Structure and Magnetic Properties of a Two-dimensional Metal-Organic Framework: $[Cu_3(bpdc)_{4/2}(pdon)_2(H_2O)_6] \cdot 2ClO_4$

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A unique 2D sheet metal-organic framework, $[Cu_3(bpdc)_{4/2}(pdon)_2(H_2O)_6]\cdot 2ClO_4$ (**2**), has been synthesized by the hydrothermal reaction of pdon with $Cu(ClO_4)_2$ (bpdc = 2,2′-bipyridyl-3,3′-dicarboxylate, pdon = 1,10-phenanthroline-5,6-dione). Compound **2** crystallizes in the orthorhombic chiral space group $P2_12_12$, with the cell parameters: $a = 12.3596(11)$, $b = 25.978(2)$, $c = 7.9585(7)$ Å, $V = 2555.3(4)$ Å^3 [$R1 = 0.068$ and $wR2 = 0.172$]. It represents a novel metal-organic framework comprising of the mixed ligands of pdon and bpdc, where the cupric atoms are bridged by alternating the μ_2- and μ_4-bpdc groups into two-dimensional positively charged layers. The bpdc ligand has resulted from the *in situ* oxidative carbon-carbon bond cleavage of the pdon ligand. Compound **2** displays antiferromagnetic interactions. Above 40 K, $\chi_m{}^{-1}$ obeys the Curie-Weiss law with $C = 1.37$ cm^3 K mol^{-1} and $\Theta = -13.95$ K.

Key words: Copper(II), Metal-Organic Framework, Crystal Structure, Magnetic Properties

Introduction

Great interest has been focused on the rapidly expanding field of crystal engineering of metal-organic frameworks (MOFs) [1] due to their intriguing network topologies as well as their potential application as functional materials in many areas such as separations and catalysis [2], gas storage [3], and magnetism [4]. Hydrothermal synthesis has been widely employed to generate MOFs with unique structures and special properties [5]. Hydrothermal reactions are often complicated and unpredictable [6]. Although such reactions may enhance the difficulty of the syntheses of purposeful material, and their rational molecular design, they can also afford some novel functional materials with enchanting structures. Additionally, some unexpected *in situ* reactions, such as ligand oxidative coupling, hydrolysis, substitution, and the simultaneous reduction and substitution, can also occur under hydrothermal conditions mediated by transition metal salts [7, 8].

1,10-Phenanthroline-5,6-dione (pdon), which is fairly distinct in its electronic character from 1,10-phenanthroline due to the two carbonyl groups, has been extensively used as a building block for the synthesis of supramolecular assemblies, since this ligand has the ability to form stable complexes with a wide variety of metal ions and carries an *o*-quinone moiety with pH-dependent electroactivity [9, 10]. Remarkably, metal complexes of this ligand potentially allow for the variation and control of redox properties over a wide range as well as for a fine tuning of the potential through pH changes [11]. Furthermore, the diketone functionality can be easily transformed into other chelating groups such as diamines, dioximes and large π-conjugated organic linkers [12]. It is also relatively prone to unexpected reactions such as reduction, hydration or carbon–carbon bond cleavage, which is particularly attractive in synthetic chemistry [13]. The carbon–carbon bond cleavage reactions under different conditions have attracted special attention. However, the exact carbon–carbon bond cleavage mechanism has not yet been established due to the few structurally

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characterized products [13, 14]. Our research group has reported a single-strand helical coordination polymer, $[Co(bpdc)(H_2O)_3]\cdot H_2O$ (**1**), in which the bpdc ligand results from the *in situ* oxidative carbon-carbon bond cleavage of the pdon ligand under hydrothermal conditions [15]. In this contribution, we present another 2D metal-organic framework, $[Cu_3(bpdc)_{4/2}(pdon)_2(H_2O)_6]\cdot 2ClO_4$ (**2**), in which the bpdc ligand also results from the *in situ* oxidative carbon-carbon bond cleavage of the pdon ligand under hydrothermal conditions. The magnetic interactions between the metal ions have been investigated.

Experimental Section

All chemicals of p. a. grade were commercially available and used without further purification. The C, H and N microanalyses were performed with a Perkin-Elmer 2400-CHNS/O elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000 – 400 cm^{-1} on a Shimadzu FT-IR-8900 spectrometer. The magnetic susceptibilities were measured using a SQUID magnetometer on crystalline samples in the temperature range of 2 to 300 K under 5 KOe.

Preparation of $[Cu_3(bpdc)_{4/2}(pdon)_2(H_2O)_6]\cdot 2ClO_4$ *(**2**)*

A mixture of $Cu(ClO_4)_2\cdot 6H_2O$ (0.365 g, 1.0 mmol) and 1,10-phenanthroline-5,6-dione (0.228 g, 1.0 mmol) was placed in a 23 mL Teflon reactor and kept under autogenous pressure at 120 °C for 7 d. The mixture was cooled to r. t., and green crystals were obtained in 42 % yield (based on the initial $Cu(ClO_4)_2\cdot 6H_2O$). Anal. for $C_{12}H_{14}CoN_2O_8$: calcd. C 41.19, H 2.29, N 8.01; found C 41.15, H 1.86, N 7.92. – IR: ν = 3437(s), 1749(s), 1578(s), 1489(w), 1431(s), 1395(s), 1304(s), 1121(s), 1082(w), 941(w), 836(m), 785(s), 755(m), 698(m), 662(m), 603(m) cm^{-1}.

X-Ray structure analysis

The reflection intensities of **2** were collected at 298(3) K using a Bruker SMART Apex II CCD area detector single-crystal diffractometer, with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å), using the $\psi/2\vartheta$ scan mode. An absorption correction was applied using the program SADABS [16]. The structure was solved by Direct Methods using SHELXS-97 [17] and refined by full-matrix least-squares methods on F^2 (SHELXL-97 [18]). All hydrogen atoms attached to the carbon atoms and the nitrogen atom were generated geometrically, and the hydrogen atoms of the water molecules were located from difference Fourier syntheses. All non-hydrogen atoms were finally refined with anisotropic displacement parameters. H atoms attached to C atoms were treated as riding, with C–H = 0.93 Å. The H atoms of the water molecules were refined with U_{iso}(H) = 1.5 U_{eq}(O). The hydrogen atom positions of the water molecule O9 were not found due to the disorder of the bpdc group. This disorder also resulted in some bond lengths being too long as well as in some unusual U values. The refinement of a split model was not attempted. Crystal data and further information on the structure determination are summarized in Table 1. Selected interatomic distances and bond angles are given in Table 2.

Table 1. Crystal and refinement data for $[Cu_3(bpdc)_{4/2}(pdon)_2(H_2O)_6]\cdot 2ClO_4$ (**2**).

Formula	$C_{48}H_{36}Cu_3N_8O_{26}Cl_2$
M_r	1402.37
Crystal size, mm^3	0.341 × 0.190 × 0.086
Crystal system	orthorhombic
Space group	$P2_12_12$
a, Å	12.3596(1)
b, Å	25.978(2)
c, Å	7.9585(7)
V, $Å^3$	2555.3(4)
Z	2
D_{calcd}, g cm^{-3}	1.82
μ(MoK_α), cm^{-1}	1.4
F(000), e	1418
hkl range	$-16 \le h \le 15$, $-34 \le k \le 34$, $-10 \le l \le 10$
$((\sin\theta)/\lambda)$max, $Å^{-1}$	0.0554
Refl. measured	18658
Refl. unique	6225
R_{int}	0.046
Param. refined	393
Flack parameter	0.00(2)
$R1(F)/wR2(F^2)$[a] (all refls.)	0.0685/0.1862
A, B values for weighting scheme[a]	0.076, 8.0
GoF (F^2)[b]	1.081
$\Delta\rho_{fin}$ (max/min), e $Å^{-3}$	1.20/−1.78

[a] $R1(F) = \|F_o| - |F_c\|/\Sigma|F_o|$, $wR2(F^2) = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w \cdot (F_o{}^2)^2]^{1/2}$, $w = [\sigma^2(F_o{}^2) + (AP)^2 + BP]^{-1}$, with $P = (\max(F_o{}^2, 0) + 2F_c{}^2)/3$; [b] $\mathrm{GoF}(F^2) = [\Sigma w(F_o{}^2 - F_c{}^2)^2/(n_{obs} - n_{param})]^{1/2}$.

CCDC 708834 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Synthesis and IR spectra

In the preparation of **2**, the bpdc ligand results from an *in situ* oxidative carbon-carbon bond cleavage of the pdon ligand under hydrothermal conditions. Repeated experiments have indicated that $Cu(ClO_4)_2\cdot 6H_2O$ plays a key role in the formation of crystalline products of **2**. We could not obtain the crystalline product **2** using other cupric salts instead of $Cu(ClO_4)_2\cdot 6H_2O$ under the same synthesis conditions.

Cu1–O3	1.978(4)	Cu1–O2	1.997(4)	Cu1–N1	2.006(5)
Cu1–N2	2.015(5)	Cu1–O1	2.246(5)	Cu2–O7$^{\#1}$	2.026(9)
Cu2–N4	2.118(1)	Cu2–O9	2.392(1)	O3–Cu1–O2	95.3(2)
O3–Cu1–N1	91.0(2)	O2–Cu1–N1	173.3(2)	O3–Cu1–N2	159.9(2)
O2–Cu1–N2	94.3(2)	N1–Cu1–N2	80.5(2)	O3–Cu1–O1	91.7(2)
O2–Cu1–O1	90.0(2)	N1–Cu1–O1	87.26(2)	N2–Cu1–O1	105.9(2)
O7$^{\#1}$–Cu2–O7$^{\#2}$	89.3(5)	N4–Cu2–O7$^{\#1}$	171.0(5)	O7$^{\#1}$–Cu2–N4	171.0(5)
O7$^{\#2}$–Cu2–N4	98.1(4)	N4–Cu2–N4$^{\#3}$	75.1(6)	O7$^{\#1}$–Cu2–O9	93.5(5)
O7$^{\#2}$–Cu2–O9	86.2(5)	N4–Cu2–O9	82.0(4)	N4$^{\#3}$–Cu2–O9	98.3(4)
N4$^{\#3}$–Cu2–O9$^{\#3}$	82.0(4)	N4–Cu2–O9$^{\#3}$	98.3(4)	O9–Cu2–O9$^{\#3}$	179.6(5)

Hydrogen bonding contacts

D–H···A	D–H	H···A	D···A	D–H···A
O1–H1c···O5$^{\#4}$	0.90	2.1049	2.977(7)	169.85
O1–H1c···O4$^{\#5}$	0.90	1.8702	2.776(6)	175.39
O2–H2d···O4	0.90	1.7616	2.613(6)	155.67
C1–H1b···O9$^{\#6}$	0.93	2.3199	3.184(1)	154.55
C8–H8a···O10$^{\#7}$	0.93	2.3967	3.210(1)	146.16

Table 2. Selected interatomic distances (Å) and angles (deg) for **2**.

Symmetry codes: #1 = $-x+3$, $-y+2$, $z-1$; #2 = x, y, $z-1$; #3 = $-x+3$, $-y+2$, z; #4 = $-1/2+x$, $5/2-y$, $3-z$; #5 = $2-x$, $2-y$, z; #6 = $3-x$, $2-y$, z; #7 = $-1/2+x$, $5/2-y$, $4-z$.

The IR spectrum of **2** shows the ν(O–H) stretching vibration of water molecules at 3437 cm^{-1}. The absorptions at 1578 and 1393 cm^{-1} can be assigned to the $\nu_{as}(CO_2^-)$ and $\nu_s(CO_2^-)$ stretching vibrations, respectively. A comparison with the characteristic carboxylate stretching vibrations of free 2,2′-bipyridyl-3,3′-dicarboxylic acid shows a significant blue-shift attributed to a coordination interaction. The strong absorptions at 1749 cm^{-1} may be attributed to the diketone group stretching vibrations of the pdon ligand, and the strong absorptions located at 1568 and 1438 cm^{-1} may be assigned to pyridyl vibrations.

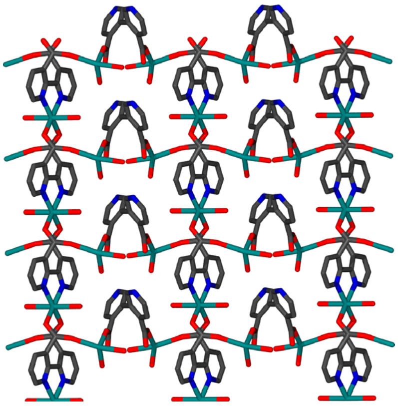

Fig. 2. Sheet parallel to (010) of **2** constructed by bpdc ligands and Cu(II) atoms (H atoms and pdon ligands have been omitted for clarity).

Structure description

Compound **2** crystallizes in the orthorhombic chiral space group $P2_12_12$. The asymmetric unit contains 1.5 Cu(II) atoms, one pdon ligand, two crystallographically independent halves of bpdc groups, three coordinated water molecules and one perchlorate anion. The Cu1 atom exhibits a significantly elongated and distorted octahedral geometry with two N atoms of a pdon ligand and four O atoms, of which two come from coordinated water molecules and two from two different bpdc ligands. The Cu1–O8 bond (2.621(2) Å) is longer than the other Cu1–N and Cu1–O bonds, the Cu1–N bond lengths are ranging from 2.012(4) to 2.013(5) Å and the Cu1–O bond lengths from 1.973(4) to 2.249(5) Å, respectively (Table 2). Each Cu2 atom also shows a slightly elongated octahedral geometry with the apical positions occupied by coordinated water molecules (O9) and the basal plane defined by two pyridyl N atoms and two carboxylate oxygen atoms (Fig. 1). The elongation

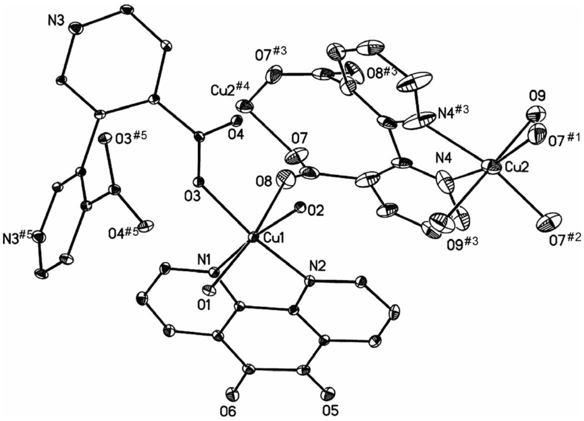

Fig. 1. ORTEP drawing showing the coordination modes of the copper atoms and the ligands (H atoms have been omitted for clarity).

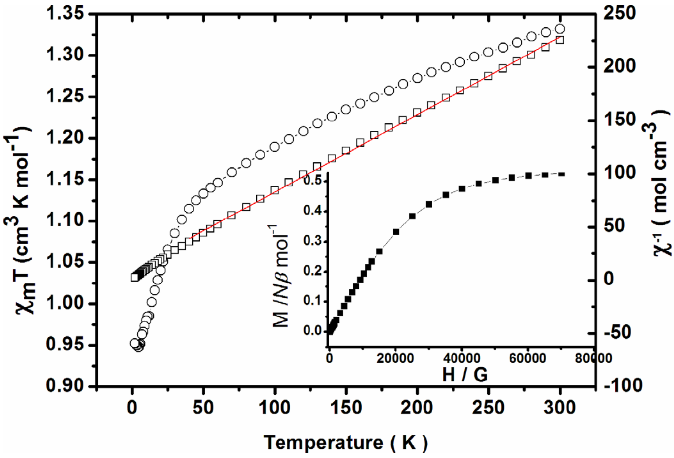

Fig. 3. Temperature dependence of the magnetic susceptibilities of **2**.

of the octahedra is due to the Cu^{2+} Jahn-Teller effect [19].

The bpdc ligands in **2** act as μ_2- and μ_4-bridges linking two and four Cu(II) ions, respectively, into a unique positively charged 2D sheet parallel to (010), as shown in Fig. 2. Each of the μ_2-bridging bpdc groups links two Cu atoms through its carboxylate O3 atoms coordinating to copper atoms. Each of the μ_4-bridging bpdc groups holds two each of the crystallographically distinct Cu1 and Cu2 atoms. The pyridyl nitrogen atoms are chelating, and the carboxylate groups adopt *anti* and *syn* coordination modes linking three copper atoms. The neighboring sheets are held together by hydrogen bonding interactions thus forming a porous three-dimensional metal-organic framework with the perchlorate anions residing in the channels, where the carbonyl oxygen atoms (O5 and O6) and the oxygen atoms of the perchlorate anions serve as hydrogen bonding acceptors receiving hydrogen atoms from the coordinated water molecules (Table 2).

Magnetic properties

The magnetic susceptibilities were measured on crystalline samples of **2** in the temperature range from 2 to 300 K under 5 KOe using a SQUID magnetometer. The $\chi_m T$ value at r. t. (1.33 cm^3 mol^{-1}) corresponds to three magnetically isolated Cu^{II} ions with $g = 2.17$. χ_m T gradually decreases from 1.33 to 1.11 cm^3 K mol^{-1} upon lowering the temperature from 300 to 40 K. Below 40 K, χ_m T decreases more steeply down to 0.95 cm^3 K mol^{-1} at 2 K (Fig. 3). This behavior suggests an overall antiferromagnetic coupling of the Cu^{II} ions in **2**. Above 40 K, $\chi_m{}^{-1}$ obeys the Curie-Weiss law with $C = 1.37$ cm^3 K mol^{-1} and $\Theta = -13.95$ K. The saturation magnetization measurements at 2 K up to an external field strength of 8 T show that the reduced magnetization is non-saturated for an $S = 1/2$ system, and the results are in good agreement with the crystal structure determination mentioned before.

Conclusion

The unique 2D metal-organic framework of **2** has been generated by hydrothermal reaction of 1,10-phenanthroline-5,6-dione with $Cu(ClO_4)_2$. The 2,2′-bipyridyl-3,3′-dicarboxylate ligand results from the *in situ* oxidative carbon-carbon bond cleavage of the phenanthroline-derived ligand. The result is significant because it demonstrates a carbon-carbon bond cleavage example under hydrothermal conditions which leads to a novel metal-organic framework.

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