One-Dimensional Copper Coordination Polymer: Preparation and Structure of Bis(1,3,5-benzenetricarboxylato)(4,4-bipyridine)copper(II)

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Recently, a variety of coordination polymers based on metalligand coordinative covalent bonding have received considerable attractions due to their novel topology and interesting functions.[1-6] In particular, much attention has been paid to porous high-dimensional coordination polymers, because of their potential zeolite-like applications.[7-10] For the preparation of this type of polymers, 1,3,5-benzenetricarboxylic acid (btcH$_3$) is widely employed because of its potential role as a multidimensional ligand.[11-13] For instance, Yaghi and co-workers reported the hydrothermal reaction between metal(II) acetate tetrahydrate, [M(OAc)$_2$·4H$_2$O: M = Co, Ni, or Zn], and btcH$_3$ to give 3-D coordination polymers of the type M$_3$(btc)$_2$·12H$_2$O.[13]

During the past years, several two- and three-dimensional coordination polymers have been prepared from transition-metal templates with mixed ligands of carboxylates and pyridyls, which can act as multidentate organic spacers. For example, a series of high-dimensional open frameworks were recently reported, in which the combinations of such organic spacers as btcH$_3$, 1,4-benzenedicarboxylic acid, pyrazine, and 4,4'-bypidine (bpy) were utilized.[14-16]

We recently reported a one-dimensional copperpyridinedicarboxylate polymer that contains square-planar Cu(II) centers exhibiting antiferromagnetic coupling.[17] We became interested in preparing high-dimensional coordination polymers with mixed ligands. In this context, we set out to prepare copper coordination polymers with btcH$_3$ and bpy by hydrothermal reactions. Unexpectedly, the hydrothermal reaction of copper nitrate [Cu(NO$_3$)$_2$·2.5H$_2$O] with the mixed ligands of btcH$_3$ and bpy gave a one-dimensional coordination polymer with an empirical formula of Cu(btcH$_2$)$_2$(bpy) (**1**). Herein, we report the preparation, structure, and thermal property of polymer **1**.

Experimental Section

Cu(NO$_3$)$_2$·2.5H$_2$O, 1,3,5-benzenetricarboxylic acid (btcH$_3$), and 4',4'-bipyridine (bpy) were purchased and used without further purifications. IR spectra were recorded with a Nicolet 320 FT-IR spectrophotometer. Themogravimetric analyses were carried out on a TA4000/SDT 2960 instrument. Elemental analyses were performed by the Korea Basic Science Institute.

Preparation of Cu(btcH$_2$)$_2$(bpy) (1). A mixture of Cu(NO$_3$)$_2$·2.5H$_2$O (0.111 g, 0.476 mmol), btcH$_3$ (0.100 g, 0.476 mmol), bpy (0.074 g, 0.476 mmol), and H$_2$O (6 mL) in the mole ratio of 1 : 1 : 1 : 700 was heated in a 23-mL Teflon-lined-reaction vessel at 180 ºC for 3 days and then cooled to room temperature by air-cooling. The blue product was collected by filtration, washed with H$_2$O (2 × 5 mL) and ethanol (2 × 5 mL), and then air-dried to give Cu(btcH$_2$)$_2$(bpy) (0.072 g, 0.129 mmol, 27.1% yield). Anal. Calcd for C$_{28}$H$_{18}$N$_2$O$_{12}$Cu (M_r = 637.98): C, 52.71; N, 4.39; H, 2.84. Found: C, 51.80; N, 4.07; H, 2.80. IR (KBr, cm^{-1}): 1699, 1613, 1552, 1430, 1395, 1289, 1169, 1116, 823, 672.

Table 1. X-ray data collection and structure refinement

formula	$C_{28}H_{18}N_2O_{12}Cu$
fw	637.98
temperature, K	295(2)
crystal system	monoclinic
space group	$C2/c$
a, Å	10.717(2)
b, Å	11.089(3)
c, Å	22.778(5)
β, deg	101.39(1)
V, Å^3	2654(1)
Z	4
d_{cal}, g cm^{-3}	1.597
μ, mm^{-1}	0.896
$T_{\min}$	0.7197
$T_{\max}$	0.9207
$F(000)$	1300
2θ range (º)	3.5-50
scan type	ω
scan speed	variable
No. of reflns measured	2439
No. of reflns unique	2309
No. of reflns with $I > 2\sigma(I)$	2019
No. of params refined	234
Max., in $\Delta\rho$ (e Å^{-3})	0.419
Min., in $\Delta\rho$ (e Å^{-3})	-0.407
GOF on F^2	1.039
R	0.0325
$wR_2{}^a$	0.0819

$^a wR_2 = \Sigma[w(F_o{}^2-F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]^{1/2}$

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Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^3 \times 10^3$)

	x	*y*	*z*	*U* (eq)[a]
Cu(1)	5000	3523(1)	7500	19(1)
O(1)	3929(1)	3538(1)	8144(1)	23(1)
O(2)	5968(1)	3437(2)	8569(1)	28(1)
O(3)	891(2)	4806(2)	9460(1)	53(1)
O(4)	1418(2)	4424(2)	10445(1)	44(1)
O(5)	6927(2)	2253(3)	10685(1)	58(1)
O(6)	6014(2)	3265(3)	11336(1)	62(1)
N(1)	5000	1728(2)	7500	21(1)
N(2)	5000	5322(2)	7500	23(1)
C(1)	4448(2)	3542(2)	9216(1)	22(1)
C(2)	3245(2)	3945(2)	9283(1)	26(1)
C(3)	2954(2)	4022(2)	9853(1)	26(1)
C(4)	3858(2)	3704(2)	10358(1)	27(1)
C(5)	5048(2)	3282(2)	10292(1)	26(1)
C(6)	5335(2)	3202(2)	9722(1)	26(1)
C(7)	4812(2)	3498(2)	8609(1)	21(1)
C(8)	1666(2)	4457(2)	9919(1)	30(1)
C(9)	6031(2)	2944(3)	10834(1)	33(1)
C(10)	3917(2)	1104(2)	7315(1)	27(1)
C(11)	3877(2)	-147(2)	7315(1)	28(1)
C(12)	5000	-800(3)	7500	22(1)
C(13)	5000	-2152(3)	7500	22(1)
C(14)	3989(2)	-2806(2)	7167(1)	27(1)
C(15)	5970(2)	5944(2)	7823(1)	27(1)

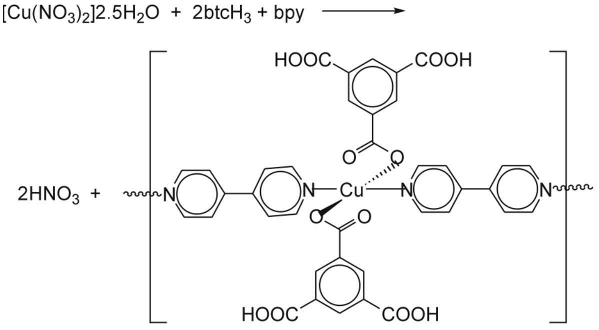
[a]Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

X-ray Structure Determination. All X-ray data were collected with the use of a Siemens P4 diffractometer equipped with a Mo X-ray tube and a graphite-crystal monochromator. The orientation matrix and unit-cell parameters were determined by least-squares analyses of the setting angles of 21 reflections in the range of $10.0^{\circ} < 2\theta < 25.0^{\circ}$. Three check-reflections were measured every 100 reflections throughout data collection and showed no noticeable variations in intensity. Intensity data were corrected for Lorenz and polarization effects. Decay corrections were also made. The intensity data were empirically corrected for absorption with ψ-scan data. All calculations were carried out with the use of the SHELXTL programs.[18]

A blue crystal of **1**, shaped as a rod of approximate dimensions of $0.60 \times 0.26 \times 0.20$ mm^3, was used for crystal- and intensity-data collection. The unit-cell parameters and systematic absences, *hkl* ($h + k = 2n + 1$) and *h*0*l* ($l = 2n + 1$), indicated two possible space groups: *Cc* (non-centrosymmetric) and *C*2/*c* (centrosymmetric). A statistical analysis of reflection intensities suggested a centrosymmetric space group, and the structure analysis converged only in *C*2/*c*. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in the difference Fourier maps. Details on crystal data and intensity data are given in Table 1. Final atomic coordinates are shown in Table 2. Selected bond distances and bond angles are given in Table 3.

Results and Discussion

Preparation. A one-dimensional Cu(II) coordination polymer with an infinite network was prepared from a mixture of $Cu(NO_3)_2 \cdot 2.5H_2O$, $btcH_3$, bpy, and H_2O in the mole ratio of 1 : 1 : 1 : 700 by heating it at 180 °C for 3 days (eq 1). Although we do not know the driving force for this reaction, the coordinative covalent bonding and the octahedral preference of the copper metal center seem to play a role.



(1)

The compound **1** is air-stable and is not soluble in common organic solvents. Its IR spectrum shows the asymmetric and symmetric carboxylate stretches for $btcH_2^{-1}$ (1699, 1430, 1395, and 1289 cm^{-1}). The disappearance of the carbonyl band (1721 cm^{-1}) in $btcH_3$ and some characteristic bands (1590 and 1532 cm^{-1}) in the free bpy suggests that both $btcH_3$ and bpy might have been coordinated to copper metals during the reaction. The formulation of **1** has been further confirmed by X-ray diffraction and elemental analysis.

Thermogravimetric analysis (TGA) shows that title polymer is stable up to 280 °C without decomposition (Figure 1). A drastic weight loss is observed from 330 to 360 °C, which corresponds to the loss of one $btcH_2^-$ ligand and one bpy

Table 3. Selected bond distances (Å) and bond angles (°)

Cu1–N1	1.990(3)	Cu1–N2	1.995(3)	Cu1–O1#1	2.034(2)
Cu1–O1	2.034(2)				
N1–Cu1–N2	180.00(1)	N1–Cu1–O1#1	90.45(4)	N2–Cu1–O1#1	89.55(5)
N1–Cu1–O1	90.45(5)	N2–Cu1–O1	89.55(4)	O1#1–Cu1–O1	179.09(9)
O2–C7–O1	121.5(2)	O3–C8–O4	124.2(2)	O6–C9–O5	124.3(2)

Symmetry transformations used to generate equivalent atoms: #1 = $-x + 1, y, -z + 3/2$; #2 = $-x + 1, y-1, -z + 3/2$.

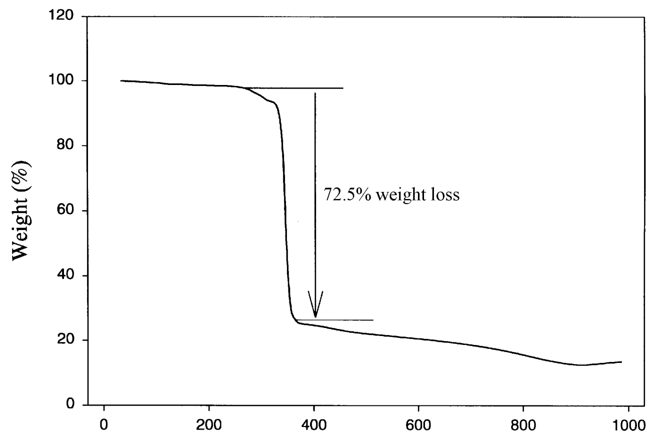


Figure 1. Thermogravimetric analysis results for **1**.

ligand. Above 505 °C, the second process occurs to give a solid residue (22.1%).

Structure. Figure 2 shows the local coordination of the copper center. The Cu1, N1, N2, C12, and C13 atoms lie on the crystallographic 2-fold rotation (C_2) axis, and this explains why this crystal has the Z value of 4 instead of 8. The coordination sphere of copper can be described as square planar, with two oxygen atoms from two btcH$_2^-$ ligands and two nitrogen atoms from two bpy ligands. The formal oxidation state of the copper metal is +2. The C-O bond distance in the coordinated and uncoordinated carboxylates are equal within experimental error.

The equatorial plane, defined by Cu1, N1, N2, O1, and O1#1 (#1 = $-x + 1, y, -z + 3/2$), is perfectly planar due to its generation by symmetry operation. Two pyridine moieties in the bpy ligand are twisted from each other by 18.1(1)°, and have the dihedral angles of 65.61(7)° and 83.76(7)° with respect to the equatorial plane. The benzene ring in the btcH$_2^-$ ligand is essentially planar with the average atomic displacement of 0.0062 Å and has the dihedral angle of 72.66(6)° with respect to the equatorial plane. Two of the three carboxylate groups are considerably twisted from the benzene ring with the dihedral angles of 17.2(1)° and 19.6 (3)°, and the remaining one (O3, O4, and C8) is relatively coplanar with the dihedral angle of 4.6(3)°. The bpy acts as a bridging ligand between two Cu metals. Interestingly, the btcH$_2$ ligand acts as a monodentate oxygen-donor ligand and does not link the Cu metals. In other words, only one (O1) out of the six carboxylate oxygens in the btcH$_2^-$ ligand is coordinated to the copper metal.

The unit-cell diagram along the *a*-axis demonstrates a one-dimensional polymeric structure of **1**, as shown in Figure 3. Each one-dimensional array is formed by the bridging bpy ligands connecting Cu metals in the *b*-axis direction. These 1-D arrays stack on top of each other along the *c*-axis with a separation of one-half of the *c*-axis length (11.4 Å). The hydrogen atoms in the carboxylate groups, which are not coordinated to the copper metal, are involved in intermolecular hydrogen bonds: O4–HO4 = 0.655 Å, O4···O3 = 2.667 Å, HO4···O3 = 2.014Å, and O4–HO4···O3 = 175.40°; O5–HO5 = 0.747 Å, O5···O2 = 2.655Å, HO5···O2 = 1.935Å, and O5–HO5···O2 = 161.69°. These hydrogen bonds are associated with the center of symmetry and *C*-centering. Williams and co-workers very recently reported that the solvothermal or hydrothermal reaction of copper(II) nitrate, terephthalic acid, and bpy in the mole ratio of 1 : 1 : 1 gives a 3-D copper polymer $[Cu_4\{(1,4\text{-}C_6H_4COO)_2\}_3(bpy)_2]$, which has a Cu(I)–Cu(II) dimeric unit.[14] On the other hand, we employed copper(II) nitrate, btcH$_3$, and bpy and obtained a 1-D copper coordination polymer.

Several attempts to enhance the dimensionality of a low-dimensional coordination polymer have recently appeared in the literature. For example, Li and co-workers reported the effect of pH on the dimensionality of coordination polymers.[19] In addition, Zaworotko and Moulton proposed the manipulation of 2D polymers to be a plausible entry into the generation of 3D polymers. Their proposed strategies are the cross-linking of 2D structures with spacer ligands and the interpenetration of identical or different 2D networks.[20,21] Furthermore, Keller and co-workers showed the dimensional control of Cu(I)–bis(4-pyridyl)ethylene coordination network by varying the solvent composition.[22] In this context, we have tried to enhance the dimensionality of polymer **1** by varying the reaction conditions such as reaction time (1–3 days), pH (3–11), mole ratio (1 : 1–3 : 1), and solvent

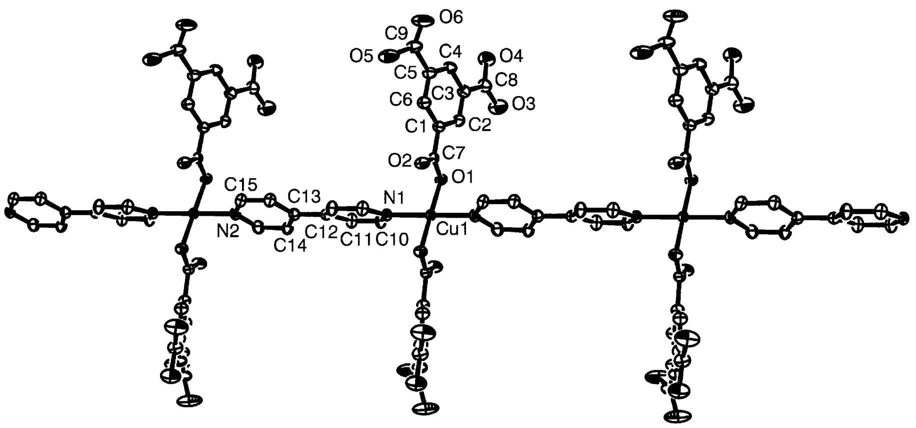


Figure 2. *ORTEP* drawing of **1** showing the atom-labeling scheme and 50% probability thermal ellipsoids.

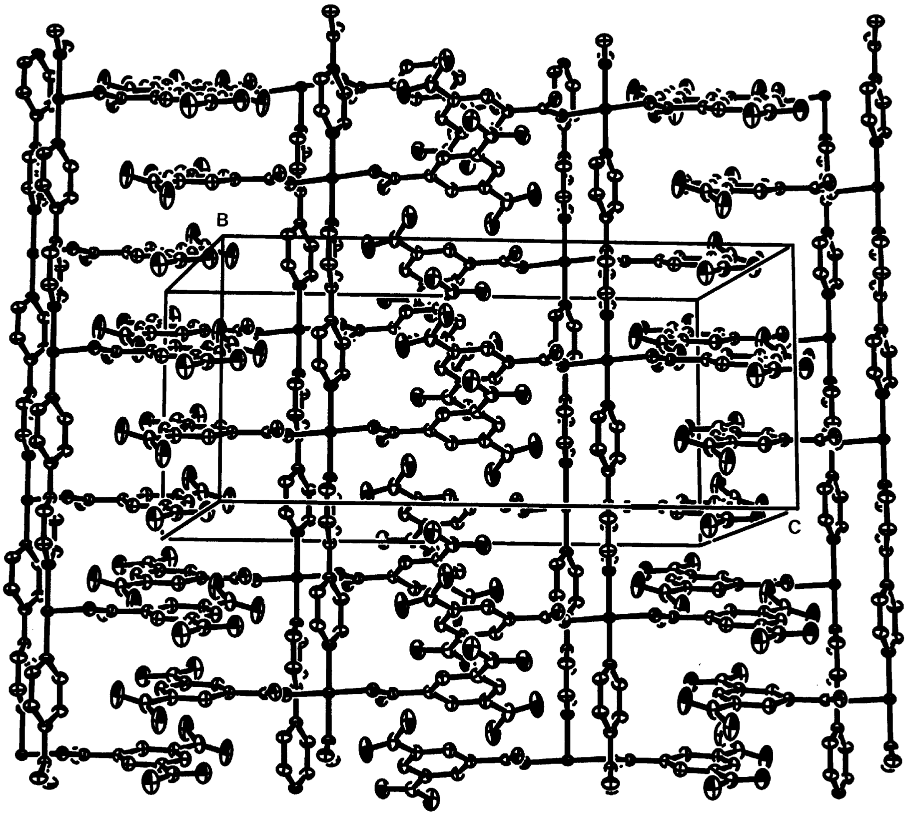


Figure 3. A packing diagram along the *a*-axis.

composition (H_2O : ROH = 4 : 1; R = Me, Et, or *n*-Bu). Variations in the reaction time or mole ratio gave the same product, which was confirmed by IR and unit-cell parameters. On the other hand, variations in the pH and solvent composition brought about the decomposition of products. In addition, instead of the bpy ligand, we tried to employ some other dipyridyl ligands (pyrazine, *trans*-1,2-bis(4-pyridyl)ethylene, *trans*-1,2-bis(4-pyridyl)ethane, and 4,4'-trimethylenedipyridine). However, these ligands gave only poorly crystalline or powder products.

In summary, we have structurally characterized $Cu(btcH_2)_2$-(bpy) (**1**), which was prepared by the hydrothermal reaction of $Cu(NO_3)_2 \cdot 2.5H_2O$ with the mixed ligands of 1,3,5-benzenetricarboxylic acid ($btcH_3$) and 4,4'-bipyridine (bpy). This polymer has a one-dimensional network and exhibits thermal stability up to 280 °C

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Supplementary Material. Tables of full bond distances and bond angles, anisotropic thermal parameters, and atomic coordinates of hydrogen atoms are available from the author Soon W. Lee.

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