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

The first year of the Long Term Project (today unfinished since the 9 shifts established for the first year will be completed the next February where the experiment for the last 3 shifts is scheduled) has been successful. Three are the main activities carried out during these first six months of project:

1. Scientific activities: 6 shifts of beamtime were scheduled in November and they were utilized to solve 12 crystal structures.
2. Beamline set-up upgrade: A new slits box and a prototype of the beam-conditioning unit have been installed.
3. Financial request for equipment: In the next call for proposals of projects of the Spanish Ministry of Education and Science a specific request for equipment has been made.

The various research groups and the BM16 team have joint their efforts to make the beamline more accessible for small molecule users, without forgetting the scientific achievements that backup our proposal. The three activities are now explained in detail.

1. Scientific achievements. A set of more than thirty crystals was tested on the diffractometer at BM16 in the beam time allocated. Good data sets were obtained for fifteen of them and among the reasons for the collection of poor data sets are twinning, the poor diffraction power, and rapid decomposition of the crystals. The final crystal structure with reasonable good parameters was obtained for twelve compounds. We present hereunder some examples of the crystal structures solved included in the milestones for the Year 1 in the proposal:

a. $(TBA)_4[Cu_2(Mempba)_2]\cdot 2H_2O$ [TBA = tetrabutylammonium and Meppba = 2-methyl-meta-phenylene(bis)oxamate]. The complex crystallizes in the monoclinic system with a $C2/c$ space group and cell parameters of a = 23.959(5) Å, b = 19.353(4) Å, c = 22.494(4) Å and β = 115.59(3)° with a volume of 9406.9(3) Å^3. The final R values are 0.117 for $I>2\sigma(I)$ and 0.131 for all the reflections. The structure consists of a dinuclear anionic unit of $[Cu_2(Mempba)_2]$ and tetrabutylammonium cations and crystallization water molecules (Figure 1). The structure confirms the formation of the homometallic precursor that can be used in a 'complexes as ligands' approach for further syntheses.

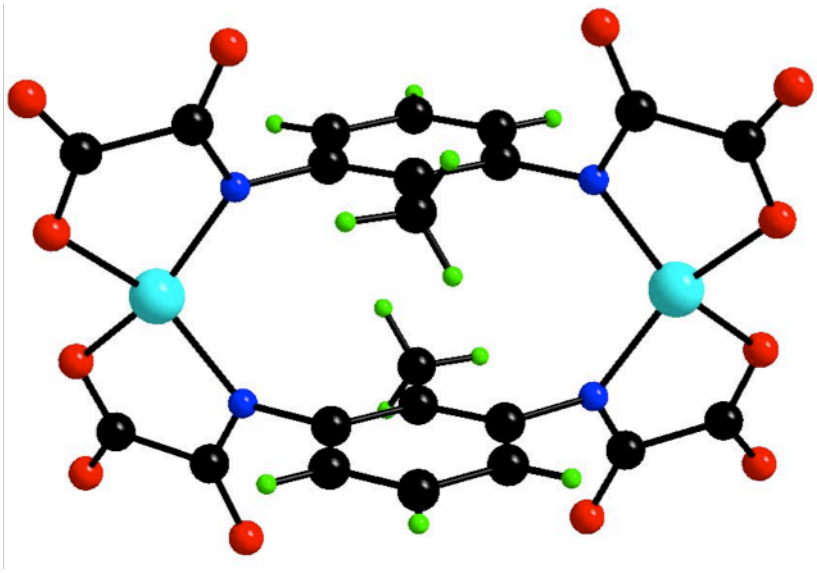

Figure 1. Dinuclear anionic unit of $(TBA)_4[Cu_2(Mempba)_2]\cdot 2H_2O$

b. $(TBA)_4[Cu_2(2,6\text{-anba})_2]$ [TBA = tetrabutylammonium and 2,6-anba = 2,6-anthracene(bis)oxamate]. The complex crystallizes in the orthorhombic system in the *Pbca* space group with cell parameters of a = 23.490(5) Å, b = 16.875(3) Å and c = 24.537(5) Å and a cell volume of 9726.3(3) Å^3. The final refining parameters are $R(I>2\sigma(I))$ = 0.072 and R(all) = 0.081. The crystal structure consists of, like in the previous example, a dinuclear anionic unit of $[Cu_2(2,6\text{-anba})_2]$ and tetrabutilammonium cations (Figure 2). The structure opens up new possibilities in the area of bis-oxamate ligands, since the body of the ligand can add new properties to the material. In this case the system undergoes a single-crystal to single-crystal transformation when the complex is excited with UV radiation. This excited state has to be characterized by X-ray diffraction and it is an important task for the next scheduled beamtime.

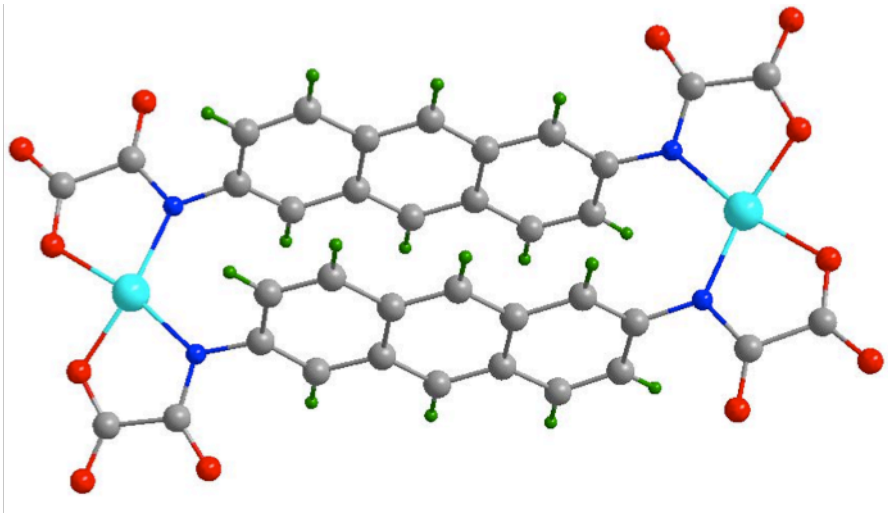

Figure 2. Anionic unit of the $(TBA)_4[Cu_2(2,6\text{-anba})_2]$ complex.

c. $[Cu(L)(H_2O)]_n$ [L= N,N'-bis-(4-carboxybenzoyl)-1,2-diaminoethane]. The complex crystallizes in the monoclinic system in the P21/c space group with cell dimensions of a = 17.858(4) Å, b = 5.9770(12) Å, c = 8.6060(17) Å and β = 100.32(3)° and cell volume of 903.7(5) Å^3. The final refinement lead to agreement parameters $R(I>2\sigma(I))$ = 0.062 and R(all) = 0.065. The crystal structure consists of chains made of the regular alternation of N,N'-bis-(4-carboxybenzoyl)-1,2-diaminoethane groups and diaquacopper(II) cations (Figure 3). The dimensionality of the complex is lower than expected but the formation of a metal-organic framework (MOF) through the coordination of a very flexible dicarboxylate is a fantastic result that can orientate the next steps of research.

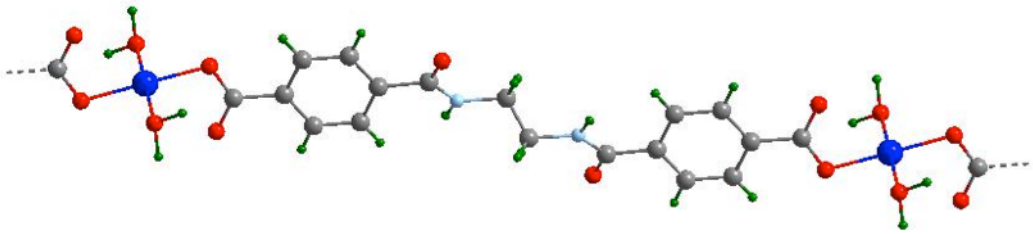

Figure 3. A view of the coordination network of the $[Cu(N,N'\text{-bis-}(4\text{-carboxybenzoyl})\text{-}1,2\text{-diaminoethane})(H_2O)]_n$

2. Beamline set-up upgrade. The major improvements have been carried out in the beam conditioning unit where a prototype from HUBER has been installed, the BCU3100. This is a modular device that bring together different beam handling systems. Among them, we can remark the monitoring system for the alignment of the diffractometer in case of beam drifts and a very accurate pair of slits, with a alignment threshold of less than 1 micrometer, to constrain reliably and with high definition the area illuminated by the beam. The technical operation of this system undergoes continuous testing by the beamline users but a specific test for small molecule complexes and different crystal sizes is planned for the next year to establish an operation protocol.

3. Financial request for equipment. In the next call for proposal of projects to be carried out from 2011 to 2013 of the Spanish Ministry of Education and Science, our research groups have include a specific entry in the budget for equipment for the BM16 beamline. This equipment consists of:

- A beamstop assembly for, especially, reduce the detector to sample distance to increase the maximum resolution reachable by the diffractometer (particularly useful for charge density experiments).
- A high-pressure cell for measurements under extreme conditions.
- Fungible goods such as cryoloops, crystalcaps, and other laboratory equipment for crystallography.
- A license for the HKL2000 softwarer program in its small molecule version for the Q210 ADSC detector. The software currently installed in the beamline for data indexing, integration and scaling is oriented to the solution of macromolecular crystal structures, therefore an update is required.