Characterizations of Core Level Electronic Structure and Interaction of Ln-M Cyano DMF Complex by Soft-X-ray Spectroscopy (in 2010)

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Previously, we discovered $Nd(DMF)_4(H_2O)_3Fe(CN)_6{\bullet}H_2O$ complex as the first material among 3d-4f cyano-bridged complexes. 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 (XAS) under variable temperature conditions by comparing X-ray crystal structure analysis. In this year, we have examined various Ln(III) ions in isostructural $Ln(DMF)_4(H_2O)_3Fe(CN)_6{\bullet}H_2O$ complexes and H/D isotope effects for some compounds [1-3].

As other types of 3d-4f molecule-based magnets, we have investigated chiral Schiff base complexes [4] to detect not only magnetic measurements but also chiroptical measurements. We have prepared several new 3d-4f chiral salen-type Schiff base binuclear (Ln(III)-M(II)) complexes, abbreviated as **GdNi**, **GdCu**, **GdZn**, **HoNi**, **HoCu**, **ErNi**, and **ErCu**. Crystal structures of **GdNi**, **GdCu** (Figure 1), **ErNi**, and **HoCu** were determined and the rest of them were confirmed their structural similarity with XRD. Temperature dependence of magnetization revealed that Ni(II) and Zn(II) were diamagnetic ions and Ln(III)-Cu(II) binuclear units indicated ferromagnetic superexchange interactions. We discussed the superexchange interactions by means of difference of $\chi_M T$ values and electronic states of Cu(II) ions observed by XAS. Moreover, we could observe characteristic chiroptical bands due to 3d-4f binuclear units in the solid states.

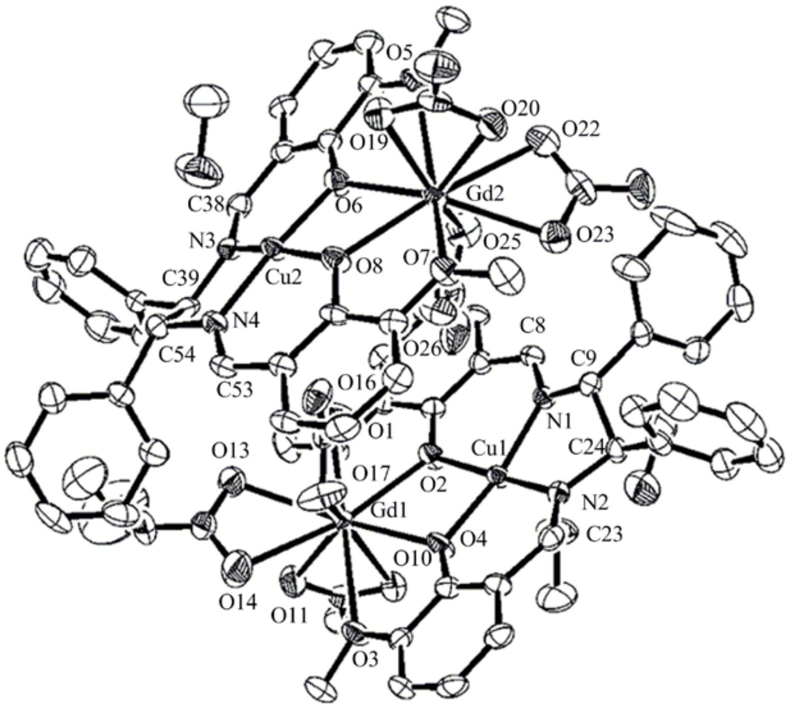

Figure 1. Crystal structure of a **GdCu** complex.

The $Cu2p_{3/2}$ and $Cu2p_{1/2}$ peaks of XAS (soft X-ray absorption spectra) were measured at KEK PF BL-19B (2010G510 and 2008G528) under variable temperature. The spectra were corrected by the standard Au sample. 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 2. 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).

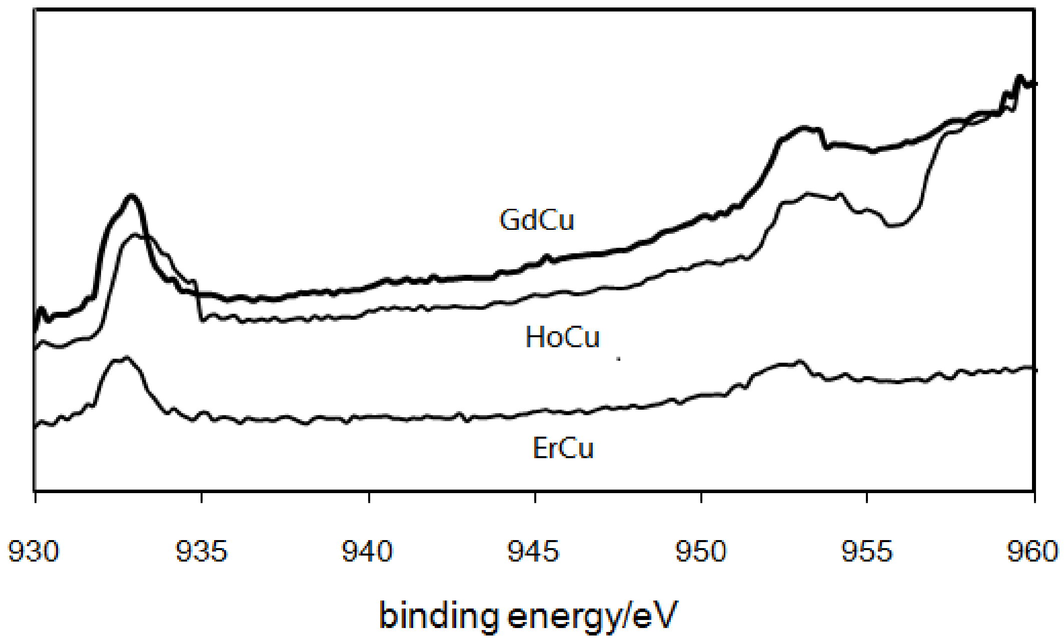

Figure 2. The XAS of $Cu2p_{1/2}$ and $Cu2p_{3/2}$ peaks for **GdCu**, **ErCu**, and **HoCu**.

In this way, 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. We discussed the superexchange interactions by means of difference of $\chi_M T$ values and electronic states of Cu(II) ions observed by XAS. So far, optical absorption (electronic) spectra (for single crystals) and MCD spectra have been employed for these asymmetric exchange systems. In this study, we could successfully observe characteristic chiroptical bands due to 3d-4f binuclear systems in the region corresponding to charge transfer bands beyond CD spectra for only 3d or 4f components. Furthermore, crystallographic study involving other systems is in progress now.

References

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[3] T. Akitsu *et al.*, Radiochim. Acta *in press*.
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