Supramolecular Assembly through the Highest Connectivity of a Keggin Polyoxometalate

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A novel supramolecular compound based on the Keggin polyoxometalate $(Hpipz)_3[PMo_{12}O_{40}]$(**1**) (pipz = piperazine) has been synthesized and characterized. X-Ray diffraction analysis reveals that the Keggin polyanion uses all of its surface oxygen atoms (36) to attract eighteen pipz units at its periphery. This represents the highest connectivity of a Keggin polyoxoanion. The electrochemical behavior of a CPE modified with **1** (**1**-CPE) has been studied.

Key words: Hydrothermal Synthesis, Supramolecular Chemistry, Keggin Polyoxometalate, Highest Connectivity, Electrochemistry

Introduction

Supramolecular chemistry has been used to understand the intermolecular interactions of molecular packing and to design new solids with desired physical and chemical properties [1]. One of the goals is to recognize and develop supramolecular synthons that are robust enough to be transferred from one network to another [2]. In the past few years, significant attention continues to focus on polyoxometalates (POMs) with respect to their intriguing architectures and potential applications in catalysis, electrochemistry, magnetism, biochemistry, and pharmaceutical chemistry [3]. As one kind of metal oxide clusters with nanosizes and abundant topologies, POMs, due to their ability to accept electrons, have been employed as inorganic building blocks for the construction of supramolecular arrays with various organic ligands. They can combine with organic *p*-electron donors, such as N-containing ligands, amino acids, polypeptides, organometallics, tetrathiafulvalene (TTF), bis(ethylenedithio)tetrathiafulvalene (ET), and perylene (per), to form POM-based hybrid materials [4]. Many studies have also shown that this kind of hybrid materials possesses some interesting specific electrical, magnetic, and optical properties.

Among the wide variety of POMs, the Keggin species $[XM_{12}O_{40}]^{n-}$ (X = B, P, Si, *etc.*; M = Mo and W) are one of the most important research topics, especially the modified Keggin derivatives. This reflects a current interest for the following reasons: the Keggin species are viewed as soluble metal oxide analogs and therefore can be used for modeling of catalytic reactions taking place on metal oxide surfaces; they are valuable building blocks for tailor-made inorganic and organic or organic hybrid materials with attractive structures and properties [5]. Due to the Keggin POMs' large number of oxygen atoms as the smart potential sites (12 terminal O atoms and 24 μ_2-O atoms) on the surface, increasing attention is currently devoted to their surface modification. However, extensive investigations have indicated that to date the highest covalent connecting number of modifying Keggin POM clusters is not more than six, and the supramolecular connecting number is twelve [6]. Therefore, the construction of highly connected Keggin POM derivatives is still a challenging issue. In fact, our group has done much work in empirically synthesizing highly connected Keggin

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POM-based compounds, including six covalent and twelve supramolecular connections of Keggin POM-based 3D networks [6]. Furthermore, stimulated by the large number of potentially coordinating oxygen atoms, and as a continuation of our research to enrich the chemistry of the saturated Keggin-based derivatives, we chose 1,4-diazacyclohexane (pipz) as the organic ligand to prepare high-connected POM-based hybrids. Herein, the synthesis and crystal structure of a new highly connected POM-based supramolecular compound, $(Hpipz)_3[PMo_{12}O_{40}]$ (**1**), is reported. A carbon paste electrode modified with compound **1** (**1**-CPE) was employed to investigate its electrochemical properties.

Results and Discussion

*Crystal structure of **1***

Single-crystal X-ray diffraction analysis reveals that **1** is constructed from one $[PMo_{12}O_{40}]^{3-}$ polyoxoanion and three $[Hpipz]^{+}$ cations, as shown in Fig. 1. The fully oxidized Keggin polyanion $[PMo_{12}O_{40}]^{3-}$ contains four $[Mo_3O_{13}]$ units and one ordered $[PO_4]^{3-}$ in the center with P–O bonds ranging from 1.519(16) to 1.545(9) Å (average 1.535 Å). The Mo–O bonds are divided into three groups: Mo–Oa (center oxygen atom) 2.479(9) – 2.497(9) Å; Mo–Ob/c (bridging oxygen atom) 1.870(7) – 1.911(7) Å, and Mo–Od (terminal oxygen atom) 1.667(6) Å. According to a bond valence sum calculation [7], all Mo atoms exhibit the oxidation state +VI (average calculated value = 6.09).

A remarkable aspect is that 12 terminal oxygen atoms of a Keggin POM are linked with 12 pipz molecules *via* supramolecular interactions (O6···N1 = 2.893 Å; O2···C2 = 3.065 Å; O2···C1 = 3.136 Å), that is to say, all terminal oxygen atoms of the Keggin POM serve to stabilize the whole structure (shown in Fig. 2, top), which is reported here for the first time. Based on the subunit, each pipz organic molecule is linked to its neighboring Keggin POMs in the same mode to form a 3D framework.

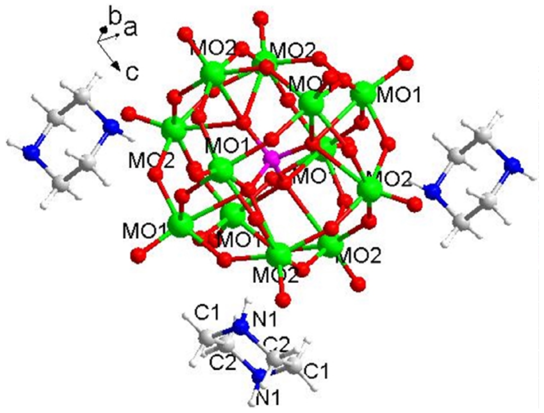

Fig. 1. Combined ball/stick representation of the molecular unit of **1**.

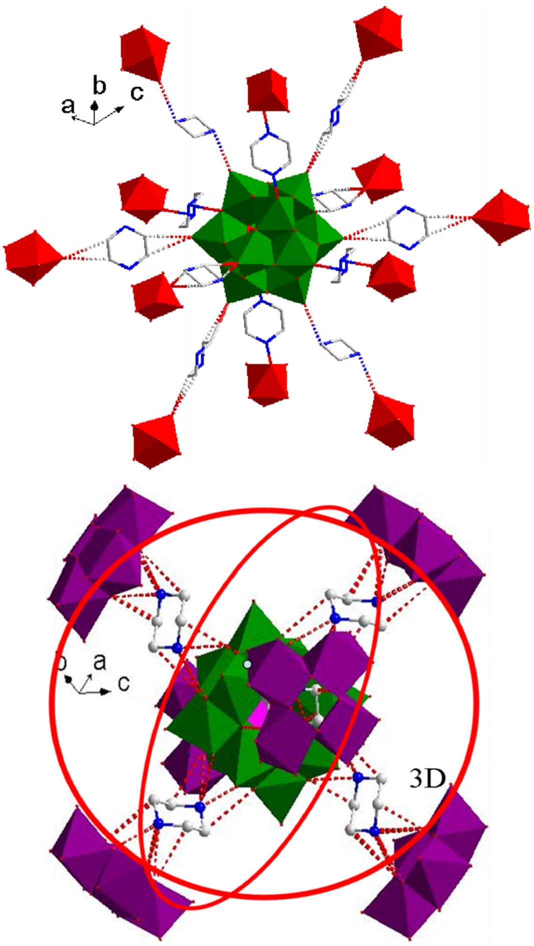

Fig. 2. Polyhedral representations of the structure formed *via* the terminal oxygen atoms and pipz molecules (top) and *via* the bridging oxygen atoms and pipz molecules (bottom).

Another fascinating structural feature is that the 24 bridging oxygen atoms of the Keggin POMs are linked with 6 pipz molecules *via* supramolecular interactions (O4···N1 = 3.113 Å; O1···N1 = 2.869 Å; O5···N1 = 3.036 Å; O4···C1 = 3.113 Å; O7···C2 = 3.214 Å), and 6 pipz molecules cap the surface window of the Keggin POMs in an octahedral manner (shown in Fig. 2, bottom). Furthermore, the subunits are extended to a 3D network in the same mode *via* other pipzs and

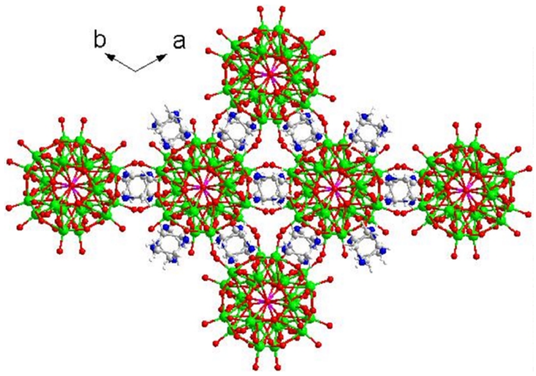

Fig. 3. View of the 3D packing of compound **1** along the crystallographic *c* axis.

their neighboring Keggin POMs. It is noted that this kind of Keggin anion capped by fragments of organic molecules is rare, and the title compound represents the first example of a six-capped structure containing Keggin POMs where all bridging oxygen atoms of the Keggin POMs serve to stabilize the whole structure.

Furthermore, the two subunits are linked to each other to form a 3D supramolecular structure. Seen along the crystallographic *c* axis, these inorganic polyanions give rise to regular chambers, and pipz organic molecules are located in the chambers to stablize the whole structure (Fig. 3).

IR spectrum

In the IR spectrum of the title compound (Fig. 4), there are four characteristic bands of POMs: 1052 cm^{-1} ascribed to ν(P–Oa), 946 cm^{-1} ascribed to ν(Mo–Ot), 858 cm^{-1} ascribed to ν(Mo–Ob–Mo) and 748 cm^{-1} ascribed to ν(Mo–Oc–Mo). The characteristic bands in the region from 1531 to 1700 cm^{-1} can be regarded to be arising from the pipz molecules.

*Voltammetric behavior of **1**-CPE*

To study the redox properties of the title compound, we used them as modifiers to fabricate chemically modified CPE, considering their insolublility in water and most organic solvents. The cyclic voltammetric behavior of **1**-CPE in 1 mol L^{-1} aqueous H_2SO_4 solution was explored at different scan rates. As shown in Fig. 5, three pairs of reversible redox peaks (I–I′, II–II′, III–III′) appear with the mean peak potentials $E_{1/2}$ = (Epc + Epa)/2 of +417 (I), +263 (II), +32 mV (III), respectively, showing three continuous two-electron processes of the Mo atoms. With increasing scan rate, the peak potentials changed gradually: the cathodic peak potentials are shifted to the negative direction and the corresponding anodic peak potentials to the positive direction. The peak-to-peak separation between the corresponding cathodic and anodic peaks thus increases, but the mean peak potentials do not change on the whole.

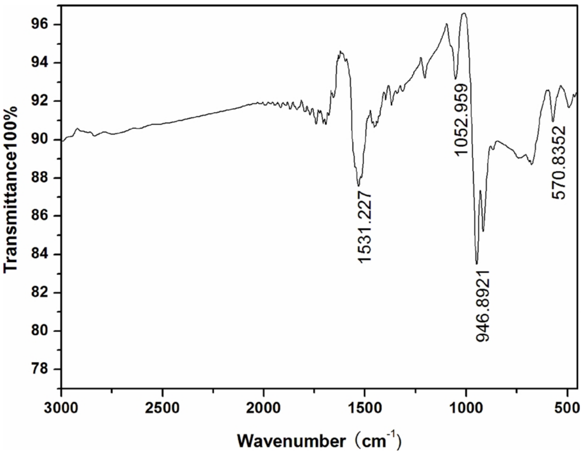

Fig. 4. IR spectrum of compound **1**.

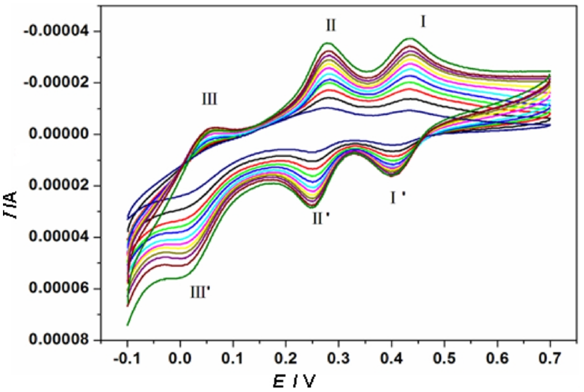

Fig. 5. The cyclic voltammograms of the **1**-CPE in 0.1 mol L^{-1} H_2SO_4 at different scan rates (from inner to outer: 50, 100, 150, 200, 250, 300, 350, 400, 450, 500, 550, 600 mV s^{-1}).

Conclusions

In summary, a novel supramolecular compound based on Keggin POMs, $(Hpipz)_3[PMo_{12}O_{40}]$, has been synthesized and characterized. In the compound, eighteen pipz molecules lie in the periphery of the Keggin POMs, and each Keggin POM provides all its surface oxygen atoms to stabilize the whole structure.

Table 1. Crystal data and parameters pertinent to the structure determination for the compound **1**.

Empirical formula	$C_{12}H_{33}Mo_{12}N_6O_{40}P_1$
*M*r	2083.67
Crystal system	trigonal (hexagonal setting)
Space group	$R\bar{3}c$
a, Å	17.893(5)
c, Å	23.583(5)
V, Å^3	6539(3)
Z	6
D_{calcd}, Mg m^{-3}	2.90
$\mu(MoK_\alpha)$, mm^{-1}	4.0
T, K	293(2)
F(000), e	5264
θ range for data collection, deg	3.15 – 27.45
Reflections collected / unique / R_{int}	20083 / 1674 / 0.0203
Data / ref. parameters	1674 / 114
GoF (F^2)[a]	1.225
$R1$ / $wR2$ [$I \geq \sigma(I)$][a]	0.0408 / 0.1168
$R1$ / $wR2$ (all data)	0.0445 / 0.1203
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	1.30 / −1.59

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$ and A and B are constants adjusted by the program; GoF = S = $[\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$, where n_{obs} is the number of data and n_p the number of refined parameters.

The title compound represents the highest connectivity of Keggin POMs. The successful isolation of the title compound provides a prototype for extending polyoxoanion coordination assemblies.

Experimental Section

General procedures

All reagents were purchased commercially and used without further purification. All syntheses were carried out in 18 mL Teflon-lined autoclaves under autogenous pressure. Distilled water was used in the reactions. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. The IR spectrum was obtained on an Alpha Centaurt FT/IR spectrometer with KBr pellets in the 400 – 4000 cm^{-1} region. Cyclic voltammograms were obtained with a CHI 660 electrochemical workstation at r. t. Platinum gauze was used as counter electrode and a Ag / AgCl electrode as a reference. A chemically bulk-modified carbon paste electrode (CPE) was used as working electrode.

Preparation of $(Hpipz)_3[PMo_{12}O_{40}]$

A mixture of α-$H_3[PMo_{12}O_{40}]\cdot xH_2O$ (0.10 mmol), pipz (0.20 mmol), NH_4VO_3(0.20 mmol) and triethylamine (trea) (0.1 mmol) was dissolved in 10 mL of distilled water at r. t. The pH value was adjusted to about 4.3 with 1.0 M HCl, and the solution was kept at 170 °C for 4 d to give black block-shaped crystals of **1** (24 % yield based on Mo). Elemental analysis of **1**, $C_{12}H_{33}Mo_{12}N_6O_{40}P$ (2083.67): calcd. C 6.90, H 1.58, N 4.02; found C 6.87, H 1.54, N 3.92.

Preparation of ***1****-CPE*

The carbon paste electrode **1**-CPE was prepared as follows: 96 mg of graphite powder and 8 mg of the title compound were mixed and ground together in an agate mortar to achieve a uniform mixture, which was added to 0.6 mL nujol with stirring. The homogenized mixture was packed into a glass tube with 1.2 mm inner diameter, and the tube surface was wiped with paper. Electrical contact was established with a copper rod through the back of the electrode.

X-Ray crystallography

Crystal data for the title compound were collected on a Rigaku Raxis Rapid IP diffractometer with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) at 273 K. A total of 20083 reflections ($3.15 \leq \theta \leq 27.45°$) were collected, 1674 of which were unique (R_{int} = 0.0203). The structure was solved by Direct Methods and refined by full-matrix least-squares on F^2 using the SHELX suite of crystallographic programs [8]. All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms at the carbon atoms were calculated at idealized positions. Crystallographic data are summarized in Table 1.

CCDC 745911 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data request/cif.

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