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Characterizations of Core Level Electronic Structure and Interaction of Ln-M Cyano DMF Complex by Soft-X-ray Spectroscopy (in 2008)

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Introduction

During searching for new functional materials acting as photo-controllable molecule-based magnets, we discovered $Nd(DMF)_4(H_2O)_3Fe(CN)_6 \cdot H_2O$ complex as the first material among 3d-4f cyano-bridged complexes [1]. However, detailed mechanism have not been elucidated especially based on correlation between crystal structures – electronic states nevertheless of systematic studies on crystal structures [2], metal-substitution [3], and other strategy to design photo-magnetic materials [4]. As one of viewpoints, we focused on flexibility of crystal structures by varying external physical conditions such as temperature.

Indeed, we have already observed quite interesting behavior by crystal structure determination of $Nd(DMF)_4(H_2O)_3Fe(CN)_6 \cdot H_2O$ complex under variable temperature conditions as follows (Figure 1, unpublished results): $C_{18}H_{36}FeN_{10}O_8Nd$, monoclinic $P2_1/n$, Z=4:
[293K] a = 17.615(6) Å, b =8.906(3) Å, c = 19.934(7) Å, β = 95.966(7)°, V = 3110(2) Å^3.
[173K] a = 17.5323(18) Å, b = 8.8685(9) Å, c = 19.827(2) Å, β = 95.879(2)°, V = 3066.5(5) Å^3.
[100K] a = 17.672(2) Å, b = 8.8249(10) Å, c = 19.537(2) Å, β = 96.147(2)°, V = 3029.6(6) Å^3.

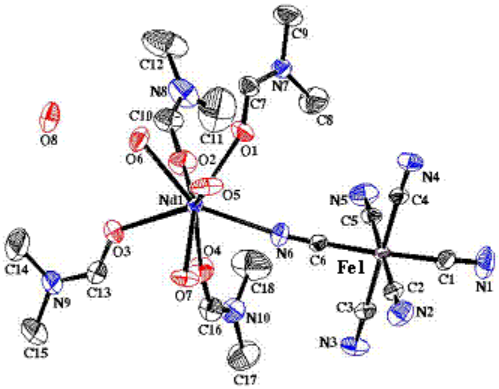

Figure 1: Crystal structure of $Nd(DMF)_4(H_2O)_3Fe(CN)_6 \cdot H_2O$

In order to discuss the role of crystal lattice (intermolecular hydrogen bonds) and coordination environment (3d electronic states coupled with 4f ions) separately, we carried out the measurements of soft X-ray absorption spectra under variable temperature conditions by comparing X-ray crystal structure analysis.

Experimental section

Preparation

Slow diffusion of aqueous solution (10 mL) of $K_3[Fe(CN)_6]$ (0.1 mmol) onto DMF solution (10 mL) of $Nd(NO_3)_6 \cdot nH_2O$ (0.1 mmol) gave rise to yellow prismatic single crystals of $Nd(DMF)_4(H_2O)_3Fe(CN)_6 \cdot H_2O$ at 298 K [1]

Soft X-ray absorption spectra

The XAS of Fe2p1/2 and Fe2p3/2 peaks were measured with BL-19B at 298 and 70 K. The spectra were corrected by the standard sample of Au.

Results and discussion

Figure 2 showed that low-spin Fe(III) ions were contained in $Nd(DMF)_4(H_2O)_3Fe(CN)_6 \cdot H_2O$ at both temperature, which indicated that the thermally-accessible structural changes is due to flexible intermolecular hydrogen bonds in crystals. The other results are omitted in this year's report, because it is preliminary level at present.

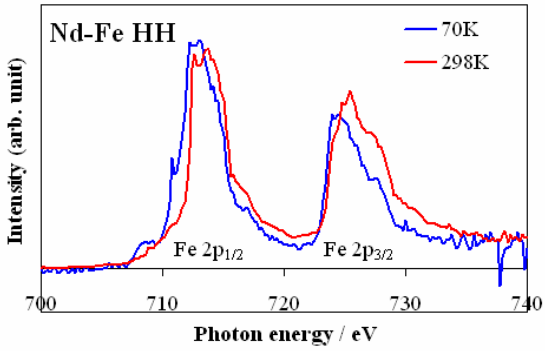

Figure 2: XAS of $Nd(DMF)_4(H_2O)_3Fe(CN)_6 \cdot H_2O$

References

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