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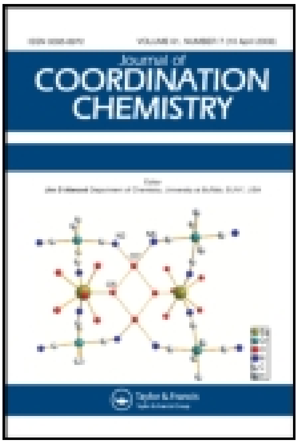

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Formation of a 1-D metal-water chain and a 2-D water-sulfate layer containing cyclic water octamers in a 3-D supramolecular network

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Formation of a 1-D metal–water chain and a 2-D water–sulfate layer containing cyclic water octamers in a 3-D supramolecular network

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A new tetranuclear complex, $\{[Cu(phen)(OH)]_4(H_2O)_2\} \cdot (SO_4)_2 \cdot 8H_2O$ (**1**) (phen = 1,10-phenanthroline), has been synthesized and characterized by elemental analysis, UV-Vis, IR, TG, and single-crystal X-ray diffraction. Complex **1** exhibits a 3-D supramolecular network with a 1-D metal–water chain consisting of tetranuclear hydroxo-bridged copper(II) clusters and water octamers and a 2-D water–sulfate layer containing cyclic water octamers with five types of $O–H \cdots O$ hydrogen-bonding motifs. The free ligand and its complex were screened for antibacterial activity against Gram-positive and Gram-negative bacteria.

Keywords: Supramolecular network; Cyclic water octamers; Metal–water chain; Water–sulfate layer

1. Introduction

Investigation of water structures in chemical and biological processes has attracted great interest [1]. Considerable attention has focused on theoretical and experimental studies of the numerous possible structures and characteristics of discrete water clusters $[(H_2O)_n$, where $n = 2–16]$ or polymeric water clusters to gain insight into the nature of water–water interactions in bulk water or ice [2]. Water clusters play a crucial role in stabilization of supramolecular systems [3] and precise structural data of water clusters in diverse surroundings provide a good understanding of the water assembly from low-nuclearity clusters to high-nuclearity clusters or from clusters to multidimensional systems [4]. A variety of water clusters such as hexamers [5], octamers [6], decamers [7], and dodecamers [8], or polymeric species of 1-D chains [9], 1-D tapes [10], or 2-D layers [11] have been reported. However, water octamers in the formation of 1-D or 2-D water morphologies have been rarely reported [12]. Herein, we report a new 3-D supramolecular network of $[Cu(phen)(OH)]_4(H_2O)_2\} \cdot (SO_4)_2 \cdot 8H_2O$ (**1**) with a 1-D metal–water chain and a 2-D water–sulfate layer containing cyclic water octamers.

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2. Experimental

2.1. *Materials and physical measurements*

All materials and reagents were obtained commercially and used without purification. C, H, and N elemental analyses were carried out with an Elementar Vario EL analyzer. UV-Vis spectra were obtained in DMF ($1.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$) for the ligand and metal complex with a Lambda 750 spectrophotometer using a 1 cm quartz cell from 200 to 800 nm. IR spectra were recorded with a Nicolet Avatar 360 FT-IR spectrometer using KBr pellets. Thermal stability studies were carried out on a ZRY-2P Thermal Analyzer.

2.2. *Synthesis of* $\{[Cu(phen)(OH)]_4(H_2O)_2\}\cdot(SO_4)_2\cdot8H_2O$ *(1)*

A mixture of $CuSO_4\cdot6H_2O$ (0.025 g, 0.1 mmol), 1,10-phenanthroline (0.020 g, 0.1 mmol), NaOH (0.30 mL, $0.65\,\mathrm{mol\,L^{-1}}$), and distilled water (10 mL) was sealed in a Teflon-lined stainless reactor (23 mL) and heated at 90°C for 3 days under autogenous pressure. Blue block crystals were obtained. Yield: 42.5%. Anal. Calcd for $C_{24}H_{28}Cu_2N_4O_{11}S$ (%): C, 40.73; H, 3.96; N, 7.92. Found: C, 40.43; H, 3.65; N, 8.21. IR data (KBr pellet, $\nu/\mathrm{cm^{-1}}$): 3408 (s), 1622 (m), 1575 (m), 1518 (m), 1429 (s), 1112 (s), 852 (s), 785 (w), 722 (m), 619 (m).

2.3. *X-ray crystallographic study*

X-ray single-crystal data of **1** were recorded on a Bruker APEX II area detector diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Semi-empirical absorption corrections were applied to the title complex using SADABS [13]. The structure was solved by direct methods [14] and refined by full-matrix least-squares on F^2 using SHELXL-97 [15]. All non-hydrogen atoms were refined anisotropically. Hydrogens were placed in geometrically calculated positions. Experimental details for X-ray data collection of **1** are presented in table 1, selected bond lengths and angles are listed in table 2, and the types of hydrogen bonds are listed in table 3.

2.4. *Antibacterial testing*

The *in vitro* antibacterial activity of the compounds was evaluated against Gram-positive bacteria (*Staphylococcus aureus*, *Candida albicans*, and *Bacillus subtilis*), and Gram-negative bacteria (*Escherichia coli* and *Pseudomonas aeruginosa*) by using the disc diffusion method. The test solutions were prepared by measuring 2 mg of all selected substances which were dissolved in 10 mL of DMF. Test solutions were added to 8 mm diameter filter paper discs and dried. The discs with tested substances and the blank (solvent) were added onto Petri dishes inoculated with the tested bacterial strains. After 24-h cultivation at 37°C, diameters of zones of inhibition were determined, and DMF was inactive under applied conditions. Commercially available ampicillin was used as reference antibacterial drug.

Table 1. Crystal data for **1**.

Empirical formula	$C_{24}H_{28}Cu_2N_4O_{11}S$
Formula weight	707.64
Temperature (K)	296(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	10.260(7)
b	11.106(8)
c	13.319(9)
α	96.299(8)
β	111.250(7)
γ	108.352(7)
Volume ($Å^3$), Z	1298.9(15), 2
Absorption coefficient μ (mm^{-1})	1.789
Calculated density ($Mg\,m^{-3}$)	1.809
F (000)	724
θ range for data collection (°)	2.31–23.50
Independent reflection	[R(int) = 0.0453]
Goodness-of-fit on F^2	1.012
Number of data collected	7914
Number of unique data	3778
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0720$, $wR_2 = 0.1841$
R indices (all data)	$R_1 = 0.1089$, $wR_2 = 0.2151$
Largest difference peak and hole ($e\,Å^{-3}$)	2.270 and −0.703

$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum(w(F_o^2 - F_c^2)^2) / \sum w(F_o^2)^2]^{1/2}$.

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

Cu(1)–O(5)	1.925(6)	Cu(2)–O(5)	1.918(6)
Cu(1)–O(6)	1.920(8)	Cu(2)–O(6)	1.904(8)
Cu(1)–O(7)	2.195(6)	Cu(2)–N(3)	2.003(7)
Cu(1)–N(1)	1.998(7)	Cu(2)–N(4)	1.972(8)
Cu(1)–N(2)	2.002(7)	Cu(2)–O(5)$^{\#1}$	2.471
O(5)–Cu(1)–O(6)	82.8(3)	N(2)–Cu(1)–O(7)	94.8(3)
O(5)–Cu(1)–O(7)	96.3(3)	N(2)–Cu(1)–N(1)	81.6(3)
O(6)–Cu(1)–O(7)	93.4(3)	O(6)–Cu(2)–O(5)	83.3(3)
O(5)–Cu(1)–N(2)	95.1(3)	O(5)–Cu(2)–N(4)	98.4(3)
O(6)–Cu(1)–N(1)	98.3(3)	O(6)–Cu(2)–N(3)	95.1(3)
N(1)–Cu(1)–O(7)	98.7(3)	N(4)–Cu(2)–N(3)	81.8(3)

Symmetry code: $^{\#1}$: $2 - x$, $1 - y$, $1 - z$.

3. Results and discussion

3.1. *Description of the crystal structure*

Single-crystal X-ray diffraction analysis revealed that **1** belongs to the triclinic system, $P\bar{1}$ space group. As shown in figure 1, the crystal structure consists of tetranuclear $\{[Cu(phen)(OH)]_4(H_2O)_2\}^{4+}$, sulfate, and crystallization water molecules. The tetranuclear $\{[Cu(phen)(OH)]_4(H_2O)_2\}^{4+}$ is centrosymmetric as reported by Zheng and Lin [16]. However, compared with the reported complex, $\{[Cu(phen)(OH)]_4(H_2O)_2\} \cdot Cl_4 \cdot 4H_2O$ (**2**) [16], sulfate takes the place of chloride and the number of lattice water molecules in **1** is eight, double that of **2**, increasing the possibility of

Table 3. Hydrogen-bonding geometry (Å, °) for **1**.

D–H···A	*d*(D–H)	*d*(H···A)	∠DHA	*d*(D···A)
O5–H26···O4	0.74	2.06	170.0	2.792(9)
O6–H25···O8$^{\#1}$	0.51	2.38	159.0	2.860(10)
O7–H1W···O1	0.83	1.86	163.2	2.668(9)
O7–H2W···O9$^{\#2}$	0.83	2.32	111.0	2.731(10)
O8–H3W···O4$^{\#3}$	0.83	1.94	174.8	2.762(9)
O8–H4W···O3$^{\#4}$	0.83	1.97	146.1	2.699(9)
O9–H5W···O1	0.83	1.99	141.4	2.684(9)
O9–H6W···O11	0.83	2.24	121.6	2.769(11)
O10–H7W···O6	0.83	1.96	165.9	2.775(10)
O10–H8W···O9$^{\#2}$	0.83	2.01	169.0	2.830(11)
O11–H9W···O10$^{\#5}$	0.83	2.05	144.3	2.767(10)
O11–H10W···O3	0.83	1.89	179.7	2.725(10)

Symmetry codes: $^{\#1}$: $1-x$, $1-y$, $1-z$; $^{\#2}$: $1-x$, $1-y$, $-z$; $^{\#3}$: $-1+x$, y, z; $^{\#4}$: $1-x$, $2-y$, $1-z$; $^{\#5}$: x, $1+y$, z.

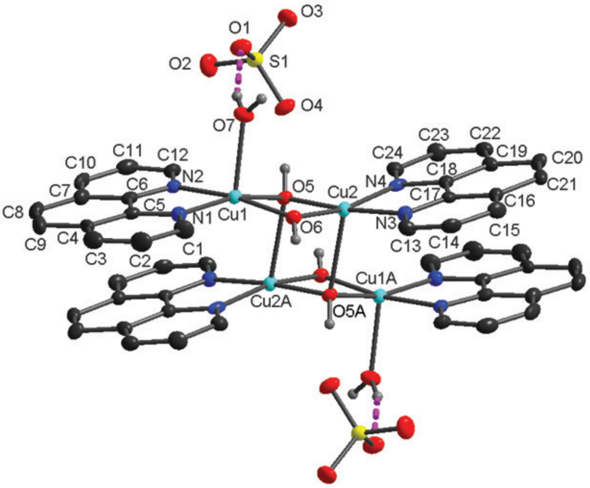


Figure 1. The coordination environment of Cu(II) in **1**. Thermal ellipsoids are shown at 30% probability and all hydrogens except those of coordinated water and hydroxyl groups are omitted for clarity.

hydrogen-bonded interactions for **1**. In **1**, two hydroxyl groups link two Cu(II) ions to form a dimeric unit with Cu1···Cu2 distance of 2.86 Å, which is further bridged to form a tetrameric unit by long Cu2–O5 bonds (2.471 Å) due to the Jahn–Teller effect [17]. Therefore, the Cu–O bond lengths range from 1.904 to 2.471 Å with an average of 2.056 Å (table 2), which is slightly shorter than the corresponding value of 2.069 Å in **2**; the Cu–N bond lengths are of the range 1.972–2.003 Å with an average of 1.994 Å (table 2), which is also shorter than **2** (2.028 Å). The differences in the bond lengths of Cu–O and Cu–N in the two complexes are probably due to spatial effect (the volume of sulfate is larger than that of chloride).

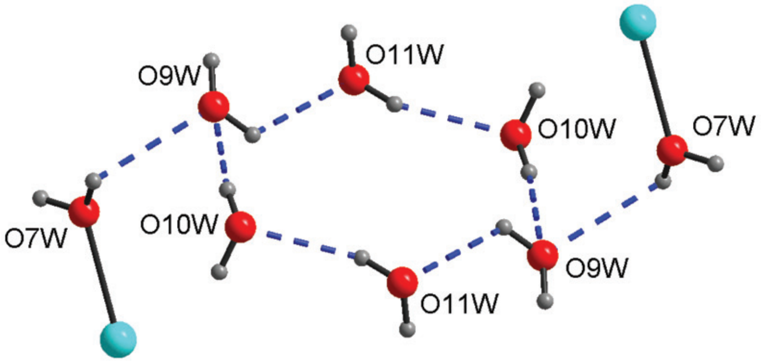


Figure 2. View of the cyclic water octamer showing the atom labeling scheme and its coordination environment.

The lattice water molecules O9W, O10W, O11W and the coordinated water molecule O7W are associated to form a water tetramer, which is further hydrogen bonded to its equivalent to yield a centrosymmetric cyclic water octamer, as shown in figure 2. The geometrical parameters of the octameric water cluster are summarized in table 3. The average $O \cdots O$ distance (2.776 Å) is slightly longer than the corresponding value in ice I_h (2.759 Å), while it is shorter than those observed in liquid water (2.854 Å). The $O \cdots O \cdots O$ angles range from 77.2° to 136.4° with an average of 109.3°, which is comparable to the value of 109.5° in ice I_c or 109.3° in the ice I_h [18]. In **1**, tetranuclear units and cyclic water octamers are arranged alternately through cooperative association of coordination interactions as well as hydrogen bonds, forming a 1-D metal–water chain structure along the *a*-axis (figure 3). On the other hand, cyclic water octamers, sulfates, and uncoordinated water (O8W) form a water–sulfate layer through $O–H \cdots O$ hydrogen bonds, in which five types of hydrogen-bonding motifs [$R_3^3(8)$, $R_4^4(12)$, $R_6^4(12)$, $R_6^6(12)$, and $R_{14}^9(32)$] can be observed, as illustrated in figure 3. Three types of water octamers have been reported [6]: (1) two dangling water molecules and a hexamer ring; (2) four dangling water molecules and a tetramer ring; and (3) an octamer ring, as shown in scheme 1. The octameric water cluster in **1** is of type A. Of the reported water oligomers, some form 1-D metal–water chains, some construct 2-D water sheets with organic ligands or anions, and some as discrete subunits help to form high-dimensional supramolecular structures [2a, 2c, 6, 8, 12b]; however, both metal–water chain and water layer structure containing water oligomers are very rare.

In **1**, the tetranuclear $\{[Cu(phen)(OH)]_4\}^{4+}$ cation are trapped in the water–sulfate layer *via* $O5–H26 \cdots O4$, $O6–H25 \cdots O8$, $O10–H7W \cdots O6$ hydrogen bonds and Cu1–O7 coordination bonds forming a 2-D supramolecular sheet. Furthermore, there are π–π stacking interactions between phen molecules of neighboring 2-D sheets (centroid-to-centroid distances of 3.46–3.61 Å), which lead to the formation of a 3-D supramolecular network along the *b*-axis (figure 4). Similar to **1**, hydrogen bonds and π–π stacking interactions join tetranuclear $\{[Cu(phen)(OH)]_4(H_2O)_2\}^{4+}$ cations into a 3-D supramolecular network of **2** [16]. However, cyclic water octamer, 1-D metal–water chain, and 2-D water–sulfate layer were not reported in **2**, which may be due to the significant decrease of lattice water molecules.

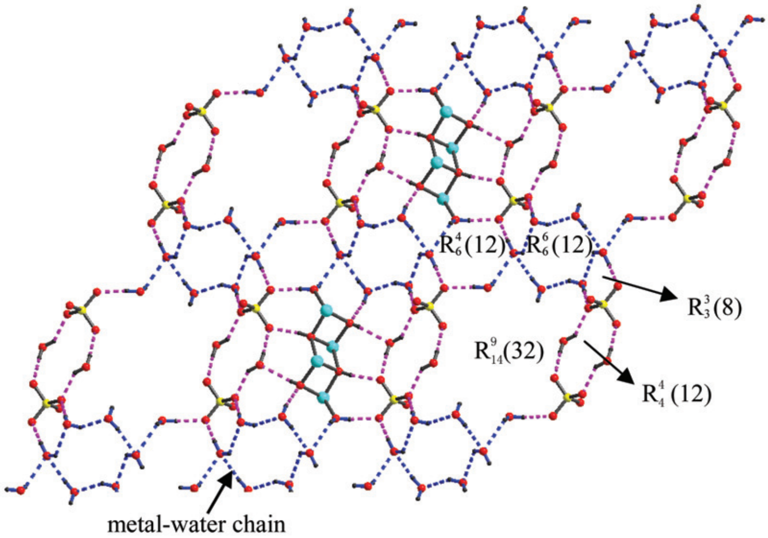
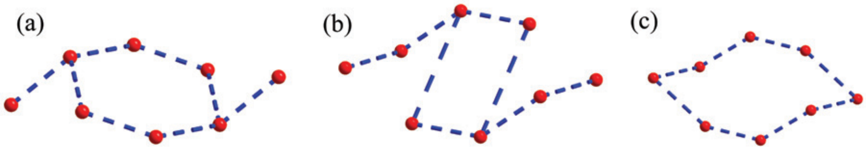


Figure 3. View of the metal–water chain and water–sulfate layer containing cyclic water octamers along the *a*-axis.



Scheme 1. The configurations of octameric water cluster.

3.2. *TG analysis*

TG analysis of **1** was carried out under N_2 with heating at 10°C min^{-1}. The complex decomposes in four decomposition steps. The first step, at 55–115°C, is loss of four lattice waters (Found: 10.5%, Calcd: 10.2%). The second of 2.7% (Calcd: 2.5%) from 205°C to 234°C corresponds to the loss of one coordinated water molecule. The third step (278–355°C) corresponds to the removal of one sulfate (Found: 14.1%, Calcd: 13.6%). Increasing temperature led to further decomposition and the final pyrolysis was completed at 835°C, giving CuO powder (Found: 22.2%, Calcd: 22.5%).

3.3. *UV-Vis spectra*

UV-Vis spectra of the ligand and its metal complex in DMF are recorded from 200 to 800 nm. Phen shows an absorption at 278 nm, attributed to $\pi \rightarrow \pi^*$ transition; the band of **1** shifts to 271 nm upon coordination. Bands at 340 and 385 nm can be attributed to ligand–metal charge transfer. Complex **1** has the d–d transition at 663 nm, indicative of "distorted square-pyramidal geometry" [19].

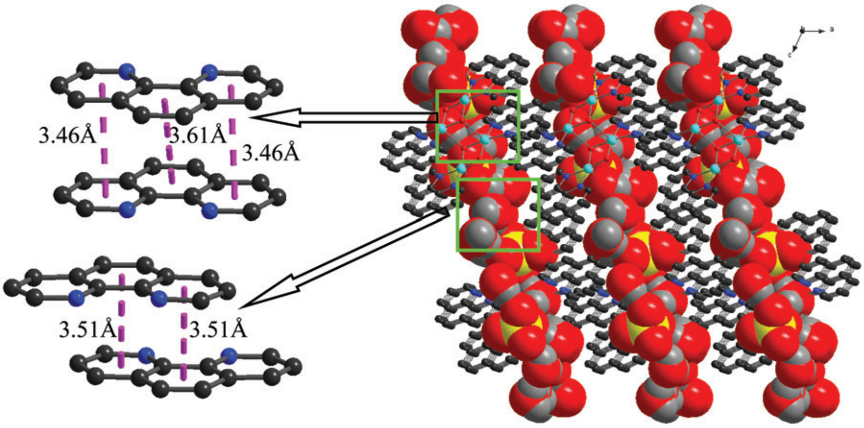


Figure 4. The 3-D supramolecular network of **1** along the *b*-axis *via* π–π stacking interactions; the water–sulfate layers are shown by a space-filling model.

Table 4. Zones of inhibition (diameter in mm) of **1** against selected bacteria, including diameter of disc (8 mm).

Compounds	*S. aureus*	*C. albicans*	*B. subtilis*	*E. coli*	*P. aeruginosa*
DMF	–	–	–	–	–
phen	–	–	–	–	–
1	12.4	9.5	10.4	8.9	9.8
$CuSO_4 \cdot 6H_2O$	10.5	8.3	10.1	8.5	9.0
Ampicillin	12	11.0	12.5	11.5	11.5

3.4. *IR spectra*

IR spectrum of phen shows the C=N band at 1585 cm^{-1}, which shifts to lower frequency at 1518 cm^{-1} in **1**, indicating coordination. The ν(O–H) of **1** exhibits a strong band at 3408 cm^{-1}; a strong absorption at 1112 cm^{-1} indicates the presence of an uncoordinated SO_4^{2-}. The aromatic ring in **1** has C=C stretching vibration at 1622 cm^{-1} and δ(C–H) modes between 852 and 726 cm^{-1}.

3.5. *Antibacterial activity results*

The antibacterial activity of **1** has been carried out against the selected microorganisms. Ampicillin was used as a standard drug. From the results given in table 4, phen exhibits no antibacterial activity, while **1** and the metal salt exhibit antibacterial activity against the tested bacteria. Complex **1** has more activity than Cu^{2+}. The increase in antibacterial activity of complex may be due to the chelation theory of Tweedy [20]. Chelation enhances the lipophilic character of the copper, which subsequently favors its permeation through the lipid layer of the cell membrane [21].

4. Conclusion

Both a 1-D metal–water chain and a 2-D water–sulfate layer containing cyclic water octamers can be observed in the 3-D supramolecular network of **1**. Coordination bonds, hydrogen bonds, and π–π stacking interactions play an important role in the formation of the 3-D supramolecular structure of **1**. Antibacterial activity screening shows that the complex has more activity than phen against the tested bacteria.

Supplementary material

Crystallographic data for **1** have been deposited with the Cambridge Crystallographic Data Center with deposition number CCDC 780276.

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