锰(II)配合物修饰的 Preyssler 型多金属氧酸盐的合成、晶体结构和催化性能

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摘要: 利用水热法合成了 1 个新的 Mn(II)-H_2biim/H_2O 配合物修饰的 Preyssler 型多金属氧酸盐,{[Mn(H_2biim)$_2$(H_2O)$_2$]$_2$[Mn(H_2biim)$_3$]$_5$Cl}[H(NaP$_5$W$_{30}$O$_{110}$)]·20H_2O (1)(H_2biim=2,2′-联咪唑),并通过单晶 X-射线衍射、元素分析、IR 光谱分析、热重分析和电化学分析等对其进行了表征,同时探讨了合成环己酮乙二醇缩酮的催化活性。结构分析表明,化合物 **1** 分子中含有 1 个[NaP$_5$W$_{30}$O$_{110}$]$^{14-}$多阴离子,其周围有 7 个游离的 Mn(II)-H_2biim/H_2O 配合物单元,分子间通过 N–H···O/OW 和 N–H···Cl 两种类型的氢键构成三维网络结构。研究表明该化合物是 1 种可重复使用、性能良好、环境友好型羰基保护催化剂。

关键词: Preyssler 结构;钨磷酸盐;锰(II)配合物;联咪唑;水热合成;催化性能

Synthesis, Crystal Structure and Catalytic Property of a Preyssler-Type Polyoxometalate Modified by Mn(II) Complexes

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Abstract: A new Preyssler-type polyoxometalate modified by Mn(II)-H_2biim/H_2O fragments, namely {[Mn(H_2biim)$_2$(H_2O)$_2$]$_2$[Mn(H_2biim)$_3$]$_5$Cl][H(NaP$_5$W$_{30}$O$_{110}$)]·20H_2O (**1**) (H_2biim=2,2′-biimidazole) has been hydrothermally synthesized, and characterized by single-crystal X-ray diffraction, elemental analysis, thermogravimetric analysis and electrochemical analysis. Its catalytic activity for synthesis of cyclohexanone ethylene ketal has been investigated. Compound **1** contains a [NaP$_5$W$_{30}$O$_{110}$]$^{14-}$ polyoxoanion, and seven isolated Mn(II)-H_2biim/H_2O complex units. A 3D framework is constructed through N−H···O/OW and N−H···Cl hydrogen bonds between H_2biim molecules and polyoxoanion or water molecules, and Cl$^-$, and π-π interactions between the imidazole rings of biimidazole ligands. It was found that compound **1** is a new environmentally friendly catalyst and has good properties in recyclings for the protection of carbonyl compound. CCDC: 967599.

Key words: preyssler structure; tungstophosphate; manganese complex; biimidazole; hydrothermal synthesis; catalytic activity

0 Introduction

The large polyoxometalate (POM) clusters, such as [NaP$_5$W$_{30}$O$_{110}$]$^{14-}$ (abbreviated as {P$_5$W$_{30}$}), [P$_8$W$_{48}$O$_{184}$]$^{40-}$, etc, have been being attracted significant attention due to their fascinating architectures and potential functions[1-8]. The Preyssler-type {P$_5$W$_{30}$} POM polyanion, having an internal cavity, is a better metal cation-

encapsulated complex[9-13]. That is to say, as a building block, {P$_5$W$_{30}$} anion can incorporate transition metals and organic groups forming inorganic-organic hybrid materials[14-16]. In recent years, a lot of research works about the applications of the Preyssler-type POMs have been reported, especially concerned the most widely used catalysts. As can be seen from the literatures′ results, the Preyssler-type POMs, as green, efficient and eco-friendly catalysts, have been used in organic synthesis, such as the esterification of organic acids[17-19], the oxidation of alcohols, aldehydes and thiols[14,20-23], the dehydration of oximes[24], the protection of carbonyl compound[25]. But the reported compounds in the literatures are mainly simple metal cation-encapsulated Preyssler′s, while the Preyssler′s derivates, i.e. transition metal (TM)-organic ligand complex-modified or extended structures have rarely been reported so far. To the best of our knowledge, E. B. Wang group successfully synthesized the first extended structures based on Preyssler anions and trivalent lanthanide cations in 2007[15]. In 2011, Wang et al. reported a new inorganic-organic hybrid compound modified by Co-1,1′-(1,4-butanediyl)bis-1H-benzimidazole complex[16], and investigated its electrocatalytic activity toward the reduction of nitrite. Recently, Yang et al. synthesized a {P$_5$W$_{30}$}-based POM containing cubic {Cu$_4$} clusters[1]. To sum up the above examples, synthesis of such inorganic-organic hybrid compounds containing some larger polyanion with higher charge is much more difficult. One of the reasons is that the organic group can form precipitate immediately in the POM system. So, the synthesis and study of these hybrids will help us to understand the interactions between organic molecules and POMs, and maybe obtain some multifunctional catalysts. In addition, 2,2′-biimidazole, as a polydentate ligand, is able to coordinate to transition metals with three reversible types: neutral (H$_2$biim), monoanion (Hbiim$^-$), and dianion (biim^{2-}) types[26-27], but few compounds involving transition metal, H$_2$biim ligands, and polyoxoanions have been reported. In our previous work, we have successfully synthesized three extended Preyssler-type polyoxometalates modified by transition metal-2,2′-

biimidazole complexes, and explored the catalytic activities for the oxidation of cyclohexanol to cyclohexanone, and found that the Preyssler POM catalysts were easily recycled recovery and reused without the loss of its catalytic activities [14]. In order to get more in-depth information of the Preyssler POMs, we endeavored to prepare new inorganic-organic hybrid compounds based on the TM-2,2′-biimidazole complexes-modified {P$_5$W$_{30}$} clusters, and to measure the crystal structures, thermal stabilities and electrochemical properties of these Preyssler-type POMs, and preliminarily explore the electrocatalytic activities toward the reduction of hydrogen peroxide, and the catalytic activities for the protection of carbonyl compound with ethanediol. Herein, we have obtained a new Mn(Ⅱ)-H$_2$biim/H$_2$O fragments-decorated Preyssler-type polyoxotungstopho-sphate, i.e. {[Mn(H$_2$biim)$_2$(H$_2$O)$_2$]$_2$[Mn(H$_2$biim)$_3$]$_5$Cl} [H(NaP$_5$W$_{30}$O$_{110}$)]· 20H$_2$O (**1**).

1 Experimental

1.1 Materials and methods

All chemicals were purchased commercially and used without further purification. The Preyssler-type tungstophosphate K$_{12.5}$Na$_{1.5}$[NaP$_5$W$_{30}$O$_{110}$]·15H$_2$O (i.e. the parent {P$_5$W$_{30}$}) was synthesized according to the reported method[28]. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 2400 CHN elemental analyzer. The elemental analyses of P, Cl, Na, Mn and W were analyzed on a Plasma-Spec-Ⅱ ICP atomic emission spectrometer. IR spectrum was recorded using KBr pellets on a Bruker AXS TENSOR-27 FTIR spectrometer in the range of 4 000 ~400 cm^{-1}. TG analysis was performed on a Pyris Diamond TG-DTA thermal analyzer at a heating rate of 10 ℃·min^{-1} from 35 to 900 ℃ in an air atmosphere. All electrochemical measurements were carried out on a CHI 604B electrochemical workstation at room temperature. The working electrode was compound **1** bulk-modified carbon paste electrode (abbreviated as 1-MCPE), prepared by hand-mixing of graphite powder with paraffin oil at a ratio of 3:50 in an agate mortar. A platinum wire was used as the counter-

electrode and Ag/AgCl (3 mol·L^{-1} KCl) as the reference electrode. The yield of cyclohexanone ethylene ketal was confirmed on a JK-GC112A Gas Chromatograph.

1.2 Synthesis of {[Mn(H₂biim)₂(H₂O)₂]₂ [Mn(H₂biim)₃]₅Cl}[H(NaP₅W₃₀O₁₁₀)]·20H₂O (1)

A mixture of $K_{12.5}Na_{1.5}[NaP_5W_{30}O_{110}]\cdot15H_2O$ (0.40 g, 0.05 mmol), H₂biim (0.09 g, 0.67 mmol), MnCl₂· 4H₂O (0.40 g, 2.02 mmol), and 20 mL of distilled water was stirred for 20 min. The resulting suspension was sealed in a Teflon-lined autoclave (30 mL) and kept at 120 ℃ for 3 d. After slow cooling to ca. 40 °C, the orange block-shape crystals were easily separated from the hot mother solution by decantation, and washed with distilled water and dried at ambient temperature (75% yield based on W). Elemental analyses Calcd. for $C_{114}H_{163}ClMn_7N_{76}NaO_{134}P_5W_{30}$(%): C, 12.61; H, 1.51; N, 9.81; P, 1.43; Na, 0.21; Cl, 0.33; Mn, 3.54; W, 50.81. Found(%): C, 12.64; H, 1.56; N, 9.79; P, 1.41; Na, 0.25; Cl, 0.35; Mn, 3.52; W, 50.85. IR (solid KBr pellet, cm^{-1}): 3 582.3 (w), 3 361.8(w), 3 174.6(m), 3 001.1(w), 2 920.2(w), 2 806.9(w), 1 624.7 (w), 1 524.5 (w), 1 404.2 (m), 1 304.0 (w), 1 163.7(m), 1 096.7(m), 929.5(s), 796.1(s), 682.9(w).

1.3 X-ray crystallography

X-ray diffraction data was collected on a Bruker Smart APEX Ⅱ CCD X-diffractometer equipped with graphite-monochromated Mo Kα radiation (λ=0.071 073 nm). An empirical absorption correction was applied using the SADABS program. Cell parameters were obtained by the global refinement of the positions of all collected reflections. The structures were solved by direct methods and refined by the full-matrix least-squares fitting on F^2 using SHELXTL-97 package[29-30]. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms on C or N atoms were added in calculated positions. Crystal data and structure refinement parameters of compound **1** are listed in Table 1. Selected bond lengths and angles are given in Table S1. Hydrogen bonds are listed in Table S2. During the refinement of compound **1**, no protonated O atom was noted on the polyanions by the bond valence sum (BVS) calculations and H protons were added due to charge-balance considerations[31]. In compound **1**, only partial lattice water molecules can be accurately assigned from the residual electron peaks, whereas the rest were directly included in the molecular formula on the basis of the elemental analyses and TG analysis. All hydrogen atoms on water molecules were directly included in the final molecular formula.

CCDC: 967599.

1.4 Electrocatalytic activity toward the reduction of hydrogen peroxide

In the potential range of 0 to −700 mV, the electrocatalytic study of compound **1** was conducted in 2 mol·L^{-1} H₂SO₄ solution at room temperature, the scan rate was 200 mV·s^{-1}. The concentrations are increased from 0 to 20 mmol for H₂O₂. The electrocatalytic activity toward the reduction of hydrogen peroxide can be evaluated by peak current changes in

Table 1 Crystal and refinement data for compound 1

Formula	$C_{114}H_{163}ClMn_7N_{76}NaO_{134}P_5W_{30}$	Z	2
Formula weight	10 855.58	D_c / (g·cm^{-3})	3.042
Crystal system	Triclinic	Abs. coeff. / mm^{-1}	15.008
Space group	$P\bar{1}$	Wavelength / nm	0.071 073
a / nm	2.060 10(11)	Temperature / K	296(2)
b / nm	2.403 35(13)	Reflections collected	60 713
c / nm	2.518 44(13)	Unique data, R_{int}	41 474, 0.045 8
α / (°)	103.502(1)	Goodness-of-fit on F^2	1.017
β / (°)	91.789(1)	θ range / (°)	1.48 to 25.00
γ / (°)	101.303(1)	R_1 ($I>2\sigma(I)$)	0.0543
V / nm³	11.850 5(11)	wR_2 (all data)	0.142 2

the CV curves.

1.5 General procedure for catalytic synthesis of cyclohexanone ethylene ketal

Acid-catalyzed synthesis of cyclohexanone ethylene ketal was used as a model reaction to evaluate the catalytic performances of compound **1**, the parent {P_5W_{30}} and $MnCl_2$. In a typical procedure, the catalyst (compound **1**, 0.12 g, 0.011 mmol) was added to a mixture of cyclohexanone (9.81 g, 0.10 mol), ethanediol (8.69 g, 0.14 mol) and cyclohexane (10 mL) in a 50 mL three-necked round-bottom flask equipped with a Dean-Stark apparatus to remove the water continuously from the reaction mixture (note: maintaining the molar ratio of W/Mn: cyclohexanone is 1:300, and these catalysts were pretreated by being dried at 200 ℃ for 2 h). After completion of the reaction, the heterogeneous catalyst remained at the bottom of the reaction vessel and can be easily separated from the organic phase containing product by decantation. The recovered catalyst was dried at

200 ℃ for 2 h and reused in a new reaction under identical experimental conditions. Each of the procedures was repeated for three cycles. The product yields were characterized by gas chromatography.

2 Results and discussion

2.1 Description of the structure

Single crystal X-ray structural analysis shows that compound **1** is composed of one Preyssler-type $[NaP_5W_{30}O_{110}]^{14-}$ polyoxoanion, two $[Mn(H_2biim)_2(H_2O)_2]^{2+}$ and five $[Mn(H_2biim)_3]^{2+}$ complex cations, one isolated Cl^- anion, and twenty lattice water molecules (Fig.1 and Fig.2a). The structural feature of the heteropolyanion subunits is essentially the same as those of the sodium derivative $[NaP_5W_{30}O_{110}]^{14-}$ previously reported in 1985 and our results (Fig.2b)[14,28]. The bond lengths and angles for all W centers exhibit normal ranges. As shown in Fig.2c and Fig.2d, there are two different coordination environments of manganese centers: Mn1/Mn2 coordinates with four nitrogen atoms from
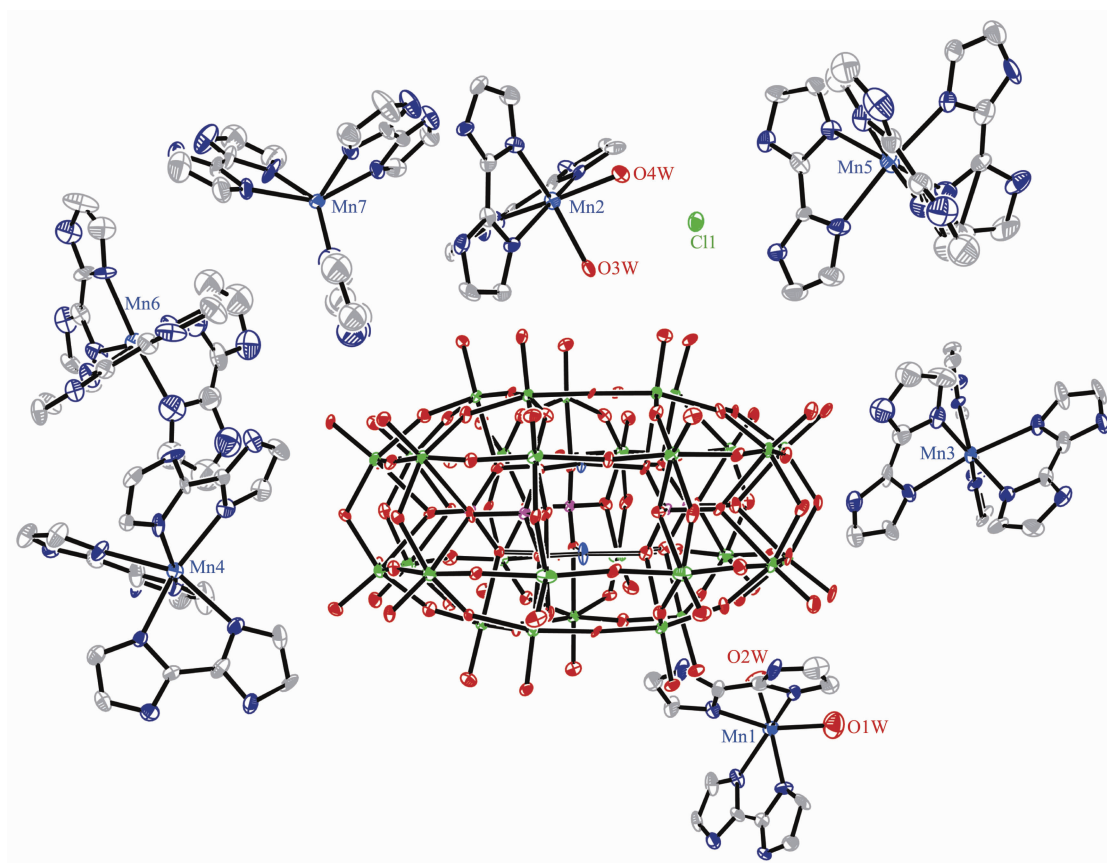
30% probability displacement ellipsoids; Hydrogen atoms and free water molecules have been omitted for clarity

Fig.1 ORTEP view of the asymmetric unit of compound **1** with atom labeling
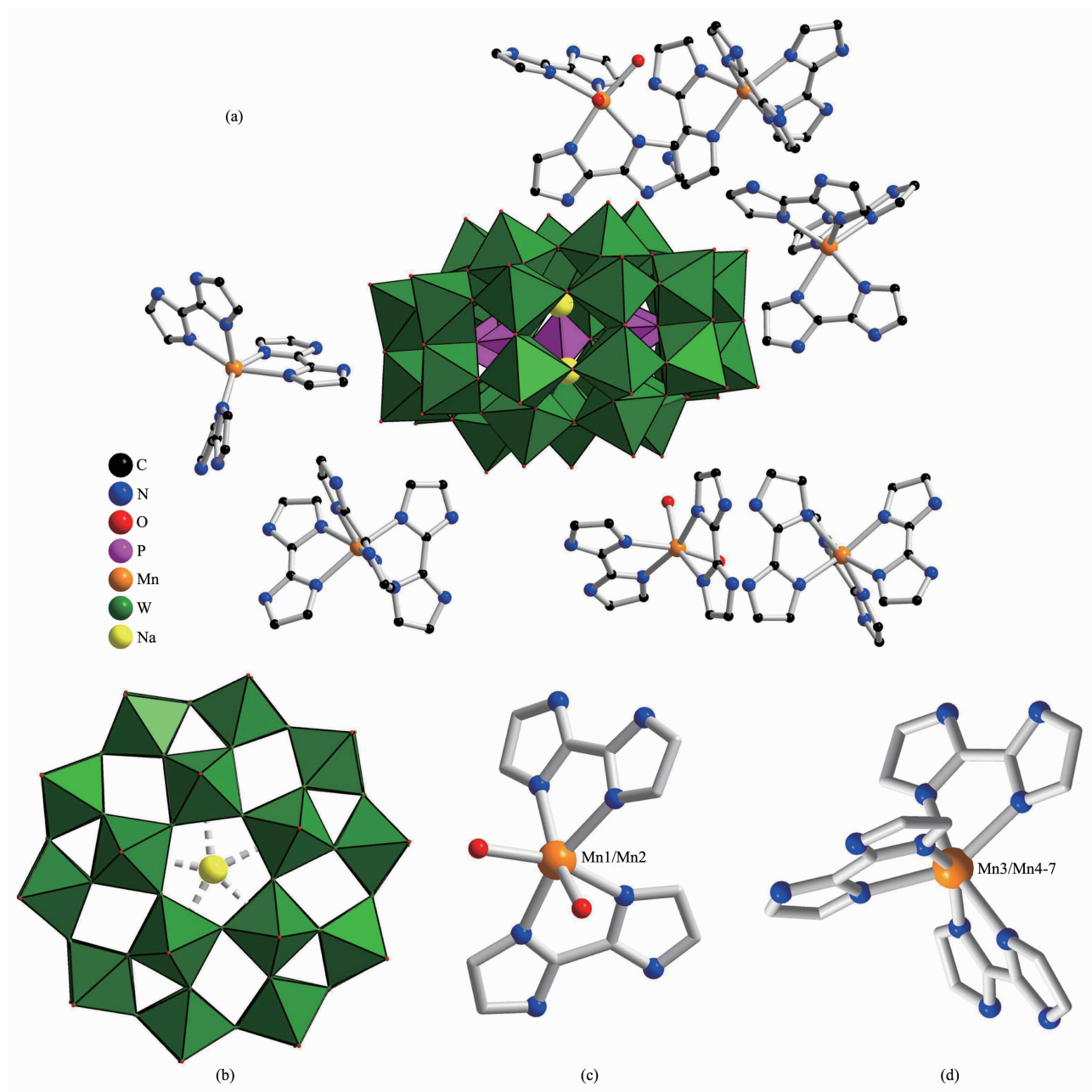
All lattice water molecules, Cl and H atoms are omitted for clarity

Fig.2　(a) Ball-and-stick/polyhedral view of compound **1**; (b) Ball-and-stick/polyhedral view of $[NaP_5W_{30}O_{110}]^{14-}$
polyanion; (c)/(d) Ball-and-stick view of the isolated $[Mn(H_2biim)_2(H_2O)_2]^{2+}$ and $[Mn(H_2biim)_3]^{2+}$ cations in **1**

two H₂biim molecules and two terminal water ligands (O1W, O2W/O3W, O4W). The bond lengths of Mn-N are in the range of 0.220 5(17)~0.233 7(16) nm, and the bond lengths of Mn-OW are 0.215 5(15)~0.222 7(13) nm. While for Mn3-Mn7 centers, their octahedral geometries are all fulfilled by six nitrogen atoms from three H₂biim molecules, and the bond lengths of Mn-N are in the range of 0.219(3)~0.233 3(19) nm. As

viewed from the packing diagram in Fig.3, a 3D supramolecular framework is formed via three kinds of hydrogen bonds of N—H⋯O, N—H⋯OW and N—H⋯Cl with the lengths of 0.271(3)~0.340(3) nm, 0.267(5) ~0.311(6) nm and 0.307(2)~0.345(2) nm between H₂biim ligands and the polyoxoanions, crystal water molecules and Cl⁻, and π-π interactions between the imidazole rings of biimidazole ligands.
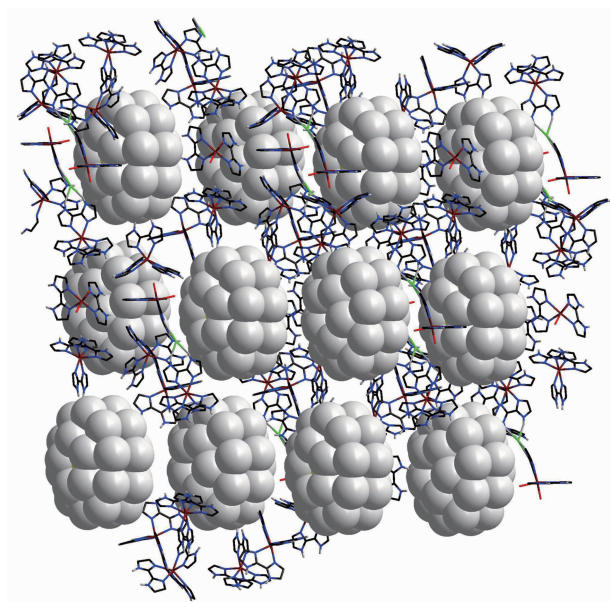
Color code is as follows: {P$_5$W$_{30}$} polyanions (grey), N (blue), Cl (green), O (red); All lattice water molecules are omitted for clarity

Fig.3　Arrangements of compound **1**

2.2　Thermogravimetric analysis

As seen from Fig.4, the TG curve of compound **1** exhibits two distinct steps of weight loss from 35 to 900 ℃. The first weight loss of 3.33% is close to the loss of twenty lattice water molecules in the temperature range of 70~300 ℃; From 300 to 640 ℃, a continuous weight loss is 24.42%, which corresponds to the removal of one Cl$^-$ ion, coordination water and H$_2$biim molecules (Calcd. 23.61%). The exothermal peaks observed at 434 and 596 ℃ in the DTA curve should be assigned to combustion of the H$_2$biim organic fragments. Additionally, the compound does not lose weight at higher than 650 ℃, this phenomenon is similar to our previous reported {P$_5$W$_{30}$}-based POMs[14], which shows that the {P$_5$W$_{30}$}
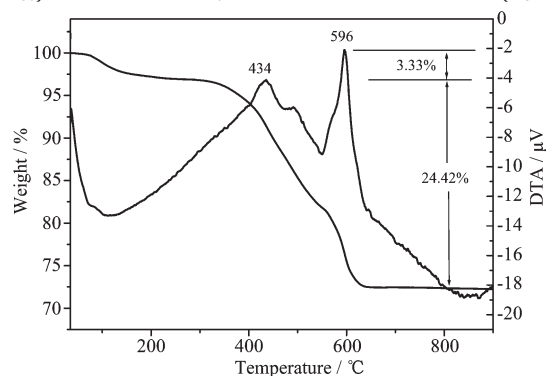

Fig.4　TG -DTA curves of compound **1**

polyoxoanion have higher thermally stabilities, and the comparison of IR spectra of compound **1** (Fig.5a), the residue after heating to 600 ℃ in air (Fig.5b), and the parent {P$_5$W$_{30}$} (Fig.5c) give a further evidence. As shown in Fig.5, the characteristic absorption bands of {P$_5$W$_{30}$} still remain for the residue sample compared with the parent {P$_5$W$_{30}$}.
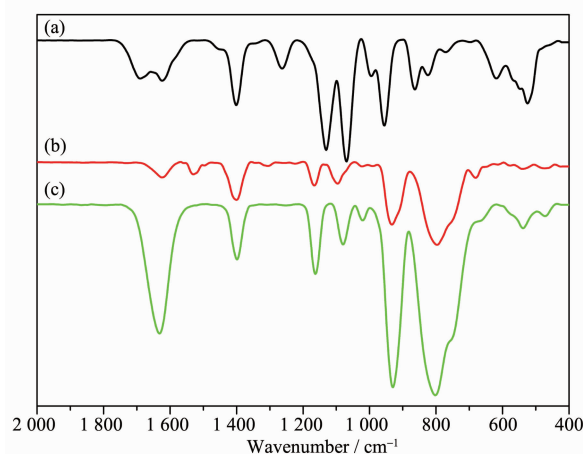

Fig.5　Comparison of IR spectra for compound **1** (a), the residue after heating to 600 ℃ in air (b), and the parent {P$_5$W$_{30}$} (c)

2.3　Electrochemical property

As shown in Fig.6, in the potential range of 0 to −700 mV, the cyclic voltammogram (CV) behavior for **1**-MCPE in 2 mol·L^{-1} H$_2$SO$_4$ solution at room temperature (scan rate: 100 mV·s^{-1}) exhibits three semireversible couples of redox peaks located at −264, −196 mV (Ⅰ-Ⅰ'); −408, −316 mV (Ⅱ-Ⅱ'); and −604, −550 mV (Ⅲ-Ⅲ'), respectively, which are
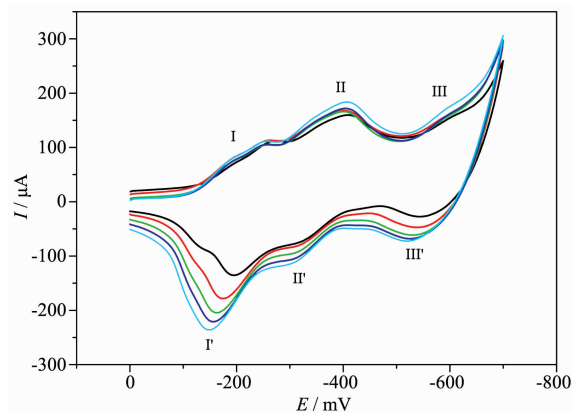
Scan rate (from inner to outer): 100, 200, 300, 400, 500 mV·s^{-1}

Fig.6　Cyclic voltammograms of **1**-MCPE in 2 mol·L^{-1} H$_2$SO$_4$ solution in the potential range of 0~−700 mV

attributed to the redox behavior of the $\{P_5W_{30}\}$ polyanion by comparing with the CV behaviors of the $\{P_5W_{30}\}$ POMs[14]. It is also can be found that the peak currents are obviously changed, and the cathodic peaks shift toward the negative direction, and the anodic peaks shift toward the positive with increasing scan rates, which shows that the redox processes of **1**-MCPE are surface-controlled[14,16].

2.4　Catalytic activity

The previous researches showed that the Preyssler-type POMs can be used as electrocatalysts for the reduction of hydrogen peroxide[14,16]. Our electrocatalytic study reveals that compound **1** also have good electrocatalytic activity toward the reduction of H_2O_2 in 2 mol·L^{-1} H_2SO_4 solution. As shown in Fig.7, **1**-MCPE exhibits the electrocatalytic behavior under the given conditions, i.e. with an increase of H_2O_2 concentration, the reduction peak currents increase while the corresponding oxidation peak currents decrease, indicating that H_2O_2 has been reduced. In
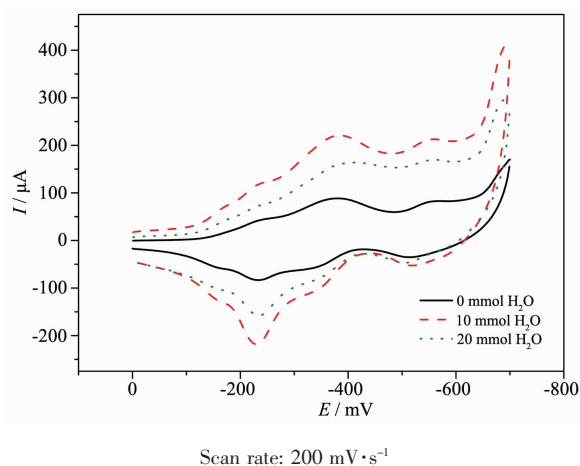
other words, the reduced specie of **1** shows electrocatalytic activity toward the reduction of H_2O_2.

It is well known that the protection of carbonyl groups is most important in multi-step preparation of many organic compounds. One of the most popular methods is to convert the carbonyl compounds into their corresponding acetals or ketals. In the traditional methods for protection of carbonyl groups, some protonic acids, HCl, H_2SO_4, etc. were generally used as catalysts, which can not be reused and recycled; especially these acids may cause serious corrosion of equipment, and produce large amounts of waste and pollution. POMs, as a kind of multifunctional catalysts, have been applied to many organic reactions, mainly due to their strong redox and acidic properties. Herein, we used compound **1** including the parent $\{P_5W_{30}\}$ as heterogeneous catalysts in the synthesis of cyclohexanone ethylene ketal, ethanediol as the carbonyl protecting group. The reaction conditions, such as the molar ratio of starting material and catalyst, reaction time, and temperature were systemically explored. The optimum conditions for the synthesis of cyclohexanone ethylene ketal were as follows: the molar ratio of cyclohexanone-ethanediol is 1:1.4, the molar ratio of the catalyst (based on W): cyclohexanone at 1:300, a reaction temperature of 98~100 ℃, a reaction time of 4 h, and 10 mL of cyclohexane water-carring agent. Catalytic performances are listed in Table 2. As seen from Table 2, compound **1** exhibits better catalytic activity than the parent $\{P_5W_{30}\}$, which shows that the $\{P_5W_{30}\}$ POM′s activity is enhanced by the introduction of Mn(II)-H$_2$biim/H$_2$O groups. Moreover, compound **1**, act as an eco-friendly heterogeneous catalyst, is easily separated and can be reused without any apparent loss of activity for the

Scan rate: 200 mV·s^{-1}

Fig.7　Cyclic voltammograms of **1**-MCPE in 2 mol·L^{-1} H_2SO_4 solution containing different concentration of H_2O_2

Table 2　Catalytic performance of compound 1 for the synthesis of cyclohexanone ethylene ketal

Entry	Catalyst	Solubility	Time / h	Yield / %
1	$\{P_5W_{30}\}$	Insoluble	4	39.4
2	MnCl$_2$	Insoluble	4	47.5
3	Compound **1**	Insoluble	4	80.2

Reaction conditions: the molar ratio of the catalyst (based on W/Mn) to cyclohexanone was 1:300; the molar ratio of cyclohexanone to ethanediol was 1:1.4 (0.10 mol of cyclohexanone); water-carring agent: 10 mL of cyclohexane; reaction at 98~100 ℃ in refluxing cyclohexane.

reaction, which indicates that the $\{P_5W_{30}\}$ skeleton has higher stability.

3　Conclusions

In summary, the successful synthesis of the new organic-inorganic hybrid compound shows that multiple Mn(II)-H$_2$biim complex cations can be introduced into the large polyoxoanion system by hydrothermal method. TM-organic complexes play an important role for stabilizing the $\{P_5W_{30}\}$ POM skeleton and enhancing POM′s activity. Compound **1** exhibits higher thermally stability and has good electrocatalytic activity toward the reduction of H$_2$O$_2$, and has better catalytic activity for the protection of carbonyl groups. The Preyssler-type POM modified by Mn(II)-H$_2$biim complex can be used in acid catalyzed organic reactions.

Supporting information is available at http://www.wjhxxb.cn

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