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Construction of organic–inorganic hybrid molybdophosphonate clusters with copper–bipyridine



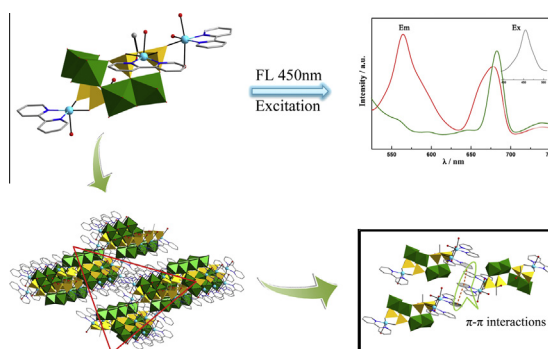
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HIGHLIGHTS

- **1** Represents the first case of transition-metal–organic ligands polyoxomolybdates.
- There exist weak π – π interactions among the bipyridine groups.
- Three Cu^{II} ions in **1** display five- and six-coordinate environments.
- Luminescent property shows the presence of LMCT transitions.

GRAPHICAL ABSTRACT



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ABSTRACT

An organic–inorganic hybrid polyoxomolybdate with formula as $[\text{Cu}(2,2'\text{-bpy})(\text{H}_2\text{O})_2]_2[\text{Cu}(2,2'\text{-bpy})(\text{H}_2\text{O})_3][(\text{O}_3\text{PCCH}_3(\text{OH})\text{PO}_3)_2\text{Mo}_4^{\text{VI}}\text{O}_{11}(\text{H}_2\text{O})_2] \cdot 7\text{H}_2\text{O}$ (**1**) (2,2'-bpy = 2,2'-bipyridine) has been successfully synthesized constructing by diphosphonate $\text{H}_2\text{O}_3\text{PC}(\text{CH}_3)(\text{OH})\text{PO}_3\text{H}_2$ (1-hydroxyethylidene-1,1-bisphosphonic acid, noted as HEDP or etidronate) under conventional aqueous solution. **1** was characterized by single-crystal X-ray diffraction, elemental analysis, IR spectroscopy, thermogravimetric (TG) analysis, and X-ray photoelectron spectroscopy (XPS). Each anion cluster of **1** can be regarded as the fusion of two $[\{\text{Cu}(2,2'\text{-bpy})(\text{H}_2\text{O})\}(\text{O}_3\text{PCCH}_3(\text{OH})\text{PO}_3)\text{Mo}_2^{\text{VI}}\text{O}_6]^{2-}$ subunits with an additional six-coordinated $[\text{Cu}(2,2'\text{-bpy})]^{2+}$ coordination cation linking on one side and there exist weak π – π interactions among the bipyridine groups. The XPS spectra indicate that the oxidation states of Mo and Cu in **1** are +6 and +2, respectively. Photoluminescence properties of **1** and the free 2,2'-bipyridine ligand have been both analyzed, showing that the presence of ligand-to-metal-charge-transfer (LMCT) transitions and metal–ligand coordination have an important effecting on the photoluminescence.

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Introduction

The design and exploration of organic–inorganic hybrid polyoxometalates (POMs) have attracted prodigious interest of researchers in synthetic chemistry, mainly due to their versatile

structural features and potential applications for catalysis, materials, photochromism and photoluminescence [1–8]. In the formation of these compounds, the oxygen atoms localized on the surface of POMs are nucleophilic and the organic ligand can graft on the POMs by substituting the terminal oxygen atoms, and also can lead to covalent interactions with electrophilic groups bearing organic groups [9]. Many organic and organometallic ligands, such as carboxylic acid, alkoxy, organosilicon, organophosphonate and

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organotin, which link to polyoxoanions, have been investigated a lot [10–13]. Among these organic ligands, diphosphonates, are a class of good modification reagents with covalent bonds and multi-functional heterogroups. In addition, diphosphonates can link up with Mo, W or V atoms to construct original architectures as new building blocks, which usually exhibit open structure types contrasting with the common Keggin and Well-Dawson type compounds. Therefore, the studies of diphosphonate-based POMs represent a more recent area in the POMs chemistry.

Over the past decade, the combination of diphosphonates with polyoxomolybdates has greatly progressed owing to the prominent work of Pope, Kortz, Dolbecq, Wang, Mialane and other groups [14–19], including the state of Mo^{VI}, Mo^V and even mixed-valent Mo^{V/VI} compounds. Among the reported compounds in this family, the TM-containing derivatives attached to the molybdodiphosphate clusters have been a subclass, which are largely explored by Zubieta's group via the approach of linking molecular oxide building blocks with appropriate organic ligands or secondary TM cations [20–22]. A vast of these compounds have been prepared under hydrothermal strategy and the structures expand to two or three dimensions [23]. Comparatively, synthesizing under conventional aqueous solution is very rare. In 2007, Kortz et al. presented the first examples of materials based on the Strandberg type polyoxoanion linked by Cu^{II} centers in aqueous acidic media with simple one-pot reaction [24]. Wang et al. reported the polyanion {V^{IV}[(Mo₂O₆)(RC(O)(PO₃)₂)]ⁿ⁻ with two {(Mo₂O₆)(RC(O)(PO₃)₂)} units connecting by a V^{IV} atom at 2010. This work further encouraged us to construct more novel molybdenum oxide architectures containing the organic component diphosphonates and secondary TM coordination cations under conventional aqueous solution.

Herein, we have introduced the TM and organic ligands as secondary metal coordination cations into the molybdodiphosphate clusters in aqueous condition. As we expected, [Cu(2,2'-bpy)(H₂O)]₂[Cu(2,2'-bpy)(H₂O)]₃[(O₃PCCH₃(OH)PO₃)₂-Mo₄^{VI}O₁₁(H₂O)]₂·7H₂O (**1**), a HEDP-based polyoxomolybdates linking three [Cu(2,2'-bpy)]²⁺ coordination fragments, has been isolated in the mixed CH₃CN/H₂O solvent. The Cu^{II} cations in **1** exhibit five- and six-coordination environments, respectively. As far as we know, **1** represents the first example of TM-organic ligands containing diphosphonate-based polyoxomolybdates under conventional aqueous solution.

Experimental

Instrument and reagent

Elemental analysis (C, H and N) was performed by a Perkin-Elmer 2400-II CHNS/O analyzer. Inductively coupled plasma (ICP) was obtained on a Perkin-Elmer Optima 2000 ICP-OES spectrometer. Infrared (IR) spectrum was recorded on a Bruker VERTEX 70 IR spectrometer in the range of 4000–400 cm⁻¹ (using KBr in pellets). XRPD data were recorded on a Philips X'Pert-MPD instrument with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) in the angular range $2\theta = 5\text{--}40^\circ$ at 293 K. TG analysis was measured on a Mettler-Toledo TGA/SDTA851^e instrument with a heating rate of 10 °C/min from 25 °C to 900 °C in N₂ flow. XPS was recorded by an Axis Ultra (Kratos, UK) photoelectron spectroscope with Al K α (1486.7 eV) irradiation. The photoluminescence property was performed on a HITACHI F-7000 fluorescence spectrophotometer in the solid state at the room temperature. Single crystals for X-ray structure analysis was performed on Bruker CCD Apex-II diffractometer with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 296 K. The structure of compound **1** was solved by direct methods and further refined by full-matrix least-squares refinements on F^2 using the SHELXL-97 software and an absorption correction was performed by the SADABS program [25,26].

All reagents were analysis grade.

Synthesis

[(n-C₄H₉)₄N]₄[Mo₈O₂₆]: The precursor was prepared according to the literature [27].

[Cu(2,2'-bpy)(H₂O)]₂[Cu(2,2'-bpy)(H₂O)]₃[(CCH₃(OH)P₂O₆)₂-Mo₄^{VI}O₁₁(H₂O)]₂·7H₂O (**1**): CuCl₂·2H₂O (0.175 g, 0.100 mmol), 2,2'-bipyridine (0.078 g, 0.500 mmol) and HEDP (0.076 g, 0.360 mmol) were dissolved in 10 mL H₂O, flowed by adding a solution of [(n-C₄H₉)₄N]₄[Mo₈O₂₆] (0.600 g, 0.270 mmol) and 2 mL DMF in acetonitrile (5 mL). The mixture was blue with some yellow precipitate. After stirring at 65 °C for 1 h, followed by cooling to room temperature and filtering. Blue rhombic crystals of **1** suitable for X-ray single-crystal diffraction were obtained by slow evaporation at room temperature after one month. Yield: 0.05 g (83.3% based on Cu). Anal. Found (%): Mo, 20.36; P, 6.82; Cu, 9.98; C, 21.97; N, 4.51; H, 2.98. Calc.: Mo, 20.47; P, 6.61; Cu, 10.17; C, 21.78; N, 4.48; H, 3.23. IR (KBr pellets): ν (cm⁻¹) = 3425 (s), 1655 (m), 1600 (m), 1483 (w), 1456 (m), 1127 (s), 1082 (s), 1033 (m), 1005 (m), 928 (s), 902 (s), 818 (w), 769 (s), 731 (s), 703 (s), 652 (s), 568 (m).

Results and discussion

Synthesis and structure

Compound **1** was synthesized starting from POM building blocks [(n-C₄H₉)₄N]₄[Mo₈O₂₆] and diphosphonate ligand HEDP as well as TM Cu^{II} ion and organic ligand 2,2'-bipyridine in the CH₃CN/H₂O (1:2) mixed solvent in the presence of DMF. The pH value of the reaction system is around 2.7 and no need further adjustment. The molar ratio of the reagent and the mixed solvent, reaction temperature and selection of starting reagent are the key to affect the formation and yield of crystals. In case the volume ratio of CH₃CN/H₂O increases to 2:1 or the solvent is pure water, the yield of the crystals is low. Whereas the solvent is pure CH₃CN, only yellow crystals [(n-C₄H₉)₄N]₂[Mo₆O₁₉] appear. In addition, we have tried to replace the [(n-C₄H₉)₄N]₄[Mo₈O₂₆] by other sources of molybdenum, such as Na₂MoO₄·2H₂O and (NH₄)₆Mo₇O₂₄·4H₂O, no isostructural analogues being obtained under the same or similar conditions. Cu^{II} ions and 2,2'-bipyridine are also unreplacable in the process of formation.

The crystal data and structure refinement detail for **1** are summarized in Table 1. Each anion cluster of **1** can be viewed as the assembly of two [{Cu(2,2'-bpy)(H₂O)}(O₃PCCH₃(OH)-PO₃)Mo₂^{VI}O₆]²⁻ subunits by corner-sharing of three oxygen atoms with an additional six-coordinated copper-bipyridine fragment linking on one side of the polyoxoanion via P–O–Cu bond (Fig. 1). The [{Cu(2,2'-bpy)(H₂O)}(O₃PCCH₃(OH)PO₃)Mo₂^{VI}O₆]²⁻ subunit is constructed by a HEDP ligand, which is anchored to the dimer of edge-sharing {Mo^{VI}O₆} octahedra through two common O atoms. The coordination mode is illustrated in Scheme 1. It should be noted that the structure of the {(O₃PCCH₃(OH)PO₃)Mo₂^{VI}O₆} cluster in **1** is totally different from those reported Mo-dimeric cluster constructed by diphosphonates, including the common {Mo₂O₄} dimeric moiety [28–31]. As is shown in Fig. 2, there are mainly three kinds of connecting modes of these clusters which have been described before. The most remarkable difference is the two P atoms are located at one profile of the edge-sharing {Mo^{VI}O₆} octahedral dimer in the {(O₃PCCH₃(OH)PO₃)Mo₂^{VI}O₆} cluster, leading to a plane basically coplanar with two Mo atoms.

In compound **1**, only three [Cu(2,2'-bpy)]²⁺ fragments act as the counterions to balance the negative charges from the polyoxoanion. We cannot find any other lattice cations. The three Cu atoms in **1** exhibit two types of coordination environments: the Cu1 ion

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