Application of X-ray Near-edge Absorption Spectroscopy on Fe(III) Spin Crossover Complexes

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The x-ray near-edge absorption spectroscopy (XANES) is known to be sensitive to the metal oxidation state, spin configuration and local environment. It is therefore widely used in spin state characterization on the Fe(II) spin crossover (SCO) system. From high spin (HS) to low spin (LS), the spin configuration changes from $(e_g^2)(t_{2g}^4)$ S=2 to $(e_g^0)(t_{2g}^6)$ S=0. The unoccupied of the anti-bonding character e_g orbital causes the shortening of Fe-ligand bond length (～0.2 Å). Based on the previous Fe K-edge XANES, the spectroscopic fingerprints of HS and LS for Fe(II) SCO complexes have been established. As for Fe(III) SCO complexes, the XANES is also expected to be different concerning the spin configuration change ($(e_g^2)(t_{2g}^3)$ S=5/2 for HS and $(e_g^0)(t_{2g}^5)$ S=1/2 for LS) and bond length differences. However, no work or paper has been published yet. Several Fe(III) reference compounds were selected for testing the application of XANES on Fe(III) SCO complexes for the first time.

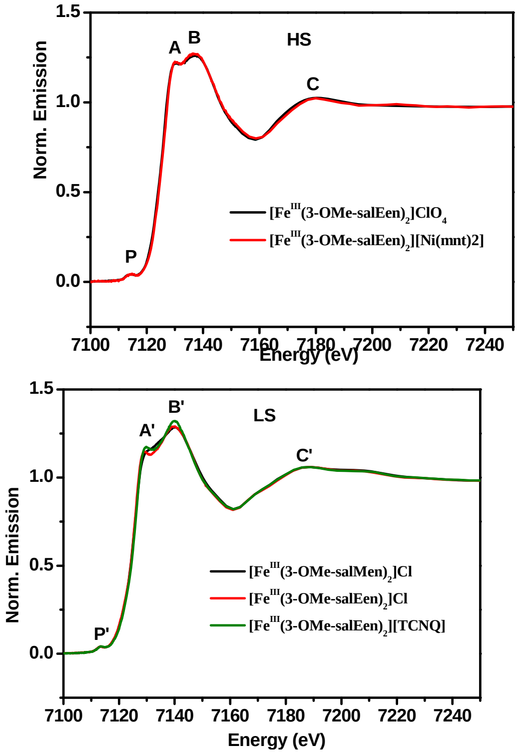

Figure 1. XANES of HS (top) and LS (bottom) Fe(III) spin crossover complexes with six-coordinated octahedral $Fe(N_4O_2)$ environment. Ligand 3-OMe-salRen (R=M and E) stands for 3-mothoxy-N-(2-ethylamino)R)-salicylaldimine (R=methyl and ethyl). TCNQ=7,7,8,8-tetracyanoquinodimethane, mnt=1,2-dicyanoethene-1,2-dithiolat.

From several different complexes with HS and LS state at room temperature determined previously by magnetic measurement, typical spectra of six-coordinated Fe(III) complexes (FeN_4O_2) is well-characterized. Which includes a weak dipole-forbidden 1s->3d pre-edge feature (P) and two absorption peaks (A and B) right after the absorption edge (figure 1). The energy positions are higher compared to the Fe(II) system as expected due to the higher oxidation state. Using a SCO compound $[Fe^{III}(3\text{-}OMe)salEen)_2]ClO_4$ with $T_{1/2}$ = 196 K for thermal dependent XANES measurement, the significant differences in HS and LS can be clearly seen (figure 2). Undergoing spin transition from HS to LS, the intensity of the main resonance A is weaker slightly and the peak position of B is shift to higher energy from 7137.4 eV to 7139.8 eV. Also the broad feature (C) arising from scattering of the photoelectron by the nearest-neighbor shell is also shift to higher energy due to the shortening of Fe-ligand distances in the LS state.

The preliminary result of iron K-edge XANES on Fe(III) spin crossover complexes demonstrates the power on characterization the oxidation and spin state. In complicated system with ferro- or antiferromagnetic interaction existing between unpaired electron, the metal spin state can only be determined unambiguously in the aid of x-ray absorption or Mossbauer spectroscopy.

Reference

Hayami, S.; Miyazaki, S.; Yamamoto, M.; Hiki, K.; Motokawa, N.; Shuto, A.; Inoue, K.; Shinmyozu, T.; and Maeda, Y.; Bull. Chem. Soc. Jpn. **79(3)**, 442–450 (2006).

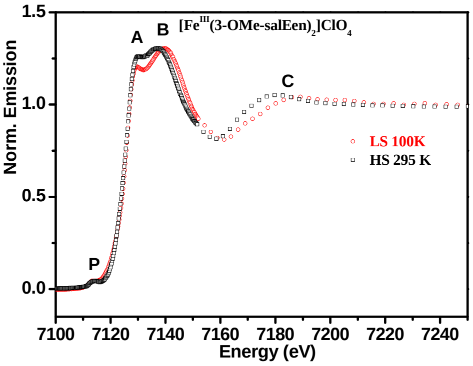

Figure 2. XANES spectra of HS (295 K) and LS (100 K) for SCO compound $[Fe^{III}(3\text{-}OMe)salEen)_2]ClO_4$ ($T_{1/2}$=196 K, determined from the thermal dependent SQUID result).