

Novel Thermally-Accessible Structural Distortion and Lattice Strain of a Chiral Cyanide-Bridged Cu (II)-Ni (II) Complex

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Abstract: We have investigated temperature dependence of crystal structure of a chiral cyanide-bridged bimetallic assembly of $[\text{CuL}_2][\text{Ni}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$ (**1**) ($\text{L} = (1R, 2R)$ -diaminocyclohexane). Cell parameters and most of bond distances decreased on cooling for **1**. However, only a long Cu-N bond of semi-coordination increases on cooling, which is the first example of negative thermal elongation of specific bond distances.

Keywords: lattice distortion, Jahn-Teller effect, copper, cyanide, temperature.

INTRODUCTION

Commonly most crystalline materials expand on heating, which is called positive thermal expansion (PTE). However some materials exhibit opposite behavior so-called negative thermal expansion (NTE), which is (anisotropic) expanding of crystal lattice on cooling [1]. The mechanism of NTE is different from materials; for example, releasing guest water molecules from host cyanide-bridged metal-organic frameworks (MOF) [2], coordination polymers showing vibration of bonds, geometrical flexibility due to d^{10} - d^{10} metallophilic interactions in cyanide-bridged MOF [3-5], and appropriate crystal arrangement and molecular shapes of organic crystalline materials [6].

Previously, we reported a chiral cyanide-bridged coordination polymer, $[\text{CuL}_2][\text{Ni}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$ (**1**) ($\text{L} = (1R, 2R)$ -diaminocyclohexane) [7]. As shown in Fig. (1), the crystal packing of **1** exhibits a zigzag one-dimensional chain structure along the crystallographic b -axis. Interestingly, one of the two axial semi-coordination Cu1-N3^i [(i) $(-x, y-1/2, -z)$] bonds of six-coordinated Cu environment of **1** was extremely long more than 3 Å, which was attributed to pseudo Jahn-Teller elongation and electrostatic interaction mainly. Since the larger d^8 ions exhibit the among the isomorphous $[\text{CuL}_2][\text{Pd}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$ [8] and $[\text{CuL}_2][\text{Pt}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$ [9], the contribution of specific crystal packing may be expected. In contrast to straight one-dimensional chain structures of $[\text{Cu}(N\text{-ethylethylenediamine})_2][\text{Ni}(\text{CN})_4]$ and the analogous d^8 metal complexes [9, 10], bent bond angles associated with the long Cu-N bond for **1** in a specific crystal packing are quite small resulting in weak interaction and less orbital overlap of typical example of π -backdonation. Furthermore, **1** and several related coordination polymers exhibited reversible releasing and containing of guest crystalline water molecules by heating and cooling. The crystal structure

determination based on powder XRD data reported by Sereda *et al.* [11-13] suggested that the resulting reversible structural changes were between zigzag (containing water molecules) and straight (losing water molecules) one-dimensional cyanide-bridges of host MOF.

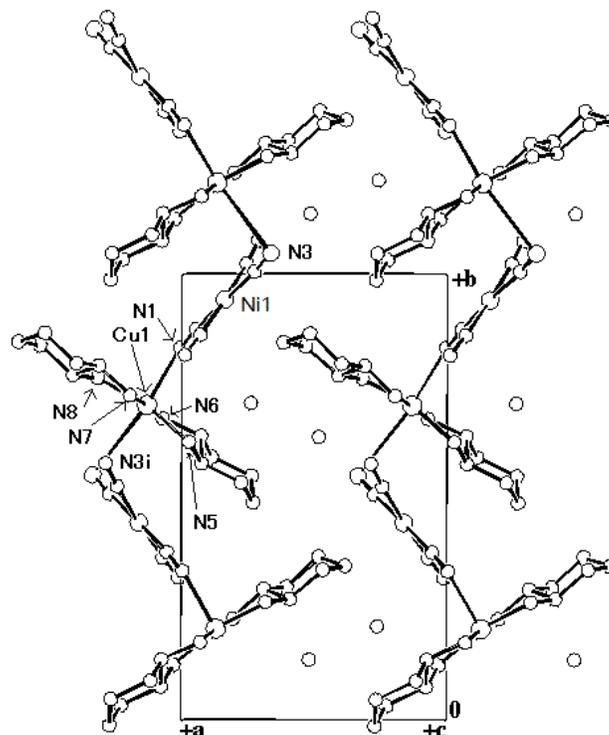


Fig. (1). Crystal structure of **1**.

Herein, we have investigated thermally accessible structural changes of **1** by cooling less than room temperature. We could successfully observe separately NTE for the long Cu-N bond and PTE for the rest of Cu coordination environment and crystal lattice isotropically. Consequently, the characteristic crystal packing to form zigzag one-dimensional chain of **1** is found to be the predominant reason

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for this long Cu-N bond exhibiting interesting temperature dependence.

MATERIALS AND METHODOLOGY

General Procedure

Chemicals and solvents of the highest commercial grade available (Kanto Chemical, Tokyo Chemical Industry, and Wako) were used as received without further purification. Preparations of **1** was carried out according to the literature [7].

Powder X-ray Diffraction

Powder XRD patterns were measured by using synchrotron radiation beamline at KEK-PF BL-8B (proposal No. 2008G526) with 8 keV ($\lambda = 1.54184 \text{ \AA}$) under variable temperature apparatus of nitrogen stream (100-300 K) equipped with a RIGAKU imaging plate. All the samples were measured for 3 min and constant ring current (440 mA).

Single Crystal X-ray Crystallography

The diffraction data were treated using SMART and SAINT [14], and absorption correction was performed using SADABS [15]. The structure was solved by direct methods using SHELXTL [16]. Non hydrogen atoms were refined anisotropically. All hydrogen atoms that could be found clearly were generated geometrically. Axis setting conversion of monoclinic cell was applied to compare with the previous data.

Crystal structural data of **1** at 100 K: $\text{C}_{16}\text{H}_{28}\text{Cu}_8\text{NiO}_2$, monoclinic, space group $P2_1$; $a = 9.7727(18)$, $b = 15.263(3)$, $c = 7.9197(15) \text{ \AA}$, $\beta = 109.613(2)^\circ$, $V = 1114.2(4) \text{ \AA}^3$, $Z = 2$, $M_r = 486.70$, $D_c = 1.451 \text{ g cm}^{-3}$, 6240 reflections measured, 4407 independent. Final $R_1 = 0.0298$, $wR_2 = 0.0880$. Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$).

Crystal structural data of **1** at 150 K: $\text{C}_{16}\text{H}_{28}\text{Cu}_8\text{NiO}_2$, monoclinic, space group $P2_1$; $a = 9.7883(7)$, $b = 15.2927(11)$, $c = 7.9461(6) \text{ \AA}$, $\beta = 109.796(10)^\circ$, $V = 1119.16(14) \text{ \AA}^3$, $Z = 2$, $M_r = 486.70$, $D_c = 1.444 \text{ g cm}^{-3}$, 6325 reflections measured, 4456 independent. Final $R_1 = 0.0232$, $wR_2 = 0.0660$. Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$).

Crystal structural data of **1** at 173 K: $\text{C}_{16}\text{H}_{28}\text{Cu}_8\text{NiO}_2$, monoclinic, space group $P2_1$; $a = 9.8014(9)$, $b = 15.3051(14)$, $c = 7.9522(7) \text{ \AA}$, $\beta = 109.85(10)^\circ$, $V = 1122.04(18) \text{ \AA}^3$, $Z = 2$, $M_r = 486.70$, $D_c = 1.441 \text{ g cm}^{-3}$, 6366 reflections measured, 4481 independent. Final $R_1 = 0.0226$, $wR_2 = 0.0654$. Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$).

Crystal structural data of **1** at 223 K: $\text{C}_{16}\text{H}_{28}\text{Cu}_8\text{NiO}_2$, monoclinic, space group $P2_1$; $a = 9.8244(7)$, $b = 15.3367(11)$, $c = 7.9683(6) \text{ \AA}$, $\beta = 110.014(10)^\circ$, $V = 1128.11(14) \text{ \AA}^3$, $Z = 2$, $M_r = 486.70$, $D_c = 1.433 \text{ g cm}^{-3}$, 6420 reflections measured, 4459 independent. Final $R_1 = 0.0237$, $wR_2 = 0.0687$. Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$).

Crystal structural data of **1** at 296 K: $\text{C}_{16}\text{H}_{28}\text{Cu}_8\text{NiO}_2$, monoclinic, space group $P2_1$; $a = 9.851(4)$, $b = 15.359(6)$, $c = 7.991(3) \text{ \AA}$, $\beta = 110.261(5)^\circ$, $V = 1134.2(8) \text{ \AA}^3$, $Z = 2$, $M_r = 486.70$, $D_c = 1.437 \text{ g cm}^{-3}$, 6482 reflections measured, 4377 independent. Final $R_1 = 0.0326$, $wR_2 = 0.0917$. Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$).

RESULTS AND DISCUSSION

Fig. (2) depicts temperature dependence (300-100 K) of powder XRD patterns of **1** measured with synchrotron radiation. Detailed examination of peaks about shifts, intensity and width indicated isotropic PTE of lattice strain.

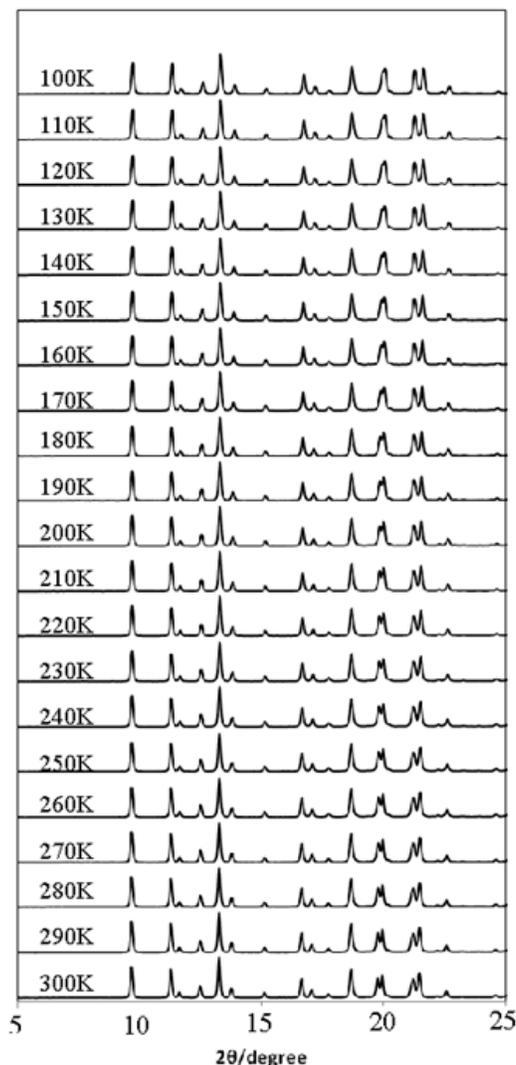


Fig. (2). Temperature dependence of XRD patterns of **1**.

If there was obvious anisotropy of crystal packing, some XRD peaks associated with might indicate irregular shifts. Recently we have reported that disagreement of direction of peak shifts by means of variable temperature powder XRD measurement [17]. For this case of a certain cyanide-bridged Cu-Ag complex, thermally induced anisotropic lattice strain was caused by structural flexibility between weak d^{10} - d^{10} metallophillic interactions and relative rigidity associated with cyanide-bridges of the $[\text{Ag}(\text{CN})_2]$ moiety and Jahn-Teller distortion of a Cu-N bond.

Single crystal structural determination of **1** measured with an X-ray generated by MoK α radiation also supports the temperature dependence of crystal lattice parameters, a , b , c , β , and V in $P2_1$ space group. Table 1 lists temperature dependence of six Cu-N bond distances of **1** around Cu coordination environment, in which Cu1-N5, Cu1-N6, Cu1-N7,

Table 1. Temperature Dependence of Cu-N Bond Distances and Tetragonality (T) of **1**

	100/K	150/K	173/K	223/K	296/K
Cu1-N1/	2.302(2)	2.303(2)	2.307(2)	2.316(2)	2.321(3)
Cu1-N3 ⁱ	3.141(3)	3.134(2)	3.137(2)	3.131(2)	3.113(4)
Cu1-N5/	2.019(2)	2.0185(17)	2.0161(17)	2.018(19)	2.013(2)
Cu1-N6/	2.006(2)	2.013(2)	2.013(2)	2.010(2)	2.013(3)
Cu1-N7/	2.027(2)	2.025(2)	2.024(2)	2.023(2)	2.022(3)
Cu1-N8/	2.038(2)	2.031(16)	2.0295(16)	2.0306(18)	2.024(2)
T of N1	0.878584	0.877931	0.875878	0.872366	0.869453
T of N3	0.643903	0.645142	0.644135	0.645289	0.648249

and Cu1-N8 are in-plane bonds linked by NH₂ groups. Whereas Cu1-N1 and Cu1-N3ⁱ bonds are long (within a normal range for Cu-N bond distances of Jahn-Teller elongation) and characteristic long axial bonds linked by NC groups. The T values denote tetragonality of distorted octahedral Cu coordination geometry whose definition is $T = \text{in-plane Cu-N bond distances} / \text{axial Cu-N bond distances}$ [18, 19].

As emphasized in Fig. (3), only the axial Cu1-N3ⁱ bond distances is elongated on cooling (NTE), though the rest of coordination bonds, namely the axial Cu1-N1 bond and the in-plane Cu1-N4 through N6 bonds are elongated by heating (PTE). The magnitude of differences of bond distances is not within e.s.d.'s and displacement parameters of Cu1 and N1 and N3 through N6 atoms exhibit normal temperature dependence.

The reason for this novel behavior is mainly attributed to appropriate crystal packing structure of **1**. Most interesting structural feature is emerged as Cu-N bond distances. However, specific reasons for lattice strain could not be found as specific interatomic distances (probably void space may be concerned). Contrary to heating behavior [11-13], releasing crystalline water accompanying by drastic structural change is not responsible for this cooling behavior. Additionally, we could not add hydrogen atoms of crystalline water molecules and we could not discuss detailed features of hydrogen bonds. However, positions of most non-hydrogen atoms were kept after changing temperature. The arrangement of rigid coordination polyhedron is kept in this temperature range not to reduce void space in the crystals. Structural or magnetic phase transition did not occur for **1** in this temperature range [7]. Some NTE materials have anisotropy of lattice vibration, contracted axis is perpendicular to the elongated axis for this case. For the case of **1**, the Cu1-N3ⁱ bonds are approximately along the bisectrix of the b and c axes or the b and a axes. However, Cu1-N1 bonds offset the flexibility of Cu1-N3ⁱ bonds in view of vibration of bonds.

Indeed, theoretical discussion suggests the possibility of both elongated and shorten Jahn-Teller distortion (so-called Jahn-Teller switching) to reduce degeneracy orbitals occupying unpaired electrons of d⁹ Cu(II) ions by coupling appropriate normal modes [20, 21]. Similar consideration may be valid for pseudo Jahn-Teller distortion systems of lower symmetry than exact O_h symmetry containing different ligands. However, to our knowledge based on a series of

investigation about the related compounds showing Jahn-Teller distortion [18, 19], we have never observed thermally accessible structural change opposite tendency against temperature dependence. In this way, both Jahn-Teller contraction in a crystal lattice and elongation on cooling (NTE be-

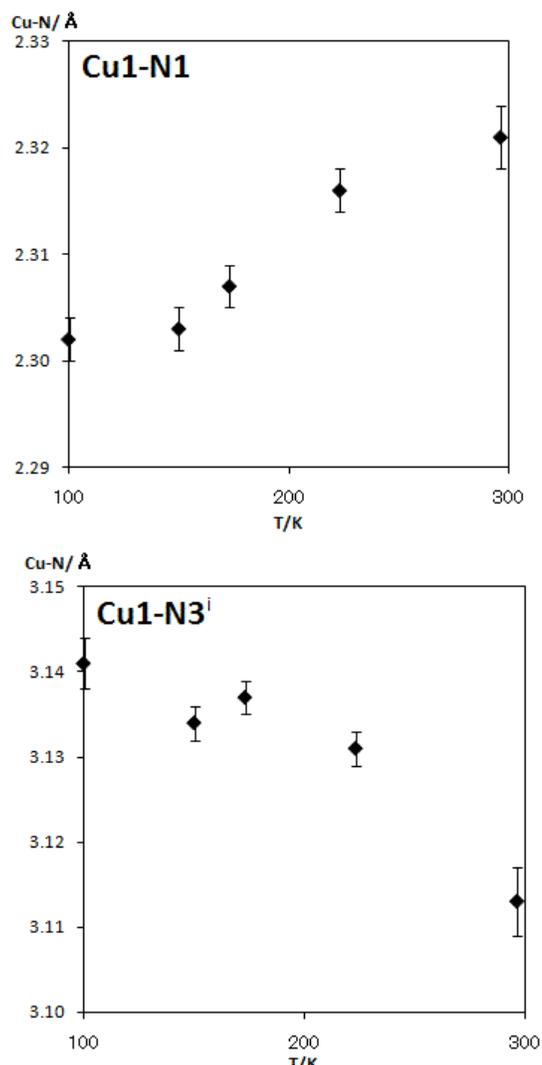


Fig. (3). Temperature dependence of short axial Cu1-N1 and long axial Cu1-N3ⁱ bond distances of **1**. Error bars denotes 1 e.s.d. ranges.

havior about a specific Jahn-Teller distorted bond) may be difficult to find for actual crystalline materials.

CONCLUSION

In summary, we have discovered a novel temperature dependence of a Jahn-Teller distorted bond for a cyanide-bridged Cu-Ni coordination polymer of zigzag one-dimensional crystal packing by chance.

SUPPLEMENTARY DATA

CCDC (779350-779354) contains the supplementary crystallographic data. These data can be obtained free of charge *via* <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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