

A Porous Supramolecular Architecture from a Copper(II) Coordination Polymer with a 3D Four-Connected 8⁶ Net

Jian-Fang Ma,* Jin Yang, Guo-Li Zheng, Li Li, and Jing-Fu Liu

Department of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China

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A novel coordination polymer $\{[\text{Cu}(\text{L}^1)(\text{L}^2)(\text{H}_2\text{O})]\cdot 5\text{H}_2\text{O}\}_n$ (**1**), where $\text{L}^1 = 1,1'-(1,4\text{-butanediyl})\text{bis}(\text{imidazole})$ and $\text{L}^2 = m\text{-phthalate}$ anion, has been obtained by using an unusual crystallization process. It crystallizes in the orthorhombic space group $Pna2_1$, which belongs to the crystal class $mm2$, with $a = 9.0521(18)$, $b = 15.401(3)$, and $c = 17.141(3)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 2389.7(8)$ Å³, and $Z = 4$. The complex **1** composing a porous supramolecular architecture displays unprecedented four-connected topology of an 8⁶ net in coordination polymer chemistry. Thermal gravimetric analysis (TGA) and X-ray powder diffraction (XRPD) patterns for **1** are discussed in detail.

Introduction

In the field of supramolecular chemistry, great interest has recently been focused on the crystal engineering of coordination frameworks due to their new topologies, intriguing architectures, intertwining phenomena, and potential applications in microelectronics, nonlinear optics, molecular selection, ion exchange, and catalysis.¹ What is particularly attractive is the novel types of structural motifs observed in these species. Supramolecular chemistry has advanced to a stage at which it is possible to select molecular building blocks that will assemble into structures with specific and desired network topologies, so that a rational design of molecular solids with potentially interesting properties is possible.² One approach to the rational design of crystalline solids has been to use organic molecules which, by their coordinating propensities, their geometry, and their relative stoichiometries, are naturally predisposed to form one of several well-categorized solid structure types or novel structure types.³ In our previous work we have studied some coordination polymers with flexible ligands used less often to design novel polymer materials.⁴ Here we aimed at coupling our interest in obtaining new frameworks with the

desire to achieve a microporous structure. In this work, we selected flexible bidentate 1,1'-(1,4-butanediyl)bis(imidazole) (L^1) ligand and m -phthalate anion (L^2) ligand which has been used to construct a coordination polymer with larger circuit.⁵ On the basis of the above selection, a polymer $\{[\text{Cu}(\text{L}^1)(\text{L}^2)(\text{H}_2\text{O})]\cdot 5\text{H}_2\text{O}\}_n$ (**1**) containing a porous architecture was obtained. To the best of our knowledge this is the first molecular architecture with the unprecedented topology of a four-connected 8⁶ net.⁶

Experimental Section

Materials. All reagents and solvents for syntheses were purchased from commercial sources and used as received.

Physical Methods. A Perkin-Elmer 240 elemental analyzer was used to collect microanalytical data, and the FT-IR spectrum was recorded from KBr pellets in range 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. TGA was performed from room temperature to 800 °C using a Perkin-Elmer TG-7 analyzer in

* To whom correspondence should be addressed. E-mail: jfma@public.cc.jl.cn.

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Table 1. Summary of X-ray Crystallographic Data for Complex **1**

chem formula	C ₁₈ H ₃₀ CuN ₄ O ₁₀
fw	526.00
color, habit	blue, needle
cryst size (mm ³)	0.147 × 0.523 × 0.125
cryst syst	orthorhombic
space group	<i>Pna</i> 2 ₁
<i>a</i> (Å)	15.401(3)
<i>b</i> (Å)	17.141(3)
<i>c</i> (Å)	9.0521(18)
α (deg)	90.00
β (deg)	90.00
γ (deg)	90.00
<i>V</i> (Å ³)	2389.7(8)
<i>Z</i> , <i>d</i> _{calcd} (g cm ⁻³)	4, 1.462
μ (Mo K α) (mm ⁻¹)	0.972
<i>F</i> (000)	1100
θ range (deg)	1.78–27.48
<i>h</i> , <i>k</i> , <i>l</i> ranges	0–19 0–22 0–11
reflcs collcd/unique	19 960/2903
reflcs obsd [<i>I</i> > 2 σ (<i>I</i>)]	2133
GOF on <i>F</i> ²	0.946
R1, ^a wR2 ^b (obsd)	0.0437, 0.1058
Δ/σ max, mean	0.001, 0.000
max, min peaks (e Å ⁻³)	0.813, -0.359

^a R1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$. ^b wR2 = $[\sum w(|F_o|^2 - |F_c|^2) / \sum w(F_o)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = (F_o^2 + 2F_c^2)/3$.

nitrogen. X-ray powder diffraction data were obtained on a Rigaku D/max 2500v PC X-ray diffractometer using Cu K α radiation.

Synthesis of 1,1'-(1,4-Butanediyl)bis(imidazole) (L¹). A mixture of imidazole (3.4 g, 50 mmol) and NaOH (2.0 g, 50 mmol) in DMSO (10 mL) was stirred at 60 °C for 1 h, and then 1,4-dichlorobutane (3.2 g, 25 mmol) was added. The mixture was cooled to room temperature after stirring at 60 °C for 2 h and then poured into 200 mL of water, and a white solid formed immediately, which weighed 4.1 g after drying in air. Anal. Calcd for C₈H₇N₂: C, 63.16; H, 7.37, N, 29.47. Found: C, 63.11; H, 7.42; N, 29.31.

Synthesis of Complex 1. A mixture of CuCl₂·2H₂O (0.171 g, 1 mmol), NaOH (0.08 g, 2 mmol), and *m*-phthalic acid (0.166 g, 1 mmol) in water was stirring for 10 min at 60 °C. Then L¹ (0.190 g, 1 mmol) was added to the solution with stirring for 30 min and a blue precipitate was obtained. The blue solid, insoluble in common organic solvents, was filtered off, washed with water, and dissolved in a minimum amount of ammonia (14 M). Suitable blue single crystals were obtained by slow evaporation of the ammoniacal solution of the solid at ambient temperature. The crystals were collected, washed with water, and dried in air (yield: 71%). Anal. Calcd for C₁₈H₃₀CuN₄O₁₀: C, 41.06; H, 5.70; N, 10.65. Found: C, 41.48; H, 5.63; N, 10.89. IR (cm⁻¹): 3432 (vs), 3127 (w), 2943 (m), 1607 (vs), 1560 (s), 1522 (m), 1449 (m), 1363 (s), 1237 (m), 1108 (s), 951 (w), 750 (m), 659 (m).

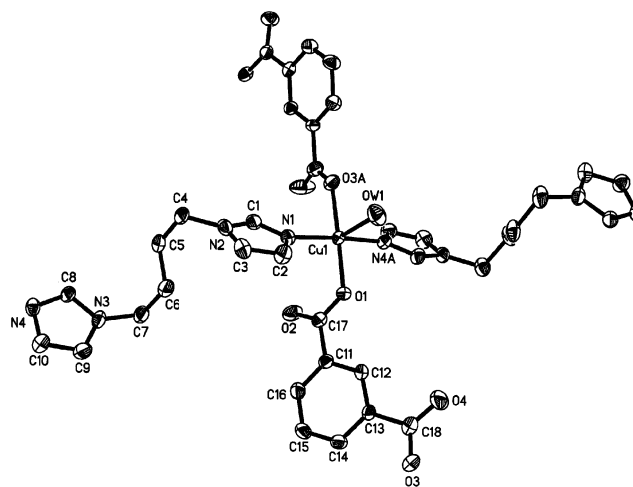
Addition of Na₂L² (1 mmol) into a solution of CuCl₂·2H₂O (1 mmol) and L¹ (1 mmol) in water also produced complex **1**. The reactions with different Cu:L¹:L² molar ratios (1:0.5:1 or 1:2:1) gave the same product **1**; this may be caused by the low solubility of **1**.

X-ray Crystallography. Crystallographic data and experimental details for structural analyses are summarized in Table 1. Single-crystal X-ray diffraction measurement of complex **1** was carried out on a Rigaku RAXIS-RAPID image plate diffractometer using the ω scan technique with Mo K α . A multiscan absorption correction was applied to the data. A total of 2903 unique reflections ($R_{int} = 0.0618$), of which 2133 had $I \geq 2\sigma(I)$, were used in all calculations. The structure was solved with the direct method of SHELXS-97⁷ and refined with full-matrix least-squares techniques

Table 2. Selected Bond Distances (Å) and Angles (deg) for {[Cu(L¹)(L²)(H₂O)]·5H₂O}_{*n*} (**1**)^a

Cu(1)–N(1)	2.000(5)	Cu(1)–O(1)	1.941(4)
Cu(1)–OW1	2.336(4)	Cu(1)–N(4) ⁱ	1.960(5)
Cu(1)–O(3) ⁱⁱ	1.960(4)		
O(1)–Cu(1)–N(4) ⁱ	89.3(2)	O(1)–Cu(1)–O(3) ⁱⁱ	177.97(19)
N(4) ⁱ –Cu(1)–O(3) ⁱⁱ	92.3(2)	O(1)–Cu(1)–N(1)	87.7(2)
N(4) ⁱ –Cu(1)–N(1)	175.2(2)	O(3) ⁱⁱ –Cu(1)–N(1)	90.6(2)
O(1)–Cu(1)–OW1	94.28(19)	N(4) ⁱ –Cu(1)–OW1	92.7(2)
O(3) ⁱⁱ –Cu(1)–OW1	86.90(19)	N(1)–Cu(1)–OW1	91.3(2)

^a Symmetry codes for **1**: (i) $x - 1/2, -y + 1/2, z - 1$; (ii) $-x + 3/2, y - 1/2, z + 1/2$. Bond lengths are given in Å and bond angles are given in deg.

**Figure 1.** ORTEP view of complex **1** showing 50% thermal probability ellipsoids.

using the SHELXL-97⁸ program. All non-hydrogen atoms were refined anisotropically, and the positions of hydrogen atoms on carbon atoms were calculated theoretically. Full-matrix least-squares refinement based on *F*² converged with R1 = 0.0437, wR2 = 0.1058, and GOF = 0.946 with Flack parameters 0.07(3). Further details are provided in the Supporting Information.

Results and Discussion

Selected bond distances and angles for complex **1** are listed in Table 2. Complex **1** is insoluble in water and common organic solvents, and the crystals suitable for X-ray diffraction analysis cannot be obtained by evaporating an appropriate solution of **1**. It is found that **1** can be dissolved in a concentrated solution of ammonia by segregating the L¹ and L² ligands from Cu cations owing to the coordinating role of ammonia toward the Cu(II) cation. So the crystals of {[Cu(L¹)(L²)(H₂O)]·5H₂O}_{*n*} (**1**) was obtained by using unusual crystallization process through evaporating an ammoniacal solution of **1**. It crystallizes in the interesting acentric orthorhombic space group *Pna*2₁, which belongs to the crystal class *mm*2.⁹ In the crystal structure (Figure 1) there is only one unique Cu(II) atom. Each Cu(II) center has a slightly distorted {CuN₂O₃} square pyramidal coordination sphere, with two nitrogen atoms from two L¹ and

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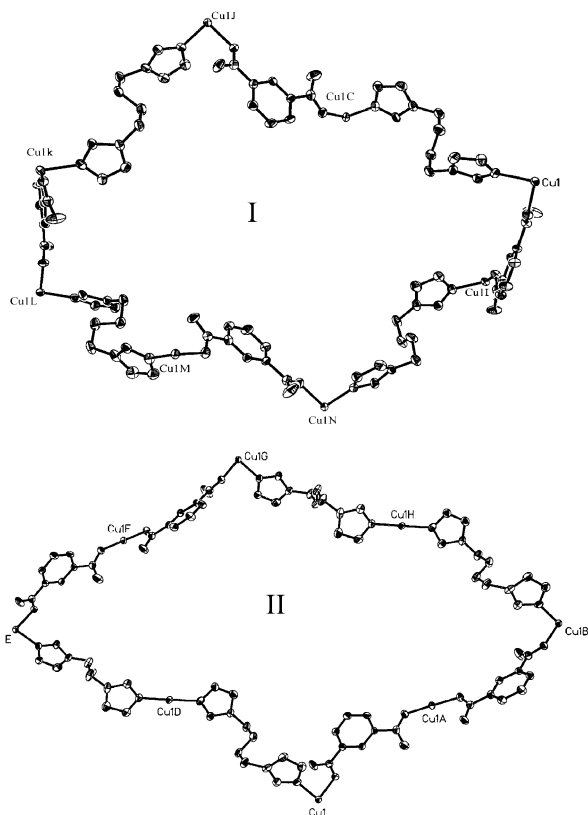


Figure 2. Two kinds of smallest eight-membered circuits in **1**. The symmetry operations are performed to generate the other seven Cu(II) sites from the CuI site of the asymmetric unit in circuits **I** and **II**.

two oxygen atoms from two L² in the base plane and one water molecule in the top site. Each L¹ is coordinated to two Cu(II) ions, and each L² bridges two Cu(II) ions using two oxygen atoms.

Cu(II) ions are connected by L¹ and L² to form 3D framework, and there are two kinds of the smallest eight-membered circuits in the network (Figure 2). Each circuit consists of eight copper(II) cations at the corners connected by four L¹ molecules and four L² anions, which make up eight edges. The length of the L¹ edge is 11.9 Å, and length of the L² edge is 9.7 Å. In circuit **I** Cu(II) ions are bridged by L¹ and L² alternatively, while in circuit **II** Cu(II) ions are bridged by ligands in the sequence of –Cu–L¹–Cu–L¹–Cu–L²–Cu–L².

It is interesting that there exist 16 eight-membered circuits through the same copper(II) ion (eight circuits **I** and eight circuits **II**). As shown in Figure 3, the same Cu(II) ion is shared by eight circuits **I** and eight circuits **II**, respectively. Wells has systematically studied the topology of three-dimensional nets, and the topology of the complex **1** can be attributed to the platonic 3D 8⁶ net, which is not specifically identified by Wells.¹⁰ Structures based on 3D four-connected nets such as well-known diamond-related structures (6⁶ net), rare NbO-like type (6⁴8²-a and 6⁴8²-b net), and PtS-like type (4²8⁴ net), which have experimentally confirmed the topologies predicted by theory, have evoked wide attention.¹¹ Wells

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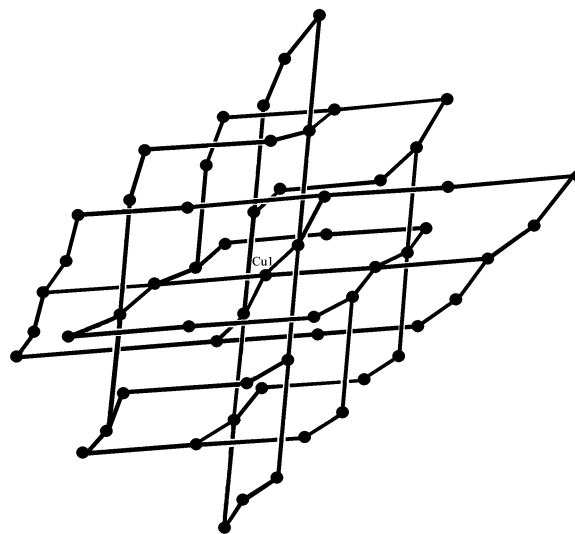


Figure 3. Schematic topology for 8⁶ nets of **1**. There exist eight circuits **I** and eight circuits **II** through the same Cu(II) ion.

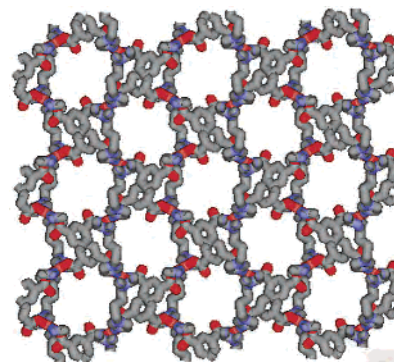


Figure 4. Channels in the 3D framework of **1**. Guest water molecules and hydrogen atoms are omitted for clarity.

listed no fewer than 20 topologically uniform examples of 3D four-connected nets, but so few types are represented in real cases. As far as we know, the present 3D four-connected 8⁶ net is first example in coordination polymer chemistry.

There exist channels in the 3D supramolecular frameworks (Figure 4). The channels are mainly occupied by the guest water molecules. Approximately 26.1% of the crystal volume is occupied by free water molecules with a volume of ca. 623 Å³ in each cell unit.¹²

When the crystals were removed from the mother liquor, they immediately lost part of the water molecules. TGA was performed after part of their water molecules had evaporated, which showed the following three strikingly clean and well-separated weight loss steps: an initial weight loss of 16.6% from room temperature to 110 °C, corresponding to the removal of remaining water molecule, followed by another weight loss of 36.8% (calcd: 36.1%) from 260 to 320 °C for evacuation of the L¹ from the frameworks. The last

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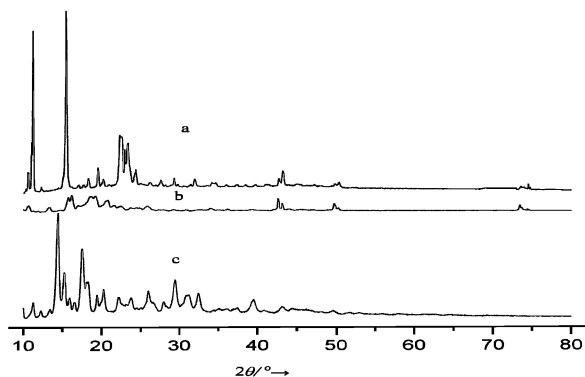


Figure 5. XRPD patterns for **1** (a) taken at room temperature, (b) after heating to 110 °C, and (c) after rehydration for 5 h.

weight loss of 28.3% (calcd: 28.5%) from 460 to 520 °C is mainly due to the combustion of L^2 . And the final product is attributed to CuO.

The XRPD pattern taken on the polycrystalline sample (Figure 5a) indicates that the structure of the bulk sample is consistent with crystal structure of **1**. The characteristic peaks of **1** began to disappear when the water molecules evolved

from the sample by heating the sample to 110 °C, and the anhydrous compound displayed poor crystallinity (Figure 5b). The structure cannot be recovered when this sample was exposed to water for a period of time. The appearance of some new sharpening peaks in the XRPD pattern of the rehydrated sample (Figure 5c) indicates that a new phase appears, and the crystallinity increases drastically with the rehydration.

In conclusion, a novel porous supramolecular architecture of the coordination polymer $\{[\text{Cu}(L^1)(L^2)(\text{H}_2\text{O})] \cdot 5\text{H}_2\text{O}\}_n$ (**1**) with unprecedented four-connected topology of 8^6 net has been synthesized. The TGA and XRPD patterns implied that the framework of the compound cannot be recovered after loss of the water molecules through heating.

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Supporting Information Available: An X-ray crystallographic file in CIF format. This material is available free of charge via Internet at <http://pubs.acs.org>.

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