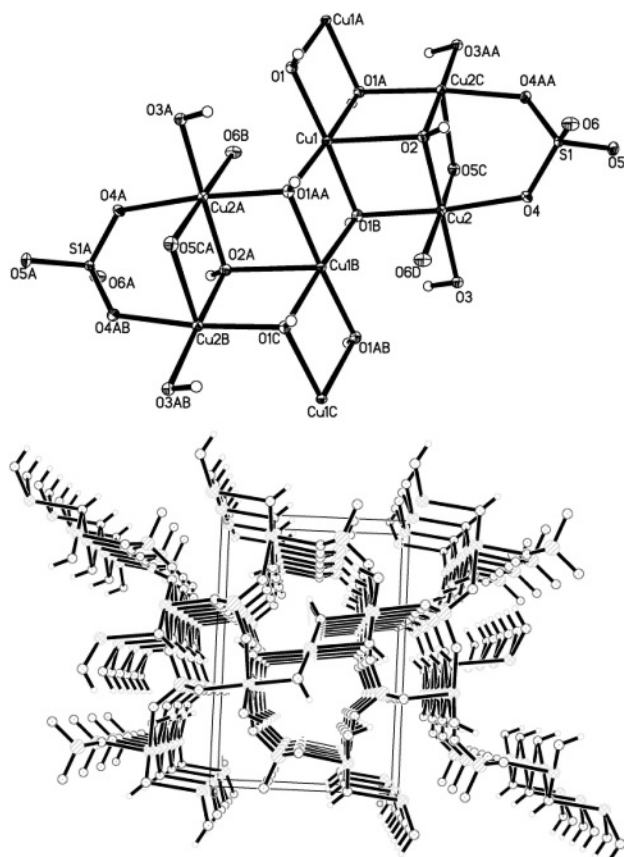


Crystal structure of catena- $(\mu_2$ -hydroxo)-tris(μ_3 -hydroxo)-(μ_6 -sulfato)-tri-copper(II), $\text{Cu}_3\text{H}_4\text{O}_8\text{S}$

Ling Huang*, Duan Qiu and Bo Zhao

College of Pharmaceutical and Chemical Engineering, Taizhou University, Linhai 317000, Zhejiang Province, P. R. China

Received April 27, 2012, accepted July 16, 2012, available online November 09, 2012, CSD no. 710086



Abstract

$\text{Cu}_3\text{H}_4\text{O}_8\text{S}$, orthorhombic, $Pnma$ (no. 62), $a = 8.283(1)$ Å, $b = 6.063(1)$ Å, $c = 12.046(2)$ Å, $V = 604.9$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0234$, $wR_{\text{ref}}(F^2) = 0.0649$, $T = 296$ K.

Table 1. Data collection and handling.

Crystal:	green blocks, size 0.40×0.45×0.50 mm
Wavelength:	Mo K_{α} radiation (0.71073 Å)
μ :	108.01 cm ⁻¹
Diffractometer, scan mode:	Bruker AXS SMART APEX II, φ and ω
$2\theta_{\text{max}}$:	54.98°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	5026, 761
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 678
$N(\text{param})_{\text{refined}}$:	71
Programs:	SHELXTL [10], SMART [11], SAINT [12]

Source of material

Except of the ligand 1,3-benzimidazole-2-sulfonic acid, which was prepared according to the literature procedure, all chemicals and solvents were of analytical grade and used as received. A

mixture of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.0968 g, 0.5 mmol), 1,3-benzimidazole-2-sulfonic acid (0.0985 g, 0.5 mmol), NaOH (0.0200 g, 0.5 mmol) and 12 mL EtOH- H_2O ($v:v = 1:1$) was sealed in a Parr Teflon-lined stainless steel vessel, and then heated at 130 °C for 5 days. Green crystals suitable for X-ray analysis were gained (yield 32% based on Cu).

IR (KBr pellet, cm⁻¹) 3563.2 s; 3378.1 s; 3260.4 s; 1534.3 w; 1424.3 w; 1090.7 br; 980.7 s; 871.8 br; 777.3 s; 734.8 s; 623.9 s; 600.8 s; 472.5 s; 426.2 s.

Experimental details

All hydroxyl H atoms were located in different Fourier maps and refined isotropically with $\text{O}-\text{H} = 0.831(9) - 0.841(9)$ Å [$U_{\text{iso}}(\text{H}) = 1.5 U_{\text{iso}}(\text{O})$].

Discussion

Polynuclear copper(II) complexes currently attracted more and more attention in the field of supramolecular chemistry and material science. In these coordination cluster, 0-D, 1-D, 2-D and 3-D frameworks have been obtained, which are of great interest in the intriguing topologies and frameworks, as well as potential applications in molecule-based magnets, catalytic materials, electrochemistry and modeling multimetallic active sites of metalloenzymes [1-3]. In the effort to design and assemble diverse multinuclear copper(II) clusters, researcher developed many synthetic strategies, such as self-assembling in the presence of simple bridging ligands, introducing linkage of Ba^{2+} or other metal ions, and polymerization of bi- or low-nuclear Cu(II) precursor [4]. It is generally believed that a novel structure of multi- or high- nuclear copper cluster can also be formed by the self-assembly of simple structure ligands with under certain conditions, e.g. Abedin *et al.* [4] have synthesized the first Cu_{36} high-nuclear copper cluster of $[\text{Cu}_{36}(\text{dpocco-4H})_{12}(\mu^3\text{-OH})_8](\text{CH}_3\text{COO})_{16} \cdot x\text{H}_2\text{O}$ by self-assembly of dpocco ligands and cupric acetate. Murugesu [5] also synthesized the Cu_{36} high-nuclear copper cluster $[\text{Cu}_{36}(\text{3-OH})_{32}(\mu\text{-OR})_8\text{Cl}_6(\text{ndpa})_8(\text{H}_2\text{O})_5\{\text{KCl}_6\}]_{32}$ ($\text{R} = \text{H}$ or Me) from tripodand $\text{N}(\text{CH}_2\text{COOH})(\text{CH}_2\text{CH}_2\text{COOH})_2$ (H_3ndpa). Using the background given above, we studied multinuclear copper(II) complexes from simply ligands, aimed at exposing their chemical behavior and exploiting new synthesis method. In this paper, we report synthesis and structure of the copper(II) polymer constructed by bridging ligands of $-\text{OH}$ and SO_4^{2-} . The complex consists of two types of coordinated Cu atoms. Four O1 atoms from crystallographically distinct μ_3 -OH bridges are coordinated to the central Cu1 atom and form a basal plane, with the square pyramidal geometry of the central ion elongated along the $\text{Cu1}-\text{O2}$ axis, giving the distances of $\text{Cu1}-\text{O1} = 1.976(2)$ and $2.005(2)$ Å, and $\text{Cu1}-\text{O2} = 2.312(3)$ Å, respectively. Cu2 is coordinated by three hydroxyl O atoms and three sulfate O atoms in an octahedral geometry. The Cu2-O distances between 1.929(2) -

* Correspondence author (e-mail: huangltzu@163.com)

2.423(2) Å are indicative of a distorted octahedron around Cu2. In fact, the complex containing two different hydroxyl bridges of μ_2 -OH and μ_3 -OH, which resulting in a one-dimensional chain constructed by [Cu₄O₄] clusters and [Cu₃O₃] clusters. As we can see, four O atoms in [Cu₄O₄] cluster are all from μ_3 -OH bridges, while [Cu₃O₃] cluster possesses one μ_2 -OH bridge and three μ_3 -OH bridges. If we ignore the linkage of O3 atoms, they are chair-like (figure, top) structural topologies [6, 7]. The neighboring Cu1...Cu1 distance for **1** is 3.0328(5) Å, which is comparable with that observed in other tetranuclear chair-like [Cu₄O₄] compounds [8, 9]. It's worth noting that there are two different coordination modes of O atoms in the SO₄²⁻: two κ -O atoms (O4, O4A), two μ_2 -O atoms (O5, O6). Furthermore, these μ_2 -O atoms of SO₄²⁻ connected neighboring Cu2 atom to form two-dimensional network (figure, bottom), given the distance Cu2...Cu2 = 2.9956(8) Å.

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
O(3)	4 <i>c</i>	0.2020(3)	3/4	0.2789(2)	0.013(1)	0.013(2)	0.013(1)	0	0.001(1)	0
Cu(1)	4 <i>c</i>	0.49518(6)	1/4	0.49890(4)	0.0127(3)	0.0078(3)	0.0121(3)	0	−0.0032(2)	0
O(1)	8 <i>d</i>	0.5470(3)	0.0066(3)	0.6020(2)	0.012(1)	0.015(1)	0.0103(9)	−0.0005(8)	0.0005(9)	0.0011(7)
O(2)	4 <i>c</i>	0.2183(3)	1/4	0.4750(2)	0.013(1)	0.013(2)	0.014(1)	0	0.000(1)	0
Cu(2)	8 <i>d</i>	0.21001(4)	0.49702(5)	0.37434(3)	0.0114(2)	0.0103(3)	0.0149(2)	−0.0003(1)	−0.0024(1)	0.0012(1)
O(4)	8 <i>d</i>	−0.0311(3)	0.4520(4)	0.3481(2)	0.011(1)	0.013(1)	0.022(1)	−0.0031(8)	0.0002(9)	0.0016(9)
S(1)	4 <i>c</i>	−0.1303(1)	1/4	0.36423(7)	0.0087(4)	0.0097(5)	0.0099(4)	0	−0.0001(4)	0
O(5)	4 <i>c</i>	−0.2623(4)	1/4	0.2827(2)	0.013(1)	0.018(2)	0.015(1)	0	−0.005(1)	0
O(6)	4 <i>c</i>	−0.1971(4)	1/4	0.4773(3)	0.025(2)	0.015(2)	0.013(1)	0	0.006(1)	0

Acknowledgments. The authors thank financial support of the Natural Science Foundation of Zhejiang Province (no. Y4110491).

References

- Bouwman, E.; Driessen, W. L.; Reedijk, J.: Model systems for type I Copper Proteins: structures of copper coordination compounds with thioether and azole-containing Ligands. *Coord. Chem. Rev.* **104** (1990) 143-172.
- Horvath, O.; Stevenson, K. L.: Photochemistry of copper(I) complexes. *Coord. Chem. Rev.* **194** (1994) 135-136, 303-324.
- Murugesu, M.; Clérac, R.; Anson, C. E.; Powell, A. K.: Structure and magnetic properties of a giant Cu₄₄^{II} aggregate which packs with a zeotypic superstructure. *Inorg. Chem.* **43** (2004) 7269-7271.
- Abedin, T. S. M.; Thompson, L. K.; Miller, D. O.; Krupicka, E.: Structural and magnetic properties of a self-assembled spheroidal triakontahexanuclear Cu₃₆ Cluster. *Chem. Commun.* (2003) 708-709.
- Murugesu, M.; Clérac, R.; Anson, C. E.; Powell, A. K.: A new type of oxygen bridged Cu₃₆^{II} aggregate formed around a central {KCl₆}₅₂ Unit, *Chem. Commun.* (2004) 1598-1599.
- Chen, J.; Wang, T. W.; Zhang, Z.; Song, Y.; Zhao, Q.; Ni, J.; Wang, Z. L.: A novel 1D coordination polymer based on rhombus [Cu₄O₄] building block: Synthesis, crystal structure and magnetic properties. *J. Mol. Struct.* **794** (2006) 154-159.
- Luo, J. -H.; Chen, L.; Yue C. -Y.; Jiang F. -L.; Hong M. -C.: Synthesis and crystal structure of a 2-D hydrogen-bonded supramolecular network {[Cu₄(OH)₄(2,2'-bpy)₄(bqdc)]·2ClO₄}_n. *Chinese J. Struct. Chem.* **26** (2007) 654-658.
- Koikawa, M.; Yamashita, H.; Tokii, T. Crystal structures and magnetic properties of tetranuclear copper(II) complexes of *N*-(2-hydroxymethylphenyl)salicylideneimine with a defective double-cubane *Inorg. Chim. Acta.* **357** (2004) 2635-2642.
- Dey, M.; Rao, C. P.; Saarenketo, P. K.; Rissanen, K.: Synthesis, structural diversity, inter-conversion and reactivity of Cu(II) complexes of hydroxy-rich molecules. *Inorg. Chem. Comm.* **5** (2002) 380-383.
- Bruker (2000). SHELXTL. Version 6.14. Bruker AXS Inc, Madison, Wisconsin, USA.
- Bruker (2002). SMART for WNT/2000. Version 5.630. Bruker AXS Inc, Madison, Wisconsin, USA.
- Bruker (2003). SAINT-Plus. Version 6.45. Bruker AXS Inc, Madison, Wisconsin, USA.