Two new hybrid molybdenum arsenate derivative constructed from [As₂Mo₆O₂₆]⁶⁻ building: Synthesis, structural characterization and photocatalysis property

Two new hybrid molybdenum arsenate derivative constructed from $[As_2Mo_6O_{26}]^{6-}$ building: Synthesis, structural characterization and photocatalysis property

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ABSTRACT

Two new inorganic-organic hybrid materials $[Cu(enMe)_2]_2\{(As_2Mo_6O_{26})\ [Cu(enMe)_2]\}\cdot 4H_2O$ (**1**) and $[As_2Mo_6(OH)_2O_{24}][Cu(H_2O)_2(phen)]_2$ (**2**) (enMe = 1,2'-propanediamine, phen = 1,10'-phenanthroline) based on $[As_2Mo_6O_{26}]^{6-}$ building blocks, denoted as $[As_2Mo_6]$, have been obtained by hydrothermal methods. **1** shows a 1-D straight chain structure constructed form $[As_2Mo_6]$ building blocks and $[Cu(enMe)_2]$ complexes, and then extended to 3-D supramolecular network by lattice water *via* hydrogen bonds interactions. **2** exhibits a new 1-D covalent ribbon with large rectangular grids formed from $[As_2Mo_6]$ building blocks connected by $[Cu(H_2O)_2(phen)]$ complexes, then extended into 3-D supramolecular network *via* hydrogen bonds and $\pi\cdots\pi$ interactions. In additional, the photocatalytic activity for methylene blue degradation under visible-light irradiation of **2** was investigated.

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1. Introduction

Polyoxometalates (POMs), which is a kind of nanoclusters constructed by the self-assembly of V, Mo, W and Nb oxides, belonging to the field of inorganic-organic hybrid materials have undergone rapid expansion in their syntheses and characterizations in recent years [1—5]. The driving force behind this research is mainly due to their novel topological and electronic versatility and application in fields as catalysis, analysis, biochemistry, materials science and medicine [6—10]. Although POMs chemistry as an old class of inorganic chemistry has been known for more than 200 years [11,12], up to now, it continues to be a considerable focus in the ongoing research because of the large number of novel POMs structures and their properties [13—15]. In the recent years, the study on functionalization of POMs to improve their application has raised a lot of academic research interests including elemental composition, solubility, redox potentials, charge density, size and shape [16—20].

Notable, a recent major advance in the burgeoning field of POM chemistry is that a good number of hybrid compounds with desirable physical-chemical properties and fascinating structures have been constructed by sensible choice of POMs and transition metal complexes (TMCs) [13,14,17,21—25]. In which the Keggin and Dawson clusters have attracted considerable attention in catalysis, photochemistry and medicine field owing to their redox properties and also to their special structural characteristics. In contrast, less attention was paid to the $[X_2M_6O_{26}]^{6-}$ (X = V and As, M = Mo and W) building blocks, although the first $[As_2Mo_6O_{26}]^{6-}$ and $[V_2Mo_6O_{26}]^{6-}$ clusters have been reported in 1976 and 1979 [26,27], respectively. In $[As_2Mo_6O_{26}]^{6-}$ and $[V_2Mo_6O_{26}]^{6-}$ clusters, there are two kinds of available surface oxygen atoms on inorganic building blocks, which will provide a significant likelihood for the derivation of differently dimensional architectures. However, to best of our knowledge, all of POMs containing $[X_2M_6O_{26}]^{6-}$ unit reported are all

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the zero-dimensional structures except two one-dimensional (1-D) chain structures constructed from $[V_2Mo_6O_{26}]^{6-}$ clusters and TMCs reported by Niu et al. [28–31]. Then, there is a remarkable challenge in the synthesis and characterization of high-dimensional POMs constructed form $[As_2Mo_6O_{26}]^{6-}$ clusters and TMCs. On the basis of the aforementioned points, we introduce the TMCs as organic-inorganic bridging fragments to link the discrete As–Mo–O motif forming extended and supported structures. Moreover, the N-containing organic ligands with electron-donating ability were introduced, which not only may act as the coordination sites to coordinate to the metal center to form the TMCs fragment, but also may provide recognition sites for hydrogen bonds and π-π stacking interactions to form interesting supramolecular structures. Following these strategies, we report here the hydrothermal syntheses and structures of two new compounds: $[Cu(enMe)_2]_2\{(As_2Mo_6O_{26})[Cu(enMe)_2]\}\cdot4H_2O$ (**1**) and $[As_2Mo_6(OH)_2O_{24}][Cu(H_2O)_2(phen)]_2$ (**2**). In compound **1**, the $[As_2Mo_6]$ units supporting two $[Cu(enMe)_2]$ TMCs interacts with other two $[Cu(enMe)_2]$ TMCs that generates the 1-D straight chain, which connects with four parallel ones by free water molecules through hydrogen bonds to form a 3-D supramolecular networks. Compound **2** possesses a new 1-D covalent ribbon with large rectangular grids formed from $[As_2Mo_6]$ building blocks connected by $[Cu(H_2O)_2(phen)]$ complexes, then extended into 3-D supramolecular network via hydrogen bonds and π···π interactions. Photocatalytic activity of **2** for decomposition of methylene blue (MB) under visible-light irradiation has been investigated, in which **2** exhibits good stability as a photocatalyst.

2. Experimental

2.1. Materials and instruments

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification.

Elemental analysis (C, H, and N) was performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. Inductively coupled plasma (ICP) element analyses were carried out on a Perkin-Elmer Optima 3300DV ICP spectrometer. IR (KBr pellets) spectrum was recorded from 400 to 4000 cm^{-1} using a Perkin-Elmer Spectrum One spectrophotometer. Powder X-ray diffraction analysis was performed on a Bruker D8 Advance powder diffractometer using Ni-filtered Cu Kα radiation at 40 kV and 30 mA, from 10° to 30° with a scan rate of 0.3° s^{-1}. The luminescent measurements were performed at room temperature using a Perkin Elmer LS55 fluorescence spectrophotometer. The excitation slit, as well as the emission slit was 2 nm. Thermogravimetric analysis was performed on a NETSCH STA 449 instrument with a heating rate of 10 °C min^{-1} in air。

2.2. Synthesis of $[Cu(enMe)_2]_2\{(As_2Mo_6O_{26})[Cu(enMe)_2]\}\cdot4H_2O$ (**1**)

A mixture of Na_3AsO_4 (0.17 g, 0.41 mmol), $(NH_4)_3Mo_7O_{24}\cdot4H_2O$ (0.13 g, 0.11 mmol), $CuCl_2\cdot2H_2O$ (0.10 g, 0.59 mmol), enMe (0.07 mL) and distilled water (15 mL) was neutralized to pH ≈ 5.0 with hydrochloric acid (4 mol L^{-1}) under stirring at room temperature for 1 h and sealed in a 25 mL Teflon-lined stainless steel reactor, then heated at 180 °C for 4 days, then the reactant mixture was cooled to room temperature to give a 30% yield (based on Mo) of **1** as purple crystals were collected by mechanical isolation and washed with distilled water. Calcd. For $C_{18}H_{58}As_2Cu_3Mo_6N_{12}O_{30}$: C, 11.76%; H, 3.18%; N, 9.14%, As, 8.15%, Cu, 10.37%, Mo, 31.30%. Found: C, 11.69%; H, 3.23%, N, 9.17%, As, 8.14%, Cu, 10.41%, Mo, 31.25%. IR (KBr pellets, v/cm^{-1}): 3236 (s), 1451 (s), 1380 (s) 1373 (w), 960 (m), 853 (s), 751 (s), 633 (s).

2.3. Synthesis of $[As_2Mo_6(OH)_2O_{24}][Cu(H_2O)_2(phen)]_2$ (**2**)

Similar to the synthesis conditions of **1**, using phen (0.07 g, 0.33 mmol) instead of enMe (0.07 mL), the pH value of reaction system was neutralized to 3.0 with hydrochloric acid (4 mol L^{-1}). The green block crystals were isolated. Yield: 20% (based on Mo). Calcd. For $C_{12}H_{13}AsCuMo_3N_2O_{15}$: C, 16.93%; H, 1.54%; N, 3.29%; As, 8.80%; Cu, 7.46%; Mo, 33.80%. Found: C, 16.89%; H, 1.57%; N, 3.32%; As, 8.78%; Cu, 7.48%; Mo, 33.77%. IR (KBr pellets, v/cm^{-1}): 3378 (s), (s), 1502 (m), 956 (s), 846 (s), 767 (s).

2.4. X-ray crystallography

All data were collected on an Agilent Technology SuperNova Eos Dual system with a (Cu-Kα, λ = 1.54178 Å for **1** and Mo-Kα, λ = 0.71073 Å for **2**) micro focus source and focusing multilayer mirror optics. The data were collected at a temperature of room temperature and processed using CrysAlis^{Pro} [32]. The structures were solved by the direct methods and refined by the full-matrix least-squares method against F^2 (SHELXL-2014) [33]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of organic ligands were localized in their calculated positions and refined using a riding model. Further details of the X-ray structural analyses are given in Table 1. Selected bond lengths and bond angles of compound **1** are listed in Table S1.

3. Results and discussion

3.1. Crystal structure of **1**

Single-crystal structural analyses reveal that **1** and **2** contain a common building unit $[As_2Mo_6O_{26}]^{6-}$. As is usually observed, the $[As_2Mo_6]$ unit of compound **1** (Fig. 1a) is similar to α-$[Mo_8O_{26}]^{4-}$ polyanion, which exhibits a highly symmetry of D_{3d}. In the $[As_2Mo_6]$ unit, all Mo atoms are located in a distorted $\{MoO_6\}$ octahedral, and Mo atoms are not in the geometric center of the octahedra, but they are closer to the vertex occupied by the terminal oxygen atoms. Six distorted $\{MoO_6\}$ octahedra joined together by edge sharing to form a flat metal oxide ring, two $\{AsO_4\}$ tetrahedra are capped with the opposite faces of the metal oxide ring. Each capped $\{AsO_4\}$ tetrahedron links to three terminal oxygen atoms within the metal oxide ring. According to the different coordination environments in the polyanions, these oxygen atoms can be divided into three groups: O_t (terminal oxygen atoms connecting to one Mo atom), with the Mo-O_t 1.702(4)-1.717(4)(4) Å; O_b (oxygen atoms connecting edge-sharing MoO_6 octahedra) with Mo-O_b 1.904(4)-1.922(4) Å; O_c (oxygen atoms connecting the AsO_4 tetrahedra and metal oxide ring) with Mo-O_c 2.275(3)-2.374(3) Å. For AsO_4, the average As—O distance is 1.697 Å, while O—As—O angles vary from 109.0(2)-110.4(2) °, which is nearly the ideal tetrahedron coordination mode.

Compound **1** consists of $[As_2Mo_6]$ units, $[Cu(enMe)_2]$ complex units and lattice water molecules. Each $[As_2Mo_6]$ unit links two adjacent identical ones by two $[Cu(2)(enMe)_2]$ bridge units via Mo–O–Cu linkages, generating a one-dimensional (1-D) straight chain of $[-As_2Mo_6-Cu(2)(enMe)_2-As_2Mo_6-]$ along the *a* axis (Fig. 1b). To the best of our knowledge, compound **1** is the first example that 1-D straight chain structure is based on $[As_2Mo_6]$ units. The bridging Cu(2) atom lies in special positions [0, 1/2, 1/2] with the site occupancy factors 0.5, which forms an octahedral configuration with two oxygen atoms from two adjacent $[As_2Mo_6]$ units and four nitrogen donors from two enMe ligands, with Cu(2)–O(8) 2.623(4) Å and the average Cu(2)–N bond length being 1.989 Å, respectively. Cu(1) atom is crystallographically non-identical with Cu(2) atom, the $[Cu(1)(enMe)_2]$ unit is terminal,