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Project CH-4330

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The aim of these measurements was the **XMCD investigation of the first {FeCo} binuclear molecules exhibiting thermal and photo-magnetic properties**. The family of Co/Fe Prussian blue analogues (PBA) are known for their photomagnetic properties and offer a large flexibility in their composition and structure that lead to tunable physical properties. One of the actual challenges in the science of magnetism is the design of nanoscale magnetic materials for the potential applications in energy efficient, switchable molecule-based information storage or electronic devices [1]. The breakthrough of the Fe/Co PBAs which behave as magnets activated upon visible light irradiation, has led to a resurgence of design and synthesis of new molecular-based magnets (Ref.6 from [1]). At 4K, the system is diamagnetic and orders ferrimagnetically upon visible light irradiation. Indeed it exhibits a reversible metal-to-metal electron-transfer between diamagnetic {Fe^{II}(low spin, S=0)-Co^{III}(low spin, S=0)} pairs and paramagnetic {Fe^{III}(low spin, S=1/2)-Co^{II}(high spin, S=3/2} pairs (Fig 2). In the photoinduced metastable state, Fe^{III} and Co^{II} ions are antiferromagnetically coupled, and the material behaves as a ferrimagnet below 20 K ([1] ref 6). We determined the nature of the coupling by XMCD measurements at K edges [2]. Going from the original three-dimensional cubic PBA to nano-scale and molecular systems, **the first dinuclear molecules** {FeCo} were recently synthesized, at the Institutes CRPP/ICMCB in Bordeaux, and represent **the elementary motif of the Co/Fe Prussian blue**. They present thermal and photo-magnetic bistability: the molecules are paramagnetic at room temperature and are diamagnetic at low temperature. Upon white light irradiation the low temperature diamagnetic state transform into a paramagnetic state (see Fig 1). The nature of Co-Fe interaction in the photo-excited state was far from being fully understood and XMCD was a technique of choice to answer this question.

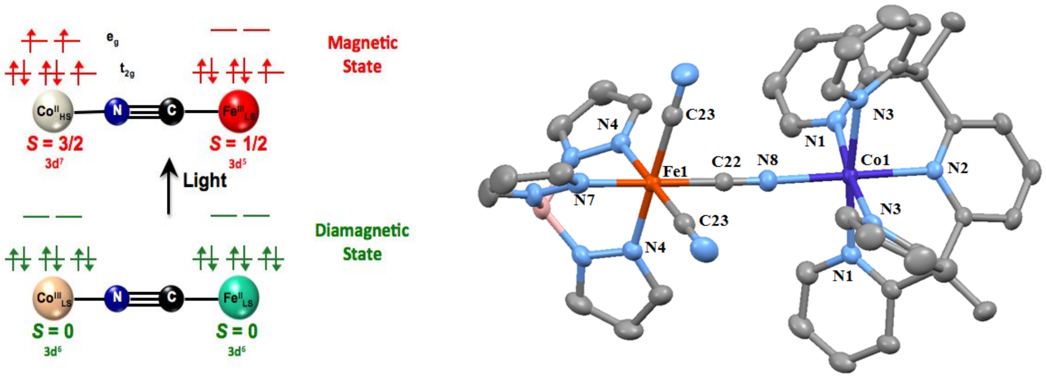

Figure 1. Scheme of ligh induced charge transfer in the Fe/Co (left) and structure of the switchable cationic {FeCo} dinuclear complex **1** (right).

The first experiment includes the investigation of the thermal induced electron transfer process at one of the family of these {FeCo} dinuclear complexes, as well as the reversibility of this property by X-ray absorption spectroscopy. The X-ray absorption spectroscopy (XAS) of an element is sensitive to its local environment (symmetry, nature of the ligands, metal-ligand distances, and bonding), and to its oxidation and spin states. Fe and Co K-edge XAS spectra were recorded for the dinuclear complex **1** at 300 K and 70 K, as it's magnetic properties from squid measurements suggested (see Fig 2.)

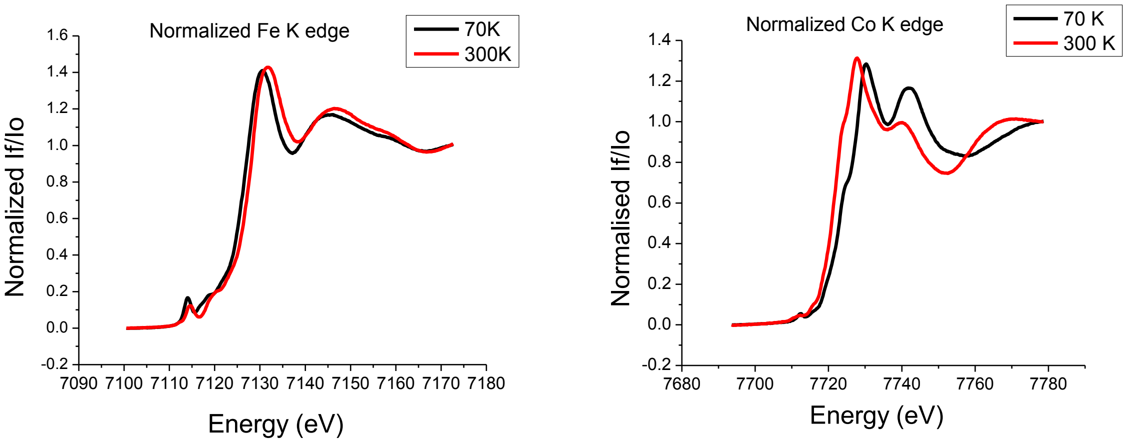

Figure 2. Fe and Co K-edge XAS spectra for 300 and 70 K.

The XAS spectra of **1** showed absorption edges at 7.132 eV (LS Fe^{III}) and 7.728 eV (HS Co^{II}) at 300 K, and the edges shifted to 7.130 eV (LS Fe^{II}) and 7.730 eV (LS Co^{III}) upon cooling to 70 K, confirming the electron transfer between the paramagnetic {Fe^{III}(low spin, S=1/2)-Co^{II}(high spin, S=3/2} state and the diamagnetic {Fe^{II}(low spin, S=0)Co^{III}(low spin, S=0)} state. By choosing the energy of 7.725 eV, we followed the thermal dependence of the XAS of Co K-edge between 300 and 70 K, which is in an perfect agreement with the squid measurements (Fig.)[1]. In heating mode, we observed reversibility of the phenomenon. (Fig. 3)

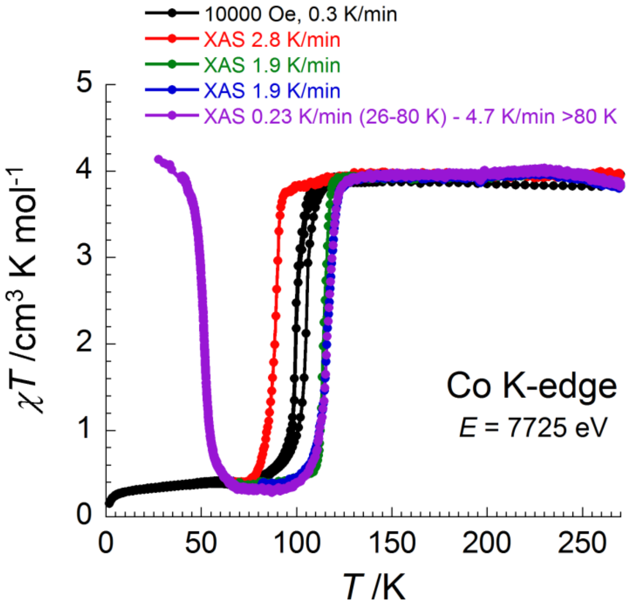

Figure 3. Temperature dependence of the χT product between 280 to 1.8 K (black curve), temperature dependence of Co K-edge XAS spectra between 300 and 70 K in cooling mode (red curve) and in heating mode (blue curve) and temperature dependence of Co K-edge XAS spectra between 20 and 300 K in heating mode (purple curve) after irradiation 7h at 2 K 940 nm LED, for a polycrystalline sample of **1** .

The second experiment includes the investigation of low temperature photoinduced paramagnetic metastable state. The Fe and Co K-edge XAS spectra were recorded at 2 K before irradiation and at 2 K after irradiation of LED 940 nm, P=1.5 mW for 7h. The XAS spectra at 2K after the irradiation of **1** showed absorption edges shifted to 7.132 eV (LS Fe^{III}) and 7.728 eV (HS Co^{II}) (Fig. 4.), confirming the photoinduced electron transfer between the diamagnetic {Fe^{II}(low spin, S=0)Co^{III}(low spin, S=0)} state at low temperature to the paramagnetic {Fe^{III}(low spin, S=1/2)Co^{II}(high spin, S=3/2} state after irradiation.

The third experiment concerns the XMCD studies of compound **1**. Since the light-induced metastable state is paramagnetic, XMCD signals were observed at Fe and Co K edges at 2 K upon light irradiation in an applied field B= +/- 17 T. (Fig. 5.). After the photo-excitation experiments, the reversibility of the thermally and photo-induced intramolecular ET was verified. The system recovered its initial state when it was warmed up to 300 K (Fig. 3, purple curve). The relaxation temperature is in a good agreement with the reflectivity studies (Fig. 6.)

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[1] The shift of 10 K, observed in fig. 3, is attributed to the use of different sweeping rate of the cooling mode between the squid and the XAS measurements.

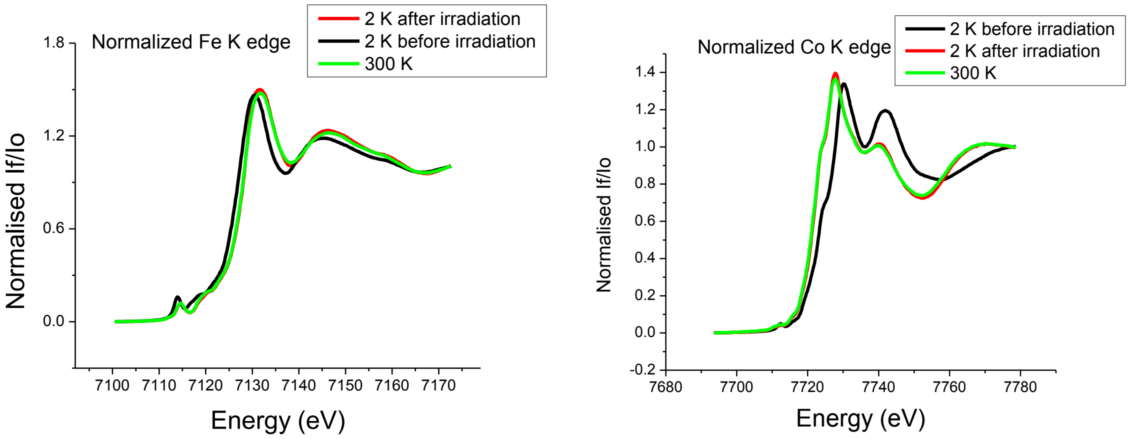

Figure 4. Fe and Co K-edge XAS spectra for 300 and 2 K, and at 2 K after irradiation with LED 940 nm for 7h (P= 1.5 mW).

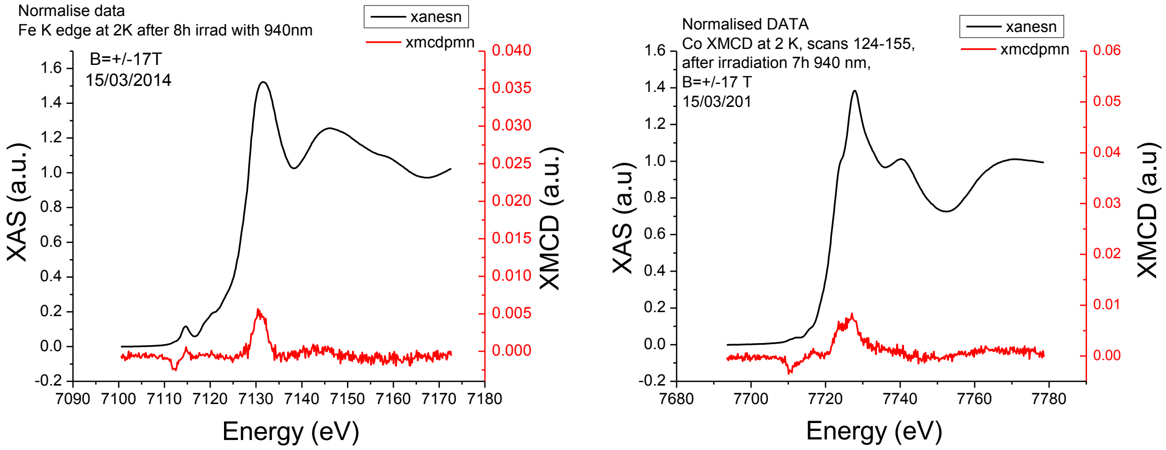

Figure 5. Isotropic (average, black) and dichroic (XMCD, red) absorption spectra at Fe (left) and Co(right) K edges.

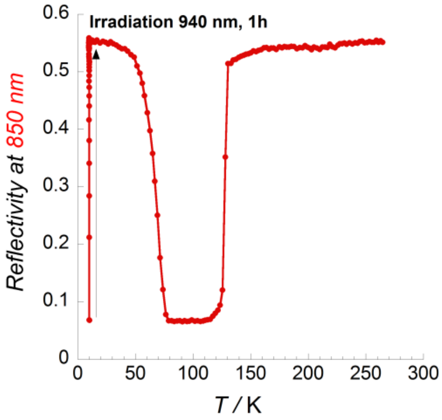

Figure 6. Absolute reflectivity of **1** at 850 nm (*R*$_{850}$) in heating mode after 1 h of LED irradiation 940 nm at 10 K.

The fourth experiment concerns the determination of the magnetic interaction (ferromagnetic vs antiferromagnetic) between the Fe^{III} and Co^{II} in the photo-induced metastable state at 2 K and with two different field values, +/-17 T and +/-8 T. The macroscopic magnetization data (Fig. 7) show no inflection point that may correspond to the presence of ferromagnetic interactions between Fe^{III} and Co^{II} ions. At both Fe and Co K edges, the dichroic signals have the same sign (positive for intense peaks corresponds to the allowed transition to the *p* levels, and negative for the very weak signals of the forbidden transitions to the *d* levels). The same signs (or directions) of the XMCD signals from cobalt and iron sites can be *preliminary* considered as a local characterization of the ferromagnetic coupling between cobalt and iron ions in the photo-induced metastablestate of compound **1**. To confirm these preliminary result and conclusions additional interpretations through theoretical calculations will be necessary.

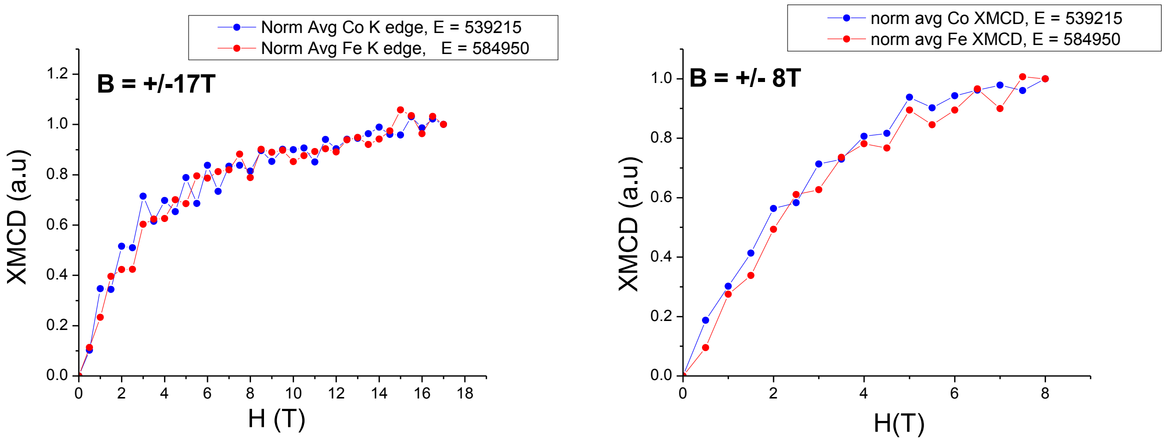

Figure 7. Magnetization curves of Fe and Co K-edge of the the photo-induced metastable state at 2 K in an applied field +/-17 T (left) and +/-8 T (right).

Finally, XMCD studies at 2K and with applied field +/-17 T were performed for the Fe^{III} and Co^{II} precursors of the complex **1** in order to be compared with the last one (Fig. 8).

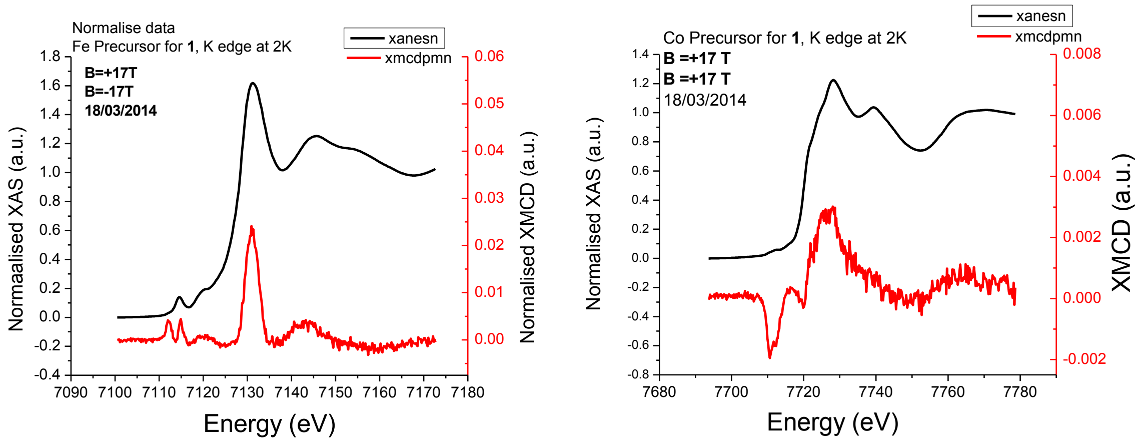

Figure 8. Isotropic (average, black) and dichroic (XMCD, red) absorption spectra at Fe K edges of the Fe^{III} precursor (left) and Co K edges for the Co^{II} precursor (right).

References

[1] Sato O., *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* **2004**, 5, 3, 203-223.

[2] Champion G. *et al. J. Am. Chem. Soc.,* **2001**, 123, 12545.