

## Anisotropy of functions and thermally structural changes for Cu(II) complexes (in 2010)

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### Introduction

In recent years, metal-organic frameworks of transition metal complexes have been attracted much attention. Since we have investigated on structures and electronic states of (chiral) copper(II) complexes, thermally-accessible structural changes of Jahn-Teller distortion (local distortion around coordination environment) and global strain of crystal lattice may be one of the important problem to be discussed closely. In this context, we have studied on thermally structural changes for several types of (cyano-bridged) Cu(II)-M bimetallic assemblies [1-5].

### Experimental section

#### Preparation

Slow diffusion of aqueous (of appropriate hydrogen or oxygen isotopes) solution of a precursor complex  $[\text{CuL}_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$  (L = bidentate amine ligand) onto aqueous solution of other metal complexes as counter anions allowed to stand at 298 K for several days to gave rise to resulting precipitates.

#### X-ray Crystallography

Powder XRD patterns of the complexes were measured at BL-8B (8 keV,  $\lambda = 1.54 \text{ \AA}$ ) at 100-300 K.

### Results and discussion

For example, we mention the study on chiral  $[\text{Cu}(\text{chxn})_2]_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$  (chxn = diaminocyclohexane; comparing with Fe, Co, and Cr or  $\text{H}_2\text{O}$ ,  $\text{D}_2\text{O}$ , and  $\text{H}_2^{18}\text{O}$  isotopes).

At 130 K, the crystal data for  $[\text{Cu}(\text{chxn})_2]_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O} \cdot n\text{H}_2\text{O}$  of these isostructural forms are Triclinic,  $P1$ ,  $Z = 1$ .

For the H form:  $a = 8.3362(11)$ ,  $b = 12.6453(16)$ ,  $c = 16.016(2) \text{ \AA}$ ,  $\alpha = 105.575(2)$ ,  $\beta = 99.017(2)$ ,  $\gamma = 95.841(2)^\circ$ ,  $V = 1587.75 \text{ \AA}^3$ .

For the D form:  $a = 8.3228(11)$ ,  $b = 12.6426(17)$ ,  $c = 16.007(2) \text{ \AA}$ ,  $\alpha = 105.579(2)$ ,  $\beta = 99.058(2)$ ,  $\gamma = 95.799(2)^\circ$ ,  $V = 1583.91 \text{ \AA}^3$ .

For the  $^{18}\text{O}$  form:  $a = 8.317(4)$ ,  $b = 12.651(6)$ ,  $c = 16.025(2) \text{ \AA}$ ,  $\alpha = 105.662(2)$ ,  $\beta = 99.080(2)$ ,  $\gamma = 95.672(2)^\circ$ ,  $V = 1585.33 \text{ \AA}^3$ .

Temperature dependence of  $[\text{Cu}(\text{chxn})_2]_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$  (the D form) indicated positive thermal expansion as global crystal lattice

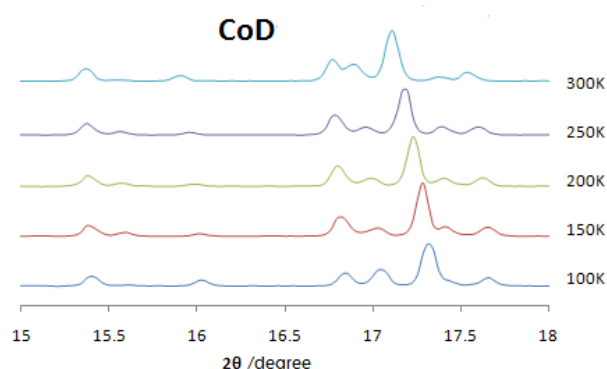
(Figure 1). Significant structural changes associated with Jahn-Teller effect were observed in mononuclear copper(II) sites rather than cyano-bridged bimetallic framework sites.

In order to understand anisotropy derived from metal-organic frameworks, local coordination bonds of mononuclear copper(II) sites are as follows:

At 100 K: axial Cu-O = 2.431(3), 2.454(3)  $\text{ \AA}$ , in-plane Cu-N = 2.753(3), 2.647(3), 2.628(3), 2.646(3)  $\text{ \AA}$ .

At 130 K: axial Cu-O = 2.4470(4), 2.4644(3)  $\text{ \AA}$ , in-plane Cu-N = 2.7639(4), 2.6286(4), 2.6373(4), 2.6524(4)  $\text{ \AA}$ .

At 296 K: axial Cu-O = 2.478(4), 2.496(4)  $\text{ \AA}$ , in-plane Cu-N = 2.811(4), 2.651(4), 2.669(4), 2.708(4)  $\text{ \AA}$ .



**Figure 1:** Temperature dependence of XRD patterns of  $[\text{Cu}(\text{chxn})_2]_3[\text{Co}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$  ( $\text{D}_2\text{O}$  isotope).

For detailed and clear discussion about anisotropy, we will investigate other bimetallic assemblies, for example  $[\text{Cu}(\text{chxn})_2][\text{Cr}_2\text{O}_7]$ , having a zig-zag arrangement of Jahn-Teller bonds against crystal lattices.

### References

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