1. PHD PROJECT DESCRIPTION (4000 characters max., including the aims and work plan, all in English)

Project title:

Porosity and dynamics in molecular crystals of coordination compounds of 3d transition metals based on N/O donor ligands

1.1. Project goals

The project is aimed at obtaining a series of porous crystalline compounds based on discrete coordination metal complexes, which contain multipodal ligands consisting of a rigid aromatic spacer and heterocyclic N/O donor moieties, and studying/modifying their structure, to deduce how this relates to their sorption properties. Furthermore, studies of dynamics, connected with cooperative molecular movements taking place in the crystals, will be investigated to uncover their mechanisms, wich could lead to potential applications in sensing devices.

1.2. Outline

Porous materials based on coordination compounds are currently one of the most fashionable topics in the field. This topic was initiated at the beginning of the current century by O. Yaghi's group, which introduced a series of isoreticular porous coordination polymers with linkers based on aromatic compounds containing dicarboxylate groups, the pore size and shape of which could be easily modified.[1] These were originally called 'metal-organic frameworks' or MOFs. However, over time, the term MOF has become very widespread and has also been applied to other porous polymeric coordination compounds.[2] The idea of generating a series of discrete coordination compounds, which would be comparable to the series of coordination polymers mentioned above, is quite a challenge and requires systematic studies with respect to the intermolecular interactions governing the formation of crystal structures.[3] The sorption properties of the obtained porous compounds would be investigated by applying gravimetric or volumetric methods. These results would be the basis for further structural modifications which could influence the size/shape of the formed voids/channels. The 'free space' available in the crystal structures is usually taken up by solvent molecules and removing these can either lead to sustaining the space or cause it to collapse. This kind of triggered single-crystal-to-single-crystal transformations would be an important part of the research.[4] These studies would allow to follow the dynamics taking place in monocrystals of the studied compounds and could help to uncover the mechanisms standing behind these processes, facilitating research towards sensing devices. As the realisation of this proposal falls under the framework of an ongoing SONATA BIS project funded by the National Science Centre, entitled: "The role of non-covalent interactions in the formation of supramolecular assemblies and the phenomenon of single-crystal-to-single-crystal transformations", the work of the PhD student would be additionally (on top of the base remuneration) funded through this grant.

1.3. Work plan

The work is planned for maximum 4 years. The first half of the year would be devoted to getting to know the subject, literature studies, getting familiar with the use of Cambridge Structural Database and programs needed for visualisation and analysis of the crystal structures, as well as synthetic lab techniques. The first year should finish with the synthesis of some heterocyclic ligands, their full basic characterisation (NMR, MS, IR, elemental analysis, and melting point determination studies), synthesis of a

range of metal-complexes and their crystallisation under different conditions. 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, which will be performed at UMK and/or at Warsaw University, solving and refining the obtained crystal structures, systematic investigation of the factors that influence the formation of particular supramolecular architectures (e.g. crystallization conditions: the effects of altering solvent, temperature), and synthetic work to modulate the obtained porous properties. This will be further supported by extended solid state studies, as well as actuating and studying single-crystal-to-single-crystal transformations.

1.4. Literature

1) (a) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O"Keeffe, O. M. Yaghi, *Systematic Design of Pore Size and Functionality in Isoreticular MOFs and Their Application in Methane Storage,* Science, 295, (2002), 469-472; (b) O. M. Yaghi, M. O"Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Reticular synthesis and the design of new materials*, Nature, 423, (2003), 705-714.

2) S. R. Batten, N. R. Champness, X.-M. Chen, J. Garcia-Martinez, S. Kitagawa, L. Öhrström, M. O"Keeffe, M. P. Suh, J. Reedijk, *Terminology of metal–organic frameworks and coordination polymers (IUPAC Recommendations 2013),* Pure Appl. Chem., 85, (2013), 1715-1724.

3) (a) L. Dobrzańska, G. O. Lloyd, H. G. Raubenheimer, L. J. Barbour, *A discrete metallocyclic complex that retains its solvent-templated channel structure on guest removal to yield a porous, gas sorbing material*, J. Am. Chem. Soc., 127, (2005), 13134-13135; (b) L. Dobrzańska, G. O. Lloyd, H. G. Raubenheimer, L. J. Barbour, *Permeability of a seemingly nonporous crystal formed by a discrete metallocyclic complex*, J. Am. Chem. Soc., 128, (2006), 698-699.

4) (a) L. Dobrzańska, G. O. Lloyd, C. Esterhuysen, L. J. Barbour, *Guest-induced conformational switching in a single crysta*l, Angew. Chem. Int. Ed., 45, (2006), 5856-5859; (b) J. Alen, L. Van Meervelt,W. Dehaen, L. Dobrzańska, *Solvent diffusion through a non-porous crystal 'caught in the act' and related single-crystal-to-single-crystal transformations in a cationic dinuclear Ag(I) complex,* CrystEngComm, 17, (2015), 8957-8964.

1.5. Required initial knowledge and skills of the PhD candidate

The candidate should have a passion for lab work (which forms a big part of the project) and be familiar with synthetic lab equipment, as well as with basic methods of compound characterisation ($^{1}H/^{13}C$ NMR in solution, MS, IR).

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

As the proposed study is on the border of synthesis/crystallography and solid-state science, the candidate after its finalisation should be well familiar with organic synthetic methods and how to obtain coordination compounds, as well as with methods for single-crystal X-ray diffraction analysis of small molecules and techniques for solid-state characterisation: powder X-ray diffraction, thermal analysis (TGA, DSC), solid-state NMR and how to study the sorption properties of the porous materials. The techniques to perform single-crystal-to-single-crystal transformations are still being developed, which has also been performed by the mentor of this proposal. Moreover, the candidate will have the opportunity to get to know the lab environment at Warsaw University and really feel part of the research community by participating in conferences and/or workshops as well as writing papers and grant proposals.