Second Year Report of the Long Term Project HS3902
Structure-property relationships in Molecule-based Magnets

This second year of the Long Term Project has been scientifically successful but, in some way, it has also been disappointing since we have been announced that the Spanish government is not going to continue financing the BM16 beamline at the ESRF. We have been unofficially informed that the last run will be the 2011/I. Concerning the scientific issues, the main activities of the last twelve months were:

1. Scientific activities: 15 shifts were allocated on 2010 and they were used to test more than 150 different crystals and solve 61 crystal structures. Several manuscripts are in different stages of preparation, two of them are submitted to publication and one has already been published.
2. Beamline set-up upgrade: One of us (Dr Jorge Pasán) has performed a stage for three months in the beamline to help in the set-up of the beamline and test the new HKL2000 data reduction software.

1. Scientific activities.

Data collection. The beamtime scheduled for 2010 were distributed in four [February (3 shifts), June (6 shifts), July (3 shifts) and November (3 shifts)].

The first beamtime (February) allocated gave no results; some crystals were tested but they yield systematically high R_{int} factors (*ca.* 28 %) without any evident reasons. Every attempt to solve the structure with these data failed. The team at BM16 performed some tests to elucidate the problem but at the end they found out nothing but the data collected some days later worked correctly.

We tried to make the most of our second beamtime of the year in June. A total of 52 data sets were collected and 26 structures solved. Among them we can remark the complex of formula $Na_4[Mn_4Cu_6(mpba)_6(H_2O)_{12}] \cdot 81H_2O$ [mpba = *N,N'*-1,3-phenylenebis(oxamate)] (Fig. 1). This compound crystallizes in the tetragonal $P4_2/mnm$ space group and cell parameters $a = b = 36.351(5)$ Å and $c = 14.943(3)$ Å with a volume of 19745(2) Å^3. Final *R*-values are somewhat higher than usual but the complexity of the structure and disorder of water molecules inside the pores account for this problem. The crystal structure is three-dimensional and it is constructed from dinuclear $[Cu_2(mpba)]$ units linked towards Mn ions to form a (10,3)-a 3D network.

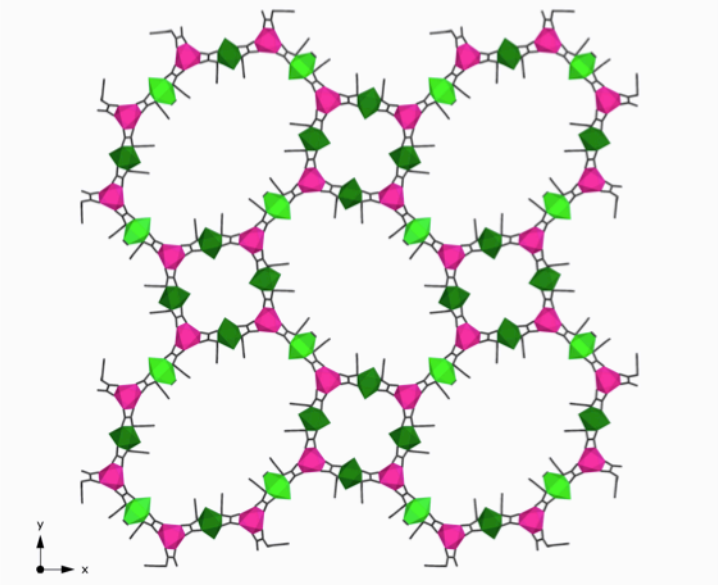

Figure 1

This metal-organic framework is an unexpected result in the coordination chemistry of the bis-oxamate ligands and it is viewed as a starting point for various experiments to prepare inclusion compounds with chiral molecules.

The third beamtime allocated (July) was mainly used to test again the crystals that did not work on the June experiment. Data sets of 28 crystals were collected, and 16 structures were solved. In particular, the two phases of the $[Cu_4Pr_4(bta)_5(H_2O)_x]\cdot yH_2O$ (H_4bta = 1,2,4,5-benzenetetracarboxylic acid) system could be solved. The phase A (Fig. 2, top) undergoes a transition to phase B (Fig. 2, bottom) at room temperature in low humidity conditions, among the small changes between the two phases, one of the bta groups changes its coordination mode and the cavities are shrunk by a 11.5% in volume. Phase A crystallizes in the P21/n space group with cell dimensions of a = 10.9527(2), b = 22.8202(4), c = 19.7589(4) Å and β = 99.6320(10)° and phase B crystallizes in the same space group with cell dimensions of a = 10.906(2), b =20.212(4), c = 19.769(4) Å and β =99.22(3)°.

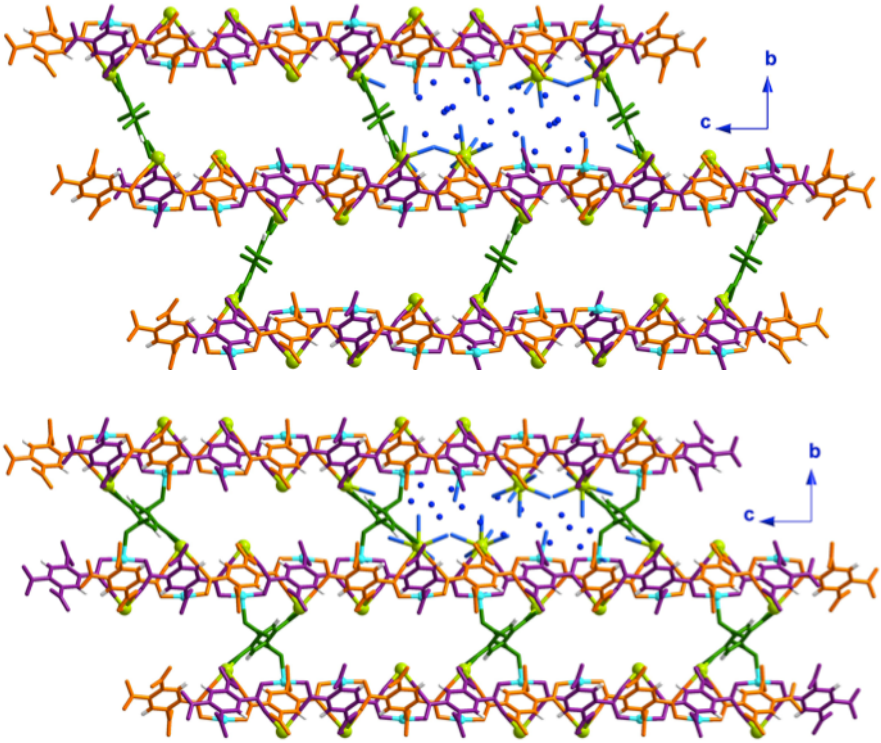

Figure 2

The fourth experiment of the year was held on November, and data sets of 27 compounds were collected, and 19 structures were solved.

In general, the reasons for low quality data collection are poor diffraction power of the crystals, rapid decomposition and loss of crystallinity during the measurement.

Publication of the results. An article has been published concerning different copper(II)-phenylenebis(oxamate) complexes in 2010 which was marked as very important paper:

- *'Oligo-m-phenyleneoxalamide Copper(II) Mesocates as Electro-Switchable Ferromagnetic Metal–Organic Wires'* E. Pardo, J. Ferrando-Soria, M.-C. Dul, R.

Lescouëzec, Y. Journaux, R. Ruiz-García, J. Cano, M. Julve, F. Lloret, L. Cañadillas-Delgado, J. Pasán, C. Ruiz-Pérez, *Chem. Eur. J.* **2010**, *16*, 12838-12851.

Two papers have been submitted to publication:

- *'Synthesis, Crystal Structures and Magnetic Properties of $M^{II}Cu^{II}$ Chains (M = Mn and Co) with Sterically Hindered Alkyl-Substituted Phenyloxamate Bridging Ligands'* J. Ferrando-Soria, E. Pardo, R. Ruiz-García, J. Cano, F. Lloret, M. Julve, Y. Journaux, J. Pasán, C. Ruiz-Pérez, *Chem. Eur. J.* **2011**, published online.

- *'Dryness Sensitive Porous 3d-4f Metal–Organic Framework with Unusual Dynamic Behaviour'* O. Fabelo, L. Cañadillas-Delgado, J. Pasán, P. Díaz-Gallifa, A. Labrador, C. Ruiz-Pérez, submitted to *Chem. Commun.*

A number of papers are in preparation, among them there is one in its final revision and it will be submitted to Angewandte Chemie:

- '*Reversible Solvatomagnetic Switching in a Sponge-Like Manganese(II)-Copper(II) 3D Open-Framework Ferrimagnet with a Pillared Square/Octogonal Layer Architecture'*.

2. Beamline set-up upgrade.

Few upgrades were carried out this year in the beamline, in part, due to the upcoming dismantling of BM16. Dr Jorge Pasán has performed a stay for three months in the beamline to help in the setup and testing the new HKL2000 data reduction software installed (financed by the Laboratorio de Rayos X y Materiales Moleculares).

The finance requested for equipment of the beamline in our scientific projects to the Spanish Ministry of Education and Science was partially approved. In this framework, the new license of the HKL2000 software was acquired. The budget for the other equipment is awaiting for final decisions about BM16.