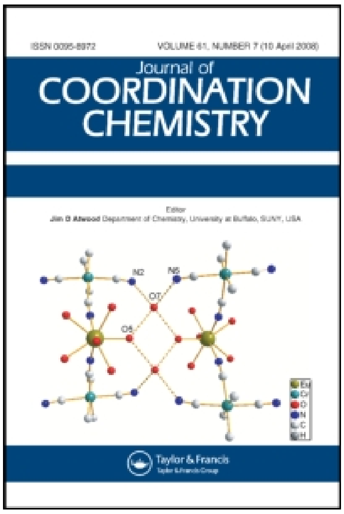

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Water tape stabilized in a 3D porous copper(I) supramolecular network

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Water tape stabilized in a 3D porous copper(I) supramolecular network

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Through hydrothermal synthesis, Cu(2-pac)$_2$ (2-pac = 2-pyrazinecarboxylic acid) reacting with 4,4′-bipyridine (abbreviated for 4,4′-bpy) in 1 : 1 molar ratio afforded a porous three dimensional supramolecule containing an infinite T4(2)8(2) water tape, showing the contribution of the water tape to the stability of the crystal host and the role of cooperative association between the water tape and the crystal host in the formation of the water tape.

Keywords: Hydrothermal synthesis; Water tape; Copper(I) supramolecular network

1. Introduction

The fundamental importance of water in physical, biological, and chemical processes has prompted intensive research, however, some properties of water still remain "anomalous" [1–6]. Water clusters are the properties of water, but there is clearly a need for better understanding how such aggregates influence the overall structure of their surroundings because the strong, directional intermolecular bonding and the capacity of water to act as a double donor and a double acceptor of hydrogen bonds make water clusters less suitable for a rigorous theory than other simple, weakly bound systems [7, 8]. Theoretical and experimental scrutiny of water clusters led to progress in preparing a variety of water clusters from $(H_2O)_2$ to $(H_2O)_{18}$ [9–21], interacting with other inorganic or organic molecules through hydrogen bonding to form more complicated functional groups.

Three morphologies of polymeric water clusters including infinite 1D-chain, [21–26] tape, [27–31] and 2D-layer [32–35] structures have been observed. Among the three morphologies, 1D water chains and tapes are of great interest because many fundamental biological processes and properties of materials [36–42] appear to depend on the unique properties of 1D water morphologies.

Here, we describe the synthesis and characterization of a porous coordination polymer, filled with a novel infinite water tape consisting of edge-shared four- and

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eight-membered water clusters, which may help to understand interactions among water clusters in more detail.

2. Experimental

2.1. *Instruments and reagents*

All the starting materials were analytical grade and purchased commercially. Elemental analyses of C, H, N were performed on Vario EL III analyzer. IR spectra were recorded on a BEQ VZNDX 550 FTIR instrument with KBr pellets within the range of 4000–400cm^{-1}.

2.2. *Synthesis of [Cu_2(2-pac)$_2$(4,4′-bpy)$_2$] • $7H_2O$ (1)*

The red complex **1** was obtained by hydrothermal synthesis of a mixture of Cu(2-pac)$_2$ (0.155 g, 0.5 mmol) and 4,4′-bpy(0.078 g, 0.5 mmol) in 15 mL H_2O, sealed in a Teflon-lined stainless container, heated at 130°C for 72 h and slowly cooled to room temperature at 5°C per hour. Yield: 24%. Anal. Calcd for **1**, $C_{30}H_{36}Cu_2N_8O_{11}$: C, 44.39; H, 4.47; N, 13.80%. Found: C, 44.42; H, 4.41; N, 12.76%. IR (KBr, cm^{-1}) 3339(s), 3105(m), 1685(s), 1596(s), 1518(w), 1469(w), 1411(s), 1340(s), 1163(s), 1060(m), 993(w), 866(m), 792(w).

2.3. *X-ray crystallography*

All single crystal X-ray experiments were performed on a Bruker Smart Apex CCD diffractometer equipped with graphite monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å) using ω and ϕ scan mode at room temperature. The single-crystal structure of complex **1** was solved by direct methods (SHELXS-97 [43]) and refined with full-matrix least-squares refinements based on F^2 using SHELXL-97 [44]. All non-H atoms were located using subsequent Fourier-difference methods. Hydrogen atoms of organic ligands were generated geometrically, and those of the water molecules were located from the difference maps. Other details of crystal data, data collection parameters and refinement statistics are given in table 1. Selected bond distances and bond angles are given in table 2.

3. Results and discussion

3.1. *Descriptions of structure*

Complex **1** was synthesized under mild hydrothermal conditions (130°C and 72 h). The red colour of **1** indicates that it is possibly a copper (1+) complex, which is consistent with the results of single crystal analysis. According to Yaghi and Chen [45, 46], under hydrothermal conditions, Cu(II) ions can be reduced to Cu(I) in the presence of 4,4′-bpy.

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

Empirical formula	$C_{30}H_{36}Cu_2N_8O_{11}$
Formula weight	811.75
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	7.6158(9)
b (Å)	13.4743(17)
c (Å)	18.232(2)
α (°)	73.661(9)
β (°)	85.305(9)
γ (°)	75.060(9)
V (Å^3)	1734.6(4)
Z	2
ρ_{Calcd} (g cm^{-3})	1.554
μ (mm^{-1})	1.296
F(000)	836
θ (°)	1.16–26.50
Indep. reflcn	5993
Data/restraint/parameters	5993/0/460
Goodness-of-fit on F^2	1.061
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0586$, $wR_2 = 0.1258$
R indices (all data)	$R_1 = 0.1817$, $wR_2 = 0.1638$
Largest peak and hole (e Å^{-3})	0.655 and −1.139

Table 2. Selected bond distances (Å) and angles (°) for **1**.

Cu(1)–O(3)	2.273(5)	Cu(1)–N(3)	2.084(6)
Cu(1)–N(6)	1.976(6)	Cu(1)–N(7)	1.981(6)
Cu(2)–O(1)	2.230(6)	Cu(2)–N(1)	2.083(6)
Cu(2)–N(5)	1.973(6)	Cu(2)–N(8)	1.970(7)
N(3)–Cu(1)–O(3)	76.6(2)	N(6)–Cu(1)–O(3)	98.7(2)
N(7)–Cu(1)–O(3)	111.2(2)	N(6)–Cu(1)–N(3)	113.0(2)
N(7)–Cu(1)–N(3)	115.5(2)	N(7)–Cu(1)–N(6)	127.3(2)
N(1)–Cu(2)–O(1)	76.8(2)	N(5)–Cu(2)–O(1)	99.7(2)
N(8)–Cu(2)–O(1)	107.0(2)	N(5)–Cu(2)–N(1)	110.5(2)
N(8)–Cu(2)–N(1)	113.1(2)	N(8)–Cu(2)–N(5)	132.7(2)

Single crystal analysis revealed that complex $[Cu_2(2\text{-pac})_2(4,4'\text{-bpy})_2]\cdot 7H_2O$ (**1**) has a 3D porous supramolecular network constructed from infinite one-dimensional chains of [Cu(2-pac)(4,4′-bpy)] through hydrogen bonding with lattice water molecules, crystallizing in triclinic, space group $P\bar{1}$. As can be seen from figure 1, the asymmetric unit of **1** contains two crystallographically distinguishable copper(I) atoms, two 4,4′-bpy ligands, two 2-pyrazinecarboxylates and seven uncoordinated water molecules. The two independent Cu(I) atoms are all coordinated with two N atoms from two 4,4′-bpy ligands, and the rest O and N atoms from one 2-pac ligand, forming an essentially tetrahedral coordination environment. As a bridging ligand, each 4,4′-bpy ligands with its terminal nitrogen atoms linked [Cu(2-pac)] units to form an infinite one dimensional chain.

Among the seven cystallographically independent free water molecules in the crytal lattice of complex **1**, O7, O8, O9, O10 and their equivalents, generated by a

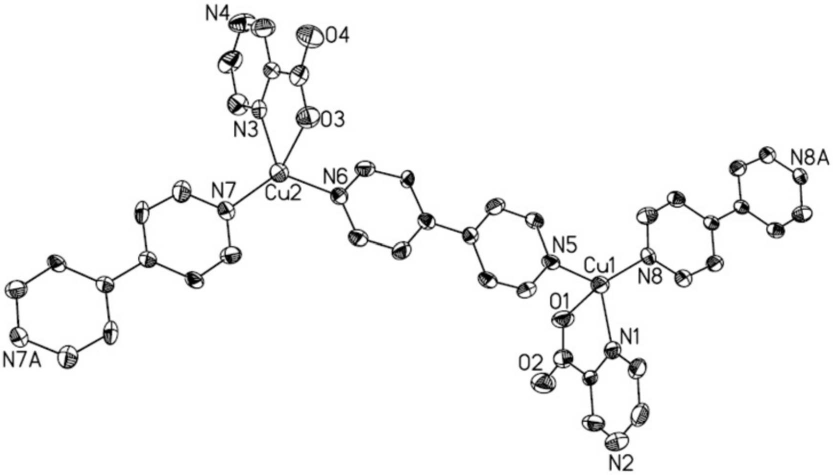

Figure 1. The coordination environment of copper ions in **1** with the thermal ellipsoids at the 30% probability level. All H atoms and lattice water molecules were omitted for clarity.

crystallographic inversion center, are associated by O–H···O hydrogen bonds in a cyclic centrosymmetric chair-like octamer, with 2.743(9) Å for O7···O8, 2.842(9) Å for O8···O9, 2.761(8) Å for O9···O10, 2.832(8) Å for O7···O10. The average O···O distance of 2.826 Å is longer than the value of 2.759 Å in ice, I_h, [47] but very similar to the O···O distance of 2.85 Å in liquid water [48]. The octamers are further self-assembled by O7···O10 hydrogen bonds with 2.9992(9) Å into extended water tapes along the b direction, consisting of fused four- and eight-membered water rings (figure 2). According to L Infantes [49], the water molecules in the channels of the framework show an interesting arrangement which give rise to a T4(2)8(2) tape, "T" means infinite tape in one dimension involving rings; "4" and "8" indicate two kinds of rings with tetramer and octamer, respectively; "2" represents two sharing water molecules. The details of hydrogen bond geometry in complex **1** are shown in table 3.

Clearly the presence of seven water molecules within the Cu^+ complex plays an important role in constructuring such a porous 3D supramolecule through hydrogen bonding, which makes the 1D structure further extended into a 3D supramolecular network. Additional hydrogen bonding interactions between oxygen atoms from carboxylate of host and water atoms from water tape of guest with 2.918(8) Å for O8···O3, 2.801(8) Å for O9···O4 and 2.723(9) Å for O10···O4 anchor the water tapes to adjacent metal–organic chains, resulting in 3D supramolecular framework, shown in figure 3.

In summary, we have experimentally presented a T4(2)8(2) water tape, showing the contribution of the water cluster to the stability of the host, and the role of the cooperative association of the water cluster and crystal host in the formation of the water cluster. The water tape pattern is very rare [49–51], and no example has been reported of the T4(2)8(2) pattern. The first T4(2)8(2) water tape in this work offers a good example for understanding water structures.

Table 3. Hydrogen bond geometry in complex **1**.

D–H···A	H···A (Å)	D···A (Å)	D–H···A (°)
O7W–H7A···O10W$^{\text{i}}$	1.95	2.832(8)	179.1
O7W–H7B···O8W$^{\text{ii}}$	1.95	2.743(9)	155.1
O8W–H8B···O9W	1.99	2.842(9)	178.7
O9W–H9B···O10W$^{\text{i}}$	1.91	2.761(8)	178.8
O10W–H10B···O7W$^{\text{iii}}$	2.53	2.992(9)	114.7
O10W–H10A···O4$^{\text{ii}}$	1.87	2.723(8)	179.1
O11W–H11B···O6W$^{\text{i}}$	2.20	3.052(14)	179.0
O11W–H11A···O5W$^{\text{iv}}$	1.86	2.706(12)	179.8
O9W–H9A···O4$^{\text{ii}}$	2.39	2.801(8)	110.6
O8W–H8A···O3$^{\text{v}}$	2.47	2.918(8)	113.8
O5W–H5A···O2$^{\text{iv}}$	2.20	2.974(9)	151.0
O5W–H5B···O2$^{\text{vi}}$	1.87	2.723(8)	179.0

(i) $-x+1, -y+1, -z+1$; (ii) $x+1, y, z$; (iii) $x-1, y, z$; (iv) $x, y, z-1$; (v) $-x, -y+1, -z+1$; (vi) $-x+2, -y+1, -z+1$.

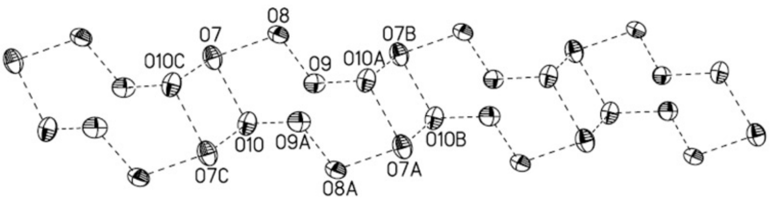

Figure 2. The 1D water T4(2)8(2) tape constructed by edge-fused cyclic octamers and tetramers with the thermal ellipsoids at the 30% probability level.

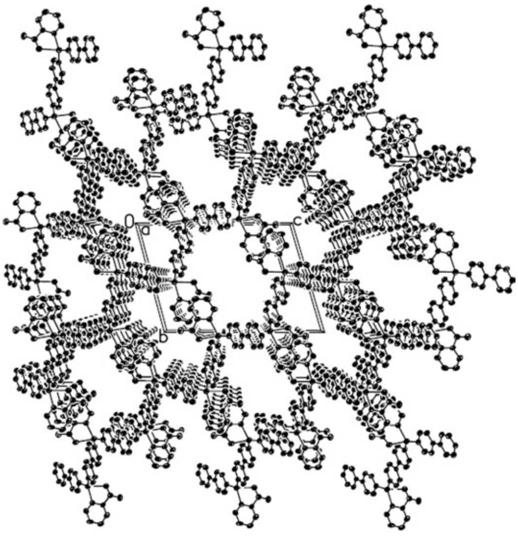

Figure 3. 3D porous supramolecular framework viewed along the a axis. The 1D water tape in the channels are omitted for clarity.

Supporting information available

Crystallographic data for the title compound has been deposited at the Cambridge Crystallographic Data Center as supplementary publications (CCDC 606599). These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK [Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk].

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