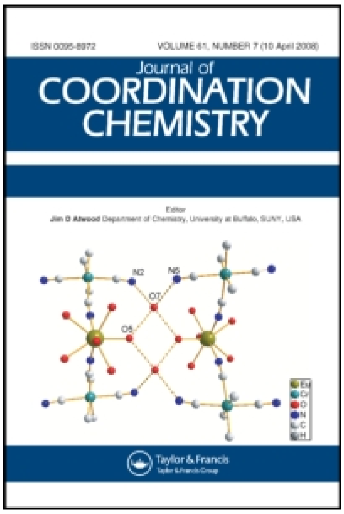

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A new tetranuclear copper(II) complex containing decameric water clusters bridged by –OH– and pyridine-2,4, 6-tricarboxylate: synthesis and magnetic characterization

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Using pyridine-2,4,6-tricarboxylic acid (H_3ptc) and 2,2-bipyridine (2,2-bipy), a tetranuclear copper(II) compound $[Cu_4(2,2\text{-bipy})_4(ptc)_2(H_2O)_2(OH)_2] \cdot 12H_2O$ (**1**) has been isolated under hydrothermal conditions. Variable temperature magnetic susceptibility of **1** from 2–300 K indicates anti-ferromagnetic interactions. The magnetic exchange coupling constants of $J = -159.4$ and $J' = -18.66\,cm^{-1}$ for **1** can be obtained through fit of the magnetic data, corresponding to two kinds of bridges, hydroxyl anions (OH^-) and pyridine carboxylate oxygen of ptc^{3-}. Moreover, decameric water clusters can also be observed, which are located between these tetranuclear copper(II) entities, forming a series of intricate $O\text{-}H \cdots O$ hydrogen bonds and stabilizing the resulting three-dimensional (3-D) hydrogen-bonded framework structure.

Keywords: Pyridine-2,4,6-tricarboxylic acid; Tetranuclear copper(II); Magnetic; Decameric water clusters

1. Introduction

Transition metal coordination polymers exhibit diverse magnetic properties based on different metal(II) ions and organic ligand linkers [1]. Especially those with short bridging ligands such as OH^- and carboxylate groups are especially favorable because they can efficiently transfer magnetic interactions between neighboring metal(II) ions forming magnetic materials [2]. Selective combination of bridging ligands and co-ligands is an effective strategy for modulating magnetic properties and assisting in understanding the magneto-structural correlations.

Coordination polymers with pyridine carboxylic acid ligands exhibit applications in areas such as gas absorption, ion exchange, magnetic materials and so on [3]. In comparison with those widely investigated pyridine mono- or dicarboxylic acid ligands, only a few examples of pyridine-2,4,6-tricarboxylic acid (H_3ptc) are reported [4]. However, H_3ptc contains a number of N- or O-coordination sites and is anticipated to form unique framework structures with intriguing properties. In this work, 2,2-bipyridine (2,2-bipy) was used as co-ligand for the following reasons: (1) only a

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few examples deal with using H_3ptc and N-containing ligands such as 4,4-bipyridine or 2,2-bipyridine [5]; and (2) chelating 2,2-bipy may help to form metal clusters as indicated in the previous reports.

Herein using H_3ptc and 2,2-bipy under hydrothermal conditions, one tetranuclear copper(II) compound $[Cu_4(2,2\text{-bipy})_4(ptc)_2(H_2O)_2(OH)_2] \cdot 12H_2O$ (**1**) can be isolated. The magnetic susceptibility of **1** at 2-300 K exhibits anti-ferromagnetic interactions with two exchange coupling constants $J = -159.4$ and $J' = -18.66\,\text{cm}^{-1}$, which can be correlated with its two bridges, OH^- and ptc^{3-} carboxylate oxygen atom, respectively.

Decameric water clusters can also be observed in **1**, which contain planar hexagonal hexameric core and four pendent waters. In comparison with widely investigated hexameric water clusters, decameric water clusters are still little known; only one such form of decameric water cluster has been reported [6].

2. Experimental

2.1. *Materials and general methods*

H_3ptc was prepared according to the literature [7]. All solvents and reagents were commercially available. Elemental analyses of carbon, hydrogen and nitrogen were carried out with a CE-440 (Leeman-Labs) analyzer. FT–IR spectra (KBr pellets) were taken on an AVATAR-370 (Nicolet) spectrometer in the 4000–400 cm^{-1} region. Variable-temperature magnetic susceptibilities were measured on a Quantum Design MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms.

2.2. *Synthesis of 1*

An aqueous solution (18 mL) containing pyridine-2,4,6-tricarboxylic acid (33.4 mg, 0.2 mmol), 2,2-bipyridine (66.8 mg, 0.4 mmol) and $Cu(ClO_4)_2 \cdot 6H_2O$ (148.4 mg, 0.4 mmol) was placed in Parr Teflon-lined stainless steel vessel (25 mL) under autogenous pressure. Several drops of triethylamine were added to adjusted pH to 8. The mixture was heated to 170°C for 72 h and then cooled to room temperature at the rate of $2^\circ\text{C} \cdot \text{h}^{-1}$; the reaction mixture was filtered and left to stand at room temperature and blue block-like crystals suitable for X-ray analysis were collected after several weeks. Yield: 46% based on Cu. Reproducibility of the synthesis is good with yield above 40%. Anal. Calcd for $C_{28}H_{33}Cu_2N_5O_{14}$: C, 42.53; H, 4.21; N, 8.86%. Found: C, 42.65; H, 4.33; N, 8.67%. IR (KBr, cm^{-1}): 3418.1(br), 3092.9(w), 1652.1(m), 1450.4(m), 1311.9(w), 1271.3(w), 1211.7(w), 1091.2(m), 798.3(w), 615.9(w), 525.3(w).

2.3. *X-ray crystallography*

Structure measurement of **1** was performed on a computer controlled Bruker APEX-II CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation with radiation wavelength 0.71073 Å by using ω-scan technique. Semi-empirical absorption corrections using SADABS were applied. The structure was solved by direct methods and refined with full-matrix least-squares using the SHELXS-97 and SHELXL-97 programs [8, 9]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically. Analytical expressions of neutral-atom scattering factors were employed and anomalous dispersion corrections were incorporated. The crystallographic data and selected bond lengths and angles are listed in tables 1 and 2, respectively.

3. Results and discussion

3.1. *Description of the structure*

As shown in figure 1, **1** has an inversion symmetry center, which comprises tetranuclear copper(II) and twelve lattice water molecules (O1 to O6 and O1A to O6A). Four copper(II) ions (Cu1, Cu2, Cu2A and Cu1A) are in **1**; the central Cu2 and Cu2A are bridged by two μ_2-OH$^-$ bridging anions at 2.913(3) Å. In contrast, Cu2 and terminal Cu1 are bridged via one ptc^{3-} carboxylate oxygen with Cu1 $\cdots$ Cu2 separation of 4.103(1) Å.

For Cu^{II} two coordination modes can be observed: Cu1 is six-coordinate by two oxygen atoms and one nitrogen atom from one tridentate chelate ptc^{3-}, one chelate

Table 1. Crystallographic data and structure refinement summary[a].

Formula	$C_{28}H_{33}Cu_2N_5O_{14}$
Fw (g mol^{-1})	790.67
Crystal size (mm^3)	0.18 × 0.16 × 0.14
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	9.1788(11)
b	11.8892(14)
c	15.2930(18)
α	79.1230(10)
β	81.959(2)
γ	78.2560
V (Å^3)	1595.7(3)
Z	2
θ range (°)	2.28 to 23.48
Limiting indices	$-11 \leq h \leq 11$
	$-14 \leq k \leq 14$
	$-18 \leq k \leq 18$
ρ (g cm^{-3})	1.646
μ (mm^{-1})	1.411
Reflections collected/unique	12288/5896
$R_{(int)}$	0.0373
Data/restraints/parameters	5896/0/442
Goodness-of-fit on F^2	1.007
$F(000)$	812
$R_1{}^a/wR_2{}^b[I>2\sigma(I)]$	0.0391/0.0733
R_1/wR_2 (all data)	0.0645/0.0831
Largest diff. peak and hole (e Å^{-3})	0.320 and 0.315

[a] $R=\Sigma(\|F_0|-|F_C\|)/\Sigma|F_0|$; [b] $wR=[\Sigma w(|F_0|^2-|F_C|^2)^2/\Sigma w(F_0{}^2)]^{1/2}$.

Table 2. Selected bond distances (Å) and angles (°)[a].

Cu(1)–O(7)	1.982(2)	Cu(1)–N(3)	2.009(3)
Cu(1)–N(4)	2.020(3)	Cu(1)–N(5)	2.040(2)
Cu(1)–O(9)	2.293(2)	Cu(1)–O(11)	2.368(2)
Cu(2)–O(8)	1.946(2)	Cu(2)–O(8)#1	1.963(2)
Cu(2)–N(2)	2.008(3)	Cu(2)–N(1)	2.010(3)
Cu(2)–O(11)	2.305(2)		
O(7)–Cu(1)–N(3)	173.00(10)	O(7)–Cu(1)–N(4)	96.67(10)
N(3)–Cu(1)–N(4)	80.73(11)	O(7)–Cu(1)–N(5)	90.17(9)
N(3)–Cu(1)–N(5)	94.26(10)	N(4)–Cu(1)–N(5)	161.59(11)
O(7)–Cu(1)–O(9)	95.13(9)	N(3)–Cu(1)–O(9)	91.21(10)
N(4)–Cu(1)–O(9)	86.46(9)	N(5)–Cu(1)–O(9)	75.89(9)
O(7)–Cu(1)–O(11)	84.59(8)	N(3)–Cu(1)–O(11)	91.46(9)
N(4)–Cu(1)–O(11)	124.01(9)	N(5)–Cu(1)–O(11)	73.54(9)
O(9)–Cu(1)–O(11)	149.43(8)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $-y+1$, $-z$.

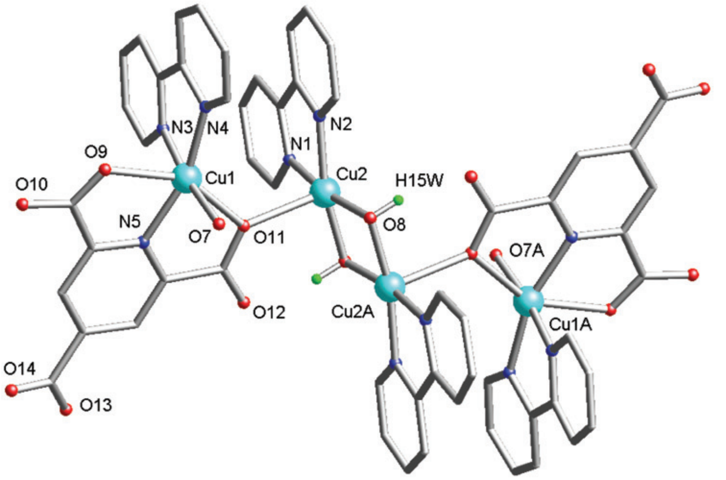
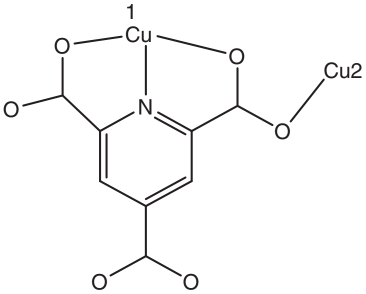


Figure 1. The tetrameric copper(II) structure of **1**.

2,2-bipy and one coordinated water (O7) forming CuN_3O_3 donor set. Cu2 is five-coordinate square pyramidal by one chelate 2,2-bipy, one ptc^{3-} carboxylate oxygen and two $–OH^-$ oxygens. The carboxylate oxygen (O11) occupies the axial site of the pyramid.

In **1**, H_3ptc is fully deprotonated ptc^{3-} and its unsymmetrical bridging coordination is shown in scheme 1: two carboxylate groups and one pyridine nitrogen are chelated to Cu1, then one un-chelate carboxylate oxygen (O11) is further coordinated to Cu2 forming bridging modes, the third carboxylate group remains uncoordinated. However, the coordination mode of ptc^{3-} is low, which may be correlated with small Cu^{II} ionic radius. When d transition metal(II) ions with small radius are used, relatively lower coordination of ptc^{3-} can be obtained; when lanthanide metal ions with large radius are used, relatively higher coordination numbers of ptc^{3-} can be obtained [4b].



Scheme 1. The unsymmetrical bridging coordination mode of ptc^{3-} in **1**.

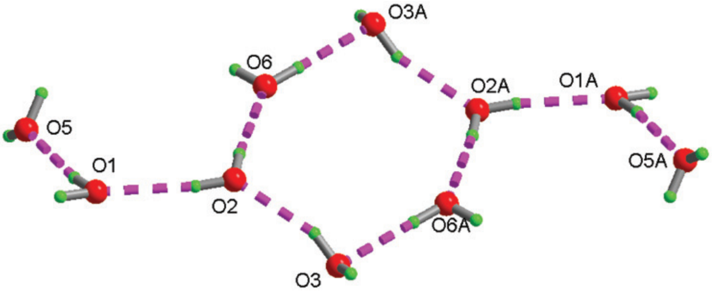


Figure 2. The detailed environment of decameric water clusters (green represents hydrogen atoms; color online only).

As shown in figure 2, lattice water molecules form centrosymmetric decameric water clusters (symmetric code A: $-x+1$, $-y+1$, $-z$), which are located between these tetranuclear copper(II) entities. The decameric water cluster contains almost planar hexagonal core and four dangling waters (figure 2). All the corresponding hydrogen bond distances and angles are listed in table 3. All hydrogen bond distances are below 3.0 Å and bond angles are larger than 150°C, indicating they are highly directional. The average O···O distance in the water cluster is 2.812 Å, comparable to those observed in the ice phase (2.77–2.84 Å) and in liquid water (2.854 Å).

Recently, a similar form of decameric water cluster has been reported in the 1-D cyano-bridged $Ln^{3+}-Cr^{3+}$ complex, which act as a template around chains [6, 10]. For **1**, these decameric water clusters also link neighboring tetranuclear copper(II) entities via a number of intricate O–H···O hydrogen bonds and form a 3-D hydrogen-bonded framework, as shown in figure 3. Similarly, the decameric water clusters also act as a template to regulate the framework structure of **1**. The corresponding intermolecular hydrogen bonds distance and angles are also listed in table 3.

3.2. *Variable-temperature magnetic susceptibility of 1*

Tetranuclear complex **1** was studied by magnetic susceptibility measurements in the 2–300 K region, as shown in figure 4, in the form of μ_{eff} *vs* T plot. The μ_{eff} value is 3.48

Table 3. Selected hydrogen bond lengths (Å) and angles (°) for **1**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
Hydrogen bonds for water clusters				
O(1)–H(2W)···O(5)#3	0.83	1.96	2.782(4)	169.7
O(2)–H(3W)···O(6)#3	0.83	1.97	2.790(5)	168.8
O(2)–H(4W)···O(1)	0.83	2.07	2.888(5)	170.2
O(3)–H(5W)···O(2)	0.83	2.00	2.798(5)	159.6
O(6)–H(11W)···O(3)#1	0.85	1.95	2.805(5)	179.4
Hydrogen bonds between water clusters and carboxylate groups				
O(4)–H(7W)···O(8)	0.83	1.92	2.739(3)	167.7
O(4)–H(8W)···O(13)#4	0.83	2.03	2.820(3)	159.6
O(5)–H(9W)···O(10)#2	0.85	1.93	2.776(3)	179.3
O(5)–H(10W)···O(14)#4	0.83	1.87	2.701(4)	176.0
O(6)–H(12W)···O(13)#4	0.83	1.95	2.770(4)	168.4
O(7)–H(13W)···O(10)#2	0.83	1.86	2.665(3)	161.0
O(7)–H(14W)···O(4)	0.83	1.81	2.644(3)	174.7
O(8)–H(15W)···O(12)#1	0.82	1.93	2.733(3)	163.3

#1 $-x+1,\ -y+1,\ -z$, #2 $-x+1,\ -y+1,\ -z+1$ #3 $x-1,\ y+1,\ z$ #4 $x,\ y-1,\ z$.

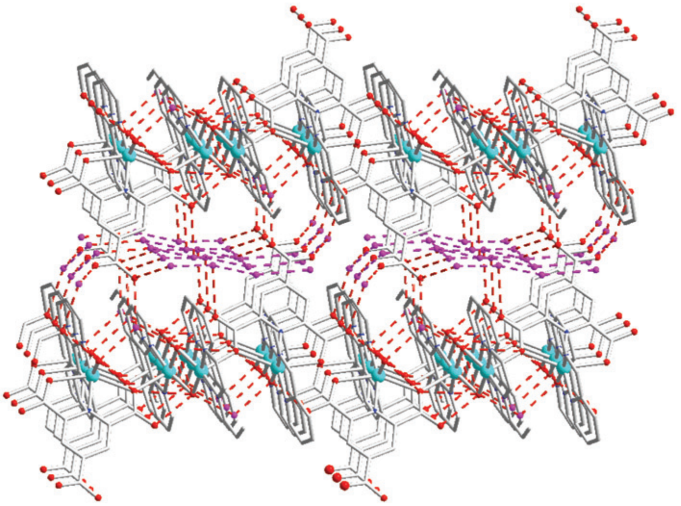


Figure 3. A 3-D supramolecular architecture of **1** (water clusters are represented in cyan; color online only).

$cm^3mol^{-1}K$ at 300 K, close to the spin-only value (3.46 $cm^3mol^{-1}K$) for a tetranuclear copper(II). As the temperature is reduced, μ_{eff} smoothly decreases to 2.19 $cm^3mol^{-1}K$ at 2 K indicating antiferromagnetic interactions between copper(II) ions dominate the magnetic properties of **1**.

To explain the magnetic exchange interactions in the centrosymmetric tetranuclear copper(II) compound, the fit about the magnetic exchange interactions are usually described by the isotropic Hamiltonian $H = -2J\ (S2 \cdot S3) - 2J'[(S1 \cdot S2) + (S3 \cdot S4)]$, where J represents exchange constant between central Cu2 and Cu2A while J' represents exchange constant between Cu2 (Cu2A) and terminal Cu1 (Cu1A). The spin labels S1, S2, S3 and S4 correspond to Cu1, Cu2, Cu2A, Cu1A as shown in the crystal

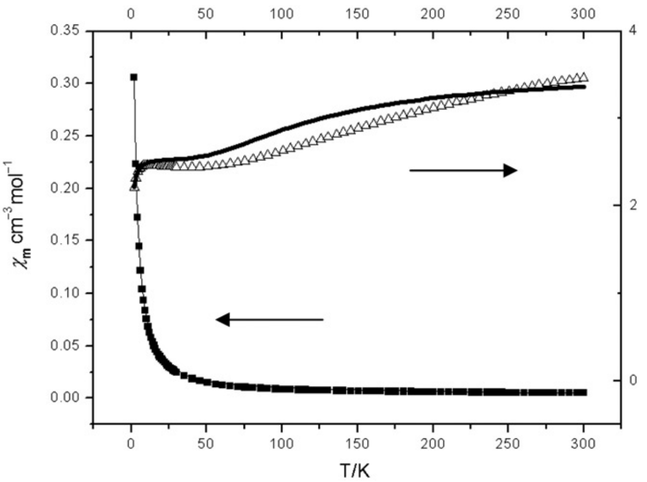


Figure 4. μ_{eff} (Δ) *vs* T and χ_{M} ($\bullet$) *vs* T plot for **1**; the solid lines represent the best fit curve.

structures. Under these conditions, the magnetic susceptibility per mole of Cu^{II} is calculated as [11]:

$$\chi_M = \frac{Ng^2\beta^2}{KT} \times \frac{10\exp(-E_1/kT) + 2\exp(-E_2/kT) + 2\exp(-E_3/kT) + 2\exp(-E_4/kT)}{5\exp(-E_1/kT) + 3\exp(-E_2/kT) + 3\exp(-E_3/kT) + 3\exp(-E_4/kT) + \exp(-E_5/kT) + \exp(-E_6/kT)} \tag{1}$$

where $E_1 = -J/2 - J'/4$; $E_2 = J/2 - J'/4$; $E_3 = J'/4 + (J^2 + J'^2)^{1/2}/2$; $E_4 = J'/4 - (J^2 + J'^2)^{1/2}/2$; $E_5 = J/2 + J'/4 + (4J^2/2 - 2JJ' + J'^2)^{1/2}/2$; $E_6 = J/2 + J'/4 - (4J^2/2 - 2JJ' + J'^2)^{1/2}/2$, N is Avogadro's number.

The magnetic susceptibility was fitted by means of least-squares methods to the theoretical expression resulting from equation (1). The best fit for the experimental data gives $J = -161.4\,\text{cm}^{-1}$, $J' = -18.46\,\text{cm}^{-1}$, $g = 2.08$. The agreement factor $R = (\chi_{\text{Obsd}} - \chi'_{\text{Calcd}})^2/(\chi_{\text{Obsd}})^2$ is 1.86×10^{-3}. The negative values of J and J' are characteristic of antiferromagnetic exchange interactions and can be attributed to hydroxide (OH^-) and ptc^{3-} carboxylate bridging, respectively. In general, the values of J and J' largely depend on Cu–O–Cu angles and Cu–O–Cu distances [12]. As for the J' value, the relatively long distances of Cu1 $\cdots$ Cu2 (4.103(3) Å), Cu1 $\cdots$ O11 (2.367(2) Å) and Cu2 $\cdots$ O11 (2.305(8) Å) cause weak anti-ferromagnetic interactions (J'). Previous relations between J and Cu–O–Cu bridging angle for copper compounds predict $J = -246$ K for 101.7°. Therefore, the J value is normal and understandable because the small Cu2–O8–Cu2A bridging angle (96.34(9)°) can reduce anti-ferromagnetic interactions between neighboring copper(II) ions [12c].

3.3. *FT–IR spectrum of 1*

In the FT–IR spectrum of **1** the broad medium absorption bands centered at $3418\,\text{cm}^{-1}$ correspond to the O–H stretching frequency of water clusters. The absence of any strong absorption bands at 1700 cm^{-1} indicates that all carboxylic groups are deprotonated. The strong bands at 1652 and 1450 cm^{-1} can be assigned to ν_{as}(COO) and ν_s(COO) of monodentate carboxylate groups [13]. All these results are in agreement with the structure of **1**.

4. Conclusion

One tetranuclear copper(II) compound $[Cu_4(2,2\text{-bipy})_4(ptc)_2(H_2O)_2(OH)_2] \cdot 12H_2O$ (**1**) has been obtained under hydrothermal conditions. The magnetic susceptibility of **1** at 2–300 K exhibits anti-ferromagnetic interactions. The magnetic exchange coupling constants $J = -159.4$ and $J' = -18.66\,cm^{-1}$ correspond to bridging OH^- and ptc^{3-}. Moreover, novel decameric water clusters also can be observed, which further assemble **1** into a 3-D hydrogen-bonded framework.

Supplementary material

CCDC-**1** 663913 contains the supplementary crystallographic data for this article. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44) 1223-336033; Email: deposit@ccdc.cam.ac.uk).

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