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A new hexamolybdate-based copper-2,2'-biimidazole coordination polymer serving as an acid catalyst and support for enzyme immobilization

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The hydrothermal reaction of (NH₄)₃[CoMo₆O₂₄H₆]·7H₂O (CoMo₆), CuCl₂·2H₂O and 2,2'-biimidazole (H₂biim) led to the formation of a new coordination polymer, namely poly[diaquabis(2,2'-biimidazole)hexa- μ_3 -oxo-octa- μ_2 -oxo-hexaoxodicopper(II)hexamolybdate(VI)], $[Cu_2Mo_6O_{20}(C_6H_6N_4)_2(H_2O)_2]_n$ (Cu- Mo_6O_{20} , at pH 2-3. It is obvious that in the formation of crystalline Cu- Mo_6O_{20} , the original Anderson-type skeleton of heteropolymolybdate $CoMo_6$ was broken and the new isopolyhexamolybdate Mo₆O₂₀ unit was assembled. In **Cu-Mo₆O₂₀**, one Mo₆O₂₀ unit connects four $[Cu(H_2biim)(H_2O)]^{2+}$ ions in a pentacoordinate mode via four terminal O atoms, resulting in a tetra-supported structure, and each Cu^{II} ion is shared by two adjacent Mo₆O₂₀ units. Infinite onedimensional chains are established by linkage between two adjacent Mo₆O₂₀ units and two Cu^{II} ions, and these chains are further packed into a three-dimensional framework by hydrogen bonds, $\pi - \pi$ interactions and electrostatic attractions. The catalytic performance of this crystalline material used as an efficient and reusable heterogeneous acid catalyst for carbonyl-group protection is discussed. In addition, Cu-Mo₆O₂₀ was applied as a new support for enzyme (horseradish peroxidase, HRP) immobilization, forming immobilized enzyme HRP/Cu-Mo₆O₂₀. HRP/Cu-Mo₆O₂₀ showed good catalytic activity and could be reused.

1. Introduction

Coordination polymers, as a type of special inorganic complex, possess novel properties and have been used as catalysts, support materials and optical and magnetism materials in many fields (Wang et al., 2014; Sun et al., 2018; Cai et al., 2005; Fedin et al., 2010). The introduction of nitrogen-containing ligands can enhance the functions of polymers through the construction of hydrogen-bond interactions with biological molecules, such as proteins. In particular, polyoxometalates (POMs), as polydentate oxygen-donor ligands with high negative charge, can coordinate with transition metal (TM) ions or TM-complex units under certain conditions, resulting in many new structures. Furthermore, POM-based inorganicorganic hybrid compounds have bifunctional effects, combining organic and inorganic components; on the other hand, POM anions can not just balance the positive charge of the TM or TM-complex cations, but can also form hydrogen bonding and covalent interactions with protein molecules via exposed O atoms. Because of their diverse structures and potential applications, POMs have attracted considerable attention. The design and synthesis of POM-based TM-coordination polymers is still a hot topic.

Enzymes that act as biological catalysts with advantages of low pollution, high selectivity and high efficiency have been

polyoxometalates

Table 1 Experimental details.

Crystal data	
Chemical formula	$[Cu_2Mo_6O_{20}(C_6H_6N_4)_2(H_2O)_2]$
$M_{ m r}$	1327.07
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	296
a, b, c (Å)	8.065 (3), 10.293 (4), 10.837 (4)
α, β, γ (°)	64.090 (5), 75.186 (5), 71.141 (5)
$V(\text{\AA}^3)$	758.8 (5)
Ζ	1
Radiation type	Μο Κα
$\mu (\text{mm}^{-1})$	3.87
Crystal size (mm)	$0.09 \times 0.07 \times 0.06$
Data collection	
Diffractometer	Bruker SMART CCD area detector
Absorption correction	Multi-scan (SADABS; Sheldrick, 2003)
T _{min} , T _{max}	0.724, 0.795
No. of measured, independent and	3875, 2639, 2409
observed $[I > 2\sigma(I)]$ reflections	,,
R _{int}	0.011
$(\sin \theta/\lambda)_{\rm max}$ (Å ⁻¹)	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.018, 0.042, 1.06
No. of reflections	2639
No. of parameters	235
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta \rho_{\rm max}, \Delta \rho_{\rm min} \ (e \ {\rm \AA}^{-3})$	0.36, -0.49

Computer programs: SMART (Bruker, 2005), SAINT (Bruker, 2005), SHELXS97 (Sheldrick, 2008), SHELXL2014 (Sheldrick, 2015) and SHELXTL (Sheldrick, 2008).

used for large-scale industrial production (DiCosimo et al., 2013; Kikukawa et al., 2018). Although free enzymes exhibit high activity as soluble homogeneous catalysts, they are difficult to isolate from the reaction system, easy to deactivate and require rigorous reaction conditions. Compared with free enzymes, immobilized enzymes show high stability, insolubility and easy separation, which allows them to be used repeatedly in continuous production. Thus, it is still a long-term task to develop environmentally friendly and biocompatible enzymesupport materials with high loading, low cost and high stabilities, including thermal, mechanical and chemical stabilities. Most importantly, the insolubility of employed supports is vital for the successful immobilization process. To our knowledge, POMs have been studied and applied in protein crystallization (Molitor et al., 2016) and protein separation (Chen et al., 2015), but these applied POMs are all water soluble and no waterinsoluble solid POM example used as a support for enzyme immobilization has been reported except in our recent work (Du et al., 2017). Having stated the above, POM-based TMcoordination polymers obtained by hydrothermal methods can meet the above requirements and may become a new type of immobilizing enzyme-support material.

Recently, our group have synthesized two Preyssler-type POM-based Cu^{II} -H₂biim (H₂biim is 2,2'-biimidazole) coordination polymers with high thermal stability and low solubility, and firstly used them as supports for enzyme immobilization (Du *et al.*, 2017). A high HRP (horseradish peroxidase)

loading (158.7 and 157.5 mg g^{-1}) and excellent reusability were observed. Obviously, the H₂biim ligand plays an important role in the construction of these functional crystalline materials. H₂biim has good biological activity (Zhang et al., 2011; Ye et al., 1999) and possesses four N atoms from two imidazole rings, so that it has a versatile coordination behaviour and forms multiple hydrogen bonds. Therefore, the construction of its complexes was considered to be a tool for crystal engineering (Tadokoro & Nakasuji, 2000). More importantly, the combination of Cu^{II}-H₂biim cations and POM anions can significantly decrease the solubility of the POM, and such insolubility is a basic requirement for support materials for enzyme immobilization. In order to construct other types of POM-based TM-H₂biim coordination polymers and explore their performance in immobilizing horseradish peroxidase (HRP), in this work, we attempted to introduce the Cu^{II} -H₂biim complex into the hexamolybdate (NH₄)₃[Co- $Mo_6O_{24}H_6$]·7H₂O (**CoMo**₆) system under hydrothermal conditions. As a result, a new crystalline hexamolybdate-based $Cu^{II}-H_2$ biim coordination polymer, $[Cu_2Mo_6(C_6H_6N_4)_2(H_2O_2O_{20}]_n$, denoted **Cu-Mo₆O₂₀**, was obtained unexpectedly, and its acid catalytic activity for carbonyl-group protection and its performance used as a support for HRP immobilization have been investigated. In addition, the catalytic activity and reusability of immobilized enzyme HRP/Cu-Mo₆O₂₀, serving as a catalyst in the co-oxidation colour reaction of phenol and 4-aminoantipyrine (4-AAP) with H_2O_2 , were also researched.

2. Experimental

All chemicals were purchased commercially and used without further purification. $(NH_4)_3$ [CoMo₆O₂₄H₆]·7H₂O was prepared and characterized according to reported procedures (Evans & Showell, 1969; Nomiya et al., 1987). HRP (isoenzyme C, product P105528, lot K1506050, E.C. 1.11.1.7, 300 Umg^{-1} , $R_Z > 3.0$, $M_w \simeq 40 \text{ kDa}$) and 4-AAP were purchased from Aladdin Biochem Technology Co. Ltd, China. Phosphate buffer solutions (PBS) $(0.1 \text{ mol } l^{-1})$ with different pH (3.5-8.5) were prepared using Na₂HPO₄, NaH₂PO₄ or H₃PO₄. The mixture of HRP and Cu-Mo₆O₂₀ was centrifuged with a TG-16G model centrifuge to obtain immobilized enzyme HRP/Cu-Mo₆O₂₀. C, H and N elemental analyses were performed on a Vario Elcube elemental analyzer. Co, Cu and Mo were analyzed on a Prodigy XP emission spectrometer. IR spectra were recorded in the range 4000–400 cm^{-1} using KBr pellets with a Bruker TENSOR-27 FT-IR spectrometer. X-ray powder diffraction (XRPD) data were obtained in the 2θ range 5–60° on a Bruker D8 Advance diffractometer using Cu K α radiation ($\lambda = 1.5418$ Å), with a step size of 0.02°. Single-crystal X-ray diffraction data were collected on a Bruker SMART APEXIIX diffractometer equipped with graphite-monochromated Mo $K\alpha$ radiation ($\lambda =$ 0.71073 Å). Thermal analysis (TG-DTA) was carried out on a Pyris Diamond TG-DTA thermal analyzer in air at a heating rate of 10 K min⁻¹. The solid-state UV spectra were recorded on a PerkinElmer Lambda 35 UV-Vis spectrophotometer. Liquid UV-Vis absorption spectra were recorded on a Lambda 35 UV–Vis spectrophotometer. Circular dichroism (CD) spectra in the wavelength range 190–250 nm were obtained on a MOS-500 automatic recording spectropolarimeter (Bio Logic, France) at room temperature using a 2 mm cell with a scan rate of 1.0 s nm^{-1} . The product of the acid-catalyzed reaction was confirmed on a JK-GC112A gas chromatograph.

2.1. Synthesis and crystallization

A mixture of $(NH_4)_3$ [CoMo₆O₂₄H₆]·7H₂O (0.482 g, 0.4 mmol), H₂biim (0.054 g, 0.4 mmol) and CuCl₂·2H₂O (0.068 g, 0.4 mmol) in deionized water (20 ml) was adjusted to pH 2–3 with 0.5 mol l⁻¹ HCl and then transferred to a 25 ml Teflonlined autoclave and kept at 393 K for 3 d. Dark-green crystals of **Cu-Mo₆O₂₀** (yield 58%, based on Mo) suitable for X-ray diffraction analysis were obtained after cooling to room temperature and filtering. Analysis calculated for C₁₂H₁₆N₈-Cu₂Mo₆O₂₂: C 10.86, H 1.22, N 8.45, Cu 9.58, Mo 43.38%; found: C 11.02, H 1.31, N 8.55, Cu 9.64, Mo 43.43%. IR (KBr, cm⁻¹): 3443 (*m*), 3299 (*m*), 3132 (*w*), 2923 (*w*), 1632 (*w*), 1530 (*w*), 1428 (*w*), 1380 (*w*), 1182 (*w*), 1085 (*w*), 941 (*m*), 903 (*vs*), 732 (*s*), 592 (*s*).

2.2. Structure determination and refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Water H atoms were found according to the residual electron-density peaks around the attached water O atom, with the O-H distances restrained to 0.85 (1) Å. The remaining H atoms were positioned in geometrically idealized positions and constrained to ride on their parent atoms, with C-H = 0.93 Å and N-H = 0.86 Å (H₂biim), and with $U_{iso}(H) = 1.2U_{eq}(C,N)$.

2.3. Acid-catalyzed synthesis of cyclohexanone ethylene ketal

One of the most common methods for protecting carbonyl groups is the condensation of aldehydes or ketones with alcohols. Selecting the acid-catalyzed synthesis of cyclohexanone ethylene ketal from cyclohexanone and glycol in cyclohexane as a model reaction (Greene & Wuts, 1999; Tao *et al.*, 2012), the catalytic activity of **Cu-Mo₆O₂₀** was evaluated. The specific experimental process referred to published methods (Li *et al.*, 2014; Liu *et al.*, 2010) and heterogeneous catalyst **Cu-Mo₆O₂₀** was easily separated from the organic phase containing the product by decantation after reaction. The catalyst was recovered and reused in a new reaction under identical experimental conditions by washing with diethyl ether or acetone.

2.4. Immobilization of enzyme and activity test of immobilized HRP

According to literature methods (Lin *et al.*, 2011; Du *et al.*, 2017) and selecting HRP as a model enzyme, the typical procedure for preparing **Cu-Mo₆O₂₀** immobilized HRP through direct adsorption was as follows: 5.0 mg of ground **Cu-Mo₆O₂₀** powder was added to 500 µl of 0.1 mol l^{-1} PBS (pH

3.5–8.5) containing different concentrations of HRP. The mixture was then stirred gently at room temperature, resulting in a suspension. The suspension was centrifuged, the supernatant liquid was slowly drawn off and the UV–Vis absorbance was measured at $\lambda = 403$ nm; meanwhile, the resulting precipitate was collected and rinsed three times with PBS to remove nonspecifically adsorbed enzyme, resulting in the immobilized enzyme, *i.e.* HRP/**Cu-Mo₆O₂₀**.

The Worthington method (Nicell & Wright, 1997; Zhou et al., 2016; Du et al., 2017) was used to test the activity of the immobilized HRP, that is, the catalytic activity of the immobilized enzyme HRP/Cu-Mo₆O₂₀ was evaluated by co-oxidation colour reaction of phenol and 4-AAP with H₂O₂ (Fig. S1 in the supporting information). The experimental procedure was as follows: solution A was prepared using 1.4 ml of 0.1 mol l^{-1} PBS (pH 3.5–8.5) containing 172 mmol l^{-1} phenol and 2.46 mmol l^{-1} 4-AAP, and was mixed with solution B consisting of 2 mmol l^{-1} H₂O₂ in 1.5 ml of 0.1 mol l^{-1} PBS, and HRP/Cu-Mo₆O₂₀ (5.0 mg) was added to the reaction mixture. The mixture was then centrifuged for 5 min at room temperature in a centrifuge tube. The rate of red product formation was proportional to the activity of immobilized HRP in the test. It can thus be monitored spectrophotometrically by tracing the formation of red product at λ = 524 nm. TOF $(mol_{product} mol_{catalyst}^{-1} s^{-1})$ was calculated to determine the activity of the immobilized and free HRP.

3. Results and discussion

3.1. Synthesis

The heptamolydate $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ and simple inorganic salt Na_2MoO_4 were both used as the starting material and, unfortunately, no crystalline material was obtained. In contrast, **Cu-Mo₆O₂₀** was successfully synthesized when $(NH_4)_3[COMo_6O_{24}H_6]\cdot 7H_2O$ was used as the precursor. Meanwhile, the elemental analysis results for Co, Cu and Mo showed that there was no Co in the crystalline sample of $C_{12}H_{16}N_8Cu_2Mo_6O_{22}$ and the found contents of Cu (9.64%) and Mo (43.43%) were consistent with their calculated values (Cu 9.58% and Mo 43.38%). While no Co was found, this further proved that the Co centre in the original precursor Anderson-type **CoMo₆** heteropolymolybdate was lost. And the formation of the isopolyhexamolybdate Mo_6O_{20} unit may be caused by fragmentation of the skeleton of the **CoMo₆** precursor and reassembly of the anion fragment.

3.2. Structure analysis

Single-crystal X-ray diffraction analysis reveals that the asymmetric unit of **Cu-Mo₆O₂₀** consists of half an $[Mo_6O_{20}]^{4-}$ isopolyanion and one $[Cu(H_2biim)(H_2O)]^{2+}$ coordination cation composed of one Cu^{II} ion, one H₂biim ligand and one coordinated H₂O molecule (Fig. 1). The geometry of $[Mo_6O_{20}]^{4-}$ is obviously quite different from those of other isopolyhexamolybdate anions, such as the famous Lindqvist-type POMs $[Mo_6O_{19}]^{2-}$, $[Mo_6O_{21}]^{6-}$, $[Mo_6O_{22}]^{8-}$ etc. (Vila-Nadal et al., 2011; Naruke & Yamase, 2005; Takara et al., 1997;



Figure 1

The asymmetric unit of the title compound, shown with 50% probability displacement ellipsoids. All H atoms have been omitted for clarity. [Symmetry codes: (i) -x + 2, -y + 1, -z; (ii) -x + 1, -y + 1, -z; (iii) x + 1, y, z.]

Qiao *et al.*, 2010), and $[Mo_6O_{20}]^{4-}$ is built from six MoO₆ octahedra that can be divided into two groups. Each group is constructed by edge-sharing MoO₆ octahedra between Mo2/Mo2ⁱ and Mo3/Mo3ⁱ, and face-sharing MoO₆ octahedra between Mo1/Mo1ⁱ and Mo3/Mo3ⁱ [symmetry code: (i) -x + 2, -y + 1, -z], and the two groups are connected by edge-sharing and corner-sharing O atoms (Fig. 2*a*). As shown in Fig. 2(*a*), there exist four triply-bridging O atoms (O6, O6ⁱ, O9 and O9ⁱ) shared by three MoO₆ octahedra belonging to Mo1/Mo2ⁱ/Mo3, Mo1ⁱ/Mo2ⁱ, Mo1/Mo1ⁱ/Mo3ⁱ and Mo1/Mo1ⁱ/

Mo3, respectively. In Cu-Mo₆O₂₀, each Cu^{II} ion adopts a slightly distorted five-coordinated square-pyramidal geometry (CuN₂O₃) by bonding to two N atoms (N1 and N2) from one H₂biim ligand, two terminal O atoms [O3ⁱⁱ and O8; symmetry code: (ii) -x + 1, -y + 1, -z] from two $[Mo_6O_{20}]^{4-}$ isopolyanions, and one O atom from a water molecule (O1W)(Fig. 2b). The two Cu1-N bond lengths are 2.021 (3) and 1.968 (3) Å, and the Cu1 $-O3^{ii}$ and Cu1-O8 bond lengths are 1.965 (2) and 2.305 (2) Å, respectively. The Cu1-O1W bond length is 1.944 (3) Å. Each $[Mo_6O_{20}]^{4-}$ unit, acting as a tetradentate ligand, coordinates with four Cu^{II} ions through four terminal O atoms, and further connects to other $[Mo_6O_{20}]^{4-}$ units one-by-one through edge-sharing O atoms (triply-bridging atoms O2 and O2ⁱⁱ) between two MoO₆ octahedra belonging to two different $[Mo_6O_{20}]^{4-}$ units, forming infinite one-dimensional (1D) zigzag isopolyanion chains (Fig. 2c), and further packing into a three-dimensional (3D) structure (Fig. 2d). As seen from Fig. 2(c), each Cu^{II} - H_2 biim/ H_2O cation links two $[Mo_6O_{20}]^{4-}$ isopolyanions, and these complex cations are appended on both sides of the isopolyanion chain, which strengthens the infinite 1D isopolyanion chain. In the 3D structure, the parallel 1D chains construct two-dimensional (2D) planes through hydrogen bonds (Figs. 3a and 3c). In addition, each pair of antiparallel neighbouring 1D chains in different 2D planes are connected by face-to-face $\pi - \pi$ stacking interactions, with the centroidcentroid distances being 3.680 Å between the imidazole rings $R_1 (N2/C2/N4/C6/C5)^{v}$ and $R_2 (C4/C3/N1/C1/N3)^{vi}$, and R_3 $(N3/C1/N1/C3/C4)^{v}$ and R_4 $(N2/C2/N4/C6/C5)^{vi}$ [symmetry codes: (v) x - 3, y + 1, z; (vi) -x - 1, -y + 1, -z + 1], together



Figure 2

The crystal structure of **Cu-Mo₆O₂₀**, showing (*a*) the crystal structure of the isopolyhexamolybdate anion, (*b*) the fragment formed by Cu^{II} ions and a $[Mo_6O_{20}]^{4-}$ isopolyanion, (*c*) a 1D chain and (*d*) a 3D framework generated by infinite 1D zigzag chains. All H atoms have been omitted for clarity. [Symmetry code: (i) -x + 2, -y + 1, -z.]

with hydrogen bonds and static electrostatic attractions among the POM anions and complex cations, generating 2D coordination polymer layers (Figs. 3b and 3d) in another direction, and are further alternately packed into a 3D supramolecular framework (Fig. 2d). In **Cu-Mo₆O₂**, there are two kinds of hydrogen bonds, *i.e.* N-H···O [2.834 (4)–3.303 (4) Å] and OW-H···O [2.654 (3) and 2.809 (3) Å] (Figs. 3c and 3d, and Table 2).

3.3. Characterization

The characteristic peaks of the polyoxoanion at 941, 903 and 732 cm⁻¹ in the IR spectrum of **Cu-Mo₆O₂₀** (Fig. S2 in the supporting information) belong to Mo $=O_{terminal}$ and Mo $-O_{bridging}$ vibrations, respectively (Li *et al.*, 2005; Haso *et al.*, 2014), and the bands at 3443–2923 cm⁻¹ are assigned to characteristic vibrations of O–H, N–H and C–H. The bands in the region 1632–1085 cm⁻¹ are associated with the imidazole ring of H₂biim. The computer-simulated and experimental XRPD patterns are illustrated in Fig. S3 of the supporting information, which shows that all major peaks are in good agreement with each other, indicating a reasonable

Table 2Hydrogen-bond geometry (Å, °).

$D - H \cdot \cdot \cdot A$	D-H	$H \cdot \cdot \cdot A$	$D \cdots A$	$D - H \cdot \cdot \cdot A$
N3-H3 B ···O9 ^{vii}	0.86	2.47	3.303 (4)	164
$N4-H4B\cdots O8^{vii}$	0.86	2.05	2.834 (4)	151
N4–H4 B ···O6 ^{vii}	0.86	2.41	3.013 (4)	128
$O1W-H1WA\cdots O4^{viii}$	0.85(1)	1.81 (1)	2.654 (3)	174 (4)
$O1W-H1WB\cdots O7^{iv}$	0.85 (1)	1.97 (1)	2.809 (3)	170 (4)

Symmetry codes: (iv) x - 1, y, z; (vii) -x + 2, -y, -z + 1; (viii) -x + 2, -y, -z.

crystalline phase purity for **Cu-Mo₆O₂₀**. The differences in intensity may be due to the preferred orientation of the crystalline powder samples. The TG–DTA curve from room temperature to 1273 K of **Cu-Mo₆O₂₀** is given in Fig. S4 of the supporting information, which shows that at 303–953 K, the total weight loss of 23.6% (calculated 22.9%) is consistent with the removal of two H₂biim ligands and two water molecules. An obvious exothermal peak at 706 K is assigned to combustion of the H₂biim organic fragments. In the range 706–953 K, there is no further weight loss, indicating that the polyanion skeleton of **Cu-Mo₆O₂₀** is retained.



Figure 3

The hydrogen bonds and π - π interactions in **Cu-Mo₆O₂₀**, showing (*a*)/(*c*) the 2D planes constructed by parallel 1D chains through hydrogen bonds and (*b*)/(*d*) the 2D planes consisting of antiparallel neighbouring 1D chains connected by face-to-face π - π stacking interactions and hydrogen bonds. Hydrogen bonds and π - π interactions are drawn as dotted and dashed lines, respectively. [Symmetry codes: (iv) x - 1, y, z; (vii) -x + 2, -y, -z + 1; (viii) -x + 2, -y, -z.]



Enzyme loading (curve **a**) and immobilized enzyme activity (curve **b**) for **Cu-Mo₆O₂₀** at different pH values.

3.4. Acid catalytic activity of Cu-Mo₆O₂₀

As we know, protection of carbonyl groups as acetals or ketals under acid catalysis is an important strategy during multiple organic reactions (Greene & Wuts, 1999). The commonly used catalysts are traditional protonic acids, e.g. anhydrous HCl, H₂SO₄ etc., or Lewis acids, such as the simple metal salts FeCl₃ and CuCl₂. These acids cannot be reused or recycled and can produce large amounts of waste and pollution, in particular, HCl or H₂SO₄ may cause serious corrosion of equipment. Thus, development of more efficient, recyclable and environmental pollution-free catalysts is a long-term goal (Tao et al., 2012; Liu et al., 2010). In our previous work, we reported the good acid catalytic performances of inorganicorganic hybrid materials constructed from Strandberg-type inorganic anions $\{P_2Mo_5\}$ (Li *et al.*, 2014) and Strandberg-type organophosphomolybdate clusters $\{(C_6H_5PO_3)_2MO_5\}$ (Wang et al., 2014). Herein, the acid catalytic activity of Cu-Mo₆O₂₀ based on isopolyoxometalate and Cu^{II} complex units was evaluated by the synthesis of cyclohexanone ethylene ketal, and the chemical equation of the catalytic reaction is shown in Scheme 1. The effect of the reaction factors, including reaction time, reactant molar ratio and dosage of catalyst, on the conversion of cyclohexanone has been discussed (Fig. S5 in the supporting information). The optimal conditions determined from Figs. S5(a-c) are as follows: a reaction time of 4 h, a ketone/alcohol ratio of 1:1.4 and a catalyst (based on Mo)/ cyclohexanone molar ratio of 1/200. Under the optimal conditions, a 92% conversion of cyclohexanone is obtained using 10 ml of cyclohexane as the water-carrying agent at reflux temperature. In light of the Cu^{II} ion being a good and homogeneous Lewis acid for the catalytic reaction (Wang et al., 2014), the introduction of Cu^{II} into the POM skeleton with the aid of an organic ligand can play an important role in the catalytic reaction. Meanwhile, the catalyst Cu-Mo₆O₂₀ can be recycled because of its insolubility and its acid catalytic activity is almost unchanged after three cycles (Fig. S6 in the supporting information). Additionally, the acid dissociation of the water molecule that coordinates to the Cu^{II} cation was considered to be the other part contributing to the catalytic activity. Furthermore, the skeleton structure of Cu-Mo₆O₂₀ may lead to the pseudo-liquid phase feature (a very remarkable property of heteropoly acids when they are used as solid catalysts is the formation of a 'pseudoliquid phase'; Lee et al., 1992), which can improve the acid strength of the compound. The above results illustrate that Cu-Mo₆O₂₀ is fairly stable and its main skeleton is retained before and after reaction, which can be further proved by powder X-ray diffraction (XRPD) (Fig. S7 in the supporting information).



3.5. Factors affecting HRP loading on $Cu\mathchar`Mo_6O_{20}$ and the activity of HRP/Cu-Mo_6O_{20}

The influence of pH, concentration of HRP solution and immobilized time on enzyme loading were studied (Figs. 4 and 5). From a comprehensive consideration of enzyme loading (curve **a** in Fig. 4) and immobilized enzyme activity (curve **b** in Fig. 4), an optimal pH of 7.5 for HRP immobili-



Figure 5

The influences of (a) concentration of HRP solution and (b) immobilized time on enzyme loading at pH 7.5 at room temperature. The concentration of HRP solution for (a) was 3.1 mg ml⁻¹ and the immobilized time for (b) was 10 h.



The relative activity of HRP/Cu-Mo₆O₂₀ after being used eight times.

zation was confirmed. As can be seen from Figs. 5(a) and 5(b), the HRP concentration and immobilization time are 3.1 mg ml^{-1} and 10 h, respectively. Under these optimum conditions, the amount of immobilized HRP reached a maximum of 300.1 mg g^{-1} , which can be calculated from the equation: HRP loading (mg g⁻¹) = $(c_0 - c)V/W_s$ (Chao *et al.*, 2013) and the standard curve of HRP (Fig. S8 in the supporting information). The maximum of HRP loading on **Cu-Mo₆O₂₀** (300.1 mg g^{-1}) is significantly higher than those on our reported Preyssler-type POM-based Cu^{II} coordination polymers (158.7 and 157.5 mg g^{-1} ; Du *et al.*, 2017), but a longer immobilization time was needed for Cu-Mo₆O₂₀. In addition, compared with other organically functionalized supports, such as mesoporous organosilica (126 mg g^{-1}) and modified chitosan (82.66 mg g^{-1}) (Zhou *et al.*, 2013; Monier *et* al., 2010), Cu-Mo₆O₂₀ also has a higher loading capacity for HRP. Moreover, the structure of Cu-Mo₆O₂₀ is unchanged before and after immobilizing HRP. As shown in Figs. S9 and



Figure 7

Linear calibration plot for H₂O₂ detection by using HRP/**Cu-Mo₆O₂₀** (HRP loading: 300.1 mg g⁻¹), $\Delta A = A$ (immobilized HRP, $\lambda = 524$ nm) – A (blank, $\lambda = 524$ nm). The reaction time was 5 min. Pure **Cu-Mo₆O₂₀** without any HRP was used to carry out control measurements to obtain a blank value.

S10 in the supporting information for $Cu-Mo_6O_{20}$ and HRP/ $Cu-Mo_6O_{20}$, respectively, the IR characteristic peaks are basically the same, and the main diffraction peaks are consistent, indicating that the structural skeleton of $Cu-Mo_6O_{20}$ is retained, also reflecting that HRP is only adsorbed on the surface of $Cu-Mo_6O_{20}$, and does not enter into the crystal lattices of the support. In order to evaluate the effect of $Cu-Mo_6O_{20}$ on the secondary structure of HRP, the CD spectra of the free HRP solution and the eluting HRP desorbed from HRP/ $Cu-Mo_6O_{20}$ were recorded (Fig. S11 in the supporting information), where the curve profiles coincide well with each other for free and desorbed HRP, showing that the secondary structure of the enzyme is retained.

Moreover, the satisfying catalytic activity of HRP/Cu-Mo₆O₂₀ is still retained after eight catalytic cycles (Fig. 6), and the activity decrease may be caused by some HRP leaching during repeated washing and prolonged exposure to high concentrations of substrate (Qiu et al., 2010). Compared with the reported immobilized HRP by pore adsorption (Zhou et al., 2013), HRP/Cu-Mo₆O₂₀ possesses better reusability. Meanwhile, HRP/Cu-Mo₆O₂₀ is also a potential material for H_2O_2 detection, and the linear range is from 2.35 $\times 10^{-6}$ to 4.0×10^{-4} mol l⁻¹ (Fig. 7). Additionally, to exclude the possibility for peroxidase activity of the carrier itself, *i.e.* pure Cu-Mo₆O₂₀ without any HRP was selected as a catalyst for the same co-oxidation colour reaction of phenol and 4-AAP with H_2O_2 to obtain a blank value, the result showing that carrier Cu-Mo₆O₂₀ has little effect on the catalytic reaction under identical reaction conditions. It was found that the red colour of the reaction solution will appear slowly after a long time (about 10 h).

4. Conclusion

The new isopolyhexamolybdate-based crystalline material Cu-Mo₆O₂₀ was successfully synthesized from the Anderson-type cobalt hexamolybdate CoMo₆ under hydrothermal conditions. **Cu-Mo₆O₂₀** is a Cu^{II} coordination polymer with a 3D structure composed of unbounded 1D chains which were constructed by $[Mo_6O_{20}]^{4-}$ isopolyanions and $[Cu(H_2biim)(H_2O)]^{2+}$ complex cations. Cu-Mo₆O₂₀ has good acid catalytic activity towards ketalation of cyclohexanone with glycol and it also exhibits a stronger adsorbtion ability towards HRP than our previously reported two cases of Preyssler-type POM-based Cu^{II}-H₂biim/ H₂O coordination polymers and some other inorganic-organic hybrid compounds, and the maximum immobilized HRP loading reaches 300.1 mg g^{-1} . The immobilized enzyme HRP/ Cu-Mo₆O₂₀ is stable and can be reused in catalytic processes. Moreover, HRP/Cu-Mo₆O₂₀ can be applied to detect trace amounts of H_2O_2 with a linear response ranging from 2.35 \times 10^{-6} to 4.0×10^{-4} mol l⁻¹.

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A new hexamolybdate-based copper-2,2'-biimidazole coordination polymer serving as an acid catalyst and support for enzyme immobilization

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Computing details

Data collection: *SMART* (Bruker, 2005); cell refinement: *SMART* (Bruker, 2005); data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

(|)

Crystal data

 $[Cu_2Mo_6O_{20}(C_6H_6N_4)_2(H_2O)_2]$ $M_r = 1327.07$ Triclinic, $P\overline{1}$ a = 8.065 (3) Å b = 10.293 (4) Å c = 10.837 (4) Å a = 64.090 (5)° $\beta = 75.186$ (5)° $\gamma = 71.141$ (5)° V = 758.8 (5) Å³

Data collection

Bruker SMART CCD area detector diffractometer phi and ω scans Absorption correction: multi-scan (SADABS; Sheldrick, 2003) $T_{\min} = 0.724, T_{\max} = 0.795$ 3875 measured reflections

Refinement

Refinement on F^2 Least-squares matrix: full $R[F^2 > 2\sigma(F^2)] = 0.018$ $wR(F^2) = 0.042$ S = 1.062639 reflections 235 parameters 2 restraints

Z = 1 F(000) = 630 $D_x = 2.904 \text{ Mg m}^{-3}$ Mo K α radiation, $\lambda = 0.71073 \text{ Å}$ Cell parameters from 2954 reflections $\theta = 2.1-31.0^{\circ}$ $\mu = 3.87 \text{ mm}^{-1}$ T = 296 KBlock, green $0.09 \times 0.07 \times 0.06 \text{ mm}$

2639 independent reflections 2409 reflections with $I > 2\sigma(I)$ $R_{int} = 0.011$ $\theta_{max} = 25.0^{\circ}, \ \theta_{min} = 2.1^{\circ}$ $h = -9 \rightarrow 9$ $k = -12 \rightarrow 5$ $l = -12 \rightarrow 11$

Hydrogen site location: mixed H atoms treated by a mixture of independent and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0182P)^2 + 0.8925P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{max} = 0.002$ $\Delta\rho_{max} = 0.36$ e Å⁻³ $\Delta\rho_{min} = -0.49$ e Å⁻³ Extinction correction: SHELXL2014 (Sheldrick, 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/sin(2\theta)]^{-1/4}$ Extinction coefficient: 0.00089 (19)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

	x	У	Ζ	$U_{ m iso}$ */ $U_{ m eq}$
Mol	0.98397 (3)	0.33719 (3)	0.03177 (3)	0.01070 (8)
Mo2	0.60552 (3)	0.61615 (3)	-0.14598 (3)	0.01038 (8)
Mo3	1.36521 (3)	0.35113 (3)	-0.13694 (3)	0.01252 (8)
Cu1	0.74909 (5)	0.03949 (4)	0.26078 (4)	0.01640 (10)
01	0.8072 (3)	0.3884 (2)	-0.0564 (2)	0.0153 (5)
O2	0.4604 (3)	0.4673 (2)	-0.0845 (2)	0.0130 (5)
03	0.4304 (3)	0.7745 (2)	-0.1873 (2)	0.0171 (5)
O4	1.1704 (3)	0.2611 (2)	-0.0937 (2)	0.0160 (5)
05	0.7053 (3)	0.6093 (3)	-0.3023 (2)	0.0205 (5)
O6	1.2507 (3)	0.3138 (2)	0.0931 (2)	0.0139 (5)
07	1.5341 (3)	0.1920 (3)	-0.1027 (2)	0.0221 (5)
08	0.9664 (3)	0.1694 (2)	0.1693 (2)	0.0179 (5)
09	0.9035 (3)	0.4712 (2)	0.1197 (2)	0.0137 (5)
O10	1.3870 (3)	0.4373 (3)	-0.3123 (2)	0.0261 (6)
N1	0.9166 (4)	-0.1542 (3)	0.3601 (3)	0.0219 (6)
N2	0.7007 (4)	0.0549 (3)	0.4419 (3)	0.0208 (6)
N3	1.0422 (4)	-0.2950 (3)	0.5499 (3)	0.0255 (7)
H3B	1.0674	-0.3268	0.6323	0.031*
N4	0.7703 (4)	-0.0341 (4)	0.6520 (3)	0.0277 (7)
H4B	0.8209	-0.0913	0.7249	0.033*
C1	0.9213 (4)	-0.1711 (4)	0.4888 (3)	0.0193 (7)
C2	0.8025 (4)	-0.0553 (4)	0.5341 (3)	0.0188 (7)
C3	1.0407 (5)	-0.2745 (4)	0.3394 (4)	0.0294 (9)
H3A	1.0670	-0.2928	0.2589	0.035*
C4	1.1183 (5)	-0.3617 (4)	0.4566 (4)	0.0315 (9)
H4A	1.2061	-0.4497	0.4707	0.038*
C5	0.5996 (5)	0.1512 (4)	0.5058 (4)	0.0259 (8)
H5A	0.5169	0.2391	0.4661	0.031*
C6	0.6412 (5)	0.0962 (4)	0.6357 (4)	0.0306 (9)
H6A	0.5920	0.1384	0.7013	0.037*
O1W	0.7698 (4)	0.0086 (3)	0.0923 (3)	0.0286 (6)
H1WA	0.795 (5)	-0.076 (2)	0.088 (4)	0.031 (11)*
H1WB	0.689 (4)	0.066 (4)	0.042 (4)	0.034 (12)*

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters $(Å^2)$

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mo1	0.00964 (14)	0.00824 (14)	0.01472 (15)	-0.00114 (10)	-0.00385 (10)	-0.00442 (11)
Mo2	0.01055 (14)	0.00962 (14)	0.01067 (14)	-0.00216 (10)	-0.00322 (10)	-0.00288 (11)
Mo3	0.01202 (14)	0.01383 (15)	0.01426 (15)	-0.00256 (11)	-0.00265 (11)	-0.00763 (12)
Cu1	0.0205 (2)	0.0121 (2)	0.0155 (2)	0.00063 (17)	-0.00799 (17)	-0.00461 (17)
01	0.0134 (11)	0.0148 (11)	0.0190 (12)	-0.0011 (9)	-0.0050 (9)	-0.0080 (10)
O2	0.0120 (11)	0.0151 (11)	0.0124 (11)	-0.0038 (9)	-0.0036 (9)	-0.0044 (10)
03	0.0161 (12)	0.0150 (12)	0.0188 (12)	-0.0014 (10)	-0.0062 (9)	-0.0050 (10)
O4	0.0148 (11)	0.0154 (12)	0.0234 (12)	-0.0027 (9)	-0.0029 (9)	-0.0131 (10)
05	0.0213 (12)	0.0219 (13)	0.0172 (12)	-0.0053 (10)	-0.0009 (10)	-0.0076 (11)
O6	0.0132 (11)	0.0125 (11)	0.0166 (12)	-0.0017 (9)	-0.0049 (9)	-0.0057 (9)
O7	0.0199 (13)	0.0208 (13)	0.0283 (14)	0.0009 (10)	-0.0068 (10)	-0.0142 (11)
08	0.0186 (12)	0.0111 (11)	0.0219 (12)	-0.0046 (9)	-0.0082 (10)	-0.0009 (10)
09	0.0130 (11)	0.0122 (11)	0.0171 (12)	-0.0028 (9)	-0.0030 (9)	-0.0065 (10)
O10	0.0269 (14)	0.0349 (15)	0.0168 (12)	-0.0090 (12)	-0.0044 (10)	-0.0083 (11)
N1	0.0239 (15)	0.0169 (15)	0.0223 (16)	-0.0009 (13)	-0.0073 (13)	-0.0060 (13)
N2	0.0228 (15)	0.0196 (15)	0.0163 (15)	-0.0003 (12)	-0.0074 (12)	-0.0047 (13)
N3	0.0262 (16)	0.0206 (16)	0.0250 (17)	0.0009 (13)	-0.0148 (13)	-0.0031 (14)
N4	0.0320 (17)	0.0306 (18)	0.0149 (15)	-0.0002 (14)	-0.0101 (13)	-0.0053 (14)
C1	0.0201 (17)	0.0138 (17)	0.0188 (18)	-0.0036 (14)	-0.0069 (14)	0.0003 (14)
C2	0.0202 (17)	0.0172 (17)	0.0161 (17)	-0.0065 (14)	-0.0040 (14)	-0.0017 (14)
C3	0.033 (2)	0.021 (2)	0.034 (2)	0.0026 (17)	-0.0087 (17)	-0.0151 (18)
C4	0.029 (2)	0.022 (2)	0.041 (2)	0.0066 (16)	-0.0157 (18)	-0.0123 (19)
C5	0.028 (2)	0.0219 (19)	0.0231 (19)	0.0049 (16)	-0.0083 (16)	-0.0095 (16)
C6	0.034 (2)	0.034 (2)	0.025 (2)	-0.0009 (18)	-0.0041 (17)	-0.0181 (18)
O1W	0.0431 (17)	0.0167 (14)	0.0300 (15)	0.0070 (12)	-0.0196 (13)	-0.0145 (12)

Atomic displacement parameters $(Å^2)$

Geometric parameters (Å, °)

Mo1-01	1.730 (2)	Cu1—08	2.305 (2)
Mo1—O8	1.739 (2)	O2—Mo3 ^{iv}	1.938 (2)
Mo1—O9	1.868 (2)	O2—Mo2 ⁱⁱ	2.236 (2)
Mo1—O4	1.961 (2)	O3—Cu1 ⁱⁱ	1.965 (2)
Mo1—O9 ⁱ	2.230 (2)	O6—Mo2 ⁱ	1.853 (2)
Mo1—O6	2.320 (2)	O9—Mo1 ⁱ	2.230 (2)
Mo1—Mo3	3.1621 (11)	O9—Mo3 ⁱ	2.367 (2)
Mo1—Mo1 ⁱ	3.1980 (14)	N1—C1	1.337 (4)
Mo2—O5	1.701 (2)	N1—C3	1.383 (5)
Mo2—O3	1.746 (2)	N2—C2	1.336 (4)
Mo2—O6 ⁱ	1.853 (2)	N2—C5	1.384 (4)
Mo2—O2	2.007 (2)	N3—C1	1.344 (4)
Mo2—O2 ⁱⁱ	2.236 (2)	N3—C4	1.374 (5)
Mo2—O1	2.332 (2)	N3—H3B	0.8600
Mo2—Mo3 ⁱ	3.3005 (12)	N4—C2	1.337 (5)
Mo3—O10	1.699 (2)	N4—C6	1.378 (5)
Mo3—O7	1.720 (2)	N4—H4B	0.8600

Mo3—O4	1.932 (2)	C1—C2	1.453 (5)
Mo3—O2 ⁱⁱⁱ	1.938 (2)	C3—C4	1.362 (5)
Mo3—O6	2.330 (2)	С3—НЗА	0.9300
Mo3—O9 ⁱ	2.367 (2)	C4—H4A	0.9300
Mo3—Mo2 ⁱ	33005(12)	C5—C6	1 356 (5)
Cu1 - O1W	1.944(3)	C5—H5A	0.9300
Cu1 O1W	1.944(3) 1.965(2)	C6 H6A	0.9300
Cul N2	1.905(2)		0.9300
Cu1—IN2	1.900(3)		0.848(10)
Cui—Ni	2.021 (3)	OIW—HIWB	0.847 (10)
01—Mo1—08	105.53 (10)	O2 ⁱⁱⁱ —Mo3—Mo1	107.91 (7)
01—Mo1—09	99.82 (10)	06-Mo3-Mo1	47.03 (5)
$O_8 M_{O1} O_9$	101.07(11)	O^{0} Mo3 Mo1	17.05 (5)
$O_1 Mo_1 O_4$	98.42(10)	$O_10 Mo_3 Mo_2^i$	142.83(0)
0^{8} Mol 0^{4}	90.42(10)	$07 M_{02} M_{02}$	142.83(9)
08 - M01 - 04	99.55(10)	$O/-MOS-MOZ^{2}$	91.19 (8)
09-M01-04	146.97 (9)	04 M05 M02 ⁴	107.00(7)
01—Mo1—09 ⁴	93.92 (9)	$O2^{m}$ —Mo3—Mo2 ^r	41.02 (6)
08—Mo1—09 ¹	160.21 (9)	O6—Mo3—Mo2 ¹	33.08 (5)
O9—Mo1—O9 ¹	77.76 (10)	$O9^{i}$ —Mo3—Mo2 ⁱ	79.92 (5)
O4—Mo1—O9 ⁱ	73.73 (9)	Mo1—Mo3—Mo2 ⁱ	77.48 (2)
O1—Mo1—O6	164.31 (9)	O1W—Cu1—O3 ⁱⁱ	88.80 (10)
O8—Mo1—O6	89.31 (9)	O1W—Cu1—N2	171.61 (13)
O9—Mo1—O6	81.63 (8)	O3 ⁱⁱ —Cu1—N2	91.04 (10)
O4—Mo1—O6	73.66 (8)	O1W—Cu1—N1	97.25 (11)
O9 ⁱ —Mo1—O6	71.01 (8)	O3 ⁱⁱ —Cu1—N1	172.79 (11)
O1—Mo1—Mo3	119.19 (8)	N2—Cu1—N1	82.40 (12)
O8—Mo1—Mo3	116.11 (8)	O1W—Cu1—O8	92.83 (11)
O9—Mo1—Mo3	111.74 (7)	O3 ⁱⁱ —Cu1—O8	90.16 (9)
04—Mo1—Mo3	35,38 (6)	N2—Cu1—O8	95.57 (11)
$O9^{i}$ Mo1 Mo3	48 38 (5)	N1—Cu1—O8	93 43 (11)
06-M01-M03	47 29 (6)	$M_0 = 01 - M_0^2$	13151(11)
Ω_1 —Mo1—Mo1 ⁱ	98 47 (7)	$Mo3^{iv}$ $O2$ $Mo2$	$146\ 84\ (12)$
O_{1}^{2} Mo1 Mo1	141.00(8)	$Mo^{2iv} = O^2 = Mo^{2ii}$	140.04(12) 104.30(0)
$O_0 M_{01} M_{01}^{i}$	141.00(0)	$M_{02} = 02 = M_{02}$	104.30(9)
$O_4 Mo_1 Mo_1$	42.93(7)	$M_{02} = O_2 = M_{02}$	106.01(9)
	10/.11(/)		1/1.89 (14)
	34.80 (6)	Mo3—O4—Mol	108.63 (10)
O6—Mo1—Mo1	71.83 (5)	Mo2 ⁱ —O6—Mo1	151.38 (11)
Mo3—Mo1—Mo1 ¹	75.714 (13)	Mo2 ⁱ —O6—Mo3	103.60 (10)
O5—Mo2—O3	103.81 (11)	Mo1—O6—Mo3	85.69 (7)
$O5-Mo2-O6^{i}$	105.88 (11)	Mo1—O8—Cu1	133.36 (11)
O3—Mo2—O6 ⁱ	99.09 (10)	Mo1—O9—Mo1 ⁱ	102.24 (10)
O5—Mo2—O2	99.76 (10)	Mo1—O9—Mo3 ⁱ	133.99 (10)
O3—Mo2—O2	96.41 (10)	Mo1 ⁱ —O9—Mo3 ⁱ	86.86 (8)
O6 ⁱ —Mo2—O2	145.72 (9)	C1—N1—C3	106.1 (3)
O5—Mo2—O2 ⁱⁱ	157.22 (10)	C1—N1—Cu1	111.6 (2)
O3—Mo2—O2 ⁱⁱ	98.12 (9)	C3—N1—Cu1	142.1 (3)
O6 ⁱ —Mo2—O2 ⁱⁱ	76.26 (9)	C2—N2—C5	106.2 (3)
O2—Mo2—O2 ⁱⁱ	71.39 (9)	C2—N2—Cu1	113.6 (2)

O5—Mo2—O1	84.46 (10)	C5—N2—Cu1	140.0 (2)
O3—Mo2—O1	170.22 (9)	C1—N3—C4	107.4 (3)
O6 ⁱ —Mo2—O1	83.37 (9)	C1—N3—H3B	126.3
O2—Mo2—O1	76.79 (8)	C4—N3—H3B	126.3
O2 ⁱⁱ —Mo2—O1	73.17 (8)	C2—N4—C6	107.6 (3)
O5—Mo2—Mo3 ⁱ	147.98 (8)	C2—N4—H4B	126.2
O3—Mo2—Mo3 ⁱ	92.04 (7)	C6—N4—H4B	126.2
O6 ⁱ —Mo2—Mo3 ⁱ	43.33 (7)	N1—C1—N3	110.8 (3)
O2—Mo2—Mo3 ⁱ	105.98 (6)	N1—C1—C2	116.3 (3)
O2 ⁱⁱ —Mo2—Mo3 ⁱ	34.67 (6)	N3—C1—C2	132.8 (3)
O1—Mo2—Mo3 ⁱ	83.25 (6)	N2—C2—N4	110.7 (3)
O10—Mo3—O7	105.13 (12)	N2—C2—C1	115.8 (3)
O10—Mo3—O4	103.31 (11)	N4—C2—C1	133.5 (3)
O7—Mo3—O4	98.59 (11)	C4—C3—N1	108.7 (3)
Q10—Mo3—Q2 ⁱⁱⁱ	102.58 (11)	С4—С3—Н3А	125.7
07—Mo3—O2 ⁱⁱⁱ	99.05 (10)	N1—C3—H3A	125.7
04—Mo3—O2 ⁱⁱⁱ	143.45 (9)	C3—C4—N3	107.0 (3)
$010 - M_0 - M_0 - 06$	158.41 (10)	C3—C4—H4A	126.5
07—Mo3—O6	96.44 (10)	N3—C4—H4A	126.5
04—Mo3—06	73.93 (8)	C6—C5—N2	108.7 (3)
$O2^{iii}$ —Mo3—O6	72.48 (8)	C6—C5—H5A	125.7
O10—Mo3—O9 ⁱ	90.22 (10)	N2—C5—H5A	125.7
O7—Mo3—O9 ⁱ	163.34 (10)	C5—C6—N4	106.9 (3)
O4—Mo3—O9 ⁱ	71.06 (9)	С5—С6—Н6А	126.6
$O2^{iii}$ —Mo3—O9 ⁱ	83.52 (8)	N4—C6—H6A	126.6
O6—Mo3—O9 ⁱ	68.49 (7)	Cu1—O1W—H1WA	125 (3)
O10—Mo3—Mo1	119.29 (8)	Cu1—O1W—H1WB	115 (3)
O7—Mo3—Mo1	119.71 (9)	H1WA—O1W—H1WB	108 (4)
O4—Mo3—Mo1	36.00 (6)		
O8—Mo1—O1—Mo2	135.03 (15)	Mo1 ⁱ —Mo1—O9—Mo3 ⁱ	97.56 (16)
O9—Mo1—O1—Mo2	29.57 (16)	C3—N1—C1—N3	0.3 (4)
O4—Mo1—O1—Mo2	-122.78 (15)	Cu1—N1—C1—N3	-175.7 (2)
O9 ⁱ —Mo1—O1—Mo2	-48.67 (15)	C3—N1—C1—C2	179.0 (3)
O6—Mo1—O1—Mo2	-64.4 (4)	Cu1—N1—C1—C2	3.1 (4)
Mo3—Mo1—O1—Mo2	-92.25 (14)	C4—N3—C1—N1	-0.4(4)
Mo1 ⁱ —Mo1—O1—Mo2	-13.94 (15)	C4—N3—C1—C2	-178.9(4)
O1—Mo1—O8—Cu1	-10.07 (19)	C5—N2—C2—N4	0.4 (4)
O9—Mo1—O8—Cu1	93.81 (16)	Cu1—N2—C2—N4	176.5 (2)
O4—Mo1—O8—Cu1	-111.59 (16)	C5—N2—C2—C1	180.0 (3)
O9 ⁱ —Mo1—O8—Cu1	-179.13 (17)	Cu1—N2—C2—C1	-3.9(4)
O6—Mo1—O8—Cu1	175.10 (16)	C6—N4—C2—N2	0.0 (4)
Mo3—Mo1—O8—Cu1	-144.49 (12)	C6—N4—C2—C1	-179.5 (4)
Mo1 ⁱ —Mo1—O8—Cu1	115.81 (14)	N1—C1—C2—N2	0.5 (5)
O1-Mo1-O9-Mo1 ⁱ	-91.91 (10)	N3—C1—C2—N2	178.9 (4)
O8—Mo1—O9—Mo1 ⁱ	159.76 (9)	N1—C1—C2—N4	179.9 (4)
O4-Mo1-O9-Mo1 ⁱ	30.7 (2)	N3—C1—C2—N4	-1.7 (7)
O9 ⁱ —Mo1—O9—Mo1 ⁱ	-0.001 (1)	C1—N1—C3—C4	-0.1 (4)

06-Mo1-09-Mo1 ⁱ	72.26 (9)	Cu1—N1—C3—C4	173.8 (3)
Mo3—Mo1—O9—Mo1 ⁱ	35.09 (9)	N1—C3—C4—N3	-0.1 (5)
O1—Mo1—O9—Mo3 ⁱ	5.65 (17)	C1—N3—C4—C3	0.3 (4)
O8—Mo1—O9—Mo3 ⁱ	-102.68 (15)	C2—N2—C5—C6	-0.7 (4)
O4-Mo1-O9-Mo3 ⁱ	128.26 (16)	Cu1—N2—C5—C6	-175.1 (3)
O9 ⁱ —Mo1—O9—Mo3 ⁱ	97.56 (16)	N2-C5-C6-N4	0.7 (5)
O6—Mo1—O9—Mo3 ⁱ	169.82 (16)	C2—N4—C6—C5	-0.4 (4)
Mo3—Mo1—O9—Mo3 ⁱ	132.65 (12)		

Symmetry codes: (i) -*x*+2, -*y*+1, -*z*; (ii) -*x*+1, -*y*+1, -*z*; (iii) *x*+1, *y*, *z*; (iv) *x*-1, *y*, *z*.

Hydrogen-bond geometry (Å, °)

$D \cdots A$	D—H··· A
3.303 (4)	164
2.834 (4)	151
3.013 (4)	128
2.654 (3)	174 (4)
2.809 (3)	170 (4)
	D…A 3.303 (4) 2.834 (4) 3.013 (4) 2.654 (3) 2.809 (3)

Symmetry codes: (iv) *x*-1, *y*, *z*; (v) -*x*+2, -*y*, -*z*+1; (vi) -*x*+2, -*y*, -*z*.