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Long Axial Cu-N Bond in $[Cu(chxn)_2][Ni(CN)_4]\cdot 2H_2O$

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Introduction

There has been tremendous interest in functional as well as synthetic design of cyanide-bridged coordination polymers in view of crystal engineering or multifunctional materials. Recently, we discovered that chiral zigzag one-dimensional complex, $[Cu(chxn)_2][Ni(CN)_4]\cdot 2H_2O$ (chxn = *trans*-cyclohexane-(*1R, 2R*)-diamine) (**1**) had a long axial Cu-N bond of 3.120(8) Å [1]. Moreover, the analogous complexes, $[Cu(chxn)_2][Pd(CN)_4]\cdot 2H_2O$ (**2**) [2] and $[Cu(chxn)_2][Pt(CN)_4]\cdot 2H_2O$ (**3**) [3], also exhibited corresponding long bonds of 3.092(8) and 3.09(1) Å, respectively. In the field of coordination chemistry, Jahn-Teller elongation of axial bonds is well known for hexacoordinated copper(II) complexes. However, the present case may be classified into semi-coordination resulting from both pseudo Jahn-Teller effect and electrostatic interaction. In order to examine detailed features of these long bonds, we tried to redetermine the crystal structure of **1** using synchrotron X-ray source preliminarily.

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 $K_2[Ni(CN)_4]$ (0.1 mmol) gave rise to blue plate-like single crystals of **1** at 298 K. Yield 80.2 %. Anal. Found; C 39.29; H 6.74; N 22.76. Calc. for $C_{16}H_{32}CuN_8NiO_2$: C 39.16; H 6.57; N 22.83. m.p. 561 K (decomposition). IR (KBr, cm^{-1}): 1038s, 1125s, 1402s, 1442w, 1591s, 1637w, 2123s, 2134s, 2858s, 2925s, 3303m, 3433s.

X-ray Crystallography

Crystal structure of **1** at room temperature was determined at BL-1B using an imaging plate detector (λ = 0.6889 Å).

Results and discussion

The cell parameters for **1** were $C_{16}H_{32}CuN_8O_2Ni$, monoclinic, $P2_1$, a = 9.8711(14) Å, b = 15.3935(23) Å, c = 7.9977(11) Å, β = 110.309(7)°, V = 1139.71(2) Å^3, Z = 2. These values are almost similar and isostructural to that measured with MoKα radiation; **1**: monoclinic, $P2_1$, a = 9.864(4) Å, b = 15.393(8) Å, c = 7.995(4) Å, β = 110.32(3)°, V = 1138.4(10) Å^3, Z = 2. **2**: $C_{16}H_{32}CuN_8O_2Pd$, monoclinic, $P2_1$, a = 9.866(3) Å, b = 15.579(4) Å, c = 8.107(3) Å, β = 110.63(2)°, V = 1166.2(7) Å^3, Z = 2. **3**: $C_{16}H_{32}CuN_8O_2Pt$, monoclinic, $P2_1$, a = 9.899(3) Å, b = 15.541(4) Å, c = 8.102(2) Å, β = 110.02(2)°, V = 1163.6(5) Å^3, Z = 2. Gradual changes of each cell parameter resulted from ionic radii of nickel(II), palladium(II), and platinum(II) ions.

The refinement of the data taken at BL-1B could be carried out, though the final R values were approximately 0.06, whose quality was similar to that of MoKα radiation. Therefore, it was confirmed that discussion on electronic density is difficult without improvements in crystallization even if using synchrotron X-ray source. Otherwise, it should be used common parameters taken from refinement in crystal structure analysis such as bond distance, displacement parameters, and their anisotropy.

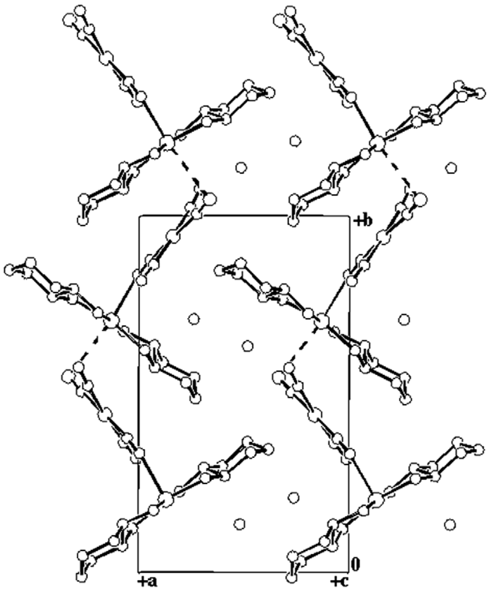

Figure 1: Crystal structure of **1**

Recently, some cyanide-bridged complexes exhibiting negative thermal expansion (the cell volume expands on cooling) have been attracted much attention. Its mechanism is not simple, and it is associated with phonon and certain flexible distortion of lattice. In this context, novel pseudo Jahn-Teller distortion for cyanide-bridged complexes **1**-**3** and temperature dependence of crystal lattice or refinement parameters should be elucidated closely.

References

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