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Łódź, 10.04.2026

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Review report of Simran Chaudhary's PhD thesis entitled " Porosity and dynamics in crystalline materials of transition metal complexes based on dipodal N-donor ligands and related solid-state phenomena "

The peer-reviewed doctoral dissertation of Simran Chaudhary, M.A., was prepared under the supervision of: Dr. hab. Liliana Dobrzańska, prof. UMK (Supervisor), and Dr. hab. Zbigniew Rafiński, prof. UMK (Co-Supervisor) at the Faculty of Chemistry, Doctoral School of Exact and Natural Sciences, Nicolaus Copernicus University in Toruń. The doctoral dissertation was funded by the National Science Centre Poland; project: Sonata Bis 2014/14/E/ST5/00611.

Copper coordination chemistry is an extremely important field of science, as its research is used in both biology and industry. Copper compounds are important in the biological field, demonstrating antibacterial and antifungal activity, and are used as pesticides and catalysts. Coordination polymers are distinguished by their porosity. Among the anticipated

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applications of MOFs is reversible gas exchange, which may be important in the fields of energy storage and separation, as well as the ability to adsorb water and utilize it in heat transfer processes. Metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) have gained significant attention for their potential in applications such as pollutant removal, fuel storage, water harvesting in arid regions, and separating specialized chemicals like pharmaceuticals. MOFs are composed of organic molecules connected by metal ion nodes.

From a formal perspective, the doctoral dissertation under review is 190 pages long. It is divided into three main chapters: Section 1: Introduction, Section 2: Experimental Part, and Section 3: Discussion and Concluding Remarks. Additionally, the work includes a list of research activities, an abstract, the purpose of the work, and references.

The aim of the doctoral thesis was:

- synthesis of dipodal imidazole based ligands and their characterization in the solid state,
- synthesis and crystallization of discrete 0D metallocycles utilizing imidazole-based ligands of different aromatic core length and rigidity, as well as substituents on imidazole moieties with application of a variety of 3d transition metal salts,
- systematic investigation of the factors that influence the formation of particular supramolecular architectures
- dynamics and sorption studies on the selected crystalline material,
- studying how modification of the ligands relates to their sorption properties.

The first section begins with an introduction to crystal engineering, followed by a description of intermolecular interactions, indicating their strengths. A description of hydrogen bonds is introduced, including a classification and a description of multifurcated hydrogen-bonded

interactions. The next section presents π - π interactions (also called aromatic stacking interactions), which are one of the most important non-covalent interactions prominent in crystalline structures of aromatic molecules and in systems containing π -bonds. Finally, weak van der Waals interactions are discussed. The next section concerns Coordination Bond: Metalloclusters vs. MOFs.

Discrete metalloclusters are obtained by coordination-driven self-assembly of metal ions and organic ligands, wherein the coordinate bond forms between the metal atom and the donor atom of the ligand, using a bottom-up approach, either through classical solution reactions or solvothermal synthesis. Coordination polymers (CPs) are extensive network structures formed by the coordination of metal ions or clusters with organic ligands. Additionally, a comparison of polymorphs and solvates and single-crystal-to-single-crystal (SC-SC) transformations is described. The next subsection describes porosity, which refers to the presence of voids or channels that allow for the diffusion and selective sorption of guest molecules. The doctoral student then discusses the research object: dipodal imidazole-based ligands. She explains the selection of such compounds in achieving the purpose of work. Pointing out that the use of N-donor ligands because M-N coordination bonds tends to be weaker and more labile compared to the M-O carboxylate coordination bond.

The next chapter (Section 2) covers the experimental work. The research techniques used are first listed: Single-Crystal X-Ray Diffraction (SC-XRD), Powder X-Ray Diffraction (PXRD), Nuclear Magnetic Resonance (NMR) Spectroscopy, Melting Point Determination, Thermogravimetric Analysis, and computer calculations. The synthesis of 12 dipodal ligands is then described. In the next subchapter, the PhD student describes the synthesis of Coordination Compounds and structural studies of

the resulting compounds. The synthesis with ligands L1, L11, and L12 is missing.

The PhD student obtained 12 structures (4 from L1, 2 from L6, 2 from L8, 2 from L11, and 2 from L12). The crystallographic data tables are missing the maximum and minimum values for the residual electron density maps. The lack of CIF files attached to the thesis prevents me from verifying the values myself.

On the following pages, the PhD student compares the crystallization of 2,7-bis(imidazol-1-ylmethyl)naphthalene (L1) from a range of solvents to the isolation of the anhydrous form (L1a) of the ligand alongside three distinct hydrates: the hemihydrate (L1.0.5H₂O, L1b), the monohydrate (L1.0.5H₂O, L1c), and the dihydrate (L1.2H₂O, L1d). The results of Hirshfeld surface analysis revealed that upon hydration, C–H···N and C–H···π hydrogen bonds progressively decrease, while hydrogen bonds involving oxygen atoms and π–π interactions become increasingly dominant.

Structural studies of compounds with the L6 ligand resulted in the production of two new polymorphs (L6a and L6b) and two distinct solid forms of L6, a monohydrate (L6c) and an anhydrous form (L6d). Crystal lattice energy calculations further confirmed that L6a is the most stable form.

However, compounds with L8 have two new conformational polymorphs L8a and L8b. Hirshfeld surface analysis confirmed, among other findings, the presence of stronger C–H···π interactions in L8b.

Crystallization of L11 led to the isolation of two new polymorphs, L11a and L11b. The C–H···π interactions are more diverse in L11a, with the involvement of methylene groups, benzene rings, and imidazole rings. For the structure of L11b, only aromatic units, i.e., benzene and imidazole rings, are involved.

With the L12 ligand no metallocycles were formed, two new coexisting polymorphs, L12a and L12b.

The next subsection concerns the obtained metallocycles. The crystals of two metallocycles based on rigid naphthalene were obtained: one with Cu(II) ion and L2, and the other with Co(II) ion and L3. Two structures were obtained with ligand L4, and one each with L5, L6, L7, L9, and L10. The PhD student obtained five structures of the 1D Coordination Polymers type.

Section 3 is about Discussion and Concluding Remarks. The reviewed work shown that imidazole-based ligands containing a rigid core, such as naphthalene could be promising candidates for constructing transiently porous metallocycles and 1D coordination polymers (CPs) suitable for small molecules adsorption. The PhD student indicated further research that could be carried out based on the obtained results.

Which of the compounds obtained do you consider the most important?

In summary, the PhD student obtained as many as 33 new crystal structures. These compounds were also studied using NMR, pxd methods, ab-initio calculations, and porosity studies. The work is clearly described and includes carefully crafted figures. It contains 249 references. The PhD candidate is the co-author of 6 publications in prestigious journals and 10 conference presentations (poster and oral presentation). She completed a one-month internship at the Vellore Institute of Technology (VIT), Vellore, Tamil Nadu, India.

I have no doubt that the dissertation submitted for my evaluation fully meets the requirements set in the Act of 20th of July, 2018, on Higher Education and Science (as amended), and in the Regulation of the Minister of Science and Higher Education of 30th January, 2018, on the detailed procedure for conducting activities in doctoral, habilitation, and professorial proceedings (Journal of Laws of 2018 , item 261). I recommend to the Council of the

Scientific Discipline of Chemical Sciences at the Faculty of Chemistry, Nicolaus Copernicus University in Toruń, that Ms. Simran Chaudhary be allowed to proceed to the subsequent stages of the doctoral process.

Furthermore, considering the high standard of the conducted research, which has resulted in measurable outcomes in the form of a series of scientific publications in renowned international journals, I also propose to the Council of the Scientific Discipline of Chemical Sciences at the Faculty of Chemistry, Nicolaus Copernicus University in Toruń, that the doctoral dissertation of Ms. Simran Chaudhary awarded distinction.

M. Szczęsny