

Thermal changes of structures and properties of pi-backdonating metal complexes (in 2010)

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Introduction

Recently, cyanide-bridged 3d-4f molecule-based magnets have attracted a great deal of attention due to their potential applications for multifunctional materials. However, detailed features of superexchange interactions are not known because of considerable spin-orbit interactions except for Gd(III) ion. Therefore, the difference of $\Delta\chi_{MT} = \chi_{MT}(\text{Ln-M}) - \chi_{MT}(\text{Ln-M}')$ between isostructural complexes (where Ln, M, and M' are (identical) paramagnetic lanthanide ions, paramagnetic transition metal ions, and diamagnetic transition metal ions, respectively) was often employed to discuss their magnetic interactions via cyanide-bridges with pi-back donation [1, 2].

In order to discuss electronic states of inner shell, we measured soft x-ray absorption spectra. Comparing with the previous cyanide-bridged 3d-4f systems, we prepared chiral Schiff base 3d-4f systems.

Experimental section

Measurements

We have prepared samples of several new 3d-4f binuclear chiral salen-type Schiff base complexes. Temperature dependence of magnetization revealed that Ni(II) and Zn(II) were diamagnetic ions and Ln(III)-Cu(II) binuclear units indicated ferromagnetic asymmetric magnetic superexchange interactions.

The Cu2p_{3/2} and Cu2p_{1/2} peaks of XAS (soft X-ray absorption spectra) for these samples were measured at KEK PF BL-19B (2010G510) under variable temperature. The spectra were corrected by the standard Au sample.

Results and discussion

In order to discuss the influence of 4f ions on Cu(II) ions in (potentially ferromagnetic) **GdCu**, **ErCu**, and **HoCu**, we measured XAS for electronic states of inner shell. The XAS spectra for **GdCu**, **ErCu**, and **HoCu** are shown in Figure 1. The Cu2p_{1/2} and Cu2p_{3/2} peaks appeared at 952 and 932 eV for all the compounds. These signals do not show the satellite structure typical of Cu(I) derivatives resulted from charge transfer involving valence states of the 3d-4f units. Consequently, the results suggest that the electronic interaction between 3d and 4f ions above 3s and 3p orbitals (namely 3d or involving ligand transitions) even at room temperature (spins are interacted but not ordered).

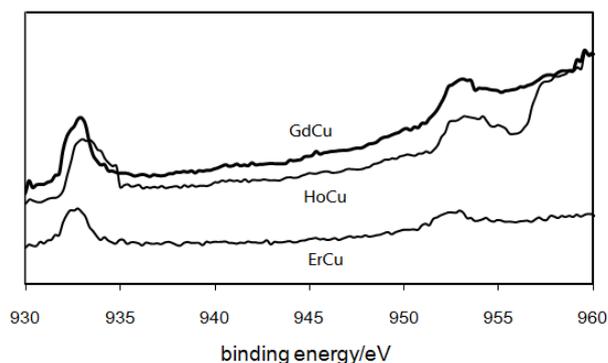


Figure 1: The XAS of Cu2p_{1/2} and Cu2p_{3/2} peaks for selected samples.

We also measured solid-state CD spectra and the corresponding diffuse reflectance electronic spectra. Since Zn(II) moieties with d¹⁰ configuration exhibit no d-d transition (12000-20000 cm⁻¹ in diffuse reflectance spectra), comparison of appropriate spectra provides not only characteristic features of Ni(II) (shoulder at 18000 cm⁻¹) and Cu(II) (peak at 19000 cm⁻¹, which may also be affected by axial ligands) or Gd(III), Er(III), and Ho(III) moieties (shoulder or spectral shift around 22000 cm⁻¹) but also bands involving chiral ligands (22000-32000 cm⁻¹) or being attributed to 3d-4f interactions. In this way, we could successfully observe characteristic CD bands around 22000 cm⁻¹ for dinuclear 3d-4f complexes including diamagnetic or paramagnetic 3d ions. Which corresponds to charge transfer shoulders of the diffuse reflectance electronic spectra. The present results suggest that chiroptical measurements of electronic states are valid for chiral 3d-4f metal complexes as multifunctional materials. The XAS data are also supported the interpretation of electronic states of d or f shells.

Further systematic investigation is now in progress now.

References

- [1] T. Akitsu et al., *Radiochim. Acta* in press.
- [2] T. Akitsu et al., *Open. Cryst. J.* 4, 16 (2011).

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