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

Project title:

Tuning the topology and magnetic properties of coordination compounds based on a ketoxime core by altering the auxiliary ligand

1.1. Project goals

The coordination compounds obtained from ketoxime type ligands through application of another auxiliary ligand have the tendency to form very diverse crystal structures ranging from discrete to higher dimensionality species. The possibility to influence the final product by pH adjustment additionally complicates the matter. The aim of the project would be to gain deeper insight and control on the formation of the supramolecular architectures and magnetic properties of the formed compounds. Moreover, the expected formation of polymorphs would be further investigated, involving crystal lattice energy calculations and crystal structure predictions (CSP), methods which are currently in development (in collaboration with a group from Imperial College London).

1.2. Outline

The chemistry of coordination compounds based on pyridyl oximes (pyNO ligands) and its derivatives is very rich structurally and embraces different types of species, starting from discrete mononuclear metal complexes, over polynuclear clusters/metallocrowns and polymeric coordination compounds.[1] One of the main reasons of this structural diversity originates from the ability of the (py)C(R)NO ligands to adopt many distinct coordination modes which is a consequence of the presence of potential O- and N- donor atoms. Applying different anions which contain additional donor atoms, such as carboxylates (different lengths and composition), thiocyanates or halides in mixed-ligand systems (pyNO-anions) additionally complicates the prediction of the final product of the synthesis. The proposed systematic studies would try to tackle an essential problem of crystal engineering[2] by making an important step towards predicting the outcome of the synthesis/crystallization for such complicated systems containing 3d-metals. Till now the reports concerning this class of complexes are rather accidental in nature. Furthermore, the focus would be put on topological analysis of the yielded species as well as the intermolecular interactions formed. Isolating polymorphic forms or their thermal induction and in-depth characterization, including lattice energy calculations, could add some value to understand the process of forming crystalline products. Moreover, the family of metal complexes based on pyridyl oximes is known for their interesting magnetic properties, including the formation of single-chain magnets.[3] Systematic studies on this class of compounds would enable the selection of such systems and studying the phenomenon in detail might enable control over the magnetic properties.

1.3. Work plan

The first couple of months would be devoted to getting to know the subject, literature studies, as well as synthetic lab techniques.

The next steps would involve:

1) Synthesis of the ketoxime-based coordination compounds (Cu(II), Ni(II), Zn(II)) with different auxiliary ligands such as Cl^-, SCN^-, NO_3^-, dicarboxylates of different length and composition.

2) Crystallization of the products under different conditions (solvent, pH, temperature).

3) Basic physico-chemical characterization of the obtained products (IR, Raman, UV-Vis (solid), melting point).

4) Single-crystal X-ray diffraction analyses of the obtained crystalline products.

5) Solving and refining the obtained crystal structures.

6) Inducing and studying thermal polymorphic transformations through application of temperature dependent PXRD (Warsaw), DSC, hot stage microscopy (Warsaw), SCXRD.

7) Involvement of CSP methods in collaboration with Imperial College London.

8) Selection of the systems to study their magnetic properties.

1.4. Literature

1) (a) I. Mylonas-Margaritis, A. Gérard, K. Skordi, J. Mayans, A. Tasiopoulos, P. McArdle, C. Papatriantafyllopoulou, *Materials*, 2020, *13*, 4084; (b) T. Afrati, C. M. Zaleski, C. Dendrinou-Samara, G. Mezei, J. W. Kampf, V. L. Pecoraro, D. P. Kessissoglou, *Dalton Trans*., 2007, 2658; (c) M. Alexiou, E. Katsoulakou, C. Dendrinou Samara, C. P. Raptopoulou, V. Psycharis, E. Manessi-Zoupa, S. P. Perlepes, D. P. Kessissoglou, *Eur. J. Inorg. Chem.,* 2005, 1964.
2) M. D. Hollingsworth, *Science,* 2002, *295*, 2410.
3) P. S. Perlepe, D. Maniaki, E. Pilichos, E. Katsoulakou, S. P. Perlepes, *Inorganics,* 2020, *8*, 39.

1.5. Required initial knowledge and skills of the PhD candidate

The candidate should have a passion for lab work and be familiar with synthetic lab equipment, as well as with basic methods of compound characterization (IR, UV-VIS).

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

The candidate after its finalization should be well familiar with the preparation of coordination compounds, methods for single-crystal X-ray diffraction analysis of small molecules and techniques for solid-state characterization: powder X-ray diffraction, thermal analysis (TGA, DSC), magnetic susceptibility. Moreover, the candidate should get some insight into computational methods enabling crystal lattice energy calculations and crystal structure predictions. Furthermore, the candidate will have the opportunity to work in another center (Warsaw University) and feel part of the research community by writing papers and grant proposals.