

## Temperature-dependent XAFS study for square-planar Hofmann-type spin crossover complex: Fe(Ethyl Isonicotinate)<sub>2</sub>Pt(CN)<sub>4</sub>

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Spin crossover (SCO) phenomenon is found in 3d transition metal complexes of  $d^4$ - $d^7$  configurations and found in the octahedral Fe(II) sites in the  $d^6$  configuration, which can be switched between high spin (HS) and low spin (LS) states by external stimuli such as temperature, pressure, or light irradiation. By changing the spin states, interesting physical and chemical phenomena appear. In addition, 2 dimensional (2D) Hofmann-type SCO compounds, possessing the cyanometalate-bridged ligands  $[M^I(CN)_2]^-$  ( $M^I = \text{Ag}$  or  $\text{Au}$ ) and  $[M^{II}(CN)_4]^{2-}$  ( $M^{II} = \text{Ni}$ ,  $\text{Pd}$ , or  $\text{Pt}$ ), become one of the candidates[1]. Recently, element-specific electronic and structural properties of the 2D Hofmann-type SCO complex Fe(pyridine)<sub>2</sub>Ni(CN)<sub>4</sub> via the temperature-dependent X-ray absorption fine structure (XAFS) and extended XAFS (EXAFS) have been reported[2]. We focus on the SCO behavior of square-planar based Hofmann-type complexes influenced by ligand molecule size with introducing oxygen atoms possessing strong electron negativity in Ethyl Isonicotinate for cyanide-bridged Fe-Pt Hofmann-type complex; Fe(Ethyl Isonicotinate)<sub>2</sub>Pt(CN)<sub>4</sub>. In this study, we aim to investigate the changes in electronic and structural properties across the SCO in Fe(Ethyl Isonicotinate)<sub>2</sub>Pt(CN)<sub>4</sub> by using XAFS and EXAFS.

Samples of Fe(Ethyl Isonicotinate)<sub>2</sub>Pt(CN)<sub>4</sub> was synthesized by direct method and vapor diffusion method. Both methods use the Mohl's salts of Fe[(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O] and K<sub>2</sub>[Pt(CN)<sub>4</sub>] with adding water. The pH of solutions was adjusted to 7.5 by adding the citric acid and 1,3-diaminopropane. Both powder and crystal samples were obtained by these reactions. Temperature-dependent XAFS and EXAFS were performed at BL-9C, Photon Factory (KEK). The samples used for XAFS measurements were diluted by BN powder and formed into pellets. The samples were cooled by the conventional closed He gas cryostat from room temperature to 11 K.

The crystal structure determined by the single-crystal X-ray diffraction (XRD) is shown in the inset of Fig. 1. The magnetization data measured by superconducting quantum interference device (SQUID) shown in Fig. 1 reveals the spin transition at 216 K with decreasing temperature and at 232 K with increasing temperature. There was the temperature width for hysteresis of 24 K.

Figure 2 shows the temperature-dependent XAFS spectra of Fe(Ethyl Isonicotinate)<sub>2</sub>Pt(CN)<sub>4</sub> for Fe *K*-edge and Pt *L*-edge. In the Fe *K*-edge XAFS spectra shown in Fig. 2 (a), the main peak positions shifts toward higher photon energy side with decreasing

temperature has been clearly observed. This can be explained by the HS-LS transitions through the changes of the crystal field strength by temperature.

Figure 2 (b) displays the Pt *L*-edge XAFS spectra of HS and LS states. Contrary to Fe *K*-edge XAFS spectra, the peak positions of the Pt *L*-edges remain unchanged across the spin transition. These results suggests the well-known property that the SCO occurs only at Fe(II) sites.

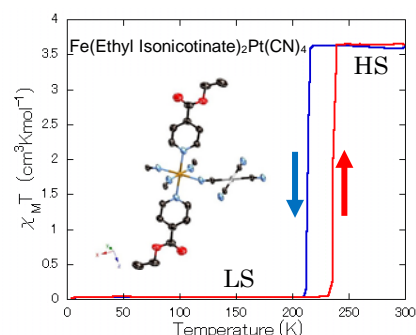


Fig. 1, Magnetic properties of Fe(Ethyl Isonicotinate)<sub>2</sub>Pt(CN)<sub>4</sub> measured by SQUID. Inset shows the crystal structure determined by single crystal XRD.

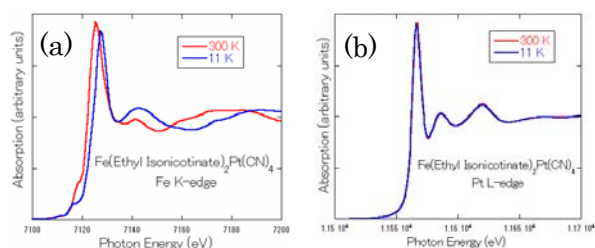


Fig. 2, Temperature-dependent XAFS spectra of Fe(Ethyl Isonicotinate)<sub>2</sub>Pt(CN)<sub>4</sub>, for (a) the Fe *K*-edge and (b) the Pt *L*-edge.

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[2] J. Okabayashi *et al.*, Inorg. Chimi. Acta **426**, 142 (2015).

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