	Experiment title: Photomagnetic Fe/Co Prussian blue analogues: From networks to cube and square molecules	**Experiment number**: CH-3621
Beamline: ID12	**Date of experiment**: from: 26/06/2013 to: 02/07/2013	**Date of report**: 16/08/2013
Shifts: 18	**Local contact(s)**: Fabrice Wilhelm	*Received at ESRF:*

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Report:

Scientific background

This proposal was devoted to the study of the local magnetic properties of photomagnetic molecules. Over the past decade there has been considerable interest in the development of tunable molecule-based materials that exhibit bistability in their physical properties as a function of external stimuli. Cyanometalates, in particular Co/Fe Prussian blue compounds, exhibit these bistable properties. At low temperatures, they are diamagnetic and order ferrimagnetically upon white light irradiation. The extended 3D structure of these systems is cubic. Going to nanoscale systems, two new complexes, $\{Fe_2Co_2\}$ and $\{Fe_4Co_4\}$, were synthesized as elementary motifs of the Co/Fe Prussian blue: a molecular cube and square, respectively ((a)Dongfeng L. et al., *J. Am. Chem. Soc.* **2008** 130, 253; (b) Zhang Y. *et al.*, Angew. Chem. Int. Ed. **2010**, 49, 3752 –3756). As for the 3D analogue, they present *magnetic bistability. The magnetic properties of the two complexes are different and the nature of Co-Fe interaction in* the photoinduced state is far from being fully understood. The aim of this proposal is to clarify the interactions as well as the magnetic state of the Fe and Co metallic ions in the thermal and photomagnetic transitions.

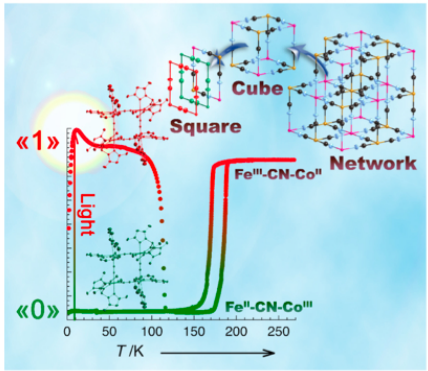

Figure 1: presentation of the square, cubic and bulk Fe/Co structures. χT measurements of the square complex $\{Fe_2Co_2\}$

Experimental details

As obtained from the synthesis, the building blocks are surrounded by solvent molecules, which have a strong influence on the photomagnetic properties of the compound. The compounds had to be protected

from desolvation in ultra high vacuum conditions. Thus the samples were deposited in a cavity on the sample holder and sealed by a kapton film. This film allows the penetration by X-rays and by the different light sources (infra-red LED and white lamp) used for photoexcitaton. We encountered a lot of difficulties to photo-excite the samples. The 17 tesla set-up of ID12 beamline has indeed no window close to the sample. We used different light sources (940 nm LED and white lamp) which beam was focalized by a lens placed at 60 cm from the sample (the smallest possible distance for the 17 tesla chamber). We were able to measure three samples: two square $\{Fe_2Co_2\}$ complexes, (i) MeObpy_$\{Fe_2Co_2\}$ that presents a spin-crossover (ii) bpy_$\{Fe_2Co_2\}$ that presents a charge transfer transition and (iii) a precursor $TpFeCN_3$ used for the synthesis which XANES and XMCD will be used as references. We measured:

1) the XANES at room temperature at Fe and Co K edges (figure 1)
2) the XANES as a function of the temperature at the Co K edge (figure 2)
3) the XANES at 2 K at Fe and Co K edges, before photoexcitation
4) the XMCD at 2 K at Fe and Co K edges after 18 hours of white light excitation
5) the XANES at room temperature at Fe and Co K edges, after relaxation

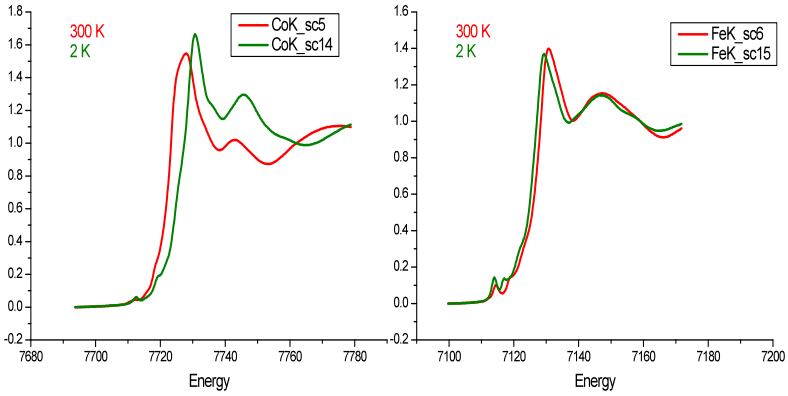

Figure 1: XANES at Co K edge (left) and Fe K edge (right) at 300 K (red) and 2 K (green) for square $\{Fe_2Co_2\}$ complexe

Results

We obtained a complete set of data for only one sample (square $\{Fe_2Co_2\}$ complexes (i)) and for the Fe precursor. The change of oxidation state of Fe and Co was clearly observed: at room temperature one observes low spin Fe(III) and high spin Co(II) and at low temperature (2 K) one observes low spin Fe(II) and low spin Co(III). The electron-transfer phenomenon was also followed as a function of the temperature (see above) by XANES at the Co K edge and compared with the magnetic data. After photoexcitation at 2 K (80 % of photoconversion) one clearly observes the charge transfer between Co and Fe ions and one gets low spin Fe(III) and high spin Co(II). At this temperature, XMCD signals have been obtained at Fe and Co K edges. These measurements will give access to the nature of the coupling between Fe and Co ions. This is a very important result to understand the magnetic properties of the compounds in its photoexcited state. The reversibility was checked: the system was back to its initial state when it was warmed up at 300 K. Only one photomagnetic sample could be completely measured because of the difficulties to prepare the sample and keep it solvated but above all to the insufficient photoexcitation conditions. We think that our light source was too far away from the sample despite the use of the focalizing lens: the distance between the lens and the sample was 60 cm. Due to these technical difficulties, we had not enough time to measure the cube $\{Fe_4Co_4\}$ complex.

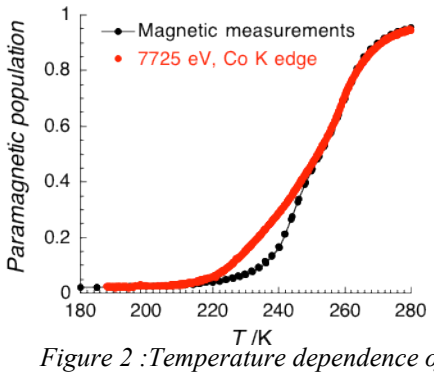

Figure 2 :Temperature dependence of paramagnetic $\{Fe_2Co_2\}$ complexe population by magnetic measurements (1000 Oe) in comparison with the XANES data at the Co K edge

After discussion with the scientists in charge of ID12, Andrei Rogalev and Fabrice Wilhelm, a modification in the 17 tesla chamber will be made for future experiments. A hole in the sample transfer part and a window could be added. The light source would be then at less than 10 cm from sample allowing a better photoexcitation of the photomagnetic samples (spin-crossover, electron-transfer, photoisomerizable compounds…).