

# Hydrothermal Synthesis, Crystal Structure, and Magnetic Property of Copper(II) Coordination Networks with Chessboard Tunnels

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A copper(II) coordination polymer, bis(isonicotinato)copper(II) dihydrate, was prepared using a hydro(solvo)thermal process and characterized by a single-crystal X-ray diffraction method and elemental analysis. Crystal data:  $[\text{Cu}(\text{II})(\text{C}_6\text{H}_4\text{O}_2\text{N})_2 \cdot 2\text{H}_2\text{O}]_n$ , monoclinic,  $Cc$ ,  $Z = 4$ ,  $a = 4.9967(5) \text{ \AA}$ ,  $b = 24.971(2) \text{ \AA}$ ,  $c = 11.110(1) \text{ \AA}$ ,  $\beta = 98.86(1)^\circ$ ,  $V = 1368.5(2) \text{ \AA}^3$ ,  $R_1 = 0.023$ , and  $wR_2 = 0.058$ . The structure is a three-dimensional metal–organic coordination network containing diamond-shaped tunnels. Magnetic studies show that the magnetic susceptibility data in the temperature range 2.0–300 K can be fitted to a Curie–Weiss law with  $\theta = -0.93 \text{ K}$  and  $C = 0.398 \text{ emu K/mol}$  ( $s = \frac{1}{2}$ ,  $g = 2.06$ ), which corresponds to an effective magnetic moment ( $\mu_{\text{eff}}$ ) per copper ion of 1.78 BM. The magnetism result indicates that there is no strong interaction between copper centers within the network structure. © 2001

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**Key Words:** hydrothermal synthesis; metal–organic frameworks; porous materials; coordination polymeric networks.

## INTRODUCTION

Because of its intrinsic microporosity of crystal structures, zeolites are of great industrial importance and find practical applications as catalysts, separation agents, and sensors (1). This has fueled continuing interest in the synthesis and applications of new types of zeolites and related microporous materials (zeotypes). Considerable recent interest in these materials has made possible the assembly of porous metal–organic ligand coordination arrays through a building block approach (2). Taking advantage of the great varieties of organic modular ligands, it could provide opportunities for the extensive formation of custom-designing frameworks to gain better control of pore size and shapes with the proper choice of metal centers (3). These building blocks contain various geometrical arrangements such as

square net (4), rectangular channel (5), honeycomb (6), brick wall (7), helix (8), and diamondoid networks (9). The applications of this type of materials in gas sorption, selective guest binding and removal, enantioselective separation, and catalysis have successfully been demonstrated (10). To explore the possibility of new family members of porous metal–organic framework materials, we hereby report the synthesis and characterization of novel porous three-dimensional metal–organic coordination frameworks,  $[\text{Cu}(\text{II})(\text{C}_6\text{H}_4\text{O}_2\text{N})_2 \cdot 2\text{H}_2\text{O}]_n$ , containing chessboard-like tunnels. The hydro(solvo)thermal method is employed in the synthesis due to its advantage in the growth of crystalline solids (11).

## EXPERIMENTAL

All reagents were commercially available and used as received. The C, H, and N microanalyses were carried out with a Perkin–Elmer 240 elemental analyzer. Thermogravimetric data were collected on a Perkin–Elmer TGA 7 analyzer under flowing oxygen.

### Synthesis of $\text{Cu}(\text{II})(\text{C}_6\text{H}_4\text{O}_2\text{N})_2 \cdot 2\text{H}_2\text{O}$ (I)

A mixture of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (1.0 mmol) and 4-cyanopyridine (1.0 mmol) was added to 10 mL of  $\text{H}_2\text{O}/\text{EtOH}$  (1:1 v/v) and treated hydro(solvo)thermally by heating at  $150^\circ\text{C}$  under autogenous pressure for 48 h. Single-phase bulk products of dark blue hexagonal columnar crystals were formed. Product crystals were filtered and air-dried. Energy-dispersed analysis (EDX) of the product crystals indicated the existence of copper atoms. The results of elemental analysis are as follows: C, 42.86; N, 7.96; H, 3.49 (c.a. C, 41.92; N, 8.15; H, 3.52). A suitable size of single-crystals was chosen for single-crystal X-ray diffraction analysis. From these results, the title compound was identified to be bis(isonicotinato)copper(II) dihydrate,  $\text{Cu}(\text{C}_6\text{H}_4\text{O}_2\text{N})_2 \cdot 2\text{H}_2\text{O}$ . It is interesting to note that, under the present

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**TABLE 1**  
Crystal Data and Structure Refinement for **1**

Identification code	<b>1</b>
Empirical formula	C <sub>12</sub> H <sub>8</sub> C <sub>10</sub> CuN <sub>2</sub> O <sub>6</sub>
Formula weight	338.30
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>Cc</i>
Unit cell dimensions	$a = 4.9967(5)$ Å, $\alpha = 90^\circ$ $b = 24.971(2)$ Å, $\beta = 98.862(10)^\circ$ $c = 11.1001(10)$ Å, $\gamma = 90^\circ$
Volume	1368.5(2) Å <sup>3</sup>
<i>Z</i>	4
Density (calculated)	1.642 mg/m <sup>3</sup>
Absorption coefficient	1.624 mm <sup>-1</sup>
<i>F</i> (000)	681
Crystal size	0.36 × 0.48 × 0.49 mm <sup>3</sup>
$\theta$ range for data collection	1.63 to 27.50°
Index ranges	$-6 \leq h \leq 6$ , $-32 \leq k \leq 32$ , $-14 \leq l \leq 14$
Reflections collected	3506
Independent reflections	3155 [ $R_{\text{int}} = 0.0230$ ]
Completeness to $\theta = 27.50^\circ$	100%
Absorption correction	Empirical
Max. and min. transmission	0.3007 and 0.2582
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	3155/2/193
Goodness-of-fit on $F^2$	1.086
Final <i>R</i> indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0230$ , $wR_2 = 0.0582$
<i>R</i> indices (all data)	$R_1 = 0.0249$ , $wR_2 = 0.0591$
Absolute structure parameter	-0.017(11)
Extinction coefficient	0.0021(5)
Largest diff. peak and hole	0.293 and -0.220 eÅ <sup>-3</sup>

Note.  $R_1 = \sum \|F_o\| - |F_c| / \sum \|F_o\|$ ,  $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$ .

experimental conditions, the 4-cyanopyridine undergoes hydrolysis reaction to become isonicotinic acid.

### Crystal Structure Determination

A single crystal of compound **1** with dimensions of 0.36 × 0.48 × 0.49 mm<sup>3</sup> was mounted on the glass fiber and data collection was performed on a Siemens-P4 four-circle diffractometer by the  $\omega$ -scan technique using graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å). A total of 3506 reflections were collected, of which 3155 are independent ( $R_{\text{int}} = 0.023$ ). *Lp* and absorption corrections were applied. The structure was solved by direct method and refined by full-matrix least-squares calculation on  $F^2$  using the SHELXTL program (12). Non-hydrogen atoms were refined anisotropically. Hydrogen atoms on pyridine rings were generated geometrically. Owing to disordered guest water molecules, hydrogen atoms were not assigned. The final refinement results are  $R_1 = 0.023$ ,  $wR_2 = 0.058$  [ $I > 2\sigma I$ ], and residual density 0.293, -0.220 eÅ<sup>-3</sup>.

**TABLE 2**  
Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for **1**;  $U(\text{eq})$  Is Defined as One-Third of the Trace of the Orthogonalized  $U^{\text{ij}}$  Tensor

	<i>x</i>	<i>y</i>	<i>z</i>	$U(\text{eq})$
Cu(1)	-7372(1)	6135(1)	11048(1)	19(1)
O(1)	-5536(5)	6706(1)	12101(2)	27(1)
N(1)	-3888(6)	8248(1)	14972(2)	24(1)
C(1)	-2877(7)	8100(1)	13983(3)	33(1)
O(2)	-8629(5)	6579(1)	13312(2)	52(1)
N(2)	-5757(5)	5551(1)	12207(2)	24(1)
C(2)	-3741(8)	7648(1)	13321(3)	33(1)
O(3)	254(4)	4392(1)	15102(2)	27(1)
C(3)	-5679(7)	7326(1)	13704(3)	28(1)
O(4)	-3741(4)	3978(1)	15018(2)	30(1)
C(4)	-6756(5)	7478(1)	14731(2)	31(1)
O(5)	-8656(15)	6222(2)	15732(5)	149(3)
C(5)	-5815(5)	7942(1)	15339(2)	28(1)
O(6)	-13116(19)	6405(4)	16663(9)	243(7)
C(6)	-6716(6)	6825(1)	13005(3)	28(1)
C(7)	-6956(5)	5076(1)	12277(3)	34(1)
C(8)	-5898(6)	4680(1)	13094(3)	34(1)
C(9)	-3489(5)	4769(1)	13856(2)	24(1)
C(10)	-2207(6)	5260(1)	13762(3)	35(1)
C(11)	-2263(5)	4340(1)	14734(2)	22(1)
C(12)	-3421(6)	5642(1)	12944(3)	34(1)

The crystallographic data for **1** are listed in Table 1. Atomic coordinates, equivalent isotropic displacement parameters, and selected distances and angles are given in Tables 2 and 3.

### Magnetic Measurements

The magnetic susceptibilities were measured on polycrystalline samples at fields of 1000 G and at temperatures ranging from 2.0 to 300 K with use of an organic matrix.

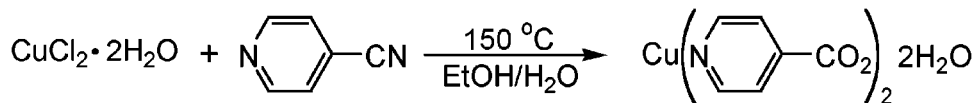
**TABLE 3**  
Selected Bond Lengths [ $\text{\AA}$ ] and Angles [ $^\circ$ ] for **1**

Cu(1)–O(3) # 1	1.965(2)	N(1)–C(5)	1.341(4)
Cu(1)–O(1)	1.977(2)	O(2)–C(6)	1.229(4)
Cu(1)–N(1) # 2	2.024(3)	N(2)–C(7)	1.337(3)
Cu(1)–N(2)	2.028(2)	N(2)–C(12)	1.337(3)
Cu(1)–O(4) # 3	2.307(2)	O(3)–C(11)	1.268(3)
O(1)–C(6)	1.276(4)	O(4)–C(11)	1.239(3)
N(1)–C(1)	1.330(5)		
O(3) # 1–Cu(1)–O(1)	170.47(10)	N(1) # 2–Cu(1)–N(2)	176.37(12)
O(3) # 1–Cu(1)–N(1) # 2	93.14(10)	O(3) # 1–Cu(1)–O(4) # 3	96.27(8)
O(1)–Cu(1)–N(1) # 2	84.11(7)	O(1)–Cu(1)–O(4) # 3	92.99(9)
O(3) # 1–Cu(1)–N(2)	90.32(7)	N(1) # 2–Cu(1)–O(4) # 3	92.98(10)
O(1)–Cu(1)–N(2)	92.30(11)	N(2)–Cu(1)–O(4) # 3	87.72(9)

Note. Symmetry transformations used to generate equivalent atoms: # 1,  $x - 1, -y + 1, z - \frac{1}{2}$ ; # 2,  $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$ ; # 3,  $x, -y + 1, z - \frac{1}{2}$ ; # 4,  $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$ ; # 5,  $x + 1, -y + 1, z + \frac{1}{2}$ ; # 6,  $x, -y + 1, z + \frac{1}{2}$ .

## RESULTS AND DISCUSSION

Compound **1** was synthesized hydro(solvo)thermally, giving 45% yield, and the characterization led to the assignment of the formula  $\text{Cu(II)(C}_6\text{H}_4\text{O}_2\text{N)}_2 \cdot 2\text{H}_2\text{O}$ . Under the reaction condition, 4-cyanopyridine was hydrolyzed to become isonicotinic acid (Eq. [1]).



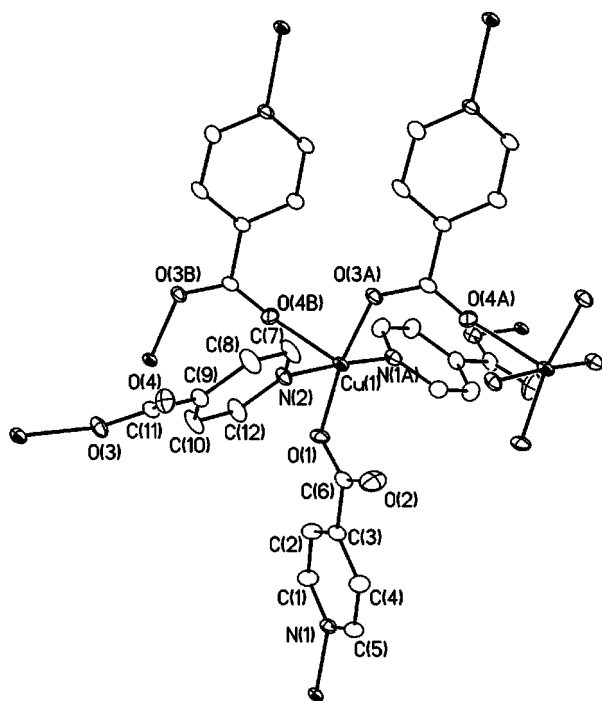
By replacing 4-cyanopyridine with 1 mmol of isonicotinic acid under the same reaction, only a single-phase monomeric copper(II) complex,  $\text{Cu(II)(C}_6\text{H}_4\text{O}_2\text{N)}_2(\text{H}_2\text{O})_2$ , was formed. This is an example to demonstrate that slow hydrolysis of 4-cyanopyridine during the reaction may play an important role in forming expanded networks (13).

Although the guest water was in a disordered form, the major framework of compound **1** can be well revealed by the X-ray single-crystal diffraction method. It possesses a three-dimensional polymeric structure containing chess-

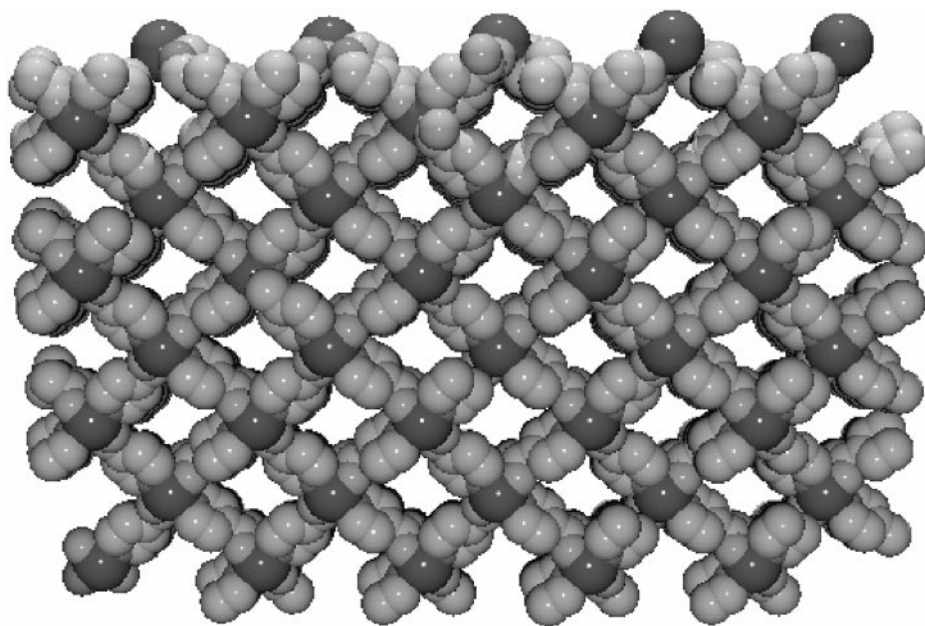
board-like channels. The building block unit of the framework is composed of an acentric  $\text{Cu(II)}$  square-pyramidal geometry linked by five isonicotinate ligands (Fig. 1). A carboxylate oxygen of isonicotinate ligand is coordinated to the apex of the square pyramid. Two nitrogen atoms of the isonicotinate ligands are coordinated to two vertices of the basal plane while the carboxylate oxygen atoms from

the other two isonicotinate ligands occupy the rest of the two vertices. With this geometrical arrangement, a square-grid layer network is expanding along the crystallographic *bc*-plane with the  $\text{Cu-Cu}$  edge distance of 8.9 Å, as shown in Fig. 2. These layers are interlinked by the apical carboxylate groups whereas they form mono copper-carboxylate-copper bridges along the crystallographic *a*-axis. As a result, linkage of these layer networks becomes a three-dimensional framework possessing chessboard-like tunnels. Each tunnel size, according to the  $\text{Cu-Cu}$  cross section, is about  $12.7 \times 11.4$  Å. Due to the electroneutrality of the host framework, the negative impact of the counter ion effect could be eliminated for guest inclusion.

The porosity of this three-dimensional framework is emphasized by a PLATON (14) analysis of the accessible solvent volume not occupied by the framework atoms ( $\text{Cu}$ ,  $\text{N}$ ,  $\text{C}$ ,  $\text{O}$ ). The calculation showed that a volume of  $318.6 \text{ \AA}^3$  (ca. 23.3% of a unit cell volume) is "solvent accessible." In **1**, guest water molecules were trapped inside the tunnels, forming hydrogen bonding with carboxylate tails that extrude into the cavities from the frameworks (with a  $\text{O} \cdots \text{O}$  distance of 2.9 Å). Thermogravimetric analysis of compound **1** indicated a weight loss of 9.7% between 30 and  $280^\circ\text{C}$ , accounting for the continuing loss of guest water molecules (ca. 10.5%). The framework integrity starts to collapse around  $330^\circ\text{C}$ . To remove the guest water molecules, the freshly grounded sample of **1** was heated at  $203^\circ\text{C}$  for 3 h. During this process, a weight loss of 10.4% (ca. 10.5%) corresponding to the loss of guest water molecules was observed. X-ray powder diffraction measurement of the dehydrated sample indicated that the framework integrity was sustained (Fig. 3). A related channel framework was also found in the case of bis(isonicotinato)iron(II) (15). Nevertheless, a different building block topology is presented in the iron(II) compound. For the iron(II) network, the carboxylate group of isonicotinate ligand is distorted from the pyridine ring (with a dihedral angle of about  $19.5^\circ$ ) and double-carboxylate bridges are formed connecting six-coordinated iron centers. The inward distortion of the pyridine ring in an iron(II) compound blocks the cavities. As a result,



**FIG. 1.** The building block unit including the asymmetric unit present in crystalline  $\text{Cu(II)(C}_6\text{H}_4\text{O}_2\text{N)}_2 \cdot 2\text{H}_2\text{O}$  with non-hydrogen atoms represented by thermal ellipsoids drawn at the 30% probability level. The carboxylate groups link the  $\text{Cu(II)}$  centers along the crystallographic *a*-axis.

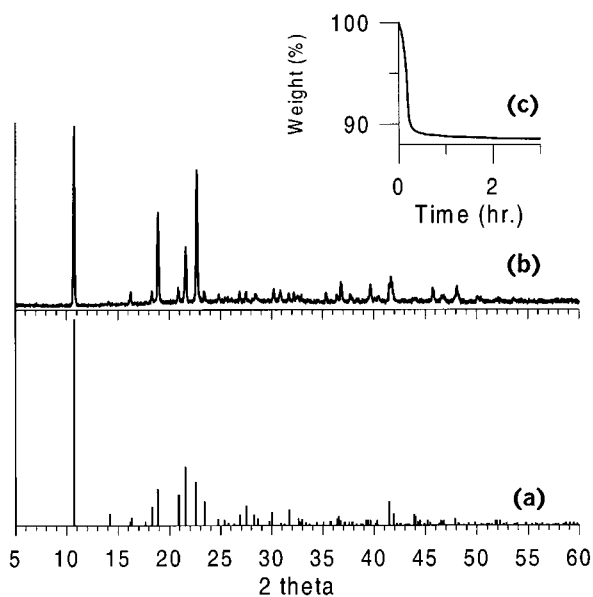


**FIG. 2.** The “chessboard” tunnels: a space-filling model of **1** with the non-hydrogen atoms along the  $a$ -axis, indicating the formation of channels (Cu–Cu cross section  $12.7 \times 11.4 \text{ \AA}$ ). Hydrogen atoms and guest molecules are omitted for clarity.

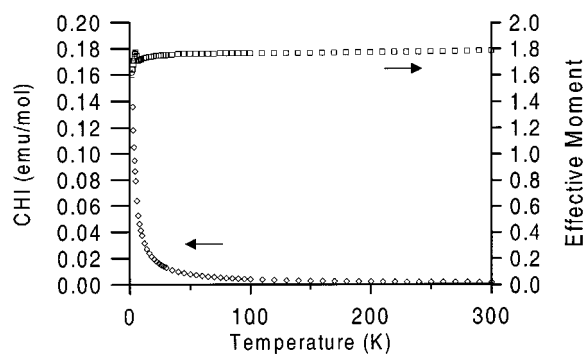
a smaller size channel is formed in bis(isonicotinato)iron(II) in comparison with the copper(II) compound **1**.

As expected, from the Cu(II)  $d^9$  configuration, the preliminary magnetic susceptibility measurement of compound

**1** has indicated paramagnetic behavior (Fig. 4). The magnetic susceptibility data in the temperature range 2.0–300 K can be fitted to a Curie–Weiss law with  $\theta = -0.93 \text{ K}$ , and  $C = 0.398 \text{ emu K/mol}$  ( $s = \frac{1}{2}$ ,  $g = 2.06$ ), which corresponds to an effective magnetic moment ( $\mu_{\text{eff}}$ ) per copper ion of 1.78 BM. These data are consistent with the copper(II) one-spin electron configuration. This result also shows that there is no strong evidence indicating the metal–metal interaction behavior within the frameworks. This could be logically expected from the geometrical arrangement of Cu(II) centers. For square–pyramidal copper (II) complexes, an unpaired electron is localized in the  $d_{x^2-y^2}$  orbital whose lobes are directed to four ligand atoms in the basal plane. As



**FIG. 3.** (a) Simulated X-ray powder pattern from single-crystal X-ray diffraction data. (b) Powder X-ray diffraction pattern of **1** after guest removal process. (c) Plot of wt% vs time, indicating removal of guest molecules at  $203^\circ\text{C}$ .



**FIG. 4.** Experimental  $\mu_{\text{eff}}$  and  $\chi$  versus temperature plots for compound **1** at a field of 1000 G.

indicated in Fig. 1, the bridging oxygen atoms (e. g., O(3A), O(4A)) of the carboxylate group occupy the vertex of the basal plane of one square pyramid and the apex of the other. Consequently, the magnetic exchange interactions of adjacent Cu(II) atoms mediated through carboxylate ligands are weak antiferromagnetic or negligible.

In conclusion, we have successfully synthesized the Cu(II) porous polymeric coordination network via hydro(solvo)thermal synthesis and characterized it. The carboxylate tails toward the inside of the cavities capable of hydrogen-bonding interaction may offer potential in selective sorption of guest molecules. Further exploration of their properties in guest sorption and catalysis is currently in progress.

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