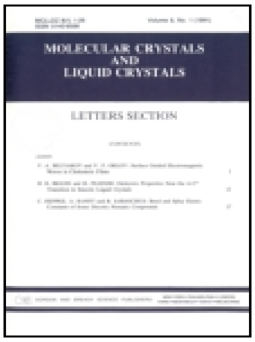

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A novel polyoxometalate-based hybrid materials composed of octamolybdate and hexamuclear copper cluster units

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ABSTRACT
Self-assemble of aqueous solution of the Cu^{2+}/molybdate/glycine system results in $\{[NaCu_6(Gly)_8(H_2O)_2][Mo_8O_{26}Cu(Gly)_2]_2\}_n \cdot n\{NaCu_6(Gly)_8(H_2O)_2\} \cdot n\{Mo_8O_{26}[Cu(Gly)(GlyH)(H_2O)_2]_2\}$ $15nH_2O$ **1**, which exhibits the 0-D + 1-D supramolecular framework and in which the copper atoms show three kinds of coordination models: (1) in quadrilateral geometry, (2) in square-pyramidal geometry, and (3) in distorted octahedral geometry. The space group of the compound is P–1, with the lattice parameters: $\alpha = 89.036(5)^\circ$, $\beta = 89.384(4)^\circ$, $\gamma = 88.337(5)^\circ$, a = 12.559(4) Å, b = 14.441 (4)Å, c = 23.063(6) Å, and Z = 1.

KEYWORDS
Amino acid; coordination models; hexanuclear copper cluster; hybrid material; polyoxometalate

1. Introduction

Polyoxometalates (POMs) have drawn tremendous attention due to their potential applications in many fields [1–5]. Amino acids and their derivatives constitute a large family of versatile ligands with flexible coordination nature and physiological importance [6–9]. The materials containing both the POM clusters and amino acids have promising applications in electrochemistry, biochemistry, and magneto-chemistry, but this area has been investigated rarely [10–15]. Many recent papers have highlighted the rich and subtle chemistry found in hybrid POMs-based compounds functionalized with Cu(II) [12–18]. The rapid progress of exploring copper-containing organic inorganic hybrid materials is driven by their interesting structures and properties [12–20]. Copper-containing compounds with amino ligands are involved in various biological functions, which are the consequence of the redox properties of the copper ion modulated by the amino ligands and of the selection of substrates by the active site [13–15,21–24]. Modulation of the reactivity is obtained mainly by changing the coordination around the copper, such as the coordination number, type, and geometry [25].

There are a few studies on the crystal structures of coordination around the copper [26–32]. Christophe investigated the various types of coordination of amino ligands to copper and the properties of the derived complexes, and the geometries of the complexes are compared and related to their redox potentials [21]. Ternary copper complexes with amino and bpy as ligands display distorted square-pyramidal coordination geometry, and show

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redox active (Cu(II)-Cu(I) couple) [24]. Diego presents an oxovanadium-copper bipyridine hybrid organic-inorganic compound with two different Cu(II) centers, in penta- and hexa-coordination modes [17].

In the copper-containing complexes, the copper centers are in tetra-, penta-, or hexa-coordination modes and forming quadrilateral geometry, square-pyramidal geometry, or octahedral geometry, respectively, presenting various types of coordination [26–32]. However, it is rarely found that the three types coordination coexisted in a complex. It is also rarely found that POM-based compounds are linked up by copper with amino ligands [12–15,32].

Herein, we report a novel compound composed of octamolybdates and coppers with glycine ligand: $\{[NaCu_6(Gly)_8(H_2O)_2][Mo_8O_{26}Cu(Gly)_2]_2\}_n \cdot n\{NaCu_6(Gly)_8(H_2O)_2\} \cdot n\{Mo_8O_{26}[Cu(Gly)(GlyH)(H_2O)_2]_2\} \cdot 15nH_2O$ **1** (Gly = NH_2CH_2COO), which exhibits the 0-D + 1-D supramolecular framework. In this compound, the copper atoms show three kinds of coordination models: (1) in quadrilateral geometry, (2) in square-pyramidal geometry, and (3) in distorted octahedral geometry.

2. Experimental

A mixture of $Na_2MoO_4 \cdot 2H_2O$ (0.5 mmol), $CuCl_2 \cdot 2H_2O$ (0.5 mmol), glycine (0.5 mmol) in H_2O (10 mL) was adjusted to 4.2, and then the resultant mixture was heated at 110°C for 3 days. The blue solution was obtained after the reaction mixture cooling to room temperature, several days later blue prism crystals were isolated at 14% yield on Mo. Anal. Calc. for **1**: C, 8.45; H, 2.16; N, 4.93; Mo, 33.74; Cu, 14.90. Found: C, 8.43; H, 2.30; N, 4.90; Mo, 33.73; Cu, 14.91. IR (solid KBr pellet/cm^{-1}): 3445s, 3253s, 1628s, 1594s, 1453m, 1408s, 1332m, 1112m, 1054m, 933s, 887s, 842m, 702s, 560s.

3. Results and discussion

Single crystal X-ray diffraction was conducted to study the structure and the crystal data and structure refinement for **1** are listed in Table 1. The space group of the compound is P–1, with the lattice parameters: $\alpha = 89.036(5)°$, $\beta = 89.384(4)°$, $\gamma = 88.337(5)$ °, $a = 12.559(4)$ Å, $b = 14.441$ (4)Å, $c = 23.063(6)$ Å, and $Z = 1$.

Single crystal X-ray diffraction study reveals that compound **1** consists of three main units: discrete $\{NaCu_6(Gly)_8(H_2O)_2\}^{5+}$, $\{Mo_8O_{26}[Cu(Gly)(GlyH)(H_2O)_2]_2\}^{2-}$, and one-dimensional $\{[NaCu_6(Gly)_8(H_2O)_2][Mo_8O_{26}Cu(Gly)_2]_2\}_n{}^{3n-}$ (Fig. 1).

The structure of $\{NaCu_6(Gly)_8(H_2O)_2\}$ (Fig. 1a) might be described as a hexanuclear copper cluster in octahedron conformation encapsules a sodium atom at the center of the octahedron. Four cis-$Cu(Gly)_2$ occupy the equatorial vertices of the octahedron, and another two copper atoms locate at the axial vertices in square pyramid configuration with four oxygen atoms from the coordination glycine and one water molecule. The $\{Mo_8O_{26}[Cu(Gly)(GlyH)(H_2O)_2]_2\}^{2-}$ (Fig. 1b) is based on octamolybdate decorated with two copper complexes, $\{CuNO_5\}$, at opposite sites. In $\{CuNO_5\}$, one oxygen atom and one nitrogen atom are from a bidentated glycine, and remainder four oxygen atoms are from two water molecules, one carboxyl of bridged glycine, and one terminal oxygen atom of octamolybdate, respectively. Noteworthy, in the third unit one hexanuclear copper cluster as a bridge connects two octamolybdates together in a slightly long Cu-O distant (2.452 Å) to

Table 1. Crystal data and structure refinement for 1.

Identification code	**1**
Empirical formula	$C_{48}H_{146}Cu_{16}Mo_{24}N_{24}Na_2O_{149}$
Formula weight	6825.07
Crystal system	Triclinic
Space group	P–1
Unit cell dimensions	$a = 12.559(4)$ Å, $\alpha = 89.036(5)$ °
	$b = 14.441(4)$ Å, $\beta = 89.384(4)$ °
	$c = 23.063(6)$ Å, $\gamma = 88.337(5)$ °
Volume	4180(2) $Å^3$
Z	1
Calculated density	2.705 g/cm^3
Absorption coefficient	3.853 mm^{-1}
F(000)	3288
Crystal size	0.1000 × 0.0800 × 0.0500 mm
Theta range for data collection	3.09 to 27.48 °
Limiting indices	$-16 \leq h \leq 15$, $-18 \leq k \leq 17$, $-29 \leq l \leq 23$
Reflections collected/unique	32,323/18,805 [*R*(int) = 0.0270]
Max. and min. transmission	0.8307 and 0.6992
Data/restraints/parameters	18,805/0/1179
Goodness-of-fit on F^2	1.053
Final *R* indices [I>2sigma(I)]	$R1 = 0.0552$, $wR2 = 0.1282$
R indices (all data)	$R1 = 0.0688$, $wR2 = 0.1375$
Largest diff. peak and hole	2.578 and −2.386 e·A^{-3}

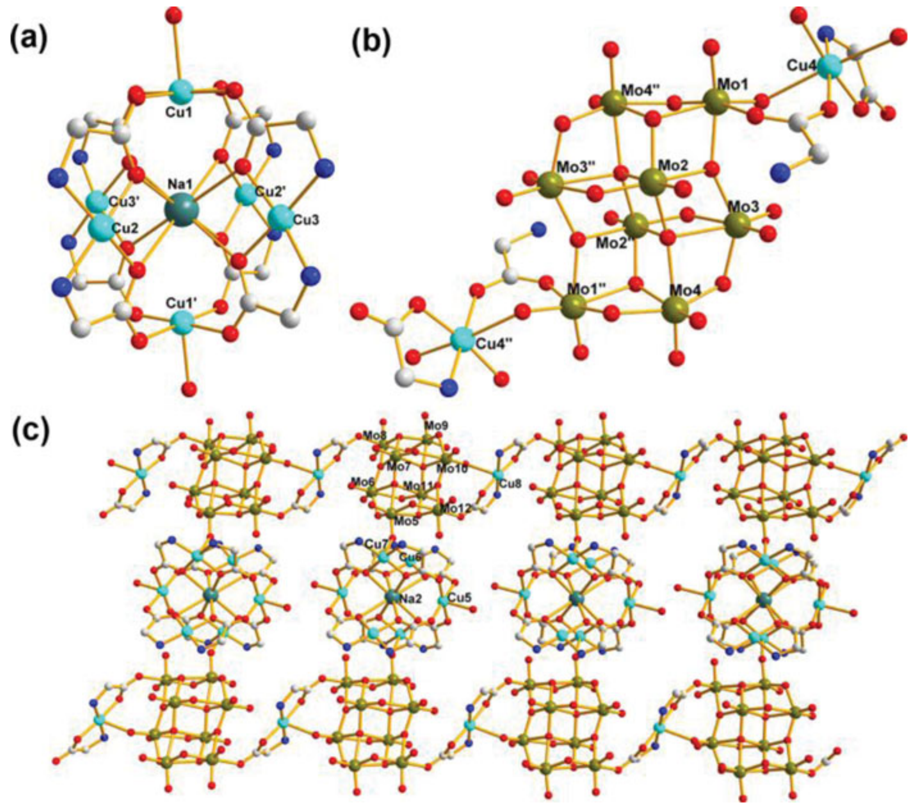

Figure 1. The three units of the compound 1: (a) $\{NaCu_6(Gly)_8(H_2O)_2\}^{5+}$; (b) $\{Mo_8O_{26}[Cu(Gly)(GlyH)(H_2O)_2]_2\}^{2-}$; and (c) $\{[NaCu_6(Gly)_8(H_2O)_2][Mo_8O_{26}Cu(Gly)_2]_2\}_n^{3n-}$ (the hydrogen atoms have been omitted for clarity, symm code: ´: -x, -y, -z; ": -x, 1-y, -z).

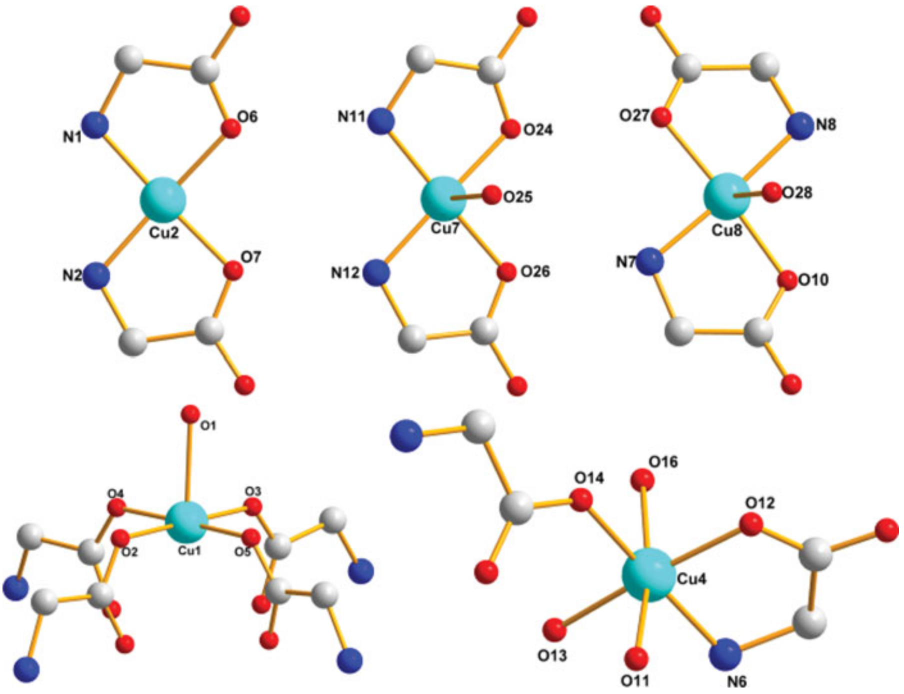

Figure 2. The coordination models of the copper atoms in compound 1 (the hydrogen atoms have been omitted for clarity).

build up $\{[NaCu_6(Gly)_8(H_2O)_2][Mo_8O_{26}]_2\}$ (abbreviated as $Cu_6(Mo_8)_2$) unit, while the trans-$Cu(Gly)_2$ group offers two remainder oxygen atoms to connect two adjacent octamolybdates of $Cu_6(Mo_8)_2$ units to form a one-dimensional ribbon-like chain as shown in Fig. 1(c). Furthermore, the weak interaction between trans-$Cu(Gly)_2$ group and octamolybdate (Cu-O bond at 2.434Å) might also increase the stability of the chain.

It is noteworthiness that in the compound **1**, the copper atoms show varying coordination models (Fig. 2). All the eight crystallographic copper atoms (shown in Fig. 1) are separated into five groups: (i) Cu2, Cu3, and Cu6 atoms are in quadrilateral geometry with two cis-coordinated glycine ligands; (ii) Cu1 and Cu5 atoms are in square-pyramidal geometry, four oxygen atoms from four glycine ligands in the equatorials positions, and one water oxygen in the axial site; (iii) Cu7 atom is in square-pyramidal geometry with two cis-coordinated glycine ligands in the equatorials positions and one oxygen from the octamolybdate ocuppied the axial site; (iv) Cu8 atom is in square-pyramidal geometry with two trans-coordinated glycine ligands in the equatorials positions and one oxygen from the octamolybdate occupied the axial site; (v) Cu4 atom is in a distorted octahedral geometry with two water oxygen atoms, one oxygen atom from the µ2-glycine-κ2O, O, one oxygen atom, and one nitrogen from the µ2-glycine-κ2N, O, and one oxygen atom from the octamolybdate.

As shown in Fig. 3, the chain-like $\{[NaCu_6(Gly)_8(H_2O)_2][Mo_8O_{26}Cu(Gly)_2]_2\}_n^{3n-}$ entities, along the ***a*** axis, are arranged one by one to form a layer in the ***ab*** plane, then the discrete $\{NaCu_6(Gly)_8(H_2O)_2\}$ and $\{Mo_8O_{26}[Cu(Gly)(GlyH)(H_2O)_2]_2\}$ are arranged to fill in alternately along the ***b***-axis and then spread along the ***a***-axis between the $\{[NaCu_6(Gly)_8(H_2O)_2][Mo_8O_{26}Cu(Gly)_2]_2\}_n^{3n-}$ layers.

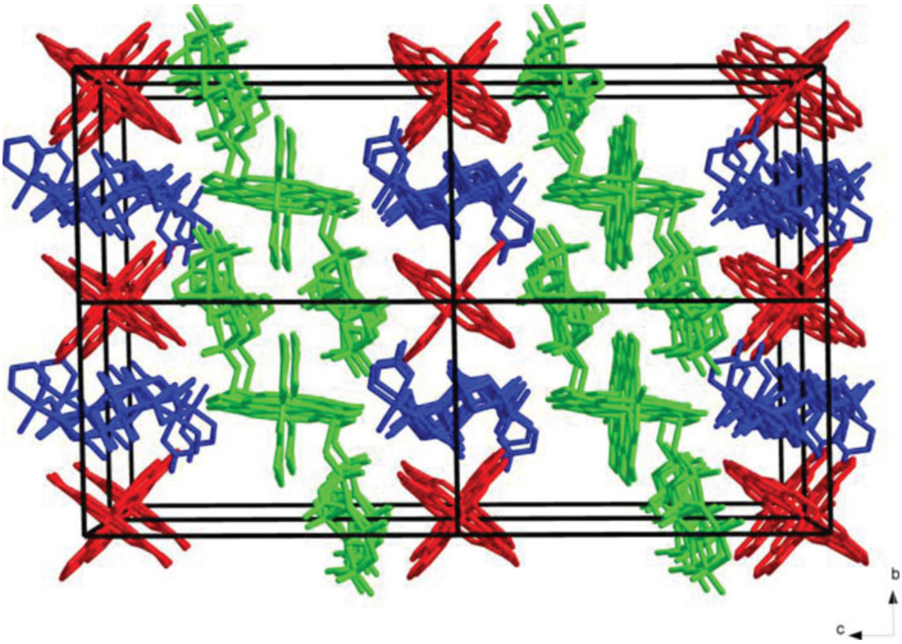

Figure 3. Cell packing for compound 1 (the hydrogen atoms and the lattice water molecules have been omitted for clarity).

4. Conclusion

In this paper, a novel compound based on hexanuclear copper cluster and octamolybdate cluster, have been synthesized and characterized. In compound **1**, the copper atoms shows varying coordinatiom models, moreover, the hetero-transition metal cluster with amino acid ligand is introduced into the compound. It might introduce the properties of hetero-transition metal cluster into POM, and provides a new strategy for the preparation of novel POM-based hybrid materials.

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References

[1] Hill, C. L., & Zhang, X. (1995). *Nature*, *373*, 324.
[2] Wu, C. D. et al. (2002). *J. Am. Chem. Soc.*, *124*, 3836.
[3] Yang, H. X. et al. (2010). *Chem. Commun.*, *46*, 2429.
[4] Müller, A., & Roy, S. (2003). *Coord. Chem. Rev.*, *245*, 153.
[5] Rarig, R. S., & Zubieta, J. (2003). *Dalton Trans.*, 1861.
[6] Xiang, S. C. et al. (2007). *J. Am. Chem. Soc.*, *129*, 15144.
[7] Hu, S. M. et al. (2001). *J. Chem. Soc., Dalton Trans.*, 2963.
[8] Aromí, G. et al. (2008). *Inorg. Chim. Acta.*, *361*, 3919.
[9] Wang, L. Y. et al. (2003). *Dalton Trans.*, 2318.
[10] Fan, D. W., Deng, Y. M., & Hao, J. C. (2010). *Amino. Acids.*, *39*, 1363.

[11] Kong, Y. M. et al. (2006). *Chem. J. Chinese Universities*, *27*, 801.
[12] An, H. Y. et al. (2007). *Inorg. Chem. Commun.*, *10*, 299.
[13] An, H. Y. et al. (2006). *Angew. Chem. Int. Ed.*, *45*, 904.
[14] Dutta, D. et al. (2010). *Dalton Trans.*, *39* (48), 11551.
[15] Wu, X.-Y. et al. (2010). *Inorganica Chimica Acta.*, *363*, 1236.
[16] Sha, J. Q. et al. (2012). *Polyhedron*, *31* (1), 422.
[17] Venegas-Yazigi, D. et al. (2011). *Inorg. Chem.*, *50* (22), 11461.
[18] Sarma, M., Chatterjee, T., & Das, S. K. (2010). *Inorg. Chem. Commun.*, *13* (10), 1114.
[19] Lan, Y. Q. et al. (2009). *Dalton Trans.*, *6*, 940.
[20] Shi, Z., Feng, S., Zhang, L., Yang, G., & Hua, J. (2000). *J. Chem. Mater.*, *12*, 2930.
[21] Place, C. et al. (1998). *Inorg. Chem.*, *37*, 4030.
[22] Owen, C. A. J. (1982). *Biochemical Aspects of Copper*, Park Ridge: New York.
[23] Beinert, H. (1991). *J. Inorg. Biochem.*, *44* (3), 173.
[24] Reddy, P. A. N., Nethaji, M., & Chakravarty, A. R. (2002). *Inorganica Chimica Acta*, *337*, 450.
[25] Solomon, E. I., Lowery, M. D., Root, D. E., & Hemming, B. L. (1995). *Mechanistic Bioinorganic Chemistry*, American Chemical Society: Washington, DC.
[26] Ames, W. M., & Larsen, S. C. (2009). *J. Biol. Inorg. Chem.*, *14*, 547.
[27] Hanna, J. V. et al. (2005). *Dalton Trans.*, 2547. doi: 10.1039/B505200A
[28] Yodoshi, M., Odoko, M., & Okabe, N. (2007). *Chem. Pharm. Bull.*, *55* (6), 853.
[29] Jones, C. E., Abdelraheim, S. R., Brown, D. R., & Viles, J. H. (2004). *J. Biological Chemistry*, *279* (31), 32018.
[30] Nicoll, A. J. et al. (2006). *J. Am. Chem. Soc.*, *128*, 9187.
[31] El-Sonbati, A. Z., Diab, M. A., El-Bindary, A. A., & Nozha, S. G. (2011). *Spectrochimica Acta Part A: Mol. Biomol. Spectroscopy*, *83*, 490.
[32] Jiang, X. Y., Wu, X. Y., Yu, R. M., Yuan, D. Q., & Chen, W. Z. (2011). *Inorg. Chem. Commun.*, *14* (9), 1546.