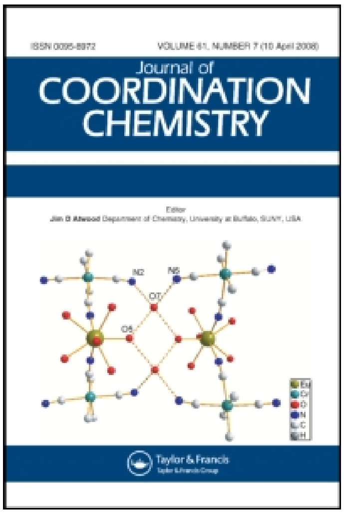

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A new hybrid material constructed from octamolybdate anion and neutral dinuclear copper units

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A new hybrid material constructed from octamolybdate anion and neutral dinuclear copper units

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A new organic–inorganic hybrid material constructed from octamolybdate anion and neutral dinuclear copper(I) units, $H_4\{[Cu_2(ophen)_2]_2[Mo_8O_{26}]\}[Cu_2(ophen)_2] \cdot H_2O$ (**1**) (Hophen = 2-hydroxy-1,10-phenanthroline), has been prepared under hydrothermal condition and characterized by elemental analysis, IR, XPS, TGA and single-crystal X-ray diffraction. Compound **1** crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 9.9091(8)$, $b = 13.3981(8)$, $c = 14.8266(10)$ Å, $\alpha = 84.6310(10)$, $\beta = 83.0620(10)^\circ$, $\gamma = 77.7800(10)$, $V = 1905.0(2)$ Å^3, $Z = 1$. Compound **1** contains a centrosymmetric polyoxoanion $\{[Cu_2(ophen)_2]_2[Mo_8O_{26}]\}^{4-}$, in which the β-$[Mo_8O_{26}]^{4-}$ is bisupported by two copper(I) coordination groups through the terminal oxygen atoms. The discrete molecules of **1** are extended into a 3-D supramolecular array through C–H$\cdots$O hydrogen bonds and strong aromatic π–π stacking contacts.

Keywords: Polyoxometalates; Hydrothermal synthesis; Octamolybdate; Dinuclear copper units

1. Introduction

Polyoxometalates (POMs) are a focus of chemical research due to their intriguing structural diversity and potential applications in catalysis, medicine and materials science [1–3]. An important advance in POM chemistry is the decoration of polyoxoanions with various organic ligands or transition metal complexes [4–6]. The introduction of transition metal complexes not only enriches the POM framework but also modifies the inorganic oxide microstructure [7–12]. Based on this strategy, a series of organic–inorganic hybrid materials have been isolated by incorporation of organic and inorganic counterparts into one structural unit [7–12].

Among the various POM structures studied, octamolybdates constitute a large family and attract special attention [13–19]. An interesting aspect of octamolybdates is the varied structural patterns in the solid state and their structural flexibility in solution [19]. Up to now, seven isomeric forms of octamolybdates have been isolated. The α-, β-, γ-, δ- and ε-isomers of octamolybdates have been crystallographically confirmed in several salts [7, 16–19]. More recently, the ζ- and η-isomer have been structurally characterized in the products of hydrothermal

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reactions [13, 14]. These octamolybdate isomers are versatile inorganic building blocks for new organic–inorganic hybrid materials [5]. A large number of octamolybdate-supported copper complexes have been synthesized and characterized; however, no octamolybdate polyoxoanions coordinated with neutral dinuclear copper complexes have been reported. Herein, we report the hydrothermal synthesis and crystal structure of octamolybdate-supported dinuclear copper(I) complexes: $H_4\{[Cu_2(ophen)_2]_2[Mo_8O_{26}]\}[Cu_2(ophen)_2] \cdot H_2O$.

2. Experimental

2.1. *General materials*

All reagents were purchased from commercial sources and used without further purification.

2.2. *Synthesis of $H_4\{[Cu_2(ophen)_2]_2[Mo_8O_{26}]\}[Cu_2(ophen)_2] \cdot H_2O$ (1)*

A mixture of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (0.62 g, 0.5 mmol), $CuCl_2 \cdot 2H_2O$ (0.17 g, 1.0 mmol), $Cu(CH_3COO) \cdot H_2O$ (0.1 g, 0.5 mmol), 1,10-phenanthroline (0.08 g, 0.4 mmol) and H_2O (15.0 g, 833.3 mmol) was stirred for 3 h in air. Then the pH was adjusted to 4.26 with hydrochloric acid (6 mol L^{-1}). The mixture was then transferred to a 30 mL Teflon-lined autoclave and kept at 165°C for 7 days. After slow cooling to room temperature, dark red block crystals of **1** were obtained, filtered off, washed with distilled water and dried in air (Yield: 75% based on Mo). Anal. Calcd for **1**: C, 31.32; H, 1.74; N, 6.09(%). Found: C, 31.23; H, 1.80; N, 6.02(%).

2.3. *Physical measurements*

C, H and N elemental analyses were performed on a Perkin–Elmer 2400II elemental analyzer. IR spectra were recorded on a Nicolet 170FT-IR spectrometer using KBr pellets in the range 4000–400 cm^{-1}. TG curves were obtained with an EXSTAR 6000 instrument under air with a heating rate of 10°C min^{-1}. XPS analyses were performed on an AXIS ULTRA spectrometer with an Al Kα ($h\nu = 1486.7$ eV) achromatic X-ray source.

2.4. *Crystal structure determination*

A dark red single crystal of **1** with approximate dimensions $0.16 \times 0.14 \times 0.13\ mm^3$ was mounted on a glass fiber capillary. The data were collected on a Bruker APEX-II CCD detector with Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293(2)K in the range $2.36 < \theta < 25.00°$. A total of 9887 (6593 unique, $R_{int} = 0.0146$) reflections were measured ($-11 \le h \le 11$, $-9 \le k \le 15$, $-16 \le l \le 17$). The structures were solved by direct methods and refined using full-matrix least-squares calculations with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were geometrically fixed to allow riding on the parent atoms to which they are attached. All calculations were performed using the SHELXTL-97 program [20]. Crystallographic data are summarized in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Description of structure*

Single crystal X-ray diffraction reveals that **1** consists of a centrosymmetric polyoxoanion $\{[Cu_2(ophen)_2]_2[Mo_8O_{26}]\}^{4-}$, four protons, one neutral dinuclear copper complex $[Cu_2(ophen)_2]$ and one lattice water molecule. The octamolybdate $[Mo_8O_{26}]^{4-}$ anion, which is built up from eight distorted MoO_6 edge-shared octahedra, is a typical β-octamolybdate. Bond valence sum calculations [21] give the values of 5.95, 6.00, 5.93 and 5.89 for Mo(1), Mo(2), Mo(3) and Mo(4), showing that all Mo sites are in the +6 oxidation state. The $\{MoO_6\}$ octahedra are distorted, and the Mo–O bonds can be divided into four categories: 1.691(3)–1.707(3) Å for Mo–O(t), 1.752(2)–2.280(3) Å for Mo–O(μ_2), 1.952(2)–2.339(2) Å for Mo–O(μ_3), and 2.165(2)–2.391(2) Å for Mo–O(μ_5); the mean values are 1.700(3), 1.943(2), 2.092(2) and 2.319(2) Å, respectively. All bond lengths are comparable to corresponding ones in $(C_6H_{16}N_4)[Mo_8O_{26}] \cdot 2H_2O$ [22]. The average Mo–O bond lengths of Mo(1)–Mo(4) are very similar (1.974–1.998 Å), indicating that the formal valence states (+6) of the Mo atoms in the anion are equivalent [23].

Table 1. Crystallographic data and structure refinement for **1**.

Formula	$C_{72}H_{48}Cu_6Mo_8N_{12}O_{33}$
Formula weight	2757.94
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	9.9091(8)
b	13.3981(8)
c	14.8266(10)
α	84.6310(10)
β	83.0620(10)
γ	77.7800(10)
Volume (Å^3)	1905.0(2)
Z	1
D_{Calcd} (Mg m^{-3})	2.399
Absorption coefficient (mm^{-1})	3.005
$F(000)$	1332
Crystal size (mm^3)	0.16 × 0.14 × 0.13
θ range for data collection (°)	2.36–25.00
Limiting indices	$-11 \le h \le 11$, $-9 \le k \le 15$, $-16 \le l \le 17$
Reflections collected	9887
Independent reflections	6593 ($R_{int} = 0.0146$)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6593/0/592
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0269$, $\omega R_2 = 0.0669$
Largest diffraction peak and hole (e Å^{-3})	0.732 and −0.562

$R_1 = \Sigma||F_o| - |F_c||/\Sigma F_o|$; $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

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

Cu(1)–O(2A)	1.868(3)	Cu(1)–N(2)	1.896(3)
Cu(1)–N(1)	2.069(3)	Cu(1)–Cu(2)	2.4216(7)
Cu(2)–O(1A)	1.889(2)	Cu(2)–N(4)	1.901(3)
Cu(2)–N(3)	2.045(3)	Cu(2)–O(3)	2.299(3)
Cu(3)–O(3A)	1.867(2)	Cu(3)–N(6)#1	1.891(3)
Cu(3)–N(5)#1	2.055(3)	Cu(3)–Cu(3)#1	2.4053(9)
Mo(1)–O(1)	1.696(2)	Mo(1)–O(2)	1.704(3)
Mo(1)–O(9)	1.891(2)	Mo(1)–O(8)	2.003(2)
Mo(1)–O(11)	2.307(2)	Mo(1)–O(13)	2.354(2)
Mo(2)–O(4)	1.704(3)	Mo(2)–O(3)	1.707(3)
Mo(2)–O(10)	1.920(2)	Mo(2)–O(9)	1.923(2)
Mo(2)–O(12)	2.280(3)	Mo(2)–O(13)	2.391(2)
Mo(3)–O(5)	1.698(3)	Mo(3)–O(6)	1.702(3)
Mo(3)–O(10)	1.897(2)	Mo(3)–O(11)#2	1.994(2)
Mo(3)–O(8)#2	2.339(2)	Mo(3)–O(13)	2.359(2)
Mo(4)–O(7)	1.691(3)	Mo(4)–O(12)	1.752(2)
Mo(4)–O(11)	1.952(2)	Mo(4)–O(8)#2	1.957(2)
Mo(4)–O(13)#2	2.165(2)	Mo(4)–O(13)	2.326(2)
O(2A)–Cu(1)–N(2)	172.66(13)	O(2A)–Cu(1)–N(1)	101.21(13)
N(2)–Cu(1)–N(1)	84.42(13)	O(2A)–Cu(1)–Cu(2)	92.55(9)
N(2)–Cu(1)–Cu(2)	82.35(9)	N(1)–Cu(1)–Cu(2)	165.20(10)
O(1A)–Cu(2)–N(4)	168.25(13)	O(1A)–Cu(2)–N(3)	99.91(12)
O(1)–Mo(1)–O(2)	104.18(13)	O(1)–Mo(1)–O(9)	103.58(12)
O(2)–Mo(1)–O(9)	100.77(12)	O(1)–Mo(1)–O(8)	100.45(11)
O(2)–Mo(1)–O(8)	96.08(11)	O(9)–Mo(1)–O(8)	146.10(10)
O(1)–Mo(1)–O(11)	90.78(11)	O(2)–Mo(1)–O(11)	162.36(11)
O(4)–Mo(2)–O(3)	105.90(13)	O(4)–Mo(2)–O(10)	97.85(12)
O(3)–Mo(2)–O(10)	101.19(12)	O(4)–Mo(2)–O(9)	98.01(12)
O(3)–Mo(2)–O(9)	102.15(12)	O(10)–Mo(2)–O(9)	146.85(10)
O(4)–Mo(2)–O(12)	164.58(11)	O(3)–Mo(2)–O(12)	89.52(11)
O(5)–Mo(3)–O(6)	104.70(13)	O(5)–Mo(3)–O(10)	100.72(12)
O(6)–Mo(3)–O(10)	101.31(12)	O(5)–Mo(3)–O(11)#2	102.96(12)
O(6)–Mo(3)–O(11)#2	97.26(11)	O(10)–Mo(3)–O(11)#2	144.94(10)
O(5)–Mo(3)–O(8)#2	91.62(11)	O(6)–Mo(3)–O(8)#2	161.94(10)
O(7)–Mo(4)–O(12)	104.31(12)	O(7)–Mo(4)–O(11)	100.80(11)
O(12)–Mo(4)–O(11)	96.73(11)	O(7)–Mo(4)–O(8)#2	100.72(11)
O(12)–Mo(4)–O(8)#2	97.40(11)	O(11)–Mo(4)–O(8)#2	150.38(10)
O(7)–Mo(4)–O(13)#2	97.45(11)	O(12)–Mo(4)–O(13)#2	158.24(10)

#1: $-x, -y+1, -z+1$; #2: $-x, -y, -z$.

As shown in figure 1, each β-$[Mo_8O_{26}]^{4-}$ anion forms covalent interactions with two neutral dinuclear copper(I) complexes $[Cu_2(ophen)_2]$ through the terminal oxygen atoms of the octamolybdate cluster with Cu–O distances of 2.299(3) Å. The three crystallographically unique copper atoms exhibit two different coordination geometries in **1**. Cu(2) displays a square-pyramidal coordination environment, defined by two nitrogens from an ophen ligand (Cu–N = 2.045(3) and 1.901(3) Å), a deprotonated hydroxy group from another ophen (Cu–O = 1.889(2) Å), the adjacent copper (Cu1–Cu2 = 2.4216(7) Å) at the equatorial position, and one oxygen from the polyoxoanion at the apical position. Cu(1) and Cu(3) adopt square-planar coordination geometry, coordinated by two nitrogens (Cu1–N = 1.896(3) and 2.069(3) Å; Cu3–N = 1.891(3) and 2.055(3) Å), one oxygen (Cu1–O = 1.868(3) Å; Cu3–O = 1.867(2) Å) from two different ophen ligands, and the adjacent copper atom (Cu1–Cu2 = 2.4216(7) Å; Cu3–Cu3A = 2.4053(9) Å, symmetry code, A: $-x, -y+1, -z+1$). All copper sites exhibit +I oxidation, confirmed by bond valence

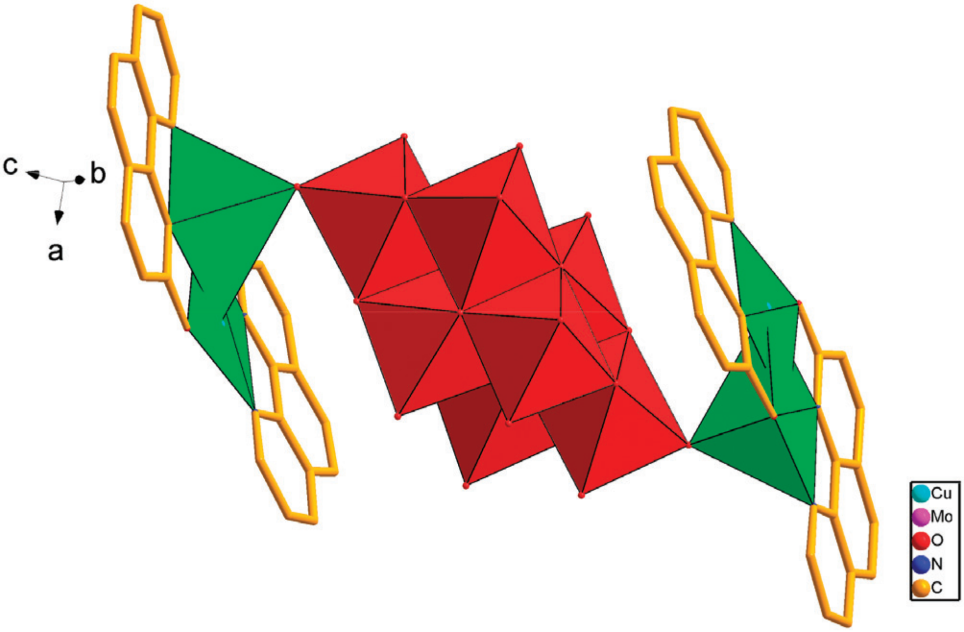

Figure 1. Polyhedral and ball/stick representation of the polyoxoanion $\{[Cu_2(ophen)_2]_2[Mo_8O_{26}]\}^{4-}$ in **1**.

sum calculations [24], which give the values of 1.35, 1.49 and 1.36 for Cu1, Cu2 and Cu3, respectively. All oxygen atoms in the $[Mo_8O_{26}]^{4-}$ anion have bond valence sums [21] in the 1.67–2.01 region, indicating that each oxygen atom in the anion is unprotonated. According to charge balance, there should be four protons in the structural unit of **1**.

Cu–Cu distances in **1** are 2.4216(7) and 2.4053(9) Å for Cu(1)–Cu(2) and Cu(3)–Cu(3A) (symmetry code, A: $-x, -y+1, -z+1$), respectively, shorter than twice the van der Waals radius of Cu^I (2.8 Å) [25] and slightly shorter than Cu^I–Cu^I separation of 2.56 Å in metallic copper, indicating bonding interactions [26]. 1,10-Phen is hydroxylated into ophen during the reaction, in which 1,10-phen reduces Cu(II) to Cu(I) [25]. The linkage between heterometal coordination groups and octamolybdate unit in **1** is similar to that in $K[\{Cu^I(2,2'\text{-bipy})\}(4,4'\text{-bipy})\{Cu^I(2,2'\text{-bipy})\}_{0.5}]_2[Mo_8O_{26}]$ [27], but different from that in $[\{Ni(phen)_2\}_2(Mo_8O_{26})]$ [13]. In the structure of the latter compound, each transition metal complex cation is attached to the octamolybdate surface by two terminal oxygen atoms of adjacent MoO_6 octahedra, to yield a neutral bimetallic cluster. However, each $[Cu_2(ophen)_2]$ group in **1** is covalently linked to the octamolybdate anion via one terminal oxygen atom, forming an anionic bimetallic cluster.

Adjacent $[Cu_2(ophen)_2]$ units in **1** are generally parallel and packed together through π–π stacking interactions. As illustrated in figure S1, groups I and II are representative of the $[Cu(1)Cu(2)(ophen)_2]$ and $[Cu(3)Cu(3A)(ophen)_2]$ (symmetry code, A: $-x, -y+1, -z+1$) fragments, respectively. Discrete molecules of **1** are extended into an interesting 1-D chain via π–π interactions between groups I and I along the *a* axis. Close contact between ophen groups of I and I is 3.160(5) Å. Furthermore, these chains

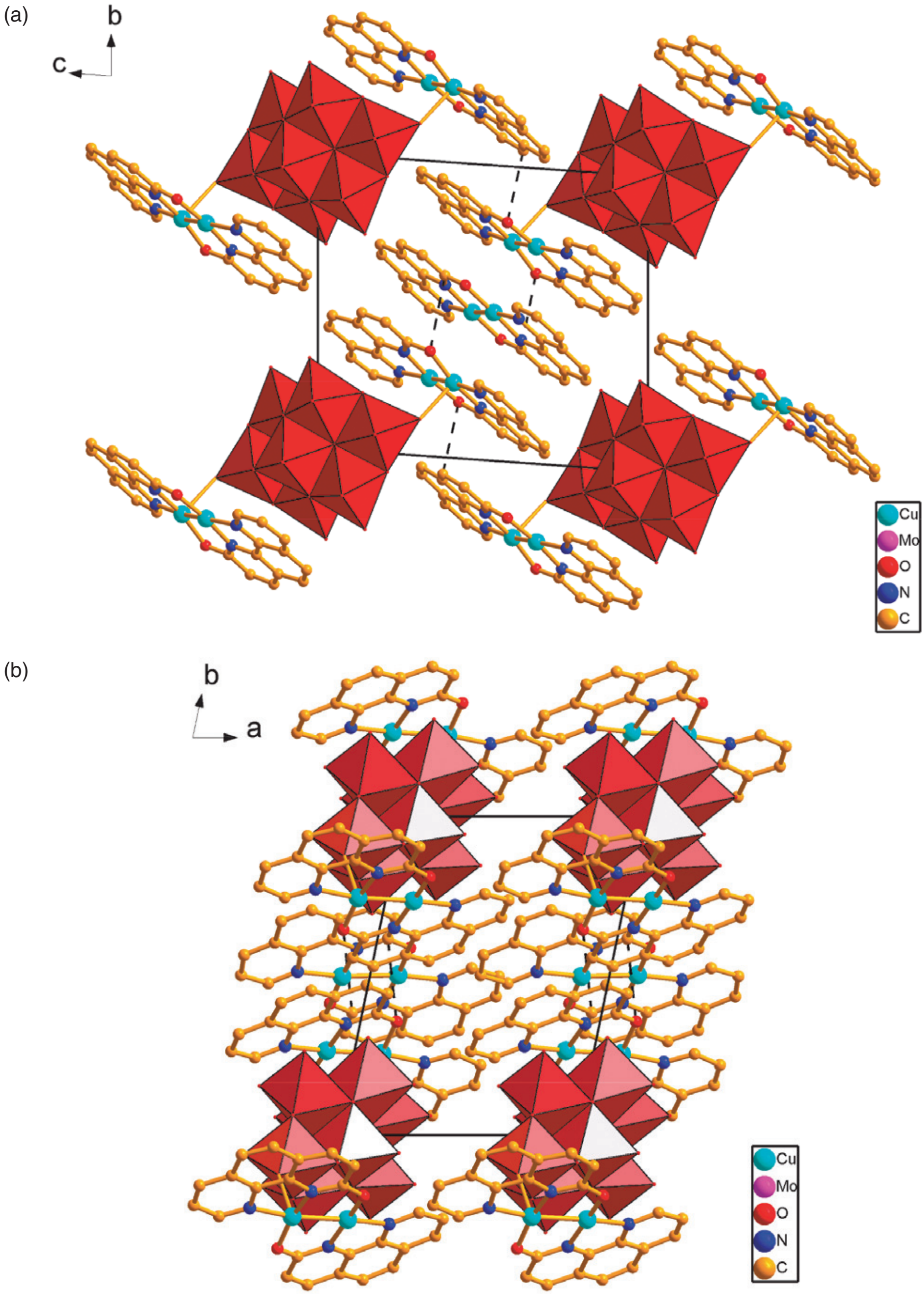

Figure 2. (a) Polyhedral and ball-stick representation of the 3-D structure of **1** along the *a*-axis. Dashed lines indicate C ··· O hydrogen bonds. All hydrogen atoms and water molecules have been omitted for clarity. (b) Polyhedral and ball-stick representation of the 3-D structure of **1** along the *c*-axis. Dashed lines indicate C ··· O hydrogen bonds. All hydrogen atoms and water molecules have been omitted for clarity.

are arranged parallel along the *bc* plane to form a 2-D network through the π–π interactions between groups I and II with the close contact distance of 3.451(5) Å. As shown in figure 2, the 2-D networks are further extended by C–H ··· O hydrogen bonds between the aromatic groups and carboxy groups from an adjacent aromatic ring (C36–O1A = 3.445(4) Å; C22–O2A = 3.408(4) Å, symmetry code, A: $-x, -y+1, -z+1$) into a 3-D supramolecular array.

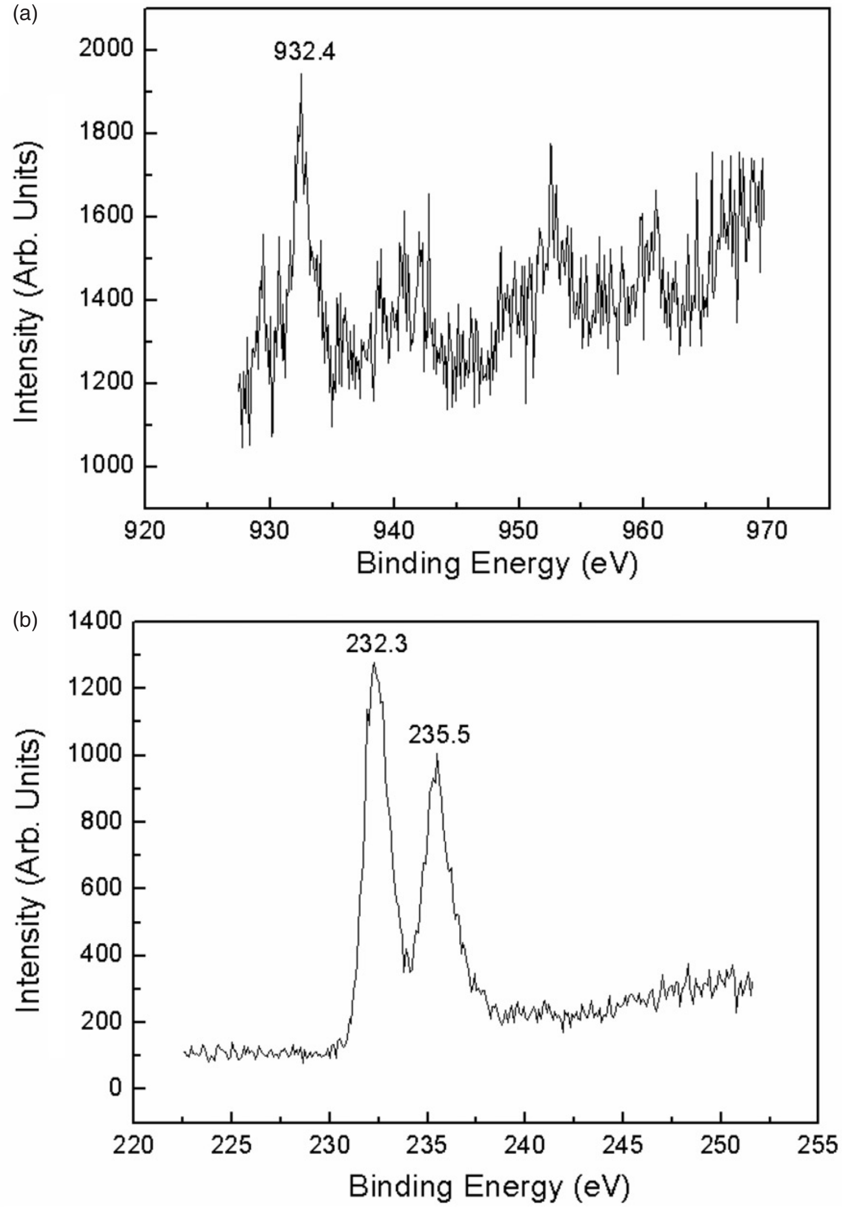

Figure 3. (a) XPS for Cu(I) in **1**, (b) XPS for Mo(VI) in **1**.

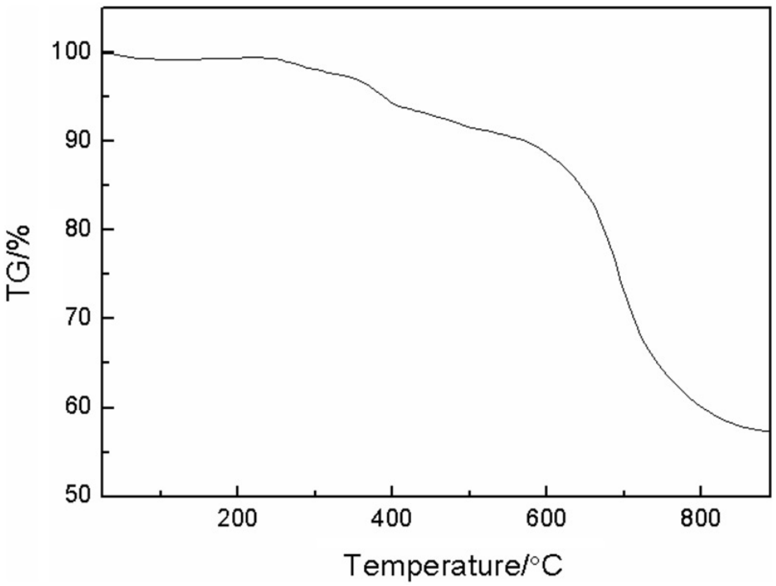

Figure 4. TG curve of **1**.

3.2. *IR, XPS spectra and TG analysis*

In the IR spectrum of **1**, characteristic peaks at 948, 933, 918, 842, 724, 710 and 668 cm^{-1} can be attributed to the Mo=O and Mo–O–Mo vibrations. Comparing the IR spectrum of **1** with that of β-$[Mo_8O_{26}]^{4-}$ [28], the shape of peaks in the 600–1000 cm^{-1} region is almost identical except for slight shifts of some peaks from coordination, indicating that the octamolybdate anion in **1** maintains the basic β-$[Mo_8O_{26}]^{4-}$ structure. This is in agreement with the single crystal X-ray diffraction analysis. Furthermore, bands in the 1143–1627 cm^{-1} region can be assigned to characteristic peaks of the ophen ligands.

The XPS spectra of **1** (figure 3) gives one peak at 932.4 eV, attributable to $Cu^+2p_{3/2}$ [23], and two peaks at 232.3 and 235.5 eV, ascribed to $Mo^{6+}3d_{5/2}$ and $Mo^{6+}3d_{3/2}$ [29], respectively, further confirming the valences of Cu and Mo.

The TG curve of **1** (figure 4) shows a total loss of 42.63% in the range of 25–890°C, which agrees with the calculated value of 43.29%. The first weight loss of 0.77% at 25–148°C corresponds to the loss of one uncoordinated water molecule per formula (Calcd 0.65%). The second weight loss of 41.86% arises from the decomposition of ophen ligands (Calcd 42.64%).

Supplementary material

Crystallographic data for the structural analysis reported in this article have been deposited with the Cambridge Crystallographic Data Centre with the deposited CCDC number 669659. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033. Email: deposit@ccdc.cam.ac.uk).

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