Proposal 16-01-683
Structural Characterization of Magnetic Metalorganic Frameworks
Time allocated: 3 shifts

Our research is focused mainly in the study of the magnetic exchange between paramagnetic centres (first transition metal lanthanide ions) through polycarboxylic groups. Sometimes the synthesis of these complexes is quite difficult and only small or epitaxially twin crystals are obtained. In the latter case we have to cut these crystals to obtain a tiny (about 70 microns in all three directions) single crystals appropriate for X-ray diffraction. In this context, synchrotron radiation becomes the only way to obtain data, good enough, to solve and refine the crystal structure of these compounds.

There are three main tasks to accomplish in the time allocated at BM16:

1. Gd(III) with succinic acid. The $\{[Gd_2(suc)_3(H_2O)_n]_n \cdot {}_nH_2O\}$ (H_2suc = succinic acid) complex grew in clusters that after scraping some tiny crystals can be obtained. They finally were too small (a few microns) for the beam size at BM16. They seem more appropriated for a micro beam line.

2. Co(II) with pyromellitic acid; $[Co_2(bta)(H_2O)_8]_n \cdot 4nH_2O$; H_4bta = 1,2,4,5-bencenetetracarboxylic acid. A good data set was collected for this complex, and after data reduction with HKL2000, it was solved and refined successfully.

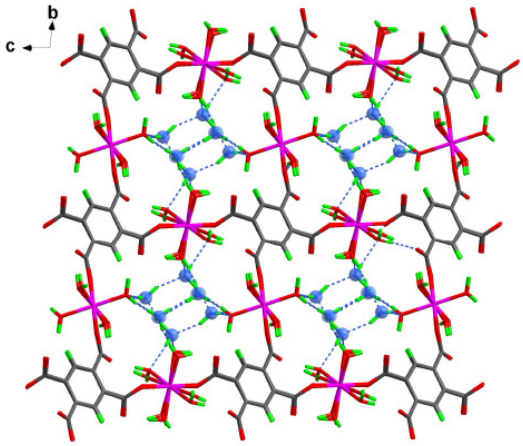

Figure 1. Projection along the *bc*-plane of the crystal structure of 1 showing the (4,4) square layers and the crystallization water molecules anchored in the porous (in blue). Hydrogen bonds are drawn as dashed lines.

3. Cu(II) with methylmalonic acid. It was not possible to improve the data set quality of those obtained in the lab diffractometer. Main problems are the twinning and the degradation of the crystals through desolvation. Although these are known problems and care was taken to avoid solvent loss during transportation to the ESRF, none of the crystals mounted worked properly.

As a result of the structure determination carried out with crystals of $[Co_2(bta)(H_2O)_8]_n \cdot 4nH_2O$ two article were published.

"(4,4) Rectangular Lattices of Cobalt(II) with 1,2,4,5-Benzenetetracarboxylic Acid: Influence of the Packing in the Crystal Structure". Fabelo O., Pasán J., Cañadillas-

Delgado L., Delgado F.S., Labrador A., Lloret F., Julve M., Ruiz-Pérez C., *Cryst. Growth & Design*, 2008, 8(11), 3984-3992.

"Well-resolved unusual alternating cyclic water tetramers embedded in a crystal host" Fabelo O., Pasán J., Cañadillas-Delgado L., Delgado F.S., Labrador A., Lloret F., Julve M., Ruiz-Pérez C. *CrystEngComm*, 2008, 10, 1743-1746.