# A Novel Polyoxo Molybdenum(V) Organophosphonate Anion Having a Sandwich Structure: Synthesis and Crystal Structure of $[N(C_2H_5)_4]_2Na_3(H_3O)_4\{Na[Mo_6O_{15}(O_3PC_6H_5)(HO_3PC_6H_5)_3]_2\}\cdot{\sim}14H_2O$

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Polyoxometalates[1] have attracted much attention not only because of their rich structural chemistry but also because of their use in catalysis.[2] There has been a great deal of research activity aimed at the so-called "reduced polyoxometalates",[3–5] as opposed to those polyoxo anions that have $nd^0$ electronic configuration at the metal center. Among the reduced polyoxometalates studied to date, polyoxo anions of vanadium have received the most attention, although a large family of macromolecular polyoxomolybdenum(V) phosphates have been described.[6] The organophosphonate group ($RPO_3^{2-}$) is known to form two-dimensional solids with metals.[7] Its tendency to lower the dimensionality of its metal compounds has been extended further in the molecular structures of vanadium polyoxo organophosphonate anions.[5a,b] In this communication we report the synthesis and structural characterization of the first polyoxo molybdenum(V) organophosphonate

$$[N(C_2H_5)_4]_2Na_3(H_3O)_4\text{-}\{Na[Mo_6O_{15}(O_3PC_6H_5)(HO_3PC_6H_5)_3]_2\}\cdot{\sim}14H_2O$$

**1**

Compound **1** was synthesized by the hydrothermal reaction of $Na_2MoO_4$, Mo, $[(C_2H_5)_4N]OH$, $C_6H_5PO_3H_2$, and $H_2O$ (2:1:2:6:300 mole ratio) at 200 °C under autogenous pressure for 3 days. The solid product consisted of clusters of dark red microcrystals and black crystalline powders. The dark red microcrystals were moderately soluble in hot water whereas the black crystals were insoluble and thus were separated by filtration from hot aqueous solution.[8] Upon cooling of the red filtrate, dark red prismatic crystals of **1**[9] were obtained in 20% isolated yield based on $Na_2MoO_4$ used. The compound may be partially dehydrated in air but is otherwise stable. The infrared spectrum exhibits bands in the region 3014–2856 cm$^{-1}$ associated with C—H stretch modes of both the phenyl group and the ethyl group of the tetraethylammonium cation. The strong bands at 1143 and 1060 cm$^{-1}$ are attributable to the P—O stretch modes of the phosphonate group. The very strong band at 961 cm$^{-1}$ establishes the presence of $Mo{=}O_t$ ($O_t$ = terminal oxo group).

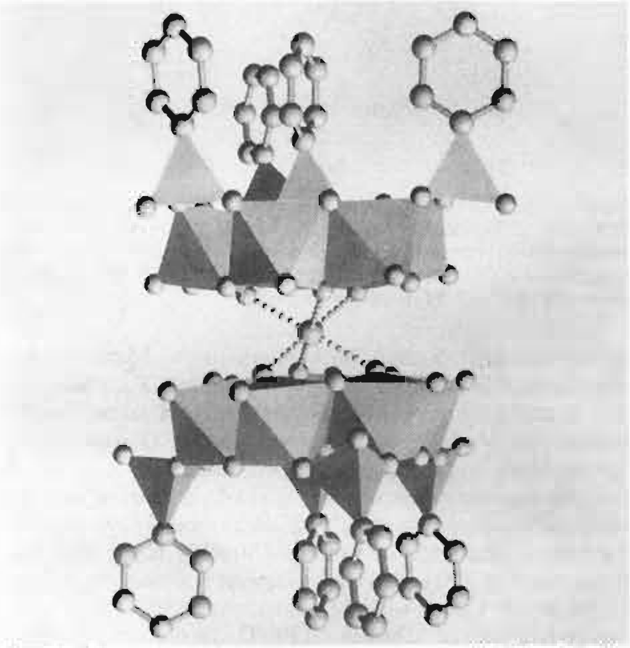

**Figure 1.** Polyhedral presentation of the structure of **1a**, $\{Na[Mo_6O_{15}(O_3PC_6H_5)(HO_3PC_6H_5)_3]_2\}^{9-}$.

X-ray structural analysis[10] revealed the presence of discrete tetraethylammonium cations and water molecules of crystallization in the lattice, some of which are disordered. The molecular anion $\{Na[Mo_6O_{15}(O_3PC_6H_5)(HO_3PC_6H_5)_3]_2\}^{9-}$ (**1a**) (Figure 1), as implied by the formula, consists of two identical hexanuclear molybdenum polyoxo phosphonate anions, $[Mo_6O_{15}(O_3PC_6H_5)(HO_3PC_6H_5)_3]^{5-}$ (**1b**), linked by a sodium cation. The six molybdenum atoms in **1b** are arranged in a circular array with

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(8) The XRD powder pattern of the black crystals shows the presence of $HMoO_3\cdot 2H_2O$ (JCPDS File 38-65) and impurity peaks.

(9) Anal. Calcd for $C_{64}H_{106}N_2O_{72}P_8Mo_{12}Na_4$: C, 21.67; H, 3.01; N, 0.79; P, 6.99; Mo, 32.46; Na, 2.59. Found: C, 21.47; H, 2.96; N, 0.72; P, 6.86; Mo, 32.89; Na, 2.65. IR (KBr pellet, cm$^{-1}$): 3422 (s, br), 3216 (s, br), 3014 (m, sh), 2927 (m, sh), 2856 (w, sh), 1635 (m), 1485 (w), 1362 (m), 1399 (s), 1143 (s), 1060 (s), 961 (vs), 748 (s), 698 (m), 569 (s).

(10) Empirical formula: $C_{32}H_{40}NO_{35.8}P_4Mo_6Na_2$. A dark red prismatic crystal measuring 0.4 × 0.3 × 0.1 mm was used for data collection. All measurements were made on a Rigaku AFC6R diffractometer with graphite-monochromated Cu K$\alpha$ radiation and a 12-kw rotation anode generator. Data were collected at 23 ± 1 °C using the $\omega$–$2\theta$ scan technique from 6.0 to 100.1° ($2\theta$); $h$ = 0 to +14, $k$ = 0 to ±17, $l$ = 0 to ±13. A total of 7069 reflections were measured; 6724 were unique ($R_{int}$ = 0.032). Crystal data: triclinic, space group $P\bar{1}$ (No. 2), $a$ = 14.726 (2) Å, $b$ = 17.786 (3) Å, $c$ = 13.706 (4) Å, $\alpha$ = 111.95 (2)°, $\beta$ = 95.69 (2)°, $\gamma$ = 79.35 (1)°, $V$ = 3271 (1) Å$^3$, $Z$ = 2, $D$(calc) = 1.784 g cm$^{-3}$. Structure solution and refinement based on 5697 reflections with $I > 3\sigma(I)$ converged at $R$ = 0.061 and $R_w$ = 0.083.

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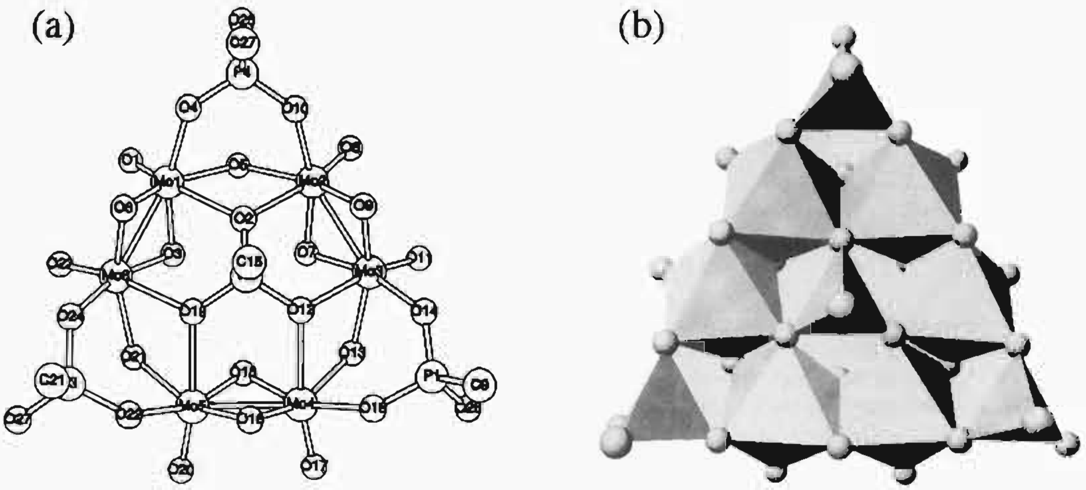

**Figure 2.** Structure of $[Mo_6O_{15}(O_3PC_6H_5)(HO_3PC_6H_5)]^{5-}$ (**1b**) showing (a) bond connectivities and the atomic labeling scheme and (b) its polyhedral presentation. The circular $Mo_6O_{24}$ core formed from edge-sharing octahedra is essentially the "Anderson structure" without a metal atom at the central octahedral site. For clarity, the carbon atoms of the phenyl group that are not connected to phosphorus are not shown. Selected interatomic distances (Å): Mo1--Mo2 (nonbonding), 3.57 (1); Mo2—Mo3, 2.583 (2); Mo1═O1, 1.69 (1); Mo1—O2, 2.345 (9), Mo1—O3, 1.93 (1); Mo1—O4, 2.09 (1); Mo1—O5, 2.12 (1); Mo1—O6, 1.95 (1).

an Mo—Mo single bond (2.586 Å) alternating with long Mo--Mo nonbonding contacts (3.57–3.59 Å) (Figure 2a). Each Mo atom is situated at the center of a $[MoO_6]$ distorted octahedron, forming the circular polyoxo metalate core $[Mo_6O_{24}]$ (Figure 2b) by sharing edges with its neighboring octahedra. The structure of this $[Mo_6O_{24}]$ core is reminiscent of $[M_7O_{24}]^{n-}$ species with the so-called "Anderson structure",[11] in which a metal atom occupies the central octahedral site of the $[Mo_6O_{24}]$ core. The four phosphonate groups are all on the same side of the plane defined by the six Mo atoms, with P—C bonds approximately perpendicular to the plane. The central $PhPO_3^{2-}$ group provides three oxygen atoms to bridge between the Mo--Mo nonbonding contacts with long Mo—O (2.31–2.34 Å) bonds trans to the short M═O double bonds (1.67–1.69 Å) while each of the remaining three $PhPO_3^{2-}$ groups on the periphery of the circle supplies two oxygen atoms to span across the Mo--Mo nonbonding contacts. In the dimeric assembly **1a**, a sodium cation is sandwiched between two identical **1b** anions. The two **1b** anions are staggered to each other so as to make the sodium cation octahedrally coordinated by oxygen atoms trans to the peripheral phosphonate oxygen atoms. The molecular anion **1a** possesses rigorous $C_i$ symmetry. (The maximum symmetry is $D_{3d}$.)

Another rather extraordinary structural feature in **1** is the presence of a trinuclear sodium–oxygen cluster, $Na_3(O_t)_4(H_2O)_{10}^{3+}$ (Figure 3), in which sodium cations are octahedrally coordinated by water molecules and the terminal oxygen atoms (Mo═$O_t$) of **1a**. Three $Na^+$-centered octahedra are linked linearly by sharing edges. A center of inversion resides at the central sodium atom. Since each of the $Na_3$ clusters is bonded to two **1a** anions through the Na—$O_t$ bonds, the sodium cluster cation and the molybdenum polyoxo anion form a one-dimensional chain running along the crystallographic *c* direction (Figure 4, supplementary material). The formation of the unusual sodium polycation may simply be the result of the high charge carried by the polyanion **1a**, which requires such a high concentration of counterion in the lattice as to cause the hexahydrated sodium cation to condense. On the other hand, the inclusion of the bulky tetraethylammonium cation in the lattice certainly indicates that other factors such as polar/nonpolar interactions play a role in the polycation formation as well.

The molecular anion **1a** may be considered a structural derivative of the $\{Na[Mo_6O_{15}(HPO_4)(H_2PO_4)_3]_2\}^{9-}$ polyanion,[12] in that all of the axial (pseudo-3-fold axis) hydroxyl groups of the phosphate are replaced by phenyl groups. While there are numerous examples of layered metal phosphonates that are structural derivatives of layered metal phosphates in this fashion,[7] to the best of our knowledge the title compound represents the first example of isostructural substitution of an organophosphonate group for a phosphate group in a polyanion.[13]

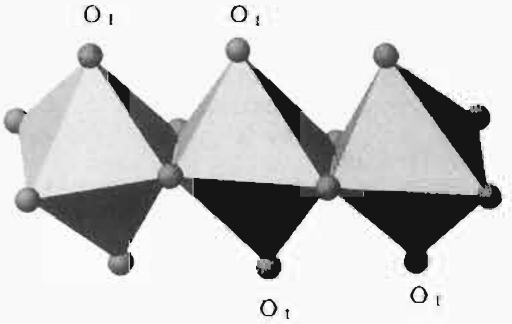

**Figure 3.** Polyhedral presentation of $Na_3(O_t)_4(H_2O)_{10}^{3+}$. Na—O bond distances range from 2.282 (9) to 2.48 (1) Å. The Na--Na distance is 3.477 (8) Å. $O_t$ is the terminal oxygen atom bonded to the Mo atom.

There is evidence[14] that polyanion **1b** is a viable molecular species by itself and the sodium cation in **1a** can be replaced by other metal cations, implying that polyanion **1b** is a large tridentate ligand. Studies aimed at elucidating the structural relations between these species are in progress.

**Supplementary Material Available:** Textual experimental details of the structure analysis, tables of crystal data and details of the structure determination, atomic positional parameters, intramolecular distances, bond angles, and anisotropic temperature factors for ordered, nonhydrogen atoms, and a figure showing a stereoview of the packing of **1** in the unit cell (Figure 4) (23 pages). Ordering information is given on any current masthead page.

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