

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

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Previously, we discovered $\text{Nd}(\text{DMF})_4(\text{H}_2\text{O})_3\text{Fe}(\text{CN})_6 \cdot \text{H}_2\text{O}$ complex as the first material among 3d-4f cyano-bridged complexes. Cyano ligands are well known as π -backdonating ones to exhibit superexchange interactions for molecule-based magnets of bimetallic assemblies. We have focused on their crystallographic aspects as well as electronic states. 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 $\text{Ln}(\text{DMF})_4(\text{H}_2\text{O})_3\text{Fe}(\text{CN})_6 \cdot \text{H}_2\text{O}$ complexes and H/D isotope effects for some compounds [1-3].

As other types of bimetallic assemblies of metal complexes, we have prepared some diastereomers of $[\text{CuL}_2][\text{M}_2\text{O}_7]$ (L is 1,2-diaminocyclohexane and its derivatives; M = Cr and W) bimetallic coordination polymers and confirmed their structural similarity and inner electronic states by means of XRD and XAS, respectively. For the first time, we have successfully observed distant vicinal effect of which chiral source is only chiral organic ligands of $[\text{CuL}_2]^{2+}$ moieties (acting as ligand complex) while probe bands for solid state CD spectra is charge transfer (CT) bands of $[\text{M}_2\text{O}_7]^{2-}$ moieties (achiral complex) with d^0 electronic configuration. The new concept (interpretation) of this observation will be important for supramolecular chirality about coordination polymers built by ligand complexes.

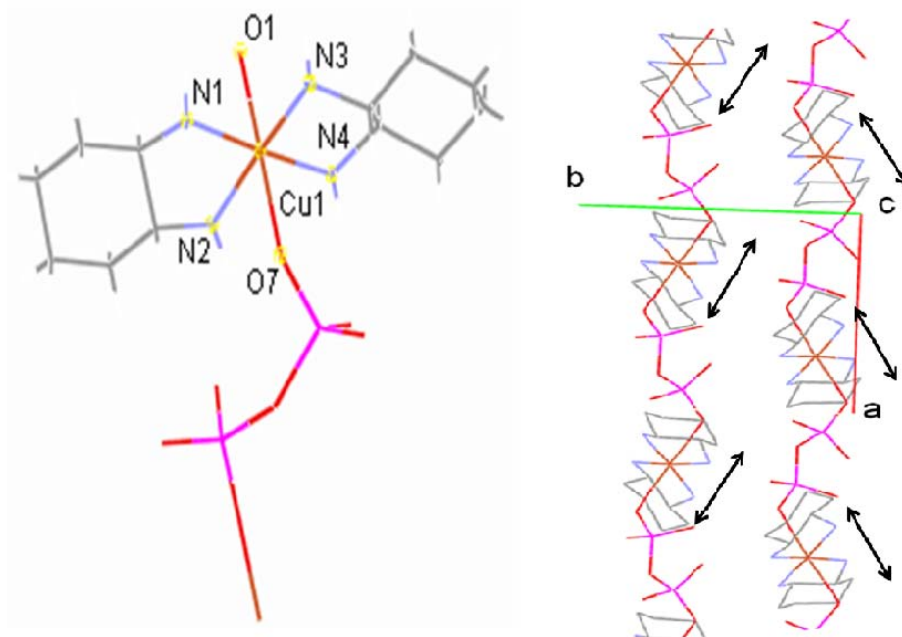


Figure 1. Crystal structure of a chiral $[\text{CuL}_2][\text{Cr}_2\text{O}_7]$ complex.

The Cu2p_{3/2} and Cu2p_{1/2} peaks of XAS (soft X-ray absorption spectra) were measured at KEK PF BL-19B (2010G510) under variable temperature. Figure 2 exhibits temperature dependence of soft X-ray absorption spectra (XAS) for a [CuL₂][W₂O₇] complex measured at 28, 50, 100, 150, 200, and 250 K. At each temperature, the Cu2p_{1/2} and Cu2p_{3/2} peaks appeared at about 932 and 952 eV, respectively. Absence of weak peak between them suggests that valence state is not copper(I) nor mixed-valence of copper(I) and copper(II) but copper(II) clearly. The bridging [Cr₂O₇]²⁻ moieties did not contribute for delocalization of charges. In addition, little difference against temperature changes indicates that electronic states of inner shell are stable.

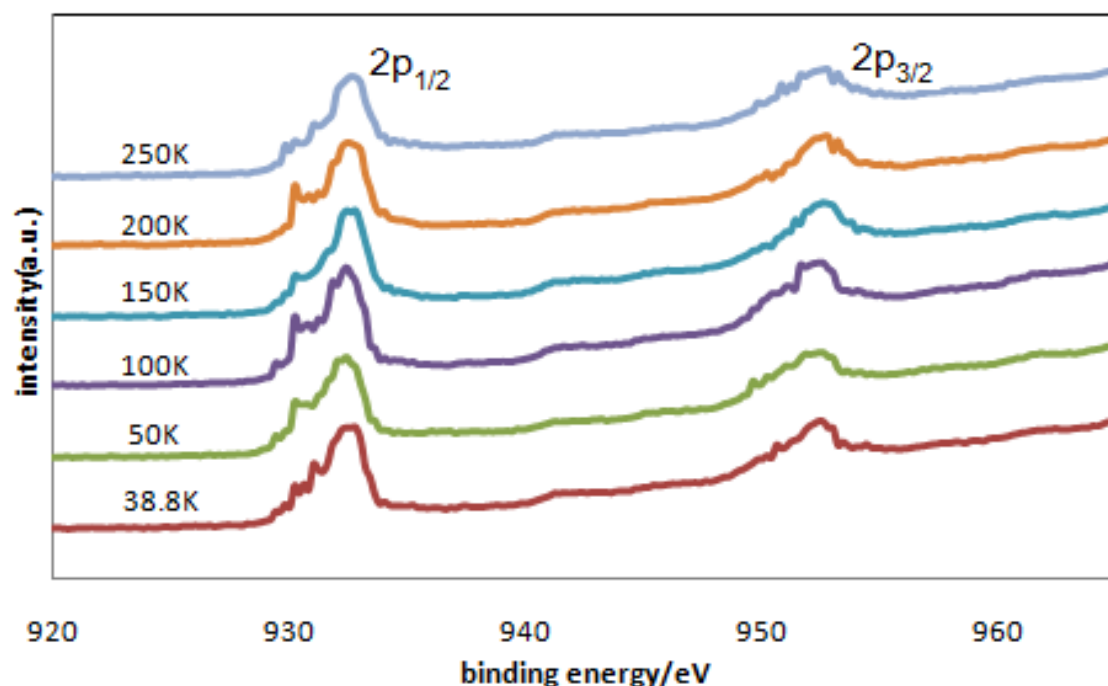


Figure 2. The XAS of Cu2p_{1/2} and Cu2p_{3/2} peaks for a chiral [CuL₂][Cr₂O₇] complex

As for solid-state spectra, systematically comparison of the related spectra and peaks of Cu-precursor at 17000 (d-d) and 32000 (CT) cm⁻¹, Cr-precursor at 20000 (CT) cm⁻¹, and W-precursor at 32000 and 40000 (CT) cm⁻¹ should be helpful for establishing assignment experimentally. It should be noted that CD bands in d-d region of Cu-precursor are attributed to vicinal effect by chiral organic ligand, while CD bands in CT region of CT band of bimetallic coordination polymers are attributed to vicinal effect by chiral complex ligand (namely the Cu-precursor). For example, a negative peak around 30000 cm⁻¹ is a typical CD band of long-range vicinal effect classified into a novel case.

In summary, we have prepared some diastereomers of [CuL₂][M₂O₇] (L is 1,2-diaminocyclohexane and its derivatives; M = Cr and W) bimetallic coordination polymers and confirmed their structural similarity and inner electronic states for selected compounds. We have successfully observed distant vicinal effect in the chiral Cu(II)-Cr(VI) or Cu(II)-W(VI) bimetallic coordination polymers. The chiral source is only chiral organic ligands of [CuL₂]²⁺ moieties while probe bands for solid state CD spectra is charge transfer bands of [M₂O₇]²⁻ moieties with d⁰ electronic configuration.

References

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