

基于双核铜簇和 $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ 阴离子的杂化化合物的合成及结构

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摘要: 通过水热合成方法得到了一个基于双核铜簇 $[\text{Cu}_2(1,4\text{-bth})_3]^{4+}$ 和 $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ 阴离子的有机-无机杂化化合物, $[\text{Cu}_2(1,4\text{-bth})_3(\text{H}_2\text{O})(\beta\text{-Mo}_8\text{O}_{26})]$ (**1**) (1,4-bth=4-(6-(1*H*-1,2,4-三氮唑-1-基)正己烷)-4*H*-1,2,4-三氮唑), 并通过元素分析、红外光谱、X-射线单晶衍射、热分析等测试对其进行了表征。晶体数据表明该化合物属于三斜晶系, $P\bar{1}$ 空间群。在化合物 **1** 中, 1,4-bth 配体都以三齿配体的形式与 3 个铜离子相连, 形成双核铜簇 $[\text{Cu}_2(1,4\text{-bth})_3]^{4+}$, 每个簇单元进一步和其相邻的 4 个同类型单元相连形成了相互平行的层状结构 $[\text{Cu}_2(1,4\text{-bth})_3]_n^{4n+}$, 层与层之间又通过 $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ 阴离子相连构成 1 个三维框架结构, 其拓扑类型为 pcu alpha-Po 简单立方格子; 热分析表明该化合物具有相对较高的热稳定性。

关键词: 有机-无机杂化物; 柔性配体; 八钼酸盐; 晶体结构

中图分类号: O614.121

文献标识码: A

文章编号: 1001-4861(2012)11-2419-06

Synthesis and Structure of One Hybrid Constructed by Dimeric Copper Clusters and $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ Polyanions

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Abstract: An organic-inorganic hybrid $[\text{Cu}_2(1,4\text{-bth})_3(\text{H}_2\text{O})(\beta\text{-Mo}_8\text{O}_{26})]$ (**1**) (1,4-bth=4-(6-(1*H*-1,2,4-triazol-1-yl)hexyl)-4*H*-1,2,4-triazole)) based on dimeric copper clusters $[\text{Cu}_2(1,4\text{-bth})_3]^{4+}$ and $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ polyanions has been synthesized and characterized by element analysis, IR spectra, single-crystal X-ray diffraction, thermal analysis. The crystallographic data shows that complex **1** crystallizes in triclinic space group $P\bar{1}$ with $a=1.195\ 1\ (2)\ \text{nm}$, $b=1.252\ 0(2)\ \text{nm}$, $c=2.146\ 0(4)\ \text{nm}$, $\alpha=85.893(3)^\circ$, $\beta=76.229(3)^\circ$, $\gamma=62.714(3)^\circ$, $V=2.769\ 0(8)\ \text{nm}^3$, $\text{C}_{30}\text{H}_{50}\text{Cu}_2\text{Mo}_8\text{N}_{18}\text{O}_{27}$, $M_r=1989.48$, $D_c=2.386\ \text{g}\cdot\text{cm}^{-3}$, $\mu(\text{Mo}\ K\alpha)=2.598\ \text{mm}^{-1}$, $F(000)=1\ 932$, $\text{GOF}=1.001$, $Z=2$, the final $R_1=0.062\ 0$ and $wR_2=0.153\ 4$ for $I>2\sigma(I)$. In complex **1**, each 1,4-bth ligand acted as a tridentate-linker to bridge three Cu^{2+} ions and dimeric copper clusters $[\text{Cu}_2(1,4\text{-bth})_3]^{4+}$ were formed. Each dimeric copper cluster is connected to four same clusters forming parallel two dimensional (2D) sheets $[\text{Cu}_2(1,4\text{-bth})_3]_n^{4n+}$. Then the $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ anions through bonded to the Cu^{2+} ions as the pillars to construct a three dimensional (3D) framework, with the pcu alpha-Po primitive cubic topology; the thermal analysis illustrate that compound **1** retains a comparatively good thermal stability. CCDC: 865416.

Key words: organic-inorganic hybrid; flexible ligand; octamolybdate; crystal structure

收稿日期: 2012-02-13。收修改稿日期: 2012-07-11。

国家自然科学基金(No.21171179), 河南省自然科学基金(No.112300410291), 河南省教育厅自然科学基金(No.2011B140025, 12A150028, 12A140017)以及周口师范学院博士启动基金资助项目。

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0 Introduction

Design and synthesis of organic-inorganic hybrid have recently aroused much interest owing to the possibility of combining the different characteristics of the components to get unusual structures or properties^[1]. Polyoxometalates (POMs), as one of the most widely used inorganic components, possess extreme variability of composition, structure, electronic properties and applications in many areas, such as catalysis, material science and biology, medicine^[2]. Octamolybdates (Mo_8), as an important member of POM family, have been extensively studied due to its diverse structures and intriguing properties. Up to date, eight isomeric forms of octamolybdates have been explored, that is, the α -, β -, γ -, δ -, ε -, ζ -, η - and θ - isomers^[3]. Su and co-workers have synthesized several hybrids based on Mo_8 polyanions and Cu-bis (imidazole) ligands. The supramolecular isomerism^[4] and the influence of the organic amine on the charge of the Cu ions in these systems were also studied^[5].

In this work, we use the octamolybdate polyanions as the inorganic building block and the bis (triazole) ligand, 4-(6-(1*H*-1,2,4-triazol-1-yl)hexyl)-4*H*-1,2,4-triazole as organic unit to construct organic-inorganic hybrid. The selection of the ligand is based on the following considerations: (i) *N*-heterocycle ligands play the important role during the construction of metal-organic frameworks (MOFs), owing to strong metal binding capability and versatile coordination modes^[6-7]; (ii) The bis(triazole) ligand combine the coordination geometry of both imidazoles and pyrazoles to provide more potential coordination sites; (iii) The ligand can act as bridges to construct high dimensional framework; (iv) The ligand has different flexibility and conformational freedom, which may provide different capacities for spatial extension. These characteristics may result the construction of diversified attractive frameworks^[8].

Herein, by utilizing the octamolybdate as inorganic building block and the flexible bis(triazole) ligand as organic unit, a three-dimensional (3D) hybrid, $[\text{Cu}_2(1,4\text{-bth})_3(\text{H}_2\text{O})(\beta\text{-Mo}_8\text{O}_{26})]$ (**1**) (1,4-bth=4-

(6-(1*H*-1,2,4-triazol-1-yl)hexyl)-4*H*-1,2,4-triazole)) has been synthesized. Thermal analysis for the compound was also performed.

1 Experimental

1.1 Materials and general methods

The 1,4-bth ligand was synthesized according to the literature method^[9]. All other chemicals were of reagent grade and used as received. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyzer. Infrared spectrum was recorded on a Vector22 Bruker Spectrophotometer with KBr pellets in the 400~4 000 cm^{-1} region. The powder XRD pattern was recorded on a Shimadzu XD-3A X-ray diffractometer. Thermogravimetric analyses (TGA) was collected on a Perkin-Elmer Pyris 1 TGA analyzer from room temperature to 800 $^{\circ}\text{C}$ with a heating rate of 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$ under nitrogen.

1.2 Synthesis of $[\text{Cu}_2(1,4\text{-bth})_3(\text{H}_2\text{O})(\beta\text{-Mo}_8\text{O}_{26})]$

A mixture of $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ (2 mmol, 480 mg), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (0.2 mmol, 240 mg), 1,4-bth (0.2 mmol, 44 mg) and H_2O (15 mL) (pH=2.93) was sealed in a 30 mL Teflon-lined bomb and heated at 175 $^{\circ}\text{C}$ for 3 d. The reaction mixture was slowly cooled to room temperature. Green virgulate crystals of **1** suitable for X-ray diffraction analysis were isolated in 41% yield. Anal. Calcd. for $\text{C}_{30}\text{H}_{50}\text{Cu}_2\text{Mo}_8\text{N}_{18}\text{O}_{27}$ (%): C, 18.11; H, 2.53; N, 12.67. Found (%): C, 18.24; H, 2.39; N, 12.58. IR for **1** (KBr)/ cm^{-1} : 3 404 (m), 3 119 (w), 1 639 (m), 1 556 (m), 1 527 (m), 1 460 (m), 1 279 (m), 1 217 (m), 1 125 (m), 1 087 (w), 1 057 (w), 944 (s), 910 (s), 893 (s), 839 (m), 712 (m), 660 (m), 646 (m), 559 (w), 520 (w), 450 (w).

1.3 X-ray crystallography

A green single crystal of **1** with dimensions of 0.23 mm×0.20 mm×0.18 mm was mounted on a Bruker Smart Apex CCD diffractometer equipped with a graphite-monochromatic $\text{Mo K}\alpha$ radiation ($\lambda=0.071\ 073$ nm) using the φ - ω scan mode in the range $1.83^{\circ}\leq\theta\leq 25.10^{\circ}$ at 298 (2) K. A total of 13 655 reflections were collected and 9 593 were independent with $R_{\text{int}}=0.054\ 4$, of which 6 507 were observed with $I>2\sigma(I)$. Raw frame data were integrated with the

Table 1 Crystallographic data for complex **1**

| | | | |
|---------------------|--|---|----------------|
| Empirical formula | $\text{C}_{30}\text{H}_{50}\text{Cu}_2\text{Mo}_8\text{N}_{18}\text{O}_{27}$ | V / nm^3 | 2.769 0(8) |
| Formula weight | 1989.48 | Z | 2 |
| Crystal size / mm | 0.23×0.20×0.18 | $D_c / (\text{g} \cdot \text{cm}^{-3})$ | 2.386 |
| Temperature / K | 298(2) | μ / mm^{-1} | 2.598 |
| Crystal system | Triclinic | $F(000)$ | 1 932 |
| Space group | $P\bar{1}$ | θ range / (°) | 1.83~25.10 |
| a / nm | 1.195 1(2) | Reflections collected / unique | 13 655 / 9 593 |
| b / nm | 1.252 0(2) | Goodness of fit on F^2 | 1.001 |
| c / nm | 2.1460(4) | R ($I > 2\sigma(I)$) | 0.062 |
| $\alpha / (^\circ)$ | 85.893(3) | wR ($I > 2\sigma(I)$) ^a | 0.1534 |
| $\beta / (^\circ)$ | 76.229(3) | Parameters | 779 |
| $\gamma / (^\circ)$ | 62.714(3) | $\Delta\rho_{\text{max}} \Delta\rho_{\text{min}} / (\text{e} \cdot \text{nm}^{-3})$ | 1 732, -862 |

^a $w=1/[\sigma^2(F_o^2)+(0.076\ 8P)^2]$ where $P=(\text{Max}(F_o^2,0)+2F_c^2)/3$.

Table 2 Selected bond lengths (nm) and angles (°) for complex **1**

| | | | | | |
|-------------------|------------|-------------------|------------|-------------------|------------|
| O(1)-Cu(1) | 0.229 6(7) | Cu(2)-O(4e) | 0.251 4(7) | O(27)-Cu(2) | 0.202 7(7) |
| Cu(2)-N(2) | 0.232 5(8) | Cu(1)-N(1) | 0.202 4(8) | Cu(1)-N(14) | 0.202 3(8) |
| Cu(1)-N(12) | 0.205 6(9) | Cu(1)-N(18) | 0.202 6(8) | Cu(2)-N(8) | 0.200 8(9) |
| Cu(1)-N(7) | 0.223 4(8) | Cu(2)-N(13) | 0.202 5(8) | Cu(2)-N(6) | 0.201 0(8) |
| N(14)-Cu(1)-N(18) | 173.3(3) | N(14)-Cu(1)-N(1) | 89.9(3) | N(14)-Cu(1)-N(12) | 83.6(3) |
| N(1)-Cu(1)-N(18) | 94.0(3) | N(18)-Cu(1)-N(12) | 92.5(3) | N(1)-Cu(1)-N(12) | 173.5(4) |
| N(1)-Cu(1)-N(7) | 89.0(3) | N(14)-Cu(1)-N(7) | 93.7(3) | N(12)-Cu(1)-N(7) | 91.8(3) |
| N(18)-Cu(1)-N(7) | 91.9(3) | N(1)-Cu(1)-O(1) | 87.6(3) | N(14)-Cu(1)-O(1) | 86.6(3) |
| N(12)-Cu(1)-O(1) | 91.6(3) | N(18)-Cu(1)-O(1) | 88.1(3) | N(8)-Cu(2)-N(6) | 92.7(4) |
| N(7)-Cu(1)-O(1) | 176.5(3) | N(6)-Cu(2)-N(13) | 170.5(4) | N(8)-Cu(2)-N(13) | 95.1(3) |
| N(6)-Cu(2)-O(27) | 87.8(3) | N(8)-Cu(2)-O(27) | 169.9(3) | N(8)-Cu(2)-N(2) | 90.3(3) |
| N(13)-Cu(2)-O(27) | 83.5(3) | N(13)-Cu(2)-N(2) | 85.9(3) | N(6)-Cu(2)-N(2) | 99.6(3) |
| O(27)-Cu(2)-N(2) | 99.5(3) | | | | |

Symmetry code: e: $x, y+1, z$.

SAINT program^[10]. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELX-97^[11]. An empirical absorption correction was applied with the program SADABS^[12]. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were set in calculated positions and refined by a riding mode, with a common thermal parameter. The final cycle of refinement converged to $R=0.087\ 6$ and $wR=0.163\ 8$ ($w=1/[\sigma^2(F_o^2)+(0.076\ 8P)^2]$ where $P=(\text{Max}(F_o^2,0)+2F_c^2)/3$). $(\Delta/\sigma)_{\text{max}}=0.000$, $S=1.001$, $(\Delta\rho)_{\text{max}}=1\ 732$ and $(\Delta\rho)_{\text{min}}=-862\ \text{e} \cdot \text{nm}^{-3}$. Crystallographic details have been summarized in Table 1. Selected bond lengths and angles for **1** are listed in Table 2.

CCDC: 865416.

2 Results and discussion

2.1 Synthesis and general characterization

Complex **1** was obtained under hydrothermal condition. The complex is stable in air and insoluble in water and common organic solvents. And all the Cu^{2+} ions in the compound were not reduced and retained their oxidation state. Comparing with the observation of Cu^+ ions in the other system^[13-14], it can be concluded that the 1,4-bth ligand in the system only acted as the tridentate-linker but not reductant, possibly due to the relatively lower molar ratio (1:10) of 1,4-bth ligand to Cu^{2+} ion^[15].

In the IR spectrum of **1**, the bands in the range

of 600~1 000 cm^{-1} show the characteristic vibrational features similar to the known $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ anion. The strong bands from 944 to 893 cm^{-1} (944 (s), 910 (s), 893 (s)) are attributed to the $\nu_{\text{as}}(\text{Mo}=\text{O})$, while multiple bands attributed to the bridging (Mo-O-Mo (Cu)) groups' absorptions are found in 839~646 cm^{-1} region (839 (m), 712 (m), 660 (m), 646 (m)). Bands in the regions of 1 450~1 650 cm^{-1} (1 639 (m), 1 556 (m), 1 527 (m), 1 460 (m)) can be assigned to the skeletal vibrations of the aromatic rings of 1,4-bth ligands. In addition, the broad band around 3 404 cm^{-1} indicates the presence of $\nu(\text{O-H})$ stretching of water molecules. The powder X-ray diffraction pattern for **1** is displayed in Fig.1. The diffraction peaks of the experimental and simulated patterns match well in key positions, indicating the phase purities of complex **1**.

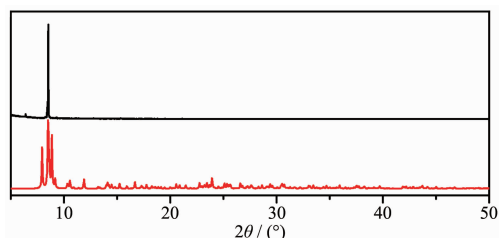
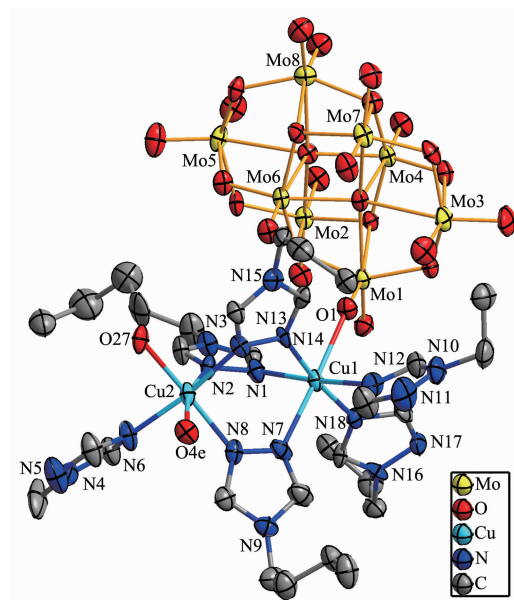


Fig.1 PXRD patterns of the simulated from the single-crystal diffraction data (bottom) and as-synthesized (top) for **1**

2.2 Structure analysis

Compound **1** crystallizes in the triclinic, $P\bar{1}$ space group. The asymmetric unit of **1** (Fig.2) contains two Cu^{2+} ions, three 1,4-bth ligands, one $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ anion and one coordinated water molecule. The $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ anion consists of eight distorted edge- and/or corner-sharing $\{\text{MoO}_6\}$ octahedra, with four kinds of O atoms, two $\mu_5\text{-O}$, four $\mu_3\text{-O}$, six $\mu_2\text{-O}$, and fourteen terminal oxygen atoms (Ot). The bond valence sum calculations^[16] reveal that all Mo atoms are in the +6 oxidation state and Cu atoms are in the +2 oxidation state. The Mo-O bond lengths (0.168 1(6)~0.252 0(6) nm) all fall in the regular range^[17].

In **1**, there are two crystallographically unique Cu^{2+} ions in the asymmetric unit. The Cu(1) ion is six-coordinated by five nitrogen atoms ((N(1), N(7), N(12), N(14), N(18)) from five 1,4-bth ligands, and one terminal oxygen atoms (O(1)) from one $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$

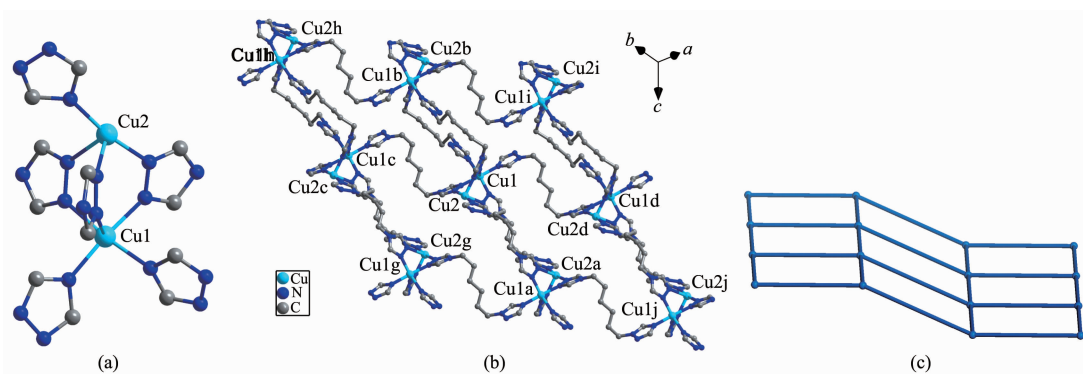


Thermal ellipsoids drawn at the 50% probability level; All H atoms are omitted for clarity; Symmetric code: e: $x, y+1, z$

Fig.2 Asymmetric unit of **1**

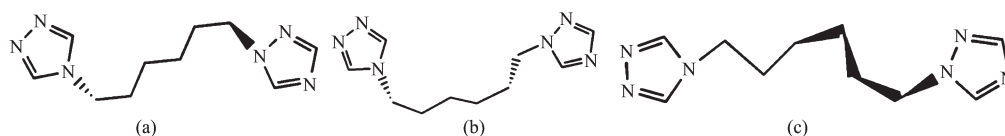
polyanion. The Cu(2) ion is also six-coordinated by four nitrogen atoms ((N(2), N(6), N(8), N(13)) from four 1,4-bth ligands, one terminal oxygen atom (O(4e)) from one $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ polyanion and one oxygen atom from coordinated water molecule (Symmetry code: e: $x, y+1, z$). Both of the coordination geometry around the copper ions can be described as the distorted octahedra. The bond distances around the Cu^{2+} ions are in the range of 0.200 8(9)~0.232 5(8) nm (Cu-N) and 0.202 7(7)~0.251 4(7) nm (Cu-O).

Interestingly, the coordination mode of the 1,4-bth ligand in complex **1** is different from those of the other bis(triazole) ligands^[18]. Each 1,4-bth ligand in **1** utilizes its three apical N atoms as the tridentate-linker to bridge three Cu^{2+} ions, and Cu (1) and Cu(2) ions are chelated by three N-N bonds from three 1,4-bth ligands to form a dimeric copper cluster $[\text{Cu}_2(1,4\text{-bth})_3]^{4+}$ with the $\text{Cu}\cdots\text{Cu}$ distance of 0.376 2 nm (Fig. 3a). Then each copper cluster is connected to four same clusters in its neighborhood by the 1,4-bth bridges forming a 2D $[\text{Cu}_2(1,4\text{-bth})_3]_n^{4n+}$ sheet with the dimensions of 1.274 nm×1.424 nm (Fig.3b). The sheet can be rationalized as a 4-connected uninodal ($4^4\cdot6^2$) topological network (Fig.3c) by considering the dimeric copper clusters as 4-connected nodes, 1,4-bth



Symmetric codes: a: $-x+2, -y, -z+1$; b: $-x+1, -y+1, -z$; c: $x-1, y+1, z$; d: $x+1, y-1, z$; g: $-x+1, -y+1, -z+1$; h: $-x, -y+2, -z$; i: $-x+2, -y, -z$; j: $-x+3, -y-1, -z+1$

Fig.3 (a) Ball-stick representation of the dimeric copper clusters; (b) Ball-stick and (c) Topological representation of the 2D $[\text{Cu}_2(1,4\text{-bth})_3]_n^{4n+}$ sheet



Scheme 1 Conformation of 1,4-bth ligand in complex 1

ligands as linkers. In addition, three kinds of conformation of 1,4-bth ligand were observed in **1**: *gauch-trans-trans-trans-gauche* (a), *gauch-trans-trans-gauche-trans* (b) and *trans-gauche-gauche-gauche-gauche* (c) (Scheme 1), resulting three kinds of $-(\text{CH}_2)-$ lengths for 1,4-bth ligand, 1.237, 1.191 and 1.328 nm, respectively. And such diverse conformation results the flexibility of positive framework ($[\text{Cu}_2(1,4\text{-bth})_3]^{4+}$), to make sure the matching of the $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ polyanions.

The neighboring $[\text{Cu}_2(1,4\text{-bth})_3]^{4+}$ sheets are parallel, and are further linked by the $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ anions through bonded to the Cu^{2+} ions as the pillars to construct the 3D framework (Fig.4). From the topological view, the 3D framework can be considered as a pcu alpha-Po primitive cubic, with the topological symbol $(4^{12} \cdot 6^3)$, by considering the dimeric copper clusters as 6-connected nodes, 1,4-bth ligands and $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ anions as linkers. In addition, the existence

of the intermolecular hydrogen bonds (Table 3) $\text{O}(27)\cdots\text{H}(27\text{C})\cdots\text{O}(8\text{e})$ and $\text{O}(27)\cdots\text{H}(27\text{D})\cdots\text{O}(9\text{f})$ (Symmetry code: f: $-x+1, -y, -z+1$), with the average distance of donor and acceptor ($d(\text{D}\cdots\text{A})$) 0.275 2 nm, further strengthen the interaction between the coordinated water molecules ($\text{O}(27)$) and $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ anions, and enhance the stability of the whole framework.

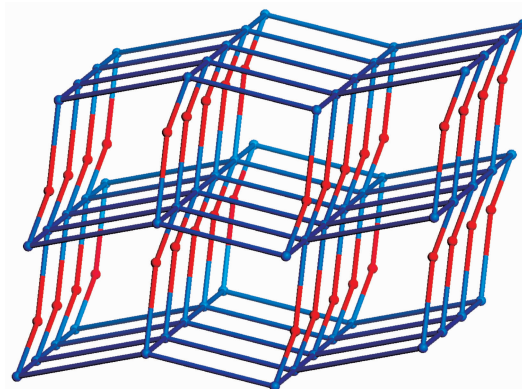


Fig.4 Schematic view of the 3D framework in **1** with the pcu alpha-Po primitive cubic topology

Table 3 Hydrogen bond lengths and bond angles for complex 1

| D-H \cdots A | $d(\text{D-H})$ / nm | $d(\text{H}\cdots\text{A})$ / nm | $d(\text{D}\cdots\text{A})$ / nm | $\angle \text{DHA}$ / ($^\circ$) |
|---|----------------------|----------------------------------|----------------------------------|------------------------------------|
| $\text{O}(27)\cdots\text{H}(27\text{C})\cdots\text{O}(8\text{e})$ | 0.096 | 0.179 | 0.274 9(10) | 174.9 |
| $\text{O}(27)\cdots\text{H}(27\text{D})\cdots\text{O}(9\text{f})$ | 0.096 | 0.185 | 0.275 6(10) | 157.0 |

Symmetry code: f: $-x+1, -y, -z+1$.

2.3 Thermal property

The thermogravimetry (TG) experiment was also performed for complex **1**. As shown in Fig.5, the TG curve displays two distinct weight loss steps with a total loss of 34.36% (Calcd. 34.12%) in the 28~800 °C. The first weight loss, 0.92% (Calcd. 0.90%) in the range of 28 ~285 °C, is ascribed to the release of the one coordinated water molecule in **1**. The second weight loss, 33.44% (Calcd. 33.12%) in the range of 285~654 °C, corresponds to the combustion of all the organic ligands in **1**. All the data above illustrate that complex **1** retains a comparatively good thermal stability.

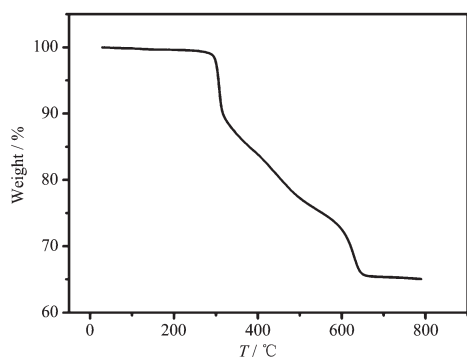


Fig.5 Thermogravimetric (TG) curve for complex **1**

3 Conclusions

In summary, a new hybrid based on flexible bis (triazole) ligands and $[\beta\text{-Mo}_8\text{O}_{26}]^{4-}$ polyanions has been synthesized. In this complex, the 1,4-bth ligands acted as tridentate-linkers and dimeric copper clusters $[\text{Cu}_2(1,4\text{-bth})_3]^{4+}$ were observed. The whole framework showed the pcu alpha-Po primitive cubic topology. The thermal analysis illustrates that complex **1** retains a comparatively good thermal stability.

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