

Encapsulation of polyoxometalates into supramolecular cages based on flexible ligands: Synthesis, structure and properties



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ABSTRACT

Three Keggin-type polyoxometalates as noncoordinating guests wrapped into supramolecular cages based on flexible ligands, named, $[\text{H}_2\text{L}][\text{HL}][\text{L}]_2[\text{PMo}_{12}\text{O}_{40}]\cdot 4\text{H}_2\text{O}$ (**1**), $[\text{HL}]_4[\text{SiW}_{12}\text{O}_{40}]$ (**2**) and $[\text{HL}]_2[\text{L}]_2[\text{PW}^{\text{V}}\text{W}^{\text{VI}}\text{O}_{38}(\text{O}_2)]\cdot 4\text{H}_2\text{O}$ (**3**) (L = 4-(3-pyridinyloxy)benzoic acid) have been synthesized via hydrothermal conditions and have been characterized by elemental analysis, IR spectroscopy, TG analysis, and single-crystal X-ray diffraction. Single-crystal X-ray diffraction analyses revealed that the Keggin polyanions are wrapped as guests in the supramolecular cages that are formed by the ligands with hydrogen bonds (O–H...O and N–H...O). Moreover, the fluorescence of the title complexes and the electrochemical properties of **1** have been investigated. In addition, the catalytical properties of compounds have also been investigated.

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1. Introduction

Polyoxometalates (POMs) as a class of inorganic compounds with potential applications in catalysis [1–4] and materials science [5,6] have attracted a lot of attention. In recent years, the method of the incorporation of POMs into the organic cages provides a useful approach for modifying structures [7–19]. POMs as a kind of excellent electron receptors can store electrons, they can also assemble into supramolecular compounds with the organic ligands. Such organic–inorganic hybrid compounds can combine the characteristics of the two components and exhibit more structural features. Especially 3D supramolecular compounds built by hydrogen bonding interaction have attracted much attention due to their properties [20,21].

Keggin-type POMs as the classic and basic compounds, occupy very important position in the field of supramolecular chemistry. In recent years, the self-assembly of the supramolecular structures based on Keggin-type POMs is becoming one of the research focuses [22–23].

It is important to choose the suitable ligands to synthesize the supramolecular cages. The structures and properties of the supramolecules can be influenced by the length and the kinds of atoms. The multidentate organic ligand, 4-(3-pyridinyloxy)benzoic acid, has the nitrogen atoms and carboxyl oxygen atoms can act as the potential hydrogen-bonding receptor to form the supramolecular frameworks. Hence, we choose the ligand

4-(3-pyridinyloxy)benzoic acid, it is beneficial to construct the cages, then POMs are wrapped in the cages.

Herein, we choose Keggin-type POMs and 4-(3-pyridinyloxy)benzoic acid as material, and get three new hybrid compounds that polyoxometalates wrapped into supramolecular cages by hydrothermal method: $[\text{H}_2\text{L}][\text{HL}][\text{L}]_2[\text{PMo}_{12}\text{O}_{40}]\cdot 4\text{H}_2\text{O}$ (**1**), $[\text{HL}]_4[\text{SiW}_{12}\text{O}_{40}]$ (**2**), $[\text{HL}]_2[\text{L}]_2[\text{PW}^{\text{V}}\text{W}^{\text{VI}}\text{O}_{38}(\text{O}_2)]\cdot 4\text{H}_2\text{O}$ (**3**) (L = 4-(3-pyridinyloxy)benzoic acid).

2. Experimental

2.1. Materials and instruments

All of the chemicals were purchased commercially and used without purification. FT-IR spectra were taken on a Nicolet 170SX spectrophotometer (as KBr pressed pellets) under room temperature. C, H, and N elemental analyses were performed with a Perkin-Elmer 2400 CHN elemental analyzer, and P, Si, Mo and W were analyzed on ICP atomic emission spectrometer. Thermo gravimetric analyses (TGA) were carried out on a STA449C integration thermal analyzer with a heating rate of 10 °C/min between room temperature to 1000 °C under nitrogen atmosphere. Fluorescent spectra for the solid samples were measured with a Hitachi F-7000 FL Spectrophotometer at room temperature.

2.2. Synthesis of compound 1

A mixture of 4-(3-pyridinyloxy)benzoic acid (0.15 mmol), $\text{M}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ (Cd, Zn...) (0.15 mmol), $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]\cdot x\text{H}_2\text{O}$

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(0.1 mmol), 10 ml H₂O was transferred and sealed in a 25 mL Teflon reactor with the pH of 1.5 adjusted with 1 M NaOH. Then this mixture was kept under autogenous pressure at 120 °C for 3 days, after the reactor was slowly cooled to room temperature over a period of 10 °C/h, yellow rodlike crystals of **1** were obtained. The crystals were picked out, washed with distilled water, and dried at room temperature (81.4% based on 4-(3-pyridinyloxy)benzoic acid). *Anal. Calc.* for C₄₈H₄₇N₄O₅₆Mo₁₂P: P, 1.12; Mo, 41.76; C, 20.88; H, 1.70; N, 2.03; Found: P, 1.20; Mo, 41.12; C, 20.94; H, 1.76; N, 2.11%. IR(KBr) ν , cm⁻¹: Four characteristic vibrations resulting from heteropolyanions with the Keggin structure: 1067 cm⁻¹, $\nu_{as}(P-Oa)$, 963 cm⁻¹, $\nu_{as}(Mo=Ot)$, 890 cm⁻¹, $\nu_{as}(Mo-Ob-Mo)$ and 785 cm⁻¹, $\nu_{as}(Mo-Oc-Mo)$; and another vibrations resulting from the L molecules: 2900 cm⁻¹ and 3050 cm⁻¹.

2.3. Synthesis of compound 2

Compound **2** was prepared in the same way as for **1**, except using H₄[SiW₁₂O₄₀] (0.1 mmol) to replace H₃PMo₁₂O₄₀, and the pH of the solution system was 1.8. Colorless rodlike crystals of **2** were obtained (20.3% based on 4-(3-pyridinyloxy)benzoic acid). *Anal. Calc.* for C₄₈H₄₀N₄O₅₂W₁₂Si: Si, 0.74; W, 59.05; C, 15.40; H, 1.06; N, 1.50; Found: Si, 0.84; W, 59.11; C, 15.47; H, 1.14; N, 1.58%. IR(KBr) ν , cm⁻¹: Four characteristic vibrations resulting from heteropolyanions with the Keggin structure 969 cm⁻¹, $\nu_{as}(Si-Oa)$, 925 cm⁻¹, $\nu_{as}(W=Ot)$, 877 cm⁻¹, $\nu_{as}(W-Ob-W)$ and 785 cm⁻¹, $\nu_{as}(W-Oc-W)$; and another vibrations resulting from the L molecules: 2889 cm⁻¹ and 3065 cm⁻¹.

2.4. Synthesis of compound 3

Compound **3** was prepared in the same way as for **1**, except using H₃[PW₁₂O₄₀] (0.1 mmol) to replace H₃PMo₁₂O₄₀, and the pH of the solution system was 1.4. Claybank block crystals of **3** were obtained (70.3% based on 4-(3-pyridinyloxy)benzoic acid). *Anal. Calc.* for C₃₆H₃₀N₃O₄₉W₁₂P: P, 0.81; W, 57.90; C, 11.33; H, 0.78; N, 1.10; Found: P, 0.90; W, 58.71; C, 12.33; H, 0.90; N, 1.16%. IR(KBr) ν , cm⁻¹: Four characteristic vibrations resulting from heteropolyanions with the Keggin structure 1083 $\nu_{as}(P-Oa)$, 980 $\nu_{as}(W=Ot)$, 894 $\nu_{as}(W-Ob-W)$ and 795 $\nu_{as}(W-Oc-W)$; and another vibrations resulting from the L molecules: 2889 cm⁻¹ and 3027 cm⁻¹.

2.5. Preparations of 1-CPE

The compound **1**-modified carbon paste electrode (**1-CPE**) was fabricated as follows: A mixture of 0.1 g graphite powder and 0.01 g compound **1** were grind together with an agate mortar and then was added 0.1 mL of mineral oil with stirring. Then the mixture was packed into a glass tube with a 1.5 mm inner diameter. Electrical contact was established with a copper wire on the back of the electrode.

2.6. X-ray crystallography

Crystal data of **1–3** were collected by a Bruker Smart Apex CCD area-detector diffractometer with graphite-monochromated Mo K α ($\lambda = 0.71073$ Å) radiation at room temperature. Absorption corrections were applied using the multiscan program SADABS. The structures were solved by direct methods and refined on F₂ by full-matrix least-squares using SHELXTL-97 on a legend computer [24]. All non hydrogen atoms were refined anisotropically. Hydrogens were located in calculated positions and refined by using a riding model. The crystal and structure refinement data for **1–3** are summarized in Table S1. The hydrogen bonds for **1–3** are listed in

Table S2. Selected bond lengths (Å) and angles (°) for **1–3** are listed in Table S3. The CCDC reference numbers are CCDC 1036120–1036122 for the title compounds.

3. Result and discussion

3.1. Synthesis

Compounds **1–3** were synthesized under hydrothermal conditions. Parallel experiments proved that the starting materials, pH value and organic compounds were crucial parts for getting the title compounds. Compounds **1–3** could be obtained without M(NO₃)₂, but the purity and yield of compounds **1–3** would improve much if the M(NO₃)₂ was added.

It is well known that the formation of POMs are mainly controlled by the pH values. Many parallel experiments showed that the value of the pH was the important factor in the formation of the compounds. In our experiments, the best pH value was 1.5 for compounds **1**, 1.8 for compound **2**, and 1.4 for compound **3**; at other values either the yields were very low or no target products could be obtained.

3.2. Description of crystal structure

3.2.1. Structure description of compound 1

Single-crystal X-ray diffraction analysis reveals that compound **1** crystallizes in the monoclinic crystal system of the P2(1)/n space group. Compound **1** consists of the Keggin-type [PMo₁₂O₄₀]³⁻, four L ligands and four water molecules (Fig. 1).

The [PMo₁₂O₄₀]³⁻ can be regarded as a {Mo₁₂O₃₆} encapsulating a {PO₄} in the center. Bond valence sum (BVS) calculations [25] indicate that all the Mo atoms are in +6 oxidation states, the P atom is in +5 oxidation states. Therefore, the ligands are protonated as H₂L and HL. There is no covalent bonds between POMs and ligands. The result shows that the charge of compound **1** is balanced by the protonated ligands, then the whole structure become neutral and stable. In compound **1**, the hydrogen bond interaction plays an important role in the formation of the whole framework. There are five kinds of hydrogen bonds between the polyanion and organic cation (Table S1). The ligands and polyanions form a 1D chains by the hydrogen bonds O23–H23···O24 and O25–H25···O18 (Fig. 2). Then the 2D layers are composed by the N–H···O (N1–H1···O26 and N2–H2···O29) between the ligands (Fig. 3). Finally, the 3D networks are constructed by N2–H2···O29 and O29–H29C···O24, and the POMs are located in the cages that formed by ligands (Fig. 4).

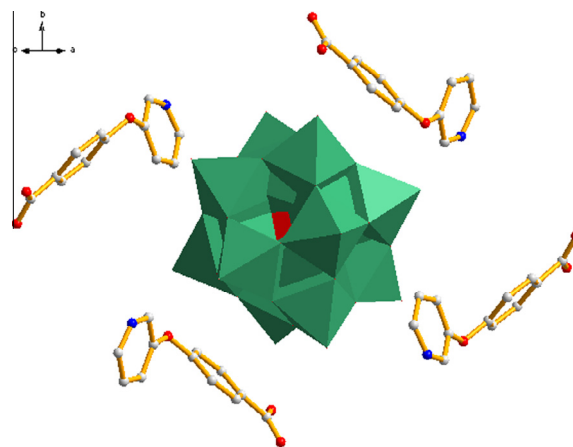


Fig. 1. Molecular structure of compound **1**.

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