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]·2H2O (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 elucidate 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]·2H2O (M=Pd and Pt) [2, 3] to compare ion size; <2> [Cu(NEthet)2][M(CN)4]·2H2O (NEten = N-ethyllethylenediamine) for combinatorial preparations by using M=Ni, Pd, and Pt to test suitable ion size; <3> [Cu(Mechxn)2][M(CN)6]2·nH2O (Mechxn = (1R, 2R)-N,N'-dimethylaminocyclohexane; M=Cr, Co, and Fe) by using different water of isotopes (1H2O, 2H2O, and H218O) for isotope effect on intermolecular hydrogen bonds.

Experimental section
Preparation
Slow diffusion of aqueous solution (10 mL) of [CuL2(H2O)2](NO3)2 (0.1 mmol) onto aqueous solution (10 mL) of K2[Pd(CN)4] (0.1 mmol) gave rise to blue plate-like single crystals of [Cu(chxn)2][Pd(CN)4]·2H2O 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]·2H2O 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]·2H2O.

References

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