ESRF	**Experiment title:** Magnetic characterization of the X-ray induced excited states in mixed valence prussian blue analogues	**Experiment number**: CH1786
Beamline: ID24	**Date of experiment**: from: 16/2/2005 to: 22/2/2005	**Date of report**: 27/2/2005 *Received at ESRF:*
Shifts: 18	**Local contact(s)**: Dr. Olivier Mathon	

Names and affiliations of applicants (* indicates experimentalists):

Dr. Serena Margadonna

School of Chemistry, University of Edinburgh, EH9 3JJ Edinburgh, UK

Prof. Kosmas Prassides

Department of Chemistry, University of Durham, DH1 3LE Durham, UK

Report:

The aim of the experiment was to employ the X-ray absorption (XAS) and magnetic circular dichroism (XMCD) techniques at the K absorption edges of Mn and Fe to characterise directly the magnetic properties of the photoswitched excited states in the prussian blue analogue $Rb_{0.7}Mn^{II}_{1.15}[Fe^{III}(CN)_6]\cdot 2H_2O$. From high-resolution synchrotron X-ray diffraction, we were able to show that in this cubic mixed valence metal cyanide, the X-ray light could induce interconversion between the ground (Mn^{II}(HS, $t_{2g}^5e_g^0$, S = 5/2)-NC-Fe^{III}(LS, $t_{2g}^5e_g^0$, S = ½)) and excited states over a broad temperature range between room temperature and 10 K (Margadonna, Prassides & Fitch, *Angew. Chem.* **2004**, *43*, 6316). Depending on the experimental conditions (illumination time, X-ray energy, temperature), a variety of internal charge transfer processes and spin transitions were triggered resulting in either continuous (second-order) or abrupt (first-order) phase transformations. We requsted beamtime on ID24 to probe the electronic and spin states of Mn and Fe in the photoinduced phases.

The high intensity and the rapid data acquisition of ID24 allowed us to follow in real time the internal redox processes which lead to the photoinduced transitions. Fig. 1a shows the evolution of the XAS spectra collected at 100 K and at the K edge of Mn as a function of time. The shift of the absorption edge is a clear signature of the X-ray induced electron transfer and of the formation of the Mn^{III}(HS, $t_{2g}^4e_g^0$, S = 2)-NC-Fe^{II}(LS, $t_{2g}^6e_g^0$, S = 0) PT1 state. The sample was then cooled down to 10 K and XAS spectra were collected as a function of time at the Mn K edge (Fig. 1b). Again we could follow the internal redox proces which leads to the formation of the Mn^{II}(IS, $t_{2g}^4e_g^1$, S = 3/2)-Fe^{III}(LS, $t_{2g}^5e_g^0$, S = ½) photoexcited PT2 state. Quite interestingly during the experiment, we could always compare the spectra of the photoinduced phases with those of non-exposed fresh sample, used throughout the experiment as reference point. At 10 K, the material comprises of ferromagnetically ordered Mn^{II} ions and a clear XMCD signal is observed. Fig. 1c shows a comparison of the XMCD spectra collected on PT2 and on non-exposed sample. There is a clear difference between the integrated intensity of the XMCD signal of the original phase and that of PT2 which is less intense by a factor of ~2/3. We note that in the original phase, the Mn^{II} ions are in their HS state with S=5/2 and a μ_{eff} of 5.9 μ_B per ion. A decrease in the integrated intensity of the XMCD signal is linearly related to a reduction in the value of the magnetic moment associated with the transition metal ion. From the XAS and XMCD spectra at 10 K, it is clear that in the PT2 phase the vast majority of the Mn ions have oxidation state of +2 with an intermediate spin state S=3/2 corresponding to 3.9 μ_B. This accounts well for the reduction in the XMCD signal upon photoexcitation. The internal redox processes and the formation of PT1 and PT2 were also followed at the Fe edge and similar effects were observed (Fig. 1d).

A careful analysis of the data is currently under way but it is already clear that the results of this experiment are far reaching. We were able to obtain unambigous evidence of the high sensitivity of this multistable molecular material to X-ray light with facile interconversion between a number of excited states with differing charge (electronic) and spin (magnetic) states at temperatures ranging from 10 K to room temperature. Such phenomena have not been reported before for a single molecular system and they open the way for the study of otherwise inaccessible electronic excited states. In particular, X-ray illumination at 10 K results in formation of an excited state with Mn^{II} in its intermidiate spin state IS. This represent the first example of a Mn^{II} IS ion in octahedral geomentry.

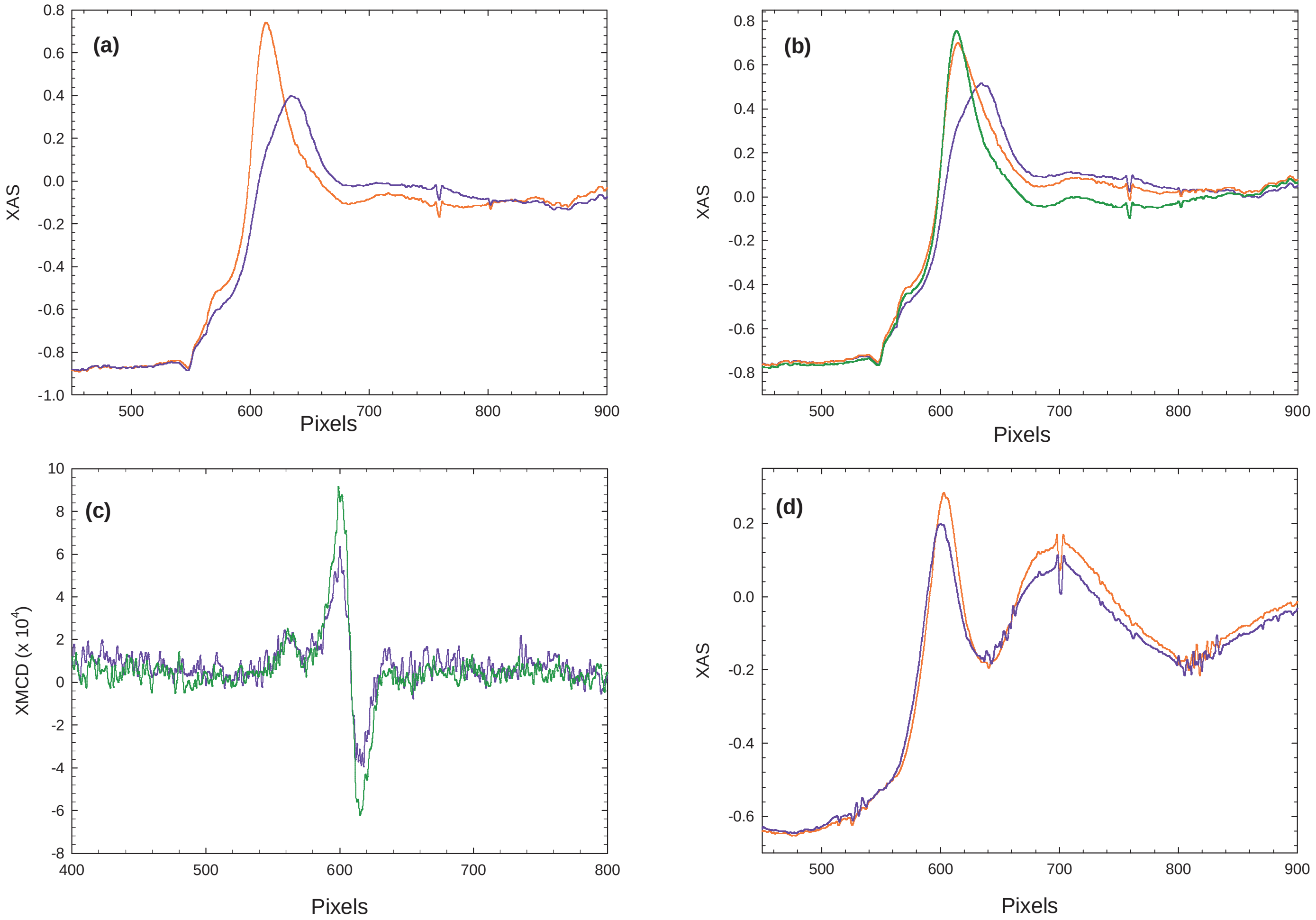

Fig. 1 (a) Time evolution of the X-ray absorption spectra at 100 K and at the Mn *K*-edge for Rb$_{0.7}$Mn$^{II}_{1.15}$[Fe^{III}(CN)$_6$]·2H$_2$O. The red spectrum corresponds to illumination time t = 0 and the blue spectrum to t = 4 hours. (b) Time evolution of the X-ray absorption spectra at 10 K and at the Mn *K*-edge. The red spectrum corresponds to illumination time t = 0 and the blue spectrum to t = 3.5 hours. The green line corresponds to the spectrum of the fresh non-exposed sample. (c) XMCD spectra (L-R) at 10 K at the Mn *K*-edge. The blue spectrum corresponds to illumination time t = 3.5 hours. The green line is the XMCD spectrum of the fresh non-exposed sample. (d) Time evolution of the X-ray absorption spectra at 100 K and at the Fe *K*-edge for Rb$_{0.7}$Mn$^{II}_{1.15}$[Fe^{III}(CN)$_6$]·2H$_2$O. The red spectrum corresponds to illumination time t = 0 and the blue spectrum to t = 3 hours.