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Solvent-dependent luminescent Cu(I) framework based on 5-(4-pyridyl)tetrazole

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ABSTRACT

A new Cu(I) coordination compound, $Cu_4(L)_4 \cdot 2EtOH$ (**1**), has been obtained from the solvothermal reaction of CuBr, HL (L = 5-(4-pyridyl) tetrazole), EtOH and $NH_3 \cdot H_2O$. The structure determination reveals that **1** has a 2D network, where each Cu(I) atom adopts a trigonal coordination mode. The 2D networks stacked in an ABAB sequence through the π–π interaction to form a 3D supramolecular framework, giving a 1D channel along the *b*-axis. The TGA and powder XRD measurements reveal that the framework is stable after removal of the guest molecules. Gas (N_2) adsorption measurement was carried out for the framework. Framework **1** shows II sorption profile with N_2, which indicates that N_2 molecules cannot diffuse into the micropore and only surface adsorption occurs. The photoluminescent research shows that compound **1** displays an interesting solvent-dependent luminescence.

1. Introduction

The rational design of metal-organic frameworks (MOFs) has attracted considerable attention because of their potential applications in catalysis [1], separation [2], ion exchange [3], and gas sorption and storage [4]. The major task of the synthesis for such MOFs is to choose appropriate metal-connecting nodes and/or organic-bridging ligands to control the formation of these complexes with required structures and properties. Long-bridged ligands or large secondary building units have been used to obtain some porous MOFs, while crystal structures with such large cavities are usually stabilized by inclusion of either suitable guests or interpenetrating lattices [5] and the absence of the guest molecules often results in low thermal stability of the host framework. Consequently, the synthesis of robust open frameworks with both high porosity and thermal stability is still a big challenge for chemists. Weak interactions such as hydrogen bonding and π–π interaction are also important in the architecture of porous MOFs [6]. The 5-substituted tetrazole derivatives, with plentiful coordinate ability and possibility, have been used extensively in the synthesis of coordination polymers with interesting structural and/or physical properties, such as luminescence, non-linear optics, ferroelectricity, magnetism and porosity [7–9]. The ligand 5-(4-pyridyl)tetrazole (HL) is an interesting multifunctional ligand having a rich store of N atoms to bind metal ions and to form hydrogen bonds. So far, a few complexes based on pyridyl-substituted tetrazole compounds have been reported in recent years [10]; the coordination chemistry of the HL ligand remains largely unexplored.

Despite the large number of solvent-dependent luminescent materials described in the literature, they are mainly organic molecule materials [11]; reports of solvent-dependent luminescent MOFs are scarce [12]. Herein, we report the synthesis, characterization and properties of HL bridged porous, two-dimensional coordination framework $Cu_4(L)_4 \cdot 2EtOH$ (**1**), which exhibits an interesting solvent-dependent luminescence.

2. Experimental

2.1. Materials and methods

The HL ligand was synthesized in accordance with the procedure reported by Demko and Sharpless [13]. The IR spectra (KBr pellets) were recorded on a Magna 750 FT-IR spectrophotometer. Powder X-ray diffraction data were recorded on a Rigaku MultiFlex diffractometer with a scan speed of $0.05–0.2^\circ\,min^{-1}$. Thermal stability studies were carried out on a NETSCHZ STA-449C thermoanalyzer under N_2 (30–800 °C range) at a heating rate of $10\,^\circ C\,min^{-1}$. Fluorescence spectra were measured with a HORIBA Jobin-Yvon FluoroMax-4 spectrometer equipped with an integrating sphere. The adsorption isotherm of N_2 (77 K) was measured in the gaseous state using ASAP-2020 volumetric adsorption equipment.

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2.2. *Synthesis of $Cu_4(C_6N_5H_4)_4 \cdot 2EtOH$ (**1**)*

In a 23-mL Teflon-lined autoclave, a mixture of CuI (0.5 mmol, 0.095 g), HL (1 mol, 1.470 g), EtOH (10 ml) and $NH_3 \cdot H_2O$ (25%, 2 ml) was stirred for about 10 min and then was heated at 150 °C for 3 days. Yellow block crystals were collected, about 0.046 g (40% yield based on Cu). Using other cuprous halides, such as CuCl, $CuCl_2$, CuBr $CuBr_2$ as metal sources by control the mole ratio of the reactants can also obtain **1.** Anal. Calcd. (%) for $C_{28}H_{28}N_{20}O_2Cu_4$: H: 4.74, C: 36.81, N: 17.18. Found: C 36.12, H 3.06, N 29.98. IR (KBr pellet, cm^{-1}): 3444b, 1620 s, 1447, 1435, 1057, 1010, 845 m, 720 s.

2.3. *Crystal structure determination*

X-ray diffraction data were collected on a Rigaku Mercury CCD X-ray diffractometer with graphite monochromated Mo-*K*α radiation ($\lambda = 0.71073$ Å) using a ω scan technique. CrystalClear software was used for data reduction and empirical absorption correction. The structure was solved by the direct methods using the Siemens SHELXTL™ Version 5 package of crystallographic software [14]. The difference Fourier maps based on the atomic positions yield all non-hydrogen atoms. The hydrogen atom positions were generated theoretically, allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters but were not refined. The structure was refined using a full-matrix least-squares refinement on F^2. All non-hydrogen atoms were refined anisotropically. The summary of crystallographic data and structure analysis is given in Table 1. The selected bond lengths and bond angles are listed in Table 2.

The hydrogen bonding information is listed in Table 3.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC: 714391. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: 44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

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

Empirical formula	C28 H28 Cu4 N20 O2
Formula weight	930.86
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P−1
a	7.223(3) Å
b	15.375(8) Å
c	16.003(8) Å
α	95.349(18)°
β	96.740(13)°
γ	98.175(11)°
V	1736.0(14) $Å^3$
Z	2
Calculated density	1.781 Mg/m^3
Crystal size	0.20 × 0.20 × 0.20 mm
Limiting indices	$-7 \leq h \leq 8$, $-18 \leq k \leq 18$, $-19 \leq l \leq 18$
Reflections collected/ unique	11163/6294
Refinement method	Full-matrix least-squares on F^2
R(int)	0.0329
Goodness-of-fit on F^2	1.033
Final R indices [$I > 2$sigma(I)]	$R_1 = 0.0525$, $\omega R_2 = 0.1545$
R indices (all data)	$R_1 = 0.0700$, $\omega R_2 = 0.1664$

$R_1 = (|F_o|-|F_c|)/|F_o|$, $\omega R_2 = [w(F_o^2-F_c^2)/w(F_o^2)^2]^{1/2}$.

Table 2
Selected bond lengths (Å) and bond angles (deg) for **1**.

Cu(1)–(1)#1	1.961 (3)	N(1)#1–Cu(1)–N(15)#2	123.79 (15)
Cu(1)–N(15)#2	1.965 (3)	N(1)#1–Cu(1)–N(19)	117.77 (15)
Cu(1)–N(19)	1.970 (3)	N(15)#2–Cu(1)–N(19)	118.44 (14)
Cu(2)–N(11)	1.965 (3)	N(11)–Cu(2)–N(5)	123.72 (15)
Cu(2)–N(5)	1.972 (3)	N(11)–Cu(2)–N(10)	118.60 (15)
Cu(2)–N(10)	1.980 (3)	N(5)–Cu(2)–N(10)	117.68 (15)
Cu(3)–N(6)#3	1.957 (3)	N(6)#3–Cu(3)–N(20)	124.23 (15)
Cu(3)–N(20)	1.958 (4)	N(6)#3–Cu(3)–N(14)#2	118.06 (15)
Cu(3)–N(14)#2	1.983 (4)	N(20)–Cu(3)–N(14)#2	117.69 (14)
Cu(4)–N(9)	1.955 (4)	N(9)–Cu(4)–N(16)	124.34 (15)
Cu(4)–N(16)	1.958 (4)	N(9)–Cu(4)–N(4)	118.07 (15)
Cu(4)–N(4)	1.978 (3)	N(16)–Cu(4)–N(4)	117.58 (15)

Symmetry codes: #1 x+1, y+1, z; #2 x+2, y+1, z+1; #3 x+1, y, z+1.

Table 3
Geometrical parameters of hydrogen bonds of 1.

	D–H	H⋯A	D⋯A	D–H⋯A
O(1)–H(1B)⋯N(2)	0.82	2.24	3.0183	158
O(2)H(2B)⋯N(17)	0.82	2.54	2.9986	116

3. Results and discussion

3.1. *Description of crystal structure*

Single-crystal X-ray analysis reveals that compound **1** crystallizes in the triclinic form with space group P-1. In **1**, each Cu(I) atom adopts a trigonal coordination mode with three nitrogen atoms (see Fig. 1) from two different tetrazole rings and one pyridyl ring [Cu–N 1.955(4)–1.983(4) Å] (see Table 2). The ligands are deprotonated to balance the charges of the whole structure according to chemical and structural information. Each L ligand serves as a μ_3-bridge to link three Cu(I) centers through three nitrogen atoms, leading to a 2D layer structure (Fig. 2a). This sheet contains six-numbered circuits (Cu_2N_4) and 32-numbered circuits ($Cu_4N_{12}C_{16}$). The Cu–Cu distances in the Cu_2N_4 rings are 3.3608(12) and 3.3628(11) Å. The cavity of each $Cu_4N_{12}C_{16}$ ring is filled with one ethanol molecule. There are O–H⋯N hydrogen bonding interactions (Table 3) between ethanol molecules and tetrazole ligands. The 2D layer structure of **1** can be rationalized as a (4.8^2) topological network (Fig. 2b) when Cu and L are regarded as three-connected nodes [15].

It should be pointed out that the adjacent layers are stacked in an ABAB sequence to form a 3D framework, in which the π–π interactions play an important role. Between the interlayers A and B, the centroid distance between pyridyl ring and tetrazole ring is

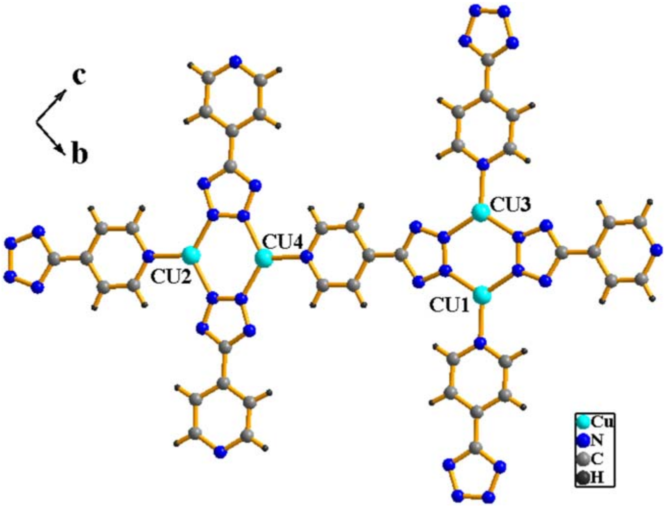

Fig. 1. The coordination environment of the Cu atoms.