PHD PROJECT DESCRIPTION

Hydrates of N-donor ligands as responsive crystalline materials: thermal transformations, water sorption, and SCSC mechanisms

1.1 Project goals: The project aims to elucidate the mechanisms of water-mediated dynamics in crystalline hydrates of N-donor ligands, with a particular focus on thermally induced transformations, including single-crystal-to-single-crystal (SC–SC) processes, and their impact on water sorption behaviour. The research will address how:
- water molecules are incorporated, ordered, and dynamically exchanged in crystal structures;
- thermal stimuli induce stepwise dehydration, structural rearrangements, and phase transitions;
- these processes influence porosity, stability, and water uptake/release properties.

A key objective is to establish structure–property relationships linking hydrogen-bonding networks, crystal packing, and transformation pathways with water sorption isotherms, enabling the rational design of functional materials for humidity control, water capture, and sensing applications.

1.2 Outline: Crystalline hydrates of organic N-donor ligands represent an important yet underexplored class of responsive molecular solids, where water molecules play an active structural and functional role. Depending on their arrangement, water molecules can: stabilize specific crystal packings, form extended hydrogen-bonding networks, act as removable or exchangeable guests, induce reversible or irreversible structural transformations. Particularly interesting are systems that exhibit: stepwise dehydration and rehydration processes, single-crystal-to-single-crystal (SC–SC) transformations upon heating or exposure to humidity, structural flexibility leading to transient or persistent porosity, selective water sorption and release behaviour. The project will explore: how ligand structure controls: water binding motifs, hydrogen-bonding networks, stability of hydrates and how thermal treatment induces: dehydration pathways and phase transitions, framework rearrangements (including SC–SC processes), how these transformations relate to: water sorption isotherms, hysteresis and reversibility, potential sensing responses (e.g. humidity-induced structural or optical changes). The long-term goal is to develop water-responsive crystalline materials with controlled uptake/release properties.

1.3 Work plan: The project is planned for 4 years and combines synthesis, crystallography, and solid-state characterization. The first half of the year would be devoted to getting to know the subject, literature studies, getting familiar with the use of the Cambridge Structural Database and programs needed for the visualisation and analysis of crystal structures. The first year should conclude with synthesis and crystallisation of selected N-donor ligands and their hydrates. Further studies can not be given a proper timeframe. Everything will depend in which direction the experiments will develop. However, they will embrace single-crystal X-ray diffraction analyses of the obtained crystalline products, solving and refining the obtained crystal structures, monitoring SC–SC transformations, systematic investigation of the factors that influence the formation of particular supramolecular architectures (e.g. crystallization conditions: the effects of altering solvent, temperature), analyses of intermolecular interactions, monitoring dehydration processes. The studies will be supported by comprehensive solid-state characterization using techniques such as PXRD, TGA, DSC, IR, solid-state NMR and measurement of water sorption isotherms.

1.4 Literature *(max. 7 listed, as a suggestion for a PhD candidate preliminary study)*

1. M. C. Etter, Encoding and decoding hydrogen-bond patterns of organic compounds, *Acc. Chem. Res.*, 23, 1990, 120–126.

2. S. Krause, N. Hosono, S. Kitagawa, Chemistry of soft porous crystals: structural dynamics and gas adsorption properties, *Angew. Chem. Int. Ed.*, 59, 2020, 15325–15341.

3. E. Jurczak, A. H. Mazurek, Ł. Szeleszczuk, D. M. Pisklak, and M. Zielińska-Pisklak, Pharmaceutical hydrates analysis—overview of methods and recent advances, *Pharmaceutics*, 12, 2020, 1–25.

4. M. Takahashi, H. Uekusa, Dehydration and Rehydration Mechanisms of Pharmaceutical Crystals: Classification Of Hydrates by Activation Energy, *J. Pharm. Sci.,* 111, 2022, 618–627.

5. S. Chaudhary, M. Wiśniewski, A. Hoser, R. M. Losus, Z. Rafiński, L. Dobrzańska, Reversible phase transformations upon water uptake/removal in crystalline material of a bipodal N- donor ligand and evaluation of the stability of the hydrates formed, *CrystEngComm*, 27, 2025, 3891–3898.

1.5 Required initial knowledge and skills of the PhD candidate

The candidate should have a strong interest in laboratory work and be familiar with standard synthetic laboratory equipment, as well as basic methods of compound characterization ($^{1}H/^{13}C$ NMR spectroscopy in solution, IR spectroscopy, and melting point determination). Familiarity with crystallography (SCXRD) and thermal analysis (TGA/DSC) will be considered an advantage.

1.6 Expected development of the PhD candidate's knowledge and skills

Upon completion of the project, the candidate is expected to have a solid understanding of organic synthesis, single-crystal X-ray diffraction analysis of small molecules as well as mechanisms of dehydration and solid-state transformations. She/he will also gain expertise in solid-state characterization techniques, including powder X-ray diffraction, thermal analysis (TGA, DSC), and solid-state NMR, as well as methods for inducing and studying single-crystal-to-single-crystal transformations. Furthermore, the candidate will have the opportunity to actively engage with the research community through participation in conferences and/or workshops, as well as through the preparation of scientific publications and grant proposals.