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Reviewer's Report on the Thesis entitled
Porosity and dynamics in crystalline materials of transition metal complexes based on dipodal N-donor ligands and related solid-state phenomena
by Ms. Simran Chaudhary

The doctoral dissertation by Ms. Simran Chaudhary has been carried out at the Faculty of Chemistry of the Nicolaus Copernicus University in Toruń (Poland) under the scientific supervision of dr hab. Liliana Dobrzańska, prof. UMK and dr hab. Zbigniew Rafiński, prof. UMK. The dissertation is formally organized into twelve chapters, divided into three main sections: (i) Introduction, (ii) Experimental Part, and (iii) Discussion and Concluding Remarks. It also includes Thesis Motivation and Aim part. In addition, it contains an abstract (in English only), a list of publications, conference presentations, internship information, funding details, a list of abbreviations, the bibliography, and an appendix with supplementary data. The thesis comprises a total of 172 pages. The first chapter serves as a comprehensive introduction to the concept of crystal engineering. It presents the definition of the field, its key principles, significance, and role in modern chemistry, particularly in materials chemistry, as well as the major challenges associated with it. The chapter also outlines the role and characteristics of intermolecular interactions, with particular emphasis on hydrogen bonding, π–π interactions, and van der Waals forces. Considerable attention is devoted to coordination bonding, especially in the context of discrete coordination compounds, metallocycles, and coordination polymers, including metal-organic frameworks (MOFs). Subsequent sections address topics central to crystal engineering and highly relevant to the dissertation, such as polymorphism, supramolecular isomerism, isostructurality, and solvates. Another important part discusses single-crystal-to-single-crystal transformations, focusing both on transformations in 0D molecular crystals, while referring to the significant contributions of the supervisors' previous studies, and on transformations in coordination polymers. The final subchapters of the introduction are devoted to porosity, gas sorption, and vapor sorption, phenomena of particular importance for the research presented in the dissertation. Special attention is given to dipodal

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imidazole-based ligands, their structural characteristics, and their role in the construction of metal complexes ranging from discrete species to extended coordination architectures. In this work, semi-rigid and flexible dipodal ligands containing imidazole groups, with varying aromatic core lengths and different substitutions on the imidazole moiety, were employed to construct the complexes investigated in the thesis. In my opinion, this chapter is written in a clear, coherent, and accessible manner, enabling even non-specialists to benefit greatly from its content. It is also worth emphasizing that the chapter is very well illustrated and presented in an engaging way. The literature review includes 249 references, 174 of which are listed in the bibliography.

The presented work fits within the ongoing, important, and ambitious research aimed at the development of new porous materials capable of adsorbing molecules. Such materials should combine high chemical stability with large surface areas and well-defined, tunable pores. While MOFs with large voids and high internal surface areas are particularly attractive for applications requiring high guest-storage capacity, discrete coordination compounds with confined cavities offer the possibility of selectively recognizing guest molecules based on factors such as size and electrostatic interactions. This makes them especially promising for sensing and separation applications. The main objectives of this project included: i) the synthesis of dipodal imidazole-based ligands and their characterization in the solid state; ii) the synthesis and crystallization of discrete 0D metallocycles using imidazole-based ligands differing in aromatic core length, rigidity, and substitution pattern on the imidazole moieties, combined with various 3d transition metal salts; iii) a systematic investigation of the factors influencing the formation of specific supramolecular architectures, including the effects of solvents and counterions; iv) dynamic and sorption studies of selected crystalline materials; and finally attempts v) examination of the relationship between ligand modification and sorption properties. The experimental part presents the synthesis and basic characterization of the dipodal ligands, their complexes, and their transformations. It also describes the experimental methodologies employed in the study, including: i) single-crystal X-ray diffraction, ii) powder X-ray diffraction, iii) NMR spectroscopy, iv) melting point determination and vi) thermogravimetric analysis, vi) computational studies, vii) gas/vapor adsorption measurements, as well as the crystallization techniques used, such as slow evaporation, vapor diffusion, solvent layering/liquid diffusion, and solvothermal synthesis. The Candidate synthesized twelve heterocyclic ligands (**L1**-**L12**) containing imidazole or pyridine units linked by either rigid or flexible aromatic spacers. Three of them (**L2**, **L3**, and **L5**) are novel compounds. Eight ligands (**L2**, **L3**, **L4**, **L5**, **L6**, **L7**, **L9**, and **L10**) were subsequently used in metal complexation studies. The initial stage of the research focused on the structural characterization of the ligands. Depending on the solvent employed, ligand **L1** was obtained in an anhydrous form as well as three distinct hydrates: hemihydrate, monohydrate, and dihydrate. Ligands **L6**, **L8**,

L11, and **L12** each form two polymorphic forms. Crystallization studies reveal two main outcomes: hydrate formation and polymorphism, governed by ligand structure. The rigid naphthalene-based ligand favors hydrates, while more flexible biphenyl-based ligands tend to form polymorphs due to increased conformational freedom. The crystal analyses of all these systems (12 analyses) reveal that dispersion forces dominate lattice stabilization in all ligands, while hydration enhances stability through strong O–H···N/O hydrogen bonds and weaker C–H···O interactions. In polymorphic systems, conformational flexibility and weak intermolecular interactions lead to diverse packing arrangements, with π–π stacking additionally stabilizing more planar structures. Thermal and PXRD analyses show that the most stable polymorphs prevail upon heating or long-term storage. The studied organic hydrates represent a promising system for vapor sorption due to their reversible water uptake and release. In particular, **L1** hydrates exhibit stepwise dehydration behavior, which is advantageous for controlled moisture adsorption at high humidity, suggesting potential applications in humidity regulation and further development of such sorption systems.

Further research led to the synthesis of 12 metallocyclic complexes based on imidazole ligands varying in aromatic core length, rigidity, and imidazole substituents, using a range of 3d transition metal ions. These include two complexes with naphthalene-based ligands: $[Cu_2(\mathbf{L2})2Cl_4]\cdot xS$ **(MC1)** and $[Co_2(\mathbf{L3})2Cl_4]\cdot 0.8CH_3CN$ **(MC2)**, three with partially embedded anthracene moiety units $[Co_2(\mathbf{L4})2Cl_4].CH_3CN$ **(MC3)**, $[Co_2(\mathbf{L4})2Br_4].4CH_3CN$ **(MC4)**, $[Co_2(\mathbf{L5})_2Br_4]$ **(MC5)**, and seven biphenyl-based systems: $[Cu_2(\mathbf{L6})2Cl_4]\cdot xS$ **(MC6)**, $[Zn_2(\mathbf{L6})_2Cl_4]\cdot xS$ **(MC7)**, $[Cd_2(\mathbf{L7})2Cl_4]\cdot 2MeOH$ **(MC8)**, $[Cu_2(\mathbf{L9})2Cl_4]\cdot CH_2Cl_2$ **(MC9)**, $[Zn_2(\mathbf{L9})_2Cl_4]\cdot xS$ **(MC10)**, $[Zn_2(\mathbf{L10})_2(Cl)_4].4DMF$ **(MC11)** and $[Zn_2(\mathbf{L10})_2(Cl)_4].1DMF$ **(MC12)**. In addition, 1D coordination polymers were also isolated during the synthesis of metallocycles, namely: $\{[Co(L3)Cl_2]\}_n$ **(CP1)**, $Cu(L_3)Cl_2]\cdot CH_3CN\}_n$ **(CP2)** and $\{[Cd(L_3)Cl_2]\cdot CH_3CN\cdot 0.2H_2O\}_n$ **(CP3)**. Their structures were characterised by single-crystal X-ray diffraction. A common feature of all obtained metallocycles is their tendency to pack into structures forming channels or discrete voids that host solvent molecules, with the frameworks stabilized by non-covalent interactions. Dynamics and sorption studies were carried out on selected crystalline materials (**MC2** leading to **MC2-a** and **MC2-b**, **MC8** leading to **MC8-a**, **MC10** leading to **MC10-a**, **MC7**, **MC9**, **CP2** leading to **CP2-a**, and **CP3** leading to **CP3a**; the structures of **MC2-a**, **MC2-b**, **MC8-a**, **MC10-a**, **CP2-a** and **CP3a** were characterised by single-crystal X-ray diffraction). The results reveal significant structural dynamics in imidazole-based metallocycles, particularly during solvent loss, which is accompanied by ligand conformational changes dependent on ligand flexibility. A spectacular single-crystal-to-single-crystal transformation has been observed for **MC10**, where the ligand changes from a C-shaped to an S-shaped conformation with a complete rearrangement of the packing motif. I am really impressed(!). Base on this part of analysis the Candidate derives two key conclusions: that rigid cores favor structural integrity and

reproducibility but limit dynamic adaptability, whereas flexible cores enable dynamic responses and potential for stimuli-responsive materials, but require strategies to mitigate the phase control. Two metallocycles exhibit measurable sorption behavior. **MC2** shows selective CO_2 uptake (2.11 wt%) despite the absence of permanent channels, indicating transient porosity. **MC7** displays lower CO_2 uptake (1.42 wt%) but enhanced H_2 adsorption (~4 mmol/g, 0.80 wt%). Both **CP2-a** and **CP3-a** adsorb H_2 and H_2O but not CO_2. **CP2-a** shows higher H_2 uptake (1.23 wt%) than **CP3-a** (0.54 wt%), while **CP3-a** has greater water adsorption (5.30 wt% vs. 3.48 wt%), with hysteresis observed in both. Overall, these systems demonstrate transient porosity enabled by framework flexibility. The analyses show that 0D metallocycles and 1D coordination polymers can rival higher-dimensional porous materials, offering a basis for next-generation systems. They also indicate that rigid naphthalene-based imidazole ligands are promising for constructing transiently porous materials for small-molecule adsorption.

The research problems addressed and resolved by the Doctoral Candidate are of high scientific significance, while the scope of the work and the breadth of the analyses performed are truly impressive. The application of a wide range of modern analytical techniques deserves particular appreciation. Her research successfully combines molecular design and synthesis with solid-state chemistry, providing valuable insight into the dynamic behavior of the investigated crystalline materials. Overall, this highly inspiring work constitutes an important achievement and opens promising perspectives for the development of novel functional materials. The doctoral dissertation demonstrates a high level of quality, both in terms of scientific content and editorial preparation. It is written in a mature and coherent manner, maintaining a very good balance between the literature review and the original experimental studies, including synthesis and physicochemical characterization. I particularly appreciate the clear and careful presentation of the results; all figures and graphs have been prepared with great attention to detail. It is worth noting that a significant part related to the thesis has already been published in *CrystEngComm* [**2025**, *27*, 3891-3898] and *RSC Advances* [**2023**, *13*, 30625-30632], where the Doctorate Student is the first author. It is worth noting that the former publication was selected for the journal cover page. She is likewise the first author of a thematically closely related article published in *Crystals* [**2025**, *15*, 289] and Polyhedron [**2022**, *224*, 115989]. In addition, she is also a co-author of two further publications: *Crystals* [**2024**, *14*, 248] and *Acta Crystallographica B* [**2024**, *80*, 19-26]. This demonstrates her dedication to Science. The thesis contains only a few minor imperfections, all of negligible importance. The list of acronyms provided at the beginning of the dissertation is useful, although it is not fully complete and is not arranged alphabetically; for example, the abbreviations „cp" (page 24) and „cpp" (page 25) are missing. In the experimental section, both degrees Celsius and Kelvin are used. I would also note that the experimental and calculated PXRD patterns refer

to different temperatures, which should be taken into account during comparison, as this may contribute in some cases to the apparent lack of homogeneity in the bulk samples. In summary, I am fully convinced that Ms. Simran Chaudhary's doctoral dissertation contains significant elements of scientific novelty. The Candidate defined the research problem well, planned it well and performed quite excellent research.

The doctoral thesis by Ms. Simran Chaudhary meets all formal requirements specified in the current Act of the Law on Higher Education and Science of Republic of Poland. Therefore, it is with great pleasure that I recommend to the Scientific Council of the Chemistry Discipline of the Nicolaus Copernicus University in Toruń that she be admitted to the next stages of the doctoral process. Furthemore, in view of the outstanding scientific quality of the conducted research, its novelty and originality, great signifficance to chemistry and materials science, as well as the candidate's evident scientific maturity, reflected in her publication records, I further respectfully appeal the Scientific Council of the Chemistry Discipline of the Nicolaus Copernicus University in Toruń to award her doctoral dissertation with distinction.

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