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DOCTORAL DISSERTATION ABSTRACT

Scientific discipline: Chemistry

Title of the doctoral dissertation: **Porosity and dynamics in crystalline materials of transition metal complexes based on dipodal N-donor ligands and related solid-state phenomena**

Doctoral dissertation abstract: Porous materials capable of adsorbing molecules have received considerable attention in recent decades due to their potential in applications like pollutant removal, gas storage, and chemical separation. Coordination bonds, known for their directionality and versatility, provide a solid foundation for creating crystalline frameworks with diverse microporous structures. While metal-organic frameworks (MOFs) have been extensively explored in the past decade, these materials often encounter challenges related to stability and scalability. Consequently, there is an increasing demand for alternative porous materials. Notably, systematic investigations into the porosity of materials based on 0D metallocycles are still limited. These materials, with their confined cavities, have the potential to selectively differentiate guest molecules based on properties such as size and electrostatic interactions, making them promising candidates for applications in sensing and separation. This thesis aimed to investigate alternative microporous crystalline materials, focusing on discrete metallocycles synthesized with semi-rigid and flexible dipodal imidazole-based ligands. During synthesizing these metallocycles, potentially porous 1D coordination polymers (CPs) were also obtained and studied. The work started with the synthesis of a series of bipodal ligands, varying in aromatic core length, rigidity, and substitution patterns, which were further utilized to construct discrete metallocycles in combination with various transition metal salts. Moreover, the solid-state studies were also performed on these ligands, revealing among others their conformational

flexibility that enhances their suitability for constructing dynamic crystalline coordination compounds. Some of the isolated coordination compounds displayed remarkable solid-state transformations, triggered via external stimuli such as heat or vacuum. For instance, metallocycle **MC2**, $[Co_2(\mathbf{L3})_2Cl_4]\cdot 0.8CH_3CN$ containing ligand 2,6-bis((2-methylimidazol-1-yl)methyl)naphthalene **(L3)**, **MC8** $[Cd_2(\mathbf{L7})_2Cl_4]\cdot 2MeOH$ constructed with 4,4′-bis((2-methyl-imidazol-1-yl)methyl)-1,1′-biphenyl **(L7)**, **MC10** $[Zn_2(\mathbf{L9})_2Cl_4]\cdot xS$ containing 4,4′-bis((1H-benzimidazol-1-yl)methyl)-1,1′-biphenyl **(L9)**, and 1D coordination polymers, **CP2**, $\{[Cu(\mathbf{L3})Cl_2]\cdot CH_3CN\}_n$ and **CP3**, $\{[Cd(\mathbf{L3})Cl_2]\cdot CH_3CN\cdot 0.2H_2O\}_n$ synthesized using ligand 2,6-bis((2-methylimidazol-1-yl)methyl)naphthalene **(L3)**, underwent structural transformations to form phases with distinct ligand conformations. These transformations were analyzed using thermogravimetric analysis, single-crystal and powder X-ray diffraction techniques, providing valuable insights into their dynamic behavior. Additionally, sorption studies revealed selective gas uptake properties, CO_2 in the case of **MC2** and H_2 in the case of **CP2** and **CP3**, highlighting potential of these materials for applications such as hydrogen storage and molecular sieving. Concluding, the results obtained demonstrate the potential of cyclic coordination compounds and low-dimensional (1D) coordination polymers with respect to their sorption properties; nevertheless, further systematic investigations are necessary for their optimization.

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