Proposal 16-01-692
Time allocated: 6 shifts

Our research involves the study of molecular-based materials, which are basically built up from two types of components: paramagnetic centres (usually transition metal or lanthanide ions, they are the spins carriers) and organic ligands (named bridging ligands because they connect different paramagnetic centres). We have synthesized single crystals of novel molecular-based magnetic materials and characterized them structural and magnetically in order to establish the magnetostructural relationships. This knowledge allows us to try the design of novel metal-organic frameworks with desired magnetic properties. The purpose of this proposal is to solve the crystal structures of novel metal-organic compounds based-on polycarboxylic acids. In the context of our magneto-structural studies, several problems were proposed to be solved at the ESRF BM16 beamline.

1. Eu(III) with 1,2,4,5-benzenetetracarboxylic acid (H_4bta). A good quality data set for complex $[Eu(bta)(H_2O)_2]\cdot[Co(H_2O)_6]_{1/2}\cdot 5H_2O$ was obtained. The data was reduced with the HKL2000 program and the structure was solved and refined properly (Figure 1).

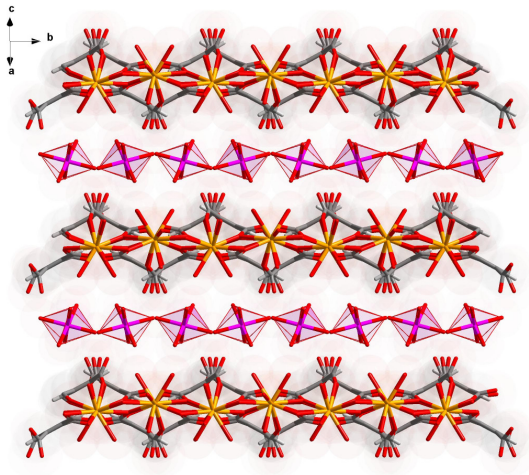

Figure 1. Perspective view of $[Eu(bta)(H_2O)_2]\cdot[Co(H_2O)_6]_{1/2}\cdot 5H_2O$ along the [101] direction showing the stacking of the layers.

2. Co(II) and Mn(II) with 1,1'-cyclohexanediacetic acid (H_2chda). The structure of the complex [Co(chda)] cannot be solved due to twinning problems. The crystals grew in the form of sheets, but after consecutive cutting up, the tiny pieces also diffract as twins or they were too small for diffracting at all. On the other hand, for the complex $[Mn_{13}(chda)_{12}(OH)_2(H_2O)_4][Naph]$ with Naph = naphtalene, we were able to obtain a good data set. The data reduction was carried out with the HKL2000 program, and it could be solved and refined (Figure 2).

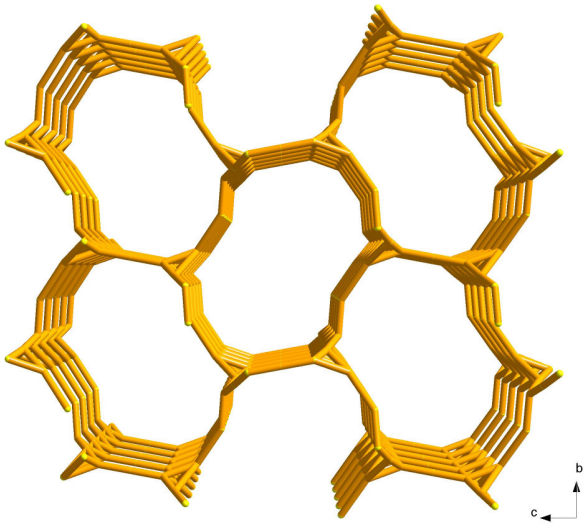

Figure 2. A central projection along the *a* axis of the manganese(II) coordination network in the complex $[Mn_{13}(chda)_{12}(OH)_2(H_2O)_4][Naph]$. Only Mn(II) ions and bridges are shown.

3. Cu(II) with methylmalonic (H_2Memal) and phenymalonic (H_2Phmal) acids. The structure of the $\{Cu(Metmal)(bpe)_4(H_2O)_n\}_n$ complex could not be solved, although extra care was taken to avoid known problems of degradation. The structure of the new phase of a phenylmalonate-conatining copper(II) complex could be solved but not refined, the quality of the data set was mediocre allowing us to visualize the structure, being the low diffraction power of the sample the main reason for the low resolution.

4. $(Ph_4P)_2M[Cu_3L_3Cl]$ [M = Co(II), Zn(II), Mn(II) and Ni(II); H_3L = mesoxalic acid]. The structures of this set of complexes were obtained in this experiment, but the result was not better than what was previously determined in the lab X-ray diffractometer. It seems that intrinsic disorder of the tetraphenylpohosponium ions in the pores of the structure, together with a rapid degradation are the main problems for the structure determination

Publications involving the solved structures within the frame of this proposal are now in progress.