

Unexpected Shielding Effect of the BF_4^- Counter Ions in the X-ray Absorption Spectrum in Crystals of a Fe^{II} Metallogrid Complex.

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Over the past few years, we have investigated the light- and temperature-induced structural changes in three oligonuclear spin crossover (SCO) complexes with grid-like arrangements. These compounds include the tetranuclear metallogrid $[\text{Fe}^{\text{II}}_4\text{L}^{\text{Me}}_4](\text{BF}_4)_4 \cdot 2\text{MeCN}$ ($\text{FE4}^{\text{Me}} \cdot \text{MeCN}$), the trinuclear $[\text{Fe}^{\text{II}}_3\text{L}^{\text{H}}_2(\text{HL}^{\text{H}})_2](\text{BF}_4)_4 \cdot 4\text{MeCN}$ ($\text{FE3}^{\text{H}} \cdot \text{MeCN}$) and the grid-like dimer $[\text{Fe}^{\text{II}}(\text{HL})_2]_2(\text{BF}_4)_4 \cdot 2\text{MeCN}$ ($\text{FE2}^{\text{H}} \cdot \text{MeCN}$), where $\text{L}^{\text{R}} = \text{R}-3,5\text{-bis}\{6-(2,2'\text{-bipyridyl})\}$ pyrazole, $\text{R} = \text{H}$ or methyl [1-4]. Through our studies, we identify a method to desolvate $\text{FE4}^{\text{Me}} \cdot \text{MeCN}$ and $\text{FE2}^{\text{H}} \cdot \text{MeCN}$ while preserving their crystallinity. During the exploration of the thermal spin crossover of the solvent-free FE4^{Me} using variable temperature single crystal X-ray diffraction (VTSCXRD) at 20KeV, we observed Hard X-ray Induced Excited Spin State Trapping (HAXIESST) at temperatures below 120K [5]. Further attempts to study the XIESST phenomenon using X-ray Absorption Spectroscopy (XAS) with soft X-rays were unsuccessful, as the tail of the fluorine spectra cover the signal of the Fe^{II} ions sample (Fig. 1 left), making it barely visible. In contrast, XAS analysis of the crystalline FE2^{H} and the powder FE3^{H} reveals strong signals corresponding to the L-edge absorption of Fe^{II} . Moreover, XAS measurements of thin films from all samples, including FE4^{Me} , exhibit prominent peaks associated with the L-edge absorption of Fe^{II} . SCXRD data collected on a FE4^{Me} crystal, from the same batch used in the XAS experiments, confirmed the presence of Fe^{II} in the sample (Fig. 1 centre). The Fe^{II} is also observed in the crystallographic data of one crystal of FE4^{Me} , out of many, taken after the XAS measurements from the sample holder. SEM/EDX analysis [6] of all crystalline samples further corroborate the presence of iron, consistent with the SCXRD findings (Fig. 1 right). The current results suggest that the shielding of the Fe^{II} spectrum by the fluorine may be related to the crystalline structure of the sample. However, the origin of this effects remains unknown, and further studies in the compound and similar metal complexes are needed to uncover this mystery that to our knowledge it is not reported yet in literature.

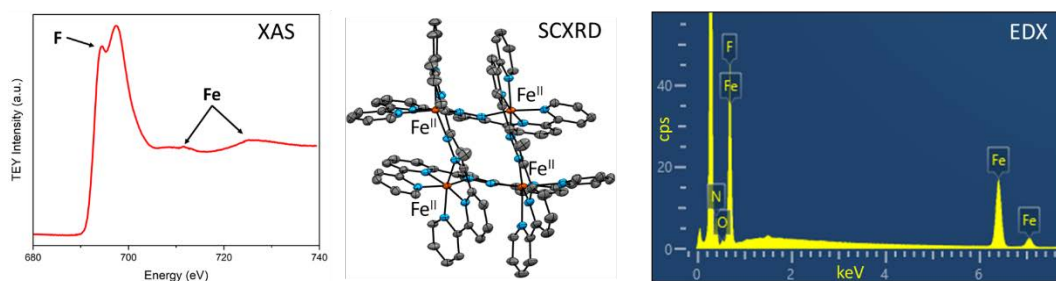


Figure 1. XAS spectrum (left), structural model of the cation (centre) and EDX spectrum (right) of FE4^{Me} .

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