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A one-dimensional copper(II) coordination polymer constructed by pyridyl-2,5-dicarboxylate: Helical structure and magnetic property

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ABSTRACT

Hydrothermal synthesis of pyridyl-2,5-dicarboxylate ($H_2\mathbf{L}$) and Cu(II) salt in the mixed solvents of water and pyridine (py) afforded one unusual 1D coordination polymer, $[Cu_4(\mathbf{L})_4(py)_4]$, with neighboring left- and right-handed helical chains. Strong π–π packing and Cu···O interactions found among neighboring chains lessen the inter-chain Cu···Cu distances to about 3.83 Å. Magnetic measurements show a ferromagnetic exchange with the $2J$ value of 27.7 cm^{-1}.

1. Introduction

The design and self-assembly of coordination polymers (CPs) have attracted great interests not only for their potential new or special characteristics as functional materials [1–5], but also for their fascinating architectures and topologies [6–10]. Especially, 1D coordination polymers are of great interests because they can be used as non-linear optical [11], magnetic [12,13], and luminescent materials [14]. Meanwhile, many interesting molecular structures, such as helical structures, have close relationship with 1D coordination polymers [15–18].

Usually, multifunctional organic bridging ligands such as multi-carboxyl acids can be utilized in the formation of various coordination polymers [19–25]. However, there is a tendency to form 2D and 3D coordination polymers for multi-carboxyl acids because such type of organic ligands possesses more coordination atoms/groups and more extending directions. For example, pyridyl-2,5-dicarboxylate ($H_2\mathbf{L}$) has been used as bridging ligands to produce many high dimensional coordination polymers without appropriate or sufficient terminal ligands [26–29]. To get 1D molecular structure, terminal ligands are very necessary for the reason that they can locate the extending positions of the metal centers [30–32]. Pyridine, as a usual organic solvent and a weak organic base, can both tune the pH of synthetic systems and act as small terminal ligands for some coordination polymers [33–35].

Herein we hydrothermally synthesize a novel 1D copper(II) coordination polymer with interesting helical structures using pyridyl-2,5-dicarboxylate as bridging ligands and pyridine as terminal ligands (Scheme 1). This compound is fully characterized by IR, EA, PXRD, TG, and single crystal X-ray diffraction. At last, magnetic property analysis is also performed.

2. Experimental section

2.1. Materials

All starting materials and solvents were commercially available without further purification. Infrared spectra were recorded on a FTS-40 infrared spectrometer as KBr pellets. Elemental analysis was performed on a Flash EA 1112 analyzer. Thermogravimetric analyses were performed under an air atmosphere at a heating rate of 10 °C/min on a Netzsch STA409 PC instrument, in the temperature range of 30–550 °C. The variable-temperature magnetic susceptibilities were measured on polycrystalline samples (ca. 13.7 mg) with a Quantum Design MPMS SQUID susceptometer operating at a magnetic field of 0.1 T in a temperature range of 2–300 K. The diamagnetic corrections were evaluated from Pascal's constants for all the constituent atoms.

2.2. Synthesis of $[Cu_4(\mathbf{L})_4(py)_4]$ **1**

A solvent mixture (7 cm^3 of water, 0.2 cm^3 of pyridine) containing $H_2\mathbf{L}$ (0.017 g, 0.1 mmol) and $Cu(CH_3COO)_2$ (0.018 g, 0.1 mmol) was placed in a Parr Teflon lined stainless steel vessel (25 cm^3), and the vessel was sealed and heated to 140 °C for 72 h, then cooled at 8 °C/h to 100 °C, held at this temperature for 12 h,

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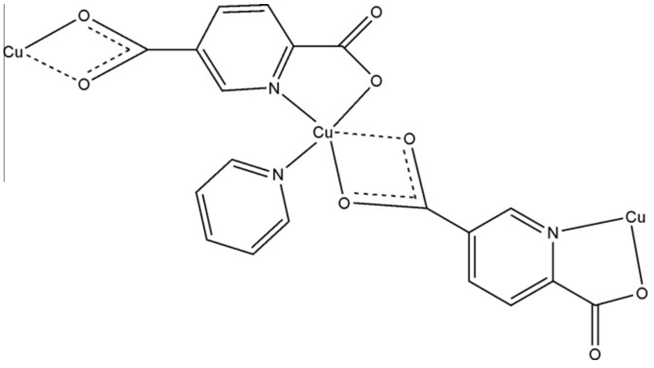

Scheme 1.

followed by cooling to room temperature at 8 °C/h. Dark blue polycrystals were carefully picked and washed with ethanol, and then dried at 70 °C. Yield: 68.75% [based on $Cu(CH_3COO)_2$]. Anal. Calcd % (found %) for $C_{12}H_8N_2O_4Cu$: C, 46.83 (47.12); H, 2.62 (2.57); N, 9.10 (9.26). IR νKBr (cm^{-1}): 1622 s, 1567 w, 1483 w, 1447 w, 1398 m, 1350 m, 1283 w, 1239 w, 1214 w, 1163 w, 1066 w, 1042 w, 957 w, 890 w, 834 m, 765 m, 694 w, 582 w, and 539 w.

2.3. Crystallography

X-ray diffraction data for single crystals were collected on a Bruker SMART APEX-II CCD diffractometer equipped with a graphite crystal and incident beam monochromator using Mo Kα radiation (λ = 0.71073 Å). Crystal data, data collection parameters, and analysis statistics for **1** are listed in Table 1. The frames were integrated in the Siemens SAINTPLUS software package, [36] and the data were corrected for absorption using the SADABS program. The structures were solved by the direct method and refined by full-matrix least-squares on F^2 using SHELXTL software. [37] The nonhydrogen atoms were refined anisotropically. The hydrogen atoms attached to carbon atoms were inserted at the calculated positions and allowed to ride on their respective parent atoms.

3. Results and discussion

3.1. General characterization

The IR spectra shows that a very strong characteristic band of C=O disappears in compound **1**, indicating two carboxylic groups of ligand **L** are all deprotonated and coordinated to metal ions.

Table 1
Crystallographic data and structure refinement summary for **1**.

Compd	1
Empirical formula	$C_{48}H_{32}Cu_4N_8O_{16}$
Formula weight	1230.98
Crystal size (mm)	0.25 × 0.24 × 0.20
Crystal system	Monoclinic
Space group	Cc
a (Å)	18.3061(16)
b (Å)	20.0855(17)
c (Å)	13.0089(11)
β (°)	109.8600(10)
Z	4
ρ_{calcd} (g cm^{-3})	1.817
μ (mm^{-1})	1.953
F (0 0 0)	2480
2θ scan range	3.92–51.00
R (int)	0.0151
Total reflections	12,390
Unique reflections	5960
R_1, $wR_2[I > 2\sigma(I)]$[a]	0.0236, 0.0585
Goodness of fit	0.985
Max/min electron density (e $Å^{-3}$)	0.193 /-0.389

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_\omega = [\sum\omega(F_o^2 - F_c^2)^2/\sum\omega(F_o^2)^2]^{1/2}$.

The XPRD of **1** determined by experiment is in a good agreement with the simulated one of single crystals, which shows that the bulk powder sample has the same components and structure as those of single crystals (Fig. S1). The thermogravimetric curve has two steps of weight loss (Fig. S2); the first one from 260 to 275 °C corresponds to the loss of the coordinating pyridine molecule, and the second from 290 to 380 °C corresponds to the decomposition of the organic dicarboxylic acid. The remaining weight of 26.5% is likely that of CuO (calcd 25.8%).

3.2. Description of crystal structure

This compound crystallized in the space group *Cc* is a one-dimensional coordination polymer. There are four copper(II) metal centers that have the same coordination environment in one asymmetric unit. Each copper(II) ion is four-coordinated by two nitrogen atoms of one pyridine and one **L** molecules and two oxygen atoms from carboxylic groups of two different **L** molecules, defining a primarily slightly distorted square planar coordination geometry (Fig. 1). The *cis* bond angles around metal centers are around the right angle, from 82.07(11) to 93.37(12)°, and the *trans* bond angles around metal centers are near to the straight angle, from 168.76(12) to 176.46(14)° (Table 2). The Cu–O and Cu–N bond dis-

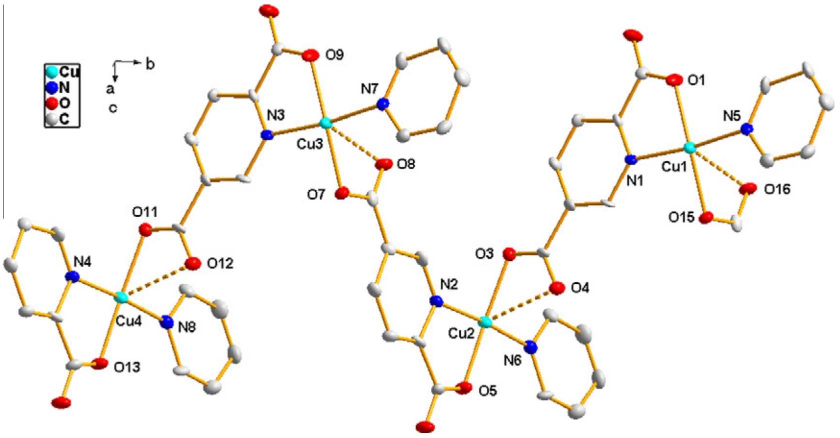

Fig. 1. Diagram showing the coordination environments around copper metal centers with displacement ellipsoids drawn at the 30% probability level. Cu···O interactions are shown by dot lines. All H atoms are omitted for clarity.