

## Temperature-dependent EXAFS study for spin crossover complex: $\text{Fe}(\text{pyridine})_2\text{Ni}(\text{CN})_4$

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Bimetallic assemblies with transition-metal complexes bridged by ligand molecules have attracted much attention for their cooperative interactions caused by transitions between high-spin (HS) and low-spin (LS) states, which result in interesting physical and chemical phenomena. The controlling of ligand field strength via external perturbations that change the coordinating ligand polymers is also one of the most fascinating subjects in molecular magnetochemistry. The complex compound  $\text{Fe}(\text{pyridine})_2\text{Ni}(\text{CN})_4$ , which was synthesized by Kitazawa *et al.* in 1996, has been regarded as one of the prototype spin crossover (SCO) complexes [4]. The Hofmann-type structures possessing two-dimensional networks bridged by cyanides with  $\text{Fe}^{2+}$  ( $3d^6$ ) SCO compounds are interesting in the synthesis of self-assemblies of new kinds of SCO molecules. However, the element-specific electronic structures, including the information about the local structural environments around Fe or Ni sites, have not been investigated explicitly because of the small size of single crystals and poly-crystalline samples. In this study, we aim to examine the changes in electronic and structural properties across the SCO transition in  $\text{Fe}(\text{pyridine})_2\text{Ni}(\text{CN})_4$  by using temperature-dependent XAFS and EXAFS.

Samples of  $\text{Fe}(\text{pyridine})_2\text{Ni}(\text{CN})_4$  were synthesized by the vapor diffusion method using the precursors of Mohr's salt,  $\text{Fe}[(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$  and  $\text{K}_2[\text{Ni}(\text{CN})_4]$ , with additional water. The pH of the solutions was adjusted to 7.5 by adding the citric acid. Most parts of the sample were obtained as poly-crystalline shapes. Temperature-dependent XAFS and EXAFS were performed at BL-9C, Photon Factory. The sample used for XAFS measurements was diluted by BN powder formed into pellets. The sample was cooled by the conventional He cryostat method from room temperature to 15 K.

The inset of Fig. 1 shows the sample structure determined by the single-crystal XRD. The magnetization data in Fig. 1 reveals the SCO transition at 200 K for decreasing temperature and 223 K for increasing temperature.

Figure 2 shows the temperature-dependent XAFS spectra of  $\text{Fe}(\text{pyridine})_2\text{Ni}(\text{CN})_4$ , for Fe and Ni *K*-edges. In the Fe *K*-edge XAFS spectra shown in Fig. 2 (a), the shifts in the main peaks originating from  $1s$  to  $4p$  electric dipole transitions can be clearly observed. The main peak positions correspond to the  $\text{Fe}^{2+}$  states. At temperatures less than 200 K, the peak positions shift to higher photon energies, which can be

explained by the decreased nearest-neighbor distance and the shift of unoccupied states toward higher energies through the increase of the crystal field strength, which induces the transition to the LS states.

Figure 1 (b) displays the Ni *K*-edge XAFS spectra of HS and LS states. Contrary to those of Fe, the peak positions of the Ni *K*-edges remain unchanged across the SCO transition. These results demonstrate the well-known property that the SCO occurs only at  $\text{Fe}^{2+}$  sites. This behavior suggests that the total volume in this compound remains unchanged across the SCO transition and the local distortion only near the Fe sites brings the SCO phenomena [2].

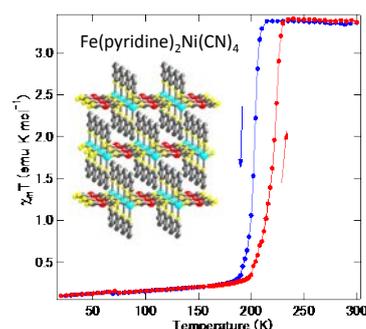


Fig. 1, Magnetic properties of  $\text{Fe}(\text{py})_2\text{Ni}(\text{CN})_4$  measured by SQUID. Inset shows the crystal structure.

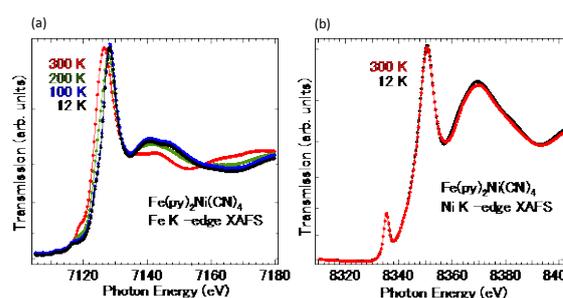


Fig. 2, XAFS spectra of  $\text{Fe}(\text{py})_2\text{Ni}(\text{CN})_4$  at varying temperatures, for (a) the Fe *K*-edge and (b) the Ni *K*-edge.

[1] T. Kitazawa *et al.*, *J. Mater. Chem.* **6**, 119 (1996).

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

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