

Synthesis and Characterization of $\text{Cs}_5\text{P}[\text{Mo}_4\text{O}_{14}(\text{OH})_2] \cdot 2\text{H}_2\text{O}$: A New Molybdophosphate Cluster with Face-Sharing MoO_6 Octahedra

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Introduction

Within the ever-growing field of (hetero)polyoxometalates, the molybdophosphate system occupies a special place as being one of the most extensively studied and quite well understood systems. Its speciation in aqueous solution as a function of pH and phosphate concentration has been established precisely by various methods such as potentiometric, NMR, Raman, and cyclic voltammetry measurements.¹ The predominant species in such solutions include $[\text{H}_x\text{P}_2\text{Mo}_5\text{O}_{23}]^{(6-x)-}$; the well-known Keggin ion $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ and its lacunary derivatives $[\text{H}_x\text{PMo}_9\text{O}_{34}]^{(9-x)-}$, $[\text{H}_x\text{PMo}_{10}\text{O}_{37}]^{(9-x)-}$, and $[\text{H}_x\text{PMo}_{11}\text{O}_{39}]^{(7-x)-}$; and the Wells–Dawson ion $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$, all built of MoO_6 octahedra sharing corners and/or edges and connected by PO_4 tetrahedra.¹ Reported here is a new molybdophosphate, $\text{Cs}_5\text{P}[\text{Mo}_4\text{O}_{14}(\text{OH})_2] \cdot 2\text{H}_2\text{O}$ (**1**), with two $\{\text{Mo}_4\text{O}_{14}(\text{OH})\}^{5-}$ fragments connected by a phosphate group. The $\{\text{Mo}_4\text{O}_{14}(\text{OH})\}^{5-}$ fragment, identified for the first time in a molybdophosphate species, contains MoO_6 octahedra sharing edges and, quite unusual for (hetero)polyoxomolybdates, faces.

Experimental Section

Our systematic exploration for novel borophosphates among the transition metals led to the initial hydrothermal synthesis of the title compound.² The original mixture contained $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, H_3BO_3 , CsCl , H_3PO_4 , and NaOH in a molar ratio of 0.5:1:1:1:1, respectively. Later, the synthesis was rationalized, and the compound was isolated as a single solid phase from an equimolar reaction of the same reactants, except boric acid ($\text{pH} \approx 7$), carried out in a Teflon-lined stainless steel autoclave (23 mL capacity,

distilled water was added to a total reaction volume of 5 mL) at 160 °C for 5 days under autogenous pressure. Colorless polyhedral crystals of the compound were collected by filtration, washed with water, and dried at room temperature (yield of ~20%). Powder X-ray diffraction analysis confirmed that the product corresponded to compound **1** (there was no amorphous phase). A study of the influence of the pH revealed that the title compound could be isolated for pH values between 2 and 7. IR (Perkin-Elmer Paragon 1000 FT-spectrometer, KBr pellet, cm^{-1}): 3582m; 3509m; 3460m; 3304m, br; 3083m, br; 1636w; 1607w; 1040s; 1017s; 941vs; 918vs; 734vs; 693s; 607m; 571s; 558m; 537m. Thermogravimetric analysis was carried out using a Cahn TG-131 apparatus in air flow of 60 mL/min and heating rate of 5 °C/min.

The replacement of phosphoric acid by arsenic(V) oxide hydrate in the previous synthesis resulted in the isostructural molybdoarsenate compound $\text{Cs}_5\text{As}[\text{Mo}_4\text{O}_{14}(\text{OH})_2] \cdot 2\text{H}_2\text{O}$ (**2**). IR (KBr pellet, cm^{-1}): 3580m; 3508m; 3448m; 3292m, br; 3068m, br; 1639w; 1609w; 947s; 922vs; 904vs; 832s; 721vs; 682s; 604m; 580m; 565m; 539w; 456m. The high-temperature (550 °C) hydrothermal synthesis and structure of compound **2** were previously reported by Hsu and Wang.³

The structure of **1** was determined from X-ray diffraction data collected on a Bruker APEX CCD diffractometer at room temperature from a colorless polyhedral crystal (0.06 × 0.08 × 0.12 mm). Molybdenum, phosphorus, and most of the oxygen atoms were located from the structure solution by direct methods, and all the remaining atoms, including the hydrogen atoms, were found by difference Fourier maps. All non-hydrogen atoms were refined with anisotropic thermal parameters. For the hydrogen atoms, the isotropic thermal parameters were fixed, and antibumping restraints were introduced. The final reliability factors converged to $R1/wR2 = 0.0191/0.0472$ for 2113 observed reflections ($I \geq 2\sigma_I$) and 134 variables. Empirical absorption corrections were applied using the SADABS V2.03 program.⁴ The structure solution and refinement (on F^2) were carried out using the SHELXTL V5.1 package.⁴ Crystallographic data and selected distances are given in Tables 1 and 2, respectively.

Results and Discussion

The structure of $\text{Cs}_5\text{P}[\text{Mo}_4\text{O}_{14}(\text{OH})_2] \cdot 2\text{H}_2\text{O}$ contains isolated $\{\text{P}[\text{Mo}_4\text{O}_{14}(\text{OH})_2]\}^{5-}$ anions, cesium cations, and water molecules. The anion, C_{2v} symmetry, is made of two

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Table 1. Crystallographic Data for $\text{Cs}_5\text{P}\{\text{Mo}_4\text{O}_{14}(\text{OH})_2\}_2 \cdot 2\text{H}_2\text{O}$ (**1**)

formula	$\text{Cs}_5\text{H}_6\text{Mo}_8\text{O}_{32}\text{P}$
fw	1981.08
space group, Z	$Cmcm$ (No. 63), 4
lattice parameters	$a = 8.8151(6)$ Å $b = 23.103(1)$ Å $c = 16.068(1)$ Å $V = 3272.4(4)$ Å ³
radiation, λ	Mo $K\alpha$, 0.710 73 Å
temp	20 °C
abs coeff	86.00 cm^{-1}
density (calcd)	4.021 g/cm^3
R1/wR2 ($I > 2\sigma_I$) ^a	0.0191/0.0472
R1/wR2 (all data) ^a	0.0208/0.0480

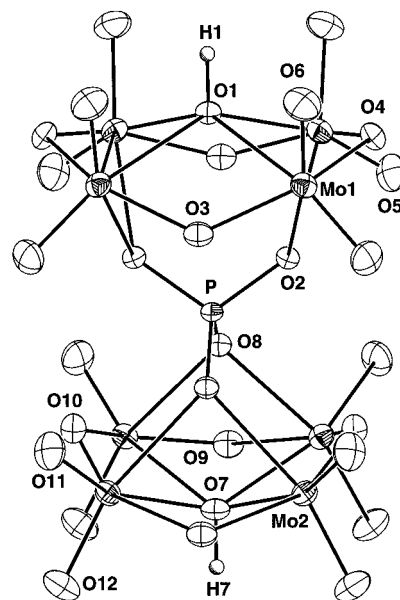
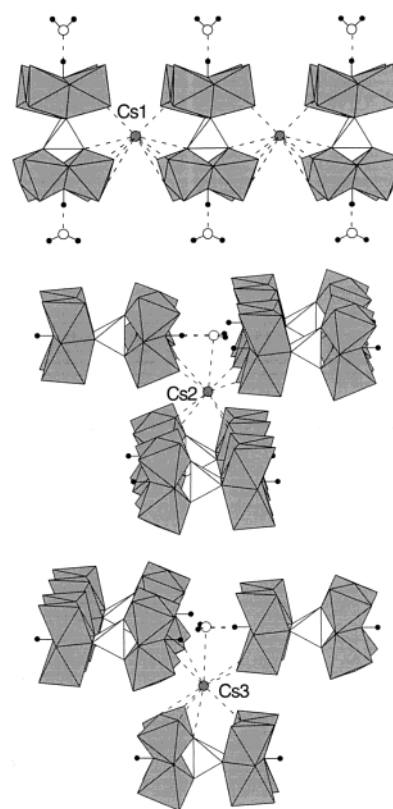
^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $wR2 = \{[\sum w[(F_o)^2 - (F_c)^2]^2] / [\sum w(F_o)^2]\}^{1/2}$ where $w = [\sigma^2(F_o)^2 + (0.0228P)^2 + 7.74P]^{-1}$ with $P = [(F_o)^2 + 2(F_c)^2]/3$.

Table 2. Selected Distances (Å) for $\text{Cs}_5\text{P}\{\text{Mo}_4\text{O}_{14}(\text{OH})_2\}_2 \cdot 2\text{H}_2\text{O}$ (**1**)

Mo1–O5	1.702(2)	Mo2–O11	1.701(2)
Mo1–O6	1.713(2)	Mo2–O12	1.707(2)
Mo1–O3	1.908(1)	Mo2–O10	1.907(1)
Mo1–O4	1.918(1)	Mo2–O9	1.922(1)
Mo1–O2	2.340(1)	Mo2–O8	2.341(1)
Mo1–O1	2.431(1)	Mo2–O7	2.430(1)
P–2 × O2	1.547(3)	P–2 × O8	1.549(3)

crystallographically inequivalent molybdate tetramers connected by a phosphate group (Figure 1). All molybdenum atoms are octahedrally coordinated and are coplanar in each tetranuclear fragment $\{\text{Mo}_4\text{O}_{14}(\text{OH})\}^{5-}$. The tetramers, one made of Mo1 and the other of Mo2 atoms, are built of two pairs of face-sharing octahedra that share edges with each other. Because of this particular arrangement of octahedra, the Mo···Mo distances alternate as long, 3.337 and 3.345 Å, for the edge-shared octahedra of Mo1 and Mo2, respectively, and short, 3.189 and 3.195 Å, for the face-shared octahedra for the Mo1 and Mo2 tetramers, respectively. The MoO_6 octahedra show the common distortion of two short (1.701(2)–1.713(2) Å), two intermediate (1.90–1.93 Å), and two long (2.33–2.44 Å) Mo–O distances (Table 2). They correspond respectively to two terminal oxygens in cis configuration, two Mo-bridging oxygen atoms in trans position, and a triply bridging Mo–O(–P)–Mo oxygen and a quadruply Mo-bridging hydroxyl group in cis configuration. Thus, each short bond is trans to a long one. The capping OH groups are bonded to all four molybdenum atoms of the tetramers. Their presence was confirmed by valence sum calculations and by the observed hydrogen bonds with distances of 2.887 and 2.713 Å for O1···Ow1 and O7···Ow2, respectively (Figure 2).⁵ The connecting phosphate group is quite a regular tetrahedron with nearly equal P–O distances of 1.547(3) and 1.549(3) Å and O–P–O angles between 107.8(2) and 110.14(7)°.

The $\{\text{Mo}_4\text{O}_{14}(\text{OH})\}^{5-}$ anion has been previously identified as a monomer in various heteropolyoxomolybdates of general formula $[(\mu_2\text{-R})\{\text{Mo}_4\text{O}_{14}(\text{OH})\}]^{n-}$ where R is an organic or organoarsenic fragment such as $\text{R}'_2\text{C}$ and $\text{R}'_2\text{As}$,^{6,7} respectively, or PhSe or OSe.⁸ Reported recently was the structure of the first compound with a dimer of two $\{\text{Mo}_4\text{O}_{14}(\text{OH})\}^{5-}$ units connected via a central arsenate group, synthesized at

**Figure 1.** Dimer $[\text{P}\{\text{Mo}_4\text{O}_{14}(\text{OH})_2\}_2]^{5-}$ made of two molybdenum tetramers $\{\text{Mo}_4\text{O}_{14}(\text{OH})\}^{5-}$ connected by a phosphate group (thermal ellipsoids at 50% probability). The cluster is of C_{2v} symmetry with the 2-fold axis vertical.**Figure 2.** Environment around the three different cesium cations. The Cs–O contacts and the hydrogen bonds are shown as broken lines.

very high temperature of 550 °C.³ The compound is isostructural with **1**, but with noticeable differences in the Mo–O distances caused by the very different distances in the connecting AsO_4 and PO_4 tetrahedra. The shorter P–O distances in **1** ($d_{\text{av}} = 1.548$ Å) compared to As–O ($d_{\text{av}} = 1.694$ Å) induce lengthening of the Mo–O distances to the oxygens of the connecting tetrahedron, $d_{\text{av}} = 2.340$ and 2.309

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NOTE

Å in **1** and **2**, respectively. Also, the two dimers of face-shared octahedra in **1** swivel closer to each other around the pivoting OH group so that the O2···O2a and O8···O8a (Figure 1) distances are much shorter in **1** than in **2**, with $d_{av} = 2.505$ and 2.730 Å, respectively. Interestingly, despite the numerous molybdophosphates, no such molybdenum tetramer was known with an organophosphorus fragment or any phosphorus-containing group analogous to the arsenic species. This, at one time, led to the speculation that perhaps the P–O bonds are too short for the supposedly rigid tetramer.⁹ Later on, however, after species with R₂C fragments and the even shorter C–O bonds were found, the thinking was changed, and compounds with P–O bonds were predicted to be possible but were never found until now.⁷

The anions in the structure alternate with cesium cations and also form hydrogen bonds with the water molecules (Figure 2). The three crystallographically independent cesium atoms display a 10-fold coordination (Cs–O distances between 3.0 and 3.7 Å), with Cs1 coordinated only by oxygen atoms of {P[Mo₄O₁₄(OH)]₂}⁵⁻ anions while Cs2 and Cs3 have one water molecule each in their coordination spheres (Figure 2).

The IR spectrum of **1** shows the same characteristic bands as those identified in the isostructural arsenate.³ Both spectra show a set of five bands in the region 3600–3000 cm⁻¹ attributed to the O–H stretching of the hydroxyl groups and the water molecules. The O–H stretching mode of the anion [(CH₃)₂AsMo₄O₁₄(OH)]²⁻ in the anhydrous tetrabutylammonium salt has been identified before as a narrow band at

3615 cm⁻¹.⁷ By analogy, the sharp band observed at 3582 cm⁻¹ in **1** is attributed to the same mode. The lower energy is easily explained by the hydrogen bond to the water molecule in **1**. Other bands in the spectrum are the following: two weak and sharp bands in 1640–1600 cm⁻¹ due to H–O–H bending vibration, two bands in 950–915 cm⁻¹ attributed to $\nu_{as}(\text{Mo}=\text{O})$, bands in the region 800–500 cm⁻¹ due to skeletal vibrations, bands at 1040 and 1017 cm⁻¹ due to P–O stretching, and one band at 571 cm⁻¹ due to O–P–O bending.¹⁰

The TGA analysis of **1** shows a two step dehydration process. The first weight loss of 1.77% is observed between 120 and 340 °C and is attributed to the loss of the two water molecules of the structure (theoretical = 1.82%). The second weight loss of 0.95% is observed between 340 and 430 °C and fits the loss of the hydroxyl group (theoretical = 0.91%).

In conclusion, the new molybdophosphate Cs₅P[Mo₄O₁₄(OH)]₂·2H₂O is the first and only example of [Mo₄O₁₄(OH)]⁵⁻ stabilized by a phosphorus-containing group. Furthermore, it has been shown that the terminal hydroxyl group can be replaced by other groups such as F, HCO₂, OCH₃, and so forth,¹¹ and it is, therefore, conceivable that the fragment can be used as a starting building unit for the construction of more complex solids. The low-temperature synthesis of **1** and **2** shows that the previously used high temperature of 550 °C for the synthesis of **2** is not necessary for the formation of dimers.³

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Supporting Information Available: X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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