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**Związki kompleksowe metali grup 10 i 11 jako potencjalne
prekursory nanomateriałów deponowanych z fazy gazowej**

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Wykaz skrótów

acac acetyloacetonian

AFM mikroskopia sił atomowych

ALD osadzanie warstw atomowych

ALIE średnia lokalna energia jonizacji

ALLYL $\text{CH}_2=\text{CH}-\text{CH}_2^-$

AMD amidynian

APT tomografia sondy atomowej

ATR osłabione całkowite odbicie

BPT bisfenylo-4-tiol

BSE elektrony wstecznie rozproszone

BTMSA bis(trimetylosililo)acetylen

BTMSE trans-bis(trimetylosililo)eten

CVD chemiczne osadzanie z fazy gazowej

1,5-COD 1,5-cykllooktadien

Cp cyklopentadienyl

DD dysocjacja dipolarna

DEA dysocjacyjny wychwyt elektronu

DI dysocjacja jonizacyjna

DMB 2,3-dimetylo-2-buten

DMCOD dimetylo-1,5-cykllooktadien

EDX analiza metodą rentgenowską z dyspersją energii

EI MS spektrometria mas z jonizacją elektronami

ESD desorpcja stymulowana elektronami

FEBID depozycja indukowana zogniskowaną wiązką elektronów

FEBIP procesy indukowane zogniskowaną wiązką elektronów

FIBID depozycja indukowana zogniskowaną wiązką jonów

GIS system dostarczania gazu

HAMD amidyna

hfac heksafluoroacetyloacetonian

HREELS wysokorozdzielcza spektroskopia strat energii elektronów

IAMDCF₃ imidoiloamidynian

IBID depozycja indukowana wiązką jonów

ⁱPr grupa izopropylowa

MFM skaningowa mikroskopia sił magnetycznych

MHY 2-metylo-1-heksen-3-yn

ND dysocjacja na fragmenty obojętne elektrycznie (dysocjacja neutralna)

ORR reakcja redukcji tlenu

PE elektrony pierwotne

RAIRS odbiciowo-absorpcyjna spektroskopia w podczerwieni

RI intensywność względna

SAM samoorganizujące się monowarstwy

^sBu grupa sekbutylowa

SE elektrony wtórne

SEM skaningowa mikroskopia
elektronowa

SERS powierzchniowo wzmocniona
spektroskopia Ramana

SPM mikroskopia sondy skanującej

TA analiza termiczna

tbaoac tert-butyloacetoacetonian

^tBu grupa tertbutylowa

TEM transmisyjna mikroskopia
elektronowa

tfac trifluoroacetyloacetonian

TNI tymczasowy jon ujemny

VTES winylotrietylosilan

VT IR zmiennotemperaturowa
spektroskopia w podczerwieni

VTMS winylotrimetylosilan

XPS spektroskopia fotoelektronów

Streszczenie

Metody osadzania z fazy gazowej takie jak, chemiczne osadzanie z fazy gazowej (CVD) oraz depozycja indukowana zogniskowaną wiązką elektronów (FEBID) lub jonów (FIBID) odgrywają istotną rolę w nanotechnologii. CVD umożliwia wytwarzanie cienkich warstw. Z kolei FEBID/FIBID pozwalają na lokalne wytwarzanie struktur 2D i 3D o precyzyjnie zdefiniowanym kształcie i rozmiarze, nawet poniżej 10 nm.

W części teoretycznej omówiono metody osadzania z fazy gazowej CVD, FEBID i FIBID ze szczególnym uwzględnieniem do tej pory stosowanych prekursorów metali z grupy 10 i 11. Zaprezentowano kryteria ich doboru w kontekście poszczególnych technik. Uwagę również poświęcono procesom indukowanym elektronami, w tym metodzie desorpcji stymulowanej elektronami (ESD). Przedstawiono także nanomateriały na bazie metali z grupy 10 i 11 otrzymane w procesach CVD, FEBID i FIBID. Na zakończenie części teoretycznej omówiono typy ligandów preferowanych w metodach osadzania z fazy gazowej i podano przykłady odpowiadających im związków koordynacyjnych.

Aktualnym problemem badawczym jest niska zawartość metalu w depozytach FEBID i FIBID, co ogranicza możliwość ich wykorzystania w sektorach wymagających materiałów wysokiej czystości. Z tego względu istotne jest poszukiwanie nowych prekursorów oraz zbadanie mechanizmów wpływających na efektywność procesów indukowanych zogniskowaną wiązką elektronów lub jonów. Poszukiwane są również nowe i przyjazne prekursory dedykowane metodzie CVD.

Niniejsza dysertacja została poświęcona badaniom nad w większości nowymi związkami kompleksowymi metali z grupy 10 i 11 z:

- 1) O,O-donorowymi karboksylanami i N-donorowymi aminami bądź amidynami $[M_2(L)_2(O_2C^tBu/R_F)_4]$ $M = Ni, Cu$; $L = RNH_2, Et_3N, NH_2(NH=)CR_F$; $R = ^tBu, ^sBu, ^iPr, Et$; $R_F = CF_3, C_2F_5$;
- 2) N,N-donorowymi imidoiloamidynianem lub amidynianem oraz z N-donorową amidyną $[Ni(NHC(CF_3)NC(CF_3)NH)_2]$, $[Au_4(\mu-(NH)_2CC_2F_5)_4]_n$ oraz $[Au_2Cl_2((NH_2(NH=)CC_2F_5)_2)]_n$;
- 3) O,O-donorowymi karboksylanami oraz β -ketoesteranami $[M_x(\mu-O_2CR)_y]$, $M = Cu, Ag$; $R = ^tBu, C(CH_3)_2C_2H_5, C_6H_5$ oraz $[Pd(CH_3COCHCO_2R)_2]$, $R = ^tBu, ^iPr, Et$.

Opracowano warunki syntezy **13** nowych związków kompleksowych. W tym dla kompleksów niklu zastosowano również metodę syntezy mechanochemicznej, która pozwoliła na istotne skrócenie czasu reakcji oraz uzyskanie wyższych wydajności. Przedstawiono struktury dla **9** wyizolowanych monokryształów, z których **4** zbadano pod kątem zastosowania w metodach osadzania z fazy gazowej. Dla otrzymanych połączeń dokonano charakterystyki składu i budowy w oparciu o metody spektroskopowe.

Dla uzyskanych kompleksów przeprowadzono badania termiczne, lotności i oddziaływania z elektronami o różnej energii (70 eV oraz 8, 20 i 200 keV). Zbadano wpływ centrum koordynacji na lotność kompleksów oraz dysocjację pod wpływem elektronów niskoenergetycznych oraz wiązki elektronów wysokoenergetycznych, a także zaproponowano mechanizm rozkładu termicznego oraz indukowanego elektronami.

Na podstawie wyników analizy termicznej ($p = \text{atm}$), eksperymentów sublimacji (10^{-2} mbar), zmiennotemperaturowej spektroskopii w podczerwieni VT IR (10^{-1} mbar) oraz EI MS (10^{-6} mbar) stwierdzono, że wszystkie badane kompleksy stanowią źródło metalu w fazie gazowej w warunkach obniżonego ciśnienia.

Kompleks $[\text{Cu}_2(\text{}^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ zastosowano w procesie CVD bez wykorzystania gazu redukującego otrzymując warstwę miedzi. Z kolei dla $[\text{Ni}_2(\text{NH}_2(\text{NH=})\text{CC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ uzyskano nanomateriał Ti-TNT20, który wykazywał aktywność fotokatalityczną.

Największą wrażliwość na elektrony niskoenergetyczne i wiązkę elektronów wysokoenergetycznych wykazały kompleksy $[\text{Cu}_2(\text{}^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ oraz $[\text{Pd}(\text{CH}_3\text{COCHCO}_2^t\text{Bu})_2]$.

Spośród badanych związków prekursorem o najniższej temperaturze odparowania w warunkach obniżonego ciśnienia i największej czułości na elektrony jest β -ketoesteran palladu(II) $[\text{Pd}(\text{CH}_3\text{COCHCO}_2^t\text{Bu})_2]$, który został wykorzystany w procesie FEBID tworząc depozyt 2D o zawartości 25 at.% Pd. Związek ten wydaje się być obiecujący jako prekursor Pd FEBID i FIBID.

Abstract

Gas-phase deposition methods, such as chemical vapor deposition (CVD) and focused electron or ion beam induced deposition (FEBID/FIBID), play a crucial role in nanotechnology. CVD enables the fabrication of thin films, while FEBID and FIBID allow for the local fabrication of 2D and 3D structures with precisely defined shapes and dimensions, even below 10 nm.

In the theoretical part, CVD, FEBID and FIBID gas-phase deposition methods were described with a special focus on the group 10 and 11 metal precursors used until now. The criteria for selecting these precursors were presented in the context of each technique. Attention is also given to electron-induced processes, including electron-stimulated desorption (ESD). Furthermore, group 10 and 11 metal-based nanomaterials obtained via CVD, FEBID, and FIBID are presented. At the end of the theoretical part the ligand types preferred in gas-phase deposition methods are described, along with examples of corresponding coordination compounds.

A current research challenge is the low metal content in FEBID and FIBID deposits, which limits their applicability in sectors that require high-purity materials. Therefore, the search for new precursors and the investigation of mechanisms influencing the efficiency of focused electron or ion beam-induced processes are essential. Additionally, there is ongoing interest in developing new and environmentally friendly precursors dedicated to the CVD method.

This dissertation is devoted to the study of mostly novel coordination compounds of group 10 and 11 metals with:

- 1) O,O-donor carboxylates or N-donor amines and amidines $[M_2(L)_2(O_2C^tBu/R_F)_4]$
 $M = Ni, Cu; L = RNH_2, Et_3N, NH_2(NH=)CR_F; R = ^tBu, ^sBu, ^iPr, Et; R_F = CF_3, C_2F_5;$
- 2) N,N-donor imidoamidinate and amidinate or N-donor amidines
 $[Ni(NHC(CF_3)NC(CF_3)NH)_2], [Au_4(\mu-(NH)_2CC_2F_5)_4]_n$ and
 $[Au_2Cl_2((NH_2(NH=)CC_2F_5)_2)]_n;$
- 3) O,O-donor carboxylates and β -ketoesterates $[M_x(\mu-O_2CR)_y], M = Cu, Ag; R = ^tBu, C(CH_3)_2C_2H_5, C_6H_5,$ and $[Pd(CH_3COCHCO_2R)_2], R = ^tBu, ^iPr, Et.$

The synthesis conditions for **13** new coordination compounds were developed. For the nickel complexes, a mechanochemical synthesis was also used, which significantly reduced the reaction time and increased product yields. Structural data were presented for **9** isolated single crystals, and **4** of which were examined for their potential application in gas-phase deposition methods. The composition and structure of the obtained compounds were characterized using spectroscopic techniques.

Thermal studies, volatility tests, and investigations of interactions with electrons of various energies (70 eV and 8, 20, and 200 keV) were carried out for the obtained complexes. The influence of the coordination center on the volatility of the complexes and their dissociation under low-energy electrons and a high-energy electron beam was examined. Additionally, mechanisms of thermal decomposition and electron-induced fragmentation were proposed.

Based on the results of thermal analysis ($p = \text{atm}$), sublimation experiments (10^{-2} mbar), variable-temperature infrared spectroscopy (VT IR, 10^{-1} mbar), and EI MS (10^{-6} mbar), it was concluded that all the investigated complexes serve as metal sources in the gas phase under reduced pressure.

The complex $[\text{Cu}_2(\text{tBuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ was used in a CVD process without a reducing gas, resulting in the formation of a copper layer. In turn, the compound $[\text{Ni}_2(\text{NH}_2(\text{NH}=\text{CC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ was used to fabricate the Ti-TNT20 nanomaterial, which exhibited photocatalytic activity.

The highest sensitivity to low-energy electrons and a high-energy electron beam was observed for the complexes $[\text{Cu}_2(\text{tBuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ and $[\text{Pd}(\text{CH}_3\text{COCHCO}_2^t\text{Bu})_2]$.

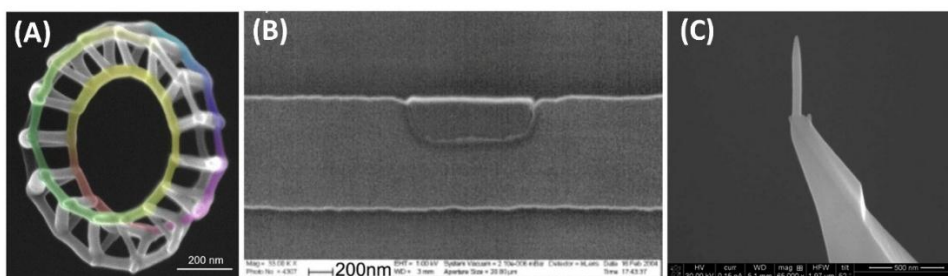
Among the studied compounds, the precursor with the lowest evaporation temperature under reduced pressure and the highest sensitivity to electrons is the palladium(II) β -ketoesterate $[\text{Pd}(\text{CH}_3\text{COCHCO}_2^t\text{Bu})_2]$, which was used in the FEBID process to form a 2D deposit containing 25 at.% Pd. This compound appears to be a promising Pd precursor for FEBID and FIBID methods.

Wstęp

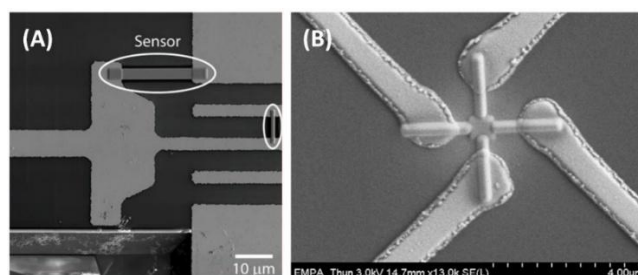
Nanotechnologia jest obecnie dynamicznie rozwijającą się dziedziną nauki. Zainteresowanie nią oraz miniaturyzacją urządzeń wynika z potencjalnych zastosowań oraz właściwości nanomateriałów, często odmiennych od tych, które wykazują materiały w skali makroskopowej. Za twórcę współczesnej nanotechnologii uznaje się amerykańskiego fizyka i laureata nagrody Nobla Richarda P. Feynmana, który w latach pięćdziesiątych, w trakcie wykładu zatytułowanego „*There's Plenty of Room at the Bottom*” przedstawił swoje rozważania na temat wykorzystania maszyn do konstruowania coraz mniejszych urządzeń, aż do poziomu molekularnego, dając tym samym początek nowemu kierunkowi badań. Pomimo, że pojęcie “nanotechnologia” zostało zdefiniowane dopiero w zeszłym stuleciu, jej nieświadome wykorzystanie towarzyszy ludziom od wieków [1–3]. Jednym z przykładów jest zastosowanie nanocząstek złota i srebra do produkcji szkła czerwonego oraz żółtego wykorzystywanego w witrażach [4]. Wytwarzano również szkła w odcieniach bieli, błękitu i turkusowego, które były opalizowane przez nanokryształy $\text{Ca}_2\text{Sb}_2\text{O}_7$ [5]. Natomiast, stal damasceńska, znana ze swojej twardości zawierała nanodruty Fe_3C oraz nanorurki węglowe [6].

Obecnie, coraz częściej prowadzone badania są skupione na aspekcie otrzymywania nanostruktur 2D i 3D o ściśle zdefiniowanym kształcie i rozmiarze oraz właściwościach, które można zastosować np. do wydajnego transportu elektronów, czy wzbudzenia optycznego. Tego typu materiały mogą być otrzymywane m.in. dzięki wykorzystaniu metod osadzania z fazy gazowej, wymagających zastosowania lotnych prekursorów, których cząsteczki są adsorbowane na powierzchni substratu i ulegają rozkładowi, z utworzeniem pożądanego nanomateriału. Taką metodę stanowi chemiczne osadzanie z fazy gazowej (CVD, *ang. chemical vapor deposition*), w której rozkład cząsteczek prekursora jest indukowany termicznie. Technika ta umożliwia wytwarzanie warstw i depozytów o różnej morfologii zawierających ziarna. Metoda ta jest wykorzystywana w nanotechnologii i mikroelektronice, na przykład w procesach tworzenia połączeń w wielowarstwowych układach scalonych [2,3,7–12]. Z kolei metody depozycji indukowanej zogniskowaną wiązką elektronów lub jonów (FEBID/FIBID, *ang. focused electron/ion beam induced deposition*), pozwalają na otrzymywanie depozytów o ściśle określonym kształcie i rozmiarze, o rozdzielczości poniżej 10 nm. Typowa zawartość metalu w depozytach FEBID mieści się w zakresie 5–40 at.%, co ogranicza ich zastosowanie w technologiach

wymagających metalu wysokiej czystości m.in. w powierzchniowo wzmocnionej spektroskopii Ramana (SERS, *ang. surface-enhanced raman spectroscopy*). Metody FEBID i FIBID umożliwiają modyfikację nanostruktur, co znajduje zastosowanie m.in. w naprawie masek fotolitograficznych (**Rysunek 1B**) i układów scalonych oraz w wytwarzaniu sond skanujących w mikroskopii sił atomowych (AFM, *ang. atomic force microscope*) (**Rysunek 1**), tomografii atomowej (APT, *ang. atom probe tomography*), czy mikroskopii magnetycznej (MFM, *ang. magnetic force microscopy*). Proces FEBID pozwala zwiększyć twardość końcówki, czy też służy do nadania właściwości przewodzących [8,13–16]. Wśród nanostruktur o właściwościach magnetycznych wyróżniają się czujniki naprężeniowo-odkształceniowe i Halla (**Rysunek 2**) [17–21].



Rysunek 1 Obrazy SEM: (A) nanodepozyt 3D PtC_x o złożonym kształcie, rozdzielczość 50 nm; (B) naprawiona metodą FEBID maska fotolitograficzna – prekursor $[Pt(\eta^5-CpMe)Me_3]$; (C) sonda do mikroskopii sił atomowych, prekursor – $[Co_2(CO)_8]$ (60 at.% Co) [22–24].



Rysunek 2 Zdjęcie SEM depozytów FEBID, (A) czujnik naprężeniowo-odkształceniowy osadzony pomiędzy stykami Au/Cr – prekursor $[Pt(\eta^5-CpMe)Me_3]$ oraz (B) czujnik Halla – prekursor $[Co_2(CO)_8]$ [18,19].

Nanomateriały na bazie metali z grupy 10 znajdują szczególne zastosowanie w nanomagnetyzmie, nanomechanice i nanosensoryce, natomiast materiały oparte na metalach z grupy 11 odgrywają kluczową rolę w nanofotonice, nanoplazmonice i nanoelektronice [17,25–30]. Niniejsza rozprawa doktorska została poświęcona nowym związkom koordynacyjnym metali z grupy 10 (Ni i Pd) oraz grupy 11 (Cu, Ag oraz Au), co podyktowane było ograniczoną ilością prekursorów o odpowiednich właściwościach dla

procesów FEBID i FIBID oraz potrzebą opracowania przyjaznych w użytkowaniu prekursorów CVD. Komercyjny prekursor $[\text{Pt}(\eta^5\text{-CpMe})\text{Me}_3]$ jest standardowo wykorzystywany w mikroskopach SEM do tworzenia przewodzącego depozytu PtC_x , gdzie zawartość metalu sięga 22–28 at.% Pt. W związku z tym w niniejszych badaniach nie podjęto próby otrzymywania związków platyny. Prekursor ten jest również stosowany w technice FIBID, jednakże uzyskiwana rozdzielczość depozytów w tym procesie jest niższa w porównaniu z metodą FEBID [14,18,31–37].

1. Wprowadzenie teoretyczne

1.1 Metody osadzania z fazy gazowej

Zgodnie z koncepcją zielonej chemii procesy technologiczne i laboratoryjne powinny dążyć do równowagi pomiędzy wpływem na środowisko, wykorzystaniem zasobów naturalnych, a opłacalnością ekonomiczną. W związku z tym współczesnym trendem naukowym i technologicznym jest dążenie do miniaturyzacji. Procesy CVD, FEBID i FIBID pozwalają na tworzenie wydajnych urządzeń przy zastosowaniu niewielkiej ilości prekursorów. Istotne jest, że w metodach FEBID i FIBID ilość używanego prekursora jest jeszcze znacznie niższa niż w CVD, co eliminuje konieczność wykorzystywania dużych ilości substancji niebezpiecznych lub szkodliwych dla zdrowia. Warto podkreślić, że niekiedy trudne jest zastosowanie tzw. przyjaznych dla środowiska związków chemicznych ze względu na brak odpowiednich właściwości, które są niezbędne do wytworzenia depozytu przy zastosowaniu konkretnych technik [4,8].

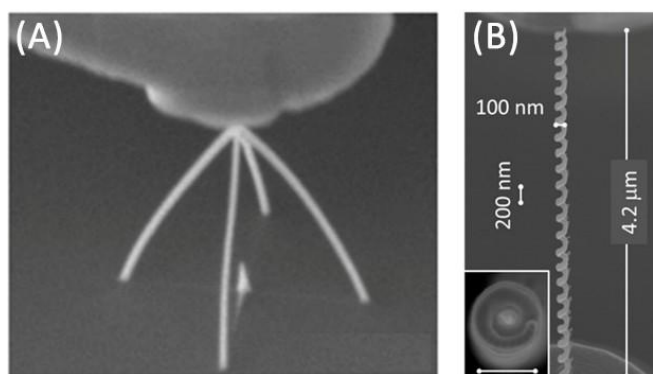
Nanomateriały mogą być wytwarzane różnymi metodami, z wykorzystaniem zarówno procesów fizycznych, jak i chemicznych. Techniki ich otrzymywania dzieli się na dwie główne kategorie: *top-down* („z góry na dół”), która polega na zmniejszaniu obiektów makro- lub mikroskalowych do rozmiarów nanometrycznych, a także *bottom-up* („z dołu do góry”) umożliwiającą budowanie materiału w wyniku łączenia atomów, a czasem cząsteczek, w kontrolowany sposób. W pierwszej z nich dominują procesy fizyczne, a w drugiej nanomateriały powstają w wyniku reakcji chemicznych. Do tej grupy można zaliczyć metody chemicznego osadzania z fazy gazowej, a także depozycję indukowaną zogniskowaną wiązką elektronów lub jonów [4,10]. CVD jest procesem znanym od lat 50-tych. XIX wieku, kiedy Bunsen po raz pierwszy zaobserwował osadzanie tlenku żelaza z chlorku żelaza i pary wodnej [8]. Natomiast techniki FEBID i FIBID są stosunkowo nowe, gdyż ich początki sięgają roku 1978, gdy gaz resztkowy w komorze mikroskopu utworzył film węglowy na powierzchni warstwy Au-Pd [38].

Techniki CVD, FEBID i FIBID umożliwiają osadzanie nanowarstw oraz tworzenie nanostruktur, przy czym wymagają zastosowania lotnych prekursorów, często związków metaloorganicznych lub koordynacyjnych [8,14].

Zaletami metody CVD są brak konieczności stosowania wysokiej próżni, możliwość regulacji szybkości osadzania oraz otrzymywania cienkich metalicznych

warstw mikro- i nanometrycznych o wysokiej czystości, na różnych powierzchniach również o złożonym kształcie [10,11,39,40].

Z kolei zaletami metod indukowanych elektronami i jonami jest możliwość tworzenia precyzyjnych depozytów, dzięki kontroli czasu przebywania wiązki elektronów lub jonów w danym punkcie (kontrola wymiarów pionowych) oraz rasteryzacja skanowania wiązki (kontrola wymiarów bocznych). Metodami FEBID i FIBID można otrzymywać depozytów o bardzo skomplikowanym kształcie (**Rysunek 1**, **Rysunek 3**) [14,26,41].



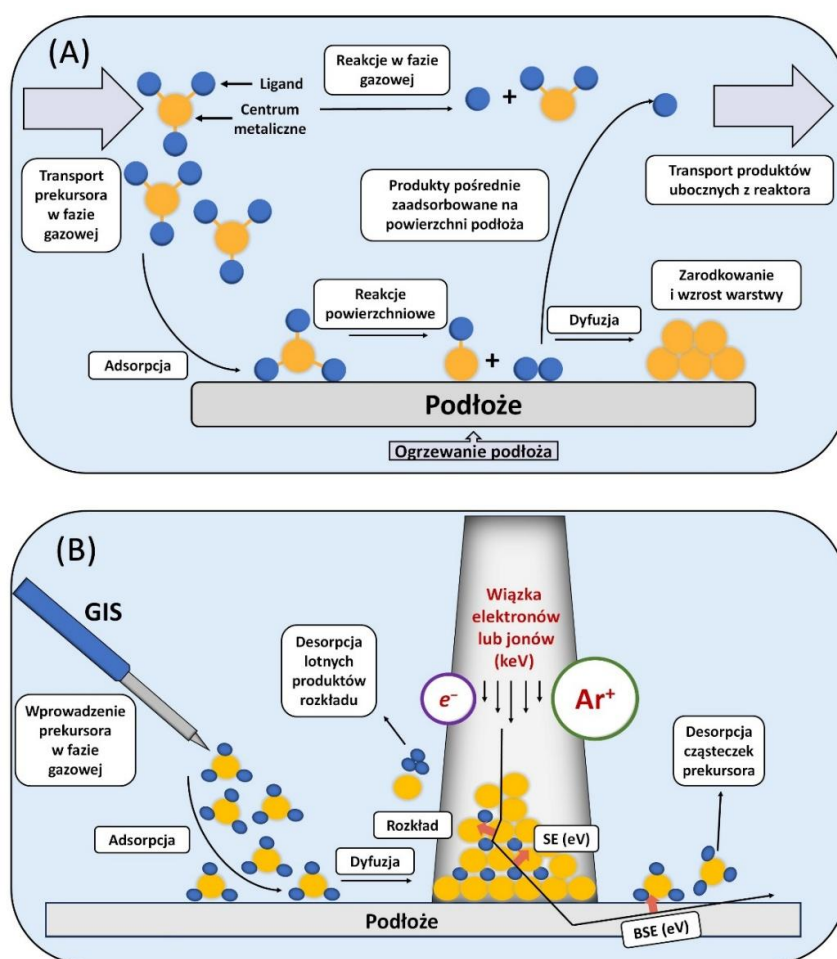
Rysunek 3 Obrazy SEM depozytu (A) FEBID Pt/C przy wykorzystaniu $[Pt(\eta^5-CpMe)Me_3]$ oraz (B) FIBID W/C z użyciem prekursora $[W(CO)_6]$ [14,26,41].

W metodzie CVD cząsteczki lotnego prekursora są transportowane w reaktorze do podłoża przy wykorzystaniu gazu nośnego, najczęściej argonu. Molekuły ulegają adsorpcji na podłożu, a następnie dysocjacji w wyniku procesów indukowanych termicznie tworząc pożądaną nanomateriał. W idealnym przypadku dochodzi do całkowitego rozkładu prekursora z wydzieleniem lotnych produktów, które są usuwane z reaktora CVD za pomocą gazu nośnego (**Rysunek 4A**). Jednakże często konieczne jest zastosowanie wysokich temperatur i czynnika redukującego np. H_2 w celu uzyskania depozytów o wysokiej czystości. Optymalizacja warunków reakcji m.in. temperatury, ciśnienia, czy przepływu gazu nośnego, minimalizuje ilość zanieczyszczeń w materiale [8,11,26].

W technikach FEBID i FIBID wykorzystywane są lotne prekursory pierwotnie dedykowane metodzie CVD, które powinny być również wrażliwe na działanie wysokoenergetycznej wiązki elektronów (FEBID), jonów (FIBID) np. Ne^+ , Ga^+ , Xe^+ lub/i elektronów niskoenergetycznych (FEBID/FIBID). W procesach FEBID i FIBID prekursor jest wprowadzany do komory mikroskopu SEM, gdzie panuje ciśnienie rzędu 10^{-6} mbar, przy użyciu systemu dostarczania gazu (GIS, ang. *gas injection system*). Następnie cząsteczki ulegają adsorpcji na podłożu i wchodzi w interakcje z wiązką cząstek

naładowanych. W idealnym przypadku dochodzi do całkowitego rozkładu prekursora z utworzeniem czystego depozytu np. metalu i wydzieleniem lotnych produktów, które wypompowywane są z komory mikroskopu SEM (**Rysunek 4B**) [8,14,26,37]. Jednakże depozyty FEBID i FIBID często zawierają dużą ilość zanieczyszczeń, ze względu na niecałkowitą dysocjację cząsteczek prekursora. Z tego względu, aby zwiększyć zawartość procentową metalu w depozycie, stosuje się procesy oczyszczania, takie jak podgrzanie podłoża, zastosowanie plazmy lub wiązki lasera, naświetlanie elektronami, czy użycie gazów reaktywnych (O_2 , H_2 , H_2O , NH_3) najczęściej po procesie osadzania, w celu usunięcia niepożądanych produktów (często jest to matryca węglowa) [37].

Warto nadmienić, że w przypadku metody FIBID procesowi depozycji towarzyszy konkurencyjne zjawisko trawienia materiału wywołane działaniem wysokoenergetycznej wiązki jonów, które może prowadzić do usuwania atomów zarówno z powierzchni substratu, jak i z osadzonego depozytu [14].



Rysunek 4 Główne etapy procesów (A) CVD oraz (B) FEBID/FIBID (ramka: fioletowa – wiązka elektronów; zielona – wiązka jonów).

Dotychczasowe badania nad prekursorami FEBID oraz FIBID wskazują na dużą złożoność tych procesów i konieczność zbadania mechanizmów oddziaływania molekuł z cząstkami naładowanymi (elektronami, jonami) w fazie gazowej i zaadsorbowanych na podłożu, w celu określenia zależności pomiędzy budową związków, a ich lotnością i wrażliwością na działanie elektronów wysokoenergetycznych oraz wtórnych, które są generowane z powierzchni substratu (*vide infra* – 1.2, 1.3).

1.2 Kompleksy jako prekursory metali w metodach CVD, FEBID oraz FIBID

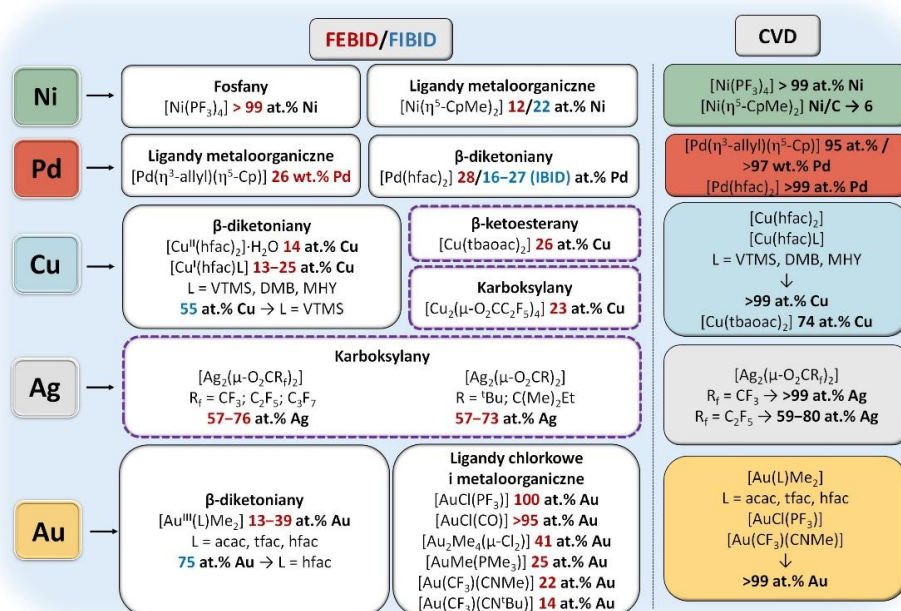
Jak wspomniano w rozdziale 1.1 lotne związki koordynacyjne znajdują zastosowanie w powyższych metodach jako tzw. prekursory stanowiące źródło metalu. Wśród znanych i wykorzystywanych prekursorów **FEBID** i **FIBID**, dla których uzyskano depozyty o wysokiej czystości znajdują się karbonylki metali: $[\text{W}(\text{CO})_6]$ (70 at.% W; 72 at.% W – He^+), $[\text{Co}(\text{CO})_3(\text{NO})]$ (50 at.% Co; 54 at.% Co – He^+), $[\text{Co}_2(\text{CO})_8]$ (95 at.% Co), jednakże są to związki toksyczne [8,42]. W kontekście znanych prekursorów **FEBID** i **FIBID** trzeba więcej powiedzieć o już wspomnianym w rozdziale 1 komercyjnie wykorzystywanym prekursorze platynowym $[\text{Pt}(\eta^5\text{-CpMe})\text{Me}_3]$ (22–28 at.% Pt). Zaletą tego związku jest stabilność termiczna, nawet przy wieloletnim użytkowaniu w temperaturze 313–353 K. Zakres ten jest szczególnie korzystny, ponieważ większość komercyjnych systemów GIS nie pozwala na ogrzewania prekursora powyżej 343 K. Ponadto uzyskiwany depozyt PtC_x wykazuje satysfakcjonujące dla tworzenia przyłączy i styków przewodnictwo elektryczne [8,18,31–37].

Należy podkreślić, że prekursory stosowane w FEBID i FIBID mogą ulegać reakcjom termicznym na powierzchni podłoża, a ich charakter jest indywidualny dla konkretnego związku, co powoduje złożoność tych procesów i odróżnia te techniki od metody CVD. W technikach indukowanych wiązką elektronów lub jonów procesy termiczne mogą być wynikiem nagrzewania podłoża spowodowanego interakcją z wiązką. Zjawisko to może prowadzić do utraty kontroli nad formowaniem depozytu oraz powstawaniem tzw. efektu “halo”. Jednak w niektórych przypadkach może również korzystnie wpływać na przebieg procesu depozycji poprzez ułatwienie dyfuzji i desorpcji lotnych produktów rozkładu, jak miało to miejsce dla związku $[\text{Cu}(\text{hfac})\text{VTMS}]$ (hfac – heksafluoroacetyloacetonian, VTMS – winylotrimetylosilan) (*vide infra* – 1.2.1) [8,16,43].

1.2.1 Prekursory metali z grupy 10 i 11

Liczba związków sprawdzanych, jako prekursorzy FEBID lub FIBID metali z grupy 10 i 11, jest niezbyt duża (**Rysunek 6**, **Rysunek 7**). Większość dotychczasowych badań koncentrowała się na testowaniu znanych prekursorów CVD w procesach FEBID i FIBID ze względu na ich potwierdzoną lotność. Jednakże w kontekście metod indukowanych elektronami lub jonami istotne jest połączenie tej właściwości z systematycznymi badaniami związków pod kątem ich wrażliwości na elektrony.

Wśród prekursorów **CVD** metali z grup 10 i 11 istotną rolę odgrywają kompleksy β -diketonianowe: $[M(\beta\text{-diketonian})_2]$ ($M = \text{Ni, Pd, Cu}$; β -diketonian = acac – acetyloacetonian, tfac – trifluoroacetyloacetonian), $[\text{Ag}(\beta\text{-diketonian})\text{L}]$ ($\text{L} = \text{PMe}_3, \text{PEt}_3, \text{VTES}$ – winylotrietylosilan, BTMSA – bis(trimetylosililo)acetylen, BTMSE – trans-bis(trimetylosililo)eten) oraz $[\text{Au}(\beta\text{-diketonian})\text{Me}_2]$, które umożliwiają otrzymanie nanomateriałów o czystości powyżej 99 at.% metalu jednak często przy zastosowaniu gazu redukującego [8,10,44].



tylko testowane w FEBID/FIBID

ALLYL – $\text{CH}_2=\text{CH}-\text{CH}_2^-$, Cp – cyklopentadienyl, DMB – 2,3-dimetylo-2-buten, MHY – 2-metylo-1-heksen-3-yn, tbaoc – tert-butyloacetoacetonian

Rysunek 5 Prekursory FEBID i FIBID oraz CVD metali grupy 10 i 11 [8,10,14,44]. Na schemacie wyróżniono (fioletową, przerywaną linią) kompleksy β -ketoesteranowe oraz karboksylanowe wykorzystywane w niniejszej pracy.

Jak wspomniano prekursory **CVD**, ze względu na lotność, stanowiły punkt wyjścia do badań w technikach **FEBID** oraz **FIBID**. W dalszej części niniejszego rozdziału omówione zostaną wyłącznie prekursory **CVD**, które były *również* testowane w procesach **FEBID** lub **FIBID**, ze względu na możliwość porównania np. czystości uzyskiwanych depozytów.

W przypadku prekursorów **CVD** niklu zastosowanie związku $[\text{Ni}(\eta^5\text{-CpMe})_2]$ prowadziło do powstania depozytu zanieczyszczonego węglem. Z kolei, gdy użyto tlen jako gaz reaktywny otrzymano warstwę tlenku niklu. Natomiast, dla $[\text{Ni}(\text{PF}_3)_4]$ otrzymano metaliczne filmy zawierające >99 at.% Ni. Te same związki zastosowane jako prekursory w technice **FEBID** (**Rysunek 5**, **Rysunek 6**) pozwoliły na uzyskanie depozytów zawierających odpowiednio 12 i 36 at.% Ni dla $[\text{Ni}(\eta^5\text{-CpMe})_2]$ oraz $[\text{Ni}(\text{PF}_3)_4]$. Z kolei w procesie **FIBID** stosując $[\text{Ni}(\eta^5\text{-CpMe})_2]$, otrzymano materiał o zawartości 22 at.% Ni [8,47].

Wykorzystanie prekursora $[\text{Pd}(\text{hfac})_2]$ w metodzie **CVD**, w obecności wodoru jako gazu redukującego, umożliwiło uzyskanie warstw o wysokiej czystości powyżej 97 at.%. Dla $[\text{Pd}(\eta^3\text{-allyl})(\eta^5\text{-Cp})]$ otrzymano materiał o zawartości palladu >95 at.% Pd. Z kolei w procesie **FEBID** (**Rysunek 5**, **Rysunek 6**) przy zastosowaniu tych prekursorów $[\text{Pd}(\text{hfac})_2]$ oraz $[\text{Pd}(\eta^3\text{-allyl})(\eta^5\text{-Cp})]$, powstały depozyty o zawartości odpowiednio 28 at.% oraz 26 at.% Pd. Natomiast stosując β -diketonian $[\text{Pd}(\text{hfac})_2]$, w metodzie **IBID**, otrzymano materiały o zawartości 16–27 at.% Pd (**Rysunek 5**, **Rysunek 7**).

Oryginalne podejście zastosowano dla octanu $[\text{Pd}_3(\mu\text{-O}_2\text{CCH}_3)_6]$. Warstwę prekursora naniesiono na podłoże krzemowe przy użyciu mokrej metody *spin coating*, a następnie naświetlono ją wiązką elektronów otrzymując depozyt o zawartości około 40 at.% Pd. Prekursor ten został wykorzystany również w taki sam sposób w eksperymentach przy użyciu wiązki Ga^+ , dając 45–65 at.% Pd [8,43,50,51].

Dla miedzi, jak wspomniano powyżej, β -diketoniany Cu(II) i Cu(I) stanowią grupę prekursorów powszechnie wykorzystywanych w procesie **CVD**. W przypadku związków miedzi(II) niezbędne jest stosowanie reduktora dla otrzymania nanomateriałów o czystości >99 at.% Cu. W **FEBID** dla $[\text{Cu}(\text{hfac})_2]\cdot\text{H}_2\text{O}$ otrzymano materiały o dużo niższej zawartości metalu 14 at.%. Natomiast w przypadku czułych na powietrze połączeń $[\text{Cu}(\text{hfac})\text{L}]$ uzyskano jedynie 13–25 at.% Cu. Zastosowanie procesu oczyszczania - w trakcie depozycji prowadzono ogrzewanie (tzw. *heat-assisted FEBID*) - do temperatury 100°C dla $[\text{Cu}(\text{hfac})\text{VTMS}]$ pozwoliło na otrzymane depozytów 3D o czystości ~100 at.%

Cu. Jednak trzeba zaznaczyć, że krystalizacja czystego depozytu miedziowego utworzyła się w matrycy węglowej.

Podczas testów FEBID dla karboksylanu miedzi(II) $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$, otrzymano depozyt o czystości 23 at.% Cu. Natomiast depozyty **FEBID** (**Rysunek 5**, **Rysunek 6**) o najwyższej zawartości metalu 26 at.% Cu uzyskano dla β -ketoesteranu $[\text{Cu}(\text{tbaoac})_2]$ ($\text{tbaoac} - \text{CH}_3\text{COCHCO}_2^t\text{Bu}$).

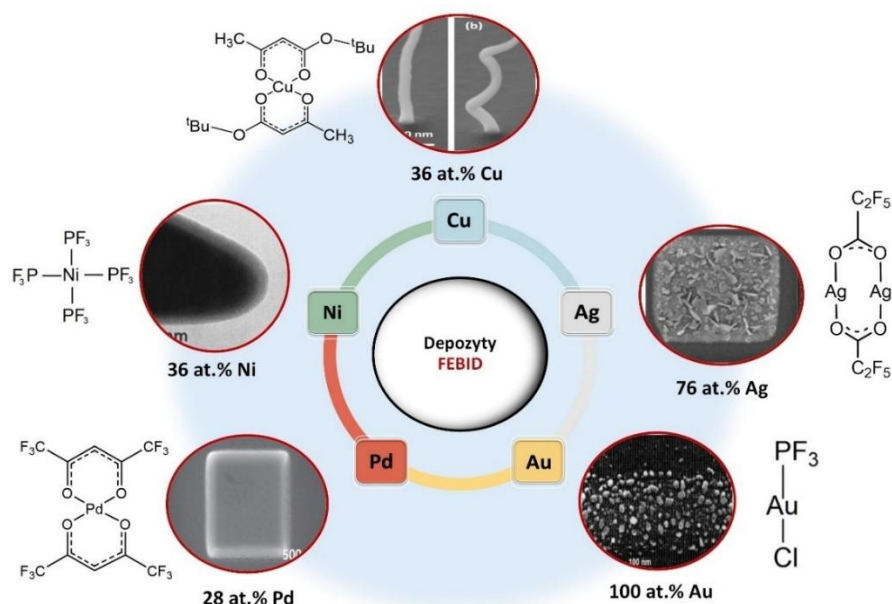
W procesie **FIBID** użycie prekursora $[\text{Cu}(\text{hfac})\text{VTMS}]$ pozwoliło na otrzymanie depozytów zawierających 55 at.% Cu (**Rysunek 5**, **Rysunek 7**) [8,14,52].

W procesie **CVD** karboksylany $[\text{Ag}_2(\mu\text{-O}_2\text{CR})_2]$, pozwoliły na uzyskanie warstw o zawartości metalu >99 at.% przy zastosowaniu wodoru jako gazu redukującego. W roli prekursorów **FEBID** testowano zarówno fluorowane, jak i niefluorowane kompleksy $[\text{Ag}_2(\mu\text{-O}_2\text{CR})_2]$, gdzie $\text{R}_F = \text{CF}_3, \text{C}_2\text{F}_5, \text{C}_3\text{F}_7$, a $\text{R} = ^t\text{Bu}, \text{C}(\text{CH}_3)_2\text{C}_2\text{H}_5$. Zawartość srebra w depozytach płaskich wynosiła 59–76 at.% Ag (76% max. dla $[\text{Ag}_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_2]$). Dotychczas w literaturze nie odnotowano nanostruktur **FEBID** o wyższej zawartości srebra. W przypadku $[\text{Ag}_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_2]$ oraz innych ligandów perfluorowanych obserwowano trójwymiarowy wzrost struktur, prowadzący do utworzenia depozytu w formie kolumny, gdzie największa zawartość Ag wynosiła około 50 at.% (**Rysunek 5**, **Rysunek 6**) [8].

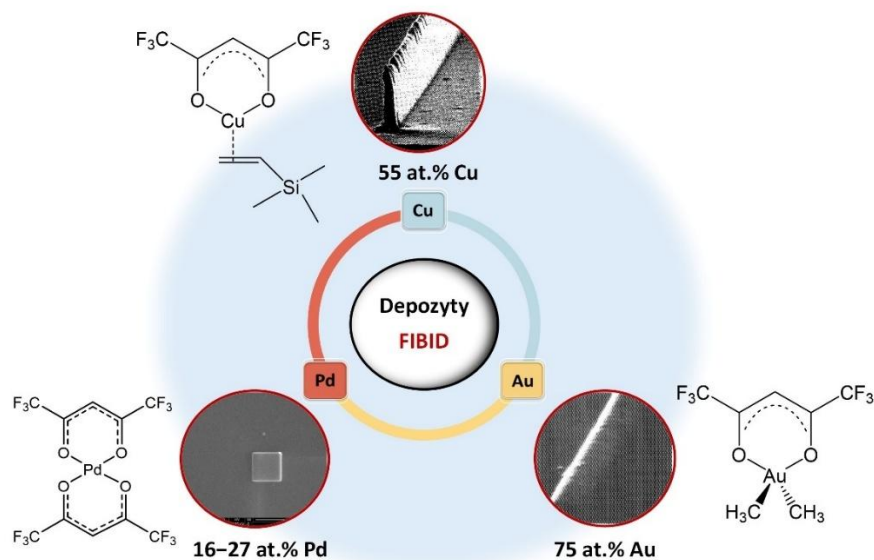
Natomiast brak jest danych literaturowych dotyczących wykorzystania związków srebra w procesie FIBID [14].

Wykorzystanie β -diketonianianów złota(III): $[\text{Au}(\text{acac})\text{Me}_2]$, $[\text{Au}(\text{tfac})\text{Me}_2]$ i $[\text{Au}(\text{hfac})\text{Me}_2]$, a także niestabilnych połączeń złota(I) $[\text{AuCl}(\text{PF}_3)]$ i $[\text{Au}(\text{CF}_3)(\text{CNMe})]$ pozwoliło na otrzymanie cienkich warstw o zawartości metalu na poziomie 85–99% w **CVD**. W procesie **FEBID** (**Rysunek 5**, **Rysunek 6**) dla $[\text{Au}(\beta\text{-diketonian})\text{Me}_2]$ otrzymano depozyty o zawartości około 13–39% metalu. Nanostruktury złota o wysokiej czystości, około 95–100 at.% Au uzyskano jedynie dla kompleksów $[\text{AuCl}(\text{PF}_3)]$ oraz $[\text{AuCl}(\text{CO})]$.

Z kolei w FIBID zastosowano $[\text{Au}(\text{hfac})\text{Me}_2]$, otrzymując depozyt zawierający 75 at.% Au, jednak zanieczyszczony galem (20 at.%) (**Rysunek 5**, **Rysunek 7**) [8,14,53].



Rysunek 6 Przykłady depozytów FEBID uzyskane przy wykorzystaniu prekursorów metali z grupy 10 i 11 [8,15,24].



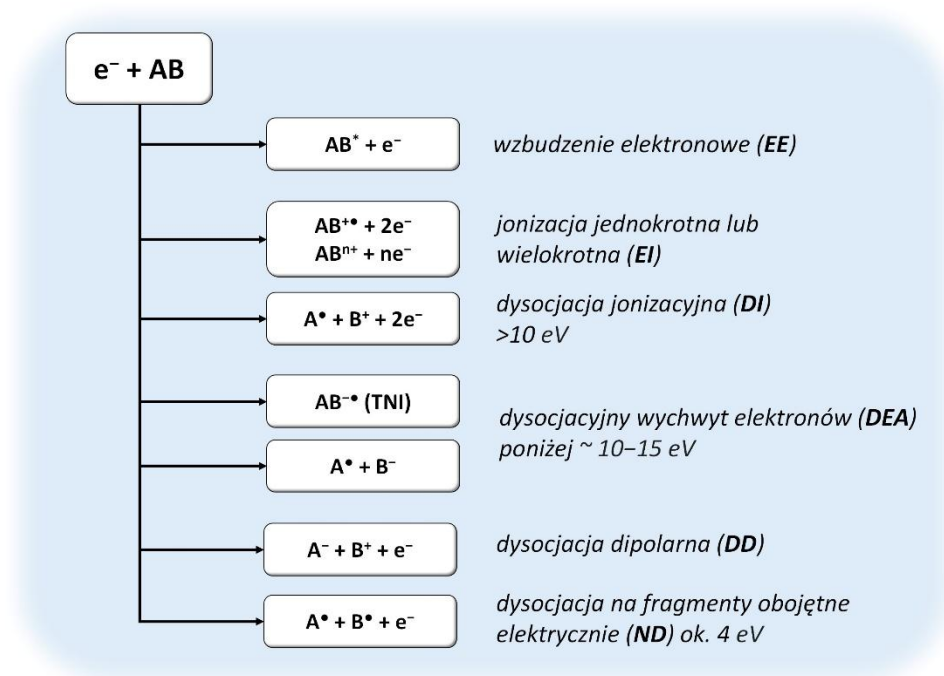
Rysunek 7 Przykłady depozytów FIBID uzyskane przy wykorzystaniu prekursorów niklu, palladu oraz złota [14,48,54].

Jak wspomniano w rozdziale 1.1 zawartość metalu w depozytach uzyskiwanych metodami indukowanymi wiązką elektronów lub jonów jest często istotnie niższa niż materiałów otrzymywanych techniką CVD. Problemem jest również stabilność prekursorów, gdyż wiele z nich jest czuła na powietrze, co wskazuje na potrzebę poszukiwania nowych przyjaznych dla użytkownika prekursorów dedykowanych tym technikom [14,42].

1.3 Procesy indukowane elektronami

W wyniku interakcji zaadsorbowanych na powierzchni cząsteczek z wiązką elektronów pierwotnych (PE, *ang. primary electrons*) następuje jonizacja oraz wzbudzenie cząsteczek, które stanowią kluczowy mechanizm początkowy procesu fragmentacji (**Rysunek 8**) [55–57] natomiast nie dochodzi bezpośrednio do rozerwania wiązań chemicznych.

W trakcie procesu FEBID w wyniku oddziaływania wiązki pierwotnej z podłożem dochodzi do zderzeń sprężystych i niesprężystych. W ich następstwie generowane są elektrony wtórne SE (SE, *ang. secondary electrons*) o energii od kilku do kilkudziesięciu eV, które wraz z powstającymi rodnikami i jonami, inicjują dalsze reakcje chemiczne i prowadzą do rozerwania wiązań chemicznych w cząsteczkach prekursora i utworzenia depozytu. Dlatego też analiza wspomnianych efektów stanowi istotny obszar badań w kontekście prekursorów FEBID, ale również FIBID, gdzie elektrony wtórne są generowane z podłoża przez wiązkę jonów. Kluczowe są procesy indukowane przez elektrony wtórne związane z: dysocjacyjnym wychwytem elektronowym (DEA, *ang. dissociative electron attachment*), jonizacją dysocjacyjną (DI, *ang. dissociative ionization*), dysocjacją dipolarną (DD, *ang. dipolar dissociation*) oraz dysocjacją na fragmenty obojętne elektrycznie (ND, *ang. neutral dissociation*) (**Rysunek 8**). Jednym z dominujących mechanizmów fragmentacji jest DEA dla energii elektronów poniżej 10–15 eV. Początek stanowi utworzenie tymczasowego jonu ujemnego (TNI, *ang. transient negative ion*) na skutek wychwytu elektronu przez cząsteczkę, który następnie ulega fragmentacji. Z kolei w trakcie procesu DI jony powstają w wyniku interakcji z elektronami o energii powyżej 10 eV. Wykrywanie cząsteczek neutralnych w procesie ND jest dość trudne, a dane na jego temat są ograniczone. Najniższą energią progową tego procesu jest energia wiązania, wynosząca około 4 eV.



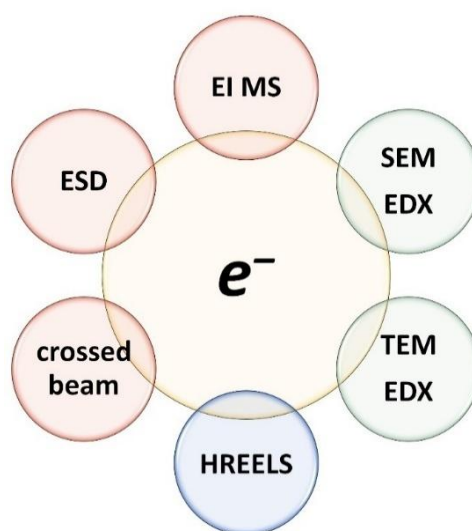
Rysunek 8 Procesy indukowane elektronami [42,55,56].

Powszechnie przyjmuje się, że przekrój czynny (*ang. cross section*) jest niski dla wyższych energii elektronów, a wyższy dla niskich energii, co wskazuje, że to elektrony wtórne odgrywają decydującą rolę w FEBIP (*ang. focused electron beam induced processing*) [25,55,58]. Na przykład, dla prekursora $[HFeCo_3(CO)_{12}]$ badania desorpcji stymulowanej elektronami (ESD, *ang. electron stimulated desorption*) wykazały, że elektrony wtórne inicjują reakcje prowadzące do dekarbonylacji, skutkując usunięciem dziewięciu z dwunastu ligandów CO [59]. Jednakże wciąż toczą się dyskusje nad udziałem elektronów PE (*ang. primary electrons*) i SE w formowaniu depozytów. Z tego względu na obecną chwilę wymagane jest przeprowadzenie indywidualnych badań dla każdego prekursora, aby określić jego przydatność i dobrać optymalne parametry procesu.

Trzeba nadmienić, że elektrony wtórne mogą prowadzić również do osadzenia pewnej ilości materiału poza obszarem naświetlania, czyli tworzenie tzw. obszaru “halo” [60,61]. Efekt “halo” jest związany z rozpraszaniem sprężystym wiązki pierwotnej, w wyniku, którego część elektronów ulega wstecznemu rozproszeniu (BSE, *ang. backscattered electrons*). Elektrony BSE powstają z obszaru większego niż średnica wiązki i mogą generować elektrony wtórne drugiego rzędu (SE2), które przyczyniają się do wzrostu efektu halo, a co za tym idzie ograniczenia rozdzielczości tworzonych nanostruktur [61,62].

Ważnym aspektem w kontekście procesów indukowanych elektronami lub jonami jest niekompletna fragmentacja prekursora spowodowana oddziaływaniem jego cząsteczek z elektronami niskoenergetycznymi. Dlatego też istotnym elementem strategii w projektowaniu nowych prekursorów FEBID i FEBID oraz doborze odpowiednich parametrów depozycji jest zbadanie procesów generowanych przez elektrony niskoenergetyczne [42,55,63].

Zrozumienie mechanizmów procesów indukowanych elektronami wysoko- i niskoenergetycznymi wymaga zastosowania szeregu metod (**Rysunek 9**). Do badań rozkładu indukowanego elektronami lub jonami wykorzystuje się techniki SEM-EDX (energia elektronów rzędu kilkudziesięciu keV) oraz TEM-EDX (rzędu kilkuset keV) (**Rysunek 9**), które umożliwiają obserwację zmian morfologii i składu próbki w wyniku oddziaływania z wiązką elektronów, co pozwala na ocenę wrażliwości związku na elektrony [55,57,64].



Rysunek 9 Schemat metod stosowanych w badaniach procesów indukowanych elektronami (pola: pomarańczowe – procesy indukowane elektronami niskoenergetycznymi, zielone – wysokoenergetycznymi, niebieskie – spektroskopia oscylacyjna).

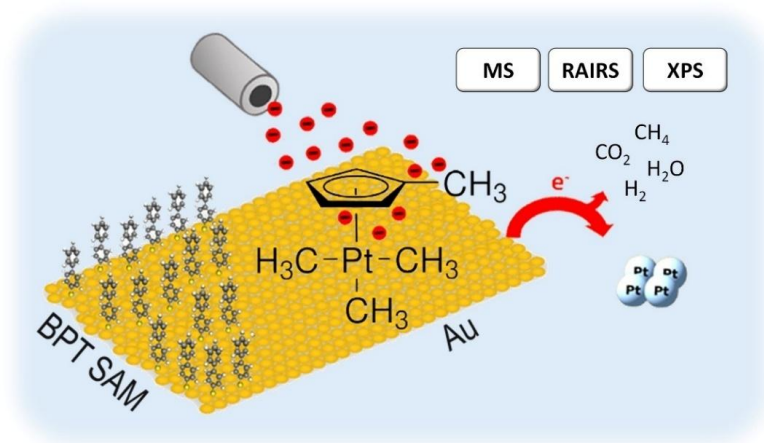
W celu analizy procesów indukowanych niskoenergetycznymi elektronami w fazie gazowej wykorzystuje się spektrometrię mas z jonizacją elektronami (EI MS). Również korzystając z techniki *crossed beam* można zbadać produkty fragmentacji na drodze DEA oraz DI, a także przekroje czynne określające prawdopodobieństwo zachodzenia danego procesu. Z kolei neutralne fragmenty lub jony generowane w wyniku oddziaływania z elektronami cząsteczek zaadsorbowanych na powierzchni mogą być analizowane przy użyciu spektrometrii mas w trakcie desorpcji stymulowanej elektronami (ESD). W badaniach wykorzystuje się także spektroskopie oscylacyjne, takie jak

wysokorozdzielcza spektroskopia strat energii elektronów (HREELS, *ang. high resolution electron energy loss spectroscopy*), która umożliwia monitorowanie zmian zachodzących w próbce poprzez analizę jej powierzchni.

1.3.1 Desorpcja stymulowana elektronami (ESD)

Wspomniano powyżej, że jedną z metod, która umożliwia określenie przydatności prekursora w metodach FEBID i FIBID jest desorpcja stymulowana elektronami (ESD) (**Rysunek 10**). Proces ten przeprowadzany jest w warunkach obniżonego ciśnienia (10^{-9} mbar), gdzie warstwa prekursora oddziałuje z elektronami niskoenergetycznymi. Dzięki tej technice możliwe jest zbadanie procesów w fazie stałej, które są inicjowane przez elektrony [62].

W procesie ESD badania przeprowadza się dla warstwy prekursora uzyskanej w procesie sublimacji, zaadsorbowanej na płytce złota pokrytej warstwą BPT (bisfenylo-4-tiol) SAM (*ang. self assembly monolayer*) (**Rysunek 10**). Podczas oddziaływania próbki z elektronami niskoenergetycznymi (eV) dynamicznie tworzą się produkty lotne, takie jak cząsteczki obojętne oraz jony fragmentacyjne. Te ostatnie są monitorowane w fazie gazowej za pomocą spektrometru mas. W celu analizy powierzchni przed i po procesie ESD wykorzystuje się techniki RAIRS (odbiciowo-absorpcyjna spektroskopia w podczerwieni, *ang. reflection adsorption infrared spectroscopy*) oraz XPS (spektroskopia fotoelektronów, *ang. X-ray photoelectron spectroscopy*). Połączenie wyników uzyskanych za pomocą tego zestawu metod pozwala na pełniejsze zrozumienie mechanizmów procesów indukowanych przez niskoenergetyczne elektrony, jakim ulegają cząsteczki prekursorów FEBID i FIBID [8].



Rysunek 10 Schemat procesu ESD na przykładzie cząsteczek prekursora $[Pt(\eta^5-CpMe)Me_3]$ zaadsorbowanych na płytce złota pokrytej warstwą BPT.

1.4 Ligandy preferowane w metodach osadzania z fazy gazowej

Na właściwości fizykochemiczne związków, w tym lotność odgrywającą kluczową rolę w technikach osadzania z fazy gazowej, wpływa wiele czynników, takich jak masa cząsteczkowa, oddziaływania międzycząsteczkowe, czy typ zastosowanych ligandów. Lotność związków można podnieść poprzez wprowadzenie podstawników zawierających fluor ze względu na ich zdolność osłabienia oddziaływań międzycząsteczkowych. Szczególnie perfluorowane podstawniki typu $R_F = CF_3$, C_2F_5 efektywnie się odpychają [42]. Wykorzystuje się również cząsteczki zawierające sterycznie rozbudowane podstawniki alkilowe $R = {}^tBu$, sBu , iPr . W celu ograniczenia możliwości tworzenia układów polimerycznych, a tym samym zwiększenia lotności połączeń można wprowadzać ligandy drugorzędowe (**Rysunek 11**) [10,42,66].

Jak omówiono w podrozdziale 1.2.1 lotne związki srebra $[Ag_2(\mu-O_2CR/R_F)_2]$, zawierające ligandy karboksylanowe, znalazły zastosowanie w metodach osadzania z fazy gazowej, takich jak CVD oraz FEBID, prowadząc do otrzymania depozytów o zróżnicowanej zawartości metalu. Jednakże, do tej pory nie zbadano ich pod kątem uzyskania pełnego zestawu danych odnośnie oddziaływania ich cząsteczek z elektronami. Z kolei przeprowadzono pod tym kątem częściową charakterystykę dla testowanego w FEBID $[Cu_2(\mu-O_2CC_2F_5)_4]$ oraz dijadrowych kompleksów zawierających drugorzędowe ligandy N-donorowe: $[Cu_2(RNH_2)_2(\mu-O_2CR_F)_4]$ z aminami alifatycznymi ($R = {}^tBu$, iPr , Et; $R_F = C_nF_{2n+1}$, $n = 1-6$) oraz $[Cu_2(NH_2(NH=)CC_2F_5)_2(\mu-O_2CR_F)_4]$ z amidynami ($R_F = CF_3$, C_2F_5 , C_3F_7 , C_4F_9) [67–70]. Stwierdzono, że kompleksy $[Cu_2(RNH_2)_2(\mu-O_2CR_F)_4]$ są dobrym źródłem metalu w fazie gazowej, a wprowadzenie aminy w pozycji aksjalnej poprawia lotność w stosunku do $[Cu_2(\mu-O_2CC_2F_5)_4]$. Wyselekcjonowane związki $[Cu_2(RNH_2)_2(\mu-O_2CC_2F_5)_4]$, gdzie $R = {}^tBu$, sBu , Et, zbadano w eksperymentach zderzeń z elektronami w fazie gazowej (*ang. cross beam*), gdzie analizie poddano jony tworzące się w efekcie procesów DI i DEA [70]. Natomiast dla $[Cu_2(EtNH_2)_2(\mu-O_2CR_F)_4]$, $R_F = C_2F_5$, C_3F_7 wykonano eksperymenty stosując wysokorozdzielczą spektroskopię strat elektronów (HREELS). Stwierdzono, że w wyniku oddziaływania z wiązką elektronów dochodzi do odsczepienia liganda aminowego [69].

Grupę kompleksów $[Cu_2(RNH_2)_2(\mu-O_2CR_F)_4]$ ($R = {}^tBu$, iPr , Et; $R_F = C_nF_{2n+1}$, $n = 1-6$) stanowiących źródło metalu wykorzystano w szeregu eksperymentów CVD, gdzie otrzymano depozyty bez zastosowania gazu redukującego [67,68,71].

Z kolei zastosowanie kompleksów miedzi(II) z amidyną $[\text{Cu}_2(\text{NH}_2(\text{NH}=\text{C})\text{CC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CR}_\text{F})_4]$ ($\text{R}_\text{F} = \text{C}_2\text{F}_5, \text{C}_3\text{F}_7$) w procesie CVD pozwoliło na otrzymanie warstw miedzi, co potwierdziło, że stanowią efektywne źródło metalu w fazie gazowej. Depozyty otrzymano w atmosferze argonu, bez udziału wodoru. Badania oddziaływania z elektronami w fazie gazowej EI MS, dla zaadsorbowanej warstwy - SEM-EDX oraz w formie czystej - TEM-EDX wykazały, że kompleks o najwyższej lotności $[\text{Cu}_2(\text{NH}_2(\text{NH}=\text{C})\text{CC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ jest wrażliwy na elektrony i może być wykorzystany w testach FEBID [72].

Do grupy lotnych związków kompleksowych, o budowie zbliżonej do karboksylanów, w których atomy tlenu zastąpiono grupami -NH lub -NR , są amidyniany (**Rysunek 11**), które znajdują komercyjne zastosowanie w technice ALD (osadzanie warstw atomowych, *ang. atomic layer deposition*) [73]. Przykładem takiego połączenia jest $[\text{Cu}_2(\mu\text{-(N}^i\text{Pr)}_2\text{C}^s\text{Bu)}_2]$, który został wykorzystany w procesie ALD do osadzania warstwy miedzi z użyciem wodoru jako drugiego reagenta. Z kolei przykładem związku zastosowanego w procesie CVD jest $[\text{Cu}_2(\mu\text{-(N}^i\text{Pr)}_2\text{CMe)}_2]$, dla którego także otrzymano warstwy miedzi [73,74]. Jednakże amidyniany tego typu nie zostały do tej pory zbadane pod kątem możliwości zastosowania w procesach indukowanych elektronami lub jonami.

Natomiast w naszej grupie badawczej otrzymano amidyniany z podstawnikami perfluorowanymi: dijądrowe miedzi(I) $[\text{Cu}_2(\mu\text{-(NH)}_2\text{CR}_\text{F})_2]$ i srebra $[\text{Ag}_2(\mu\text{-(NH)}_2\text{CR}_\text{F})_2]$ oraz trijądrowe palladu $[\text{Pd}_3(\mu\text{-(NH)}_2\text{CR}_\text{F})_6]\cdot x\text{Et}_2\text{O}$ [75]. Dla nich wykonano systematyczne badania dotyczące stabilności termicznej i lotności oraz zbadano je pod kątem oddziaływania z elektronami nisko- i wykoenergetycznymi, wykorzystując metody EI MS, SEM-EDX oraz TEM-EDX. Związki te wykazały niską wrażliwość na działanie elektronów nisko- i wykoenergetycznych, co nie jest korzystne z punktu widzenia ich zastosowania w procesach FEBID i FIBID. Jednak wykazują właściwości termiczne odpowiednie dla wykorzystania w procesie CVD. W analogiczny sposób scharakteryzowano lotne monojądrowe, niesymetryczne imidoiloamidyniany miedzi(II) $[\text{Cu}(\text{NHC}(\text{CH}_3)\text{NC}(\text{R}_\text{F})\text{NH})_2]$ ($\text{R}_\text{F} = \text{CF}_3, \text{C}_2\text{F}_5$) [76].

Przedstawione dane z jednej strony pozwalają na zaproponowanie obiecujących podstawników i ligandów, a z drugiej ujawniają istotne braki w obecnym stanie wiedzy, wskazując na potrzebę dalszych, systematycznych badań nad opracowywaniem nowych prekursorów dedykowanych dla poszczególnych metodach osadzania z fazy gazowej.

Cele pracy

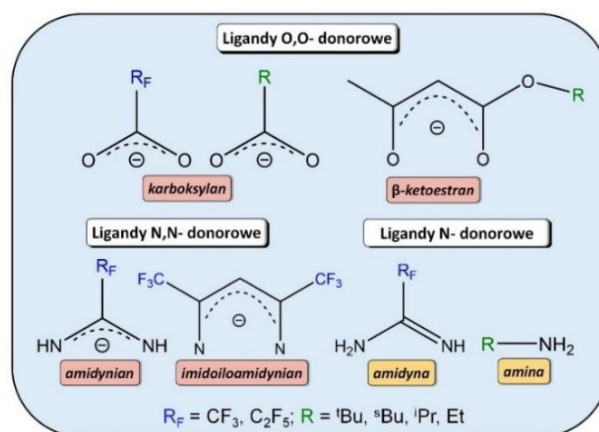
Procesy wywołane przez elektrony lub jony często prowadzą do powstawania depozytów o niskiej zawartości metalu. Jednym z obecnych wyzwań jest zwiększenie zawartości metalu w depozytach uzyskiwanych metodami FEBID i FIBID, co bezpośrednio wpływa na funkcjonalność otrzymywanych nanostruktur [8,14,25,42,77]. Wymaga to zarówno poszukiwania nowych prekursorów dedykowanych tym technikom, jak i szczegółowego zbadania procesów termicznych oraz indukowanych elektronami, które wpływają na wydajność procesu dysocjacji.

Dlatego też celem pracy było:

opracowanie metod syntezy nowych, potencjalnych prekursorów FEBID i FIBID metali z grupy 10 oraz 11, a następnie przeprowadzenie dla nich systematycznych badań umożliwiających zrozumienie zależności między ich strukturą – w tym roli centrum koordynacji, a lotnością, stabilnością termiczną i czułością na elektrony.

Aby osiągnąć cele główne, niezbędne było zrealizowanie następujących zadań badawczych:

- opracowanie metody syntezy nowych związków koordynacyjnych metali: Ni, Pd, Cu, Ag oraz Au z przedstawionymi poniżej ligandami: **1)** O,O- i N-, **2)** N,N- lub N-, a także **3)** O,O-donorowymi (**Rysunek 11**), dedykowanych do metod osadzania z fazy gazowej oraz ich charakterystyka pod względem składu i struktury przy wykorzystaniu metod spektroskopowych, rentgenowskiej analizy strukturalnej oraz w oparciu o obliczenia teoretyczne;

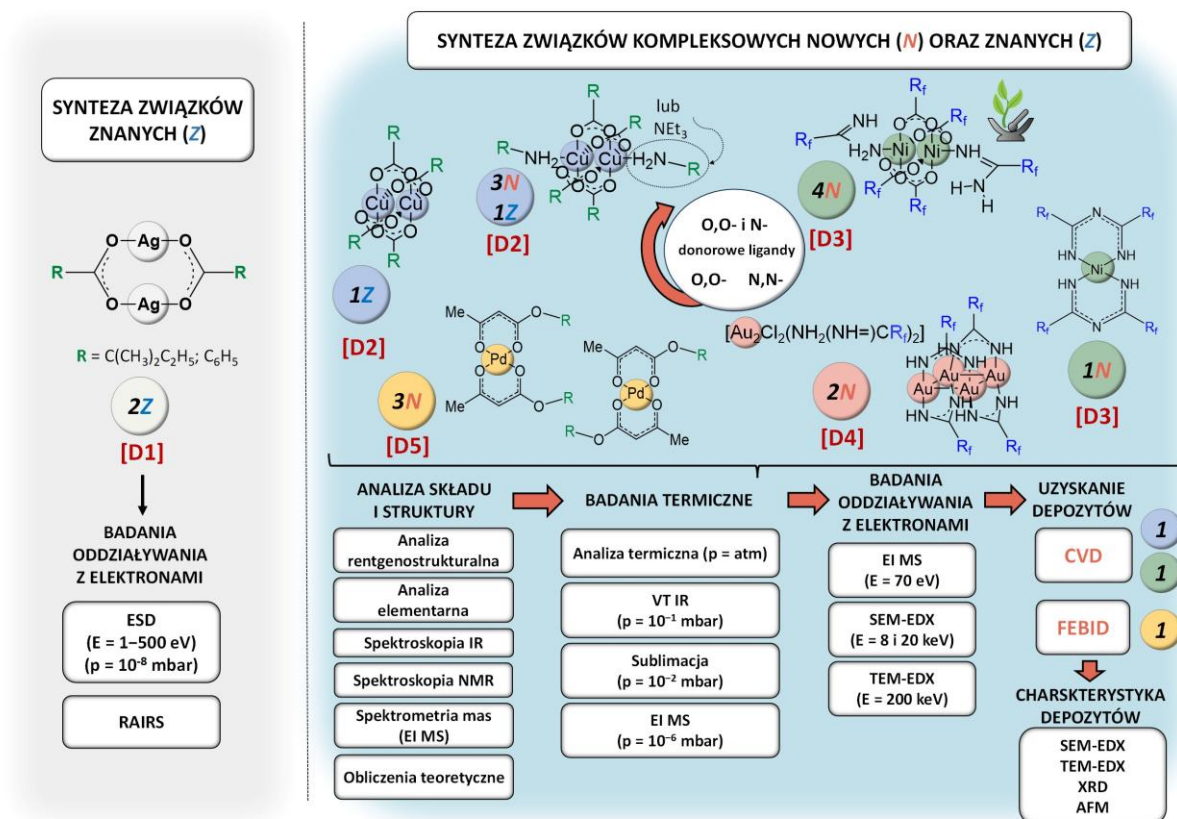


Rysunek 11 Wzory wykorzystanych ligandów: karboksylan (R/R_FCO_2), β -ketoesteran ($CH_3COCHCO_2R$), amidynian $R_FC(NH)_2$, imidoiloamidynian ($NHC(CF_3)NC(CF_3)NH$), amidyna ($R_FC(=NH)NH_2$) i amina (RNH_2).

- określenie stabilności termicznej i lotności nowych związków oraz wybranych połączeń literaturowych, które dotąd nie były analizowane pod tym kątem, a także zbadanie procesów i reakcji termicznych podczas ogrzewania pod ciśnieniem atmosferycznym i obniżonym;
- zbadanie oddziaływania związków koordynacyjnych metali oraz ich cząsteczek zaadsorbowanych na powierzchni substratu z elektronami wysoko- i niskoenergetycznymi;
- selekcja prekursorów do odpowiednich technik osadzania z fazy gazowej oraz otrzymanie depozytów w procesach CVD oraz FEBID, ich charakterystyka i próby zastosowania.

Dyskusja wyników

2.1 Metodologia

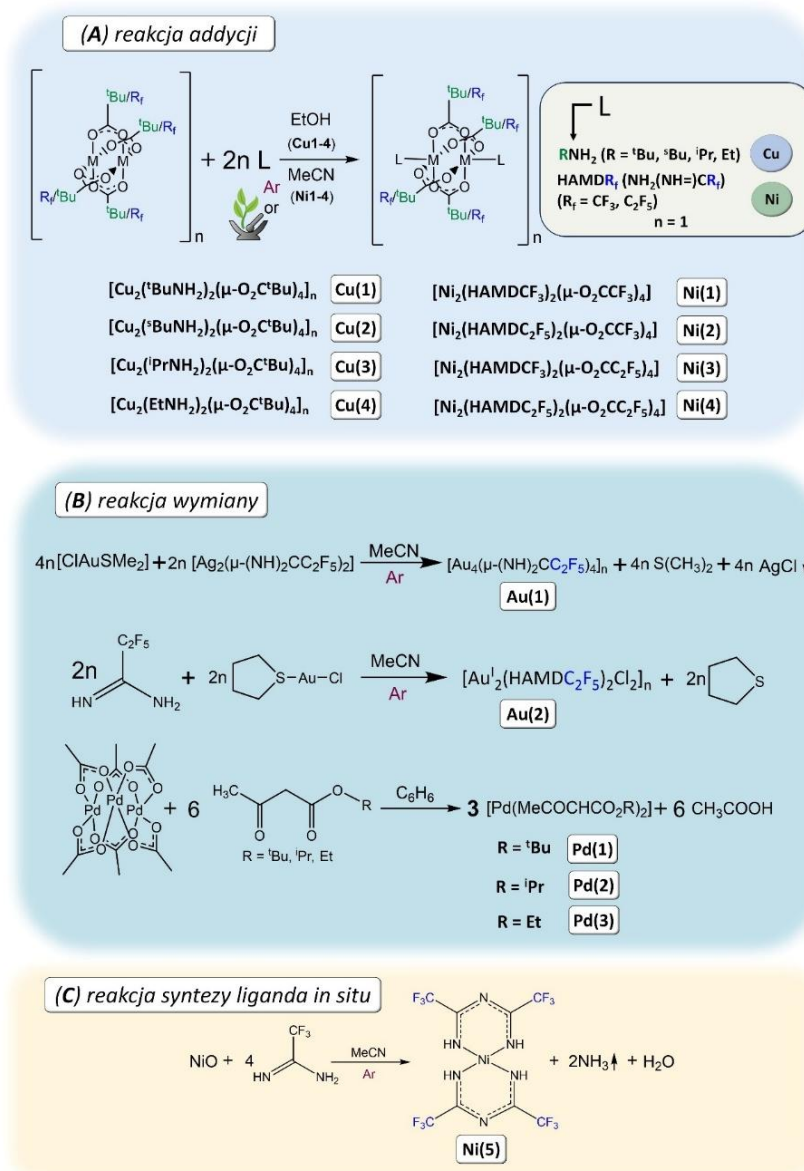


Rysunek 12 Metodologia badań zastosowana przy realizacji rozprawy doktorskiej.

2.2 Otrzymywanie kompleksów metali z grupy 10 i 11

W rozdziale 1.2 wykazano, że brakuje stabilnych prekursorów metali z grupy 10 i 11, które umożliwiałyby uzyskanie depozytów FEBID i FIBID o wysokiej czystości, bez konieczności stosowania procesu oczyszczania [8,14].

W ramach rozprawy doktorskiej opracowano metody syntezy (**Rysunek 13**) szeregu nowych związków kompleksowych metali z grupy 10 i 11, które tworzyły się na drodze reakcji: a) addycji **Cu(1)–Cu(4)** [D2], **Ni(1)–Ni(4)** [D3], b) wymiany **Pd(1)–Pd(3)** [D5], **Au(1), Au(2)** [D4], c) powstawania liganda *in situ* **Ni(5)** [D3].



Rysunek 13 Otrzymywanie nowych związków kompleksowych na drodze reakcji: addycji (A) **Cu(1)–Cu(4)** [D2], **Ni(1)–Ni(4)** [D3], wymiany (B) **Pd(1)–Pd(3)** [D5], **Au(1), Au(2)** [D4] i syntezy liganda *in situ* (C) **Ni(5)** [D3].

Wykorzystanie czułych na powietrze ligandów takich jak amidyny, a także kompleksów złota(I) jako substratów, wymagało zastosowania warunków beztlenowych. Istotnym jest, że uzyskane produkty wykazywały stabilność na powietrzu rzędu miesięcy **Ni(1)–Ni(4)** [D3], **Au(1)** [D4], czy tygodni **Au(2)** [D4] (*Rysunek 13*), co znacząco ułatwia ich użytkowanie, a w wypadku **Ni(5)** było to kilka dni [D2].

W przypadku związków z ligandami O,O- i N- donorowymi otrzymano nowe karboksylanowe kompleksy miedzi(II) z aminami alifatycznymi **Cu(1)–Cu(5)** [D2] oraz niklu(II) z amidyną **Ni(1)–Ni(4)** [D3].

Nowe kompleksy miedzi(II) **Cu(1)–Cu(4)** [D2] oraz znany w literaturze związek **Cu(5)** [D2] zsyntetyzowano zgodnie z uprzednio opracowaną procedurą, na drodze reakcji piwalanu miedzi(II) (w niniejszej pracy dla uproszczenia zastosowano nazwę zwyczajową *piwalan* zamiast systematycznej 2,2-dimetylopropionian) $[\text{Cu}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ **Cu(6)** [D2] z odpowiednią aminą, uzyskując układy polimeryczne $[\text{Cu}_2(\text{amina})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$, które są źródłem lotnych nośników metalu (*vide infra* – 2.4). Wydajność reakcji dla kompleksów **Cu(1)–Cu(4)** [D2] była na poziomie 60–70%.

Z kolei związki niklu(II) z perfluorowanymi amidynami na bazie karboksylanów $[\text{Ni}_2(\text{NH}_2(\text{NH}=\text{CR}_\text{F})_2(\mu\text{-O}_2\text{CR}_\text{F})_4)]$ ($\text{R}_\text{F} = \text{CF}_3, \text{C}_2\text{F}_5$) **Ni(1)–Ni(4)** [D3] (*Rysunek 12*, *Rysunek 13*) otrzymano na drodze reakcji karboksylanu niklu $[\text{Ni}_2(\mu\text{-O}_2\text{CR}_\text{F})_4]$ z odpowiednią amidyną. Należy podkreślić, że dla kompleksów **Ni(1)–Ni(4)** [D3] opracowano również warunki syntezy mechanochemicznej, która pozwoliła na skrócenie czasu syntezy z 24 h do kilku minut i uniknięcie użycia rozpuszczalnika, wpisując się tym samym w trend zielonej chemii. Wydajność syntezy metodą „klasyczną” wynosiła około 40%, natomiast zastosowanie metody mechanochemicznej pozwoliło na uzyskanie wyższej wartości, na poziomie 70%.

W trakcie prowadzonych badań ustalono również warunki otrzymywania nowych związków złota(I): amidynianu **Au(1)** oraz kompleksu z amidyną i ligandem chlorkowym **Au(2)** [D4] na drodze reakcji wymiany (*Rysunek 12*, *Rysunek 13*) osiągając wydajności na poziomie odpowiednio 70% i 40%.

W przypadku kompleksu z ligandem N,N-donorowym opracowano warunki syntezy nowego imidoiloamidynianu niklu(II) **Ni(4)** [D3], w trakcie której *in situ* powstaje symetryczny imidoiloamidynian podczas kondensacji amidyny w acetonitrylu. Otrzymany w wyniku reakcji produkt poddano oczyszczaniu metodą sublimacji, uzyskując końcową wydajność procesu około 13%.

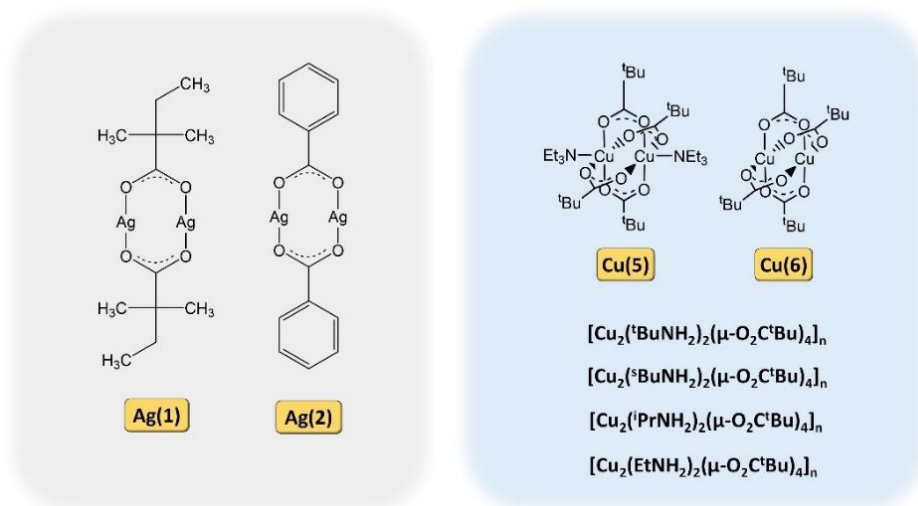
Natomiast dla kompleksów palladu **Pd(1)–Pd(3)** [D5] opracowano metodę syntezy, gdzie produkt tworzy się w reakcji octanu palladu(II) z β -ketoestrem (**Rysunek 12**, **Rysunek 13**). Dla tego typu związków uzyskano wysoką wydajność syntezy, sięgającą 70%.

Poprzez powolne odparowywanie rozpuszczalnika, w temperaturze pokojowej wyhodowano dziewięć monokryształów (*vide infra* – 2.3.1) odpowiednich do pomiarów dyfrakcyjnych (**Rysunek 15**):

- **Cu(1a)** $\rightarrow$ $[\text{Cu}_3(^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_6]_n$
- **Cu(2a)** $\rightarrow$ $[\text{Cu}_3(^s\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_6]_n$
- **Cu(3a)** $\rightarrow$ $[\text{Cu}_3(^i\text{PrNH}_2)_2(\mu_3\text{-OH})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$
- **Cu(4a)** $\rightarrow$ $[\text{Cu}_{20}(\text{EtNH}_2)_6(\mu_3\text{-OH})_{24}(\text{OH})(\text{H}_2\text{O})_5(\text{NO}_3)(\mu\text{-O}_2\text{C}^t\text{Bu})_8](^t\text{BuCO}_2)_6 \cdot 13\text{H}_2\text{O}$
- **Ni(5a)** $\rightarrow$ $[\text{Ni}(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH}_2)_2] \cdot (\text{NH}_4) \cdot (\text{CF}_3\text{CONH}) \cdot (\text{CF}_3\text{CONH}_2) \cdot \text{H}_2\text{O}$
- **Au(1)** $\rightarrow$ $[\text{Au}_4(\mu\text{-(NH)}_2\text{CC}_2\text{F}_5)_4]_n$
- **Pd(1)** $\rightarrow$ $[\text{Pd}(\text{MeCOCHCO}_2^t\text{Bu})_2]$
- **Pd(2)** $\rightarrow$ $[\text{Pd}(\text{MeCOCHCO}_2^i\text{Pr})_2]$
- **Pd(3)** $\rightarrow$ $[\text{Pd}(\text{MeCOCHCO}_2\text{Et})_2]$

Chcąc wykonać zaawansowane badania metodą ESD dla prekursora FEBID $[\text{Ag}_2(\mu\text{-O}_2\text{CC}(\text{CH}_3)_2\text{C}_2\text{H}_5)_2]$ (**Ag1**) i związku $[\text{Ag}_2(\mu\text{-O}_2\text{CC}_6\text{H}_5)_2]$ z podstawnikiem aromatycznym (**Ag2**) [D1] wykonano syntezy zgodnie z procedurą literaturową [78] (**Rysunek 12**, **Rysunek 14**) (*vide infra* – 2.5.2).

Grupy analizowanych związków uzupełniono o znane w literaturze kompleksy miedzi(II) $[\text{Cu}_2(\text{Et}_3\text{N})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]$ **Cu(5)** oraz $[\text{Cu}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ **Cu(6)** [D2] (**Rysunek 12**, **Rysunek 14**). Umożliwiło to zbadanie wpływu wprowadzenia aminy o wyższej rzędowości oraz karboksylanu analogicznego do $[\text{Ag}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_2]$ stosowanego w FEBID (57 at.% Ag) [8], a także oceny zmian właściwości fizykochemicznych wynikających ze zmodyfikowania sfery koordynacyjnej piwalanu miedzi(II) poprzez wprowadzenie N-donorowej aminy (*vide infra* – rozdział 2.4, 2.5).



Rysunek 14 Wzory literaturowe poddanych badaniom związków kompleksowych srebra(I) **Ag(1)**, **Ag(2)** [D1] oraz miedzi(II) **Cu(5)**, **Cu(6)** [D2] wraz z pozostałymi kompleksami piwalanowymi miedzi(II) **Cu(1)–Cu(4)**.

2.3 Budowa nowych związków kompleksowych

W celu określenia składu wyizolowanych nowych połączeń wykorzystano zarówno metody rentgenostrukturalne: **Cu(1a)–Cu(4a)** [D2], **Ni(5a)** [D3], **Au(1)** [D4], **Pd(1)–Pd(3)** [D5], jak i spektroskopowe: **Cu(1)–Cu(6)** [D2], **Ni(1)–Ni(5)** [D3], **Au(1)** i **Au(2)** [D4], **Pd(1)–Pd(3)** [D5].

2.3.1 Rentgenowska analiza strukturalna monokryształów

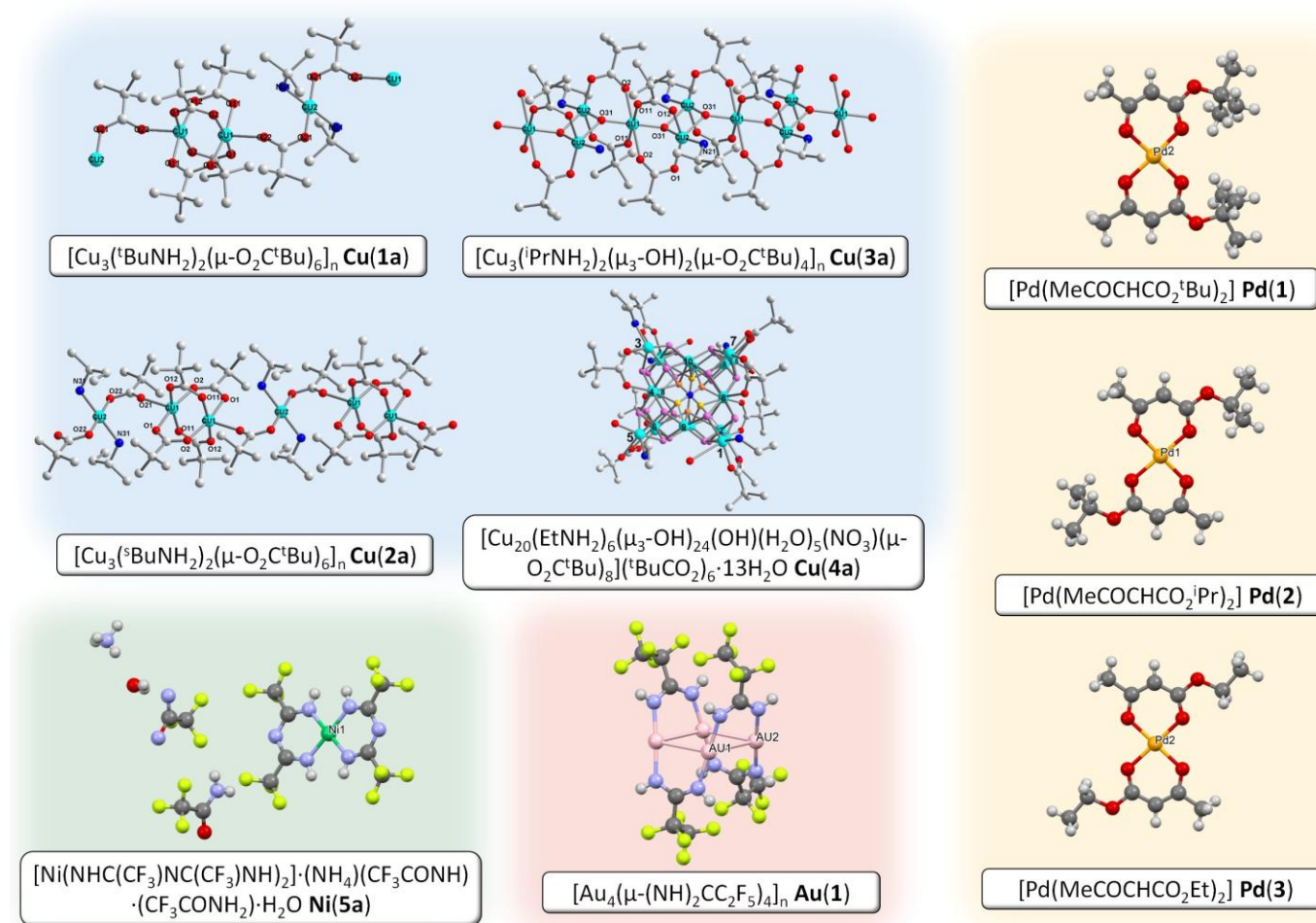
Na drodze utraty liganda aminowego z kompleksów piwalanowych o budowie ogólnej $[\text{Cu}_2(\text{amina})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ otrzymano trzy nowe **Cu(1a)–Cu(3a)** [D2], polimeryczne połączenia miedzi oraz dwudziestojądrowy kompleks **Cu(4a)** [D2] (**Rysunek 15**). Rentgenowska analiza strukturalna wykazała, że kompleksy **Cu(1a)** oraz **Cu(2a)** [D2] krystalizują w tej samej grupie przestrzennej $P2_1/n$ tworząc łańcuchy zbudowane z naprzemiennie ułożonych dimerów o strukturze koła łopatkowego (*ang. paddle-wheel*) oraz jednostek monojądrowych, połączonych razem asymetrycznymi mostkami karboksylowymi typu *syn-anti*. W strukturze obu związków zaobserwowano obecność mostków *syn-syn* w jednostce dimeru. W związku **Cu(3a)** [D2] krystalizującym w grupie przestrzennej $P\bar{1}$, podobnie jak dla **Cu(1a)** i **Cu(2a)** [D2], obserwowano tworzenie się układów polimerycznych, jednak ich topologia różniła się istotnie od wcześniejszych struktur, ponieważ w łańcuchu obserwowano mostki typu $\mu_3\text{-OH}$ łączące jony miedzi(II). Z kolei inicjatorem utworzenia odmiennej struktury dla kompleksu

dwudziestojądrowego $[\text{Cu}_{20}(\text{EtNH}_2)_6(\mu_3\text{-OH})_{24}(\text{OH})(\text{H}_2\text{O})_5(\text{NO}_3)(\mu\text{-O}_2\text{C}^t\text{Bu})_8](^t\text{BuCO}_2)_6 \cdot 13\text{H}_2\text{O}$ **Cu(4a)** [D2] prawdopodobnie był znajdujący się w centrum anion azotanowy(V). Stwierdzono, że związek **Cu(4a)** krystalizuje w układzie rombowym, w grupie przestrzennej Pbc_a. Osiem jonów miedzi(II) zlokalizowano w wierzchołkach zniekształconego sześcianu, natomiast pozostałe dwanaście na środkach jego krawędzi. Ponadto, jony miedzi(II) połączone były za pomocą 24 grup hydroksylowych, rozmieszczonych po cztery na każdej ścianie sześcianu, tworzących mostki typu $\mu_3\text{-OH}$, oraz ośmiu mostków karboksylanowych typu *syn-syn*. W pracy zostały scharakteryzowane wspomniane już dijądrowe karboksylanowe kompleksy miedzi(II) z aminami alifatycznymi $[\text{Cu}_2(\text{amina})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$, dla których nie uzyskano monokryształów. Ze względu na zbyt dużą masę cząsteczkową dla **Cu(4a)** i tworzenie polimerów koordynacyjnych **Cu(1a)–Cu(3a)** [D2], związki te nie zostały zbadane pod kątem możliwości zastosowania ich w metodach osadzania z fazy gazowej.

W przypadku niklu otrzymano związek $[\text{Ni}(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH})_2] \cdot (\text{NH}_4)(\text{CF}_3\text{CONH}) \cdot (\text{CF}_3\text{CONH}_2) \cdot \text{H}_2\text{O}$ **Ni(5a)** [D3] (*Rysunek 15*) krystalizujący w układzie P $\bar{1}$. W jednostce asymetrycznej obserwowano cząsteczki kompleksu $[\text{Ni}(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH})_2]$ **Ni(5)** [D3] wraz z kationem amonowym, amidanem (CF_3CONH^-), cząsteczką amidu (CF_3CONH_2) oraz wody. W sferze koordynacyjnej niklu znajdowały się chelatowo związane dwa symetryczne ligandy imidoiloamidynianowe. Analiza powierzchni Hirshfelda wykazała obecność licznych oddziaływań międzycząsteczkowych w strukturze **Ni(5a)** [D3], co nie jest korzystne w kontekście potencjalnego zastosowania tego związku w metodach osadzania z fazy gazowej.

Natomiast dla złota uzyskano stabilny na powietrzu amidynian złota(I) **Au(1)** [D4] (*Rysunek 15*), krystalizujący w grupie przestrzennej I2/a. Obserwowano tetrameryczne podjednostki złożone z czterech kationów złota(I) połączonych ze sobą mostkami amidynianowymi oraz silnymi wiązaniami aurofilowymi (około 3.03 Å). Natomiast tetrametry związane były ze sobą wyłącznie słabymi wiązaniami aurofilowymi (około 3.3 Å) tworząc nieskończone łańcuchy. Analiza powierzchni Hirshfelda wykazała, że najliczniejsze oddziaływania międzycząsteczkowe stanowią jedynie kontakty typu F $\cdots$ F, co przyczynia się do lotności, a więc sprzyja potencjalnemu zastosowaniu **Au(1)** [D4] w metodach osadzania z fazy gazowej.

Dla wszystkich β -ketoesteranów palladu **Pd(1)–Pd(3)** [D5] udało się wyizolować monokryształy z chelatowo związanymi ligandami O,O-donorowymi (*Rysunek 15*). Dla połączenia **Pd(1)** [D5] obserwowano ułożenie grup tert-butyłowych w pozycji *cis*, natomiast dla **Pd(2)** oraz **Pd(3)** [D5] odpowiednio grupy izopropylowe i etylowe znajdowały się w położeniu *trans*. Na podstawie analizy powierzchni Hirshfelda, we wszystkich strukturach stwierdzono, że dominującą rolę odgrywają słabe międzycząsteczkowe oddziaływania van der Waalsa, co wraz z niewielką masą cząsteczkową kompleksów sugerowało możliwość potencjalnego zastosowania tych związków w metodach osadzania z fazy gazowej.



Rysunek 15 Struktury krystaliczne: karboksylanowych kompleksów miedzi(II) z aminami alifatycznymi **Cu(1a)–Cu(4a)** [D2], imidoiloamidynianu niklu(II) **Ni(5a)** [D3] i amidynianu złota(I) **Au(1)** [D4] oraz β -ketoesteranów palladu(II) **Pd(1)–Pd(3)** [D5].

2.3.2 Metody spektroskopowe

Analizę widm w podczerwieni (IR), magnetycznego rezonansu jądrowego (NMR), spektrometrii mas z jonizacją elektronami (EI MS) zastosowano, w celu potwierdzania koordynacji ligandów oraz zaproponowania budowy nowych kompleksów, dla których nie uzyskano monokryształów. W oparciu o nią potwierdzano również budowę kompleksów, dla których została przeprowadzona analiza rentgenostrukturalna, a także fakt otrzymania połączeń literaturowych ($[\text{Ag}_2(\mu\text{-O}_2\text{CC}(\text{CH}_3)_2\text{C}_2\text{H}_5)_2]$ **Ag(1)**, $[\text{Ag}_2(\mu\text{-O}_2\text{CC}_6\text{H}_5)_2]$ **Ag(2)** **[D1]** oraz $[\text{Cu}_2(\text{Et}_3\text{N})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]$ **Cu(5)**, $[\text{Cu}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ **Cu(6)** **[D2]**). Wykorzystano również metody obliczeniowe w celu określania sposobu koordynacji N-donorowej amidyny w karboksylanowych kompleksach niklu(II) **Ni(1)–Ni(4)** oraz tworzenie symetrycznego imidoiloamidynianu, związanego w kompleksie **Ni(5)** **[D3]**.

Dla dijądrowych karboksylanowych kompleksów miedzi(II) z aminami w pozycji aksjalnej $[\text{Cu}_2(\text{amina})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ **Cu(1)–Cu(4)** **[D2]** w oparciu o analizę widm EI MS, w których obserwowano jony trijądrowe potwierdzono tworzenie polimerów koordynacyjnych. W widmie IR kompleksu $[\text{Cu}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ **Cu(6)** **[D2]**, który znany jest jako układ polimeryczny $[\text{Cu}_2(\mu_3\text{-O}_2\text{C}^t\text{Bu})_2(\mu_2\text{-O}_2\text{C}^t\text{Bu})_2]_n$ obserwowano dwa pasma przypisane drganiom ν_{asCOO} . Analogiczne sygnały były również obecne widmach $[\text{Cu}_2(\text{amina})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ **Cu(1)–Cu(4)** **[D2]**, co świadczy o tworzeniu się tego typu układów.

Z kolei dla karboksylanowych związków niklu(II) z amidynami $[\text{Ni}_2(\text{HAMDR}_F)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (HAMD – $(\text{NH}_2(\text{NH}=\text{CR}_F))$) **Ni(1)–Ni(4)** **[D3]**, w oparciu o wyniki analizy widm EI MS, w których obserwowano jony $[\text{Ni}_2(\text{HAMDR}_F)(\text{O}_2\text{CR}_F)_3]^+$ oraz $[\text{Ni}_2(\text{HAMDR}_F)_2(\text{O}_2\text{CR}_F)]^+$, potwierdzono koordynację obu ligandów oraz tworzenie układów dijądrowych. Na podstawie analizy widm IR oraz w oparciu o obliczenia teoretyczne zaproponowano mostkowy sposób koordynacji karboksylanów oraz dwa sposoby wiązania amidyny, jednej cząsteczki w dimerze poprzez grupę $=\text{NH}$, a drugiej przez NH_2 .

Dla imidoiloamidynianu niklu(II) $[\text{Ni}(\text{IAMDCF}_3)_2]$ (IAMDCF₃ – $\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH}$) **Ni(5)** **[D3]**, na podstawie teoretycznego widma IR zasymulowanego w oparciu o strukturę kompleksu **Ni(5a)** **[D3]** wykazano tworzenie monojądrowego kompleksu z chelatowo skoordynowanymi ligandami imidoiloamidynianowymi. Dodatkowo, analiza wspomnianych widm IR potwierdziła tworzenie związku zawierającego symetryczne ligandy imidoiloamidynianowe, co

odróżnia go od wcześniej uzyskanych w grupie badawczej niesymetrycznych imidoiloamidynianów miedzi(II) [76].

Na podstawie widm IR dla amidynianu złota(I) $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ **Au(1)** [D4] potwierdzono deprotonację amidyny i wiązanie liganda amidynianowego poprzez atomy azotu do jonów złota ($\nu_{\text{Au-N}}$ ok. 563 cm^{-1}). Dla chlorkowego kompleksu złota(I) z amidyną $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ **Au(2)** [D4] w oparciu o spektroskopię w podczerwieni potwierdzono jej N-donorową koordynację oraz wiązanie anionów chlorkowych do jonów złota(I).

W przypadku kompleksów palladu(II) z β -ketoesteranami $[\text{Pd}(\text{CH}_3\text{COCHCO}_2\text{R})_2]$ $\text{R} = ^t\text{Bu}, ^i\text{Pr}, \text{Et}$ **Pd(1)–Pd(3)** [D5] tworzenie układu monojądrowego i chelatowy sposób koordynacji ligandów potwierdzono również w oparciu analizę widm IR eksperymentalnych oraz teoretycznych, a także ^1H , ^{13}C NMR, które potwierdziły deprotonację cząsteczki β -ketoestru. Wyniki te zostały potwierdzone również w oparciu o analizę widm EI MS, w których obserwowano jony molekularne $[\text{Pd}(\text{CH}_3\text{COCHCO}_2\text{R})_2]^+$.

2.4 Badanie stabilności termicznej i lotności

Jak wspomniano w rozdziale 1 lotność jest jedną z kluczowych cech prekursorów w metodach CVD, FEBID i FIBID. Badania przeprowadzone zarówno pod ciśnieniem atmosferycznym, jak i obniżonym, pozwalają na określenie zdolności związku do generowania lotnych nośników metalu oraz oszacowanie temperatury jego sublimacji. W celu określenia właściwości termicznych badanych związków, w niniejszej pracy zastosowano szereg metod takich jak: klasyczna analiza termiczna ($p = \text{atm}$), sublimacja pod obniżonym ciśnieniem ($p = 10^{-2}\text{ mbar}$), zmiennotemperaturowa spektroskopia w podczerwieni (VT IR, *ang. variable temperature infrared spectroscopy*) ($p = 10^{-1}\text{ mbar}$) oraz wspomniana już spektrometria mas z jonizacją elektronami (EI MS, *ang. electron impact mass spectrometry*) ($p = 10^{-6}\text{ mbar}$).

2.4.1 Analiza termiczna

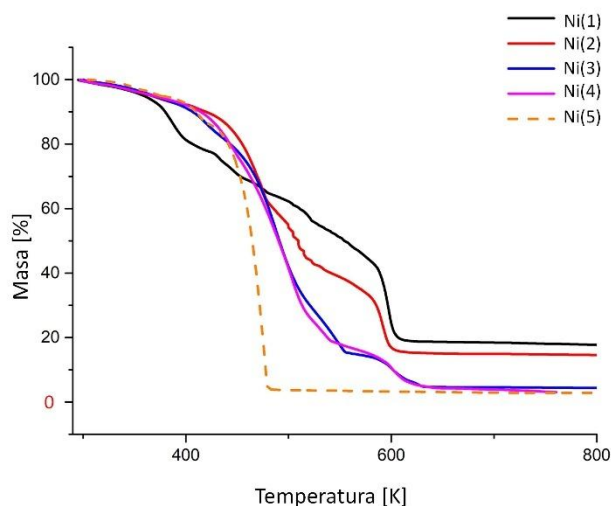
Analizę termiczną (TA) wykonano w celu określenia stabilności termicznej kompleksów oraz identyfikacji stałych i gazowych produktów rozkładu.

Z punktu widzenia możliwości zastosowania związku w roli prekursora w metodach osadzania z fazy gazowej korzystne jest kiedy już w warunkach analizy termicznej dochodzi do generowania lotnych nośników metalu. W efekcie, po procesie ogrzewania nie obserwuje się pozostałości lub jej masa jest poniżej zawartości metalu w związku. Takie zachowanie może świadczyć o znacznej stabilności termicznej związku. Należy tutaj jednak zaznaczyć, że zbyt duża stabilność termiczna może być problemem dla rozkładu związku w warunkach procesu CVD. Z drugiej strony potencjalne prekursory o niskiej stabilności ulegają przedwczesnemu rozkładowi, co skutkuje utratą kontroli nad przebiegiem procesu osadzania.

Należy zaznaczyć, że rozkład termiczny związków w warunkach analizy TA nie wyklucza ich z grona potencjalnych prekursorów stosowanych w technikach osadzania z fazy gazowej. Wynika to z faktu, że procesy te prowadzone są w warunkach obniżonego ciśnienia ($\text{CVD} \rightarrow 10^{-1}$ mbar; $\text{FEBID, FIBID} \rightarrow 10^{-6}$ mbar), co może skutkować obniżeniem temperatury transferu cząsteczek do fazy gazowej. W związku z tym analiza termiczna stanowi wstępny etap w ocenie przydatności danego związku.

Na podstawie wyników analizy termicznej stwierdzono, że karboksylanowe związki miedzi(II) z aminami $[\text{Cu}_2(\text{amina})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ **Cu(1)–Cu(4)**, pomimo polimerycznej budowy oraz $[\text{Cu}_2(\text{Et}_3\text{N})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]$ **Cu(5)** [D2], a także kompleksy niklu z amidynami $[\text{Ni}_2(\text{NH}_2(\text{NH=})\text{CR}_F)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ **Ni(3)** i **Ni(4)** [D3], w warunkach prowadzenia procesu tworzą nośniki metalu w fazie gazowej, co było również obserwowane dla prekursora FEBID $[\text{Ag}_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_2]$ (*Rysunek 17*). Dodatkowo wyniki uzyskane dla związków niklu świadczą o tym, że długość perfluorowanego łańcucha ma wpływ na tworzenie się finalnych produktów rozkładu, a występowanie grup C_2F_5 sprzyja generowaniu lotnych nośników metalu [8,76].

Spośród badanych związków efekt sublimacji był obserwowany wyraźnie dla imidoiloamidynian niklu(II) **Ni(5)** [D3] (*Rysunek 16*).



Rysunek 16 Analiza termograwimetryczna dla kompleksów **Ni(1)–Ni(5)** [D3].

Z kolei dla amidynianu $[\text{Au}_4(\mu\text{-(NH)}_2\text{CC}_2\text{F}_5)_4]_n$ **Au(1)** [D4] masa pozostałości po procesie była bliska wartości teoretycznej dla złota, co świadczy o utracie ligandów amidynianowych w trakcie procesu i wskazuje na tworzenie metalu jako finalnego produktu rozkładu. W przypadku wcześniej badanych w naszej grupie badawczej amidynianów miedzi(I) $[\text{Cu}_2(\mu\text{-AMDC}_2\text{F}_5)_2]$ i srebra(I) $[\text{Ag}_2(\mu\text{-AMDC}_2\text{F}_5)_2]$ (AMD – $(\text{NH})_2\text{CC}_2\text{F}_5$) potwierdzono, że związki te stanowią źródło metali w fazie gazowej już pod ciśnieniem atmosferycznym. Różnice te prawdopodobnie wynikają z dimerycznej budowy tych związków w odniesieniu do łańcucha złożonego z tetramerów dla kompleksu złota(I) [76].

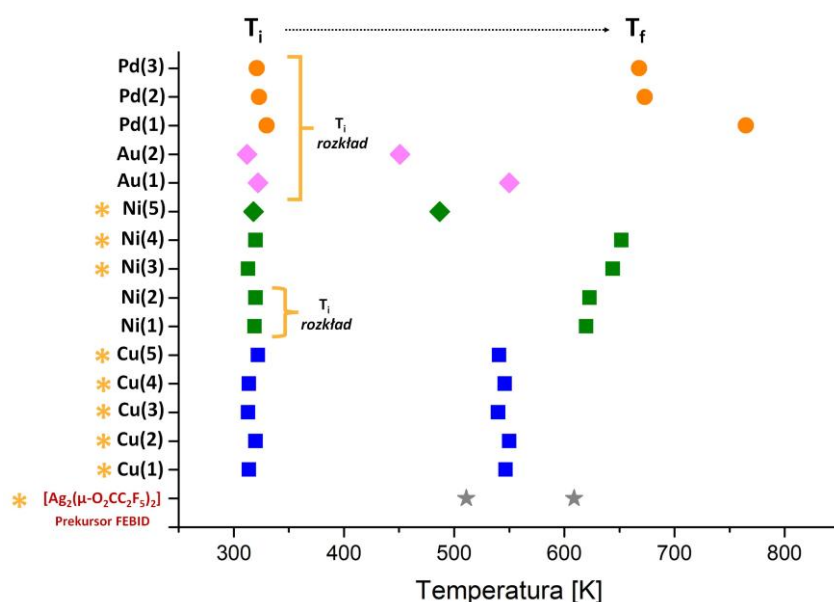
W przypadku $[\text{Au}_2\text{Cl}_2((\text{NH}_2(\text{NH}=\text{CC}_2\text{F}_5)_2)]_n$ **Au(2)** [D4] pierwszy etap procesu odpowiada wydzielaniu chlorowodoru, powstałego w wyniku deprotonacji cząsteczek amidyny poprzez aniony chlorkowe, co jest zgodne z wynikami VT IR oraz EI MS (*vide infra* – 2.4.3, 2.5.1). Masa pozostałości po procesie była bliska wartościom teoretycznym dla złota. Świadczy to o jego tworzeniu się jako końcowego produktu rozkładu, co zostało potwierdzone również w oparciu o uzyskany dyfraktogram proszkowy.

Natomiast, dla β -ketoesteranów palladu **Pd(1)–Pd(3)** [D5] na termogramach obserwowano jedynie jeden etap rozkładu z utworzeniem finalnie palladu i węgla. Stanowią, więc one przykład związków, które wymagają zastosowania obniżonego ciśnienia w celu transportu nośników metalu do fazy gazowej (*vide infra* – 2.4.2, 2.4.4).

Podsumowując, dla związków wchodzących w skład niniejszej rozprawy doktorskiej obserwowano szerszy zakres temperaturowy pomiędzy temperaturą

początkową T_i , a końcową T_f w porównaniu do prekursora FEBID [$\text{Ag}_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_2$] (będzie on stanowił pewien odnośnik w przeprowadzonych badaniach) (**Rysunek 17**). Temperatury T_i odnotowano w zakresie 314–330 K. Natomiast najniższą temperaturę T_f obserwowano dla kompleksu [$\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2$]_n **Au(2)** [**D4**] (451 K), a najwyższą dla [$\text{Pd}(\text{tbaoac})_2$] **Pd(1)** [**D5**] (765 K). Warto nadmienić, że temperatura odparowania prekursorów w zakresie 373–573 K jest uznawana za korzystną w procesie CVD [79,80].

Na podstawie wyników analizy termicznej stwierdzono, że kompleksy [$\text{Cu}_2(\text{amina})_2(\mu\text{-O}_2\text{C}^i\text{Bu})_4$]_n **Cu(1)–Cu(4)** [**D2**] oraz [$\text{Ni}_2(\text{HAMDR}_F)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4$] **Ni(3)**, **Ni(4)** [**D3**] wykazują parametry korzystne z punktu widzenia zastosowania ich w procesie CVD ze względu na ich stabilność termiczną oraz możliwość generowania lotnych nośników metalu w stosunkowo niskich temperaturach. Potencjalnie związki **Cu(5)** [**D2**] oraz **Ni(5)** [**D3**] są obiecujące, ale wymagają dalszego zbadania w celu pełnej oceny ich przydatności.

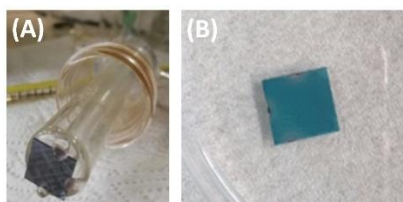


★ – prekursor FEBID, związki z: ■ – karboksylanami i ligandem N-donorowym, ◆ – ligandami N,N- lub N-donorowymi oraz ● – O,O-donorowymi, gwiazdką (*) – związki, które częściowo przechodzą do fazy gazowej w trakcie procesu

Rysunek 17 Temperaturowe początkowe (T_i) i końcowe (T_f) procesów obserwowanych podczas analizy termicznej dla związków (od dołu): [$\text{Ag}_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_2$], **Cu(1)–Cu(5)** [**D2**], **Ni(1)–Ni(5)** [**D3**], **Au(1)** i **Au(2)** [**D4**], **Pd(1)–Pd(3)** [**D5**].

2.4.2 Sublimacja

Zdolność związków do sublimacji jest pożądaną cechą w metodach osadzania z fazy gazowej. W celu oceny lotności potencjalnych prekursorów oraz wyznaczenia ich temperatury sublimacji, przeprowadzono takie próby w warunkach obniżonego ciśnienia (10^{-2} mbar). Zastosowanie sublimatora z uchwytem na podłożu krzemowe umożliwiło przygotowanie na nim warstw związków (**Rysunek 18**), które następnie wykorzystano w badaniu oddziaływania zaadsorbowanych na powierzchni cząsteczek z wiązką elektronów wysokoenergetycznych (*vide infra* – 2.5). Ze względu na wcześniej wyznaczoną zależność eksperymentalną sublimacja stanowi również wstępny etap dla oszacowania odpowiedniej temperatury GIS. Przykładowo temperatura sublimacji dla $[\text{Ag}_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_2]$ wynosiła 423 K, a w systemie GIS zastosowano temperaturę 423–453 K [8].



Rysunek 18 (A) Zdjęcie sublimatora z podłożem krzemowym, (B) warstwa uzyskana dla kompleksu $[\text{Cu}_2(\text{tBuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ **Cu(1)** [**D2**] w procesie sublimacji.

Próbie sublimacji podjęto dla wszystkich nowych związków oraz **Cu(5)**, **Cu(6)** [**D2**]. Jednak kompleksy $[\text{Ni}_2(\text{HAMDR}_F)_2(\mu\text{-O}_2\text{CR}_F)_4]$ **Ni(1)–Ni(3)** [**D3**] oraz $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ **Au(2)** [**D4**] jej nie ulegały.

Na podstawie wyników dla piwalanowych kompleksów miedzi(II) $[\text{Cu}_2(\text{amina})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ stwierdzono, że addycja liganda drugorzędowego w postaci aminy pierwszorzędowej **Cu(1)–Cu(4)** do piwalanu **Cu(6)** [**D2**] obniża temperaturę sublimacji o około 35–55 K. Natomiast związek **Cu(5)** z aminą trzeciorzędową [**D2**] nie ulegał sublimacji, ale był źródłem piwalanu miedzi **Cu(6)**, w niższej o ok. 25 K temperaturze [**D2**], co również jest korzystne z punktu widzenia zastosowania.

Z kolei temperatura sublimacji dla $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ **Ni(4)** [**D3**] była o 30 K wyższa w porównaniu z analogicznym kompleksem miedzi(II) $[\text{Cu}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (rozdział 1.4) otrzymanym w ramach badań prowadzonych w naszej grupie badawczej [72]. Należy też nadmienić, że wszystkie kompleksy $[\text{Cu}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CR}_F)_4]$ ($\text{R}_F = \text{CF}_3, \text{C}_2\text{F}_5, \text{C}_3\text{F}_7, \text{C}_4\text{F}_9$) ulegały

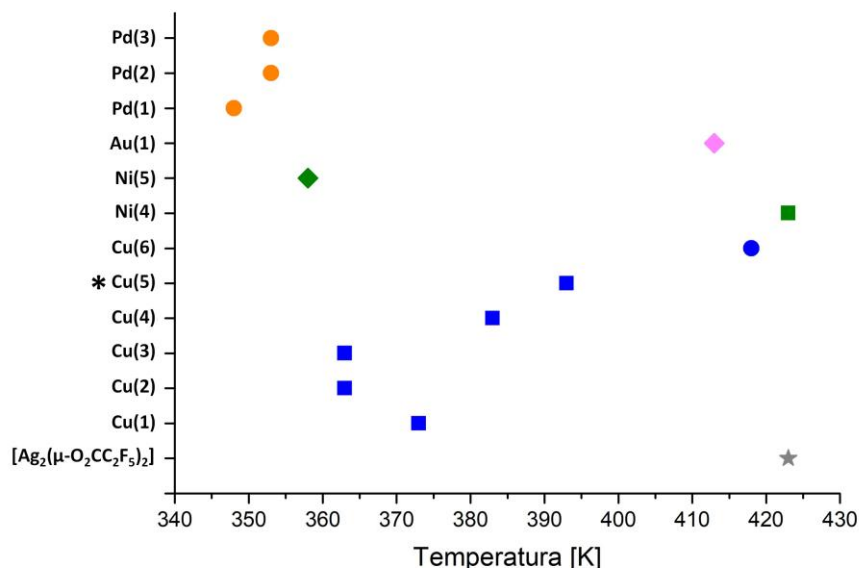
sublimacji w przeciwieństwie do analogów niklowych. Zaobserwowane różnice sugerują istotny wpływ centrum koordynacyjnego na parametry fizykochemiczne związków.

Dla symetrycznego imidoiloamidynianu niklu $[\text{Ni}(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH})_2]$ **Ni(5)** [D3] odnotowano z kolei niższą temperaturę sublimacji (358 K) niż dla kompleksów miedzi(II) z niesymetrycznymi imidoiloamidynianami $[\text{Cu}(\text{NHC}(\text{CH}_3)\text{NC}(\text{R}_F)\text{NH})_2]$ ($\text{R}_F = \text{CF}_3, \text{C}_2\text{F}_5$) (373 K) [76].

Natomiast amidynian złota(I) $[\text{Au}_4(\mu\text{-(NH)}_2\text{CC}_2\text{F}_5)_4]_n$ **Au(1)** [D4] (413 K) sublimował w stosunkowo wysokiej temperaturze 413 K, jednak wciąż niższej niż dla prekursora FEBID $[\text{Ag}_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_2]$ (423 K) [8]. Może to być związane z obecnością słabych wiązań aurofilowych pomiędzy jednostkami tetramerycznymi (2.3.1). W przypadku kompleksów, $[\text{Cu}_2(\mu\text{-AMDC}_2\text{F}_5)_2]$ odnotowano niższą (373 K), a dla $[\text{Ag}_2(\mu\text{-AMDC}_2\text{F}_5)_2]$ analogiczną (413 K) temperaturę sublimacji. Zaobserwowane różnice mogą wynikać z niższej masy amidynianu miedzi.

Dla $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ **Au(2)** [D4] podjęto próbę sublimacji, którą przeprowadzono do osiągnięcia temperatury 353 K. Zaobserwowane różnice w kształcie i położeniu pasm w widmach IR kompleksu wyjściowego oraz powstałej warstwy wskazują, że zaadsorbowane zostały cząsteczki amidynianu złota(I) $[\text{Au}_4(\mu\text{-(NH)}_2\text{CC}_2\text{F}_5)_4]_n$ **Au(1)** [D4], będącego produktem rozkładu termicznego kompleksu **Au(2)** [D4], w efekcie deprotonacji amidyny i wydzielania się chlorowodoru (*vide infra* – 2.4.4). Intensywność sygnałów była jednak niewielka, co wskazuje na utworzenie się cienkiej warstwy związku.

β -ketoesterany palladu **Pd(1)–Pd(3)** [D5] charakteryzowały się najniższymi temperaturami sublimacji (348 oraz 353 K) spośród uzyskanych połączeń. Istotny jest fakt, że temperatura ta (**Rysunek 19**) jest już zbliżona do temperatury około 333 K, w jakiej wykorzystywany jest komercyjny prekursor platynowy pod dużo niższym ciśnieniem (10^{-6} mbar) [8]. Jak już wspomniano (2.3.1) na podstawie analizy powierzchni Hirshfelda stwierdzono, że największy udział mają oddziaływania $\text{H}\cdots\text{H}$, które są typowe dla słabych oddziaływań typu van der Waalsa. Słabe oddziaływania międzycząsteczkowe występujące dla kompleksów **Pd(1)–Pd(3)** [D5] sprzyjają ich lotności, co czyni je potencjalnymi kandydatami do zastosowań w procesach osadzania z fazy gazowej, szczególnie FEBID i FIBID, gdzie ze względu na specyfikę aparatury wymagane jest zastosowanie stosunkowo niskich temperatur parowania lub sublimacji (313–353 K) pod ciśnieniem 10^{-6} mbar.



★ – prekursor FEBID, związki z: ■ – karboksylanami i ligandem N-donorowym, ◆ – ligandami N,N-donorowymi oraz ● – O,O-donorowymi

Rysunek 19 Temperatury sublimacji ($p = 10^{-2}$ mbar) dla związków (od dołu): $[Ag_2(\mu-O_2CC_2F_5)_2]$, **Cu(1)–Cu(6)** [D2], **Ni(4)** i **Ni(5)** [D3], **Au(1)** [D4], **Pd(1)–Pd(3)** [D5].

Dla piwalanowych kompleksów miedzi(II) **Cu(1)–Cu(6)** [D2], imidoiloamidynianu niklu(II) **Ni(5)** [D3], amidynianu złota(I) **Au(1)** [D4], β-ketoesteranów palladu(II) **Pd(1)–Pd(3)** [D5] obserwowano niższą lub porównywalną w przypadku $[Ni_2(HAMDC_2F_5)_2(\mu-O_2CC_2F_5)_4]$ **Ni(4)** [D3], temperaturę sublimacji względem prekursora FEBID $[Ag_2(\mu-O_2CC_2F_5)_2]$ (**Rysunek 19**) [8,81]. Czyni to je atrakcyjnymi kandydatami pod kątem wykorzystania w metodzie CVD, a także procesach FEBID i FIBID z użyciem eksperymentalnego systemu GIS.

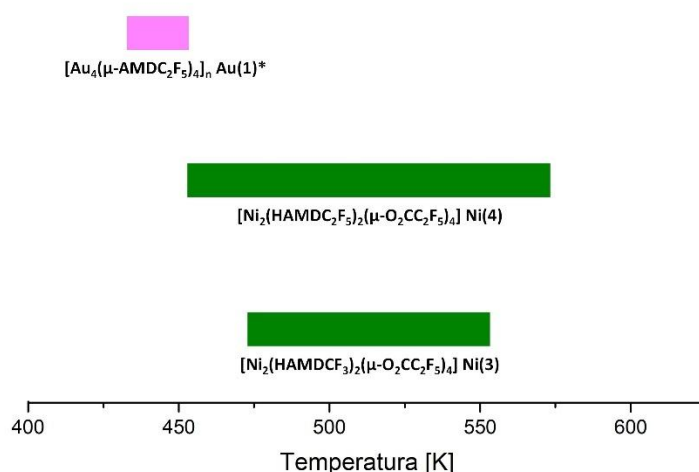
2.4.3 Zmiennotemperaturowa spektroskopia w podczerwieni

Widma zmiennotemperaturowej spektroskopii w podczerwieni (VT IR) zarejestrowano w celu zbadania składu fazy gazowej w trakcie ogrzewania kompleksów, a także oszacowania ich temperatur odparowania, pod kątem procesu CVD, ponieważ ciśnienie zastosowane w reaktorze CVD jest zbliżone do panującego podczas analizy VT IR ($p = 10^{-1}$ mbar).

Do badań wybrano kompleksy niklu(II) z karboksylanami i amidynami $[Ni_2(HAMDR_F)_2(\mu-O_2CR_F)_4]$ **Ni(1)–Ni(4)** [D3] w celu oceny wpływu centrum koordynacji

na temperaturę, w której generowane są lotne nośniki metalu, względem wcześniej opisywanych kompleksów miedzi(II) $[\text{Cu}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CR}_\text{F})_4]$ [72].

W widmach związków $[\text{Ni}_2(\text{HAMDR}_\text{F})_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$, gdzie $\text{R}_\text{F} = \text{CF}_3$, C_2F_5 obserwowano pasma charakterystyczne dla cząsteczek kompleksu **Ni(3)** [D3] w zakresie 473–553 K oraz dla **Ni(4)** [D3] w temperaturze 453–573 K (**Rysunek 20**). Z kolei w przypadku połączeń trifluorooctanowych $[\text{Ni}_2(\text{HAMDR}_\text{F})_2(\mu\text{-O}_2\text{CCF}_3)_4]$ **Ni(1)** oraz **Ni(2)** [D3] w widmach VT IR nie zarejestrowano pasm świadczących o występowaniu cząsteczek kompleksów pierwotnych w fazie gazowej. Obecność połączeń **Ni(3)** oraz **Ni(4)** [D3] w fazie gazowej potwierdza, że karboksylany zawierające grupy C_2F_5 sprzyjają generowaniu nośników metalu [75,76]. Trzeba również zaznaczyć, że w przypadku związku **Ni(4)** [D3] zawierającego wyłącznie pentafluorowane podstawniki $\text{R}_\text{F} = \text{C}_2\text{F}_5$ obserwowano niższą temperaturę odparowania (453 K) w stosunku do kompleksu **Ni(3)** (473 K) [D3]. Istotny jest również fakt, że temperatura odparowania dla związków miedzi(II) $[\text{Cu}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CR}_\text{F})_4]$ $\text{R}_\text{F} = \text{CF}_3$, C_2F_5 , C_3F_7 , C_4F_9 (353–553 K) [72] była niższa o około 100 K wskazując, że zmiana centrum koordynacji $\text{Cu} \rightarrow \text{Ni}$ wpływa na jej podwyższenie temperatury odparowania.



Rysunek 20 Zakresy temperatur, w których obserwowano nowe komplekсы w fazie gazowej (VT IR, $p = 10^{-1}$ mbar) dla związków (od dołu): **Ni(3)**, **Ni(4)** [D3] oraz **Au(1)** wygenerowanego w trakcie ogrzewania **Au(2)** [D4].

Wykonano również pomiary dla związku złota(I) $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ **Au(2)** [D4], który w warunkach sublimacji (10^{-2} mbar) ulegał rozkładowi, aby określić skład fazy gazowej w trakcie jego ogrzewania.

Analiza widm VT IR dla kompleksu **Au(2)** [D4] potwierdziła wydzielanie chlorowodoru w trakcie procesu i obecność amidynianu złota(I) **Au(1)** w fazie gazowej [D4] począwszy

od 433 K do 453 K (**Rysunek 20**), co jest zgodne z wynikami analizy termicznej oraz próby sublimacji (**2.4.1**, **2.4.2**). Nośnik złota, czyli związek **Au(1)** [**D4**] był obserwowany w węższym zakresie temperatur niż wspomniane kompleksy niklu **Ni(3)** oraz **Ni(4)** 433–453 K, co może być mniej korzystne pod kątem zastosowania **Au(2)** [**D4**] w metodzie CVD, chociaż z drugiej strony niższa temperatura odparowania jest w niej pożądana.

Podsumowując związki **Ni(3)** oraz **Ni(4)** [**D3**] były obiecującymi kandydatami do wykorzystania w procesie CVD. Natomiast **Au(2)** [**D4**] jest interesujący ze względu na możliwość generowania lotnych nośników metalu w formie **Au(1)**, ale jego próba wykorzystania nie będzie klasycznym przykładem procesu CVD. Natomiast, należy zaznaczyć, że efektywne generowanie nośnika metalu w efekcie reakcji chemicznej było już wykorzystane dla kompleksów $[\text{Ag}(\text{NH}_2^t\text{Bu})_2](\text{R}_\text{F}\text{CO}_2) \cdot x\text{H}_2\text{O}$ ($\text{R}_\text{F} = \text{CF}_3$, $x = 0.5$; $\text{R}_\text{F} = \text{C}_2\text{F}_5$, C_5F_{11} , C_6F_{13} , $x = 0$) [82].

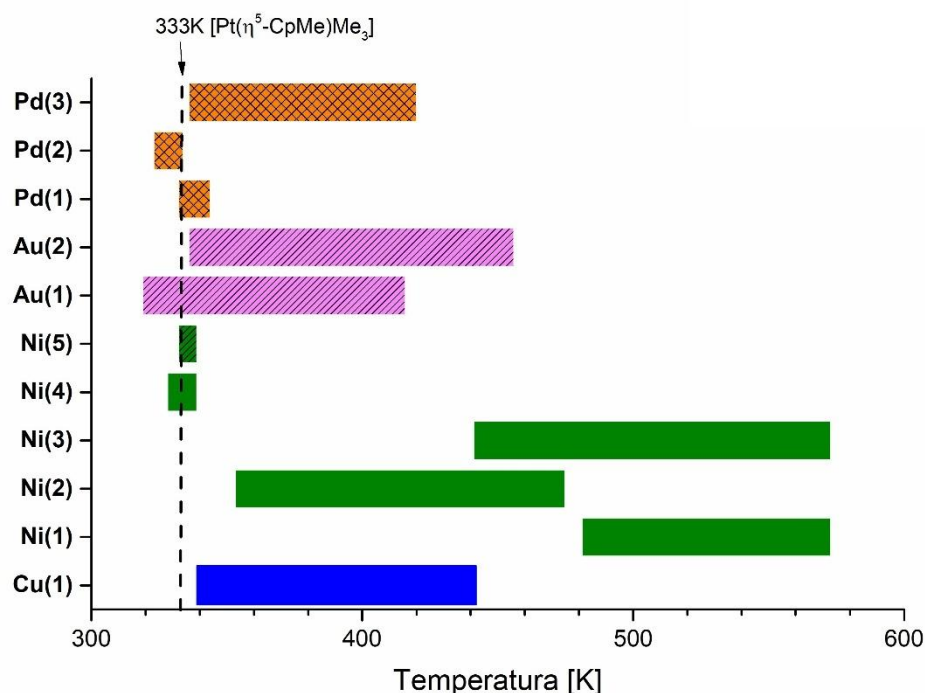
2.4.4 Spektrometria mas z jonizacją elektronami

Widma spektrometrii mas (EI MS) zarejestrowano techniką jonizacji elektronami, która wymaga przejścia próbki do fazy gazowej, w celu sprawdzenia możliwości tworzenia przez badane związki kompleksowe lotnych nośników metalu, w warunkach obniżonego ciśnienia $p = 10^{-6}$ mbar (analogicznego jak w komorze mikroskopu SEM podczas procesu FEBID). Ogrzewanie prowadzono w zakresie temperatur 313–573 K. Badania systematyczne przeprowadzono dla grup $[\text{Ni}_2(\text{HAMDR}_\text{F})_2(\mu\text{-O}_2\text{CR}_\text{F})_4]$ **Ni(1)–Ni(4)** [**D3**], $[\text{Pd}(\text{CH}_3\text{COCHCO}_2\text{R})_2]$ **Pd(1)–Pd(3)** [**D5**], $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ **Au(1)** [**D4**], **Au(2)** [**D4**] oraz wybrano kompleks **Cu(1)** [**D2**] gdyż był najbardziej wrażliwy na działanie wiązki elektronów wysokoenergetycznych (*vide infra* – **2.5.3**).

Na wykresie poniżej (**Rysunek 21**) przedstawiono zakresy temperatur występowania jonów fragmentacyjnych zawierających metal. Skład obserwowanych jonów zostanie omówiony w rozdziale **2.5.1** (**Tabela 1**). Dla wymienionych wyżej kompleksów jony fragmentacyjne zawierające metal zaczynano obserwować już w zakresie temperatur 319–339 K (**Rysunek 20**) dla **Cu(1)**, **Ni(4)**, **Ni(5)**, **Au(1)**, **Au(2)**, **Pd(1)–Pd(3)** zbliżonym do temperatury stosowania komercyjnego prekursora platynowego $[\text{Pt}(\eta^5\text{-CpMe})\text{Me}_3]$ (ok. 333 K).

Zakresy temperaturowe, w których obserwowano jony zawierające metal (**Rysunek 21**) były relatywnie szerokie dla **Cu(1)** [**D2**] (339–442 K), **Ni(1)–Ni(3)** [**D3**] (353–573 K), **Au(1)** [**D4**] (319–416 K oraz 336–456 K), a także w przypadku **Pd(3)** [**D5**] (336–420 K).

Ponadto w oparciu o analizę widm potwierdzono stabilność termiczną związków **Ni(5)** [D3], **Au(1)** [D4], **Pd(1)–Pd(3)** [D5].



Rysunek 21 Wyniki analizy EI MS. Zakres temperatur, w których obserwowano jony zawierające metal dla nowych kompleksów (od dołu): **Cu(1)** [D2], **Ni(1)–Ni(5)** [D3], **Au(1)** i **Au(2)** [D4], **Pd(1)–Pd(3)** [D5].

Podsumowując (rozdział 2.4), na podstawie omówionych wyżej wyników, stwierdzono, że badane kompleksy **Cu(1)–Cu(6)** [D2], **Ni(1)–Ni(5)** [D3], **Au(1)** i **Au(2)** [D4], **Pd(1)–Pd(3)** [D5] stanowią źródło metalu w fazie gazowej.

2.5 Badania oddziaływania cząsteczek z elektronami

2.5.1 Spektrometria mas z jonizacją elektronami

Wrażliwość badanych związków na działanie elektronów niskoenergetycznych (70 eV) można ocenić na podstawie wspomnianej wcześniej analizy widm EI MS. Należy jeszcze raz podkreślić, że warunki eksperymentalne panujące podczas pomiaru ($\sim 10^{-6}$ mbar) są zbliżone do tych, jakie występują w komorze mikroskopu SEM w trakcie procesów FEBID lub FIBID.

Na podstawie dotychczas uzyskanych danych EI MS, zebranych w naszej grupie badawczej, stwierdzono, że obecność jonu molekularnego może świadczyć o niskiej wrażliwości związku na elektrony niskoenergetyczne. Z kolei występowanie jonu

pseudomolekularnego oraz jonów $[M]^+$ wskazuje na większą podatność związku na fragmentację, a tym samym na jego większą wrażliwość na elektrony niskoenergetyczne [8,70,76].

Kompleks **Cu(1) [D2]** został wybrany do analizy ze względu na najwyższą czułość na wysokoenergetyczne elektrony (*vide infra* – 2.5.3). W jego widmach nie zaobserwowano jonów molekularnych i pseudomolekularnych (**Tabela 1**). Natomiast zarejestrowano jon metalu $[Cu]^+$ o $RI_{\max} = 14\%$ **[D2]** (RI – intensywność względna). Zidentyfikowano również fragment charakterystyczny dla aminy $[C_3H_9N]^{+*}$ oraz dijadrowy $[Cu_2(O_2C^tBu)_2]^{+*}$, co wskazuje na wysoką czułość badanego kompleksu na działanie niskoenergetycznych elektronów w fazie gazowej. Obecność tych jonów świadczy również o większej wrażliwości wiązania Cu-N na elektrony niskoenergetyczne niż Cu-O. Obserwowano także fragmenty $[(CH_3)_2C=CH_2]^{+*}$ oraz $[CO_2]^{+*}$ świadczące o fragmentacji karboksylanu prowadzącej do powstania lotnych produktów rozkładu, które mogą relatywnie łatwo desorbować z powierzchni podłoża już w trakcie procesu.

W widmach kompleksów $[Ni_2(NH_2(NH=)CR_F)_2(\mu-O_2CR_F)_4]$ **Ni(1)–Ni(4) [D3]** nie zidentyfikowano jonów molekularnych. Jony pseudomolekularne $[Ni_2(NH_2NH_2CC_2F_5)(O_2CCF_3)_3]^+$, $[Ni_2(NH_2NH_2CC_2F_5)(O_2CC_2F_5)_3]^+$ były widoczne jedynie dla dwóch z nich **Ni(2)** oraz **Ni(4) [D3]** (**Tabela 1**). Z kolei fragmenty odpowiadające tworzeniu jonu metalu $[Ni]^+$ były obserwowane na niskim poziomie dla wszystkich **Ni(1)–Ni(4) $\rightarrow RI_{\max} = 3\%$ [D3]** (**Tabela 1**). W przypadku analogicznych literaturowych związków miedzi(II) $[Cu_2(NH_2(NH=)CC_2F_5)_2(\mu-O_2CR_F)_4]$, brak jonu molekularnego, a także niska intensywność jonów pseudomolekularnych $[Cu_2(HAMDC_2F_5)_2(O_2CR_F)_3]^+$ na poziomie $RI = 2\text{--}8\%$ oraz jednocześnie wysoka intensywność dla fragmentu $[Cu_2F]^+$ (97%), który stanowił końcowy produkt rozkładu świadczyły o ich wysokiej wrażliwości na działanie elektronów niskoenergetycznych [72],[76]. Wynika z tego, że zmiana centrum koordynacji Cu $\rightarrow$ Ni powoduje obniżenie wrażliwości na elektrony niskoenergetyczne, przy zachowaniu większej czułości wiązań M-N w stosunku do M-O.

Z kolei dla związku niklu **Ni(5) [D3]** względna intensywność jonu molekularnego osiągnęła wartość na poziomie 99%, co świadczy o jego niskiej czułości na elektrony (**Tabela 1**). Związek ten wykazywał najmniejszą wrażliwość na działanie niskoenergetycznych elektronów.

Dla $[Au_4(\mu-(NH)_2CC_2F_5)_4]_n$ **Au(1) [D4]** w widmach masowych obserwowano jon molekularny $[Au_2(NH_2NH_2CC_2F_5)_2]^{+*}$ wskazujący na rozerwanie wiązań w jednostce tetramerycznej, a także jon pseudomolekularny $[Au_2(NH_2NH_2CC_2F_5)]^+$ (**Tabela 1**).

Natomiast obecność fragmentów $[\text{Au}_3(\text{NHNHCC}_2\text{F}_5)_2]^+$ oraz $[\text{Au}_4(\text{NHNHCC}_2\text{F}_5)]^+$ świadczy o możliwości fragmentacji tetrameru.

W przypadku $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ **Au(2)** **[D4]** nie zidentyfikowano jonu molekularnego, ale obserwowano jony $[\text{Au}_2(\text{NHNHCC}_2\text{F}_5)_2]^{+\bullet}$, $[\text{HCl}]^{+\bullet}$, $[\text{H}_2\text{Cl}]^+$ potwierdzające wydzielanie chlorowodoru na początku procesu. Warto przypomnieć, że obecność tych jonów jest związana z termicznym rozkładem kompleksu **Au(2)** **[D4]** (2.4.2). W widmach dla związków złota(I) nie stwierdzono obecności fragmentów odpowiadających jonowi $[\text{M}]^+$ (*Tabela 1*).

Dla wszystkich badanych związków $[\text{Pd}(\text{CH}_3\text{COCHCO}_2\text{R})_2]$ **Pd(1)–Pd(3)** **[D5]** zaobserwowano jony molekularne $[\text{Pd}(\text{CH}_3\text{COCHCO}_2\text{R})_2]^{+\bullet}$ (*Tabela 1*), które dla kompleksów **Pd(2)** oraz **Pd(3)** osiągnęły intensywność na poziomie 100% odpowiednio w 330 K oraz w zakresie 388–416 K, co świadczy o ich niskiej wrażliwości na elektrony niskoenergetyczne (*Tabela 1*). W widmach nie stwierdzono obecności fragmentów metalu $[\text{M}]^+$. Dla wszystkich kompleksów obserwowano jony $[\text{CH}_3\text{CHO}]^{+\bullet}$ oraz $[\text{CO}_2]^{+\bullet}$ świadczące o tworzeniu lotnych produktów rozkładu, które mogą być łatwo usuwalne w trakcie procesów indukowanych elektronami [83].

Tabela 1 Zestawienie danych spektrometrii mas (EI MS) dla związków: (od góry) **Cu(1)** [D2], **Ni(1)–Ni(5)** [D3], **Au(1)** i **Au(2)** [D4], **Pd(1)–Pd(3)** [D5].

Badany związek	Jon		
	Molekularny	Pseudomolekularny	[M] ⁺
Cu(1)	—		[Cu] ⁺
Ni(1)	—		[Ni] ⁺
Ni(2)	—	[Ni ₂ (NHNH ₂ CC ₂ F ₅)(O ₂ CCF ₃) ₃] ⁺	[Ni] ⁺
Ni(3)	—		[Ni] ⁺
Ni(4)	—	[Ni ₂ (NHNH ₂ CC ₂ F ₅)(O ₂ CC ₂ F ₅) ₃] ⁺	[Ni] ⁺
*Ni(5)	[Ni(NHC(CF ₃)NC(CF ₃)NH) ₂] ⁺⁺	[Ni(NHC(CF ₃)NC(CF ₃)NH)] ⁺	[Ni] ⁺
Au(1)	[Au ₂ (NHNHCC ₂ F ₅) ₂] ⁺⁺	[Au ₂ (NHNHCC ₂ F ₅)] ⁺	—
Au(2)	—	[Au ₂ (NHNHCC ₂ F ₅) ₂] ⁺⁺	—
Pd(1)	[Pd(CH ₃ COCHCO ₂ ^t Bu) ₂] ⁺⁺	[Pd(CH ₃ COCH ₂ CO ₂ ^t Bu)] ⁺	—
*Pd(2)	[Pd(CH ₃ COCHCO ₂ ⁱ Pr) ₂] ⁺⁺	[Pd(CH ₃ COCH ₂ CO ₂ ⁱ Pr)] ⁺	—
*Pd(3)	[Pd(CH ₃ COCHCO ₂ Et) ₂] ⁺⁺	[Pd(CH ₃ COCHCO ₂ Et)] ⁺	—

* Jon molekularny:

RI_{max} = 99% (332–339 K) **Ni(5)**

RI_{max} = 100% (330 K) **Pd(2)**, (388–416 K) **Pd(3)**

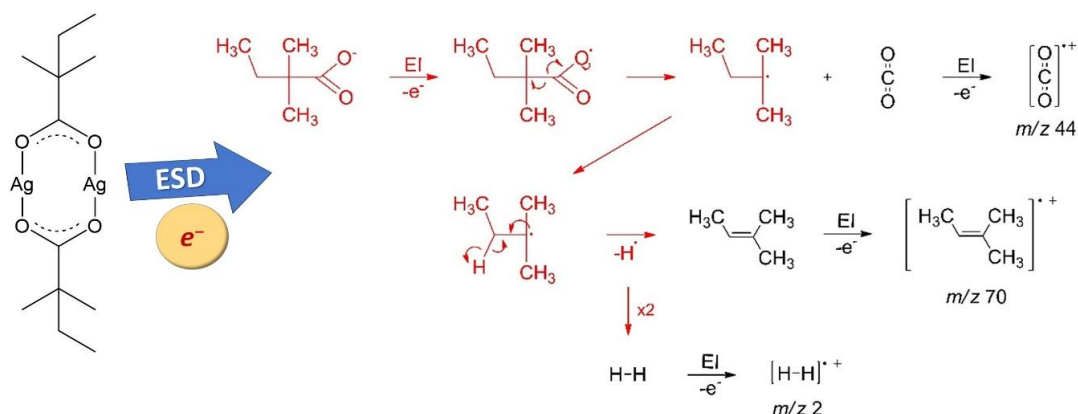
Warto zaznaczyć, że dla wszystkich badanych związków (**Tabela 1**) obserwowano jony fragmentacyjne zawierające metal, co świadczy o tworzeniu jego lotnych nośników.

2.5.2 Desorpcja stymulowana elektronami

Jak wspomniano w rozdziale (1.2) karboksylany srebra stanowią istotną grupę prekursorów w technice FEBID. W związku z tym, w ramach współpracy międzynarodowej, przeprowadzono badania desorpcji stymulowanej elektronami (ESD), których interpretacji dokonano w oparciu o analizę warstw metodą RAIRS; desorbowanych z powierzchni produktów przy użyciu spektrometrii mas EI MS oraz obliczeń teoretycznych ALIE (*ang. average local ionization energy*). Do badań wykorzystano [Ag₂(μ-O₂CC(CH₃)₂C₂H₅)₂] z rozgałęzionym podstawnikiem alifatycznym **Ag(1)** [D1], który w procesie FEBID umożliwił uzyskanie depozytu o zawartości 73 at.% Ag [8] oraz związek [Ag₂(μ-O₂CC₆H₅)₂], zawierający podstawnik aromatyczny **Ag(2)** [D1].

Na podstawie widm RAIRS stwierdzono, że cząsteczki związków zaadsorbowane na powierzchni BPT SAM są zorientowane pionowo do powierzchni. W widmach masowych dla **Ag(1)** [D1] obserwowano jon [C₅H₁₀]⁺⁺ świadczący o możliwości

przekształcenia się tego rodnika w stabilny alken, który może ulegać desorpcji w trakcie procesu (**Rysunek 22**).



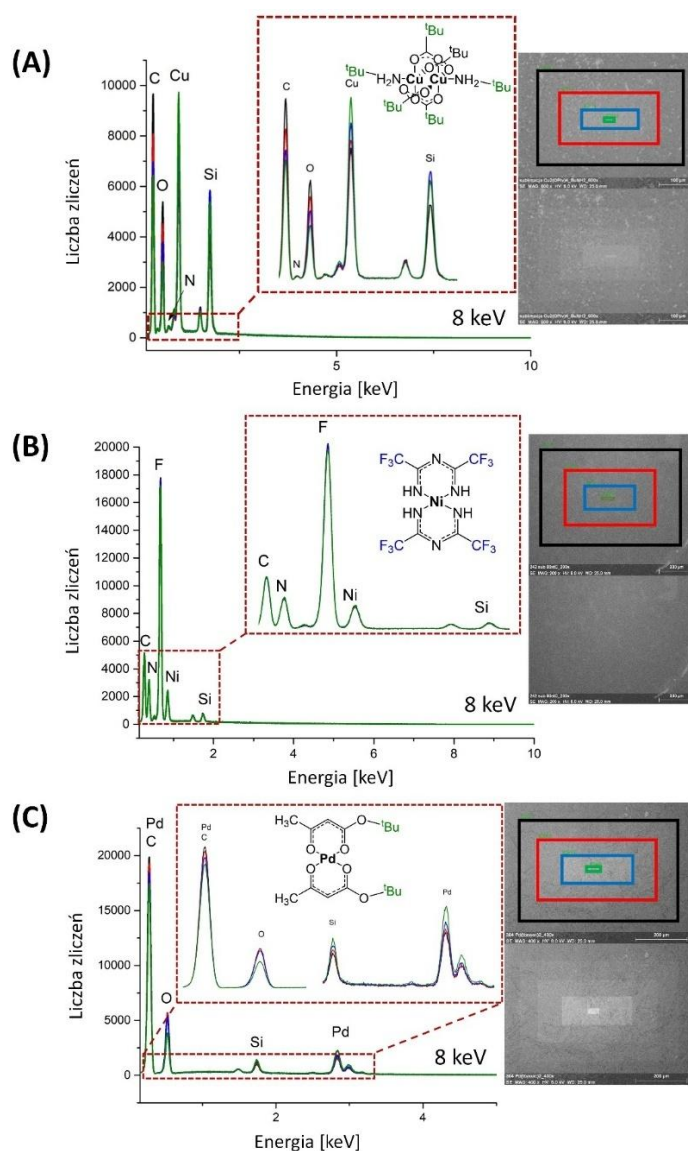
Rysunek 22 Mechanizm fragmentacji $[Ag_2(\mu-O_2CC(CH_3)_2C_2H_5)_2]$ **Ag(1)** [**D1**] indukowany przez elektrony niskoenergetyczne, 1–500 eV (fragmenty czerwone – odpowiadają procesom zachodzącym na powierzchni próbki, czarne – lotne produkty ulegające jonizacji w spektrometrze mas).

Z obliczeń ALIE wynika, że korzystne miejsce dla jonizacji, $[Ag_2(\mu-O_2CC(CH_3)_2C_2H_5)_2]$ **Ag(1)** [**D1**], w których energia jest najmniejsza, znajduje się w obrębie grupy karboksylanowej. Sugeruje to, że w wyniku jonizacji przy udziale elektronów, dochodzi do wydzielenia cząsteczki CO_2 . Z kolei dla związku $[Ag_2(\mu-O_2CC_6H_5)_2]$ **Ag(2)** [**D1**] występowanie wiązań wielokrotnych w pierścieniu aromatycznym sprzyja usuwaniu elektronów na drodze interakcji z elektronami pierwotnymi. Jednakże proces ten nie prowadzi do dysocjacji wiązań, co jest przyczyną obserwowanej wysokiej stabilności benzoesanu.

Podsumowując, wyniki zawarte w pracy [**D1**] stwierdzono, że związki zawierające ligandy karboksylanowe o alifatycznych łańcuchach mogą być obiecujące w technice FEBID, gdyż grupa $-COO$ łatwo oddysocjowuje w procesach indukowanych elektronami o energii z zakresu 1–500 eV, a powstające cząsteczki CO_2 efektywnie desorbują z powierzchni podłoża. Z kolei powstający rodnik alkilowy przekształca się w stabilny i lotny węglowodór [**D1**] (**Rysunek 22**).

2.5.3 Wrażliwość związków na wiązkę wysokoenergetycznych elektronów

W celu oceny wrażliwości badanych związków na wiązkę wysokoenergetycznych elektronów, wykorzystano skaningową (SEM) oraz transmisyjną (TEM) mikroskopię elektronową. Analizę SEM-EDX przy energiach elektronów wynoszących 8 i 20 keV przeprowadzono dla warstw kompleksów, sublimowanych na podłożu krzemowym. Widma EDX rejestrowano bezpośrednio podczas analizy SEM, a zmniejszenie obszaru skanowania skutkowało zwiększeniem dawki elektronów. Badania przeprowadzono dla kompleksów, dla których otrzymano warstwy w procesie sublimacji, czyli **Cu(1)–Cu(5)**, **Ni(4)**, **Ni(5)**, **Au(1)**, **Pd(1)–Pd(3)** (2.4.2).

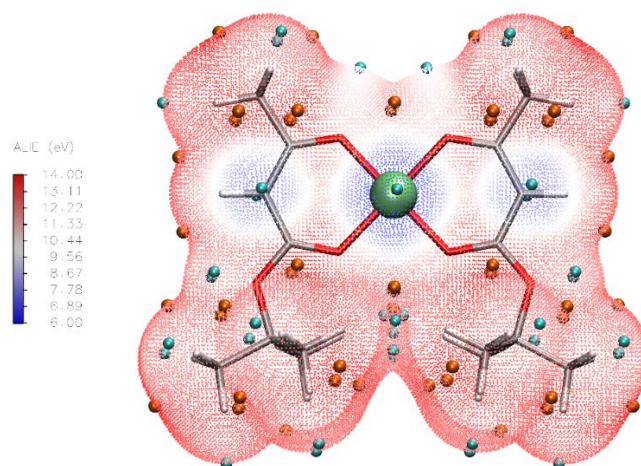


Rysunek 23 Widma SEM-EDX (8 keV) z poszczególnych obszarów skanowania dla warstw wybranych kompleksów: **Cu(1)** [D2], **Ni(5)** [D3] oraz **Pd(1)** [D5] na substracie krzemowym.

Dla kompleksów miedzi $[\text{Cu}_2(\text{amina})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ **Cu(1)–Cu(5)**, $[\text{Cu}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ **Cu(6)** [D2] i niklu $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ **Ni(4)** [D3] zawierających ligandy karboksylanowe stwierdzono, że związki te są wrażliwe na działanie wiązki elektronów wysokoenergetycznych (8 i 20 keV). Na podstawie zmiany intensywności sygnałów charakterystycznych dla poszczególnych pierwiastków oraz zdjęć SEM po procesie naświetlania stwierdzono, że kompleks **Cu(1)** [D2] zawierający *tert*-butyloaminę (**Rysunek 23A**) jest najbardziej wrażliwy na elektrony wysokoenergetyczne spośród grupy kompleksów zawierających jednocześnie ligandy typu O,O- i N-donorowego. Zawartość procentowa miedzi zwiększyła się z 8.4 → 14.1 at. % dla elektronów o energii 8 keV oraz z 1.8 → 2.5 at. % dla 20 keV.

Imidoiloamidynian niklu(II) **Ni(5)** [D3] oraz amidynian złota(I) **Au(1)** [D4] wykazują niską wrażliwość na działanie wiązki elektronów wysokoenergetycznych (**Rysunek 23B**). W widmach EDX obserwowano jedynie nieznaczny spadek intensywności sygnału charakterystycznego dla fluoru, co świadczy o ich stabilności.

W przypadku β -ketoesteranów palladu(II) **Pd(1)–Pd(3)** [D5] zawartość metalu pozostawała niemal niezmienną pod wpływem oddziaływania z wiązką elektronów o energii 20 keV. Natomiast przy 8 keV, we wszystkich przypadkach obserwowano wzrost intensywności sygnału charakterystycznego dla palladu. Na podstawie obserwowanych zmian w morfologii powierzchni widocznych na zdjęciach SEM oraz zmian intensywności sygnałów poszczególnych pierwiastków w widmach EDX można stwierdzić, że kompleks **Pd(1)** [D5] (**Rysunek 23C**) wykazuje największą wrażliwość na działanie wysokoenergetycznych elektronów. Z tego względu dla tego związku wykonano obliczenia ALIE podobnie, jak dla wcześniej opisywanych kompleksów srebra **Ag(1)** i **Ag(2)** [D1]. Wyniki obliczeń wskazują, że jonizacja kompleksu zachodzi w obszarze metalu oraz grupie -CH pierścienia chelatowego (**Rysunek 24**), co prowadzi do powstawania fragmentów zawierających grupę karbonylową. Jest to zgodne z wynikami spektrometrii mas, które potwierdziły tworzenie się CH_3CHO i CO_2 jako lotnych produktów fragmentacji, relatywnie łatwo ulegających desorpcji z powierzchni podłoża, co jest tak istotne z punktu zastosowania w metodach FEBID i FIBID.



Rysunek 24 Mapa średniej lokalnej energii jonizacji (ALIE) nałożona na strukturę kompleksu **Pd(1)** [D5].

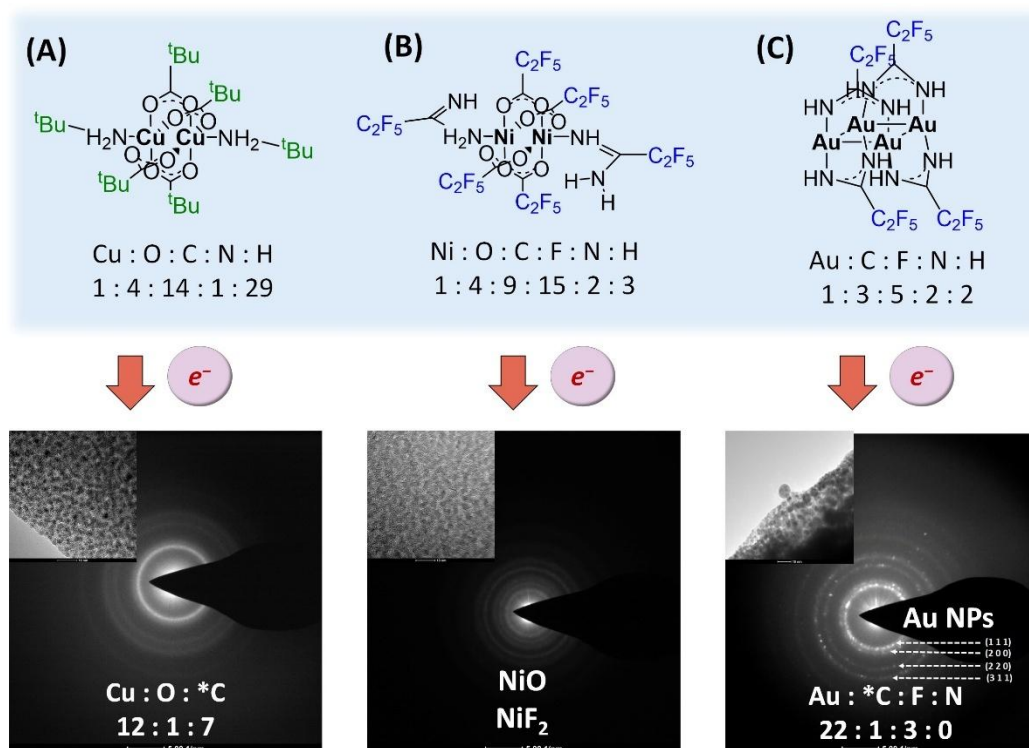
Na podstawie wyników analizy SEM-EDX do przeprowadzenia pomiarów TEM-EDX wyselekcjonowano związki $[\text{Cu}_2(\text{tBuNH}_2)_2(\mu\text{-O}_2\text{CtBu})_4]_n$ **Cu(1)** [D2], $[\text{Ni}_2(\text{NH}_2(\text{NH}=\text{CC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ **Ni(4)** [D3], $[\text{Au}_4(\mu\text{-(NH)}_2\text{CC}_2\text{F}_5)_4]_n$ **Au(1)** [D4], dla których uzyskano warstwy w procesie sublimacji i wykazujące największą wrażliwość na elektrony wysokoenergetyczne spośród badanej grupy kompleksów (2.4.2, 2.5.3).

Pomiary TEM-EDX wykonano przy energii 200 keV (**Rysunek 25**). Podczas obrazowania TEM zaobserwowano zmiany morfologii badanych związków, w tym formowanie się krystalitów. W przypadku związku **Cu(1)** [D2] (**Rysunek 25A**) w widmie EDX zarejestrowano sygnał charakterystyczny dla miedzi oraz słaby sygnał tlenu, ponadto nie obserwowano sygnału dla azotu. Wskazuje to na możliwość usunięcia liganda karboksylanowego oraz aminy w trakcie oddziaływania próbki z wiązką elektronów wysokoenergetycznych.

Z kolei dla kompleksu niklu(II) **Ni(4)** [D3] w widmach EDX obserwowano sygnały charakterystyczne dla niklu, tlenu i fluoru. Zarejestrowany dyfraktogram proszkowy potwierdził, że produktami rozkładu indukowanego wiązką elektronów wysokoenergetycznych są NiO i NiF₂ (**Rysunek 25B**). Tworzenie się fluorku odnotowano również dla analogicznego kompleksu miedzi $[\text{Cu}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ [72], analizowanego w identycznych warunkach pomiarowych. Uzyskane rezultaty wskazują, że amidyna prawdopodobnie może być skutecznie usuwana w trakcie oddziaływania z wiązką elektronów o energii 200 keV.

W przypadku amidynianu złota(I) **Au(1)** [D4] (**Rysunek 25C**) zarejestrowany dyfraktogram potwierdził tworzenie się nanocząstek złota. W widmach EDX

zaobserwowano sygnały charakterystyczne dla złota, węgla (w dużej mierze pochodzącego od membrany) i fluoru. Brak sygnału charakterystycznego dla azotu świadczył o zerwaniu wiązań Au–N w warunkach pomiarowych i utworzeniu się lotnych produktów zawierających azot. Warta podkreślenia jest wysoka zawartość złota w utworzonym materiale.



Rysunek 25 Zestawienie wyników TEM, EDX, XRD dla związków: **Cu(1)** [D2], **Ni(4)** [D3] i **Au(1)** [D4] z uwzględnieniem zmiany stosunku atomowego w związku pierwotnym (panel górny) oraz materiale po naświetlaniu (panel dolny, *C – siatka TEM była pokryta błoną węglową).

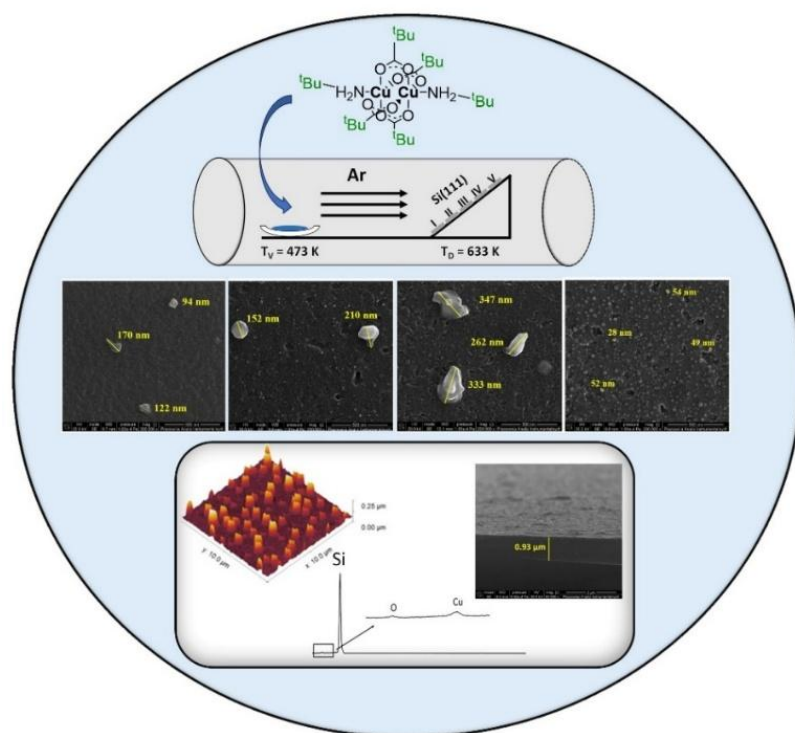
2.6 Charakterystyka otrzymanych nanomateriałów CVD oraz FEBID

W oparciu o przeprowadzone badania termiczne, testy lotności, a także wrażliwość na elektrony nisko- i wysokoenergetyczne wybrano związki do otrzymania depozytów w procesie CVD oraz do testów FEBID.

2.6.1 Depozyty otrzymane w procesie CVD

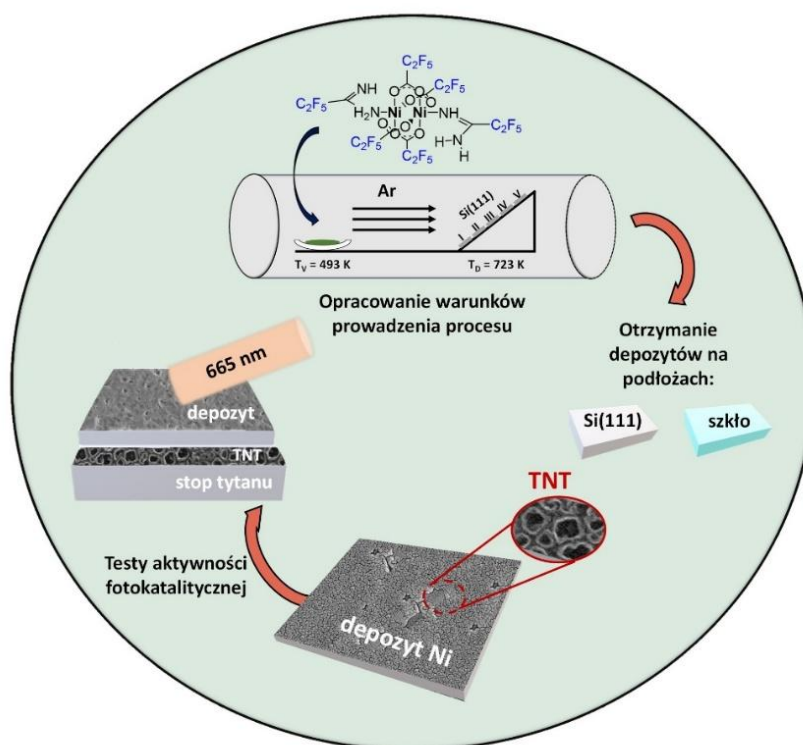
Do uzyskania materiałów CVD wybrano karboksylanowe kompleksy: miedzi(II) $[\text{Cu}_2(\text{tBuNH}_2)_2(\mu\text{-O}_2\text{CtBu})_4]_n$ **Cu(1)** **[D2]** oraz niklu(II) $[\text{Ni}_2(\text{NH}_2(\text{NH}=\text{CC}_2\text{F}_5)_2(\mu\text{-O}_2\text{C-C}_2\text{F}_5)_4)]$ **Ni(4)** **[D3]**. Oba związki, wykazywały odpowiednią lotność (co omówiono w rozdziale 2.4). Dla obu kompleksów zaproponowano warunki prowadzenia procesu CVD na podstawie wyników omówionych w podrozdziałach 2.4.1, 2.4.2, 2.4.3. Osadzanie przeprowadzono w reaktorze typu *hot-wall*, bez użycia wodoru jako gazu redukującego. Zastosowano temperatury odparowania (T_v) i depozycji (T_D) wynoszące 473 K oraz 633 K dla prekursora **Cu(1)** **[D2]**, a także 493 K oraz 723 K dla kompleksu **Ni(4)** **[D3]**.

Dla związku **Cu(1)** **[D2]** uzyskane depozyty na podłożu krzemowym charakteryzowały się niejednorodną morfologią, z widoczną zmianą wielkości i kształtu ziaren o średnicy od 30–50 nm do ok. 350 nm w zależności od długości drogi transportu prekursora. Zarejestrowane widma SEM-EDX potwierdziły obecność miedzi w depozycie oraz występowanie prawdopodobnie niewielkiej ilości tlenku miedzi. Analiza metodą AFM potwierdziła, że na powierzchni warstwy znajdują się struktury o wysokości 250–360 nm (*Rysunek 26*).



Rysunek 26 Zestawienie wyników CVD dla depozytów uzyskanych przy wykorzystaniu prekursora **Cu(1)** $[Cu_2(tBuNH_2)_2(\mu-O_2C^tBu)_4]_n$ [D2].

W przypadku wykorzystania kompleksu **Ni(4)** [D3] otrzymano depozyty na różnych podłożach w tym krzemie, szkle oraz podłożu z nanorurkami TiO_2 (Ni-TNT20) (**Rysunek 27**). Uzyskane wyniki SEM wskazują, że morfologia powierzchni depozytów zależy nie tylko od drogi transportu, podobnie jak w przypadku **Cu(1)** [D2], lecz również od rodzaju zastosowanego podłoża [D3]. W widmach EDX dla uzyskanych materiałów zaobserwowano obecność sygnałów charakterystycznych dla niklu i tlenu, a także niewielkiej intensywności sygnały pochodzące od węgla i fluoru. Warto podkreślić, że opracowano warunki dla otrzymywania nanomateriału Ni-TNT20, który wykazywał aktywność fotokatalityczną w reakcji utleniania błękitu metylenowego [D3].



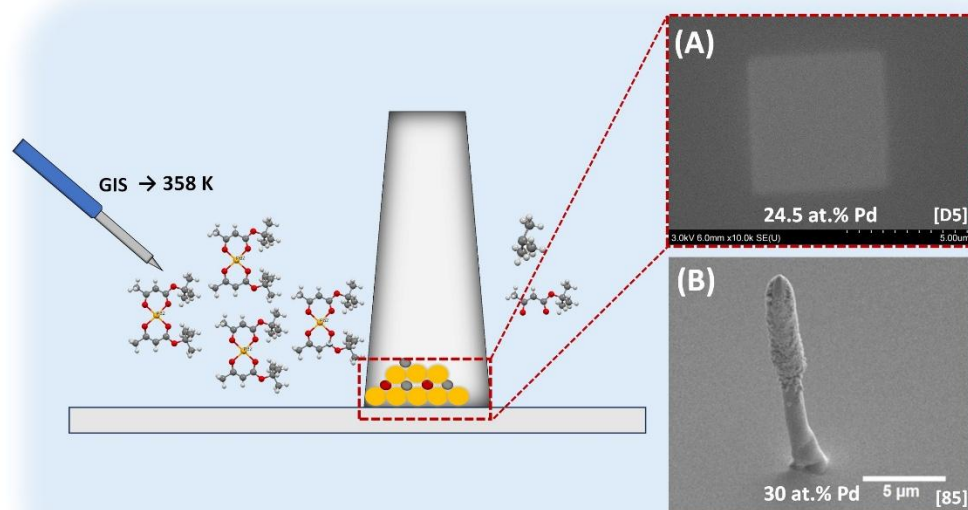
Rysunek 27 Nikłowe depozyty CVD uzyskane przy wykorzystaniu prekursora **Ni(4)** $[Ni_2(NH_2(NH=)CR_f)_2(\mu-O_2CR_f)_4]$ **[D4]**.

Podsumowując, sprawdzane w roli prekursorów CVD kompleksy **Cu(1)** **[D2]** oraz **Ni(4)** **[D3]** stanowią źródło metalu w fazie gazowej i są obiecującymi prekursorami w metodzie CVD. Co więcej, rezultaty te mogą stanowić podstawę do dalszych badań nad zastosowaniem tych związków w komercyjnych reaktorach CVD, w ściśle kontrolowanych warunkach i na przykład z uwzględnieniem wykorzystania gazu redukującego dla związku **Ni(4)** **[D3]**.

2.6.2 Depozyty FEBID

Na podstawie uzyskanych wyników (rozdziały 2.4, 2.5) zaproponowano β -ketoesterany palladu(II), jako grupę potencjalnych prekursorów FEBID. Do testów FEBID wybrano związek $[Pd(CH_3COCHCO_2^tBu)_2]$ **Pd(1)** **[D5]** ze względu na jego wrażliwość na elektrony niskoenergetyczne, jak i na wiązkę elektronów wysokoenergetycznych, co wskazywało na możliwość efektywnej dysocjacji w trakcie procesu. Kluczową zaletą kompleksu jest jego stosunkowo niska temperatura sublimacji, wynosząca pod ciśnieniem 10^{-2} mbar, 348 K, która już jest porównywalna do komercyjnego prekursora platynowego $[Pt(\eta^5-CpMe)Me_3]$ (około 333 K, pod ciśnieniem

10^{-6} mbar). Dla związku **Pd(1)** [D5] uzyskano depozyt ($T_{GIS} = 358$ K, 20 keV, 0.5 nA) w kształcie kwadratu [D5] (*Rysunek 28*) o zawartości: 24.5 at.% Pd, 56.7 at.% C oraz 18.8 at.% O, co jest zbliżone do wyników dla związku literaturowego zawierającego ten sam typ liganda O,O-donorowego $[Cu(CH_3COCHCO_2^tBu)_2]$ (26 at.% Cu) [8].



Rysunek 28 Depozyty FEBID: (A) 2D oraz 3D (B) uzyskane przy wykorzystaniu prekursora **Pd(1)** $[Pd(CH_3COCHCO_2^tBu)_2]$ [D5] [84].

Badania z wykorzystaniem tego prekursora kontynuowano w ramach współpracy międzynarodowej [84] i otrzymano trójwymiarowy depozyt o zawartości palladu wynoszącej około 30%. W tym przypadku ilość węgla została zredukowana o około 90% w stosunku do pierwotnej zawartości w kompleksie, co podkreśla konieczność dalszych badań. Wzrost wertykalny depozytu wskazuje, że związek **Pd(1)** jest obiecujący do wykorzystania w metodach z użyciem skupionej wiązki elektronów lub jonów [84].

Warto zaznaczyć, że zmiany warunków eksperymentalnych często prowadzą do różnic w składzie depozytu. W związku z tym kontynuacja tych badań i zastosowanie innych parametrów procesu może prowadzić do uzyskania depozytów o wyższej czystości.

Podsumowanie i wnioski

Wybrano ligandy i opracowano warunki syntezy **13 nowych** związków kompleksowych metali z grupy 10 i 11 z:

ligandami O,O- i N-donorowymi

- $[\text{Cu}_2(\text{RNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ ($R = {}^s\text{Bu}, {}^i\text{Pr}, \text{Et}$) **Cu(1)–Cu(4)** z mostkowo skoordynowanymi karboksylanami oraz aminą alifatyczną, które otrzymano w reakcji piwalanu miedzi(II) z aminą alifatyczną,
- $[\text{Ni}_2(\text{NH}_2(\text{NH}=\text{CR}_f)_2(\mu\text{-O}_2\text{CR}_f)_4)]$ ($R_f = \text{CF}_3, \text{C}_2\text{F}_5$) **Ni(1)–Ni(4)**, w których występują mostkujące karboksylany i dwa sposoby wiązania amidyny poprzez grupę $=\text{NH}$ i $-\text{NH}_2$, które otrzymano w reakcji amidyny z $[\text{Ni}_2(\mu\text{-O}_2\text{CR}_f)_4]$.

Związki niklu otrzymano również z wykorzystaniem syntezy mechanochemicznej, co pozwoliło na skrócenie czasu syntezy z 24 h do kilku minut, uniknięcie użycia rozpuszczalnika oraz zwiększenie wydajności reakcji z 40% do 70%.

ligandami N,N- lub N-donorowymi

- $[\text{Ni}(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH})_2]$ **Ni(5)** powstający na drodze reakcji liganda *in situ*, który chelatowo wiąże się do Ni(II) przez dwa atomy azotu,
- $[\text{Au}_4(\mu\text{-(NH)}_2\text{C}_2\text{F}_5)_4]_n$ **Au(1) stabilny na powietrzu** tetramer z mostkowo wiązanymi amidynianami, który otrzymano na drodze reakcji wymiany $[\text{Ag}_2(\mu\text{-(NH)}_2\text{C}_2\text{F}_5)_2]$ z $[\text{Au}(\text{tht})\text{Cl}]$.
- $[\text{Au}_2\text{Cl}_2(\text{NH}_2(\text{NH}=\text{CC}_2\text{F}_5)_2)]_n$ **Au(2) stabilny na powietrzu** kompleks chlorkowy z amidyną, który otrzymano na drodze reakcji amidyny z $[\text{Au}(\text{SMe}_2)\text{Cl}]$.

ligandami O,O-donorowymi

- $[\text{Pd}(\text{CH}_3\text{COCHCO}_2\text{R})_2]$ ($R = {}^t\text{Bu}, {}^i\text{Pr}, \text{Et}$) **Pd(1)–Pd(3)**, gdzie forma: *cis* dla $R = {}^t\text{Bu}$ oraz *trans* dla kompleksów zawierających grupy ${}^i\text{Pr}$ oraz Et . Otrzymano je na drodze reakcji wymiany β -ketoestru z octanem palladu.

Wyizolowano **9** monokryształów, przy czym **5** z nich ze względu na dużą masę cząsteczkową lub silne oddziaływania międzycząsteczkowe nie było dalej badane pod kątem procesów osadzania z fazy gazowej:

- $[\text{Cu}_3({}^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_6]_n$ **Cu(1a)**
- $[\text{Cu}_3({}^s\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_6]_n$ **Cu(2a)**

- $[\text{Cu}_3(\text{}^i\text{PrNH}_2)_2(\mu_3\text{-OH})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ **Cu(3a)**
- $[\text{Cu}_{20}(\text{EtNH}_2)_6(\mu_3\text{-OH})_{24}(\text{OH})(\text{H}_2\text{O})_5(\text{NO}_3)(\mu\text{-O}_2\text{C}^t\text{Bu})_8](^t\text{BuCO}_2)_6 \cdot 13\text{H}_2\text{O}$ **Cu(4a)**
- $[\text{Ni}(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH}_2)_2] \cdot (\text{NH}_4)(\text{CF}_3\text{CONH}) \cdot (\text{CF}_3\text{CONH}_2) \cdot \text{H}_2\text{O}$ **Ni(5a)**

oraz

4, dla których wykonano badania pod kątem potencjalnego wykorzystania w metodach osadzania z fazy gazowej:

- $[\text{Au}_4(\mu\text{-(NH)}_2\text{CC}_2\text{F}_5)_4]_n$ **Au(1)**
- $[\text{Pd}(\text{MeCOCHCO}_2^t\text{Bu})_2]$ **Pd(1)**
- $[\text{Pd}(\text{MeCOCHCO}_2^i\text{Pr})_2]$ **Pd(2)**
- $[\text{Pd}(\text{MeCOCHCO}_2\text{Et})_2]$ **Pd(3)**.

Przeprowadzone badania termiczne, lotności i wpływu elektronów o różnej energii pozwoliły na sformułowanie wniosków i uogólnień:

1) $[\text{Cu}_2(\text{RNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ **Cu(1)–Cu(4)**

- Nowe kompleksy $[\text{Cu}_2(\text{RNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ ($\text{R} = ^t\text{Bu}, ^s\text{Bu}, ^i\text{Pr}, \text{Et}$) **Cu(1)–Cu(4)** stanowią źródło metalu nawet pod ciśnieniem atmosferycznym.
- Wprowadzenie liganda drugorzędowego w postaci aminy alifatycznej wpływa na obniżenie temperatury sublimacji ($p = 10^{-2}$ mbar), a $[\text{Cu}_2(^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ generuje lotne nośniki metalu już od 339 K ($p = 10^{-6}$ mbar).
- Związek $[\text{Cu}_2(^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ **Cu(1)** jest najbardziej czuły na elektrony nisko- i wysokoenergetyczne.

Związek $[\text{Cu}_2(^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ **Cu(1)** umożliwił otrzymanie depozytu metalu w procesie CVD bez wykorzystania gazu redukującego, potwierdziło to jego zdolność do efektywnego generowania lotnych nośników metalu w fazie gazowej. Właściwości tego kompleksu wskazują również na jego potencjalną przydatność jako prekursora w technikach FEBID i FIBID.

2) $[\text{Ni}_2(\text{NH}_2(\text{NH=})\text{CR}_F)_2(\mu\text{-O}_2\text{CR}_F)_4]_n$ **Ni(1)–Ni(4)**

- Związki $[\text{Ni}_2(\text{HAMDR}_F)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]_n$ **Ni(3)**, **Ni(4)** generują lotne nośniki metalu nawet pod ciśnieniem atmosferycznym, a także w warunkach zbliżonych do procesu CVD ($p = 10^{-1}$ mbar) w zakresie 453–573 K.
- Spośród badanych połączeń jedynie $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]_n$ **Ni(4)** ulega sublimacji w temperaturze 423 K ($p = 10^{-2}$ mbar). Natomiast, wszystkie kompleksy

$[\text{Ni}_2(\text{HAMDR}_F)_2(\mu\text{-O}_2\text{CR}_F)_4]$ **Ni(1)–Ni(4)** generują lotne nośniki metalu w warunkach obniżonego ciśnienia już od 328 K ($p = 10^{-6}$ mbar).

- Związek $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ **Ni(4)** był najbardziej czuły na elektrony niskoenergetyczne i wysokoenergetyczną wiązkę elektronów.

*Zastosowanie w procesie CVD $[\text{Ni}_2(\text{NH}_2(\text{NH=})\text{CR}_F)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ **Ni(3)**, **Ni(4)**, bez wykorzystania gazu redukującego potwierdziło jego zdolność do efektywnego generowania lotnych nośników metalu w fazie gazowej i pozwoliło na otrzymanie materiałów Ni-TNT20, które wykazują aktywność fotokatalityczną.*

3) $[\text{Ni}(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH})_2]$ **Ni(5)**

- Związek przechodzi do fazy gazowej pod ciśnieniem atmosferycznym.
- Sublimuje w stosunkowo niskiej temperaturze 358 K pod obniżonym ciśnieniem ($p = 10^{-2}$ mbar).
- Wykazuje niską wrażliwość na elektrony niskoenergetyczne i wiązkę elektronów wysokoenergetycznych.

Właściwości tego kompleksu wskazują na jego potencjalną przydatność jako prekursora w metodzie CVD.

4) $[\text{Au}_4(\mu\text{-(NH)}_2\text{CC}_2\text{F}_5)_4]_n$ **Au(1)** oraz $[\text{Au}_2\text{Cl}_2(\text{NH}_2(\text{NH=})\text{CC}_2\text{F}_5)_2]_n$ **Au(2)**

- $[\text{Au}_4(\mu\text{-(NH)}_2\text{CC}_2\text{F}_5)_4]_n$ **Au(1)** sublimuje w temperaturze 413 K pod obniżonym ciśnieniem ($p = 10^{-2}$ mbar). Jest to związane z występowaniem oddziaływań międzycząsteczkowych w kompleksie $[\text{Au}_4(\mu\text{-(NH)}_2\text{CC}_2\text{F}_5)_4]_n$, w których najliczniejsze są kontakty typu $\text{F}\cdots\text{F}$. Zarówno one, jak i występujące słabe wiązania aurofilowe między tetramerami sprzyjają lotności tego związku.
- Oba związki generują lotne nośniki metalu w warunkach obniżonego ciśnienia już od 319 K ($p = 10^{-6}$ mbar).
- W warunkach zbliżonych do procesu CVD $[\text{Au}_2\text{Cl}_2(\text{NH}_2(\text{NH=})\text{CC}_2\text{F}_5)_2]_n$ **Au(2)** ($p = 10^{-1}$ mbar) ulega rozkładowi z wydzielaniem chlorowodoru i amidynianu złota(I), który jest nośnikiem metalu w fazie gazowej w zakresie 433–453 K.
- $[\text{Au}_4(\mu\text{-(NH)}_2\text{CC}_2\text{F}_5)_4]_n$ **Au(1)** wykazuje niską wrażliwość na wiązkę elektronów wysokoenergetycznych (8 i 20 keV).

*Właściwości tych kompleksów wskazują na potencjalną przydatność amidynianu złota(I) **Au(1)** jako prekursora w metodzie CVD, który może być również rozważany jako potencjalny kandydat do testów FEBID.*

5) [**Pd**(CH₃COCHCO₂R)₂] **Pd(1)–Pd(3)**

- Słabe oddziaływania międzycząsteczkowe ułatwiają transfer cząsteczek do fazy gazowej.
- Kompleksy sublimują w stosunkowo niskiej temperaturze 348–353 K pod ciśnieniem $p = 10^{-2}$ mbar i generują lotne nośniki metalu w warunkach obniżonego ciśnienia już od 323 K ($p = 10^{-6}$ mbar).
- Związki są wrażliwe na elektrony niskoenergetyczne i wiązkę elektronów wysokoenergetycznych, co koreluje z obliczeniami średniej lokalnej energii jonizacji (ALIE).

Związek [**Pd**(CH₃COCHCO₂^tBu)₂] **Pd(1)** wykorzystano w procesie FEBID ze względu na najniższą temperaturę sublimacji. Stosując $T_{GIS} = 358$ K otrzymano depozyt 2D zawierający 25 at.% Pd. Właściwości tego kompleksu wskazują również na jego potencjalną przydatność jako prekursora w technice FIBID.

Podsumowując:

Zastosowana metodologia pozwoliła na zaproponowanie przyjaznych dla użytkownika prekursorów do zastosowań w metodach CVD oraz FEBID.

Zebrany materiał badawczy pozwolił na sformułowanie następujących uogólnień:

- Potwierdzono istotny wpływ centrum koordynacji na właściwości kompleksów. Zmiana jonu centralnego z Cu → Ni w związku [M₂(NH₂(NH=)CC₂F₅)₂(μ-O₂CC₂F₅)₄] obniża lotność oraz wrażliwość na elektrony nisko- i wysokoenergetyczne.
- Połączenia zawierające ligandy N,N-donorowe są stabilne termicznie i lotne, ale wykazują niską wrażliwość na elektrony nisko- i wysokoenergetyczne.
- Najbardziej odpowiednimi prekursorami mogącymi mieć zastosowanie w metodach osadzania z fazy gazowej, zwłaszcza FEBID i FIBID są związki zawierające ligandy O,O- donorowe, takie jak **karboksylany, czy β-ketoesterany**, gdyż grupa -COO stosunkowo łatwo dysocjuje w procesach indukowanych elektronami, a powstające cząsteczki CO₂ oraz towarzyszące im węglowodory mogą łatwo odszczepiać się z powierzchni podłoża.

Wykaz prac wchodzących w skład rozprawy doktorskiej

[D1] Martinović P.; Rohdenburg M.; **Butrymowicz A.**; Sarigül S.; Huth P.; Denecke R.; Szymańska I. B.; Swiderek P. Electron-Induced Decomposition of Different Silver(I) Complexes: Implications for the Design of Precursors for Focused Electron Beam Induced Deposition, *Nanomaterials* **2022**, 12, 1687, doi:10.3390/nano12101687 (IF = 5.7; MNiSW = 100)

[D2] **Butrymowicz-Kubiak A.**; Luba W.; Madajska K.; Muzioł T.; Szymańska I.B. Pivalate complexes of copper(II) with aliphatic amines as potential precursors for depositing nanomaterials from the gas phase, *New J. Chem.*, **2024**, 48, 6232, doi:10.1039/d3nj04959k (IF = 2.7; MNiSW = 70)

[D3] **Butrymowicz-Kubiak A.**; Topolski A.; Muzioł T. M.; Szymańska I. B. Nickel complexes based on perfluorinated amidine for applications in gas-assisted methods and photocatalysis, *Dalt. Trans.*, **2025**, *praca przyjęta do druku*, doi: 10.1039/D5DT00550G (IF = 3.5; MNiSW = 140)

[D4] **Butrymowicz-Kubiak A.**; Muzioł T.M.; Madajski P.; Szymańska I.B. New Gold(I) Complexes as Potential Precursors for Gas-Assisted Methods: Structure, Volatility, Thermal Stability, and Electron Sensitivity, *Molecules*, **2025**, 30, 146, doi:10.3390/molecules30010146 (IF = 4.2; MNiSW = 140)

[D5] **Butrymowicz-Kubiak A.**; Muzioł T.M.; Kaczmarek Kędziera A.; Jureddy C.S.; Maćkosz K.; Utke I.; Szymańska I.B. New palladium(II) β -ketoesterates for Focused Electron Beam Induced Deposition: Synthesis, structures, and characterization, *Dalt. Trans.*, **2024**, 53, 13662, doi:10.1039/d4dt01287a (IF = 3.5; MNiSW = 140)

Spis rysunków

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Dorobek naukowy

Publikacje będące podstawą rozprawy doktorskiej:

- [D1] Martinović P.; Rohdenburg M.; **Butrymowicz A.**; Sarigül S.; Huth P.; Denecke R.; Szymańska I. B.; Swiderek P. Electron-Induced Decomposition of Different Silver(I) Complexes: Implications for the Design of Precursors for Focused Electron Beam Induced Deposition, *Nanomaterials* **2022**, 12, 1687, doi:10.3390/nano12101687 (IF = 5.7; MNiSW = 100)
- [D2] **Butrymowicz-Kubiak A.**; Luba W.; Madajska K.; Muzioł T.; Szymańska I.B. Pivalate complexes of copper(II) with aliphatic amines as potential precursors for depositing nanomaterials from the gas phase, *New J. Chem.*, **2024**, 48, 6232, doi:10.1039/d3nj04959k (IF = 2.7; MNiSW = 70)
- [D3] **Butrymowicz-Kubiak A.**; Topolski A.; Muzioł T. M.; Szymańska I. B. Nickel complexes based on perfluorinated amidine for applications in gas-assisted methods and photocatalysis, *Dalt. Trans.*, **2025**, *praca zaakceptowana*, doi: 10.1039/D5DT00550G (IF = 3.5; MNiSW = 140)
- [D4] **Butrymowicz-Kubiak A.**; Muzioł T.M.; Madajski P.; Szymańska I.B. New Gold(I) Complexes as Potential Precursors for Gas-Assisted Methods: Structure, Volatility, Thermal Stability, and Electron Sensitivity, *Molecules*, **2025**, 30, 146, doi:10.3390/molecules30010146 (IF = 4.2; MNiSW = 140)
- [D5] **Butrymowicz-Kubiak A.**; Muzioł T.M.; Kaczmarek Kędziera A.; Jureddy C.S.; Maćkosz K.; Utke I.; Szymańska I.B. New palladium(II) β -ketoesterates for Focused Electron Beam Induced Deposition: Synthesis, structures, and characterization, *Dalt. Trans.*, **2024**, 53, 13662, doi:10.1039/d4dt01287a (IF = 3.5; MNiSW = 140)

Publikacje spoza rozprawy:

- 1) Jureddy C.S., Maćkosz K., **Butrymowicz-Kubiak A.**, Szymańska I.B., Hoffman P., Utke I. Direct writing of nanostructures with electron beam using palladium β -diketoesterate complex, *Beilstein J. Nanotechnol.*, **2025**, 16, 530–539, doi:10.3762/bjnano.16.41 (IF = 2.6; MNiSW = 100)

- 2) Szymańska I.B.; Madajska K.; **Butrymowicz A.**; Barwiolek M. Copper(II) Perfluorinated Carboxylate Complexes with Small Aliphatic Amines as Universal Precursors for Nanomaterial Fabrication, *Materials* **2021**, 14, 7451, <https://doi.org/10.3390/ma14237451> (IF = 3.7; MNI_{SW} = 140),

Patent:

K. Madajska, **A. Butrymowicz**, I. B. Szymańska, Związki miedzi(I), miedzi(II) i palladu(II) z amidynianami o perfluorowanym łańcuchu alkilowym oraz sposób ich wytwarzania, Pat.243245 (Biuletyn Urzędu Patentowego 07.03.2022)

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- 1) Grants4NCUStudents (kierownik grantu): 90-SIDUB.6102.66.2022.G4NCUS5, *The application of new complexes of group 10 and 11 in chemical vapour deposition method(CVD)*, 2022, **A. Butrymowicz-Kubiak**, W. Luba, M. Jaros, W. Ciarkowska,
- 2) Grants4NCUStudents (kierownik grantu): 90-SIDUB.6102.41.2022.G4NCUS4, *New nickel and gold precursors for focused electron/ion beam*, 2022, **A. Butrymowicz-Kubiak**, W. Luba,

- 3) Grants4NCUStudents (członek zespołu): 90-SIDUB.6102.83.2021.G4NCUS1, *Studies of key processes for finding new FEBID/FIBID precursors*, 2021, K. Madajska, **A. Butrymowicz-Kubiak**,
- 4) Stypendystka w ramach projektu badawczego SONATA BIS: „Rola oddziaływań niekowalencyjnych w organizacji układów supramolekularnych i fenomen transformacji strukturalnych w monokryształach”, Wydział Chemii UMK”, Zakres prac: Synteza związków koordynacyjnych Au(I) na bazie ligandów heterocyklicznych. Fizykochemiczna charakterystyka uzyskanych połączeń koordynacyjnych. Krystalizacja. Badania strukturalne otrzymanych produktów krystalicznych i analiza termiczna (23.09–23.12.2024), kierownik projektu: dr hab. Liliana Dobrzańska, prof. UMK.

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Prezentacje ustne:

- 1) **Aleksandra Butrymowicz-Kubiak**, Katarzyna Madajska, Tadeusz Muzioł, Anna Kaczmarek-Kędziera, Wiktoria Luba, Chinmai S. Jureddy, Krzysztof Maćkosz, Ivo Utke, Iwona B. Szymańska, *Electron interactions with new potential FEBID precursors of nickel, palladium, copper and gold*, FEBIP 2024 : 9th Workshop of Focused Electron Beam Induced Processing, Uniwersytet Goethego, Frankfurt nad Menem, Niemcy, 21-24.07.2024;
- 2) **Aleksandra Butrymowicz-Kubiak**, Tadeusz M. Muzioł, Anna Kaczmarek-Kędziera, Chinmai S. Jureddy, Krzysztof Maćkosz, Ivo Utke, Iwona B. Szymańska, *Electron-molecule interaction studies for new Pd(II) complexes and preliminary FEBID tests*, MultiChem Working Group meeting, Frankfurt nad Menem, Niemcy, 25-26.07.2024;
- 3) **Aleksandra Butrymowicz-Kubiak**, Wiktoria Luba, Katarzyna Madajska, Tadeusz Muzioł, Iwona Szymańska, *Pivalate complexes of copper(II) with aliphatic amines as potential precursors for depositing nanomaterials from the gas phase*, XVII Seminarium Kopernikańskie, Uniwersytet Mikołaja Kopernika, Toruń, Polska, 06-07.06.2024;
- 4) **Aleksandra Butrymowicz**, Wiktoria Luba, Tadeusz Muzioł, Iwona B. Szymańska, *Copper(II) complexes with pivalate and small aliphatic amines as potential precursors in vapour deposition methods*, XXVIII International Conference on Coordination and

Bioinorganic "Recent progress in coordination, bioinorganic and applied inorganic chemistry", Smolenice, Słowacja, 5-10.06.2022;

- 5) **Aleksandra Butrymowicz**, Iwona Szymańska, *New palladium(II) complexes with perfluorinated amidinates as precursors in vapor deposition methods*, 1st HighLIGHTing Science Meeting and PANIC, Wrocław, Polska, 26-28.05.2021;
- 6) **Aleksandra Butrymowicz**, Iwona Szymańska, *Nowe kompleksy miedzi(I) i miedzi(II) z N'-tert-butylo-N,N-dimetyloformamidyną*, Władcy chemii: 51. Ogólnopolska Szkoła Chemii, Wrocław, Polska, 08-10.11.2019.

Postery:

- 1) **Aleksandra Butrymowicz-Kubiak**, Tadeusz Muzioł, Anna Kaczmarek-Kędziera, Chinmai Jureddy, Krzysztof Maćkosz, Ivo Utke, Iwona Szymańska, *New Pd(II) β -ketoesterates complexes as potential FEBID precursors*, 9th EuChemS Chemistry Congress (ECC), Dublin, Irlandia, 07-11.07.2024;
- 2) **Aleksandra Butrymowicz-Kubiak**, Iwona B. Szymańska, *Nowe związki kompleksowe palladu(II) z β -ketoestrami jako potencjalne prekursorzy FEBID*, 65. Zjazd Naukowy Polskiego Towarzystwa Chemicznego. Toruń, Polska, 18-22.09.2023;
- 3) **Aleksandra Butrymowicz**, Iwona Szymańska, Tadeusz Muzioł, *New palladium(II) complexes with O,O- and N,N-donor ligands for nanomaterials fabrication*, The 5th International Conference on Functional Molecular Materials (FunMat 2023), Uniwersytet Jagielloński, Kraków, Polska, 29-31.03.2023;
- 4) **Aleksandra Butrymowicz**, Iwona Szymańska, *New Nickel(II) perfluorinated amidine-carboxylate and imidoylamidinate complexes as potential precursors in vapour deposition methods*, 44th International Conference on Coordination Chemistry, Rimini, Włochy, 28.08-02.09.2022;
- 5) **Aleksandra Butrymowicz**, Katarzyna Madajska, Wiktoria Luba, Tadeusz Muzioł, Iwona B. Szymańska, *Copper(II) complexes with pivalate and small aliphatic amines as precursors for nanomaterial fabrication*, FEBIP 2022: 8th Workshop of Focused Electron Beam Induced Processing, Kraków, Polska 13-15.07.2022;
- 6) **Aleksandra Butrymowicz**, Iwona B. Szymańska, *New gold(I) and gold(II) complexes with amidinates as potential precursors for vapor deposition methods*, FIT4NANO Workshop, Kraków, Polska 11-13.07.2022;
- 7) **Aleksandra Butrymowicz**, Iwona Szymańska, *New volatile palladium(II) and nickel(II) perfluorinated amidine derivatives as potential precursor in FEBID/FIBID*

methods, 4th EuFN and FIT4NANO Joint Workshop/Meeting, Wiedeń, Austria, 27-30.09.2021.

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- 1) Iwona B. Szymańska, Katarzyna Madajska, **Aleksandra Butrymowicz-Kubiak**, *Fluorinated or non-fluorinated precursors for FEBID/FIBID process?*, FIT4NANO Workshop 2024, Durrës, Albania, 16-20.09.2024;
- 2) Iwona B. Szymańska, Katarzyna Madajska, **Aleksandra Butrymowicz-Kubiak**, *Badanie oddziaływania elektronów z kompleksami w celu znalezienia nowych prekursorów FEBID*, 65. Zjazd Naukowy Polskiego Towarzystwa Chemicznego. Toruń, Polska, 18-22.09.2023;
- 3) Benedykt Ryszard Jany, Katarzyna Madajska, **Aleksandra Butrymowicz-Kubiak**, Iwona Szymańska, Franciszek Krok, *Method of Testing Decomposition Results of the Metal-organic: precursors for IBID Applications using Gallium FIB*, FIT4NANO Workshop, Lizbona, Portugalia 17-19.07.2023;
- 4) Iwona Szymańska, **Aleksandra Butrymowicz-Kubiak**, Katarzyna Madajska, *Ni, Pd, Cu, and Ag FEBID/FIBID potential precursors' interactions with electrons*, FIT4NANO Workshop, Lizbona, Portugalia 17-19.07.2023;
- 5) Wiktoria Luba, **Aleksandra Butrymowicz**, Tadeusz Muzioł, Iwona Szymańska, *Pivalate complexes of copper(II) with aliphatic amines as potential precursors for CVD and FEBID methods*, The 5th International Conference on Functional Molecular Materials (FunMat 2023), Kraków, Polska, 29-31.03.2023;
- 6) Iwona Szymańska, **Aleksandra Butrymowicz**, Katarzyna Madajska, *Coordination chemistry influence on new FEBID precursors development*, The 5th International Conference on Functional Molecular Materials (FunMat 2023), Kraków, Polska, 29-31.03.2023;
- 7) Petra Martinović, Markus Rohdenburg, **Aleksandra Butrymowicz**, Selma Sarigül, Paula Huth, Reinhard Denecke, Iwona B. Szymańska, Petra Swiderek, *Electron-induced decomposition of different silver(I) complexes: implications for the design of precursors for focused electron beam induced deposition*, FEBIP 2022: 8th Workshop of Focused Electron Beam Induced Processing, Kraków, Polska, 13-15.07.2022;
- 8) Iwona B. Szymańska, **Aleksandra Butrymowicz**, Katarzyna Madajska, *How coordination chemistry limits new FEBID precursors development?*, FEBIP 2022: 8th Workshop of Focused Electron Beam Induced Processing, Kraków, Polska,

13-15.07.2022;

- 9) Benedykt Ryszard Jany, Katarzyna Madajska, **Aleksandra Butrymowicz**, Iwona B. Szymańska, Franciszek Krok, *New Cu precursors for ion beam induced deposition under Gallium FIB*, FIT4NANO Workshop, Kraków, Polska 11-13.07.2022;
- 10) Katarzyna Madajska, **Aleksandra Butrymowicz**, Iwona B. Szymańska, *Selection of coordination compounds for the study of interactions with a focused ion beam*, FIT4NANO Workshop, Kraków, Polska 11-13.07.2022;
- 11) Potential FEBID/FIBID precursors of groups 10 and 11 with O- and N-donor ligands, Katarzyna Madajska, **Aleksandra Butrymowicz**, Iwona Szymańska, 4th EuFN and FIT4NANO Joint Workshop/Meeting, Wiedeń, Austria, 27-30.09.2021.

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Article

Electron-Induced Decomposition of Different Silver(I) Complexes: Implications for the Design of Precursors for Focused Electron Beam Induced Deposition

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Abstract: Focused electron beam induced deposition (FEBID) is a versatile tool to produce nanostructures through electron-induced decomposition of metal-containing precursor molecules. However, the metal content of the resulting materials is often low. Using different Ag(I) complexes, this study shows that the precursor performance depends critically on the molecular structure. This includes Ag(I) 2,2-dimethylbutanoate, which yields high Ag contents in FEBID, as well as similar aliphatic Ag(I) carboxylates, aromatic Ag(I) benzoate, and the acetylide Ag(I) 3,3-dimethylbutynyl. The compounds were sublimated on inert surfaces and their electron-induced decomposition was monitored by electron-stimulated desorption (ESD) experiments in ultrahigh vacuum and by reflection–absorption infrared spectroscopy (RAIRS). The results reveal that Ag(I) carboxylates with aliphatic side chains are particularly favourable for FEBID. Following electron impact ionization, they fragment by loss of volatile CO₂. The remaining alkyl radical converts to a stable and equally volatile alkene. The lower decomposition efficiency of Ag(I) benzoate and Ag(I) 3,3-dimethylbutynyl is explained by calculated average local ionization energies (ALIE) which reveal that ionization from the unsaturated carbon units competes with ionization from the coordinate bond to Ag. This can stabilise the ionized complex with respect to fragmentation. This insight provides guidance with respect to the design of novel FEBID precursors.

Keywords: focused electron beam induced deposition; silver precursors; precursor design; electron-induced chemistry; electron-stimulated desorption

1. Introduction

Silver(I) carboxylates have lately received increasing attention regarding their application in focused electron beam induced deposition (FEBID) [1–3]. FEBID is a direct-write method, which is performed in electron microscopes and generates precisely defined metal nanostructures through electron-induced decomposition of suitable precursor molecules [4]. Gaseous precursors are injected into the vacuum chamber of the microscope, physisorb on a substrate surface, and are then dissociated under the focused electron beam. Ideally, this leads to pure metal deposits while volatile organic compounds are pumped away [4]. Unfortunately, the organic ligands often become incorporated in the deposits leading to unwanted contaminations. Without applying post-deposition purification methods, the metal content of typical FEBID deposits fabricated from metal-

containing precursors typically lies in the range 5–40 atom% [3,5,6]. This impedes possible applications requiring, e.g., high electrical conductivity.

The first reported deposition of silver (Ag) via FEBID used the carboxylate complex Ag(I) 2,2-dimethylbutanoate ($[\text{Ag}_2(\mu\text{-O}_2\text{CC}(\text{CH}_3)_2\text{C}_2\text{H}_5)_2]$) as precursor [7]. Ag FEBID nanostructures are of interest because pure Ag is suitable for plasmonic applications due to small optical losses in the visible regime [7]. Carboxylate complexes have been successfully used in chemical vapour deposition (CVD) resulting in high purity thin metal films [8–12]. FEBID of Ag from Ag(I) 2,2-dimethylbutanoate was enabled by a fully integrated and heated gas injection system (GIS) that can handle Ag compounds despite their relatively low vapour pressures [7]. The results have revealed that Ag(I) 2,2-dimethylbutanoate is a promising FEBID precursor that produces high purity deposits with Ag contents of up to 73 atom% [7]. Recently, the fluorinated complex Ag(I) pentafluoropropionate ($[\text{Ag}_2(\mu\text{-O}_2\text{CCF}_5)_2]$) was also used for FEBID resulting in deposits with high silver contents of up to 76 atom% [3].

The design of suitable FEBID precursors requires insight into the mechanisms that govern their electron-induced decomposition [13]. As demonstrated herein for the case of Ag(I) complexes, the efficient decomposition of the precursors depends decisively on the structure of the organic ligands that are coordinated to the metal. In the case of carboxylate ligands, the electron-induced fragmentation is thought to be driven by electron ionization (EI) leading to release of thermodynamically stable and volatile CO_2 (Figure 1). This was deduced previously from studies on the electron-induced decomposition of thin surface layers of the coordination polymer Cu(II) oxalate and of the metal organic framework HKUST-1 [14,15], the latter being a three-dimensional coordination polymer consisting of Cu^{2+} ions that are linked by trivalent benzene-1,3,5-tricarboxylate anions. However, it was also observed that the removal of elements other than the metal during electron irradiation was much more efficient for Cu(II) oxalate than in the case of HKUST-1 [14], underlining that the loss of CO_2 from the carboxylate is not the only factor that governs the efficiency of decomposition. In fact, it was proposed that the facile decomposition of Cu(II) oxalate is related to a reaction pathway that can convert the entire oxalate unit to the stable volatile product molecule CO_2 [16].

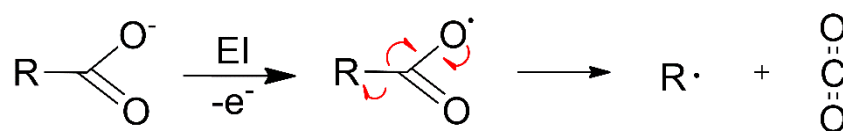


Figure 1. Fragmentation of carboxylate ligands in metal complexes initiated by ionization following electron impact, as proposed earlier [14–17]. Red arrows indicate the electron rearrangement that leads to release of CO_2 and an organic radical $\text{R}^\bullet$.

Aiming at design strategies for precursors to be used in FEBID of Ag nanostructures, we report here surface science studies conducted in a clean ultrahigh vacuum (UHV) environment that investigate the electron-induced decomposition of Ag(I) complexes with different ligands. Volatile compounds released upon electron impact from a precursor layer were analysed by use of mass spectrometry (MS) in an electron-stimulated desorption (ESD) experiment. Complementarily, reflection–absorption infrared spectroscopy (RAIRS) was employed to monitor chemical changes in the precursor layer upon electron exposure. Although the studies were conducted with much lower primary electron energies (herein 50 eV, exceptionally 100 or 500 eV) than typically used in FEBID (>1 keV) [4], it is widely accepted that low-energy secondary electrons drive much of the precursor fragmentation that occurs under the electron beam [13,18–20]. Therefore, the present approach can reveal the typical decomposition reactions that are also relevant to the actual FEBID process.

We studied, in particular, the electron-induced decomposition of Ag(I) 2,2-dimethylbutanoate (Figure 2, (1)) as an example of a precursor that performs well in FEBID and

compared its electron-induced decomposition to a carboxylate complex with aromatic side group, namely, Ag(I) benzoate (Figure 2, (2)), and an organometallic acetylide compound with a Ag-C bond, Ag(I) 3,3-dimethyl-1-butyne (Figure 2, (3)). Furthermore, a fully deuterated Ag(I) 2,2-dimethylbutanoate and several Ag(I) carboxylates with different alkyl groups (Figure 2, (4–7)) were included to support the conclusions. Note that the volatile Ag(I) carboxylate complexes have a dimeric structure, as shown in Figure 2 [21], while Ag(I) 3,3-dimethyl-1-butyne (3) has been described as a polymeric material [22] but is represented in Figure 2 by its monomeric form. Samples were prepared by sublimating these compounds onto self-assembled monolayers (SAMs) of 4-biphenylthiol (BPT) on Au surfaces that were fully cross-linked by electron irradiation prior to the sublimation. The cross-linked BPT (cl-BPT) SAM does not, by itself, give rise to ESD signals and suppresses unwanted adsorption of vapours on the Au support during handling of the samples under ambient conditions [23]. This approach thus ensures that ESD stems entirely from the sublimate layers. The results reveal that the ligands of Ag(I) 2,2-dimethylbutanoate and other compounds containing alkylated carboxylate ligands can be converted to volatile products by electron irradiation, while this is not the case for the aromatic carboxylate ligand and the alkynyl ligand. This work thus provides guidance for the choice of suitable Ag(I) carboxylate precursors for FEBID.

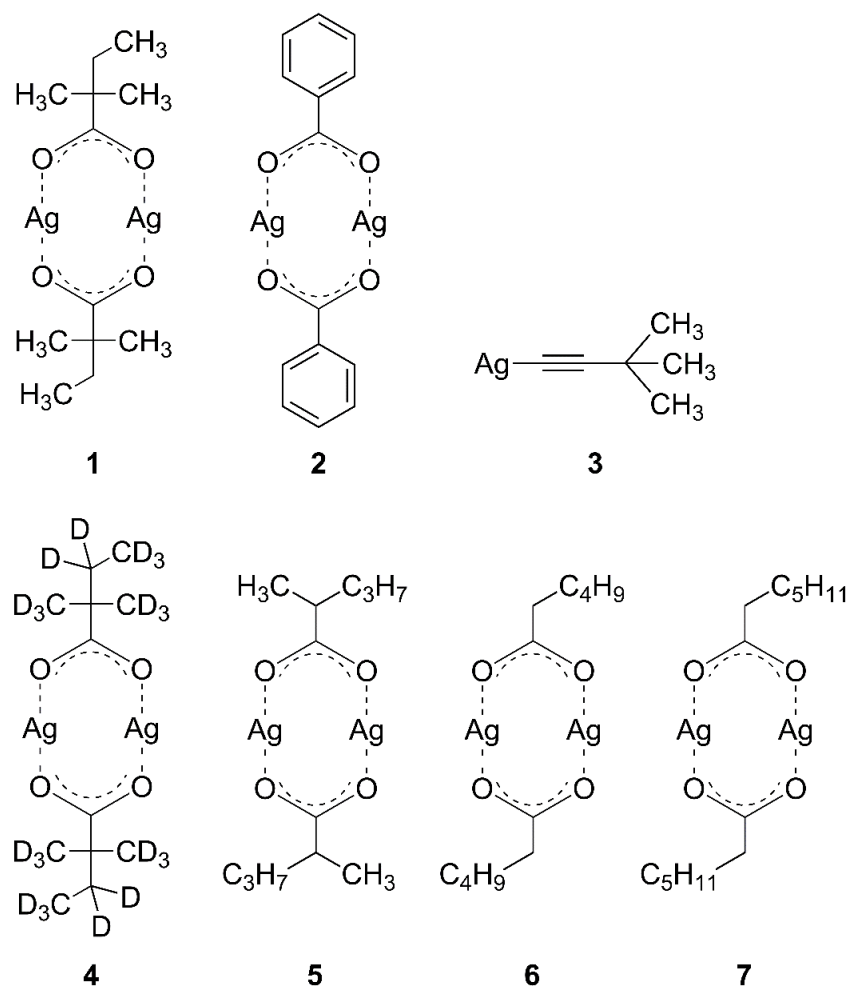


Figure 2. Silver(I) complexes used in the present study: Ag(I) 2,2-dimethylbutanoate (1); Ag(I) benzoate (2); Ag(I) 3,3-dimethyl-1-butyne (3); Ag(I) 2,2-dimethylbutanoate- d_{11} (4); Ag(I) 2-methylpentanoate (5); Ag(I) hexanoate (6); Ag(I) heptanoate (7). The volatile Ag(I) carboxylate complexes (1–2, 4–7) have a dimeric structure [21], while Ag(I) 3,3-dimethyl-1-butyne (3) has been described as a polymeric material [22] but is shown here in its monomeric form for simplicity.

2. Materials and Methods

2.1. Precursor Synthesis

Ag(I) carboxylates (Ag(I) 2,2-dimethylbutanoate, Ag(I) benzoate, Ag(I) 2,2-dimethylbutanoate- d_{11} , Ag(I) 2-methylpentanoate, Ag(I) hexanoate, and Ag(I) heptanoate) were synthesised from the corresponding carboxylic acids (2,2-dimethylbutanoic acid (Alfa Aesar, Haverhill, MA, USA, 97%)), benzoic acid (Merck, Darmstadt, Germany, 99%), 2,2-dimethylbutanoic acid d_{11} (CDN Isotopes, Quebec, Canada, 98.4% d_{11}), 2-methylpentanoic acid (Sigma-Aldrich, St. Louis, MO, USA, 98%), hexanoic acid (Alfa Aesar, Haverhill, MA, USA, 98+%), heptanoic acid (SAFC, St. Louis, MO, USA, 97%)), and silver nitrate (Alfa Aesar, Haverhill, MA, USA, 99.9+%) using a simple precipitation reaction modified from a protocol reported previously [21]. A solution of the carboxylic acid (3.5 mmol) and potassium hydroxide (Riedel-de-Haën, Seelze, Germany, >85%, 3.5 mmol) in a water–ethanol mixture (1:1 *v/v*) was stirred and an equal volume of a solution of silver nitrate in water (3.5 mmol) was slowly added. A white precipitate formed, which was filtered, washed with water and ethanol, and dried in vacuo. Ag(I) 3,3-dimethyl-1-butynyl was obtained from Oliver Feddersen Clausen (www.modularflow.com) and used as received.

2.2. Sample Preparation

In line with experiments reported previously [23] and except for samples used in XPS experiments, all Ag(I) compounds were sublimated on a cl-BPT SAM, which was grown beforehand on an Au surface (200 nm Au on 5 nm Ti on boron-doped silicon, Georg Albert PVD). Prior to the preparation of the SAM, the Au surface was cleaned by immersion in peroxymonosulfuric acid (H_2SO_4/H_2O_2 3:1 *v/v*), followed by rinsing with distilled water and ethanol. Each cleaning step was conducted for at least 15 min using ultrasonication. The cleaned Au surface was immersed in a 1 mM solution of BPT (Sigma-Aldrich, St. Louis, MO, USA, 97%) in ethanol for 72 h and then washed with ethanol and dried in a nitrogen stream. RAIRS confirmed the formation of the BPT SAM. For cross-linking, the BPT SAM was exposed to an electron dose of 40,000 $\mu C/cm^2$ at $E_0 = 500$ eV. This was sufficient to terminate desorption of H_2 according to MS. Sublimation was conducted using a glassware sublimation apparatus. The cl-BPT-SAM was mounted on the coldfinger of the apparatus and the Ag(I) compound (amounts ranging from 1 to 15 mg depending on the compound) was filled into the flask. Sublimation was performed by evacuating the flask to 5×10^{-2} mbar and heating it to 200 °C (240 °C for Ag(I) benzoate) while the coldfinger was flushed with cooling water throughout the sublimation process. Samples inspected by optical microscopy and by XPS were prepared by sublimating the Ag(I) compounds onto cleaned Au substrates without SAM. All sublimated samples were characterised using RAIRS.

2.3. Electron-Stimulated Desorption (ESD) Experiments

ESD experiments were performed in a home-built UHV chamber described before [14,16]. The setup is equipped with a flood gun (SPECS FG15/40, SPECS Surface Nano Analysis GmbH, Berlin, Germany) for electron exposure and a quadrupole mass spectrometer (QMS) residual gas analyser (RGA) (Stanford Research Systems, Sunnyvale, CA, USA) with mass range m/z 1–300 for analysing the desorbing products. The electron gun delivers a divergent electron beam with a tunable energy in the range of 1–500 eV and with current densities measured on the sample between 10 and 30 $\mu A/cm^2$. The setup consists of a main chamber and a small transfer chamber that can be evacuated and vented separately and is used to insert the sublimate samples. The samples were mounted on Cu sample holders, which were cleaned beforehand in the main chamber by electron irradiation at $E_0 = 500$ eV. After inserting the samples, the transfer chamber was evacuated to a pressure of 1×10^{-8} mbar, allowing for sample transfer into the main chamber by use of a linear manipulator. The pressure in the main chamber was constantly kept below 5×10^{-9} mbar. To further reduce ESD from the Cu sample holder, the sample holders were covered

by a Cu mask, which was kept in vacuum between experiments and exposes approximately 2 cm² of the sample surface to the electron beam. The mask is electrically insulated from the sample and is held at chamber ground potential.

Most ESD experiments were carried out using an electron energy of $E_0 = 50$ eV. Selected experiments were, in addition, performed at 100 or 500 eV. To accurately measure the sample current and therefore the electron exposure, a positive bias was applied to the sample. This prevents secondary electrons, which are produced upon irradiation, from escaping. For 50 eV (100 eV, 500 eV), the flood gun energy was set to 45 eV (90 eV, 480 eV) while a positive bias of +5 eV (+10 eV, +20 eV) was applied. The ESD experiments were performed at room temperature. The desorbing neutral products, which have desorption cross-sections that are typically orders of magnitude higher than those of ions [24], were analysed by MS in a selected m/z range after EI at 70 eV in the ion source of the QMS. The QMS was also used to measure mass spectra of 2-methyl-2-butene, CO₂ and H₂O, which were needed as reference to fit the ESD data of Ag(I) 2,2-dimethylbutanoate. Note that the RGA employed in this study discriminates against high m/z ratios, which impedes the usage of listed reference MS data [17].

2.4. Reflection–Absorption Infrared Spectroscopy (RAIRS)

RAIRS was used to confirm the successful sublimation of the Ag(I) compounds on cl-BPT SAMs and to monitor their decomposition in an ex situ experiment after electron exposure. RAIR spectra were measured as described previously [25] with an evacuated FTIR spectrometer (IFS 66v/S, Bruker Optics GmbH, Ettlingen, Germany) by accumulating 400 scans in the range between 4000 and 750 cm^{−1} with a resolution of 4 cm^{−1} using an aperture of 2.0 mm. The spectrometer is equipped with a grazing incidence reflection unit and a liquid nitrogen-cooled MCT detector with sufficient sensitivity down to 750 cm^{−1}. During measurements, the sample chamber was evacuated to 5–8 mbar and the system was purged with N₂ to eliminate residual vapours such as CO₂ and H₂O. A fully deuterated hexadecanethiol (HDT) SAM grown on a Au surface was used to measure background spectra.

2.5. Attenuated Total Reflection (ATR) and Transmission Infrared Spectroscopy

ATR infrared spectroscopy (ATR–IR) [26] was used to verify the integrity of the Ag(I) precursors prior to sublimation. The spectra were measured using a FTIR Spectrometer (Nicolet™ Summit, Thermo Scientific™, Waltham, MA, USA) with a monolithic germanium ATR crystal by accumulating 16 scans in the range between 4000 and 550 cm^{−1}. In addition, transmission infrared spectra were measured on the evacuated FTIR spectrometer that was also used for RAIRS. For this, a mixture containing 0.1% of the Ag(I) compound and 99.9% KBr were pressed into a pellet. A pure KBr pellet was used as background.

2.6. Optical Microscopy

Optical microscopy (×40) was used to take photos of sublimated layers of Ag(I) 2,2-dimethylbutanoate, Ag(I) benzoate, and Ag(I) 3,3-dimethyl-1-butyne. A Motic BA210 LED microscope (Motic, Barcelona, Spain) was used for this purpose.

2.7. X-Ray Photoelectron Spectroscopy

All XPS measurements were performed with a VG ESCALAB 220I XL spectrometer (Thermo Scientific™, Waltham, MA, USA) at room temperature and with a background pressure < 1 × 10^{−8} mbar. To excite the photoelectrons, non-monochromatised Al K_{α1,2} (1486.6 eV) radiation was used. The samples were attached to the sample holder by double-sided carbon tape, which also provides conducting contact.

All measurements were carried out in normal emission. To focus the emitted electrons, a lens mode characterised by a small angular acceptance ($\approx \pm 4^\circ$) and a large detection

area ($\varnothing$ 5 mm) was used. The hemispherical electron energy analyser was operated in constant analyser energy mode. The detail spectra were recorded with pass energy of 50 eV. The photoelectron current was accumulated over 30 ms, parallel in six channeltrons, with energy steps of 0.1 eV. Each range was scanned four times, using an alternating recording mode.

All XPS data were processed using Unifit software (Version 2022, Unifit Scientific Software GmbH, Leipzig, Germany) [27]. For all detail spectra, the excitation satellites were subtracted. A charge correction was applied by setting the major C 1s signal to a binding energy of 285 eV. As background function, the sum of a first order polynomial and Shirley function was used. The spectra were fitted using Voigt profiles. Within one spectrum, the Gaussian and Lorentzian widths were kept the same for all signals as well as doublet separations, if applicable. Peak height ratios within doublets were kept fixed, respecting the quantum mechanically derived intensity ratios.

2.8. Computational Methods

DFT-based geometry optimisation of Ag(I) compounds was carried out using the Gaussian16 software package (rev. C.01, Gaussian, Inc., Wallingford, CT, USA) [28]. The B3LYP/def2-TZVPP [29–32] model chemistry was employed including empirical dispersion corrections according to Grimme's D3 method [33] involving Becke–Johnson damping (GD3BJ) [34]. The location of minimum structures on the potential energy surface was verified by the absence of imaginary frequencies in vibrational analyses. The average local ionization energy (ALIE) [35] was calculated in a three-dimensional grid out of the DFT wavefunction with the Multiwfn software (Version 3.8, Tian Lu, Beijing, China) [36].

3. Results

3.1. Characterisation of Sublimated Precursor Layers

Prior to electron irradiation, the integrity of the Ag(I) compounds after sublimation was verified and the structure and thickness of the sublimate layers were characterised. IR spectra of Ag(I) 2,2-dimethylbutanoate, Ag(I) benzoate, and Ag(I) 3,3-dimethyl-1-butyryl are shown in Figure 3. RAIRS data for the sublimate layers are compared to spectra of the as-prepared compounds recorded by transmission IR spectroscopy in KBr pellets and by ATR-IR. For each compound, all data were obtained from material resulting from the identical synthesis batch. Full range spectra of Ag(I) 2,2-dimethylbutanoate and Ag(I) benzoate are presented in Figure S1 (Supplemental Materials) and the detailed assignment of the bands is summarised in Tables S1–S3 (Supplemental Materials).

The transmission IR spectra of Ag(I) 2,2-dimethylbutanoate (Figure 3a) and Ag(I) benzoate (Figure 3b) obtained from the as-synthesised compounds agree well with previous results [21,37–39]. However, the positions of the asymmetric carboxylate stretching vibration $\nu_{as}(\text{COO}^-)$ at 1544 and 1553 cm^{-1} are indicative of a dominant contribution of ligands with a monodentate coordination [40–43]. The transmission IR spectrum of Ag(I) benzoate exhibits an additional band at 1517 cm^{-1} , which is characteristic of a bridging coordination [40–43]. Only the bridging coordination is observed in the ATR-IR and RAIR spectra of both Ag(I) 2,2-dimethylbutanoate and Ag(I) benzoate. This is consistent with the presence of Ag(I) dimers bridged by two carboxylate ligands as also deduced earlier from mass spectra of gaseous Ag(I) 2,2-dimethylbutanoate [21]. As all spectra for a particular compound shown in Figure 3 have been obtained from the same synthesis batch, we conclude that the presence of unidentate species in the transmission spectra results from a phase transition induced by the high pressure applied when preparing the KBr pellets. In contrast, the RAIRS data support that sublimation preserves the dimer structure.

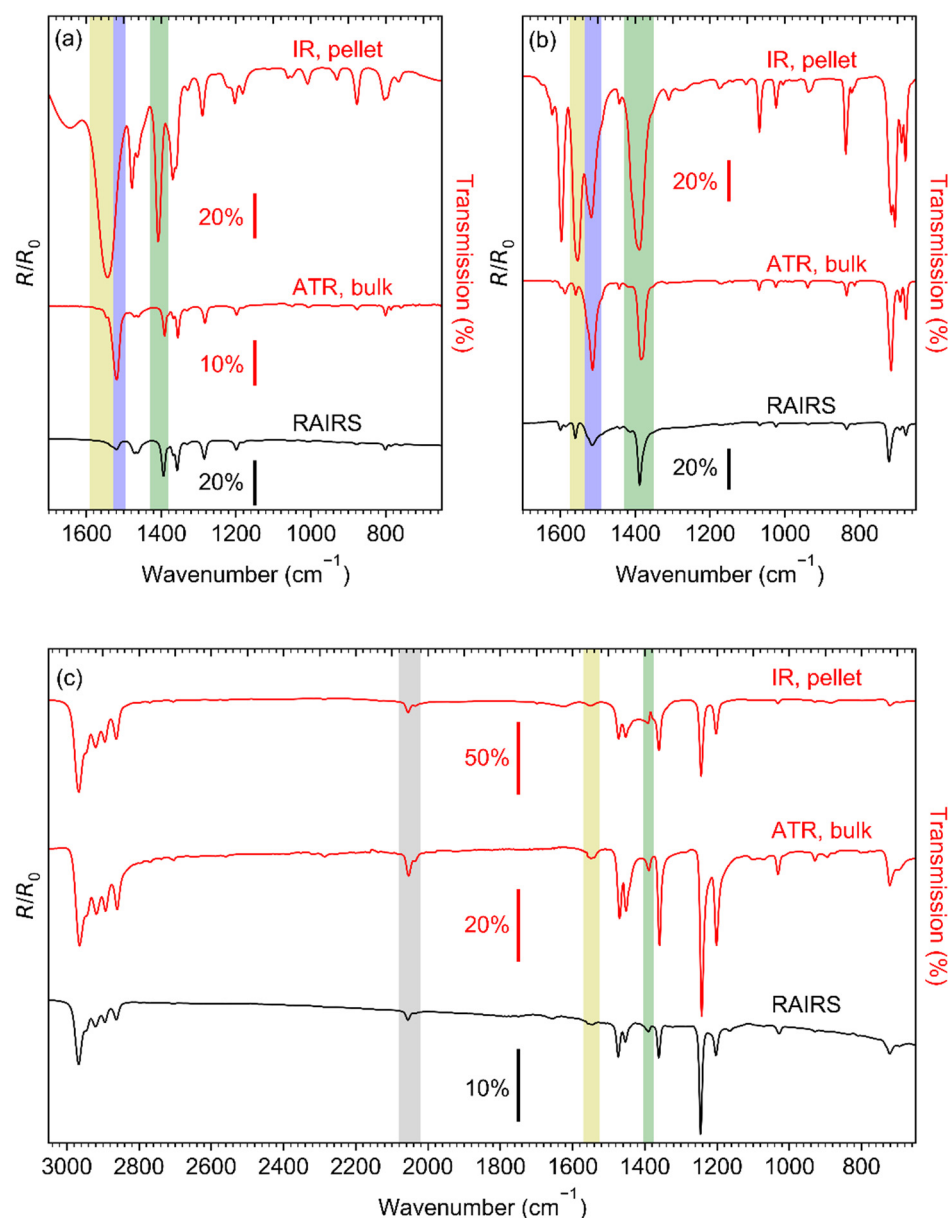


Figure 3. Infrared spectra of (a) Ag(I) 2,2-dimethylbutanoate, (b) Ag(I) benzoate, and (c) Ag(I) 3,3-dimethyl-1-butynyl. The two upper spectra in each frame were recorded in transmission from KBr pellet (IR) and by attenuated total reflectance (ATR) from the as-synthesised compound. The bottom spectra (RAIRS) were recorded in reflection from the compounds sublimated onto cl-BPT/Au substrates. The coloured bands highlight particular vibrational modes: $\nu_{as}(\text{COO}^-)$ in monodentate coordination (yellow), $\nu_{as}(\text{COO}^-)$ in bridging coordination (blue), $\nu_s(\text{COO}^-)$ (green), $\nu(\equiv\text{CH})$ (grey).

The intensity of $\nu_{as}(\text{COO}^-)$ is low as compared to $\nu_s(\text{COO}^-)$ in the RAIR spectra obtained from both carboxylate complexes (Figure 3a,b). In contrast, $\nu_{as}(\text{COO}^-)$ has a high intensity in ATR-IR. This indicates that despite the lack of specific binding sites on the cl-BPT SAM, the molecules assume on average a near-upright orientation (Figure 4). In this case, the transition dipole moment (TDM) of $\nu_{as}(\text{COO}^-)$ is close to parallel to the underlying Au surface and therefore the band has a low intensity according to the surface selection rule [44]. In contrast, the TDM of $\nu_s(\text{COO}^-)$ is near perpendicular to the surface so that this vibration is well visible.

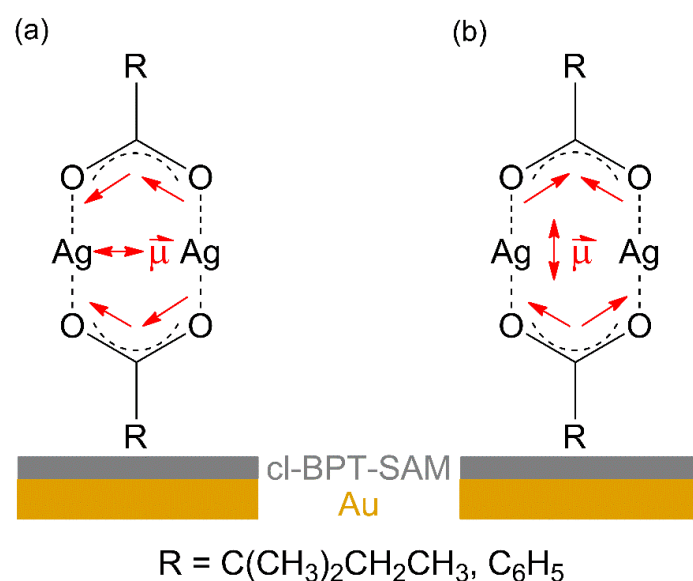


Figure 4. Qualitative model of the average arrangement of Ag(I) 2,2-dimethylbutanoate and Ag(I) benzoate when sublimated onto the cl-BPT/Au substrates as derived from RAIRS. For molecules standing near upright, the transition dipole moment (TDM) of $\nu_{as}(\text{COO}^-)$ is close to parallel to the substrate leading to low intensity (a) and the TDM $\nu_s(\text{COO}^-)$ is near perpendicular to the substrate (b).

All of the IR spectra obtained from Ag(I) 3,3-dimethyl-1-butyne (Figure 3c) are in excellent agreement with those of free 3,3-dimethyl-1-butyne [45,46] except that coordination to Ag(I) ions is obvious from the missing CH stretching vibration of the acetylene unit $\nu(\equiv\text{CH})$, which would be located at 3309 cm^{-1} (see Figure S1 and Table S3, Supplemental Materials). Note that the spectra show additional small and broader bands around 1550 and 1390 cm^{-1} . These are the characteristic $\nu_{as}(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$ bands of carboxylate ligands (compare Tables S1 and S2, Supplemental Materials) indicative of an impurity resulting from CO_2 uptake. This is in line with previous reports that Ag(I) alkynes tend to incorporate CO_2 into their Ag-C bond leading to formation of Ag(I) carboxylates [47].

At an electron energy of 50 eV , applied in most of the irradiation experiments shown in Sections 3.2 and 3.3, the effective attenuation length of electrons in a material is typically of the order of 1 nm [48]. Sufficiently thin sublimite layers are thus needed to be able to fully decompose the sample by electron irradiation. As shown in Section 3.2, complete decomposition was achieved for sublimite layers of Ag(I) 2,2-dimethylbutanoate but not in the cases of Ag(I) benzoate and Ag(I) 3,3-dimethyl-1-butyne. As the aim of this study is to relate the decomposition efficiency to the molecular structure of the Ag(I) complexes, we must rule out that incomplete decomposition results from a sublimite thickness that is beyond the penetration depth of the electron beam. Therefore, we used infrared spectroscopy (see Figure S2 and Table S4, Supplemental Materials) to establish that the amount of sublimite material in the samples of Ag(I) benzoate and Ag(I) 3,3-dimethyl-1-butyne does not exceed that present in Ag(I) 2,2-dimethylbutanoate samples. Furthermore, we examined the homogeneity of the samples by visual inspection using optical microscopy (Figure S3, Supplemental Materials) and XPS (Table S5 and Figure S4, Supplemental Materials). It is not trivial to relate this information to a sublimite thickness because, as obvious from the microscopic images, the material is not homogeneously distributed on the supporting surface. In fact, formation of islands is often encountered when layers are grown from the gas phase [23]. Additionally, according to the RAIRS data (Figure S2), the actual amount of sublimite varies somewhat between individual samples. This most likely relates to slight variations in the sublimation conditions (temperature, pressure) from one experiment to the next. In particular, the flux and temperature of the cooling water could not be quantitatively controlled. However, as outlined in part 2 of the

Supplemental Materials, the intensity of RAIRS spectra depends linearly on the amount of material that is probed within the thickness regime considered herein [25,49]. Based on this and on a quantitative analysis of the XPS intensities derived from reported procedures [50,51], we can safely conclude that the amount of material present in the sublimates of Ag(I) benzoate and Ag(I) 3,3-dimethyl-1-butynyl generally did not exceed the amount of material present in sublimates of Ag(I) dimethylbutanoate. This conclusion is important for the evaluation of the results presented in Section 3.2.

3.2. Electron-Induced Decomposition of Ag(I) 2,2-dimethylbutanoate, Ag(I) Benzoate, and Ag(I) 3,3-dimethyl-1-butynyl

The effect of electron irradiation on the sublimated layers of Ag(I) 2,2-dimethylbutanoate, Ag(I) benzoate, and Ag(I) 3,3-dimethyl-1-butynyl was compared using RAIRS, as shown in Figure 5. A complete loss of the vibrational bands is observed in the case of Ag(I) 2,2-dimethylbutanoate (Figure 5a) after an electron exposure of 1 C/cm² at 50 eV. RAIRS data recorded after increasing exposures and presented in Figure S5 (Supplemental Materials) reveal that an exposure of 1 C/cm² is, in fact, needed for a complete conversion of the sublimate. In contrast, only a minor loss of intensity is observed for Ag(I) benzoate (Figure 5b) and Ag(I) 3,3-dimethyl-1-butynyl (Figure 5c), despite the somewhat lower amount of material in the sublimate (see Table S4, Supplemental Materials). This reveals a significantly lower sensitivity towards electron irradiation for the latter two compounds as compared to Ag(I) 2,2-dimethylbutanoate, despite a comparable or even lower average sublimate thickness.

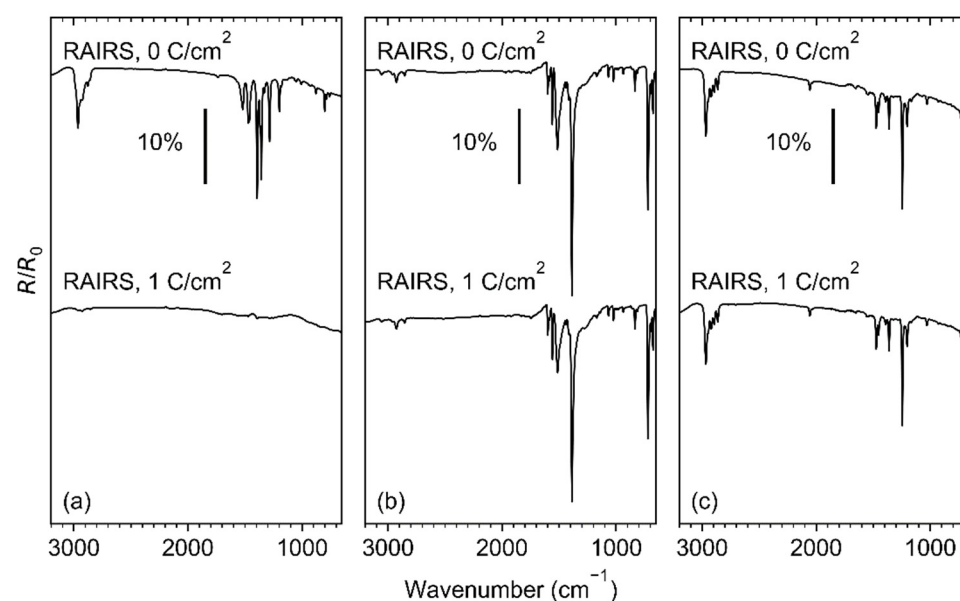


Figure 5. RAIR spectra of (a) Ag(I) 2,2-dimethylbutanoate and (b) Ag(I) benzoate, and (c) Ag(I) 3,3-dimethyl-1-butynyl before (0 C/cm²) and after irradiation (1 C/cm²) at $E_0 = 50$ eV.

During irradiation, electron-stimulated desorption (ESD) of neutral species from the sublimate layers was monitored by EI-MS, which produces, in the QMS ion source, the cations and fragments thereof discussed below. Figure 6 shows mass spectra acquired during the initial stages of irradiation from the same samples of the three Ag(I) complexes, as presented in Figure 5. The ESD mass spectrum of Ag(I) 2,2-dimethylbutanoate (Figure 6a) reveals desorption of H₂ and CO₂ as indicated by the most intense signals at m/z 2 (H₂^{•+}) and m/z 44 (CO₂^{•+}). While some H₂ is generally present as dominant background gas (see bottom curves in each frame of Figure 6), CO₂ stems exclusively from the decomposition of the sublimate layer. Additional signals at m/z 70 (C₅H₁₀^{•+}) and m/z 55 (C₅H₁₀^{•+})-

CH_3^+) that are also absent from the background gas are characteristic of desorption of a hydrocarbon compound and are thus accompanied by signals in the ranges of C_3 fragments (m/z 39 (C_3H_3^+) and m/z 41–43), C_2 fragments (m/z 26–29), and C fragments (m/z 13–15 with m/z 15 assigned to CH_3^+). Further signals at m/z 16 (O^+) and m/z 12 (C^+) relate to the fragmentation pattern of CO_2 (see below). The signal m/z 18 (H_2O^+) gives evidence of a certain amount of humidity that is present, in particular, in the background gas of the vacuum chamber.

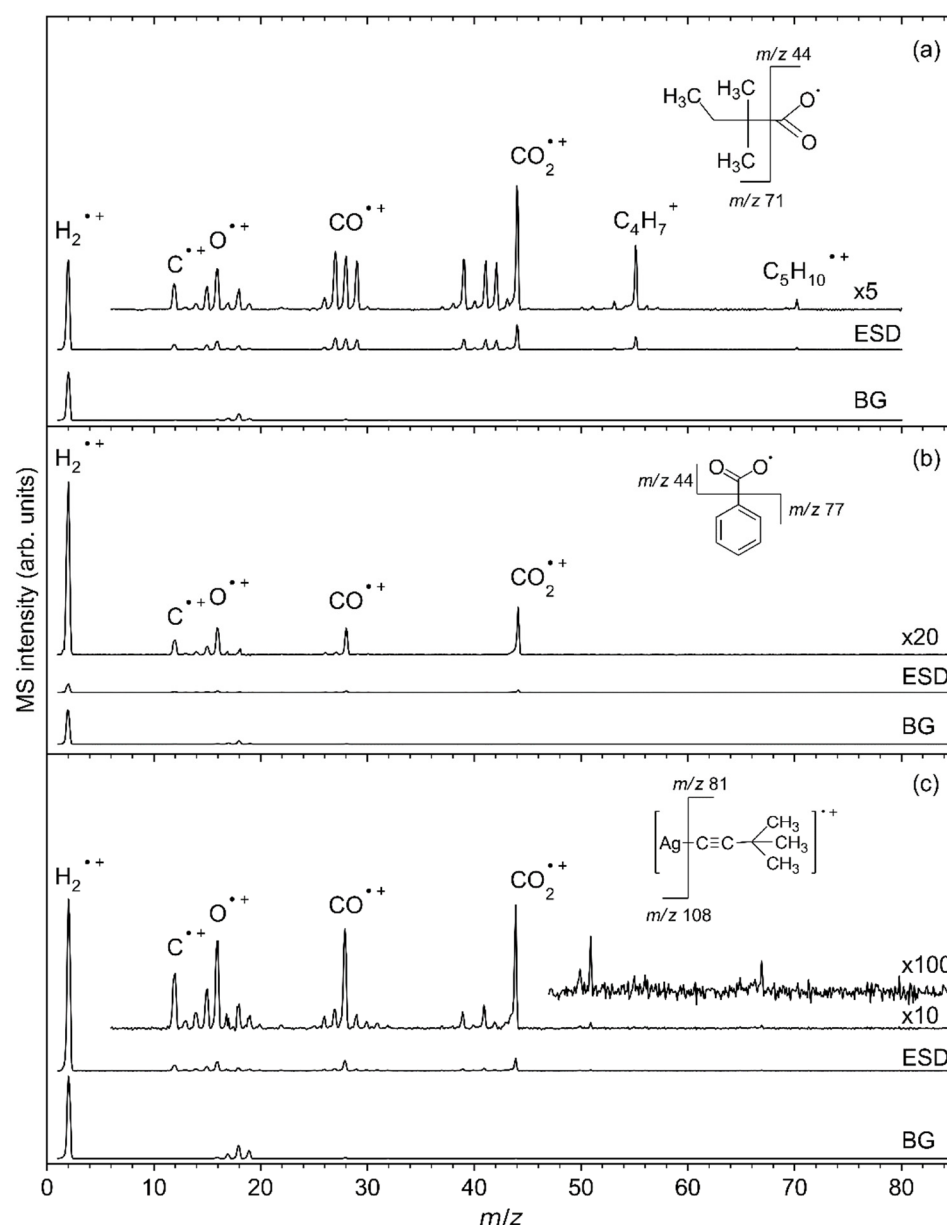


Figure 6. Mass spectra of the volatile species produced upon ESD ($E_0 = 50$ eV) from (a) Ag(I) 2,2-dimethylbutanoate and (b) Ag(I) benzoate, and (c) Ag(I) 3,3-dimethyl-1-butyryl as well as background MS measured directly before each irradiation. All ESD MS were corrected by subtracting the respective background mass spectrum (BG). Note that the dominant fragments in (c) give evidence that a carboxylate impurity has formed in the Ag(I) 3,3-dimethyl-1-butyryl sample.

It is important to note that ESD was only observed for sufficiently thin sublimite layers. At larger sublimite thickness, the MS intensities decreased strongly while the RAIR spectrum changed to that also obtained by ATR-IR from the bulk material (Figure S6, Supplemental Materials). We take this as indication that sublimation has produced

larger crystallites with size beyond the penetration depth of the electron beam. This most likely leads to charge accumulation which repels the impinging electrons leading to loss of ESD intensity.

The ESD mass spectrum of Ag(I) 2,2-dimethylbutanoate (Figure 6a) was modelled by overlapping reference mass spectra of 2-methyl-2-butene, CO₂ and H₂O (Figure 7, see also Figure S7 in Supplemental Materials for individual reference MS data). The same QMS as for the ESD experiments was used to record reference mass spectra during leaking of the individual gases into the vacuum chamber. This provides for a more reliable analysis than the use of literature data because the sensitivity of the instrument decreases towards higher m/z ratios [17]. We note that three different alkenes can be formed by cleaving a hydrogen radical from the alkyl radical C₅H₁₁[•] that is released upon loss of CO₂ from Ag(I) 2,2-dimethylbutanoate (Figure 8). The mass spectra of these three C₅H₁₀ isomers are very similar [52] so that a unique assignment is not strictly possible. However, 2-methyl-2-butene was selected for the analysis of the ESD mass spectrum and we also refer to the desorbing product as such in the following discussion because it is the most stable of these isomers (see Figure 8). In this analysis, the intensity of the mass spectrum of 2-methyl-2-butene was first scaled so that the height of the m/z 70 signal matches the ESD mass spectrum. Next, the spectrum of CO₂ was scaled and added so that the overall intensity of the m/z 44 signal in the ESD data was well reproduced. Finally, the same procedure was applied to H₂O based on the m/z 18 signal. The resulting modelled mass spectrum provides a reasonable reproduction of the ESD mass spectrum (Figure 7) and thus supports that Ag(I) 2,2-dimethylbutanoate yields CO₂ and 2-methyl-2-butene as most likely isomer of C₅H₁₀ under electron irradiation. Overall, this indicates that electron-induced fragmentation leads to loss of the entire alkyl side group, which would yield a C₅H₁₁[•] radical. As obvious from our analysis, the radical converts to the stable olefin prior to desorption (see also Section 4). This latter reaction must proceed by loss of atomic hydrogen that can recombine to H₂, thus explaining the increase in the m/z 2 signal under electron irradiation as compared to the residual gas background spectrum (Figure 6a).

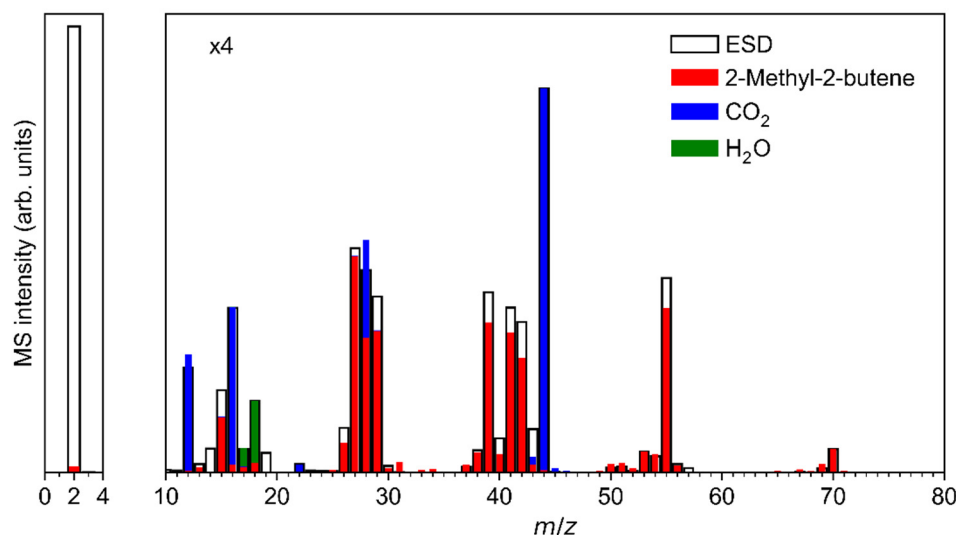


Figure 7. Reproduction of the mass spectrum (m/z 0–80) of the volatile species produced upon ESD ($E_0 = 50$ eV) from Ag(I) 2,2-dimethylbutanoate from Figure 6a as a superposition of contributions from CO₂, H₂O, and 2-methyl-2-butene. The experimental ESD data were fitted by mass spectra obtained from the pure compounds: first, the spectrum of 2-methyl-2-butene was scaled to the ESD intensity at m/z 70; next, the spectrum of CO₂ was added with scaling factor so that the ESD intensity at m/z 44 was reproduced; and last, the spectrum of H₂O was added with scaling factor set to reproduce the ESD intensity of m/z 18.

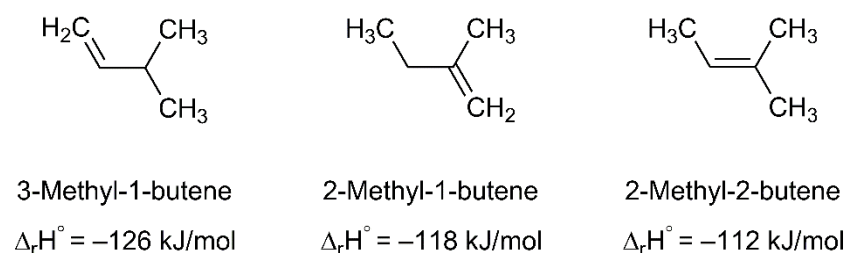


Figure 8. Different alkenes that can be formed after hydrogen radical loss from the $C_5H_{11}^\bullet$ radical produced upon electron irradiation of Ag(I) 2,2-dimethylbutanoate. The enthalpy of reaction at standard conditions ($\Delta_r H^\circ$) for hydrogenation of the double bond that yields the same final product C_5H_{12} in each case indicates that 2-methyl-2-butene is the most stable among these isomers [53,54].

We note that significant H_2 desorption from the cl-BPT SAM can be ruled out because cross-linking was always performed until ESD of H_2 had ceased (see Section 2.2). This was also verified by exposing a cl-BPT SAM to ambient conditions before it was reintroduced into UHV and further irradiated, which then resulted in negligible ESD of H_2 (see Figure S8, Supplemental Materials). As a further test to confirm the origin of the H_2 ESD signal, perdeuterated Ag(I) 2,2-dimethylbutanoate was also investigated. In this case, ESD recorded upon electron irradiation at 100 eV shows patterns that correspond closely to the nondeuterated analogue (Figure S9 and Table S6, Supplemental Materials). Note that the ESD pattern of the nondeuterated Ag(I) 2,2-dimethylbutanoate at 100 eV (Figure S9) agrees closely with the result for 50 eV. The deuterated compound in fact shows desorption of D_2 (m/z 4) upon electron irradiation, which supports the hypothesis that atomic hydrogen (H or D) released from the $C_5H_{11}^\bullet$ ($C_5D_{11}^\bullet$) radical is the origin of 2-methyl-2-butene. However, D_2 is accompanied by even stronger signals of HD (m/z 3) and H_2 (m/z 2). Considering the high isotope purity (98.4%) of the acid used in the synthesis of perdeuterated Ag(I) 2,2-dimethylbutanoate and the lack of ESD from the supporting cl-BPT SAM, we relate the formation of HD and H_2 to the electron-induced fragmentation of small quantities of H_2O present as residual humidity (see above). This also indicates that H_2O must contribute to ESD of H_2 from nondeuterated Ag(I) 2,2-dimethylbutanoate.

Note that differently branched alkyl chains on the carboxylate ligands show analogous fragmentation behaviour. In all isomers of Ag(I) 2,2-dimethylbutanoate but also in the case of Ag(I) heptanoate, desorption of an olefin resulting from loss of CO_2 and an additional H atom is observed in ESD performed at 100 eV (Figure S10, Supplemental Materials). Additionally, the ligands are again completely lost within an exposure of 1 C/cm^2 according to RAIRS (Figure S11, Supplemental Materials).

In the case of Ag(I) benzoate (Figure 6b), the ESD intensity is considerably smaller than for Ag(I) 2,2-dimethylbutanoate. While the lower intensity as such may relate to the somewhat lower amount of sublimate, it is remarkable that only H_2 , CO_2 , traces of H_2O , and possibly some CO desorb under electron irradiation. In contrast, desorption of products that relate to the phenyl (C_6H_5) group of the benzoate ligand is absent. This indicates that, in contrast to carboxylate ligands with alkyl groups, the aromatic ring is not converted to a volatile product after electron-induced loss of CO_2 . The origin of this different behaviour is discussed in Section 4.

Finally, ESD of Ag(I) 3,3-dimethyl-1-butyne (Figure 6c) is dominated again by desorption of CO_2 showing the same characteristic signals at m/z 44, 28, 16, and 12. This is unexpected from the molecular structure of this compound but in line with the carboxylate infrared bands seen in RAIRS of thin sublimate layers (Figure 3c). ESD also shows small hydrocarbon signals. A fragment with m/z 81 that represents the mass of the entire ligand is, in addition, visible in the case of a thicker sublimate layer irradiated at higher electron energy (Figures S12 and S13, Supplemental Materials). However, based on the particularly small loss of intensity in RAIRS of the thinner sublimate under electron exposure (Figure 5c) and considering previous reports that the elemental composition of Ag(I)

3,3-dimethyl-1-butyne powder did not change under electron irradiation in an electron microscope [7], we propose that ESD of the 3,3-dimethyl-1-butyne ligand rather stems from molecules that have reacted with CO_2 from the ambient during sample handling than from pristine Ag(I) 3,3-dimethyl-1-butyne. The obvious lack of sensitivity of Ag(I) 3,3-dimethyl-1-butyne towards electron irradiation is also discussed further in Section 4.

3.3. Kinetics of ESD from Ag(I) 2,2-dimethylbutanoate

Further insight into the electron-induced decomposition of Ag(I) 2,2-dimethylbutanoate upon irradiation with an energy of 50 eV was obtained by recording the evolution of ESD signals with characteristic m/z ratios as function of time. Note that RAIRS data for the samples described in this section are included in Figure S2 and Table S4 (Supplemental Materials). The experiments monitored m/z 44 that relates to desorption of CO_2 and m/z 55, representative of 2-methyl-2-butene or its isomers. Both signals increase abruptly at the start of irradiation followed by a decay, which is particularly steep in the case of CO_2 (Figure 9, top). During this decay, the current that is transmitted through the sample (Figure 9, bottom) increases slowly but steadily. This effect can result from depletion of the sublimite layer and thus increased transmission of electrons to the substrate or from trapping of some positive charge in the layer that accelerates the electrons towards the sample. However, the increasing current indicates that the simultaneous decrease in the ESD intensity does not result from deflection of the electron beam due to negative charging of the sample but must relate to the decomposition kinetics of the sample. Notably, the desorption rate of 2-methyl-2-butene decreases more slowly than that of CO_2 . This supports that CO_2 is released via the initial electron-induced fragmentation while 2-methyl-2-butene is formed in a subsequent and somewhat slower reaction step that involves loss of atomic hydrogen.

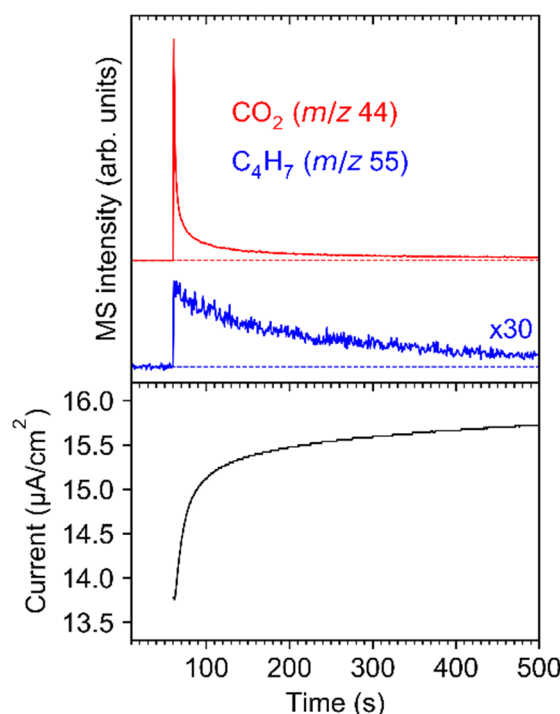


Figure 9. ESD as function of time during electron irradiation of Ag(I) 2,2-dimethylbutanoate at $E_0 = 50$ eV monitored for m/z 44 (top panel, red, representative of CO_2) and m/z 55 (top panel, blue, representative of 2-methyl-2-butene). The sudden step increase in the ESD signals marks the start of irradiation. During irradiation, the current was measured on the sample (bottom panel), reaching a value of $16.46 \mu\text{A}/\text{cm}^2$ after a total exposure of $0.4 \text{ C}/\text{cm}^2$.

The experiment was repeated with several individual samples to confirm the different ESD kinetics for CO₂ and 2-methyl-2-butene. Figure 10 shows two experiments where the irradiation was interrupted to reveal effects of possible aging of the sample upon contact to ambient conditions during transfer from UHV to RAIRS (Figure 10a) or in UHV (Figure 10b). In both cases, a slower decay or even an initial slight increase in the ESD signal of 2-methyl-2-butene was observed after the start of irradiation, in line with the result of the experiment shown in Figure 9. This effect was also observed in the case of an additional experiment performed at electron energy of 500 eV (Figure S14, Supplemental Materials). Note that variations in the time-dependent ESD curves between samples possibly relate to the morphology of the individual samples that may exhibit different crystallite sizes due to fluctuations of the temperature during sublimation. A more detailed investigation of this effect was, however, beyond the scope of the present work.

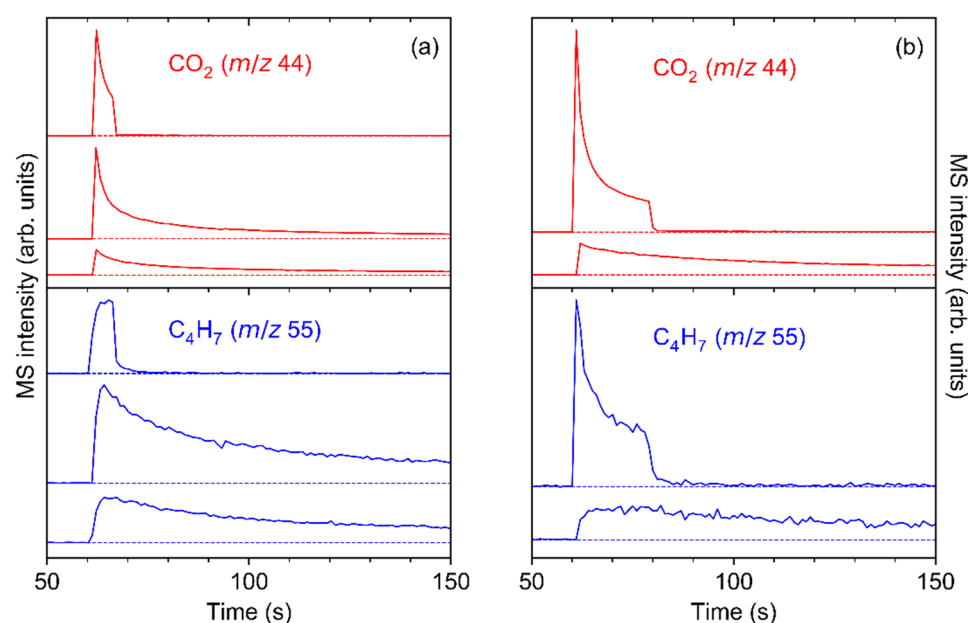


Figure 10. ESD as function of time during electron irradiation of Ag(I) 2,2-dimethylbutanoate at $E_0 = 50$ eV for m/z 44 (top of panel, red, representative of CO₂) and m/z 55 (bottom of panel, blue, representative of 2-methyl-2-butene). (a) The irradiation was interrupted after an exposure of 60 $\mu\text{C}/\text{cm}^2$ (first row, average current 14.0 $\mu\text{A}/\text{cm}^2$) and 1400 $\mu\text{C}/\text{cm}^2$ (second row, average current 17.0 $\mu\text{A}/\text{cm}^2$) before the last exposure of 100,000 $\mu\text{C}/\text{cm}^2$ (third row, average current 16.9 $\mu\text{A}/\text{cm}^2$). In between irradiations, the sample was retrieved from UHV for RAIRS. (b) The irradiation was interrupted for 90 min after 180 $\mu\text{C}/\text{cm}^2$ (first row, average current 13.0 $\mu\text{A}/\text{cm}^2$) and the sample left in UHV until irradiation was resumed with an exposure of 400,000 $\mu\text{C}/\text{cm}^2$ (second row, average current 17.1 $\mu\text{A}/\text{cm}^2$). Except for the first row, the graphs are clipped to the initial period of irradiation for better visualisation.

Figure 10 also reveals that irradiated sublimable layers of Ag(I) 2,2-dimethylbutanoate are subject to further chemical modification when handled in ambient conditions. For the sample that remained in UHV when electron exposure was interrupted, ESD resumed with similar intensity as seen at the end of the first electron exposure when the irradiation was switched on again (Figure 10b). In contrast, when the sample was exposed to ambient conditions prior to the next irradiation, the ESD intensity for both m/z 44 and m/z 55 was significantly higher than at the end of the previous irradiation (Figure 10a). This indicates that electron irradiation activates the sublimable towards reaction with constituents of air. This effect may be akin to the uptake of CO₂ by Ag(I) 3,3-dimethyl-1-butynyl, as discussed in Section 3.1. In line with a previous theoretical study [55], we tentatively propose that Ag⁺ ions remaining in the sublimable layer after electron-induced fragmentation of Ag(I) 2,2-dimethylbutanoate react with CO₂ from the ambient atmosphere upon handling in air.

When resuming electron irradiation, this additional CO₂ is released in addition to that produced from the remaining intact Ag(I) compound.

Finally, we compare the time scales for decomposition of Ag(I) 2,2-dimethylbutanoate as observed in ESD and RAIRS. As can be estimated from Figures 9 and 10, the CO₂ ESD signal decays to a level near the baseline within an electron exposure of the order of a few 10 mC/cm² at an electron energy of 50 eV. In contrast, an electron exposure of the order of 0.1 C/cm² is required for the same sample to achieve a visible reduction in the RAIRS intensities (Figure S15, Supplemental Materials). The rapid decay of the CO₂ ESD signal is similar to earlier results for Cu(II) oxalate and related coordination polymers grown on a surface in a layer-by-layer process [16]. On the other hand, exposures of an order of only 10 mC/cm² were necessary for the RAIRS signals to disappear for the thinnest investigated layers of Cu(II) oxalate while the required exposures clearly increased with the thickness of the layers [16]. This general behaviour indicates that only the fragments produced in the uppermost layers of the materials desorb rapidly while diffusion from layers further from the vacuum interface and possibly also inelastic scattering of the electron beam within the layer limits the ESD process at later stages of the irradiation. However, as seen in Figure 5, sublimates of Ag(I) 2,2-dimethylbutanoate can in fact be completely decomposed when a sufficiently long electron exposure is applied.

4. Discussion

The ESD and RAIRS data presented above reveal that Ag(I) 2,2-dimethylbutanoate and similar aliphatic Ag(I) carboxylates are decomposed more efficiently under electron irradiation than Ag(I) benzoate and Ag(I) 3,3-dimethyl-1-butynyl. The different decomposition behaviour of the three types of compounds can result from (i) different fragmentation efficiencies upon electron impact and (ii) reactions that are specific to particular fragments released by the initial electron–molecule interaction. These two effects are discussed herein. Furthermore, reactions with ambient vapours prior to electron irradiation play a role in the decomposition Ag(I) 3,3-dimethyl-1-butynyl.

As proposed before [14,16,17], the electron-induced fragmentation of precursors with carboxylate ligands is most likely triggered by ionization (see Figure 1). The present results indicate that carboxylate ligands with saturated side chains are more efficiently removed from the sublimate layer than the aromatic benzoate ligand. This is reminiscent of earlier results for surface grown coordination polymers showing that CO₂ is more efficiently released from Cu(II) oxalate than from HKUST-1 [14]. While the oxalate dianion consists of two carboxylate groups that are directly bound to each other, the trivalent linker of HKUST-1 contains an aromatic ring as also present in Ag(I) benzoate. The comparably low efficiency of CO₂ loss from HKUST-1 and Ag(I) benzoate thus suggests that the aromatic ring stabilises the material with respect to fragmentation under electron irradiation. This effect is not included in the fragmentation mechanism represented in Figure 1, which assumes that ionization removes an electron from the negatively charged carboxylate group. To substantiate the hypothesis that the aromatic ring counteracts the depicted fragmentation channel, we investigated the average local ionization energy (ALIE) [56] of Ag(I) 2,2-dimethylbutanoate and Ag(I) benzoate, also including Ag(I) 3,3-dimethyl-1-butynyl as another example with unsaturated structural unit (Figure 11). For both carboxylate compounds, the ALIE reveals particularly low values at the Ag atoms in line with the coordinate bond donation that shifts electron density from the negatively charged carboxylate group to the positively charged Ag. Ionization thus leads preferably to removal of electron density from these coordinate bonds similar to the simplified model depicted in Figure 1. However, in the case of Ag(I) benzoate (Figure 11b), additional sites with relatively low values of the ALIE are localised on the aromatic ring. This points to an increased probability that ionization occurs from the hydrocarbon side group in Ag(I) benzoate. The possibility to delocalise the resulting charge over the ring is expected to counteract dissociation following ionization. This provides an explanation for the lower CO₂ yield upon electron irradiation of Ag(I) benzoate as compared to Ag(I) 2,2-

dimethylbutanoate where the ALIE is high on the alkyl side group. The calculation thus reveals that the side group of the carboxylate ligands can have an effect on the efficiency of the electron-induced fragmentation of a metal carboxylate complex.

Note that a similar fragmentation becomes possible when Ag(I) 3,3-dimethyl-1-butyne reacts with CO₂ under ambient conditions to form again a carboxylate complex (see Sections 3.1 and 3.2). However, here again, concurrent ionization from the triple bond most likely lowers the fragmentation efficiency upon ionization. This also rationalises the low sensitivity of Ag(I) 3,3-dimethyl-1-butyne itself towards electron irradiation [7]. In analogy to the situation in Ag(I) benzoate, ionization from the unsaturated CC triple bond of the ligand is most favourable. This is again visualised by the ALIE calculated for the monomeric structure of Ag(I) 3,3-dimethyl-1-butyne (Figure 11c). The ALIE is particularly low, also compared to Ag(I) benzoate, on the triple bond. We note that the stability of Ag alkynyls is also supported by reports that such compounds can form under mild conditions when an alkynyl hydrocarbon is adsorbed onto a Ag(111) surface in the presence of O₂ [57]. The persistence of the vibration $\nu(\text{C}\equiv\text{C})$ under electron irradiation (Figure 5 and Table S3, Supplemental Materials) further indicates that ionization of Ag(I) 3,3-dimethyl-1-butyne does not lead to polymerization as known in the case of olefins [58], which we attribute to steric hindrance by the bulky tertiary butyl group.

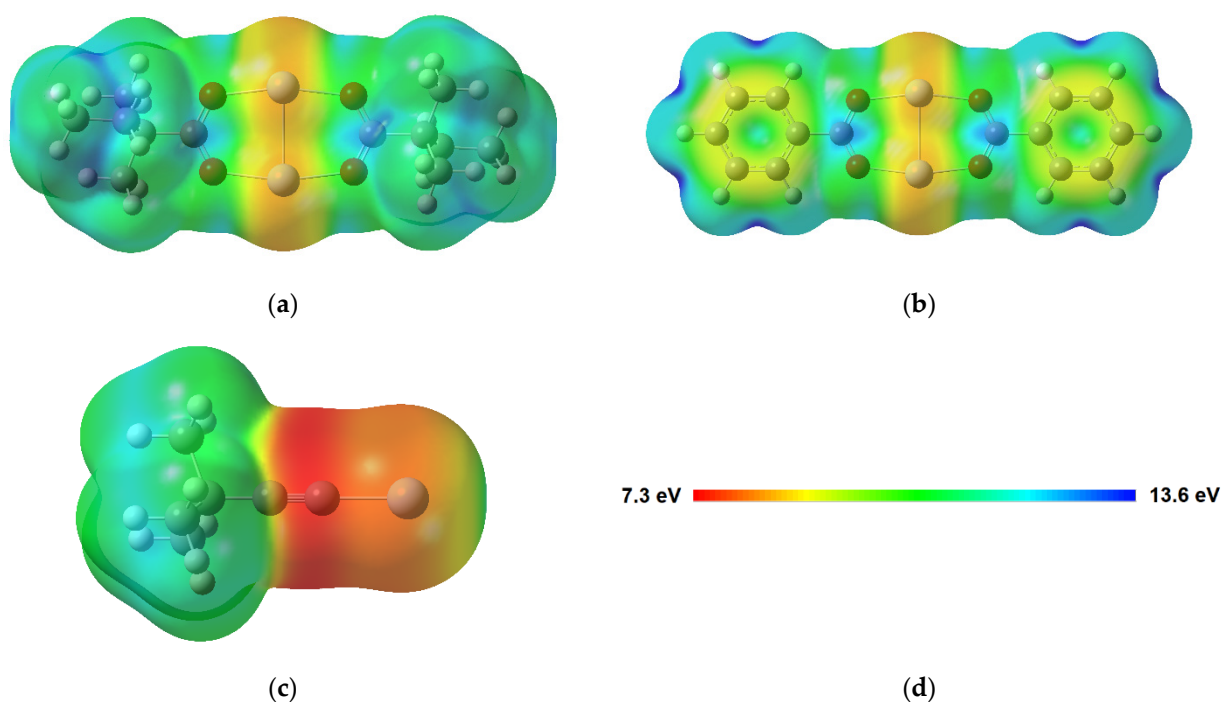


Figure 11. Average local ionization energy (ALIE) mapped onto the molecular surface (0.001 a.u. electron density isosurface) for (a) Ag(I) 2,2-dimethylbutanoate and (b) Ag(I) benzoate dimers, as well as (c) the monomer of Ag(I) 3,3-dimethyl-1-butyne calculated at the B3LYP-GD3BJ/def2TZVPP level. (d) The colour code represents the distribution of ALIE in each molecule.

Molecular radical fragments that are released by the initial electron–molecule interaction can undergo different reactions depending on their structure and on reaction partners that may be available in their vicinity. The ESD results (Section 3.2) show that the radical $\cdot\text{C}_5\text{H}_{11}$ released upon electron-induced loss of CO₂ from Ag(I) 2,2-dimethylbutanoate converts to a stable and volatile olefin that can desorb and thereby remove carbon from a deposit during the FEBID process. Figure 12 summarises this sequence of reactions. In principle, radical species can also add to double bonds [17], but these are absent from the intact adjacent molecules. Additionally, the radical site carries bulky substituents that hinder the approach towards a reaction partner. Stabilisation by transfer or loss of

hydrogen is thus apparently the most rapid reaction. We note that a saturated product resulting from recombination of the hydrogen radical with a second $\cdot\text{C}_5\text{H}_{11}$ radical is not visible in the ESD data (Figure 6). This can be deduced from the lack of MS signals at m/z 57 and m/z 72 that are characteristic of a hydrocarbon C_5H_{12} [52].

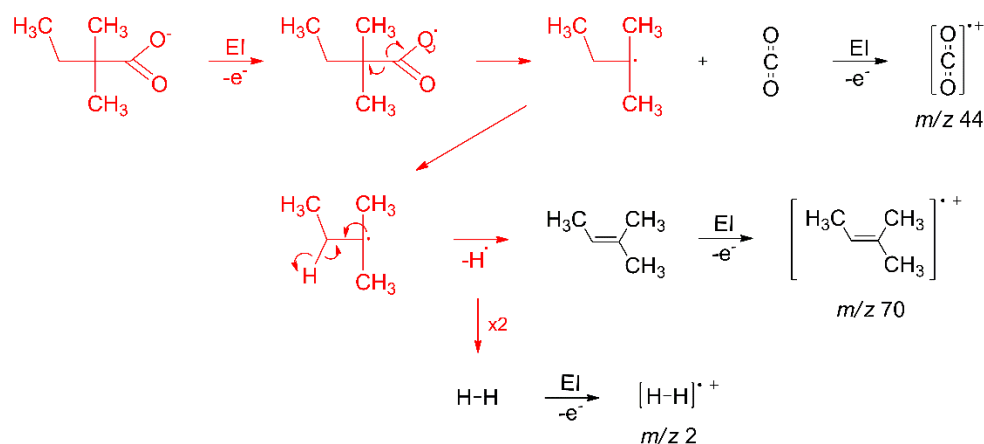


Figure 12. Mechanism of the electron-induced decomposition of Ag(I) 2,2-dimethylbutanoate to stable volatile reaction products. The electron-induced fragmentation and subsequent loss of atomic hydrogen from the radical fragment proceed on the surface (red) while stable volatile products desorb to be identified by their characteristic fragments formed after ionization in the ion source of the MS (black).

In contrast to the case of the saturated alkyl radical $\cdot\text{C}_5\text{H}_{11}$ released from Ag(I) 2,2-dimethylbutanoate, stabilisation of the phenyl radical $\cdot\text{C}_6\text{H}_5$ that results from expulsion of CO_2 in the case of Ag(I) benzoate by loss of atomic hydrogen is not favourable. Such a reaction would lead to a highly strained ring structure with a triple bond. Recombination reactions between phenyl radicals are thus more likely to occur. This has been extensively reported in the case of BPT and related SAMs [59], and has also been applied here in the preparation of the cl-BPT SAMs used as support for the sublimates layers. The lack of signals relating to ESD of the phenyl ring or of a benzene molecule (C_6H_6) that would result from recombination of the phenyl radical $\cdot\text{C}_6\text{H}_5$ with a hydrogen radical released from another molecule under electron irradiation strongly supports that cross-linking is also the most likely reaction of $\cdot\text{C}_6\text{H}_5$ in the sublimates layer. Overall, both the different fragmentation probability of Ag(I) 2,2-dimethylbutanoate and Ag(I) benzoate and the different reactivity of the radical species released upon electron impact rationalise the ESD and RAIRS results (Section 3.2) and support that aliphatic carboxylate ligands are superior ligands for FEBID precursors.

5. Conclusions

We investigated the electron-induced decomposition of Ag(I) 2,2-dimethylbutanoate, a precursor that yields deposits with high Ag contents in FEBID [7] and compared its reactivity under irradiation to other Ag(I) carboxylates with different hydrocarbon structures attached to the carboxylate group. In addition, the fragmentation behaviour of Ag(I) 3,3-dimethyl-1-butyne was studied. ESD and RAIRS experiments performed on sublimates on an inert surface in combination with calculations of the average local ionization energy (ALIE) of the different Ag(I) compounds yield a comprehensive picture of the factors that determine the efficiency of ligand removal as result of electron irradiation. In particular, carboxylates with saturated hydrocarbon structure are decomposed with high efficiency to yield CO_2 and an alkene that derives from the hydrocarbon group by loss of atomic hydrogen. In contrast, loss of hydrogen from a phenyl radical that is released upon electron-induced expulsion of CO_2 from the ligand of Ag(I) benzoate is not favourable because it would result in a highly strained ring structure with triple bond. Aromatic

radicals therefore preferably react by cross-linking with other fragments and thus retain carbon in the nonvolatile deposit formed under electron exposure.

Another factor that determines the electron-induced fragmentation of the Ag(I) compounds is the site within the molecule from which an electron is removed upon ionization. As shown by the calculations, the ALIE is lowest on the carboxylate group in the case of Ag(I) 2,2-dimethylbutanoate. Ionization thus preferably destabilises the carboxylate group and triggers expulsion of CO₂. In contrast, CC double or triple bonds, such as present in Ag(I) benzoate and Ag(I) 3,3-dimethyl-1-butyne, represent alternative sites within the molecule where electron density can be easily removed. Loss of an electron from multiple CC bonds, however, does not favour dissociation. This rationalizes the slow decomposition of Ag(I) benzoate under electron exposure as obvious from the present RAIRS results and provides an explanation for the high stability of Ag(I) 3,3-dimethyl-1-butyne, as noted previously. As a general guideline for the design of novel FEBID precursors, our results thus indicate that aliphatic carboxylate ligands are a preferential choice because (i) ionization upon electron impact in fact removes charge preferably from the carboxylate group and (ii) this triggers decomposition to stable volatile products.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/nano12101687/s1>, Figure S1: Full range infrared spectra of Ag(I) 2,2-dimethylbutanoate and Ag(I) benzoate. Table S1: Vibrational band positions and assignments for Ag(I) 2,2-dimethylbutanoate [21,40–43]. Table S2: Vibrational band positions and assignments for Ag(I) benzoate [37–43]. Table S3: Vibrational band positions and assignments for Ag(I) 3,3-dimethyl-1-butyne [45,46]. Figure S2: ATR spectra and RAIR spectra of sublimates of Ag(I) 2,2-dimethylbutanoate, Ag(I) benzoate, and Ag(I) 3,3-dimethyl-1-butyne used in the different experiments. Table S4: Comparison of RAIRS and ATR intensities for average sublimite thickness estimation [26]. Figure S3: Optical microscopy of sublimite layers of Ag(I) 2,2-dimethylbutanoate, Ag(I) benzoate, and Ag(I) 3,3-dimethyl-1-butyne. Table S5: XPS Au signals used for an estimate of the sublimite thickness. Figure S4: Simulated relative attenuation of XPS Au4d and Au4f signals for sublimite layers [50]. Figure S5: RAIRS of Ag(I) 2,2-dimethylbutanoate before and after the electron exposures. Figure S6: RAIRS and ESD of sublimates with increasing amount of Ag(I) 2,2-dimethylbutanoate. Figure S7: ESD mass spectra recorded from sublimates of Ag(I) 2,2-dimethylbutanoate and mass spectra of CO₂, H₂O, and 2-methyl-2-butene. Figure S8: ESD mass spectra to exclude additional H₂ production from cl-BPT SAM during irradiation. Figure S9: ESD mass spectra recorded from sublimates of Ag(I) 2,2-dimethylbutanoate and perdeuterated Ag(I) 2,2-dimethylbutanoate. Table S6: ESD signals and assignments for Ag(I) 2,2-dimethylbutanoate and perdeuterated Ag(I) 2,2-dimethylbutanoate. Figure S10: ESD mass spectra recorded from sublimates of Ag(I) 2,2-dimethylbutanoate, Ag(I) 2-methylpentanoate, Ag(I) hexanoate, and Ag(I) heptanoate. Figure S11: RAIR spectra of Ag(I) 2,2-dimethylbutanoate, Ag(I) 2-methylpentanoate, Ag(I) hexanoate, and Ag(I) heptanoate before and after electron irradiation. Figure S12: RAIR spectra of Ag(I) 3,3-dimethyl-1-butyne before and after irradiation. Figure S13: ESD mass spectra recorded from a thick sublimite layer of Ag(I) 3,3-dimethyl-1-butyne. Figure S14: ESD kinetic experiment of Ag(I) 2,2-dimethylbutanoate. Figure S15: RAIRS of Ag(I) 2,2-dimethylbutanoate recorded before and after different electron exposures. References [14,21,25,26,37–43,45,46,49–51] are cited in the supplementary materials.

Author Contributions: P.M. synthesised the Ag(I) carboxylates, prepared and characterised the samples, performed electron irradiation experiments, prepared the figures, drafted the manuscript, and managed the references; A.B. participated in the synthesis of the compounds and in electron irradiation experiments; S.S. contributed the data shown in Figure S6 from her bachelor thesis; M.R. performed the ALIE calculations and participated in the XPS experiments and analysis; P.H. performed the XPS measurements and analysed the XPS data. R.D. checked the interpretation of the XPS data and their modelling; I.B.S. contributed information on the properties of the compounds; P.S. composed the final manuscript and performed the modelling of the XPS data. All authors have read and agreed to the published version of the manuscript.

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Supporting Information

Electron-Induced Decomposition of Different Silver(I) Complexes: Implications for the Design of Precursors for Focused Electron Beam Induced Deposition

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1. Infrared spectra of Ag 2,2-dimethylbutanoate and Ag benzoate

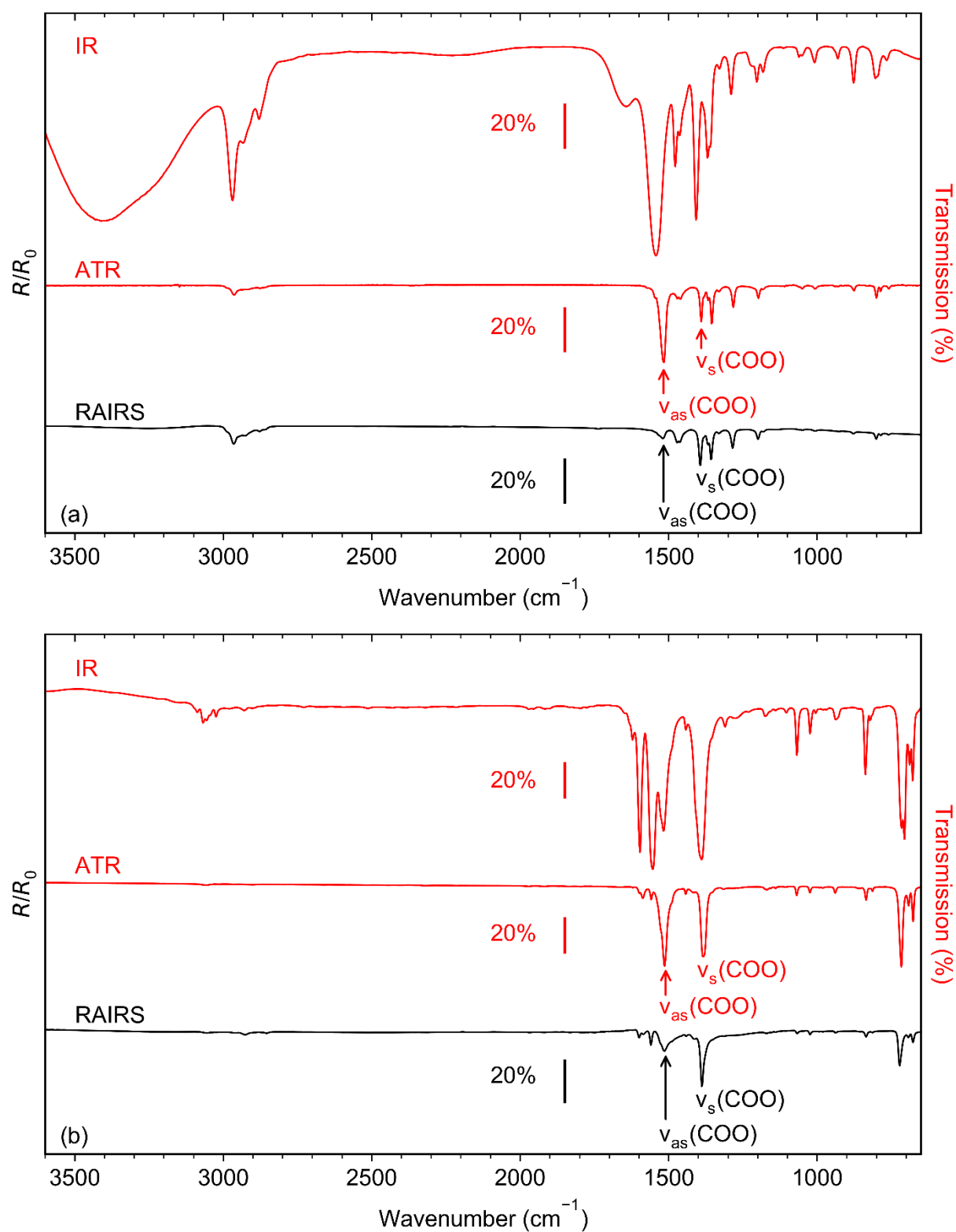


Figure S1. Infrared spectra of (a) Ag(I) 2,2-dimethylbutanoate and (b) Ag(I) benzoate. The two upper spectra in each frame were recorded in transmission from KBr pellet (IR) and by attenuated total reflectance (ATR) from the as-synthesized compound. The bottom spectrum (RAIRS) was recorded in reflection from the compounds sublimated onto cl-BPT/Au substrates. The data are the same as shown for a smaller range of wavenumbers in Figure 2 of the main manuscript.

Table S1. Vibrational band positions and assignments for Ag(I) 2,2-dimethylbutanoate.

Ag(I) 2,2-dimethylbutanoate				
Assignment^a	bulk IR (cm⁻¹)	bulk ATR (cm⁻¹)	RAIRS (cm⁻¹)	bulk IR (cm⁻¹)^b
<i>N</i> (CH)	2969 2934 2880	2962 2919 2875	2963 2929 2877	
$\nu_{as}(\text{COO}^-)$ of monodentate coordination ^c	1544	1547		1548
$\nu_{as}(\text{COO}^-)$ of bridging coordination ^c		1515	1520	
$\delta_{as}(\text{CH}_3)$, $\delta(\text{CH}_2)$	1477 1464	1471	1471	1477
$\nu_s(\text{COO}^-)$	1408	1389	1394	1405
$\delta_s(\text{CH}_3)$	1369 1359	1356	1357	1366 1357
$\delta_w(\text{CH}_2)$, $\delta_t(\text{CH}_2)$	1290	1282	1285	1290
Skeletal vibrations	1220 1204 1183 1061 1050 1008 930 877 800	1198 1182 1061 1051 1007 930 876 800	1200 1182 1062 1050 1008 928 877 800	

a ν = stretching, δ = deformation, δ_r = rocking, δ_w = wagging, δ_t = twisting.

b from KBr pellet [1].

c see Ref. [2–5].

Table S2. Vibrational band positions and assignments for Ag(I) benzoate.

Ag(I) benzoate				
Assignment^{a,b}	bulk IR (cm⁻¹)	bulk ATR (cm⁻¹)	RAIRS (cm⁻¹)	bulk IR (cm⁻¹)^b
$\nu(\text{CH})$	3088, 3068, 3056, 3024, 2930	3050, 2900	3060, 2928, 2855	3050 vw
	1622	1622		
$\nu(\text{CC})$	1598	1599	1602	1596 vs
$\nu_{\text{as}}(\text{COO}^-)$ of monodentate coordination ^c	1553	1559	1562	1553 vs 1560 ^d
$\nu_{\text{as}}(\text{COO}^-)$ of bridging coordination ^c	1517	1514	1516	1518 ^d
$\nu(\text{CC})$	1442	1418	1415	1407-1447 s-w ^e
$\nu_{\text{s}}(\text{COO})$	1390	1384	1390	1412 s 1397 sh
$\nu(\text{CC})$	1310	1315	1314	1306 vw
$\beta(\text{CH})$	1069	1069	1068	1067 w
$\beta(\text{CH})$	1025	1025	1024	1023 vw
$\beta_{\text{s}}(\text{COO}^-)$	838	835	837	842 w
$\gamma(\text{CH})$	820	814	813	817 vw
$\gamma_{\text{s}}(\text{COO}^-)$	716	716	724	711 s
$\phi(\text{CC})$	679	676	681	683 sh

a Nomenclature is ν = stretching, β = in plane deformation / angle deformation, γ = out of plane deformation, ϕ = out of plane ring deformation. Note that assignments for last four entries are not unique, see also Ref. [6].

b from KBr pellet and Nujol. [7].

c see Ref. [2–5].

d values for Ag stearate from Ref. [3].

e values for different alkali benzoates, see Ref. [8].

Table S3. Vibrational band positions and assignments for Ag(I) 3,3-dimethyl-1-butyne.

Ag(I) 3,3-dimethyl-1-butyne				
Assignment^{a,b}	bulk IR (cm⁻¹)	bulk ATR (cm⁻¹)	RAIRS (cm⁻¹)	liquid IR^b
$\nu(\equiv\text{CH})$	-	-	-	3309 s
$\nu(\text{CH}_3)$	2966	2966	2967	2971 s
	2947	2944	2947	2954 sh
	2920	2918	2920	2935 vw
	2895	2893	2894	2906 m
	2863	2860	2863	2872 s
$\nu(\text{C}\equiv\text{C})$	2056	2053	2056	2106 m
$\nu_{\text{as}}(\text{COO}^-)$ of monodentate coordination ^c	1551	1548	1550	
$\nu_{\text{s}}(\text{COO})^{\text{c}}$	1393	1389	1390	
$\delta(\text{CH}_3)$	1472	1471	1473	1476 m
	1453	1452	1453	1456 m
	1361	1359	1361	1367 s
$\delta_{\text{r}}(\text{CH}_3) + \nu(\text{CC})$	1244	1242	1245	1248 s
$\nu(\text{CC}) + \delta(\text{CH}_3)$	1203	1202	1204	1204 m
$\nu(\text{CC}_3)$	884	895	894	882 m

a ν = stretching, δ = deformation, δ_{r} = rocking

b data for tert-butylacetylene from Ref. [9], compare also Ref. [10] for assignments.

c Bands resulting from formation of carboxylate complex by insertion of CO₂ into the Ag-C bond.

2. Estimate of the thickness of sublimated samples

All sublimated samples were inspected by reflection absorption infrared spectroscopy (RAIRS) prior to electron irradiation. Infrared spectra obtained by attenuated total reflectance (ATR-IR) measurements were used as reference by which we deduce, from the RAIRS data, information on how the absolute amounts of material present in the sublimates of Ag(I) 2,2-dimethylbutanoate, Ag(I) benzoate, and Ag(I) 3,3-dimethyl-1-butynyl compare to each other. Some samples were, in addition, investigated by optical microscopy and X-ray photoelectron spectroscopy (XPS) to obtain more insight into the distribution of the material on the surface. We explain here the arguments on which the conclusions presented in the main manuscript are based.

The RAIRS data for all samples that were used in the experiments presented in the main text are shown in Figure S2, together with the ATR-IR spectra of Ag(I) 2,2-dimethylbutanoate, Ag(I) benzoate, and Ag(I) 3,3-dimethyl-1-butynyl. The infrared intensities were evaluated to obtain a rough estimate of the relative average thickness of the sublimate layers. This analysis is based on a comparison of ATR-IR and RAIRS intensities for selected bands. The intensities are measured as the peak height because the width of the bands in the different spectra is comparable. To support this procedure, we argue that the penetration depth of the evanescent IR wave into the samples pressed onto the ATR crystal should be similar for all three compounds. We use the ATR-IR intensities of bands with similar wavenumber as reference (see Table S4) to avoid wavenumber-dependent distortion of the spectra [11] and have checked by gradually increasing the force applied by the ATR piston that the intensities were in saturation. Furthermore, and in line with previous results (see for instance Refs. [12–14]), our estimate assumes that, for sufficiently thin molecular layers, the RAIRS intensities increase linearly with the amount of material as long as the average orientation of the molecules remains the same. Such orientation effects are absent from the present RAIRS data which show, for each compound, a generally constant pattern (Figure S2). The obvious intensity fluctuations between different samples of the same compound included in Figure S2 thus reflect variations in the amount of material present in the samples.

For each of the three Ag(I) compounds, the band intensities in RAIRS summarized in Table S4 are compared to those found in the ATR-IR spectra. Most importantly, the ratio between the RAIRS intensity of the sample used in the ESD experiment (Figures 5 and 6 of main manuscript) and the ATR-IR intensity is higher for Ag(I) 2,2-dimethylbutanoate than for the other two compounds. This indicates that the average thickness of Ag(I) benzoate and Ag(I) 3,3-dimethyl-1-butynyl sublimate layers does not exceed that of Ag(I) 2,2-dimethylbutanoate. Based on this result, the decomposition efficiency of the three compounds can be safely compared as described in Section 3.2 of the main manuscript.

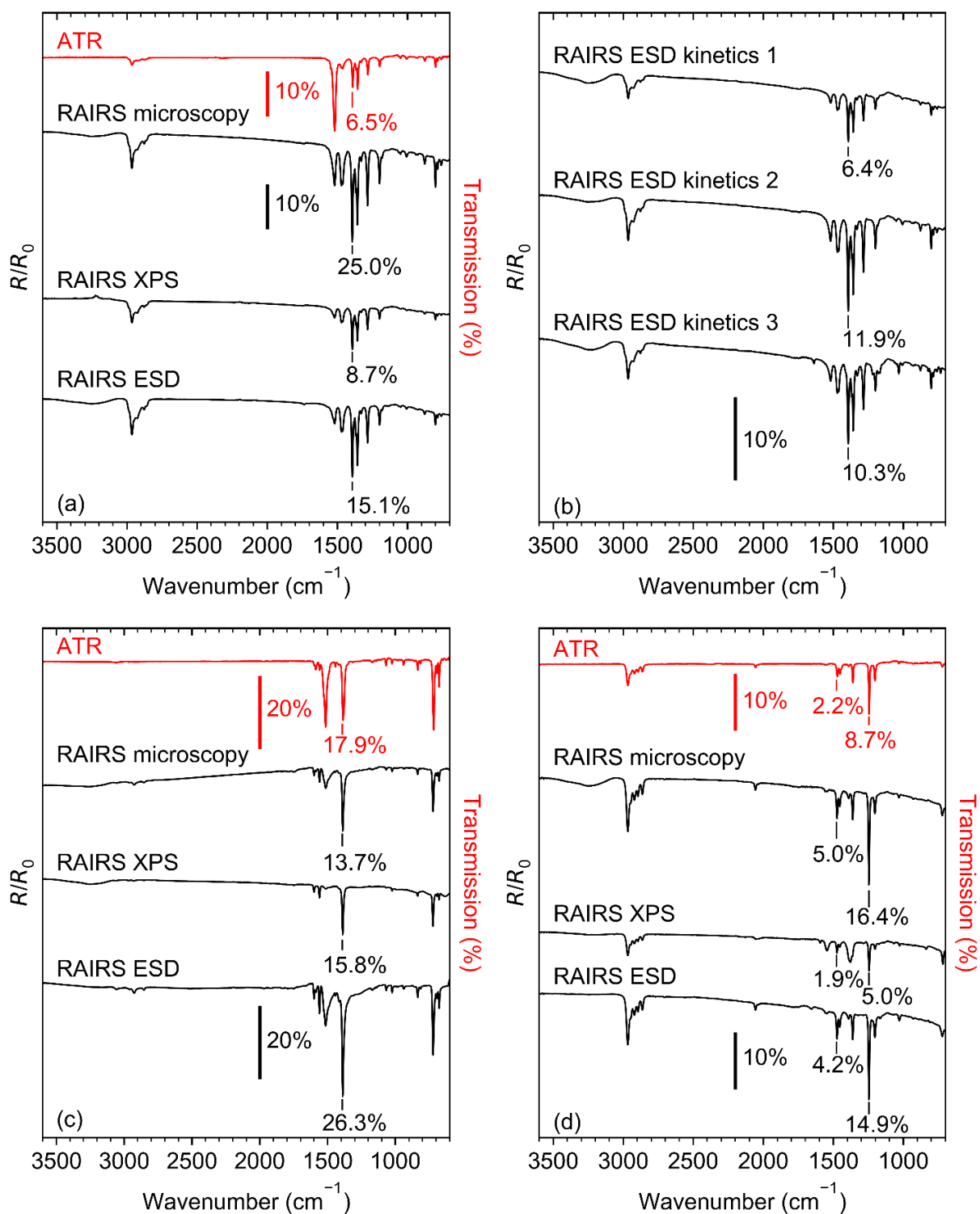


Figure S2. ATR spectra (red) and RAIR spectra (black) of sublimates of (a,b) Ag(I) 2,2-dimethylbutanoate, (c) Ag(I) benzoate, and (d) Ag(I) 3,3-dimethyl-1-butyryl used in the different experiments presented in this work. The labels indicate in which experiments the RAIRS samples were subsequently used. See Table S4 for details.

Table S4. RAIRS intensities of selected bands for samples used in the experiments described in the main text and corresponding ATR intensities given in % as used as reference for an estimate of the average sublimate thickness. Values in parentheses establish a comparison between intensities in RAIRS and ATR with the latter being set to 100 for convenience. It is assumed that ATR intensities reflect the same amount of material for all three compounds.

	Ag(I) 2,2-dimethyl-butanoate	Ag(I) benzoate	Ag(I) 3,3-dimethyl-1-butyne
Selected band ^a	$\nu_s(\text{COO}^-)$ 1390 cm^{-1}	$\nu_s(\text{COO}^-)$ 1390 cm^{-1}	$\delta(\text{CH}_3)$ 1360 cm^{-1}
ATR ^b	6.5% (100)	17.9% (100)	8.7% (100)
RAIRS microscopy (Figure S3)	25.0% (385)	13.7% (77)	16.4% (189)
RAIRS ESD (Figures 5 and 6)	15.1% (232)	26.3% (145)	14.9% (171)
RAIRS XPS (Figure S2)	8.7% (134)	15.8% (88)	5.0% (57)
RAIRS ESD kinetics 1 (Figure 9)	6.4% (98)		
RAIRS ESD kinetics 2 (Figure 10a)	11.9% (183)		
RAIRS ESD kinetics 3 (Figure 10b)	10.3% (158)		

^a The analysis is based on vibrational bands with similar wavenumbers to avoid effects of wavenumber dependence of the ATR data. See Ref. [11].

Optical microscopy (Figure S3) shows that the sublimate layers of Ag(I) 2,2-dimethylbutanoate and Ag(I) benzoate exhibit larger agglomerated crystallites while the sublimate of Ag(I) 3,3-dimethyl-1-butyne is more homogeneous. We note that according to the RAIRS intensities (Table S4), the sample of Ag(I) 2,2-dimethylbutanoate used in microscopy was thicker than samples used in electron irradiation experiments. However, even this amount of material is thin enough to warrant that the orientation of the molecules in the sublimate is governed by the surface (see also Section 3.1 of main manuscript). In contrast, the RAIR spectrum of a sublimate that has been prepared from a larger amount of material (see RAIRS denoted 5 mg in Figure S6) has a significantly higher intensity and closely matches the ATR-IR spectrum indicating that the orientation of the molecules is no longer governed by the surface. This effect most likely indicates that larger crystallites begin to grow independently of the underlying surface and dominate the RAIR spectrum. This suggests that the agglomerated crystallites seen in Figure S3a are not dominant in RAIRS. As the optical microscopy image does not allow to conclude on the presence of a thin layer between the crystals, XPS was used as a further tool to characterize the sample.

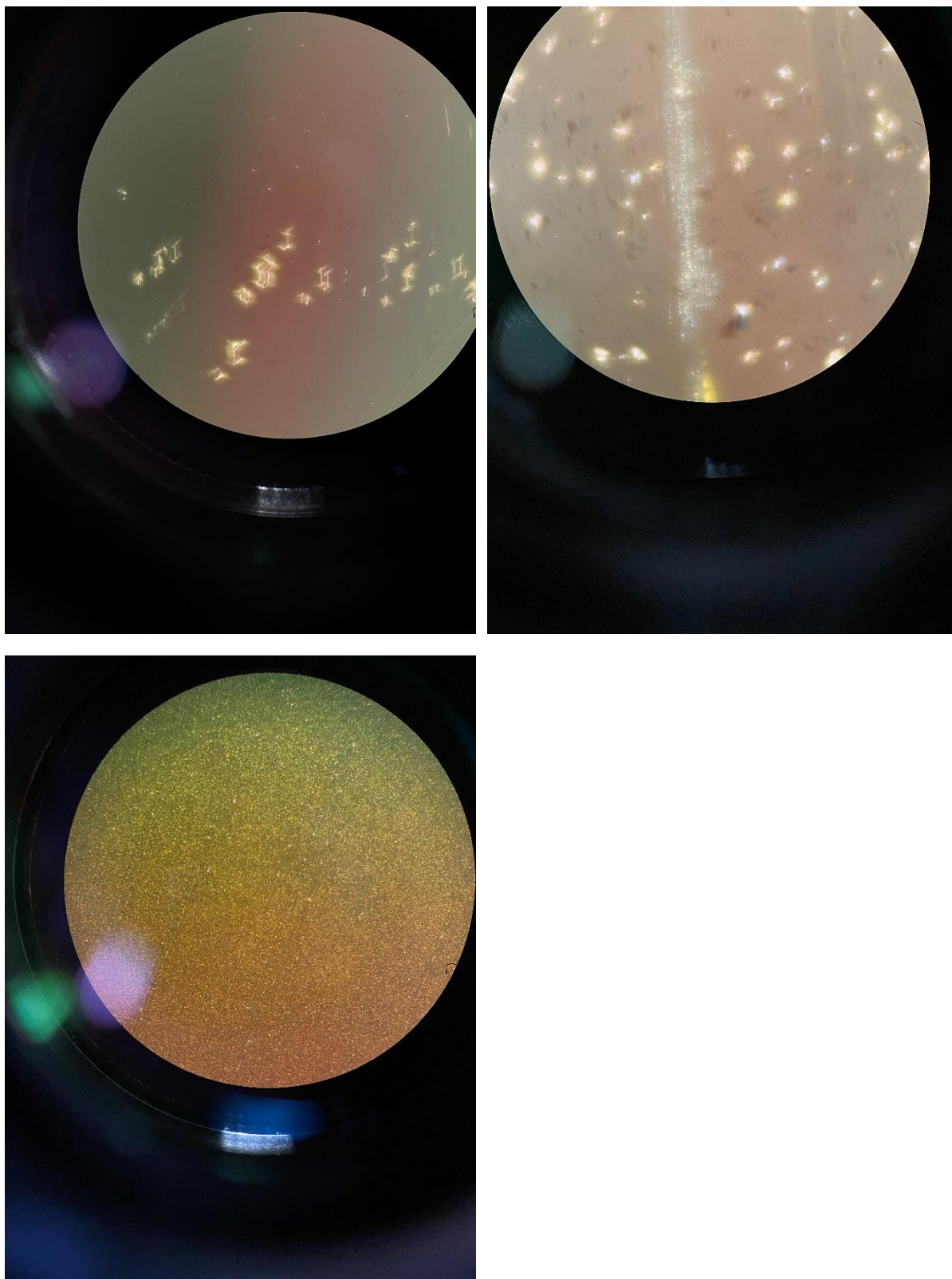


Figure S3. Optical microscopy (40x) of sublimate layers of (a) Ag(I) 2,2-dimethylbutanoate, (b) Ag(I) benzoate, and (c) Ag(I) 3,3-dimethyl-1-butynyl prepared on Au substrates without cl-BPT SAM. The circular view field has a physical diameter of 0.5 mm.

XPS has been performed to obtain more information on the surface coverage of the sublimate layers. To this end, the Ag(I) complexes were sublimated on Au substrates without cl-BPT SAM and the attenuation of signals for electron emission from Au4d and Au4f levels from the underlying substrate, which possess different kinetic energies, was evaluated using the software UNIFIT 2021 [15]. This analysis assumes a uniform thickness which is calculated from the ratio of the integrated intensities of the two signals after correction for the respective ionization cross sections and the spectrometer transmission function taking account of the different electron effective attenuation lengths of the Au4d and Au4f photoelectrons (See equation (10) in Ref. [15]). Values for the attenuation length of 33 Å for Au4d photoelectrons and 39 Å for Au4f photoelectrons were obtained for Ag(I) 2,2-dimethylbutanoate (density of 1.15 g/cm³) using the NIST Electron Effective-Attenuation-Length Database [16]. The same values were used for the other two compounds where densities have not been reported. The thicknesses derived from these values under the assumption of a homogeneous surface coverage are summarized in Table S5.

Table S5. XPS Au signals used for an estimate of the sublimate thickness.

	Ag(I) 2,2-dimethylbutanoate	Ag(I) benzoate	Ag(I) 3,3-dimethyl-1-butynyl
Area Au 4d	36	48	44
Area Au 4f	63	52	54
Ratio Au4d/Au4f	0.57	0.92	0.82
Thickness according to equation (12) [15]	12 nm	1.7 nm	4.4 nm
Conclusion from models shown in Figure S4	Majority of the substrate must be covered by sublimate	Up to 1/3 of surface may be void of sublimate	Up to 10% of the substrate may be void of sublimate

According to optical microscopy (Figure S3), the assumption of a homogeneous thickness is questionable in the case of the sublimate layers considered here. Therefore, we discuss here the effect of partial surface coverage on the intensity ratio of the Au4d and Au4f signals using a simple model. In the simplest case, the model describes a surface covered by an amount of material that, when homogeneously distributed, results in a thickness d . We then consider situations where the same amount of material covers only a fraction A of the surface and the material is stacked again with homogeneous thickness d/A within this area. The intensity of a photoelectron signal that stems with initial intensity I_0 from the underlying Au surface then results as

$$I = I_0 \cdot (1 - A) + I_0 \cdot A \cdot e^{-d/A\lambda}.$$

Here, λ is the electron effective attenuation length for a given photoelectron kinetic energy. Using this equation and the values for the attenuation length given above, the resulting intensities for Au4d and Au4f were calculated and their ratio is plotted as function of surface coverage A in Figure S4a (enlargement thereof in Figure S4b) for a series of thicknesses d .

Note that for a value of $A = 1$ and the thicknesses listed in Table S5, the plots would in fact reproduce the experimental intensity ratios. A modified version of this model (Figure S4c and enlargement thereof in Figure S4d) reflects a certain roughness. Again, the model represents an amount of material that, when homogeneously distributed, results in a thickness d and the material is simply redistributed when describing partial coverage. However, in this case the thickness in 50% of the covered area is reduced by 1/3 while it is increased by the same amount in the remaining 50%. In this case, the intensity of a given photoelectron signal as compared to a bare Au surface would result as

$$I = I_0 \cdot (1 - A) + 0.5 \cdot I_0 \cdot A \cdot e^{-2d/3A\lambda} + 0.5 \cdot I_0 \cdot A \cdot e^{-4d/3A\lambda}.$$

Both models yield qualitatively similar results. In particular, Figure S4 shows that an intensity ratio of 0.57 as observed for Ag(I) dimethylbutanoate is a strong indication that the Au substrate is in fact predominantly covered by the sublimate layer. Considering that the sublimate sample of Ag(I) dimethylbutanoate used for XPS was significantly thinner than the one imaged by optical microscopy (see RAIRS data in Table S4), we conclude that the crystallites seen in Figure S3a most likely have grown on top of a more homogeneous layer that covered the entire substrate. The result is less clear for Ag(I) benzoate and Ag(I) 3,3-dimethyl-1-butynyl. According to Figure S4, the intensity ratio of 0.82 obtained for the latter would also be consistent with a layer that is on average thicker than 4.4 nm but leaves a minor part of the substrate (<10%) uncovered. An even larger part of the surface can be void of sublimate in the case of Ag(I) benzoate. In this case the amount of sublimate would even more exceed that of a homogeneous 1.7 nm layer. However, the intensity ratios as function of fraction of covered surface obtained from the two models suggest that at least 66% of the surface would even need to be covered by sublimate of Ag(I) benzoate to reproduce the experimental ratio of 0.92. The infrared results (Table S4) suggest that the amount of material present in the sublimate of Ag(I) benzoate used for XPS is about 65% of the amount of Ag(I) dimethylbutanoate used for XPS. Taken together, this would translate to an average thickness of the of Ag(I) benzoate sublimate that is unlikely to exceed that of Ag(I) dimethylbutanoate. An analogous estimate for Ag(I) 3,3-dimethyl-1-butynyl arrives at the same conclusion. Based on these arguments, we can safely conclude that the amount of material present in the sublimates of Ag(I) benzoate and Ag(I) 3,3-dimethyl-1-butynyl generally did not exceed the amount of material present in sublimates of Ag(I) dimethylbutanoate. This conclusion is important for the evaluation of the results presented in Section 3.2 of the main manuscript.

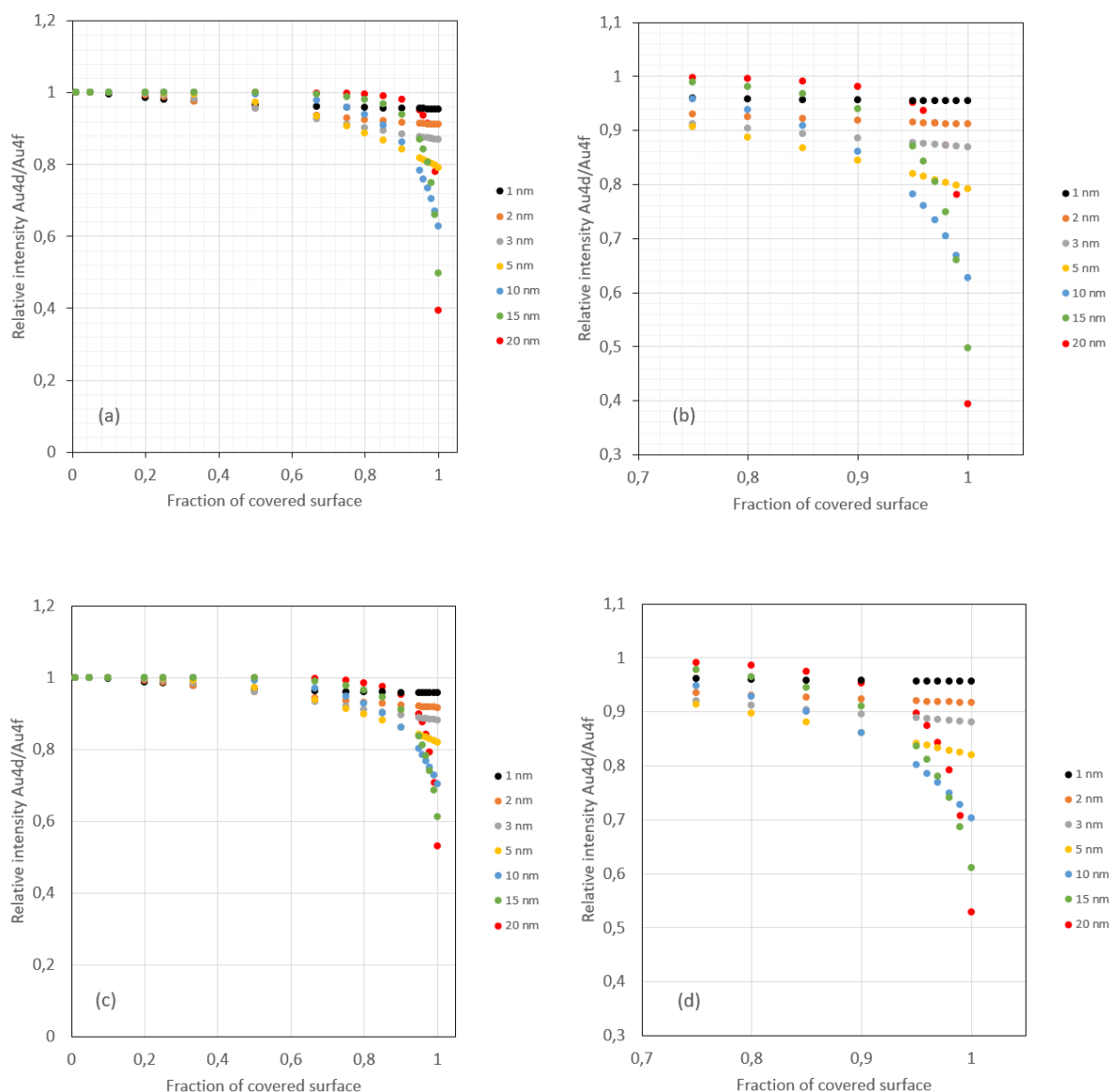


Figure S4. Simulated relative attenuation of XPS Au4d and Au4f signals for sublimates layers produced from different amounts of material stated as homogeneous thickness for a fully covered surface in the plot. For partial coverage the same amount of material is either contained with homogeneous thickness within the covered areas (a,b) or its thickness is reduced by 1/3 in 50% of the covered area while it is increased by the same amount in the remaining 50% (c,d). See text for further details of the model.

3. Electron-induced decomposition of Ag(I) 2,2-dimethylbutanoate

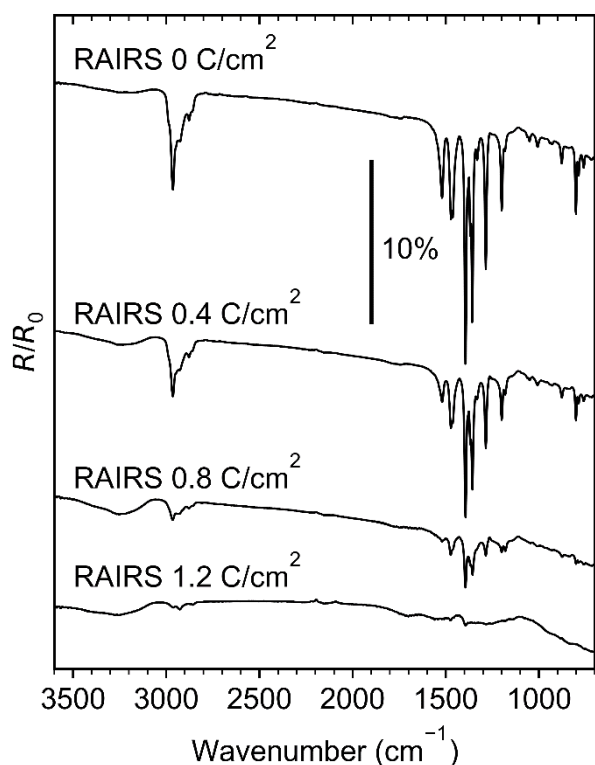


Figure S5. RAIRS of Ag(I) 2,2-dimethylbutanoate recorded before (0 C/cm^2) and after the electron exposures stated in the graph at an electron energy of 50 eV.

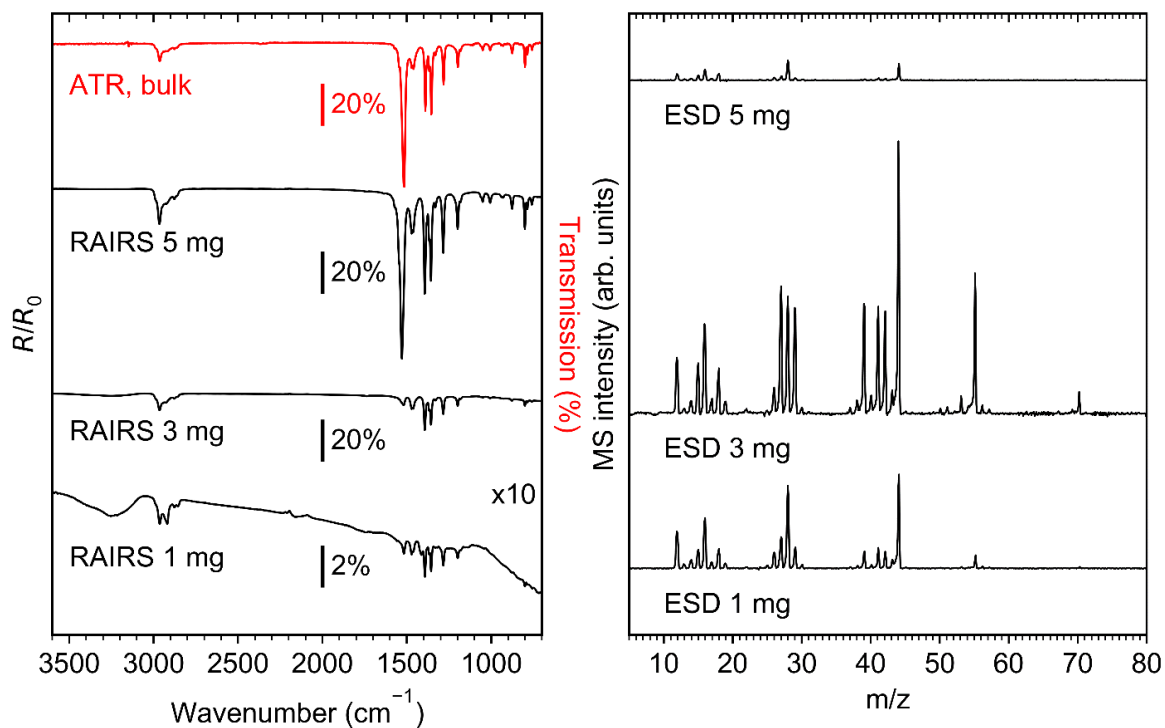


Figure S6. RAIRS of sublimates prepared from increasing amounts of Ag(I) 2,2-dimethylbutanoate as indicated in the graph and comparison to ATR-IR of the same compound (left) as well as ESD mass spectra obtained from these samples upon electron irradiation at 50 eV.

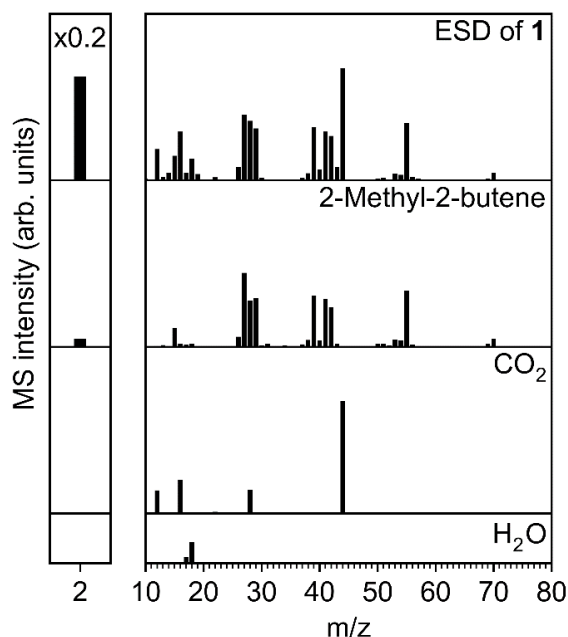


Figure S7. Mass spectrum (m/z 0-80) of the volatile species produced upon ESD ($E_0 = 50$ eV) from Ag(I) 2,2-dimethylbutanoate and mass spectra obtained using the same QMS upon leaking of CO_2 , H_2O , and 2-methyl-2-butene into the vacuum chamber.

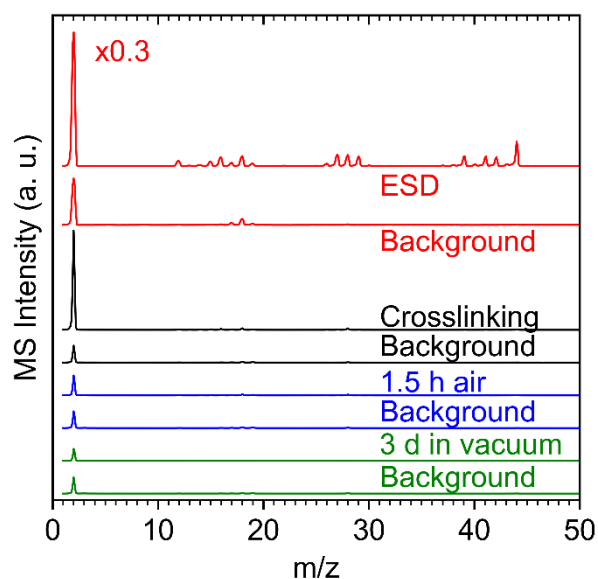


Figure S8. Red: ESD mass spectrum recorded during electron irradiation ($E_0 = 50$ eV) of Ag(I) 2,2-dimethylbutanoate. Black: ESD mass spectrum ($E_0 = 500$ eV) recorded during electron-induced crosslinking of a BPT-SAM. Blue: ESD mass spectrum ($E_0 = 500$ eV) recorded from the same cl-BPT-SAM after 1.5 h exposure to ambient conditions. Green: ESD mass spectrum ($E_0 = 500$ eV) recorded from the same cl-BPT-SAM after 3 days storing in vacuum. Note that the spectra represent raw data that have not been corrected by subtracting the background spectra recorded before the start of the respective irradiation experiment and included here as bottom curves of each data. The result shows that electron irradiation of a cl-BPT SAM does not lead to production of H_2 above the level present in the vacuum chamber as residual gas.

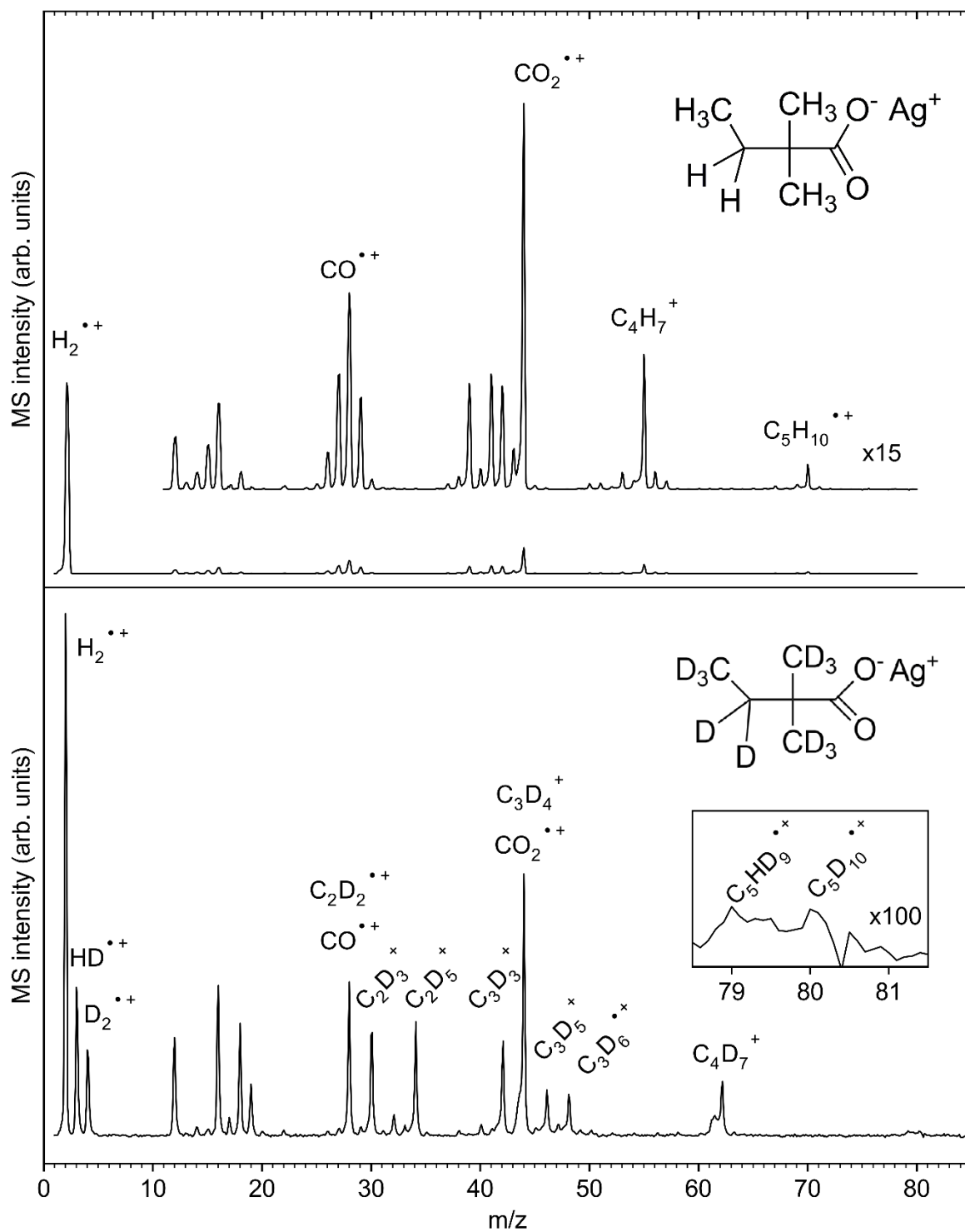


Figure S9. ESD mass spectra recorded from sublimates of Ag(I) 2,2-dimethylbutanoate (top) and perdeuterated Ag(I) 2,2-dimethylbutanoate (bottom) upon electron irradiation at 100 eV. The higher energy was used to obtain higher ESD intensities. The signals are also listed in Table S6.

Table S6. ESD signals and assignments for Ag(I) 2,2-dimethylbutanoate and perdeuterated Ag(I) 2,2-dimethylbutanoate as seen in Figure S9.

Ag 2,2-dimethylbutanoate		Perdeuterated Ag 2,2-dimethylbutanoate			
Fragment	m/z	Fragment	m/z	H exchanged fragment	m/z
[C ₅ H ₁₀] ^{•+}	70	[C ₅ D ₁₀] ^{•+}	80	[C ₅ HD ₉] ^{•+}	79
C ₄ H ₇ ⁺	55	C ₄ D ₇ ⁺	62	C ₄ HD ₆ ⁺	61
[CO ₂] ^{•+}	44				
[C ₃ H ₆] ^{•+}	42	[C ₃ D ₆] ^{•+}	48		
C ₂ H ₅ ⁺	41	C ₃ D ₅ ⁺	46		
C ₃ H ₄ ⁺	40 weak	[CO ₂] ^{•+} , C ₃ D ₄ ⁺	44		
C ₃ H ₃ ⁺	39	C ₃ D ₃ ⁺	42		
		C ₃ D ₂ ⁺	40		
C ₂ H ₅ ⁺	29	C ₂ D ₅ ⁺	34		
CO ^{•+} , [C ₂ H ₄] ^{•+}	28	[C ₂ D ₄] ^{•+}	32 weak		
C ₂ H ₃ ⁺	27	C ₂ D ₃ ⁺	30		
[C ₂ H ₂] ^{•+}	26	CO ^{•+} , [C ₂ D ₂] ^{•+}	28		
[H ₂ O] ^{•+}	18				
O ^{•+} , [CH ₄] ^{•+}	16	[CD ₄] ^{•+}	20 weak	[CHD ₃] ^{•+}	19
CH ₃ ⁺	15	[H ₂ O] ^{•+} , CD ₃ ⁺	18		
CH ₂ ^{•+}	14	O ^{•+} , CD ₂ ^{•+}	16		
C ^{•+}	12	C ^{•+}	12		
		[D ₂] ^{•+}	4		
		[HD] ^{•+}	3		
[H ₂] ^{•+}	2	[H ₂] ^{•+}	2		

4. Electron-induced degradation of Ag carboxylates with different alkyl side chain

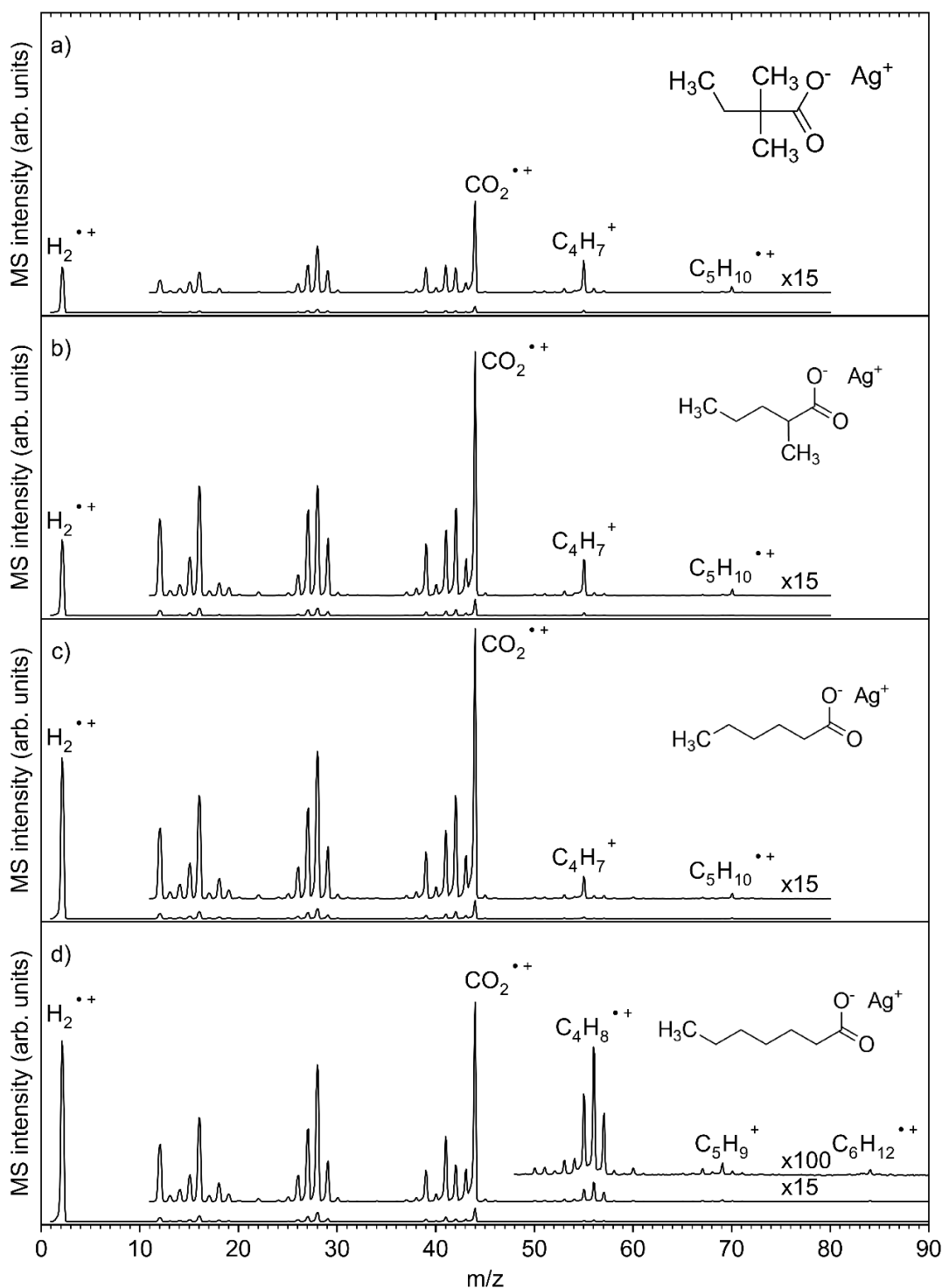


Figure S10. ESD mass spectra of the volatile species produced from sublimates of (a) Ag(I) 2,2-dimethylbutanoate, (b) Ag(I) 2-methylpentanoate, (c) Ag(I) hexanoate, and (d) Ag(I) heptanoate upon electron irradiation at 100 eV. The higher energy was used to obtain higher ESD intensities.

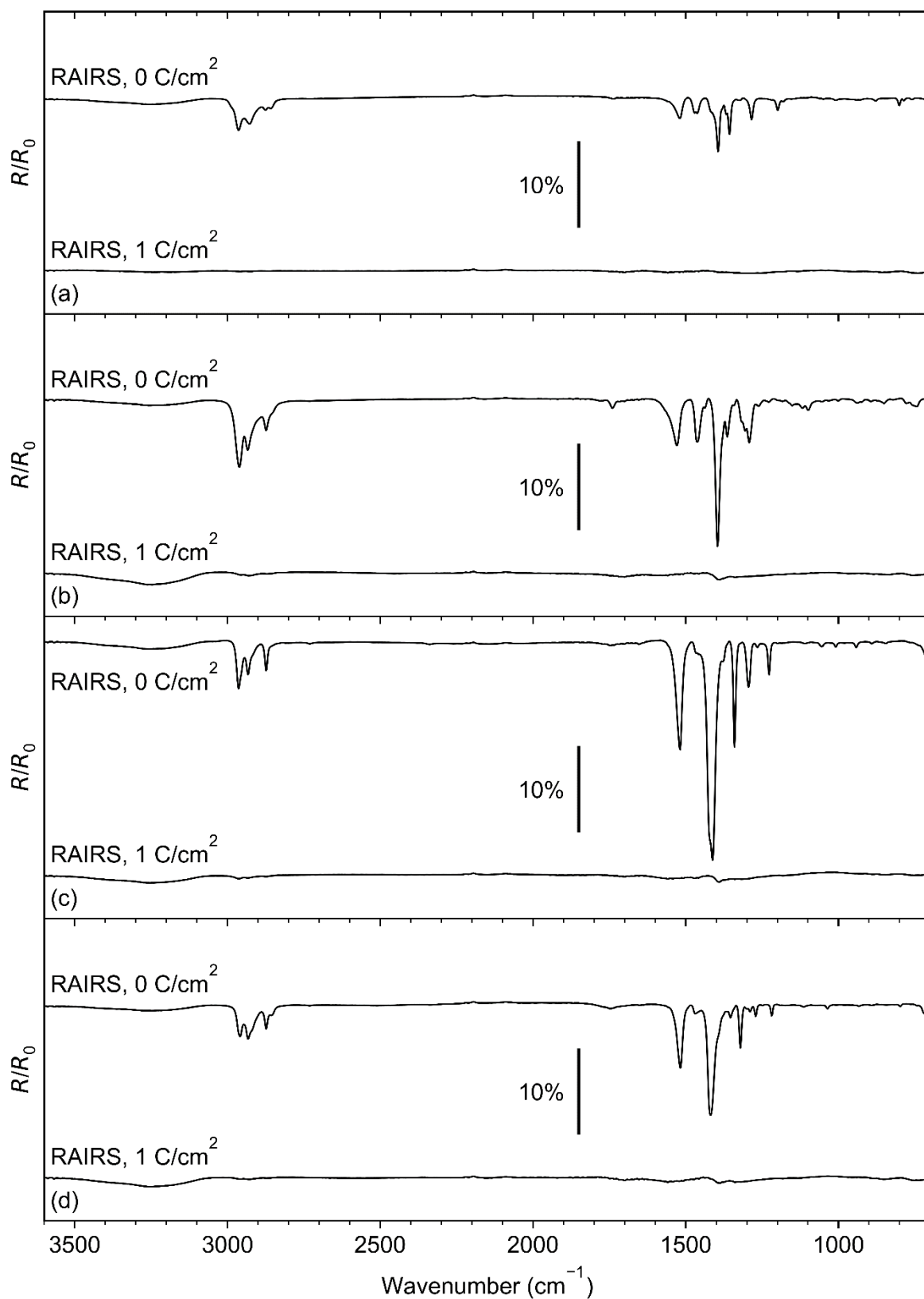


Figure S11. RAIR spectra of (a) Ag(I) 2,2-dimethylbutanoate, (b) Ag(I) 2-methylpentanoate, (c) Ag(I) hexanoate, and (d) Ag(I) heptanoate before (0 C/cm^2) and after electron irradiation (1 C/cm^2) at $E_0 = 100 \text{ eV}$.

5. Electron-induced degradation of a thick Ag(I) 3,3-dimethyl-1-butynyl sublimate

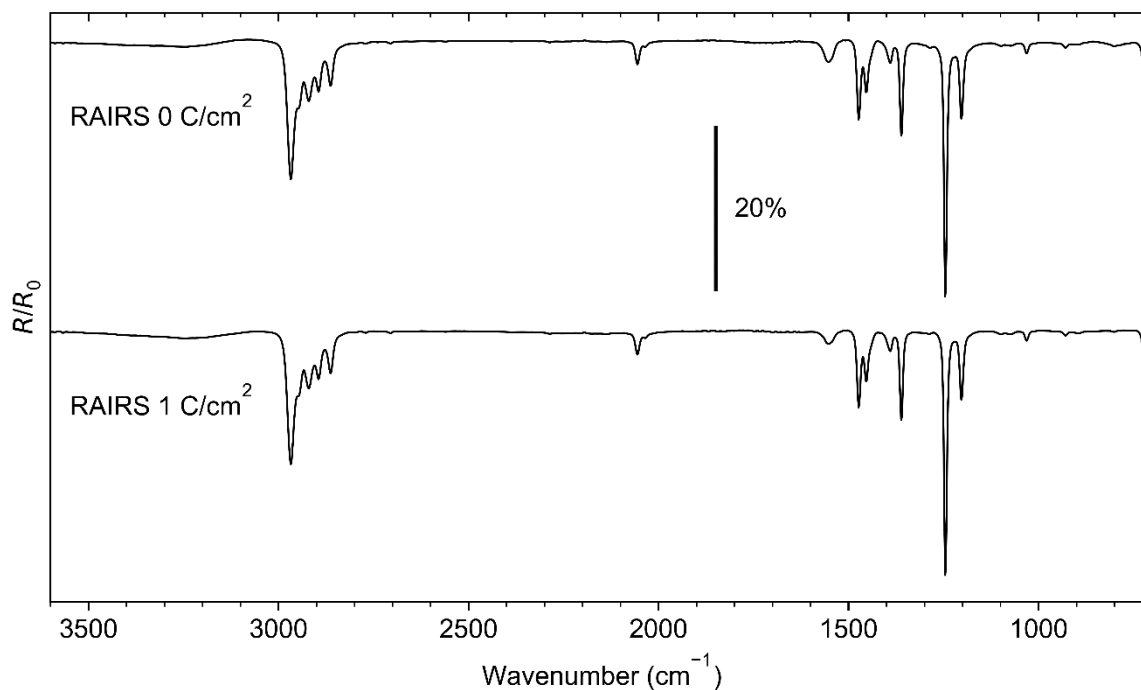


Figure S12. RAIR spectra of Ag(I) 3,3-dimethyl-1-butynyl before (0 C/cm²) and after irradiation (1 C/cm²) with $E_0 = 100$ eV.

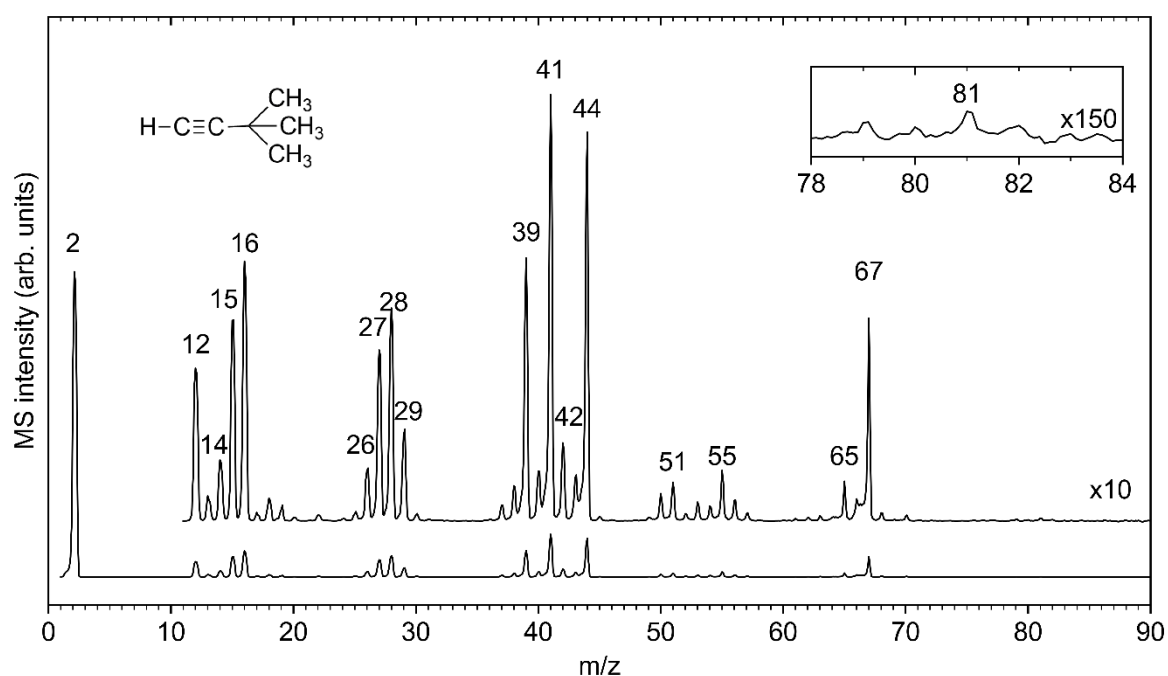


Figure S13. ESD mass spectra of the volatile species produced upon electron irradiation at 100 eV from a thick sublimate layer of Ag(I) 3,3-dimethyl-1-butynyl as also shown in Figure S12.

6. ESD kinetic experiments

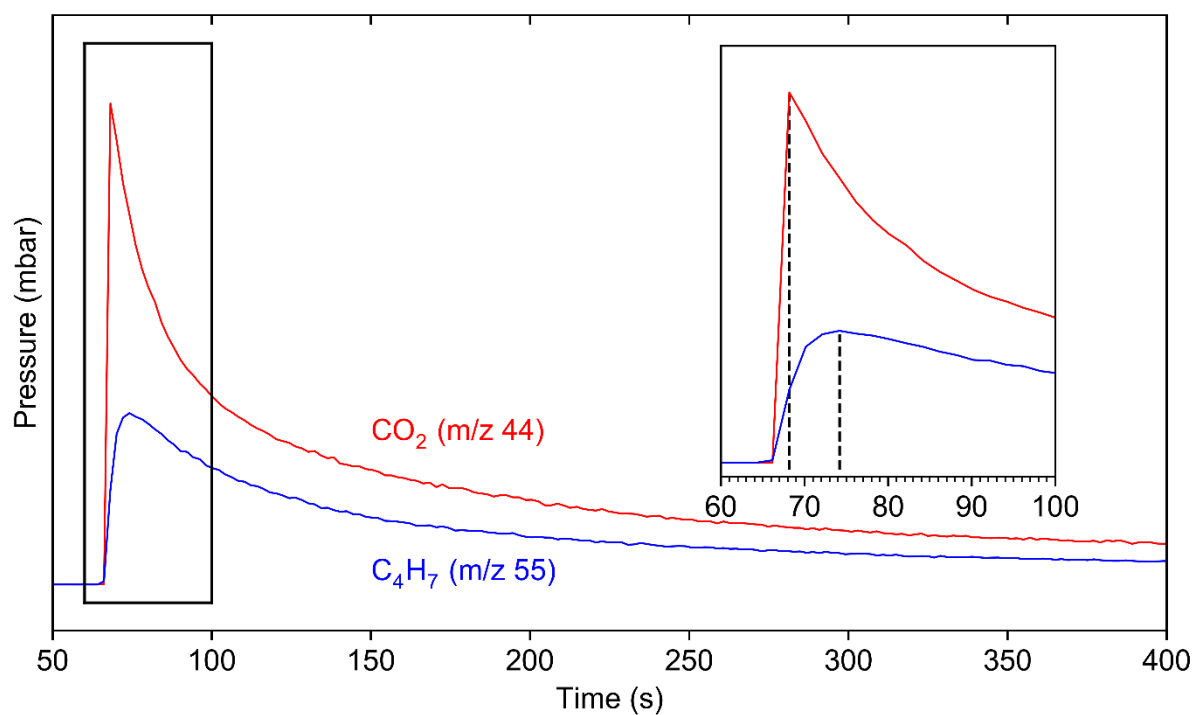


Figure S14. ESD as function of time during electron irradiation of Ag(I) 2,2-dimethylbutanoate at $E_0 = 500$ eV for m/z 44 (red, representative of CO_2) and m/z 55 (blue, representative of 2-methyl-2-butene). The sudden step increase of the ESD signals marks the start of irradiation. During irradiation, the average current measured on the sample amounted to $1.4 \mu\text{A}/\text{cm}^2$.

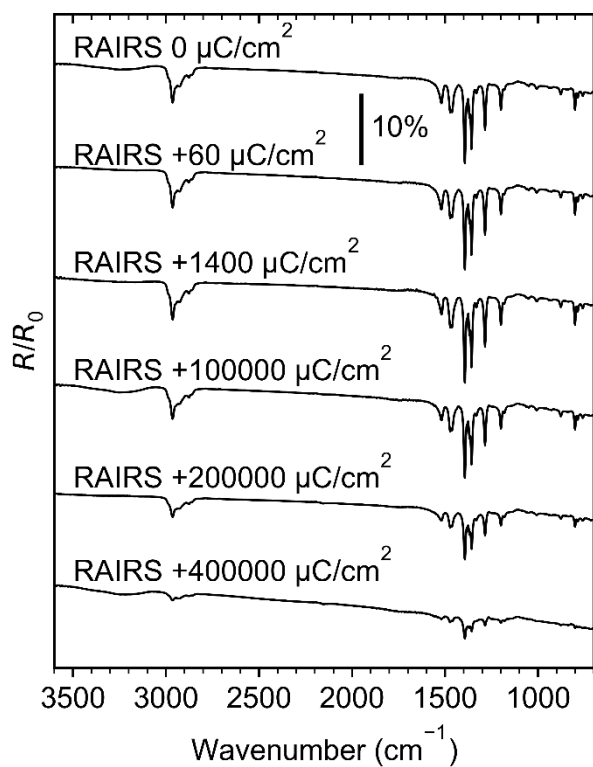


Figure S15. RAIRS of Ag(I) 2,2-dimethylbutanoate recorded before (0 C/cm^2) and after the electron exposures stated in the graph at an electron energy of 50 eV. The spectra were recorded during the experiment shown in Figure 9b of the main manuscript. Note that Figure 9b contains only the first three electron irradiation cycles after which ESD intensities were generally small.

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Pivalate complexes of copper(II) with aliphatic amines as potential precursors for depositing nanomaterials from the gas phase†

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New copper(II) complexes with pivalate and primary aliphatic amines $[\text{Cu}_2(\text{RNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$, where $\text{R} = {}^t\text{Bu}$, ${}^s\text{Bu}$, ${}^i\text{Pr}$, and Et were synthesised and characterised. These and the known complexes with tertiary triethylamine $[\text{Cu}_2(\text{Et}_3\text{N})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]$ were investigated for use as precursors in chemical vapour deposition (CVD) and focused electron beam induced deposition (FEBID) methods by thermal analysis and sublimation experiments. TGA studies have shown that copper derivatives in the gas phase occur even at atmospheric pressure. For preliminary CVD experiments, the selected copper compound $[\text{Cu}_2({}^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ was used. Moreover, the so-called 'sensitivity' to high-energy electrons studied in thin layers of compounds was confirmed by observations using electron microscopes. These results reveal that the obtained complexes can be promising for the vapour deposition methods. Additionally, the used pivalate-amine ligand system allowed four single crystals to grow through partial release of the secondary ligand in the air. The following multi-nuclear complexes $[\text{Cu}_3({}^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_6]_n$, $[\text{Cu}_3({}^s\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_6]_n$, $[\text{Cu}_3({}^i\text{PrNH}_2)_2(\mu_3\text{-OH})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$, and $[\text{Cu}_{20}(\text{EtNH}_2)_6(\mu_3\text{-OH})_{24}(\text{OH})(\text{H}_2\text{O})_5(\text{NO}_3)(\mu\text{-O}_2\text{C}^t\text{Bu})_8]({}^t\text{BuCO}_2)_6 \cdot 13\text{H}_2\text{O}$ were characterized.

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† Electronic supplementary information (ESI) available: Table S1: Crystal data and structure refinement for (1a–4a); Table S2: Bond lengths [Å] and angles [°] for $[\text{Cu}_3({}^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_6]_n$ (1a); Table S3: Bond lengths [Å] and angles [°] for $[\text{Cu}_3({}^s\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_6]_n$ (2a); Table S4: Bond lengths [Å] and angles [°] for $[\text{Cu}_3({}^i\text{PrNH}_2)_2(\mu_3\text{-OH})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (3a); Table S5: Bond lengths [Å] and angles [°] for $[\text{Cu}_{20}(\text{EtNH}_2)_6(\mu_3\text{-OH})_{24}(\text{OH})(\text{H}_2\text{O})_5(\text{NO}_3)(\mu\text{-O}_2\text{C}^t\text{Bu})_8]({}^t\text{BuCO}_2)_6 \cdot 13\text{H}_2\text{O}$ (4a); Fig. S1: Chain topology in $[\text{Cu}_3({}^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_6]_n$ (2a) shows alternately arranged paddlewheel and mononuclear motifs; Fig. S2: Packing diagram of $[\text{Cu}_{20}(\text{EtNH}_2)_6(\mu_3\text{-OH})_{24}(\text{OH})(\text{H}_2\text{O})_5(\text{NO}_3)(\mu\text{-O}_2\text{C}^t\text{Bu})_8]({}^t\text{BuCO}_2)_6 \cdot 13\text{H}_2\text{O}$ (4a) viewed along a axis. For the clarity of the picture hydrogen atoms are omitted; Fig. S3: The solvation sphere around the cluster (a) and hydrogen bonds in the crystal network (b). The selected hydrogen bond pathways between clusters are marked in green (for cluster···solvation sphere···cluster pattern) and in magenta (for cluster···solvation sphere···solvation sphere···cluster pattern); Fig. S4: ATR-IR spectrum for the compounds of the general formulae: $[\text{Cu}_2(\text{RNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (1–5) and single crystals formed during crystallization (1a–3a). The coloured bands highlight the ranges of the particular vibrational modes: (ν_{NH_2}) (yellow), (ν_{asCOO}) (green), (ν_{sCOO}) (blue), (ν_{CH_3}) (grey); Fig. S5: ATR-IR spectrum for the compound $[\text{Cu}_2({}^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (1) (black) and $[\text{Cu}_3({}^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_6]_n$ (1a) (grey); Fig. S6: ATR-IR spectrum for the compound $[\text{Cu}_2({}^s\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (2) (black) and $[\text{Cu}_3({}^s\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_6]_n$ (2a) (grey); Fig. S7: ATR-IR spectrum for the compound $[\text{Cu}_2({}^i\text{PrNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (3) (black) and $[\text{Cu}_3({}^i\text{PrNH}_2)_2(\mu_3\text{-OH})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (3a) (grey); Fig. S8: ATR-IR spectrum for the compound $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (4); Fig. S9: ATR-IR spectrum for the compound $[\text{Cu}_2(\text{Et}_3\text{N})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (5); Fig. S10: Thermal decomposition of $[\text{Cu}_2({}^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (1) (TG, DTG, DTA curves); Fig. S11: Thermal decomposition of $[\text{Cu}_2({}^s\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (2) (TG, DTG, DTA curves); Fig. S12: Thermal decomposition of $[\text{Cu}_2({}^i\text{PrNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (3) (TG, DTG, DTA curves); Fig. S13: Thermal decomposition of $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (4) (TG, DTG, DTA curves); Fig. S14: Thermal decomposition of $[\text{Cu}_2(\text{Et}_3\text{N})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (5) (TG, DTG, DTA curves); Fig. S5: Transmission electron microscope (TEM) diffraction pattern for the TGA final residue of CuO: (A) $[\text{Cu}_2({}^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (2), (B) $[\text{Cu}_2({}^i\text{PrNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (3), (C) $[\text{Cu}_2(\text{Et}_3\text{N})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (5); Fig. S6: Infrared spectra for the compound $[\text{Cu}_2({}^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (2) before (grey) and after sublimation (black) at 363 K ($p = 10^{-2}$ mbar); Fig. S7: Infrared spectra for the compound $[\text{Cu}_2({}^s\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (2) before (grey) and after sublimation (black) at 363 K ($p = 10^{-2}$ mbar); Fig. S8: Infrared spectra for the compound $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (4) before (grey) and after sublimation (black) at 383 K ($p = 10^{-2}$ mbar); Fig. S9: Infrared spectra for the compound $[\text{Cu}_2(\text{Et}_3\text{N})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (5) before (grey) and after sublimation attempt (black) at 393 K ($p = 10^{-2}$ mbar); $[\text{Cu}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (0) (blue); Fig. S20: Infrared spectra for the compound $[\text{Cu}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (0) before (grey) and after sublimation (black) at 418 K ($p = 10^{-2}$ mbar); Table S6: Mass spectrometry with electron ionization (EI MS) results for the complex $[\text{Cu}_2({}^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (1); Fig. S21: Examined scan areas' EDX spectra (8 keV) for $[\text{Cu}_2({}^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (2) deposited on a silicon wafer; Fig. S22: Examined scan areas' EDX spectra (20 keV) for $[\text{Cu}_2({}^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (2) deposited on a silicon wafer; Fig. S10: Examined scan areas' EDX spectra (8 keV) for $[\text{Cu}_2({}^i\text{PrNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (3) deposited on a silicon wafer; Fig. S11: Examined scan areas' EDX spectra (20 keV) for $[\text{Cu}_2({}^i\text{PrNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (3) deposited on a silicon wafer; Fig. S12: Examined scan areas' EDX spectra (8 keV) for $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (4) deposited on a silicon wafer; Fig. S13: Examined scan areas' EDX spectra (20 keV) for $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (4) deposited on a silicon wafer; Fig. S14: Examined scan areas' EDX spectra (8 keV) for $[\text{Cu}_2(\text{Et}_3\text{N})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (5) deposited on a silicon wafer; Fig. S15: Examined scan areas' EDX spectra (20 keV) for $[\text{Cu}_2(\text{Et}_3\text{N})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (5) deposited on a silicon wafer; Fig. S16: Examined scan areas' EDX spectra (8 keV) for $[\text{Cu}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (0) deposited on a silicon wafer; Fig. S30: Examined scan areas' EDX spectra (20 keV) for $[\text{Cu}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (0) deposited on a silicon wafer; Fig. S31: Composition analysis of the obtained materials using $[\text{Cu}_2({}^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (1), (A) for deposit obtained on the second substrate, (B) for deposit obtained on the fourth substrate; Fig. S17: SEM image to show the thickness of the copper layer obtained using $[\text{Cu}_2({}^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (1) for deposit fomed on the second substrate. CCDC 2261736 (1a), 2261751 (2a), 2261785 (3a) and 2261768 (4a). For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d3nj04959k>

1. Introduction

Copper is an abundant element in the earth's crust with relatively low cost but high electrical and heat conductivity. Therefore, it is an excellent candidate for use in commercial applications in fields such as nanoelectronics or data storage.¹

Nanomaterials are attractive research topics due to the possibility of use in different fields, such as nano- and optoelectronic devices; magnetic-, gas-, thermal-, and bio-sensors, as well as plasmonic structures.^{2,3} The various nanomanufacturing technologies, such as optical/electron-beam lithography, nanoimprint lithography (NIL), atomic layer deposition (ALD), chemical mechanical polishing (CMP), or laser nanopatterning, allow for the fabrication of nanostructures and devices.^{4–7} Their significant disadvantage is the problem with the production of high-resolution 3D deposits. In comparison, the focused electron beam induced deposition (FEBID) technique enables the formation of two- and three-dimensional nanostructures of precisely defined shapes and sizes, in the order of even 5–10 nm.^{8–10} High lateral resolution can be achieved by controlling the electron beam's location and pulse duration. In the case of FEBID, volatile precursor molecules are introduced through the gas injection system (GIS) onto the substrate surface, where they adsorb and are decomposed by a focused electron beam in the order of keV energy. The FEBID method involves the advantages of direct-write lithographic processes, among others, high spatial resolution specific to the site, maskless, and resistance, as well as obtaining deposits on non-planar surfaces. Many factors influence the performance of the processes, including the dissociation of the precursor molecules adsorbed on the substrate by interactions with high-energy electrons. The efficiency of deposit formation is also affected by secondary electrons generated by the substrate and can cause the expansion of the deposit, forming the so-called “halo” area. It is important to note that there is still a lack of suitable, stable, and user-friendly precursors to obtain pure copper deposits with a defined 2D and 3D shape without post-deposition purification.^{2,3,11–14}

The FEBID method requires a precursor with sufficient volatility and limited thermal decomposition. For this reason, the volatile precursors used in chemical vapour deposition (CVD) are considered applicable. Significantly, these compounds are often not characterised and optimised for the electron induced FEBID process. Therefore, research focusing on combining volatility with electron sensitivity and thermal stability is crucial for the design and synthesis of new precursors. Among the metal precursors of 11 group elements, the high metal content in the deposit was achieved for the complexes: $[\text{Ag}_2(\mu\text{-O}_2\text{CC}(\text{Me})_2\text{Et})_2]$ (73 at% Ag), $[\text{Ag}_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_2]$ (76 at% Ag), $[\text{Ag}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_2]$ (57 at% Ag), and $[\text{AuCl}(\text{PF}_3)]$ (pure Au crystals). In the case of copper the following compounds have been tested: $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (23 at% Cu), $[\text{Cu}(\text{hfac})_2]\cdot\text{H}_2\text{O}$ (14 at% Cu) (hfac – hexafluoroacetylacetonate), $[\text{Cu}(\text{tbaoc})_2]$ (26 at% Cu) (tbaoc – *tert*-butylacetoacetate), $[\text{Cu}(\text{hfac})\text{VTMS}]$ (20 at% Cu) (VTMS – vinyltrimethylsilane), $[\text{Cu}(\text{hfac})\text{MHY}]$ (13 at% Cu) (MHY – 2-methyl-1-hexen-3-yne), and $[\text{Cu}(\text{hfac})\text{DMB}]$

(13 at% Cu) (DMB – 3,3-dimethyl-1-butene).^{8,15–18} These studies suggested that the electron beam decomposition is influenced not only by the ligand but also by the coordination centre.

We decided to investigate copper(II) compounds with pivalate (2,2-dimethylpropanoate) and amines because our previous studies on complexes with perfluorinated carboxylates and small aliphatic amines $[\text{Cu}_2(\text{RNH}_2)_2(\mu\text{-O}_2\text{CR}_f)_4]$, where R = ^tBu, ⁱPr, Et; $\text{R}_f = \text{C}_n\text{F}_{2n+1}$, $n = 1\text{--}6$ have indicated that the introduction of a secondary amine ligand improves volatility and causes that they are a good source of metals in the gas phase.^{19,20} Moreover, the compounds $[\text{Cu}_2(\text{RNH}_2)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$, where R = ^tBu, ^sBu, Et and $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CC}_3\text{F}_7)_4]$, have been studied in terms of low-energy electron–molecule interactions for their possible application in the FEBID method.^{21,22} Generally, the number of copper(II) compounds with non-fluorinated carboxylate and various amines are described.^{23–27} Among them, the pivalate complex containing triethylamine $[\text{Cu}_2(\text{Et}_3\text{N})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]$ is discussed. The magnetic properties were studied for this compound of the ‘paddle wheel’ structure with *syn-syn* bridging carboxylates, similar to copper(II) acetate.²⁸ However, the research has not been concerned with investigating gas-phase processes.

In this work, we present the study of volatility and interaction of electrons for new, user-friendly, copper(II) complexes with pivalate and small aliphatic amines $[\text{Cu}_2(\text{RNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$, R = ^tBu, ^sBu, ⁱPr, Et, known as $[\text{Cu}_2(\text{Et}_3\text{N})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]$,²⁸ and the substrate $[\text{Cu}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$,²⁹ which may be an alternative to the previously studied carboxylates in the CVD and FEBID methods.⁸ The aim of introducing amine as a secondary ligand was to verify how it would modify the physicochemical properties of complexes. Therefore, we would like to test whether non-fluorinated complexes, where a bulky *tert*-Butyl substituent should increase the volatility of the compounds, can be an alternative to the fluorinated analogues.^{19–22}

In addition, single crystals of $[\text{Cu}_3(\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_6]_n$, $[\text{Cu}_3(\text{sBuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_6]_n$, $[\text{Cu}_3(\text{PrNH}_2)_2(\mu_3\text{-OH})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$, and $[\text{Cu}_{20}(\text{EtNH}_2)_6(\mu_3\text{-OH})_{24}(\text{OH})(\text{H}_2\text{O})_5(\text{NO}_3)(\mu\text{-O}_2\text{C}^t\text{Bu})_8][\text{Cu}(\text{CO}_2)_6\cdot 13\text{H}_2\text{O}]$ were obtained during the synthesis of the polymeric complexes $[\text{Cu}_2(\text{RNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ and their structures are also described in this paper.

2. Experimental

2.1 Materials

tert-Butylamine ^tBuNH₂ (98%), *sec*-butylamine ^sBuNH₂ (99%), isopropylamine ⁱPrNH₂ (≥ 99.5%), ethylamine EtNH₂ (2.0 mol dm^{−3} THF solution), and triethylamine Et₃N (99%) were purchased from Sigma Aldrich (Saint Louis, MO, USA), absolute ethanol (≥ 99.8%) – from Honeywell (Charlotte, USA). Copper(II) pivalate $[\text{Cu}_2(\mu_3\text{-O}_2\text{C}^t\text{Bu})_2(\mu_2\text{-O}_2\text{C}^t\text{Bu})_2]_n$ (for simplicity, we will use a formula $[\text{Cu}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]$) was prepared as earlier reported²⁹ using pivalic acid (99%) purchased from Sigma Aldrich (Saint Louis, MO, USA), sodium hydroxide (p.a) purchased from Avantor (Avantor Performance Materials, Poland S.A.), and copper(II) nitrate trihydrate (99%) purchased from Chempur (Poland). All reagents were used as received. The Si(111) substrates

were obtained from the Institute of Microelectronics and Photonics, Center for Electronic Materials Technology in Warsaw (Lukasiewicz Research Network, Poland). The Si substrates for the CVD experiments were prepared by immersion in the HF:HNO₃:H₂O (1:4:5) mixture, rinsing with acetone, ethanol, and water, and then dried in an argon stream. Each step was conducted for at least 10 min using ultrasonication.

2.2 Instrumentation

IR spectra were registered with a Vertex 70V spectrometer (Bruker Optik, Leipzig, Germany) using a reflective-single reflection diamond ATR unit (200–4000 cm⁻¹). Electron impact mass spectra (EI MS) were registered using an AutoSpec Premier (Waters) over the temperature range 313–573 K. C, H, and N content was found out using a Vario MACRO CHN ELEMENTAR Analysensysteme GmbH, Langenselbold, Germany. Thermal studies (TGA/DTA) were measured using an SDT 2960 TA analyser (New Castle, DE, USA) (dry N₂; heating rate 2.5 K min⁻¹), heating range up to 583–698 K, and sample mass (7–13 mg). Preliminary deposition experiments were carried out using the homemade horizontal hot-wall CVD reactor on silicon substrates Si(111) in argon within 60 min. The vaporisation temperature T_V was 473 K, whereas the deposition temperature T_D was 633 K. The morphology and composition of deposited materials were studied using scanning electron microscopy: Quanta 3D FEG (FEI, Hillsboro, OR, USA) and SEM-LEO 1430VP, Ltd, Cambridge, UK (operating voltage 8 and 20 kV), equipped with an energy dispersive X-ray spectrometer (EDS) Quantax 200 with detector Xflash 4010 (Bruker AXS microanalysis GmbH, Berlin, Germany), which was also used in preliminary electron sensitivity tests. Transmission electron microscopy (TEM G2 F20X-Twin 200 kV FEI, Hillsboro, OR, USA) was used to characterize the thermal analysis residue, test the sensitivity of compounds to the high-energy electrons (200 keV), and confirm the composition of the CVD deposited materials. A sample for TEM testing was prepared by dissolving a compound in anhydrous ethanol (99.8%), applying a drop on a carbon-coated nickel mesh with holes (Lacey type 400 mesh) and evaporating the solvent at room temperature. In the case of the CVD deposits, the sample surface was scratched using a TEM grid (Lacey type 400 mesh). Energy-dispersive X-ray spectroscopy (EDX, RTEM model SN9577, 134 eV, EDAX, FEI, Hillsboro, OR, USA) spectra and selected area (electron) diffraction patterns were recorded to identify the chemical elements. Atomic force microscopy (AFM) analysis of deposits was performed using a Veeco microscope (Veeco, Plainview, NY, USA).

2.3 Software

All graphical data were further processed with OriginPro 9.1. TA Universal Analysis (New Castle, DE, USA) was used to analyse thermograms. Grain sizes in the deposits were determined by OCI, University of Wisconsin, Madison, WI, USA.

2.4 Synthesis

All syntheses were carried out at normal conditions in the air.

[Cu₂(μ-O₂C^tBu)₄]_n (**0**), (0.5 mmol) was placed in a round-bottomed flask, and 10 cm³ of anhydrous ethanol was added,

followed by the dropwise addition of amine (1 mmol), RNH₂, where R = ^tBu (**1**), ^sBu (**2**), ⁱPr (**3**), Et (**4**) (THF solution) or Et₃N (**5**). The resulting dark blue or dark green solution was stirred for 1 h. Next, the solvent was evaporated in the air at room temperature. The reaction products [Cu₂(amine)₂(μ-O₂C^tBu)₄]_n were blue powders. Yields range between 60% and 70%.

In addition, the solvent was under slow evaporation (275–283 K) to give crystals with the following formulas [Cu₃(^tBuNH₂)₂(μ-O₂C^tBu)₆]_n (**1a**), [Cu₃(^sBuNH₂)₂(μ-O₂C^tBu)₆]_n (**2a**), and [Cu₃(ⁱPrNH₂)₂(μ₃-OH)₂(μ-O₂C^tBu)₄]_n (**3a**).

The crystal [Cu₂₀(EtNH₂)₆(μ₃-OH)₂₄(OH)(H₂O)₅(NO₃)(μ-O₂C^tBu)₈](^tBuCO₂)₆·13H₂O (**4a**) was obtained using the same procedure as for (**1a–3a**). It should be noted that a limited number of crystals (**4a**) have been obtained. It has been observed that the nitrate anion played a key role in the growth of this single crystal. Its presence is due to the use of copper(II) nitrate for the synthesis of [Cu₂(μ-O₂C^tBu)₄]_n (**0**). The phenomenon of the formation of this complex (**4a**) seemed interesting, and we decided to describe it, although, due to its core size, Cu₂₀, it is beyond the scope of this paper. Removal of the nitrate impurity from the substrate (**0**) resulted in the complex [Cu₂(EtNH₂)₂(μ-O₂C^tBu)₄]_n formation, whose structure is more promising for application in vapor deposition methods.

[Cu₂(^tBuNH₂)₂(μ-O₂C^tBu)₄]_n (**1**). Cu₂O₈N₂H₅₈C₂₈ (calc./found) C 49.61/49.62, N 4.13/4.26, H 8.62/8.64; IR (3327, 3256, 2957, 2924, 2901, 2868, 1626, 1578, 1551, 1477, 1458, 1406, 1364, 1254, 1223, 1119, 1022, 937, 895, 789, 683, 617, 555, 436, 380, 314 cm⁻¹). Yield: 70%.

[Cu₂(^sBuNH₂)₂(μ-O₂C^tBu)₄]_n (**2**). Cu₂O₈N₂H₅₈C₂₈ (calc./found) C 49.61/49.11, N 4.13/4.05, H 8.62/8.30; IR (3333, 3236, 3134, 2959, 2926, 2901, 2868, 1626, 1580, 1549, 1477, 1460, 1414, 1362, 1221, 1178, 1146, 1076, 1053, 1028, 1005, 941, 895, 820, 789, 665, 617, 552, 432, 390, 368, 314 cm⁻¹). Yield: 66%.

[Cu₂(ⁱPrNH₂)₂(μ-O₂C^tBu)₄]_n (**3**). Cu₂O₈N₂H₅₄C₂₆ (calc./found) C 48.05/47.99, N 4.31/4.29, H 8.38/8.33; IR (3331, 3248, 2957, 2930, 2903, 2868, 1626, 1578, 1545, 1479, 1462, 1416, 1364, 1225, 1186, 1159, 1069, 1043, 937, 897, 789, 660, 619, 555, 436, 390, 368, 312 cm⁻¹). Yield: 65%.

[Cu₂(EtNH₂)₂(μ-O₂C^tBu)₄]_n (**4**). Cu₂O₈N₂H₅₀C₂₄ (calc./found) C 46.36/47.70, N 4.51/4.30, H 8.11/8.28; IR (3287, 3142, 2959, 2930, 2872, 1603, 1547, 1520, 1481, 1416, 1358, 1223, 1173, 1055, 1022, 937, 893, 787, 704, 611, 550, 436, 386, 311, 241 cm⁻¹). Yield: 60%.

[Cu₂(Et₃N)₂(μ-O₂C^tBu)₄]_n (**5**). The performed X-ray diffraction measurements for the single-crystal confirmed that the cell parameters are identical with [Cu₂(Et₃N)₂(μ-O₂C^tBu)₄] reported by M. Mikuriya *et al.* (CCDC 1209041) and synthesised using more amine (copper(II) pivalate: amine molar ratio = 1:3).²⁸ IR (2972, 2957, 2932, 2899, 2847, 2793, 1618, 1481, 1456, 1418, 1375, 1360, 1225, 1196, 1159, 1115, 1092, 1072, 1047, 1007, 937, 897, 835, 818, 789, 737, 617, 530, 440, 388, 312, 270 cm⁻¹). Yield: 62%.

Spectral data for the complexes (**1a–3a**) which formed single crystals are given in the following sections.

[Cu₃(^tBuNH₂)₂(μ-O₂C^tBu)₆]_n (**1a**). Cu₃O₁₂N₂H₇₆C₃₈ IR (3327, 3252, 2955, 2924, 2903, 2868, 1626, 1578, 1547, 1477, 1458, 1406, 1364, 1256, 1219, 1111, 1022, 937, 895, 789, 683, 615, 554, 540, 436, 382, 368, 347, 312 cm⁻¹).

$[\text{Cu}_3(^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_6]_n$ (**2a**). $\text{Cu}_3\text{O}_{12}\text{N}_2\text{H}_{76}\text{C}_{38}$ IR (3335, 3238, 3123, 2955, 2928, 2905, 2866, 1624, 1580, 1547, 1477, 1460, 1408, 1360, 1219, 1182, 1148, 1074, 1051, 1028, 1003, 970, 935, 895, 818, 791, 667, 617, 596, 554, 532, 494, 430, 372, 316 cm^{-1}).

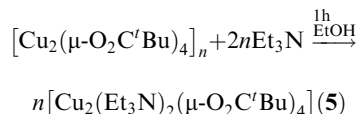
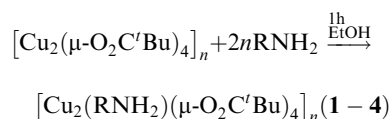
$[\text{Cu}_3(^i\text{PrNH}_2)_2(\mu_3\text{-OH})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (**3a**). $\text{Cu}_3\text{O}_{10}\text{N}_2\text{H}_{56}\text{C}_{26}$ IR (3564, 3331, 3306, 3202, 3123, 2957, 2928, 2868, 1624, 1576, 1549, 1481, 1414, 1360, 1221, 1165, 1092, 1061, 1043, 939, 893, 789, 673, 613, 548, 492, 436, 390, 366, 312 cm^{-1}).

2.5 X-ray crystal structure determinations

The single-crystal diffraction data for compounds (**1a–4a**) were collected at 100 K using an XtaLAB Synergy (Dualflex) diffractometer with HyPix detector, $\text{CuK}\alpha$ radiation $\lambda = 1.54178$ Å. For all studied compounds, the data reduction was performed in CrysAlis Pro³⁰ and the Gaussian absorption correction was applied. For (**2a**), twinning with three domains was detected, and the refinement process was performed using the HKLF 5 flag. The structures were solved using the direct methods and refined with a full-matrix least-squares procedure on F^2 (SHELX-97).³¹ Heavy atoms were refined with anisotropic displacement parameters, whereas hydrogen atoms were assigned to calculated positions with thermal displacement parameters fixed to a value of 20% or 50% higher than those of the corresponding carbon atoms. Hydrogen atoms attached to nitrogen and oxygen atoms were located from difference Fourier maps. In the final stage of the refinement, TWIN command was applied for (**1a**). In the reported structures, several restraints (DFIX, DANG, DELU, ISOR) were applied mainly for *tert*-butyl groups of the pivalate anion, aliphatic chains of amines, and water molecules. For some amine and pivalate ligands, a positional and rotational disorder was also observed. In the case of (**3a**), the instability of this compound should be noted. It results in slightly elevated refinement parameters. However, these crystals were measured several times, and the best data set was obtained for the fresh sample. During the data collection, the radiation damage was observed. Hence, the complete data set could not be used for the refinement, and a reasonable limit had to be selected to assure a relatively complete data set with rational acceptable quality. All figures were prepared using the DIAMOND³² and ORTEP-3³³ software. The results of the data collection and refinement have been summarized in ESI† (Table S1), such as selected bond lengths and angles (Table S2–S5, ESI†). CCDC 2261736, 2261751, 2261785, and 2261768 contain the supplementary crystallographic data for the compounds (**1a**), (**2a**), (**3a**), and (**4a**), respectively.†

3. Results and discussion

In the ethanol solution, amine molecules are coordinated to copper(II), and complexes of formula $[\text{Cu}_2(\text{RNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$, where $\text{R} = ^t\text{Bu}$, ^sBu , ^iPr , Et, and $[\text{Cu}_2(\text{Et}_3\text{N})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$, were formed:



The obtained complexes (**1–5**) were blue, fine-crystalline powders, stable in air for months. Single crystal X-ray experiments confirmed the identity of the obtained compound (**5**) with that described in the literature.²⁸

In addition, four single-crystals with the following formulas $[\text{Cu}_3(^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_6]_n$ (**1a**), $[\text{Cu}_3(^s\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_6]_n$ (**2a**), $[\text{Cu}_3(^i\text{PrNH}_2)_2(\mu_3\text{-OH})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (**3a**), and $[\text{Cu}_{20}(\text{EtNH}_2)_6(\mu_3\text{-OH})_{24}(\text{OH})(\text{H}_2\text{O})_5(\text{NO}_3)(\mu\text{-O}_2\text{C}^t\text{Bu})_8](^t\text{BuCO}_2)_6 \cdot 13\text{H}_2\text{O}$ (**4a**) were isolated through the crystallization process. During the crystal growth, a decrease in the amine-to-metal ratio ($\text{RNH}_2:\text{Cu}$) from 2:2 (**1–4**) to 2:3 or less (**1a–4a**) was observed. The amounts of compounds (**1a–4a**) were relatively small; therefore, only the main products (**1–5**) were studied for their potential use in CVD and FEBID methods.

3.1 Crystallography

Structure of $[\text{Cu}_3(^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_6]_n$ (1a**).** Compound (**1a**) crystallises in the monoclinic space group $P2_1/n$ with Cu2 atoms located on an inversion centre (Fig. 1). The structure is composed of chains running along *a* axis built of alternately arranged paddlewheel and mononuclear units connected by a *syn-anti* O21 carboxylate bridge (Fig. 2). Hence, all three carboxylate anions present in the asymmetric unit act as bridges, but those involved in the paddlewheel (O1 and O11 anions) are found in the *syn-syn* coordination mode, and their *tert*-butyl groups show rotational disorder (0.55/0.45). The distance between two copper atoms connected by the *syn-syn* bridge Cu1–Cu1 $[1 - x, 1 - y, 1 - z]$ is much shorter (2.602 Å) than for

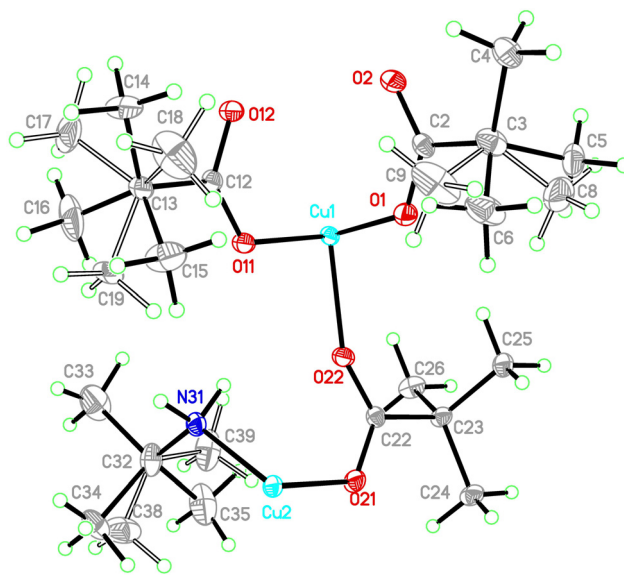


Fig. 1 The asymmetric unit of $[\text{Cu}_3(^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_6]_n$ (**1a**) with a numbering scheme and thermal displacement ellipsoids at 30% probability.

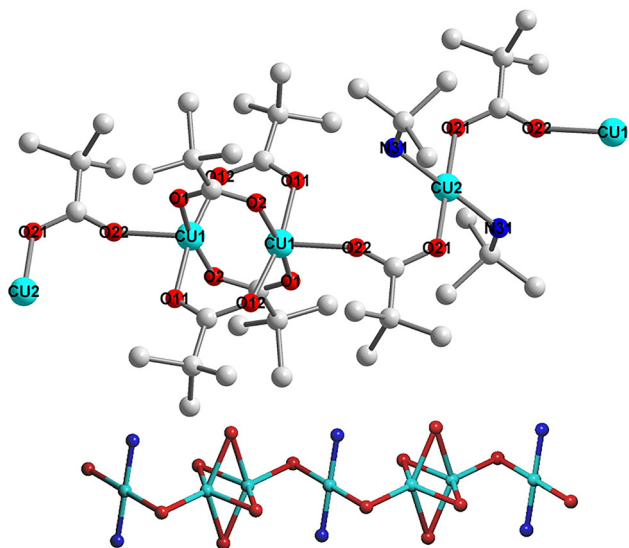


Fig. 2 Chain topology in $[\text{Cu}_3(\text{tBuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_6]_n$ (**1a**) shows alternately arranged paddlewheel and mononuclear motifs. For clarity of the figure, all hydrogen atoms as well as minor populations of the *tert*-butyl groups in O1 and O11 bonded carboxylate anions are omitted. Chain topology given in the presentation based on the analysis performed in TOPOS (bottom) (copper in cyan, carboxylate in red, and amine in blue).³⁷

bonded by the *syn-anti* bridge (Cu1–Cu2: 4.701 Å). The coordination sphere adopts a square pyramid geometry for the Cu1 atom ($\tau_5 = 0.005$)³⁴ and square planar for Cu2 ($\tau'_4 = 0.000$).³⁵ Cu1 is coordinated to four oxygen atoms from carboxylate anions forming the basal plane of the square pyramid (Cu1–O: 1.947(2)–1.977(2) Å). In the apical position, the O22 atom (Cu1–O22: 2.136(2) Å) is found from the next carboxylate anion. In the monomeric unit, the Cu2 square planar coordination sphere is composed of two N31 nitrogen atoms from amines (1.994(3) Å) and two O21 atoms from the carboxylate anions (1.964(2) Å) in *trans* positions. For the amine, the *tert*-butyl group also revealed rotational disorder (0.50/0.45). The O1 and O11 *syn-syn* bridges in the paddlewheel are symmetrical, whereas the O21 carboxylate anion forms an asymmetric bridge due to the Jahn–Teller effect, resulting in an elongation of the Cu1–O22 bond.

Between those chains seem to be weak van der Waals interactions. The crystal network is composed of rather loosely arranged infinite chains running along *a* axis (Fig. 3). Nevertheless, the analysis performed in PLATON³⁶ did not show any voids. Inside the chain, there are N31–H31...O22 and C25–H25...O12 $[1 - x, 1 - y, 1 - z]$ hydrogen bonds.

Structure of $[\text{Cu}_3(\text{tBuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_6]_n$ (2a**).** Compound (**2a**) is similar to (**1a**) in the space group $P2_1/n$ (Fig. 4); the content, coordination modes, and topology of the chain are identical (Fig. S1, ESI†). Same coordination sphere geometry is comparable in both complexes. The cell parameters are close, but slightly denser packing is observed for (**2a**). The packing patterns are analogous. However, the important distinction relies on the direction of chain propagation – along the $[100]$ direction in (**1a**) and $[010]$ direction in (**2a**). In the latter case, it coincides with the direction of the twofold axis.

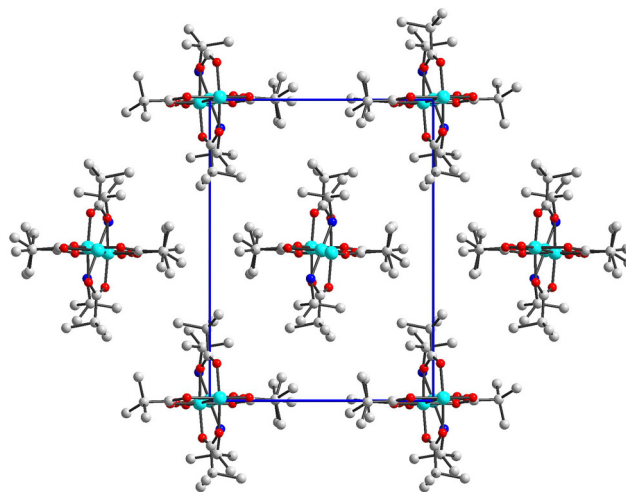


Fig. 3 Packing diagram of $[\text{Cu}_3(\text{tBuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_6]_n$ (**1a**) along *a* axis. Hydrogen atoms are omitted for the clarity of the figure.

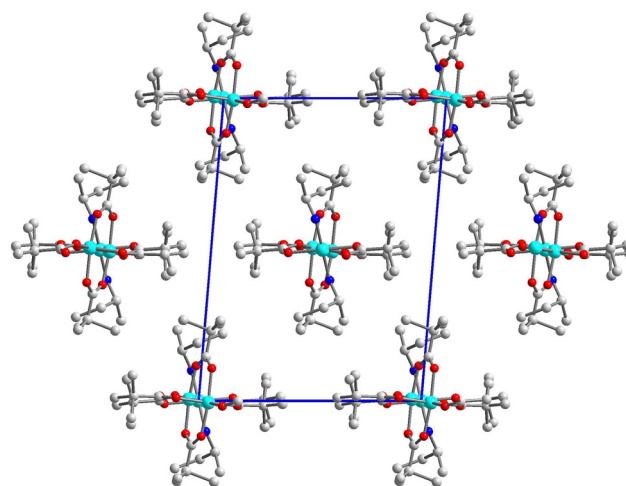


Fig. 4 Packing diagram of $[\text{Cu}_3(\text{tBuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_6]_n$ (**2a**) along *b* axis. Hydrogen atoms are omitted for the clarity of the figure.

Structure of $[\text{Cu}_3(\text{tBuNH}_2)_2(\mu_3\text{-OH})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (3a**).** This compound (**3a**) crystallises in the triclinic $P\bar{1}$ space group with the Cu1 atom located in the inversion centre (Fig. 5). Some comments are needed for the crystal quality, which is much lower than other structures presented in this paper. This compound is unstable, and diffraction disappears in time due to radiation damage. Hence, the refinement required to limit the number of frames included in the data processing and, in consequence, also the completeness. It also resulted in higher refinement parameters. Nevertheless, the main features can be established and discussed. Infinite chains are formed similarly to (**1a**) and (**2a**). However, the topology of this compound is different (Fig. 6). The chain consists of the trimetallic repeating motif around the central hydroxyl group, creating μ_3 bridges. Cu1 and Cu2 atoms are also connected by bridging pivalates, whereas two Cu2 atoms are coupled by two $\mu_3\text{-OH}$ bridges. It results in a significant shortening of this Cu–Cu

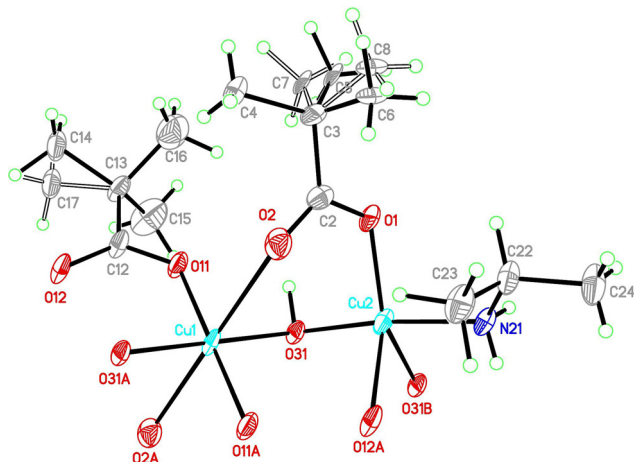


Fig. 5 The structure of $[\text{Cu}_3(\text{PrNH}_2)_2(\mu_3\text{-OH})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (**3a**) with numbering scheme and thermal displacement ellipsoids at 30% probability.

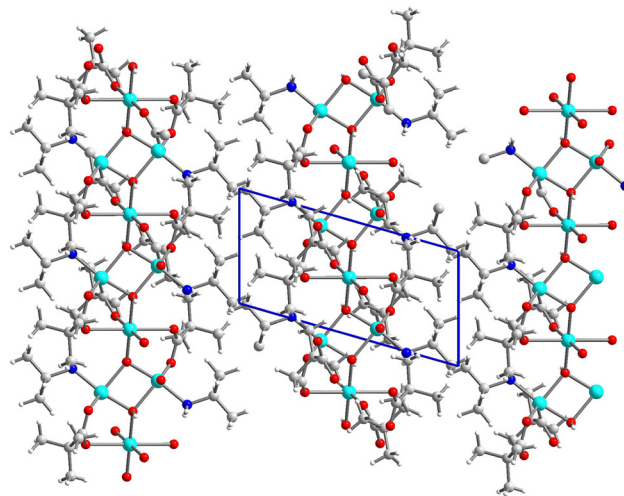


Fig. 7 Packing diagram of $[\text{Cu}_3(\text{PrNH}_2)_2(\mu_3\text{-OH})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (**3a**) shows parallel oriented chains running along *a* axis.

distance (3.079 Å for Cu2–Cu2 vs. 3.239 and 3.713 Å for Cu1–Cu2). Cu1 and Cu2 differ in the coordination sphere geometry. Cu1 shows a strongly elongated octahedral geometry with axial positions occupied by O2 atoms. The equatorial plane is formed by two O11 atoms from the carboxylate and two O31 from hydroxyl groups. Cu2 was found in a strongly distorted pentacoordinate environment ($\tau_5 = 0.522$). The analysis performed in SHAPE³⁸ indicates that the trigonal bipyramid ($S_{\text{TBPY-5}} = 2.750$) better matches than the square pyramid ($S_{\text{SPY-5}} = 4.977$). This coordination sphere consists of O31 hydroxyl groups, two oxygen atoms from carboxylates, and nitrogen of terminally bonded isopropylamine. Therefore, two Cu2 polyhedra share the common edge and the common vertex with Cu1 (Fig. 7).

The packing of (**3a**) shows parallel arranged chains running along *a* axis. They interact *via* weak van der Waals interactions, but the chains are densely packed, and no voids are observed. These weak interactions are related to hydrophobic aliphatic chains exposed to the outer part of the chain. The N–H...O and O31–H31...O hydrogen bonds were found only inside the chain.

Structure of $[\text{Cu}_{20}(\text{EtNH}_2)_6(\mu_3\text{-OH})_{24}(\text{OH})(\text{H}_2\text{O})_5(\text{NO}_3)(\mu\text{-O}_2\text{-C}^t\text{Bu})_8][(\text{C}^t\text{BuCO}_2)_6 \cdot 13\text{H}_2\text{O}]$ (4a**).** The icosanuclear compound (**4a**)

crystallises in the orthorhombic *Pbca* space group, with half of the structure given by the above formula present in the asymmetric unit. Twenty copper atoms form a distorted cube with edges ranging from 5.599 to 5.947 Å, and adjacent Cu atoms are separated by 2.9–3.1 Å (Fig. 8). Eight copper(II) ions are located in the vertices of the cube (Cu1, Cu3, Cu5, and Cu7), whereas twelve remaining ions (Cu2, Cu4, Cu6, Cu8, Cu9, and Cu10) are found approximately in centres of the cube edges. Metal centres are connected *via* 24 hydroxyl groups located by four on every cube face, forming μ_3 bridges and eight *syn-syn* bridging pivalates. They form a cage with a small aperture (*ca.* 3.9–4.2 Å) and space big enough to host a rotationally disordered nitrate anion, which is also involved in the bridging coordination of all copper(II) ions located on the cube edges except Cu8. Detection of nitrate anions requires comments. In this system, for one nitrate, there are twenty copper atoms. It comes from a slight impurity in the substrate ($[\text{Cu}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (**0**)) and was only visible in this complex. The coordination spheres of Cu1, Cu3, and Cu5 are completed by N-bonded ethylamine and $\text{H}_2\text{O}/\text{OH}^-$ ligands. It should be noted that to balance the core charge, one water molecule per cube must be deprotonated, forming

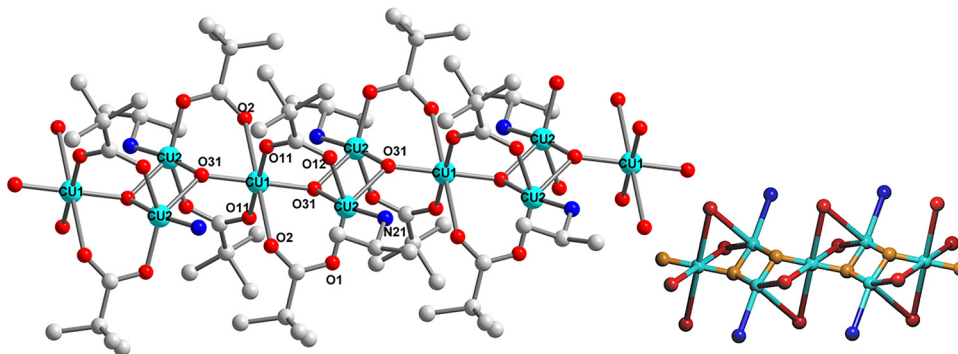


Fig. 6 Chain topology of the $[\text{Cu}_3(\text{PrNH}_2)_2(\mu_3\text{-OH})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (**3a**) with metal atoms and coordinated atoms numbered (left) and presentation based on the analysis performed in TOPOS³⁷ (right) (copper in cyan, hydroxyl group in orange, carboxylate in red, and amine in blue).

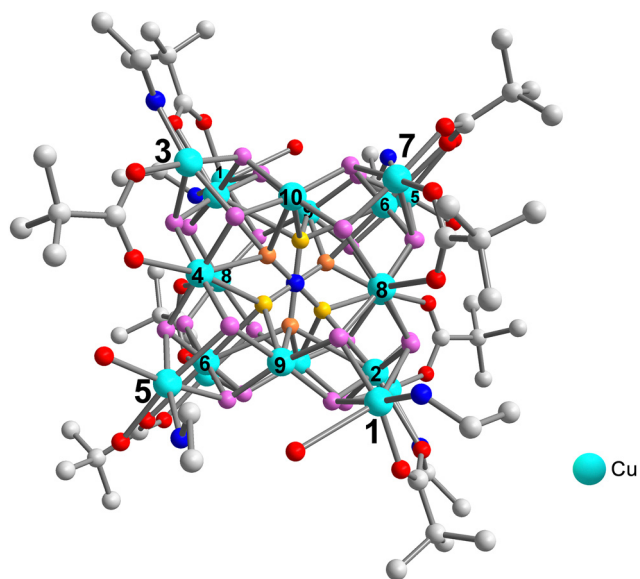


Fig. 8 The perspective view of $[\text{Cu}_{20}(\text{EtNH}_2)_6(\mu_3\text{-OH})_{24}(\text{OH})(\text{H}_2\text{O})_5(\text{NO}_3)(\mu\text{-O}_2\text{C}^t\text{Bu})_8](^t\text{BuCO}_2)_6 \cdot 13\text{H}_2\text{O}$ (**4a**) with a selective numbering scheme. Numbers refer to corresponding copper atoms, e.g., 3 = Cu3.

a hydroxyl group. We are not able to distinguish if O85 or O86 (both coordinated to the Cu5 atom) consists of the hydroxyl group. The cavities between cubes are filled with crystallization water molecules and uncoordinated pivalates, resulting in dense packing. The latter species are involved in hydrogen bonding to four hydroxyl groups placed on every cube face. Hence, they lock the cage entry (Fig. 9).

Such a very complicated cluster structure results in many coordination types. All copper(II) ions are distinguished based on the type of surrounding ligands, their amount, and the type of coordination mode. There are penta- (Cu3 ($\tau_5 = 0.127$), Cu7

($\tau_5 = 0.127$)), Cu8 ($\tau_5 = 0.020$), Cu9 ($\tau_5 = 0.115$), and Cu10 ($\tau_5 = 0.063$);³⁴ and hexacoordinate (Cu1, Cu2, Cu4, Cu5, and Cu6) copper(II) ions. Bridging hydroxyl group coordination is a common feature for all Cu(II) ions. Three μ_3 -bridging OH in mutual *cis* position groups are coordinated to every Cu(II) located in the cube vertices, whereas copper(II) ions at edge centres coordinate four hydroxyl groups. For Cu2, Cu4, and Cu6, the elongated octahedra are completed by one oxygen atom coming from pivalate and one from nitrate anions.

Packing along *a* axis shows some small voids. However, the analysis performed in PLATON³⁶ shows that cavities account for 157.5 Å³ (1.1% of the volume cell) split over eight positions (*ca.* 20 Å³ per void). This volume is too small even for water molecules, and hence, these spaces are inaccessible for any solvent molecules. The crystal network is maintained mainly by a robust framework of hydrogen bonds. There are a large number of crystallization water molecules and uncoordinated carboxylic anions surrounding the icosanuclear cluster which isolate those clusters and they cannot interact directly – there is no evidence of hydrogen bonding between clusters. However, these clusters tightly bind water molecules and anions, forming a solvation sphere (Fig. S3, ESI†). Moreover, there are also strong interactions between components of this solvation sphere. Hence, interactions between clusters are possible for two patterns: cluster...solvation sphere...cluster or cluster...solvation sphere...solvation sphere...cluster.

3.2 Infrared spectra analysis

In the infrared spectrum of the substrate $[\text{Cu}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (**0**), characteristic two bands for asymmetric stretching vibrations of the carboxylate group ($\nu_{\text{as}}\text{COO}$) were found: 1578 and 1530 cm⁻¹ (Table 1 and Fig. S20, ESI†). This indicates the existence of two coordination modes of carboxylate, which was previously confirmed by the X-ray diffraction measurements for

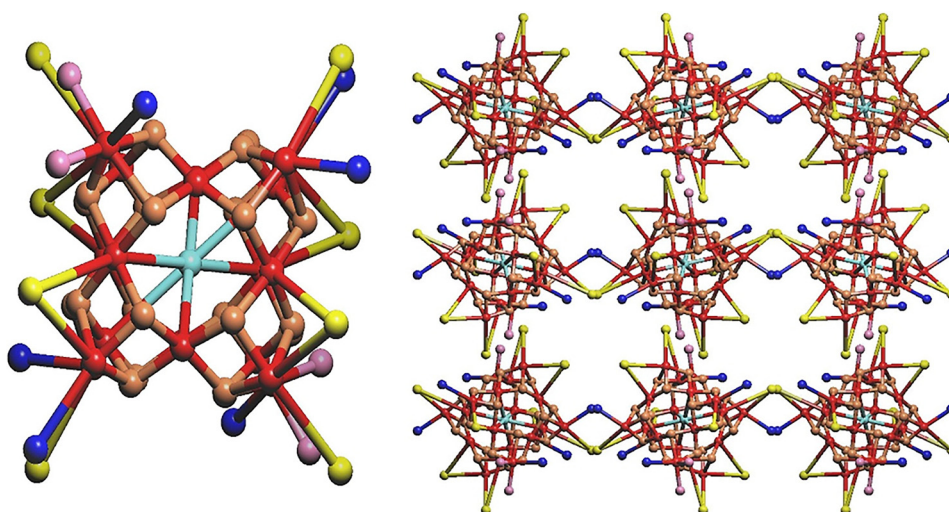


Fig. 9 The topology of $[\text{Cu}_{20}(\text{EtNH}_2)_6(\mu_3\text{-OH})_{24}(\text{OH})(\text{H}_2\text{O})_5(\text{NO}_3)(\mu\text{-O}_2\text{C}^t\text{Bu})_8](^t\text{BuCO}_2)_6 \cdot 13\text{H}_2\text{O}$ (**4a**) and packing of those cubes. Uncoordinated pivalates and crystallization water molecules are omitted for the clarity of the picture. The analysis and the figure were prepared in TOPOS³⁷ (copper atoms are given in red, bridging hydroxyl groups in orange, ethylamine in blue, nitrate in light blue, terminal water/hydroxyl group in violet, and pivalate in yellow).

Table 1 Selected IR absorption bands (cm^{-1}) of the studied compounds (0–5)

Compound	ν'_{asCOO}					$\Delta\nu_{\text{COO}}$
	ν_{asNH_2}	ν_{sNH_2}	ν_{asCOO}	$+\delta\text{NH}_2$	ν_{sCOO}	
$[\text{Cu}_2(\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (1)	3327	3256	1626	1551	1406	220 145
$[\text{Cu}_2(\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^i\text{Bu})_4]_n$ (2)	3333	3236	1626	1549	1414	212 135
$[\text{Cu}_2(\text{PrNH}_2)_2(\mu\text{-O}_2\text{C}^i\text{Bu})_4]_n$ (3)	3331	3248	1626	1545	1416	210 129
$[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{C}^i\text{Bu})_4]_n$ (4)	3287	3142	1603	1547	1416	187 131
$[\text{Cu}_2(\text{Et}_3\text{N})_2(\mu\text{-O}_2\text{C}^i\text{Bu})_4]$ (5)	—	—	1618	—	1418	200
$[\text{Cu}_2(\mu\text{-O}_2\text{C}^i\text{Bu})_4]_n$ (0)	—	—	1578 1530	—	1412	166 118
$^t\text{BuNH}_2$	3347	3283		1597 ^a		
$^i\text{BuNH}_2$	3365	3287		1600 ^a		
$^i\text{PrNH}_2$	3357	3280		1600 ^a		
EtNH_2	3362	3298		1599 ^a		

^a δNH_2 only.

the single-crystal and described in the literature.³⁹ For the complexes (1–4) (Table 1 and Fig. S4–S8, ESI[†]), two bands, which can be assigned to ν_{asCOO} vibrations, were also observed. The first is over the range 1626–1603 cm^{-1} , and the second is at 1551–1545 cm^{-1} (overlapping with δNH_2). The signals for symmetric stretching vibration (ν_{sCOO}) were registered over the range of 1416–1406 cm^{-1} . Two bands assigned to ν_{asCOO} suggest two coordination modes of the carboxylate for the compounds (1–4) similar to the copper(II) pivalate (0) (3.1 Crystallography). Note that in the infrared spectrum of the complex $[\text{Cu}_2(\text{Et}_3\text{N})_2(\mu\text{-O}_2\text{C}^i\text{Bu})_4]$ (5) (Table 1 and Fig. S9, ESI[†]), one band for asymmetric stretching vibrations was observed: 1618 cm^{-1} . The same value was reported in the literature for the single crystal, in which the *syn-syn* carboxylate coordination mode was confirmed.²⁸

The characteristic bands for asymmetric and symmetric vibration of the amine molecule for the complexes (1–4) were found as follows: 3333–3287 cm^{-1} (ν_{asNH_2}) and 3256–3142 cm^{-1} (ν_{sNH_2}), respectively. The coordination shifts of the signals relative to the free ligand were in the range of 75–20 cm^{-1} and 156–27 cm^{-1} .^{40–43}

The IR spectra of single crystals (1a–3a) (Fig. S4–S7, ESI[†]) also exhibit two characteristics ν_{asCOO} (*syn-syn* and *syn-anti* coordination modes of pivalates) and one ν_{sCOO} band of the carboxylate ligand. The values for these asymmetric and symmetric stretching vibrations are similar to results for (1–3), which suggest the same carboxylate coordination modes. The typical bands of the amine molecule ν_{NH_2} were identified over the range 3335–3123 cm^{-1} . However, in the far IR region for single crystals (1a–2a), the weak additional bands at 540 cm^{-1} , 368 cm^{-1} , and 347 cm^{-1} (1a) and at 532 cm^{-1} and 494 cm^{-1} (2a) were detected. For the complex (2a), no band at 390 cm^{-1}

observed for (2) was registered. Moreover, compound (3a) spectra show the signal at 3564 cm^{-1} characteristics for O–H stretching vibration of the hydroxyl group (Fig. S7, ESI[†]).

3.3 Thermal analysis

Thermal analysis was performed to study the behaviour of the complexes during heating under a nitrogen atmosphere and to determine the temperature of the final decomposition. For the studied complexes, the three (1–4) or two (5) decomposition stages were observed (Table 2 and Fig. 10, Fig. S10–S14, ESI[†]). The temperature of the decomposition process onset changed between 313 K and 322 K (T_i), while the temperature of the final product formation was from 540 K to 550 K (T_f). The aforementioned ranges of T_i and T_f are narrow, in contrast to the previously described complexes with perfluorinated carboxylates: $[\text{Cu}_2(\text{BuNH}_2)_2(\mu\text{-O}_2\text{CR}_f)_4]$, $[\text{Cu}_2(\text{PrNH}_2)_2(\mu\text{-O}_2\text{CR}_f)_4]$, and $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CR}_f)_4]$ ($\text{R}_f = \text{CF}_3, \text{C}_2\text{F}_5, \text{C}_3\text{F}_7, \text{C}_4\text{F}_9$).^{19,20}

TEM diffraction patterns and EDX spectra for the residues revealed that the decomposition product is metallic copper for the complexes (1–4). In the case of the compound (5), with a tertiary amine, a mixture of copper(I) and (II) oxides was identified (Fig. S15, ESI[†]). The lower residue mass compared to the theoretical value of copper for the compounds (1–5) (Table 2) indicates that these complexes are the source of metal carriers in the gas phase at atmospheric pressure. This makes them promise to use in CVD and FEBID applications.

Table 2 Thermal analysis results

Complex	Temperature [K]			Residue [%]		
	T_i	T_m	T_f	Found	Calc.	Residue
$[\text{Cu}_2(\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^i\text{Bu})_4]_n$ (1)	314	352	362	3.10	18.75	Cu
	362	424	436			
	436	534	547			
$[\text{Cu}_2(\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^i\text{Bu})_4]_n$ (2)	320	360	376	3.94	18.75	Cu
	376	431	449			
	449	530	550			
$[\text{Cu}_2(\text{PrNH}_2)_2(\mu\text{-O}_2\text{C}^i\text{Bu})_4]_n$ (3)	313	354	365	4.99	19.56	Cu
	356	413	431			
	431	530	540			
$[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{C}^i\text{Bu})_4]_n$ (4)	314	357	368	5.92	20.44	Cu
	368	420	432			
	432	533	546			
$[\text{Cu}_2(\text{Et}_3\text{N})_2(\mu\text{-O}_2\text{C}^i\text{Bu})_4]$ (5)	322	367	387	6.81	20.23	Cu_2O
	387	531	541			+ CuO

 T_i , initial temperature; T_m , maximum temperature; T_f , final temperature.

3.4 Sublimation experiments

In this study, we would like to verify the volatility of new copper(II) complexes (1–5) in relation to the previously known $[\text{Cu}_2(\mu\text{-O}_2\text{C}^i\text{Bu})_4]_n$ (0) (Fig. S20, ESI[†]). Moreover, these experiments allowed obtaining layers of compounds on the silicon substrate, which were then analysed in terms of interaction with a high-energy electron beam (*vide infra* – 3.6 SEM/EDX and TEM observations). The sublimation experiments were performed under reduced pressure (10^{-2} mbar) in a glass sublimator with a special holder for a silicon wafer.

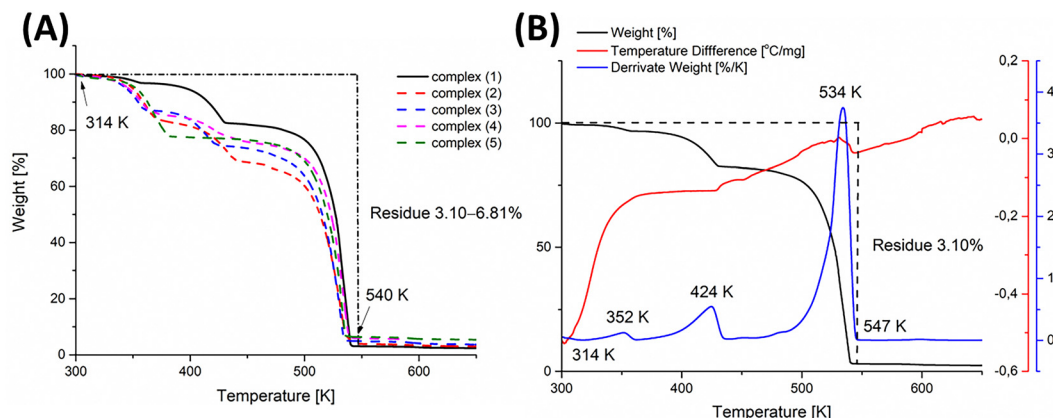


Fig. 10 (A) Thermogravimetric curves (TG) for the complexes: (1) $[\text{Cu}_2(\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (black line), (2) $[\text{Cu}_2(\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (red dashed line), (3) $[\text{Cu}_2(\text{PrNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (blue dashed line), (4) $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (pink dashed line), (5) $[\text{Cu}_2(\text{Et}_3\text{N})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (green dashed line); (B) thermogravimetric analysis (TGA) (black line), derivative thermogravimetry (DTG) (blue line), differential thermal analysis (DTA) (red line) for the complex (1).

The spectra for the complexes (1–4) in the solid phase and their thin layers deposited on silicon substrates are very similar and exhibit bands $\nu_{\text{as}}\text{COO}$, $\nu'_{\text{as}}\text{COO} + \delta\text{NH}_2$, and $\nu_{\text{s}}\text{COO}$, which are characteristics of coordinated amine and carboxylate ligands (Fig. 11 and Fig. S16–S18, ESI[†]). Thinner coverages were obtained for the complexes (2) and (3), resulting in visible noise that made it difficult to precisely assign the $\nu_{\text{as}}\text{NH}_2$ and $\nu_{\text{s}}\text{NH}_2$ bands. This fact does not affect the final statement that the complexes (1–4) sublime at the temperatures listed below (Table 3). Only for the layer formed at 393 K using the compound (5), the lack of characteristic bands for the complex was observed (Fig. S19, ESI[†]). The spectrum indicates that the main product of the process is $[\text{Cu}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_2]_n$ (0) (Fig. S19 and S20, ESI[†]). These data suggest that new complexes (1–4) can be promising precursors for application in vapour deposition methods, in contrast to the complex with tertiary amine (5). These pivalate complexes with primary amines (1–4) sublime at

Table 3 Sublimation temperatures for the complexes (1–5) ($p = 10^{-2}$ mbar)

Compound	Sublimation temperature [K]
$[\text{Cu}_2(\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (1)	373
$[\text{Cu}_2(\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (2)	363
$[\text{Cu}_2(\text{PrNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (3)	363
$[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (4)	383
$[\text{Cu}_2(\text{Et}_3\text{N})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (5)	393*
$[\text{Cu}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_2]_n$ (0)	418

10^{-2} mbar, at temperatures lower by 35–55 K relative to the copper(II) pivalate (Table 3), which indicates that the introduction of the primary amine to the coordination sphere as the secondary ligand, improves volatility. It should be noted that this temperature may be suitable for FEBID experiments where, typically, $T_{\text{max}} = \sim 353\text{--}363$ K ($p = 10^{-3}\text{--}10^{-4}$ mbar) is required.⁵

Moreover, the described collision experiments for the complexes with perfluorinated carboxylates demonstrate that the compounds $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]_n$, $[\text{Cu}_2(\text{BuNH}_2)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]_n$, and $[\text{Cu}_2(\text{BuNH}_2)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]_n$ were detected in the gas phase at 353 or 373 K, whereas the $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]_n$ molecules were observed at 423 K. This fact suggests that introducing a secondary ligand in the form of a small primary amine improves the volatility of the copper(II) complexes.²²

3.5 Mass spectra analysis

The mass spectra (EI MS) of the selected complex $[\text{Cu}_2(\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (1) were registered between 313–573 K (Fig. 12 and Table S6, ESI[†]). Based on these results, we could verify that the studied complex is capable of generating volatile metal carriers, check its sensitivity to the low-energy electrons (70 eV), and study how the composition of the gas phase changes during heating under reduced pressure (*ca.* 10^{-6} mbar). The compound (1) was chosen for this test since it showed the highest sensitivity to high-energy electrons (*vide infra* – 3.6 SEM/EDX and TEM observations).

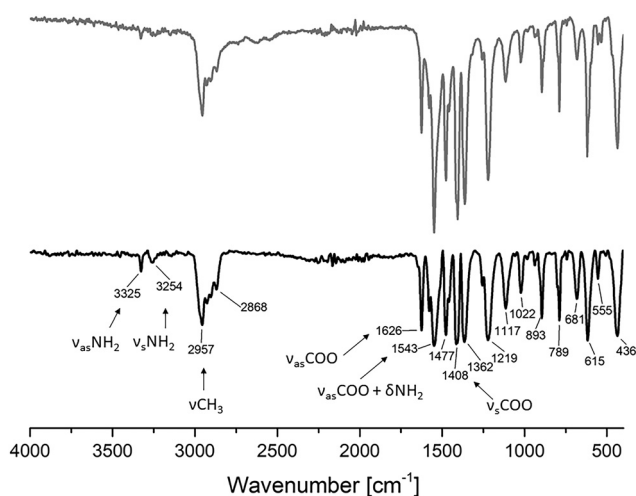


Fig. 11 Infrared spectra for the compound $[\text{Cu}_2(\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (1) before (gray) and after sublimation (black) at 373 K ($p = 10^{-2}$ mbar).

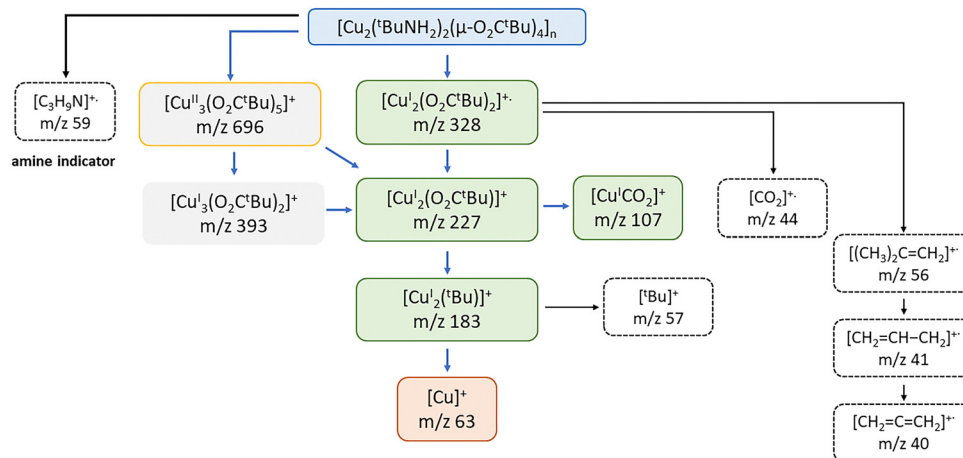


Fig. 12 Fragmentation scheme for the most important fragments of $[\text{Cu}_2(\text{tBuNH}_2)_2(\mu\text{-O}_2\text{CtBu})_4]_n$ (**1**) (Cu(II) – yellow frame, ions occurring in small quantities – grey assignment, non-metallated fragments – black, dashed frame).

For the complex $[\text{Cu}_2(\text{tBuNH}_2)_2(\mu\text{-O}_2\text{CtBu})_4]_n$ (**1**), no molecular or pseudomolecular ions were detected in the spectra (Fig. 12 and Table S6, ESI†). However, the above-mentioned studies (3.4 Sublimation experiments) indicated that compound (**1**) can be transferred to the gas phase at 373 K, even under higher pressure (10^{-2} mbar). Therefore, it suggests the high sensitivity of the complex (**1**) to the low-energy electrons, which caused its effective decomposition.

At the beginning (339 K), simultaneously fragments typical for amine and metallated ions were observed, e.g.: $[\text{C}_3\text{H}_9\text{N}]^+$, $[\text{C}_3\text{H}_8\text{N}]^+$, $[\text{C}_2\text{H}_4\text{N}]^+$, $[\text{Cu}_2(\text{O}_2\text{CtBu})]^+$, and $[\text{Cu}_2(\text{O}_2\text{CtBu})_2]^+$ (Fig. 12 and Table S6, ESI†). The mentioned fragments containing copper were detected up to 432 K and achieved the highest relative intensity: 50% RI and 33% RI at 381 K, respectively. Notably, the intensity of $[\text{Cu}_2(\text{O}_2\text{CtBu})]^+$ was the most significant among the observed metallated fragments (Table S6, ESI†). This suggests that the Cu–N bond is more sensitive to the electrons than Cu–O. Moreover, identified ions containing Cu(I) (Fig. 12 and Table S6, ESI†) indicate Cu(II) reduction during the fragmentation. The formation of the ion $[\text{Cu}]^+$ ($m/z = 63$) between 368 K and 383 K suggests that copper is the final product of low-energy electron induced fragmentation ($\text{RI}_{\text{max}} = 14\%$, 368 K and 372 K).

Above 442 K, the metallated ions were not registered, whereas the intensities for non-metallated fragments significantly increased (Table S6, ESI†), which indicates the beginning of the thermal decomposition process. The formation of products, such as $[\text{C}_4\text{H}_{10}]^+$, $[(\text{CH}_3)_2\text{C}=\text{CH}_2]^+$, and $[\text{CO}_2]^+$, is related to a reaction pathway that can transform carboxylate unit to the volatile carbon dioxide and isobutene molecules.

The studied complex (**1**) exhibits the low temperature of the metallated fragments generation as well as is highly sensitive towards low-energy electron interactions. Therefore, it seemed to be a promising candidate for FEBID tests.

3.6 SEM/EDX and TEM observations

The sensitivity to the high-energy electrons of thin layers of complexes deposited on silicon substrate was studied using

SEM/EDX at 8 and 20 keV energy. For these studies, we chose the complexes (**1–4**) and compound (**0**) as references to determine the effect of amines upon irradiation. EDX spectra were taken during the SEM analysis, each of them recorded for 30 s. The scanning area was reduced, which caused an increase in the dose of electrons. Moreover, TEM (200 keV) measurements were performed for the compounds (**0**) and (**1**).

The SEM images for the sublimate layers indicated that a homogeneous layer covering the entire substrate was obtained for the complexes (**3**) and (**4**) (Fig. S23–S26, ESI†). We note that in the case of other samples, the material is not homogeneously distributed on the surfaces (Fig. 13 and Fig. S21, S22, S27–S30, ESI†). As previously described in Section 3.4, for sample (**5**), the main product of the sublimation was the $[\text{Cu}_2(\mu\text{-O}_2\text{CtBu})_2]_n$. This data and SEM images reveal that the presence of tertiary amine Et_3N caused a decrease in the temperature of volatile metal carrier generation, but a lower homogeneity of the sample is also observed compared to the compound (**0**), for which a dense and homogenous layer was obtained.

The microscopic observations and EDX spectra showed that the compound (**1**) is the most sensitive to the high-energy electron beam (Fig. 13). Among the other compounds, the effect of electron irradiation on the sublimated layers was visible for the complexes (**0**) (Fig. S29 and S30, ESI†), (**4**) (Fig. S25 and S26, ESI†), and (**5**) (Fig. S27 and S28, ESI†). Moreover, as a result of the interaction between electrons and samples (**0**), (**1**), and (**5**), morphological changes in SEM images were also observed.

During TEM imaging, changes in the structure of the samples (**1**) and (**0**) were detected. The microscopic observations confirmed that tested compounds are sensitive to the high-energy electron beam (200 keV). After a few seconds of irradiation, we observed circular structures surrounded by amorphous carbon in TEM images (Fig. 14(A) and (B)). In both samples, the diffraction patterns confirmed the crystallinity of the formed material and the formation of copper nanoparticles (Fig. 14(C) and (D)). The EDX spectra of the TEM obtained

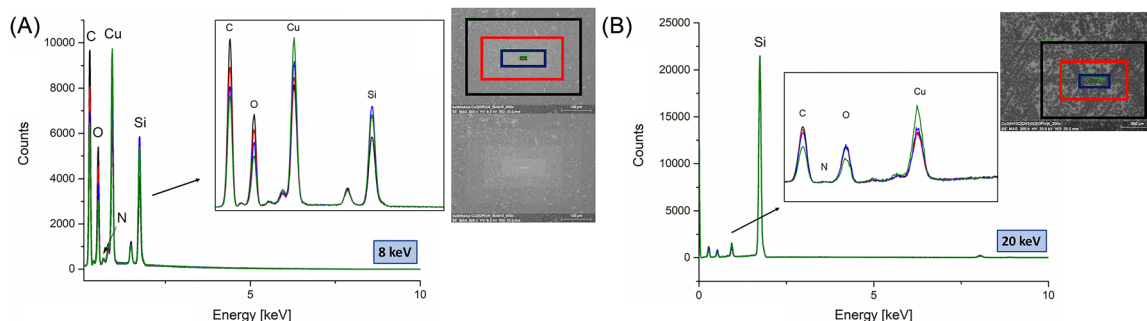


Fig. 13 Examined scan areas' EDX spectra for the complex $[\text{Cu}_2(\text{tBuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (**1**) layer on a silicon wafer: (A) –8 keV, (B) –20 keV.

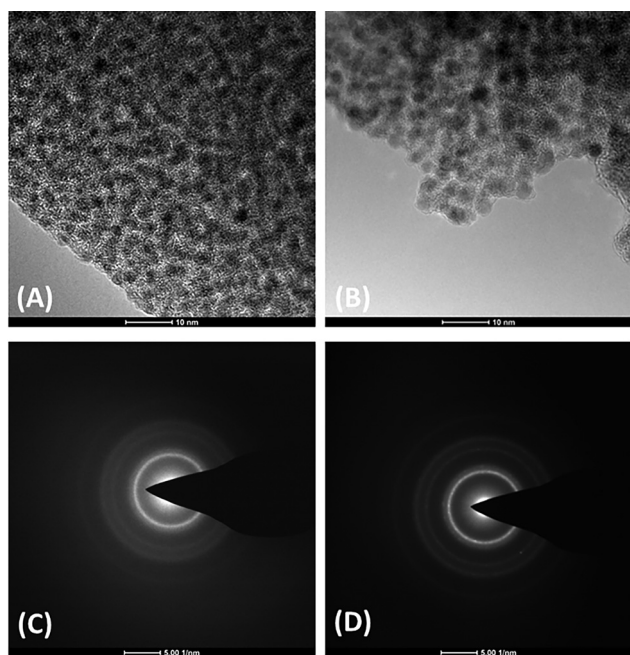


Fig. 14 Image of sample (A) – $[\text{Cu}_2(\text{tBuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (**1**) and (B) – $[\text{Cu}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (**0**) after a few seconds of interaction with a focus high-energy electron beam (200 keV). Diffraction pattern, which confirms the presence of copper nanoparticles for (C) – $[\text{Cu}_2(\text{tBuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (**1**) and (D) – $[\text{Cu}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (**0**).

Table 4 TEM-EDX data for the complex (**1**) and (**0**)

Element	Atomic content of the element [at%]	
	$[\text{Cu}_2(\text{tBuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (1)	$[\text{Cu}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (0)
Cu	60.74	49.31
O	5.04	3.54
C ^a	34.20	42.39

^a TEM grid covered with carbon.

material showed the following atomic contents of the elements: (**1**) –60.74 at% Cu, 5.04 at% O and (**0**) –49.31 at% Cu, 3.54 at% O (Table 4). It should be noted that the TEM grid was covered with carbon, which affects semiquantitative measurement. As a result of the interaction of the complex (**1**) with the electron beam (200 keV), the carboxylate ligand was removed.

The significant copper and slight oxygen content confirmed this. The absence of a signal from nitrogen suggests that the Cu–N bond was broken under the conditions of TEM observation. This is consistent with previous data from EI MS experiments, in which Cu–N bonds were also the most sensitive to break due to electrons (3.5 Mass spectra analysis). The data obtained for the compound (**0**) indicate that the carboxylate ligand was removed due to electron beam exposure during TEM analysis.

Summarising, the microscopic observations confirmed that the compounds (**1**) and (**0**) are sensitive to the high-energy electron beam and can be potentially used as FEBID precursors. It is worth noting that the decomposition of the compounds strongly depends on the beam power and electron dose. SEM/EDX observations suggest incomplete electron induced decomposition. A different behaviour was observed when electrons with an energy of 200 keV (TEM) were used; Cu is the final product of decomposition.

3.7 Preliminary chemical vapour deposition (CVD) experiments

CVD experiments were carried out in a homemade hot-wall horizontal reactor in argon without using a reducing agent. We selected the compound $[\text{Cu}_2(\text{tBuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (**1**) to check the generation of volatile metal carriers during heating, which is important for use in CVD and FEBID methods. Moreover, this complex showed the highest sensitivity towards electron irradiation, which is significant in FEBID.

The surface morphology of the formed deposits varied in the grains' size and shape due to the length of the vapor transport way in the CVD reactor (Fig. 15). The silicon surface is covered by a heterogeneous layer (Fig. 15(A)–(C), (A1)–(C1)) in which irregular and elongated grains were observed. In the SEM images, the formed structures exhibited a size of about 94–170 nm (Fig. 15(A) and (A1)), 152–210 nm (Fig. 15(B) and (B1)), and 262–347 nm (Fig. 15(C) and (C1)) in diameter. For the longest transport way (Fig. 15(D) and (D1)), a less homogenous surface was observed. The grains were approximately 28–54 nm in size and formed a film, but holes with a diameter of 96–124 nm were in it detected.

For the deposits (Fig. 15(A) and (C)), EDX spectra were registered (Fig. S31, ESI†). The materials that were obtained

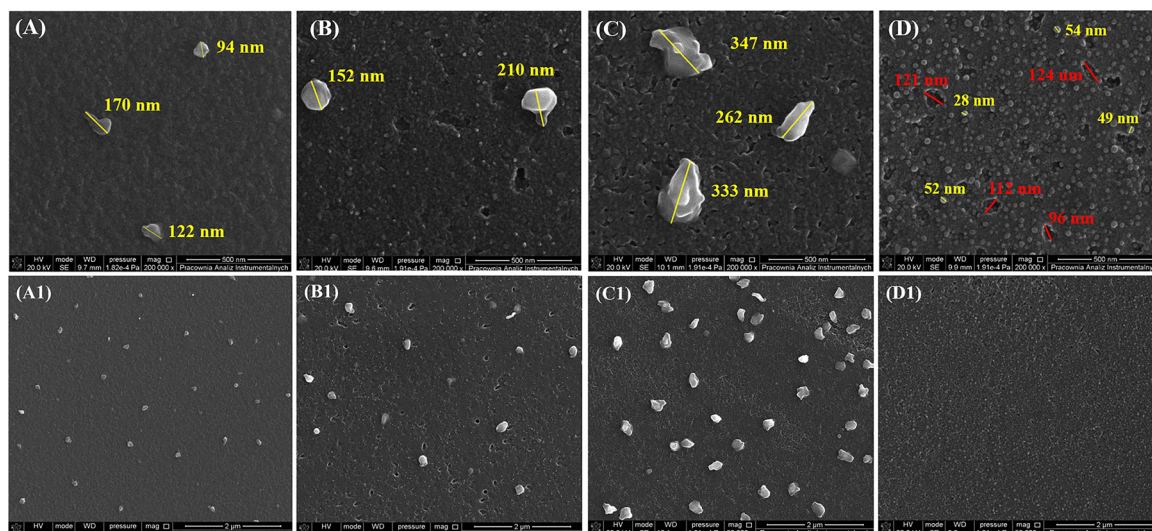


Fig. 15 SEM images of deposits formed using the precursor $[\text{Cu}_2(\text{tBuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (**1**), $\text{Mag} = 200\,000\times$ (A)–(D) and $50\,000\times$ (A1)–(D1), (orderly with the increasing transport way length), $T_V = 473\text{ K}$, $T_D = 633\text{ K}$, $\text{Si}(111)$, Ar .

were thin, with a thickness of about $0.93\text{--}0.97\text{ }\mu\text{m}$ (Fig. S32, ESI†); consequently, the signals from copper and low intensity from oxygen were observed. This suggests the formation of copper and a small amount of copper oxide.

Atomic force microscopy (AFM) was also performed to investigate the spatial structure of the deposits. The AFM images show that the depicted coverings are not continuous and homogeneous. Interestingly, single three-dimensional deposits were

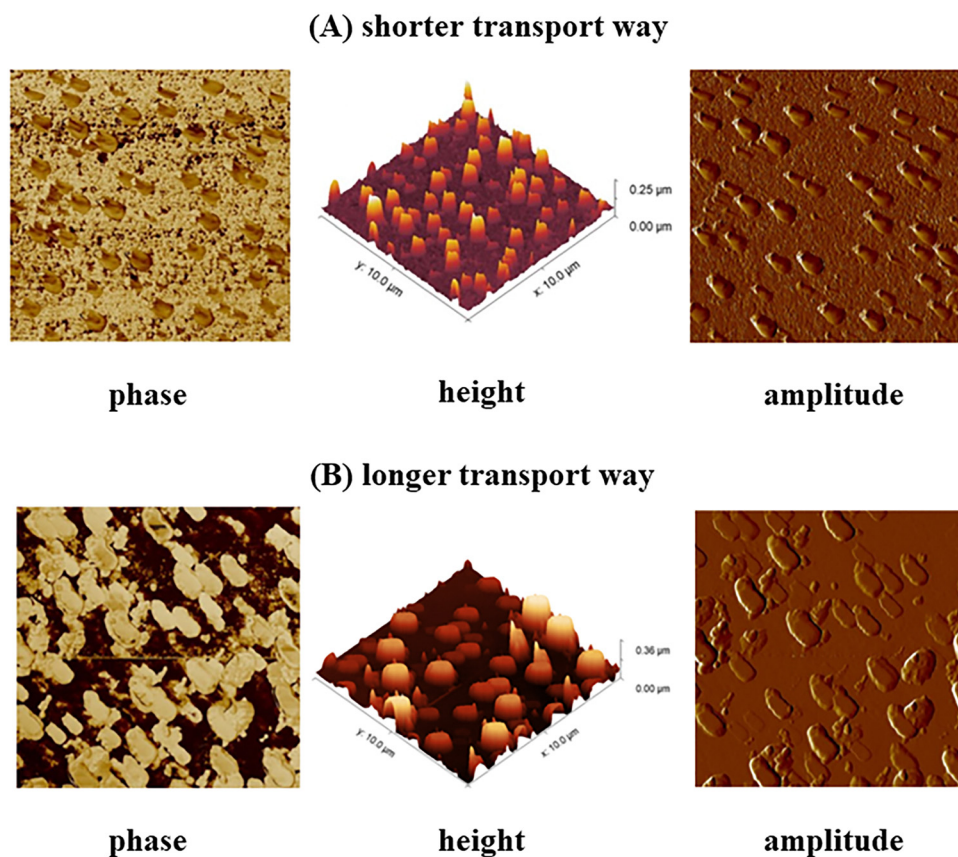


Fig. 16 AFM images of deposits obtained using the compound $[\text{Cu}_2(\text{tBuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (**1**): (A) the shorter transport way – deposit B; (B) the longer transport way – deposit D.

observed, indicating that vertical growth is dominant during deposition using this precursor. The height of the structures ranged from 250 to 360 nm (Fig. 16). The roughness parameters increased with the length of the transport way and achieved $R_a = 19.0$ nm, $R_q = 28.3$ nm for the deposit (B), $R_a = 43.4$ nm, $R_q = 58.3$ nm for the deposit (D).

These promising results can be used for further research to apply this potential precursor in commercial CVD reactors under controlled conditions.

4. Conclusions

Copper(II) compounds of the general formula $[\text{Cu}_2(\text{RNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$, where R = $t\text{Bu}$ (1), $s\text{Bu}$ (2), $i\text{Pr}$ (3), Et (4) and also $[\text{Cu}_2(\text{Et}_3\text{N})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]$ (5) were synthesized by the reaction of copper(II) pivalate with aliphatic amines. Additionally, single crystal X-ray diffraction revealed the formation of complexes: $[\text{Cu}_3(t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_6]_n$ (1a), $[\text{Cu}_3(s\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_6]_n$ (2a), $[\text{Cu}_3(i\text{PrNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_6]_n$ (3a), and $[\text{Cu}_{20}(\text{EtNH}_2)_6(\mu_3\text{-OH})_{24}(\text{OH})(\text{H}_2\text{O})_5(\text{NO}_3)(\mu\text{-O}_2\text{C}^t\text{Bu})_8](t\text{BuCO}_2)_6 \cdot 13\text{H}_2\text{O}$ (4a), which have been grown in the air through amine ligand partial release. The crucial role of nitrate anion for the last (4a) is suggested.

The IR spectra analysis suggested the bridging coordination mode of carboxylate and confirmed the N-bonding amine for all studied compounds. The results of mass spectrometry and sublimation experiments demonstrated that synthesized compounds (1–5) are a source of copper carriers in the gas phase. The thermal analysis data also revealed that copper can be transported to the gaseous phase even at atmospheric pressure. Moreover, electron impact mass spectra analysis for $[\text{Cu}_2(t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (1) exhibited its sensitivity towards the low-energy electrons irradiation and demonstrated the possibility of decomposition into copper. Based on the study of the complexes' interactions with high-energy electrons, it can be concluded that the compound $[\text{Cu}_2(t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (1) is the most sensitive on high-energy electron exposure (at 8, 20, and 200 keV). The CVD preliminary experiments confirmed that the compound $[\text{Cu}_2(t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (1) is the source of metal in the gas phase. The metallated materials with varying 3D structures were deposited under an argon atmosphere by heating the precursor at 473 K and depositing at 633 K. These results indicate that introducing *tert*-butylamine to copper(II) pivalate improved volatility and increased electron sensitivity, which suggests that new complex $[\text{Cu}_2(t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (1) can be potentially tested under typical FEBID conditions for the preparation of nanostructures composed of copper.

Data availability statement

The data presented in this study are available on request from the corresponding author.

Author contributions

All the authors discussed the results. K. M. and I. B. S. conceptualization and methodology; A. B.-K. and W. L. investigations, A. B.-K., and W. L. figures preparations, A. B.-K. original draft preparation; T. M. X-ray structural measurements, visualization and structure description, I. B. S. supervision. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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Supplementary Materials:

Pivalate complexes of copper(II) with aliphatic amines as potential precursors for depositing nanomaterials from the gas phase

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X-ray crystal structure determination

Table S1 Crystal data and structure refinement for **(1a–4a)**.

Identification code	(1a)	(2a)	(3a)	(4a)
Empirical formula	C38 H76 Cu3 N2 O12	C38 H76 Cu3 N2 O12	C26 H56 Cu3 N2 O10	C82 H207 Cu20 N7 O72
Formula weight	943.62	943.62	747.34	3732.48
Temperature [K]	100(2) K	100(2) K	100(2) K	100(2) K
Wavelength [Å]	1.54184 Å	1.54184 Å	1.54184 Å	1.54184 Å
Crystal system, space group	Monoclinic, P2 ₁ /n	Monoclinic, P2 ₁ /n	Triclinic, P $\bar{1}$	Orthorhombic, Pbca
Unit cell dimensions [Å] and [°]	a = 11.6627(5) Å α = 90° b = 12.4671(6) Å β = 92.366(4)° c = 16.7859(9) Å γ = 90°	a = 12.5325(5) Å α = 90° b = 11.1446(4) Å β = 94.728(4)° c = 17.1279(7) Å γ = 90°	a = 6.2514(12) Å α = 109.72(2)° b = 12.462(4) Å β = 99.887(15)° c = 12.7926(14) Å γ = 103.83(2)°	a = 20.1618(5) Å α = 90° b = 25.4106(6) Å β = 90° c = 28.8931(7) Å γ = 90°
Volume [Å ³]	2438.6(2) Å ³	2384.10(17) Å ³	875.5(4) Å ³	14802.6(6) Å ³
Z, Calculated density [Mg×m ⁻³]	2, 1.285 Mg/m ³	2, 1.314 Mg/m ³	1, 1.417 Mg/m ³	4, 1.675 Mg/m ³
Absorption coefficient [mm ⁻¹]	1.958 mm ⁻¹	2.002 mm ⁻¹	2.532 mm ⁻¹	3.784 mm ⁻¹
F(000)	1002	1002	393	7688
Crystal size [mm]	0.160 x 0.100 x 0.040 mm ³	0.130 x 0.060 x 0.040 mm ³	0.100 x 0.030 x 0.020 mm ³	0.080 x 0.050 x 0.030 mm ³
Theta range for data collection [°]	2.635 to 74.499°	4.739 to 68.227°	3.819 to 68.199°	3.189 to 74.501°
Limiting indices	-13 ≤ h ≤ 14, -15 ≤ k ≤ 15, -20 ≤ l ≤ 20	-15 ≤ h ≤ 15, -13 ≤ k ≤ 13, -20 ≤ l ≤ 20	-7 ≤ h ≤ 6, -13 ≤ k ≤ 13, -20 ≤ l ≤ 20	-12 ≤ h ≤ 25, -31 ≤ k ≤ 31, -34 ≤ l ≤ 35
Reflections collected/unique	18846	6871	6231	59548
Completeness [%] to theta [°]	99.9 %	98.0 %	88.7 %	99.7 %
Absorption correction	Gaussian	Analytical	Gaussian	Gaussian
Max. and min. transmission	1.000 and 0.618	0.921 and 0.798	1.000 and 0.806	0.932 and 0.816
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data/restraints/parameters	4859 / 42 / 333	6871 / 32 / 276	2831 / 29 / 199	14603 / 51 / 898
Goodness-of-fit on F ²	1.025	1.034	1.032	1.045
Final R Indices [I>2sigma(I)]	R1 = 0.0478, wR2 = 0.1244	R1 = 0.0716, wR2 = 0.1940	R1 = 0.1094, wR2 = 0.2815	R1 = 0.0432, wR2 = 0.1240
R indices (all data)	R1 = 0.0528, wR2 = 0.1275	R1 = 0.0934, wR2 = 0.2117	R1 = 0.1846, wR2 = 0.3288	R1 = 0.0486, wR2 = 0.1277
Largest diff. peak and hole [e.Å ⁻³]	0.684 and -0.790 e.Å ⁻³	1.036 and -0.601 e.Å ⁻³	1.919 and -1.063 e.Å ⁻³	1.635 and -0.898 e.Å ⁻³

Table S2 Bond lengths [Å] and angles [°] for [Cu₃(^tBuNH₂)₂(μ-O₂C^tBu)₆]_n (**1a**).

Cu(1)-O(1)	1.947(2)
Cu(1)-O(2)#1	1.954(2)
Cu(1)-O(12)#1	1.973(2)
Cu(1)-O(11)	1.977(2)
Cu(1)-O(22)	2.136(2)
Cu(1)-Cu(1)#1	2.6022(8)
Cu(2)-O(21)	1.964(2)
Cu(2)-O(21)#2	1.964(2)
Cu(2)-N(31)#2	1.994(3)
Cu(2)-N(31)	1.994(3)
O(1)-Cu(1)-O(2)#1	169.07(9)
O(1)-Cu(1)-O(12)#1	90.79(10)
O(2)#1-Cu(1)-O(12)#1	88.89(10)
O(1)-Cu(1)-O(11)	89.67(10)
O(2)#1-Cu(1)-O(11)	88.54(10)
O(12)#1-Cu(1)-O(11)	168.77(9)
O(1)-Cu(1)-O(22)	93.74(10)
O(2)#1-Cu(1)-O(22)	97.00(10)
O(12)#1-Cu(1)-O(22)	102.40(8)
O(11)-Cu(1)-O(22)	88.76(8)
O(21)-Cu(2)-O(21)#2	180.0
O(21)-Cu(2)-N(31)#2	84.95(10)
O(21)#2-Cu(2)-N(31)#2	95.05(10)
O(21)-Cu(2)-N(31)	95.05(10)
O(21)#2-Cu(2)-N(31)	84.95(10)
N(31)#2-Cu(2)-N(31)	180.00(14)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x+2,-y+1,-z+1

Table S3 Bonds lengths [Å] and angles [°] for [Cu₃(^sBuNH₂)₂(μ-O₂C^tBu)₆]_n (**2a**).

Cu(1)-O(12)#1	1.940(4)
Cu(1)-O(11)	1.952(4)
Cu(1)-O(2)#1	1.974(3)
Cu(1)-O(1)	1.978(4)
Cu(1)-O(21)	2.160(3)
Cu(1)-Cu(1)#1	2.6277(13)
Cu(2)-O(22)	1.962(4)
Cu(2)-O(22)#2	1.962(4)
Cu(2)-N(31)	2.023(6)
Cu(2)-N(31)#2	2.023(6)
O(12)#1-Cu(1)-O(11)	168.46(16)
O(12)#1-Cu(1)-O(2)#1	90.93(19)
O(11)-Cu(1)-O(2)#1	89.03(18)
O(12)#1-Cu(1)-O(1)	89.3(2)
O(11)-Cu(1)-O(1)	88.40(19)
O(2)#1-Cu(1)-O(1)	168.12(15)
O(12)#1-Cu(1)-O(21)	95.69(16)
O(11)-Cu(1)-O(21)	95.61(16)
O(2)#1-Cu(1)-O(21)	101.92(14)
O(1)-Cu(1)-O(21)	89.88(14)
O(12)#1-Cu(1)-Cu(1)#1	82.74(12)
O(11)-Cu(1)-Cu(1)#1	85.86(12)
O(2)#1-Cu(1)-Cu(1)#1	81.07(10)
O(1)-Cu(1)-Cu(1)#1	87.18(11)
O(21)-Cu(1)-Cu(1)#1	176.67(10)
O(22)-Cu(2)-O(22)#2	180.0
O(22)-Cu(2)-N(31)	92.3(2)
O(22)#2-Cu(2)-N(31)	87.7(2)
O(22)-Cu(2)-N(31)#2	87.7(2)
O(22)#2-Cu(2)-N(31)#2	92.3(2)
N(31)-Cu(2)-N(31)#2	180.0
C(2)-O(1)-Cu(1)	119.6(3)
C(2)-O(2)-Cu(1)#1	127.2(3)
C(12)-O(11)-Cu(1)	121.1(4)
C(12)-O(12)-Cu(1)#1	125.1(4)
C(22)-O(21)-Cu(1)	148.8(3)

C(22)-O(22)-Cu(2)	111.2(3)
C(32)-N(31)-Cu(2)	120.0(6)
Cu(2)-N(31)-H(31A)	107.3
Cu(2)-N(31)-H(31B)	107.3
Cu(2)-N(31)-H(31C)	107.3
Cu(2)-N(31)-H(31D)	107.3

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x+1,-y+2,-z+1

Table S4 Bonds lengths [Å] and angles [°] for [Cu₃(ⁱPrNH₂)₂(μ₃-OH)₂(μ-O₂C^tBu)₄]_n (**3a**).

Cu(1)-O(31)#1	1.951(6)
Cu(1)-O(31)	1.951(6)
Cu(1)-O(11)#1	1.975(8)
Cu(1)-O(11)	1.975(7)
Cu(2)-O(31)	1.936(7)
Cu(2)-O(1)	1.950(9)
Cu(2)-N(21)	1.990(8)
Cu(2)-O(12)#1	2.083(9)
Cu(2)-O(31)#2	2.127(7)
O(31)#1-Cu(1)-O(31)	180.0(5)
O(31)#1-Cu(1)-O(11)#1	83.6(3)
O(31)-Cu(1)-O(11)#1	96.4(3)
O(31)#1-Cu(1)-O(11)	96.4(3)
O(31)-Cu(1)-O(11)	83.6(3)
O(11)#1-Cu(1)-O(11)	180.0
O(31)-Cu(2)-O(1)	93.0(3)
O(31)-Cu(2)-N(21)	171.3(4)
O(1)-Cu(2)-N(21)	94.1(4)
O(31)-Cu(2)-O(12)#1	92.8(3)
O(1)-Cu(2)-O(12)#1	140.0(3)
N(21)-Cu(2)-O(12)#1	85.1(4)
O(31)-Cu(2)-O(31)#2	81.6(3)
O(1)-Cu(2)-O(31)#2	135.1(3)
N(21)-Cu(2)-O(31)#2	89.8(3)
O(12)#1-Cu(2)-O(31)#2	84.8(3)
C(2)-O(1)-Cu(2)	115.6(8)
Cu(2)-O(31)-Cu(1)	112.9(4)
Cu(2)-O(31)-Cu(2)#2	98.4(3)
Cu(1)-O(31)-Cu(2)#2	131.1(4)
Cu(2)-O(31)-H(31)	103.9
Cu(1)-O(31)-H(31)	103.9
Cu(2)#2-O(31)-H(31)	103.9

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x+2,-y+1,-z+1

Table S5 Bond lengths [Å] and angles [°] for [Cu₂₀(EtNH₂)₆(μ₃-OH)₂₄(OH)(H₂O)₅(NO₃)(μ-O₂C^tBu)₈](^tBuCO₂)₆·13H₂O (**4a**).

Cu(1)-O(1)	1.924(3)
Cu(1)-N(81)	1.976(3)
Cu(1)-O(105)	1.986(2)
Cu(1)-O(110)	2.026(2)
Cu(1)-O(101)	2.274(2)
Cu(1)-Cu(9)	2.9024(7)
Cu(1)-Cu(2)	2.9926(7)
Cu(2)-O(102)	1.942(2)
Cu(2)-O(101)	1.944(2)
Cu(2)-O(106)	1.967(2)
Cu(2)-O(105)	1.982(2)
Cu(2)-Cu(3)	3.0575(7)
Cu(3)-O(11)	1.935(2)
Cu(3)-N(76)	1.983(3)
Cu(3)-O(107)	1.984(2)
Cu(3)-O(106)	2.010(2)
Cu(3)-O(102)	2.258(2)
Cu(3)-Cu(10)	2.9937(7)
Cu(3)-Cu(4)	3.0279(7)
Cu(4)-O(102)	1.950(2)
Cu(4)-O(108)	1.959(3)
Cu(4)-O(103)	2.008(2)
Cu(4)-O(107)	2.016(2)
Cu(4)-O(90)	2.374(4)
Cu(4)-O(12)	2.414(2)
Cu(4)-O(88)	2.428(4)
Cu(5)-N(91)	1.987(4)
Cu(5)-O(103)	1.998(2)
Cu(5)-O(85)	2.025(3)
Cu(5)-O(109)	2.044(3)
Cu(5)-O(86)	2.289(4)
Cu(5)-O(108)	2.325(3)
Cu(5)-Cu(6)	2.9733(7)
Cu(6)-O(104)	1.932(2)
Cu(6)-O(109)	1.962(2)

Cu(6)-O(103)	1.978(2)
Cu(6)-O(112)#1	1.995(2)
Cu(6)-Cu(7)	3.0012(7)
Cu(7)-O(21)	1.923(3)
Cu(7)-O(31)	1.930(3)
Cu(7)-O(111)	1.984(2)
Cu(7)-O(112)#1	2.026(2)
Cu(7)-O(104)	2.245(2)
Cu(7)-Cu(8)	2.9532(7)
Cu(7)-Cu(10)#1	2.9568(7)
Cu(8)-O(101)	1.933(2)
Cu(8)-O(104)	1.939(2)
Cu(8)-O(110)	1.976(2)
Cu(8)-O(111)	1.978(2)
Cu(8)-O(32)	2.274(2)
Cu(9)-O(108)#1	1.932(3)
Cu(9)-O(105)	1.939(2)
Cu(9)-O(110)	1.970(2)
Cu(9)-O(109)#1	1.982(2)
Cu(9)-O(90)#1	2.228(4)
Cu(10)-O(111)#1	1.955(2)
Cu(10)-O(107)	1.957(2)
Cu(10)-O(106)	1.961(2)
Cu(10)-O(112)	1.964(2)
Cu(10)-O(88)	2.209(4)
Cu(10)-O(89)	2.308(5)
O(1)-Cu(1)-N(81)	94.63(12)
O(1)-Cu(1)-O(105)	93.49(11)
N(81)-Cu(1)-O(105)	170.65(11)
O(1)-Cu(1)-O(110)	166.22(11)
N(81)-Cu(1)-O(110)	92.03(11)
O(105)-Cu(1)-O(110)	79.07(9)
O(1)-Cu(1)-O(101)	114.95(11)
N(81)-Cu(1)-O(101)	102.83(11)
O(105)-Cu(1)-O(101)	77.80(8)
O(110)-Cu(1)-O(101)	75.09(8)
O(1)-Cu(1)-Cu(9)	125.49(9)
N(81)-Cu(1)-Cu(9)	129.02(9)

O(105)-Cu(1)-Cu(9)	41.68(7)
O(110)-Cu(1)-Cu(9)	42.66(6)
O(101)-Cu(1)-Cu(9)	88.39(6)
O(1)-Cu(1)-Cu(2)	95.49(8)
N(81)-Cu(1)-Cu(2)	142.22(9)
O(105)-Cu(1)-Cu(2)	40.99(6)
O(110)-Cu(1)-Cu(2)	86.52(6)
O(101)-Cu(1)-Cu(2)	40.51(6)
Cu(9)-Cu(1)-Cu(2)	70.552(17)
O(102)-Cu(2)-O(101)	94.50(9)
O(102)-Cu(2)-O(106)	85.29(9)
O(101)-Cu(2)-O(106)	175.63(9)
O(102)-Cu(2)-O(105)	173.98(10)
O(101)-Cu(2)-O(105)	86.27(9)
O(106)-Cu(2)-O(105)	94.39(9)
O(102)-Cu(2)-Cu(1)	141.73(7)
O(101)-Cu(2)-Cu(1)	49.44(7)
O(106)-Cu(2)-Cu(1)	129.56(7)
O(105)-Cu(2)-Cu(1)	41.10(6)
O(102)-Cu(2)-Cu(3)	47.50(7)
O(101)-Cu(2)-Cu(3)	138.04(7)
O(106)-Cu(2)-Cu(3)	40.27(7)
O(105)-Cu(2)-Cu(3)	133.55(7)
Cu(1)-Cu(2)-Cu(3)	153.15(2)
O(11)-Cu(3)-N(76)	91.26(13)
O(11)-Cu(3)-O(107)	96.50(10)
N(76)-Cu(3)-O(107)	167.95(13)
O(11)-Cu(3)-O(106)	175.55(10)
N(76)-Cu(3)-O(106)	93.11(12)
O(107)-Cu(3)-O(106)	79.05(9)
O(11)-Cu(3)-O(102)	102.75(10)
N(76)-Cu(3)-O(102)	109.95(12)
O(107)-Cu(3)-O(102)	77.35(9)
O(106)-Cu(3)-O(102)	76.47(9)
O(11)-Cu(3)-Cu(10)	135.18(8)
N(76)-Cu(3)-Cu(10)	129.64(11)
O(107)-Cu(3)-Cu(10)	40.23(7)
O(106)-Cu(3)-Cu(10)	40.47(6)

O(102)-Cu(3)-Cu(10)	81.80(6)
O(11)-Cu(3)-Cu(4)	88.84(8)
N(76)-Cu(3)-Cu(4)	148.68(11)
O(107)-Cu(3)-Cu(4)	41.20(7)
O(106)-Cu(3)-Cu(4)	87.83(6)
O(102)-Cu(3)-Cu(4)	40.08(6)
Cu(10)-Cu(3)-Cu(4)	65.981(16)
O(11)-Cu(3)-Cu(2)	141.03(8)
N(76)-Cu(3)-Cu(2)	94.96(10)
O(107)-Cu(3)-Cu(2)	84.79(7)
O(106)-Cu(3)-Cu(2)	39.24(6)
O(102)-Cu(3)-Cu(2)	39.36(6)
Cu(10)-Cu(3)-Cu(2)	62.880(15)
Cu(4)-Cu(3)-Cu(2)	66.714(16)
O(102)-Cu(4)-O(108)	177.58(11)
O(102)-Cu(4)-O(103)	98.42(9)
O(108)-Cu(4)-O(103)	83.25(10)
O(102)-Cu(4)-O(107)	84.18(9)
O(108)-Cu(4)-O(107)	94.21(10)
O(103)-Cu(4)-O(107)	176.80(10)
O(102)-Cu(4)-O(90)	102.84(13)
O(108)-Cu(4)-O(90)	75.66(13)
O(103)-Cu(4)-O(90)	80.40(12)
O(107)-Cu(4)-O(90)	100.89(12)
O(102)-Cu(4)-O(12)	91.79(9)
O(108)-Cu(4)-O(12)	89.81(10)
O(103)-Cu(4)-O(12)	94.85(9)
O(107)-Cu(4)-O(12)	83.17(9)
O(90)-Cu(4)-O(12)	165.10(12)
O(102)-Cu(4)-O(88)	77.86(12)
O(108)-Cu(4)-O(88)	100.02(13)
O(103)-Cu(4)-O(88)	106.15(12)
O(107)-Cu(4)-O(88)	76.17(12)
O(12)-Cu(4)-O(88)	157.65(12)
O(102)-Cu(4)-Cu(3)	48.19(7)
O(108)-Cu(4)-Cu(3)	130.91(8)
O(103)-Cu(4)-Cu(3)	141.13(7)
O(107)-Cu(4)-Cu(3)	40.41(7)

O(90)-Cu(4)-Cu(3)	121.15(11)
O(12)-Cu(4)-Cu(3)	71.00(6)
O(88)-Cu(4)-Cu(3)	87.57(10)
N(91)-Cu(5)-O(103)	171.17(15)
N(91)-Cu(5)-O(85)	94.03(16)
O(103)-Cu(5)-O(85)	91.82(11)
N(91)-Cu(5)-O(109)	94.82(15)
O(103)-Cu(5)-O(109)	79.18(9)
O(85)-Cu(5)-O(109)	170.97(11)
N(91)-Cu(5)-O(86)	85.19(18)
O(103)-Cu(5)-O(86)	101.40(13)
O(85)-Cu(5)-O(86)	90.40(16)
O(109)-Cu(5)-O(86)	92.10(14)
N(91)-Cu(5)-O(108)	97.60(15)
O(103)-Cu(5)-O(108)	74.69(9)
O(85)-Cu(5)-O(108)	101.80(11)
O(109)-Cu(5)-O(108)	75.26(9)
O(86)-Cu(5)-O(108)	167.22(14)
N(91)-Cu(5)-Cu(6)	134.56(13)
O(103)-Cu(5)-Cu(6)	41.36(7)
O(85)-Cu(5)-Cu(6)	130.62(10)
O(109)-Cu(5)-Cu(6)	41.02(7)
O(86)-Cu(5)-Cu(6)	86.39(10)
O(108)-Cu(5)-Cu(6)	82.77(7)
O(104)-Cu(6)-O(109)	175.49(10)
O(104)-Cu(6)-O(103)	93.87(10)
O(109)-Cu(6)-O(103)	81.69(10)
O(104)-Cu(6)-O(112)#1	87.07(10)
O(109)-Cu(6)-O(112)#1	97.39(10)
O(103)-Cu(6)-O(112)#1	178.37(10)
O(104)-Cu(6)-Cu(5)	132.86(7)
O(109)-Cu(6)-Cu(5)	43.16(7)
O(103)-Cu(6)-Cu(5)	41.87(7)
O(112)#1-Cu(6)-Cu(5)	136.80(7)
O(104)-Cu(6)-Cu(7)	48.40(7)
O(109)-Cu(6)-Cu(7)	136.04(8)
O(103)-Cu(6)-Cu(7)	138.28(7)
O(112)#1-Cu(6)-Cu(7)	42.11(7)

Cu(5)-Cu(6)-Cu(7)	152.75(2)
O(21)-Cu(7)-O(31)	89.04(12)
O(21)-Cu(7)-O(111)	175.83(11)
O(31)-Cu(7)-O(111)	93.30(10)
O(21)-Cu(7)-O(112)#1	98.19(11)
O(31)-Cu(7)-O(112)#1	168.22(12)
O(111)-Cu(7)-O(112)#1	78.95(9)
O(21)-Cu(7)-O(104)	106.09(10)
O(31)-Cu(7)-O(104)	108.60(10)
O(111)-Cu(7)-O(104)	76.43(9)
O(112)#1-Cu(7)-O(104)	78.43(9)
O(21)-Cu(7)-Cu(8)	142.00(8)
O(31)-Cu(7)-Cu(8)	87.09(8)
O(111)-Cu(7)-Cu(8)	41.72(6)
O(112)#1-Cu(7)-Cu(8)	92.79(7)
O(104)-Cu(7)-Cu(8)	41.03(6)
O(21)-Cu(7)-Cu(10)#1	135.28(9)
O(31)-Cu(7)-Cu(10)#1	128.13(9)
O(111)-Cu(7)-Cu(10)#1	40.98(6)
O(112)#1-Cu(7)-Cu(10)#1	41.38(7)
O(104)-Cu(7)-Cu(10)#1	86.44(6)
Cu(8)-Cu(7)-Cu(10)#1	72.434(17)
O(21)-Cu(7)-Cu(6)	93.99(8)
O(31)-Cu(7)-Cu(6)	147.87(9)
O(111)-Cu(7)-Cu(6)	85.88(7)
O(112)#1-Cu(7)-Cu(6)	41.33(7)
O(104)-Cu(7)-Cu(6)	40.06(6)
Cu(8)-Cu(7)-Cu(6)	71.062(17)
Cu(10)#1-Cu(7)-Cu(6)	68.152(16)
O(101)-Cu(8)-O(104)	96.68(9)
O(101)-Cu(8)-O(110)	84.47(9)
O(104)-Cu(8)-O(110)	170.67(9)
O(101)-Cu(8)-O(111)	171.84(9)
O(104)-Cu(8)-O(111)	84.13(9)
O(110)-Cu(8)-O(111)	93.43(9)
O(101)-Cu(8)-O(32)	99.48(9)
O(104)-Cu(8)-O(32)	96.61(9)
O(110)-Cu(8)-O(32)	92.32(9)

O(111)-Cu(8)-O(32)	88.47(9)
O(101)-Cu(8)-Cu(7)	142.49(7)
O(104)-Cu(8)-Cu(7)	49.48(7)
O(110)-Cu(8)-Cu(7)	131.74(7)
O(111)-Cu(8)-Cu(7)	41.89(6)
O(32)-Cu(8)-Cu(7)	73.41(6)
O(108)#1-Cu(9)-O(105)	172.57(11)
O(108)#1-Cu(9)-O(110)	95.34(10)
O(105)-Cu(9)-O(110)	81.61(9)
O(108)#1-Cu(9)-O(109)#1	86.30(11)
O(105)-Cu(9)-O(109)#1	94.99(10)
O(110)-Cu(9)-O(109)#1	165.67(10)
O(108)#1-Cu(9)-O(90)#1	79.80(13)
O(105)-Cu(9)-O(90)#1	107.56(13)
O(110)-Cu(9)-O(90)#1	107.19(13)
O(109)#1-Cu(9)-O(90)#1	87.12(13)
O(108)#1-Cu(9)-Cu(1)	131.25(8)
O(105)-Cu(9)-Cu(1)	42.95(7)
O(110)-Cu(9)-Cu(1)	44.20(7)
O(109)#1-Cu(9)-Cu(1)	126.16(7)
O(90)#1-Cu(9)-Cu(1)	130.07(11)
O(111)#1-Cu(10)-O(107)	95.08(10)
O(111)#1-Cu(10)-O(106)	168.79(9)
O(107)-Cu(10)-O(106)	80.89(9)
O(111)#1-Cu(10)-O(112)	81.17(9)
O(107)-Cu(10)-O(112)	165.02(10)
O(106)-Cu(10)-O(112)	100.02(10)
O(111)#1-Cu(10)-O(88)	102.65(13)
O(107)-Cu(10)-O(88)	82.76(13)
O(106)-Cu(10)-O(88)	87.29(13)
O(112)-Cu(10)-O(88)	112.20(14)
O(111)#1-Cu(10)-O(89)	99.84(14)
O(107)-Cu(10)-O(89)	113.74(14)
O(106)-Cu(10)-O(89)	91.35(14)
O(112)-Cu(10)-O(89)	81.22(14)
O(111)#1-Cu(10)-Cu(7)#1	41.73(7)
O(107)-Cu(10)-Cu(7)#1	127.58(7)
O(106)-Cu(10)-Cu(7)#1	134.62(7)

O(112)-Cu(10)-Cu(7)#1	42.99(7)
O(88)-Cu(10)-Cu(7)#1	126.25(11)
O(111)#1-Cu(10)-Cu(3)	131.29(7)
O(107)-Cu(10)-Cu(3)	40.91(7)
O(106)-Cu(10)-Cu(3)	41.69(7)
O(112)-Cu(10)-Cu(3)	134.64(7)
O(88)-Cu(10)-Cu(3)	92.59(11)
O(89)-Cu(10)-Cu(3)	115.10(13)
Cu(7)#1-Cu(10)-Cu(3)	140.41(2)
C(2)-O(1)-Cu(1)	121.3(2)
C(12)-O(11)-Cu(3)	126.5(2)
C(12)-O(12)-Cu(4)	127.1(2)
C(22)-O(21)-Cu(7)	123.4(2)
C(32)-O(31)-Cu(7)	125.8(2)
C(32)-O(32)-Cu(8)	126.7(2)
C(79)-N(76)-Cu(3)	125.0(5)
C(77)-N(76)-Cu(3)	118.3(4)
Cu(3)-N(76)-H(76B)	107.7
Cu(3)-N(76)-H(76C)	106.1
Cu(3)-N(76)-H(76D)	106.1
C(82)-N(81)-Cu(1)	119.6(2)
Cu(1)-N(81)-H(81A)	107.4
Cu(1)-N(81)-H(81B)	107.4
C(92)-N(91)-Cu(5)	107.3(6)
C(94)-N(91)-Cu(5)	122.1(7)
Cu(5)-N(91)-H(91A)	110.3
Cu(5)-N(91)-H(91B)	110.3
Cu(5)-N(91)-H(91C)	106.8
Cu(5)-N(91)-H(91D)	106.8
N(87)-O(88)-Cu(10)	123.7(3)
N(87)-O(88)-Cu(4)	130.3(3)
Cu(10)-O(88)-Cu(4)	89.85(15)
N(87)-O(89)-Cu(10)	120.2(3)
N(87)-O(90)-Cu(9)#1	124.1(3)
N(87)-O(90)-Cu(4)	132.1(3)
Cu(9)#1-O(90)-Cu(4)	90.24(15)
Cu(5)-O(85)-H(85A)	117.8
Cu(5)-O(85)-H(85B)	125.0

Cu(5)-O(86)-H(86A)	113.3
Cu(5)-O(86)-H(86B)	136.5
Cu(8)-O(101)-Cu(2)	117.71(11)
Cu(8)-O(101)-Cu(1)	94.55(9)
Cu(2)-O(101)-Cu(1)	90.05(8)
Cu(8)-O(101)-H(101)	116.4
Cu(2)-O(101)-H(101)	116.4
Cu(1)-O(101)-H(101)	116.4
Cu(2)-O(102)-Cu(4)	118.56(12)
Cu(2)-O(102)-Cu(3)	93.14(9)
Cu(4)-O(102)-Cu(3)	91.73(9)
Cu(2)-O(102)-H(102)	116.0
Cu(4)-O(102)-H(102)	116.0
Cu(3)-O(102)-H(102)	116.0
Cu(6)-O(103)-Cu(5)	96.77(10)
Cu(6)-O(103)-Cu(4)	113.43(11)
Cu(5)-O(103)-Cu(4)	102.14(10)
Cu(6)-O(103)-H(103)	114.2
Cu(5)-O(103)-H(103)	114.2
Cu(4)-O(103)-H(103)	114.2
Cu(6)-O(104)-Cu(8)	126.74(12)
Cu(6)-O(104)-Cu(7)	91.54(9)
Cu(8)-O(104)-Cu(7)	89.49(9)
Cu(6)-O(104)-H(104)	113.9
Cu(8)-O(104)-H(104)	113.9
Cu(7)-O(104)-H(104)	113.9
Cu(9)-O(105)-Cu(2)	120.59(12)
Cu(9)-O(105)-Cu(1)	95.37(10)
Cu(2)-O(105)-Cu(1)	97.91(10)
Cu(9)-O(105)-H(105)	113.4
Cu(2)-O(105)-H(105)	113.4
Cu(1)-O(105)-H(105)	113.4
Cu(10)-O(106)-Cu(2)	106.95(10)
Cu(10)-O(106)-Cu(3)	97.84(10)
Cu(2)-O(106)-Cu(3)	100.49(10)
Cu(10)-O(106)-H(106)	116.3
Cu(2)-O(106)-H(106)	116.3
Cu(3)-O(106)-H(106)	116.3

Cu(10)-O(107)-Cu(3)	98.86(10)
Cu(10)-O(107)-Cu(4)	111.23(11)
Cu(3)-O(107)-Cu(4)	98.39(10)
Cu(10)-O(107)-H(107)	115.3
Cu(3)-O(107)-H(107)	115.3
Cu(4)-O(107)-H(107)	115.3
Cu(9)#1-O(108)-Cu(4)	113.98(14)
Cu(9)#1-O(108)-Cu(5)	93.89(10)
Cu(4)-O(108)-Cu(5)	92.98(10)
Cu(9)#1-O(108)-H(108)	117.1
Cu(4)-O(108)-H(108)	117.1
Cu(5)-O(108)-H(108)	117.1
Cu(6)-O(109)-Cu(9)#1	106.55(11)
Cu(6)-O(109)-Cu(5)	95.82(10)
Cu(9)#1-O(109)-Cu(5)	101.69(11)
Cu(6)-O(109)-H(109)	116.6
Cu(9)#1-O(109)-H(109)	116.6
Cu(5)-O(109)-H(109)	116.6
Cu(9)-O(110)-Cu(8)	118.16(11)
Cu(9)-O(110)-Cu(1)	93.14(9)
Cu(8)-O(110)-Cu(1)	101.49(10)
Cu(9)-O(110)-H(110)	113.8
Cu(8)-O(110)-H(110)	113.8
Cu(1)-O(110)-H(110)	113.8
Cu(10)#1-O(111)-Cu(8)	125.24(11)
Cu(10)#1-O(111)-Cu(7)	97.29(10)
Cu(8)-O(111)-Cu(7)	96.40(10)
Cu(10)#1-O(111)-H(111)	111.6
Cu(8)-O(111)-H(111)	111.6
Cu(7)-O(111)-H(111)	111.6
Cu(10)-O(112)-Cu(6)#1	114.97(12)
Cu(10)-O(112)-Cu(7)#1	95.63(10)
Cu(6)#1-O(112)-Cu(7)#1	96.56(10)
Cu(10)-O(112)-H(112)	115.5
Cu(6)#1-O(112)-H(112)	115.5
Cu(7)#1-O(112)-H(112)	115.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

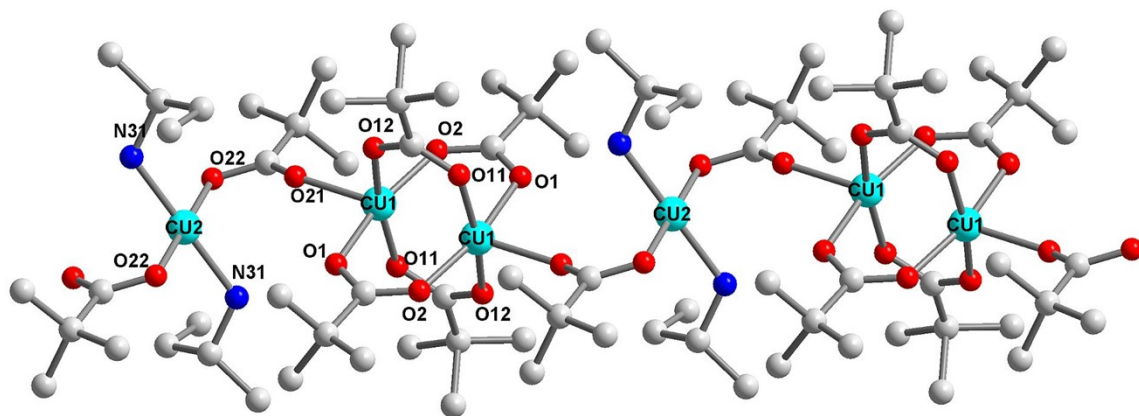


Figure S1 Chain topology in $[\text{Cu}_3(\text{sBuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_6]_n$ (**2a**) shows alternately arranged paddlewheel and mononuclear motifs.

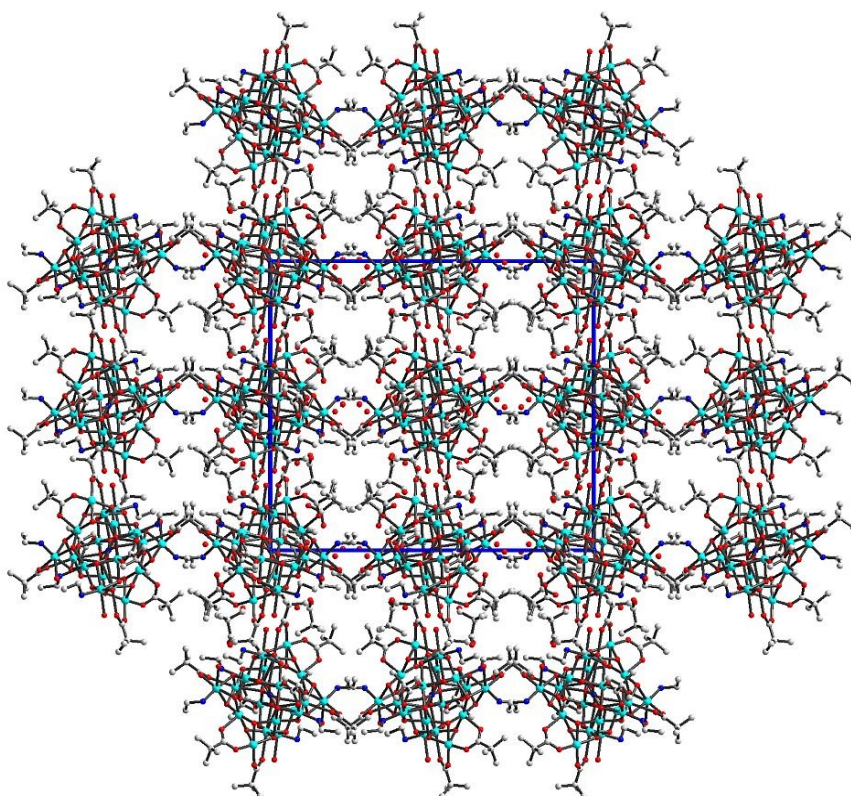


Figure S 2 Packing diagram of $[\text{Cu}_{20}(\text{EtNH}_2)_6(\mu_3\text{-OH})_{24}(\text{OH})(\text{H}_2\text{O})_5(\text{NO}_3)(\mu\text{-O}_2\text{C}^t\text{Bu})_8](^t\text{BuCO}_2)_6 \cdot 13\text{H}_2\text{O}$ (**4a**) viewed along a axis. For the clarity of the picture hydrogen atoms are omitted.

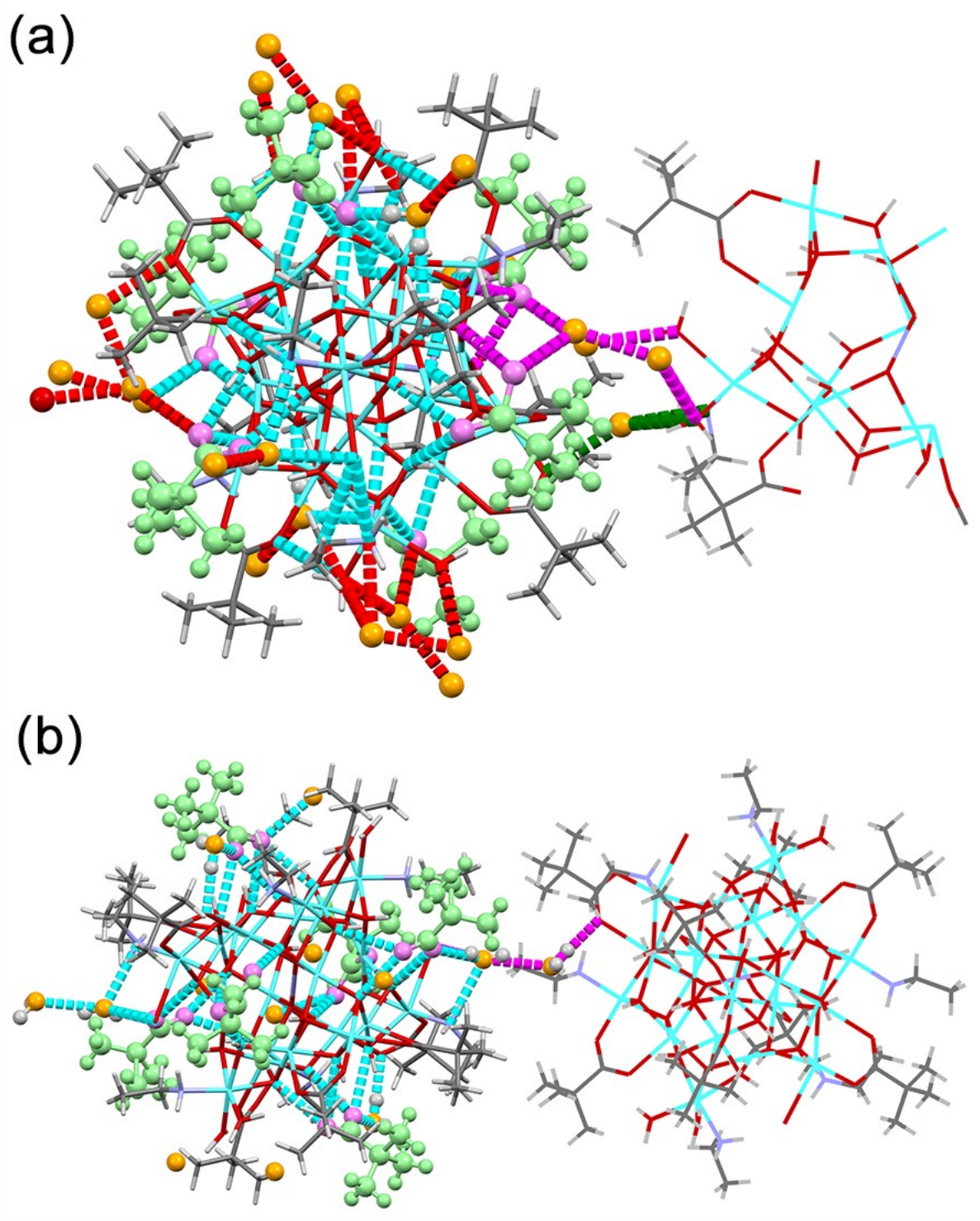


Figure S 3 The solvation sphere around the cluster (a) and hydrogen bonds in the crystal network (b). The selected hydrogen bond pathways between clusters are marked in green (for cluster...solvation sphere...cluster pattern) and in magenta (for cluster...solvation sphere...solvation sphere...cluster pattern).

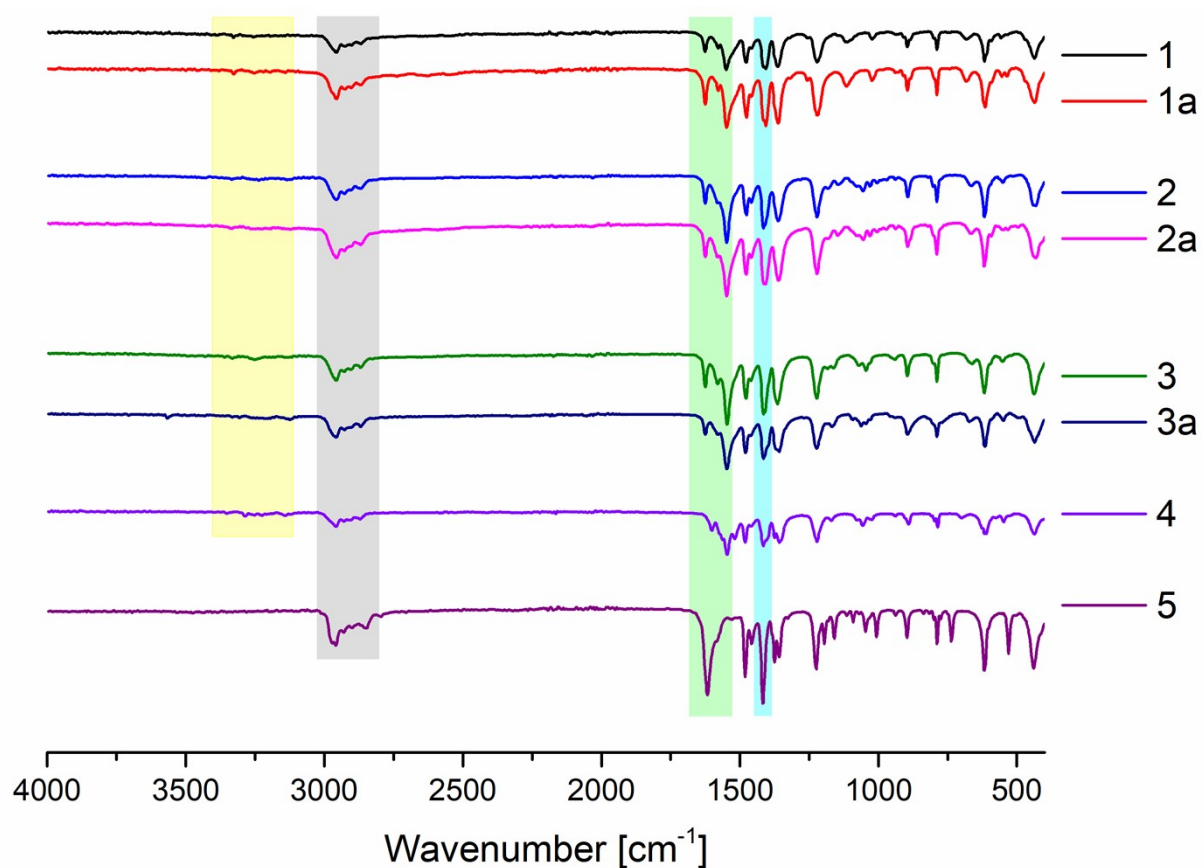


Figure S 4 ATR-IR spectrum for the compounds in the general formulas: $[\text{Cu}_2(\text{RNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (**1–5**) and single crystals formed during crystallization (**1a–3a**). The coloured bands highlight the ranges of the particular vibrational modes: (νNH_2) (yellow), ($\nu_{\text{as}}\text{COO}$) (green), ($\nu_{\text{s}}\text{COO}$) (blue), (νCH_3) (grey).

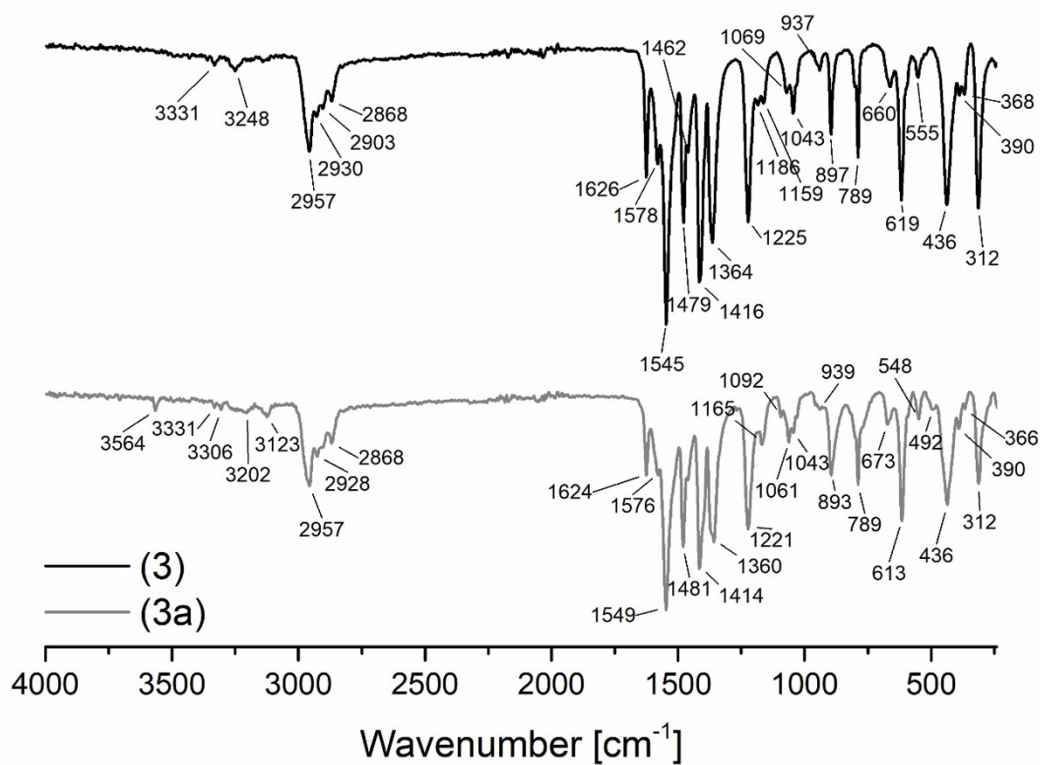


Figure S7 ATR-IR spectrum for the compound $[\text{Cu}_2(i\text{PrNH}_2)_2(\mu\text{-O}_2\text{C'Bu})_4]_n$ (**3**) (black) and $[\text{Cu}_3(i\text{PrNH}_2)_2(\mu_3\text{-OH})_2(\mu\text{-O}_2\text{C'Bu})_4]_n$ (**3a**) (grey).

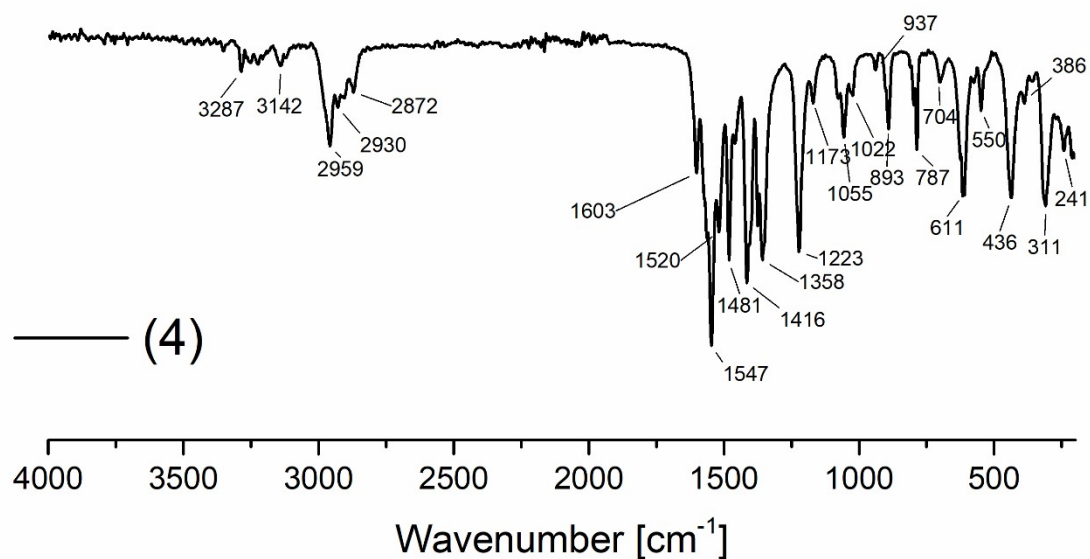


Figure S8 ATR-IR spectrum for the compound $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{C'Bu})_4]_n$ (**4**).

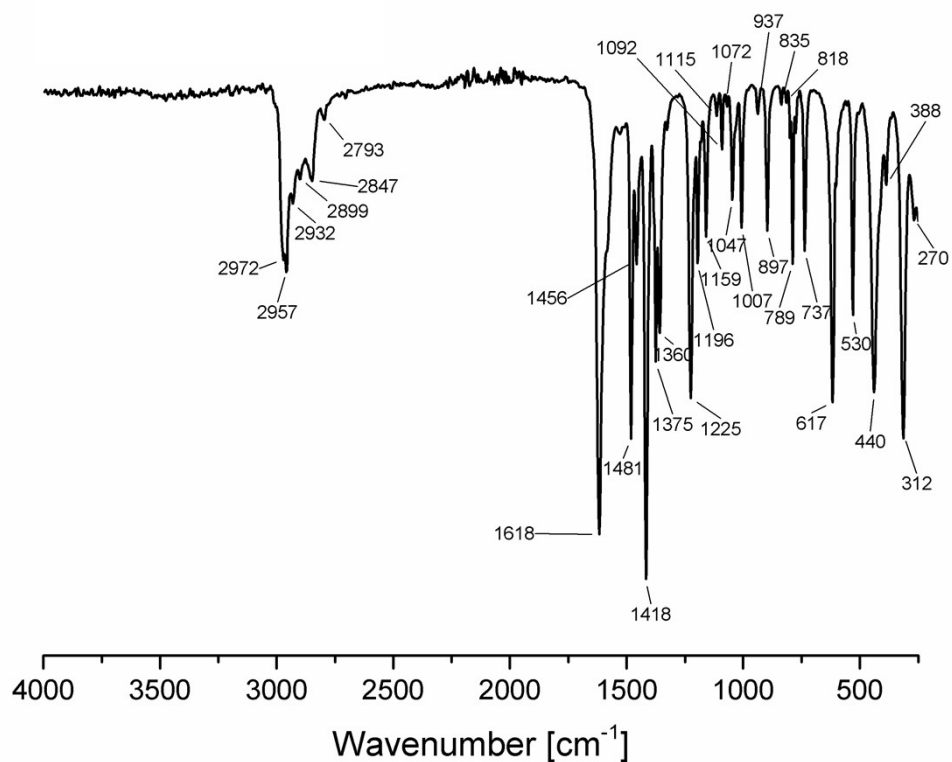


Figure S9 ATR-IR spectrum for the compound $[\text{Cu}_2(\text{Et}_3\text{N})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]$ (**5**).

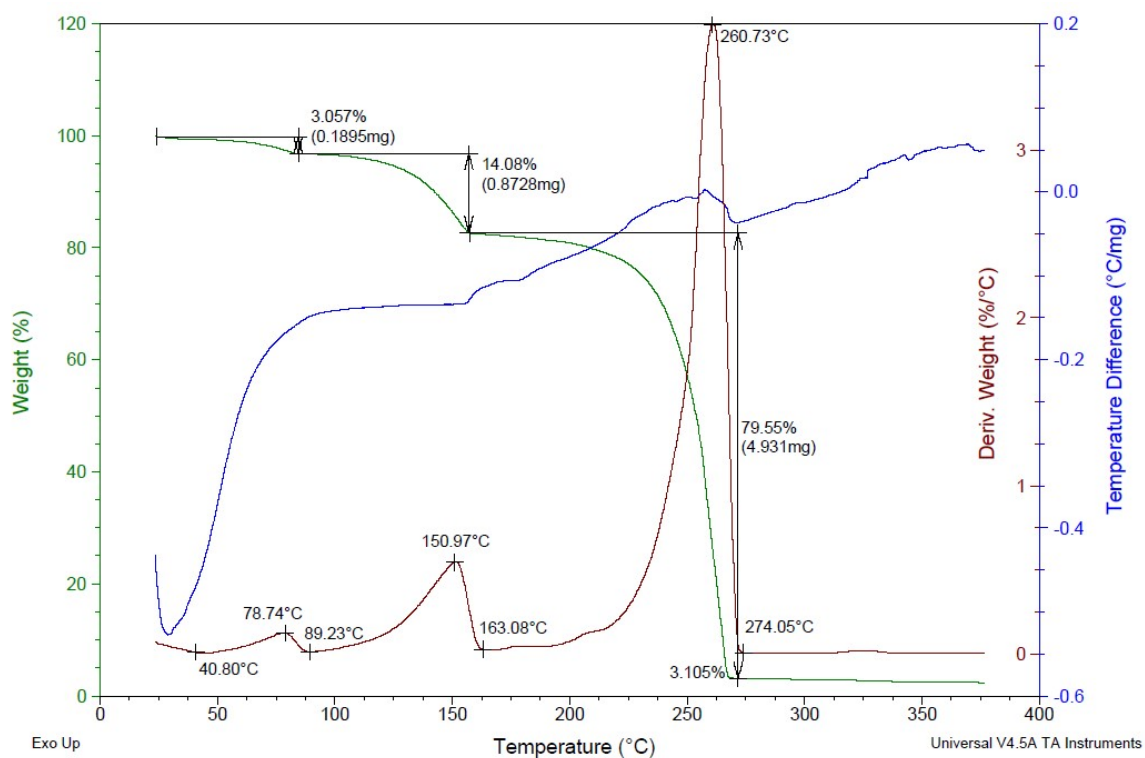


Figure S10 Thermal decomposition of $[\text{Cu}_2(t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (**1**) (TG, DTG, DTA curves).

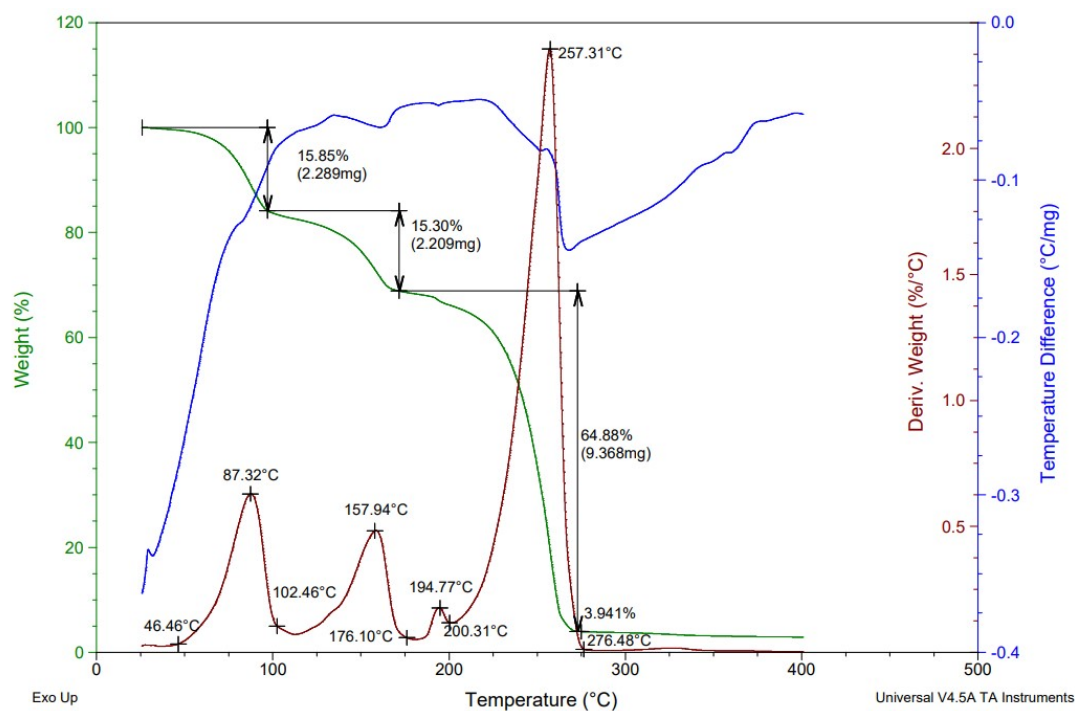


Figure S11 Thermal decomposition of $[\text{Cu}_2(\text{sBuNH}_2)_2(\mu\text{-O}_2\text{C}^i\text{Bu})_4]_n$ (**2**) (TG, DTG, DTA curves).

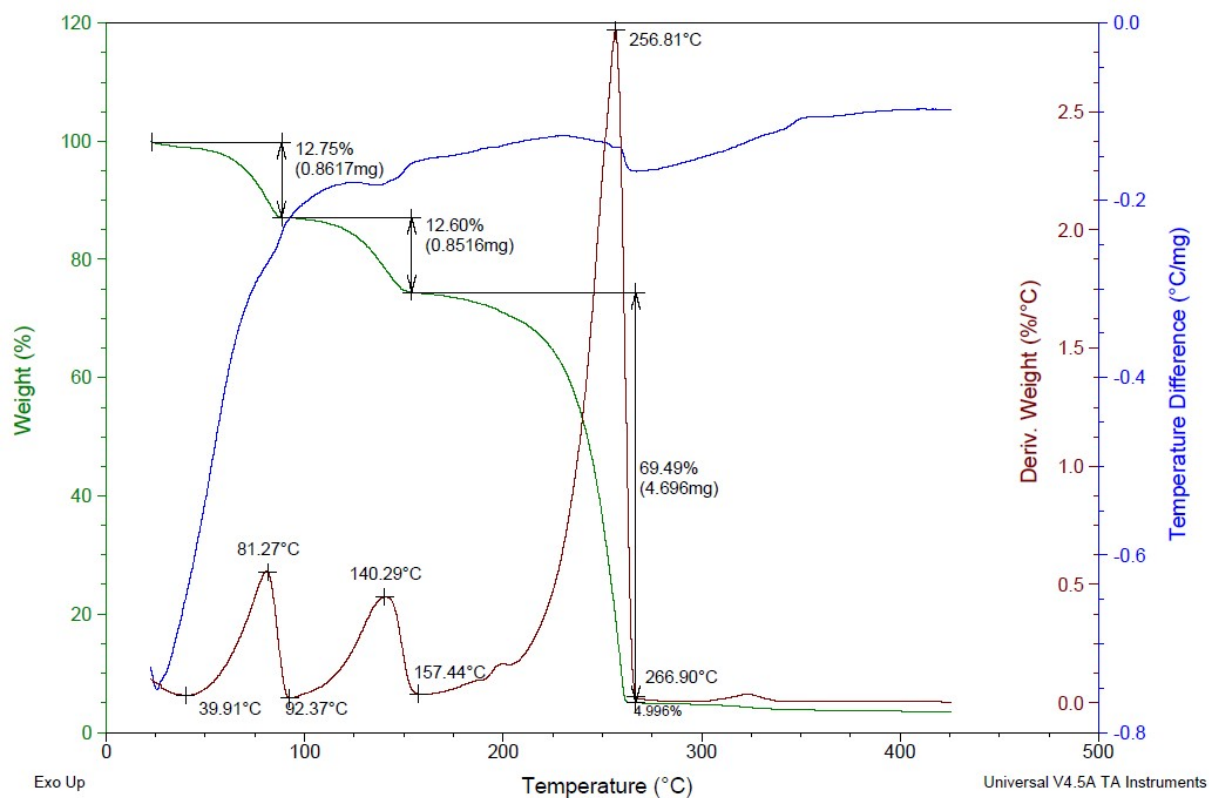


Figure S12 Thermal decomposition of $[\text{Cu}_2(\text{iPrNH}_2)_2(\mu\text{-O}_2\text{C}^i\text{Bu})_4]_n$ (**3**) (TG, DTG, DTA curves).

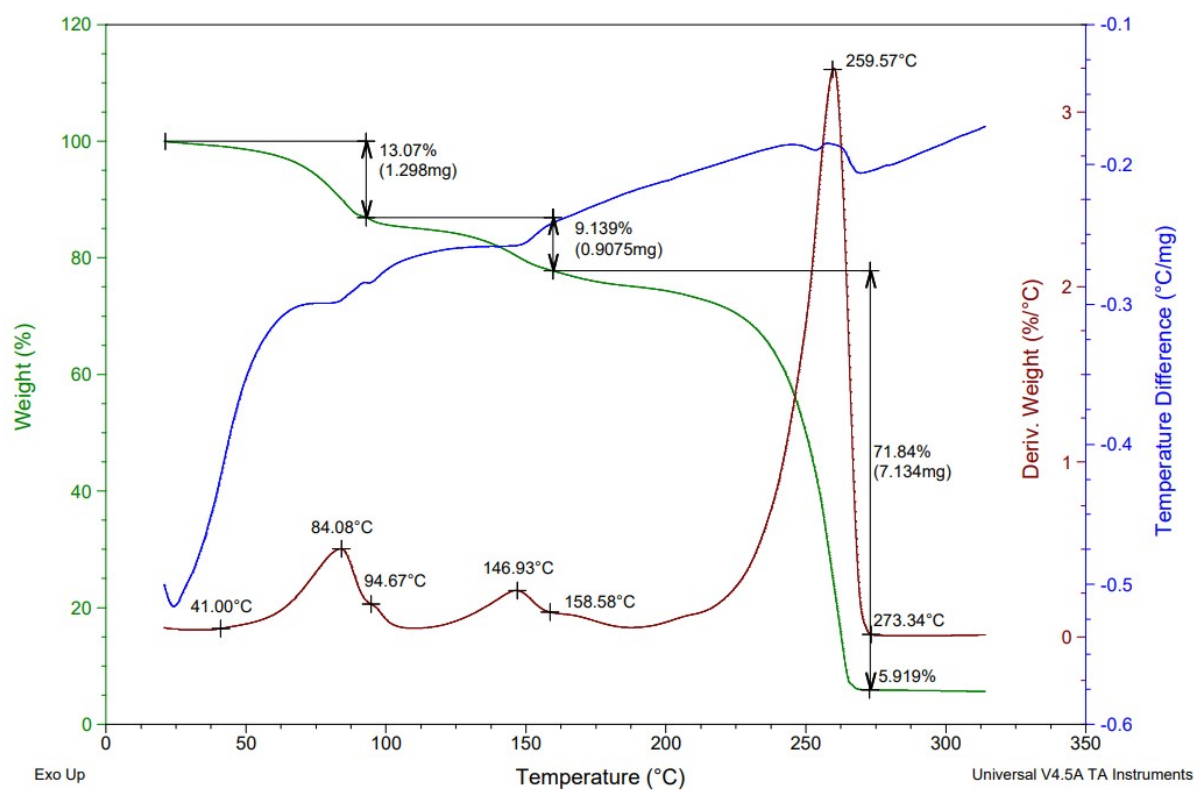


Figure S13 Thermal decomposition of $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (**4**) (TG, DTG, DTA curves).

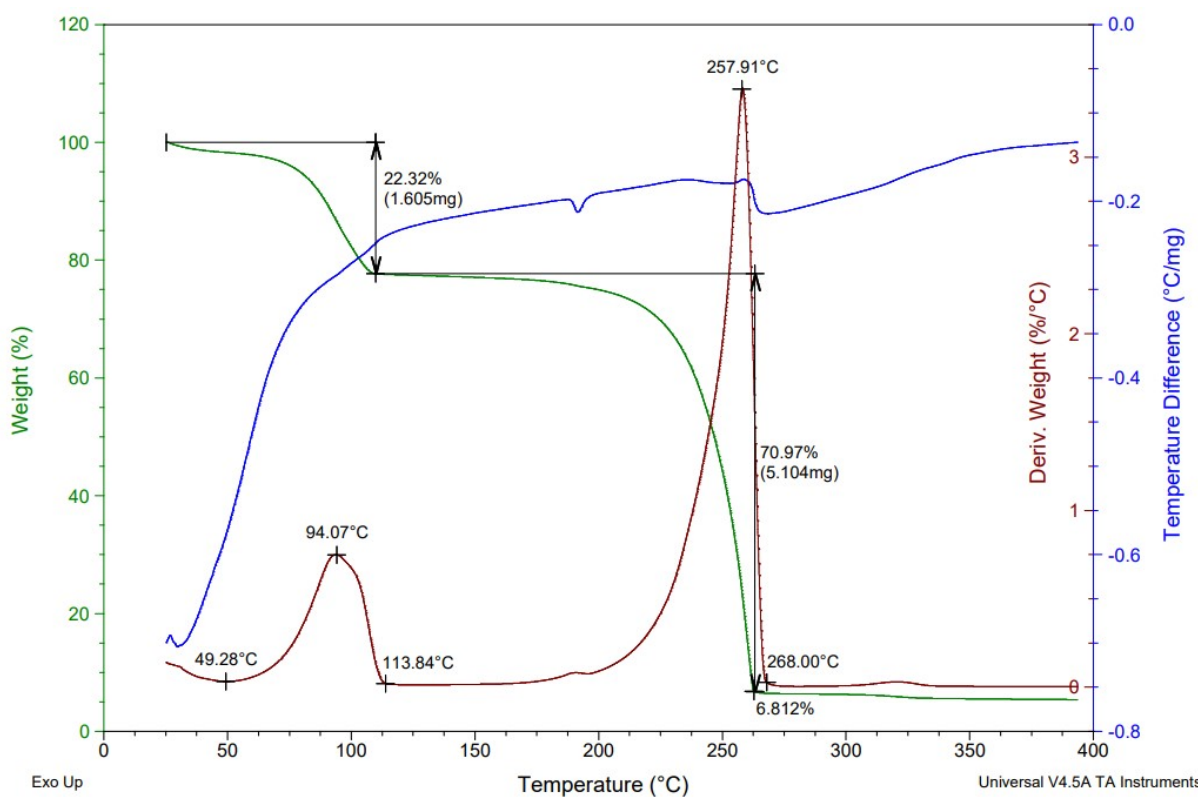


Figure S14 Thermal decomposition of $[\text{Cu}_2(\text{Et}_3\text{N})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]$ (**5**) (TG, DTG, DTA curves).

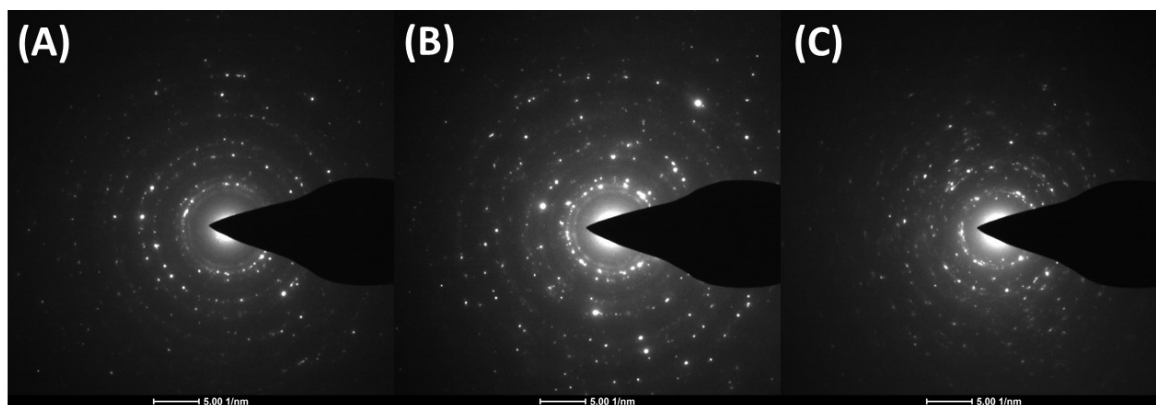


Figure S15 Transmission electron microscope (TEM) diffraction pattern for the TGA final residue: (A) $[\text{Cu}_2(\text{}^s\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (**2**), (B) $[\text{Cu}_2(\text{}^i\text{PrNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (**3**), and (C) $[\text{Cu}_2(\text{Et}_3\text{N})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]$ (**5**).

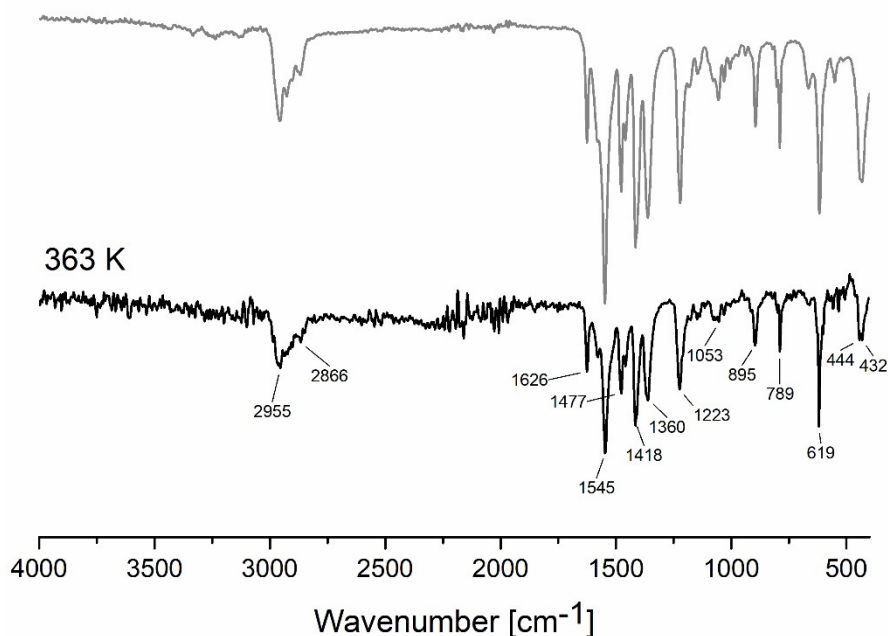


Figure S16 Infrared spectra for the compound $[\text{Cu}_2(\text{}^s\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (**2**) before (grey) and after sublimation (black) at 363 K ($p = 10^{-2}$ mbar).

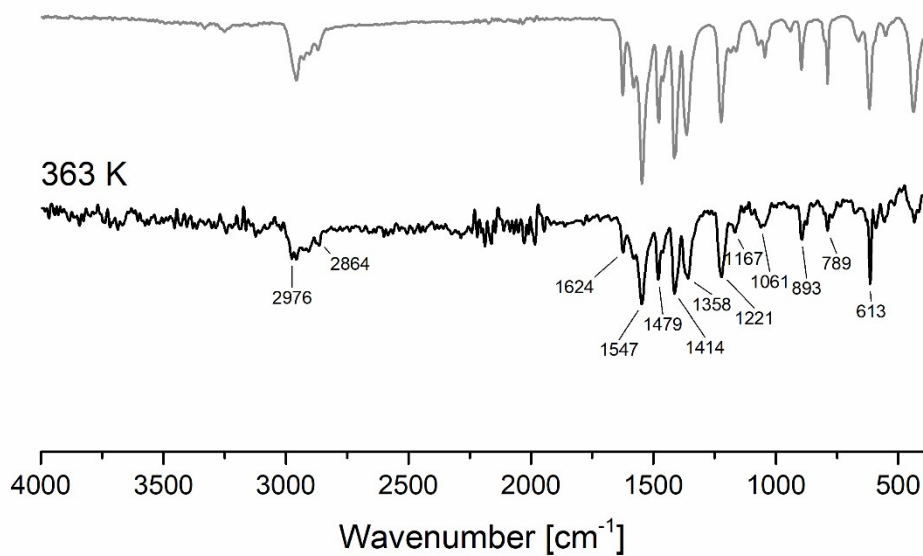


Figure S17 Infrared spectra for the compound $[\text{Cu}_2(\text{iPrNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (**3**) before (grey) and after sublimation (black) at 363 K ($p = 10^{-2}$ mbar).

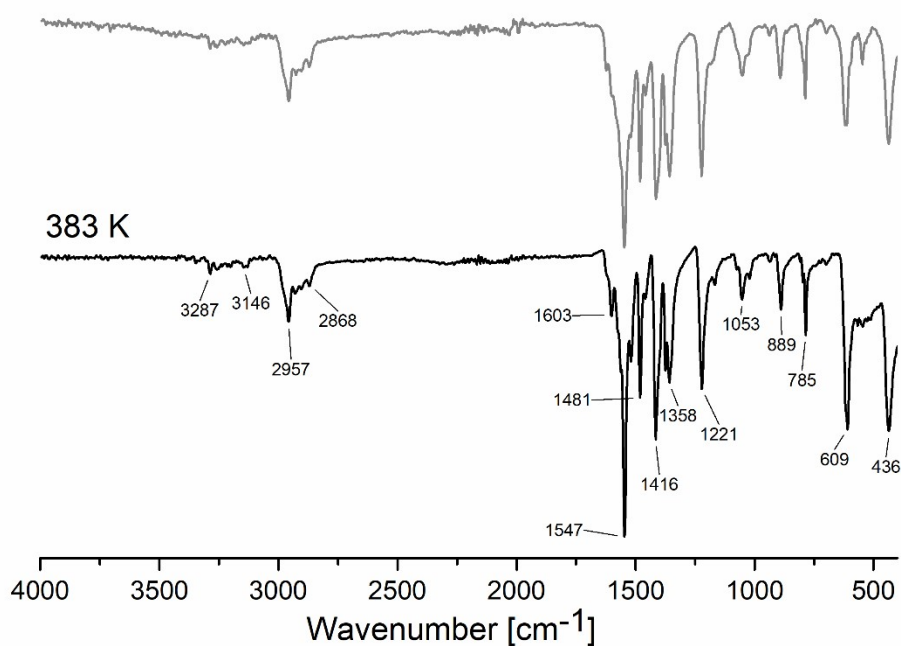


Figure S18 Infrared spectra for the compound $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (**4**) before (grey) and after sublimation (black) at 383 K ($p = 10^{-2}$ mbar).

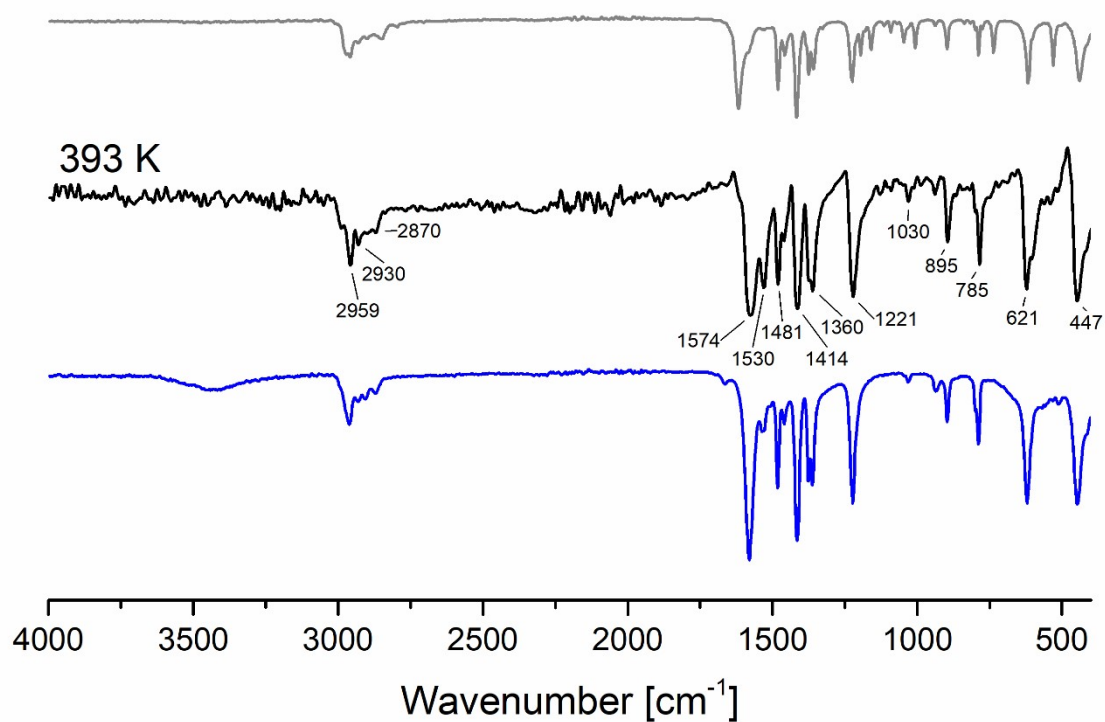


Figure S19 Infrared spectra for the compound $[\text{Cu}_2(\text{Et}_3\text{N})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]$ (**5**) before (grey) and after sublimation attempt (black) at 393 K ($p = 10^{-2}$ mbar), $[\text{Cu}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (**0**) (blue).

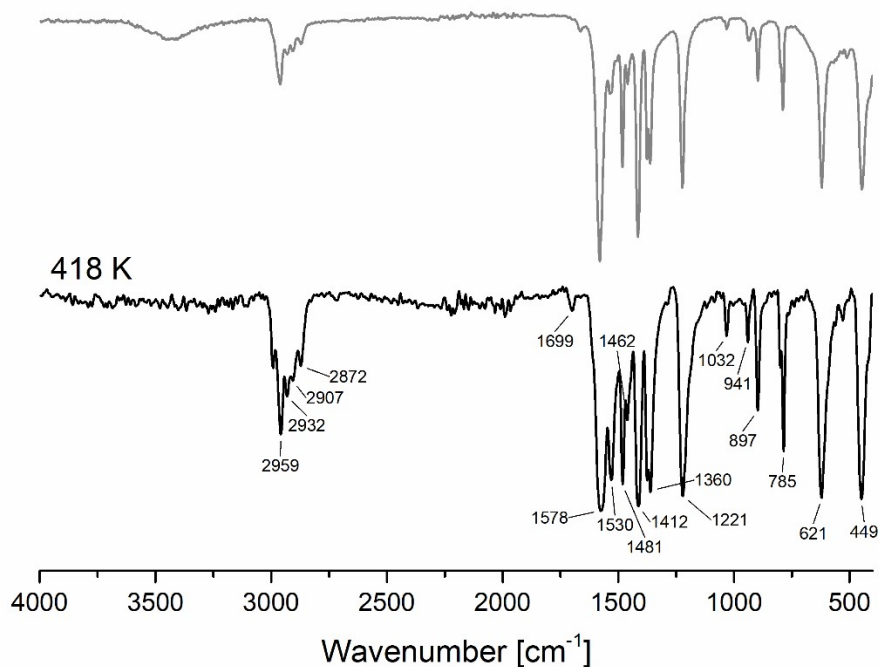


Figure S20 Infrared spectra for the compound $[\text{Cu}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (**0**) before (grey) and after sublimation (black) at 418 K ($p = 10^{-2}$ mbar).

Table S6 Mass spectrometry with electron ionization (EI MS) results for the complex $[\text{Cu}_2(^t\text{BuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]$ (**1**).

Fragments	m/z	Relative Intensity (RI) [%]				
		350 K	370 K	417 K	487 K	525 K
$[\text{C}_2\text{H}_2\text{N}]^+ / [\text{CH}_2=\text{C}=\text{CH}_2]^{+\cdot}$	40	6	11	45	50	40
$[\text{C}_2\text{H}_3\text{N}]^+ / [\text{CH}_2=\text{CH}-\text{CH}_2]^{+\cdot}$	41	1	21	8	10	—
$[\text{C}_2\text{H}_4\text{N}]^+ / [\text{CH}_2\text{CO}]^+$	42	26	35	92	94	88
$[\text{CO}_2]^{+\cdot}$	44	3	1	2	8	—
$[\text{C}_2\text{H}_7\text{N}]^+ / [\text{COOH}]^{+\cdot}$	45	1	—	33	100	25
$[(\text{CH}_3)_2\text{C}=\text{CH}_2]^{+\cdot}$	56	2	2	12	21	—
$[^t\text{Bu}]^+$	57	4	1	29	24	—
$[\text{C}_3\text{H}_8\text{N}]^+ / [\text{C}_4\text{H}_{10}]^{+\cdot}$	58	48	100	100	99	100
$[\text{C}_3\text{H}_9\text{N}]^{+\cdot}$	59	100	26	5	5	8
$[\text{Cu}]^+$	63	1	11	1	—	—
$[\text{C}_3\text{H}_7\text{CO}_2]^+$	87	1	—	5	5	—
$[\text{CuCO}_2]^+$	107	1	6	—	—	—
$[\text{Cu}_2(^t\text{Bu})]^+$	183	3	2	8	—	—
$[\text{Cu}_2(\text{O}_2\text{C}^t\text{Bu})]^+$	227	14	27	36	—	—
$[\text{Cu}_2(\text{O}_2\text{C}^t\text{Bu})_2]^{+\cdot}$	328	12	25	23	—	—
$[\text{Cu}_3(\text{O}_2\text{C}^t\text{Bu})_2]^+$	393	—	6	—	—	—
$[\text{Cu}_3(\text{O}_2\text{C}^t\text{Bu})_5]^+$	696	1	4	—	—	—

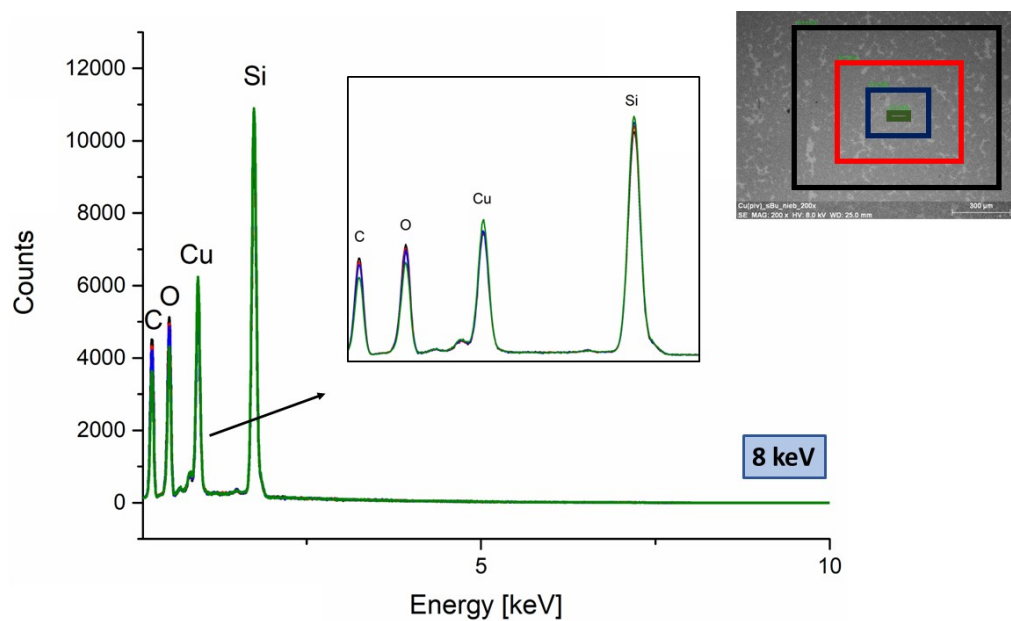


Figure S21 Examined scan areas' EDX spectra (8 keV) for $[\text{Cu}_2(\text{sBuNH}_2)_2(\mu\text{-O}_2\text{C}'\text{Bu})_4]_n$ (2) layer on a silicon wafer.

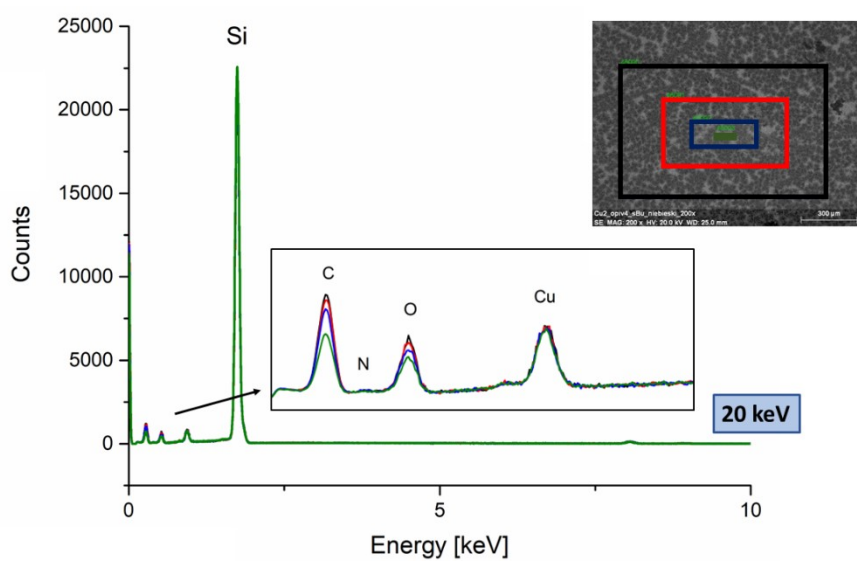


Figure S22 Examined scan areas' EDX spectra (20 keV) for $[\text{Cu}_2(\text{sBuNH}_2)_2(\mu\text{-O}_2\text{C}'\text{Bu})_4]_n$ (2) layer on a silicon wafer.

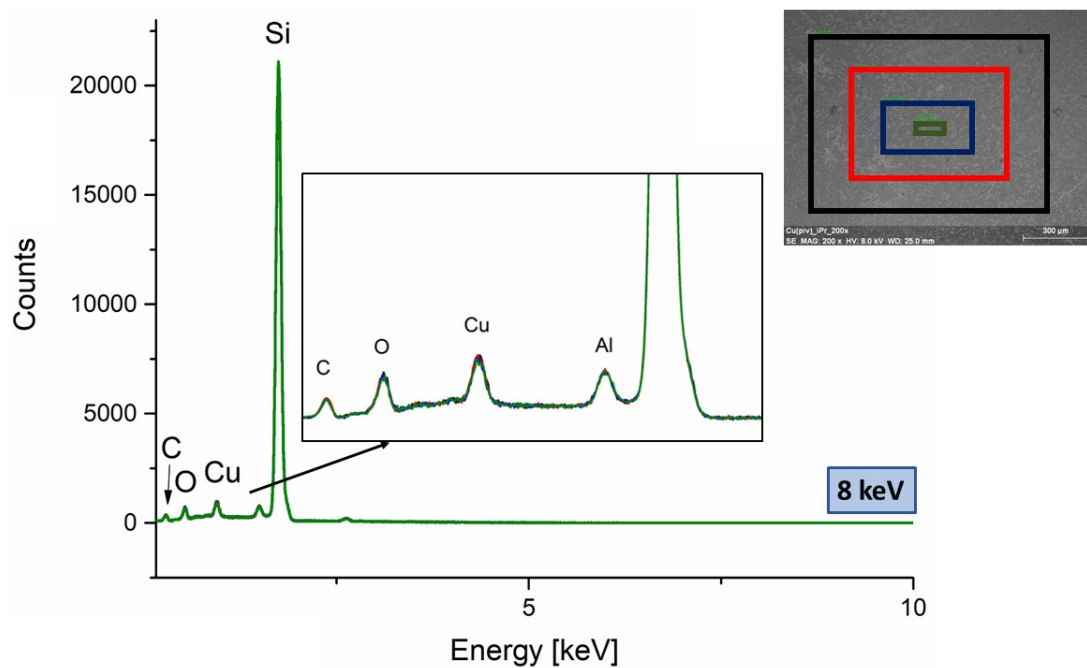


Figure S23 Examined scan areas' EDX spectra (8 keV) for $[\text{Cu}_2(\text{iPrNH}_2)_2(\mu\text{-O}_2\text{C'Bu})_4]_n$ (3) layer on a silicon wafer.

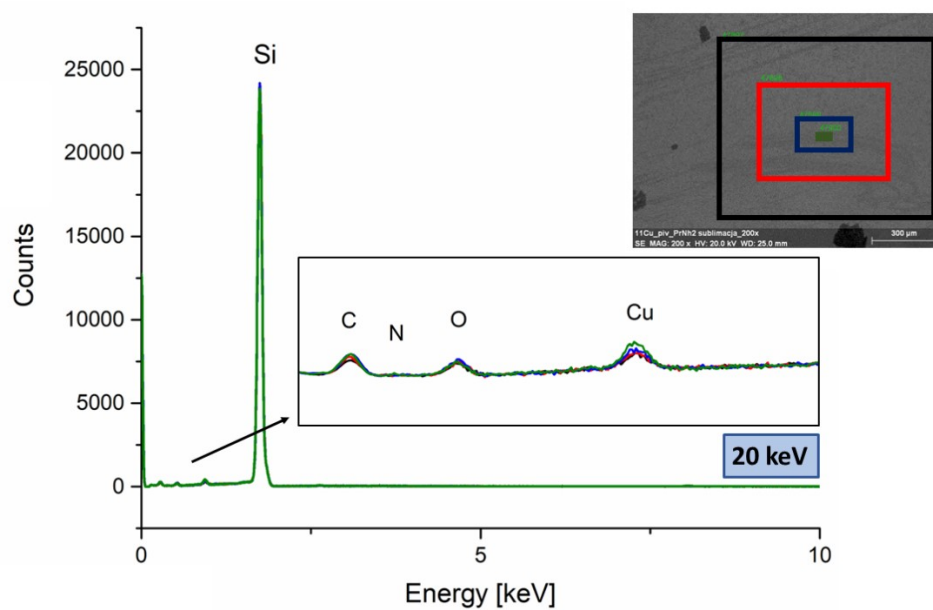


Figure S24 Examined scan areas' EDX spectra (20 keV) for $[\text{Cu}_2(\text{iPrNH}_2)_2(\mu\text{-O}_2\text{C'Bu})_4]_n$ (3) layer on a silicon wafer.

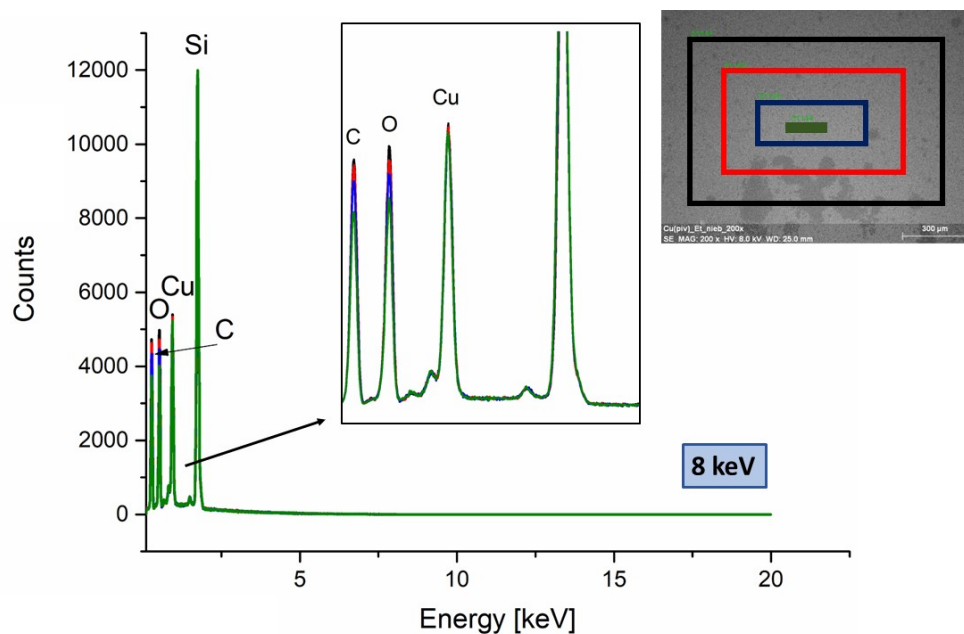


Figure S25 Examined scan areas' EDX spectra (8 keV) for $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (**4**) layer on a silicon wafer.

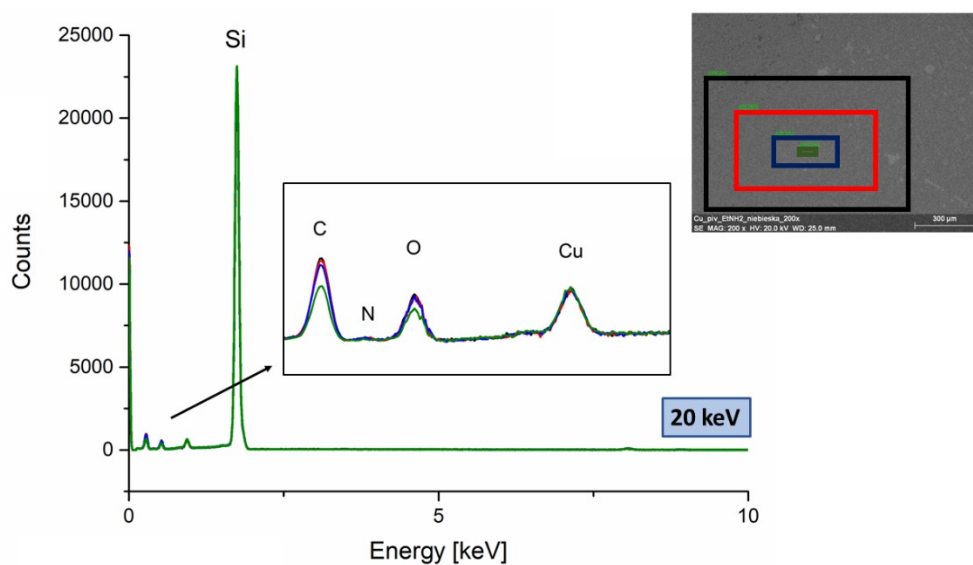


Figure S26 Examined scan areas' EDX spectra (20 keV) for $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (**4**) layer on a silicon wafer.

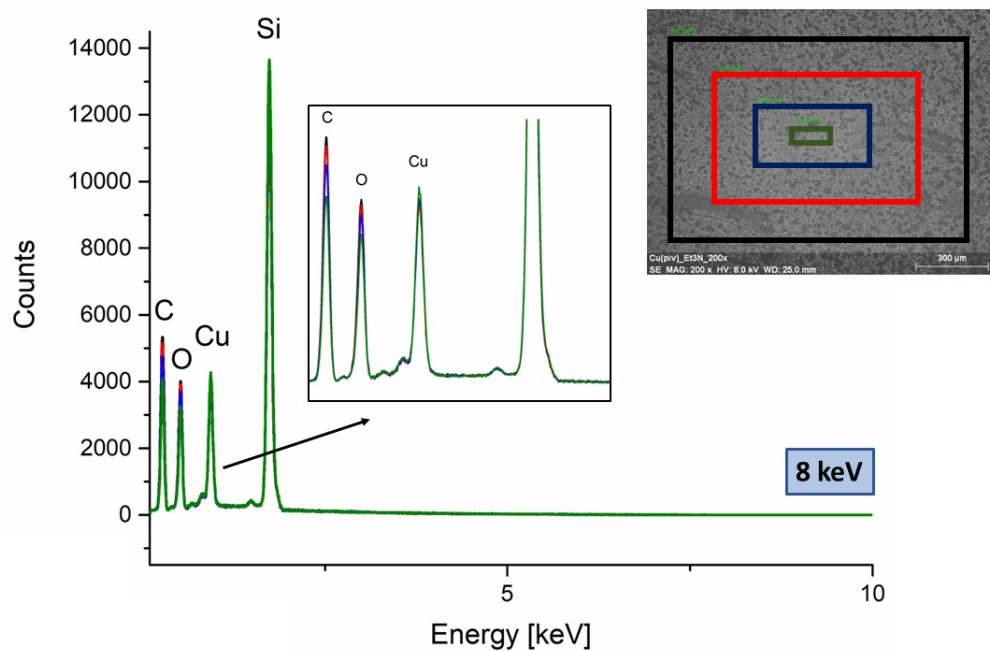


Figure S27 Examined scan areas' EDX spectra (8 keV) for $[\text{Cu}_2(\text{Et}_3\text{N})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]$ (**5**) layer on a silicon wafer.

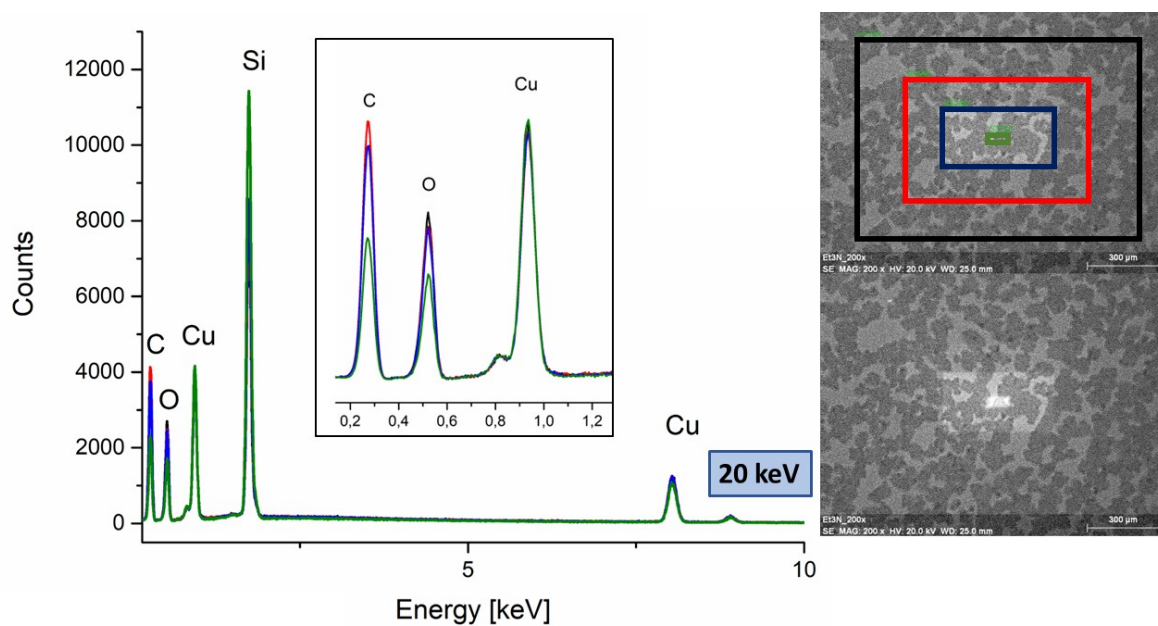


Figure S28 Examined scan areas' EDX spectra (20 keV) for $[\text{Cu}_2(\text{Et}_3\text{N})_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]$ (**5**) layer on a silicon wafer.

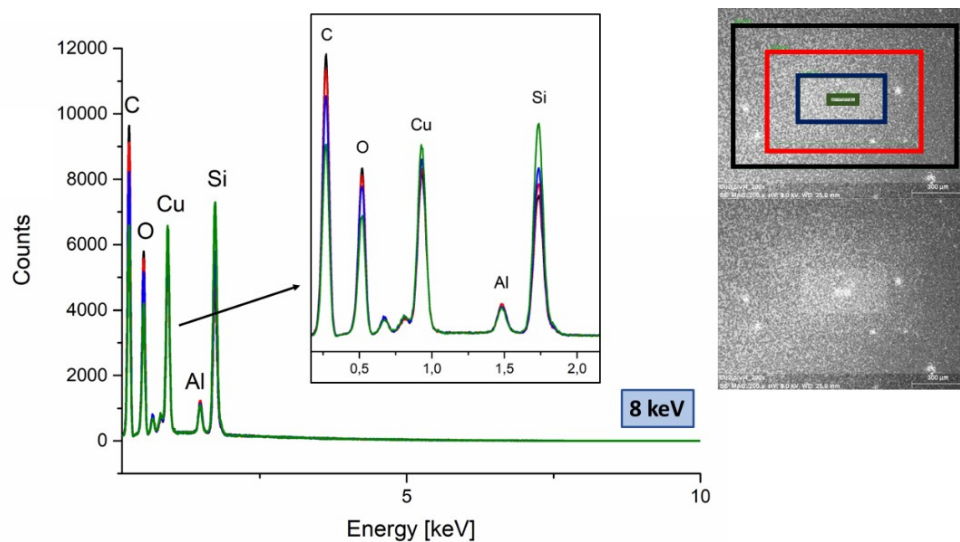


Figure S29 Examined scan areas' EDX spectra (8 keV) for $[\text{Cu}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (0) layer on a silicon wafer.

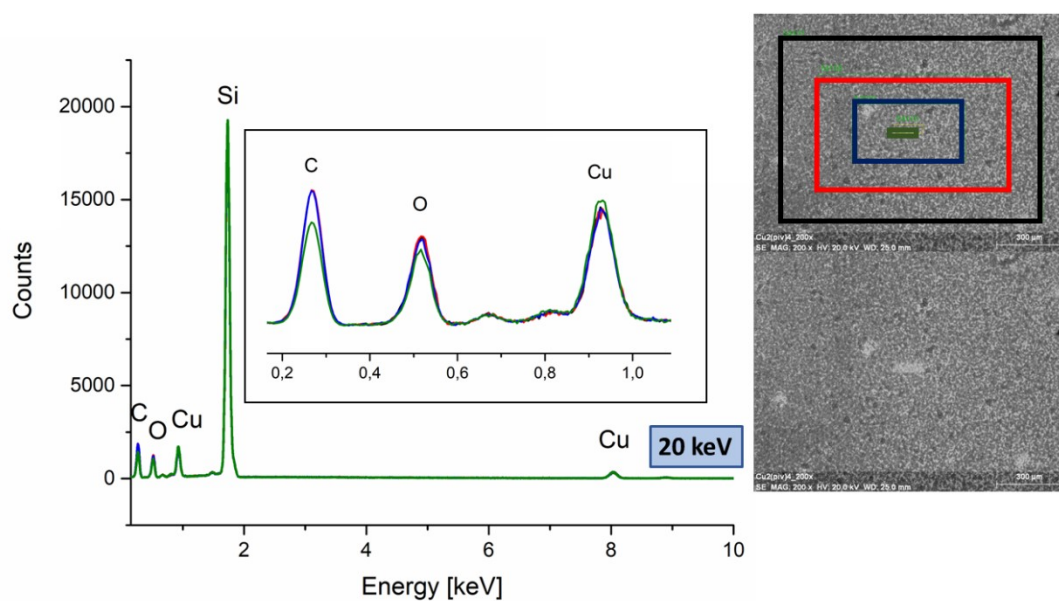


Figure S30 Examined scan areas' EDX spectra (20 keV) for $[\text{Cu}_2(\mu\text{-O}_2\text{C}^t\text{Bu})_2]_n$ (0) layer on a silicon wafer.

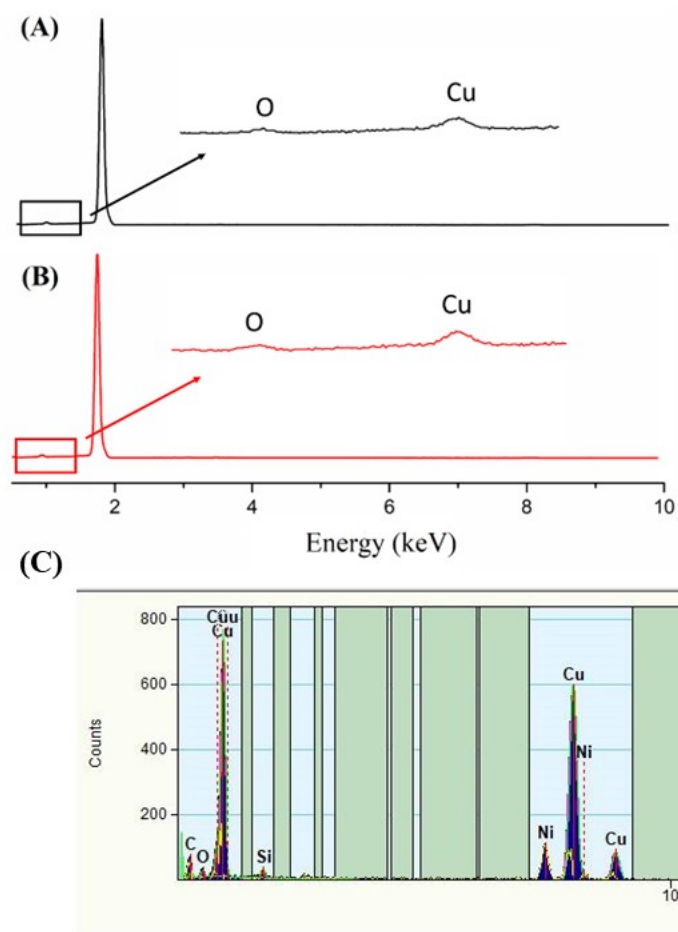


Figure S31 Composition analysis of the obtained materials using $[\text{Cu}_2(\text{tBuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (**1**), (A) for deposit obtained on the second substrate, (B) for deposit obtained on the fourth substrate, (C) EDX spectra from TEM obtained on the fourth substrate.

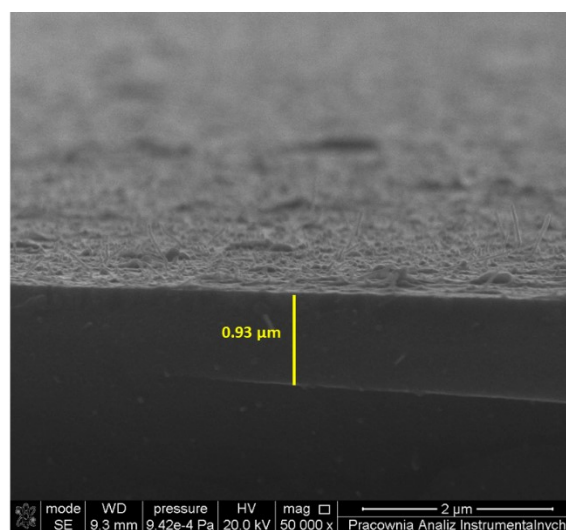


Figure S32 SEM image to show the thickness of the copper layer obtained materials using $[\text{Cu}_2(\text{tBuNH}_2)_2(\mu\text{-O}_2\text{C}^t\text{Bu})_4]_n$ (**1**) for deposit obtained on the second substrate.

PAPER

Nickel complexes based on amidine for applications in gas-assisted methods and photocatalysis†

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The new nickel(II) complexes were investigated as potential precursors for gas-assisted methods: chemical vapor deposition and focused electron or ion beam induced deposition, which are techniques to produce nanomaterials. We report the conventional and mechanochemical 'green' synthesis of amidine-carboxylate $[\text{Ni}_2(\text{NH}_2(\text{NH}=\text{CR}_f)_2(\mu\text{-O}_2\text{CR}_f)_4]$ ($\text{R}_f = \text{CF}_3, \text{C}_2\text{F}_5$) and imidoamidinate $[\text{Ni}(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH}_2)]$ complexes with perfluorinated substituents and their characteristics. Infrared spectroscopy, electron impact mass spectrometry, and density-functional theory calculations were used to confirm the formation of dinuclear amidine-carboxylate and mononuclear imidoamidinate complexes. Additionally, the structure of $[\text{Ni}(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH}_2)] \cdot (\text{NH}_4)(\text{NHOCF}_3) \cdot (\text{NH}_2\text{OCCF}_3) \cdot (\text{H}_2\text{O})$ was solved using single crystal X-ray diffraction. Thermal stability and volatility of the studied compounds were investigated using thermal analysis and sublimation experiments. These results show that $[\text{Ni}_2(\text{NH}_2(\text{NH}=\text{CC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4)]$ and $[\text{Ni}(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH}_2)]$ sublime over a range of 358–423 K under 10^{-2} mbar pressure. Electron impact mass spectrometry of complexes and microscopy studies (SEM/EDX and TEM/EDX) reveal that $[\text{Ni}_2(\text{NH}_2(\text{NH}=\text{CC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4)]$ is the most sensitive to low- and high-energy electrons. For this compound, the nickel-based materials were grown on silicon, glass, and finally titania nanotubes using the chemical vapor deposition (CVD) process. Kinetic tests have shown that the modification of titania nanotubes with nickel strengthens this material's photocatalytic activity in methylene blue photodegradation. The obtained results indicate that the selected compound may be a promising precursor for vapor deposition techniques.

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1. Introduction

Nanomaterials offer significant advantages for a wide range of applications in the nanotechnology sector, including electronics, magnetism, mechanics, and non-noble catalysts.^{1–5} The significant interest devoted to nickel-based nanomaterials stems from their ferromagnetic properties at room temperature, making them ideal for application in modern industry, e.g., magnetic data storage in electronic devices, magnetic sensing, and magnetic force microscopy tips. NiO thin films are employed in various technologies as hole extraction layers for solar cells, displays, light-emitting diodes or photocatalysts.^{6–19}

These deposits can be prepared using various techniques, including vapor deposition methods, e.g. chemical vapor deposition (CVD) and focused electron/ion beam induced deposition (FEBID/FIBID).^{1,20,21} The advantages of CVD include its reproducibility, high deposition rate for a large substrate area and conformal coverage of complex shapes.^{1,22} While FEBID and FIBID offer the unique benefit of enabling the fabrication of 2D and 3D nanostructures with precisely defined dimensions.^{1,2,20,21,23} The CVD precursors exhibit volatility, which is also essential for applications of complexes in FEBID and FIBID. Therefore, they were considered suitable for use in these processes.^{1,24} In FEBID, the dissociation of adsorbed precursor molecules is initiated by a focused electron beam (keV). However, the influence of secondary electrons (eV) produced from the substrate is essential for nanostructure growth. These types of electrons are also significant in FIBID, where they are generated by a focused ion beam.^{1,2,21,23}

The low metal content of FEBID and FIBID deposits, which can impact their functionality, is still a topic of ongoing research. The choice of the precursor is crucial for the successful growth of nanostructures: its chemical nature and dis-

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sociation behaviour determine the composition of the grown material. The following nickel compounds have been tested in FEBID: $[\text{Ni}(\eta^5\text{-CpMe})_2]$ and $[\text{Ni}(\text{PF}_3)_4]$ (12–36 at% Ni).²⁵ Likewise, the deposits for the precursor $[\text{Ni}(\eta^5\text{-CpMe})_2]$ (22 at% Ni) were obtained using an ion beam (FIBID).^{1,26} However, fabricated materials with a high content of this metal without post-deposition purification have still not been obtained.^{2,21,27–30}

In our recent study, a series of $[\text{Cu}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CR}_f)_4]$ ($\text{HAMDC}_2\text{F}_5\text{-(NH}_2\text{(NH=)CC}_2\text{F}_5\text{))}$ compounds have been tested as potential precursors in CVD and FEBID methods. The studies indicate that $[\text{Cu}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ may be potentially used in these techniques for the fabrication of a metallic film by CVD and can be considered a FEBID precursor.³¹ The goal of the present work was to systematically investigate the influence of modifications to the coordination center on volatility and electron sensitivity, using the newly synthesized dinuclear nickel(II) amidine-carboxylate $[\text{Ni}_2(\text{HAMDR}_f)_2(\mu\text{-O}_2\text{CR}_f)_4]$, where $\text{R}_f = \text{CF}_3$, C_2F_5 . Moreover, a new mononuclear imidoamidinate $[\text{Ni}(\text{IAMMDC}_3)_2]$ ($\text{IAMMDC}_3\text{-NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH}$) complex with perfluorinated substituents, which should increase volatility, was investigated. In this study, a green, solvent-free synthesis route was applied to synthesize amidine-carboxylate compounds. The thermal stability and suitability of the complexes for producing metalated volatile species were studied under atmospheric and reduced pressure. The most promising compound $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ was tested in the CVD process. The developed process has been used to obtain potentially useful Ni-TiO₂ photocatalytic materials, considering that TiO₂-based materials are good examples of common semiconductor photocatalysts. Their activity results from the existence of valence (VB) and conduction (CB) bands in solid titania that are relatively close to each other (band gap is *ca.* 3.0–3.4 eV).³² It means that the energy needed to generate free electrons (e_{CB}^-) and holes (h_{VB}^+) in TiO₂ is close to the border of UV and visible light (*ca.* 380 nm). Thus, there is a real possibility of activation of photocatalytic materials in sunlight by TiO₂ modification, *e.g.* with nickel.^{33–36} We also investigate the electron-induced decomposition of the studied complex molecules in the gas phase and their adsorption on a substrate to provide insight into the design of FEBID and FIBID precursors.

In addition, the single crystal of $[\text{Ni}(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH})_2](\text{NH}_4)(\text{NHOC}_2\text{F}_5)(\text{NH}_2\text{OCC}_2\text{F}_5)\cdot\text{H}_2\text{O}$ was grown, which allowed the structure of this compound to be solved. Moreover, Hirshfeld surface analysis was performed to investigate intermolecular interactions in the crystal structure.

2. Experimental

2.1. Materials

Anhydrous acetonitrile (99.8%) and isobutyronitrile (99%) were purchased from Sigma Aldrich (Saint Louis, MO, USA); NiO (99.99%) and trifluoroacetamide $\text{CF}_3\text{C(=NH)NH}_2$ (HAMDCF₃) (85%) were obtained from Alfa Aesar (Haverhill,

MA, USA); and trifluoroacetamide $\text{CF}_3\text{C(=NH)NH}_2$ (HAMDCF₃) (90%) and pentafluoropropylamide $\text{C}_2\text{F}_5\text{C(=NH)NH}_2$ (HAMDC₂F₅) (98.7%) were obtained from Apollo Scientific (Stockport, UK). Nickel(II) perfluorinated carboxylates $[\text{Ni}_2(\mu\text{-O}_2\text{CR}_f)_4]$ ($\text{R}_f = \text{CF}_3$ and C_2F_5) were synthesized following the improved procedure mentioned in the literature,³⁷ using $\text{NiCO}_3\cdot\text{Ni(OH)}_2\cdot 2\text{H}_2\text{O}$ (p.a.) from Avantor Performance Materials Poland (Gliwice, Poland) and CF_3COOH (99%) and $\text{C}_2\text{F}_5\text{COOH}$ (97%) from Sigma Aldrich (Saint Louis, MO, USA). The Si(111) wafers were purchased from the Institute of Microelectronics and Photonics, Centre for Electronic Materials Technology in Warsaw–Lukasiewicz Research Network (Warsaw, Poland). The Si(111) substrates for the CVD experiments were prepared by rinsing for at least 10 min using ultrasonication with acetone, ethanol, and water, then immersing in the $\text{HF}:\text{HNO}_3:\text{H}_2\text{O}$ (1 : 4 : 5) mixture, rinsing twice for at least 10 min with water, and then drying under an argon stream. Glass substrates (borosilicate glass microscope slides) were purchased from Alchem (Warszawa, Poland). The glass substrates for CVD experiments were prepared by rinsing for at least 10 min using ultrasonication with acetone, ethanol, and water, and then dried in an argon stream. Titanium foil (Ti6Al4 V, 0.2 mm thick) was provided by Bimo Tech Sp. z o.o., (Wrocław, Poland). Acetone, 96% ethanol, and 40% HF were used for TNT (titanium nanotubes) substrate preparation, and methylene blue was used for kinetic tests. All these chemicals were purchased from Avantor Performance Materials Poland (Gliwice, Poland). Al_2O_3 (p.a.) was used in the mechanical cleaning of the TNT surface and was provided by Sigma Aldrich (Saint Louis, MO, USA). All reagents were used as received.

2.2. Instrumentation

IR spectra were recorded with a Vertex 70v spectrometer (Bruker Optik, Leipzig, Germany) using a reflective-single reflection diamond ATR unit (200–4000 cm^{-1}). Electron impact mass spectra (EI MS) were recorded using an AutoSpec Premier, Waters Corporation (Milford, MA, USA) over a temperature range of 313–573 K. The C, H, and N contents were determined using a Vario MACRO CHNS ELEMENTAR Analysensysteme (GmbH, Langenselbold, Germany). Thermal studies (TGA/DTA) were performed using an SDT 2960 TA analyzer (New Castle, DE, USA; dry N₂; heating rate 2.5 K min^{−1}) in a heating range of up to 1273 K and a sample mass of 3–10 mg. The sublimation experiments were performed under reduced pressure (10^{−2} mbar) in a glass sublimator with a special holder for the silicon substrate. Variable temperature infrared spectra of vapours (VT IR) were recorded using a PerkinElmer Spectrum 2000 spectrometer (Waltham, MA, USA) over a range 400–4000 cm^{-1} with a medium slit width and a peak resolution of 2.0 cm^{-1} . A glass vessel with the precursor sample (~100 mg) was placed in the homemade reactor tube and heated (from 333 to 613 K) under dynamic vacuum (10^{−1} mbar). Deposition experiments were carried out using a homemade horizontal hot-wall CVD reactor on silicon Si(111), glass (within 60 min), and TNT20 layer on Ti6Al4 V alloy (within

30 min) substrates in argon. The vaporization temperatures T_V were 473 K and 493 K, whereas the deposition temperatures T_D were 723 K and 763 K. The morphology and composition studies of layers of the compounds were performed using scanning electron microscopy using a Quanta 3D FEG, FEI (Hillsboro, OR, USA) and SEM-LEO 1430VP (Cambridge, UK) microscopes (operating voltage 8 and 20 kV), equipped with an energy-dispersive X-ray spectrometer (EDS) Quantax 200 with an Xflash 4010 detector (Bruker AXS microanalysis GmbH, Berlin, Germany), which was also used in preliminary electron sensitivity tests. Transmission electron microscopy using Tecnai G² F20X-Twin and Tecnai G² 20X-TWIN 200 kV, FEI (Hillsboro, OR, USA) microscopes was used to characterize the thermal analysis residue and to test the sensitivity of compounds to high-energy electrons (200 keV). The samples for the TEM experiments were prepared by dissolving the compounds in anhydrous ethanol (99.8%), applying a drop on a carbon-coated copper grid (Lacey type, 400 mesh), and evaporating the solvent at room temperature. The morphology and composition studies of layers of the compounds were performed by scanning electron microscopy using a Quanta 3D FEG (FEI, Hillsboro, OR, USA) microscope and a LEO 1430VP, Ltd, Cambridge, UK (operating voltage 8 and 20 kV) SEM equipped with an energy dispersive X-ray spectrometer (EDS) Quantax 200 with an Xflash 4010 detector (Bruker AXS microanalysis GmbH, Berlin, Germany) which was also used in preliminary electron sensitivity tests. Atomic force microscopy (AFM) analysis of deposits was performed using a Veeco microscope, Veeco (Plainview, NY, USA). Kinetics of methylene blue photodegradation was monitored with an Agilent 8453 spectrophotometer equipped with an Agilent 89090 Peltier temperature controller at 298.1 K by recording spectra of the methylene blue solution in a range 500–800 nm every few minutes. The UV irradiation was carried out using an Emita VP-60 lamp, 180 W, $\lambda_{\max}$ = 365 nm, Famed (Łódź, Poland). The Vis irradiation was performed under a 100 W halogen bulb. The distance between the used lamps and the irradiated solutions was 15 cm. The electrochemical formation of TiO₂ nanotubes was carried out using a PowerLab dual output DC power supply 605D-II equipped with wires with clips.

2.3. DFT calculations

The geometry optimization of the studied compounds and corresponding ligands, based partially on the available crystal structure, was conducted using the M06/6-311G(d,p) method to ensure consistent treatment of the organic ligands and metal complexes and remain consistent, aligning to previous work.³¹ The DFT calculations were performed using Gaussian16 (Wallingford, CT, USA).³⁸

2.4. Software

All graphical data were further processed using OriginPro 9.1. TA Universal Analysis (New Castle, DE, USA) was used to analyze thermograms. Grain size in the deposits was determined by ImageJ, LOCI, University of Wisconsin (Madison, WI, USA). To assign the volatile decomposition products in VT

IR experiments, the recorded spectra were compared with the spectra of molecules in the gas phase collected in SpectraBase.³⁹ Diagrams illustrating the synthesis of compounds 1–5 and the VT IR mechanism were drawn using ChemDraw Ultra version 12.0 (Cambridge, MA, USA). CrystalExplorer 21.5 (revision 608bb32)⁴⁰ was used to calculate Hirshfeld surfaces. All figures of the crystal structures were prepared using DIAMOND 4 version 4.6.8⁴¹ and ORTEP-3⁴² software.

2.5. Synthesis

Synthesis of $[\text{Ni}_2(\text{NH}_2(\text{NH}=\text{CR}_f)_2(\mu\text{-O}_2\text{CR}_f)_4]$ ($\text{R}_f = \text{CF}_3$, C_2F_5) (denoted as $[\text{Ni}_2(\text{HAMDR}_f)_2(\mu\text{-O}_2\text{CR}_f)_4]$ for convenience) (1–4). Complexes 1–4 were synthesized by using two different methods: synthesis in solvent (**Sol**) and mechanochemically (**Mech**), so-called a green chemistry synthesis method. Syntheses were carried out using a glove box under an argon atmosphere.

(Sol) $[\text{Ni}_2(\mu\text{-O}_2\text{CR}_f)_4]$, where $\text{R}_f = \text{CF}_3$ and C_2F_5 (0.5 mmol), was placed in a round-bottomed flask, and 20 cm³ of anhydrous acetonitrile was added, followed by the introduction of trifluoroacetamide or pentafluoropropylamide (HAMDR_f, 1 mmol) to the stirring solution. The resulting marine colour solution was stirred for 24 h. After this time, the solvent was removed under reduced pressure (10^{−2} mbar).

(Mech) $[\text{Ni}_2(\mu\text{-O}_2\text{CR}_f)_4]$, where $\text{R}_f = \text{CF}_3$ and C_2F_5 (0.5 mmol), and trifluoroacetamide or pentafluoropropylamide (HAMDR_f, 1 mmol) were placed in a mortar. Next, the mixture was ground for 5 minutes.

The isolated compounds were green solids, stable in air for months. Yields ranged between (**Sol**) – 40% and 45%; (**Mech**) – 62% and 71%. No single crystals suitable for X-ray structure analysis were obtained for compounds 1–4, despite efforts to grow them from the solution.

Synthesis of $[\text{Ni}(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH}_2)_2]$ (denoted as $[\text{Ni}(\text{IAMDCF}_3)_2]$ for convenience) (5). The synthesis was carried out using Schlenk glassware and a glove box under an argon atmosphere. NiO (1 mmol) was added to 2 cm³ acetonitrile and mixed, and then trifluoroacetamide (2 mmol) was introduced to the reaction mixture and stirred over seven days. The unreacted nickel(II) oxide was removed by filtration and washed with anhydrous acetonitrile. The solvent was evaporated in air. The orange product required purification by sublimation (353 K, 10^{−2} mbar) to give an orange solid stable in air for weeks. Yield: 13%. No analogue product was formed when pentafluoropropylamide was used, even when the reaction conditions were varied.

The reaction was also carried out in isobutyronitrile and the orange single crystals suitable for X-ray structure analysis were grown by slow evaporation of the solvent at room temperature in air $[\text{Ni}(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH}_2)_2] \cdot (\text{NH}_4)(\text{NHOCF}_3) \cdot (\text{NH}_2\text{OCCF}_3) \cdot \text{H}_2\text{O}$ (denoted, for convenience $[\text{Ni}(\text{IAMDCF}_3)_2] \cdot (\text{NH}_4)(\text{NHOCF}_3) \cdot (\text{NH}_2\text{OCCF}_3) \cdot \text{H}_2\text{O}$) (5a) ($\text{NiO}_2\text{N}_{10}\text{H}_{14}\text{C}_{12}\text{F}_{18}$).

$[\text{Ni}_2(\text{HAMDCF}_3)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (1). $\text{Ni}_2\text{O}_8\text{N}_4\text{H}_6\text{C}_{12}\text{F}_{18}$ (calc./found) % C 18.16/18.19, H 0.76/1.05, N 7.06/7.22; $T = 533$ K

(*m/z*, RI %) $[\text{Ni}(\text{HAMDCf}_3)]^+$ (170, 2), $[\text{Ni}(\text{HN}=\text{C}=\text{NH})(\text{O}_2\text{CCF}_3)]^+ / [\text{Ni}(\text{AMDCf}_3)(\text{CO}_2)]^+$ (213, 2), $[\text{Ni}(\text{NCCF}_3)(\text{CF}_3\text{CO})]^+$ (264, 11), $[\text{Ni}_2(\text{HAMDCf}_3)(\text{AMDCf}_3)(\text{O}_2\text{CCF}_3)(\text{NH}_3)]^+$ (469, 11); IR (ATR) 3524, 3373, 3325, 3262, 3194, 1717, 1668, 1576, 1450, 1267, 1190, 1140, 1036, 922, 847, 797, 725, 665, 606, 523, 419, 320, 289, 216 cm^{-1} . Yield: (A) – 45%; (B) – 70%.

$[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (2). $\text{Ni}_2\text{O}_8\text{N}_4\text{H}_6\text{C}_{14}\text{F}_{22}$ (calc./found) % C 18.82/18.86, H 0.68/1.05, N 6.27/6.53; $T = 425$ K (*m/z*, RI %) $[\text{Ni}(\text{HAMDC}_2\text{F}_5)(\text{CO}_2)]^+$ (264, 4), $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\text{O}_2\text{CCF}_3)]^+$ (551, 1), $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)(\text{AMDC}_2\text{F}_5)(\text{O}_2\text{CCF}_3)]^+$ (552, 1), $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\text{O}_2\text{CCF}_3)(\text{NH}_3)]^+$ (570, 4), $[\text{Ni}(\text{AMDC}_2\text{F}_5)_2(\text{O}_2\text{CCF}_3)_2(\text{NH}_3)_2(\text{CO})]^+$ (668, 32); IR (ATR) 3514, 3373, 3325, 3325, 3271, 3206, 1715, 1668, 1566, 1456, 1373, 1335, 1186, 1142, 1028, 851, 770, 795, 727, 673, 521, 434, 384, 295, 231 cm^{-1} . Yield: (A) – 41%; (B) – 62%.

$[\text{Ni}_2(\text{HAMDCf}_3)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (3). $\text{Ni}_2\text{O}_8\text{N}_4\text{H}_6\text{C}_{16}\text{F}_{26}$ (calc./found) % C 19.34/17.49, H 0.61/1.08, N 5.64/5.96; $T = 496$ K (*m/z*, RI %) $[\text{Ni}_2(\text{AMDCf}_3)(\text{O}_2\text{CC}_2\text{F}_5)]^+$ (390, 9), $[\text{Ni}(\text{HAMDCf}_3)_2(\text{O}_2\text{CC}_2\text{F}_5)]^+$ (445, 5), $[\text{Ni}_2(\text{HAMDCf}_3)(\text{O}_2\text{CC}_2\text{F}_5)(\text{CF}_3)]^+$ (460, 27), $[\text{Ni}_3(\text{HAMDCf}_3)(\text{AMDCf}_3)_2(\text{CN})]^+$ (536, 23), $[\text{Ni}_2(\text{AMDCf}_3)(\text{O}_2\text{CC}_2\text{F}_5)_2]^+$ (553, 7); IR (ATR) 3520, 3373, 3327, 3269, 3196, 1713, 1678, 1576, 1429, 1325, 1209, 1155, 1030, 864, 824, 731, 667, 586, 540, 419, 295, 224 cm^{-1} . Yield: (A) – 45%; (B) – 71%.

$[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (4). $\text{Ni}_2\text{O}_8\text{N}_4\text{H}_6\text{C}_{18}\text{F}_{30}$ (calc./found) % C 19.77/20.87, H 0.55/1.80, N 5.12/5.94; $T = 329$ K (*m/z*, RI %) $[\text{Ni}(\text{HAMDC}_2\text{F}_5)(\text{O}_2\text{CC}_2\text{F}_5)]^+$ (383, 4), $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\text{O}_2\text{CC}_2\text{F}_5)]^+ / [\text{Ni}_2(\text{AMDC}_2\text{F}_5)(\text{O}_2\text{CC}_2\text{F}_5)_2]^+$ (603, 2), $[\text{Ni}_3(\text{HAMDC}_2\text{F}_5)(\text{O}_2\text{CC}_2\text{F}_5)_2(\text{NH}_3)]^+$ (681, 4), $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)(\text{O}_2\text{CC}_2\text{F}_5)_3]^+$ (767, 33), $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\text{O}_2\text{CC}_2\text{F}_5)_3(\text{CC}_2\text{F}_5)]^+$ (1060, 6); IR (ATR) 3526, 3375, 3323, 3244, 3198, 1713, 1680, 1551, 1429, 1325, 1207, 1153, 1026, 899, 824, 773, 731, 671, 586, 542, 422, 382, 295, 226 cm^{-1} . Yield: (A) – 40%; (B) – 65%.

$[\text{Ni}(\text{IMAMDCf}_3)_2]$ (5). $\text{NiN}_6\text{H}_4\text{C}_8\text{F}_{12}$ (calc./found) % C 25.29/24.44, H 2.55/3.88, N 11.80/11.74; $T = 334$ K (*m/z*, RI %) $[\text{Ni}(\text{HN}=\text{C}=\text{NH})]^+$ (100, 6), $[\text{Ni}(\text{NCCF}_3)]^+$ (153, 5), $[\text{Ni}(\text{NHNH}_2\text{CCF}_3)]^+$ (170, 11), $[\text{Ni}(\text{NHCNCNH})_2]^+$ (194, 9), $[\text{Ni}(\text{NHCNCNH})_2(\text{NH}_3)]^+$ (211, 18), $[\text{Ni}(\text{NH}_2\text{CNCNH})_2(\text{NH}_3)_2]^+$ (230, 53), $[\text{Ni}(\text{CF}_3\text{NCCF}_3\text{N})]^+$ (236, 11), $[\text{Ni}(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH})]^+$ (264, 13), $[\text{Ni}(\text{NH}_2\text{C}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH})]^+$ (265, 66), $[\text{Ni}(\text{CNC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NC})]^+$ (286, 40), $[\text{Ni}(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH})_2]^+$ (470, 99); IR (ATR) 3366, 3285, 3047, 1609, 1547, 1495, 1339, 1288, 1202, 1150, 1088, 959, 837, 775, 752, 646, 590, 544, 459, 397, 378, 276 cm^{-1} . Yield: 13%.

2.6. X-ray crystal structure determination

The single-crystal diffraction data for compound $[\text{Ni}(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH})_2] \cdot (\text{NH}_4)(\text{NHOCF}_3) \cdot (\text{NH}_2\text{OCCF}_3) \cdot \text{H}_2\text{O}$ (5a) were collected at 100 K using an XtaLAB Synergy (Dualflex) diffractometer with a HyPix detector, $\text{CuK}\alpha$ radiation $\lambda = 1.54184$ Å. The data reduction was performed using CrysAlis Pro for the studied compound,⁴³ and the Gaussian absorption correction was applied. The compound's structure was solved using direct methods and refined with a full-matrix least-squares

procedure on F^2 (SHELXT).⁴⁴ All heavy atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to nitrogen or oxygen atoms were located on the difference electron density maps and refined isotropically. For the $\text{C}_{32}(\text{NH})\text{O}$ group a rotational disorder is observed with oxygen and nitrogen atoms sharing the same positions and with 0.55:0.45 occupancies. Hence, EXYZ and EADP commands were used for this group. In the final model one hydrogen atom attached to disordered N_{32} amidate nitrogen atom is missing. For the water molecule two geometrical restraints for O–H bond lengths (DFIX) were applied.

The results of data collection and refinement have been summarized in the ESI (Table S1†), such as selected bond lengths and angles (Table S2†). CCDC 2375574† contains supplementary crystallographic data for compound 5a.

2.7. Covering of Ti6Al4 V with titania nanotubes

TiO_2 nanotube layers (TNT) were formed on the Ti6Al4 V titanium alloy during the anodic oxidation process (20 V, 20 min). Before anodization, the foil was cut into 1 cm × 7 cm pieces, which had been rubbed with sandpaper (2500 grit). Then, the cut foils were washed three times in an ultrasonic bath for 15 min in acetone, ethanol, and water, respectively. Just before the electrolysis, each piece of foil was immersed for 30 s in the $\text{HF}:\text{HNO}_3:\text{H}_2\text{O}$ mixture (1:4:5). After anodization, the titanium foils were washed with deionized water containing a small portion of Al_2O_3 powder in an ultrasonic bath for 5 min and then washed again in pure deionized water for 15 min. Finally, the foils were dried in an argon stream and cut into 1 cm × 1 cm pieces.³²

2.8. Photocatalytic activity tests of TNT and Ni-TNT deposits

The photocatalytic activity of titania nanotubes formed at a potential 20 V modified by the CVD technique using $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (4) as a precursor (Ni-TNT20) and without modification (TNT20) has been tested in the methylene blue (MB) degradation process under UV irradiation. The starting concentration of MB in the reaction mixture (3 cm^3) was 1×10^{-5} mol dm^{-3} . Tests were repeated three times for the solution: without the catalyst (REF) and with the immersed 1 cm^2 of the deposit (TNT20 and Ni-TNT20). To achieve an equilibrium in MB adsorption processes on the surfaces (or the reactor glass), each solution prepared for the experiment was kept in darkness for 3 hours before UV irradiation. Changes in the absorbance were recorded spectrophotometrically after 50 μl of the reaction mixture was added to 600 μl of deionized water placed in a quartz cuvette (blank) (total cuvette volume: 1400 μl). The next spectrum was recorded after adding the next 50 μl of the reaction mixture to the previous solution in the cuvette (recorded as a new blank, vol.: 650 μl). This procedure was repeated several times.

3. Results and discussion

In the acetonitrile solvent or by a direct mechanochemical 'green' process, two amidine molecules are coordinated by

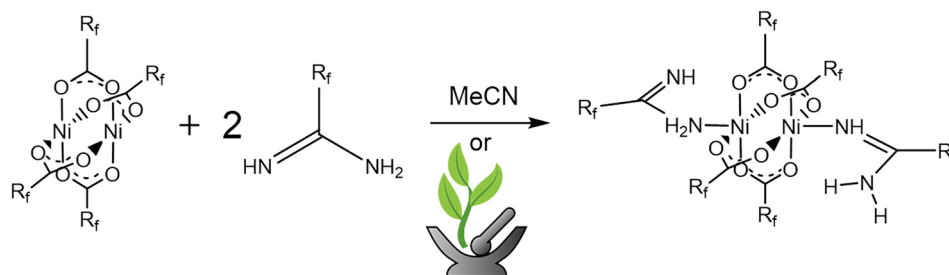


Fig. 1 Reaction scheme for the synthesis of nickel complexes $[\text{Ni}_2(\text{HAMDR}_f)_2(\mu\text{-O}_2\text{CR}_f)_4]$, where $\text{R}_f = \text{CF}_3$ and C_2F_5 (1–4).

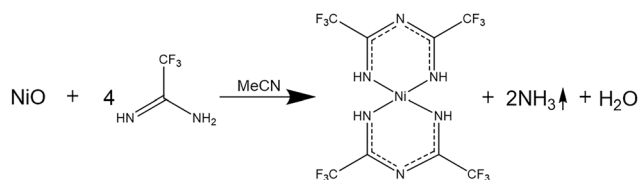


Fig. 2 Reaction scheme for the synthesis of the nickel complex $[\text{Ni}(\text{IMAMDCF}_3)_2]$ (5).

dinuclear nickel(II) carboxylate and complexes of formula $[\text{Ni}_2(\text{HAMDR}_f)_2(\mu\text{-O}_2\text{CR}_f)_4]$, where $\text{R}_f = \text{CF}_3$ and C_2F_5 , (1–4) were formed (Fig. 1).

In the case of compound 5 during the nickel(II) oxide reaction with a perfluorinated amidine, a new imidoamidinate ligand $(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH})$ is formed *in situ* as a result of condensation of 4 amidine molecules with the released ammonia. This is consistent with data reported for perfluorinated amidine.⁴⁵ Next, it is coordinated in the chelate mode to the metal centre, forming the mononuclear complex of the formula $[\text{Ni}(\text{IMAMDCF}_3)_2]$. Compound 5 required purification by the sublimation process (at 353 K). In addition, the reaction was also carried out in isobutyronitrile and single crystals of $[\text{Ni}(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH})_2](\text{NH}_4)$

$(\text{NH}_4\text{OCCF}_3)(\text{NH}_2\text{OCCF}_3)\cdot\text{H}_2\text{O}$ (5a) were formed (Fig. 2). The yield of compound 5a was relatively small; therefore, only complex 5 was studied for its potential use in CVD and FEBID methods.

The obtained compounds (1–4) were green solid, stable in air for months, orange powder (5) stable in air for weeks, or orange crystals (5a) stable in air for days.

3.1. Crystallography

$[\text{Ni}(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH})_2](\text{NH}_4)(\text{NH}_4\text{OCCF}_3)(\text{NH}_2\text{OCCF}_3)\cdot\text{H}_2\text{O}$ (5a) crystallises in the triclinic $P\bar{1}$ space group with all atoms located in the general positions. In the asymmetric unit, a nickel(II) block with two imidoamidinate ligands, amide molecule, amide anion, ammonium cation, and water molecule are found. Note that in the N_{32} amide, a hydrogen atom is missing because it cannot be located on the difference electron density map due to rotational disorder of this group (Fig. 3).

The Ni atom has a square planar geometry ($\tau_4 = 0.014$, $\tau'_4 = 0.010$)^{46,47} comprising four nitrogen atoms with Ni–N distances being 1.8587(17)–1.8642(18) Å. The valence angles range from 89.66(8) to 90.43(8)° and from 178.42(8) to 179.59(8)° (Table S2†). In packing along the a axis we observe columns of nickel moieties. The voids between those molecules are filled

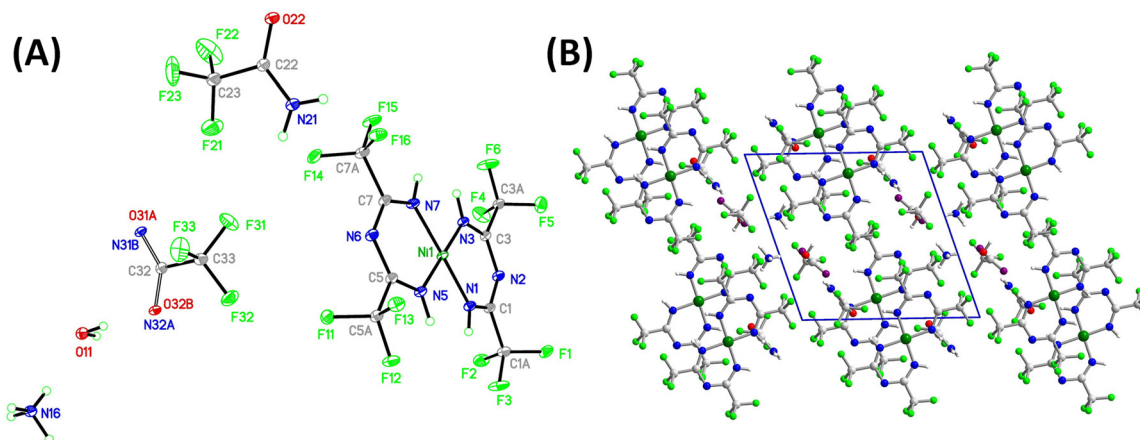


Fig. 3 (A) The structure of $[\text{Ni}(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH})_2](\text{NH}_4)(\text{NH}_4\text{OCCF}_3)(\text{NH}_2\text{OCCF}_3)\cdot\text{H}_2\text{O}$ (5a) with ellipsoids at the level of 30% probability (dark green – nickel atom; dark blue – nitrogen atoms; grey – carbon atoms; green – fluorine atoms; red – oxygen atoms; disordered N_{32} group – violet) and (B) the crystal network of (5a) along the a axis.

with amide, amidate, ammonium cation and water molecules providing an important contribution to the crystal network stability, which is maintained mainly by a robust network of inter-

molecular hydrogen bonds. The following hydrogen bonds are found $\text{N-H}_{\text{im}} \cdots \text{O}_{\text{aq}}$, $\text{N-H}_{\text{im}} \cdots \text{N}_{\text{am}}$, $\text{N-H}_{\text{am}} \cdots \text{O}_{\text{am}}$, $\text{N-H}_{\text{am}} \cdots \text{O}_{\text{aq}}$, $\text{N-H}_{\text{cat}} \cdots \text{N}_{\text{im}}$, $\text{N-H}_{\text{cat}} \cdots \text{N}_{\text{am}}$, $\text{N-H}_{\text{cat}} \cdots \text{O}_{\text{aq}}$, $\text{N-H}_{\text{cat}} \cdots \text{F}_{\text{am}}$, $\text{O-H}_{\text{aq}} \cdots \text{N}_{\text{am}}$

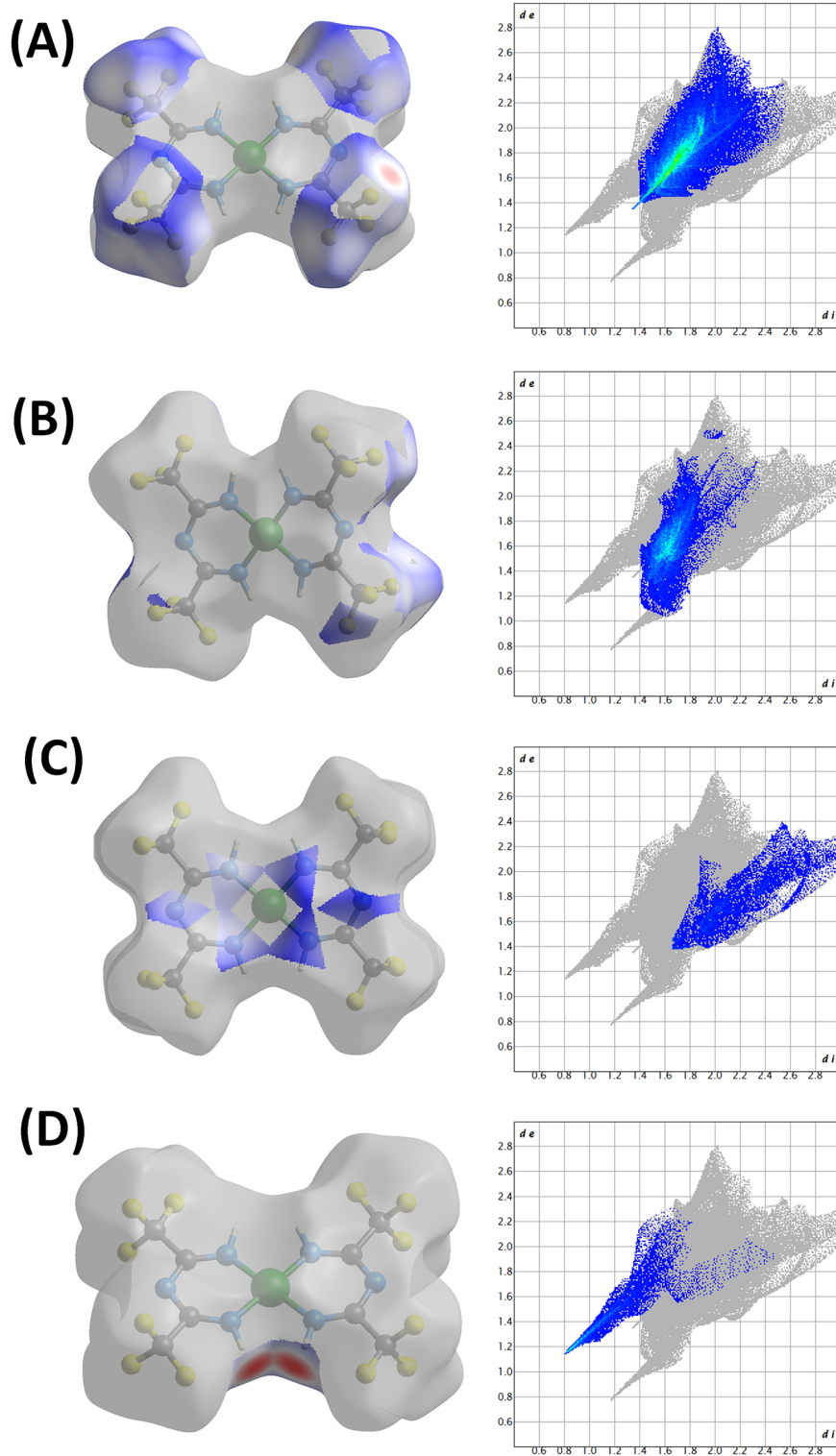


Fig. 4 Hirshfeld surfaces (left) and fingerprints (right) of selected interactions created in the crystal network of $[\text{Ni}(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH}_2)_2] \cdot (\text{NH}_4)(\text{NH}_2\text{OCCF}_3) \cdot (\text{H}_2\text{O})$ (**5a**) for the $[\text{Ni}(\text{IMAMDCF}_3)_2]$ molecule: (A) for $\text{F} \cdots \text{F}$ (40.7%), (B) for $\text{F} \cdots \text{H}$ (17.9%), (C) for $\text{N} \cdots \text{F}$ (6.4%), and (D) for $\text{H} \cdots \text{O}$ (5.6%).

and $\text{O-H}_{\text{aq}} \cdots \text{N}_{\text{im}}$ involving all hydrogen atoms of $-\text{NH}$ and $-\text{NH}_2$ groups, ammonium cations as well as from water molecules. Hence, such bonds are formed between different units but not between identical moieties. This pattern is completed by $\text{C-F} \cdots \pi$ (Fig. S1†) intermolecular interactions between the chelate ring amidine molecules and $\pi-\pi$ interactions between the chelate ring of nickel units involved in zipper formation. It is confirmed by the projection of those interactions on the Hirshfeld surface showing many short $\text{H} \cdots \text{N}$, $\text{H} \cdots \text{O}$ and also $\text{F} \cdots \text{C}$ interactions (Fig. 4). The $\text{F} \cdots \text{F}$ contacts are the most numerous as there are many exposed fluorine atoms in those units. The presence of numerous short intermolecular interactions in the crystal structure may suggest that compound $[\text{Ni}(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH})_2] \cdot (\text{NH}_4)(\text{NHOCF}_3) \cdot (\text{NH}_2\text{OCCF}_3) \cdot \text{H}_2\text{O}$ (**5a**) is not suitable for use in vapor deposition methods. However, it should be noted that only a limited amount of this complex was obtained (**5a**), therefore, it was not possible to determine its sublimation temperature.

3.2. Infrared spectral analysis supported by DFT calculations

$[\text{Ni}_2(\text{HAMDRf})_2(\mu\text{-O}_2\text{CRf})_4]$ (**1–4**). In the infrared spectra of the complexes $[\text{Ni}_2(\text{HAMDRf})_2(\mu\text{-O}_2\text{CRf})_4]$ (**1–4**), the bands at *ca.* 1674 cm^{-1} and shoulder peak at *ca.* 1715 cm^{-1} result from the overlapping of the signals attributed to $\nu_{\text{as}}\text{COO}$ and νCN groups, Fig. 6 and Fig. S2–S5†, which is consistent with the theoretical results (Fig. 5). The signals for symmetric stretching vibration were observed over a range of $1456\text{--}1429 \text{ cm}^{-1}$ and the calculated parameter $\Delta\nu = \nu_{\text{as}}\text{COO} - \nu_{\text{s}}\text{COO}$, were *ca.* 215 cm^{-1} for the compounds with trifluoroacetates (**1**) and (**2**)

and *ca.* 250 cm^{-1} for pentafluoropropionates (**3**) and (**4**) (Table S3†). The $\Delta\nu$ values are close to the $\Delta\nu\text{RCO}_2\text{Na}$ for sodium trifluoroacetate (223 cm^{-1}) and pentafluoropropionate (268 cm^{-1}), respectively, indicating the bridging coordination mode of the carboxylate ligands.

The new nickel(II) complexes $[\text{Ni}_2(\text{HAMDRf})_2(\mu\text{-O}_2\text{CRf})_4]$ (**1–4**) are similar to the previously described copper(II) compounds $[\text{Cu}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CRf})_4]$ ³¹ where amidine was coordinated by the $=\text{NH}$ group. However, a second possibility, implying binding by the NH_2 group, was also theoretically considered. Based on the calculation results for the nickel(II) complexes with $=\text{NH}$ bonded amidine, we expect the presence of three bands in the region typical of stretching vibrations of the N-H bonds (Fig. 5). However, five bands in this area of the NH_2 and $=\text{NH}$ groups stretching vibrations ($3526\text{--}3194 \text{ cm}^{-1}$) were observed (Table S3† and Fig. 5, 6). The difference in the number of bands in the theoretical (Fig. 5) and experimental spectra (Fig. 5, 6 and Fig. S5†) depends on the coordination mode. Therefore, calculation of the spectrum of $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ for which one amidine is bonded by $=\text{NH}$ and the second by NH_2 group have been performed (Fig. 5). The simulated spectrum (Fig. 5) shows two sets of the asymmetric vibration characteristic of the NH_2 group and one band each for νNHCNH_2 , $\nu_{\text{s}}\text{NH}_2$ and $\nu=\text{NH}$, which is consistent with the experimental data (Table S3† and Fig. 5, 6). These theoretical and experimental results led us to propose the coordination of one amidine by $=\text{NH}$ and the second by the NH_2 group. Based on these results and previously reported data for $[\text{Cu}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CRf})_4]$,³¹ it can

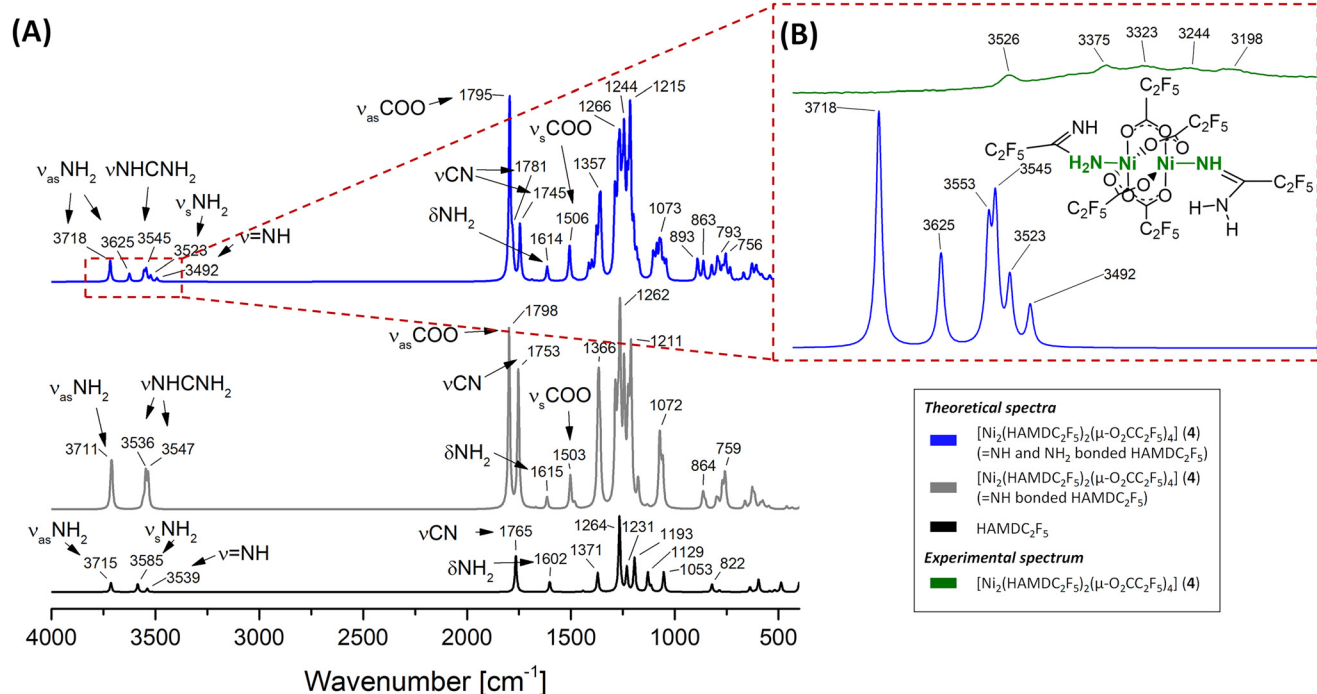


Fig. 5 Theoretical IR spectrum (DFT M06/6-311G(d,p)) for $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (**4**): $=\text{NH}$ and NH_2 bonded amidine (blue), $=\text{NH}$ bonded amidine (grey), and HAMDC_2F_5 (black) – (A). The enlarged region of experimental (green) and theoretical (blue) spectra – (B) for complex **4**.

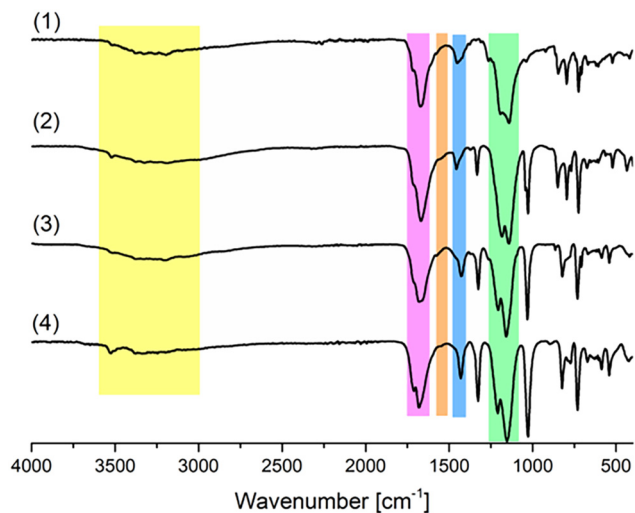


Fig. 6 ATR-IR spectrum for compounds $[\text{Ni}_2(\text{HAMDCF}_3)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (1), $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (2), $[\text{Ni}_2(\text{HAMDCF}_3)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (3), and $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (4); the coloured bands highlight the ranges of the particular vibrational modes: νNH_2 and $\nu=\text{NH}$ (yellow), $\nu_{\text{as}}\text{COO} + \nu\text{CN}$ (pink), δNH_2 (orange), $\nu_{\text{s}}\text{COO}$ (blue), and νCF (green).

be concluded that the metal centre plays a crucial role in the coordination mode of amidine.

$[\text{Ni}(\text{IMAMDCF}_3)_2]$ (5). The crystal structure analysis of $[\text{Ni}(\text{IMAMDCF}_3)_2] \cdot 2(\text{HAMDCF}_3) \cdot 2\text{H}_2\text{O}$ (5a) (see Section 3.1) indicates the formation of a symmetric imidoamidinate ligand. However, the potential formation of unsymmetrical imidoamidinate ligand similar to earlier results for Cu(II) complexes

$[\text{Cu}(\text{NHC}(\text{CH}_3)\text{NC}(\text{R}_f)\text{NH})_2]$ ($\text{R}_f = \text{CF}_3, \text{C}_2\text{F}_5$) was possible.⁴⁸ The theoretical calculations were performed to confirm symmetric ligand formation and simplify the assignment of bands to individual vibrations. The theoretical spectrum for this compound shows two bands νCH_3 (Fig. 7). In addition, it should be noted that the amount of the bands characteristic of νCF is different compared to experimental results, which denies the formation of the unsymmetrical ligand.

The calculation for the symmetrical imidoamidinate $[\text{Ni}(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH})_2]$ (5) showed the stretching vibration characteristic band of the NH groups is at 3538 cm^{-1} and deformation band δCNH at 1495 cm^{-1} (Fig. 7), which correspond to the bands 3285 cm^{-1} and 1495 cm^{-1} in the experimental IR spectrum (Fig. S6†). The signals matching the νNH_2 , and δNH_2 were not observed, which revealed the deprotonation of the ligand formed *in situ* (Fig. 7). Moreover, the two bands νCH_3 visible in the calculated spectrum (Fig. 7B) of the complex with asymmetric imidoamidinate were not recorded (Fig. S6†). These results confirm the formation of the $[\text{Ni}(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH})_2]$ complex (5), where only perfluorinated substituents are present.

The interpretation of these data is important for the evaluation of the infrared results of the layers of compounds 4 and 5 deposited on the silicon substrate (*vide infra* – see Section 3.6), which were then analysed in terms of their interaction with a high-energy electron beam.

3.3. Thermal analysis

Thermal analysis was performed to study the behaviour of the complexes during heating under a nitrogen atmosphere and to

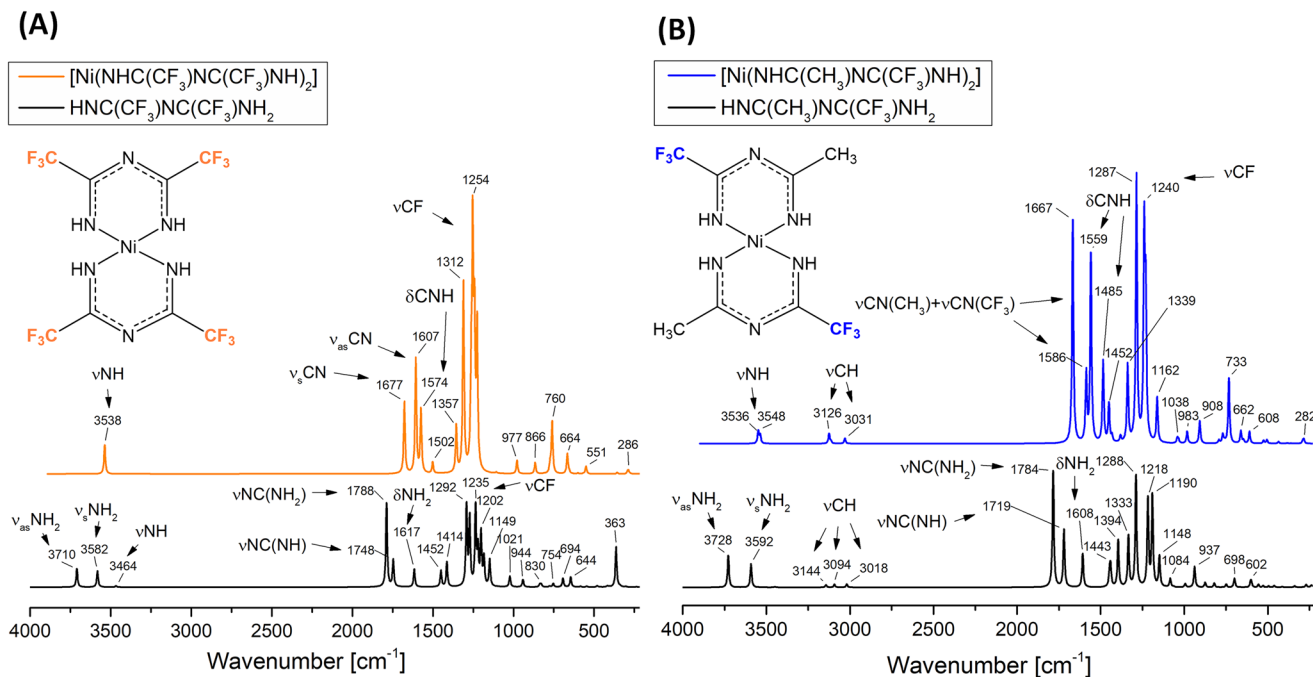


Fig. 7 Theoretical IR spectrum (DFT M06/6-311G(d,p)) of $[\text{Ni}(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH})_2]$ (5) – (A) and $[\text{Ni}(\text{NHC}(\text{CH}_3)\text{NC}(\text{CF}_3)\text{NH})_2]$ – (B) (nickel compounds – blue line, IMAMD – black line).

determine the temperature of the final decomposition. These data revealed that the decomposition of complexes 1–5 proceeds in several overlapping endothermic steps for the compound (1) as well as endothermic and exothermic processes for complexes 2–5 (Fig. 8 and Fig. S7–S11†). In the case of complex 5, an endothermic process associated with melting was observed at 318 K.

The thermograms show that the thermal decomposition of perfluorinated amidine-carboxylate (1–4) and imidoamidinate (5) nickel(II) complexes begin at a temperature (T_i) of 313–320 K, whereas the final decomposition temperature (T_f) ranged between 620 and 652 K for compounds 1–4 and is higher than that for complex 5 by about 150 K (Table S4†). The T_i values are lower for the complexes with pentafluoropropylamidine (2) and (4), in comparison with the previously described copper(II) amidine-carboxylate complexes $[\text{Cu}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ and $[\text{Cu}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ by about 71 K and 44 K, respectively. However, T_f achieved higher values by 37 K and 97 K, as well. The lower T_i temperature can be advantageous for using compounds as metal sources in vapor deposition processes. On the other hand, the broader ‘temperature window’ ($T_f - T_i$) for nickel(II) compounds is more promising for the FEBID process.

For complexes 3, 4, and 5, a significantly lower residue mass compared to the theoretical content of nickel in the molecule was observed. These results reveal that the compounds are a source of metal carriers in the gas phase under atmospheric pressure. TEM diffraction patterns for the residue revealed that the decomposition product is metallic nickel for complex 5 (Fig. S12†). In contrast, for complexes 1 and 2, the remaining mass after thermal analysis is higher than the nickel content. Therefore, the final product for compound 1 was additionally studied using TEM-EDX (Fig. S13†), which

showed the presence of Ni, F, and O (*ca.* 67:24:9), which suggests that the residue may include Ni, NiO, and NiF_2 .

The lower residue for compounds $[\text{Ni}_2(\text{HAMD})_2(\mu\text{-O}_2\text{CR}_f)_4]$ where $\text{R}_f = \text{C}_2\text{F}_5$ (3) and (4) suggest these complexes are a better source of metal carriers than analogues with $\text{R}_f = \text{CF}_3$, and therefore they are more attractive for potential use in vapor deposition methods. The thermal analysis results indicate that the length of the perfluorinated carbon chain affects the production of volatile metal carriers and the formation of final products under atmospheric pressure conditions. In addition, it should be noted that the mononuclear imidoamidinate complex (5) is the most effective source of nickel carriers under atmospheric pressure conditions.

3.4. Mass spectral analysis

The electron impact mass spectra (EI MS) of complexes 1–5 were recorded between 313 and 573 K (Tables S5–S9†). Based on these results, we can verify whether these complexes are capable of generating volatile metal carriers, check their sensitivity to low-energy electrons in the gas phase (70 eV), and study how the composition of the gas phase changes during heating under reduced pressure ($\sim 10^{-6}$ mbar). It is important to note that during the FEBID process in the SEM chamber, the conditions are quite similar to the EI MS experiments.

For complexes 1–4, no molecular ions were detected in the EI MS spectra (Tables S5–S8†). However, metallated fragments containing *N,N*- and *O,O*-donor ligands were identified. Moreover, the VT IR studies for complexes 3 and 4 (*vide infra* see Section 3.5) and sublimation experiments for compound 4 (*vide infra* – see Section 3.6) show that they can be transferred to the gas phase, even under higher pressure (10^{-1} – 10^{-2} mbar). Therefore, the absence of molecular ions indicates that the $[\text{Ni}_2(\text{HAMDR}_f)_2(\mu\text{-O}_2\text{CR}_f)_4]$ complexes are highly sensitive to low-energy electrons, which results in their rapid decomposition.

Dinickel ions containing both ligands, amidine and carboxylate, have been identified, *e.g.*, $[\text{Ni}_2(\text{HAMDR}_f)(\text{O}_2\text{CR}_f)_3]^+$ and $[\text{Ni}_2(\text{HAMDR}_f)_2(\text{O}_2\text{CR}_f)(\text{NH}_3)]^+$ confirming the coordination of these ligands (Fig. 9 and Fig. S14, Tables S5–S8†). Moreover, a number of dinuclear fragments were present as dominant at various temperatures (Tables S5–S8†). For all complexes (1–4), the presence of trinuclear ions was also observed (Fig. 9). Additionally, for compounds 3 and 4, the formation of higher-mass fragments cannot be excluded, based on the registration of tetranuclear fragments $[\text{Ni}_4(\text{HAMDR}_f)(\text{O}_2\text{CC}_2\text{F}_5)_3(\text{CO}_2)_4]^+$.

In general, in the EI MS spectra, the metallated fragments were detected over a range of 481–573 K for 1, 353–475 K for 2, 441–573 K for 3, and 328–339 K for 4, and the high %RI of the metallated ions was observed as follows: 8–11% RI from 530 K to 550 K for 1, 30–42% RI 425–441 K for 2, 100% RI at 488–490 K, 511–515 K for 3, and 6–40% RI at 328–329 K for 4. The relatively low temperatures of occurrence of the metallated ions for compounds 2 and 4 (Fig. 9 and Tables S5–S8†) is advantageous in terms of introducing them to the FEBID or FIBID process using a commercial GIS system, which requires around 333 K.⁴⁹

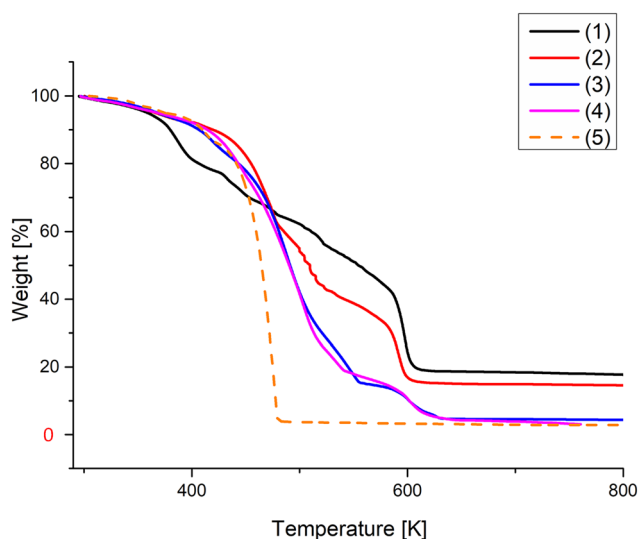
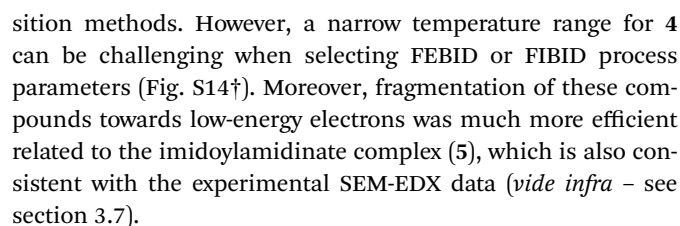


Fig. 8 Thermogravimetric curves (TG) for complexes $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (1) (black), $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (2) (blue), $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (3) (red), $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (4) (pink), and $[\text{Ni}(\text{IAMDC}_2\text{F}_5)_2]$ (5) (orange).



Considering the previous discussion, compounds **2** and **4** exhibit the most promising potential for use in vapor depo-



In the spectra recorded for compounds **1–4** (Fig. S15–S22†), the first volatile products formed upon heating were recorded

at 333 K. From this temperature to 613 K, bands characteristic of free amidine molecules were identified at *ca.* 3570 cm^{-1} ($\nu_{\text{as}}\text{NH}_2$), *ca.* 3450 cm^{-1} ($\nu_{\text{s}}\text{NH}_2$), *ca.* 1780 cm^{-1} (νCN), and *ca.* 1590 cm^{-1} (δNH_2) (Fig. S15–S22†). The increasing number of signals from 453 K for **4** in the NH stretching vibration area: 3568 cm^{-1} $\nu_{\text{as}}\text{NH}_2$, 3500 cm^{-1} νNH , 3448 cm^{-1} $\nu_{\text{s}}\text{NH}_2$, 3249 cm^{-1} $\nu = \text{NH}$, and the appearance of the bands: 1732 cm^{-1} , 1706 cm^{-1} $\nu_{\text{as}}\text{COO} + \nu\text{CN}$, 1591 cm^{-1} δNH_2 , and 1435 cm^{-1} $\nu_{\text{s}}\text{COO}$ suggest a transfer of the complex molecules to the gas phase (Fig. S21 and S22†). A similar effect was observed for complex **3** from 473 K (Fig. S19 and S20†). The complex molecules were observed over a range of 473–553 K (Fig. S19 and S20†) for **3** and 453–573 K for **4** (Fig. S21 and S22†) and the highest intensity of their bands were recorded at 513 K for both **3** and **4**. This is promising for their application in vapor deposition methods and is consistent with thermal analysis results (see Section 3.3), which indicated volatile metal carrier generation even at atmospheric pressure. However, a wider temperature window was observed for complex **4**.

Moreover, the occurrence of other bands: $\text{R}_f\text{C}\equiv\text{N}$ for **3** (493–533 K) and **4** (473–553 K), CO for **3**, **4** (573–613 K), R_fCOOH for **4** (593–613 K), and CF_3CFO for **3** (593–613 K) (Table S10†), provides evidence of formation volatile degradation products. These results suggest that the coordination centre and different coordination modes of amidine influence the decomposition mechanism, differing from previously reported data for $[\text{Cu}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$,³¹ where Cu-AMD species, $\text{Cu}_2(\text{O}_2\text{CR}_f)_4$, HAMD, R_fCOOH , CF_3CFO , CF_2O , CO_2 , and CO were observed.

The lack of bands characteristic of trifluoroacetate complexes $[\text{Ni}_2(\text{HAMDR}_f)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ $\text{R}_f = \text{CF}_3$ (**1**), C_2F_5 (**2**) (Fig. S15–S18†) indicate that the presence of the C_2F_5 group in the carboxylate enhances the evaporation.

Based on the VT IR spectra analysis of the thermal decomposition pathways of compounds **3** and **4** were proposed (Fig. 11).

The new nickel(II) compounds $[\text{Ni}_2(\text{HAMDR}_f)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (**3**) and $[\text{Ni}_2(\text{HAMDR}_f)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (**4**) are promising for future use in the CVD process and other vapor deposition methods. However, the nickel complex $[\text{Ni}_2(\text{HAMDR}_f)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ evaporation was started at a higher temperature (473 K (**3**) and 453 K (**4**)) compared to $[\text{Cu}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$, for which the metal carriers were detected from 353 K.³¹ This may be related to the formation of bonds between molecular units, as observed in the mass spectra (see Section 3.4), where trinuclear and tetranuclear fragments were detected. This indicates that the coordination centre has a significant impact on volatility and thermal decomposition mechanism. Notably, the lower transition temperature of complex **4** to the gas phase led to its selection for CVD studies (*vide infra* – see Section 3.8) and the preparation of materials for photoactivity studies (*vide infra* – see Section 3.9).

3.6. Sublimation experiments

Sublimation is a desired property for the application of complexes in vapor deposition methods such as CVD and FEBID or FIBID. Sublimation experiments were carried out to verify the volatility of the potential precursors as well as to determine the sublimation temperature of entire compound molecules.

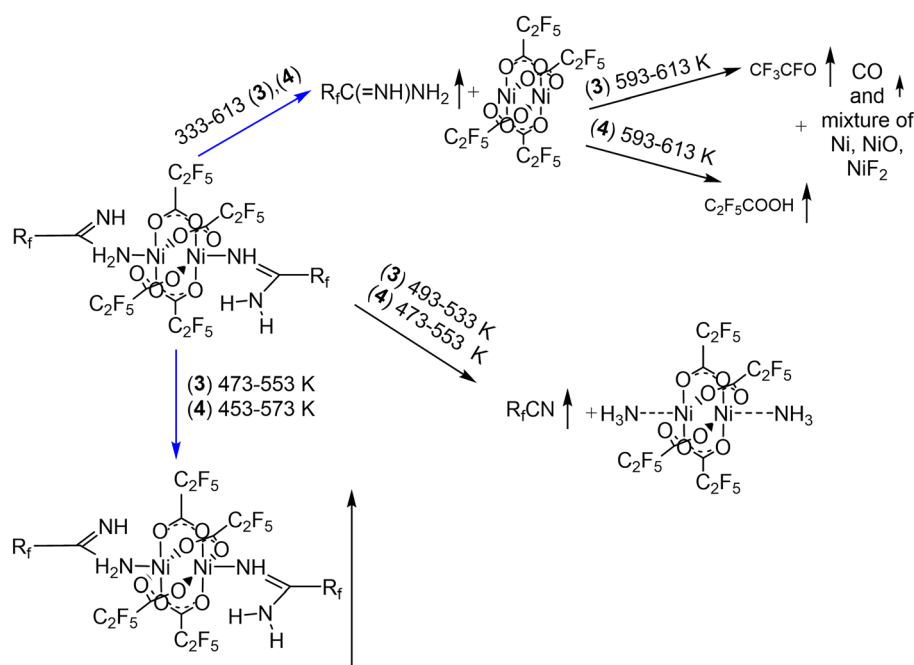


Fig. 11 Proposed reaction pathways of $[\text{Ni}_2(\text{HAMDR}_f)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ $\text{R}_f = \text{CF}_3$ (**3**) and C_2F_5 (**4**) thermal decomposition at 10^{-2} mbar based on VT IR studies (blue arrow – main reaction pathways; vertical arrows – gaseous products).

For these studies, we chose compounds **4** and **5**, which are the source of metal carriers in the gas phase even under atmospheric pressure (see Section 3.3). Moreover, our previous studies reveal that the copper(II) amidine-carboxylate complex $[\text{Cu}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ seemed to be a promising candidate for CVD and FEBID applications.³¹ It was, therefore, crucial to see what effect the change of coordination centre would have on volatility, among other things. These experiments were carried out in a classical glass sublimator under a pressure of 10^{-2} mbar with a special holder for the silicon substrate. Moreover, they allowed for obtaining layers of compounds **4** and **5**, which were then studied in terms of interaction with a high-energy electron beam (SEM/EDX) (*vide infra* – see Section 3.7), as for the compounds previously tested by us.^{31,50–52}

For complex $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (**4**), the process was performed at 423 K. In the infrared spectrum of the layer deposited on the silicon substrate, the bands characteristic of coordinated amidine and carboxylate ligands were observed: νCN (1715 cm^{-1}), $\nu_{\text{as}}\text{COO}$ (1666 cm^{-1}), δNH_2 (1543 cm^{-1}), $\nu_{\text{s}}\text{COO}$ (1427 cm^{-1}) (Fig. 12C). The thin layer spectrum shows shifts in the positions of bands in the region corresponding to the stretching vibrations of N–H groups. Moreover, an increase in the intensity of the νCN band was observed, along with slight changes in the shape of bands in the $830\text{--}550\text{ cm}^{-1}$ region, probably resulting from some structure rearrangement.

On the basis of the theoretical spectra (see Section 3.2), we propose that the reduction in the number of signals characteristic of the NH group, together with changes in the intensities of the bands characteristic of νCN and $\nu_{\text{as}}\text{COO}$, may be related to a change in the coordination mode of the amidine. In the theoretical spectra for $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (**4**) with $=\text{NH}$ bonded amidine (Fig. 5), we observed three bands in the NH region and similar intensities of bands νCN and $\nu_{\text{as}}\text{COO}$. Furthermore, the enhanced intensity of the δNH_2 in the IR spectrum of adsorbed molecules provides next evidence for this change. These facts do not affect the conclusion that complex $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (**4**) sublimates at a temperature of 423 K.

In the case of compound **5**, the sublimation occurred at 358 K. The IR spectra of the original in the solid phase and layer cannot be directly compared because complex **5** was purified by sublimation. However, the infrared spectrum of sublimate layers exhibits bands νNH , νCN , νCF , and δCNH (Fig. 6), which are characteristic of coordinated imidoamidinate (see Section 3.2).

The EDX spectra confirmed the presence of nickel, nitrogen, carbon, and fluorine for complexes **4** and **5**, as well as oxygen for the compound **4** (*vide infra* – see section 3.7).

In summary, the analysis of the infrared and EDX spectra of compound (**4**) and (**5**) layers provide their transfer to the gas phase. The low evaporation temperature for compound (**5**)

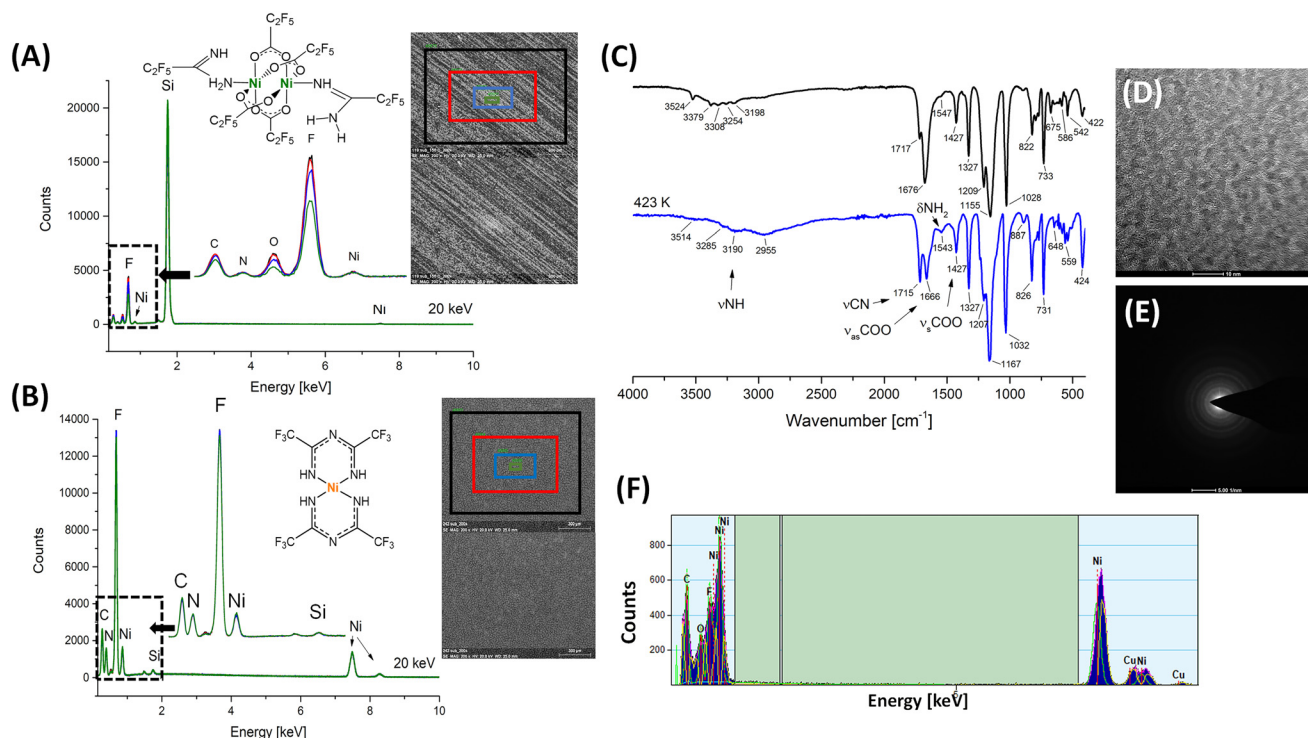


Fig. 12 EDX spectra (20 keV) of sublimed $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (**4**) – (A) and $[\text{Ni}(\text{IMAMDC}_2\text{F}_3)_2]$ (**5**) – (B) layered on a Si(111) substrate (Mag = 200 $\times$) (top view SEM images of irradiated areas of the sublimed film: top image with marked areas corresponding to the EDX plots, bottom image: morphological changes after irradiation), infrared spectra for compound **4** (black) and its adsorbed layer (blue) at 423 K ($p = 10^{-2}$ mbar) (C), TEM image of the sample (**4**) after several seconds of interaction with high-energy (200 keV) electrons (D), TEM diffraction pattern (E), and TEM-EDX spectrum (F).

makes it attractive for future use in vapor deposition processes.

3.7. SEM/EDX observation and TEM/EDX studies of $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ and $[\text{Ni}(\text{IMAMDCF}_3)_2]$

To assess the sensitivity of the compounds to high energy electrons and their usefulness in the FEBID and FIBID methods, a scanning electron microscope (SEM) and a transmission electron microscope (TEM) were used. These experiments are important for evaluating the precursor's initial effectiveness in the FEBID and FIBID processes and provide insight into the design of new precursors. The sensitivity of thin layers of complexes **4** and **5** resublimated on the silicon substrate (see Section 3.6) was studied using SEM/EDX at 8 and 20 keV energy. EDX spectra were recorded during the SEM analysis. The scanning area was reduced, which caused an increase in the dose of electrons. Moreover, TEM (200 keV) measurements were performed for the compound (**4**).

The SEM images show that the sublimated layers obtained for complex $[\text{Ni}(\text{IMAMDCF}_3)_2]$ (**5**) are homogeneously distributed on the silicon surface (Fig. 12 and Fig. S23†). We note that in the case of $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (**4**) samples, the surface is not homogeneously covered (Fig. 12). In the EDX spectra (20 keV) of $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (**4**) thin layer deposited on a silicon substrate, changes in the signal intensity for individual elements constituting the precursor were detected (Fig. 12A). As the electron dose was increased, a decrease in the amount of carbon, oxygen, and fluorine in the sample was observed. However, no morphological changes in SEM images and intensities of individual elements in EDX spectra (20 keV) were observed for compound $[\text{Ni}(\text{IMAMDCF}_3)_2]$ (**5**) (Fig. 12B). Only a negligible change in the intensity of the fluorine signal was noted when 8 keV was used (Fig. S23†). The microscopic observations and EDX spectra showed that the amidine-carboxylate compound (**4**) is more sensitive to the high-energy electron beam than the imidoylamidinate complex (**5**).

During TEM imaging, changes in the structure of the sample (**4**) were detected. The microscopic observations confirmed that the tested compound is sensitive to the high-energy electron beam (200 keV). After a few seconds of irradiation, the formation of circular structures surrounded by amorphous carbon in TEM images was observed (Fig. 12D). The diffraction patterns confirmed the crystallinity of the formed material and the formation of nickel(II) oxide and nickel(II) fluoride (Fig. 12E). Notably, in the case of $[\text{Cu}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$, the formation of CuF_2 as the final product was also noted under similar experimental conditions.³¹ In addition, characteristic signals of nickel, fluorine, oxygen, and carbon were present in the TEM-EDX spectra (Fig. 12F). It should be noted that the TEM grid was covered with carbon, which affects the semiquantitative measurement. The results suggest that the Ni–N bond was broken under the experimental conditions.

These data show that electron-induced decomposition strongly depends on beam power and electron dose. Moreover,

the type of the donor ligand influences electron-induced fragmentation and should be an essential factor in the selection of precursors for FEBID and FIBID methods. The microscopic observations and TEM-EDX spectra reveal that the amidine-carboxylate complex (**4**) is sensitive to the high-energy electron beam and may be potentially tested under experimental FEBID and FIBID conditions.

In summary, these data indicate that Ni-ligand bonds with *N*-donor amidines and *O,O*-donor carboxylates are more sensitive to electrons than *N,N*-donor imidoylamidinate ligand. These results indicate that the type of coordination sphere influences electron-induced fragmentation and should be an important factor in selecting precursors for FEBID/FIBID. Moreover, they suggest that the formation of thermodynamically stable and volatile CO_2 during electron-induced fragmentation may be crucial for the dissociation process *via* a focused electron or ion beam.⁴⁸

3.8. CVD experiments

CVD experiments were carried out in a homemade hot-wall horizontal reactor in argon without using a reducing agent. We selected compound $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (**4**) to confirm the generation of volatile metal carriers during heating, which is important for use in vapor deposition techniques. Moreover, we aimed to prepare the material on titania nanotubes for its use in preliminary photocatalytic activity studies (*vide infra* – see Section 3.9). To achieve this, we first carried out deposition on a silicon substrate to determine the parameters for the process. We also decided to carry out CVD experiments on glass to check the effects of the substrate.

Based on the VT IR analysis, an evaporation temperature of 493 K was selected (see Section 3.5), when the bands characteristic of compound **4** achieved the highest intensity. The temperature of 723 K (T_D) was chosen according to the thermal analysis results to achieve the precursor's decomposition on the silicon substrates placed according to the increasing transport pathway (Fig. S24†).

The silicon substrates (III–V) are covered by homogeneous and densely packed grains (Fig. 13), in which a wider grain size with a 50–80 nm diameter was observed (Fig. 13B). No significant differences in the deposit shape were visible but the cover density increased from III by IV to V substrates (Fig. 13). Moreover, they differ in the number of observed cubic forms (Fig. 13A and B). The thickness of the obtained layers reached approximately 150 nm (Fig. 13D). The influence of the precursor transport pathway on surface morphology was evident.

Atomic force microscopy was performed to investigate the spatial structure of the deposits. The AFM images revealed that the deposited material formed a continuous and homogeneous coating. The materials deposited on the IV substrate ranged in height up to 73 nm (Fig. 13E), with the formation of cubic structures observed. The EDX spectra revealed the presence of signals characteristic of nickel and oxygen, with negligible amounts of carbon and fluorine (Fig. 13F).

As demonstrated by the materials obtained for the fourth substrate (Fig. S24†), which had the same distance between

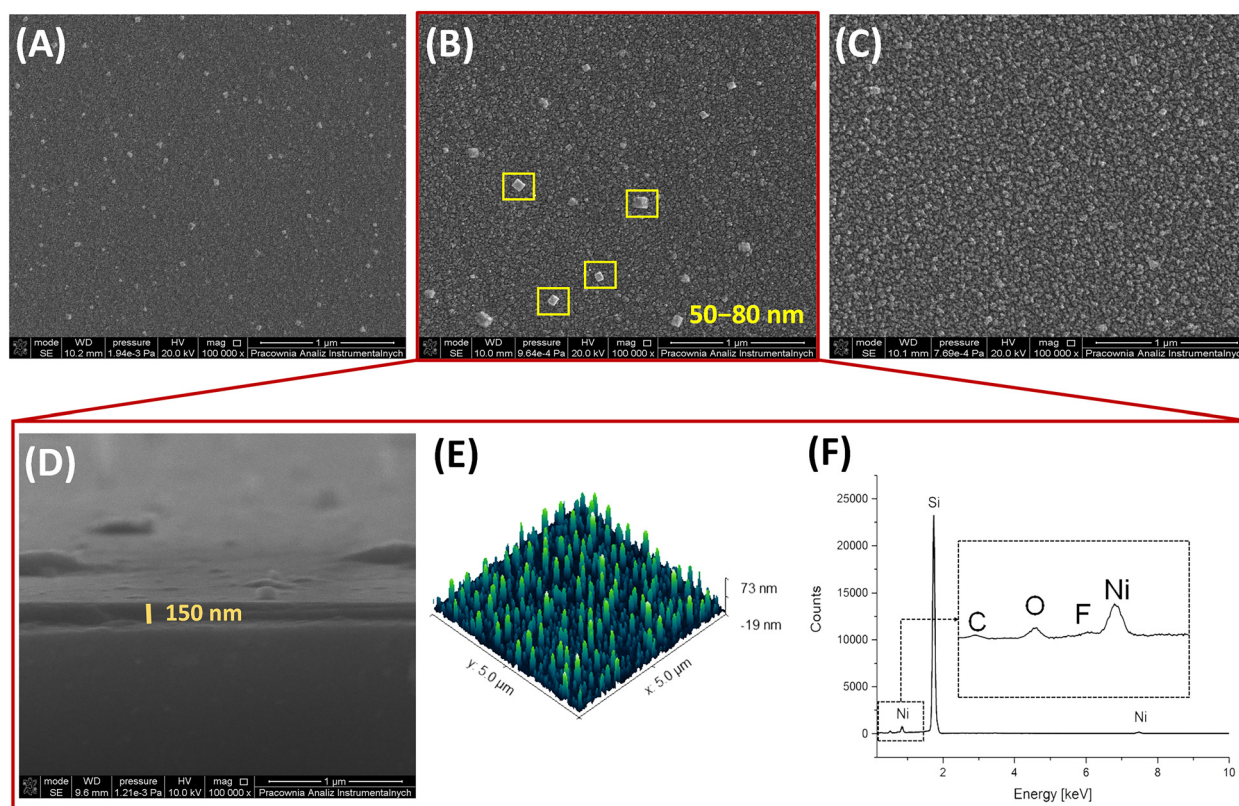


Fig. 13 SEM images of CVD deposits formed using the precursor $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (**4**), Mag = 100 000 $\times$ (A)–(C) (orderly with the increasing transport way length: III, IV, and V substrates), (D) cross-section of the IV deposit, (E) AFM images and (F) composition analysis of the deposit material obtained on the fourth substrate, $T_V = 493$ K, $T_D = 723$ K, Si(111), Ar.

the precursor and substrate, differences were observed in the materials deposited on: silicon, glass, and TNT (Fig. 14). The formation of cubic structures was not observed on glass (Fig. 14B), in contrast to the deposits formed on silicon (Fig. 14A). In the case of the material deposited on titania nanotubes, the SEM image shows more densely packed grains with visible gaps (Fig. 14C and Fig. S25[†]), compared to the material formed on glass and Si(111), with the resulting layer exhibiting a thickness of approximately 1 μm (Fig. 14D). In the EDX spectra, the signals characteristic of nickel, titanium, and oxygen were observed. Moreover, low-intensity signals corresponding to carbon and fluorine were detected (Fig. 14E). These results indicate that the morphology of the deposits varied depending on the type of substrate (Fig. 14). Similarly, the influence of the precursor transport pathway on deposit morphology was evident (Fig. 13).

The CVD experiments confirmed that complex $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (**4**) is a source of metal carriers in the gas phase and may be a promising precursor for future CVD experiments, *e.g.* using reducing gas. The results we obtained and the used parameters are the basis for further research.

3.9. Preliminary photocatalytic activity tests

The materials obtained by the CVD process were investigated for their potential application in photocatalysis. Taking into

account the photocatalytic activity of titania nanotubes synthesised electrochemically at 20 V (TNT20) and modified by the CVD technique using $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (**4**) as a precursor (Ni-TNT20) have been tested for their potential photoactivity in the reaction of methylene blue photodegradation. Changes in the spectra of the MB aqueous solution during its photocatalytic degradation are presented in Fig. 15B and Table S11[†].

Based on the observed changes, a wavelength 665 nm was selected for the monitoring of MB photodegradation. The recorded absorbance–time dependencies at this wavelength were linear (Fig. 15C).

It means that the absorbance depends only on one reactant, or the reaction progress is low. Taking into account significant changes in the MB concentration (Fig. 15), the last possibility cannot be applied and changes in the concentration of only one reactant decide the absorbance–time dependence. The above graph (Fig. 15C) also shows that without catalysts, methylene blue solution even under irradiation of the UV lamp remains relatively stable. However, the addition of titania-based substrates causes a distinct acceleration of the photodegradation process, especially for nickel CVD modified material. Analogous tests in visible light demonstrated the absence of photocatalytic activity of the obtained substrates (Fig. S26 and Table S12[†]).

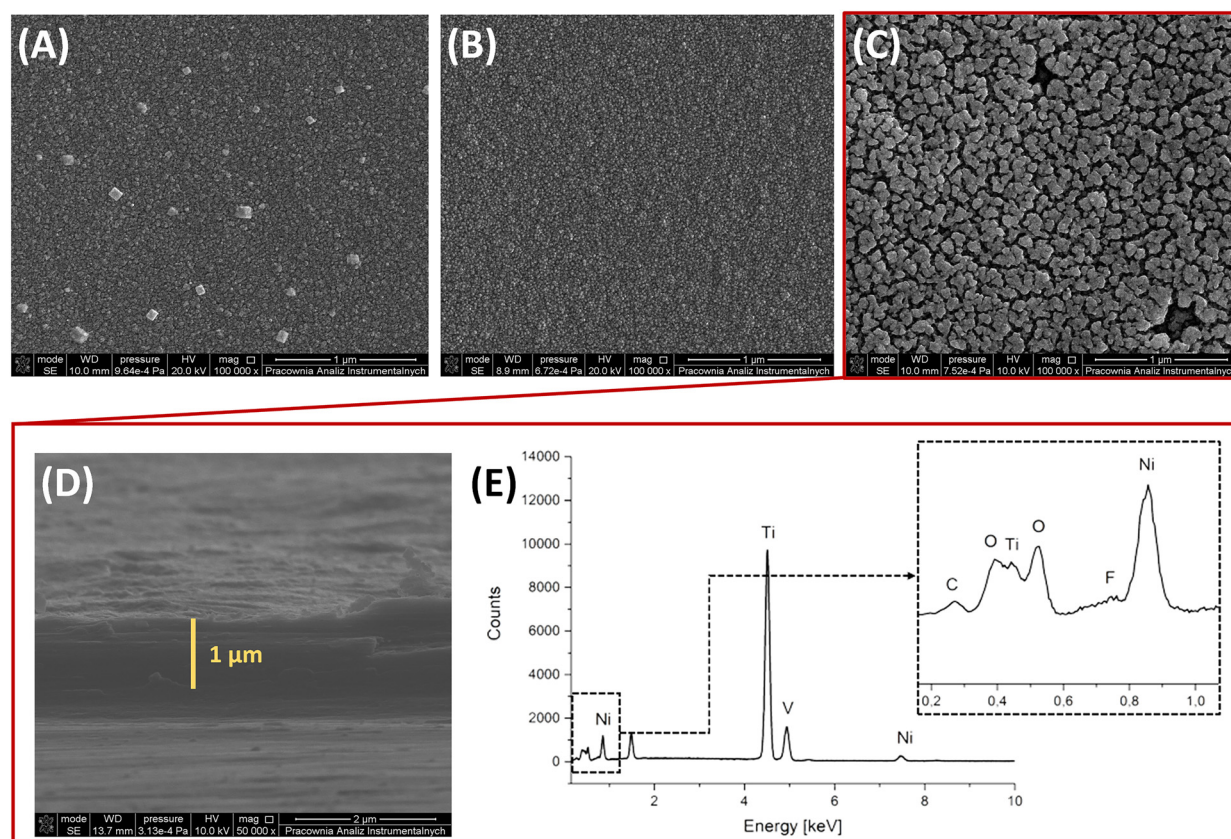


Fig. 14 SEM images of deposits formed using the precursor $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (**4**) (Mag = 100 000 $\times$, $T_V = 493$ K, $T_D = 723$ K, Ar), on different substrates: (A) Si(111), (B) glass, and (C) titania nanotubes. (D) Cross-section for deposits on the (C) substrate and (E) its composition analysis.

Explanation of the meaning of the kinetic parameters describing the absorbance–time dependencies is relatively simple. In the studied reaction, the rate of the whole process depends on the substrate surface (S) and MB concentration. The reaction can be written as:

$$\text{rate} = -\frac{d[\text{MB}]}{dt} = k^{\text{II}}S[\text{MB}] \quad (1)$$

where k^{II} is a second-order rate constant.

However, because the size of the substrates was the same in all samples (1 cm²), the expression $k^{\text{II}}S$ can be treated as a constant. Additionally, the $A = f(t)$ dependence linearity is saved even when more than 25% of the starting MB is degraded. It means that excess of the organic dye over the catalyst active sites is important, and, under the reaction conditions, the MB concentration can also be treated as constant. Thus, eqn (1) changes to form (2), which expresses the zero-order kinetic dependence:

$$-\frac{d[\text{MB}]}{dt} = k_{\text{obs}} \quad (2)$$

where $k_{\text{obs}} = k^{\text{II}}S[\text{MB}]$.

An integral form of eqn (2) leads to linear dependence that can be applied to describe the kinetic tests (3):

$$[\text{MB}] = -k_{\text{obs}}t + [\text{MB}]_0 \quad (3)$$

k_{obs} rate constants for three repetitions of the kinetic measurements for REF, TNT20, and Ni-TNT20 are shown in (Fig. 15D).

The conducted tests have demonstrated that a stable in the dark MB aqueous solution undergoes slow changes when exposed to UV light. However, this change increases *ca.* 6 times when a TNT20 material is applied and more than 9 times, when Ni-TNT20 is immersed in the MB solution, for the first set of tests. Test repetitions using the same 1 cm² catalyst substrates washed with water and acetone and dried revealed that the substrates can be applied more than once, besides the gradually decreasing photoactivity. The problem of the TiO₂ photocatalyst deactivation is known in the literature. It results mainly from adsorption processes occurring during photocatalysis. Y.S. You *et al.* noticed that aromatic reactants (*e.g.* methylene blue) have a high affinity to the titania surface and may cause its deactivation.⁵³ The role of deposition of the decomposed organic dyes in the titania photocatalysts is also described by Kaewgun and Lee.⁵⁴ The authors suggest that carbonaceous deposits may also play a role in that process.

The results of the kinetic tests clearly show that Ti6Al4 V foil covered with titania nanotubes synthesized at 20 V is a good catalyst in the tested system, and TNT20 modification

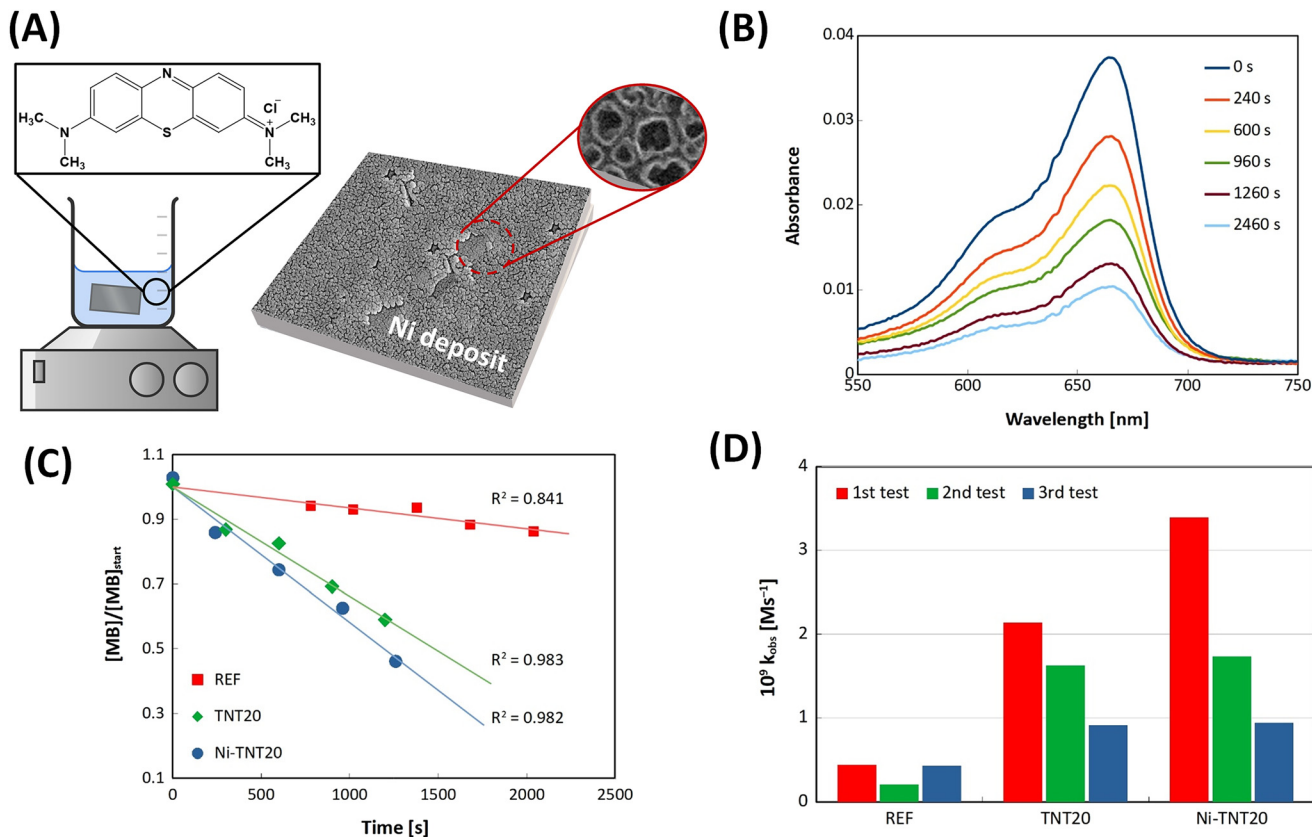


Fig. 15 (A) Scheme of the material used in photoactivity tests; (B) spectral changes in the aqueous MB solution during its photocatalytic degradation with Ni-TNT20 as a catalyst. $[MB]_0 = 0.01$ mM, $T = 298.1$ K, $l = 1$ cm; (C) the absorbance–time dependencies for the studied substrates (TNT20 and Ni-TNT20) and the sample without the substrate (REF) during the first UV irradiation. $[MB]_0 = 1 \times 10^5$ mol dm $^{-3}$, $T = 298.1$ K; (D) values of k_{obs} for three repetitions of the kinetic tests for REF, TNT20, and Ni-TNT20.

with nickel can additionally strengthen its catalytic activity. Such a change in photoactivity expands the possible application of the studied materials.

4. Conclusions

The conventional and mechanochemical synthesis methods of new nickel(II) amidine-carboxylate $[Ni_2(HAMDR_f)_2(\mu-O_2CR_f)_4]$ ($R_f = CF_3, C_2F_5$) and imidoamidinate $[Ni(IMAMDCF_3)_2]$ complexes were developed. Additionally, single crystal X-ray diffraction revealed the formation of the mononuclear complex $[Ni(NHC(CF_3)NC(CF_3)NH_2)_2] \cdot (NH_4)(NHOCF_3) \cdot (NH_2OCCF_3) \cdot H_2O$ and demonstrated the chelating ligand coordination by nitrogen atoms. The IR and EI MS analysis confirmed the amidine and carboxylate coordination for $[Ni_2(HAMDR_f)_2(\mu-O_2CR_f)_4]$, $R_f = CF_3$ and C_2F_5 and imidoamidinate formation for $[Ni(IMAMDCF_3)_2]$. For nickel(II) imidoamidinate, chelating ligand coordination was proposed using infrared spectral analysis and confirmed by DFT calculations. The dominant role played by short intermolecular interactions with solvating molecules in the crystal structure of $[Ni(IMAMDCF_3)_2] \cdot (NH_4)(NHOCF_3) \cdot (NH_2OCCF_3) \cdot H_2O$ was confirmed by Hirshfeld

surface analysis, which reduced volatility. The thermal analysis data indicated that the $[Ni_2(HAMDR_f)_2(\mu-O_2CC_2F_5)_4]$ and $[Ni(IMAMDCF_3)_2]$ complexes can be transported to the gaseous phase even at atmospheric pressure. The EI MS experiments showed that all studied compounds are the source of metal in the gas phase even at a temperature of 328 K ($p = 10^{-6}$ mbar), which suggests that they could be introduced into the SEM microscope chamber *via* the GIS system. The fragmentation behaviour of the compounds in the gas phase reveals that the amidine-carboxylate complexes are more sensitive to low-energy electrons than imidoamidinate. Based on the study of the interactions of complexes with high-energy electrons, it can be concluded that compound $[Ni_2(HAMDC_2F_5)_2(\mu-O_2CC_2F_5)_4]$ is sensitive to high-energy electron exposure (at 8, 20, and 200 keV). Variable temperature infrared spectroscopy demonstrated that the complexes with pentafluoropropionate $[Ni_2(HAMDR_f)_2(\mu-O_2CC_2F_5)_4]$ ($R_f = CF_3, C_2F_5$) are a source of nickel carriers in the gas phase even from 453 K. The $[Ni(IMAMDCF_3)_2]$ sublimation occurs at 358 K, while $[Ni_2(HAMDC_2F_5)_2(\mu-O_2CC_2F_5)_4]$ requires 423 K ($p = 10^{-2}$ mbar). These results showed that *N,N*-imidoamidinate increased the volatility of the nickel compound but at the same time, it decreased sensitivity to low- and high-energy electrons. Our studies indicate that a change in the coordination

center from Cu to Ni decreases the volatility of amidine-carboxylate complexes. $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ is not as suitable as copper for applications in FEBID and FIBID processes. However, the CVD experiments confirmed that it is a source of nickel in the gas phase and enhances the growth of metallated-based materials by precursor evaporation at 493 K and deposit formation at 723 K on silicon, glass, and titania nanotubes synthesized on 20 V (TNT20) substrates. Kinetic tests of TNT20 and Ni-TNT20 have shown that their modification with nickel strengthens their photocatalytic activity in methylene blue photodegradation. $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ can be considered for practical use in CVD applications and for modification of TiO_2 properties.

Supplementary materials

Q5 Table S1 Crystal data and structure refinement for compound $[\text{Ni}(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH}_2)_2 \cdot (\text{NH}_4)(\text{NHOCF}_3) \cdot (\text{NH}_2\text{OCCF}_3) \cdot \text{H}_2\text{O}]$ (5a); Table S2 Bond lengths [$\text{\AA}$] and angles [$^\circ$] for compound $[\text{Ni}(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH}_2)_2 \cdot (\text{NH}_4)(\text{NHOCF}_3) \cdot (\text{NH}_2\text{OCCF}_3) \cdot \text{H}_2\text{O}]$ (5a); Fig. S1 Hirshfeld surfaces (left) and fingerprints (right) of selected interactions created in the crystal network of $[\text{Ni}(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH}_2)_2 \cdot (\text{NH}_4)(\text{NHOCF}_3) \cdot (\text{NH}_2\text{OCCF}_3) \cdot \text{H}_2\text{O}]$ (5a) for the $[\text{Ni}(\text{IMAMDCF}_3)_2]$ molecule: (A) for $\text{H} \cdots \text{F}$ (4.9%), (B) for $\text{F} \cdots \text{N}$ (4.8%), (C) $\text{N} \cdots \text{H}$ (3.7%), (D) for $\text{F} \cdots \text{C}$ (3.3%), and (E) for $\text{C} \cdots \text{F}$ (2.9%); Table S3 Selected IR absorption bands (cm^{-1}) of the studied compounds $[\text{Ni}_2(\text{HAMDR}_f)_2(\mu\text{-O}_2\text{CR}_f)_4]$ (1–4); Fig. S2 ATR-IR spectrum for compound $[\text{Ni}_2(\text{HAMDCF}_3)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (1) (black) and the reactants $[\text{Ni}_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (red) and HAMDCF_3 (blue); Fig. S3 ATR-IR spectrum for compound $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (2) (black) and the reactants $[\text{Ni}_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (red) and HAMDC_2F_5 (blue); Fig. S4 ATR-IR spectrum for compound $[\text{Ni}_2(\text{HAMDCF}_3)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (3) (black) and the reactants $[\text{Ni}_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (red) and HAMDCF_3 (blue); Fig. S5 ATR-IR spectrum for compound $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (4) (black) and the reactants $[\text{Ni}_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (red) and HAMDC_2F_5 (blue); Fig. S6 Infrared spectrum of $[\text{Ni}(\text{IMAMDCF}_3)_2]$ (5); Table S4 Thermal analysis results; Fig. S7 Thermal decomposition of $[\text{Ni}_2(\text{HAMDCF}_3)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (1) (TG, DTG, DTA curves); Fig. S8 Thermal decomposition of $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (2) (TG, DTG, DTA curves); Fig. S9 Thermal decomposition of $[\text{Ni}_2(\text{HAMDCF}_3)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (3) (TG, DTG, DTA curves); Fig. S10 Thermal decomposition of $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (4) (TG, DTG, DTA curves); Fig. S11 Thermal decomposition of $[\text{Ni}(\text{IMAMDCF}_3)_2]$ (5) (TG, DTG, DTA curves); Fig. S12 Transmission electron microscopy (TEM) diffraction pattern for the TGA residue (Ni) for $[\text{Ni}(\text{IMAMDCF}_3)_2]$ (5); Fig. S13 TEM analysis results of the residue after thermal decomposition of $[\text{Ni}_2(\text{HAMDCF}_3)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (1), (A) – TEM image, (B) – EDX spectrum and (C) – atomic content of the elements; Fig. S14 Temperature ranges for the metallated fragments for compounds 1–5. The ions which achieved the highest relative intensity are marked in the diagram; Table S5 EI MS results for the $[\text{Ni}_2(\text{HAMDCF}_3)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ complex (1); Table S6 EI MS

results for the $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ complex (2); Table S7 EI MS results for the $[\text{Ni}_2(\text{HAMDCF}_3)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ complex (3); Table S8 EI MS results for the $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ complex (4); Table S9 EI MS results for the $[\text{Ni}(\text{IMAMDCF}_3)_2]$ complex (5), Fig. S15 Temperature variable infrared spectra (VT IR) for the vapor formed during the $[\text{Ni}_2(\text{HAMDCF}_3)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (1) heating (333–473 K); Fig. S16 Temperature variable infrared spectra (VT IR) for the vapor formed during the $[\text{Ni}_2(\text{HAMDCF}_3)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (1) heating (473–613 K); Fig. S17 Temperature variable infrared spectra (VT IR) for the vapor formed during the $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (2) heating (333–473 K); Fig. S18 Temperature variable infrared spectra (VT IR) for the vapor formed during the $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (2) heating (473–613 K); Fig. S19 Temperature variable infrared spectra (VT IR) for the vapor formed during the $[\text{Ni}_2(\text{HAMDCF}_3)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (3) heating (333–473 K) (bands characteristic for: free HAMD – black, complex – green); Fig. S20 Temperature variable infrared spectra (VT IR) for the vapor formed during the $[\text{Ni}_2(\text{HAMDCF}_3)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (3) heating (473–613 K) (bands characteristic for: free HAMD – black, complex – green, complex and HAMD – blue assignment); Fig. S21 Temperature variable infrared spectra (VT IR) for the vapor formed during the $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (4) heating (333–473 K) (bands characteristic for: free HAMD – black, complex – green, complex and HAMD – blue assignment); Fig. S22 Temperature variable infrared spectra (VT IR) for the vapor formed during the $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (4) heating (473–613 K) (bands characteristic for: free HAMD – black, complex – green, complex and HAMD – blue assignment); Table S10 Vibrational band positions and assignments for gaseous products of thermal decomposition of $[\text{Ni}_2(\text{HAMDR}_f)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (3) and $[\text{Ni}_2(\text{HAMDR}_f)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (4), where $\text{R}_f = \text{CF}_3$ (3), C_2F_5 (4); Fig. S23 Examined scan areas' EDX spectra (8 keV) for the $[\text{Ni}(\text{IMAMDCF}_3)_2]$ (5) layer deposited on a Si(111) substrate (Mag = 200 $\times$); Fig. S24 CVD reactor scheme with marked substrates numbered according to the length of the transport path; Fig. S25 SEM images of deposits formed using the precursor $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (4) ($T_V = 493 \text{ K}$, $T_D = 723 \text{ K}$, Ar), on titania nanotubes, (A) – Mag = 25 000 $\times$, (B) – Mag = 50 000 $\times$, (C) – 100 000 $\times$; Table S11 The k_{obs} values for methylene blue photocatalytic degradation under a UV lamp without (REF) and with TNT20 or Ni-TNT20 substrates as catalysts. Repetitions were carried out using the same substrates; Table S12 The k_{obs} values for methylene blue photocatalytic degradation under a Vis lamp without (REF) and with TNT20 and Ni-TNT20 substrates as catalysts; Fig. S26 The absorbance–time dependencies for the studied substrates (TNT20 and Ni-TNT20) and the sample without the substrate (REF) during Vis light irradiation. $[\text{MB}]_0 = 1 \times 10^5 \text{ mol dm}^{-3}$, $T = 298.1 \text{ K}$.

Author contributions

I.B.S: conceptualization; A.B.-K synthesized nickel(II) complexes and prepared the samples; A.B.-K and I.B.S character-

ized the samples; A.B.-K prepared the figures and drafted the manuscript; T.M: X-ray structural measurements; A.B.-K and T. M: visualization and structure description; A.T performed photocatalytic activity tests, provided a description of the applied methodology, visualized, and discussed the obtained results; A.B.-K managed the references. All authors checked the interpretation of the data, composed the final manuscript, and read and agreed to the published version of the manuscript.

Data availability

The data supporting this article have been included as part of the ESI.† Crystallographic data for **5a** have been deposited at the CCDC under 2375574† and can be obtained from https://www.ccdc.cam.ac.uk/data_request/cif.

Conflicts of interest

There are no conflicts to declare.

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Supplementary Materials:

Nickel complexes based on amidine for applications in gas-assisted methods and photocatalysis

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Table S 1 Crystal data and structure refinement for the compound $[\text{Ni}(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH}_2)_2] \cdot (\text{NH}_4)(\text{NHOC}(\text{CF}_3)) \cdot (\text{NH}_2\text{OC}(\text{CF}_3)) \cdot \text{H}_2\text{O}$ (**5a**).

Identification code	(5a)
Empirical formula	C12 H13 F18 N9 Ni O3
Formula weight	732.02
Temperature [K]	100(2)
Wavelength [Å]	1.54184
Crystal system, space group	Triclinic, P-1
Unit cell dimensions [Å] and [°]	a = 9.04000(18) α = 70.687(2) b = 11.8822(2) β = 79.653(2) c = 12.1180(3) γ = 81.9191(16)
Volume [Å ³]	1203.80(5)
Z, Calculated density [Mg×m ⁻³]	2, 2.017
Absorption coefficient [mm ⁻¹]	2.871
F(000)	724
Crystal size [mm ³]	0.090 x 0.060 x 0.040
Theta range for data collection [°]	3.905 to 77.770
Limiting indices	-11 ≤ h ≤ 11 -15 ≤ k ≤ 15 -15 ≤ l ≤ 15
Reflections collected/unique	8742
Completeness [%] to theta [°]	100.0 %
Absorption correction	Analytical
Max. and min. transmission	0.905 and 0.829
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	8742 / 2 / 407
Goodness-of-fit on F ²	1.032
Final R Indices [I > 2σ(I)]	R1 = 0.0415, wR2 = 0.1168
R indices (all data)	R1 = 0.0421, wR2 = 0.1173
Largest diff. peak and hole [eÅ ⁻³]	0.655 and -0.650

Table S 2 Bond lengths [Å] and angles [°] for the compound [Ni(NHC(CF₃)NC(CF₃)NH)₂](NH₄)(NH₂OCCF₃)·H₂O (**5a**).

Ni(1)-N(1)	1.8587(17)
Ni(1)-N(5)	1.8628(18)
Ni(1)-N(7)	1.8642(18)
Ni(1)-N(3)	1.8633(18)
N(1)-Ni(1)-N(5)	89.93(8)
N(1)-Ni(1)-N(7)	178.42(8)
N(5)-Ni(1)-N(7)	89.97(8)
N(1)-Ni(1)-N(3)	89.66(8)
N(5)-Ni(1)-N(3)	179.59(8)
N(7)-Ni(1)-N(3)	90.43(8)
C(1)-N(1)-Ni(1)	127.61(15)
Ni(1)-N(1)-H(1)	116.2
Ni(1)-N(3)-H(3)	116.2
C(5)-N(5)-Ni(1)	127.09(15)
Ni(1)-N(5)-H(5)	116.5
Ni(1)-N(7)-H(7)	116.3

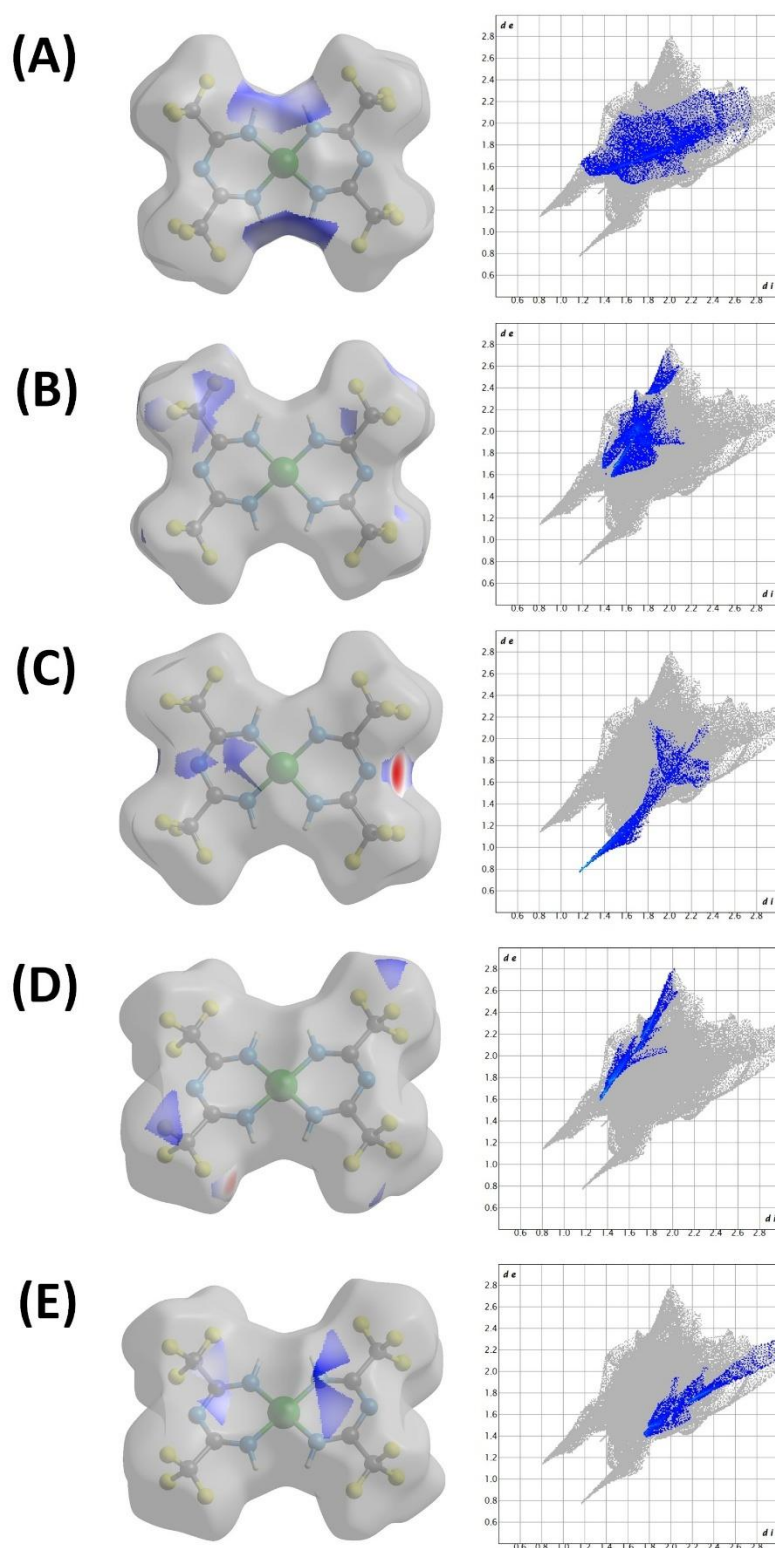


Figure S 1 Hirshfeld surfaces (left) and fingerprints (right) of selected interactions created in the crystal network of $[\text{Ni}(\text{NHC}(\text{CF}_3)\text{NC}(\text{CF}_3)\text{NH}_2)]\cdot(\text{NH}_4)(\text{NH}_2\text{OCCF}_3)\cdot\text{H}_2\text{O}$ (**5a**) for $[\text{Ni}(\text{IMAMDCF}_3)_2]$ molecule: (A) for $\text{H}\cdots\text{F}$ (4.9%), (B) for $\text{F}\cdots\text{N}$ (4.8%), (C) $\text{N}\cdots\text{H}$ (3.7%), (D) for $\text{F}\cdots\text{C}$ (3.3%), and (E) for $\text{C}\cdots\text{F}$ (2.9%).

Table S 3 Selected IR absorption bands (cm^{-1}) of the studied compounds $[\text{Ni}_2(\text{HAMDR}_i)_2(\mu\text{-O}_2\text{CR}_i)_4]$ (**1–4**).

Compound	νNH^*	$\nu\text{CN (sh)}$	$\nu_{\text{as}}\text{COO}$	δNH_2	$\nu_{\text{s}}\text{COO}$	$\Delta\nu\text{COO}$
$[\text{Ni}_2(\text{HAMDCF}_3)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (1)	3524 3373 3325 3265 3194	1717	1668	1576	1450	218
$[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (2)	3514 3373 3325 3271 3206	1715	1668	1566	1456	212
$[\text{Ni}_2(\text{HAMDCF}_3)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (3)	3520 3373 3327 3269 3196	1713	1678	1576	1429	249
$[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (4)	3526 3375 3323 3244 3198	1713	1680	1551	1429	251
HAMDCF₃	3350 3163	1670	—	1575	—	—
HAMDC₂F₅	3362 3130	1664	—	1593	—	—

* $\nu_{\text{as}}\text{NH}_2$, $\nu_{\text{s}}\text{NH}_2$, $\nu=\text{NH}$

$\Delta\nu\text{CF}_3\text{CO}_2\text{Na} = 223 \text{ cm}^{-1}$, $\Delta\nu\text{C}_2\text{F}_5\text{CO}_2\text{Na} = 268 \text{ cm}^{-1}$; $[\text{Ni}_2(\mu\text{-O}_2\text{CCF}_3)_4]$ [cm^{-1}]: 1665 $\nu_{\text{as}}\text{COO}$, 1449 $\nu_{\text{s}}\text{COO}$; $[\text{Ni}_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ [cm^{-1}]: 1713, 1641 $\nu_{\text{as}}\text{COO}$, 1431 $\nu_{\text{s}}\text{COO}$

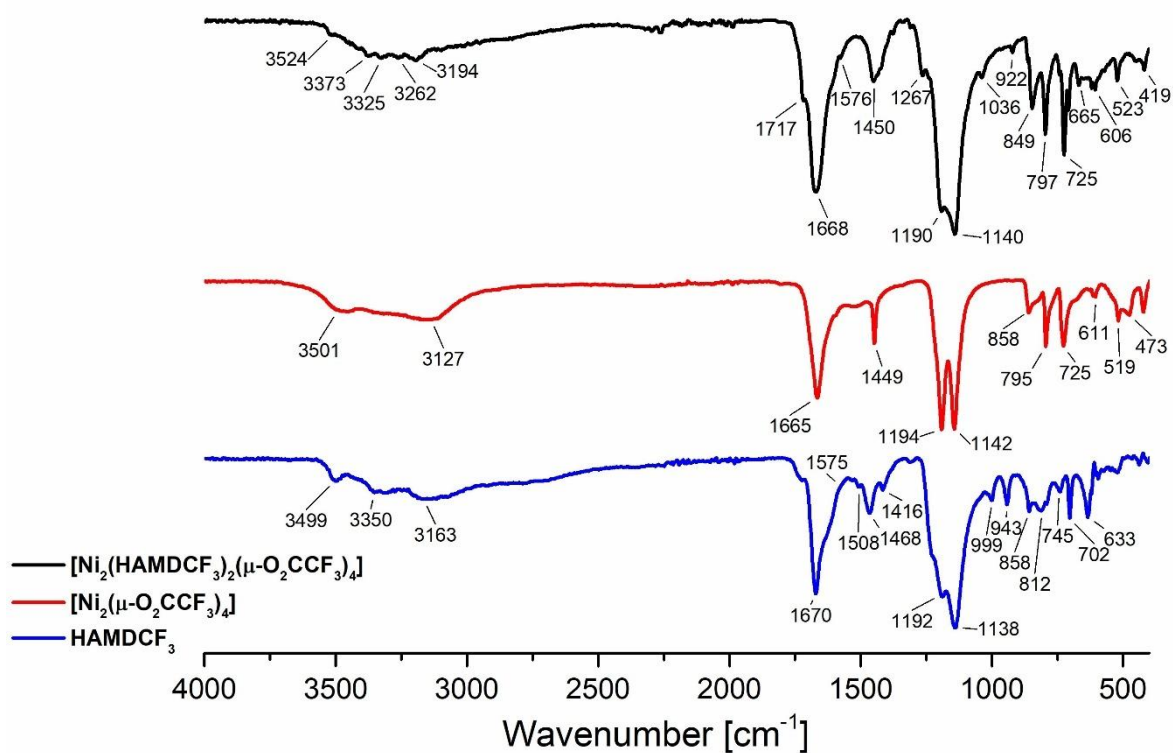


Figure S 2 ATR-IR spectrum for the compound $[\text{Ni}_2(\text{HAMDCF}_3)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (1) (black) and for the reactants $[\text{Ni}_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (red), HAMDCF_3 (blue).

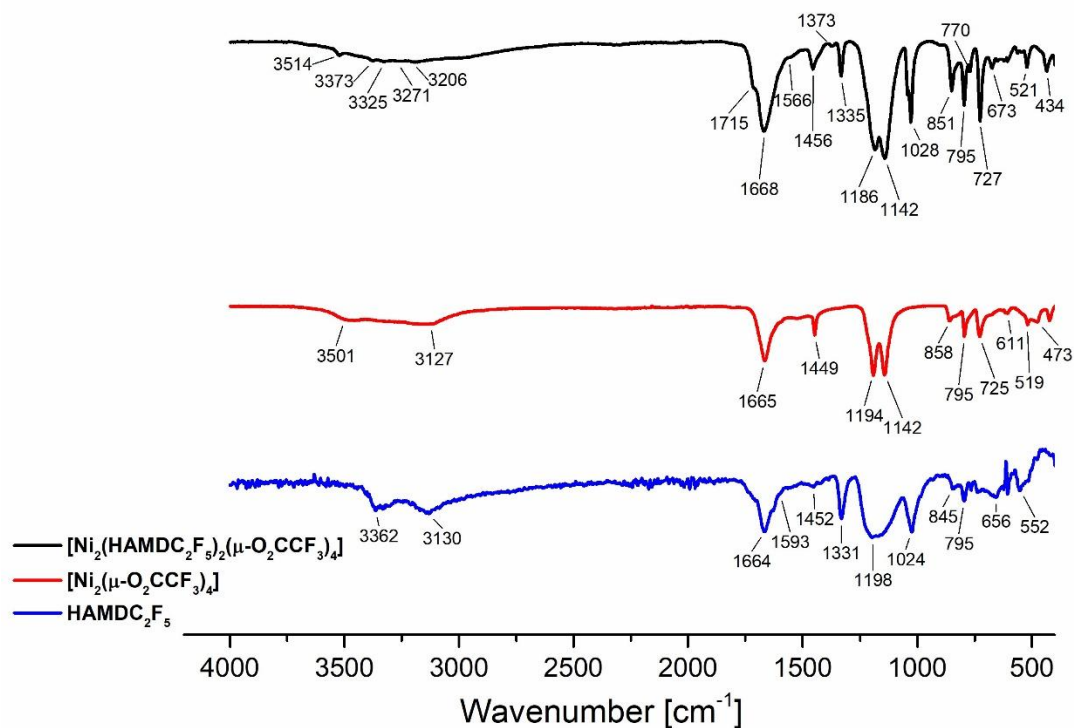


Figure S 3 ATR-IR spectrum for the compound $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (2) (black) and for the reactants $[\text{Ni}_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (red), HAMDC_2F_5 (blue).

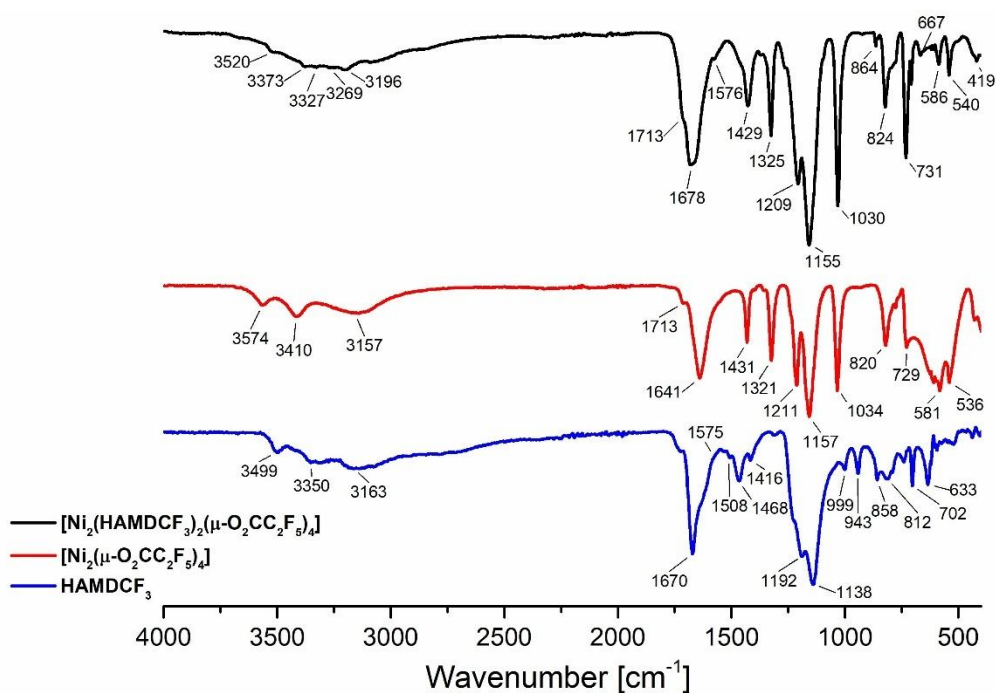


Figure S 4 ATR-IR spectrum for the compound $[\text{Ni}_2(\text{HAMDCF}_3)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (**3**) (black) and for the reactants $[\text{Ni}_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (red), HAMDCF_3 (blue).

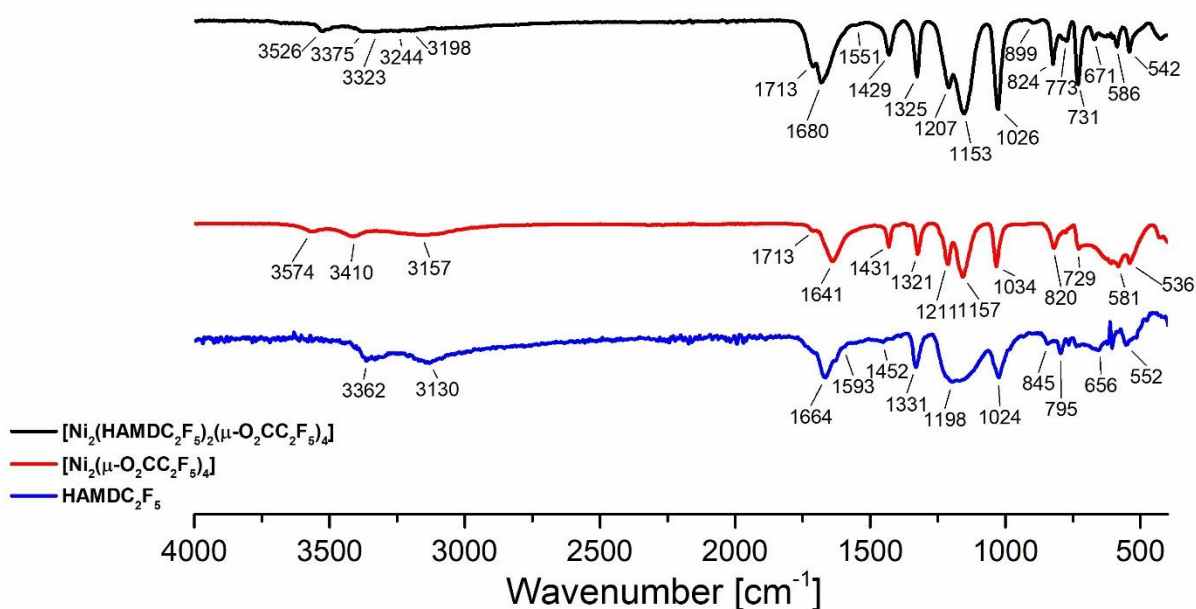


Figure S 5 ATR-IR spectrum for the compound $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (**4**) (black) and for the reactants $[\text{Ni}_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (red), HAMDC_2F_5 (blue).

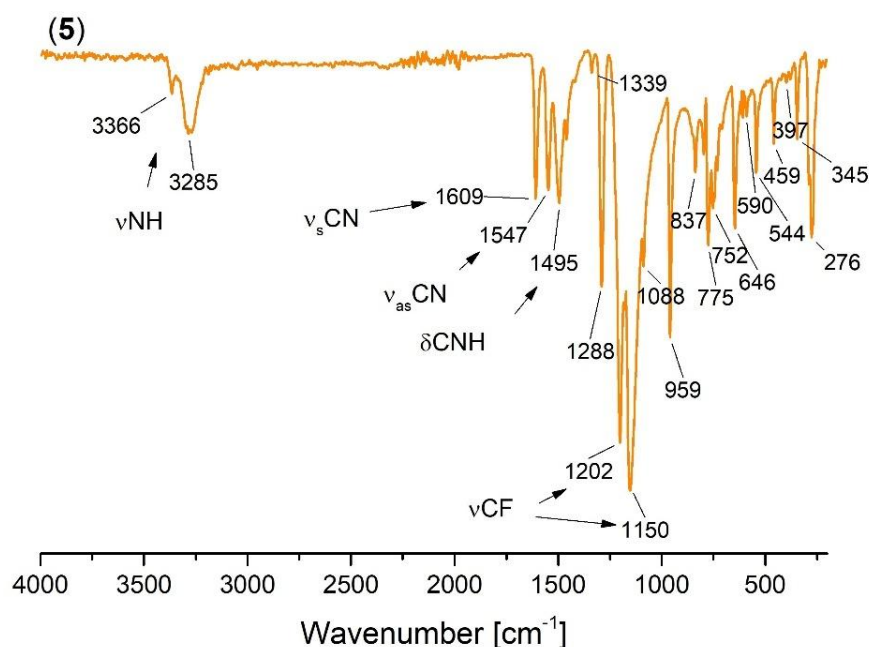


Figure S 6 Infrared spectrum of the $[\text{Ni}(\text{IMAMDCF}_3)_2]$ (5).

Table S 4 Thermal analysis results.

Complex	Temperature [K]			Residue [%]	
	T_i	T_m	T_f	Found	Calc.
$[\text{Ni}_2(\text{HAMDCF}_3)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (1)	319	387	406	19.33	14.83 (Ni)
	406	432 445 477 519	529		
	529	597	620		
$[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (2)	320	342 375	395	16.63	13.17 (Ni)
	395	474	485		
	485	507	528		
	528	591	623		
$[\text{Ni}_2(\text{HAMDCF}_3)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (3)	313	488	562	5.65	11.82 (Ni)
	562	601	644		
$[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (4)	320	503	547	4.54	10.74 (Ni)
	547	600	652		
$[\text{Ni}(\text{IMAMDCF}_3)_2]$ (5)	318	345 369	378	3.97	12.47 (Ni)
	378	413	423		
	423	474	487		

T_i , initial temperature; T_m , maximum temperature; T_f , final temperature

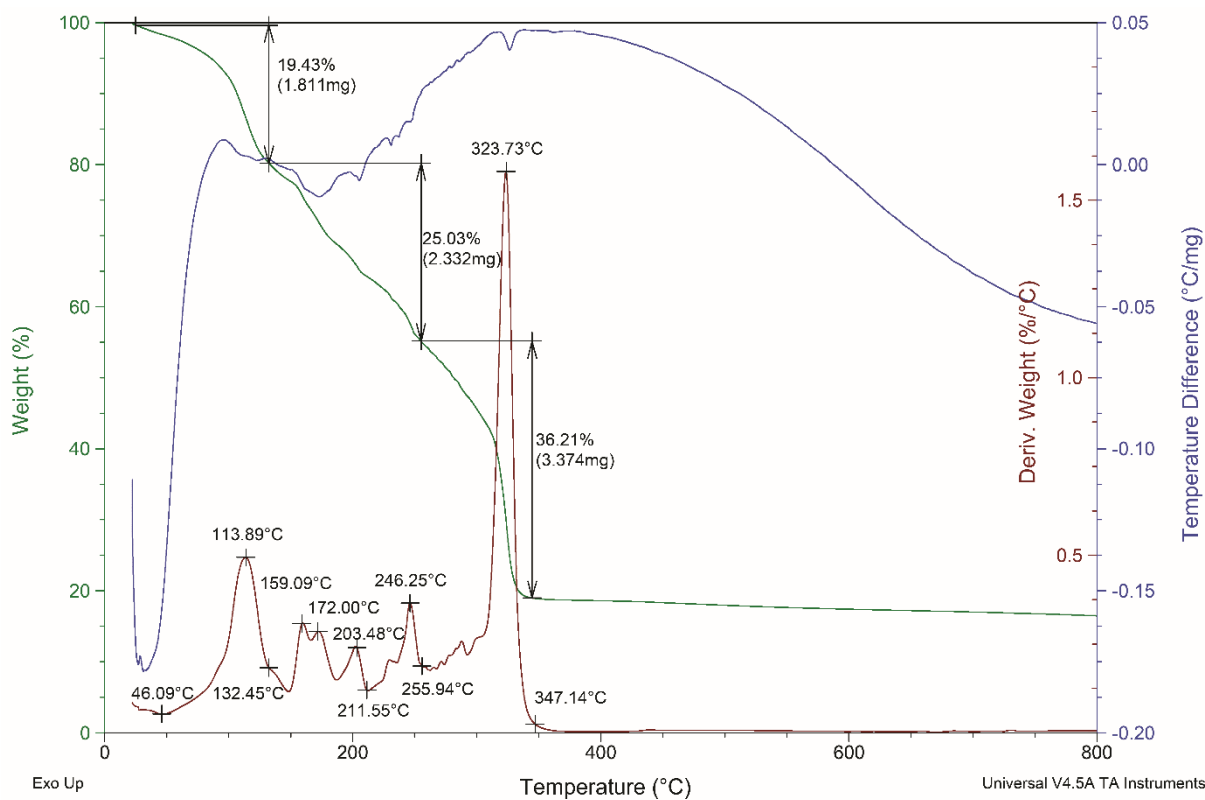


Figure S 7 Thermal decomposition of $[\text{Ni}_2(\text{HAMDCF}_3)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (1) (TG, DTG, DTA curves).

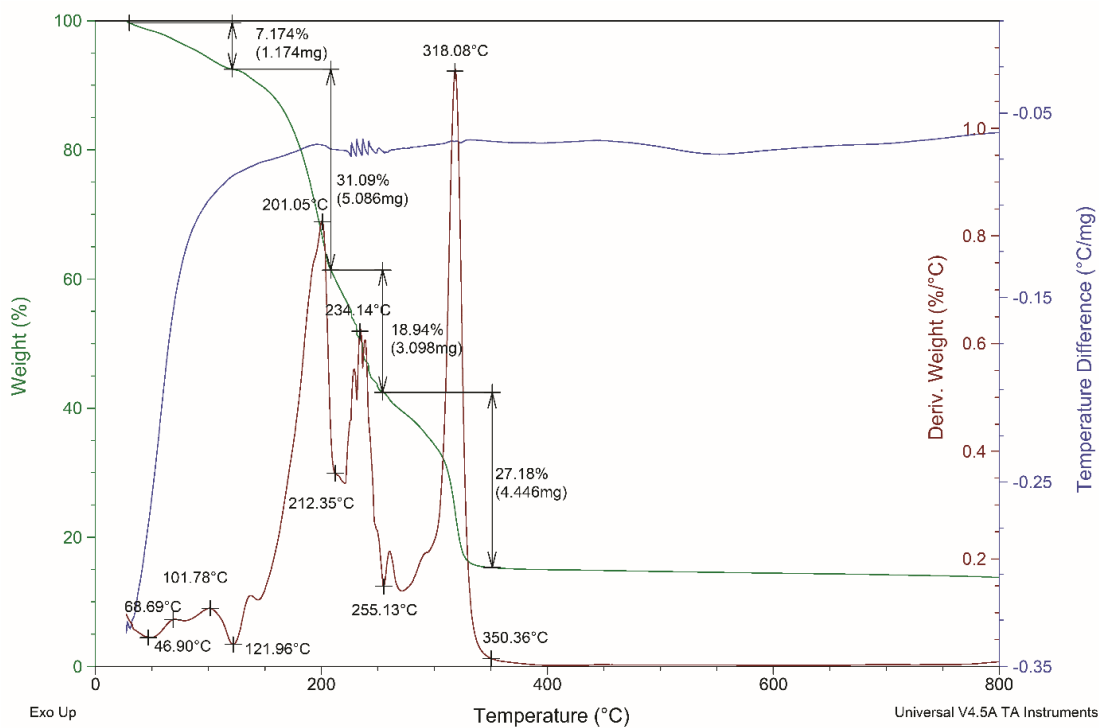


Figure S 8 Thermal decomposition of $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (2) (TG, DTG, DTA curves).

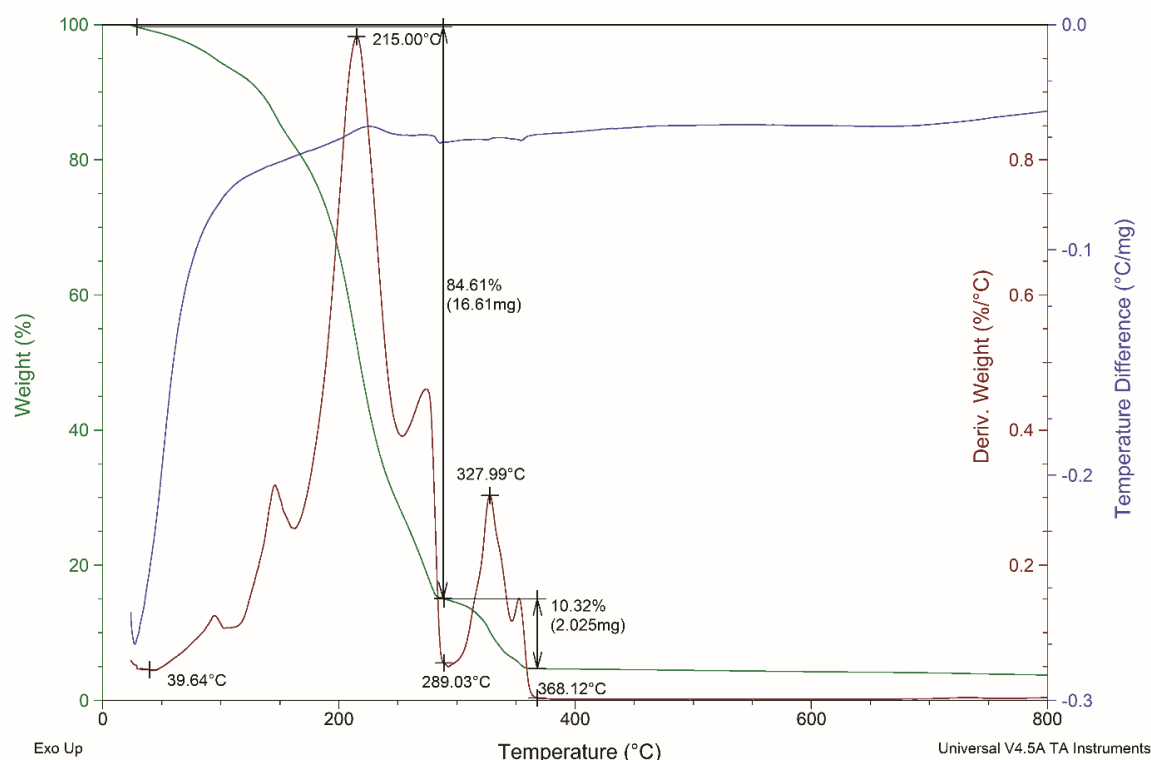


Figure S 9 Thermal decomposition of $[\text{Ni}_2(\text{HAMDCF}_3)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (**3**) (TG, DTG, DTA curves).

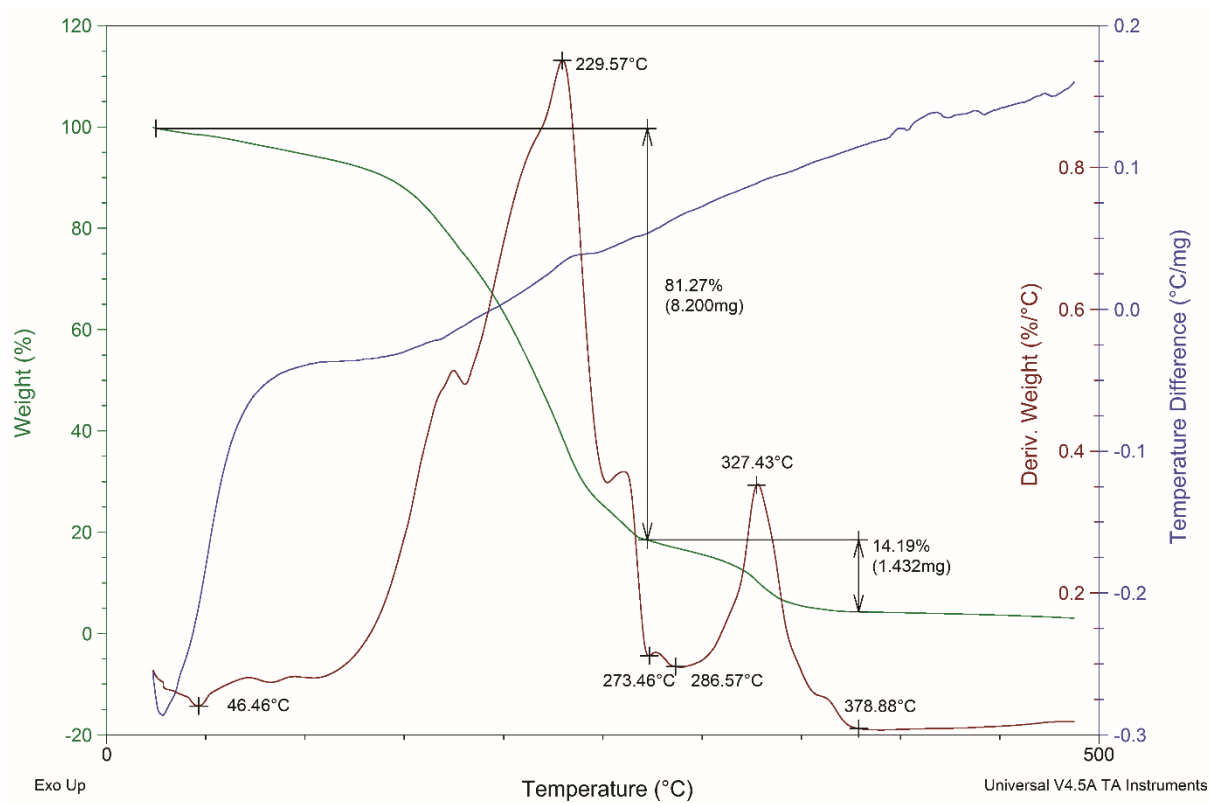


Figure S 10 Thermal decomposition of $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (**4**) (TG, DTG, DTA curves).

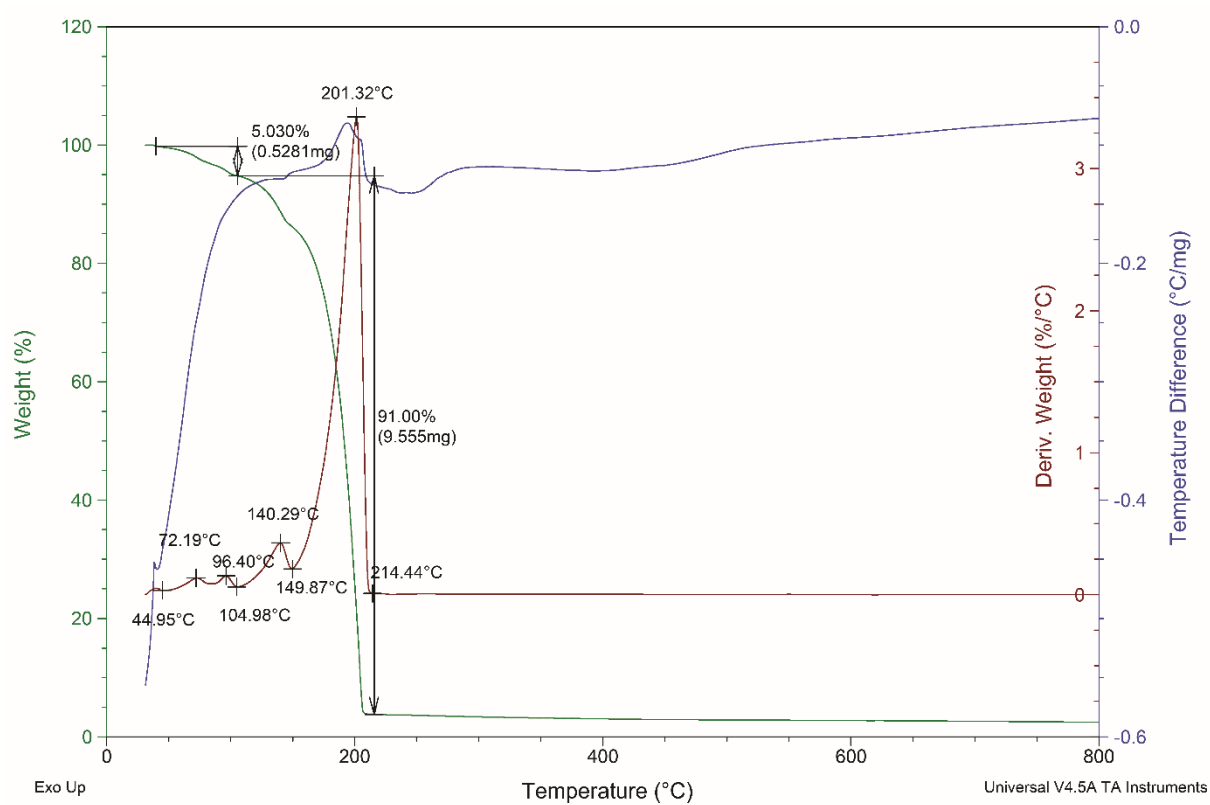


Figure S 11 Thermal decomposition of $[\text{Ni}(\text{IMAMDCF}_3)_2]$ (5) (TG, DTG, DTA curves).

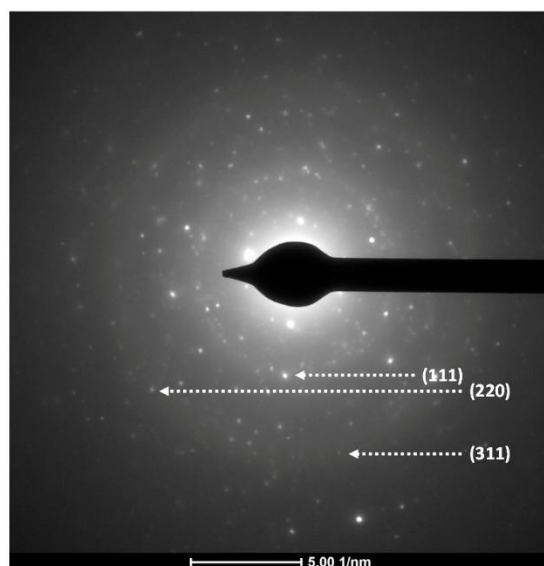


Figure S 12 Transmission electron microscope (TEM) diffraction pattern for the TGA residue (Ni) for $[\text{Ni}(\text{IMAMDCF}_3)_2]$ (5).

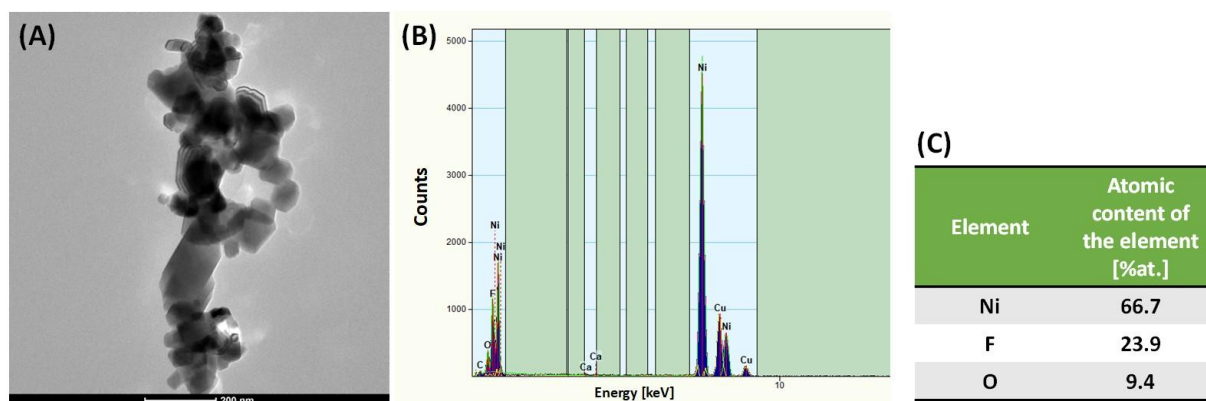


Figure S 13 TEM analysis results of the residue after thermal decomposition of $[\text{Ni}_2(\text{HAMDCF}_3)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (1), (A) – TEM image, (B) – EDX spectrum and (C) – atomic content of the elements.

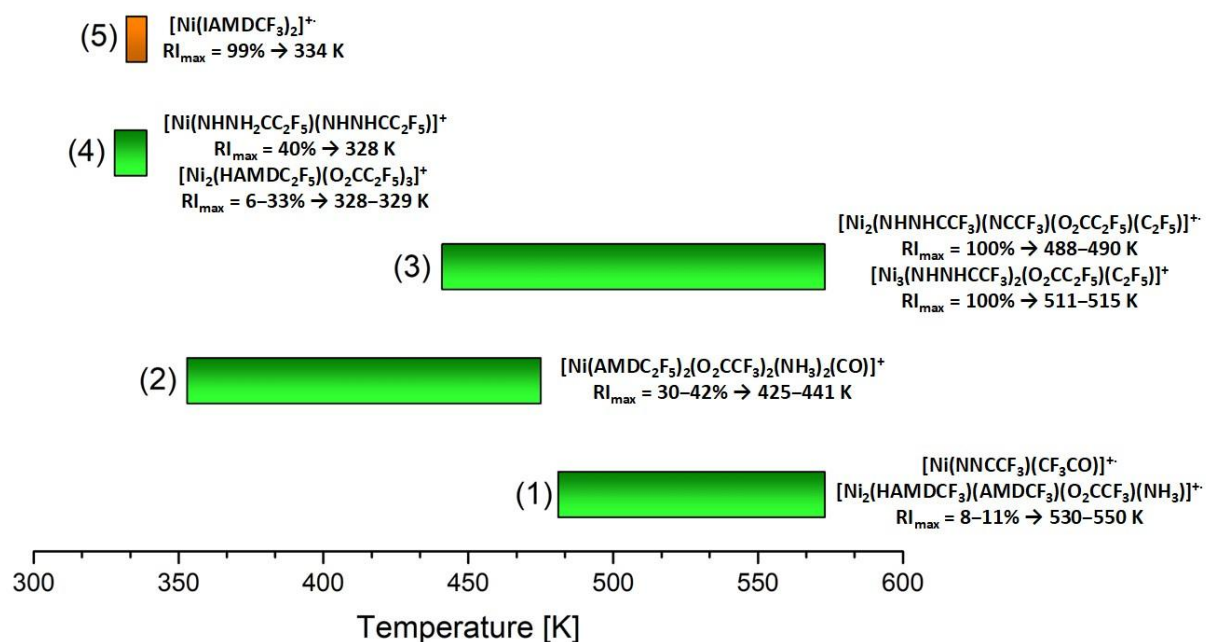


Figure S 14 Temperature ranges for the metallated fragments for compounds (1–5). The ions which achieved the highest relative intensity are marked in the diagram.

Table S 5 EI MS results for the complex $[\text{Ni}_2(\text{HAMDCF}_3)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (**1**).

Fragments	m/z	Relative Intensity (RI) [%]			
		466 K	481 K	533 K	573 K
$[\text{F}_2]^+$	38	—	<1	1	1
$[\text{HN}=\text{C}=\text{N}]^+$	41	1	3	1	1
$[\text{HN}=\text{C}=\text{NH}]^{++}$	42	2	9	5	1
$[\text{CO}_2]^+$	44	34	52	99	89
$[\text{CO}_2\text{H}]^{++}$	45	31	63	36	50
$[\text{Ni}]^+$	58	—	—	1	<1
$[\text{CF}_3]^+$	69	100	100	100	100
$[\text{CF}_3\text{CN}]^{++}$	95	4	5	3	4
$[\text{CF}_3\text{CNH}]^+$	96	2	3	4	1
$[\text{CF}_3\text{CNH}_2]^{++}$	97	3	4	2	4
$[\text{NHNH}_2\text{CCF}_3]^{++}$	112	10	16	9	1
$[\text{CF}_3\text{CO}_2\text{H}]^+$	114	1	1	1	1
$[\text{Ni}(\text{NHNH}_2\text{CCF}_3)]^+$	170	—	—	2	—
$[\text{Ni}(\text{HN}=\text{C}=\text{NH})(\text{O}_2\text{CCF}_3)]^+$ $[\text{Ni}(\text{NHNHCCF}_3)(\text{CO}_2)]^+$	213	—	—	2	—
$[\text{Ni}(\text{NNCCF}_3)(\text{CF}_3\text{CO})]^{++}$	264	—	1	11	1
$[\text{Ni}_2(\text{NHNH}_2\text{CCF}_3)(\text{NHNHCCF}_3)(\text{O}_2\text{CCF}_3)(\text{NH}_3)]^{++}$	469	—	1	11	<1
$[\text{Ni}_3(\text{NHNHCCF}_3)(\text{O}_2\text{CCF}_3)_2(\text{NH}_3)]^+$	530	—	—	—	2

Table S 6 EI MS results for the complex $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (2).

Fragments	m/z	Relative Intensity (RI) [%]			
		353 K	358 K	425 K	451 K
$[\text{F}_2]^+$	38	<1	1	1	—
$[\text{HN}=\text{C}=\text{N}]^+$	41	4	8	1	—
$[\text{HN}=\text{C}=\text{NH}]^+$	42	13	15	5	1
$[\text{CO}_2]^+$	44	100	100	76	73
$[\text{CO}_2\text{H}]^+$	45	14	47	28	19
$[\text{Ni}]^+$	58	1	1	3	—
$[\text{CF}_3]^+$	69	49	70	100	100
$[\text{CF}_2\text{CN}]^+$	76	2	3	25	23
$[\text{C}_2\text{F}_4]^+$	100	11	9	8	4
$[\text{CF}_3\text{CO}_2\text{H}]^+$	114	1	1	1	—
$[\text{C}_2\text{F}_5]^+$	119	45	26	14	6
$[\text{C}_2\text{F}_4\text{CN}]^+$	126	1	1	18	22
$[\text{C}_2\text{F}_5\text{CNH}]^+$	146	4	3	6	2
$[\text{C}_2\text{F}_5\text{CNH}_2]^+$	147	<1	<1	<1	—
$[\text{NHNH}_2\text{CC}_2\text{F}_5]^+$	162	62	40	10	1
$[\text{Ni}(\text{NHNHCC}_2\text{F}_5)]^+$	219	1	1	2	—
$[\text{Ni}_2(\text{NHNHCCF}_3)(\text{NH}_3)]^+$	244	<1	<1	8	3
$[\text{Ni}(\text{NHNHCC}_2\text{F}_5)(\text{HN}=\text{C}=\text{N})]^+$	260	<1	1	4	2
$[\text{Ni}(\text{NHNHCC}_2\text{F}_5)(\text{HN}=\text{C}=\text{NH})]^+$	261	<1	<1	1	—
$[\text{Ni}(\text{NHNH}_2\text{CC}_2\text{F}_5)(\text{HN}=\text{C}=\text{NH})]^+$	262	<1	<1	2	—
$[\text{Ni}(\text{NHNH}_2\text{CC}_2\text{F}_5)(\text{CO}_2)]^+$	264	<1	<1	4	2
$[\text{Ni}_2(\text{NHNHCC}_2\text{F}_5)(\text{O}_2\text{CCF}_3)_2(\text{CF}_3)]^{2+}$	286	—	—	3	1
$[\text{Ni}(\text{CF}_3)_2(\text{C}_2\text{F}_5)]^+$	315	—	<1	10	2
$[\text{Ni}(\text{NHNHCC}_2\text{F}_5)(\text{O}_2\text{CCF}_3)]^+$	332	4	2	—	—
$[\text{Ni}_2(\text{NHNH}_2\text{CC}_2\text{F}_5)(\text{O}_2\text{CCF}_3)_4\text{-H}]^{2+}$	364	<1	1	24	—
$[\text{Ni}(\text{NHNHCC}_2\text{F}_5)_2]^+$	380	2	1	—	—
$[\text{Ni}_2(\text{NHNHCC}_2\text{F}_5)_2(\text{O}_2\text{CCF}_3)]^+$	551	<1	—	1	—
$[\text{Ni}_2(\text{NHNH}_2\text{CC}_2\text{F}_5)(\text{NHNHCC}_2\text{F}_5)(\text{O}_2\text{CCF}_3)]^+$	552	—	<1	1	—

$[\text{Ni}_2(\text{NHNH}_2\text{CC}_2\text{F}_5)_2(\text{O}_2\text{CCF}_3)(\text{NH}_3)]^+$	570	—	—	4	1
$[\text{Ni}_2(\text{NHNH}_2\text{CC}_2\text{F}_5)(\text{O}_2\text{CCF}_3)_3]^+$	617	3	2	—	—
$[\text{Ni}_2(\text{NHNH}_2\text{CC}_2\text{F}_5)_3(\text{NH}_3)]^+$	619	1	1	19	4
$[\text{Ni}(\text{NHNHCC}_2\text{F}_5)_2(\text{O}_2\text{CCF}_3)_2(\text{NH}_3)_2(\text{CO})]^+$	668	<1	2	32	24
$[\text{Ni}_2(\text{NHNHCC}_2\text{F}_5)_2(\text{O}_2\text{CCF}_3)_3]^+$	777	7	5	—	—
$[\text{Ni}_3(\text{NHNH}_2\text{CC}_2\text{F}_5)_3(\text{O}_2\text{CCF}_3)_2]^+$	888	—	—	—	—

Table S 7 EI MS results for the complex $[\text{Ni}_2(\text{HAMDCF}_3)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (**3**).

Fragments	m/z	Relative Intensity (RI) [%]			
		441 K	458 K	496 K	573 K
$[\text{F}_2]^+$	38	<1	1	—	—
$[\text{HN}=\text{C}=\text{N}]^+$	41	1	1	—	—
$[\text{HN}=\text{C}=\text{NH}]^{++}$	42	4	3	—	—
$[\text{CO}_2]^+$	44	80	100	22	92
$[\text{CO}_2\text{H}]^+$	45	98	31	34	15
$[\text{Ni}]^+$	58	<1	2	—	—
$[\text{CF}_3]^+$	69	100	75	83	100
$[\text{CF}_2\text{CN}]^+$	76	4	11	7	—
$[\text{CF}_3\text{CNH}]^+$	96	5	4	—	—
$[\text{CF}_3\text{CNH}_2]^{++}$	97	38	10	13	7
$[\text{C}_2\text{F}_4]^+$	100	83	32	50	71
$[\text{NHNH}_2\text{CCF}_3]^{++}$	112	9	8	—	—
$[\text{C}_2\text{F}_5]^+$	119	68	26	36	40
$[\text{C}_2\text{F}_5\text{CO}_2\text{H}]^{++}$	164	<1	<1	—	—
$[\text{Ni}(\text{NHNHCCF}_3)]^+$	169	1	1	—	—
$[\text{Ni}(\text{NHNH}_2\text{CCF}_3)]^+$	170	1	3	—	—
$[\text{Ni}(\text{NHNHCCF}_3)(\text{NCN})]^{++}$	209	2	1	—	—
$[\text{Ni}(\text{NHNH}_2\text{CCF}_3)(\text{NCN})]^+$	210	1	1	—	—
$[\text{Ni}(\text{NHNHCCF}_3)(\text{CF}_3\text{CN})]^+$	264	1	14	—	—
$[\text{Ni}(\text{NHNHCCF}_3)_2(\text{NH}_3)]^{++}$	297	—	—	5	1
$[\text{Ni}(\text{O}_2\text{CC}_2\text{F}_5)(\text{CF}_3\text{NH})]^{++}$	305	—	1	—	—
$[\text{Ni}(\text{NHNHCCF}_3)(\text{O}_2\text{CC}_2\text{F}_5)]^{++}$	332	2	2	—	—
$[\text{Ni}_2(\text{NHNHCCF}_3)(\text{O}_2\text{CC}_2\text{F}_5)]^+$	390	—	<1	9	1
$[\text{Ni}_2(\text{NHNH}_2\text{CCF}_3)(\text{O}_2\text{CC}_2\text{F}_5)]^+$	391	—	<1	—	—
$[\text{Ni}_3(\text{O}_2\text{CC}_2\text{F}_5)(\text{HNCNC})]^+$	392	—	<1	10	2
$[\text{Ni}_2(\text{O}_2\text{CC}_2\text{F}_5)_2]^{++}$	442	—	<1	19	4
$[\text{Ni}(\text{NHNH}_2\text{CCF}_3)_2(\text{O}_2\text{CC}_2\text{F}_5)]^+$	445	20	2	5	—
$[\text{Ni}_2(\text{NHNH}_2\text{CCF}_3)(\text{NHNHCCF}_3)_2]^{++}$	450	<1	2	—	—

$[\text{Ni}_2(\text{NHNH}_2\text{CCF}_3)(\text{O}_2\text{CC}_2\text{F}_5)(\text{CF}_3)]^{++}$	460	<1	1	27	17
$[\text{Ni}_2(\text{NHNH}_2\text{CCF}_3)(\text{NHNHCCF}_3)(\text{O}_2\text{CCF}_3)(\text{NH}_3)]^{++}$	469	2	17	—	—
$[\text{Ni}_2(\text{NHNH}_2\text{CCF}_3)_2(\text{O}_2\text{CC}_2\text{F}_5)(\text{NH}_3)]^+$	520	1	5	—	—
$[\text{Ni}_3(\text{NHNH}_2\text{CCF}_3)(\text{NHNHCCF}_3)_2(\text{CN})]^+$	536	—	1	23	5
$[\text{Ni}_2(\text{NHNHCCF}_3)(\text{O}_2\text{CC}_2\text{F}_5)_2]^+$	553	<1	1	7	—
$[\text{Ni}_2(\text{NHNHCCF}_3)(\text{NCCF}_3)(\text{O}_2\text{CC}_2\text{F}_5)(\text{C}_2\text{F}_5)]^{++}$	604	1	2	—	—
$[\text{Ni}_2(\text{O}_2\text{CC}_2\text{F}_5)_3]^+$	605	<1	1	77	13
$[\text{Ni}_3(\text{NHNH}_2\text{CCF}_3)(\text{O}_2\text{CC}_2\text{F}_5)_2(\text{NH}_3)]^+$	629	—	1	6	—
$[\text{Ni}_3(\text{NHNHCCF}_3)_2(\text{O}_2\text{CC}_2\text{F}_5)(\text{C}_2\text{F}_5)]^+$	680	<1	2	86	21
$[\text{Ni}_2(\text{NHNHCCF}_3)(\text{O}_2\text{CC}_2\text{F}_5)_3]^{++}$	716	2	2	—	—
$[\text{Ni}_3(\text{NHNHCCF}_3)(\text{O}_2\text{CC}_2\text{F}_5)_3(\text{NH}_3)]^+$	793	—	—	—	5
$[\text{Ni}_2(\text{NHNHCCF}_3)_2(\text{O}_2\text{CC}_2\text{F}_5)_3]^+$	827	1	1	—	—
$[\text{Ni}_3(\text{O}_2\text{CC}_2\text{F}_5)_4(\text{NH}_3)]^+$	845	—	<1	13	46
$[\text{Ni}_3(\text{O}_2\text{CC}_2\text{F}_5)_5]^+$	989	—	<1	24	—
$[\text{Ni}_4(\text{NHNHCCF}_3)(\text{O}_2\text{CC}_2\text{F}_5)_3(\text{CO}_2)_4]^{++}$	1013	—	1	4	—
$[\text{Ni}_3(\text{NHNH}_2\text{CCF}_3)(\text{NHNHCCF}_3)_2(\text{O}_2\text{CC}_2\text{F}_5)_3(\text{CF}_3)(\text{NH}_3)]^{++}$	1085	—	<1	2	5

Table S 8 EI MS results for the complex $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (**4**).

Fragments	m/z	Relative Intensity (RI) [%]			
		324 K	328 K	329 K	332 K
$[\text{HN}=\text{C}=\text{N}]^+$	41	10	<1	—	—
$[\text{HN}=\text{C}=\text{NH}]^{++}$	42	20	1	1	3
$[\text{CO}_2]^+$	44	28	37	5	69
$[\text{CO}_2\text{H}]^{++}$	45	100	22	3	34
$[\text{Ni}]^+$	58	—	1	—	—
$[\text{CF}_3]^+$	69	32	25	5	100
$[\text{CF}_2\text{CN}]^+$	76	1	<1	<1	5
$[\text{C}_2\text{F}_4]^+$	100	18	16	4	80
$[\text{C}_2\text{F}_5]^+$	119	14	17	3	56
$[\text{C}_2\text{F}_4\text{CN}]^+$	126	—	—	<1	3
$[\text{C}_2\text{F}_5\text{CNH}]^+$	146	<1	2	<1	1
$[\text{C}_2\text{F}_5\text{CNH}_2]^+$	147	1	1	<1	6
$[\text{NHNH}_2\text{CC}_2\text{F}_5]^{++}$	162	3	3	1	13
$[\text{C}_2\text{F}_5\text{CO}_2\text{H}]^{++}$	164	3	9	—	—
$[\text{Ni}(\text{NHNHCC}_2\text{F}_5)]^+$	219	—	8	<1	1
$[\text{Ni}(\text{NHNH}_2\text{CC}_2\text{F}_5)]^+$	220	—	10	<1	—
$[\text{Ni}(\text{O}_2\text{CC}_2\text{F}_5)]^+$	221	—	4	<1	—
$[\text{Ni}(\text{NHNHCC}_2\text{F}_5)(\text{HN}=\text{C}=\text{NH})]^+$	261	—	1	—	—
$[\text{Ni}(\text{NHNH}_2\text{CC}_2\text{F}_5)(\text{HN}=\text{C}=\text{NH})]^+$	262	—	2	—	—
$[\text{Ni}(\text{NHNH}_2\text{CC}_2\text{F}_5)(\text{NHNHCC}_2\text{F}_5)]^+$	381	—	40	1	—
$[\text{Ni}(\text{NHNHCC}_2\text{F}_5)(\text{O}_2\text{CC}_2\text{F}_5)]^{++}$	382	—	16	<1	—
$[\text{Ni}_4(\text{O}_2\text{CC}_2\text{F}_5)(\text{C}_2\text{F}_5)(\text{NH}_3)]^+$	533	—	4	1	2
$[\text{Ni}(\text{NHNH}_2\text{CC}_2\text{F}_5)_2(\text{O}_2\text{CC}_2\text{F}_5)]^+$	545	—	13	1	—
$[\text{Ni}_2(\text{NHNH}_2\text{CC}_2\text{F}_5)_2(\text{O}_2\text{CC}_2\text{F}_5)]^+$ $[\text{Ni}_2(\text{NHNHCC}_2\text{F}_5)(\text{O}_2\text{CC}_2\text{F}_5)_2]^+$	603	—	15	2	1
$[\text{Ni}_2(\text{O}_2\text{CC}_2\text{F}_5)_3]^+$	605	—	12	2	2
$[\text{Ni}_2(\text{NHNH}_2\text{CC}_2\text{F}_5)_2(\text{O}_2\text{CC}_2\text{F}_5)_2]^{++}$ $[\text{Ni}_2(\text{NHNHCC}_2\text{F}_5)(\text{O}_2\text{CC}_2\text{F}_5)_3]^{++}$	766	—	—	—	1
$[\text{Ni}_2(\text{NHNH}_2\text{CC}_2\text{F}_5)(\text{O}_2\text{CC}_2\text{F}_5)_3]^+$	767	—	6	33	—
$[\text{Ni}_2(\text{NHNHCC}_2\text{F}_5)_2(\text{O}_2\text{CC}_2\text{F}_5)_2(\text{CO}_2)]^{++}$	808	—	1	3	—

$[\text{Ni}_2(\text{NHNH}_2\text{CC}_2\text{F}_5)(\text{HN}=\text{C}=\text{NH})(\text{O}_2\text{CC}_2\text{F}_5)_3]^+$	809	—	<1	—	—
$[\text{Ni}_3(\text{NHNHCC}_2\text{F}_5)(\text{O}_2\text{CC}_2\text{F}_5)_3(\text{NH}_3)]^+$	843	—	1	7	—
$[\text{Ni}_2(\text{NHNH}_2\text{CC}_2\text{F}_5)(\text{NHNHCC}_2\text{F}_5)(\text{O}_2\text{CC}_2\text{F}_5)_3]^{++}$	928	—	9	—	—
$[\text{Ni}_2(\text{NHNH}_2\text{CC}_2\text{F}_5)_2(\text{O}_2\text{CC}_2\text{F}_5)_3(\text{CC}_2\text{F}_5)]^+$	1060	—	<1	6	—
$[\text{Ni}_4(\text{NHNH}_2\text{CC}_2\text{F}_5)(\text{O}_2\text{CC}_2\text{F}_5)_3(\text{CO}_2)_4]^+$	1061	—	<1	10	1

Table S 9 EI MS results for the complex [Ni(IMAMDCF₃)₂] (5).

Fragments	m/z	Relative Intensity (RI) [%]		
		332 K	334 K	339 K
[CH ₃ CN] ⁺ / [HN=C=N] ⁺	41	2	–	15
[NH=C–NH] ⁺	42	1	–	41
[NH=C–NH ₂] ⁺	43	2	3	43
[CF ₂] ⁺	50	12	7	16
[Ni] ⁺	58	2	2	45
[CF ₃] ⁺	69	90	62	100
[CF ₂ CN] ⁺	76	8	3	–
[Ni(HN=C=NH)] ⁺	100	2	6	2
[N ₂ CCF ₃] ⁺	109	–	–	3
[NHNHCCF ₃] ⁺	111	–	–	3
[NHNH ₂ CCF ₃] ⁺	112	–	–	–
[C ₂ F ₄ CN] ⁺	126	–	–	3
[Ni(NCCF ₃)] ⁺	153	1	5	–
[Ni(NHNH ₂ CCF ₃)] ⁺	170	3	11	2
[Ni(NHCNCNH) ₂] ⁺	194	2	9	2
[Ni(NHCNCNH) ₂ (NH ₃)] ⁺	211	8	18	4
[Ni(NH ₂ CNCNH) ₂ (NH ₃) ₂] ⁺	230	75	53	9
[Ni(CF ₃ NCCF ₃ N)] ⁺	236	11	10	–
[Ni(NHC(CF ₃)NC(CF ₃)NH)] ⁺	264	3	13	3
[Ni(NH ₂ C(CF ₃)NC(CF ₃)NH)] ⁺	265	14	66	13
[Ni(CNC(CF ₃)NC(CF ₃)NC)] ⁺	286	48	40	3
[Ni(NHC(CF ₃)NC(CF ₃)NH)(NHC(CF ₃)NCCF ₂ N)] ⁺	450	–	–	2
[Ni(NHC(CF ₃)NC(CF ₃)NH) ₂] ⁺	470	18	99	24

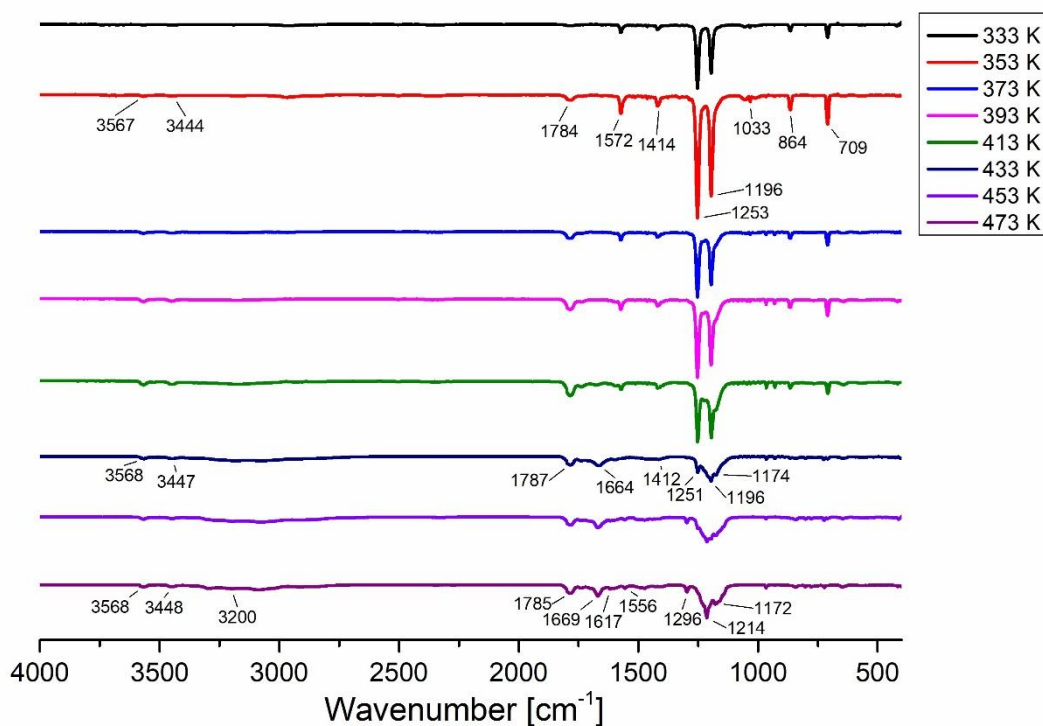


Figure S 15 Temperature variable infrared spectra VT IR for the vapor formed during the $[\text{Ni}_2(\text{HAMDCF}_3)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (1) heating (333–473 K).

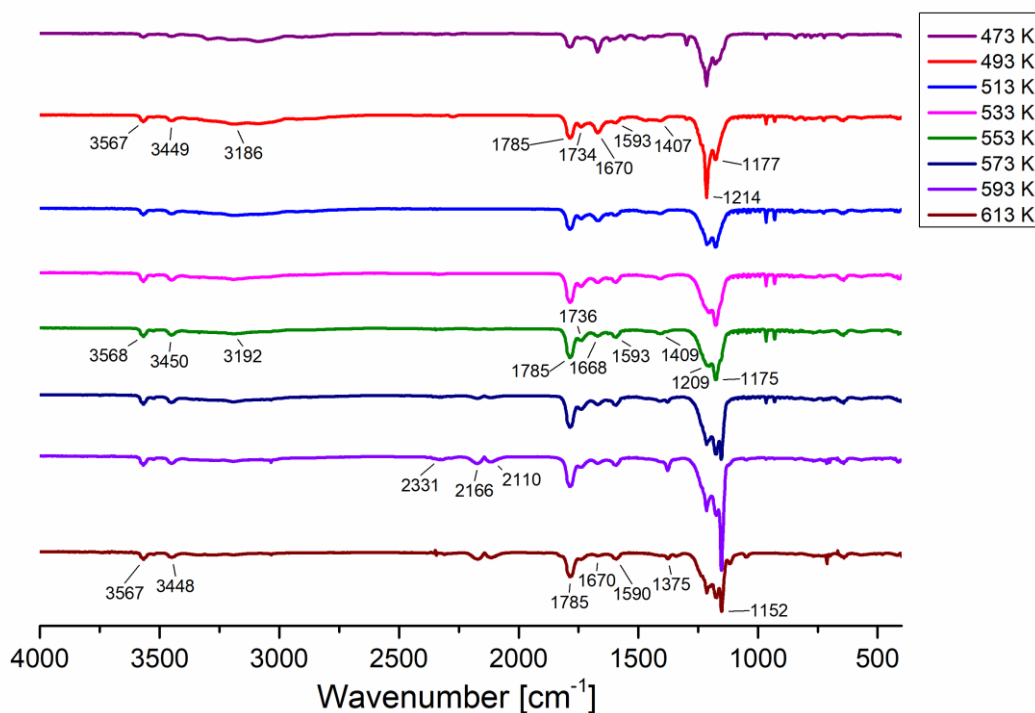


Figure S 16 Temperature variable infrared spectra VT IR for the vapor formed during the $[\text{Ni}_2(\text{HAMDCF}_3)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (1) heating (473–613 K).

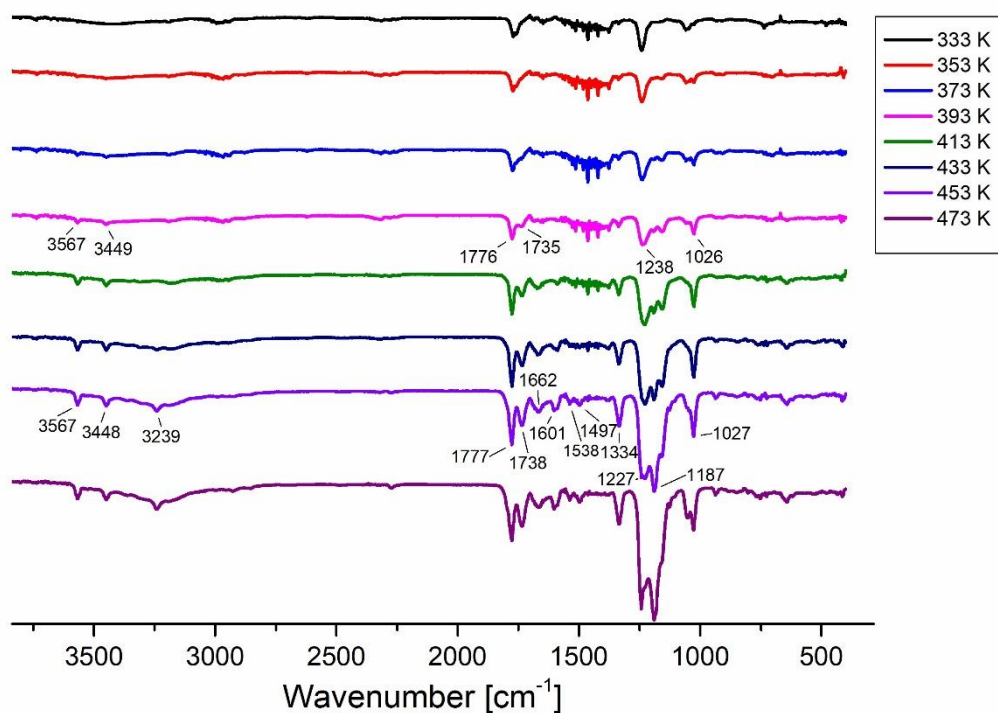


Figure S 17 Temperature variable infrared spectra VT IR for the vapor formed during the $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (**2**) heating (333–473 K).

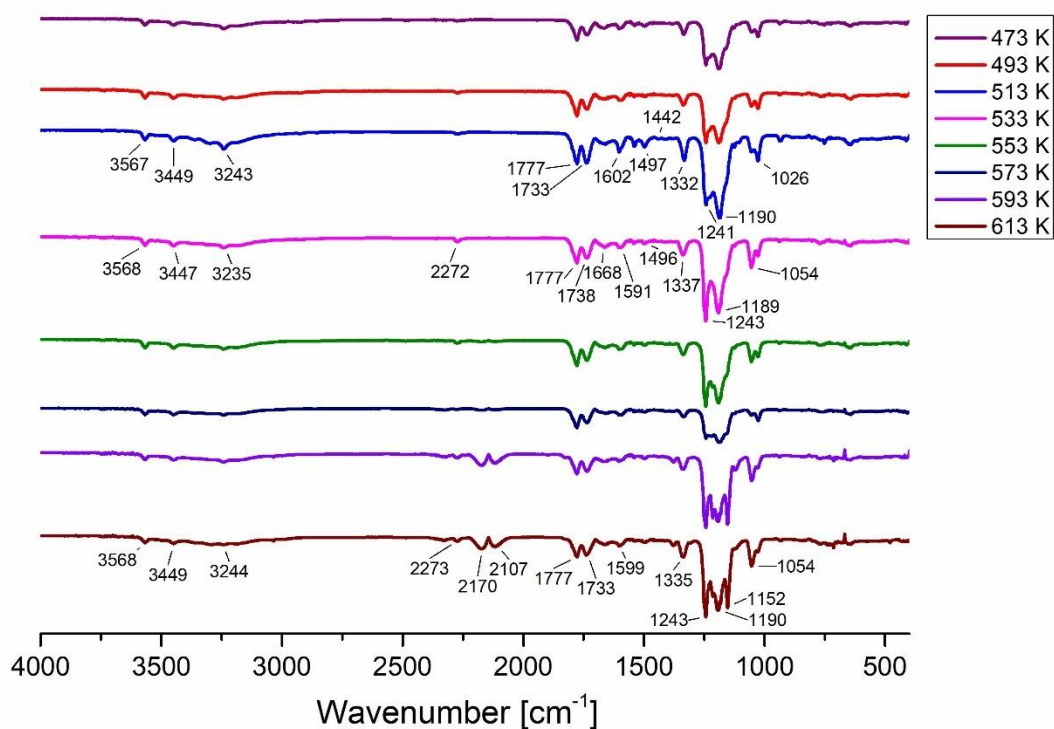
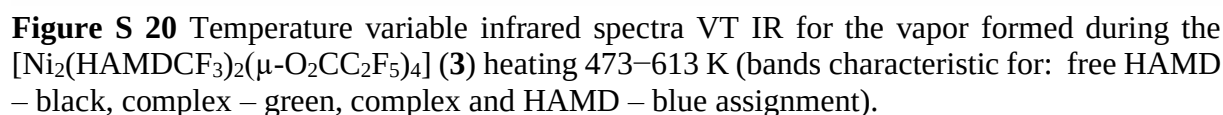
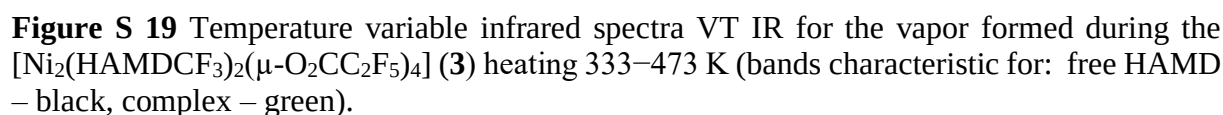


Figure S 18 Temperature variable infrared spectra VT IR for the vapor formed during the $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CCF}_3)_4]$ (**2**) heating (473–613 K).



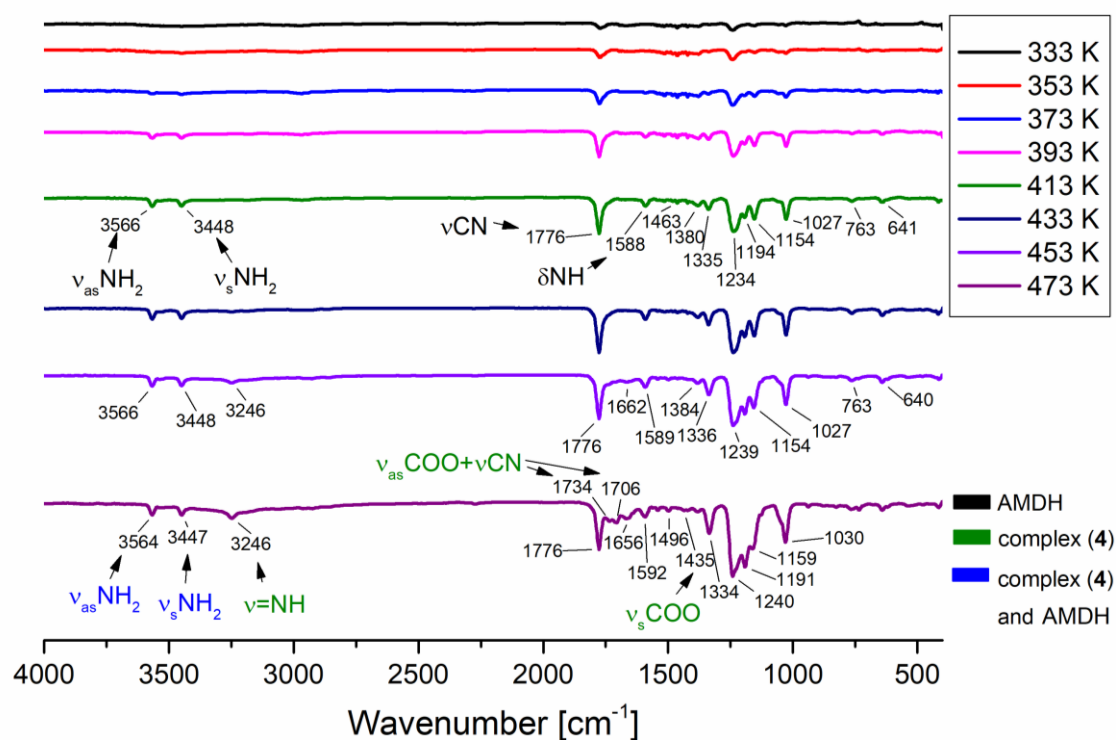


Figure S 21 Temperature variable infrared spectra VT IR for the vapor formed during the $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (**4**) heating 333–473 K (bands characteristic for: free HAMD – black, complex – green, complex and HAMD – blue assignment).

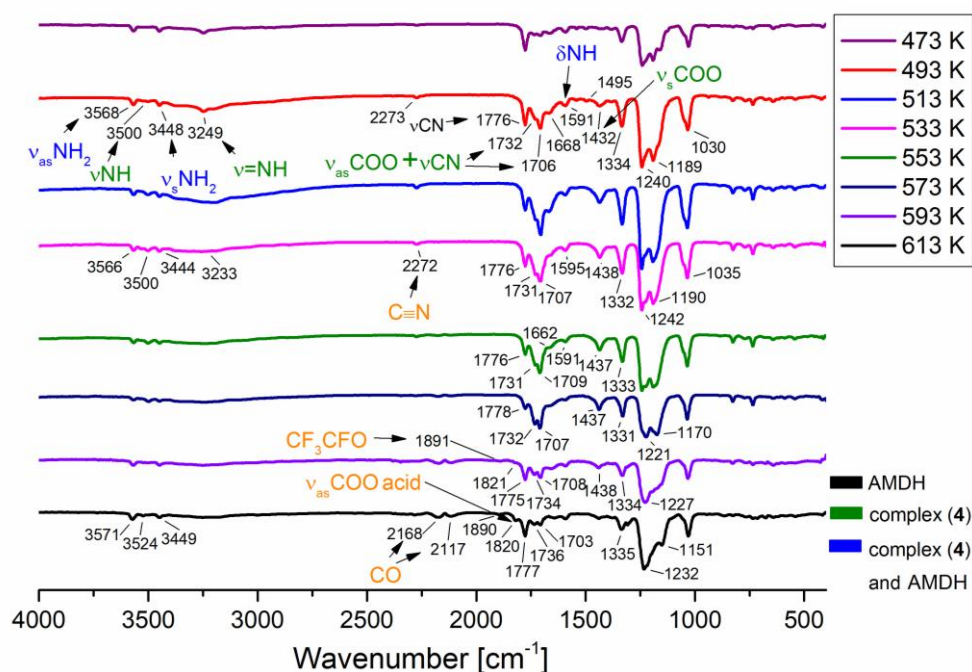


Figure S 22 Temperature variable infrared spectra VT IR for the vapor formed during the $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (**4**) heating 473–613 K (bands characteristic for: free HAMD – black, complex – green, complex and HAMD – blue assignment).

Table S 10 Vibrational band positions and assignments for gaseous products of thermal decomposition of $[\text{Ni}_2(\text{HAMDR}_f)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (**3**) and $[\text{Ni}_2(\text{HAMDR}_f)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (**4**), where $\text{R}_f = \text{CF}_3$ (**3**), C_2F_5 (**4**).

Assignment (ca.) [cm ⁻¹]	(1)	(2)	(3)	(4)
$\nu\text{C}\equiv\text{N}$ ($\text{R}_f\text{C}\equiv\text{N}$)	—	2273	2272	2274
νCO (CO)	2166 2110	2170 2107	2168 2117	2168 2117
νCO_2	2331	—	—	—
$\nu_{\text{as}}\text{COO}$ (<i>acid</i>)	—	—	1820	—
$\nu\text{C}=\text{O}$ (CF_3CFO)	—	—	—	1890
νCF (CF_3CFO)	—	—	—	1253 1199

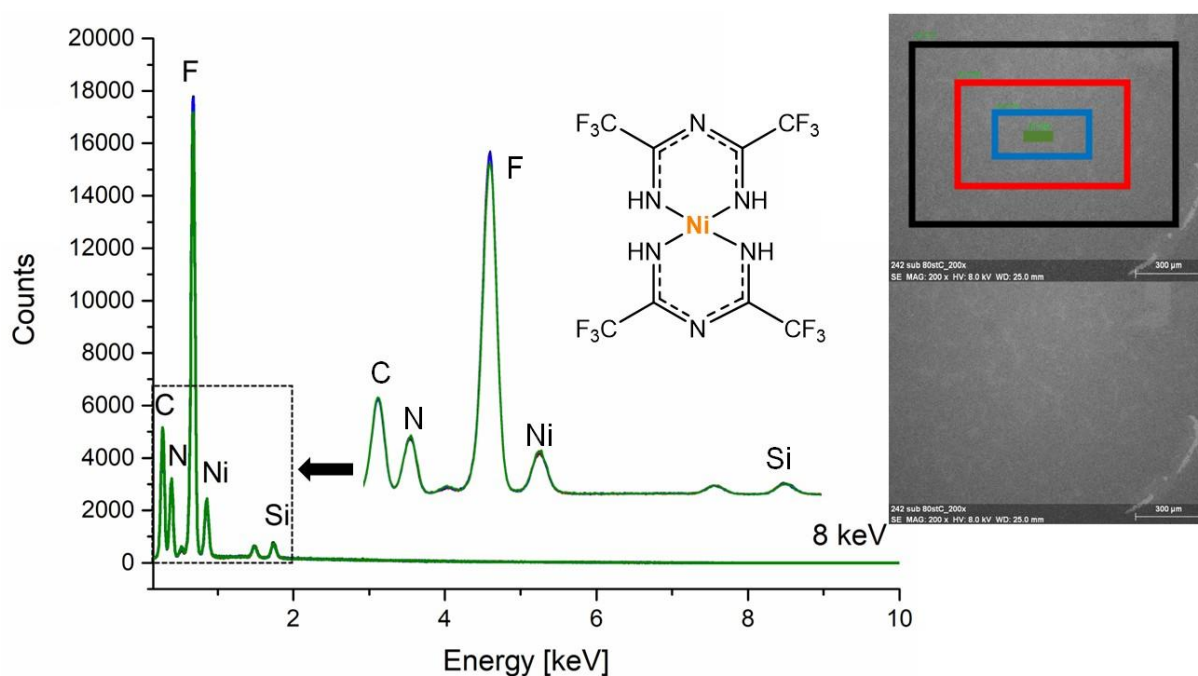


Figure S 23 Examined scan areas' EDX spectra (8 keV) for the $[\text{Ni}(\text{IMAMDCF}_3)_2]$ (**5**) layer deposited on a Si(111) substrate (Mag = 200x).

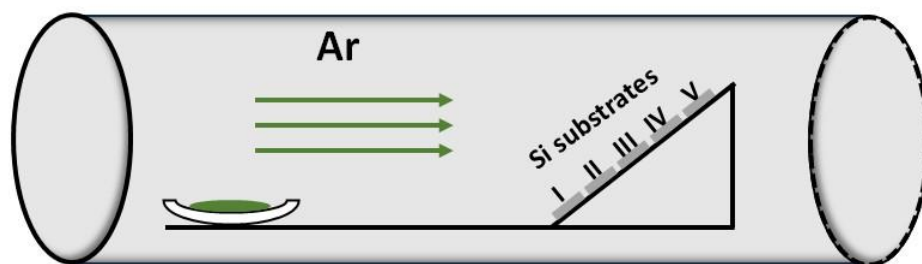


Figure S 24 CVD reactor scheme with marked substrates, numbered according to the length of the transport path.

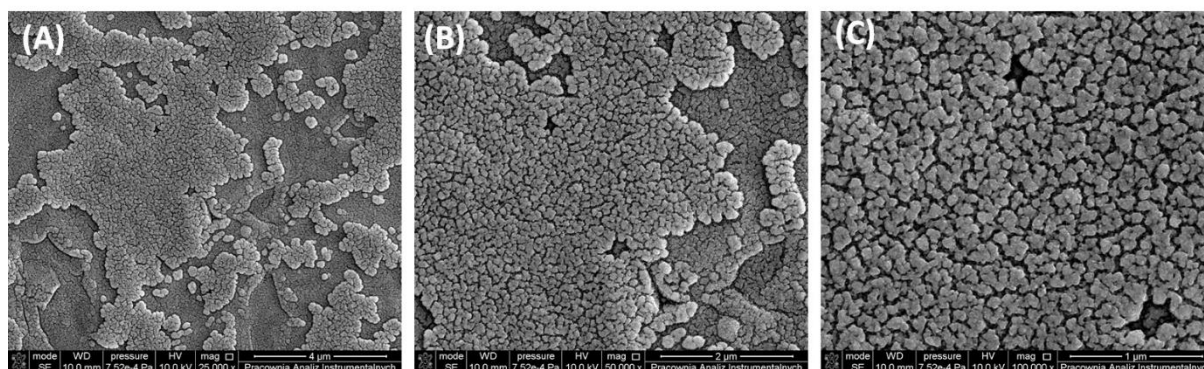


Figure S 25 SEM images of deposits formed using the precursor $[\text{Ni}_2(\text{HAMDC}_2\text{F}_5)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$ (**4**) ($T_V = 493 \text{ K}$, $T_D = 723 \text{ K}$, Ar), on titania nanotubes, (A) – Mag = 25000x, (B) – Mag = 50000x, (C) – 100000x.

Table S 11 The k_{obs} values for methylene blue photocatalytic degradation under UV-lamp without (REF) and with TNT20 or Ni-TNT20 substrates as catalysts. Repetitions were carried out using the same substrates.

Substrate	Test number	$10^9 k_{\text{obs}} [\text{Ms}^{-1}]$
REF	1	0.44 ± 0.11
	2	0.21 ± 0.01
	3	0.43 ± 0.15
TNT20	1	2.14 ± 0.16
	2	1.63 ± 0.09
	3	0.91 ± 0.02
Ni-TNT20	1	3.39 ± 0.27
	2	1.73 ± 0.10
	3	0.94 ± 0.13

Table S 12 The k_{obs} values for methylene blue photocatalytic degradation under Vis-lamp without (REF) and with TNT20 and Ni-TNT20 substrates as catalysts.

Substrate	$10^9 k_{\text{obs}} [\text{Ms}^{-1}]$
REF	0.35 ± 0.04
TNT20	0.23 ± 0.03
Ni-TNT20	0.33 ± 0.07

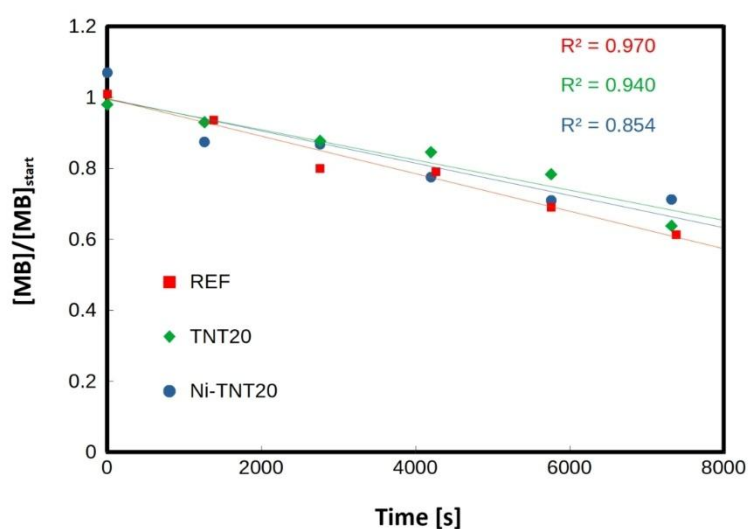


Figure S 26 The absorbance-time dependencies for the studied substrates (TNT20 and Ni-TNT20) and the sample without the substrate (REF) during the Vis irradiation. $[\text{MB}]_0 = 1 \cdot 10^5 \text{ mol/dm}^3$, $T = 298.1 \text{ K}$.

Article

New Gold(I) Complexes as Potential Precursors for Gas-Assisted Methods: Structure, Volatility, Thermal Stability, and Electron Sensitivity

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Abstract: We report the synthesis and characterization of new, user-friendly gold(I) $[\text{Au}_4(\mu\text{-(NH)}_2\text{CC}_2\text{F}_5)_4]_n$ coordination polymer and $[\text{Au}_2\text{Cl}_2(\text{NH}_2(\text{NH}=\text{CC}_2\text{F}_5)_2)]_n$ complex. These compounds were investigated for potential application as precursors in chemical vapor deposition (CVD) and focused electron/ion beam-induced deposition (FEBID/FIBID), which are additive methods to produce nanomaterials. Single-crystal X-ray diffraction, elemental analysis, and infrared spectroscopy were used to determine the complexes' composition and structure. We studied their thermal stability and volatility using thermal analysis and variable-temperature infrared spectroscopy (VT IR) and by conducting sublimation experiments. The gold(I) amidinate $[\text{Au}_2(\mu\text{-(NH)}_2\text{CC}_2\text{F}_5)_2]_n$ sublimates at 413 K under 10^{-2} mbar pressure. The electron-induced decomposition of the complexes' molecules in the gas phase and of their thin layers on silicon substrates was analyzed using electron impact mass spectrometry (EI MS) and microscopy studies (SEM/EDX), respectively, to provide insights for FEBID and FIBID precursor design. The $[\text{Au}_2\text{Cl}_2(\text{NH}_2(\text{NH}=\text{CC}_2\text{F}_5)_2)]_n$ hydrogen chloride molecules evolved during heating, with the formation of gold(I) amidinate. The obtained results revealed that the new gold(I) amidinate may be a promising source of metal for nanomaterial fabrication by gas-assisted methods.

Keywords: chemical vapor deposition; focused electron beam-induced deposition; focused ion beam-induced deposition; Hirshfeld surface analysis; volatile compounds; volatility study; nanomaterials; electron interactions; gold(I) complexes; thermal properties



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1. Introduction

Gold is an ideal candidate for modern industrial applications due to its high conductivity and resistance to electromigration, which makes it valued for use in electrical contacts [1,2]. Furthermore, this metal has attracted increasing attention for its plasmonic and optoelectronic applications, e.g., in direct nanoemitters or high-performance sensors, integrated optical circuits, and optoelectronic devices [3–5]. Gold nanoparticles with a homogenous size distribution are used in Surface-Enhanced Raman Spectroscopy (SERS), an important field of plasmonic research. Moreover, they are invaluable in new anti-cancer therapies, where they are used for targeted drug delivery or bioimaging [6–10].

The ability of miniaturization is an essential aspect of modern technology. Fabrication at the nanoscale level often involves the formation of 2D and 3D nanomaterials with different functionalities. Nanodeposits with outstanding magnetic, electrical, optical, mechanical, and catalytic properties can be produced by various gas-assisted methods,

e.g., chemical vapor deposition (CVD), atomic layer deposition (ALD), focus electron beam-induced deposition (FEBID), and focus ion beam-induced deposition (FIBID) [11–14]. These processes need coordination compounds as the metal source in the gas phase [6,11]. CVD is a widely used method in which deposits are formed on a heated substrate by a decomposition reaction of adsorbed precursor molecules [15]. ALD differs from CVD in the introduction of a gas precursor. In ALD, two compounds are introduced separately in pulses and undergo sequential and self-limiting surface reactions [16]. FEBID and FIBID are relatively new emerging methods. These direct deposition techniques for nanofabrication also need volatile and appropriately sensitive precursors. Molecules are adsorbed on a substrate surface and decomposed under the influence of a focused electron or ion beam (keV) [6,11]. In the FEBID process, the influence of secondary electrons (eV) produced from the substrate is essential for nanostructure growth. This type of electrons are also significant in the FIBID process, where they are generated by a focused ion beam. Therefore, combining volatility with electron/ion sensitivity and thermal stability is crucial for designing new FEBID and FIBID precursors.

Commercially available CVD precursors are often tested in FEBID and FIBID processes. However, the applied gold compounds are air-sensitive and thermally unstable, which makes their storage and fabrication problematic for FEBID and FIBID processes. Therefore, new and user-friendly gold precursor molecules are needed to overcome this issue. High-purity gold films have been generated by the CVD method from a number of volatile gold complexes. Some of the most important gold compounds used are β -diketonates and complexes with the so-called small ligands $[\text{Au}_2\text{Me}_4(\mu\text{-Cl}_2)]$, $[\text{AuCl}(\text{SMe}_2)]$, $[\text{AuCl}(\text{PMe}_3)]$, and $[\text{AuMe}(\text{PMe}_3)]$ [6,17]. In contrast, the amount of FEBID and FIBID precursors is limited. The first FEBID experiments on gold(III) β -diketonate complexes were carried out using $[\text{Au}(\text{acac})\text{Me}_2]$ (acac–acetylacetonate), $[\text{Au}(\text{tfac})\text{Me}_2]$ (tfac–trifluoroacetylacetonate), and $[\text{Au}(\text{hfac})\text{Me}_2]$ (hfac–heksafluoroacetylacetonate). The metal content in the deposits varied in the range of 30–39 at.% Au. The highest value, 91 at.% Au, was achieved for $[\text{Au}(\text{tfac})\text{Me}_2]$ in FEBID experiments when co-injected water was applied as the oxidizing gas, while the gold(I) complexes $[\text{AuCl}(\text{PF}_3)]$ and $[\text{AuCl}(\text{CO})]$ produced high-purity FEBID deposits at the level of 95–100 at.% Au without post-deposition purification. However, these precursors are highly air-sensitive, which complicates their practical use [3,6,18]. In the case of the FIBID method, only $[\text{Au}(\text{hfac})\text{Me}_2]$ has been tested (75 at.% Au) [11,19,20].

One group of volatile coordination compounds is that of non-fluorinated amidinates such as $[\text{Au}(\text{N}^i\text{Pr})_2\text{CMe}_2]$, $[\text{Au}(\text{N}^i\text{Pr})_2\text{C}^n\text{Bu}_2]$ [21], and gold(I) 5,5-bicyclic amidinate [22], studied for their potential application as precursors in atomic layer deposition (ALD) and chemical vapor deposition (CVD). However, these compounds have not been even preliminarily studied for their applicability in electron- or ion-driven processes. Relatively new compounds are perfluorinated amidinates with the general formula $(\text{NH})_2\text{CR}_f\text{—}(\text{R}_f\text{—perfluorinated group})$. On the other hand, perfluorinated substituents increase compound volatility due to reduced interactions between molecules caused by the repulsion of the fluorine atoms [23]. Among the perfluorinated compounds, are silver(I) and mercury(II) complexes such as $[\text{Ag}((\text{NH})_2\text{CCF}_3)]$, $[\text{Ag}((\text{NH})_2\text{CC}_2\text{F}_5)]$, $[\text{Hg}((\text{NH})_2\text{CC}_2\text{F}_5)_2]$ [24], which have not been investigated for use in gas phase deposition processes. Only the mentioned silver(I) and new copper(I) amidinates have been recently studied by us for their potential application in the FEBID and FIBID processes by electron interaction investigations [25].

Based on that motivation, we here present a synthesis method for new air-stable gold(I) $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (AMD– $(\text{NH})_2\text{CC}_2\text{F}_5$) and $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (AMDH– $\text{NH}_2(\text{NH=})\text{CC}_2\text{F}_5$) complexes containing the perfluorinated C_2F_5 substituent that should be promising for their volatility features. Furthermore, we demonstrate the crystal structure and intermolecular interactions of the molecules based on Hirshfeld surface analysis

for a gold(I) amidinate. This approach can be employed to prescreen and score new potential precursors for vapor deposition methods. The compounds' thermal stability was determined under atmospheric pressure, and their suitability for the production of metallated volatile species under reduced pressure was studied. Moreover, the low-energy electron interactions of Au(I) amidinate in the gas phase was investigated. The electron beam sensitivity of gold(I) amidinate was studied using electron microscopy imaging. Furthermore, a thermal decomposition mechanism for $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ is proposed. Therefore, we investigated whether new user-friendly complexes can be used in CVD and as an alternative to the unstable gold(I) and gold(III) compounds previously tested in FEBID and FIBID [6].

2. Experimental Section

2.1. Materials

Anhydrous acetonitrile (99.8%), chloro(dimethylsulfide)gold(I) $[\text{Au}(\text{SMe}_2)\text{Cl}]$ (>97.0%), and tetrahydrothiophene (tht) (99%) were purchased from Sigma Aldrich (Saint Louis, MO, USA), $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ ($\geq 99.9\%$) from Pol-Aura (Zawroty, Poland), AgNO_3 (99.9%) from Chempur (Piekary Śląskie, Poland), $\text{C}_2\text{F}_5\text{C}(\text{=NH})\text{NH}_2$ (HAMD- C_2F_5) (98.7%) from Apollo Scientific (Stockport, UK), and ethanol (96%) and NaHCO_3 (p.a) from Avantor Performance Materials Poland (Gliwice, Poland). $[\text{Au}(\text{tht})\text{Cl}]$ [26] and $[\text{Ag}_2((\text{NH})_2\text{CC}_2\text{F}_5)_2]$ [25] were prepared as earlier reported. Ag_2CO_3 was synthesized in the reaction of AgNO_3 and NaHCO_3 , as described previously [27]. All reagents were used as received. The Si(111) substrates were purchased from the Institute of Microelectronics and Photonics, Center for Electronic Materials Technology in Warsaw–Lukasiewicz Research Network (Warsaw, Poland).

2.2. Instrumentation

IR spectra were registered with a Vertex 70V spectrometer (Bruker Optik, Leipzig, Germany) using a reflective single-reflection diamond ATR unit ($200\text{--}4000\text{ cm}^{-1}$). Electron impact mass spectra (EI MS) were registered using an AutoSpec Premier, Waters Corporation (Milford, MA, USA) over the temperature range of $313\text{--}573\text{ K}$. The C, H, and N content was determined using a Vario MACRO CHN ELEMENTAR Analysensysteme (GmbH, Langenselbold, Germany). Thermal studies (TGA/DTA) were performed using an SDT 2960 TA analyzer (New Castle, DE, USA; dry N_2 ; heating rate 2.5 K min^{-1}), in a heating range up to 1273 K and a sample mass of 3 and 10 mg. Variable-temperature infrared spectra (VT IR) were registered using a PerkinElmer Spectrum 2000 spectrometer (Waltham, MA, USA) over the range of $400\text{--}4000\text{ cm}^{-1}$ with a medium slit width and a peak resolution of 2.0 cm^{-1} . A glass vessel with the precursor sample ($\sim 100\text{ mg}$) was placed in a homemade reactor tube and heated (from 333 to 693 K) under a dynamic vacuum ($p = 10^{-1}\text{ mbar}$). The sublimation experiments were performed under reduced pressure (10^{-2} mbar) in a glass sublimator with a special holder for a silicon substrate. The morphology and composition studies of layers of the compounds were performed using scanning electron microscopy with Quanta 3D FEG, FEI (Hillsboro, OR, USA) and SEM-LEO 1430VP, Ltd., (Cambridge, UK) microscopes (operating voltage 8 and 20 kV), equipped with the energy-dispersive X-ray spectrometer (EDS) Quantax 200 with an Xflash 4010 detector Bruker AXS microanalysis GmbH (Berlin, Germany), which was also used in preliminary electron sensitivity tests. Transmission electron microscopy, TEM G2 F20X-Twin 200 kV FEI (Hillsboro, OR, USA) was used to characterize the thermal analysis residue and test the sensitivity of the compounds to high-energy electrons (200 keV). The samples for the TEM experiments were prepared by dissolving the compounds in anhydrous ethanol (99.8%), applying a drop on a carbon-coated copper mesh with holes (Lacey type, 400 mesh), and evaporating the solvent at room temperature. Energy-dispersive X-ray spectroscopy, EDX, RTEM model SN9577,

134 eV, EDAX, FEI, (Hillsboro, OR, USA) spectra and selected-area (electron) diffraction patterns were recorded to identify the chemical compositions.

2.3. Software

All graphical data were further processed with OriginPro version 9.1. TA Universal Analysis (New Castle, DE, USA) was used to analyze the thermograms. To assign the decomposition products in VT IR experiments, the registered spectra were compared with the spectra of molecules in the gas phase collected in SpectraBase (<https://spectrabase.com/>, accessed on 12 July 2024) [28]. Diagrams indicating the synthesis of the compounds (1), (2) and the VT IR mechanism were drawn using ChemDraw Ultra version 12.0 (Cambridge, MA, USA). CrystalExplorer 21.5 (revision 608bb32) [29] was used to calculate Hirshfeld surfaces. All figures of the crystal structures were prepared using DIAMOND 4 version 4.6.8 [30] and ORTEP-3 (version 1.0.3) [31] software.

2.4. Synthesis

2.4.1. Synthesis of $[\text{Au}_4(\mu\text{-(NH)}_2\text{CC}_2\text{F}_5)_4]_n$ (Denoted, for Convenience, $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$) (1)

$[\text{Au}(\text{SMe}_2)\text{Cl}]$ (0.28 mmol) was added to 20 cm³ of anhydrous acetonitrile; then, $[\text{Ag}_2(\text{NH})_2\text{CC}_2\text{F}_5)_2]$ (0.14 mmol) was introduced to the solution, which was stirred for 24 h. The silver(I) chloride formed during the reaction was filtered and washed with acetonitrile. The solvent from the filtrate was removed under reduced pressure (10^{-2} mbar) to obtain a white solid, insoluble in available organic solvents and stable in argon atmosphere and air for months. Yield: 73% (1). White single crystals suitable for X-ray structure analysis were grown by slow evaporation from the mother liquor for complex (1) at room temperature.

2.4.2. Synthesis of $[\text{Au}_2\text{Cl}_2(\text{NH}_2(\text{NH}=\text{CC}_2\text{F}_5)_2)]_n$ (Denoted, for Convenience, $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$) (2)

$[\text{Au}(\text{tht})\text{Cl}]$ (0.12 mmol) was added to 20 cm³ of anhydrous acetonitrile; then, $\text{C}_2\text{F}_5\text{CNHNH}_2$ (0.12 mmol) was introduced to the solution and stirred for 24 h. The mixture was then filtered, and the solvent from the filtrate was removed under reduced pressure (10^{-2} mbar) to obtain a white-pink solid, insoluble in available organic solvents and stable in argon atmosphere for months and in air for weeks. Yield: 43% (2). No single crystals suitable for X-ray structure analysis were obtained for compound (2), despite efforts to grow them.

$[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1) $\text{Au}_4\text{N}_8\text{H}_8\text{C}_{12}\text{F}_{20}$ (calc./found) % H 0.56/0.47, % C 10.06/9.84, % N 7.83/7.87; EI MS T = 328 K (*m/z*, RI %) $[\text{Au}(\text{NHCNH})]^+$ (239, 4), $[\text{Au}(\text{NHNH}_2\text{CCF})]^{+\bullet}$ (271, 1), $[\text{Au}_2(\text{NHNHCC}_2\text{F}_5)_2]^{2+}/[\text{Au}(\text{NHNHCC}_2\text{F}_5)]^{+\bullet}$ (358, 2), $[\text{Au}_2(\text{NH}_2)]^+$ (410, 1), $[\text{Au}_2(\text{NHCNH})]^{2+}$ (436, 3), $[\text{Au}_2(\text{NHNHCC}_2\text{F}_5)]^+$ (555, 21), $[\text{Au}_2(\text{NHNHCC}_2\text{F}_5)(\text{HCN})]^+$ (582, 6), $[\text{Au}_2(\text{NHNHCC}_2\text{F}_5)(\text{NHCNH})]^+$ (597, 19), $[\text{Au}_2(\text{NHNHCC}_2\text{F}_5)_2]^{+\bullet}$ (716, 100), $[\text{Au}_3(\text{NHNHCC}_2\text{F}_5)_2]^+$ (913, 2), $[\text{Au}_4(\text{NHNHCC}_2\text{F}_5)]^+$ (949, 8); IR (3412 (m), 3344 (m), 1614 (s), 1512 (w), 1325 (m), 1202 (s), 1171 (s), 1146 (s), 1030 (s), 826 (w), 748 (m), 685 (m), 563 (m), 455 (w), 365 (w), 311 (w) cm⁻¹). Yield: 73%.

$[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (2) $\text{Au}_2\text{N}_4\text{H}_6\text{C}_6\text{F}_{10}\text{Cl}_2$ (calc./found) % H 0.77/0.90, % C 9.13/9.81, % N 7.10/7.23; EI MS T = 339 K (*m/z*, RI %) $[\text{HCl}]^{+\bullet}$ (36, 17), $[\text{H}_2^{35}\text{Cl}]^+$ (37, 67), $[\text{H}_2^{37}\text{Cl}]^+$ (39, 22), $[\text{Au}(\text{NH})]^{+\bullet}$ (212, 11), $[\text{Au}(\text{HNCNH}_2)]^+$ (240, 3), $[\text{Au}(\text{NHNH}_2\text{CCF})]^{+\bullet}$ (271, 2), $[\text{Au}(\text{NHC}_2\text{F}_5)]^{+\bullet}$ (331, 2), $[\text{Au}(\text{NNCC}_2\text{F}_5)]^{+\bullet}$ (356, 5), $[\text{Au}_2(\text{NHNHCC}_2\text{F}_5)_2]^{2+}/[\text{Au}(\text{NHNHCC}_2\text{F}_5)]^{+\bullet}$ (358, 6), $[\text{Au}_2(\text{NHNHCC}_2\text{F}_5)_2]^{+\bullet}$ (716, 4), $[\text{Au}_3(\text{NHNCC}_2\text{F}_5)]^+$ (751, 3); IR (3499 (w), 3360 (w), 3233 (m), 3163 (m), 1678 (s), 1611 (m), 1491 (w), 1429 (w), 1387 (w), 1329 (m), 1286 (w), 1213 (s), 1186 (s), 1155 (s), 1024 (s), 804 (w), 775 (w), 735 (w), 694 (w), 625 (m), 600 (m), 565 (w), 527 (w), 484 (w), 434 (w), 386 (m), 338 (m), 247 (w) cm⁻¹). Yield: 43%.

2.5. X-Ray Crystal Structure Determinations

Single-crystal diffraction data for compound (**1**) were first collected at MX14-2 beam-line (BESSY II synchrotron (HZB, Berlin, Germany) at 100 K. The structure was processed using *xdsapp* [32,33]. The structure was solved using direct methods and refined with a full-matrix least-squares procedure on F^2 (SHELX-2018/1) [34]. All heavy atoms were refined with anisotropic displacement parameters. Hydrogen atoms of NH groups were found from the difference electron density map and refined with isotropic thermal displacement parameters fixed at a value 20% higher than that of the corresponding nitrogen atoms. However, due to the gold presence resulting in a high absorption coefficient, also high difference peaks were observed. Hence, the data collection was repeated at 100 K using a XtaLAB Synergy (Dualflex) diffractometer (Rigaku) with a HyPix detector, MoK α radiation $\lambda = 0.71073$ Å. Data reduction was performed in CrysAlis Pro for the studied compound [35], and the Gaussian absorption correction was applied. Those data were used for the final refinement steps with the model from the synchrotron data. The data collection and refinement results are summarized in Supplementary Materials (Table S1), such as selected bond lengths and angles (Table S2). CCDC 2378410 contains supplementary crystallographic data for compound (**1**). These data can be freely obtained from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3. Results and Discussion

In anhydrous acetonitrile, chloro(dimethylsulfide)gold(I) reacts with silver(I) amidinate to produce gold(I) amidinate (**1**). The reaction proceeds with the precipitation of silver(I) chloride (Figure 1).

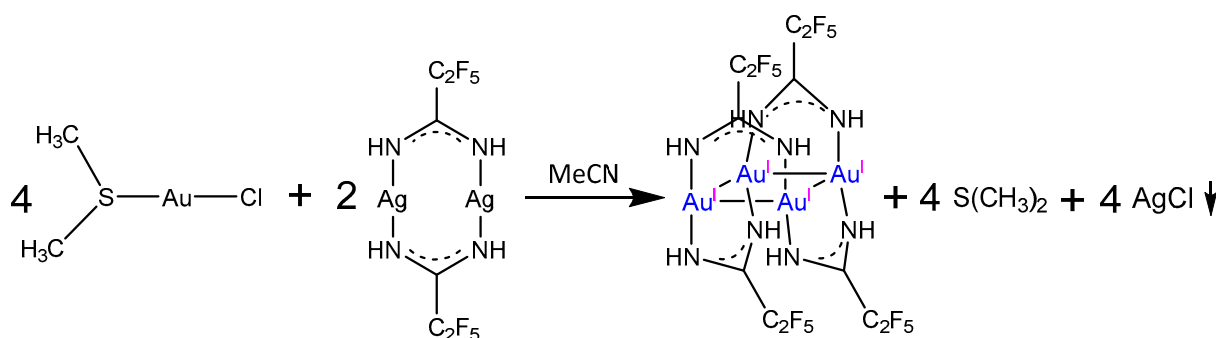


Figure 1. Reaction scheme for the synthesis of the gold(I) complex $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (**1**).

Chloro(amidine)gold(I) (**2**) was formed in the reaction of chloro(tetrahydrothiophene)gold(I) with amidine in anhydrous acetonitrile (Figure 2).



Figure 2. Reaction scheme for the synthesis of the gold(I) complex $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (**2**).

The obtained compounds are white (**1**) or white-pink solids (**2**), both being stable for months in argon atmosphere, whereas in air, (**1**) is stable for months, and (**2**) for weeks.

3.1. Crystallography

$[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (**1**) is a coordination polymer and crystallizes in the monoclinic $I2/a$ space group with half of the molecule shown by the above formula in the asymmetric unit and Au1 and Au3 atoms located at the twofold axis (Figures 3, 4 and S1,

Tables S1 and S2). A tetramer, composed of four gold(I) cations forming an almost perfect rhombus (the Au...Au...Au angles are 66.38 and 113.92°) is the principal motif. The gold(I) cations are connected by amidinate anions as well as aurophilic interactions, with Au...Au distances being 3.035 and 3.046 Å. The $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]$ tetramers are connected by aurophilic interactions into zigzag chains running along the *a* axis, with Au1...Au2 distances being 3.361 Å (only slightly longer than 3.329 Å—the Au1...Au3 separation in the tetramer) and the Au2...Au1...Au2 angle being 82.15° (Figure 5). Adjacent tetramers in such chains also interact by N2-H2...N1[−1/2 + *x*, 1 − *y*, *z*] hydrogen bonds. The chain topology was determined in TOPOS, and the environment around the gold atoms was established, assuming that the gold and nitrogen atoms were the closest neighbors. The coordination numbers determined in this way were 7, 5, and 5 for the Au1, Au2, and Au3 atoms, respectively. In the coordination sphere of every gold(I) cation, there are two nitrogen atoms bound at 2.012(3) and 2.012(3) Å for Au1, 2.002(3) and 2.012(3) Å for Au2, and 2.017(3) and 2.017(3) Å for Au3. The chains are arranged into an *ab* layer mainly via non-covalent weak F...F interactions created between N11 amidinate anions. Finally, the 3D network is formed by F...F contacts formed by N1 amidinate anions from adjacent layers. It should be noted that this structure is maintained either by aurophilic and hydrogen bonds (Figure S2) in the chain or by F...F interchain contacts. The F...F contacts are the most numerous intermolecular interactions in the crystal network, and the red spots on the Hirshfeld surface indicate that some of those contacts are short [36,37].

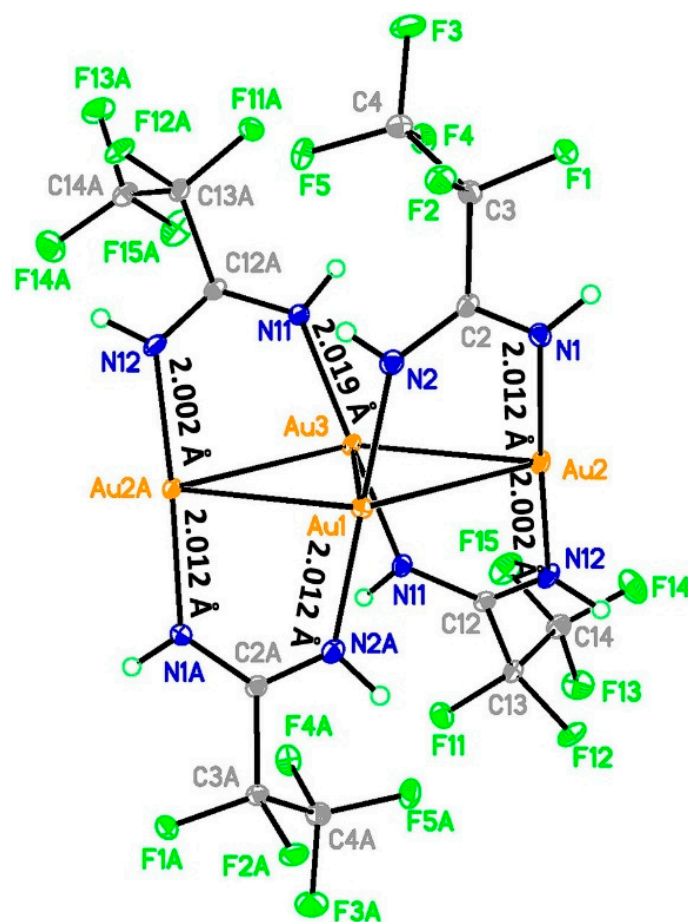


Figure 3. The tetramer structure of $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1) with ellipsoids at the level of 30% probability (yellow—gold atoms; blue—nitrogen atoms; gray—carbon atoms; green—fluorine atoms).

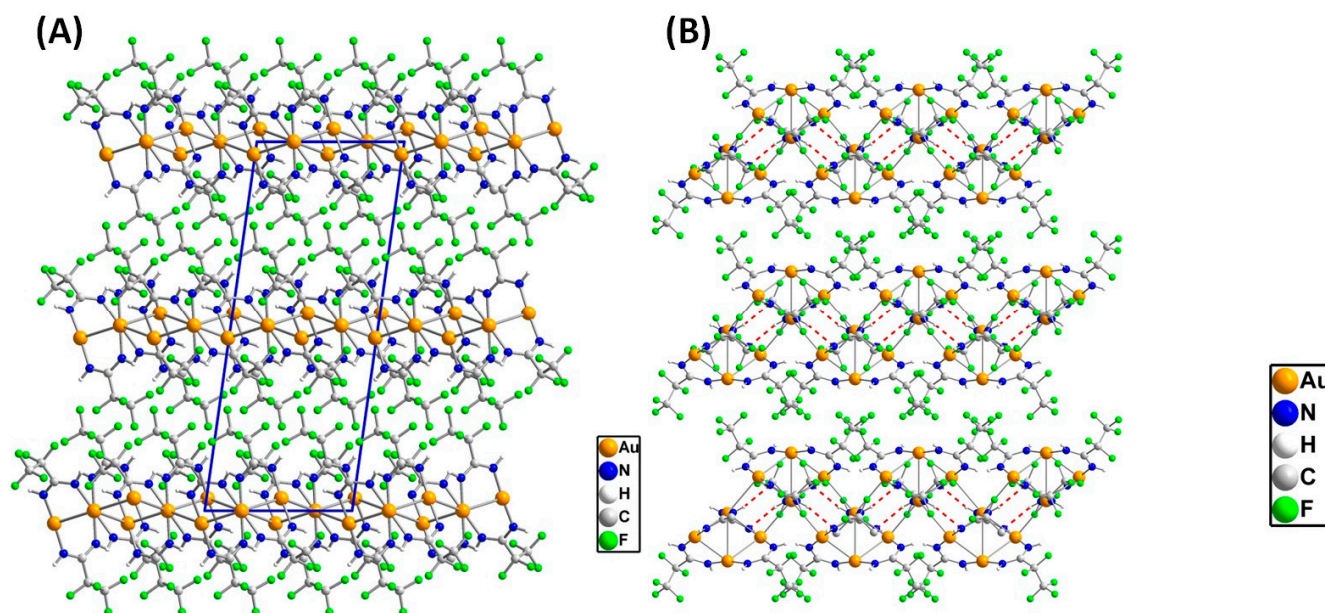


Figure 4. The crystal network of $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (**1**) along the b axis (in blue is marked the unit cell) (A) and the crystal structure projected in the ab plane (the hydrogen bonds are marked with a red dashed line) (B) (yellow—gold atoms; blue—nitrogen atoms; gray—carbon atoms; green—fluorine atoms).

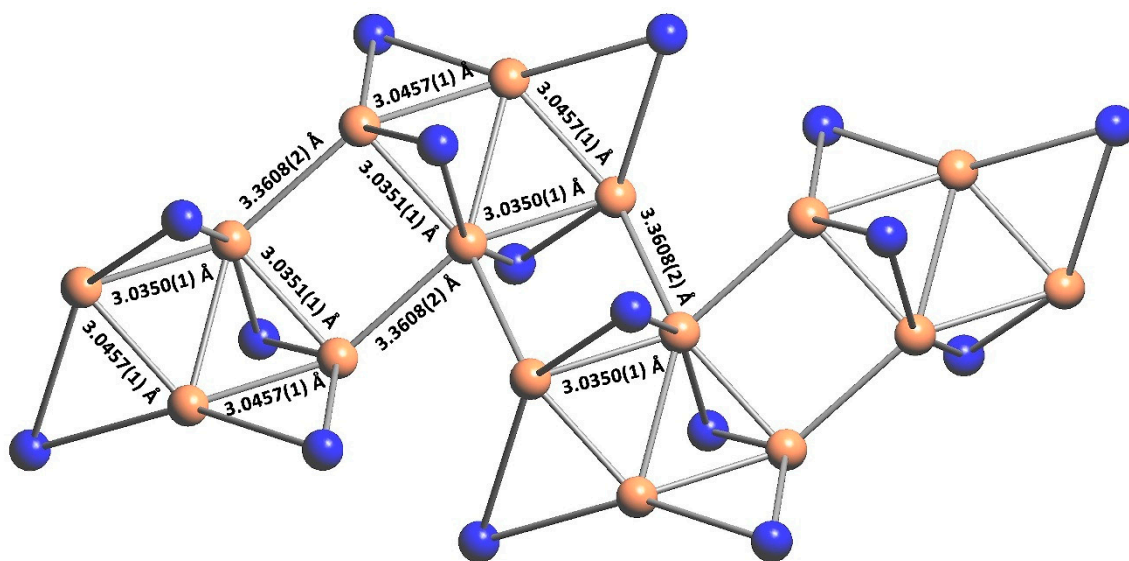


Figure 5. The chain topology in $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (**1**) shows the zigzag-pattern axis (gold in orange, AMD in blue) based on the analysis performed in TOPOS (Version 5.5.2.2) [38].

Summarizing, the polymeric structure is maintained by aurophilic and hydrogen bonds (Figures 4 and S2), whereas for interchain interactions, F...F contacts prevail, being the most numerous, with some short distances detected as it is evidenced by the red spots on the Hirshfeld surface (Figures 6, S3 and S4). The presence of weak intermolecular interactions is advantageous in terms of application using the CVD method $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (**1**) and when introducing the compound via the GIS during the FEBID or FIBID process, which requires the use of volatile precursor molecules.

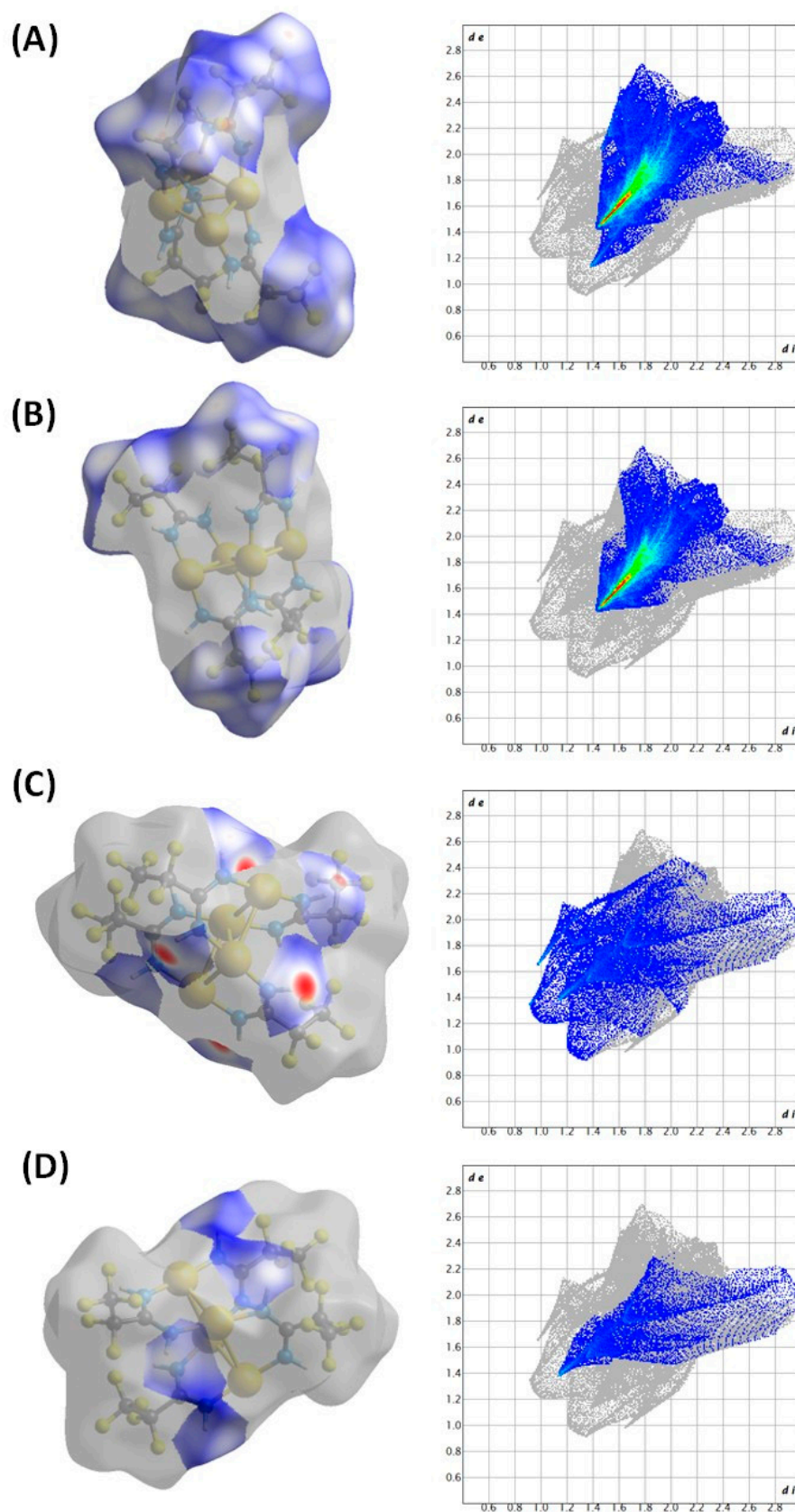


Figure 6. Hirshfeld surfaces (left) and fingerprints (right) of selected interactions created in the crystal network of $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1): (A) for $\text{F} \cdots \text{all}$ (65.6%), (B) for $\text{F} \cdots \text{F}$ (53.1%), (C) for $\text{H} \cdots \text{all}$ (20.4%), (D) for $\text{H} \cdots \text{F}$ (9.5%). In brackets, a given surface area included as a percentage of the total surface area is shown.

3.2. Infrared Spectra Analysis

In the infrared spectrum of the compound $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (**1**) (Figure 7), bands at 1614 cm^{-1} (**1**), characteristic of asymmetric stretching vibrations $\nu_{\text{as}}\text{NCN}$, as well as at 1512 cm^{-1} , typical of symmetric $\nu_{\text{s}}\text{NCN}$ stretching vibrations of the NCN group, were observed (Table 1), which confirmed the deprotonation of amidine and the formation of the amidinate complex. Moreover, the formation of the Au–N bond resulted in the appearance of a signal around 563 cm^{-1} . The resolved crystal structure (Section 3.1) and EI MS (Section 3.4) results also indicated the formation of a gold(I) amidinate complex.

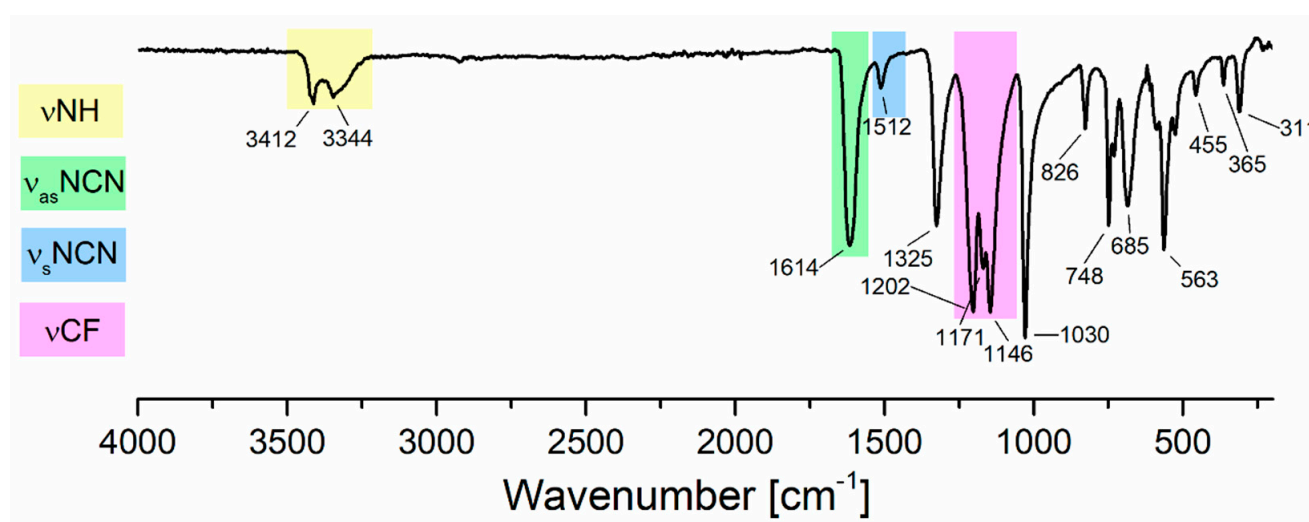


Figure 7. ATR-IR spectrum of the compound $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (**1**). The colored bands highlight the ranges of the particular vibrational modes: (νNH) (yellow), ($\nu_{\text{as}}\text{NCN}$) (green), ($\nu_{\text{s}}\text{NCN}$) (blue), (νCF) (pink).

Table 1. Selected IR absorption bands (cm^{-1}) of the studied compounds (**1**) and (**2**).

Compound	νNH	νNH_2	$\nu=\text{NH}$	$\nu\text{C}=\text{N}$	δNH_2	$\nu_{\text{as}}\text{NCN}$	$\nu_{\text{s}}\text{NCN}$	$\nu\text{Au-N}$
$[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1)	3412 3344	–	–	–	–	1614	1512	563
$[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (2)	–	3233	3163	1678	1611	–	–	565
HAMDC_2F_5	–	3362	3130	1664	1593	–	–	–

The band of $\nu\text{Au-Cl} = 338\text{ cm}^{-1}$ in the $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (**2**) spectrum.

For the complex $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (**2**) (Figure S5), bands characteristic of the amidine molecule were observed in the spectrum, i.e., $\nu_{\text{as}}\text{NH}_2$ at 3360 cm^{-1} ; $\nu_{\text{s}}\text{NH}_2$ 3233 cm^{-1} ; $\nu=\text{NH}$ at 3163 cm^{-1} ; νCN at 1678 cm^{-1} ; δNH_2 1611 cm^{-1} . The coordination shifts of these signals relative to the free amidine were $\nu\text{NH}_2 \rightarrow 129\text{ cm}^{-1}$; $\nu=\text{NH} \rightarrow 33\text{ cm}^{-1}$; $\nu\text{CN} \rightarrow 14\text{ cm}^{-1}$; and $\delta\text{NH}_2 \rightarrow 18\text{ cm}^{-1}$, confirming the coordination of this ligand. Moreover, the existence of signals for stretching vibrations, i.e., $\nu\text{Au-N}$ at 565 cm^{-1} and $\nu\text{Au-Cl}$ at 338 cm^{-1} [39], confirmed the formation of a bond between gold and the N-donor amidine as well as a of bond between chloride and the gold atoms. The TEM-EDX analysis of the complex (**2**) also confirmed the presence of chlorine atoms (Figure S6). Based on these data, we propose the formation of the chloro(amidine)gold(I) complex $[\text{Au}_2(\text{HAMDC}_2\text{F}_5)_2\text{Cl}_2]_n$ (**2**).

This data interpretation is crucial for the evaluation of the infrared result from the layers of compound (**1**) deposited on the silicon substrate (Section 3.5).

3.3. Thermal Analysis

Thermal analysis was performed to study the behavior of the complexes during heating under a nitrogen atmosphere and to determine the temperature of the final decomposition. These data revealed that the decomposition of complex (1) proceeded in a single main endothermic step. In the case of compound (2), two consecutive endothermic steps were observed (Figure 8, Table 2). The thermal process began at a temperature (T_i) of ca. 317 K, with the maximum rate occurring at 527 K for (1) and 411 K for (2) (T_m). The final decomposition temperature (T_f) was 550 K (1) and 451 K (2), respectively (Table 2). The compounds (1) and (2) final residues are close to the theoretical content of gold in the respective molecules (Table 2). This indicated that for (1), the amidinates were lost. For complex (2), hydrogen chloride (377 K) was released in the first stage, amidinates detached in the second, and metallic gold formed as the final decomposition product. These results were confirmed by the TEM diffraction patterns of the formed residues, which revealed characteristic signals of metallic gold for both complexes (1) and (2) (Figure 9). Contrary to our previous results for the copper(I) and silver(I) amidinates $[\text{Cu}_2(\mu\text{-AMDC}_2\text{F}_5)_2]$ and $[\text{Ag}_2(\mu\text{-AMDC}_2\text{F}_5)_2]$, indicating that they are sources of metal carriers in the gas phase under atmospheric pressure in nitrogen [25], the gold(I) complexes (1) and (2) decomposed to the theoretically predicted amounts of metallic gold. That behavior can be justified by the different structures of the molecules.

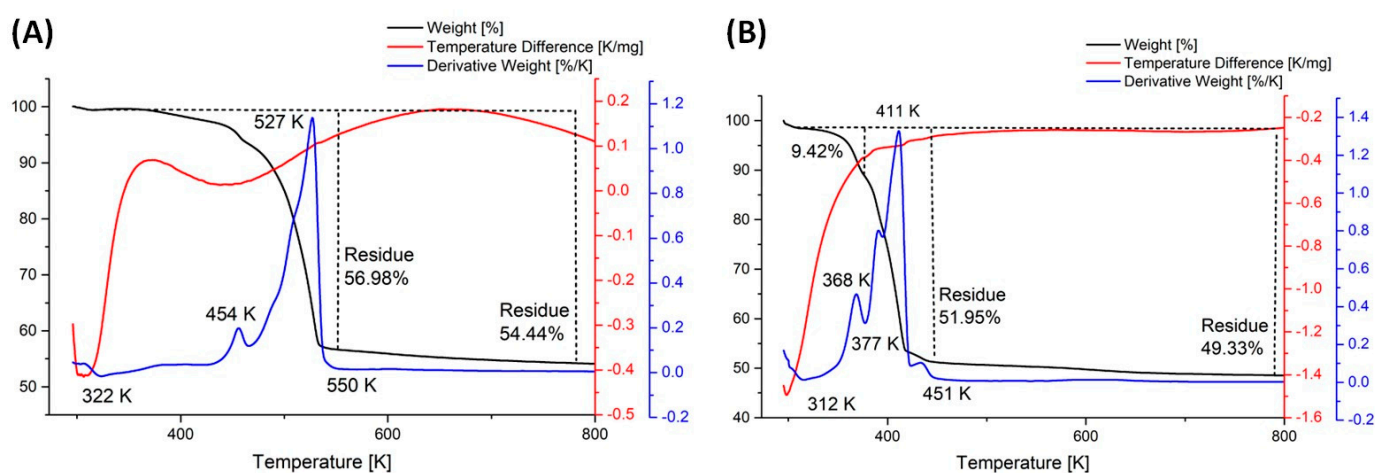


Figure 8. Thermogravimetric analysis (TGA) (black line), derivative thermogravimetry (DTG) (blue line), and differential thermal analysis (DTA) (red line) of the complex $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1) (A) and $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (2) (B).

Table 2. Thermal analysis results.

Complex	Heat Effect	Temperature [K]			Residue [%]	
		T_i	T_m	T_f	Found [%]	Calc. [%]
$[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1)	Endo	322	527	550	56.98	55.01 (Au)
$[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (2)	Endo	312	368	377	51.95	49.99 (Au)
	Endo	377	411	451		

T_i , initial temperature; T_m , maximum temperature; T_f , final temperature.

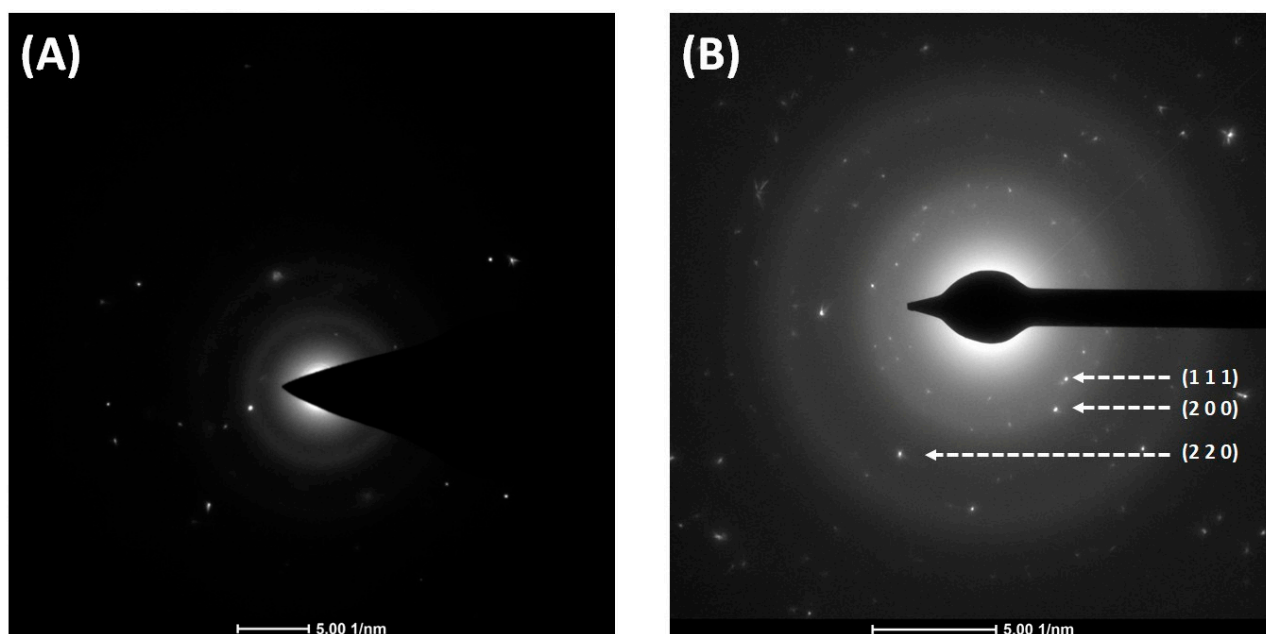


Figure 9. Transmission electron microscope (TEM) diffraction pattern of the TGA final residues of $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1) (A) and $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (2) (B), with the diffraction pattern of gold marked in white.

3.4. Mass Spectra Analysis

The electron impact mass spectra (EI MS) of the complexes (1) and (2) were registered between 313 and 573 K. Based on these results, we could verify whether these compounds are capable of generating volatile metal carriers, check their sensitivity to low-energy electrons (70 eV), and study how the composition of the gas phase changed during heating under high vacuum ($\sim 10^{-6}$ mbar). It is important to note that during the FEBID or FIBID process in the SEM chamber, the conditions were quite similar to those of the EI MS experiments.

In the EI MS spectra, the metallated fragments were detected in relatively low temperatures, i.e., from 319 to 416 K for (1) and from 336 to 456 K for (2), which is promising for application in vapor deposition methods. These fragments achieved the following highest relative intensities: 100% RI from 326 K to 341 K and from 352 K to 403 K (1) and 63% RI at 343 K (2).

In the case of the compound $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1), the high %RI of the ion $[\text{Au}_2(\text{NHNHCC}_2\text{F}_5)_2]^+\bullet$ (RI = 100%) (Figure S8) indicates its stability and not highly efficient low-energy electron-induced fragmentation. Moreover, row of dinuclear fragments were present as dominant under the process conditions (Figure 10). This suggests a thermal and electron-induced reaction resulting in the breaking of the polymer chains. However, based on the $[\text{Au}_3(\text{NHNHCC}_2\text{F}_5)_2]^+$ and $[\text{Au}_4(\text{NHNHCC}_2\text{F}_5)]^+$ ions, the formation of higher mass fragments cannot be excluded. Due to the limited measuring range up to m/z 1100, it was not possible to record them.

The EI MS results for $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (2) showed that the compound released HCl upon heating (electron-induced ions $[\text{HCl}]^+\bullet$ and $[\text{H}_2\text{Cl}]^+$ were detected) and converted to gold(I) amidinate, and fragments were obtained, as observed in the fragmentation of compound (1) (Figure S7, Table S4). Moreover, the ion $[\text{Au}_2(\text{NHNHCC}_2\text{F}_5)_2]^+\bullet$ confirmed amidine deprotonation and amidinate formation. The low %RI for the $\text{Au-AMDC}_2\text{F}_5$ fragment and high %RI for the $[\text{Au}(\text{NH})]^+\bullet$ ($\text{RI}_{\text{max}} = 63\%$) indicated an efficient electron-induced fragmentation. The signals m/z 87 and 88 (Table S4) are indicative of an

impurity in the form of $[\text{Au}(\text{tht})\text{Cl}]$, resulting from the volatile tetrahydrothiophene used during synthesis.

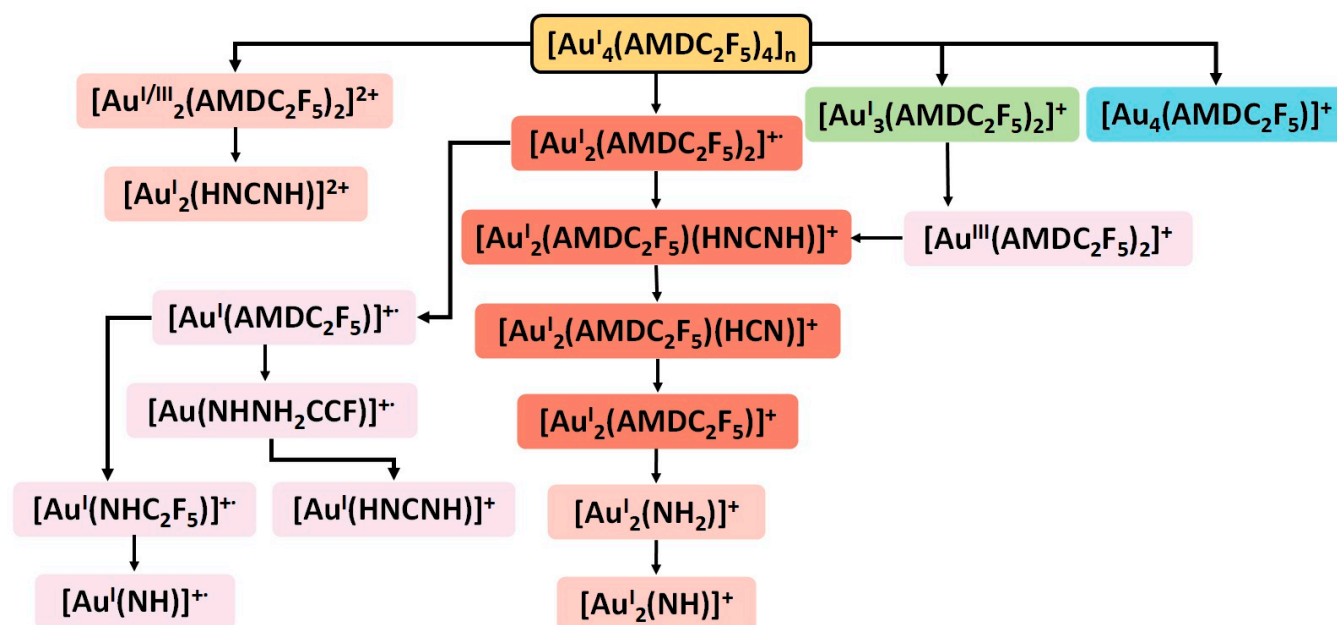


Figure 10. Fragmentation scheme for the metallated fragments of $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1); assignment: blue—tetranuclear ions, green—trinuclear ions, red—dinuclear ions, pink—mononuclear ions (brighter fields—ions occurring in small quantities).

Moreover, the signals characteristic for the ions, e.g., $[\text{CF}_2]^+$, $[\text{CF}_3]^+$, $[\text{CF}_2\text{CN}]^+$, $[\text{C}_2\text{F}_4\text{CN}]^+$, $[\text{NHNH}_2\text{CC}_2\text{F}_5]^+\bullet$, indicated the fragmentation of compounds (1), (2) and are related to a reaction pathway that can transform the amidinate unit to volatile fluorinated molecules.

Summarizing, the $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1) and $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (2) complexes can be promising for use in the CVD, FEBID, and FIBID processes because the effective generation of volatile metal carriers, e.g., gold amidinates in EI MS was observed at relatively low temperatures (from 319 K (1) and 339 K (2)). Therefore, it can be assumed that the investigated compounds can be introduced into the microscope chamber via the GIS system at a temperature similar to that used for the commercial platinum precursor $[\text{Pt}(\mu^5\text{-CpMe})\text{Me}_3]$, which is about 333 K [6,18]. Moreover, $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (2) decomposed to gold(I) amidinate and fragmented in the carbon-free fragment $[\text{Au}(\text{NH})]^+\bullet$ with high efficiency. This is important because one of the problems associated with FEBID is the carbon contamination of structures [6,18]. Moreover, the complexes (1) and (2) are sensitive to low-energy electron interactions. Therefore, they seem to be promising candidates for CVD applications and FEBID or FIBID tests.

3.5. Sublimation Experiments

Sublimation is a desired property for complexes that are used in vapor deposition methods such as CVD and FEBID or FIBID. Sublimation experiments were carried out to verify the volatility of the new gold(I) complexes (1) and (2) and determine the sublimation temperature of entire compound molecules. These experiments were carried out in a classical glass sublimator under a pressure of 10^{-2} mbar with a special holder for a silicon substrate. Moreover, they allowed for obtaining layers of compound (1), which was then studied in terms of interaction with a high-energy electron beam (Section 3.7).

The infrared spectrum of a $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1) thin layer deposited on a silicon substrate was very similar to that obtained in the solid phase and exhibited the

bands νNH , $\nu_{\text{as}}\text{NCN}$, $\nu_{\text{s}}\text{NCN}$, and νCF , which are characteristic of coordinated amidinate (Figure 11). There were some additional bands around $800\text{--}500\text{ cm}^{-1}$, probably resulting from some primary polymeric structure rearrangement. This fact does not affect the conclusion that the complex sublimes at a temperature of 413 K . In the case of the compound $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (2), the sublimation experiment was conducted up to 353 K . The differences in the shape and position of the bands in the spectra of the original complex and the formed layer during the process (Figure S9) indicate that decomposition products dominated in the layer. However, signals characteristic of gold(I) amidinate were also observed in the spectrum due to decomposition of the complex (2), but their intensity was small. Furthermore, the SEM-EDX spectra analysis of the deposited layer showed Cl, F, N, and C, which confirmed that compound (2) decomposed into organic species (Figure S10), while the negligible intensity of the Au signal indicated gold(I) amidinate formation. On the other hand, the recorded TEM diffraction pattern of non-volatile residue revealed that the final product of the decomposition was gold nanoparticles (Figure S11).

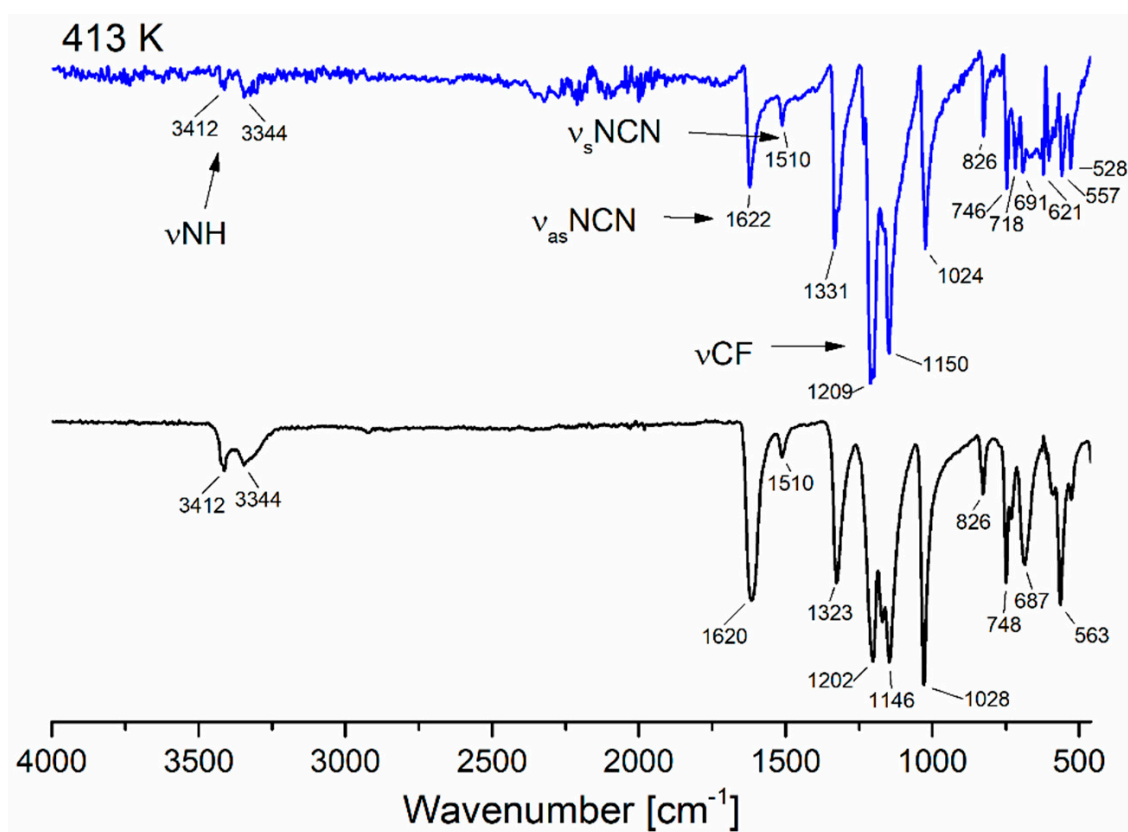


Figure 11. Infrared spectra of the compound $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1) before (black) and after sublimation (blue) at 413 K ($p = 10^{-2}\text{ mbar}$).

The compounds' volatility is usually discussed in relation to the molecular weight and the interactions occurring in the solid state. The good volatility of complex (1) can be justified by the polymeric structure maintained by the aurophilic and hydrogen bonds in the chain and the $\text{F}\cdots\text{F}$ contacts dominating in the crystal network. The aurophilic interactions ($2.5\text{--}3.5\text{ \AA}$) are a significant stabilization factor responsible for an evaporation temperature increase [18]. However, in compound (1), those bonds are short inside the tetramers, whereas they are much longer ($3.361\text{ \AA}$) and weaker between adjacent tetrameric motifs. Moreover, the huge number of intermolecular $\text{F}\cdots\text{F}$ contacts providing significant electrostatic repulsion also affects volatility. Hence, both factors—weak aurophilic bonds

between tetramers and interactions between partially negatively polarized fluorine atoms—are responsible for the lowering of the evaporation temperature [23].

The advantage of $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (**1**) with N,N-donor ligands is its slightly lower evaporation temperature compared to that of the O,O-donor carboxylate (423 K , 10^{-1} mbar), which is a well-known FEBID precursor $[\text{Ag}_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_2]$ (76 at.% Ag) [6,40].

3.6. Variable-Temperature Infrared Spectroscopy (VT IR)

The compound $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (**2**) was studied using the VT IR method to determine the composition of the gas phase formed during the heating of the complex. Moreover, we could verify that the studied complex was capable of generating volatile metal carriers under higher pressure (10^{-1} mbar) than during the sublimation attempt and under which it decomposed (Sections 3.3 and 3.5).

In the spectra registered for the compound $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (**2**) (Figure 12), the first volatile products formed upon heating were recorded at 333 K . At this temperature, a band characteristic for HCl molecules was detected at 2982 cm^{-1} . This indicated that for the complex $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (**2**), the generation of volatile gold carriers is driven by a thermal process resulting in the release of hydrogen chloride, amidine deprotonation, and the formation of gold(I) amidinate $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (**1**), which was also deduced from the EI MS studies and the sublimation experiments (Sections 3.4 and 3.5). The VT IR spectra at the temperature of 433 K and 453 K showed the bands νNH (3446 , 3343 cm^{-1}), and $\nu_{\text{as}}\text{NCN}$ (1660 cm^{-1}) (Figure 12), characteristic for the gold(I) amidinate. However, the occurrence of the bands characteristic for free amidine, i.e., νNH (3510 cm^{-1}), νCN (1776 cm^{-1}), and $\nu\text{C}\equiv\text{N}$ (2271 cm^{-1}), in the temperature range of $373\text{--}453\text{ K}$, suggest that a decomposition products' mixture was formed simultaneously (Figure 12).

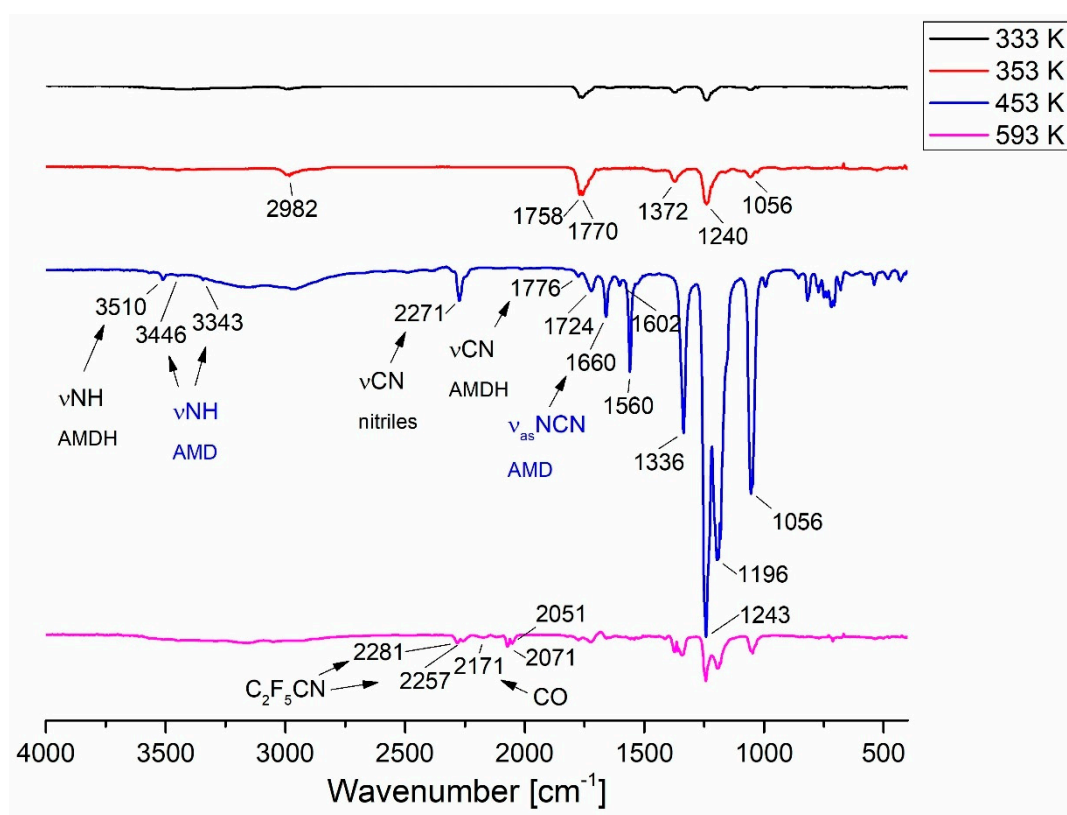


Figure 12. VT IR spectra of $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (**2**) in the temperature range of $333\text{--}593\text{ K}$ ($p = 10^{-1}$ mbar).

In summary, it was confirmed that the amidine complex $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (2) generates metal carriers in the gas phase in the form of gold(I) amidinate and can be considered for use in vapor deposition processes.

3.7. SEM/EDX Observation and TEM/EDX Studies of $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1) Adsorbed Thin Layers

To assess the sensitivity of the compounds to high-energy electrons and their usefulness in the FEBID and FIBID methods, a scanning electron microscope (SEM) and a transmission electron microscope (TEM) were used. These experiments are important to evaluate the precursor's initial effectiveness in the FEBID and FIBID process and provide insights for the design of new precursors. The sensitivity of thin layers of complex (1) resublimated on a silicon substrate (Section 3.5) was studied using SEM/EDX at 8 and 20 keV energy. EDX spectra were recorded during the SEM analysis. The scanning area was reduced, which caused an increase in the dose of electrons. Moreover, TEM (200 keV) measurements were performed for compound (1). The EDX spectra recorded for each area showed that changes in the intensity of the signals characteristic of individual elements (C, N, and Au) were observed when irradiation at 8 keV was performed (Figure 13 and Figure S12). Only a decrease in the fluorine signal intensity was observed. Based on these results and the morphological changes observed in SEM, we propose that complex (1) is sensitive to a high-energy electron beam (Figure 14). With the use of 20 keV, the changes in signal intensity for individual elements (C, N, F, and Au) remained at the same level, and no morphological changes in the SEM image were observed (Figure S12).

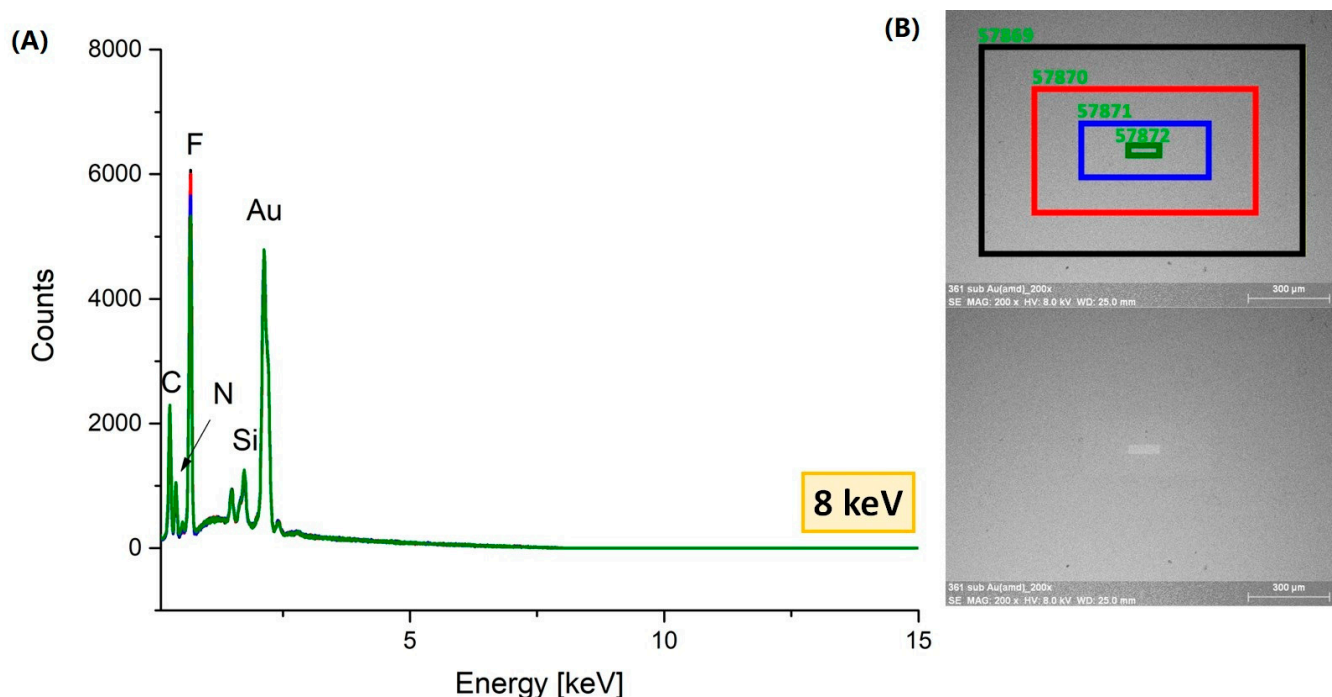


Figure 13. EDX spectra (8 keV) of sublimed $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1) on a Si(111) substrate (Mag = 200×) (A). Top view of SEM images of irradiated areas of the sublimed film (B); top image: marked areas corresponding to the EDX plots; bottom image: morphological changes after irradiation; black, red, blue, and green rectangles—orderly with largest to smallest area of scanning, the colors correspond to changes in signals intensity in the EDX spectrum.

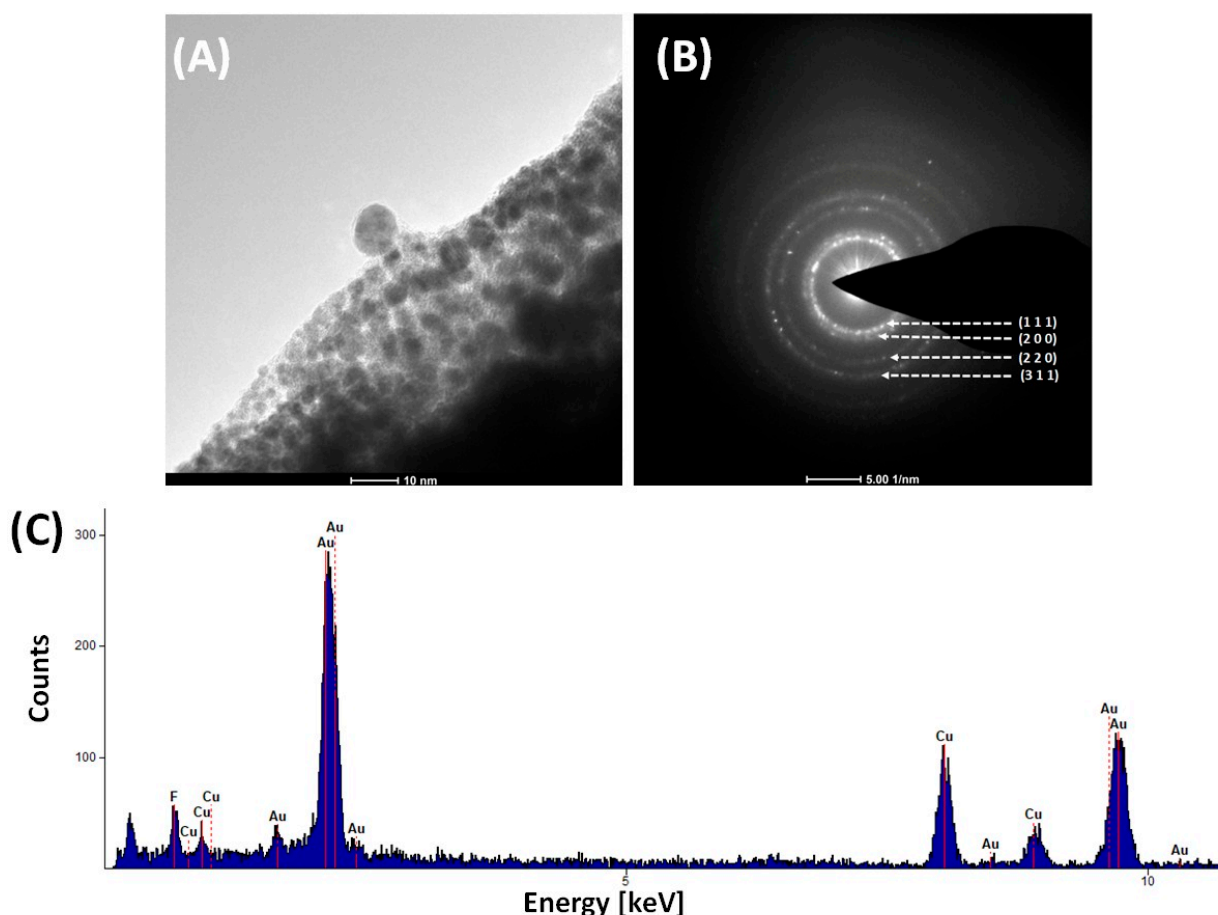


Figure 14. TEM imaging for $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (**1**): image of the sample after several seconds of interaction with high-energy (200 keV) electrons (A), TEM diffraction pattern (B), TEM-EDX spectrum (C).

Moreover, the mentioned vaporized layer of compound (**1**) was heated at 613 K, following the thermal analysis, under conditions close to those of the CVD process. Notably, characteristic signals for Au and C were observed, while no signals for F and N were detected in the EDX spectrum (Figure S13), which is an encouraging result for the potential application of compound (**1**) in the CVD process. These results suggest a more efficient thermal removal of the organic ligand from the surface relative to the electron irradiation. However, this hypothesis requires confirmation through further experiments.

In the TEM imaging (200 keV) that was performed for $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (**1**), changes in the structure of the sample were observed. After a few seconds of irradiation, the TEM images revealed grains surrounded by amorphous carbon (Figure 14A). The diffraction patterns confirmed the formed material's crystallinity and gold nanoparticle formation (Figure 14). The TEM EDX spectra from TEM showed signals characteristic of gold, fluorine, and carbon, but no nitrogen signal was detected. It should be noted that the TEM mesh was covered with a carbon membrane (Table 3). As a result of the interaction of the complex (**1**) with the electron beam (200 keV), a decomposition product formed, which was identified as crystalline gold. The absence of a signal from nitrogen indicates that the Au-N bond was broken under the conditions of the TEM observations. Moreover, the fluorine signal suggests that a carbon fluoride matrix was formed.

Table 3. TEM-EDX data for the complex $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1).

Element	Atomic Content of the Element [%at.] after Irradiation	Atomic Content of the Element [%at.] of the Complex
	$[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1)	
Au	83.02	1
F	13.13	5
C	3.84 *	3
N	—	2

* TEM grid covered with carbon.

In summary, the microscopic observations confirmed that compound (1) demonstrates sensitivity to high-energy electrons and can potentially be tested under experimental FEBID or FIBID conditions. It should be noted that the decomposition of complex (1) strongly depends on the beam power and electron dose.

4. Conclusions

Synthesis methods of new gold(I) complexes based on the fluorinated amidine with the formulas $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1) and $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (2) were developed. For $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1), single-crystal X-ray diffraction studies revealed the formation of a stable coordination polymer composed of $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]$ (1) tetramers and demonstrated the presence of bridging amidinates as well as aurophilic bonds in the chain. Additionally, the IR and EI MS spectra analysis confirmed the amidinate formation and the coordination of gold by nitrogen atoms. The relatively low evaporation temperature, 413 K ($p = 10^{-2}$ mbar), can be related to the structural features—aurophilic interactions, which are short in the tetramer and much longer and weaker between adjacent repeating motifs—and the dominant role of weak repulsive F...F intermolecular interactions between adjacent chains, confirmed by Hirshfeld surface analysis. In the case of the complex $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (2), the EI MS results indicated the formation of dinuclear gold amidinate fragments released upon the thermal loss of HCl. The thermal analysis data indicated that the compounds decomposed at the atmospheric pressure, with loss of amidinate for (1) and (2) and hydrogen chloride in the first step for (2). On the other hand, the EI MS spectra analysis showed that both gold(I) complexes were the source of metal in the gas phase, even at the temperature of 319 K ($p = 10^{-6}$ mbar). This fact suggests that the studied complexes could be introduced into the SEM microscope chamber via the GIS system. The VT IR spectra confirmed the release of HCl from $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (2) and the formation of gold(I) amidinate over the temperature range of 433–453 K. $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1) sublimation occurs at 413 K ($p = 10^{-2}$ mbar), which is similar to what observed for the sublimation of the FEBID precursor $[\text{Ag}_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_2]$. These results indicate that the new gold(I) amidinate is a metal source in the gas phase and can be tested under typical CVD conditions. Based on the study of the complex' interactions with high-energy electrons, it can be concluded that the compound $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1) is sensitive to high-energy electron exposure (8 and 200 keV). Moreover, $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$, unlike previously tested gold(I) and gold(III) complexes, is air-stable and user-friendly, shows satisfactory volatility, is susceptible to an electron beam, and can be considered for practical use in the FEBID and FIBID processes.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules30010146/s1>, Table S1 Crystal data and structure refinement for the compound $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1); Table S2 Bond lengths [Å] and angles [°] for the compound $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1); Figure S1 The asymmetric part of structure of $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1)

with ellipsoids at the level of 30% probability (yellow—gold atoms; blue—nitrogen atoms; gray—carbon atoms; green—fluorine atoms); Figure S2 Crystal structure projected in the *ab* plane of $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1) (hydrogen bonds H...N are marked with a red dashed line); Figure S3 Hirshfeld surfaces (left) and fingerprints (right) of selected interactions created in the crystal network of $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1): (A) for F...H (9.2%), (B) for H...H (5.3%), (C) for Au...F (3.4%), (D) for Au...H (3.4%). In brackets, a given surface area included as a percentage of the total surface area is shown; Figure S4 Hirshfeld surfaces (left) and fingerprints (right) of selected interactions created in the crystal network of $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1): (A) for H...Au (2.7%), (B) for N...H (2.6%), (C) for H...N (2.6%), (D) for Au...Au (2.3%). In brackets, a given surface area included as a percentage of the total surface area is shown; Figure S5 ATR-IR spectrum for the compound $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (2) (blue), HAMDC_2F_5 (red), and $[\text{Au}(\text{tht})\text{Cl}]$ (black); Figure S6 Results of TEM-EDX analysis obtained for the complex $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (2) after a few seconds of interaction with a focus high-energy electron beam (200 keV), (A)—TEM image, (B) TEM-EDX spectrum, and (C) atomic content of the element; Table S3 Electron impact mass spectrometry (EI MS) results for the compound $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1); Table S4 Electron impact mass spectrometry (EI MS) results for the compound $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (2); Figure S7 Fragmentation scheme for the most important ions of $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (2) (HAMDC_2F_5 ; $\text{AMD}(\text{NH})_2\text{CC}_2\text{F}_5$), assignment: grey—non-metallated ions, red—dinuclear ions, pink—mononuclear ions; Figure S8 EI MS spectra, where the $[\text{Au}_2(\text{AMD})_2]^+$ ion achieved relative intensity at the level of 100%; Figure S9 Infrared spectra for the compound $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (2) before (black) and after sublimation (blue) at 353 K ($p = 10^{-2}$ mbar); Figure S10 EDX spectra (20 keV) of product adsorbed on a Si(111) substrate during the sublimation test of $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (2); Figure S11 Transmission electron microscope image for gold nanoparticles formed after sublimation process for the complex $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (2) (A), TEM diffraction pattern (B), and energy-dispersive X-ray spectroscopy (EDX) spectrum (TEM grid covered with carbon) (C); Figure S12 EDX spectra (20 keV) of sublimed $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1) on a Si(111) substrate (Mag = 200×) (A). Top view SEM images of irradiated areas of the sublimed film (B): top: with marked areas corresponding to the EDX plots; bottom: morphological changes after irradiation; black, red, blue, and green rectangles – orderly with largest to smallest area of scanning, the colors correspond to changes in signals intensity in the EDX spectrum; Figure S13 SEM images of vaporized layer of the compound $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1) after heat treatment at 613 K: Mag = 10,000 ×—(A); Mag = 50,000 ×—(B); Mag = 100,000 ×—(C). SEM image—(D) and EDX spectrum—(E) of studied area.

Author Contributions: I.B.S. conceptualization; A.B.-K. synthesized the complexes and prepared the samples; A.B.-K. and I.B.S. characterized the samples; A.B.-K. prepared the figures and drafted the manuscript; T.M.M. performed the X-ray structural measurements; A.B.-K. and T.M.M. performed visualization and structure description; P.M. TEM/EDX performed the measurements and their analysis. All authors have read and agreed to the published version of the manuscript.

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New Gold(I) Complexes as Potential Precursors for Gas-Assisted Methods: Structure, Volatility, Thermal Stability, and Electron Sensitivity

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Table S1. Crystal data and structure refinement for the compound $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (**1**).

Identification code	(1)
Empirical formula	C ₁₂ H ₈ Au ₄ F ₂₀ N ₈
Formula weight	1432.13
Temperature [K]	100(2)
Wavelength [Å]	0.71073
Crystal system, space group	Monoclinic, I2/a
Unit cell dimensions [Å] and [°]	a = 8.99189(19) α = 90 b = 12.6776(3) β = 98.034(2) c = 22.7927(5) γ = 90
Volume [Å ³]	2572.77(10)
Z, Calculated density [Mg×m ⁻³]	4, 3.697
Absorption coefficient [mm ⁻¹]	22.906
F(000)	2528
Crystal size [mm ³]	0.150 x 0.040 x 0.020
Theta range for data collection [°]	2.796 to 26.370
Limiting indices	-11 ≤ h ≤ 10 -15 ≤ k ≤ 15 -28 ≤ l ≤ 28
Reflections collected/unique	15417
Completeness [%] to theta [°]	99.6 %
Absorption correction	Gaussian
Max. and min. transmission	0.854 and 0.277
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	2625 / 0 / 200
Goodness-of-fit on F ²	1.035
Final R Indices [I > 2σ(I)]	R ₁ = 0.0145, wR ₂ = 0.0355
R indices (all data)	R ₁ = 0.0171, wR ₂ = 0.0364
Largest diff. peak and hole [eÅ ⁻³]	1.184 and -0.916

Table S2. Bond lengths [Å] and angles [°] for the compound [Au₄(μ-AMDCC₂F₅)₄]_n (**1**).

Au(1)-N(2)#1	2.012(3)
Au(1)-N(2)	2.012(3)
Au(1)-Au(2)#1	3.03500(14)
Au(1)-Au(2)	3.03506(14)
Au(1)-Au(3)	3.3288(2)
Au(1)-Au(2)#2	3.36078(18)
Au(1)-Au(2)#3	3.36078(18)
Au(2)-N(12)	2.002(2)
Au(2)-N(1)	2.012(2)
Au(2)-Au(3)	3.04568(14)
Au(3)-N(11)#1	2.019(2)
Au(3)-N(11)	2.019(2)
N(2)#1-Au(1)-N(2)	177.79(14)
N(2)#1-Au(1)-Au(2)#1	78.40(7)
N(2)-Au(1)-Au(2)#1	102.84(7)
N(2)#1-Au(1)-Au(2)	102.84(7)
N(2)-Au(1)-Au(2)	78.40(7)
Au(2)#1-Au(1)-Au(2)	113.925(6)
N(2)#1-Au(1)-Au(3)	91.11(7)
N(2)-Au(1)-Au(3)	91.11(7)
Au(2)#1-Au(1)-Au(3)	56.963(3)
Au(2)-Au(1)-Au(3)	56.962(3)
N(2)#1-Au(1)-Au(2)#2	74.07(7)
N(2)-Au(1)-Au(2)#2	104.20(7)
Au(2)#1-Au(1)-Au(2)#2	147.724(4)
Au(2)-Au(1)-Au(2)#2	88.653(3)
Au(3)-Au(1)-Au(2)#2	138.924(3)
N(2)#1-Au(1)-Au(2)#3	104.20(7)
N(2)-Au(1)-Au(2)#3	74.07(7)
Au(2)#1-Au(1)-Au(2)#3	88.652(3)
Au(2)-Au(1)-Au(2)#3	147.724(4)
Au(3)-Au(1)-Au(2)#3	138.924(3)
Au(2)#2-Au(1)-Au(2)#3	82.152(6)
N(12)-Au(2)-N(1)	174.93(10)
N(12)-Au(2)-Au(1)	103.69(7)
N(1)-Au(2)-Au(1)	81.17(7)

N(12)-Au(2)-Au(3)	81.23(7)
N(1)-Au(2)-Au(3)	99.66(7)
Au(1)-Au(2)-Au(3)	66.381(5)
N(12)-Au(2)-Au(1)#2	82.20(7)
N(1)-Au(2)-Au(1)#2	99.25(7)
Au(1)-Au(2)-Au(1)#2	91.346(4)
Au(3)-Au(2)-Au(1)#2	147.922(4)
N(11)#1-Au(3)-N(11)	170.06(15)
N(11)#1-Au(3)-Au(2)#1	77.88(7)
N(11)-Au(3)-Au(2)#1	107.77(7)
N(11)#1-Au(3)-Au(2)	107.77(7)
N(11)-Au(3)-Au(2)	77.88(7)
Au(2)#1-Au(3)-Au(2)	113.312(7)
N(11)#1-Au(3)-Au(1)	94.97(7)
N(11)-Au(3)-Au(1)	94.97(7)
Au(2)#1-Au(3)-Au(1)	56.655(3)
Au(2)-Au(3)-Au(1)	56.656(3)
C(2)-N(1)-Au(2)	125.1(2)
Au(2)-N(1)-H(1)	117.5
C(2)-N(2)-Au(1)	129.3(2)
Au(1)-N(2)-H(2)	115.4
C(12)-N(11)-Au(3)	128.5(2)
Au(3)-N(11)-H(11)	115.8
C(12)-N(12)-Au(2)	125.8(2)
Au(2)-N(12)-H(12)	117.1

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1/2, y, -z+1$ #2 $-x+1, -y+1, -z+1$ #3 $x-1/2, -y+1, z$

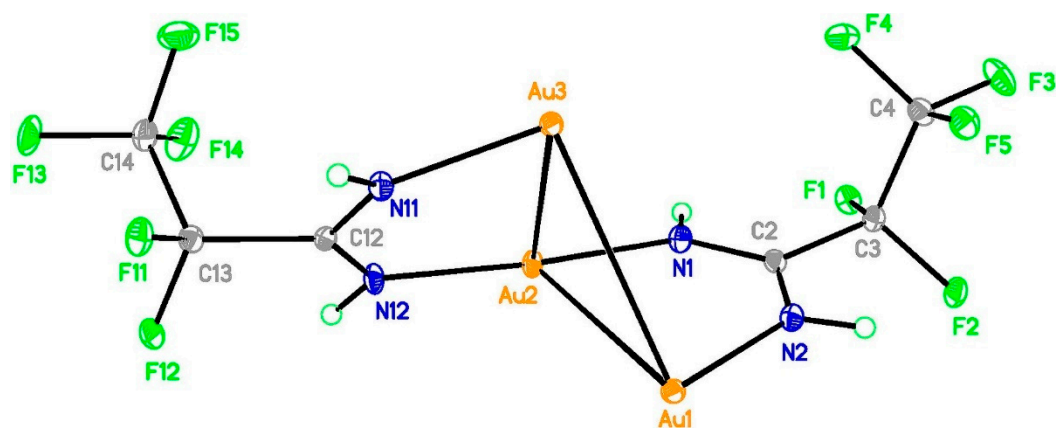


Figure S1. The asymmetric part of structure of $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (**1**) with ellipsoids at the level of 30% probability (yellow – gold atoms; blue – nitrogen atoms; gray – carbon atoms; green – fluorine atoms).

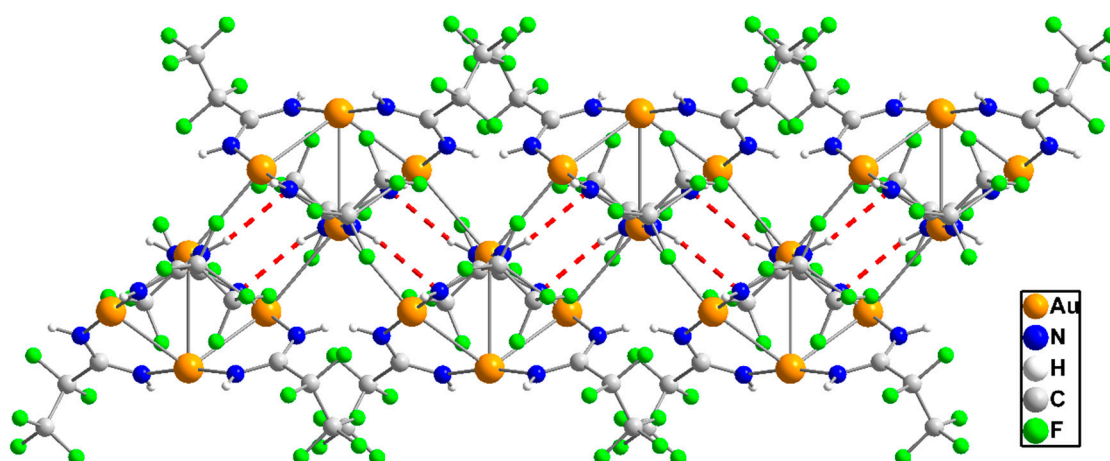


Figure S2. Crystal structure projected in the ab plane of $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (**1**) (hydrogen bonds $\text{H}\cdots\text{N}$ are marked with a red dashed line).

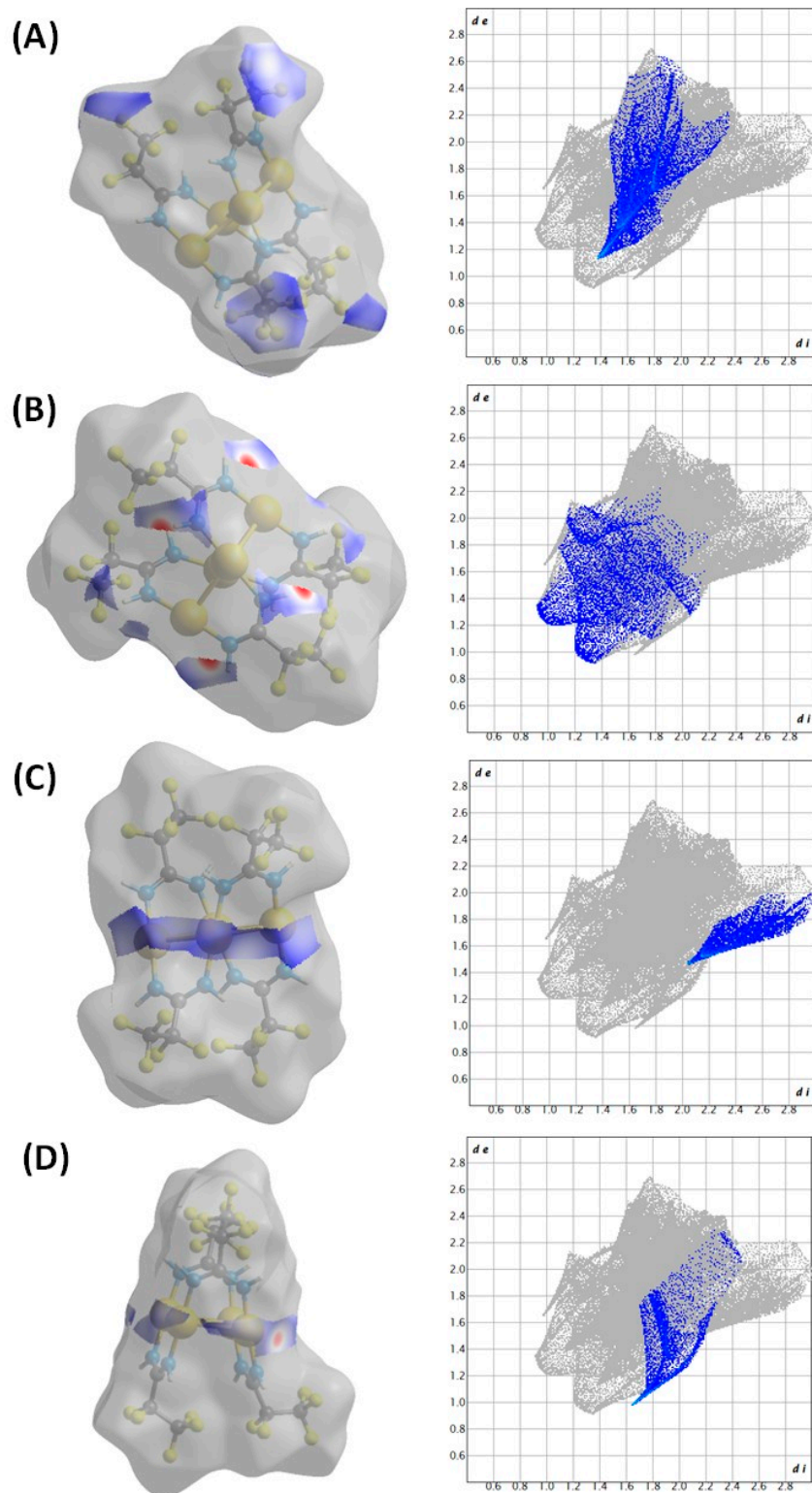


Figure S3. Hirshfeld surfaces (left) and fingerprints (right) of selected interactions created in the crystal network of $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1): (A) for $\text{F}\cdots\text{H}$ (9.2%), (B) for $\text{H}\cdots\text{H}$ (5.3%), (C) for $\text{Au}\cdots\text{F}$ (3.4%), (D) for $\text{Au}\cdots\text{H}$ (3.4%). In brackets, a given surface area included as a percentage of the total surface area is shown.

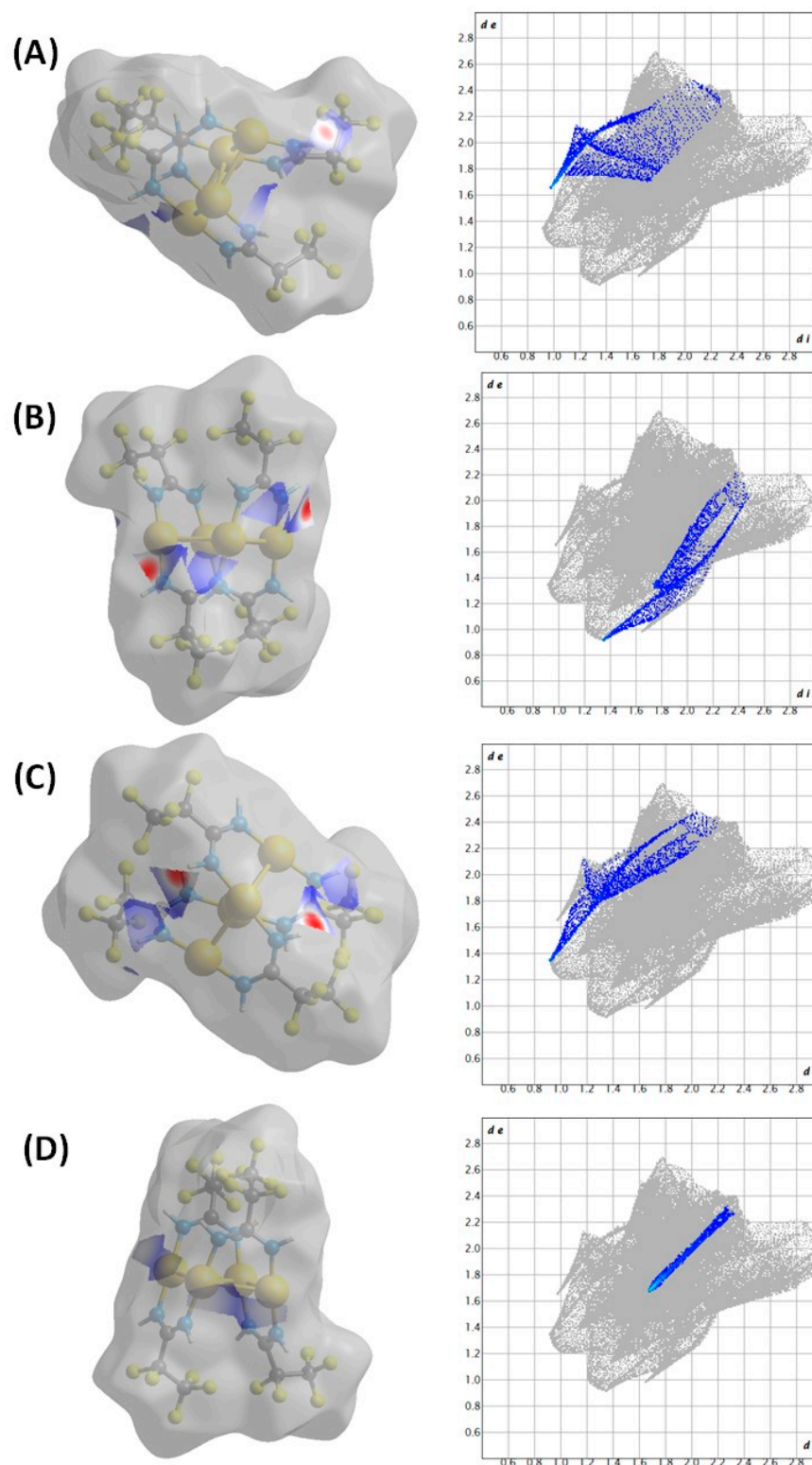


Figure S4. Hirshfeld surfaces (left) and fingerprints (right) of selected interactions created in the crystal network of $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1): (A) for $\text{H}\cdots\text{Au}$ (2.7%), (B) for $\text{N}\cdots\text{H}$ (2.6%), (C) for $\text{H}\cdots\text{N}$ (2.6%), (D) for $\text{Au}\cdots\text{Au}$ (2.3%). In brackets, a given surface area included as a percentage of the total surface area is shown.

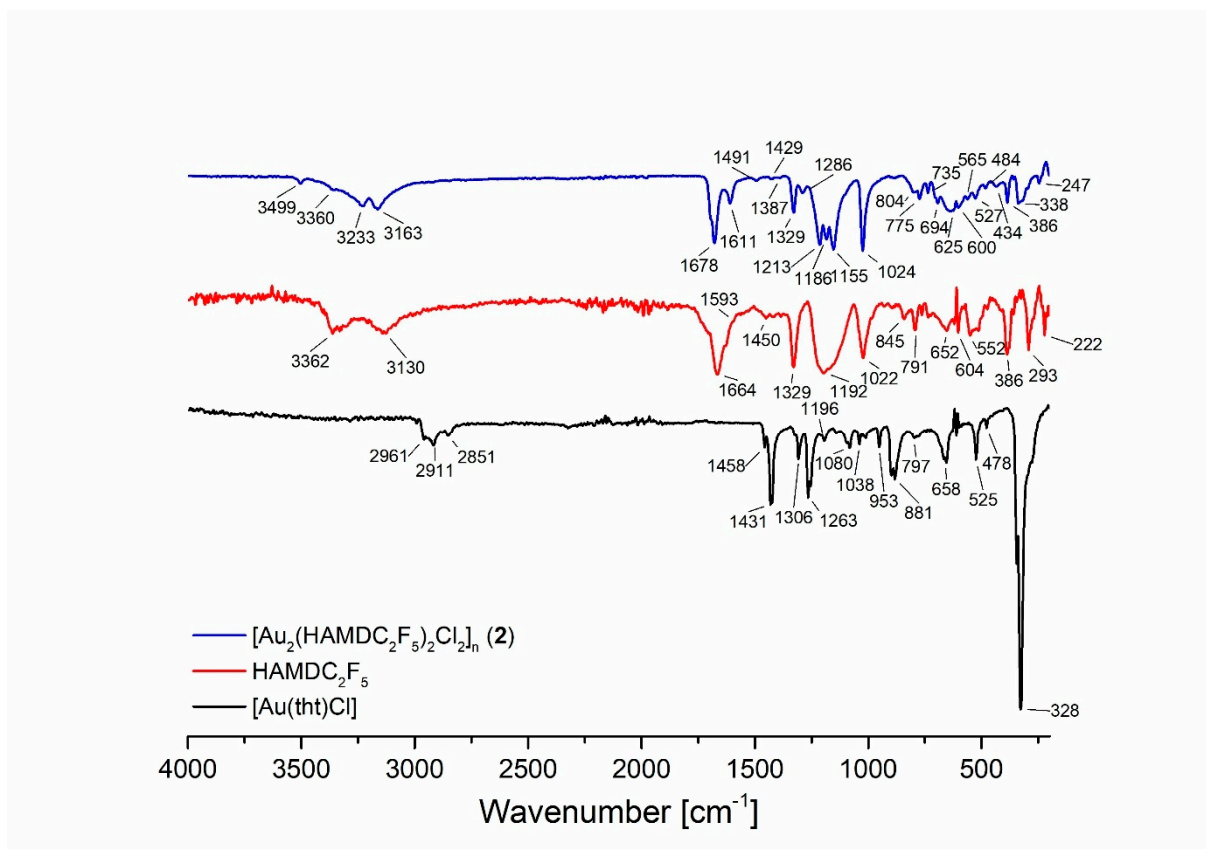
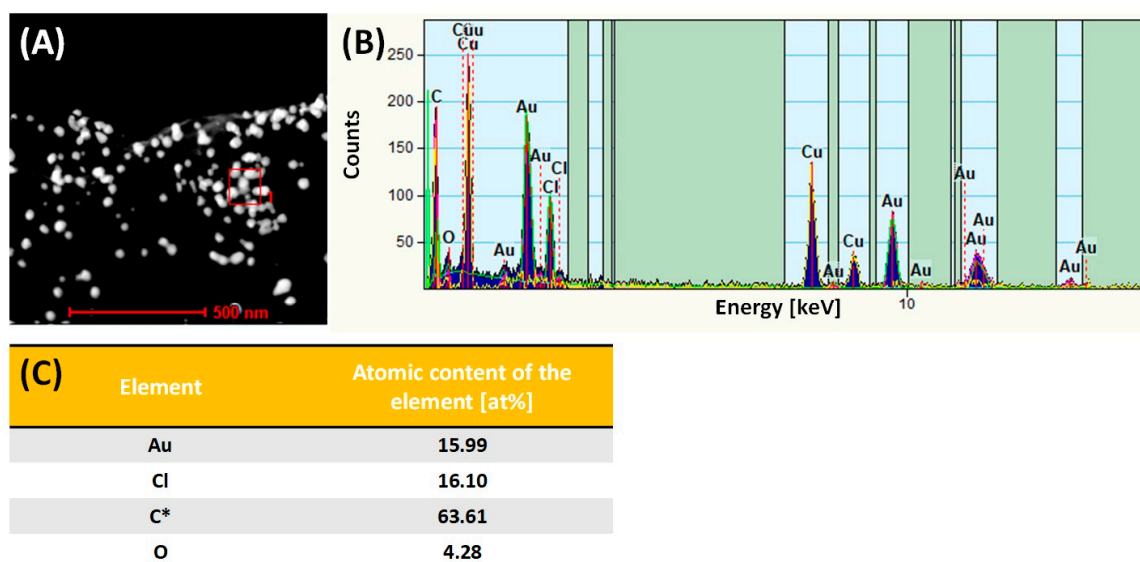


Figure S5. ATR-IR spectrum for the compound $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (**2**) (blue), HAMDC_2F_5 (red), and $[\text{Au}(\text{tht})\text{Cl}]$ (black).



*TEM grid covered with carbon

Figure S6. Results of TEM-EDX analysis obtained for the complex $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (**2**) after a few seconds of interaction with a focus high-energy electron beam (200 keV), (A) – TEM image, (B) TEM-EDX spectrum, and (C) atomic content of the element.

Table S3. Electron impact mass spectrometry (EI MS) results for the compound $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (**1**).

Fragments	m/z	Relative Intensity (RI) [%]				
		324 K	328 K	339 K	352 K	406 K
$[\text{HN}=\text{C}=\text{N}]^+$	41	5	—	3	2	—
$[\text{HN}=\text{C}=\text{NH}]^{++}$	42	47	2	4	4	1
$[\text{HN}=\text{C}-\text{NH}_2]^{++}$	43	7	3	6	6	10
$[\text{FC}_2\text{H}]^{++}$	44	25	25	52	55	100
$[\text{FCN}]^{++}$	45	69	1	8	12	2
$[\text{CF}_2]^+$	50	4	2	6	—	—
$[\text{CF}_3]^+$	69	60	12	40	38	59
$[\text{CF}_2\text{CN}]^+$	76	5	3	7	7	15
$[\text{C}_2\text{F}_4]^+$	100	6	3	4	4	7
$[\text{C}_2\text{F}_5]^+$	119	20	8	10	10	14
$[\text{C}_2\text{F}_4\text{CN}]^+$	126	4	2	4	4	11
$[\text{NHCC}_2\text{F}_5]^+$	146	1	2	1	—	1
$[\text{NHNHC}_2\text{F}_5]^+$	149	71	13	9	7	—
$[\text{NHNH}_2\text{CC}_2\text{F}_5]^{++}$	162	9	12	19	20	22
$[\text{Au}(\text{NH})]^{++}$	212	16	—	—	—	—
$[\text{Au}(\text{HNCNH})]^+$	239	2	4	4	5	1
$[\text{Au}(\text{NHNH}_2\text{CCF})]^{++}$	271	—	1	—	—	—
$[\text{Au}(\text{NHC}_2\text{F}_5)]^{++}$	331	8	—	—	—	—
$[\text{Au}_2(\text{NHNHCC}_2\text{F}_5)_2]^{2+}$ / $[\text{Au}(\text{NHNHCC}_2\text{F}_5)]^{++}$	358	—	2	3	2	—
$[\text{Au}_2(\text{NH}_2)]^+$	410	—	1	1	—	—
$[\text{Au}_2(\text{HNCNH})]^{2+}$	436	—	3	3	2	1
$[\text{Au}(\text{NHNHCC}_2\text{F}_5)_2]^+$	519	2	—	—	—	—
$[\text{Au}_2(\text{NHNHCC}_2\text{F}_5)]^+$	555	1	21	30	25	12
$[\text{Au}_2(\text{NHNHCC}_2\text{F}_5)(\text{HCN})]^+$	582	—	6	6	5	1
$[\text{Au}_2(\text{NHNHCC}_2\text{F}_5)(\text{HNCNH})]^+$	597	—	19	21	19	14
$[\text{Au}_2(\text{NHNHCC}_2\text{F}_5)_2]^{++}$	716	—	100	100	100	95
$[\text{Au}_3(\text{NHNHCC}_2\text{F}_5)_2]^+$	913	—	2	—	—	1
$[\text{Au}_4(\text{NHNHCC}_2\text{F}_5)]^+$	949	—	8	3	4	8

Table S4. Electron impact mass spectrometry (EI MS) results for the compound $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (**2**).

Fragments	m/z	Relative Intensity (RI) [%]			
		336 K	339 K	344 K	363 K
$[\text{HCl}]^{+\bullet}$	36	2	17	25	24
$[\text{H}_2^{35}\text{Cl}]^+$	37	9	67	100	100
$[\text{H}_2^{37}\text{Cl}]^+$	39	2	22	30	31
$[\text{HN}=\text{C}=\text{NH}]^{+\bullet}$	42	3	18	22	10
$[\text{HN}=\text{C}-\text{NH}_2]^{+\bullet}$	43	8	6	35	—
$[\text{FC}_2\text{H}]^{+\bullet}$	44	100	29	—	23
$[\text{FCN}]^{+\bullet}$	45	1	4	—	17
$[\text{CF}_2]^+$	50	2	1	7	3
$[\text{CF}_3]^+$	69	16	26	59	24
$[\text{CF}_2\text{CN}]^+$	76	—	6	17	5
$[\text{C}_4\text{H}_7\text{S}]^+$	87	—	100	8	10
$[\text{CF}_4]^{+\bullet} / [\text{C}_4\text{H}_8\text{S}]^{+\bullet}$	88	1	62	6	9
$[\text{C}_2\text{F}_4]^+$	100	3	4	5	—
$[\text{C}_2\text{F}_5]^+$	119	12	18	29	10
$[\text{C}_2\text{F}_4\text{CN}]^+$	126	—	4	12	—
$[\text{NHCC}_2\text{F}_5]^+$	146	5	8	14	—
$[\text{NHNH}_2\text{CC}_2\text{F}_5]^{+\bullet}$	162	22	4	—	—
$[\text{Au}(\text{NH})]^{+\bullet}$	212	—	11	52	52
$[\text{Au}(\text{HNCNH}_2)]^+$	240	—	3	—	—
$[\text{Au}(\text{NHNH}_2\text{CCF})]^{+\bullet}$	271	—	2	4	3
$[\text{Au}(\text{NHC}_2\text{F}_5)]^{+\bullet}$	331	—	2	9	—
$[\text{Au}(\text{NNCC}_2\text{F}_5)]^{+\bullet}$	356	—	5	37	3
$[\text{Au}_2(\text{NHNHCC}_2\text{F}_5)_2]^{2+}$ $/[\text{Au}(\text{NHNHCC}_2\text{F}_5)]^{+\bullet}$	358	—	6	8	—
$[\text{Au}_2(\text{NHNHCC}_2\text{F}_5)_2]^{+\bullet}$	716	—	4	—	—
$[\text{Au}_3(\text{NHNCC}_2\text{F}_5)]^+$	751	—	3	—	—

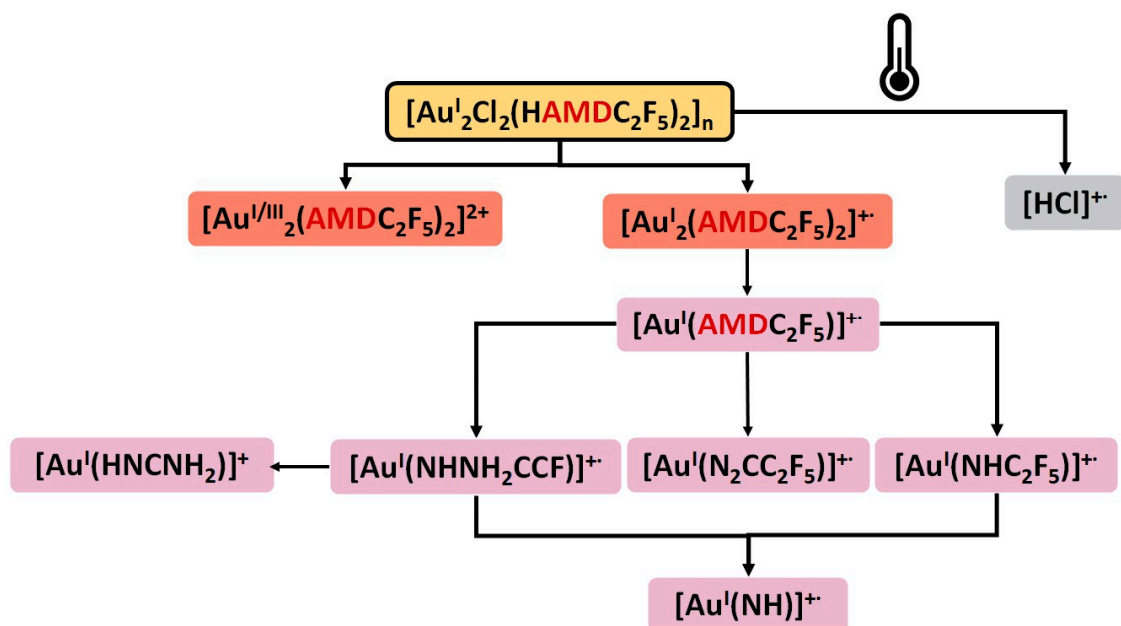


Figure S7. Fragmentation scheme for the most important ions of $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (2) (HAMD – $\text{NHNH}_2\text{CC}_2\text{F}_5$; AMD – $(\text{NH})_2\text{CC}_2\text{F}_5$), assignment: grey – non-metalled ions, red – dinuclear ions, pink – mononuclear ions.

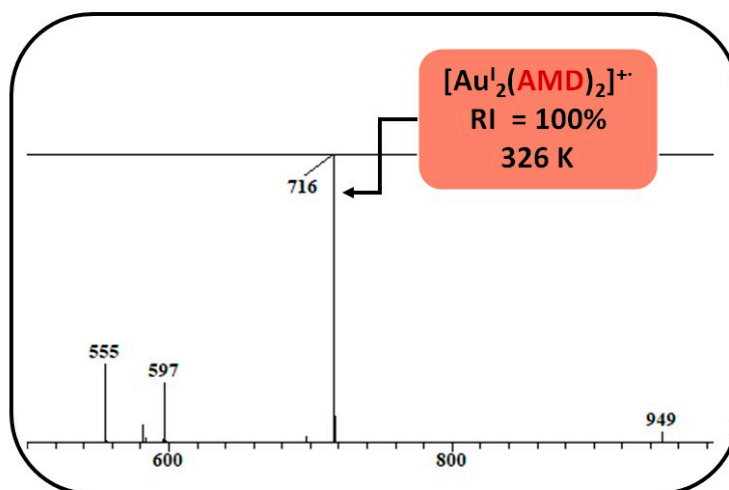


Figure S8. EI MS spectra, where the $[\text{Au}_2(\text{AMD})_2]^{+}$ ion achieved relative intensity at the level of 100%.

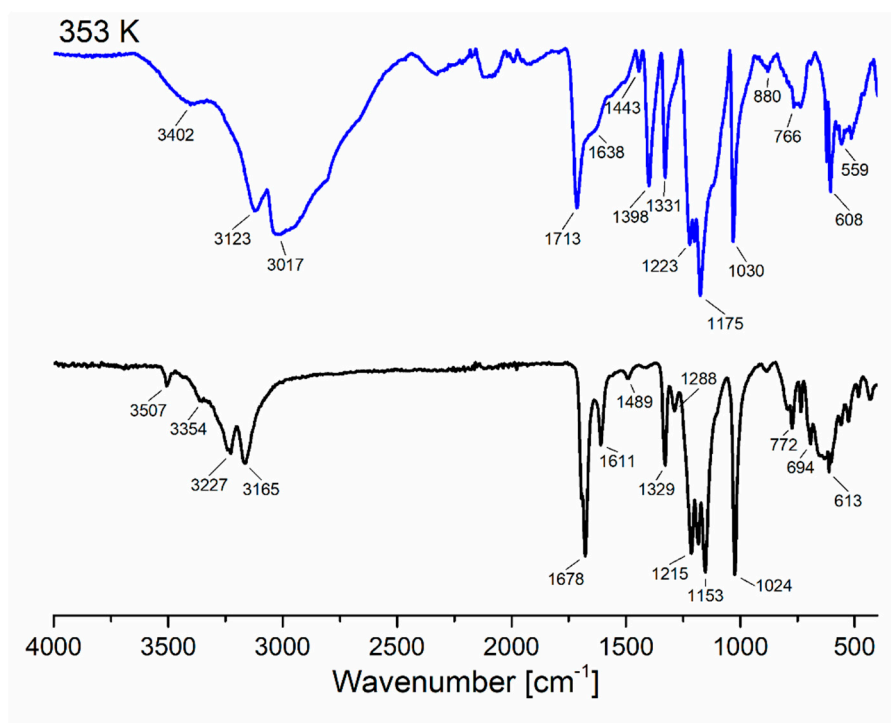


Figure S9. Infrared spectra for the compound $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (**2**) before (black) and after sublimation (blue) at 353 K ($p = 10^{-2}$ mbar).

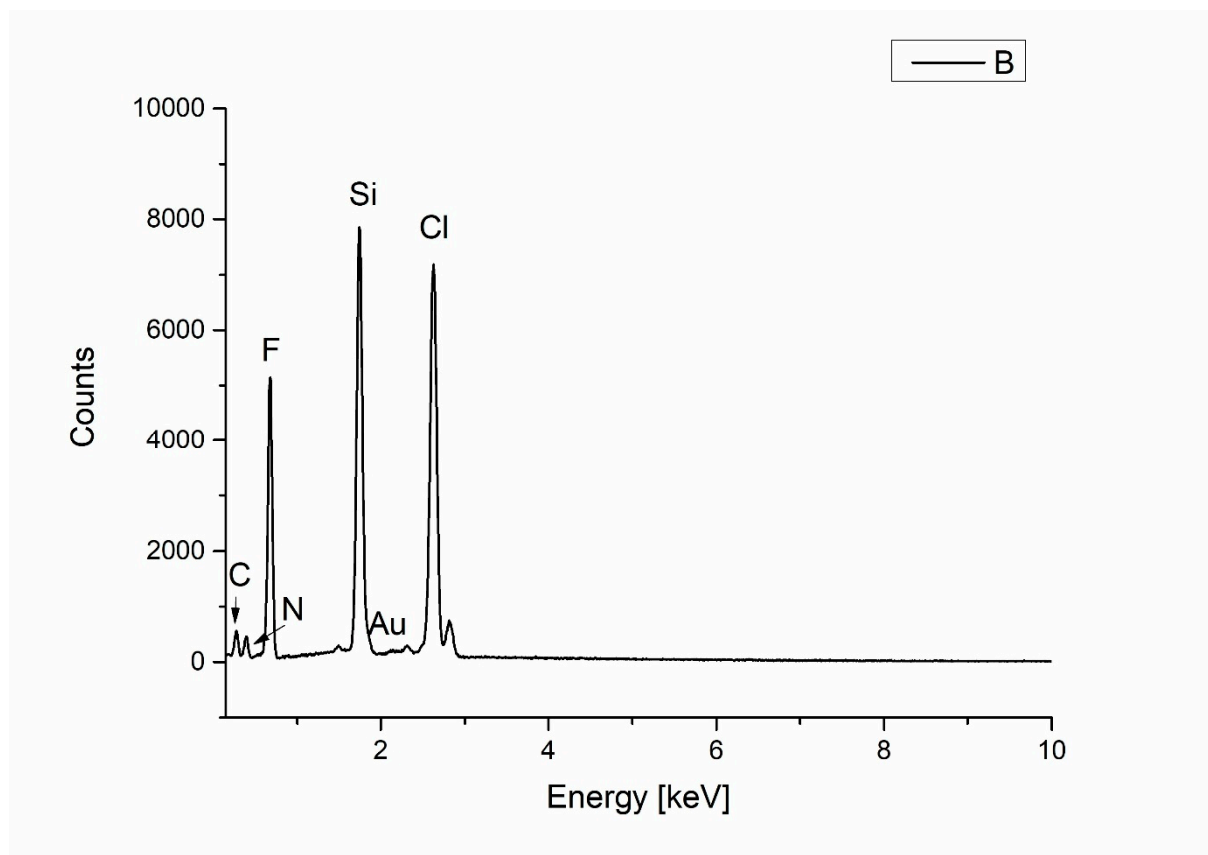


Figure S10. EDX spectra (20 keV) of product adsorbed on a Si(111) substrate during the sublimation test of $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (**2**).

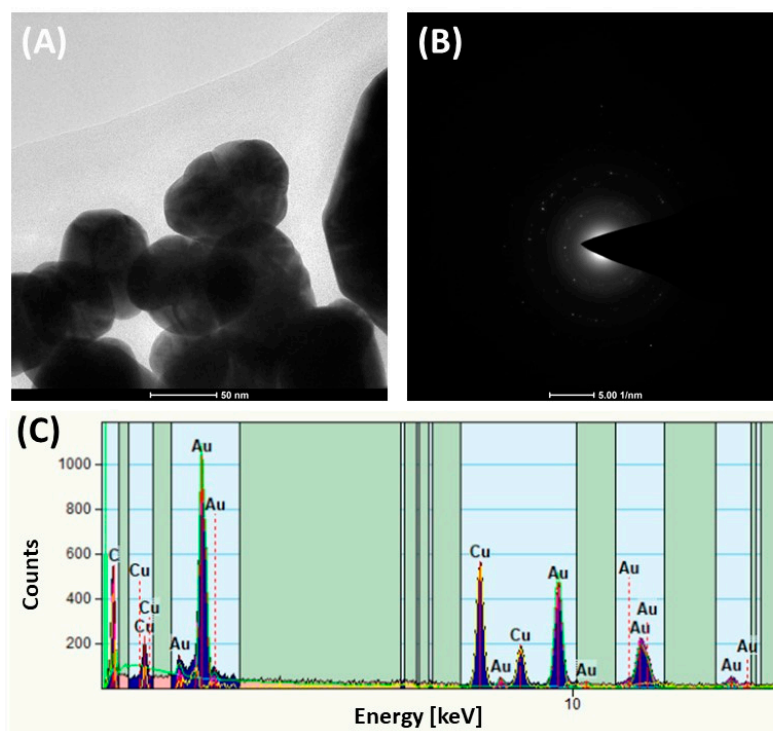


Figure S11. Transmission electron microscope image for gold nanoparticles formed after sublimation process for the complex $[\text{Au}_2\text{Cl}_2(\text{HAMDC}_2\text{F}_5)_2]_n$ (**2**) (A), TEM diffraction pattern (B), and energy-dispersive X-ray spectroscopy (EDX) spectrum (TEM grid covered with carbon) (C).

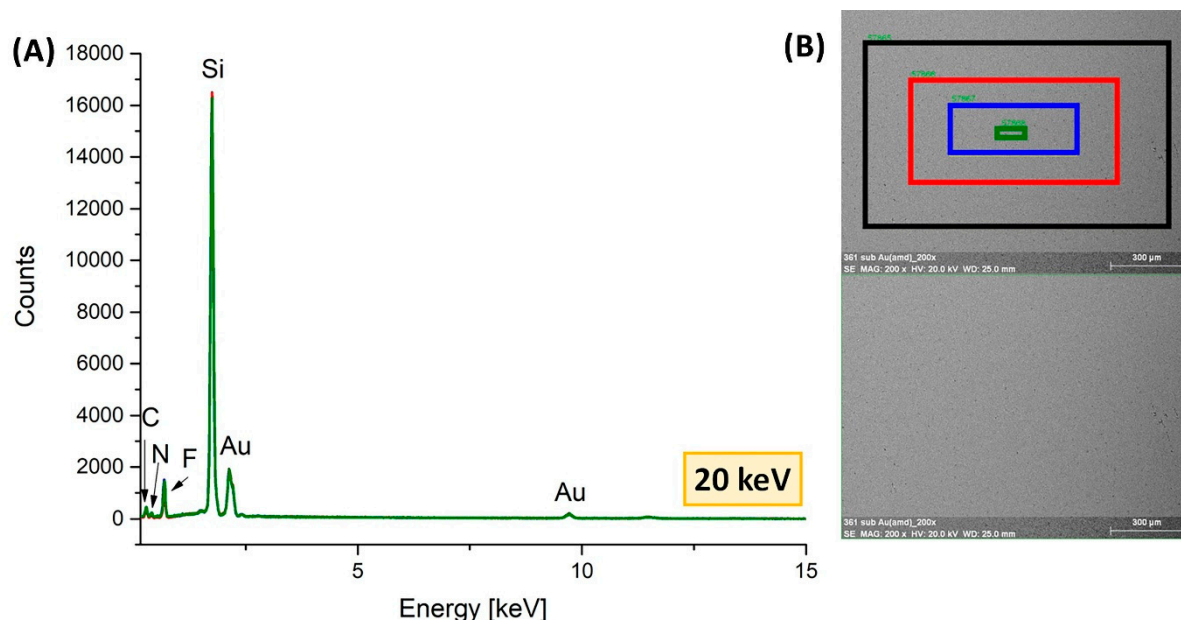


Figure S12. EDX spectra (20 keV) of sublimed $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (**1**) on a Si(111) substrate (Mag = 200×) (A). Top view SEM images of irradiated areas of the sublimed film (B): top: with marked areas corresponding to the EDX plots; bottom: morphological changes after irradiation; black, red, blue, and green rectangles – orderly with largest to smallest area of scanning, the colors correspond to changes in signals intensity in the EDX spectrum.

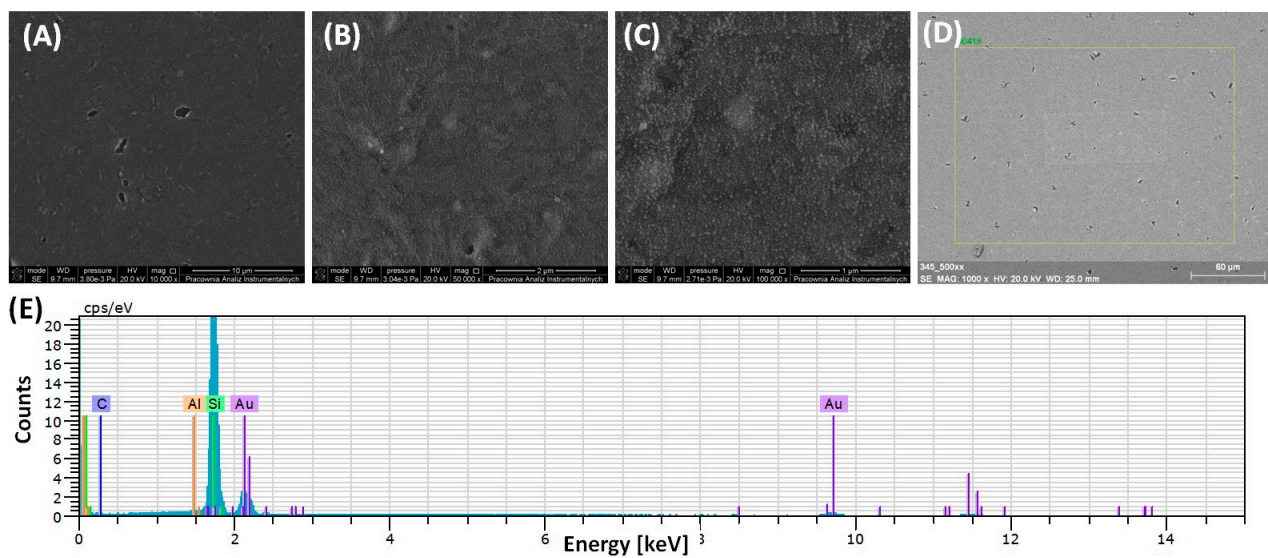


Figure S13. SEM images of vaporized layer of the compound $[\text{Au}_4(\mu\text{-AMDC}_2\text{F}_5)_4]_n$ (1) after heat treatment at 613 K: Mag = 10 000 x – (A); Mag = 50 000 x – (B); Mag = 100 000 x – (C). SEM image – (D) and EDX spectrum – (E) of studied area.

PAPER

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13662New palladium(II) β -ketoesterates for focused
electron beam induced deposition: synthesis,
structures, and characterization†A. Butrymowicz-Kubiak, ^a T. M. Muzioł, ^a A. Kaczmarek-Kędziera, ^a
C. S. Jureddy,^b K. Maćkosz,^b I. Utke ^b and I. B. Szymańska ^{*a}

We report the synthesis and characterization of new palladium(II) β -ketoesterate complexes $[\text{Pd}(\text{CH}_3\text{COCHCO}_2\text{R})_2]$ with alkyl substituents $\text{R} = {}^t\text{Bu}, {}^i\text{Pr}, \text{Et}$. These compounds can have potential use in focused electron beam induced deposition (FEBID), which is a direct write method for the growth of structures at the nanoscale. However, it is still a major challenge to obtain deposits with a high metal content, and new precursor molecules are needed to overcome this. Single crystal X-ray diffraction, infrared spectroscopy, nuclear magnetic resonance spectroscopy, and density-functional theory calculations were used to confirm the compounds' composition and structure. Using thermal analysis and sublimation experiments, we investigate their thermal stability and volatility. These studies show that the palladium complexes sublime over the range 348–353 K under 10^{-2} mbar pressure. The electron-induced decomposition of the complex molecules in the gas phase and their thin layers on silicon substrates were analysed using electron impact mass spectrometry (EI MS) and microscopy studies (SEM/EDX). They confirm that the precursor electron-induced fragmentation depends on the molecular structure. The obtained results reveal that $[\text{Pd}(\text{CH}_3\text{COCHCO}_2{}^t\text{Bu})_2]$ with *cis*-positioned *tert*-butyl groups may be a promising FEBID precursor, and we carried out preliminary deposition experiments using this compound.

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1. Introduction

Palladium-based nanomaterials are attractive as current transducer materials for hydrogen safety sensors also in optical fiber technology, as a catalyst among others in fuel cells to improve the kinetics of reactions, *e.g.*, the oxygen reduction reaction (ORR), and in nanoelectronics as, *e.g.*, capacitors, resistors, and contacts.^{1–9}

The focused electron beam induced deposition (FEBID) method is a versatile tool in an SEM microscope for producing 2D- and 3D-nanostructures of any pattern by direct writing without involving masks, reducing the further steps to deposit materials. Outstanding 3D nanostructures were obtained by precise control of the electron beam,^{10–12} which have pro-

perties that can play important roles in the fields of nanophotonics, nanoplasmonics, nanomagnetism, nanomechanics, nanoelectronics, and nanosensors.^{13–19} These nanodeposits, even of sub-10 nm size, can also serve as a prototype for the fundamental understanding of the size effect on the properties of materials. An ongoing research topic is producing pure metal deposits. This effect can be achieved by delivering volatile molecules to the surface, where they are adsorbed and decomposed under the influence of a focused electron beam (keV). The primary electrons (PE) of the beam generate secondary electrons (SE) with lower energy (eV) in the substrate. The molecule dissociation may involve several processes, such as dissociative electron attachment (DEA), dissociative ionization (DI), dipolar dissociation (DD), and dissociation into neutrals (ND). Their effectiveness depends on the precursor molecule and the substrate type. The probability of bond-breaking in the molecule (interaction cross-section) for high energy electrons (PE) is lower compared to that for low energy electrons (SE). Therefore, the latter are the driving force of deposit formation. FEBID precursors are expected to generate thermodynamically favourable volatile decomposition by-products under electron-induced fragmentation, which are easily desorbed.^{13,20–30} All the mechanisms involved in the deposition process are dependent on the precursor molecule itself and on the experimental

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parameters. In this context, synthesizing and testing new precursors to understand the mechanisms involved plays an important role.^{29,31}

High-purity metal deposits (95–100 at%) have been found for iron, tungsten, cobalt carbonyls, and gold halogen-containing molecules. Unfortunately, the mentioned types of precursors are often toxic or decompose when exposed to air or moisture. High-purity silver deposits (57–76%) were also obtained from stable silver(I) carboxylates $[\text{Ag}_2(\mu\text{-O}_2\text{CR})_2]$, ($\text{R} = \text{CF}_3$, C_2F_5 , $t\text{-Bu}$, $\text{C}(\text{Me})_2\text{Et}$). However, the literature data review reveals that the metal content of typical FEBID deposits, produced from metal precursors without post-deposition purification methods, is usually in the range of 5–40 at%.^{21,23,24,29,32–34}

Palladium, similar to platinum, belongs to the 10 group of elements. The platinum cyclopentadienyl organometallic compounds $[\text{Pt}(\eta^5\text{-Cp})\text{Me}_3]$ (4–21.5 at% Pt) and $[\text{Pt}(\eta^5\text{-CpMe})\text{Me}_3]$ (22–28 at% Pt) are used in commercially available gas-injection systems (GIS) in SEM microscopes. Trimethyl(methylcyclopentadienyl)platinum(IV) is the most commonly used in the FEBID method. A major advantage of this precursor is the fact that it can be used repeatedly for years without thermal decomposition in the range of 313 K to 353 K, which is a relatively low temperature and attractive for FEBID precursors.^{35–42} The palladium complexes $[\text{Pd}(\eta^3\text{-allyl})(\eta^5\text{-Cp})]$ and $[\text{Pd}(\text{hfac})_2]$ (hfac – hexafluoroacetylacetonate) were tested in FEBID resulting in purity at the level of 26 ± 5 at% Pd and 28 at% Pd, respectively, whereas deposits for $[\text{Pd}_3(\text{O}_2\text{CCH}_3)_6]$ (40 ± 5 at% Pd) were produced by electron beam irradiation of spin-coated films.^{7,23,43,44}

To the best of our knowledge, the literature data concerning Pd(II) β -ketoesterates are limited to the $[\text{Pd}(\text{AAEMA})_2]$ (AAEMA – deprotonated form of 2-(acetoacetoxy)ethyl methacrylate), which has been used for the synthesis of a polymer-supported palladium catalyst. The obtained material with catalytically active sites exhibits several properties, including selectivity for the reduction of quinolines and nitroarenes, as well as the possibility of conversion of aliphatic and aromatic carboxylic acid into esters.^{45–52} β -Ketoesterate complexes are a group of precursors that, due to their volatile nature, have been used in vapour deposition methods such as chemical vapour deposition (CVD) and were also tested for FEBID. This class of molecules contains a chelate ring, which makes the compound more volatile than the complexes of non-chelating ligands because it prevents the formation of multinuclear structures and can lead to the formation of metal carriers in the gas phase.^{53,54} The reported deposition of metals *via* CVD used β -ketoesterate complexes: $[\text{Cu}(\text{maoac})_2]$ (maoac – methyl acetoacetate), $[\text{Cu}(\text{eaoac})_2]$ (eaoac – ethyl acetoacetate), $[\text{Cu}(\text{tbaaac})_2]$ ^{55,56} (tbaaac – *tert*-butyl acetoacetate), $[\text{Fe}(\text{tbaaac})_3]$,⁵⁷ $[\text{Zr}(\text{tbaaac})_3]$,⁵⁸ and $[\text{Hf}(\text{tbaaac})_4]$ ⁵⁹ as precursors. In FEBID, only one copper(II) β -ketoesterate complex $[\text{Cu}(\text{tbaaac})_2]$ with 26 at% Cu has been used so far.^{23,60,61} This compound has been chosen for the FEBID experiments because the β -ketoesterate ligand can be converted into stable and volatile molecules such as carbon dioxide and isobutylene.²⁹

Deposits in the form of nanowires and nanohelices have been obtained by heating the GIS and substrate up to 373 K.^{23,29,61}

The goal of the present work is to develop a synthesis method for new mononuclear palladium(II) complexes $[\text{Pd}(\text{CH}_3\text{COCHCO}_2\text{R})_2]$, where $\text{R} = t\text{-Bu}$, $i\text{-Pr}$, Et (ipaoac – isopropyl acetoacetate) with a relatively low molecular weight that should be promising for volatility. Ketoesters used as ligands should generate volatile by-products under the influence of an electron beam. Moreover, we demonstrate the crystal structure and intermolecular interactions of the molecules based on Hirshfeld analysis. The compounds' thermal stability was determined under atmospheric pressure, and their suitability for the production of metallated volatile species under reduced pressure was studied. We also investigate electron-induced decomposition in the gas phase and the interaction of adsorbed molecules with an electron beam and have discussed them based, among other things, on the average local ionisation energy (ALIE) calculations. Moreover, we selected the most promising compound $[\text{Pd}(\text{tbaaac})_2]$ and tested its behaviour in the FEBID process.

2. Experimental

2.1 Materials

Palladium(II) acetate (98%) was purchased from Sigma Aldrich (Saint Louis, MO, USA); *tert*-butyl acetoacetate (97%), and ethyl acetoacetate ($\geq 99\%$) from Thermo Scientific (Waltham, Massachusetts, USA), isopropyl acetoacetate ($>97\%$) from Tokyo Chemical Industry Co., Ltd (TCI), benzene (p.a) from Avantor (Avantor Performance Materials, Poland S.A.), and benzene- d_6 (99.96%) from ARMAR Chemicals (Döttingen, Switzerland). The Si(111) substrates for sublimation experiments were purchased from the Institute of Microelectronics and Photonics, Center for Electronic Materials Technology in Warsaw (Lukasiewicz Research Network, Poland). Si(100) with a native oxide layer was used as a substrate for FEBID deposit composition studies.

2.2 Instrumentation

IR and variable temperature infrared spectra (VT IR) spectra were registered with a Vertex 70 V spectrometer (Bruker Optik, Leipzig, Germany) using a reflective-single reflection diamond ATR unit ($200\text{--}4000\text{ cm}^{-1}$) and Specac's heated transmission cell holder ($400\text{--}4000\text{ cm}^{-1}$), respectively. VT IR spectra were recorded in the 303–513 K temperature range at pressures below 1 hPa. Electron impact mass spectra (EI MS) were registered using an AutoSpec Premier (Waters) over the temperature range 313–573 K. C and H contents were determined with a Vario MACRO CHN ELEMENTAR Analysensysteme GmbH, Langenselbold, Germany. Nuclear Magnetic Resonance (NMR) spectra were obtained using Bruker Avance III 700 MHz and Bruker Avance III 400 MHz spectrometers at the following parameters: ^1H : 400 and 700 MHz, TMS; ^{13}C (proton-decoupled): 100 and 176 MHz, TMS; solvent C_6D_6 , 295.5–300.4 K. Thermal studies (TGA/DTA) were performed on

an SDT 2960 TA analyser (New Castle, DE, USA) (dry N₂; heating rate 2.5 K min⁻¹, heating range up to 1273 K; sample mass 7–10 mg). The melting points were measured with Fisher Scientific (DUBUQUE, IOWA 52001, USA) Boetius apparatus. The sublimation experiments were performed under reduced pressure (10⁻² mbar) in a glass sublimator with a special holder for a silicon substrate. The morphology and composition studies of layers of the compounds were performed using scanning electron microscopy: Quanta 3D FEG (FEI, Hillsboro, OR, USA) and SEM-LEO 1430VP, Ltd, Cambridge, UK (operating voltage 8 and 20 kV) equipped with an energy dispersive X-ray spectrometer (EDS) Quantax 200 with an Xflash 4010 detector (Bruker AXS microanalysis GmbH, Berlin, Germany) which was also used in preliminary electron sensitivity tests. XRD data were collected with a Philips X'PERT diffractometer with an X'Celerator Scientific detector (Malvern Panalytical Ltd, Malvern, UK). Diffractograms were registered in the 5–120° 2θ range, using Cu Kα radiation and sample spinning (step size – 0.02°, program. res. slit – 0.5, exposure time – 60 s or 75 s per degree). X'Pert HighScore Plus software and ICDD (PDF 00-005-0681) file were used for phase identification. The FEBID experiments were performed using a Hitachi S3600 SEM, equipped with a custom heating stage. The square deposit was carried out at an acceleration voltage of 20 kV and beam current of 0.5 nA as measured on a silicon substrate. The substrate temperature was held at 343 K and GIS was at 358 K. The deposit morphologies were analysed using a Hitachi S4800 SEM. The compositions were measured with an energy dispersive X-ray spectroscopy (EDS) system from EDAX. The chemical composition of the deposits was validated from the EDX measurements taken using Oxford instruments. The EDX study was performed with a 6 keV electron beam with 500 pA, the signals were collected for 60 s, and the obtained composition was corrected using STRATAGEM thin film correction software for the silicon substrate.

2.3 DFT calculations

The geometry optimization for the analysed compounds and corresponding ligands, starting from the available crystal structures, was carried out with the B3LYP-D3/def2-TZVPP approach in order to ensure the uniform treatment of the organic ligand and the metal complexes and for consistency with the previous work.²¹ The characteristics of the stationary points on the potential energy surface were verified by harmonic vibrational analysis. Average local ionization energy (ALIE)⁶² was estimated with the same approach. All DFT calculations were performed using Gaussian16 (Wallingford, CT, USA)⁶³ and ALIE was generated with Multiwfn.⁶⁴

2.4 Software

All graphical data were further processed with OriginPro 9.1. TA Universal Analysis (New Castle, DE, USA) was used to analyse thermograms. A schematic diagram indicating the synthesis of the compounds (1–3) was drawn using ChemDraw Ultra 12.0 (Mid-Cambridge, MA, USA). All figures of crystal

structures were prepared using DIAMOND⁶⁵ and ORTEP-3⁶⁶ software.

2.5 Synthesis

All syntheses were carried out under normal conditions in the air. [Pd₃(O₂CCH₃)₆] (0.1 mmol) was placed in a round-bottomed flask, and 35 cm³ of benzene was added, followed by adding an excess of β-ketoester (1.2 mmol), MeCOCH₂COOR, where R = ^tBu (1), ⁱPr (2), Et (3), dropwise. The resulting dark-orange solution was stirred for 24 h and then placed in the crystalliser. The obtained compounds were orange solids and stable without moisture access for months. The compound (2) required purification by sublimation. Yields were 70% (1), 60% (2), and 80% (3), respectively. Orange single crystals suitable for X-ray structure analysis were grown by slow evaporation from the mother liquor for all complexes (1–3) at room temperature.

[Pd(tbaoc)₂] (1) PdO₆H₂₆C₁₆ (calc./found) % C 45.67/45.61, H 6.23/6.26; EI MS *T* = 336 K (*m/z*, RI %) [Pd(CH₃COCH₂)⁺ (163, 20), [Pd(CH₃COCHCO)⁺ (190, 32), [Pd(CH₃COCH₂CO₂H)⁺ (208, 64), [Pd(CH₃COCH₂CO₂^tBu)⁺ (264, 9), [Pd(CH₃COCH₂CO₂)₂]⁺⁺ (308, 100), [Pd(CH₃COCHCO₂^tBu)(CH₃COCH₂CO₂)⁺⁺ (364, 11), [Pd(CH₃COCHCO₂^tBu)₂]⁺⁺ (420, 30); IR (ATR, 2968, 2926, 1576, 1551, 1503, 1462, 1447, 1408, 1389, 1368, 1302, 1250, 1155, 1061, 1030, 997, 968, 841, 800, 777, 748, 685, 642, 608, 501, 461, 444, 382, 359, 334, 297, 257 cm⁻¹); ¹H NMR (400 MHz, C₆D₆, TMS), 1.28/1.33 ppm (18H, OC(CH₃)₃, s/s), 1.64/1.67 ppm (6H, CH₃CO, s/s), 4.79/4.79 ppm (2H, CH, s/s), ¹³C NMR (400 MHz, C₆D₆, TMS), 24.00/24.22 ppm (CH₃CO), 28.15/28.33 ppm (OC(CH₃)₃), 80.96/81.56 ppm (OC(CH₃)₃), 87.15/87.36 ppm (CH), 171.71/172.12 ppm (COO), 186.75/187.14 ppm (CH₃CO).

[Pd(ipaoac)₂] (2) PdO₆H₂₂C₁₄ (calc./found) % C 42.81/41.53, H 5.65/5.48; *T* = 328 K (*m/z*, RI %) [Pd(CH₃COCH₂)⁺ (163, 29), [Pd(CH₃COCHCO)⁺ (190, 43), [Pd(CH₃COCH₂CO₂ⁱPr)⁺ (250, 35), [Pd(CH₃COCHCO₂ⁱPr)(CH₃COCHCO)⁺⁺ (333, 5), [Pd(CH₃COCHCO₂ⁱPr)₂]⁺⁺ (392, 49); IR (ATR, 2978, 2928, 2872, 1576, 1547, 1514, 1456, 1414, 1371, 1281, 1180, 1142, 1111, 1059, 1030, 997, 972, 908, 822, 791, 772, 745, 685, 644, 609, 590, 523, 494, 463, 438, 355, 322, 289, 255 cm⁻¹); ¹H NMR (700 MHz, C₆D₆, TMS), 0.94/1.02 ppm (12H, OCH(CH₃)₂, d/d), 1.69/1.70 ppm (6H, CH₃CO, s/s), 4.84/4.85 ppm (2H, CH, s/s), 4.97 (2H, OCH(CH₃)₂, m), ¹³C NMR (700 MHz, C₆D₆, TMS), 21.58/21.62 ppm (OC(CH₃)₂), 24.01/24.22 ppm (CH₃CO), 68.90/68.96 ppm (OCH(CH₃)₂), 86.24/86.62 ppm (CH), 171.03/171.28 ppm (COO), 187.17/187.62 ppm (CH₃CO).

[Pd(eaoac)₂] (3) PdO₆H₁₈C₁₂ (calc./found) % C 39.52/39.55, H 4.98/4.92; *T* = 339 K (*m/z*, RI %) [Pd(CH₃COCH₂)⁺ (163, 19), [Pd(CH₃COCHCO)⁺ (190, 22), [Pd(CH₃COCHCO₂Et)(CH₃COCHCO)⁺⁺ (319, 5), [Pd(CH₃COCHCO₂Et)₂]⁺⁺ (364, 58); IR (ATR, 2982, 2930, 2899, 1574, 1547, 1503, 1476, 1449, 1404, 1366, 1273, 1177, 1059, 1016, 989, 966, 864, 816, 770, 683, 606, 511, 473, 415, 318, 291, 258 cm⁻¹); ¹H NMR (400 MHz, C₆D₆, TMS), 0.81/0.88 ppm (6H, OCH₂CH₃, t/t), 1.67/1.68 ppm (6H, CH₃CO, s/s), 3.85 ppm (4H, OCH₂CH₃, q), 4.82/4.83 ppm (2H, CH, s/s), ¹³C NMR (400 MHz, C₆D₆, TMS), 13.65/13.89 ppm

(OCH₂CH₃), 23.99/24.19 ppm (C(CH₃CO), 61.13/61.58 ppm (OCH₂CH₃), 85.82/86.13 ppm (CH), 171.36/171.68 ppm (COO), 187.37/187.77 ppm (CH₃CO).

2.6 X-ray crystal structure determination

The single-crystal diffraction data for the compounds (1–3) were collected at 100 K using an XtaLAB Synergy (Dualflex) diffractometer with HyPix detector, CuK α radiation λ = 1.54184 Å. The data reduction was performed in CrysAlis Pro for all studied compounds,⁶⁷ and the Gaussian absorption correction was applied. The compounds' structures were solved using direct methods and refined with a full-matrix least-squares procedure on F^2 (SHELX-97).⁶⁸ All heavy atoms were refined with anisotropic displacement parameters. Hydrogen atoms were assigned at calculated positions with thermal displacement parameters fixed to a value of 20% or 50% higher than those of the corresponding carbon atoms.

The results of the data collection and refinement have been summarized in the ESI (Table S1), such as selected bond lengths and angles (Tables S2–S4†). CCDC 2335314, 2335316, and 2335315 contain supplementary crystallographic data for the compounds (1), (2), and (3), respectively.†

Powder X-ray diffraction (PXRD) with a Cu-K α radiation source was used for the composition analyses of the complexes [Pd(tbaoac)₂] (1) (Fig. S1) and [Pd(ipaoac)₂] (2) (Fig. S2†). The experimental data were collected in the 2θ range of 5–50° (step: 0.02, exposure time: 75 s per degree). The theoretical powder diffraction patterns were calculated in Mercury.⁶⁹

3. Results and discussion

In the benzene solution, the palladium(II) complexes of the general formula [Pd(MeCOCHCO₂R)₂], where R = *t*Bu (1), *i*Pr (2), Et (3) were formed *via* the deprotonation of the suitable β -ketoester (Fig. 1).

The obtained compounds were an orange solid with needle-shaped crystals (1–3), and stable in air for months. The com-

pound (2) required purification by a sublimation process (at 353 K).

3.1 Crystallography

The compound [Pd(tbaoac)₂] (1) crystallizes in the triclinic $P\bar{1}$ space group with two complex molecules in the asymmetric unit arranged almost perpendicularly (82.7°) (Fig. 2). The β -ketoesterates act as chelates, and their *tert*-butyl groups show *cis*-positions. The Pd atom has a square planar geometry comprising four oxygen atoms with Pd–O distances being 1.963–2.001 Å. In packing, we observe uniformly dispersed molecules with the shortest Pd...Pd distances in the crystal achieving 6.161, 6.398, and 6.559 Å. The crystal network is maintained mainly by an almost perpendicularly oriented chelate ring forming π – π intermolecular interactions and C–H... π interactions between C8–H8, C23–H23, and C38–H38 and the chelate ring (Fig. S3†). It is confirmed by the projection of those interactions on a Hirshfeld surface (Fig. 3 and S4†). The H...H and C...H contacts are the most numerous, and red spots indicate that some of them are short.^{70–72} It is further supported by energy calculations showing that dispersion energy prevails in this system (Fig. 4). The presence of C11–H11...O32 and C21–H21...O2[1 – *x*, 1 – *y*, 2 – *z*] hydrogen bonds is also confirmed by red spots for H...O and O...H surfaces and significantly smaller contribution of the electrostatic term in the total energy. Hence, it is obvious that hydrogen atoms of the *tert*-butyl groups are involved in the electrostatic and dispersion interactions in the crystal network of the complex (1) (Fig. 4). The presence of weak intermolecular interactions is advantageous in terms of introducing a compound into GIS *via* the FEBID process, which requires the use of volatile precursor molecules.

The complex [Pd(ipaoac)₂] (2) crystallizes in a monoclinic, $P2_1/n$ space group with a palladium atom positioned at the inversion centre and half of the molecule in the asymmetric unit (Fig. 5). The coordination sphere adopts a square planar geometry and is composed of four oxygen atoms coming from two β -ketoesterates. In contrast to the compound (1), the isopropyl substituents in the *trans* position were observed. The

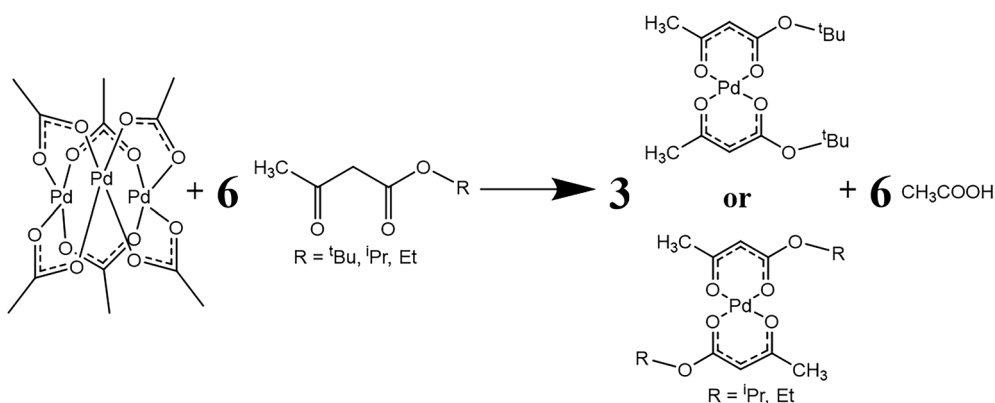


Fig. 1 Reaction scheme for the synthesis of palladium complexes [Pd(tbaoac)₂] (1), [Pd(ipaoac)₂] (2), and [Pd(eaoac)₂] (3).

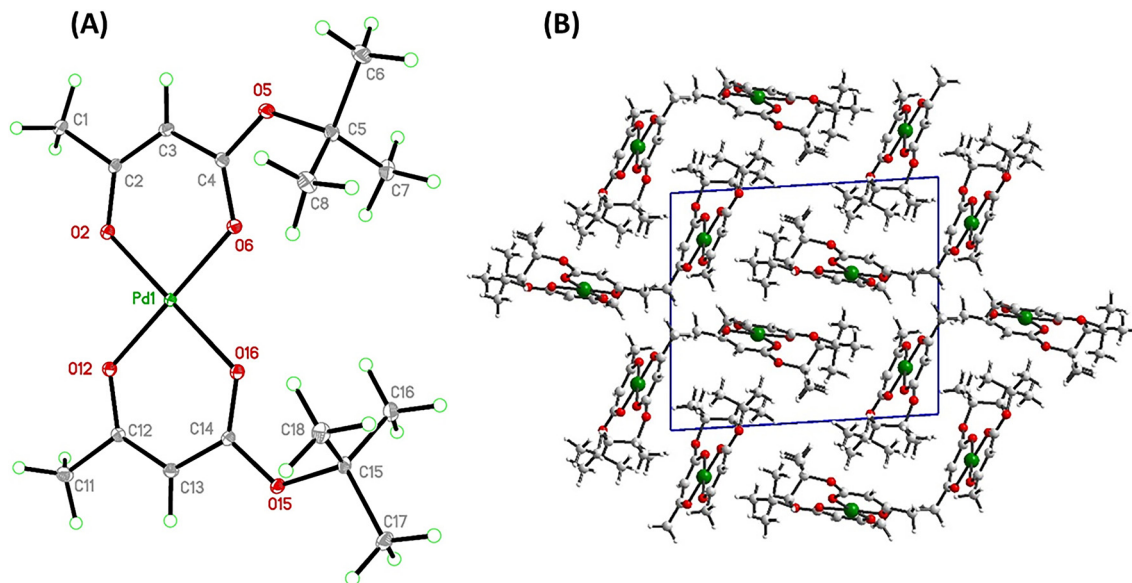


Fig. 2 The structure of $[\text{Pd}(\text{tbaoc})_2]$ (1): (A) thermal ellipsoid at the level of 30% probability, and (B) packing along the a axis.

bond distances between Pd–O fall within 1.981–1.999 Å, and the shortest Pd...Pd distance in the structure is 4.353 Å. In the packing along the a axis, we observe columns composed of stacked complex molecules. Similarly to the compound (1), numerous π – π interactions appear between chelate rings (Fig. S5†). The interaction landscape is completed by Pd...chelate ring interactions as well as by a robust network of $\text{C1-H1A}\cdots\text{O1}[1+x, y, z]$ hydrogen bonds. It is confirmed by the Hirshfeld surface with dominating weak interactions as well as energy calculations between adjacent molecules (Fig. S6 and S7†).

The $[\text{Pd}(\text{eaoac})_2]$ (3) compound with ethyl groups in *trans*-positions crystallizes in the triclinic $P\bar{1}$ space group with two crystallographically independent molecules in the unit cell (Fig. 6 and S8†). The asymmetric part of the unit consists of half of each molecule. In contrast to the compound (1), both molecules are almost parallel (3.6°), and the $\text{C4-C4}[-x, 1-y, 2-z]\cdots\text{C14}[-x, 1-y, 2-z]\cdots\text{C14}[1+x, y, -1+z]$ torsion angle is 144.2° . The ethyl group is coplanar with the chelate ring with torsion angles being close to 180° . The coordination sphere geometry is square planar as it was observed also in the complexes (1) and (2). The bond distances for Pd1–O fall within 1.9833(15)–1.9923(15) Å and 1.9881(15)–1.9917(16) Å for Pd2–O. The distance Pd...Pd in the crystal exceeds 6.235 Å. The energy landscape is completed by $\text{C1-H1B}\cdots\text{chelate ring}$ interactions, whereas no hydrogen bonds were detected. It can be surprising because the Hirshfeld surface shows *ca.* 30% of $\text{H}\cdots\text{O}$ contacts (Fig. S9 and S10†). However, it should be noted that they are usually long or they are missing appropriate geometry to consider them as hydrogen bonds.^{73,74} Hence, mainly weak van der Waals interactions contribute to the total energy (Fig. S11–S13†).

Summarizing, in all the reported structures we detected a square planar environment of the palladium(II) cations. However, there are significant distinctions in crystal packing

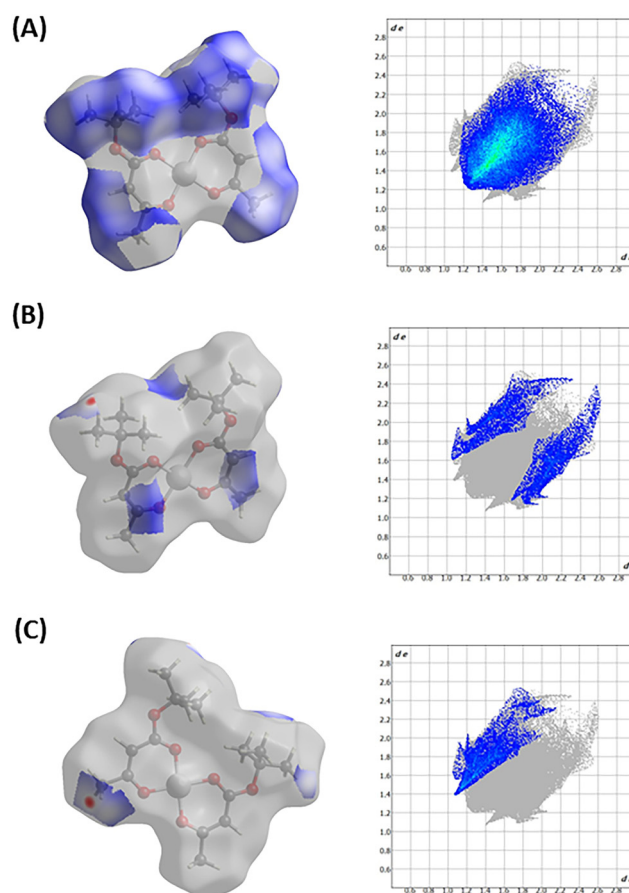


Fig. 3 Hirshfeld surfaces (left) and fingerprints (right) of selected interactions created in the crystal network of $[\text{Pd}(\text{tbaoc})_2]$ (1) for Pd1 molecule: (A) for $\text{H}\cdots\text{H}$ (63.0%), (B) for $\text{C}\cdots\text{H}$ and $\text{H}\cdots\text{C}$ (11.5%), and (C) for $\text{H}\cdots\text{O}$ (9.7%). In brackets, a given surface area included as a percentage of the total surface area is shown.

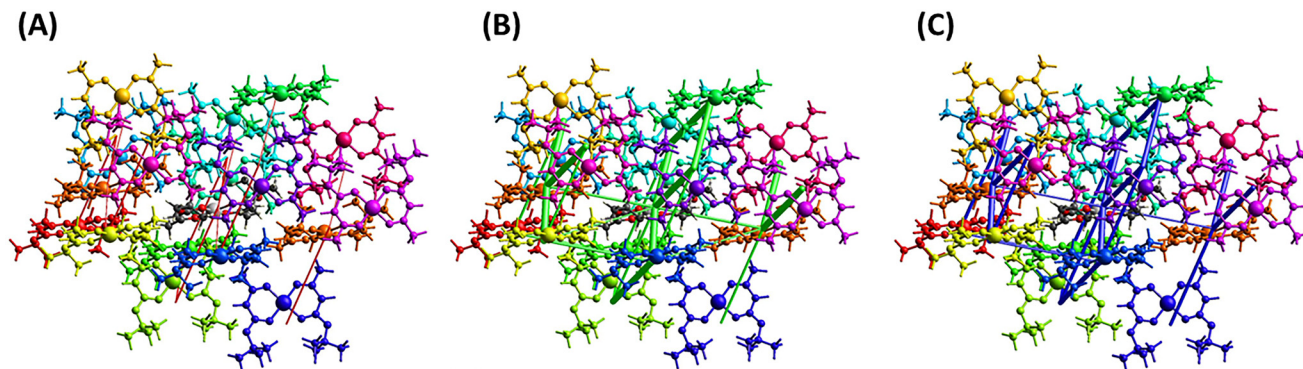


Fig. 4 Interaction energy: (A) electrostatic, (B) dispersion, and (C) total in the crystal network of $[\text{Pd}(\text{tbaoac})_2]$ (1) for the Pd1 molecule.

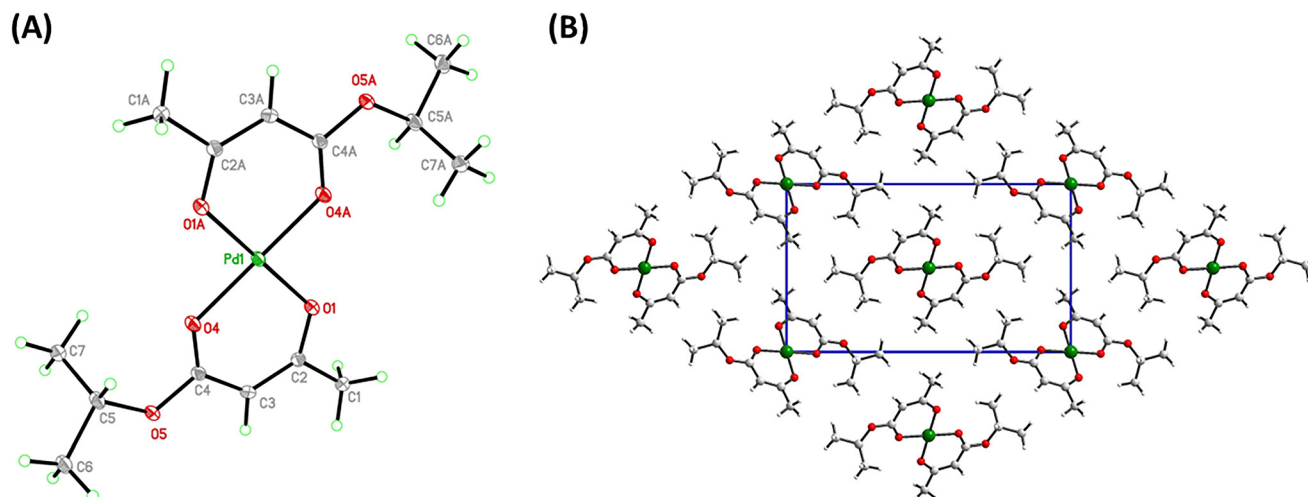


Fig. 5 The structure of $[\text{Pd}(\text{ipaoac})_2]$ (2): (A) with the numbering scheme and (B) packing along the a axis.

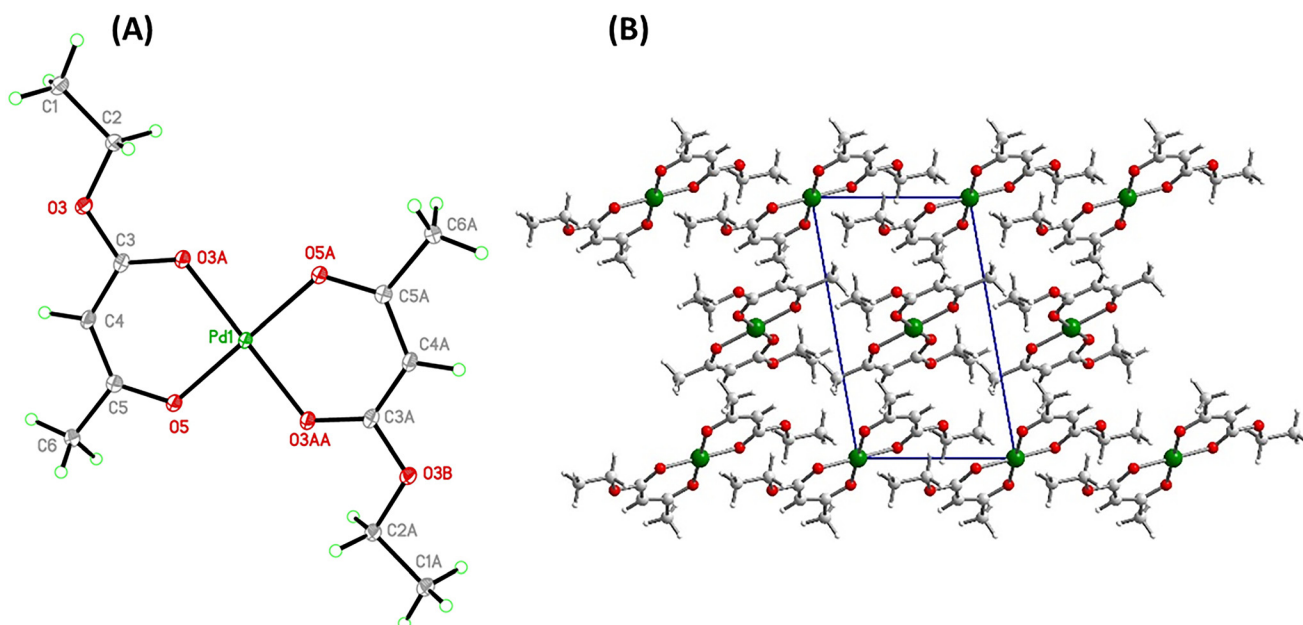


Fig. 6 The structure of $[\text{Pd}(\text{eaoac})_2]$ (3): (A) thermal ellipsoid at the level of 30% probability, (B) packing along the a axis.

and crystal network organization despite any solvent-accessible voids being observed, and all structures are densely packed. The differences between the three molecule structures are significant. For (1), the form with *tert*-butyl groups in the *cis*-positions crystalized, whereas for (2) (isopropyl) and (3) (ethyl), *trans*-placed forms were obtained, indicating that substituents play an important role. It might be surprising that the biggest groups were found in the *cis* positions. It can be rationalized by maintaining significant separations between them and also by interactions in the crystal network. The cell volume changes because of different crystallographic motifs – in (1) two independent molecules were found in the asymmetric part, and in (3) two halves of the molecule were independent, whereas in (2) only half of the molecule occurred in the asymmetric unit. Even the orientation of two independent blocks is different – in (1), they are almost perpendicularly positioned, and in (3), they are practically coplanar but tilted in the plane. The common feature is that in all reported structures, π - π interactions are important, and Hirshfeld surfaces indicate that H...H contacts prevail. Hence, dispersion energy is the main factor contributing to the network stability. In the reported three structures strong hydrogen bonds are missing. Therefore, we can hypothesize that those compounds should be promising in FEBID experiments. We expect that weak intermolecular forces should facilitate molecule transfer to the gas phase which is important in the FEBID method. It is confirmed by the results of sublimation experiments (*vide infra* – 3.7 Sublimation experiments section).

3.2 Infrared spectroscopy

In the infrared spectra of the complexes (1–3), the characteristic band of the δ CH group was observed in the range

1180–1155 cm^{-1} (Fig. 7), which confirms the ligand deprotonation and the formation of the β -ketoesterate. The crystal structures (see 3.1 Crystallography section), and ^1H and ^{13}C NMR spectra (*vide infra* – 3.4 Nuclear magnetic resonance spectroscopy section) also indicate deprotonation. Moreover, the strong band in the region 1514–1503 cm^{-1} typical to $\nu\text{C}=\text{C}$ has been registered. In addition, two characteristic bands for the stretching vibrations ($\nu\text{C}=\text{O}$) of the β -ketoesterate ($\text{C}=\text{O}$) $\text{CH}(\text{C}=\text{O})\text{O}$ group were observed. One was registered at *ca.* 1576 cm^{-1} , and the second was at 1549 cm^{-1} (Table 1, Fig. 7, and Fig. S14–S16†). The coordination shifts of these signals relative to the free protonated ligands (Fig. S17†) towards lower values of the wave numbers were at about 162 cm^{-1} and 165 cm^{-1} . This confirms the β -ketoesterate coordination by both O atoms of $\text{C}=\text{O}$ groups (see 3.1 Crystallography and 3.4 Nuclear magnetic resonance spectroscopy sections).

Moreover, the formation of the chelate ring results in the appearance of a high-intensity signal around 770 cm^{-1} . This band corresponds to the deformation vibration of the chelat-

Table 1 Selected IR absorption bands (cm^{-1}) of the studied compounds (1–3)

	$\nu\text{C}=\text{O}^a$	$\nu\text{C}=\text{C}$	$\delta\text{C}-\text{H}$	$\nu\text{Pd}-\text{O}$
[Pd(tbaoac) ₂] (1)	1576 1551	1503	1155	501
[Pd(ipaoac) ₂] (2)	1576 1547	1514	1180	523
[Pd(eaoac) ₂] (3)	1574 1547	1503	1177	511

^a The $\nu\text{C}=\text{O}$ bands of protonated ligands (tbaoacH, ipaoacH, eaoacH): 1740–1736 cm^{-1} and *ca.* 1714 cm^{-1} .

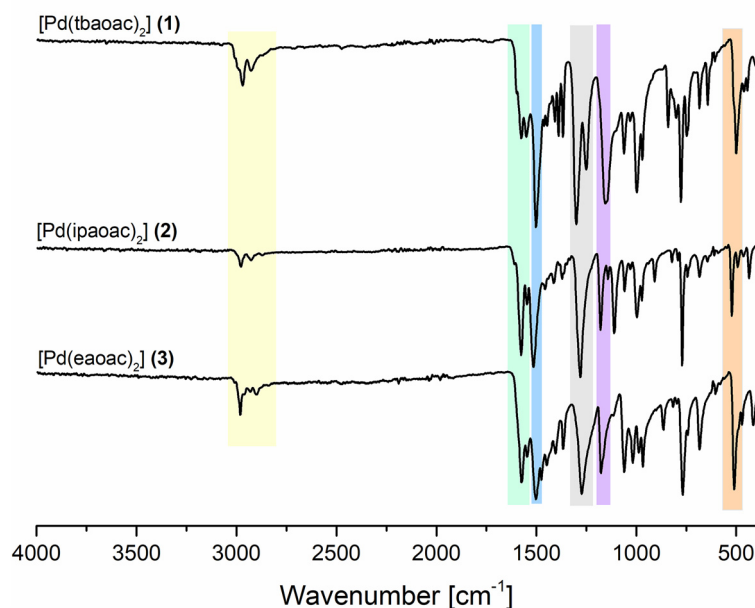


Fig. 7 ATR-IR spectra for compounds: [Pd(tbaoac)₂] (1), [Pd(ipaoac)₂] (2), and [Pd(eaoac)₂] (3). The coloured bands highlight the ranges of the particular vibrational modes: $\nu\text{C}-\text{H}$ (yellow), $\nu\text{C}=\text{O}$ (green), $\nu\text{C}=\text{C}$ (blue), $\nu\text{C}-\text{O}$ (grey), $\delta\text{C}-\text{H}$ (violet), $\nu\text{Pd}-\text{O}$ (orange).

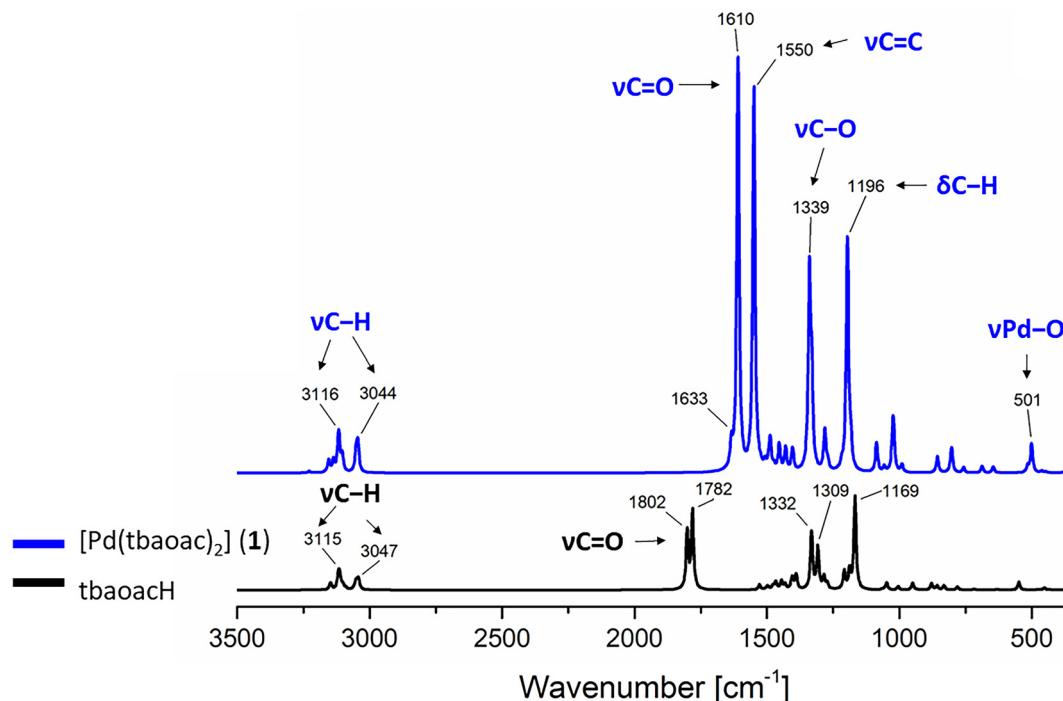


Fig. 8 Theoretical infrared spectrum calculated by DFT B3LYP-D3/def2-TZVPP for the compound $[\text{Pd}(\text{tbaoac})_2]$ (1) (blue line) and ligand tbaoach (black line).

ing ring ($\delta\text{C-O-C}$). The existence of signals for stretching vibrations ($\nu\text{Pd-O}$) over the range $523\text{--}501\text{ cm}^{-1}$ confirms the coordination by oxygen atoms (Fig. 7, S14–S16[†]). Additionally, the band in the region $1302\text{--}1273\text{ cm}^{-1}$ has been assigned to $\nu\text{C-O}$ stretching vibration of the ester group. The signals over the range $2982\text{--}2926\text{ cm}^{-1}$ ($\nu\text{C-H}$) were also detected. They can be assigned to the stretching vibration of the substituents: methyl (1–3) and *tert*-butyl (1), iso-propyl (2) or ethyl (3) groups. Notably, our experimental results are consistent with those previously reported for the copper and zinc complexes $[\text{Cu}(\text{tbaoac})_2]$, $[\text{Zn}(\text{tbaoac})_2]$, and $[\text{Zn}(\text{ipaoac})_2]$.^{56,75} This data interpretation is important for the infrared result evaluation of the layers of the compounds deposited on the silicon substrate (*vide infra* – 3.7 Sublimation experiments section), which were then analysed in terms of their interaction with a high-energy electron beam.

In order to assign frequencies and confirm the coordination of β -ketoesters in experimental spectra, the theoretical calculations of the harmonic vibrational frequencies were carried out. The calculation showed the stretching vibrations characteristic of the C=O groups are *ca.* 1612 cm^{-1} (1–3) (Fig. 8, Fig. S18 and S19[†]). These bands shift towards lower values by: (1) $\rightarrow 192$ and 172 cm^{-1} , (2) $\rightarrow 194$ and 174 cm^{-1} , and (3) $\rightarrow 194$ and 173 cm^{-1} as compared to theoretical spectra of the corresponding β -ketoesters, which confirm ligand coordination. Note that the theoretical spectra show the deformation band $\delta\text{C-H}$, which indicates the deprotonation of β -ketoesters and is consistent with the experimental IR and NMR data (*vide infra* – 3.4 Nuclear magnetic resonance spectroscopy section).

3.3 Average local ionization energy (ALIE)

In order to confirm the preferred ionisation sites during the electron–molecule interaction, the average local ionisation energy (ALIE) was calculated. For these studies, we chose the complex (1), which showed the highest sensitivity towards electron irradiation (*vide infra* – 3.8 EDX and SEM observation after sublimation experiments section). ALIE calculations demonstrate the possibility of predicting reaction pathways and the resulting ions formed by the initial electron–molecule interaction. These theoretical studies were previously applied for silver(i) carboxylates, among others, for $[\text{Ag}_2(\mu\text{-O}_2\text{CC}(\text{Me})_2\text{Et})_2]$, which was used as a FEBID precursor and yields 73 at% Ag.^{21,23}

The calculated data for the complex (1) show that the blue-marked regions localised on the metal atom and $-\text{CH}$ groups of the chelate ring have relatively low ALIE values (Fig. 9). This suggests ionisation of the compound (1) at these regions and, therefore, formation of fragments containing ester and carbonyl groups, and the possibility of the generation of the decomposition products proposed for all complexes (1–3) (*vide infra* – 3.6 Mass spectra analysis section). Ionization, therefore, causes the formation of fragments containing ester and carbonyl groups. This is in line with the EI MS results showing that the palladium(II) β -ketoesterate complexes undergo fragmentation with high efficiency to yield CH_3CHO and CO_2 (m/z 44) (Tables S5–S7[†]). These product formation suggests that the palladium(II) β -ketoesterate complexes may be promising for the FEBID method because of the tendency of the coordinated ligands to decompose into stable volatile products, which can be easily removed from the surface during deposition.²¹

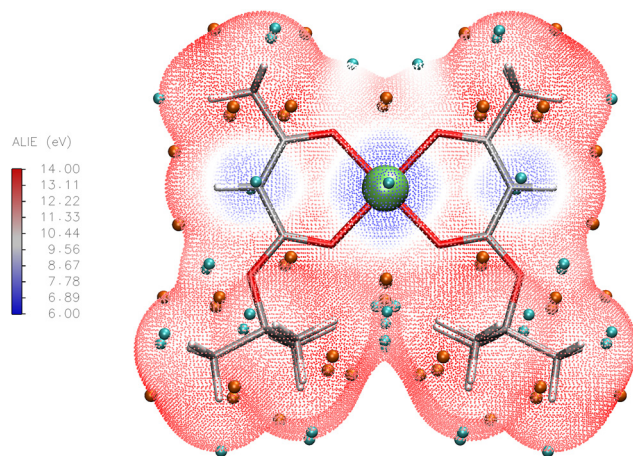


Fig. 9 Average local ionization energy (ALIE) mapped onto the molecular surface for the complex $[\text{Pd}(\text{tbaoac})_2]$ (1).

3.4 Nuclear magnetic resonance spectroscopy

In the ^1H NMR and ^{13}C NMR spectra for the complexes (1–3) two sets of signals were identified. This suggests that the two forms of the compounds exist in the benzene solution. The ^1H NMR spectra (Fig. S20, S24, and S28†) for the compounds

(1–3) indicate the deprotonation of ligands and formation of chelate complexes with the loss of singlet around 3.0 ppm characteristic for the $-\text{CH}_2$ group of the β -ketoesters and the appearance of signals $\delta(\text{CH})$ at approximately 4.8 ppm (Fig. S21, S25, and S29†). Additionally, two sets of signals attributed to *tert*-butyl (1), iso-propyl (2), ethyl (3) and methyl (1–3) substituents were observed. The integration ratios of the peaks for both forms were 1 : 3 for (1) and 1 : 1 for (2) and (3).

In the ^{13}C NMR spectra (Fig. S22, S26, and S30†), we also noted two sets of signals. The deprotonation of the β -ketoester group was confirmed by the detection of the signals $\delta(\text{CH})$ between 85.8 and 87.4 ppm (1–3). The loss of protons was also indicated by the disappearance of the peak $\delta(\text{CH}_2)$ around 50 ppm (Fig. S23, S27, and S31†). The signals characteristic for the carbon atoms in the ester and keto groups were found in the 171.0–172.1 ppm and 186.8–187.8 ppm ranges. The calculated coordination shifts ($\Delta C_{\text{coord}} = \delta C_{\text{coord}} - \delta C_{\text{ligand}}$) attributed to the coordination of the β -ketoesters were $\Delta C_{\text{ester}} = 3.63$ to 5.05 ppm and $\Delta C_{\text{keto}} = 11.30$ to 12.69 ppm, which confirm the coordination of the O-donor β -ketoesters to the palladium(II) ion. There are also two sets of signals assigned to the carbon atoms in the *tert*-butyl (1), iso-propyl (2), ethyl (3), and methyl (1–3) groups.

3.5 Thermal analysis

In order to determine the final decomposition temperature and the degradation products, thermal analysis was carried out to study the behaviour of the complexes during heating under a nitrogen atmosphere. These data revealed that the decomposition of the complexes (1–3) proceeds in a single exothermic process. In the case of the complex (1), an endothermic process associated with melting was observed immediately before the onset of the exothermic stage (Table 2, Fig. 10, Fig. S32–S33†). It has been confirmed using the Boetius apparatus that the compound (1) melts at around 403–408 K and decomposes above this temperature.

Table 2 Thermal analysis results

Complex	Heat effect	Temperature [K]			Found residue [%]
		T_i	T_m	T_f	
$[\text{Pd}(\text{tbaoac})_2]$ (1)	<i>endo/exo</i>	330	413	765	30.81
$[\text{Pd}(\text{ipaoac})_2]$ (2)	<i>exo</i>	323	420	673	36.07
$[\text{Pd}(\text{eaoac})_2]$ (3)	<i>exo</i>	321	410	668	38.08

T_i , initial temperature; T_m , maximum temperature; T_f , final temperature.

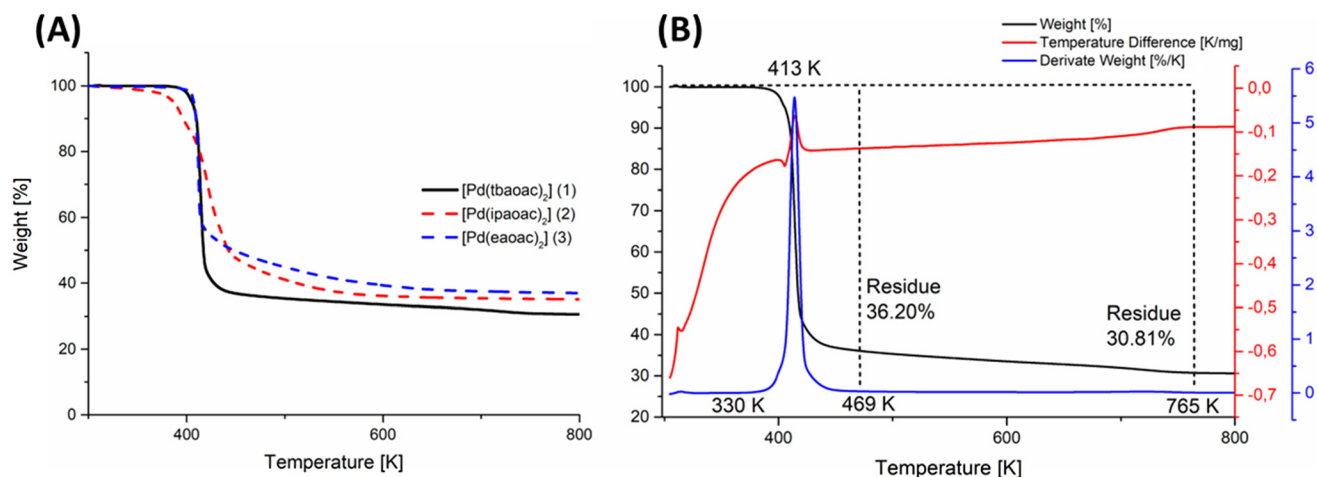


Fig. 10 (A) Thermogravimetric curves (TG) for the complexes: $[\text{Pd}(\text{tbaoac})_2]$ (1) (black line), $[\text{Pd}(\text{ipaoac})_2]$ (2) (red dashed line), and $[\text{Pd}(\text{eaoac})_2]$ (3) (blue dashed line); (B) thermogravimetric analysis (TGA) (black line), derivative thermogravimetry (DTG) (blue line), and differential thermal analysis (DTA) (red line) for the complex (1).

The weight loss was observed over the entire temperature range, up to the end of the process. For the complexes (1–3), a higher residue mass compared to the theoretical content of palladium (Table 2) was observed. The theoretical values for the compounds are as follows: 25.29% for (1), 27.09% for (2), and 29.18% for (3). The diffraction pattern of palladium for the final decomposition products of the compounds (2) and (3) were registered (Fig. S34†) (PDF 00-005-0681). We suspect the presence of amorphous carbon, which would explain the continuous change in mass. However, it was not possible to verify the final solid decomposition product due to its amorphous nature. In addition, EDX spectra for the residue (3) confirmed the presence of palladium, but the identification of carbon in the sample was prevented by the negligible difference in the peak position between palladium and carbon.

The VT IR spectra for the compound in the solid state were registered to investigate the thermal stability of the complexes and to monitor the structural changes caused by heating (Fig. S35†). The VT IR spectra under reduced pressure (<1 hPa) show that the complex (1) is stable up to 413 K, as confirmed by the bands' characteristics of coordinated β -ketoesterate detected over the temperature range 303–413 K: ν C–H (2974, 2928 cm^{-1}), ν C=O (1585, 1553 cm^{-1}), ν C=C (1506 cm^{-1}), ν C–O (1302 cm^{-1}), δ C–H (1159 cm^{-1}), and ν Pd–O (500 cm^{-1}). Moreover, at 413 K, we observed an additional band at 1720 cm^{-1} , indicating the presence of a ligand. This signal, as well as those at 1369 cm^{-1} and 1151 cm^{-1} , was registered up to 513 K, but their intensities decreased. For the compound (1) the maximum temperature of the decomposition process in the thermogram was noted at 413 K (DTG), and agrees well with the results of the VT IR of the solid.

3.6 Mass spectra analysis

The electron impact mass spectra (EI MS) of the complexes (1–3) were registered between 313 and 573 K (Fig. S36–37, Tables S5–S7†). Based on these results, we can verify whether these complexes are capable of generating volatile metal carriers, check their sensitivity to low-energy electrons (70 eV),

and study how the composition of the gas phase changes during heating under reduced pressure ($\sim 10^{-6}$ mbar). It is important to note that during the FEBID process in the SEM chamber, the conditions are quite similar to the EI MS experiments (*vide infra* – 3.9 Preliminary FEBID experiments section).

In the EI MS spectra, the metallated fragments were detected over the range 332–344 K for (1), 323–334 K for (2), and 336–420 K for (3).

The molecular ions $[\text{Pd}(\text{CH}_3\text{COCHCO}_2\text{R})_2]^{++}$ were observed from 336 K for the compounds (1) and (3), and 323 K for the complex (2), confirming the composition of the volatile complexes (Fig. S36†). These fragments achieved the highest relative intensity as follows: 39% RI at 337 K (1), 100% RI at 330 K (2), and 100% RI from 388 K to 416 K (3) (Fig. S37†). The lower %RI for the compound (1) and detection of other palladium-containing fragments, *e.g.* $[\text{Pd}(\text{CH}_3\text{COCH}_2\text{CO}_2)_2]^{++}$ (*ca.* RI = 100%) and $[\text{Pd}(\text{CH}_3\text{COCH}_2\text{CO}_2\text{H})]^+$ (*ca.* RI = 59%) indicate its more efficient electron-induced fragmentation (Table S5†). On the other hand, RI = 100% of $[\text{Pd}(\text{CH}_3\text{COCHCO}_2\text{R})_2]^{++}$ for the complexes (2) and (3) points to lower sensitivity to low-energy electrons of these molecules (Fig. S37†). Moreover, other metallated ions such as $[\text{Pd}(\text{CH}_3\text{COCHCO})]^+$ and $[\text{Pd}(\text{CH}_3\text{COCH}_2)]^+$ have been identified for all studied complexes (Fig. 11).

The signal characteristics for the ions, *e.g.*, $[\text{CH}_3\text{CO}]^+$, $[\text{CH}_3\text{CHO}]^+/\text{CO}_2^+$, and $[\text{CH}_3\text{COCH}]^+/\text{[(CH}_3)_2\text{C}=\text{CH}_2]^+$ give evidence of the formation of volatile acetyl, acetaldehyde, carbon dioxide, acetone, and isobutene molecules, which is in line with experiments reported for $[\text{Cu}(\text{tboac})_2]$ and SIMS experiments for tboacH.^{56,76}

Summarizing, the palladium(II) β -ketoesterates can be promising for use in the FEBID process because the effective generation of volatile metal carriers in EI MS was observed at relatively low temperatures (323–336 K). This fact allowed us to assume that the studied precursors can be introduced into the microscope chamber *via* the GIS system at a temperature similar to the commercially available platinum precursor $[\text{Pt}(\mu^5\text{-CpMe})\text{Me}_3]$, which requires around 333 K.³⁴ Therefore, $[\text{Pd}(\text{tboac})_2]$ seems promising in the role of a FEBID precursor because it can be transferred to the gas phase at relatively low

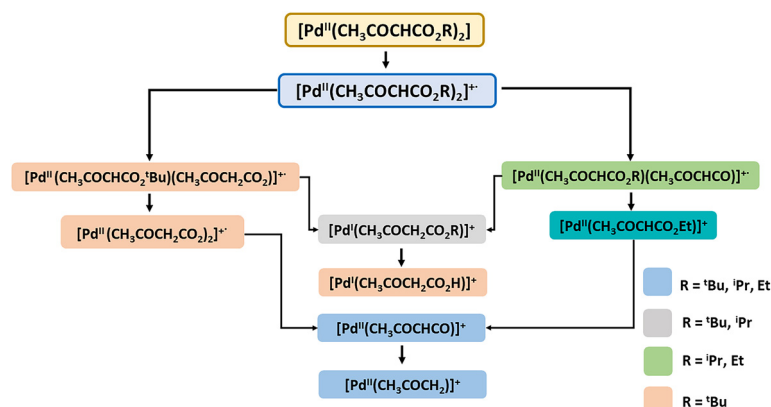


Fig. 11 Fragmentation scheme for the metallated fragments of $[\text{Pd}(\text{tboac})_2]$ (1), $[\text{Pd}(\text{ipaoac})_2]$ (2), and $[\text{Pd}(\text{eaoac})_2]$ (3).

temperature, and its fragmentation towards low-energy electrons was much more efficient relative to compounds (2) and (3).

3.7 Sublimation experiments

Sublimation experiments were carried out to confirm the volatility of new palladium(II) β -ketoesterate complexes (1–3) and determine the sublimation temperature of entire compound molecules. Moreover, these experiments allowed obtaining layers of the compounds (1–3) on the silicon substrate, which were then studied in terms of interaction with a high-energy electron beam (*vide infra* –3.8 EDX and SEM observation after sublimation experiments section). The IR spectra confirm the successful sublimation of the complexes (1–3) with a thin layer formation on the silicon substrate (Fig. 12, Fig. S38–S39†). It should be noted that the IR spectra of the complex (2) in the solid phase and layer cannot be directly compared because it was purified by sublimation. The infrared spectra of sublimate layers for the complexes (1) and (3) are in agreement with results for pure compounds and exhibit bands ν C–H, ν C=O, ν C=C, ν C–O, and δ C–H, which are characteristic of coordinated β -ketoesterates. These signals are also present for the layer of the compound (2), confirming the sublimation of the [Pd(ipaoac)₂] (Fig. S38†). In the case of the compound (1) layer, there are only slight differences in the shape and intensity of the bands, which are around 680–500 cm^{–1}. On the other hand, for the layer of [Pd(eaoac)₂] (3), the smooth band ν C=C was observed, in contrast to the spectrum in the solid phase. The complexes with substituents ^tBu in *cis*-positions (1) or ⁱPr and Et in *trans*-positions (2–3) exhibit only a slight difference in sublimation temperature. However, the studies indicate that the [Pd(tbaoac)₂] (1) has the lowest sublimation temperature

Table 3 Sublimation temperatures for the complexes (1–3) ($p = 10^{-2}$ mbar)

Compound	Sublimation temperature [K]
[Pd(tbaoac) ₂] (1)	348
[Pd(ipaoac) ₂] (2)	353
[Pd(eaoac) ₂] (3)	353

(348 K) (Table 3). These experiments consider the prediction of initial temperatures using a GIS in the SEM chamber during the FEBID process. The advantage of the obtained compounds (1–3) is a low evaporation temperature as compared to non-fluorinated FEBID precursors [Cu(tbaoac)₂] and [Pd(acac)₂] for which were reported: 368 K and 373–433 K, respectively. In contrast, the fluorinated β -diketonate [Pd(hfac)₂] evaporates over the range 319–328 K; however, the pressure was not quantified.^{23,56} The low evaporation temperature of the palladium(II) β -ketoesterates (1–3) makes them attractive for future use in the FEBID process and other vapor deposition methods.

3.8 EDX and SEM observation after sublimation experiments

The SEM images show that the sublimate layers obtained for the complexes (1) and (3) are homogeneously distributed on the silicon surface (Fig. 13, Fig. S40, S43 and S44†). On the other hand, the sample (2) was heterogeneously covered, and brighter and darker areas were observed (Fig. S41–S42†). Moreover, in the case of the compound (3), the SEM image shows that the layer is formed by needle-shaped objects (Fig. S43 and S44†).

The sensitivity to the high-energy electrons of thin layers of the complexes deposited on the silicon substrate was tested

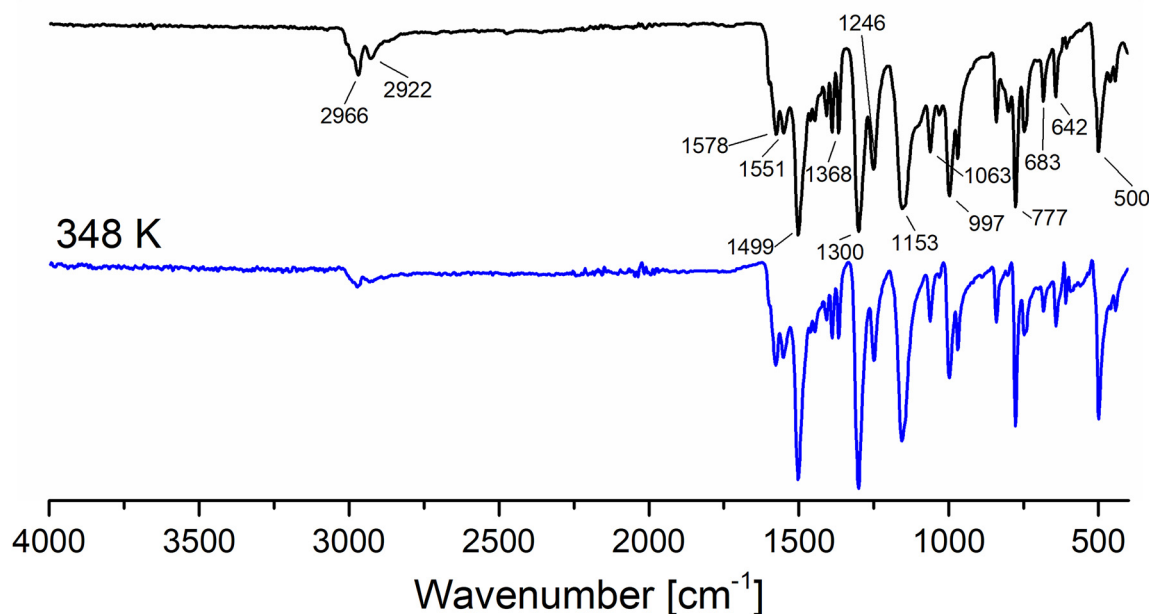


Fig. 12 Infrared spectra for the compound [Pd(tbaoac)₂] (1) before (black) and after sublimation (blue) at 348 K ($p = 10^{-2}$ mbar).

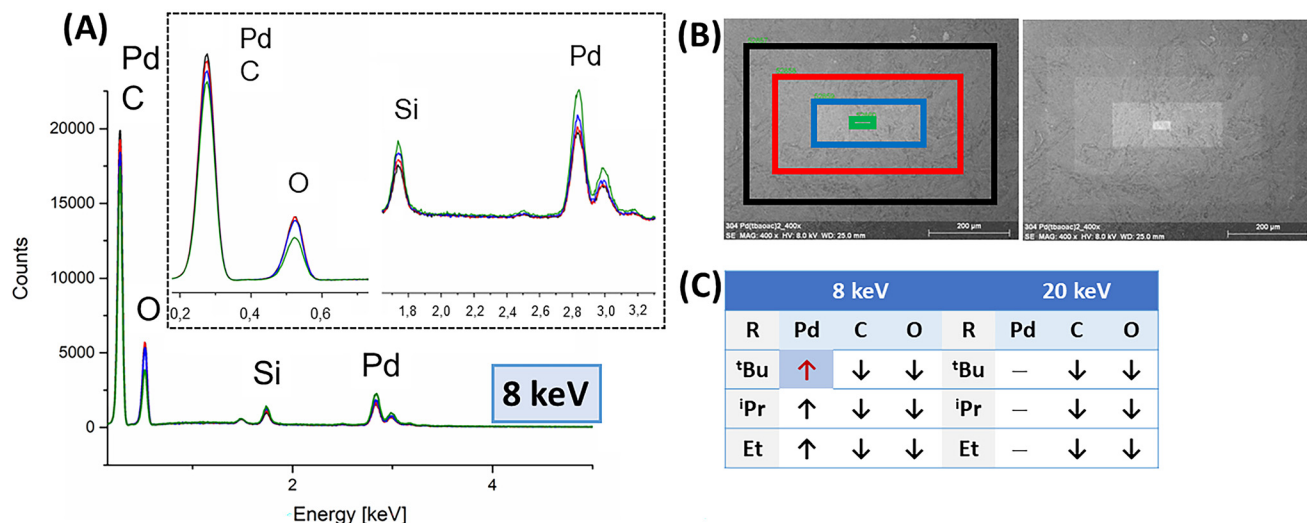


Fig. 13 (A) EDX spectra (8 keV) of sublimed $[\text{Pd}(\text{tbaoac})_2]$ (1) layer on a Si(111) substrate (Mag = 400 $\times$). (B) Top view SEM images of irradiated areas of the sublimed film: left image with marked areas corresponding to the EDX plots, right image: morphological changes after irradiation; (C) changes in the intensity of individual elements after irradiation with 8 keV and 20 keV beams (↑ increase, ↓ decrease, — no changes).

using SEM/EDX at 8 and 20 keV energy. EDX spectra were taken during the SEM analysis, each recorded for 30 seconds. During this experiment the electron dose was increased reducing the scanning area. The EDX spectra recorded for each area showed that the content of carbon and oxygen decreased with an increasing dose for 8 keV and 20 keV beams (1–3) (Fig. 13, Fig. S40–44[†]). The palladium content remained almost unchanged under the influence of a 20 keV electron beam, whereas after irradiation with 8 keV the signal intensity of this metal increased in all cases. It should be noted that the changes in palladium intensity were most significant for the complex (1). Based on the morphological changes in SEM images and intensities of individual elements in the EDX spectra, we propose that the complex (1) is the most sensitive to the high-energy electron beam (Fig. 13, and Fig. S40[†]). The slight effect of electron irradiation on the sublimed layers was visible for the complexes (2) and (3) (Fig. S41–44[†]). However, morphological changes in the SEM images were observed only for the compound (2) (Fig. S41–42[†]). These results indicate that not only the type of the substituents but also their position in space may significantly influence electron-induced fragmentation and should be an important factor in the selection of precursors for FEBID.

3.9 Preliminary FEBID experiments

Among the three synthesized complexes, the above characterization experiments and theoretical calculations showed that $[\text{Pd}(\text{tbaoac})_2]$ has the highest sensitivity towards electron irradiation, implying efficient dissociation. Moreover, we chose $[\text{Pd}(\text{tbaoac})_2]$ because low sublimation temperatures allow the substrate to remain at lower temperatures, opening the door to perform deposits on temperature sensitive substrates or layers. A square deposit was performed using the electron beam with

lithography software, which allows steering of the e-beam on the substrate. The substrate was held at 343 K to avoid condensation and thermal decomposition, while the gas injection system was kept at 358 K to effectively evaporate the $[\text{Pd}(\text{tbaoac})_2]$ (1). The SEM image of the FEBID deposit was obtained (Fig. 14). The deposit composition with the correction reveals palladium 24.5 at%, carbon 56.7 at%, and oxygen 18.8 at%. No halo deposits were observed around the square e-beam patterns. The obtained deposit was similar in composition to the deposits obtained using $[\text{Cu}(\text{tbaoac})_2]$.⁴⁴ However, variation of composition with the change in experimental conditions is often observed. Therefore, future experiments with varying experimental parameters to validate the extent of metal content that can be obtained will be performed.

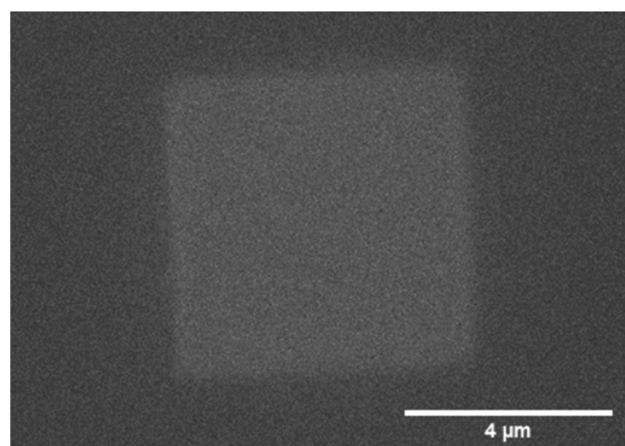


Fig. 14 SEM image of a FEBID deposit using $[\text{Pd}(\text{tbaoac})_2]$ (1). The square deposit was performed with a GIS temperature of 358 K and stage at 343 K using a 20 keV electron beam.

4. Summary and conclusions

New palladium(II) compounds of the general formula $[\text{Pd}(\text{MeCOCHCO}_2\text{R})_2]$, where $\text{R} = \text{'Bu}, \text{'Pr}, \text{Et}$, were synthesized by the direct reaction of palladium(II) acetate and suitable β -ketoesters. The single-crystal X-ray diffraction revealed the formation of stable mononuclear Pd(II) complexes and demonstrated the chelating ligand coordination. Additionally, IR and NMR spectra analysis confirmed β -ketoester deprotonation and chelation of the formed anions, as well as the structure and composition of the studied compounds. The dominant role of weak intermolecular interactions in the structures of the complexes was confirmed by Hirshfeld surface analysis, that is important for compound volatility. The thermal analysis data indicated that pressure reduction is required to transfer palladium carriers to the gas phase. On the other hand, the EI MS experiments showed that palladium(II) β -ketoesterates are the source of metal in the gas phase even at the temperature of 323 K ($p = 10^{-6}$ mbar). This fact suggested that the studied complexes could be introduced into the SEM microscope chamber *via* the GIS system. The fragmentation behaviour of the complex molecules in the gas phase with low-energy electrons reveals the highest sensitivity to the low energy electrons of the compound (1) and more efficient fragmentation, which correlate with the ALIE calculations. The compound's sublimation ($p = 10^{-2}$ mbar) occurs from 348 to 353 K. The layers of the Pd(II) β -ketoesterates deposited on the silicon surface interact with high energy electron beams (8 and 20 keV). The most volatile and sensitive towards electron irradiation is $[\text{Pd}(\text{tbaoac})_2]$ existing in the *cis* form. The preliminary FEBID experiments revealed that the compound $[\text{Pd}(\text{tbaoac})_2]$ may be supplied with GIS in the 348–358 K range. The metal content in the deposited structures was identified at *ca.* 24.5 at%. To further increase the metal content, the variation of deposition parameters and post-purification methods can be applied. $[\text{Pd}(\text{tbaoac})_2]$ can also be tested for more complicated 2D and 3D structure growth. In summary, from the point of view of the future design of new FEBID precursors, our results suggest that β -ketoesterate complexes can be considered as the metal source for the nanostructures' growth.

Author contributions

I.B.S: conceptualization; A.B.-K synthesized palladium(II) complexes and prepared the samples; A.B.-K and I.B.S characterized the samples; A.B.-K prepared the figures and drafted the manuscript; T.M: X-ray structural measurements; A.B.-K and T.M: visualization; T.M: structure description; A.K.-K and A.B.-K performed the theoretical calculations, description of the applied computational methodology, and discussion of the obtained DFT results; C.S.J, K.M, and A.B.-K, performed FEBID experiments; K.M: EDX measurements for FEBID deposit; C.S.J and I.U: discussion of the obtained FEBID results; I.U.: con-

ceptualisation and interpretation of the FEBID data; A.B.-K managed the references. All authors checked the interpretation of the data, composed the final manuscript, and have read and agreed to the published version of the manuscript.

Data availability

The data supporting this article have been included as part of the ESI.† Table S1 Crystal data and structure refinement for (1–3); Table S2 Bond lengths [Å] and angles [°] for $[\text{Pd}(\text{tbaoac})_2]$ (1), Table S3 Bond lengths [Å] and angles [°] for $[\text{Pd}(\text{ipaoac})_2]$ (2); Table S4 Bond lengths [Å] and angles [°] for $[\text{Pd}(\text{eaoac})_2]$ (3); Fig. S1 Experimental (blue) and calculated (red) XRD patterns of the $[\text{Pd}(\text{tbaoac})_2]$ (1); Fig. S2 Experimental (blue) and calculated (red) XRD patterns of the $[\text{Pd}(\text{ipaoac})_2]$ (2); Fig. S3 C–H... π interactions between C8–H8, C23–H23, C38–H38, and chelate ring (green dashed lines) and between chelate rings (blue dashed lines) in the compound $[\text{Pd}(\text{tbaoac})_2]$ (1); Fig. S4 Hirshfeld surfaces (left) and fingerprints (right) of selected interactions created in the crystal network of $[\text{Pd}(\text{tbaoac})_2]$ (1) for the Pd2 molecule: (A) for H...H (63.5%), (B) for O...H (11.2%), (C) for C...H and H...C (11.1%), and (D) for H...O (10.0%). In brackets, there is a given surface area included as a percentage of the total surface area; Fig. S5 π – π interactions between palladium ions and the chelate ring (orange dashed lines) and O...H hydrogen bonds (magenta dashed lines) in the compound $[\text{Pd}(\text{ipaoac})_2]$ (2); Fig. S6 Hirshfeld surfaces (left) and fingerprints (right) of selected interactions created in the crystal network of $[\text{Pd}(\text{ipaoac})_2]$ (2): (A) for H...H (67.0%), (B) for H...O (18.1%), and (C) for C...Pd (3.5%). In brackets, there is a given surface area included as a percentage of the total surface area; Fig. S7 Interaction energy: (A) electrostatic, (B) van der Waals, and (C) total in the crystal network of $[\text{Pd}(\text{ipaoac})_2]$ (2); Fig. S8 The structure of $[\text{Pd}(\text{eaoac})_2]$ (3) with the numbering scheme; Fig. S9 Hirshfeld surfaces (left) and fingerprints (right) of selected interactions created in the crystal network of $[\text{Pd}(\text{eaoac})_2]$ (3) for the Pd1 molecule: (A) for H...H (53.1%), (B) for O...H (29.7%), and (C) for C...H (7.4%). In brackets, there is a given surface area included as a percentage of the total surface area; Fig. S10 Hirshfeld surfaces (left) and fingerprints (right) of selected interactions created in the crystal network of $[\text{Pd}(\text{eaoac})_2]$ (3) for the Pd2 molecule: (A) for H...H (58.1%), (B) for H...O (25.9%), (C) for C...O (4.0%), and (D) for C...C (3.6%). In brackets, there is a given surface area included as a percentage of the total surface area; Fig. S11 Interaction energy: (A) electrostatic, (B) van der Waals, and (C) total in the crystal network of $[\text{Pd}(\text{eaoac})_2]$ (3) for the Pd1 molecule; Fig. S12 Interaction energy: (A) electrostatic, (B) van der Waals, and (C) total in the crystal network of $[\text{Pd}(\text{eaoac})_2]$ (3) for the Pd2 molecule; Fig. S13 Interaction energy: (A) electrostatic, (B) van der Waals, and (C) total in the crystal network of $[\text{Pd}(\text{eaoac})_2]$ (3) for Pd1 and Pd2 molecules; Fig. S14 ATR-IR spectrum for the compound $[\text{Pd}(\text{tbaoac})_2]$ (1); Fig. S15 ATR-IR spectrum for the com-

pound [Pd(ipaoac)₂] (2); Fig. S16 ATR-IR spectrum for the compound [Pd(eaoac)₂] (3); Fig. S17 ATR-IR spectra for the protonated ligands: MeCOCH₂CO₂^tBu – tbaoacH (black), MeCOCH₂CO₂ⁱPr – ipaoacH (blue), and MeCOCH₂CO₂Et – eaoacH (grey); Fig. S18 Theoretical infrared spectrum calculated by DFT B3LYP-D3/def2-TZVPP for the compound [Pd(ipaoac)₂] (2) (blue line) and the ligand ipaoacH (black line); Fig. S19 Theoretical infrared spectrum calculated by DFT B3LYP-D3/def2-TZVPP for the compound [Pd(eaoac)₂] (3) (blue line) and the ligand eaoacH (black line); Fig. S20 ¹H NMR spectrum of the compound [Pd(tbaoac)₂] (1); Fig. S21 ¹H NMR spectrum of the tbaoacH – MeCOCH₂CO₂^tBu; Fig. S22 ¹³C NMR spectrum of the compound [Pd(tbaoac)₂] (1); Fig. S23 ¹³C NMR spectrum of the tbaoacH – MeCOCH₂CO₂^tBu; Fig. S24 ¹H NMR spectrum of the compound [Pd(ipaoac)₂] (2); Fig. S25 ¹H NMR spectrum of the ipaoacH – MeCOCH₂CO₂ⁱPr; Fig. S26 ¹³C NMR spectrum of the compound [Pd(ipaoac)₂] (2); Fig. S27 ¹³C NMR spectrum of the ipaoacH – MeCOCH₂CO₂ⁱPr; Fig. S28 ¹H NMR spectrum of the compound [Pd(eaoac)₂] (3); Fig. S29 ¹H NMR spectrum of the compound eaoacH – MeCOCH₂CO₂Et; Fig. S30 ¹³C NMR spectrum of the compound [Pd(eaoac)₂] (3); Fig. S31 ¹³C NMR spectrum of the eaoacH – MeCOCH₂CO₂Et; Fig. S32 Thermogram of [Pd(ipaoac)₂] (2) (TG, DTG, DTA curves); Fig. S33 Thermogram of [Pd(eaoac)₂] (3) (TG, DTG, DTA curves); Fig. S34 XRD analysis of the residue after TGA of [Pd(ipaoac)₂] (2) and [Pd(eaoac)₂] (3); Fig. S35 VT IR spectra in the solid state for the compound [Pd(tbaoac)₂] (1) in the temperature range 303–513 K; Fig. S36 EI MS spectra, where the molecular ions appeared: (A) – [Pd(tbaoac)₂] (1) at the temperature 336 K, (B) – [Pd(ipaoac)₂] (2) at 323 K and (C) – [Pd(eaoac)₂] (3) at 336 K, and (D) – isotopic pattern simulation for the molecular ion [Pd(tbaoac)₂]⁺; Fig. S37 EI MS spectra, where the molecular ions achieved the highest relative intensity: (A) – [Pd(tbaoac)₂] (1) at 337 K, (B) – [Pd(ipaoac)₂] (2) at 330 K and (C) – [Pd(eaoac)₂] (3) at 388 K, and (D) – [Pd(eaoac)₂] (3) at 416 K; Table S5 EI MS results for the complex [Pd(tbaoac)₂] (1); Table S6 EI MS results for the complex [Pd(ipaoac)₂] (2); Table S7 EI MS results for the complex [Pd(eaoac)₂] (3); Fig. S38 Infrared spectra for the compound [Pd(ipaoac)₂] (2) after sublimation (blue) at 353 K (*p* = 10^{−2} mbar); Fig. S39 Infrared spectra for the compound [Pd(eaoac)₂] (3) before (black) and after sublimation (blue) at 353 K (*p* = 10^{−2} mbar); Fig. S40 Examined scan areas' EDX spectra (20 keV) for the [Pd(tbaoac)₂] (1) layer deposited on a Si(111) substrate (Mag = 200×); Fig. S41 Examined scan areas' EDX spectra (8 keV) for the [Pd(ipaoac)₂] (2) layer deposited on a Si(111) substrate (Mag = 200×); Fig. S42 Examined scan areas' EDX spectra (20 keV) for the [Pd(ipaoac)₂] (2) layer deposited on a Si(111) substrate (Mag = 200×); Fig. S43 Examined scan areas' EDX spectra (8 keV) for the [Pd(eaoac)₂] (3) layer deposited on a Si(111) substrate (Mag = 200×); Fig. S44 Examined scan areas' EDX spectra (20 keV) for the [Pd(eaoac)₂] (3) layer deposited on a Si(111) substrate (Mag = 200×). CCDC 2335314, 2335316, and 2335315† contain supplementary crystallographic data for the compounds [Pd(tbaoac)₂] (1), [Pd(ipaoac)₂] (2), and [Pd(eaoac)₂] (3), respectively.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Supplementary Materials:

New palladium(II) β -ketoesterates for Focused Electron Beam Induced Deposition: Synthesis, structures, and characterization

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X-ray crystal structure determination

Table S 1 Crystal data and structure refinement for (1–3).

Identification code	(1)	(2)	(3)
Empirical formula	C16 H26 O6 Pd	C14 H22 O6 Pd	C12 H18 O6 Pd
Formula weight	420.77	392.71	364.66
Temperature [K]	100(2) K	100(2) K	100.15 K
Wavelength [Å]	1.54184 Å	1.54184 Å	1.54184 Å
Crystal system, space group	Triclinic, P-1	Monoclinic, P2 ₁ /n	Triclinic, P-1
Unit cell dimensions [Å] and [°]	a = 10.23141(11) Å α = 91.9303(9)° b = 12.95320(14) Å β = 98.1743(9)° c = 14.56071(17) Å γ = 100.3549(9)°	a = 4.35329(10) Å α = 90° b = 10.3794(3) Å β = 93.392(2)° c = 17.7657(5) Å γ = 90°	a = 7.0247(2) Å α = 89.994(3)° b = 8.6043(3) Å β = 80.180(3)° c = 11.5706(4) Å γ = 79.606(3)°
Volume [Å ³]	1875.53(4) Å ³	801.33(4) Å ³	677.46(4) Å ³
Z, Calculated density [Mg×m ⁻³]	4, 1.490 Mg/m ³	2, 1.628 Mg/m ³	2, 1.788 Mg/m ³
Absorption coefficient [mm ⁻¹]	8.207 mm ⁻¹	9.558 mm ⁻¹	11.252 mm ⁻¹
F(000)	864	400	368
Crystal size [mm]	0.140 x 0.060 x 0.030 mm ³	0.130 x 0.040 x 0.020 mm ³	0.1 x 0.03 x 0.02 mm ³
Theta range for data collection [°]	3.072 to 74.503°	4.937 to 74.504°	3.879 to 74.475°
Limiting indices	-12 ≤ h ≤ 12 -16 ≤ k ≤ 16 -16 ≤ l ≤ 18	-5 ≤ h ≤ 4 -12 ≤ k ≤ 12 -17 ≤ l ≤ 22	-8 ≤ h ≤ 8 -10 ≤ k ≤ 7 -14 ≤ l ≤ 14
Reflections collected/unique	68027	5007	8513
Completeness [%] to theta [°]	99.9 %	98.6 %	99.9 %
Absorption correction	Gaussian	Gaussian	Gaussian
Max. and min. transmission	0.908 and 0.490	0.942 and 0.422	0.920 and 0.433
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data/restraints/parameters	7650 / 0 / 432	1605 / 0 / 100	2756 / 0 / 179
Goodness-of-fit on F ²	1.052	1.112	1.092
Final R Indices [I > 2σ(I)]	R1 = 0.0184, wR2 = 0.0500	R1 = 0.0346, wR2 = 0.0948	R1 = 0.0261, wR2 = 0.0746
R indices (all data)	R1 = 0.0189, wR2 = 0.0503	R1 = 0.0384, wR2 = 0.0981	R1 = 0.0286, wR2 = 0.0765
Largest diff. peak and hole [e. Å ⁻³]	0.372 and -0.545 e. Å ⁻³	0.980 and -0.906 e. Å ⁻³	0.919 and -0.990 e. Å ⁻³

Table S 2 Bond lengths [Å] and angles [°] for [Pd(tbaoac)₂] (**1**).

Pd(1)-O(12)	1.9657(11)
Pd(1)-O(2)	1.9710(11)
Pd(1)-O(6)	1.9947(11)
Pd(1)-O(16)	1.9978(11)
Pd(2)-O(22)	1.9628(11)
Pd(2)-O(32)	1.9660(11)
Pd(2)-O(36)	1.9972(11)
Pd(2)-O(26)	2.0010(11)
O(12)-Pd(1)-O(2)	85.30(5)
O(12)-Pd(1)-O(6)	179.55(5)
O(2)-Pd(1)-O(6)	94.70(4)
O(12)-Pd(1)-O(16)	94.88(4)
O(2)-Pd(1)-O(16)	179.71(5)
O(6)-Pd(1)-O(16)	85.11(4)
C(2)-O(2)-Pd(1)	122.69(10)
C(4)-O(6)-Pd(1)	122.82(10)
C(12)-O(12)-Pd(1)	122.83(10)
C(14)-O(16)-Pd(1)	122.59(10)
O(22)-Pd(2)-O(32)	84.38(5)
O(22)-Pd(2)-O(36)	178.04(5)
O(32)-Pd(2)-O(36)	94.34(5)
O(22)-Pd(2)-O(26)	94.95(5)
O(32)-Pd(2)-O(26)	175.70(5)
O(36)-Pd(2)-O(26)	86.44(5)
C(22)-O(22)-Pd(2)	122.88(10)
C(24)-O(26)-Pd(2)	121.38(10)
C(32)-O(32)-Pd(2)	123.17(10)
C(34)-O(36)-Pd(2)	122.89(10)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1

Table S 3 Bond lengths [Å] and angles [°] for [Pd(ipaoac)₂] (**2**).

Pd(1)-O(1)#1	1.9811(19)
Pd(1)-O(1)	1.9811(19)
Pd(1)-O(4)	1.999(3)
Pd(1)-O(4)#1	1.999(3)
O(1)#1-Pd(1)-O(1)	180.00(9)
O(1)#1-Pd(1)-O(4)	85.23(8)
O(1)-Pd(1)-O(4)	94.77(8)
O(1)#1-Pd(1)-O(4)#1	94.78(8)
O(1)-Pd(1)-O(4)#1	85.22(8)
O(4)-Pd(1)-O(4)#1	180.0
C(2)-O(1)-Pd(1)	122.62(18)
C(4)-O(4)-Pd(1)	122.20(19)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1

Table S 4 Bond lengths [Å] and angles [°] for [Pd(eaoac)₂] (**3**).

Pd(1)-O(3A)#1	1.9923(15)
Pd(1)-O(3A)	1.9923(15)
Pd(1)-O(5)#1	1.9833(15)
Pd(1)-O(5)	1.9833(15)
Pd(2)-O(13A)#2	1.9917(16)
Pd(2)-O(13A)	1.9917(16)
Pd(2)-O(15)	1.9881(15)
Pd(2)-O(15)#2	1.9881(15)
O(3A)#1-Pd(1)-O(3A)	180.0
O(5)#1-Pd(1)-O(3A)	85.40(6)
O(5)#1-Pd(1)-O(3A)#1	94.60(6)
O(5)-Pd(1)-O(3A)#1	85.40(6)
O(5)-Pd(1)-O(3A)	94.60(6)
O(5)#1-Pd(1)-O(5)	180.0
C(3)-O(3A)-Pd(1)	122.01(14)
C(5)-O(5)-Pd(1)	122.94(16)
O(13A)#2-Pd(2)-O(13A)	180.0
O(15)-Pd(2)-O(13A)	94.64(6)
O(15)-Pd(2)-O(13A)#2	85.36(6)
O(15)#2-Pd(2)-O(13A)#2	94.64(6)
O(15)#2-Pd(2)-O(13A)	85.36(6)
O(15)-Pd(2)-O(15)#2	180.0
C(13)-O(13A)-Pd(2)	122.04(14)
C(15)-O(15)-Pd(2)	122.60(16)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x,-y+1,-z+2

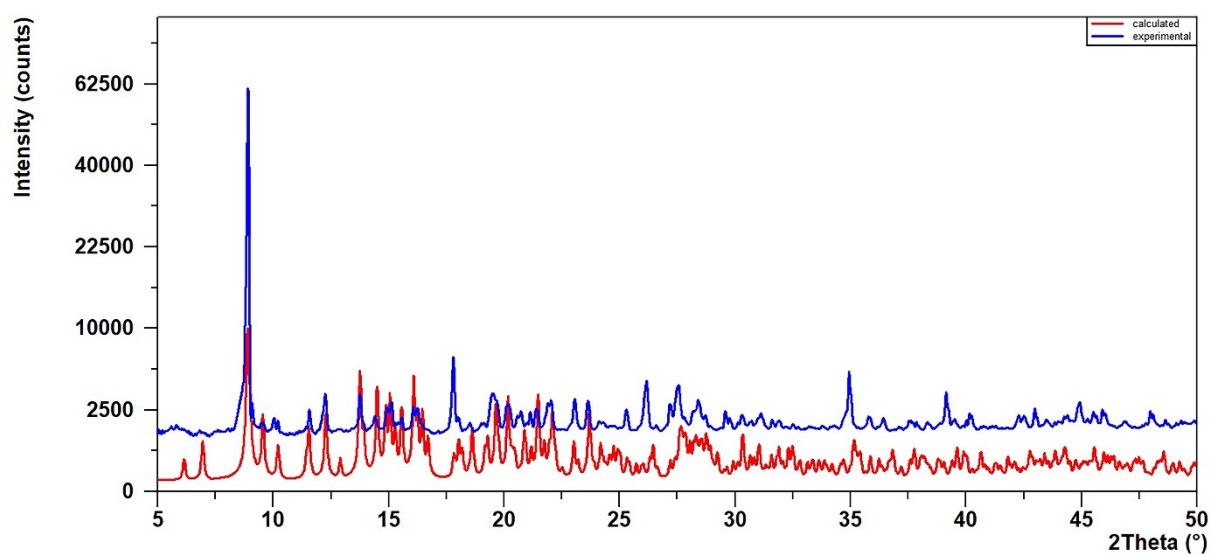


Figure S 1 Experimental (blue) and calculated (red) XRD patterns of the [Pd(tbaoac)₂] (1).

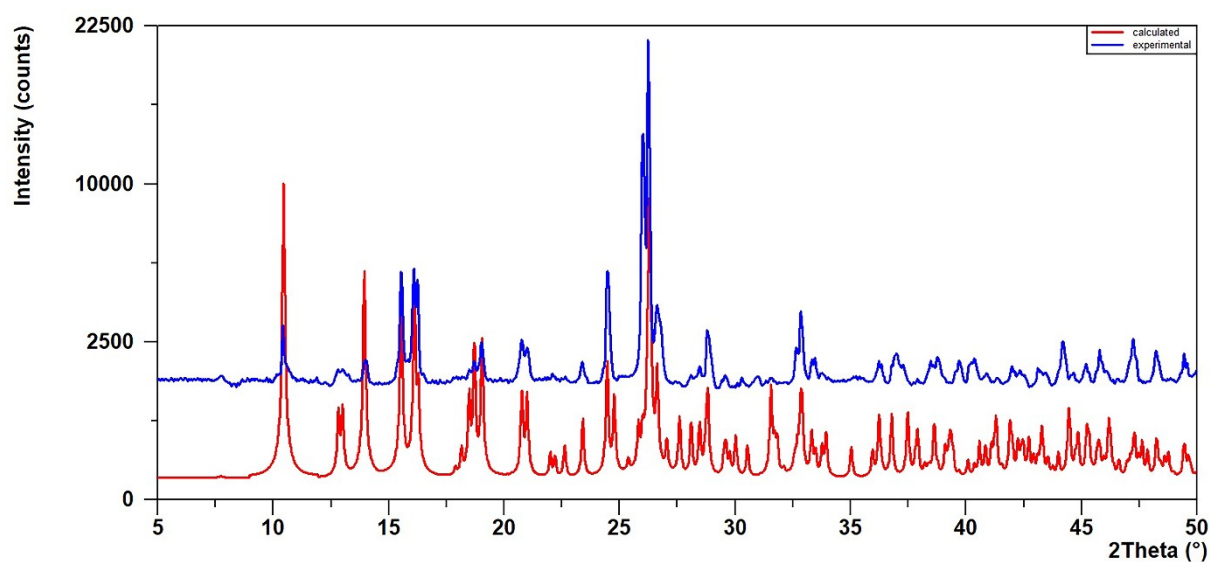


Figure S 2 Experimental (blue) and calculated (red) XRD patterns of the [Pd(ipaoac)₂] (2).

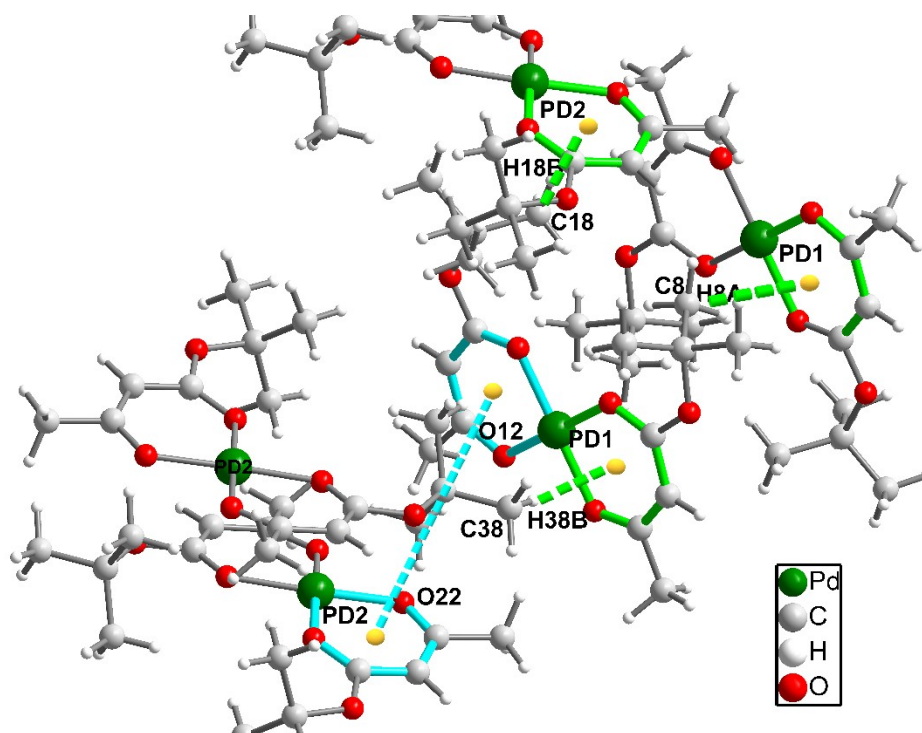


Figure S 3 C-H... π interactions between C8-H8, C23-H23, C38-H38, and chelate ring (green dashed lines) and between chelate rings (blue dashed lines) in the compound $[\text{Pd}(\text{tbaoac})_2]$ (**1**).

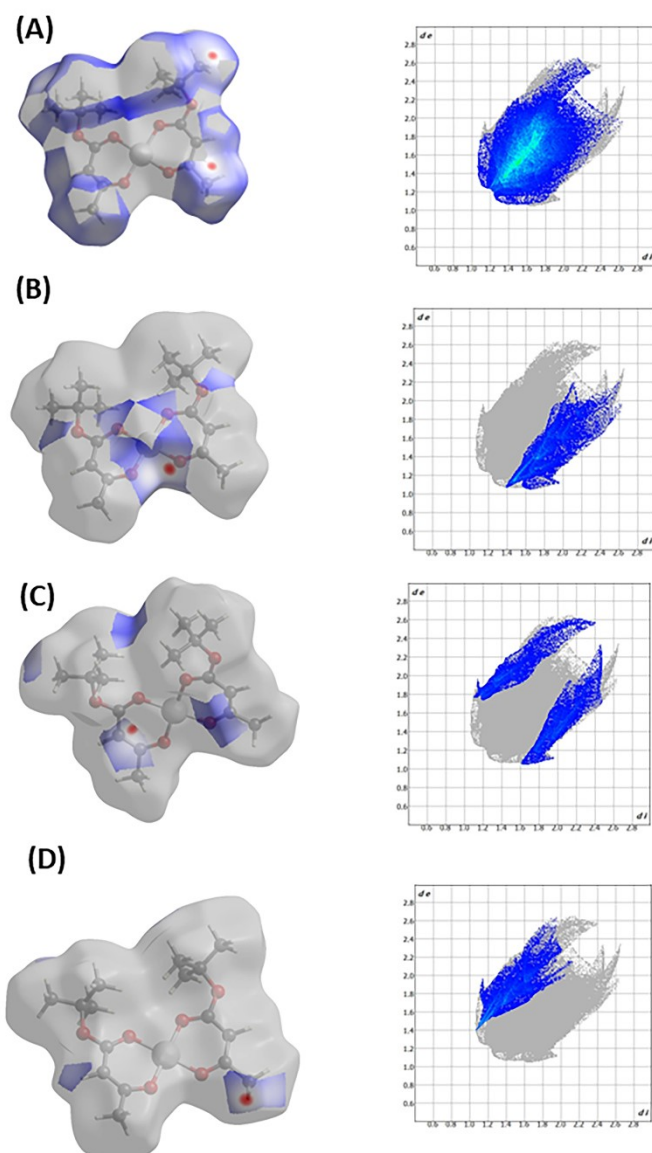


Figure S 4 Hirshfeld surfaces (left) and fingerprints (right) of selected interactions created in the crystal network of [Pd(tbaoac)₂] (1) for Pd₂ molecule: (A) for H...H (63.5%), (B) for O...H (11.2%), (C) for C...H and H...C (11.1%), and (D) for H...O (10.0%). In brackets, there is a given surface area included as a percentage of the total surface area.

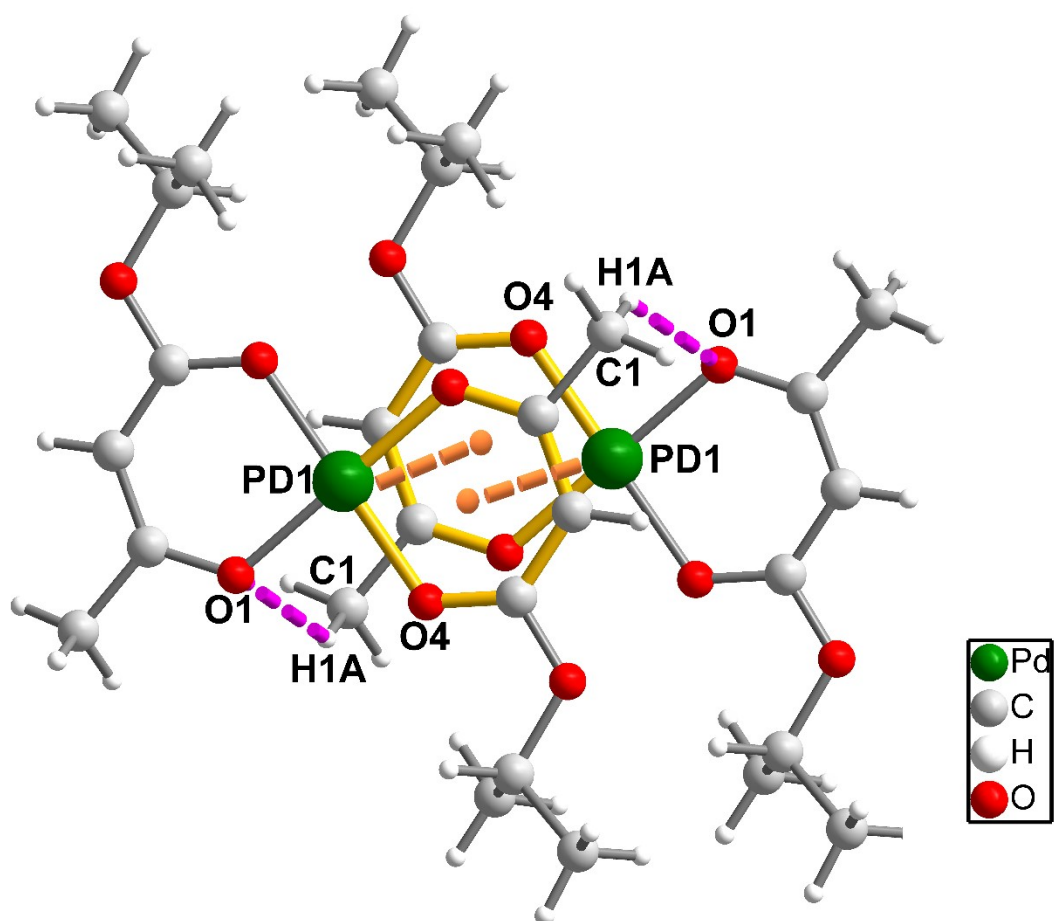


Figure S 5 π - π interactions between palladium ion and chelate ring (orange dashed lines) and O...H hydrogen bonds (magenta dashed lines) in the compound $[\text{Pd}(\text{ipaoac})_2]$ (2).

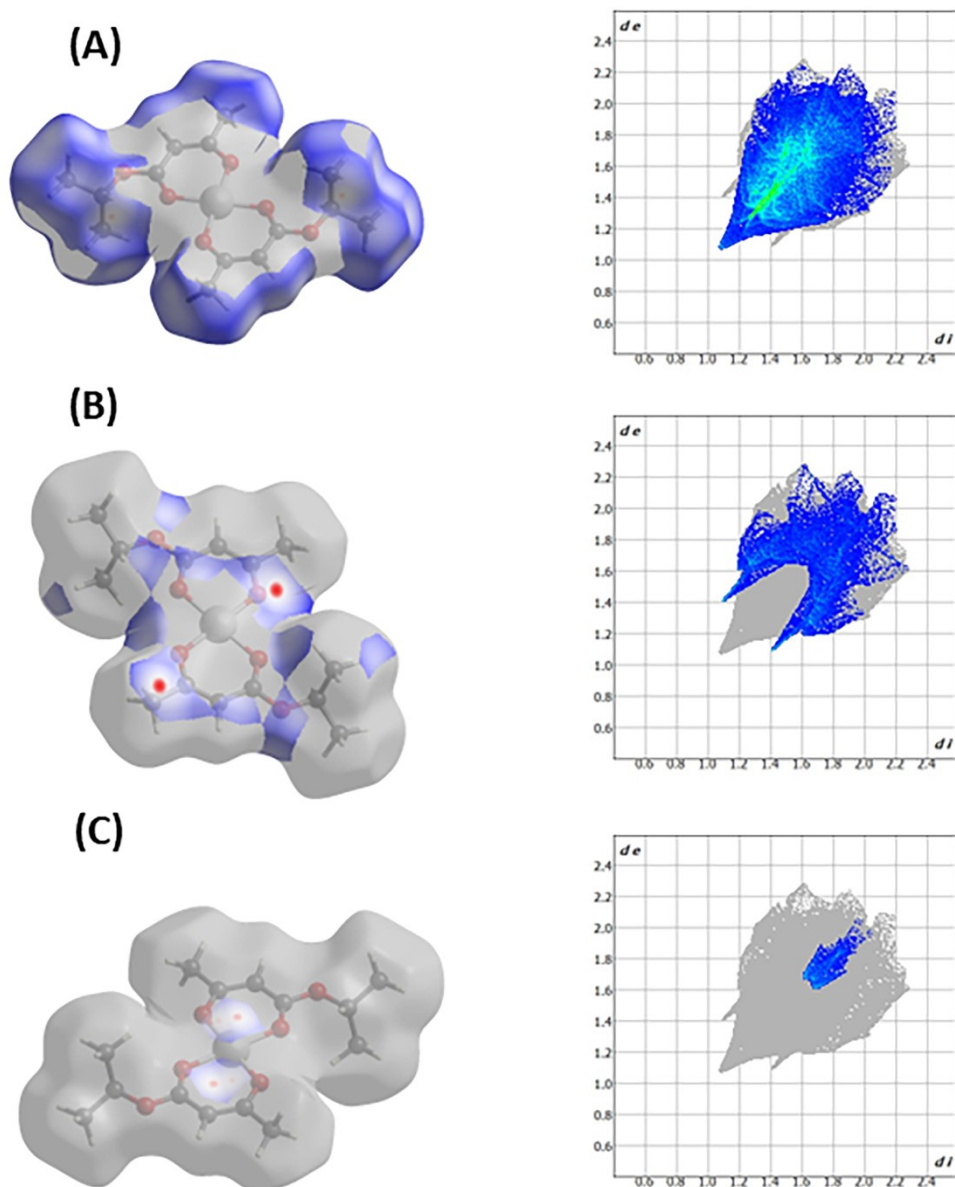


Figure S 6 Hirshfeld surfaces (left) and fingerprints (right) of selected interactions created in the crystal network of $[\text{Pd}(\text{ipaoac})_2]$ (**2**): (A) for $\text{H}\cdots\text{H}$ (67.0%), (B) for $\text{H}\cdots\text{O}$ (18.1%), and (C) for $\text{C}\cdots\text{Pd}$ (3.5%). In brackets, there is a given surface area included as a percentage of the total surface area.

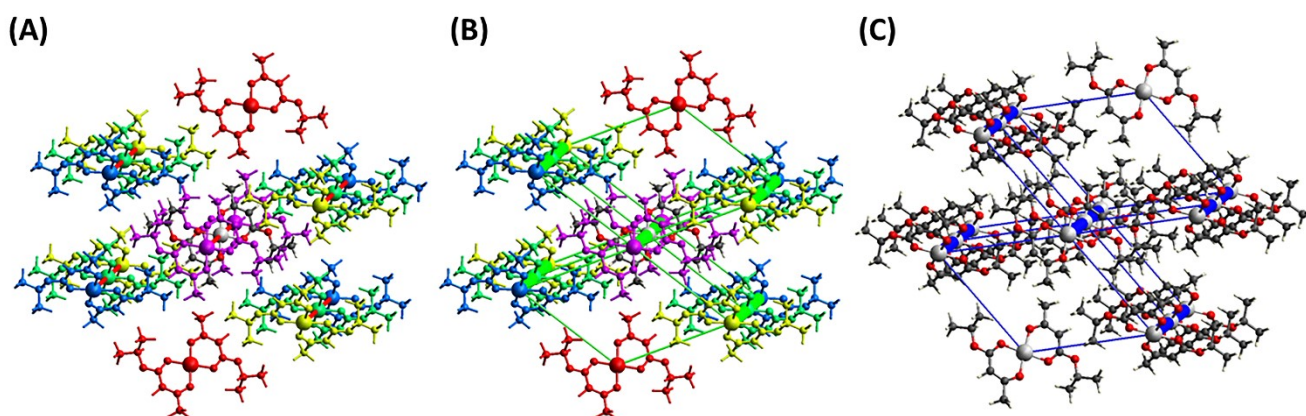


Figure S 7 Interactions energy: (A) – electrostatic, (B) – van der Waals, and (C) – total in the crystal network of $[\text{Pd}(\text{ipaoac})_2]$ (2).

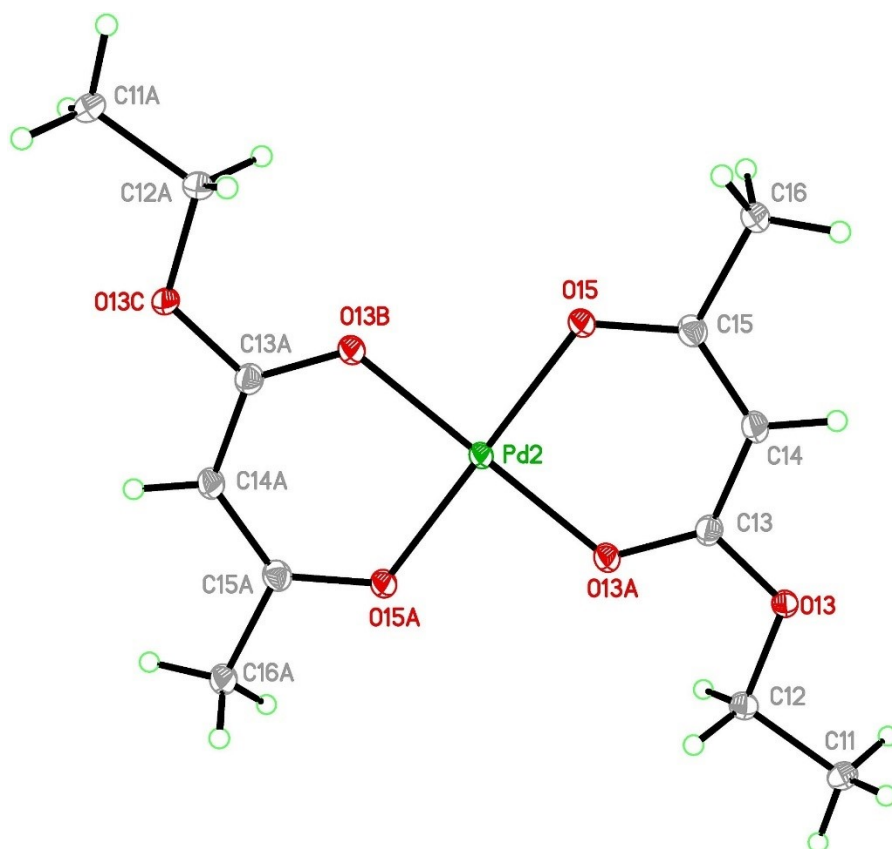


Figure S 8 The structure of $[\text{Pd}(\text{eaoac})_2]$ (3) with the numbering scheme.

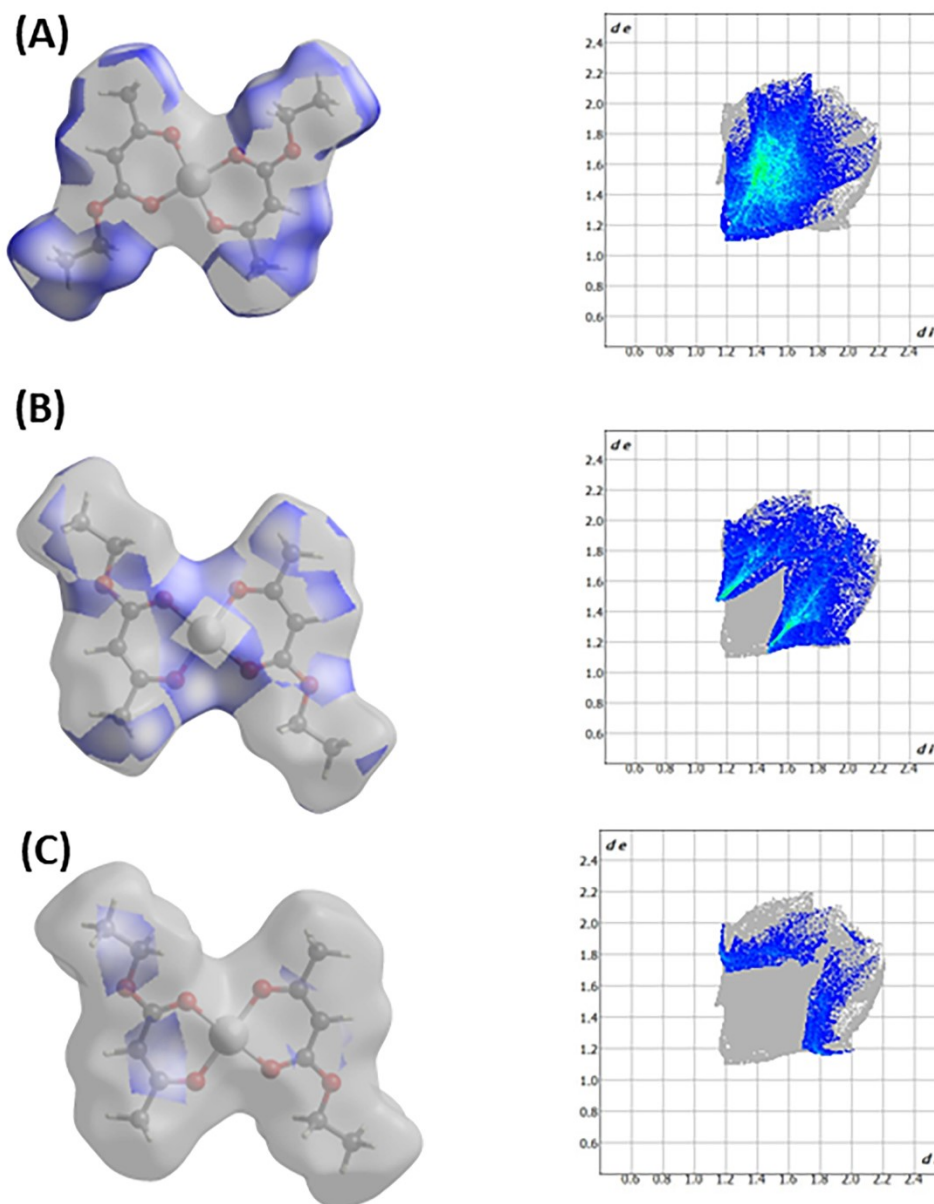


Figure S 9 Hirshfeld surfaces (left) and fingerprints (right) of selected interactions created in the crystal network of $[\text{Pd}(\text{eaoac})_2]$ (**3**) for Pd1 molecule: (A) for H...H (53.1%), (B) for O...H (29.7%), and (C) for C...H (7.4%). In brackets, there is a given surface area included as a percentage of the total surface area.

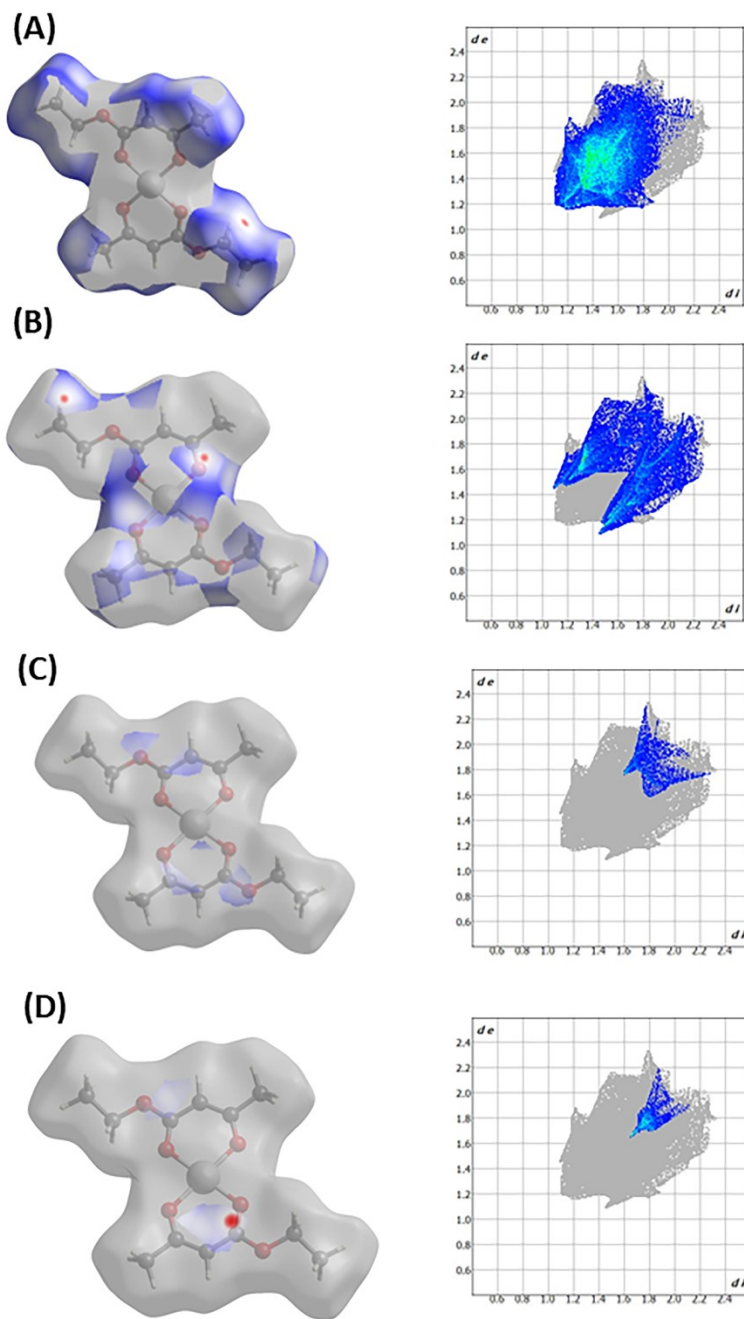


Figure S 10 Hirshfeld surfaces (left) and fingerprints (right) of selected interactions created in the crystal network of $[\text{Pd}(\text{eaoac})_2]$ (**3**) for Pd2 molecule: (A) for H...H (58.1%), (B) for H...O (25.9%), (C) for C...O (4.0%), and (D) for C...C (3.6%). In brackets, there is a given surface area included as a percentage of the total surface area.

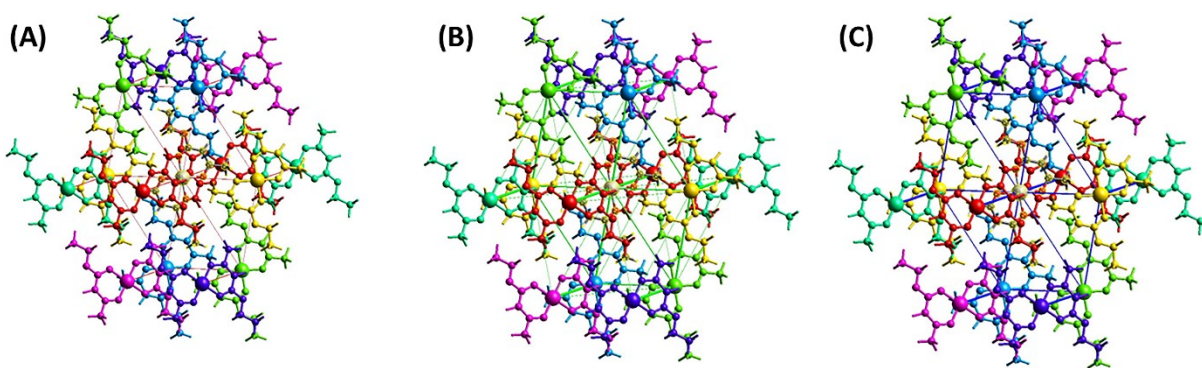


Figure S 11 Interactions energy: (A) – electrostatic, (B) – van der Waals, and (C) – total in the crystal network of $[\text{Pd}(\text{eaoac})_2]$ (**3**) for Pd1 molecule.

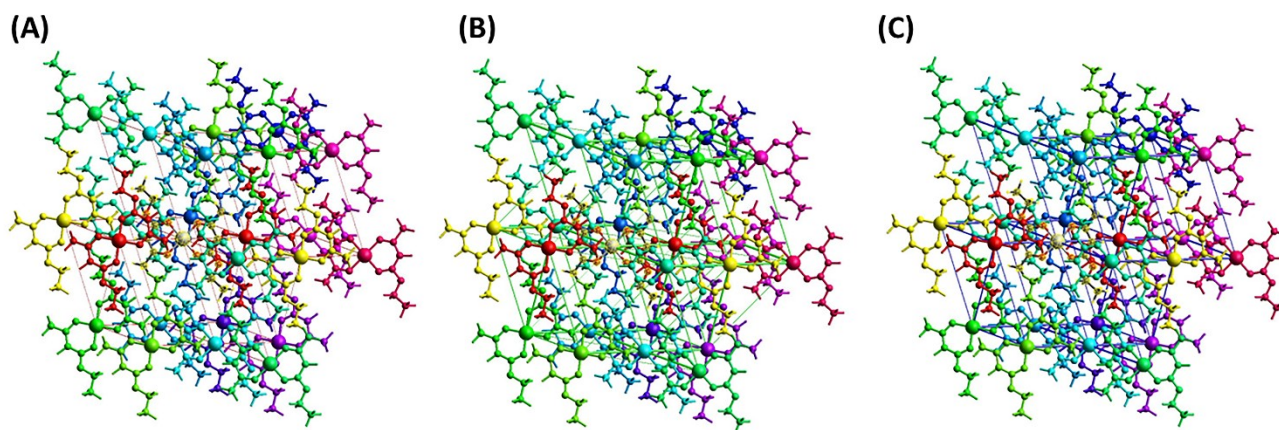


Figure S 12 Interactions energy: (A) – electrostatic, (B) – van der Waals, and (C) – total in the crystal network of $[\text{Pd}(\text{eaoac})_2]$ (**3**) for Pd2 molecule.

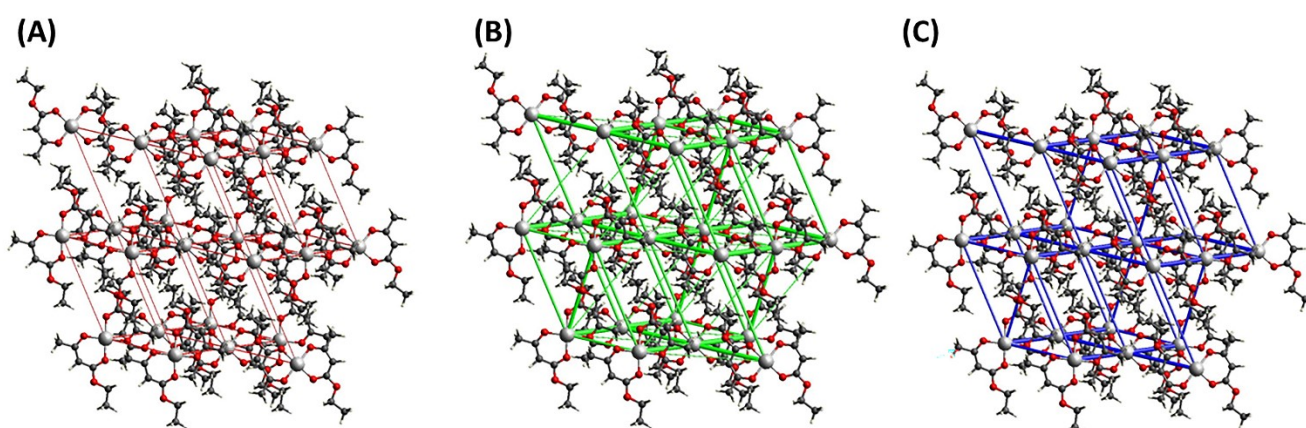


Figure S 13 Interactions energy: (A) – electrostatic, (B) – van der Waals, and (C) – total in the crystal network of $[\text{Pd}(\text{eaoac})_2]$ (**3**) for Pd1 and Pd2 molecules.

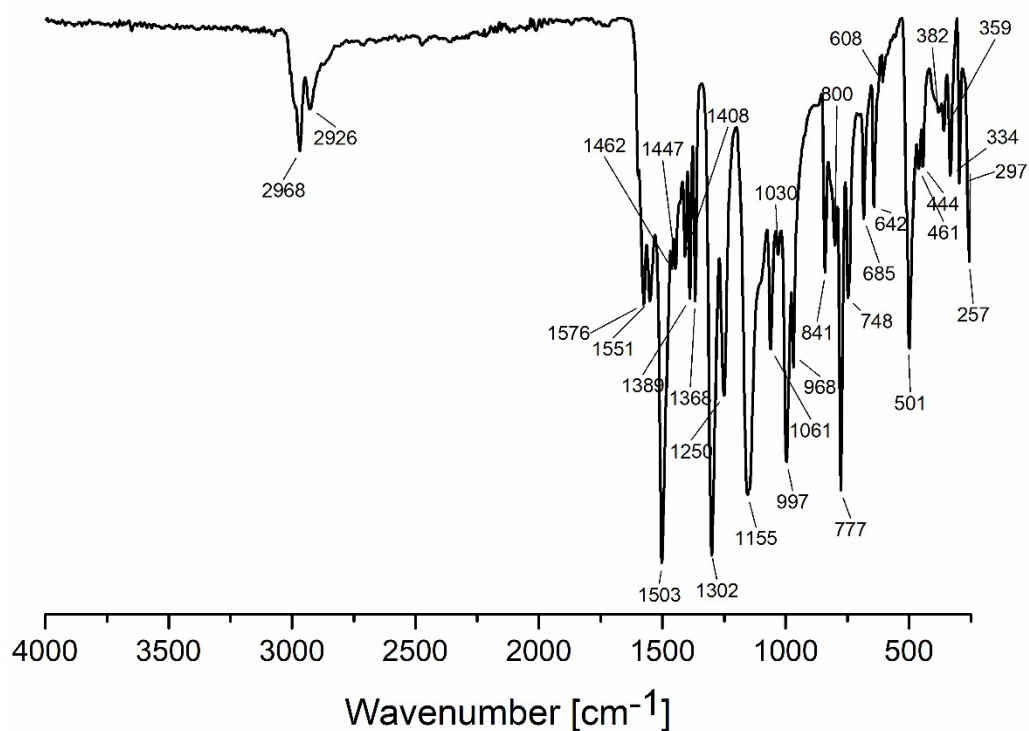


Figure S 14 ATR-IR spectrum for the compound $[\text{Pd}(\text{tbaoac})_2]$ (1).

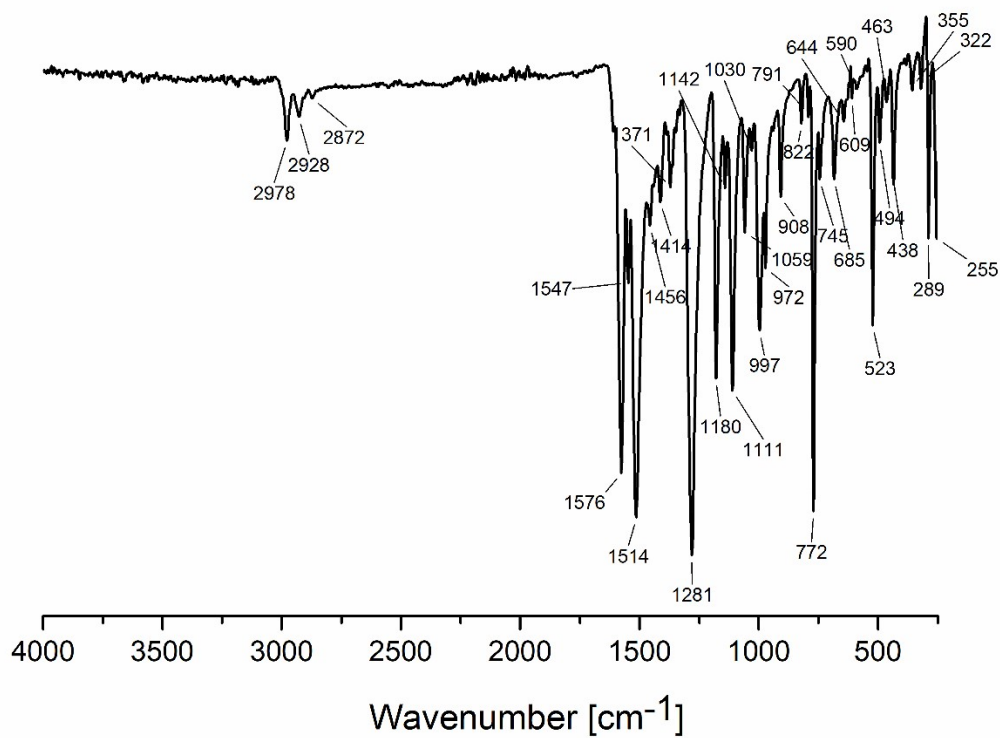


Figure S 15 ATR-IR spectrum for the compound $[\text{Pd}(\text{ipaoac})_2]$ (2).

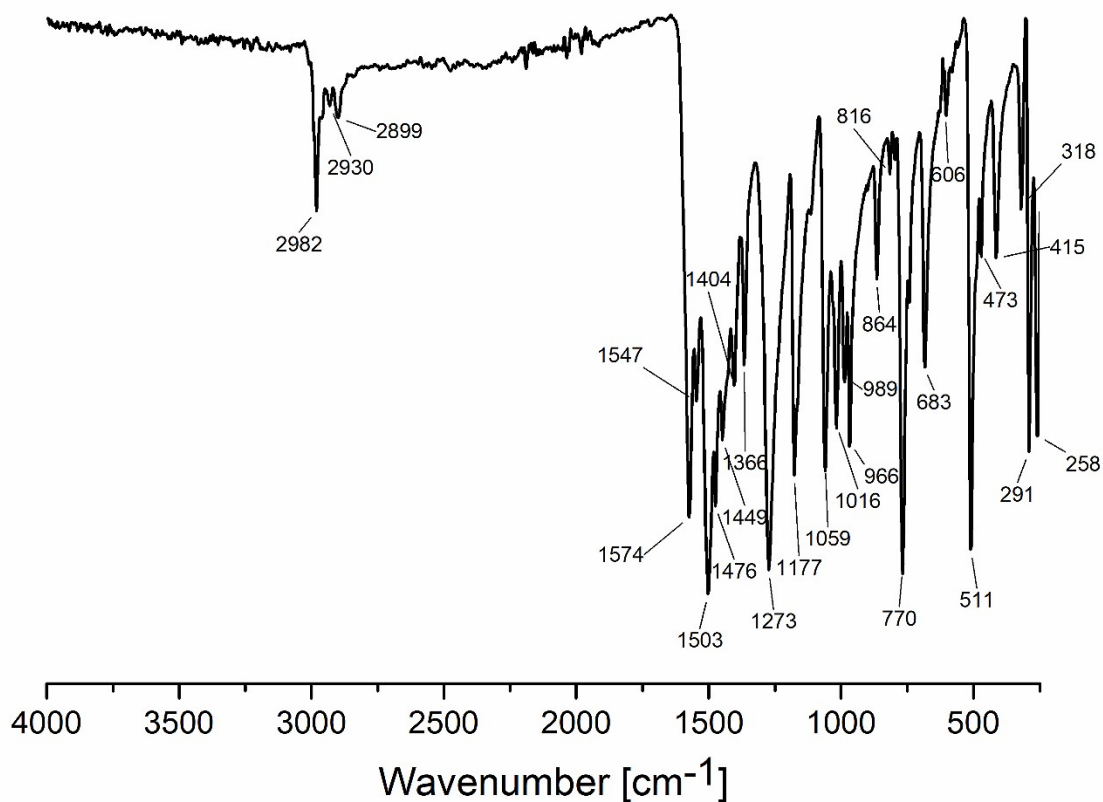


Figure S 16 ATR-IR spectrum for the compound $[\text{Pd}(\text{eaoac})_2]$ (**3**).

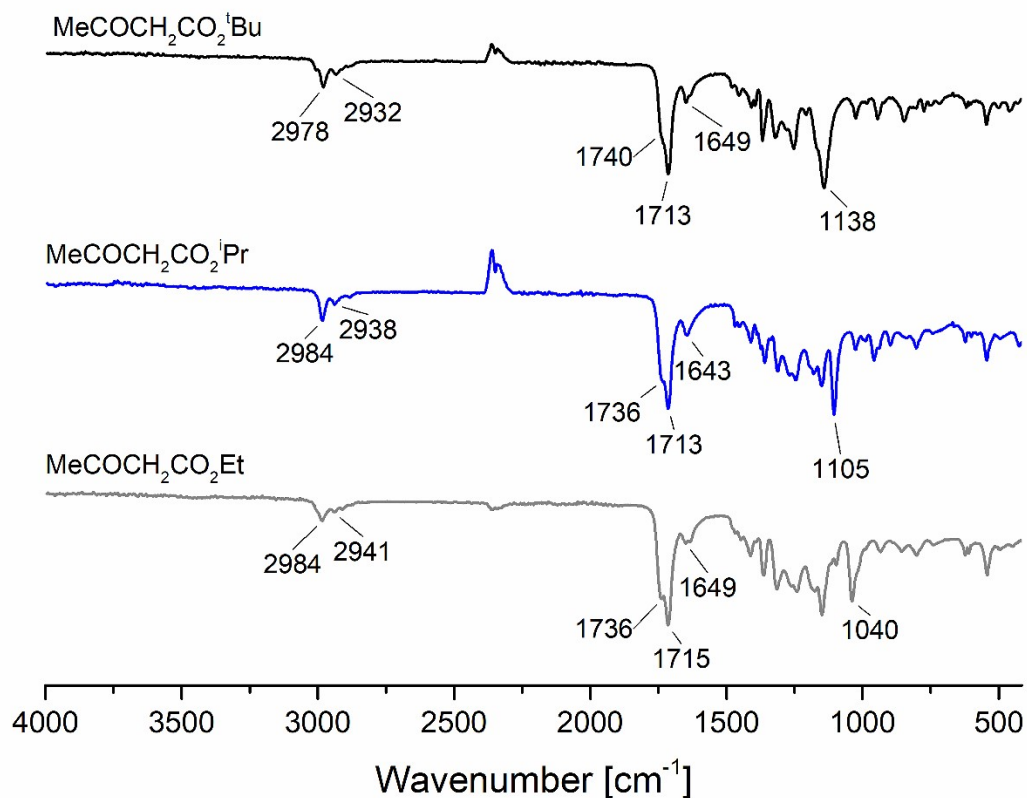


Figure S 17 ATR-IR spectra for the protonated ligands: $\text{MeCOCH}_2\text{CO}_2^t\text{Bu}$ – tbaoacH (black), $\text{MeCOCH}_2\text{CO}_2^i\text{Pr}$ – ipaoacH (blue), and $\text{MeCOCH}_2\text{CO}_2\text{Et}$ – eaoacH (grey).

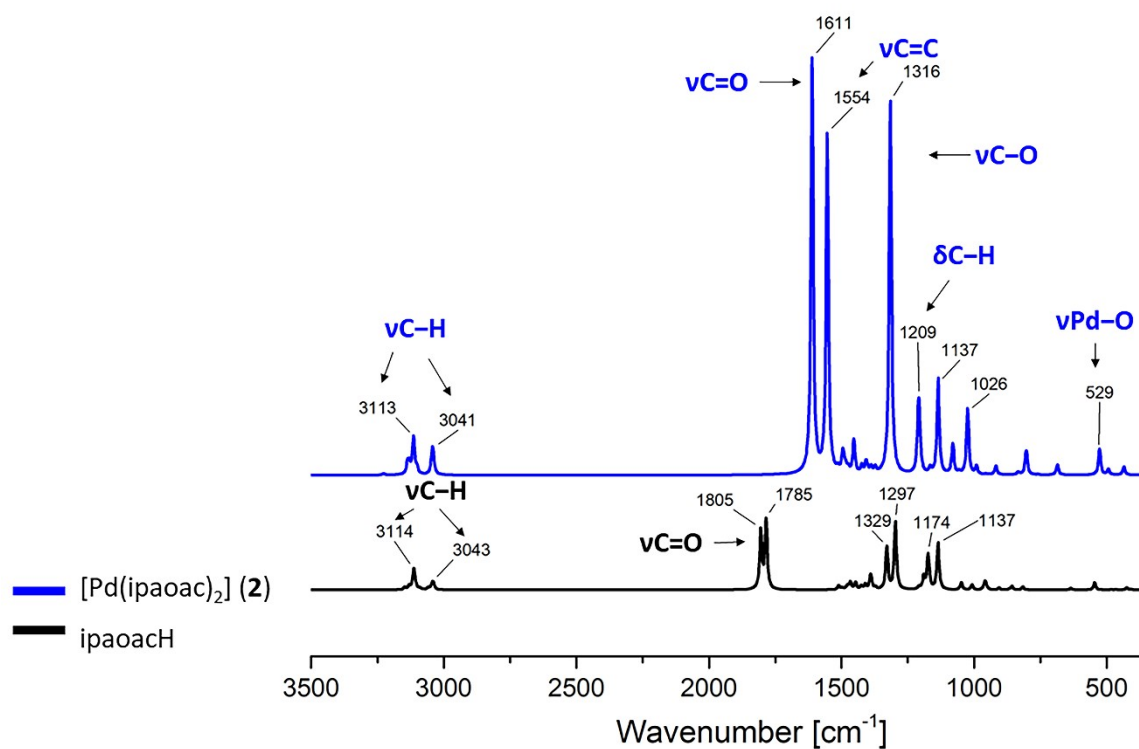


Figure S 18 Theoretical infrared spectra calculated by DFT B3LYP-D3/def2-TZVPP for the compound [Pd(ipaoac)₂] (**2**) (blue line) and ligand ipaoach (black line).

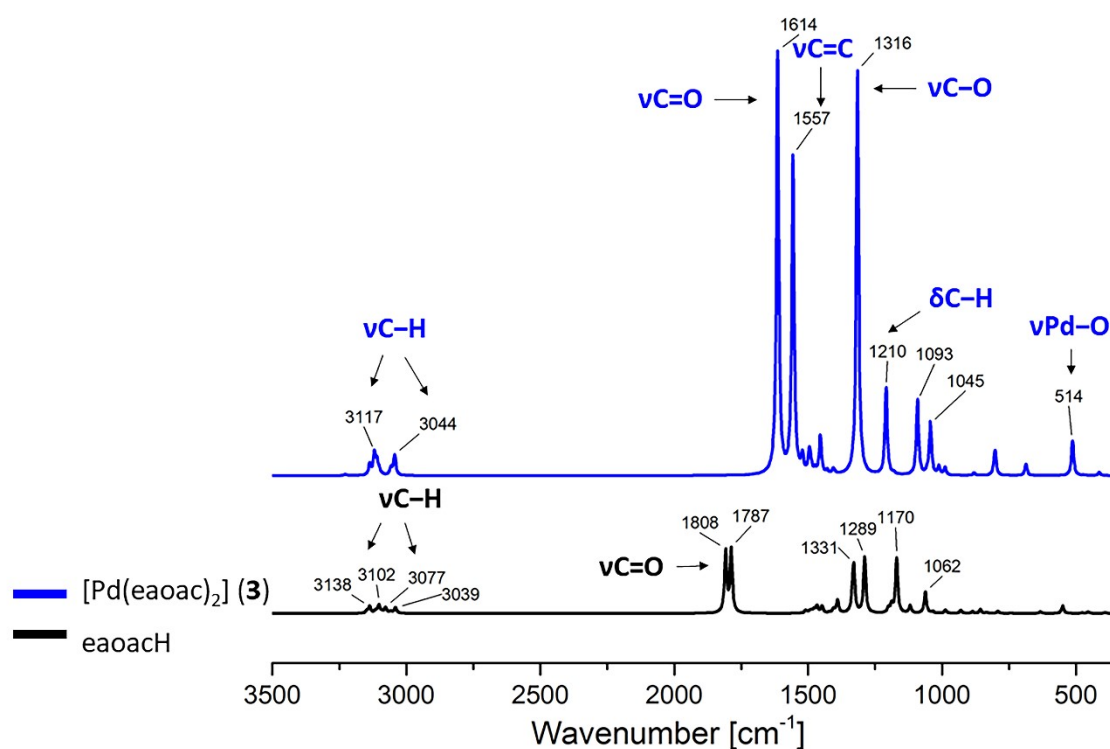


Figure S 19 Theoretical infrared spectra calculated by DFT B3LYP-D3/def2-TZVPP for the compound [Pd(eaoac)₂] (**3**) (blue line) and ligand eaoach (black line).

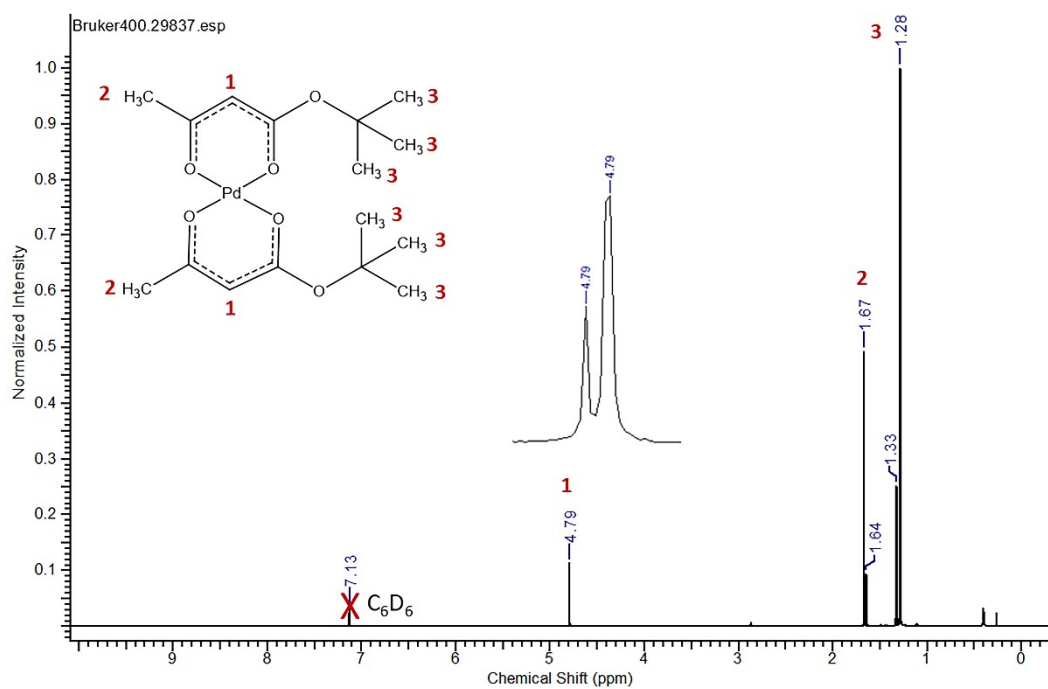


Figure S 20 ^1H NMR spectrum of the compound $[\text{Pd}(\text{tbaoac})_2]$ (1).

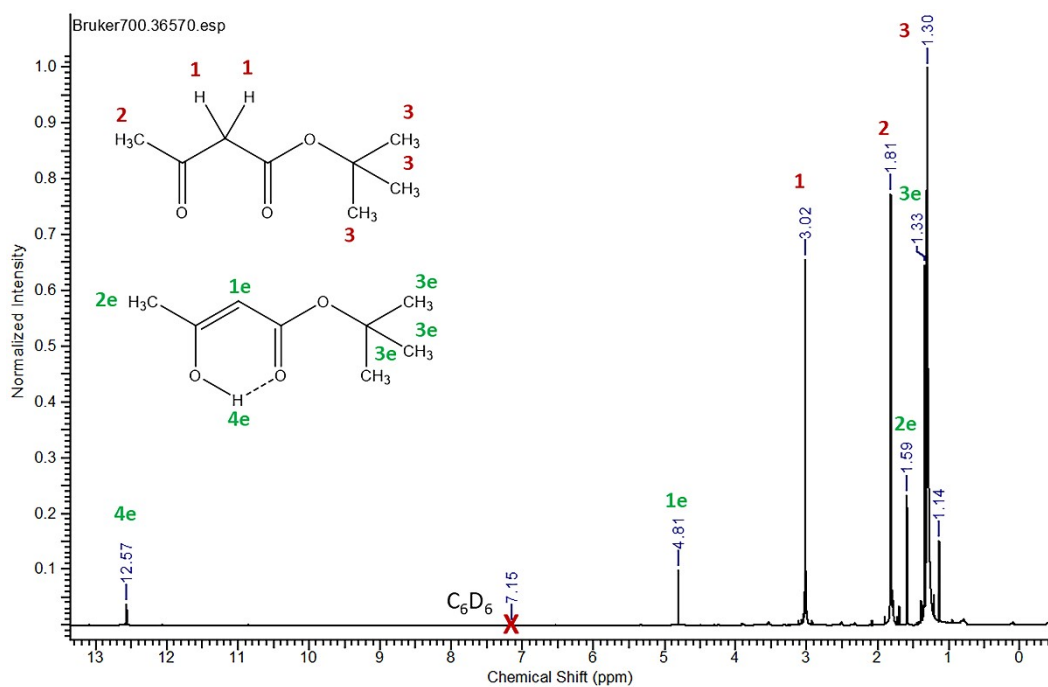


Figure S 21 ^1H NMR spectrum of the $\text{tbaoacH} - \text{MeCOCH}_2\text{CO}_2^t\text{Bu}$.

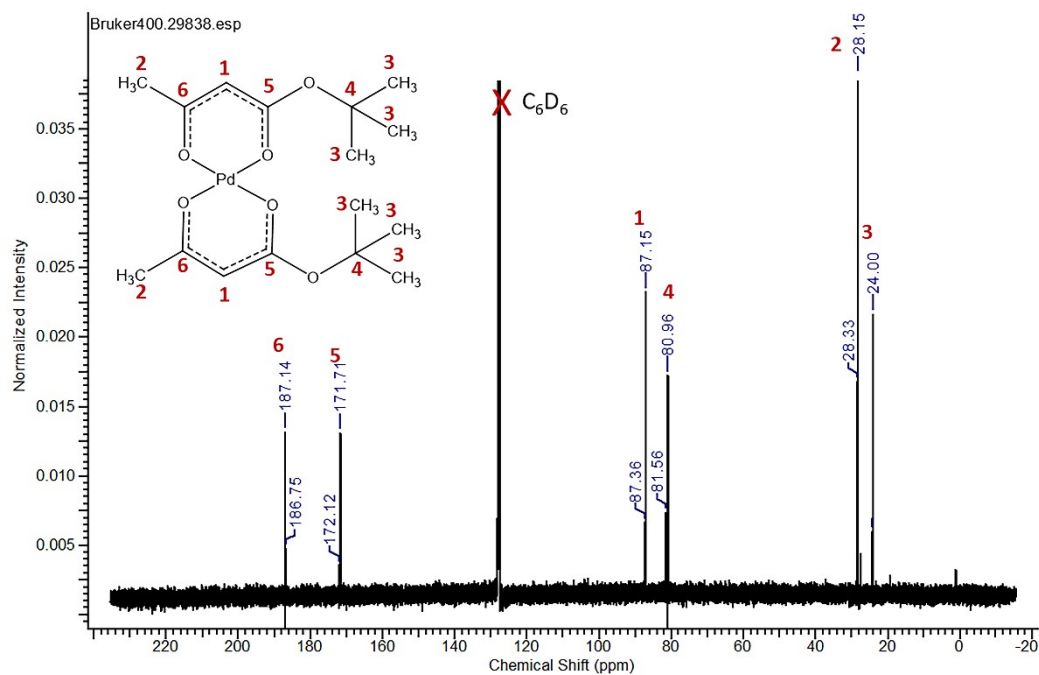


Figure S 22 ^{13}C NMR spectrum of the compound $[\text{Pd}(\text{tbaoac})_2]$ (1).

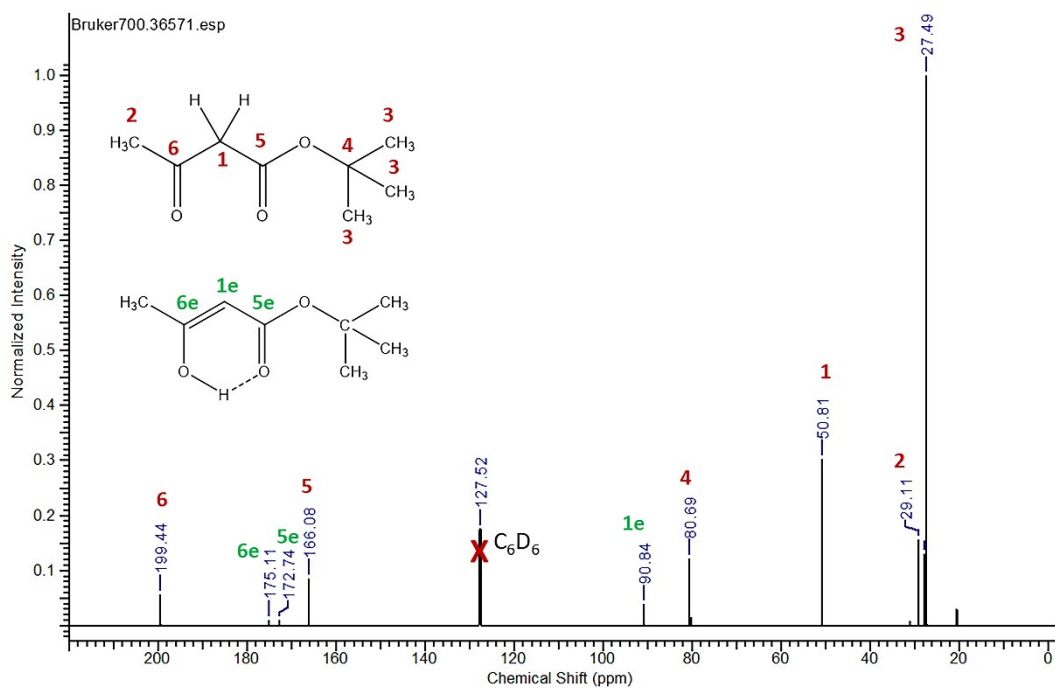


Figure S 23 ^{13}C NMR spectrum of the $\text{tbaoacH} - \text{MeCOCH}_2\text{CO}_2^t\text{Bu}$.

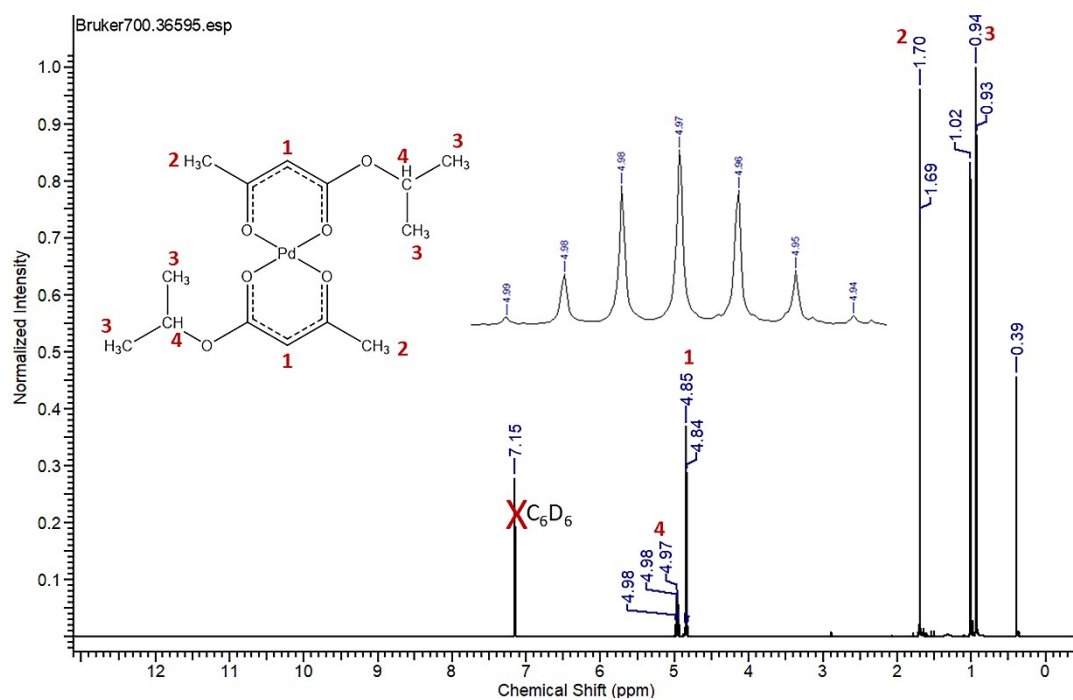


Figure S 24 ^1H NMR spectrum of the compound $[\text{Pd}(\text{ipaoac})_2]$ (2).

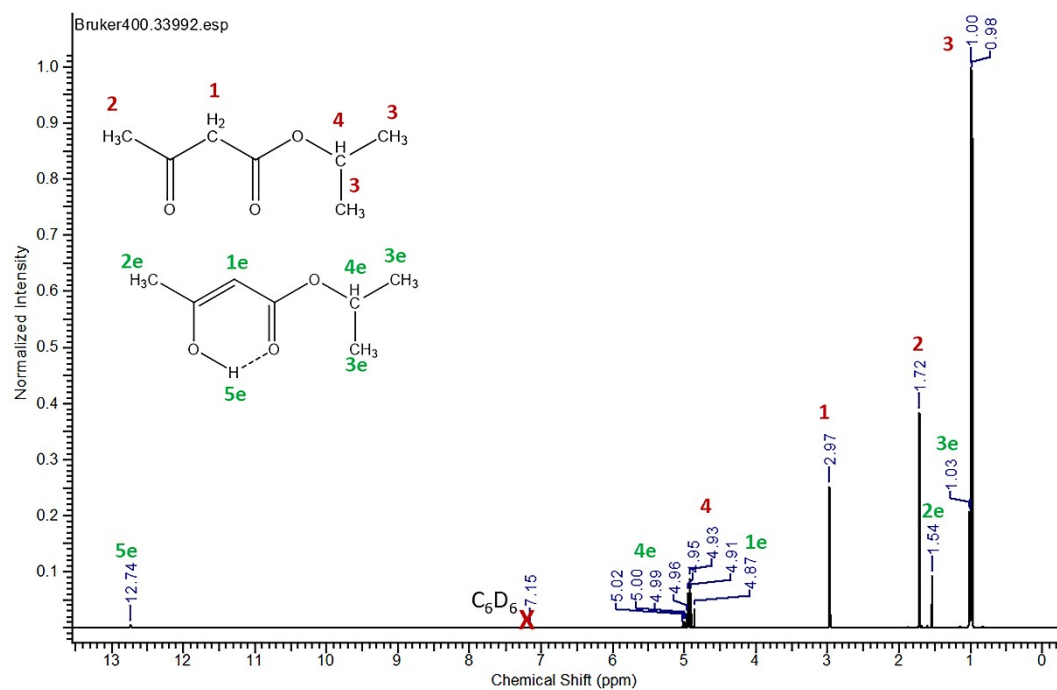


Figure S 25 ^1H NMR spectrum of the ipaoacH – $\text{MeCOCH}_2\text{CO}_2^i\text{Pr}$.

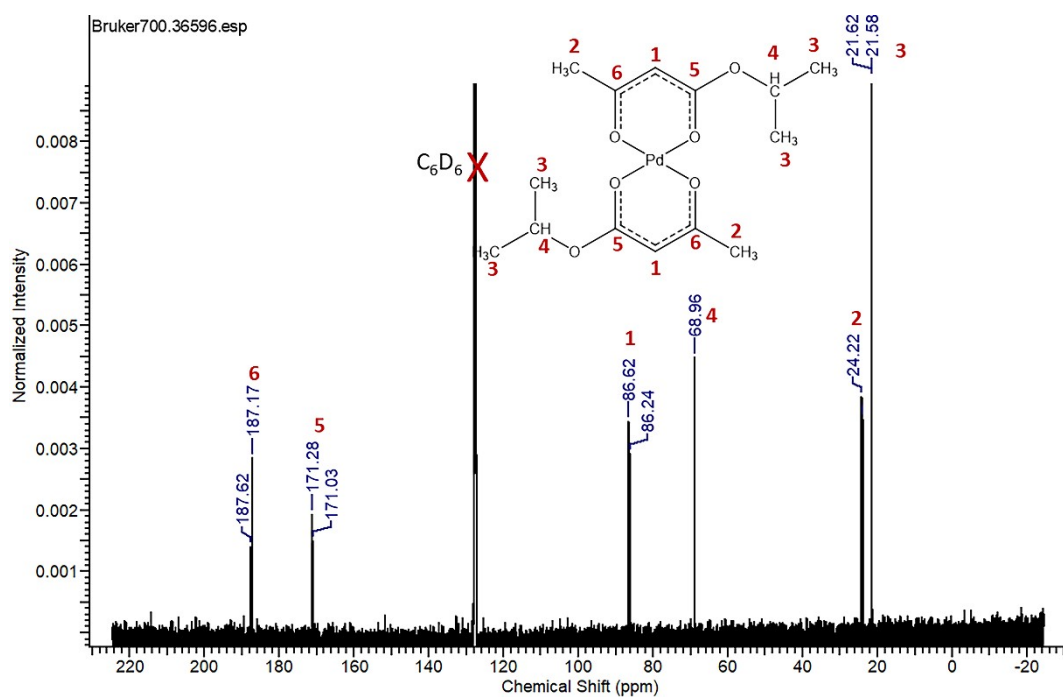


Figure S 26 ^{13}C NMR spectrum of the compound $[\text{Pd}(\text{ipaoac})_2]$ (2).

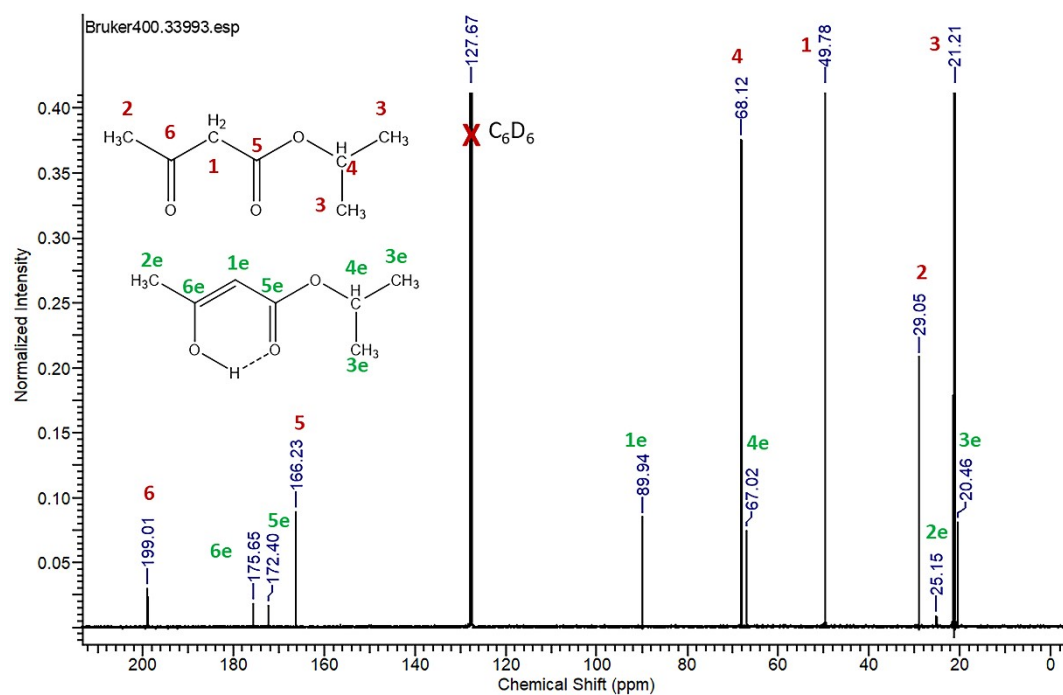


Figure S 27 ^{13}C NMR spectrum of the ipaoacH – $\text{MeCOCH}_2\text{CO}_2^i\text{Pr}$.

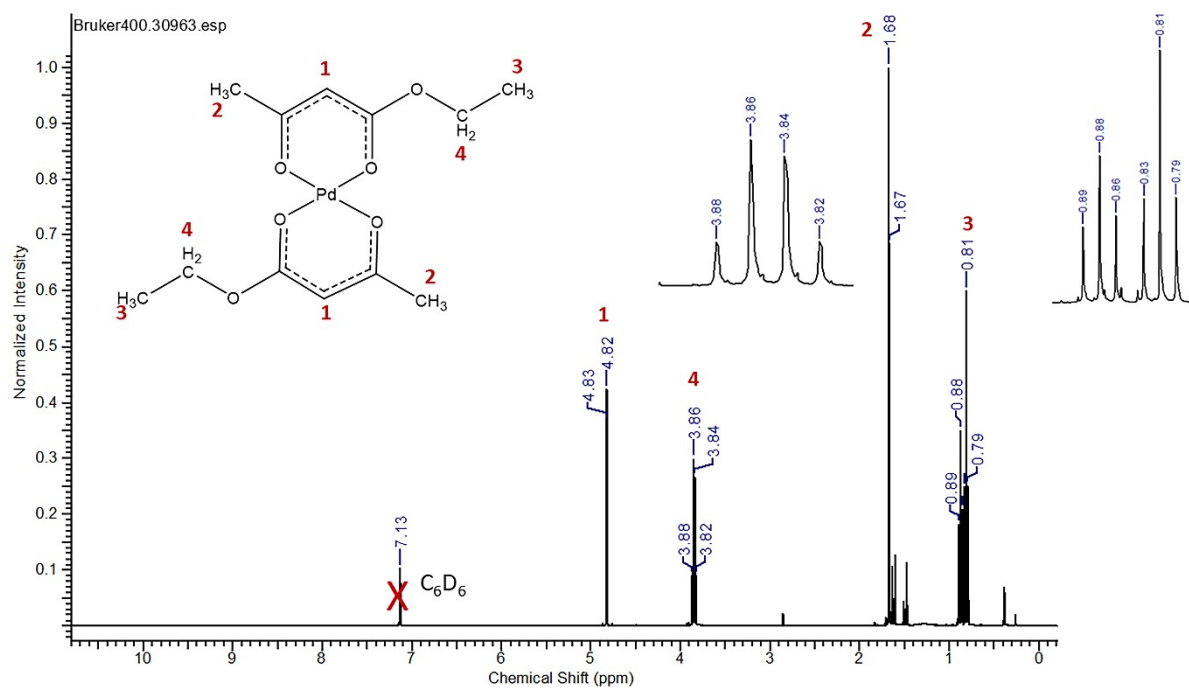


Figure S 28 ^1H NMR spectrum of the compound $[\text{Pd}(\text{eaoac})_2]$ (3).

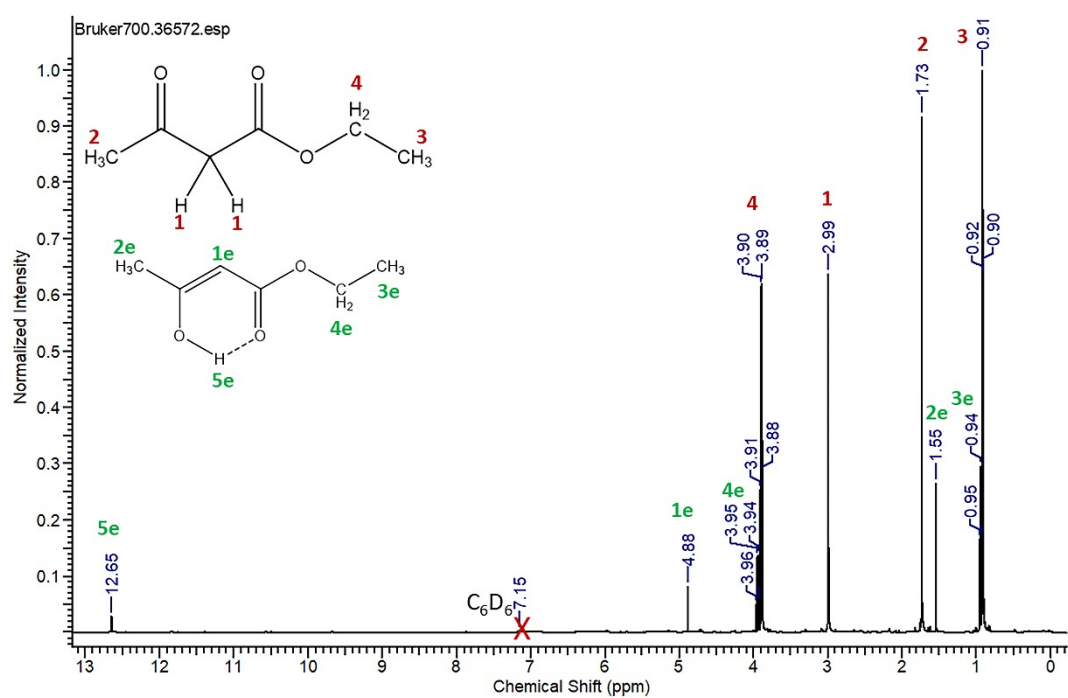


Figure S 29 ^1H NMR spectrum of the compound $\text{eaoacH} - \text{MeCOCH}_2\text{CO}_2\text{Et}$.

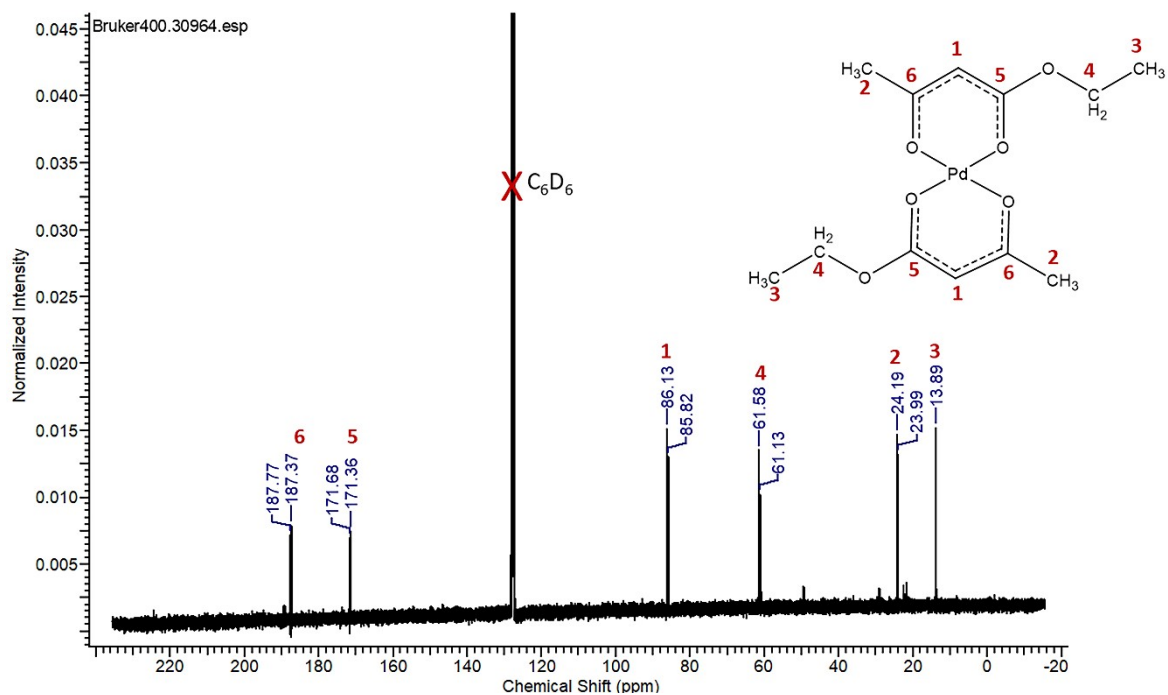


Figure S 30 ^{13}C NMR spectrum of the compound $[\text{Pd}(\text{eaoac})_2]$ (3).

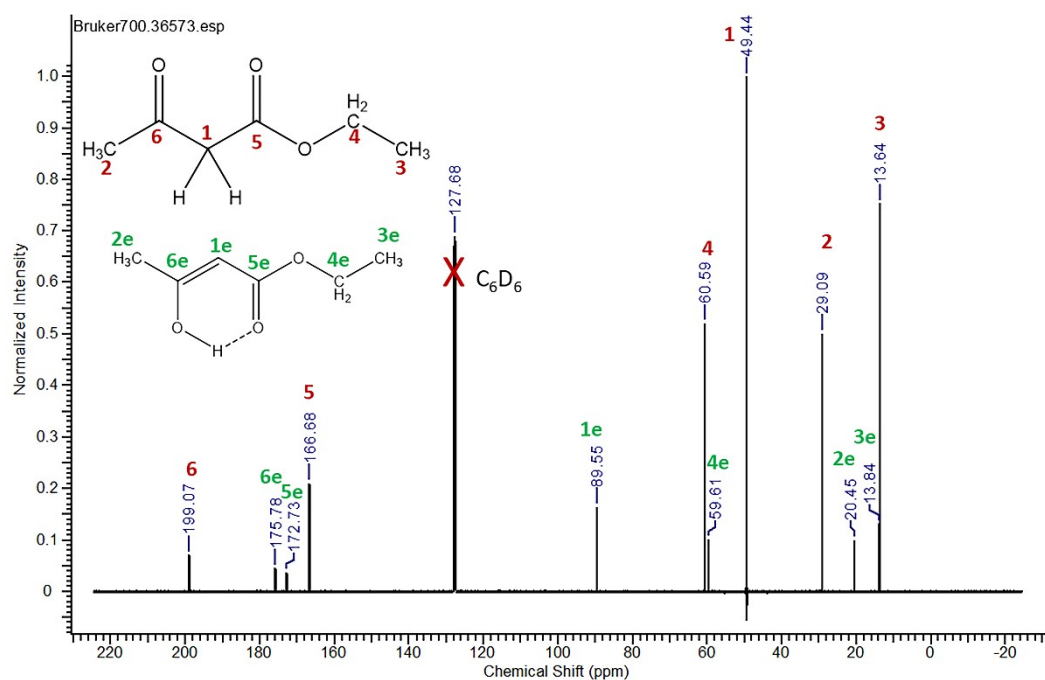


Figure S 31 ^{13}C NMR spectrum of the compound $\text{eaoacH} - \text{MeCOCH}_2\text{CO}_2\text{Et}$.

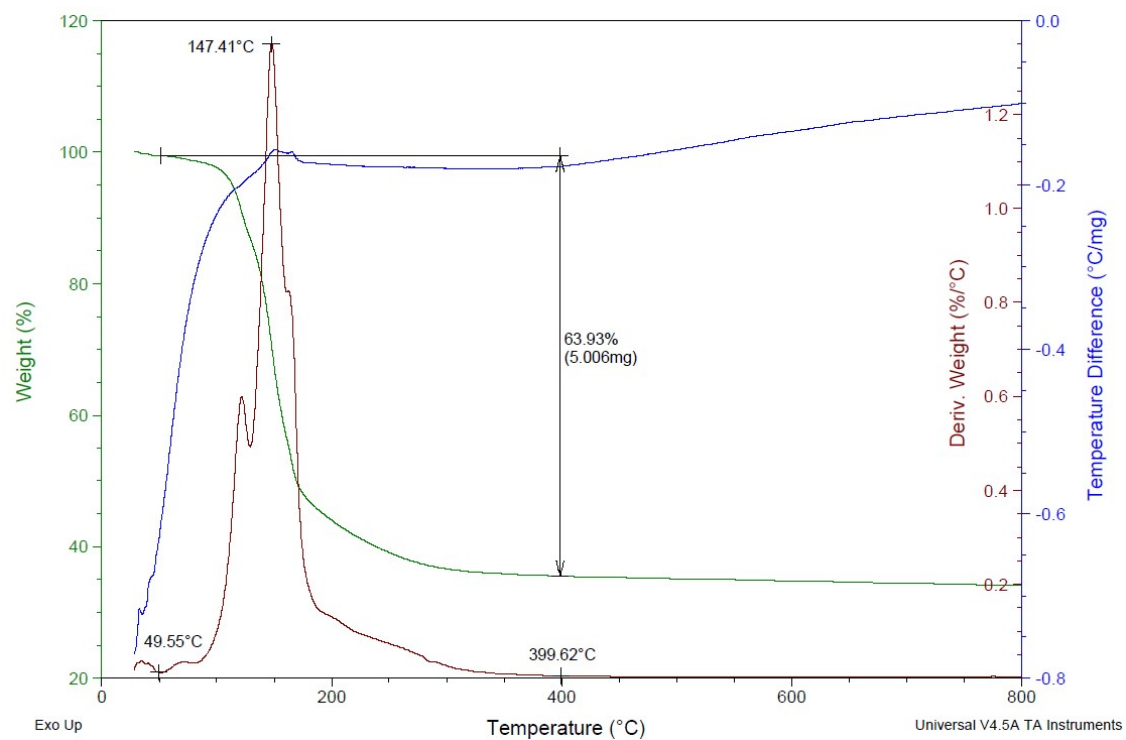


Figure S 32 Thermogram of $[\text{Pd}(\text{ipaoac})_2]$ (2) (TG, DTG, DTA curves).

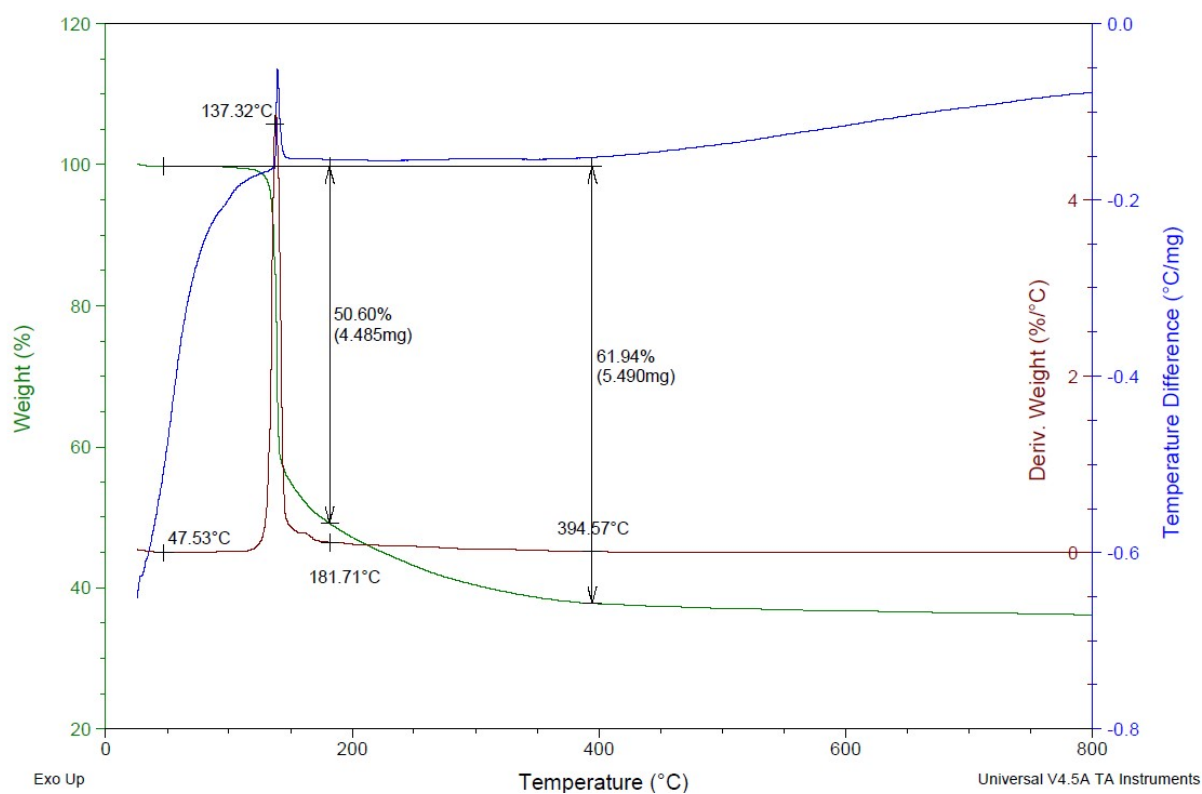


Figure S 33 Thermogram of $[\text{Pd}(\text{eaoac})_2]$ (3) (TG, DTG, DTA curves).

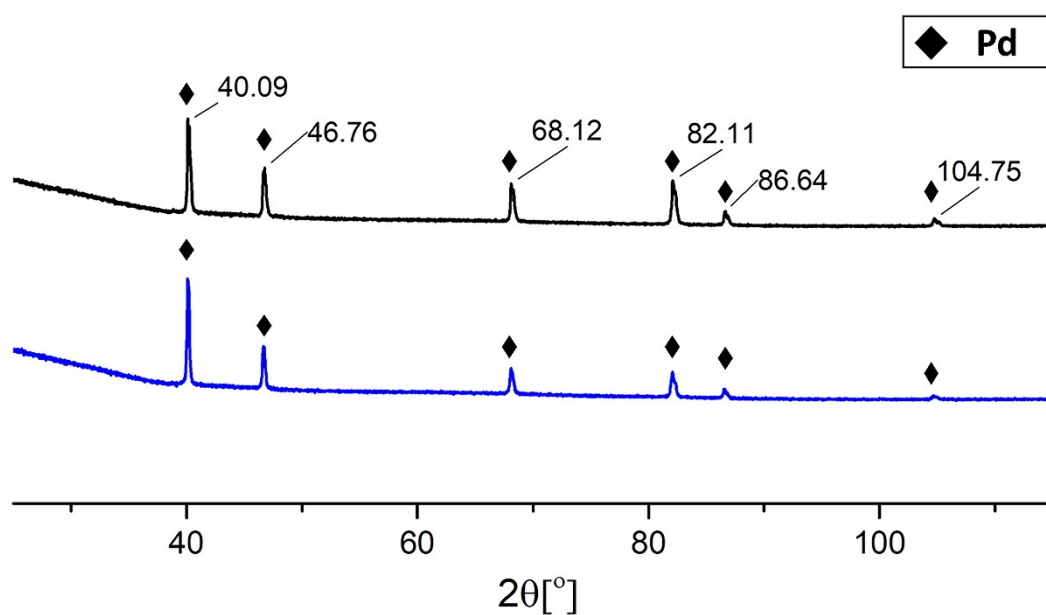


Figure S 34 XRD analysis of the residue after thermal analysis of $[\text{Pd}(\text{ipaoac})_2]$ (2) and $[\text{Pd}(\text{eaoac})_2]$ (3).

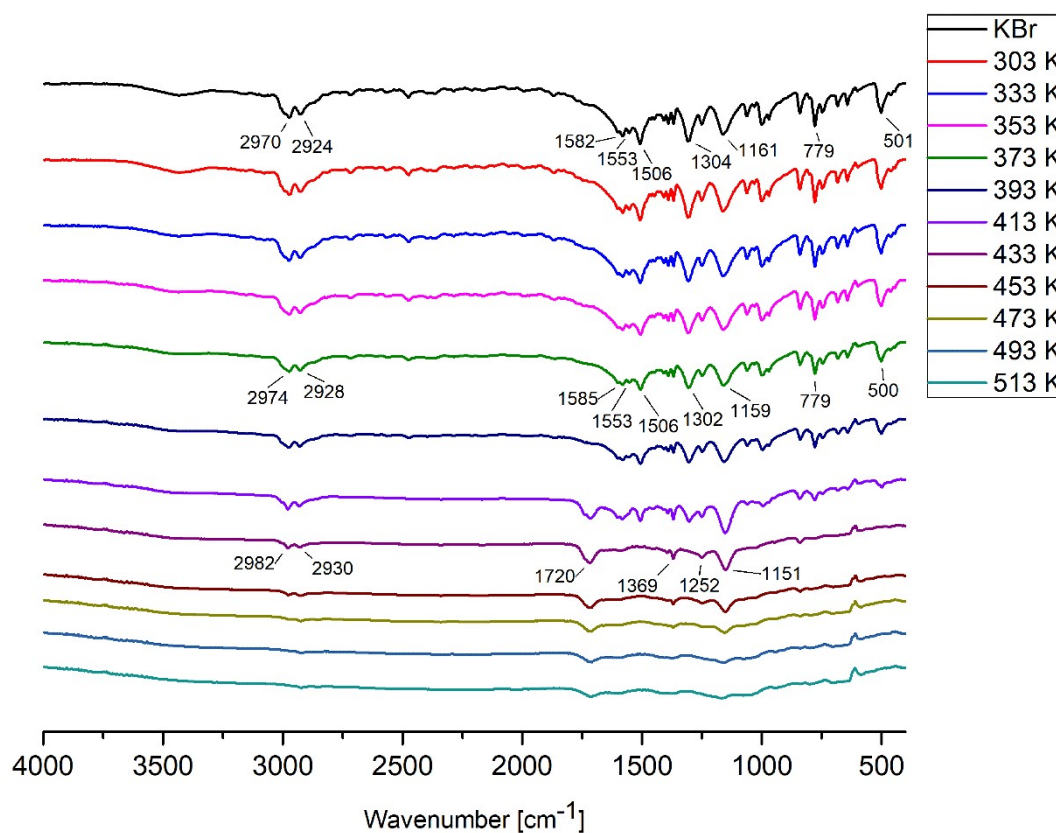


Figure S 35 VT IR spectra in the solid state for the compound $[\text{Pd}(\text{tbaoac})_2]$ (1) in the temperature range 303–513 K.

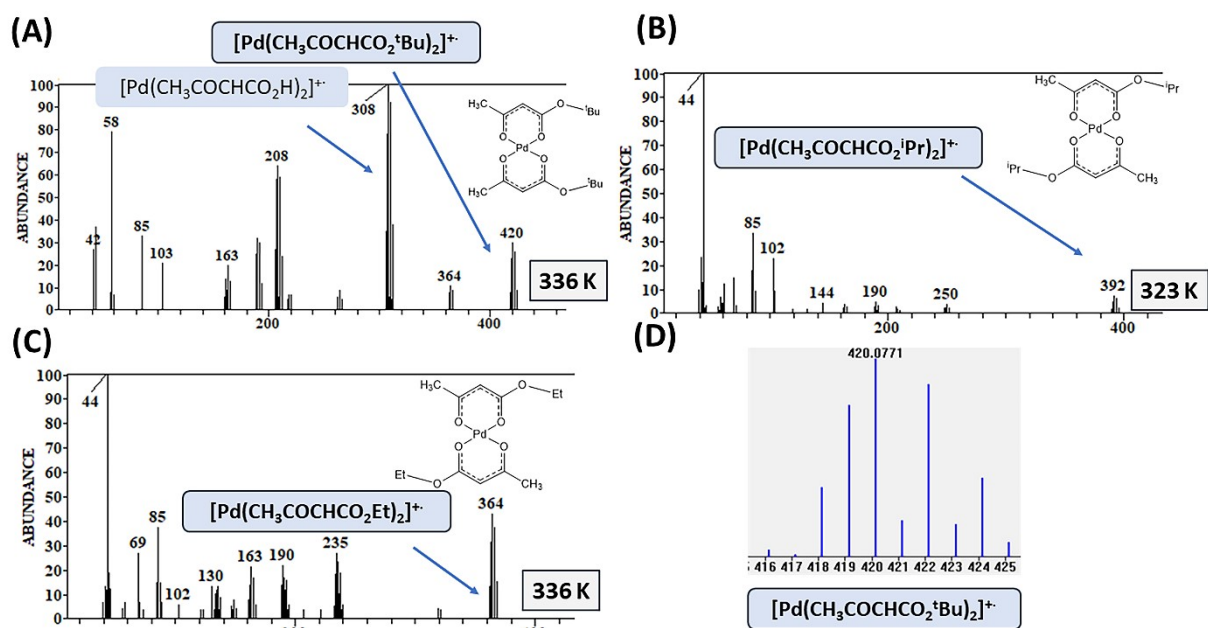


Figure S 36 EI MS spectra, where the molecular ions appeared: (A) – $[\text{Pd}(\text{tbaoac})_2]$ (**1**) at the temperature 336 K, (B) – $[\text{Pd}(\text{ipaoac})_2]$ (**2**) at 323 K and (C) – $[\text{Pd}(\text{eaoac})_2]$ (**3**) at 336 K, and (D) – isotopic pattern simulation for the molecular ion $[\text{Pd}(\text{tbaoac})_2]^+$.

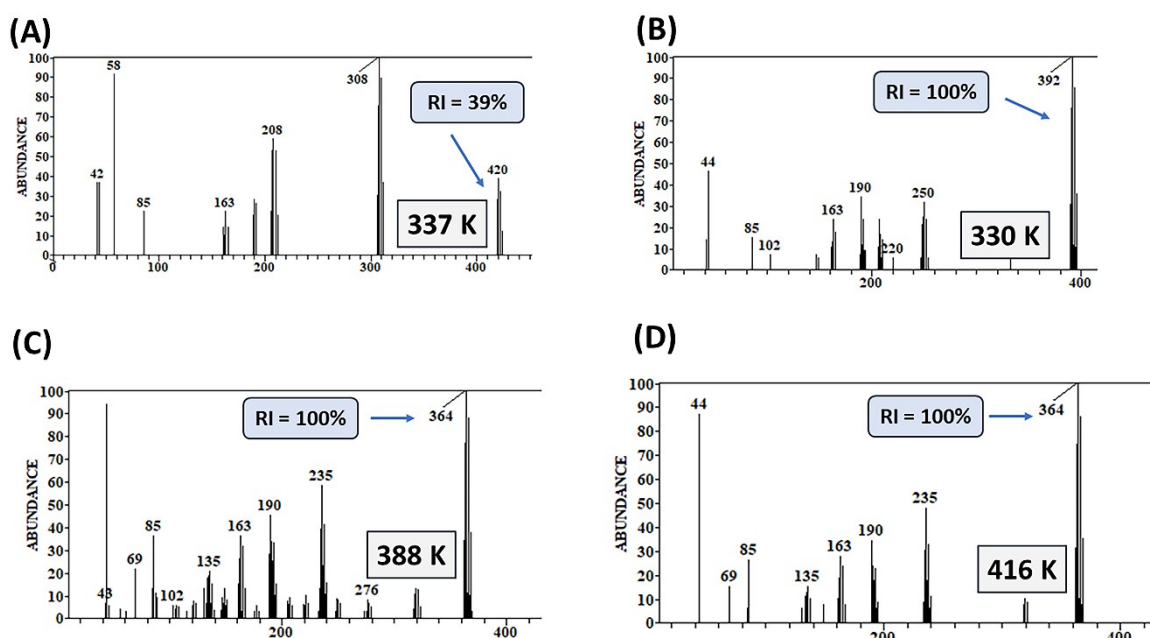


Figure S 37 EI MS spectra, where the molecular ions achieved the highest relative intensity: (A) – $[\text{Pd}(\text{tbaoac})_2]$ (**1**) at the temperature 337 K, (B) – $[\text{Pd}(\text{ipaoac})_2]$ (**2**) at 330 K and (C) – $[\text{Pd}(\text{eaoac})_2]$ (**3**) at 388 K, and (D) – at 416 K.

Table S 5 EI MS results for the complex [Pd(tbaoac)₂] (**1**).

Fragments	m/z	Relative Intensity (RI) [%]			
		336 K	342 K	349 K	365 K
[CHCO] ⁺	41	—	2	1	1
[CH ₂ =CO] ⁺	42	27	48	4	4
[CH ₃ CO] ⁺	43	—	6	14	11
[CH ₃ CHO] ⁺ /[CO ₂] ⁺	44	37	51	100	100
[CO ₂ H] ⁺	45	—	2	11	7
[HCOOH] ⁺	46	—	3	64	37
[CH ₃ COCH] ⁺ /[(CH ₃) ₂ C=CH ₂] ⁺	56	—	4	1	<1
[CH ₃ COCH ₂] ⁺ /[^t Bu] ⁺	57	8	8	1	1
[(CH ₃) ₂ CO] ⁺ /[C ₄ H ₁₀] ⁺	58	79	100	1	1
[CH ₃ CO ₂ H] ⁺	60	7	9	38	20
[CH ₃ COCH ₂ C] ⁺ /[^t BuC] ⁺	69	—	2	—	—
[CH ₃ COCH ₂ CO] ⁺ /[^t BuCO] ⁺	85	33	23	—	—
[CH ₃ COCH ₂ CO ₂ H] ⁺ /[^t BuOCHO] ⁺	102	—	2	—	—
[CH ₃ COCH ₂ C(OH) ₂] ⁺ /[^t BuOCHOH] ⁺	103	21	33	—	—
[Pd(CH ₃ COCH ₂)] ⁺	163	20	6	—	—
[Pd(CH ₃ COCHCO)] ⁺	190	32	5	—	—
[Pd(CH ₃ COCH ₂ CO ₂ H)] ⁺	208	64	7	—	—
[Pd(CH ₃ COCH ₂ CO ₂ ^t Bu)] ⁺	264	9	1	—	—
[Pd(CH ₃ COCH ₂ CO ₂) ₂] ⁺	308	100	5	—	—
[Pd(CH ₃ COCHCO ₂ ^t Bu)(CH ₃ COCH ₂ CO ₂)] ⁺	364	11	1	—	—
[Pd(CH ₃ COCHCO ₂ ^t Bu) ₂] ⁺	420	30	2	—	—

Table S 6 EI MS results for the complex [Pd(ipaoac)₂] (**2**).

Fragments	m/z	Relative Intensity (RI) [%]			
		323 K	328 K	332 K	349 K
[CHCO] ⁺	41	—	—	—	—
[CH ₂ =CO] ⁺	42	23	18	22	30
[CH ₃ CO] ⁺	43	12	9	17	9
[CH ₃ CHO] ⁺ /[CO ₂] ⁺	44	100	100	100	100
[CO ₂ H] ⁺	45	2	2	—	12
[HCOOH] ⁺	46	3	3	—	32
[CH ₃ COCH] ⁺	56	3	2	—	—
[CH ₃ COCH ₂] ⁺	57	2	2	—	—
[(CH ₃) ₂ CO] ⁺	58	7	5	—	9
[CH ₃ CO ₂ H] ⁺	60	4	22	—	9
[CH ₃ COCH ₂ C] ⁺	69	15	12	—	45
[CH ₃ COCH ₂ CO] ⁺	85	33	82	24	19
[ⁱ PrCO ₂] ⁺	87	9	23	—	—
[CH ₃ COCH ₂ CO ₂ H] ⁺	102	23	75	—	15
[CH ₃ COCH ₂ C(OH) ₂] ⁺	103	9	37	—	—
[CH ₃ COCH ₂ CO ₂ ⁱ Pr] ⁺	144	4	22	—	—
[Pd(CH ₃ COCH ₂)] ⁺	163	4	29	—	—
[Pd(CH ₃ COCHCO)] ⁺	190	2	43	—	—
[Pd(CH ₃ COCH ₂ CO ₂ ⁱ Pr)] ⁺	250	4	35	—	—
[Pd(CH ₃ COCHCO ₂ ⁱ Pr)(CH ₃ COCHCO)] ⁺	333	—	5	—	—
[Pd(CH ₃ COCHCO ₂ ⁱ Pr) ₂] ⁺	392	7	49	98	—

Table S 7 EI MS results for the complex [Pd(eaoac)₂] (**3**).

Fragments	m/z	Relative Intensity (RI) [%]				
		336 K	339 K	375 K	419 K	422 K
[CHCO] ⁺	41	—	4	—	—	—
[CH ₂ CO] ⁺	42	13	24	—	3	—
[CH ₃ CO] ⁺	43	12	13	12	16	14
[CH ₃ CHO] ⁺ /[CO ₂] ⁺	44	100	100	100	100	100
[CO ₂ H] ⁺	45	19	64	—	4	6
[HCOOH] ⁺	46	12	16	6	6	5
[CH ₃ COCH] ⁺	56	4	8	5	4	—
[CH ₃ COCH ₂] ⁺	57	—	—	—	4	—
[(CH ₃) ₂ CO] ⁺	58	7	9	—	—	—
[CH ₃ CO ₂ H] ⁺	60	—	8	—	7	8
[CH ₃ COCH ₂ C] ⁺	69	27	25	27	22	18
[CH ₃ COCH ₂ CO] ⁺	85	37	34	36	32	24
[CH ₃ COCH ₂ CO ₂ H] ⁺ /[OCHCO ₂ Et] ⁺	102	6	6	5	6	—
[CH ₃ COCH ₂ CO ₂ Et] ⁺	130	13	14	12	13	9
[Pd(CH ₃ COCH ₂)] ⁺	163	21	19	29	20	—
[Pd(CH ₃ COCHCO)] ⁺	190	22	22	32	23	—
[Pd(CH ₃ COCHCOOEt)] ⁺	235	27	29	40	30	—
[Pd(CH ₃ COCHCO ₂ Et)(CH ₃ COCHCO)] ⁺	319	4	5	7	7	—
[Pd(CH ₃ COCHCO ₂ Et) ₂] ⁺	364	43	58	66	57	—

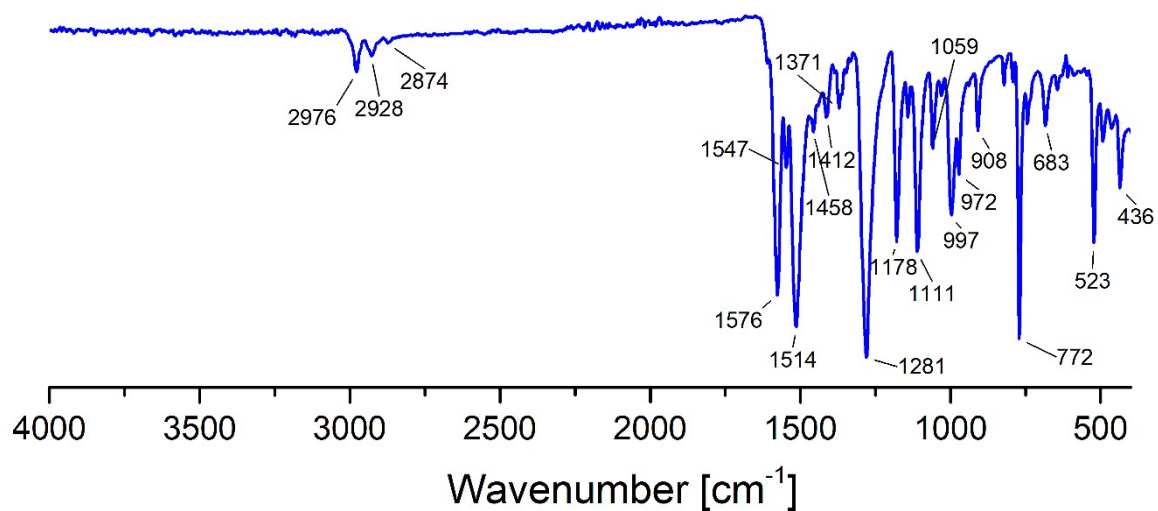


Figure S 38 Infrared spectrum for the compound [Pd(ipaoac)₂] (**2**) after sublimation (blue) at 353 K ($p = 10^{-2}$ mbar).

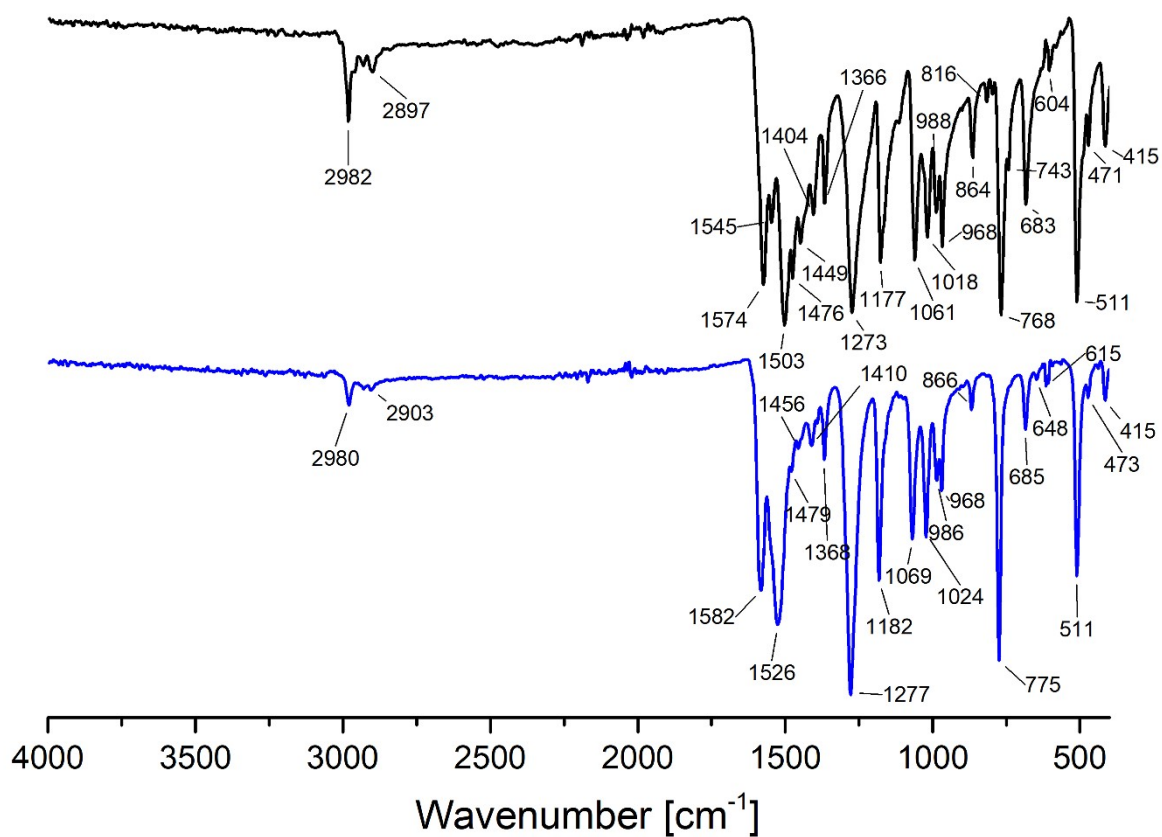


Figure S 39 Infrared spectra for the compound [Pd(eaoac)₂] (**3**) before (black) and after sublimation (blue) at 353 K ($p = 10^{-2}$ mbar).

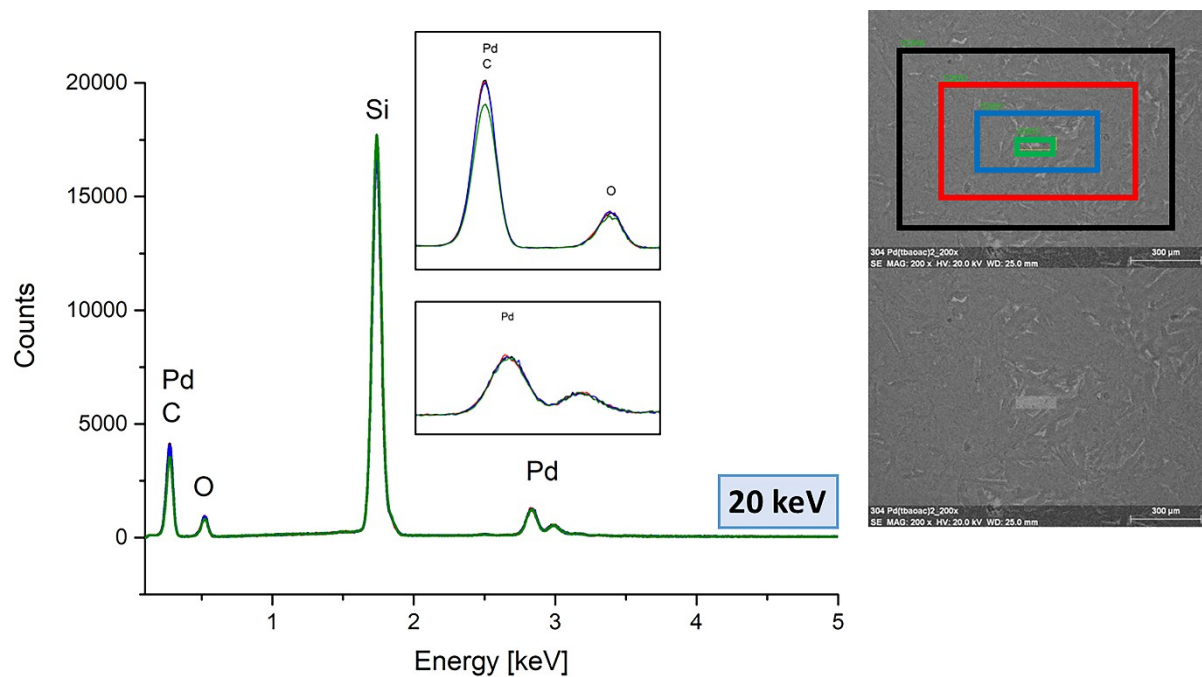


Figure S 40 Examined scan areas' EDX spectra (20 keV) for the $[\text{Pd}(\text{tbaoac})_2]$ (1) layer deposited on a Si(111) substrate (Mag = 200x).

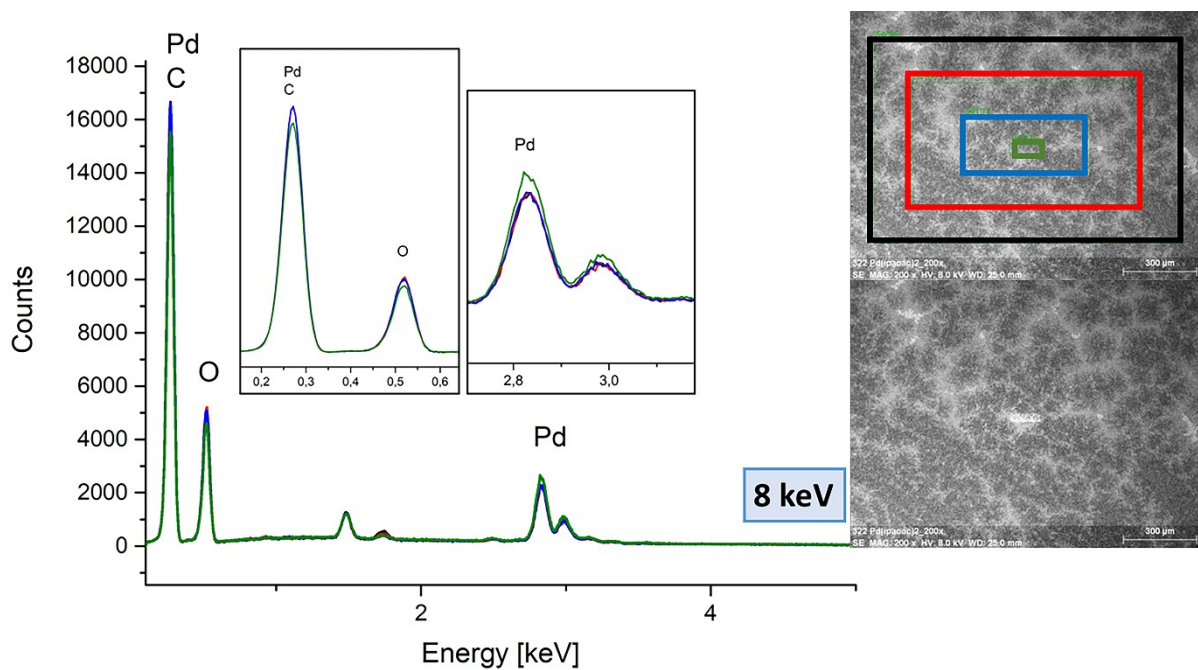


Figure S 41 Examined scan areas' EDX spectra (8 keV) for the $[\text{Pd}(\text{ipaoac})_2]$ (2) layer deposited on a Si(111) substrate (Mag = 200x).

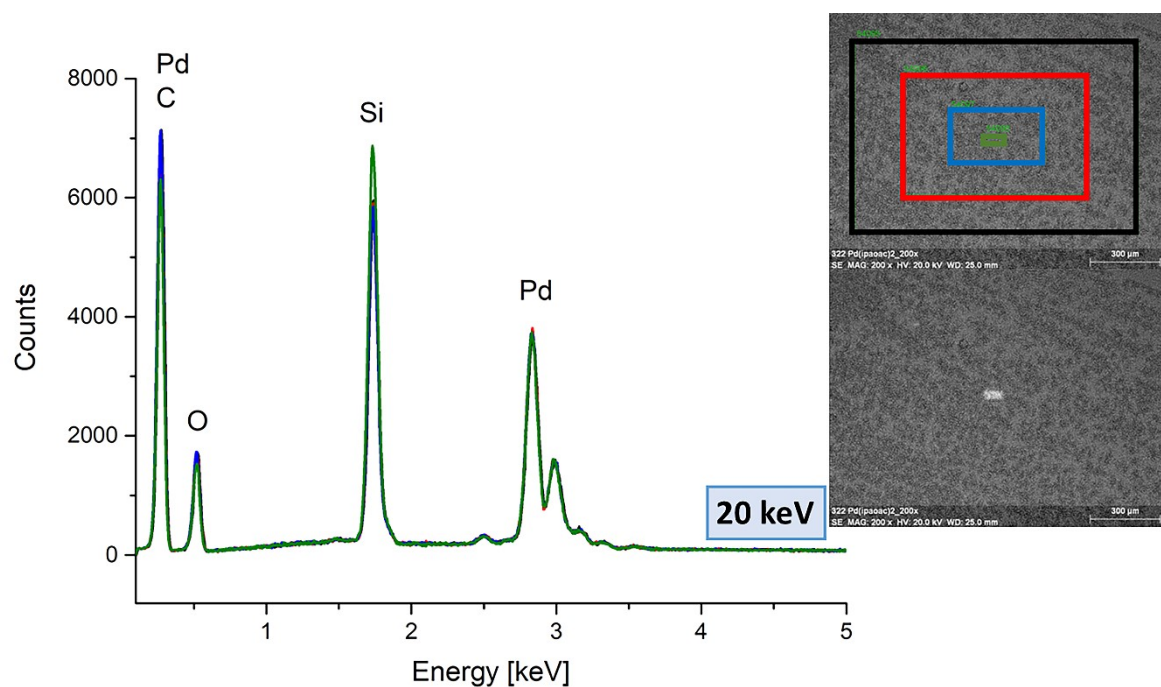


Figure S 42 Examined scan areas' EDX spectra (20 keV) for the [Pd(ipaoac)₂] (2) layer deposited on a Si(111) substrate (Mag = 200x).

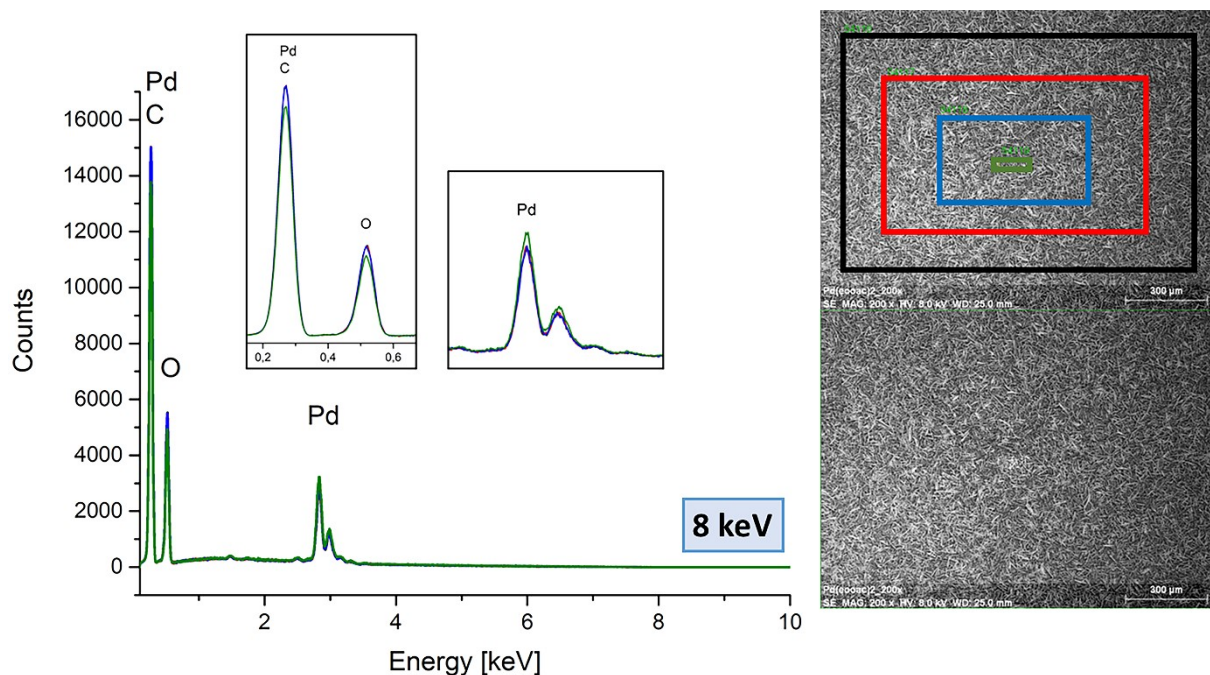


Figure S 43 Examined scan areas' EDX spectra (8 keV) for the [Pd(eaoac)₂] (3) layer deposited on a Si(111) substrate (Mag = 200x).

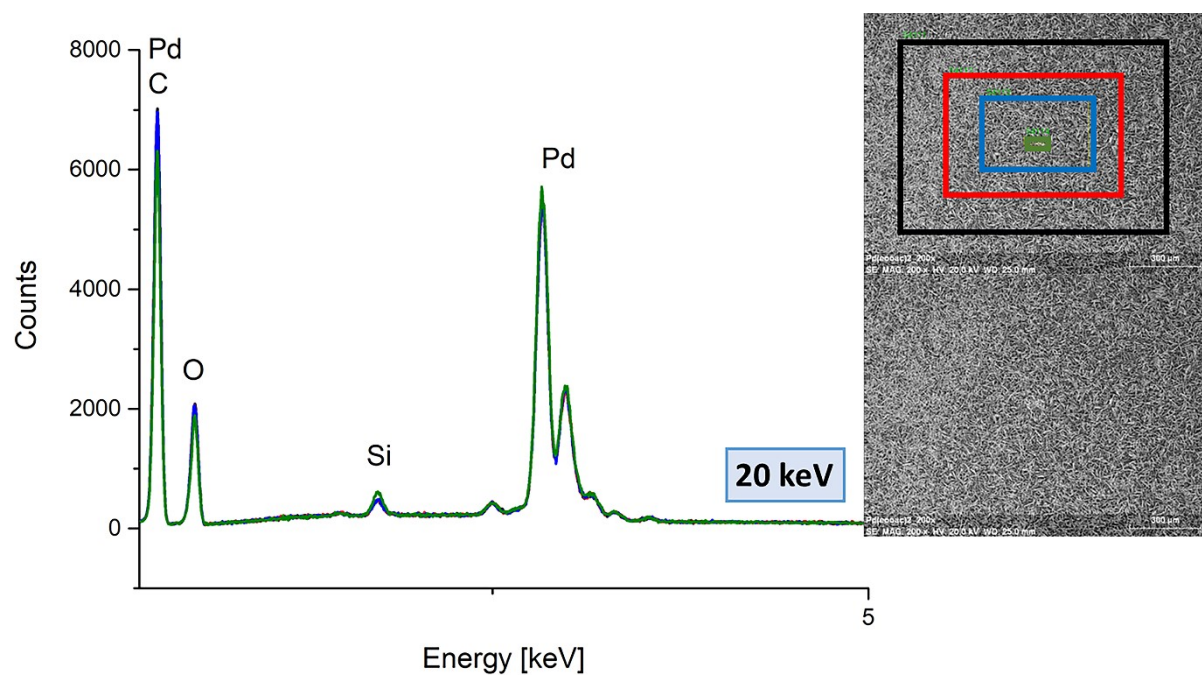


Figure S 44 Examined scan areas' EDX spectra (20 keV) for the $[\text{Pd}(\text{eaoac})_2]$ (**3**) layer deposited on a Si(111) substrate (Mag = 200x).

Toruń, dnia 29.05.2025

Mgr Aleksandra Butrymowicz-Kubiak

.....
(tytuł, stopień, imię i nazwisko kandydata/współautora)

Szkoła Doktorska Nauk Ścisłych i Przyrodniczych AST

Wydział Chemii

Uniwersytet Mikołaja Kopernika w Toruniu

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.....
(jednostka zatrudniająca kandydat/współautora)

**Rada Dyscypliny Chemia
Uniwersytetu Mikołaja Kopernika
w Toruniu**

Oświadczenie o współautorstwie

Niniejszym oświadczam, że w pracy:

[D1] Martinović P., Rohdenburg M., **Butrymowicz A.**, Sarigül S., Huth P., Denecke R., Szymańska I. B., Swiderek P., Electron-Induced Decomposition of Different Silver(I) Complexes: Implications for the Design of Precursors for Focused Electron Beam Induced Deposition, *Nanomaterials* 2022, 12, 1687 mój udział polegał na:

- syntezie związków kompleksowych srebra,
- uczestnictwie w przeprowadzaniu eksperymentów ESD.

[D2] **Butrymowicz-Kubiak A.**, Luba W.; Madajska K.; Muzioł T.M.; Szymańska I.B. Pivalate complexes of copper(II) with aliphatic amines as potential precursors for depositing nanomaterials from the gas phase, *New J. Chem.*, 2024, 48, 6232 mój udział polegał na:

- syntezie związków kompleksowych miedzi(II) wraz z otrzymaniem monokryształów odpowiednich do pomiarów dyfraktometrycznych,
- charakterystyce otrzymanych związków w oparciu o metody spektroskopowe: IR, EI MS,
- opracowaniu warunków otrzymywania warstw kompleksów w procesie sublimacji,
- opracowaniu uzyskanych wyników dotyczących stabilności termicznej kompleksów, lotności i wrażliwości na elektrony: analizy termicznej, EI MS, IR, SEM-EDX, TEM-EDX,
- opracowaniu warunków otrzymywania warstw miedzi w procesie CVD i charakterystyka depozytów w oparciu o SEM-EDX, AFM,
- omówieniu i interpretacji uzyskanych wyników,
- przygotowaniu części rysunków i tabel znajdujących się w manuskrypcie,
- przygotowaniu manuskryptu.

[D3] **Butrymowicz-Kubiak A.**; Topolski A.; Muzioł T.M.; Szymańska I.B. Nickel complexes based on perfluorinated amidine for applications in gas-assisted methods and photocatalysis, *Dalt. Trans.*, 2025, (*praca zaakceptowana do druku*) mój udział polegał na:

- współtworzeniu merytorycznej koncepcji badań,
- syntezie związków kompleksowych niklu(II) wraz z otrzymaniem monokryształu odpowiedniego do pomiarów dyfraktometrycznych,
- wykonaniu oraz charakterystyce analizy powierzchni Hirshfelda otrzymanego monokryształu (wspólnie z dr Tadeusz Muzioł),
- charakterystyce otrzymanych związków w oparciu o metody spektroskopowe (IR, EI MS), rentgenostrukturalne, a także obliczenia teoretyczne,
- opracowaniu warunków otrzymywania warstw kompleksów w procesie sublimacji, wykonaniu pomiarów VT IR,
- opracowaniu warunków otrzymywania warstw na bazie niklu w procesie CVD na różnych podłożach, w tym przygotowanie materiału poddanego testom aktywności forokatalitycznej,
- przygotowaniu rysunków i tabel znajdujących się w manuskrypcie,
- omówieniu i interpretacji uzyskanych wyników,
- przygotowaniu manuskryptu,
- komunikacji z redakcją czasopisma podczas procesu publikacji.

[D4] **Butrymowicz-Kubiak A.**; Muzioł T.M.; Madajski P.; Szymańska I.B. New Gold(I) Complexes as Potential Precursors for Gas-Assisted Methods: Structure, Volatility, Thermal Stability, and Electron Sensitivity, *Molecules*, 2025, 30, 146 mój udział polegał na:

- współtworzeniu merytorycznej koncepcji badań,
- syntezie związków kompleksowych złota(I) wraz z otrzymaniem monokryształu odpowiedniego do pomiarów dyfraktometrycznych,
- charakterystyce otrzymanych związków w oparciu o metody spektroskopowe (IR, EI MS), rentgenostrukturalne,
- opracowaniu warunków otrzymywania warstw kompleksów w procesie sublimacji, wykonanie pomiarów VT IR,
- opracowaniu warunków otrzymywania warstw na bazie niklu w procesie CVD na różnych podłożach, w tym przygotowanie materiału poddanego testom aktywności forokatalitycznej,
- omówieniu i interpretacji uzyskanych wyników,
- przygotowaniu rysunków i tabel znajdujących się w manuskrypcie,
- przygotowaniu manuskryptu.

[D5] **Butrymowicz-Kubiak A.**; Muzioł T.M.; Kaczmarek Kędziera A.; Jureddy C.S.; Maćkosz K.; Utke I.; Szymańska I.B. New palladium(II) β -ketoesterates for Focused Electron Beam Induced Deposition: Synthesis, structures, and characterization, *Dalt. Trans.*, 2024, 53, 13662 mój udział polegał na:

- współtworzeniu merytorycznej koncepcji badań,
- syntezie związków kompleksowych palalldu(II) wraz z otrzymaniem monokryształów odpowiednich do pomiarów dyfraktometrycznych,
- charakterystyce otrzymanych związków w oparciu o metody spektroskopowe (IR, ^1H , ^{13}C NMR, EI MS), rentgenostrukturalne, a także obliczenia teoretyczne (widm IR wspólnie wykonane z dr hab. Anna Kaczmarek-Kędziera),
- wykonaniu oraz charakterystyce analizy powierzchni Hirshfelda otrzymanych monokryształów,
- opracowaniu warunków otrzymywania warstw kompleksów w procesie sublimacji,
- otrzymaniu depozytu FEBID (wspólnie z dr Krzysztof Maćkosz i doktorantką C. S. Jureddy)
- omówieniu i interpretacji uzyskanych wyników,

- przygotowaniu rysunków i tabel znajdujących się w manuskrypcie,
- przygotowaniu manuskryptu.

.....
(podpis)

Informacja o przetwarzaniu danych osobowych

Na podstawie Rozporządzenia Parlamentu Europejskiego i Rady (UE) 2016/679 z dnia 27 kwietnia 2016 r. w sprawie ochrony osób fizycznych w związku z przetwarzaniem danych osobowych i w sprawie swobodnego przepływu takich danych oraz uchylenia dyrektywy 95/46/WE, zwanego dalej „RODO”, informujemy, że:

1. Administratorem Pana/Pani danych osobowych będzie Uniwersytet Mikołaja Kopernika w Toruniu z siedzibą przy ul. Gagarina 11, 87-100 Toruń (dalej: Uczelnia, ADO).
2. Pana/Pani dane osobowe w związku z postępowaniem o nadanie stopnia naukowego będą przetwarzane:
 - a. na podstawie art. 6 ust. 1 lit. c) RODO – obowiązek prawny wynikający z przepisów ustawy z dnia 20 lipca 2018 r. Prawo o szkolnictwie wyższym i nauce (Dz. U. z 2020, poz. 85);
 - b. na podstawie art. 6 ust. 1 lit. f) RODO – prawnie uzasadniony interes ADO:
 - do ustalenia, obrony lub dochodzenia roszczeń – przez okres do przedawnienia roszczeń, lub przez okres prowadzenia postępowania przez właściwe organy lub sądy w przypadku dochodzenia roszczeń,
 - na potrzeby wewnętrzne tworzenia zestawień, analiz i statystyk – przez okres obowiązywania umowy,
 - na potrzeby prowadzenia ewidencji korespondencji przychodzącej i wychodzącej – wieczyście,
 - na potrzeby marketingu produktów i usług ADO.
3. Z zastrzeżeniem przepisów powszechnie obowiązującego prawa przysługują Panu/Pani prawa, które zrealizujemy na wniosek o:
 - a. Żądanie dostępu do danych osobowych oraz prawo ich sprostowania,
 - b. Żądanie usunięcia lub ograniczenia przetwarzania.
4. Przysługuje Panu/Pani również prawo wniesienia sprzeciwu na przetwarzanie danych osobowych.
5. Podanie przez Pana/Panią danych osobowych jest niezbędne do wykonania celu wymienionego w pkt 2 lit. a i b., a brak ich podania uniemożliwi otwarcie i przeprowadzenie postępowania.
6. Przysługuje Panu/Pani prawo wniesienia skargi do Prezesa Urzędu Ochrony Danych Osobowych.
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9. W stosunku do Pana/Pani nie będą prowadzone działania polegające na podejmowaniu decyzji w sposób zautomatyzowany, nie będą one również podlegały zautomatyzowanemu profilowaniu.
10. Jeżeli chce Pan/Pani skontaktować się z Uczelnią w sprawach związanych z przetwarzaniem danych osobowych, w szczególności w związku z wniesieniem wniosku o realizację przysługujących praw prosimy o kontakt pod adresem e-mail: iod@umk.pl lub adresem korespondencyjnym: UMK w Toruniu, ul. Gagarina 11, 87-100 Toruń, z dopiskiem „IOD”, dostępny jest również kontakt telefoniczny: 56 611 27 42.



Toruń, dnia 29.05.2025

dr hab. Iwona B. Szymańska

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(tytuł, stopień, imię i nazwisko kandydata/współautora)
Uniwersytet Mikołaja Kopernika w Toruniu

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(jednostka zatrudniająca kandydat/współautora)

**Rada Dyscypliny Chemia
Uniwersytetu Mikołaja Kopernika
w Toruniu**

Oświadczenie o współautorstwie

Niniejszym oświadczam, że w pracy:

[D1] Martinović P.; Rohdenburg M.; **Butrymowicz A.**; Sarigül S.; Huth P.; Denecke R.; Szymańska I. B.; Swiderek P. Electron-Induced Decomposition of Different Silver(I) Complexes: Implications for the Design of Precursors for Focused Electron Beam Induced Deposition, *Nanomaterials* **2022**, 12, 1687, doi:10.3390/nano12101687 mój udział polegał na przygotowaniu informacji na temat właściwości badanych związków, uczestnictwie w dyskusji wyników i korekcie manuskryptu;

[D2] Butrymowicz-Kubiak A.; Luba W.; Madajska K.; Muzioł T.; Szymańska I.B. Pivalate complexes of copper(II) with aliphatic amines as potential precursors for depositing nanomaterials from the gas phase, *New J. Chem.*, **2024**, 48, 6232, doi:10.1039/d3nj04959k mój udział polegał na przygotowaniu koncepcji i metodologii badań, moderowaniu dyskusji wyników, korekcie manuskryptu i komunikacji z redakcją czasopisma podczas procesu publikacji;

[D3] Butrymowicz-Kubiak A.; Topolski A.; Muzioł T. M.; Szymańska I. B. Nickel complexes based on perfluorinated amidine for applications in gas-assisted methods and photocatalysis, *Dalt. Trans.*, **2025**, praca przyjęta do druku, mój udział polegał na przygotowaniu koncepcji i metodologii badań, częściowej charakterystyce próbek, moderowaniu dyskusji wyników i korekcie manuskryptu oraz mentoringu podczas komunikacji z redakcją czasopisma;

[D4] Butrymowicz-Kubiak A.; Muzioł T.M.; Madajski P.; Szymańska I.B. New Gold(I) Complexes as Potential Precursors for Gas-Assisted Methods: Structure, Volatility, Thermal Stability, and Electron Sensitivity, *Molecules*, **2025**, 30, 146, doi:10.3390/molecules30010146, mój udział polegał na przygotowaniu koncepcji badań, częściowej charakterystyce próbek, moderowaniu dyskusji wyników, korekcie manuskryptu i częściowo komunikacji z redakcją czasopisma podczas procesu publikacji;

[D5] Butrymowicz-Kubiak A.; Muzioł T.M.; Kaczmarek Kędziera A.; Jureddy C.S.; Maćkosz K.; Utko I.; Szymańska I.B. New palladium(II) β -ketoesterates for Focused Electron Beam Induced Deposition: Synthesis, structures, and characterization, *Dalt. Trans.*, **2024**, 53, 13662, doi:10.1039/d4dt01287a mój udział polegał na przygotowaniu koncepcji badań, częściowej charakterystyce próbek, moderowaniu dyskusji wyników, korekcie manuskryptu i komunikacji z redakcją czasopisma podczas procesu publikacji.

.....
(podpis)

Informacja o przetwarzaniu danych osobowych

Na podstawie Rozporządzenia Parlamentu Europejskiego i Rady (UE) 2016/679 z dnia 27 kwietnia 2016 r. w sprawie ochrony osób fizycznych w związku z przetwarzaniem danych osobowych i w sprawie swobodnego przepływu takich danych oraz uchylenia dyrektywy 95/46/WE, zwanego dalej „RODO”, informujemy, że:

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 - b. na podstawie art. 6 ust. 1 lit. f) RODO – prawnie uzasadniony interes ADO:
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 - na potrzeby wewnętrzne tworzenia zestawień, analiz i statystyk – przez okres obowiązywania umowy,
 - na potrzeby prowadzenia ewidencji korespondencji przychodzącej i wychodzącej – wiece,yscie,
 - na potrzeby marketingu produktów i usług ADO.
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 - a. Żądanie dostępu do danych osobowych oraz prawo ich sprostowania,
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5. Podanie przez Pana/Panią danych osobowych jest niezbędne do wykonania celu wymienionego w pkt 2 lit. a i b., a brak ich podania uniemożliwi otwarcie i przeprowadzenie postępowania.
6. Przysługuje Panu/Pani prawo wniesienia skargi do Prezesa Urzędu Ochrony Danych Osobowych.
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8. Na dzień zbierania Pana/Pani danych osobowych nie planujemy przekazywać ich poza EOG (obejmujący Unię Europejską, Norwegię, Lichtenstein i Islandię), nie wykluczając tego w przyszłości, o czym zostanie Pan/Pani poinformowania ze stosownym wyprzedzeniem.
9. W stosunku do Pana/Pani nie będą prowadzone działania polegające na podejmowaniu decyzji w sposób zautomatyzowany, nie będą one również podlegały zautomatyzowanemu profilowaniu.
10. Jeżeli chce Pan/Pani skontaktować się z Uczelnią w sprawach związanych z przetwarzaniem danych osobowych, w szczególności w związku z wniesieniem wniosku o realizację przysługujących praw prosimy o kontakt pod adresem e-mail: iod@umk.pl lub adresem korespondencyjnym: UMK w Toruniu, ul. Gagarina 11, 87-100 Toruń, z dopiskiem „IOD”, dostępny jest również kontakt telefoniczny: 56 611 27 42.

Toruń, dnia 29.05.2025

dr Tadeusz Muzioł

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(tytuł, stopień, imię i nazwisko kandydata/współautora)
Uniwersytet Mikołaja Kopernika w Toruniu

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(jednostka zatrudniająca kandydat/współautora)

Rada Dyscypliny
Uniwersytetu Mikołaja Kopernika
w Toruniu

Oświadczenie o współautorstwie

Niniejszym oświadczam, że w pracy:

Butrymowicz-Kubiak A.; Luba W.; Madajska K.; Muzioł T.M.; Szymańska I.B. Pivalate complexes of copper(II) with aliphatic amines as potential precursors for depositing nanomaterials from the gas phase, New J. Chem., 2024, 48, 6232 mój udział polegał na wykonaniu pomiarów dyfraktometrycznych, rozwiązaniu i udokładnieniu struktur, opracowaniu otrzymanych wyników, a także ich opisie.

Butrymowicz-Kubiak A.; Topolski A.; Muzioł T.M.; Szymańska I.B. Nickel complexes based on perfluorinated amidine for applications in gas-assisted methods and photocatalysis, Dalt. Trans., 2025, (praca zaakceptowana do druku) mój udział polegał na wykonaniu pomiarów dyfraktometrycznych, rozwiązaniu i udokładnieniu struktur, wykonaniu obliczeń przy użyciu powierzchni analizy Hirshfelda, opracowaniu otrzymanych wyników, a także ich opisie.

Butrymowicz-Kubiak A.; Muzioł T.M.; Madajski P.; Szymańska I.B. New Gold(I) Complexes as Potential Precursors for Gas-Assisted Methods: Structure, Volatility, Thermal Stability, and Electron Sensitivity, Molecules, 2025, 30, 146 mój udział polegał na wykonaniu pomiarów dyfraktometrycznych, rozwiązaniu i udokładnieniu struktur, wykonaniu obliczeń przy powierzchni analizy Hirshfelda, opracowaniu otrzymanych wyników, a także ich opisie.

Butrymowicz-Kubiak A.; Muzioł T.M.; Kaczmarek Kędziera A.; Jureddy C.S.; Maćkosz K.; Utke I.; Szymańska I.B. New palladium(II) β -ketoesterates for Focused Electron Beam Induced Deposition: Synthesis, structures, and characterization, Dalt. Trans., 2024, 53, 13662 mój udział polegał na wykonaniu pomiarów dyfraktometrycznych, rozwiązaniu i udokładnieniu struktur, opracowaniu otrzymanych wyników, a także ich opisie.

Tadeusz Muzioł
.....
(podpis)

Informacja o przetwarzaniu danych osobowych

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3. Z zastrzeżeniem przepisów powszechnie obowiązującego prawa przysługują Panu/Pani prawa, które zrealizujemy na wniosek o:
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Bremen, 7.5.2025

Prof. Dr. Petra Swiderek
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University of Bremen
(entity employing the candidate/co-author)

Scientific Discipline Council
at the Nicolaus Copernicus University
in Toruń

Co-authorship Statement

I hereby declare that in the work Martinović P., Rohdenburg M., Butrymowicz A., Sarigül S., Huth P., Denecke R., Szymańska I. B., Swiderek P., Electron-Induced Decomposition of Different Silver(I) Complexes: Implications for the Design of Precursors for Focused Electron Beam Induced Deposition, Nanomaterials 2022, 12, 1687 my contribution consisted of composing the final manuscript and performing the modelling of the XPS data.

22.05.2025

X Prof. Dr. Petra Swiderek

Signiert von: Petra Swiderek
(signature)

Information on the processing of personal data

Pursuant to Regulation (EU) 2016/679 of the European Parliament and of the Council of 27 April 2016 on the protection of natural persons with regard to the processing of personal data and on the free movement of such data and repealing Directive 95/46/EC, hereinafter referred to as RODO [General Data Protection Regulation], we inform as follows:

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Leipzig, 20.05.2025

Dr., M.Sc., Markus Rohdenburg

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(entity employing the co-author)

Scientific Discipline Council
at the Nicolaus Copernicus University
in Toruń

Co-authorship Statement

I hereby declare that in the work Martinović P., Rohdenburg M., Butrymowicz A., Sarigül S., Huth P., Denecke R., Szymańska I. B., Swiderek P., Electron-Induced Decomposition of Different Silver(I) Complexes: Implications for the Design of Precursors for Focused Electron Beam Induced Deposition, Nanomaterials 2022, 12, 1687 my contribution consisted of performing computational calculations and participating in XPS experiments and analysis.

.....
(signature)

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Bremen, 21.05.2025

Dr. Petra Martinović.....
(title, degree, first and last name of the candidate/co-author)

.....
(entity employing the candidate/co-author)

Scientific Discipline Council
at the Nicolaus Copernicus University
in Toruń

Co-authorship Statement

I hereby declare that in the work Martinović P., Rohdenburg M., Butrymowicz A., Sarigül S., Huth P., Denecke R., Szymańska I. B., Swiderek P., Electron-Induced Decomposition of Different Silver(I) Complexes: Implications for the Design of Precursors for Focused Electron Beam Induced Deposition, *Nanomaterials* 2022, 12, 1687 my contribution consisted of synthesising the Ag(I) carboxylates, preparing and characterising the samples, performing electron irradiation experiments, preparing the figures, drafting the manuscript, and managing the references.

eSigned by:

05/21/2025 @ 14:05 UTC
.....
(signature)

Information on the processing of personal data

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Page 3 of 3



Warszawa, dnia 27.05.2025

mgr Wiktoria Luba

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(tytuł, stopień, imię i nazwisko kandydata/współautora)

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(jednostka zatrudniająca kandydat/współautora)

Rada Dyscypliny
Uniwersytetu Mikołaja Kopernika
w Toruniu

Oświadczenie o współautorstwie

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.....
(podpis)

 Podpisano przez/ Signed by:
WIKTORIA
LUBA
Data/ Date: 28.05.2025 02:12
mSzafir

Informacja o przetwarzaniu danych osobowych

Na podstawie Rozporządzenia Parlamentu Europejskiego i Rady (UE) 2016/679 z dnia 27 kwietnia 2016 r. w sprawie ochrony osób fizycznych w związku z przetwarzaniem danych osobowych i w sprawie swobodnego przepływu takich danych oraz uchylenia dyrektywy 95/46/WE, zwanego dalej „RODO”, informujemy, że:

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6. Przysługuje Panu/Pani prawo wniesienia skargi do Prezesa Urzędu Ochrony Danych Osobowych.
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Toruń, dnia 27.05.2025

Dr Katarzyna Madajska

.....
(tytuł, stopień, imię i nazwisko kandydata/współautora)

.....
(jednostka zatrudniająca kandydat/współautora)

**Rada Dyscypliny Wydziału Chemii
Uniwersytetu Mikołaja Kopernika
w Toruniu**

Oświadczenie o współautorstwie

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Katarzyna Madajska
.....
(podpis)

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Toruń, dnia 29.05.2025

dr Adrian Topolski

(tytuł, stopień, imię i nazwisko kandydata/współautora)

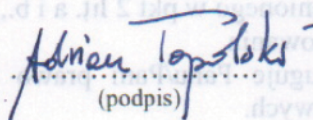
Wydział Chemii, Uniwersytet Mikołaja Kopernika w Toruniu

(jednostka zatrudniająca kandydat/współautora)

**Rada Dyscypliny Wydziału Chemii
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w Toruniu**

Oświadczenie o współautorstwie

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(podpis)

Informacja o przetwarzaniu danych osobowych

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Toruń, dnia 21.05.2025

mgr Piotr Madajski

.....
(tytuł, stopień, imię i nazwisko kandydata/współautora)

Uniwersytet Mikołaja Kopernika w Toruniu

.....
(jednostka zatrudniająca kandydat/współautora)

**Rada Dyscypliny Wydziału Chemii
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Piotr Madajski

.....
(podpis)

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Toruń, 19. maja 2025

Anna Kaczmarek-Kędziera
Zespół Modelowania Molekularnego
Katedra Chemii Materiałów, Adsorpcji i Katalizy
Wydział Chemii UMK

Rada Dyscypliny Nauki Chemiczne
Uniwersytetu Mikołaja Kopernika w Toruniu

Oświadczenie o współautorstwie

Niniejszym oświadczam, że w pracy:

A. Butrymowicz-Kubiak, T. M. Muzioł, A. Kaczmarek Kędziera, C. S. Jureddy, K. Maćkosz,
I. Utke, I. B. Szymańska

*New palladium(II) β -ketoesterates for Focused Electron Beam Induced Deposition: Synthesis,
structures, and characterization*

Dalton Trans., **2024**, 53, 13662

mój udział polegał na przeprowadzeniu obliczeń teoretycznych dla badanych związków, analizie średniej lokalnej energii jonizacji (ALIE), zredagowaniu części manuskryptu dotyczącej uzyskanych wyników obliczeń dla ALIE oraz sprawdzeniu ostatecznej wersji manuskryptu.

Anna Kaczmarek-Kędziera
Anne Kaczmarek-Kędziera

Thun, 08/05/2025

Dr inż. Krzysztof Maćkosz
(title, degree, first and last name of the candidate/co-author)

Empa
(entity employing the candidate/co-author)

Scientific Discipline Council
at the Nicolaus Copernicus University
in Toruń

Co-authorship Statement

I hereby declare that in the work Butrymowicz-Kubiak A.; Muzioł T.M.; Kaczmarek Kędziera A.; Jureddy C.S.; Maćkosz K.; Utke I.; Szymańska I.B. New palladium(II) β -ketoesterates for Focused Electron Beam Induced Deposition: Synthesis, structures, and characterization, Dalt. Trans., 2024, 53, 13662 my contribution consisted of performing FEBID experiments and EDX measurements for the FEBID deposits.

**Krzysztof
Mackosz**
Digitally signed by
Krzysztof Mackosz
Date: 2025.05.20
10:58:11 +02'00'
(signature)

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Pursuant to Regulation (EU) 2016/679 of the European Parliament and of the Council of 27 April 2016 on the protection of natural persons with regard to the processing of personal data and on the free movement of such data and repealing Directive 95/46/EC, hereinafter referred to as RODO [General Data Protection Regulation], we inform as follows:

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 - b. pursuant to art. 6.1(f) of the RODO - legitimate interest of the ADO:
 - for the establishment, defence or assertion of claims - for the period until the statute of limitations for claims, or for the period of proceedings by the competent authorities or courts in the event of a claim,
 - for internal purposes of compilation, analysis and statistics - for the duration of the contract,
 - for the purpose of keeping records of incoming and outgoing mail – indefinitely,
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 - a. request access to and the right to rectify your personal data,
 - b. request to erase or restrict processing.
4. You also have the right to object to the processing of your personal data.
5. Providing your personal data is necessary in order to fulfil the purpose mentioned in point 2(a) and 2(b), and failure to do so will make it impossible to open and conduct the proceedings.
6. You have the right to lodge a complaint with the President of the Office for Personal Data Protection.
7. Your personal data may be made available to reviewers or public administration bodies, courts, court enforcement officers within the scope of situations provided for by law.
8. As of the date of collecting your personal data, we have no plans to transfer it outside the EEA (comprising the European Union, Norway, Liechtenstein and Iceland), without excluding it in the future, of which you will be informed in due time.
9. No automated decision-making activities will be carried out on you, nor will you be subject to automated profiling.
10. If you wish to contact the University on matters relating to the processing of your personal data, in particular in relation to making a request for the exercise of your rights, please contact us by email at iod@umk.pl or mailing to UMK w Toruniu, ul. Gagarina 11, 87-100 Toruń, with the reference "IOD", telephone contact is also available: 56 611 27 42.

Thun,08.05.2025

Dr Ivo Utke

.....
(title, degree, first and last name of the candidate/co-author)

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Scientific Discipline Council
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Ivo
Utke

Digital
unterscriben von
Ivo Utke
Datum: 2025.05.08
11:11:03 +02'00'

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(signature)

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Pursuant to Regulation (EU) 2016/679 of the European Parliament and of the Council of 27 April 2016 on the protection of natural persons with regard to the processing of personal data and on the free movement of such data and repealing Directive 95/46/EC, hereinafter referred to as RODO [General Data Protection Regulation], we inform as follows:

1. The controller of your personal data will be the Nicolaus Copernicus University in Toruń with its seat at Gagarina 11, 87-100 Toruń (hereinafter: the University, ADO).
2. Your personal data in connection with the proceedings for the award of the degree will be processed:
 - a. pursuant to 6.1(c) of the RODO - legal obligation under the provisions of the Act of 20 July 2018 - Law on Higher Education and Science (Journal of Laws of 2020, item 85);
 - b. pursuant to art. 6.1(f) of the RODO - legitimate interest of the ADO:
 - for the establishment, defence or assertion of claims - for the period until the statute of limitations for claims, or for the period of proceedings by the competent authorities or courts in the event of a claim,
 - for internal purposes of compilation, analysis and statistics - for the duration of the contract,
 - for the purpose of keeping records of incoming and outgoing mail – indefinitely,
 - for marketing purposes of ADO's products and service.
3. Subject to the provisions of generally applicable law, you have rights which we will exercise upon request to:
 - a. request access to and the right to rectify your personal data,
 - b. request to erase or restrict processing.
4. You also have the right to object to the processing of your personal data.
5. Providing your personal data is necessary in order to fulfil the purpose mentioned in point 2(a) and 2(b), and failure to do so will make it impossible to open and conduct the proceedings.
6. You have the right to lodge a complaint with the President of the Office for Personal Data Protection.
7. Your personal data may be made available to reviewers or public administration bodies, courts, court enforcement officers within the scope of situations provided for by law.
8. As of the date of collecting your personal data, we have no plans to transfer it outside the EEA (comprising the European Union, Norway, Liechtenstein and Iceland), without excluding it in the future, of which you will be informed in due time.
9. No automated decision-making activities will be carried out on you, nor will you be subject to automated profiling.
10. If you wish to contact the University on matters relating to the processing of your personal data, in particular in relation to making a request for the exercise of your rights, please contact us by email at iod@umk.pl or mailing to UMK w Toruniu, ul. Gagarina 11, 87-100 Toruń, with the reference "IOD", telephone contact is also available: 56 611 27 42.