Synthesis and Characterization of Cs$_5$P[Mo$_4$O$_{14}$(OH)]$_2$·2H$_2$O: A New Molybdophosphate Cluster with Face-Sharing MoO$_6$ Octahedra

Eddy Dumas and Slavi C. Sevov*

University of Notre Dame, Department of Chemistry and Biochemistry, Notre Dame, Indiana 46556

Received August 24, 2001

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. The predominant species in such solutions include [H$_x$PMo$_{12}$O$_{40}$]$^{6-}$$^{-}$$^{-}$; the well-known Keggin ion [PMo$_{12}$O$_{40}$]$^{6-}$$^{-}$, and its lacunary derivatives [H$_x$PMo$_{11}$O$_{39}$]$^{6-}$$^{-}$$^{-}$, [H$_x$PMo$_{10}$O$_{39}$]$^{6-}$$^{-}$, and [H$_x$PMo$_{9}$O$_{34}$]$^{6-}$$^{-}$; and the Wells−Dawson ion [P$_2$Mo$_{10}$O$_{40}$]$^{6-}$, all built of MoO$_6$ octahedra sharing corners and/or edges and connected by PO$_4$ tetrahedra. Recent studies related to compound 1 were introduced. The final reliability factors converged to R1/wR2 = 0.08/0.12 mm.

Experimental Section

Our systematic exploration for novel borophosphates among the transition metals led to the initial hydrothermal synthesis of the title compound. The original mixture contained Na$_2$MoO$_4$, H$_3$BO$_3$, CsCl, H$_3$PO$_4$, 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 mixture of Cs$_5$As[Mo$_4$O$_{14}$(OH)]$_2$·2H$_2$O, Cs$_2$Mo$_2$O$_7$, and structure of compound 2 were carried out using the SHELXTL V5.1 package. The structure solution and refinement (on $F^2$) were carried out using the SHELXTL V5.1 package. Crystallographic data and selected distances are given in Tables 1 and 2, respectively.

Results and Discussion

The structure of compound 1 was determined from X-ray diffraction data collected on a Bruker APEX CCD diffractionometer at room temperature from a colorless polyhedral crystal (0.06 × 0.08 × 0.12 mm). The high-temperature syntheses of Cs$_5$As[Mo$_4$O$_{14}$(OH)]$_2$·2H$_2$O and Cs$_5$P[Mo$_4$O$_{14}$(OH)]$_2$·2H$_2$O were carried out using the SHELXTL V5.1 package. Crystallographic data and selected distances are given in Tables 1 and 2, respectively.

For the hydrogen atoms, the remaining atoms, including the hydrogen atoms, were found by difference Fourier maps. All non-hydrogen atoms were refined with anisotropic thermal parameters. Empirical absorption corrections were applied using the SADABS V2.03 program. The structure solution and refinement (on $F^2$) were carried out using the SHELXTL V5.1 package. The structure solution and refinement (on $F^2$) were carried out using the SHELXTL V5.1 package.

Published on Web 12/14/2001

* Author to whom correspondence should be addressed. E-mail: ssevov@nd.edu.


crystallographically inequivalent molybdate tetramers connected by a phosphate group (Figure 1). All molybdenum atoms are octahedrally coordinated and are coplanar in each tetratomic fragment \{MoO$_4$$_{12}$(OH)$_5$\}$^{5-}$. The tetramers, one made of Mo1 and the other of Mo2 atoms, are built of two pairs of face-sharing octahedra that share edges with each other. Because of this particular arrangement of octahedra, the Mo•••Mo distances alternate as long, 3.337 and 3.345 Å, for the edge-shared octahedra of Mo1 and Mo2, respectively, and short, 3.189 and 3.195 Å, for the face-shared octahedra for the Mo1 and Mo2 tetramers, respectively. The MoO$_6$ octahedra show the common distortion of two short Mo distances in \{MoO$_4$$_{12}$(OH)$_5$\}$^{5-}$. The shorter Mo distances alternate as long, 3.345 Å) compared to As distances (1.93 Å) in the connecting AsO$_4$ tetrahedra. The shorter P-O distances are to the oxygens of the connecting tetrahedron, \{MoO$_4$$_{12}$(OH)$_5$\}$^{5-}$ units connected via a central arsenate group, synthesized at a very high temperature of 550 °C. The compound is isostructural with I, 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 I (d$_{ov}$ = 1.548 Å) compared to As–O (d$_{ov}$ = 1.694 Å) induce lengthening of the Mo–O distances to 3.345 Å.

The \{MoO$_4$$_{12}$(OH)$_5$\}$^{5-}$ anion has been previously identified as a monomer in various heteropolyoxomolybdates of general formula \{[(x$_2$)R](MoO$_4$$_{12}$(OH)$_5$)\}$^{5-}$ where R is an organic or organoarsenic fragment such as R'$_2$C and R'$_2$As, respectively. PhSe or OSe. Reportedly the structure of the first compound with a dimer of two \{MoO$_4$$_{12}$(OH)$_5$\}$^{5-}$ units connected via a central arsenate group, synthesized at a very high temperature of 550 °C. The compound is isostructural with I, 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 I (d$_{ov}$ = 1.548 Å) compared to As–O (d$_{ov}$ = 1.694 Å) induce lengthening of the Mo–O distances to 3.345 Å.

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 \( R_2 C \) fragments 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 \( \{\text{P}[\text{Mo}_4\text{O}_{14}(\text{OH})]\}_2^\text{−} \) 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.\(^8\) 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 \([\text{(CH}_3)_2\text{AsMo}_4\text{O}_{14}(\text{OH})]^\text{2−} \) 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 \( \nu_\text{as}(\text{Mo}=\text{O}) \), 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 Cs\(_5\)P[Mo\(_4\)O\(_{14}\)(OH)]\(_5\)\(2\text{H}_2\text{O} \) is the first and only example of [Mo\(_4\)O\(_{14}\)(OH)]\(^5\text{−}\) 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, HCO\(_2\), OCH\(_3\), 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.\(^3\)

Acknowledgment. We thank the National Science Foundation (Grant DMR-9701550) for the financial support.

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.

IC010900W