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Coordination structure analysis of a vapochromic and spin-crossover complex Fe(4,4'-bipyridine)Ni$(CN)_4$·$n$$H_2O$

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Introduction

Spin-crossover(SCO) Fe^{II} complexes are a promising source for new functional molecular switches because they can alternate between a high-spin and a low-spin state depending on the circumstances and show variations in magnetism, color and structure. We recently prepared a new Fe^{II} complex Fe(4,4'-bpy)Ni$(CN)_4$·2.5H_2O(**1**), where 4,4'-bpy is 4,4'-bipyridine. This compound itself did not show SCO. However, it absorbed volatile organic vapor such as ethanol and acetone with change of its color, and **1** containing such organic molecules showed SCO phenomena. The appearance of the SOC depended on the species of the organic molecules absorbed. In the cases of ethanol and acetone, one-step spin transition(ST) and two-step ST were observed, respectively. For detailed examination, its crystal structure is necessary. Although **1** could be obtained as powder, no crystalline sample has been prepared. In this project, we attempted to obtain structural information of **1** from EXAFS spectra.

Experimental

Fe and Ni K-edge XAFS spectra of **1** and its related compound Fe$(py)_2$Ni$(CN)_4$ (**2**), whose structure is considered to be similar to that of **1**, were measured at ambient temperature in the transmission mode at BL-9C station of PF-KEK. The curve fitting of the FT function was carried out over the real space range of r = 1 - 6 Å considering single and multi scattering paths.

Results and Discussion

FT functions of $k^3\chi(k)$ observed for **1** and **2** are shown in Fig.1. At a glance, similarity of the FT functions between the two compounds is remarkable. This finding suggests the structural similarity of the surroundings of Fe and Ni in both compounds.

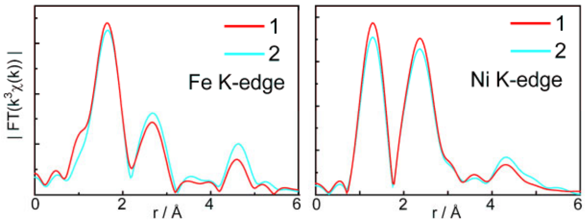

Fig.1 FT magnitude observed for **1** and **2**.

The curve fitting for the spectra of **2** was carried out based on the structure determined by the single crystal X-ray diffraction analysis.[1] A network structure formed by nearly straight Ni-C-N-Fe linkages is characteristic of **2**. The results of the fitting were good as shown in Fig.2. This confirmed that multi scattering effects coming from the Ni-C-N-Fe linkage give significant influence on the EXAFS spectra. The similarity observed between the EXAFS spectra of **1** and **2** strongly supports the existence of the Ni-C-N-Fe linkage and the network structure in **1**.

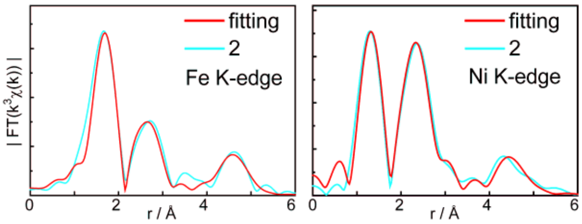

Fig.2 Observed spectrum of **2** and the best-fit results for **2**.

Considering the results of this EXAFS study together with results from elementary analysis, IR and powder X-ray diffraction, a structure shown in Fig.3 can be estimated for **1**. The Ni-C-N-Fe linkages make a 2D network. The 2D networks are stacked to form a layered structure and 4,4'-bpy, which is a bidentate ligand with a straight shape, makes a bridge between the stacked 2D networks. As a result, **1** has a 3D framework. This 3D framework has vacant space between the networks and between 4,4'-bpys for absorbing water and guest molecules.

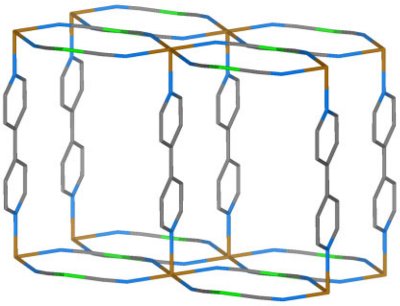

Fig.3 Estimated structure for **1** drawn with a cylinder model.

References

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