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Separated observation of Jahn-Teller and lattice distortion in thermal structural changes of copper(II) complexes (in 2009)

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Introduction

A chiral complex, $[Cu(chxn)_2][Ni(CN)_4]\cdot 2H_2O$ (chxn = (*1R, 2R*)-diaminocyclohexane) had a long axial Cu-N bond of 3.120(8) Å [1] and also exhibited negative thermal elongation associated with this long Cu-N bond. In order to elucidated appropriate factors about crystal packing to observe lattice and Jahn-Teller distortion separately, we measured variable temperature XRD patterns for some cases : <1> $[Cu(chxn)_2][M(CN)_4]\cdot 2H_2O$ (M=Pd and Pt) [2, 3] to compare ion size; <2> $[Cu(NEten)_2][M(CN)_4]\cdot 2H_2O$ (NEten = *N*-ethylethylenediamine) for combinatorial preparations by using M=Ni, Pd, and Pt to test suitable ion size; <3> $[Cu(Mechxn)_2]_3[M(CN)_6]_2\cdot nH_2O$ (Mechxn = (*1R, 2R*)-*N,N*'-dimethyldiaminocyclohexane; M=Cr, Co, and Fe) by using different water of isotopes (^1H_2O, ^2H_2O, and $H_2{}^{18}O$) for isotope effect on intermolecular hydrogen bonds.

Experimental section

Preparation

Slow diffusion of aqueous solution (10 mL) of $[CuL_2(H_2O)_2](NO_3)_2$ (0.1 mmol) onto aqueous solution (10 mL) of $K_2[Pd(CN)_4]$ (0.1 mmol) gave rise to blue plate-like single crystals of $[Cu(chxn)_2][Pd(CN)_4]$ at 298 K [3]. The rest of samples were prepared similar way by employing the corresponding ligands (L), cyanide precursors, and water of isotopes.

X-ray Crystallography

Powder XRD patterns of the complexes were measured at BL-8B (8 keV, λ = 1.54 Å) at 100-300 K.

Results and discussion

For example, XRD patterns at 100-300 K of $[Cu(chxn)_2][Pd(CN)_4]\cdot 2H_2O$ are shown in Figure 1. It suggested that the crystal lattice exhibited positive thermal expansion isotropically. Moreover, the magnitude of peak shift due to 100 K temperature change is almost comparable to substitution of Pd(II) to Pt(II) ion. Therefore, the novel negative thermal elongation of long axial Cu-N of Jahn-Teller distortion observed in 2008 may be attributed to unique crystal packing of $[Cu(chxn)_2][M(CN)_4]\cdot 2H_2O$.

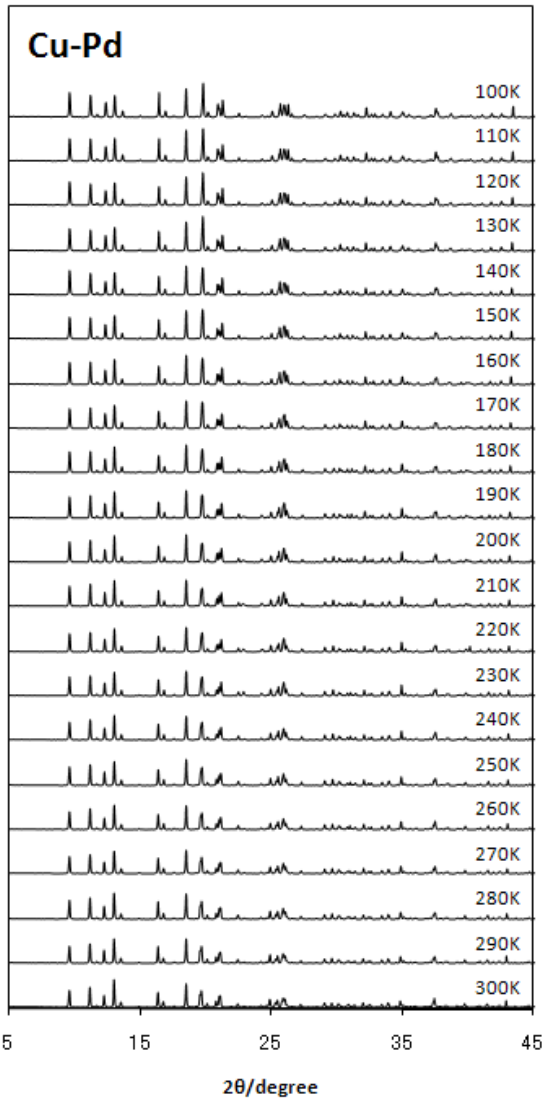

Figure 1: XRD patterns of $[Cu(chxn)_2][Pd(CN)_4]\cdot 2H_2O$.

References

[1] T. Akitsu et al., Inorg. Chem. 145, 9826 (2006).
[2] T. Akitsu et al., Inorg. Chim. Acta 342, 36 (2008).
[3] T. Akitsu et al., Acta Crystallogt. E65, m406 (2009).

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