Introduction

A 3d-4f complex, Nd(DMF)₄(H₂O)₃Fe(CN)₆•H₂O, was known to exhibit photo-induced magnetic changes [1]. The factors of this unique behavior were investigated in view of crystal structures [2] and metal-substitution [3] in order to design photo-magnetic materials [4]. As one of viewpoints, we focused on flexibility of crystal structures Nd(DMF)₄(H₂O)₃Fe(CN)₆•H₂O. In 2008 we found that it showed negative thermal expansion along the a-axis. Intermolecular hydrogen bonds play an important role in this behavior. In order to elucidate <1> effect of Ln(III) ion size <2> effect of H/D isotope of intermolecular hydrogen bonds, and <3> separate observation between lattice (hydrogen bonds) and coordination sphere (electronic states of low-spin Fe(III) ion), we compared with various analogous Ln(DMF)₄(H₂O)₃Fe(CN)₆•H₂O or Ln(DMF)₄(D₂O)₃Fe(CN)₆•D₂O complexes and measured XAS under variable temperature condition.

Experimental section

Preparation

Slow diffusion of aqueous solution (10 mL) of K₃[Fe(CN)₆] (0.1 mmol) onto DMF solution (10 mL) of Nd(NO₃)ₓ•nH₂O (0.1 mmol) gave rise to yellow prismatic single crystals of Nd(DMF)₄(H₂O)₃Fe(CN)₆•H₂O at 298 K [1]. The other samples were prepared in a similar way with the corresponding Ce, Sm, Gd, and Er metal sources and water or DMF ligands of different isotopes.

Soft X-ray absorption spectra

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

Results and discussion

For example, Figure 1 shows XAS of Fe₂p₁/₂ and Fe₂p₃/₂ for Sm(DMF)₄(H₂O)₃Fe(CN)₆•H₂O (SmFeHH) at 298 and 70 K and Sm(DMF)₄(D₂O)₃Fe(CN)₆•D₂O (SmFeDH) at 298 K. In contrast to thermally-induced anisotropic structural changes of the crystal lattice, all the spectra suggest low-spin Fe(III) ions at both temperature. Moreover, H/D isotope of intermolecular hydrogen bonds were observed slightly. One of the important factors of the thermal behavior may be not local coordination environment but intermolecular hydrogen bonds.

References


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