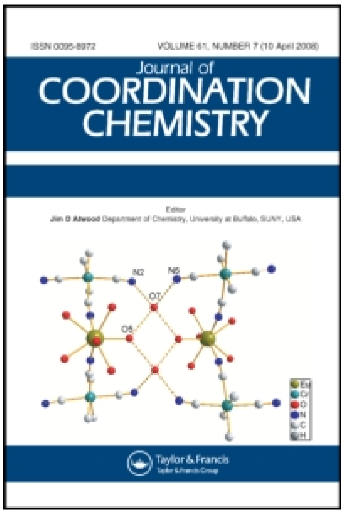

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Synthesis, crystal structure, and characterization of a new high-dimensional phosphomolybdate architecture built from silver-complex fragments and hexa-connected P_2Mo_5 clusters

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A new 3-D organic–inorganic hybrid phosphomolybdate, $[Ag(bipy)]_4(H_2P_2Mo_5O_{23}) \cdot 3H_2O$ (**1**) (bipy = 4,4′-bipyridine) has been hydrothermally synthesized and characterized by elemental analyses, IR, TG, and fluorescent properties. Compound **1** crystallizes in the monoclinic space group $C2/c$ with $a = 23.830(5)$, $b = 21.030(4)$, $c = 24.501(5)$ Å, $\beta = 110.38(3)^\circ$, $V = 11510(4)$ Å^3, $Z = 8$, and R_1 (wR_2) = 0.0507 (0.1210). It contains unique 3-D metal organic frameworks based on silver-complex fragments and hexa-connected P_2Mo_5 clusters via covalent bonds and represents the highest connection numbers of P_2Mo_5 clusters to date.

Keywords: Fluorescent; Phosphomolybdate; Hexa-connected

1. Introduction

Rational design and controlled synthesis of organic-inorganic hybrid materials based on polyoxometalates (POMs) is of interest for intriguing frameworks and topologies [1–6], and for their potential applications in functional materials, nanotechnology, and biological recognition [7–9]. There are many promising synthetic strategies for construction of novel POM materials. One is to connect well-defined POM building units as inorganic bridging groups with transition metal complexes (TMCs) via covalent bonds under hydrothermal or solvothermal conditions. The incorporation of TMCs can dramatically influence the microstructures and properties of final products, so the merits of POMs and TMCs work together to build POM-based metal organic frameworks with charming structures and unique properties.

In the process of constructing organic-inorganic hybrid compounds based on POMs, biphosphopentamolybdate clusters (P_2Mo_5) as excellent building blocks seized our attention because of the following two considerations: First, the relative higher charge densities of P_2Mo_5 clusters make stronger interactions with TMCs for constructing 3-D

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organic-inorganic hybrid materials; the P_2Mo_5 clusters have smaller volume compared to other POMs with equivalent negative charges which increases the charge densities per volume. Second, P_2Mo_5 clusters could be effortlessly synthesized by mixing Na_2MoO_4 and H_3PO_4 under pH-controlled hydrothermal conditions. Based on the aforementioned conditions, some organic-inorganic hybrid compounds constructed from P_2Mo_5 clusters have been explored in recent years. For example, Lu *et al.* [10] reported $[Cu(phen)(H_2O)]_3[(PO_4)_2Mo_5O_{15}] \cdot 5H_2O$ and $HNa[Cu(bpy)(H_2O)]_2[(PO_4)_2Mo_5O_{15}] \cdot 6H_2O$ (phen = 1,10-phenanthroline, bpy = 2,2′-bipyridine) exhibiting 1-D chains based on the P_2Mo_5 clusters and copper-complex fragments. Armatas *et al.* [11] and Burkholder *et al.* [12] synthesized a series of POM compounds based upon P_2Mo_5 subunits. Upreti and Ramanan [13] reported three new organic-inorganic hybrid materials $\{NH_3C_6H_4NH_3\}_7[Mo_5O_{15}\{PO_3(OH)\}_2]_2[HMo_5O_{15}\{PO_3(OH)\}_2]_2 \cdot 21H_2O$, $\{NH_3C_6H_4NH_3\}_2[Mo_5O_{15}\{PO_3(OH)\}_2] \cdot 4H_2O$, and $\{NH_3C_6H_4NH_3\}_2\{NH_2C_6H_4NH_3\}[Mo_5O_{15}\{PO_4\}\{PO_3(OH)\}] \cdot 3H_2O$ crystallized in the presence of *o*, *m* and *p*-phenylenediammonium ions [13]. Our group has reported $[H_2bipy]_2Cu(bipy)_2\}Mo_5P_2O_{23}] \cdot 4H_2O$ (bipy = 4,4′-bipyridine) which exhibits a 3-D framework of 1-D channels built from $\{Cu(bipy)2\}_n^{2n+}$ coordination polymer sheets pillared by $[Mo_5P_2O_{23}]^{6-}$ clusters [14]. $(H_2bipy)_{0.5}\{[Ni(H_2O)_5][Ni(Hbipy)(H_2O)_4][Mo_5P_2O_{23}]\}$ and $(H_2bipy)_{0.5}\{[Co(H_2O)_5][Co(Hbipy)(H_2O)_4][Mo_5P_2O_{23}]\}$ are also reported by Wang and coworkers [15]. To date, no high-connected frameworks based upon P_2Mo_5 clusters have been observed. The reason is probably that previous chemists often chose copper, cobalt, and nickel metal ions which possess relatively higher coordination numbers. The connection modes of these metal ions brought on high steric hindrance. To mitigate the steric hindrance in transition metal complex fragments, we chose silver ions with low coordination numbers as the source of metal ions to construct TMCs which provide relatively lower steric hindrance for construction of high-connected 3-D organic-inorganic hybrid compounds. Herein, we report a new 3-D phosphomolybdate architecture, $[Ag(bipy)]_4(H_2P_2Mo_5O_{23}) \cdot 3H_2O$ (**1**), which contains unique 3-D organic-inorganic hybrid frameworks constructed from silver-complex fragments and hexa-connected P_2Mo_5 clusters via covalent bonds. In this compound, the P_2Mo_5 cluster exhibits the highest connection mode reported, linked by six silver-complex fragments. The fluorescence of **1** has also been investigated.

2. Experimental

2.1. *General methods and materials*

All chemicals purchased were reagent grade and used without purification. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Ag, P and Mo were measured with a Leaman inductively coupled plasma (ICP) spectrometer. Water contents were determined by TG analyses on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of $10^{\circ}C\,min^{-1}$. IR spectra were recorded in the range $400–4000\,cm^{-1}$ on an Alpha Centaurt FT/IR spectrophotometer with pressed KBr pellets. Photoluminescence spectrum was measured using a FL-2T2 instrument (SPEX, USA) with a 450-W xenon lamp monochromated by double grating (1200 grooves/mm).

2.2. *Synthesis of (1)*

The mixture of $AgNO_3$ (0.1 g, 0.59 mmol), 4,4′-bipy (0.05 g, 0.32 mmol), $Na_2MoO_4 \cdot 2H_2O$ (0.1 g, 0.06 mmol), and H_3PO_4 (85%, 0.15 g, 1.30 mmol) in a molar ratio of about 10: 5.3: 1: 21.7 in H_2O (5 mL, 277.78 mmol) was adjusted to pH (5–6) by adding NaOH (1 mol L^{-1}), then the mixture was stirred for 30 min in air. The mixture was transferred to a Teflon-lined autoclave (23 mL) and kept at 140°C for 5 days. After slow cooling to room temperature, yellow crystals were filtered, washed with distilled water, and dried in a desiccator at room temperature to give a yield of 40% based on Mo. Elemental analysis for $C_{40}H_{40}Ag_4Mo_5N_8O_{26}P_2$ (2021.92), Calcd: C 23.76, H 1.99, N 5.54, Ag 21.34, P 3.06, Mo 23.79%; found: C 23.72, H 2.05, N 5.60, Ag 21.27, P 3.15, Mo, 23.70%. Selected IR (KBr pellet, cm^{-1}): 3434 (s), 1606 (s), 1532 (w), 1418 (w), 1132 (m), 1050 (w), 1003 (w), 906 (s), 809 (m), 667 (s), 569 (w), 529 (w).

2.3. *X-ray crystallography*

The suitable single crystal was mounted on a glass fiber and the crystallographic data of **1** were collected at 150(2) K on a Rigaku R-axis Rapid IP diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and IP technique. Empirical absorption correction was applied. The structure of **1** was solved by the direct method and refined by full-matrix least-squares on F^2 using the SHELXTL-97 crystallographic software package [16]. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. The H atoms on the carbon were included in calculated positions. The H atoms on water cannot be found from the weak residual electron peaks but were directly included in the final molecular formula. Crystal data and structure refinement for **1** are summarized in table 1. Selected bond lengths and angles of **1** are given in table S2.

3. Results and discussion

3.1. *Structure description*

Compound **1** has been synthesized under hydrothermal condition and characterized by single crystal X-ray diffraction analysis. In the fundamental unit of **1**, a propeller-like hexa-connected architecture is generated from individual P_2Mo_5 clusters and six silver complex fragments (figure 1). As well known, the P_2Mo_5 clusters can be viewed as a ring of five distorted MoO_6 octahedra with two capped PO_4 tetrahedra on each side [10]. Each phosphate subunit shares three oxo-groups with the molybdate ring. One of these oxo-groups is μ_2-bridging, linking one molybdenum site and the phosphorus and the other two adopt a μ_3-bridging mode, linking two molybdenum sites and the phosphorus. Valence bond calculations confirm that all Mo's in the P_2Mo_5 clusters are in +6 oxidation state [17]. In silver-complex fragments, Ag1 and Ag2 are coordinated in distorted tetrahedral geometry, with two N atoms from two 4,4′-bipy and two O atoms from two adjacent P_2Mo_5 clusters; Ag3 and Ag4 have distorted T-shaped coordination, where the two nitrogens are from two 4,4′-bipy and one O is from a P_2Mo_5 cluster. The Ag–N and Ag–O distances are in the range 2.105(7)–2.203(7) Å and

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{40}H_{40}Ag_4Mo_5N_8O_{26}P_2$
Mr	2021.92
T (K)	150(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$C2/c$
Units of dimensions (Å, °)	
a	23.830(5)
b	21.030(4)
c	24.501(5)
α	90
β	110.38(3)
γ	90
V (Å^3)	11510(4)
Z	8
D_{calcd} (Mg m^{-3})	2.334
μ (mm^{-1})	2.526
$F(000)$	7776
θ range for data collection (°)	3.05–25.00
Limiting indices	$-28 \le h \le 28$, $-24 \le k \le 24$, $-25 \le l \le 29$
Reflections collected/unique	41,635/10,085 [$R_{(int)} = 0.0738$]
Completeness to $\theta = 25.00$	99.5%
Goodness-of-fit	1.011
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0507$, $wR_2 = 0.1210$
R indices (all data)	$R_1 = 0.0724$, $wR_2 = 0.1330$

$R_1 = \sum||F_o|-|F_c||/\sum|F_o|$; $wR_2 = \sum\left[w\left(F_o^2 - F_c^2\right)^2\right]\Big/\sum\left[w\left(F_o^2\right)^2\right]^{1}$.

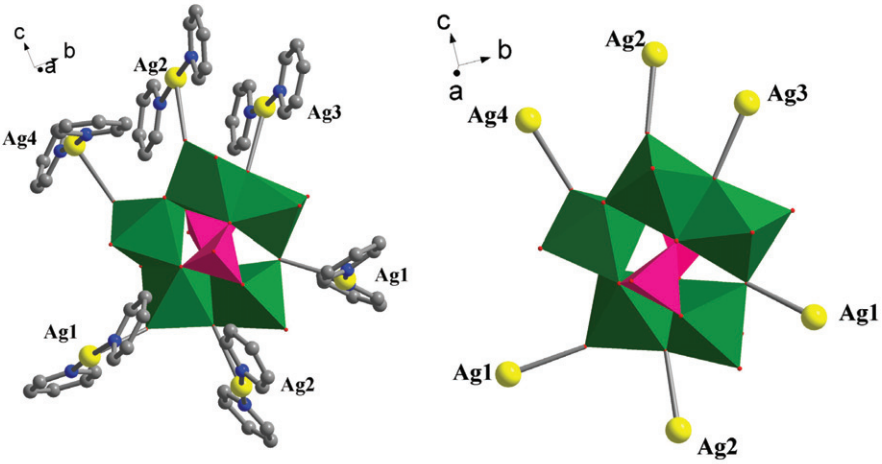

Figure 1. (a) Combined polyhedral and ball/stick representation of the molecular structural unit of **1**. (b) The view of coordination details of P_2Mo_5 clusters. The bipy ligands were drawn in half parts for clarity. All hydrogen atoms and water molecules have been omitted for clarity.

2.644(1)–2.789(2) Å [18], respectively. According to the different linking modes, silver complex fragments may be divided into three types as shown in figure 1(b): (i) the Ag(1 or 2) subunit links to two P_2Mo_5 clusters through two oxygens, one from a terminal oxygen of MoO_6 octahedra, and the other from μ_2-oxo group (Mo–O–Mo); (ii) the Ag(3) is bound to one P_2Mo_5 cluster via only one oxygen from a μ_2-oxo group (Mo–O–Mo); and (iii) Ag(4) complex is similar to the Ag(3) complex, but from a

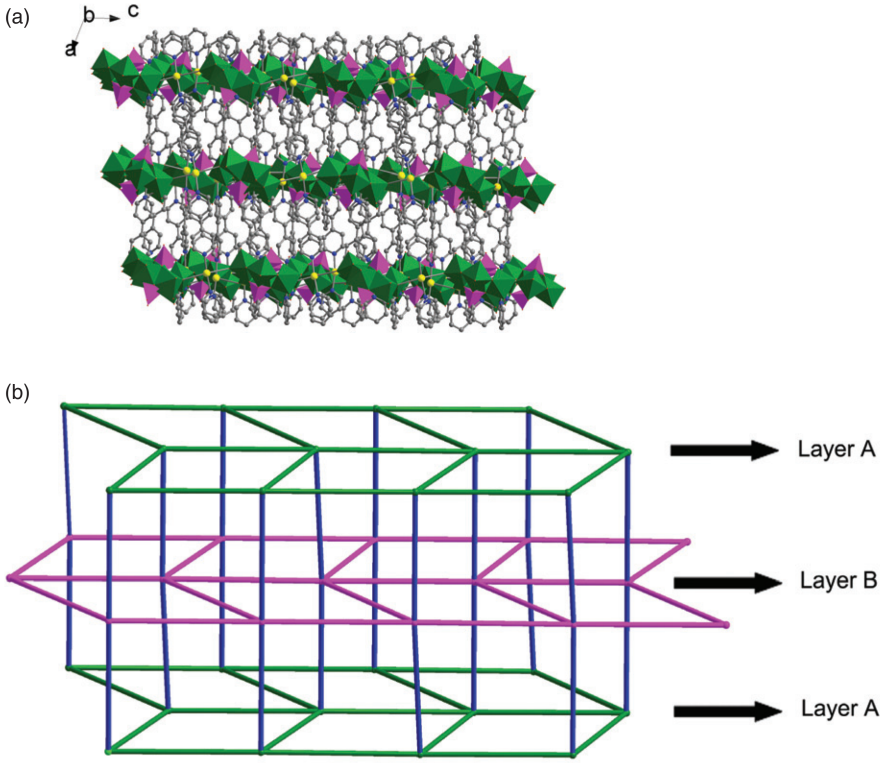

Figure 2. (a) The 3-D framework in **1**. (b) A schematic illustration of the 3-D framework of **1**. The green moiety represents the 2-D layer structure of Layer A, the purple moiety represents Layer B and the blue moiety represents the silver-complex fragments.

terminal oxygen of MoO_6 octahedra. So each P_2Mo_5 cluster is bridged by six $[Ag(bipy)]_n^{n+}$ subunits to assemble two kinds of 1-D infinite chains [figure S1 (a)]: (i) chain A is a 1-D zigzag chain where the Ag(1) subunits connect the propeller-shaped P_2Mo_5 clusters with the distances of adjacent Ag1's of 10.565(2) Å; and (ii) chain B is a 1-D linear chain with the distances of adjacent Ag2's of 12.449(3) Å. The two types of chains are all like propellers, P_2Mo_5 as center, two of six silver complexes as linkers of chains, and the other four as blades in four directions. Adjacent propeller-shaped chains are linked to constitute 2-D layers via covalent bonding (Ag–O) where the P_2Mo_5 clusters are nodes [figure S1 (b)]. In 2-D layers, two sorts of approximate parallelogram grids were generated with distances of inserted silver subunits as Ag4–Ag4, 5.653(2) Å; and Ag3–Ag3, 3.581 Å. Furthermore, the 2-D layers in two different directions extended to 3-D metal-organic frameworks with the help of the inserted TMC subunits via covalent bonding (Ag–N and Ag–O) as shown in figure 2(a). Schematic illustration of the 3-D framework is shown in figure 2(b). The detailed 3-D architectures are provided in figure S2.

3.2. *IR spectrum*

The IR spectrum of **1** (figure S3) between 4000 and 400 cm^{-1} exhibits two strong bands in the 666–907 cm^{-1} range associated with ν_{sym} (Mo$=$O) and ν_{asym} (Mo$=$O) and

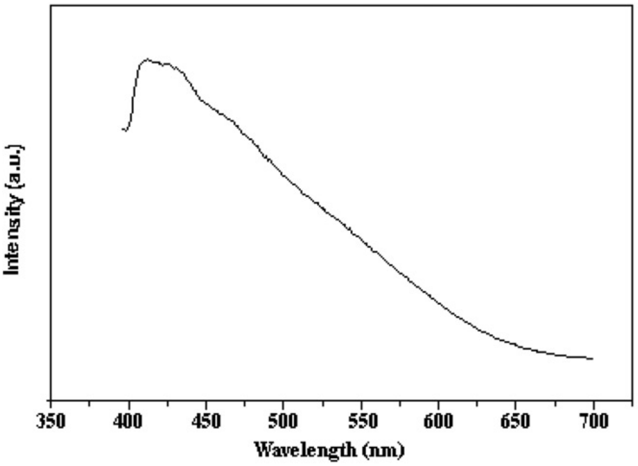

Figure 3. Emission spectrum (maximum = 413 nm) and excitation spectrum (maximum = 320 nm) of **1** in the solid state at room temperature.

a medium intensity band in the 560–590 $\mathrm{cm^{-1}}$ region attributed to ν(Mo–O–Mo). A series of medium intensity bands in the 1000–1610 $\mathrm{cm^{-1}}$ range is associated with 4,4′-bipy, and a broad and strong band at about 3434 $\mathrm{cm^{-1}}$ is associated with the water of crystallization.

3.3. *Thermogravimetric analysis*

The thermal stability of **1** has been determined on single crystalline samples in nitrogen by thermogravimetric analysis (TGA). The TGA curve of **1** exhibits two weight losses: one (2.75%) from 140 to 180°C is attributed to loss of coordinated water (calculated 2.67%); another (30.78%) from 300 to 450°C corresponds to removal of 4,4′-bipy (calculated: 30.90%).

3.4. *Photoluminescence spectrum*

The emission of **1** in the solid state at room temperature is depicted in figure 3. Compound **1** exhibits intense blue photoluminescence with an emission maximum at 413 nm with $\lambda_{ex} = 320$ nm. According to previous observations [19, 20], this emission band is probably assigned to emission of ligand-to-metal charge transfer (LMCT). This indicates that **1** may be an excellent candidate for photoactive materials [21, 22].

4. Conclusion

We successfully combined the merits of P_2Mo_5 clusters and transition metal complex fragments synthesizing a new 3-D hexa-connected P_2Mo_5 cluster structure which represents the highest connection of P_2Mo_5 clusters. The successful design and synthesis of **1** not only confirm the advantages of hydrothermal methods in preparing new organic-inorganic hybrid materials but also may suggest a way to control the connection numbers of POMs by altering the reactive metal ions. More work in this field is underway.

Supplementary materials

The IR and photoluminescence spectra of **1** and the additional tables are available. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as deposition numbers CCDC-689965 for **1**. The data can be obtained, free of charge, from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK via fax: (+44 1223 336033) or Email (deposit@ccdc.cam.ac.uk).

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