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Short communication

A new supramolecular compound based on Keggin-type phosphomolybates with mixed-ligand and mixed-valence Cu(I/II): $[Cu(I)(phen)_2]_2\{[Cu(II)]_2(phen)_4PTA\}[H_3PMo_8^{VI}Mo_4^{V}O_{40}]$



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GRAPHICAL ABSTRACT



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ABSTRACT

With an aim to obtain a new supramolecular compound based on Keggin-type polyoxometalates with mixed-ligand: $[Cu(I)(phen)_2]_2\{[Cu(II)]_2(phen)_4PTA\}[H_3PMo_4^VMo_8^{H}O_{40}]$ (phen = 1,10-phenanthroline, PTA = terephthalic acid) has been synthesized under hydrothermal conditions and structurally characterized by elemental analyses, IR, X-ray single crystal diffraction, TG analyses and XPS. In the title compound, the Keggin-type phosphomolybates anions, butterfly-shaped $[Cu(I)(phen)_2]^+$ subunits and dumbbell-shaped {[Cu(II]]_2(phen)_4PTA}²⁺ subunits are alternately connected to form chiral helical chains *via* hydrogen bonds along b axis, and the adjacent chiral helical chains are connected in the way of sharing butterfly-shaped [Cu(I)(phen)_2]⁺ subunits and dumbbell-shaped {[Cu(II]]_2(phen)_4PTA}²⁺ subunits to form 3D supramolecular reticular framework. As expected, the title compound with mixed-ligands (phen and PTA) has been successfully synthesized, inconceivably, the title compound also contains mixed-valence Cu (Cu(I) in butterfly-shaped [Cu(I)(phen)_2]⁺ subunits; Cu(II) in dumbbell-shaped {[Cu(II]]_2(phen)_4PTA}²⁺ subunits). The preliminary analyses show that mixed-valence Cu(I/II) may be due to the reduction of Cu(II) (from CuCl_2) to Cu(I) (in butterfly-shaped [Cu(I) (phen)_2]⁺ subunits) by N-containing compound. The successful results of this work provide a new idea that supramolecular materials with attractive structures and novel properties, which could be designed and

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Received 2 December 2018; Received in revised form 24 January 2019; Accepted 25 January 2019 Available online 26 January 2019 1387-7003/ © 2019 Elsevier B.V. All rights reserved. synthesized by introducing of mixed-ligands into the supramolecular materials. Additionally, the electrocatalytic property of the title compound to H_2O_2 has been studied.

Supramolecular chemistry has been defined as the understanding of intermolecular interactions in the context of crystal packing and shown spectacular advances in the last couple of decades as a consequence of their interesting structural chemistry and unusual properties [1-4]. Hereinto, the organic-inorganic hybrid supramolecular materials have received extremely intensive interest, because inorganic components could combine with organic components to obtain unusual structures and inconceivable properties [5,6]. Polyoxometalates (POMs), as one kind of well-known inorganic components with nucleophilic oxygenenriched surfaces and oxygen atoms on the surface forming hydrogen bonds with organic components, could be viewed as important inorganic building blocks for constructing organic-inorganic hybrid materials [7-10]. So the syntheses of organic-inorganic hybrid materials based on POMs are very significant. Usually, a promising tool for these materials' design is the evaluation and use of organic ligands under hydrothermal conditions, such as POM-based metal-organic frameworks (POM-MOFs) [11-16]. Inspired by POM-MOFs, POMs and mixedligand coordination metal ions might be introduced into the organicinorganic hybrid supramolecular to get attractive structures and novel properties. Therefore, it remains a formidable challenge to rationally design the organic-inorganic hybrid supramolecular material based on POMs and mixed-ligands with affecting its structure and properties.

Hence, a motivation for providing a new inspirational method to design and synthesize organic-inorganic hybrid supramolecular materials based on POMs with distinctive structure and properties by introducing mixed-ligands coordinated metal ions has been put forward. Then, Keggin-type phosphomolybates, mixed-ligands (PTA and phen) and CuCl₂ have been chosen in the present experiment. The following points are taken into consideration: (1) The Keggin-type POMs with abundant surface oxygen atoms are coordination potential sites for hydrogen bonds towards surface hydrogen atoms of organic ligands in all directions [17-19]. (2) The copper ions have different coordination numbers (4 or 6) and could easier coordinate with the O, N, S atoms of the organic ligands [20,21]. (3) On the one hand, phen with a good π electron conjugated system is also an indispensable factor for the construction of aryl stacking supported supramolecular structures [22,23], on the other hand, PTA has a linear ribbon structure with four terminal O atoms, flexible coordination fashion and excellent coordination ability [24,25]. As expect, an organic-inorganic hybrid supramolecular

compound based on Keggin-type phosphomolybates containing mixedligand and mixed-valence Cu(I/II) with helical chains: [Cu(I) (phen)₂]₂{[Cu(II)]₂(phen)₄PTA}[H₃PMo₈^{VI}Mo₄^VO₄₀] has been obtained and characterized. In addition, the structure characteristics, formation of mixed-valence and the electrocatalytic to H₂O₂ of the title compound were also discussed.

All reagents were purchased commercially and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. IR spectra were recorded in the range of 400-4000 cm⁻¹ on a VERTEX-70 Fourier FT-IR spectrophotometer with pressed KBr pellets. Thermogravimetric analyses (TGA) were recorded on a Mettler TGA/SDTA851e thermal analyzer under dynamic nitrogen atmosphere with a heating rate of 10 °C·min⁻¹. X-ray powder diffraction (XRPD) patterns of samples were recorded with a Rigaku D/max-III-B (Tokyo, Japan) diffractometer with Cu K_a irradiation ($\lambda = 1.54178$ Å). The X-ray photoelectron spectra (XPS) of the title compound were obtained with an X-ray photoelectron spectrometer (ESCALAB 250Xi, Thermo Scientific). Crystal data for the title compound was collected on Bruker SMART-CCD diffractometers, with Mo-K_{α} monochromated radiation ($\lambda = 0.71073$ Å) at 296 K. The structures were solved by directed methods and refined by using the SHELXTL (full-matrix least-squares on F^2) and Olex2 1.2 programs packages. All the atoms (not including hydrogen atoms) were refined anisotropically. The positions of hydrogen atoms on carbon atoms were generated geometrically. The crystal data and structure refinements of the title compound are summarized in Table S1. Selected bond lengths and angles are listed in Table S2.

The title compound was synthesized by the hydrothermal method from a mixture of $(NH_4)_6M_{07}O_{24}$ ' $4H_2O$ (1 mmol), CuCl₂:2H₂O (1 mmol), phen (1 mmol), PTA (1.5 mmol), H₃PO₄ (0.02 mmol), NaOH (1 mmol) and H₂O (0.83 mmol) in a molar ratio 1:1:1:1.5:0.02:1:0.83. The resulting suspension was stirred for 2–3 h, then sealed in a telfonlined reactor with 75% filling and heated at 180 °C for 7 days. After slow cooling to room temperature over a period of 24 h, black like block crystals were filtered, washed with water, and dried at room temperature. Yield: 43% based on Mo. Calcd for the title compound $C_{104}H_{68}Cu_4Mo_{12}N_{16}O_{44}P$ (3238.): C, 33.92; H, 1.74; N, 5.19. Found: C, 28.93; H, 1.74, N, 5.19. IR (KBr pellet, cm⁻¹): 3072(m), 1946(m), 1629(m), 1522(m), 1431(m), 1346(m), 1311(w), 1226(w), 1149(w),



Fig. 1. Ball/stick representation of the asymmetric unit of the title compound.

1110(m), 1062(s), 965(s), 722(s) (Fig. S1).

100 mg graphite powder and *ca.* 20 mg (the title compound sample) were mixed and ground together by agate mortar and pestle to achieve an even, dry mixture. The mixture 0.2 mL nujol was added and stirred with a glass rod. Then the homogenized mixture was used to pack 3 mm inner diameter glass tubes, and the surface was wiped with weighing paper. Electrical contact was established with copper rod through the back of the electrode.

Single-crystal X-ray diffraction analysis reveals that the title compound consists of [Cu(I)(phen)₂]⁺ subunits (abbreviated to Cu1 subunit), {[Cu (II)₂(phen)₄PTA}²⁺ subunits (abbreviated to Cu2 subunit) and $[H_{2}PMo_{4}^{V}Mo_{8}^{V}O_{40}]^{4-}$ polyoxoanion (abbreviated to PMo12) (Fig. 1). Within the Cu1 subunit, the Cu(I) is four-coordinated by phen N-donors. The Cu2 subunit structure consists of two Cu(II) ions, four phen molecules and one PTA molecule, the Cu(II) is six-coordinated by two N-donors of phen and of O-donors PTA. Cu1 subunits, Cu2 subunits and PMo12 clusters are alternately connected to form chiral helical chains via hydrogen bonds along b axis. The adjacent chiral helical chains are connected in way of sharing butterfly-shaped Cu1 subunits and dumbbell-shaped Cu2 subunits to form 3D supramolecular reticular framework, which reveals that the intermolecular hydrogen bonds play vital role to construct the higher dimensional framework (Fig. 2). The bond distance of Cu9-N is 2.068, 1.995, 2.213, 2.006 and 2.011 Å for Cu9-N1, Cu9-N2, Cu9-N6, Cu9-N7, and Cu9-O19, respectively. The P-O distances are in the range of 1.435(7)–1.650(8) Å with an average bond length 1.529 Å, while the O–P–O angles vary from 63.9(4)° to 111.3(4)°. Relevant Mo–O bonds can be classified into three groups, Mo-O_t bonds, Mo-O_{b/c} bonds and Mo-O_a bonds, and the bond distances fall in the ranges of 1.649(5)-1.657(4) Å, 1.770(8)-1.911(5) Å, and 2.358(7)-2.442(8) Å, respectively. The distance of hydrogen bonds is presented in Table S3.

It is interesting that there are different valence of copper ions in the title compound. Within butterfly-shaped Cu1 subunit, Cu(I) is coordinated by four N atoms of PTA molecules. Cu(II) is six-coordinated by four N atoms of PTA molecules and two O atoms of phen molecule.



Fig. 3. TGA curve of the title compound.

Two Cu(II) ions, four phen molecules and two PTA molecules are combined to form dumbbell-shaped Cu2 subunits. The helical direction of the helical chain is determined by the Cu2 subunits. Then Cu1 subunits and Cu2 subunits are connected to each other along b axis, which are supported by π ... π stacking interactions. In this way, an interesting chiral helical chain is formed along b axis.

The thermal weight of the title compound is shown in Fig. 3. For the title compound, TGA shows that weight loss start at 100 °C and ends at 400 °C. The first weight loss is in the temperature range of 100–260 °C, which is corresponding to the release of phen ligand in the title compound (calc 39.15%). The second weight loss at 390 °C is ascribed to PTA ligands (calc 4.46%). At last, the total weight loss is 45.52% (calc

Fig. 2. View of the H-bonding interactions among the PMo12, Cu1 subunits and Cu2 subunits in the supramolecular layered framework of the title compound. The Hbonding interactions are indicated by blue dotted lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)





Fig. 4. Showing the bulk product are in good agreement with the calculated patterns based on the results from single-crystal X-ray diffraction.

43.61%), which is consistent with the molecular formula of the title compound.

As shown in the Fig. 4, the title compound has a strong diffraction peak in the range of $5-50^{\circ}$. The measured data of the title compounds are in agreement with the peak pattern of the single crystal simulated data, and the characteristic peak positions are in agreement, indicating that the title compound is a pure phase.

For the title compound, the main chemical constituents of the cluster anion were determined by XPS measurements. According to referring to the XPS manual [26], the Mo–O inner binding energy of $Mo^{5+}3d_{3/2}$ and $Mo^{5+}3d_{5/2}$ are 233.9 eV and 231.0 eV, respectively, P–O bond in $P^{5+}2p_{3/2}$ inner electron binding energy is 133.1 eV.

The bond valence sum calculations (BVS) indicate one out of three Cu atoms are in the +1 oxidation state in compound [27], four out of twelve Mo atoms are in the +5 oxidation state for compound. Hence, addition of three protons is necessary to balance the charge of compound in the molecular formula, which are supported by the XPS measurements (Fig. 5).

Cyclic voltammetry (CV) was used to test electrocatalytic reduction of activity for H_2O_2 of the title compound in $1 \text{ mol}\cdot\text{L}^{-1}$ H_2SO_4 solution as buffer solution at the scan rate 50 mV·s⁻¹ and are shown in Fig. 6. In the potential range from +600 to -200 mV, there are three pairs of



Fig. 6. The cyclic voltammograms of title compound in 1 mol/L H_2SO_4 solutions at different scan rates (20, 50, 110, 140, 170 and 200 mV/s).



Fig. 7. The cyclic voltammograms of title compound in $1 \text{ mol/L } H_2SO_4$ containing 2; 4; 8; 16 mmol H_2O_2 . Scan rate: 100 mV/s.



Fig. 5. XPS of the title compound.

reversible redox peaks at -0.079 V, +0.213 V, and +0.358 V, of $E_{1/}$ $_2 = (E_{cp} + E_{ap}) / 2$ for the title compound. The redox peaks I-I', II-II', and III-III' correspond to three consecutive two-electron processes of Mo. The value of peak-to-peak separation between the corresponding anodic and cathodic peaks (ΔE_p) is 55, 4 and 3 mV, respectively, which is smaller than the theoretical value of reversible two-electron process controlled by ideal diffusion. And it indicates that the surface electrochemical process is not ideal and reversible. When scan rate was varied from 50 to 300 mV/s, the cathodic peak current increases as well as the corresponding anode peak current. Moreover, the cathodic peak potentials shift towards the negative direction and the corresponding anodic peak potentials shift to the positive direction with increasing scan rates. It is interesting that the cathodic and anodic peak potentials increase gradually when the scan rates varied from lower to higher, indicating that these redox processes are irreversible. It was worth mentioning that Cu signal isn't discovered in this potential range and may be covered by a strong current of Mo.

As everyone knows, POMs have good electrocatalytic ability, the title compound were employed to detect H_2O_2 to evaluate its electrocatalytic activity. When the scan rate is 50 mV·s⁻¹, the reduction peak and oxidation peak area increase with the increase of H_2O_2 concentration. With the increase of the reduction peak current, the corresponding oxidation peak current decreases gradually. In addition, with high scan rate, the significant catalytic current is still found, demonstrating higher electrocatalytic activity towards electroreduction of H_2O_2 (Fig. 7).

In summary, the supramolecular material based on Keggin-type polyoxometalates with mixed-ligand was synthesized under hydrothermal conditions and were structurally characterized. Based on the analysis of structures of the title compound, the Keggin-type phosphomolvbates anions, butterfly-shaped [Cu(I)(phen)2]⁺ subunits and dumbbell-shaped $\{[Cu(II)]_2(phen)_4PTA\}^{2+}$ subunits are alternately connected to form chiral helical chains via hydrogen bonds and π ... π stacking interactions along b axis. The helical structure is the most stable form of the structure of the title compound, and the helical direction of the helical chain is determined by the Cu2 subunits. It is interesting that there are two distinct valence of copper ions in the title compound. The preliminary analysis shows that mixed-valence Cu may be due to the reduction of Cu(II) (from CuCl₂) to Cu(I) (in butterflyshaped [Cu(I)(phen)₂]⁺ subunits) by N-containing compound. Additionally, the electrochemical property of the title compound has been carried out, and the results show that Cu signal was not found in this potential range, possibly because it was covered by a strong current in Mo. The successful results of this work provide a new idea that supramolecular materials with attractive structures and novel properties, which could be designed and synthesized by introducing of mixed-ligands into the supramolecular materials.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.inoche.2019.01.037.

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