A Novel Asymmetric Chair-like **Hydroxyl**-bridged Tetra-copper Compound: Synthesis, Supramolecular Structure and Magnetic Property

Xiao-Feng Wang^{a,*}, Ke-Jie Du^a, Hong-Qing Wang^a, Xue-Li Zhang^{b,*} and Chang-Ming Nie^a

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 (H_3BTC). 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 H_2O and one BTC^{3-} occupied each terminal coordinated site. In addition, the magnetic property has been investigated.

Keywords: Copper • Asymmetric tetranuclear cluster • X-ray diffraction • Thermal stability •

Magnetic property

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 polynuclear 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 π - π 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 (μ_2 - or μ_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 H_3BTC = benzene tricarboxylic acid), which can be readily ambient synthesized and further characterized by powder X-ray diffraction (PXRD), elemental 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⁻¹. Diffraction studies on single crystals were conducted with a Bruker SMART APEX-II CCD diffractometer equipped with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 296 K using an ω -2 θ scan mode. Powder X-ray diffraction (PXRD) data were collected on a Rigaku D/max 2200 diffractometer with Cu-K α 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 [Cu₄(bpy)₄(OH)₄(H₂O)(BTC)]NO₃·8H₂O

A mixture of Cu(NO₃)₂·3H₂O (238 mg, 1 mmol), bpy (96 mg, 0.5 mmol) in 15 mL EtOH, was stirred 30 mins, and then a solution of H₃BTC (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 C₄₉H₅₇Cu₄N₉O₂₂: 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 α 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 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 $[\text{Cu}_4(\text{bpy})_4(\text{OH})_4(\text{H}_2\text{O})(\text{BTC})]\text{NO}_3 \cdot 8\text{H}_2\text{O}$ 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 $[\text{Cu}_4(\text{bpy})_4(\text{OH})_4(\text{H}_2\text{O})(\text{BTC})]^+$ cation, one NO_3^- anion as counter-ion, along with eight lattice water molecules. The identical chair-like $[\text{Cu}_4(\mu_3\text{-OH})_2(\mu_2\text{-OH})_2]$ core has been observed in the reported analogues compounds. As depicted in Figure 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 $\mu_3\text{-OH}$ 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 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 $\mu\text{-OH}$. 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^{3-} for Cu4 with the Cu4-O5 length of 2.237(4) Å. In contrast to the reported orthodox $\text{Cu}_4(\text{OH})_4$ core analogues ended with same terminal coordination groups in the central symmetric P-1 space group, the result indicates that $[\text{Cu}_4(\text{bpy})_4(\text{OH})_4(\text{H}_2\text{O})(\text{BTC})]\text{NO}_3 \cdot 8\text{H}_2\text{O}$ (**1**) 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 $\text{Cu}_4(\text{OH})_4$ core could be considered as the *trans*-assembly dimerization of two identical dinuclear $[\text{Cu}(\mu_2\text{-OH})_2\text{Cu}]$ motifs via head-to-tail connection through the out-of-plane Cu-O(H) bonds [18,19] rather than the cubane $\text{Cu}_4(\text{OH})_4$ core *cis*-assembly via face-to-face connection[24,25]. Therefore, the corresponding parameters are identical for the symmetric dimmerized orthodox $\text{Cu}_4(\text{OH})_4$ core analogues. However, the parameters of $[\text{Cu}(\mu_2\text{-OH})_2\text{Cu}]$ motifs in compound **1** are dissimilar. The distances of Cu1...Cu2 in one $[\text{Cu}(\mu_2\text{-OH})_2\text{Cu}]$ motif is 2.907 Å, while the Cu3...Cu4 in another Cu_2 -motif is 2.899 Å. Moreover, it is interesting that the pairs angles of Cu-O-Cu in the two

$[\text{Cu}(\mu_2\text{-OH})_2\text{Cu}]$ motifs of the asymmetric $[\text{Cu}_4(\text{bpy})_4(\text{OH})_4(\text{H}_2\text{O})(\text{BTC})]$ unit are also slight different, the angles of Cu1-O1-Cu2 and Cu1-O2-Cu2 are 99.33(17) and 94.81(15)° in one $[\text{Cu}(\mu_2\text{-OH})_2\text{Cu}]$ motif, or those of Cu3-O3-Cu4 and Cu3-O4-Cu4 are 96.06(17) and 97.32(17)° in another Cu_2 -motif, respectively. The key reason might be the structural distortion derived from the both terminal Cu(II) coordinated with different spatial size axial ligands (H_2O or BTC^{3-}) to form an asymmetric chair-like $[(\text{H}_2\text{O})\text{Cu}_4(\text{OH})_4(\text{BTC})]$ core.

The full deprotoned BTC^{3-} , plays not only a mono-dentate co-ligand to coordinate Cu4 via one carboxyl O atom, but also as acceptors through O atoms form uncoordinated carboxylate group to connect the hydrogen bonds with coordinated $\mu\text{-OH}$ and water molecule. As depicted in Figure 2a, the O6 of the carboxylate from BTC^{3-} forms one intramolecular hydrogen bond with the coordinated $\mu_3\text{-OH}$ (the distance of 2.834 Å and the $\angle\text{O3-H3A}\cdots\text{O6} = 118.7^\circ$). On other hand, the one coordinated -OH and one aqua form two intermolecular hydrogen bonds with one carboxyl segment from a adjacent Cu_4 -units (the distance of 2.707 Å and the $\angle\text{O1W-H1Wb}\cdots\text{O7b} = 165.7^\circ$, or the distance of 2.814 Å and the $\angle\text{O1-H1A}\cdots\text{O8b} = 117.2^\circ$, respectively), while another coordinated $\mu_2\text{-OH}$ and $\mu_3\text{-OH}$ form two intermolecular hydrogen bonds with one carboxyl segment from another adjacent Cu_4 -units (the distance of 2.750 Å and the $\angle\text{O4A-H4A}\cdots\text{O9a} = 126.0^\circ$, or the distance of 2.915 Å and the $\angle\text{O2-H2A}\cdots\text{O10a} = 160.6^\circ$, respectively). Through the hydrogen bonds, the $[(\text{H}_2\text{O})\text{Cu}_4(\text{OH})_4(\text{BTC})]^+$ cores were constructed a cation supramolecular layer with hexagonal hollows, which are filled with NO_3^- counter-ions and eight lattice water molecules. Considered the coordination and H-bonds, each $\text{Cu}_4(\text{OH})_4(\text{bpy})_4$ segment and BTC^{3-} can be both considered as the 3-connected nodes. Therefore, compound **1** can be simplified into the two-dimensional honeycomb networks with (6, 3) topology (Fig. 3). Moreover, the pyridyl fragment of bpy molecules are aslant anchored on both outsides of the supramolecular layer. The resulting layers are further packed in slanted AB style interactive stacking to construct a 3-D supramolecular architecture through the interdependently embedded bpy rings, which are resulted from the strong interlayer $\pi\text{-}\pi$ stacking interactions between the adjacent bpy planes with the closest with the mean stacking distance of 3.46-3.65 Å.

3.2 Thermal Analysis

Thermogravimetric analyses for $[\text{Cu}_4(\text{bpy})_4(\text{OH})_4(\text{H}_2\text{O})(\text{BTC})]\text{NO}_3 \cdot 8\text{H}_2\text{O}$ has been measured under a flow of N_2 gas from room temperature to 750°C at a heating rate of $10^\circ\text{C}/\text{min}$. Differential scanning calorimetry (DSC) behavior presents one broad absorption heat peak during 30 to 160°C , and two weak absorption peaks at 190 and 217°C , respectively, which indicate the corresponding physical (dehydration) or chemical reactions (decomposing). The TGA of the as-synthesized sample showed gradual loss of $12.8\text{ wt\%}$ (calcd: 11.76%) from below 160°C which belongs to the loss of eight lattice and one coordinated water molecules per $[\text{Cu}_4(\text{bpy})_4(\text{OH})_4(\text{H}_2\text{O})(\text{BTC})]\text{NO}_3 \cdot 8\text{H}_2\text{O}$ formula unit, and then the weight was rapidly lost (42.1%) with further raising the temperature to 310°C which matches the expected value of $45.3\text{ wt\%}$ for the removal of four bpy molecules. Upon 500°C the final decomposed residue presumably is $\text{Cu}_2(\text{OH})_2\text{CO}_3$ with the $34.3\text{ wt\%}$ remaining mass (calcd: 32.1% based on Cu).

3.3 Magnetic Properties

Variable-temperature magnetic properties of $[\text{Cu}_4(\text{bpy})_4(\text{OH})_4(\text{H}_2\text{O})(\text{BTC})]\text{NO}_3 \cdot 8\text{H}_2\text{O}$ have been studied with a magnetic field of 1000 Oe under normal pressure in the region of $2\text{--}300\text{ K}$. As shown in Figure 3, the magnetic behavior of title compound is illustrated in the form of χ_M vs. T and $\chi_M T$ vs. T plots. At room temperature, the $\chi_M T$ value of $1.59\text{ cm}^3\text{mol}^{-1}\text{K}$ is slightly higher than the expected value of $1.50\text{ cm}^3\text{mol}^{-1}\text{K}$ for four uncoupled $S = 1/2$ Cu(II) centers with a g value of 2.0 [26]. Upon cooling to 12 K , the $\chi_M T$ values decrease gradually to $1.408\text{ cm}^3\text{mol}^{-1}\text{K}$, along with a slight floating of $1.418\text{ cm}^3\text{mol}^{-1}\text{K}$ at 11 K (insert in Figure 3), and then sharply drop down to a minimum of $1.15\text{ cm}^3\text{mol}^{-1}\text{K}$ at 2 K . The $1/\chi_M$ versus T plot can be well-fitted by the Curie–Weiss law above 30 K , giving a Weiss constant of $-21.1(1)\text{ K}$ (see Figure S5). The negative θ value indicates the dominant antiferromagnetic exchanges within $\text{Cu}_4(\text{OH})_4$ cluster.

Besides the long distance of $\text{Cu}\cdots\text{Cu}$ within H-bond layer (10.87 and $11.21\text{ \AA}$) or $\text{Cu}\cdots\text{Cu}$ separated by $\pi\text{--}\pi$ stacking ($11.83\text{ \AA}$), the structural distortion (as mentioned above and see Figure 4) leads to the magnetic coupling parameters in the isotropic asymmetric Cu_4 -unit are still too complicated to be evaluated. It has been assumed the absence of magnetic interaction between the terminal Cu(II) ions ($\text{Cu}2\cdots\text{Cu}4$ above $5.55\text{ \AA}$) and the long sides of butterfly Cu_4 -unit ($\text{Cu}1\cdots\text{Cu}4$ and $\text{Cu}2\cdots\text{Cu}3$) due to the relatively larger separation. Hence, the experimental $\chi_M T$ data had to be fitted using the modified analytical express equation being used in study of the

zigzag linear tetranuclear system [18, 27], which is derived from Heisenberg-Dirac-vanVleck (HDVV) spin Hamiltonian model $\hat{H} = -2J_a(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_3 \cdot \hat{S}_4) - 2J_b\hat{S}_1 \cdot \hat{S}_3$. The J_a or J_b represent the distinct superexchange coupling between two Cu(II) atoms of intra- or inter-dimer $[\text{Cu}(\mu_2\text{-OH})_2\text{Cu}]$ motifs, respectively. Taking into account the TIP term, the best fit parameters to the magnetic data were found to be $J_a = -0.27 \text{ cm}^{-1}$, $J_b = 0.09 \text{ cm}^{-1}$, $g = 1.96$ and $\text{TIP} = 4.70 \times 10^{-4}$, which are different from that of hydroxo-bridged symmetric compounds, with positive J_a and J_b that indicated the ferromagnetic coupling within $\text{Cu}_4(\text{OH})_4$ core [18].

4. Conclusions

In conclusion, we have successfully prepared an unprecedented tetra-copper compound based on asymmetric chair-like hydroxo-bridged $[\text{Cu}_4(\text{bpy})_4(\text{OH})_4(\text{H}_2\text{O})(\text{BTC})]$ cores, where the terminal ligands are coordinated aqua and deprotonated BTC^{3-} , respectively. Through the hydrogen bonds between the BTC^{3-} and coordination $-\text{OH}/\text{H}_2\text{O}$, the compound **1** forms the honeycomb supramolecular layer. The overall variational-temperature magnetic behavior of this compound indicates the predominant antiferromagnetic coupling inside the chair-like $\text{Cu}_4(\text{OH})_4$ magnetic unit.

5. Acknowledgements

This work was financially supported by the National Science Foundation of China (Grant No. 11375082, 11275090 and 11175080) and the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry (SRF for ROCS, SEM to Dr. X. W.).

Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC No 1486080. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK: fax: (+44) 01223-336-033; e-mail: deposit@ccdc.cam.ac.

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/>

References

- [1] C. J. Brown, F. D. Toste, R. G. Bergman, K. N. Raymond, *Chem. Rev.* **2015**, *115*, 3012–3035.
- [2] H. -B. Xu, X. -M. Chen, Q. -S. Zhang, L. -Y. Zhang, Z. -N. Chen, *Chem. Commun.* **2009**, 7318–7320.
- [3] X. -F. Wang, X. -L. Qi, F. -N. Shi, J. Rocha, *J. Mol. Struct.* **2011**, *1004*, 26–30.
- [4] M. Kiguchi, J. Inatomi, Y. Takahashi, R. Tanaka, T. Osuga, T. Murase, M. Fujita, T. Tada, S. Watanabe, *Angew. Chem. Int. Ed.* **2013**, *52*, 6202–6205.
- [5] C. M. Zaleski, S. Tricard, E. C. Depperman, W. Wernsdorfer, T. Mallah, M. L. Kirk, V. L. Pecoraro, *Inorg. Chem.* **2011**, *50*, 11348–11352.
- [6] W.-X. Zhang, Y.-Y. Yang, S.-B. Zai, S. W. Ng, X.-M. Chen, *Eur. J. Inorg. Chem.* **2008**, 679–685.
- [7] B. Berkoff, K. Griffiths, A. Abdul-Sada, G. J. Tizzard, S. J. Coles, A. Escuer, G. E. Kostakis, *Dalton Trans.* **2015**, *44*, 12788–12795.
- [8] T. Liu, Y.-J. Zhang, Z.-M. Wang, S. Gao, *J. Am. Chem. Soc.* **2008**, *130*, 10500–10501.
- [9] A. J. Tasiopoulos, W. Wernsdorfer, K. A. Abboud, G. Christou, *Angew. Chem. Int. Ed.* **2004**, *43*, 6338–6342.
- [10] D. I. Alexandropoulos, T. N. Nguyen, L. Cunha-Silva, T. F. Zafiropoulos, A. Escuer, G. Christou, T. C. Stamatatos, *Inorg. Chem.* **2013**, *52*, 1179–1183.
- [11] P.-P. Yang, X.-F. Gao, H.-B. Song, S. Zhang, X.-L. Mei, L.-C. Li, D.-Z. Liao, *Inorg. Chem.* **2011**, *50*, 720–722.
- [12] M.-H. Zeng, M.-X. Yao, H. Liang, W.-X. Zhang, X.-M. Chen, *Angew. Chem. Int. Ed.* **2007**, *46*, 1832–1835.
- [13] Y.-Z. Zheng, M. Speldrich, H. Schilder, X.-M. Chen, P. Kögerler, *Dalton Trans.* **2010**, *39*, 10827–10829.
- [14] F. He, M.-L. Tong, X.-L. Yu, X.-M. Chen, *Inorg. Chem.* **2005**, *44*, 559–565.
- [15] A. J. Tasiopoulos, W. Wernsdorfer, K. A. Abboud, G. Christou, *Polyhedron* **2005**, *24*, 2505–2512.
- [16] R. Dey, B. Bhattacharya, E. Colacio, D. Ghoshal, *Dalton Trans.* **2013**, *42*, 2094–2016.
- [17] A. Hazra, S. Bonakala, K. K. Bejagam, S. Balasubramanian, T. K. Maji, *Chem. Eur. J.* **2016**, *22*, 7792–7799.
- [18] Y. -Q. Zheng, D. -Y. Cheng, B. -B. Liu, W. -X. Huang, *Dalton Trans.* **2011**, *40*, 277–286.
- [19] X. Li, D.-Y. Cheng, J. -L. Lin, Z.-F. Li, Y. -Q. Zheng, *Cryst. Growth Des.* **2008**, *8*, 2853–2861.
- [20] S. Balboa, R. Carballo, A. Castineiras, J. M. Gonzalez-Perez, J. Niclos-Gutierrez, *Polyhedron* **2008**, *27*, 2921–2930.
- [21] J. -H. Luo, L. Chen, C. -Y. Yue, F. -L. Jiang, M. -C. Hong, *Jiegou Huaxue (Chin. J. Struct. Chem.)* **2007**, *26*, 654–658.
- [22] G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, Göttingen, Germany, **1997**.
- [23] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, Göttingen, Germany, **1997**.
- [24] J. Sletten, A. Sørensen, M. Julve, Y. Journaux, *Inorg. Chem.* **1990**, *29*, 5054–5058.
- [25] R. Carballo, B. Covelo, E. M. Vazquez-Lopez, E. Garcia-Martinez, A. Castineiras, *Z. Anorg. Allg. Chem.* **2002**, *628*, 907–908.
- [26] S. R. Breeze, S. Wang, J. E. Greedan, N. P. Raju, *J. Chem. Soc., Dalton Trans.* **1998**, 2327–2334.
- [27] C. Zeng, Y. Zang, G. Wang, A. Dai, *Acta Chim. Sinica*, **1990**, *48*, 678–685.

The Tables and Figures Captions

Table 1

Crystallographic data and structure refinement of $[\text{Cu}_4(\text{bpy})_4(\text{OH})_4(\text{H}_2\text{O})(\text{BTC})]\text{NO}_3 \cdot 8\text{H}_2\text{O}$.

Table 2

Selected bond lengths ($\text{\AA}$) and angles ($^\circ$) in $[\text{Cu}_4(\text{bpy})_4(\text{OH})_4(\text{H}_2\text{O})(\text{BTC})]\text{NO}_3 \cdot 8\text{H}_2\text{O}^{\text{a}}$.

Figure 1

The coordination environment of Cu(II) centers in the asymmetric $\text{Cu}_4(\text{OH})_4$ cation unit. Thermal ellipsoids are drawn at the 30% probability level. H atoms of bpy and BTC are omitted for clarity.

Figure 2

(a) The H bonding motif of the $\text{Cu}_4(\text{bpy})_4(\text{OH})_4$ unit (the segments of bpy rings are omitted for clarity) and (b) The π - π stacking interactions of bpy rings.

Figure 3

(a) The planform view of the honeycomb-like H-bond layer structure with cavities (marked with yellow oval); (b) $\text{Cu}_4(\text{bpy})_4(\text{OH})_4$ or BTC^{3-} respectively as two different three connected H-bond nodes; (c) the (6,3) topological net, (d) The side view of the H-bond layer and (e) the space-filled presentation of the slide AB style packing of adjacent layers.

Figure 4

The TGA and DSC curves for $[\text{Cu}_4(\text{bpy})_4(\text{OH})_4(\text{H}_2\text{O})(\text{BTC})]\text{NO}_3 \cdot 8\text{H}_2\text{O}$.

Figure 5

The $\chi_{\text{M}}T$ ($\circ$) and χ_{M} ($\square$) vs T plots for **1** (insert the low temperature region). The red solid lines are the fits of the data.

Figure 6

Coupling scheme for the tetranuclear $\text{Cu}_4(\text{OH})_4$ unit.

Table 1. Crystallographic data for **1**.

Empirical formula	C ₄₉ H ₅₇ Cu ₄ N ₉ O ₂₂
Formula weight	1378.24
Temperature	296(2)
Crystal system	Triclinic
space_group	<i>P</i> 1
Unit cell dimensions	<i>a</i> = 10.3896(4) Å <i>b</i> = 12.5152(5) Å <i>c</i> = 12.8954(5) <i>α</i> = 115.252(2) ° <i>β</i> = 99.823(2) ° <i>γ</i> = 104.892(2) °
Volume/ Å ³	1388.22(9)
<i>Z</i>	1
<i>D</i> _{calc.} / g·cm ⁻³	1.649
Absorpt coefficient / mm ⁻¹	1.600
<i>F</i> (000)	706
<i>R</i> _{int}	0.022
Reflections collected	22888
Independent reflections	10963
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	10023
Refinement method	Full-matrix least-squares on <i>F</i> ²
Number of parameters	753
Goodness-of-fit on <i>F</i> ²	1.041
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0326, <i>wR</i> ₂ = 0.0910
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0366, <i>wR</i> ₂ = 0.0937
Δρ _{max} (e·Å ⁻³)	0.541
Δρ _{min} (e·Å ⁻³)	-0.585

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

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)

a) The numbering scheme is shown in Figure 1.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

A copper complex based on the asymmetric chair-like hydroxo-bridged tetra-copper $[\text{Cu}_4(\text{bpy})_4(\text{OH})_4(\text{H}_2\text{O})(\text{BTC})]$ units has been synthesized and characterized. In addition, the magnetic property of the compound was investigated.

Xiao-Feng Wang,* Ke-Jie Du,
Hong-Qing Wang, Xue-Li Zhang*
and Chang-Ming Nie

**An Novel Asymmetric
Chair-like Hydroxyl-bridged
Tetra-copper Compound:
Synthesis, Supramolecular
Structure and Magnetic
Property**