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

Project title:

Design and magnetism of copper, nickel, and zinc heterometallic materials

1.1. Project goals

The aim of research project is design, structural and spectroscopic study on new heterometallic materials of copper, nickel, and zinc and to determine magnetic properties that will allow to characterize the interaction of electron spins of metal centers. and may improve the interpretation of magnetic properties of newly synthesized materials. The aim is also to correlate magnetism with advanced spectroscopic studies using synchrotronic radiation and theoretical modelling, which can improve and help in better interpretation of magnetic properties of newly synthesized materials.

1.2. Outline

The research efforts on molecular materials are targeting the construction of novel materials with high performance for applications in the fields such as magnetic and optoelectronic devices, nonlinear optics, and luminescence, biological or medicine-related materials. An important feature of molecular materials such as heterometallic complexes is the ability to create bridges by linkers playing an important role as carriers of magnetic interactions between metal centers. These interactions may significantly affect the magnetic properties of the system compared to identical single metallic units [1]. The materials of proposed research belong to a series of thiocyanate bridged Cu(II)-Ni(II), Cu(II)-Cr(III), Cu(II)-Zn(II), Ni(II)-Cr(III), Ni(II)-Zn(II) building blocks: Cu-amine-Ni-NCS, Cu-amine-Cr-NCS, Cu-amine-Zn-NCS, Ni-amine-Cr-NCS, Ni-amine-Zn-NCS, where amine is aliphatic or heterocyclic amine derivative. The new heterometallic compounds with potential structural diversity being 3D, 2D, 1D and 0D topologies will be obtained and characterized by X-ray crystallography, UV-Vis, IR, XRD, XAS, fluorescence spectroscopy and magnetic measurements. Among the 0D molecular magnets, a variety of structures, such as heterometallic thiocyanato bridged binuclear [2], trinuclear [3], tetranuclear [4], pentanuclear [5] compounds, deserves attention. Most of them show weak ferromagnetic or antiferromagnetic interactions. A few examples of heterometallic 2D structures bridging by thiocyanate ligands with ferromagnetic coupling between metal centers are known. The first molecular magnet based on thiocyanate bridging heterometallic 2D complex has been reported. [6] Among a few known 3D thiocyanato-bridged heterometallic complexes, some examples was reported, which shows reversible ordered-disordered phase transition [7]. There are only about twenty literature reports on compounds with Ni-NCS system. Such compounds may show ferro- and piezoelectric properties or multi-step thermosensitive dielectric response directly connected with reversible structural phase transitions or act as an ionic liquid with thermochromic properties, frequency-regulated dielectric switches or semiconductors. On the other hand, reports on heterometallic complexes based on Zn-NCS are also extremely rare. This provides an appropriate approach to adjusting magnetic properties through the proper selection of auxiliary ligands defining the topology and other structural factors limiting the dimensionality of the network using thiocyanate as linkers. These studies will allow to answer questions about what is the structure of such compounds, what are their magnetism and whether there is a correlation between the structure and magnetic properties of these materials. The answer to this and the above questions will allow us to better understand the mechanism of action of potential molecular magnets and will in the future better plan the synthesis of new materials with potential magnetic activity, determining the relevance and importance of the research presented in the project.

1.3. Work plan

1. Preparation and identification of selected series of copper, nickel and zinc compounds

2. Structural and spectroscopic studies using elemental analysis, metal analysis (voltammetry, ASA, ICP), powder X-ray diffraction analysis, single crystal X-ray diffraction method, and spectroscopic methods (UV-Vis, IR, XAS, fluorimetry).

3. Detailed EPR studies and the determination of the magnetic susceptibility

4. DFT modelling of magnetic properties to support the interpretation of the experimental data

5. Determination of structure-magnetism correlations for all the series of compounds and analysis their potential application as molecular magnets

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

[1] J.R. Gispert (ed.). Coordination chemistry. Wiley-VCH, Weinheim, Germany, 2008.

[2] R. González, A. Acosta, R. Chiozzone, C. Kremer, D. Armentano, G. De Munno, M. Julve, F. Lloret, J. Faus, Inorg. Chem. 51 (2012) 5737–5747.

[3] A. Bieńko, J. Kłak, J. Mroziński, R. Boča, I. Brüdgam, H. Hartl, Dalton Trans., (2007) 2681–2688.

[4] J. Ribas, C. Diaz, R. Costa, J. Tercero, X. Solans, M. Font-Bardía, H. Stoeckli-Evans, Inorg. Chem., 37 (1998) 233–239.

[5] Y.-P. Quan, P. Yin, N.-N. Han, A.-H. Yang, H.-L. Gao, J.-Z. Cui, W. Shi, P. Cheng, Inorg. Chem. Comm., 12 (2009) 469–472.

[6] M. Mousavi, V. Béreau, C. Duhayon, P. Guionneauc, J.-P. Sutter, Chem. Commun. 48 (2012) 10028–10030.

[7] K.-P. Xie, W.-J. Xu, C.-T. He, B. Huang, Z.-Y. Du, Y.-J. Su, W.-X. Zhang, X.-M. Chena, CrystEngComm. 18 (2016) 4495–4498.

1.5. Required initial knowledge and skills of the PhD candidate

Knowledge of the principles and techniques of the subject disciplines.

Knowledge of the design, synthesis and spectroscopic studies on transition metal coordination compounds

Knowledge of the selected spectroscopic methods, UV-Vis, IR.

Organizational and project management skills.

English written and oral communication skills.

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

Advanced knowledge of the principles and techniques of the subject disciplines.

Advanced knowledge of the design, synthesis and spectroscopic studies on transition metal coordination compounds

Knowledge of the elemental analysis, metal analysis (voltammetry, ASA, ICP), powder X-ray diffraction analysis, spectroscopic methods (UV-Vis, IR, XAS), and single crystal X-ray diffraction method.

Knowledge of the EPR spectra and the determination of the magnetic susceptibility.

Knowledge of the fluorescence methods and fluorescence imaging methods.

Organizational and project management skills.

Advanced English written and oral communication skills.