

단 신

1차원 Cu(II) 배위 고분자의 합성 및 구조: [Cu(bdcH)₂(bipyen)] (bdc=1,3-benzenedicarboxylate; bipyen=*trans*-1,2-bis (4-pyridyl)ethylene)

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Preparation and Structure of One-Dimensional Copper(II) Coordination Polymer: [Cu(bdcH)₂(bipyen)] (bdc=1,3-benzenedicarboxylate; bipyen=*trans*-1,2-bis(4-pyridyl)ethylene)

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Recently, a variety of coordination polymers based on metal-ligand coordinative covalent bonding have received considerable attraction due to their novel topologies and interesting functions.¹⁻⁶ In particular, research interest has been focused on 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 (btcl₃) is widely employed because of its potential role as a multidimensional ligand.¹¹⁻¹⁵

We have been continually interested in preparing coordination polymers with dicarboxylate ligands. For instance, we have obtained a 3-D zinc,¹¹ 3-D cobalt,¹⁵ 2-D Ni,¹⁶ 1-D Cu,¹⁷ 2-D La,¹⁸ and 2-D cobalt¹⁹ coordination polymers by hydrothermal reactions. Very recently, we reported the structure of [Cu(btcl₂)₂(bpy)], which was hydrothermally prepared from copper nitrate (Cu(NO₃)₂·2.5H₂O), btcl₁, and 4,4'-bipyridine (bpy). Interestingly, this polymer has a one-dimensional network despite the potential of the btcl₁ as a multidimensional ligand.²⁰

In order to gain more insight into the connectiv-

ity pattern and its ensuing structures of the mixed-ligand systems of carboxylates and pyridyls, we decided to prepare another copper coordination polymer based on 1,3-benzenedicarboxylic acid (isophthalic acid, bdcH₂) and *trans*-1,2-bis(4-pyridyl)ethylene (bipyen). The hydrothermal reaction of Cu(NO₃)₂·2.5H₂O with bdcH₂ and bipyen gave a one-dimensional coordination polymer with an empirical formula of [Cu(bdcH)₂(bipyen)] (1). Herein, we report the preparation, structure, and thermal property of polymer 1.

EXPERIMENTAL SECTION

Cu(NO₃)₂·2.5H₂O, bdcH₂, and bipyen were purchased. IR spectra were recorded with a Nicolet Avatar 320 FT-IR spectrophotometer. Thermogravimetric analyses were carried out on a TA4000/SDT 2960 instrument. Elemental analyses were performed by the National Center for Inter-University Research Facilities.

Preparation of Cu(bdcH)₂(bipyen) (1). A mix-

ture of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (0.175 g, 0.602 mmol), bdcl_1 (0.100 g, 0.602 mmol), bipyen (0.110 g, 0.602 mmol), and H_2O (6 mL) in the mole ratio of 1:1:1:700 was heated in a 23-mL Teflon-lined reaction vessel at 150 °C for 2 days and then cooled to room temperature by air-cooling. The blue product was collected by filtration, washed with H_2O (2×5 mL) and ethanol (2×5 mL), and then air-dried to give blue crystals of $\text{Cu}(\text{bdcl}_1)_2(\text{bipyen})$ (0.141 g, 0.203 mmol, 80.8% yield). Anal. Calcd for $\text{C}_{28}\text{H}_{18}\text{N}_2\text{O}_{12}\text{Cu}$ ($M_r = 576.00$): C, 58.39; N, 4.86; H, 3.50. Found: C, 58.22; N, 4.89; H, 3.52. IR (KBr): 3440, 3012, 1864, 1697, 1626, 1573, 1425, 1371, 1261, 1159, 1067, 934, 827, 798.730, 555 cm^{-1} .

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 monochromator. The orientation matrix and unit-cell parameters were determined by the least-squares analyses of the setting angles of 24 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. The intensity data were empirically corrected for absorption with ψ -scan data. Decay corrections were also made. All calculations were carried out with the use of SHELXTL programs.²¹

A blue crystal of **1**, shaped as a block of approximate dimensions of $0.30 \times 0.28 \times 0.14 \text{ mm}^3$, was used for crystal- and intensity-data collection. The unit-cell parameters and systematic absences of $h0l$ ($l = 2n+1$) and $0k0$ ($k = 2n+1$) unambiguously indicated $P2_1/c$ as a space group. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in the difference Fourier maps and were refined isotropically. Details on crystal data and

Table 1. X-ray data collection and structure refinement

formula	$\text{C}_{28}\text{H}_{18}\text{CuN}_2\text{O}_8$
fw	576.00
temperature, K	293(2)
crystal system	monoclinic
space group	$P2_1/c$
<i>a</i> , Å	11.529(2)
<i>b</i> , Å	13.575(2)
<i>c</i> , Å	15.908(4)
β , deg	106.41(2)
<i>V</i> , Å ³	2388.2(8)
<i>Z</i>	4
d_{calc} , g cm ⁻³	1.602
μ , mm ⁻¹	0.974
T_{min}	0.7200
T_{max}	0.9212
$F(000)$	1180
2θ range (°)	3.5–50
scan type	ω
scan speed	variable
No. of reflns measured	4366
No. of reflns unique	4143
No. of reflns with $I > 2\sigma(I)$	3041
No. of params refined	432
Max. in $\Delta\rho$ (e \AA^{-3})	0.235
Min. in $\Delta\rho$ (e \AA^{-3})	-0.317
<i>GOF</i> on F^2	1.048
<i>R</i>	0.0385
wR_2^a	0.0814

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

refinement details are given in Table 1. Selected bond lengths and bond angles are given in Table 2.

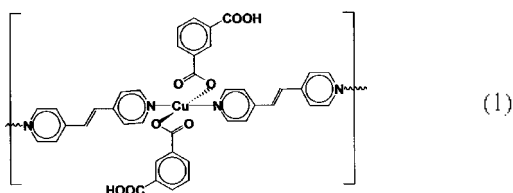
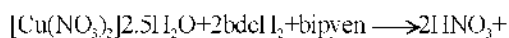
Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center, CCDC No. 190620 for **1**. Copies of this information may be obtained free of charge from: The director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk/conts/retrieving.html>).

Table 2. Selected bond lengths (Å) and bond angles (°)

Cu1-O1	1.916(2)	Cu1O5	1.926(2)	Cu1N1	2.082(2)
Cu1-N2	2.091(2)				
O1-Cu1-O5	177.33(9)	O1Cu1-N1	89.79(9)	O5Cu1N1	90.57(9)
O1-Cu1-N2	89.55(9)	O5Cu1-N2	90.20(9)	N1Cu1N2	177.48(10)

RESULTS AND DISCUSSION

Preparation. A one-dimensional Cu(II) coordination polymer with an empirical formula of $[\text{Cu}(\text{bdcH})_2(\text{bipyen})]$ (**1**) was prepared by heating a mixture of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$, bdcH_2 , bipyen , and H_2O in the mole ratio of 1:1:1:700 at 150°C for 2 days (eq 1). A very closely related polymer $[\text{Cu}(\text{btcl}_2)_2(\text{bpy})]$ was recently reported by our group.²⁰



The compound **1** is air- and moisture-stable and is not soluble in common organic solvents. The IR spectrum of **1** shows the asymmetric and symmetric carboxylate stretches for bdcH^- (1697 , 1626 , 1573 , and 1371 cm^{-1}).^{22,23} The shift of the carbonyl bands in the free bdcH_2 and the disappearance of some characteristic bands (1592 and 1460 cm^{-1}) in the free bipyen suggest that both bdcH_2 and bipyen might have been coordinated to copper metals during the reaction. A broad band at 3440 cm^{-1} can be assigned to the OH stretch in the uncoordinated car-

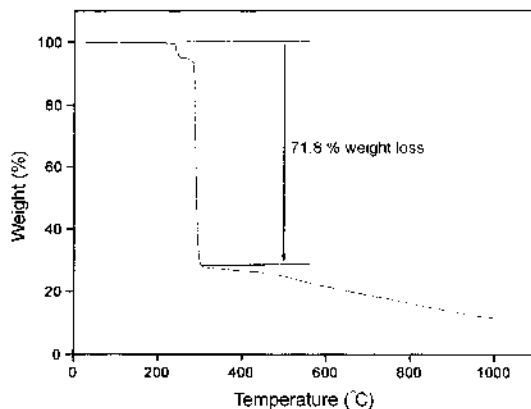


Fig. 1. Thermogravimetric analysis results for **1**.

boxylate group. The formulation of **1** has been further confirmed by X-ray diffraction and elemental analysis.

Thermogravimetric analysis (TGA) shows that the title polymer is stable up to 240°C without decomposition (Fig. 1). A drastic weight loss occurs from 280 to 305°C , which corresponds to the loss of two bdcH^- ligands and one bipyen ligand. In comparison, the $[\text{Cu}(\text{btcl}_2)_2(\text{bpy})]$ polymer related to polymer **1** is stable up to 280°C .²⁰

Structure. Fig. 2 shows the local coordination of the copper center. The coordination sphere of copper can be described as square planar, with two oxygen atoms from two bdcH^- ligands and two nitrogen atoms from two bipyen ligands. The for-

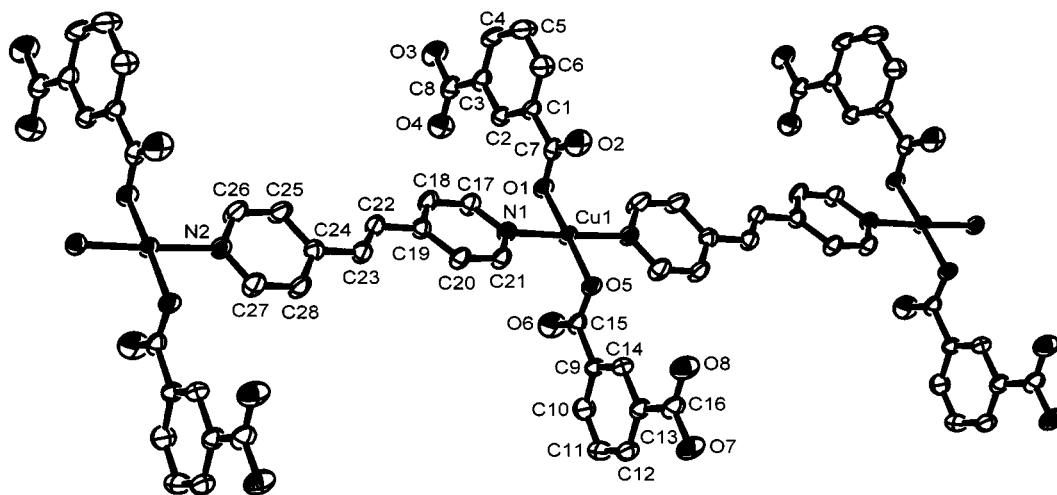


Fig. 2. ORTEP drawing of **1** showing the atom-labeling scheme and 50% probability thermal ellipsoids.

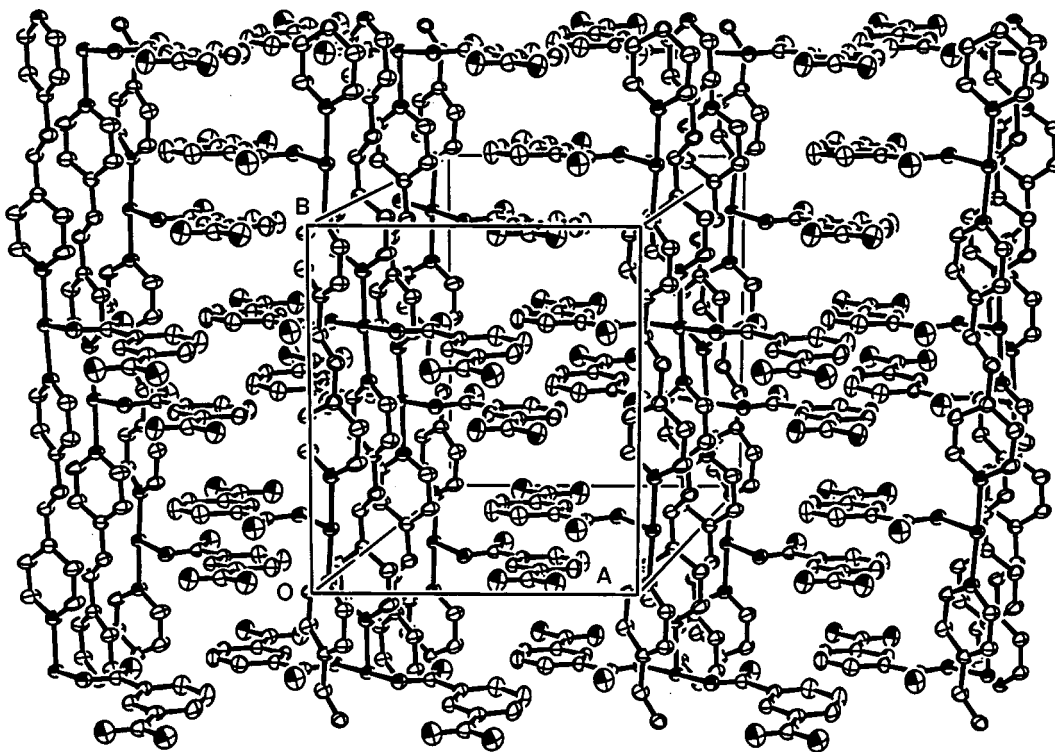


Fig. 3. A packing diagram along the *c*-axis.

mal oxidation state of the copper metal is +2. The C-O bond lengths in the coordinated and uncoordinated carboxylate groups are equal within experimental error.

The equatorial plane, defined by Cu1, N1, N2, O1, and O5, is relatively planar with an average atomic displacement of 0.0443 Å. Two pyridine moieties in the bipyen ligand are twisted from each other by 17.9(2)°. The benzene ring in the bdeH⁻ ligand is almost planar with an average atomic displacement of 0.0007 Å and is essentially perpendicular to the equatorial plane with a dihedral angle of 87.0(1)°. The bipyen acts as a bridging ligand between two Cu metals. Interestingly, the bdeH⁻ ligand acts as a monodentate oxygen-donor ligand and does not link Cu metals; that is, only one (O1) out of the four carboxylate oxygens in the bdeH⁻ ligand is coordinated to the copper metal.

The packing diagram along the *c*-axis demonstrates a one-dimensional polymeric structure of **1** (Fig. 3). Each one-dimensional array is formed by

the bridging bipyen ligands linking Cu metals in the *b*-axis direction. These 1-D arrays stack on top of each other along the *c*-axis. The hydrogen atoms in the uncoordinated carboxylate groups are involved in intermolecular hydrogen bonds: O3...HO3=1.139 Å, O3...O8=2.601 Å, HO3...O8=1.465 Å, and O3...HO3...O8=175.57°. O7...HO7=1.325 Å, O7...O4=2.668 Å, HO7...O4=1.343 Å, and O7...HO7...O4=179.31°. O7...HO7=1.325 Å, O7...O3=3.501 Å, HO7...O3=2.621 Å, and O7...HO7...O3=121.57°. The overall bonding parameters and framework pattern of **1** are essentially the same as those found for [Cu(bdeH₂)₂-(bpy)] that we previously reported.²⁰ Chen and co-workers very recently reported an intriguing result that the hydrothermal reaction of Cu(NO₃)₂·3H₂O with bdeH₂ and bpy at 180 °C gave a 3-dimensional, mixed-valence Cu(I,II) polymer [Cu₂(bdeO)-(bpy)] (bdeOH=2-hydroxy-1,3-benzenedicarboxylate).²⁴ They rationalized the formation of the bdeO³⁻ fragment on the basis of the in situ oxidation of the bde²⁻ ion under the hydrothermal condi-

tions. By contrast, our reaction system consisting of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$, bdcH_2 , and bipycn at 150°C gave a 1-dimensional copper(II) coordination polymer, and the oxidation of bdcH^- ligand was not observed.

In summary, we have structurally characterized $\text{Cu}(\text{bdcH})_2(\text{bipycn})$ (**1**), which was prepared by the hydrothermal reaction of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ with the mixed ligands of 1,3-benzenedicarboxylic acid (bdcH_2) and *trans*-1,2-bis(4-pyridyl)ethylene (bipycn). This polymer has a one-dimensional network and exhibits thermal stability up to 240°C .

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