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# Hydrothermal synthesis and crystal structure of 3D 2-fold interpenetrating Cu(I) complexes

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## Abstract

This paper presents a novel and distinctive metal-organic compound $Cu(4,4'\text{-bpy})(H_2PO_4)\cdot 2H_2O$ (4,4′-bpy = 4,4′-dipyridyl) **1** with intriguing structure motifs of interpenetrating networks. Furthermore, IR, element analysis, and TGA were employed to characterize it. Compound **1** belongs to monoclinic system, space group *P2/n*, $a = 8.4828(15)$ Å, $b = 8.8988(16)$ Å, $c = 17.862(3)$ Å, $\beta = 102.575(2)°$, $V = 1316.0(4)$ Å$^3$, $Z = 4$, $R_1 = 0.0472$.

*Keywords:* Hydrothermal synthesis; Cooper; Chain; Networks; 4,4′-bpy; Interpenetrating networks

## 1. Introduction

The synthesis of hybrid inorganic–organic porous materials is still attractive [1–6], due to its potential applications in catalysis, sensing, ion exchanging, separations, shape selective absorption, optical devices, gas storage, or molecular based magnetism [7–13]. Particularly attractive are the novel types of supramolecular intertwinings formed from the 2D or 3D interpenetrated species with equal topology that still need a rational classification [27]. In fact, lots of oxygen-donor and/or nitrogen-donor ligands have been employed to construct different topologies such as multiple-nuclear, chain, networks, cluster, helices, rotaxanes, catenanes, and so on [14–17]. Among the numerous ligands employed in this area, the most prevalent is the rigid linear connector 4,4′-bpy or analogues, which can be employed to construct 1D linear [19] or zigzag-like [20] chain, 2D square grid [21] or interwoven honeycomb [22], and 3D diamondoid [23] frameworks, in terms of their bridging [18] or monodentate coordination mode. But there exists few example of supramolecular intertwinings formed from the 4,4′-bpy or analogues in literature.

Herein, we selected the rigid 4,4′-bpy ligands to construct basal skeleton and $H_2PO_4^-$ anions as decorated groups to balance the positive charge of copper ions. Consequently, a unique compound with 3D 2-fold interpenetrating networks was obtained from the rigid 4,4′-bpy ligand and $H_2PO_4^-$ anion. Furthermore, the TG-DTA was employed to evaluate the flexibility of the interpenetrating networks in **1**.

## 2. Experimental

### 2.1. Materials and physical measurements

All reagents were bought from commercial sources without further purification. IR(KBr pellets) spectra was recorded in the 400–4000 cm$^{-1}$ range using a Perkin–Elmer Spectrum One FTIR spectrometer. And elemental analysis was carried out on Elementar Vario ELIII microanalyzer.

### 2.2. Synthesis

An aqueous solution (10 ml) of $Cu(NO_3)_2\cdot 3H_2O$(0.24 g, 1 mmol), 4,4′-bpy(0.38 g, 2 mmol) and $NaH_2PO_4$(0.16 g, 1 mmol) in a ratio 1:2:1 was sealed in a 23-ml Teflon-lined reactor and heated at 180 °C for three days under autogenous pressure. After cooled to room temperature (5 °C/h), red sheet crystal was obtained (yield 60% based on Cu). And then filtered off, washed with distilled water and dried in air. Element analysis calcd for **1**(%): C 34.05, H 4.00, N 7.94; found: C34.15, H 4.12, N 8.04. Main IR(KBr) (cm$^{-1}$): 3050(s), 1601(s), 1533(m), 1414(m), 1155(s),1218(m),1057(s), 965(s), 815(s), 733(m),650(m).

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Table 1
Crystal data and structure refinement for **1**

| | |
|---|---|
| Empirical formula | **1** ($C_{10}H_{14}PN_2O_6Cu$) |
| fw | 349.72 |
| Temp. (K) | 293(2) |
| Wavelength (Å) | 0.71073 |
| Cryst syst | Monoclinic |
| Space group | *P*2/*n* |
| *a* (Å) | 8.4828(15) |
| *b* (Å) | 8.8988(16) |
| *c* (Å) | 17.862(3) |
| *β* (deg) | 102.575(2) |
| *Z* | 4 |
| vol ($Å^3$) | 1316.0(4) |
| Density ($mg/m^3$) | 1.765 |
| *F*(000) | 708 |
| GOF on $F^2$ | 1.063 |
| Final *R* indices [$I>2(I)$] | *R*1: 0.0472, *ωR*2: 0.1204 |
| Largest diff. peak and hole ($e/Å^3$) | 0.01 and 0.00 |

Table 2
Selected bond lengths (Å) angles (°) for **1**

| | | | |
|---|---|---|---|
| Cu(1)–N(1) | 1.911(3) | P(1)–O(4) | 1.507(3) |
| Cu(1)–N(2)#1 | 1.913(3) | P(1)–O(3) | 1.529(3) |
| Cu(1)–O(1) | 2.338(4) | P(1)–O(2) | 1.539(4) |
| P(1)–O(1) | 1.487(3) | O(4)–P(1)–O(3) | 109.39(18) |
| N(1)–Cu(1)–N(2)#1 | 155.85(18) | O(1)–P(1)–O(2) | 109.15(19) |
| O(1)–P(1)–O(4) | 113.0(2) | O(4)–P(1)–O(2) | 109.1(3) |
| O(1)–P(1)–O(3) | 109.9(3) | O(3)–P(1)–O(2) | 106.0(3) |
| N(1)–Cu(1)–N(2)#1 | 155.85(18) | N(2)#1–Cu(1)–O(1) | 101.25(15) |
| N(1)–Cu(1)–O(1) | 102.54(15) | | |

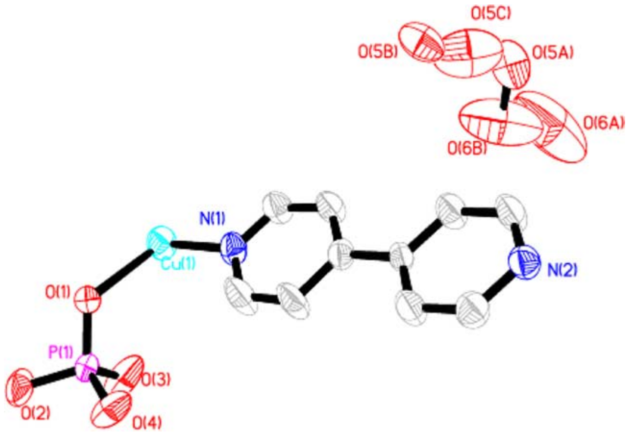

Fig. 1. The asymmetrical unit of **1**. Hydrogen atoms were omitted for clarity. Symmetry code: #1 $x-1/2,-y+1,z+1/2$; #2 $x+1/2,-y+1,\ z-1/2$; #3 $-x+3/2,\ y,\ -z+1/2$.

### 2.3. X-ray crystallography

A red sheet-like single crystal of **1** with dimension 0.13×0.12×0.15 mm was chosen for data collection on a single X-ray diffraction. Data collection was performed on a Bruker SMART 1000 CCD bidimensional detector using Mo-Kα radiation. Data was integrated and corrected for absorption using the Bruker programs SAINT SADABS and SMART. The structure was then solved with direct methods and refined using SHELXL−97. All non-hydrogen atoms (phosphor, oxygen, carbon, copper, nitrogen atoms) were located first in difference Fourier maps, whereas hydrogen atom positions were placed in calculated positions [24]. Further details of X-ray structure analysis are given in Table 1, and selected distance and angles are presented in Table 2.

## 3. Results and discussion

### 3.1. Description of the crystal structure of 1

X-ray diffraction analysis reveals that complex **1** is a member of interpenetrating nets with small chambers, based on long $Cu^I$ chain via hydrogen bonds. The asymmetric unit of **1** consists of one $Cu^I$ ion, one $H_2PO_4^-$ anion, one monodentate bpy ligand, and two distorted water molecules (Fig. 1). The $Cu^I$ ion is three coordinated, in a slightly distorted planar triangular geometry with a $C_{2v}$ symmetry, by one oxygen atom (Cu–O 2.338 Å)of $H_2PO_4^-$ anion and two nitrogen atoms (Cu—N 1.911 Å)of two independent monodentate 4,4′-bpy. And the rigid 4,4′-bpy ligands are employed to connect the metal-nodes to furnish the long zigzag $Cu^I$ chain(because of the node with a $C_{2v}$ symmetry). The bent angle of this zigzag chain is 155.85° for N(1)–Cu(1)–N(2)1, and the distance of adjacent two metallic ions was 10.921 Å for Cu–4,4′-bpy–Cu. In addition, the superfluous 4,4′-bpy ligands also play a role in deoxidizing $Cu^{II}$ ion to $Cu^I$ ion (bond valence calculations give values of 1.0 for Cu atom [25]). Seen from Fig. 2, the long chain shows two modes of A and B, in an interlaced array (see Fig. 2). Further, two As or Bs allow to link together through hydrogen bonds from $H_2PO_4^-$ anions (O3···H–O4: 2.504 Å, 152°) to form similar 2D nets (12.1×21.4 $Å^2$), named AA or BB (Fig. 3). Moreover, four As or Bs can also link together via hydrogen bonds from $H_2PO_4^-$ anions (O3···H–O4: 2.504 Å 152°, O1···H–O2: 2.530 Å 133.7°) to furnish another similar 2D nets (13.840×8.483 $Å^2$), named AAAA (consists of two modes of AAAA1 and AAAA2) or BBBB (contains two modes of BBBB1 and BBBB2)(Fig. 4). Following, two kinds of 3D networks with large voids (12.1×21.4×12.7 $Å^3$) are furnished from AA+AAAA or BB+BBBB, named D1 and D2. From further analysis of the structure of **1**, three unique features are apparent: (1) 3D interpenetrating entities (Fig. 5): the long chain A from D1 or B from D2 penetrates into the center of window BBBB or AAAA with π–π stacking effect (the offset distance is 3.6 Å), respectively. The last step of cyclization takes place between AAAA/or BBBB and BB/or AA, respectively; (2) the connected $H_2PO_4^-$ anions in a distinctive geometry of ribbon, construct from the infinite $H_2PO_4^-$ anions via two kinds of hydrogen bonds (O3···H–O4: 2.504 Å 152°, O1···H–O2: 2.530 Å 133.7°), and each $H_2PO_4^-$ anion performs four-hydrogen bonds(two as H-donor and two as H-acceptor) with adjacent two $H_2PO_4^-$ anions, resulted in mutually perpendicular four-membered rings (4Rs) of 4R1(O1–O2–O1–O2)