Coordinating and hydrogen bonding ability of a bifunctional 2D paddle-wheel copper(II) coordination polymer

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A B S T R A C T

A new copper(II) complex of formula $\{[Cu_2(H_2btc)_2(dmf)_2]\cdot 4dmf\}_n$ (1) [H_4btc = 1,2,4,5-benzenetetracarboxylic acid, dmf = dimethylformamide] has been synthesised and its structure determined by X-ray diffraction. The structure displays a new square grid of "paddle-wheel" tetracarboxylate-bridged dicopper(II) units with an intradimer copper–copper separation of 2.619(2) Å. The dmf molecules are retained through weak axial coordinative bonds and hydrogen bonding interactions with the carboxylic groups of the porous neutral network of 4^4 net topology. The magnetic behaviour of 1 corresponds to a strong antiferromagnetic coupling within each dicopper(II) unit ($J = -343$ cm^{-1} with the Hamiltonian being defined by $\mathbf{H} = -J\,\mathbf{S}_1\cdot\mathbf{S}_2$). Complex 1 does not adsorb N_2 but it exhibits certain absorption of CO_2 with a hysteretic desorption behaviour typical of flexible MOFs.

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1. Introduction

The rational design and synthesis of porous coordination polymers, known as metal–organic frameworks (MOFs), is a very interesting subject of current research in the field of crystal engineering [1,2]. Due to their diverse structural architectures and net topologies, this new class of multifunctional materials has potential applications in different areas, like catalysis, gas storage, ion exchange, molecular electronics and spintronics [3–9]. The selection of an appropriate ligand is one of the most important steps in order to obtain the desired compound in the reticular synthesis of porous coordination polymers. Aromatic carboxylate ligands have been widely used for the construction of new coordination polymers of variable dimensionality. Among them, 1,2,4, 5-benzenetetracarboxylic acid (hereafter noted H_4btc) [10–12], is particularly well-suited for the preparation of multifunctional coordination polymers due to several reasons: (a) the high symmetry and great conformational flexibility of its four carboxylic groups; (b) the occurrence of up to four deprotonation degrees [$H_nbtc^{(4-n)-}$ with $n = 0$–3] that makes possible the adoption of very

different coordination modes in its interaction with metal ions; (c) and the ability to establish additional weak hydrogen-bonds with guest molecules (like solvents or gases) when acting either as hydrogen-bond acceptor or donor through the carbonyl and carboxylic oxygen atoms, respectively [13–33].

Our target in this area is to synthesize and explore the magnetism and host–guest chemistry of new porous coordination polymers with the $H_nbtc^{(4-n)-}$ ($n = 0$–3) ligand and divalent first-row transition metal ions. Consequently, we are particularly interested in the "paddle-wheel" tetracarboxylate-bridged dimetallic core, $[M_2^{II}(RCOO)_4S_2]$ (M = Cu, Fe, and Zn with S = H_2O, MeOH or dmf for instance) [34], which is a well-recognised square secondary building unit (SBU) used for the construction of a variety of nD MOFs (n = 2 or 3) with varying net topologies (Scheme 1) [35]. Herein we report the synthesis, X-ray crystal structure, magnetic properties, thermal and gas sorption behaviour of the novel 2D copper(II) coordination polymer of formula $\{[Cu_2(H_2btc)_2(dmf)_2]\cdot 4dmf\}_n$ (1). Interestingly, 1 is a rare example of bifunctional MOF, whereby the dmf molecules are kept through weak axial coordinative bonds at each copper(II) ion and hydrogen bonding interactions with the carboxylic groups of the H_2btc^{2-} ligands.

2. Experimental

2.1. Synthesis

An ethanolic solution (4 mL) of $CuCl_2$ (17.05 mg, 1 mmol) was added into a solution of H_4btc (25.82 mg, 1 mmol) in dmf (4 mL). The resulting solution was stirred for 30 min, filtered and allowed to evaporate at room temperature. X-ray quality green prisms of **1** were obtained after a few days. They were picked by hand and air-dried. Yield ca. 40% (based on copper). *Anal.* Calc. for $C_{19}H_{25}$ CuN_3O_{11} (**1**): C, 42.67; H, 4.68; N, 7.85. Found: C, 42.34; H, 4.57; N, 7.76%.

2.2. X-ray crystallography data collection and refinement

The powder diffractogram of **1** was obtained using an ENRAF–NONIUS FR590 powder diffractometer with INEL120 detector (Debye–Scherrer geometry).

For the determination of the crystal structure by X-ray diffraction, a single-crystal of **1** was mounted on a Bruker Apex II diffractometer and the diffraction data were collected at 293(2) K by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An absorption correction was applied using SADABS [36]. The crystallographic structure was solved by direct methods. The refinements were carried out with the SHELXL-97 program [37]. All refinements were made by full-matrix least-squares on F^2, with anisotropic displacement parameters for all non-hydrogen atoms. All hydrogen atoms were placed at calculated positions and then included in the structure factor calculation in a riding model using SHELXL-97 defaults. The graphical manipulations were carried out with Diamond v.3.2 software [38]. A summary of crystal data and structure determination is given in Table 1. Selected bond lengths and angles are listed in Table 2 and hydrogen bonds are given in Table 3.

2.3. Physical measurements

The C, H, N elemental analyses were conducted using a Perkin Elmer CHN 2400 apparatus.

The infrared spectrum was recorded with a Thermo Nicolet 380 FT-IR apparatus equipped with Smart Orbit Diamond ATR system.

The thermogravimetric analysis (TGA) was performed on a very small amount (2 mg) of crystalline powdered sample of **1** under a dry N_2 atmosphere with a Mettler Toledo TGA/STDA 851^e thermobalance operating at a heating rate of 10 °C min^{-1}.

N_2 and CO_2 adsorption–desorption isotherms were recorded on a Micromeritics ASAP-2020 automated analyser at 77 and 273 K, respectively. Samples were degassed for 5 h at variable temperatures in the 30–175 °C range and at 10^{-6} Torr prior to analysis. BET, Langmuir and Dubinin-Radushkevich models were used to determine the values of the surface area.

Variable-temperature (2–300 K) magnetic susceptibility measurements under a magnetic field of 1.0 T were carried out on a polycrystalline sample of **1** with a SQUID magnetometer. The experimental data were corrected for the diamagnetic contributions of the constituent atoms and the sample holder, as well as for the temperature-independent paramagnetism (TIP) of the copper(II) ion (60×10^{-6} cm^3 mol^{-1}).

Table 1
Crystal data and refinement details of {[$Cu_2(H_2btc)_2(dmf)_2$]·4dmf}$_n$ (**1**).

Empirical formula	$C_{19}H_{25}CuN_3O_{11}$
Formula weight (g mol^{-1})	M_r = 534.96 g/mol
Crystal colour	green
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	10.4860(8)
b (Å)	10.8132(8)
c (Å)	10.8268(8)
α (°)	90.123(4)
β (°)	99.936(4)
γ (°)	101.413(4)
V (Å^3)	1184.5(2)
Z	2
Density (g cm^{-3})	1.500
μ (mm^{-1})	0.984
Reflections collected	26301
Unique reflections	4487
R_{int}	0.0318
R_1, wR_2 [$I < 2\sigma(I)$]	0.0392, 0.1097
R_1, wR_2 (all data)	0.0456, 0.1141
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.675, −0.466

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

Cu1–O1	1.967 (2)	O1–Cu1–O6	89.01(8)
Cu1–O6	1.968(2)	O1–Cu1–O9	96.94(8)
Cu1–O9	2.124(2)	O6–Cu1–O9	95.06(9)
Cu1–O2^i	1.952(2)	O1–Cu1–O2^i	168.74(9)
Cu1–O5^i	1.960(2)	O1–Cu1–O5^i	89.58(8)

* Symmetry code: (i) = $1 - x$, $1 - y$, $1 - z$.

Table 3
Hydrogen bonds (Å, deg).*

D–H···A	D–H	H···A	D···A	<D–H···A
O4–H4···O10	0.8200	1.8200	2.639(4)	175.00
O7–H7···O11	0.8200	1.7900	2.577(7)	162.00

* D = donor and A = acceptor.

3. Results and discussion

3.1. Description of the structure

Compound **1** crystallises in the triclinic $P\bar{1}$ space group. Its crystal structure consists of square grid copper(II) layers with a
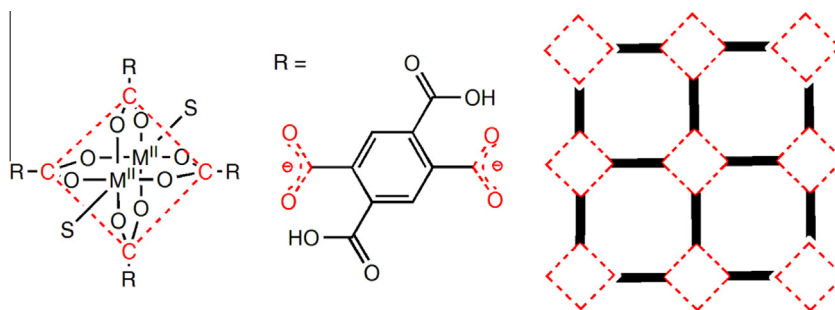
Scheme 1. MOF with a square-grid topology resulting from the self-assembly of square paddle-wheel dimetallic SBUs by the H_2btc^{2-} ligand (M = Cu with S = dmf).