



# A novel asymmetric chair-like hydroxyl-bridged tetra-copper compound: Synthesis, supramolecular structure and magnetic property



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## ABSTRACT

A new polynuclear Cu(II) compound,  $[\text{Cu}_4(\text{bpy})_4(\text{OH})_4(\text{H}_2\text{O})(\text{BTC})]\text{NO}_3 \cdot 8\text{H}_2\text{O}$  (**1**), was prepared by self-assembly from the solution of copper(II) nitrate and two kinds of ligands, 2,2'-bipyridine (bpy) and benzene-tricarboxylic acid ( $\text{H}_3\text{BTC}$ ). Single crystal structure analysis reveals that **1** features a rare asymmetric chair-like hydroxyl-bridged tetra-copper cluster:  $[\text{Cu}_4(\text{OH})_4]$  core along with one  $\text{H}_2\text{O}$  and one  $\text{BTC}^{3-}$  occupied each terminal coordinated site. In addition, the magnetic property has been investigated.

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## 1. Introduction

The discrete poly-nuclear metallic cluster-based coordination complexes attract widespread attentions not only derived from their potential applications as functional materials in catalysis [1], optics [2,3], electron transport [4] and molecule-based magnets [5–7], but also from their relatively simple core structures, which are provided the pretty better opportunities to deeply understand its structure-properties relationship. Therefore, a numerous poly-nuclear cluster materials, especially molecular-based magnets, have been harvested to employ the small ligands (which offer the shorter and stronger magnetic exchange pathways [8–10], such as formic, cyanide, halogen and azide), and have exhibited the interesting magnetization [11–13]. However, the slightly structural changing of the molecular-based materials might perform intriguing varieties of the magnetic phenomena. In many cases, the counter-ions, co-ligands and the lattice guest species also put effects in the magnetic performances, which commonly through the

supramolecular interactions including the hydrogen bond or  $\pi$ - $\pi$  stacking, besides the spin ground states and minimal spin polytopes constitutes of the central transition metal ions [14–17]. Consequently, it is necessary to rational prepare and investigate magnetic properties of more complexes and its variant analogues in order to correspondingly establish the unique structural-activity relationship for the molecular magnetism.

Among the commonly used assemble modules, the hydroxyl feature smaller donor atom size and routine ( $\mu_2$ - or  $\mu_3$ -) bridging models, so the hydroxyl-bridged metal polynuclear clusters are the suitable candidates to investigate the magneto-structural correlation. Currently, a series poly-nuclear copper complexes based well-known hydroxyl-bridged dinuclear  $[\text{Cu}(\mu_2\text{-OH})_2\text{Cu}]$  units had been step-like synthesized and characterized: monomer, dimer (also considered as chair-like type tetra-copper complex) and trimer of dicopper  $[\text{Cu}(\text{OH})_2\text{Cu}]$  cluster [18,19].

However, the chair-like type hydroxyl-bridged tetra-copper compounds have been prepared are scant and all are symmetric cluster [20,21]. Herein, we report a new asymmetric chair-like type tetra-nuclear copper complex,  $[\text{Cu}_4(\text{bpy})_4(\text{OH})_4(\text{H}_2\text{O})(\text{BTC})]\text{NO}_3 \cdot 8\text{H}_2\text{O}$  (**1**, bpy = 2,2'-bipyridine and  $\text{H}_3\text{BTC}$  = benzene tricarboxylic acid), which can be readily ambient synthesized and further characterized by powder X-ray diffraction (PXRD), elemental

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analysis (EA), thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC).

## 2. Experimental

### 2.1. Materials and physical methods

Chemical reagents were commercially purchased and used without further purification. The C, H and N elemental analyses were carried out with a Vario EL elemental analyzer. The Fourier Transform infrared (FT-IR) spectrum was recorded on a Shimadzu IRPrestige-21 spectrometer using KBr pellets. Thermogravimetric measurements were carried out in a nitrogen stream with a Netzsch STA409PC apparatus with a heating rate of 10 °C min<sup>-1</sup>. Diffraction studies on single crystals were conducted with a Bruker SMART APEX-II CCD diffractometer equipped with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 296 K using an  $\omega$ -2 $\theta$  scan mode. Powder X-ray diffraction (PXRD) data were collected on a Rigaku D/max 2200 diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 1.5418$  Å). Variable-temperature magnetic susceptibility measurements were performed using a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer.

### 2.2. Synthesis of [Cu<sub>4</sub>(bpy)<sub>4</sub>(OH)<sub>4</sub>(H<sub>2</sub>O)(BTC)]NO<sub>3</sub>·8H<sub>2</sub>O

A mixture of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (238 mg, 1 mmol), bpy (96 mg, 0.5 mmol) in 15 mL EtOH, was stirred 30 mins, and then a solution of H<sub>3</sub>BTC (0.2 mmol, 0.034 g) in aqueous ammonia (25%, 10 mL) were added dropwise. Filtered and kept the deep blue solution in the dark at room temperature for 10 days. Blue block-shaped crystals were obtained in 38% yield (based on Cu). Elemental analysis (%): Calcd. for C<sub>49</sub>H<sub>57</sub>Cu<sub>4</sub>N<sub>9</sub>O<sub>22</sub>: C, 42.70; H, 4.17; N, 9.15. Found: C, 42.83; H, 4.13; N, 9.09.

### 2.3. X-ray crystallographic structure determination

The X-ray diffraction data was collected using a Bruker APEX-II CCD diffractometer with graphite-monochromated Mo-K $\alpha$  radiation. Structure was solved by direct methods using SHELXTL and refined by full-matrix least-squares on  $F^2$  using SHELX-97 programs [22,23]. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed by geometrical considerations and were added to the structure factor calculation. However, although the single crystal structure was solved in the chiral P1 space group, the Flack value of 0.389(9) indicated the **1** should be the racemic twinning crystal. The crystallographic data of compound **1** are shown in Table 1. Selected bond angles and lengths are listed in Table 2.

## 3. Results and discussion

### 3.1. Description of the structure

Single crystal X-ray analysis reveals that **1** crystallizes in the triclinic system with the chiral P1 (No.1) spacegroup. The asymmetric unit is composed of [Cu<sub>4</sub>(bpy)<sub>4</sub>(OH)<sub>4</sub>(H<sub>2</sub>O)(BTC)]<sup>+</sup> cation, one NO<sub>3</sub><sup>-</sup> anion as counter-ion, along with eight lattice water molecules. The identical chair-like [Cu<sub>4</sub>( $\mu_3$ -OH)<sub>2</sub>( $\mu_2$ -OH)<sub>2</sub>] core has been observed in the reported analogues compounds. As depicted in Fig. 1, both centre Cu(II) ions (Cu1 and Cu3) are square pyramidal coordination spheres with two N atoms of bpy, two O atom from -OH in the equatorial plane while one O atom from  $\mu_3$ -OH occupied the axial position. The distances of Cu-N are about 2 Å, while the range of Cu-O bond lengths are 1.904(3)–2.434(4) Å for Cu1 or

**Table 1**

Crystallographic data and structure refinement of [Cu<sub>4</sub>(bpy)<sub>4</sub>(OH)<sub>4</sub>(H<sub>2</sub>O)(BTC)]NO<sub>3</sub>·8H<sub>2</sub>O.

Empirical formula	C <sub>49</sub> H <sub>57</sub> Cu <sub>4</sub> N <sub>9</sub> O <sub>22</sub>
Formula weight	1378.24
Temperature	296(2)
Crystal system	Triclinic
space_group	P1
Unit cell dimensions	$a = 10.3896(4)$ Å $b = 12.5152(5)$ Å $c = 12.8954(5)$ Å $\alpha = 115.252(2)^\circ$ $\beta = 99.823(2)^\circ$ $\gamma = 104.892(2)^\circ$
Volume/Å <sup>3</sup>	1388.22(9)
Z	1
$D_{\text{calc}}/\text{g}\cdot\text{cm}^{-3}$	1.649
Absorpt coefficient/mm <sup>-1</sup>	1.600
$F(000)$	706
$R_{\text{int}}$	0.022
Reflections collected	22888
Independent reflections	10963
Observed reflections [ $I > 2\sigma(I)$ ]	10023
Refinement method	Full-matrix least-squares on $F^2$
Number of parameters	753
Goodness-of-fit on $F^2$	1.041
Final R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0326$ , $wR_2 = 0.0910$
R indices (all data)	$R_1 = 0.0366$ , $wR_2 = 0.0937$
$\Delta\rho_{\text{max}}$ (e·Å <sup>-3</sup> )	0.541
$\Delta\rho_{\text{min}}$ (e·Å <sup>-3</sup> )	-0.585

**Table 2**

Selected bond lengths (Å) and angles (°) in [Cu<sub>4</sub>(bpy)<sub>4</sub>(OH)<sub>4</sub>(H<sub>2</sub>O)(BTC)]NO<sub>3</sub>·8H<sub>2</sub>O<sup>a</sup>.

Cu1–O1	1.905(3)	Cu1–O2	1.962(4)
Cu1–N1	2.013(4)	Cu1–N2	1.987(5)
Cu1–O3	2.434(4)		
Cu2–O1	1.909(4)	Cu2–O1W	2.230(4)
Cu2–N3	2.014(5)	Cu2–N4	2.009(4)
Cu2–O2	1.985(3)		
Cu3–O2	2.288(4)	Cu3–O3	1.943(4)
Cu3–N5	2.018(5)	Cu3–N6	2.025(4)
Cu3–O4	1.927(4)		
Cu4–O3	1.958(3)	Cu4–O4	1.928(4)
Cu4–N7	2.010(4)	Cu4–N8	1.999(5)
Cu4–O5	2.239(4)		
Cu1–O1–Cu2	99.29(17)	Cu1–O2–Cu2	94.85(15)
Cu1–O2–Cu3	99.63(17)	Cu1–O3–Cu3	95.41(16)
Cu1–O3–Cu4	105.82(15)	Cu2–O2–Cu3	109.14(16)
Cu3–O3–Cu4	96.01(16)	Cu3–O4–Cu4	97.35(17)

<sup>a</sup> The numbering scheme is shown in Fig. 1.

1.934(3)–2.288(4) Å for Cu3, respectively. The equatorial plane of both terminal Cu(II) ions (Cu2 and Cu4) are also coordinated by two N atoms of bpy, two O atoms of  $\mu$ -OH. The Cu–O bond lengths are in the region of 1.928(4)–1.958(3) Å. It is intriguing that the axial terminal ligands of both terminal Cu(II) are different: an aqua for Cu2 with the Cu2–O1W length of 2.227(4) Å, while BTC<sup>3-</sup> for Cu4 with the Cu4–O5 length of 2.237(4) Å. In contrast to the reported orthodox Cu<sub>4</sub>(OH)<sub>4</sub> core analogues ended with same terminal coordination groups in the central symmetric P-1 space group, the result indicates that [Cu<sub>4</sub>(bpy)<sub>4</sub>(OH)<sub>4</sub>(H<sub>2</sub>O)(BTC)]NO<sub>3</sub>·8H<sub>2</sub>O (**1**) is a rare asymmetric example of hydroxyl-bridged chair-like tetra-copper complex in chiral P1 space group.

As the Zheng's reported, the hydroxyl-bridged chair-like Cu<sub>4</sub>(OH)<sub>4</sub> core could be considered as the *trans*-assembly dimerization of two identical dinuclear [Cu( $\mu_2$ -OH)<sub>2</sub>Cu] motifs via head-to-tail connection through the out-of-plane Cu–O(H) bonds [18,19] rather than the cubane Cu<sub>4</sub>(OH)<sub>4</sub> core *cis*-assembly via face-to-face connection [24,25]. Therefore, the corresponding parameters are identical for the symmetric dimmerized orthodox Cu<sub>4</sub>(OH)<sub>4</sub> core

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