Chemistry

8B/2008G526

Separated observation of Jahn-Teller and lattice distortion in thermal structural changes of copper(II) complexes (in 2008)

Takashiro AKITSU*[1]
[1] Department of Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kazurazaka, Shinjuku-ku, Toyo 162-8601, Japan

Introduction

It is well known that copper(II) complexes exhibit long axial coordination bonds due to Jahn-Teller effect. Both possibilities (elongation and compression) will lead to show so-called negative thermal expansion for proper lattice systems or to discuss Jahn-Teller and lattice distortion separately. These viewpoint may be important to design multifunctional materials. Recently, we found that a certain chiral zigzag one-dimensional Cu(II)-Ni(II) 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, we examined the magnitude of Jahn-Teller distortion caused by substitution to Pd(II) or Pt(II) ions [2] and stereochemistry of ligands [2, 3]. In order to examine thermally accessible structural changes (without phase transition), we carried out structural determination of **1** by using single crystals at several temperature points and preliminary data collection to determine crystal structures based on powder diffraction patterns for a series of Ni(II), Pd(II), and Pt(II) complexes

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 [1]. 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).

X-ray Crystallography

Crystal structure of **1** at 300, 200, and 90 K was determined with BL-8B using an imaging plate detector (λ = 0.6889 Å). For comparison, we measured it at 296, 223, 173, 150, and 100 K using a CCD diffractometer in a laboratory with MoKα radiation (λ = 0.71073 Å).

The results of powder measurements are omitted in this year's report, because it is preliminary level at present.

Results and discussion

The selected cell parameters and bond distances of **1** under various conditions are as follows:
(As for all data, $C_{16}H_{32}CuN_8O_2Ni$, monoclinic, $P2_1$, Z=2)
[300K, λ = 0.6889 Å] a = 9.8565(19) Å, b = 15.415(7) Å, c = 7.9888(7) Å, β = 110.217(12)°, V = 1138.8(2) Å^3, Cu1-N1=3.104(4) Å, Cu1-N3=2.339(4) Å, Cu1-N5=2.011(3) Å, Cu1-N6=2.016(3)Å, Cu1-N7=2.027(3) Å, Cu1-N8=2.033(2) Å.
[200K, λ = 0.6889 Å] a = 9.8612(8) Å, b = 15.3897(11) Å, c = 7.989(2) Å, β = 110.203(11)°, V = 1137.9(3) Å^3 , Cu1-N1=3.119(4) Å, Cu1-N3=2.317(4) Å, Cu1-N5=2.024(3) Å, Cu1-N6=2.041(3)Å, Cu1-N7=2.033(3) Å, Cu1-N8=2.020(3) Å.
[90K, λ = 0.6889 Å] a = 9.8081(19) Å, b = 15.4107(12) Å, c = 8.0062(7) Å, β = 110.2789(15)°, V = 1143.46(16) Å^3, Cu1-N1=3.125(3) Å, Cu1-N3=2.320(2) Å, Cu1-N5=2.015(2) Å, Cu1-N6=2.020(2)Å, Cu1-N7=2.026(2) Å, Cu1-N8=2.037(2) Å.
[296K, λ = 0.71073 Å] a = 9.851(4) Å, b = 15.359(6) Å, c = 7.991(3) Å, β = 110.261(5)°, V = 1134.2(8) Å^3, Cu1-N1=3.112(2) Å, Cu1-N3=2.321(3) Å, Cu1-N5=2.013(3) Å, Cu1-N6=2.013(3)Å, Cu1-N7=2.024(3) Å, Cu1-N8=2.021(3) Å.
[223K, λ = 0.71073 Å] a = 9.8244(7) Å, b = 15.3367(11) Å, c = 7.9683(6) Å, β = 110.0140(10)°, V = 1128.11(14) Å^3, Cu1-N1=3.131(2) Å, Cu1-N3=2.315(2) Å, Cu1-N5=2.0104(18) Å, Cu1-N6=2.018(2)Å, Cu1-N7=2.0305(19) Å, Cu1-N8=2.0224(18) Å.
[173K, λ = 0.71073 Å] a = 9.8014(9) Å, b = 15.3051(14) Å, c = 7.9552(7) Å, β = 109.8500(10)°, V = 1122.04(18) Å^3, Cu1-N1=3.137(2) Å, Cu1-N3=2.3074(19) Å, Cu1-N5=2.0237(17) Å, Cu1-N6=2.0296(18)Å, Cu1-N7=2.0163(18) Å, Cu1-N8=2.0133(17) Å.
[150K, λ = 0.71073 Å] a = 9.7883(7) Å, b = 15.2927(11) Å, c = 7.9461(6) Å, β = 109.7960(10)°, V = 1119.16(14) Å^3, Cu1-N1=3.143(2) Å, Cu1-N3=2.295(3) Å, Cu1-N5=2.026(3) Å, Cu1-N6=2.015(3)Å, Cu1-N7=2.024(3) Å, Cu1-N8=2.027(3) Å.
[100K, λ = 0.71073 Å] a = 9.7727(18) Å, b = 15.263(3) Å, c = 7.9297(15) Å, β = 109.613(2)°, V = 1114.2(4) Å^3, Cu1-N1=3.142(2) Å, Cu1-N3=2.295(4) Å, Cu1-N5=2.032(4) Å, Cu1-N6=2.022(4)Å, Cu1-N7=2.012(4) Å, Cu1-N8=2.025(4) Å.

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).

* akitsu@rs.kagu.tus.ac.jp