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Project CH-4036

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Scientific background

This project is dedicated to solution studies of electron transfer molecules with XANES and XMCD measurements. As previously done for the Co/Fe bulk Prussian blue analogs and also molecular objects, the electron-transfer phenomenon (Figure 1) has been studied by XMCD measurements at the Co and Fe K edges [1,2], to answer the question regarding the spin and oxidation states of the different metal ions in the diamagnetic and paramagnetic states, and also to probe the nature of the Co-Fe magnetic interaction inside the molecule. XMCD at Fe and Co K edges are particularly well adapted to the measurements in solids.

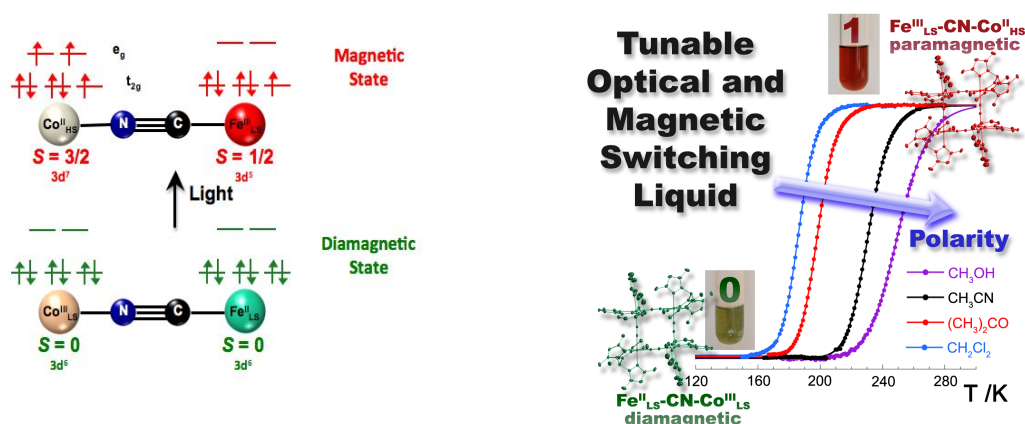


Figure 1. Scheme of thermal- and light-induced electron transfer in the Fe/Co unit (left) and magnetic measurements in solution for the {FeCo} square 1 (right).

Recently, we focused on electron-transfer properties in diluted solutions of these systems in order to estimate the intrinsic properties of the isolated molecules independently of a crystal packing or a network. In order to have a good solubility, we have synthesized new molecules with functionalized ligands. Two new $\{\text{Fe}_2\text{Co}_2\}$ complexes have been prepared and they exhibit the thermal- and light-induced electron transfer in the solid state and in solutions [3a,b]. As expected, the solutions display the properties of the isolated molecules with an electron-transfer crossover (Boltzmann population) rather than a phase transition linked to crystal packing effects in the solid state. Interestingly, we have shown with a combination of UV-Visible and magnetic studies in solutions that the electron-transfer can be tuned by the nature and the polarity of the solvent [3, Fig. 1 Right]. A positive shift of 60 K for the electron transfer temperature has been observed when the solvent is more polar. The objective of this proposal is to follow the electron transfer in solutions using local techniques.

Experimental details

In cooperation with the ID12 beamline scientists, we have designed a specific glass cell adapted for the solution measurements. We focused on one Fe_2Co_2 square [3] soluble in methanol (freezing point at 176 K). We have tested two different concentrations ($C=3 \cdot 10^{-2}$ Mol/L and $C=2 \cdot 10^{-3}$ Mol/L). For each concentration, we measured:

- 1) the XANES at room temperature at Fe and Co K edges.
- 2) the XANES at 200 K and 225 K at Fe and Co K edges to check if we are able to follow the electron transfer in solution above the freezing point of the solvent.
- 3) the XANES as a function of the temperature at the Co K edge (several cycles to check the stability of the solution).
- 4) the XANES at 200 K at Fe and Co K edges under X-ray irradiation during several hours
- 5) the XANES at room temperature at Fe and Co K edges to check the reversibility.

Results

The first experiment consists of the investigation of the thermal induced electron transfer process in solution for one of the $\{\text{FeCo}\}$ tetranuclear complex, 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 tetranuclear complex at 300 K and 200 K, as its magnetic properties from squid measurements suggested an electron transfer at 260 K (see Fig 2).

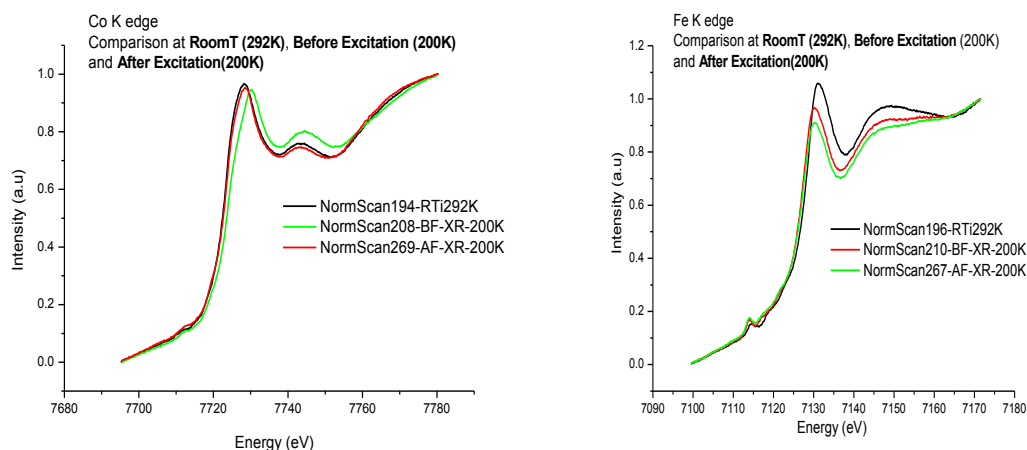


Figure 2. Fe and Co K-edge XAS spectra for 300 and 200 K for the preparation **1** ($3 \cdot 10^{-2}$ Mol/L).

The XAS spectra of **1** showed absorption edges at 7.132 eV (LS FeIII) and 7.728 eV (HS CoII) at 300 K. By choosing the energy of 7725 eV, we followed the thermal dependence of the XAS of Co K-edge between 300 and 200 K. The observed curve is in an perfect agreement with the squid measurements between 300 K and 220 K, but below 220 K, we observed a partial formation of Co(II). By measuring the XAS of Fe and Co edges at 200 K for several hours, we observed in these conditions the presence of Co(III) and Fe(II), as expected for the diamagnetic state, but also the presence of Co(II). In heating mode, we observed a good reversibility of the phenomenon for the Co K edge (Fig. 3). but not for the Fe ion. These data suggests some degradation of the sample.

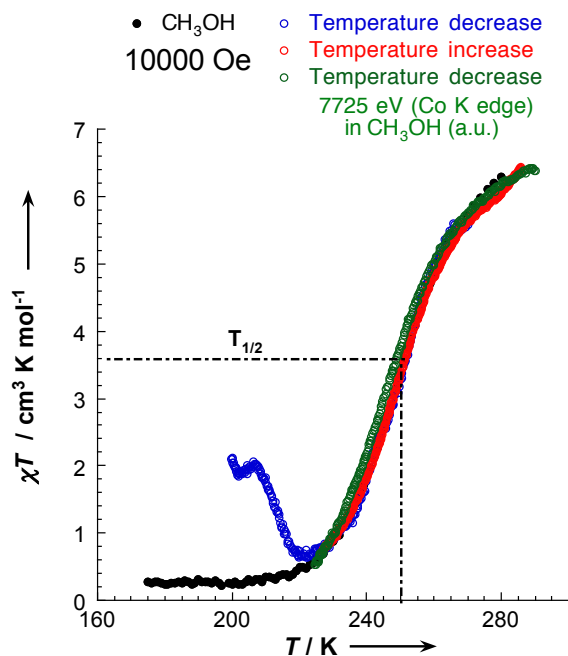


Figure 3. Temperature dependence of the χT product between ≈ 80 to 1.8 K (black curve), temperature dependence of Co K-edge XAS spectra between 300 and 200 K in cooling mode (blue curve) and in heating mode (red curve) and again in second cooling mode between 300 and 240 K (green).

The second experiment includes the investigation of the second solution (less concentrated, $C=2 \cdot 10^{-3}$ Mol/L) with a reduced flux to avoid the degradation of the sample. By choosing the energy of 7725 eV, we followed the thermal dependence of the XAS of Co K-edge between 300 and 225 K, and observed a good reversibility (Figure 4). During a second cooling at 225 K, we observed the stability of the signals (over 5 hours) on the Fe and Co K edges. In these conditions, we confirm the electron transfer in temperature (Figure 5) and its reversibility.

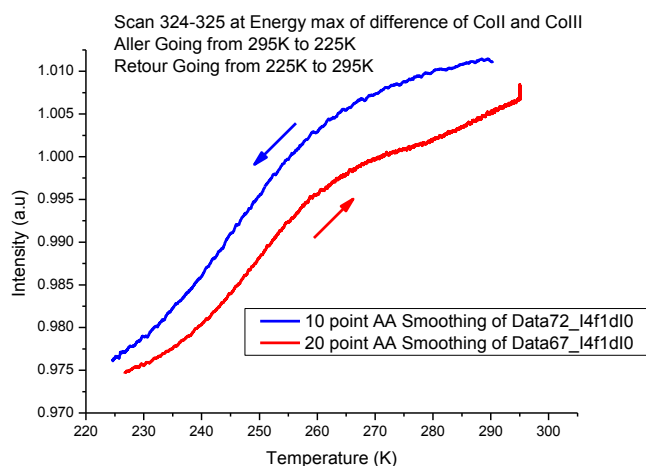


Figure 4. Temperature dependence of Co K-edge XAS spectra between 300 and 225 K in cooling mode (blue curve) and in heating mode (red curve) on preparation **2** ($2 \cdot 10^{-3}$ Mol/L).

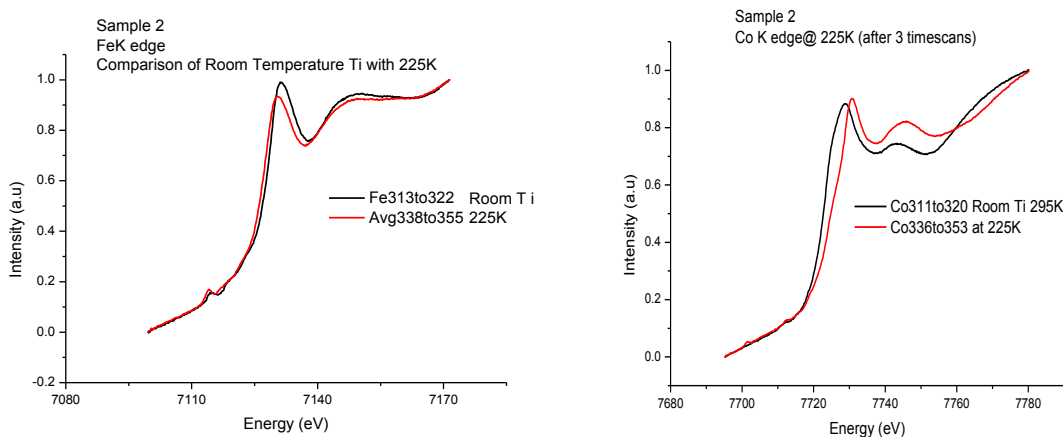


Figure 5. Fe and Co K-edge XAS spectra for 300 (black) and 225 K (red) for the preparation **2** ($2 \cdot 10^{-3}$ Mol/L).

The sample was placed at 200 K, and exposed the sample to X-ray beam. In these conditions, the Co(II) is transformed in Co(III) whereas the Fe stayed in +II oxidation state (Figure 6). This confirms the photoreduction of Co(III) in Co(II) at 200 K.

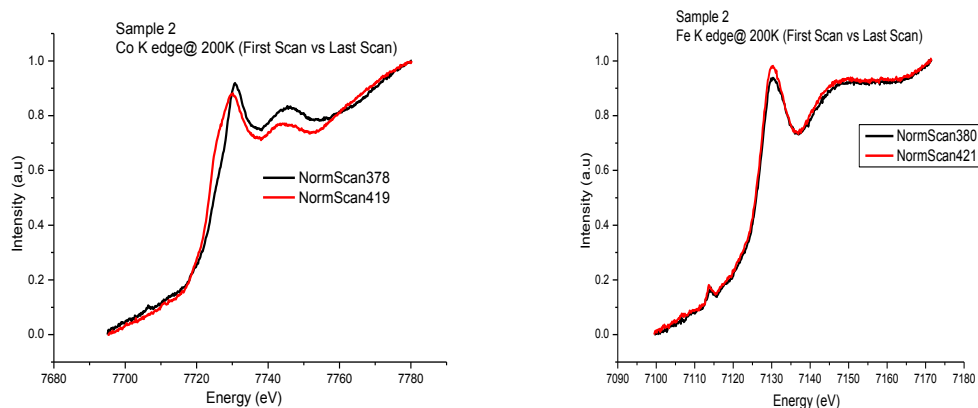


Figure 6. Co and Fe K-edge XAS spectra at 225 K before irradiation (black) and after 6 hours of X-ray irradiation (red) for the preparation 2 ($2 \cdot 10^{-3}$ Mol/L).

In conclusion, we were able to thermally-induce the electron-transfer inside the solution and to follow the local change of spin and oxidation states of Fe and Co ions. We have also observed at 200 K in the diamagnetic state the photoreduction using X-ray irradiation of Co(II) in Co(III) where the Fe maintained in Fe(II).

References

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