

Multicomponent Polyanions. 53. Structure of Tetrakis(trimethylammonium) Tetra- μ -oxo-bis(triaqua-hexadeca-oxo(trioxophenylphosphato)hexamolybdate) Dihydrate, $[\text{NH}(\text{CH}_3)_3]_4[\{(\text{C}_6\text{H}_5\text{P})\text{Mo}_6\text{O}_{21}(\text{H}_2\text{O})_3\}_2]\cdot 2\text{H}_2\text{O}$

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Abstract

The title compound crystallized in the monoclinic space group $P2_1/n$ (No. 14) [$a = 11.211(5)$, $b = 12.862(3)$, $c = 23.05(1)$ Å, $\beta = 94.37(3)^\circ$, $V = 3314(2)$ Å³, $Z = 2$]. The polyanion can be regarded as a dimer of a phenylphosphonatohexamolybdate, $(\text{C}_6\text{H}_5\text{P})\text{Mo}_6\text{O}_{23}(\text{H}_2\text{O})_3$, linked by four O atoms. In this monomeric unit the six molybdenum octahedra are grouped into two parts consisting of four and two edge-sharing octahedra, respectively. These two parts are connected by two corner-sharing O atoms to form a bent Mo_6 ring. The phenylphosphonate group coordinates to the Mo_6 ring from the narrow side as a tripodal ligand. The $\{(\text{C}_6\text{H}_5\text{P})\text{Mo}_6\text{O}_{21}(\text{H}_2\text{O})_3\}_2$ units form layers parallel to (001) and the structure is stabilized by hydrogen bonds between water and neighboring anions. The monomeric unit has been shown to be a key structure in the process of deducing the aqueous solution structures of the $(\text{C}_6\text{H}_5\text{P})\text{Mo}_6^{2-}$ and $(\text{C}_6\text{H}_5\text{P})\text{Mo}_7^{4-}$ species found in a previous equilibrium study of the $\text{H}^+ - \text{MoO}_4^{2-} - (\text{C}_6\text{H}_5\text{P})\text{O}_3^-$ system.

1. Introduction

A polyoxometalate is an aggregated oxoanion formed by dehydrative condensation of monooxometalates such as vanadate, molybdate or tungstate. When only one type of transition metal is involved, so-called isopolyoxometalates (isopolyanions) are formed and when at least one additional element such as P, Si or As (often regarded as an aggregation centre) takes part in the formation, so-called heteropolyoxometalates (heteropolyanions) are formed. Since Berzelius reported the first examples of polyoxometalate in 1826 (Berzelius, 1826), extensive efforts have been made to synthesize polyoxometalates and to investigate the structures, properties and practical use of such compounds.

At the Department of Inorganic Chemistry, Umeå University, the equilibria of aqueous polyoxometalate systems have long been studied by means of potentiometry and spectroscopic methods such as NMR. These

investigations give the most probable speciation of the systems in question. Using the formation constants obtained, each system can then be modeled at various concentrations, as long as the ionic medium and the temperature are not changed. It is, however, only the empirical formula which can be determined by such studies and, generally, neither the molecular formula nor the structure of the species are obtainable directly from the equilibrium analysis, although some structural information can be obtained from NMR. Therefore, other methods have to be used to obtain the direct structural information of the species. Several attempts have been made to isolate the species as crystals and to determine their solid-state structure. Large Angle X-ray Scattering (LAXS) data have also been recorded in order to obtain structural information in solution. The structure found in the isolated crystal is not necessarily the same as that in aqueous solution. However, if the chemical formula of the polyanion in the crystal agrees with the composition obtained from the equilibrium analysis, it is likely that the structure in solution is analogous or closely related to that in the solid state.

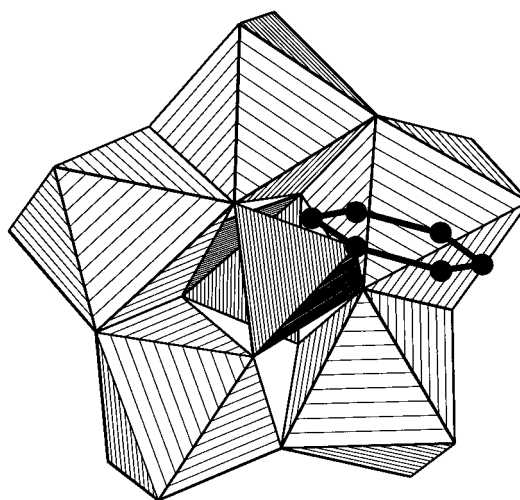


Fig. 1. A polyhedral representation of the $(\text{C}_6\text{H}_5\text{P})_2\text{Mo}_5\text{O}_{21}^{4-}$ anion.

In a combined potentiometric and ^{31}P NMR equilibrium analysis of the three-component system $\text{H}^+ - \text{MoO}_4^{2-} - (\text{C}_6\text{H}_5\text{P})\text{O}_3^{2-}$ (Yagasaki *et al.*, 1987), three different compositions of phenylphosphonato-polyoxomolybdates were found; $\text{Mo}_5(\text{PhP})_2$, Mo_6PhP and Mo_7PhP ($\text{C}_6\text{H}_5\text{P}$ is designated PhP for simplicity). This speciation study was performed in a 0.600 M NaCl medium, where $[\text{Na}^+]$ was kept constant while $[\text{Cl}^-]$ was allowed to vary. The crystal structure of the $\text{Mo}_5(\text{PhP})_2$ species has been determined previously (Lyxell & Strandberg, 1988). The polyanion was found to have the common structure for X_2M_5 -type heteropolyoxometalates (Fig. 1) and the formula was confirmed to be $(\text{C}_6\text{H}_5\text{P})_2\text{Mo}_5\text{O}_{21}^{4-}$. The structures of the other two polyanions have so far only been proposed (Yagasaki *et al.*, 1987). In order to determine the solution structures of the Mo_6PhP and Mo_7PhP species and to verify that $\text{Mo}_2(\text{PhP})_2$ in solution has the X_2M_5 -type structure, a LAXS study on concentrated solutions has recently been performed (Lyxell *et al.*, 1998). In the determination of the solution structure it is essential to know the crystal structure of the relevant species as a starting model. Therefore, many attempts to crystallize the species using a variety of different counterions have been made. Eventually, the trimethylammonium cation gave suitable crystals for the single crystal X-ray diffraction method. The crystals were obtained from an acidic (pH = 1) solution of Mo/PhP = 6 with $[\text{PhP}] \approx 12 \text{ mM}$. As can be seen in the distribution diagram in Fig. 2, the predominant species at these conditions is the $\text{Mo}_6\text{PhP}^{2-}$ polyanion. It was thus expected that the

crystals would give the structure of the polyanion species and a structure determination on this crystalline phase has therefore been carried out.

2. Experimental

2.1. Chemicals

All the chemicals used were commercially available and were used without further purification: sodium molybdate dihydrate (E. Merck, p.a.), phenylphosphonic acid (Fluka, purum), trimethylamine hydrochloride (Schuchardt, chemical grade), sodium chloride (E. Merck, p.a.) and hydrochloric acid (E. Merck, p.a.).

2.2. Preparation

Aqueous solutions of 1.5 M sodium molybdate (0.75 ml) and 0.625 M phenylphosphonic acid (0.3 ml), giving a Mo/PhP ratio of 6, and 0.4 g of sodium chloride, to give 0.6 M Na^+ medium, were mixed and diluted with water to give a 15 ml solution. The pH was then adjusted to *ca.* 1.0 by adding concentrated hydrochloric acid under vigorous stirring. Finally, 0.7 ml of 2.4 M trimethylamine hydrochloride was added. The small amount of precipitation which formed immediately was not removed. The resulting mixture was subjected to very slow evaporation in air at room temperature. Colorless tabular crystals appeared after several months. An amount of a yellow-greenish-yellow crystalline compound was also obtained, which was confirmed by IR to be the trimethylammonium salt of dodecamolybdophosphate. Thus, the phenylphosphonic acid partially became phosphoric acid by hydrolysis.

2.3. Intensity measurement and calculations

Intensity data were collected on a Syntex R3 automated four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$, 50 kV and 30 mA). The background was measured on each side of every reflection for a time equal to the duration of the peak measurement. Cell parameters were derived by least-squares refinement from 19 reflections with programs supplied with the diffractometer system. All other calculations were carried out by *Xtal3.2* programs (Hall *et al.*, 1992). The intensity data were corrected for the Lp factor. An empirical absorption correction was applied; 13 reflections evenly distributed in the range $4.8 < 2\theta < 53.0^\circ$ with a step scan of 10° around its diffraction vector were measured, with the relative transmission factor 0.740–1.000. The structure was solved by direct methods and subsequent difference-Fourier synthesis, and refined by full-matrix least-squares calculations. H atoms were not located. The extinction correction was

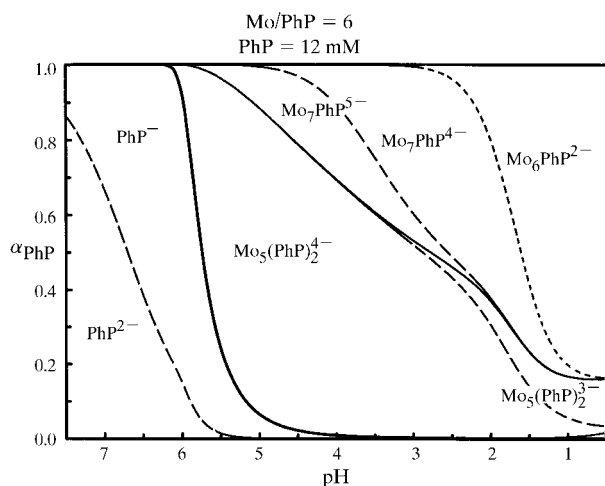


Fig. 2. Diagram showing the cumulative distribution of phenylphosphonate species, α_{PhP} , as a function of pH at Mo/PhP = 6. Each species is represented by an area and its fraction is represented by the area's vertical height at that pH. The curves have been calculated using the formation constants from the equilibrium analysis study (Yagasaki *et al.*, 1987). Full drawn curves separate species which give different ^{31}P NMR resonances. Dashed curves separate species which cannot be differentiated due to rapid exchange on the NMR time scale.

Table 1. *Experimental details*

Crystal data	
Chemical formula	C ₂₄ H ₆₆ N ₄ O ₅₀ Mo ₁₂ P ₂
Chemical formula weight	2424
Cell setting	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	11.211 (5)
<i>b</i> (Å)	12.862 (3)
<i>c</i> (Å)	23.05 (1)
β (°)	94.37 (3)
<i>V</i> (Å ³)	3314 (2)
<i>Z</i>	2
<i>D_x</i> (Mg m ⁻³)	2.429
Radiation type	Mo <i>K</i> α
Wavelength (Å)	0.71073
No. of reflections for cell parameters	19
θ range (°)	9.0–10.5
μ (mm ⁻¹)	2.34
Temperature (K)	293
Crystal form	Tabular
Crystal size (mm)	0.4 × 0.2 × 0.1
Crystal color	Colorless
Data collection	
Diffractometer	Syntex R3
Data collection method	θ - 2θ scans
Absorption correction	φ scan
<i>T_{min}</i>	0.740
<i>T_{max}</i>	1.000
No. of measured reflections	14 937
No. of independent reflections	12 059
No. of observed reflections	9763
Criterion for observed reflections	<i>I</i> > 3.0 σ (<i>I</i>)
<i>R_{int}</i>	0.012
θ_{max} (°)	32.58
Range of <i>h, k, l</i>	0 → <i>h</i> → 16 -10 → <i>k</i> → 19 -34 → <i>l</i> → 34
No. of standard reflections	3
Frequency of standard reflections (min)	Every 50 reflections
Refinement	
Refinement on	<i>F</i>
<i>R</i>	0.037
<i>wR</i>	0.059
<i>S</i>	1.12
No. of reflections used in refinement	9722
No. of parameters used	416
H-atom treatment	H atoms not located
(Δ/σ) _{max}	0.002
$\Delta\rho_{max}$ (e Å ⁻³)	1.618
$\Delta\rho_{min}$ (e Å ⁻³)	-1.165
Extinction method	Zachariasen (1967)
Extinction coefficient	18 (2) × 10 ²
Source of atomic scattering factors	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV, Tables 2.2B and 2.3.1)
Computer programs	
Data reduction	<i>Xtal DIFDAT SORTRF ADDREF</i> (Hall <i>et al.</i> , 1992)
Structure solution	<i>Xtal GENEV GENSIN GENTAN</i> (Hall <i>et al.</i> , 1992)
Structure refinement	<i>Xtal CRYLSQ</i> (Hall <i>et al.</i> , 1992)
Preparation of material for publication	<i>Xtal BONDLA CIFIO</i> (Hall <i>et al.</i> , 1992)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

	$U_{eq} = (1/3)\Sigma_i \Sigma_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j$			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Mo1	0.60267 (3)	-0.02607 (3)	0.32540 (2)	0.0244 (1)
Mo2	0.90916 (3)	0.03211 (3)	0.38842 (1)	0.0204 (1)
Mo3	0.94724 (3)	0.25190 (3)	0.46273 (2)	0.0227 (1)
Mo4	0.70864 (3)	0.34569 (3)	0.53612 (2)	0.0261 (1)
Mo5	0.48896 (3)	0.16967 (2)	0.53511 (1)	0.0193 (1)
Mo6	0.37143 (3)	0.07516 (3)	0.39245 (2)	0.0214 (1)
P	0.65386 (8)	0.19398 (7)	0.41274 (4)	0.0175 (3)
O12	0.7615 (3)	-0.0240 (3)	0.3573 (1)	0.025 (1)
O16	0.4372 (3)	-0.0293 (3)	0.3440 (1)	0.025 (1)
O23	0.9922 (2)	0.1102 (2)	0.4515 (1)	0.022 (1)
O34	0.8234 (3)	0.3460 (2)	0.4790 (2)	0.028 (1)
O45	0.5973 (3)	0.2641 (3)	0.5762 (2)	0.028 (1)
O56	0.3930 (3)	0.1463 (2)	0.4666 (2)	0.025 (1)
O1	0.6028 (5)	0.0667 (5)	0.2733 (2)	0.045 (2)
O1'	0.5987 (4)	-0.1390 (4)	0.2868 (2)	0.042 (2)
O2	0.9485 (4)	0.1011 (3)	0.3302 (2)	0.035 (2)
O2'	0.9972 (3)	-0.0769 (3)	0.3889 (2)	0.034 (2)
O3	0.9971 (4)	0.3107 (3)	0.4026 (2)	0.033 (2)
O3'	1.0541 (4)	0.2800 (3)	0.5172 (2)	0.037 (2)
O4	0.6221 (4)	0.4495 (3)	0.5144 (3)	0.045 (2)
O4'	0.7949 (5)	0.3878 (4)	0.5958 (2)	0.047 (2)
O5	0.3914 (3)	0.1454 (3)	0.5875 (2)	0.031 (1)
O5'	0.5770 (3)	0.0593 (2)	0.5403 (1)	0.025 (1)
O6	0.3544 (4)	0.1762 (4)	0.3453 (2)	0.040 (2)
O6'	0.2309 (3)	0.0274 (4)	0.3944 (2)	0.037 (2)
O2 _{aq}	0.8249 (3)	-0.0310 (3)	0.4736 (2)	0.031 (1)
O34 _{aq}	0.8339 (3)	0.1723 (3)	0.5411 (2)	0.027 (1)
O5 _{aq}	0.3930 (5)	0.3294 (3)	0.5183 (2)	0.040 (2)
O16P	0.5797 (3)	0.0964 (2)	0.3964 (1)	0.021 (1)
O23P	0.7884 (3)	0.1703 (2)	0.4133 (1)	0.022 (1)
O45P	0.6197 (3)	0.2330 (2)	0.4723 (1)	0.020 (1)
O1 _w	0.2427 (5)	0.3710 (5)	0.4240 (3)	0.059 (3)
N1	0.1732 (5)	0.3110 (5)	0.2251 (3)	0.047 (3)
N2	0.8394 (9)	0.6343 (6)	0.3790 (3)	0.063 (4)
C1	0.6165 (4)	0.2969 (3)	0.3629 (2)	0.024 (1)
C2	0.5237 (5)	0.3640 (5)	0.3751 (3)	0.039 (2)
C3	0.4860 (7)	0.4413 (7)	0.3351 (4)	0.054 (4)
C4	0.5423 (7)	0.4513 (7)	0.2839 (4)	0.055 (4)
C5	0.6354 (6)	0.3849 (5)	0.2716 (3)	0.042 (3)
C6	0.6730 (5)	0.3083 (4)	0.3115 (2)	0.031 (2)
C11	0.2949 (9)	0.311 (1)	0.2033 (5)	0.067 (5)
C21	0.170 (1)	0.368 (1)	0.2811 (4)	0.076 (6)
C31	0.129 (1)	0.203 (1)	0.2287 (6)	0.077 (6)
C12	0.879 (3)	0.5300 (9)	0.3832 (8)	0.15 (1)
C22	0.921 (3)	0.699 (2)	0.3462 (6)	0.15 (1)
C32	0.723 (2)	0.652 (3)	0.349 (1)	0.19 (2)

made according to the formalism of Zachariasen (1967). Scattering factors used were for Mo³⁺, P⁰, O⁻ (anionic O atoms), O⁰ (water O atom), N⁰ and C⁰, and anomalous dispersion was considered (*International Tables for X-ray Crystallography*, 1974). Crystal data and experimental conditions are summarized in Table 1.†

† Lists of atomic coordinates, anisotropic displacement parameters and structure factors have been deposited with the IUCr (Reference: AB0384). Copies have been obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Selected geometric parameters (\AA , $^\circ$)

Mo1—O12	1.874 (3)	Mo5—O5 _{aq}	2.338 (4)
Mo1—O16	1.936 (3)	Mo5—O45P	2.286 (3)
Mo1—O1	1.692 (5)	Mo5—O5	1.719 (4)
Mo1—O1'	1.702 (5)	Mo5—O5'	1.728 (3)
Mo1—O5 ⁱ	2.523 (4)	Mo6—O16	1.929 (3)
Mo1—O16P	2.300 (3)	Mo6—O56	1.938 (4)
Mo2—O12	1.897 (3)	Mo6—O5' ⁱ	2.365 (3)
Mo2—O23	1.945 (3)	Mo6—O6	1.695 (5)
Mo2—O2	1.696 (4)	Mo6—O6'	1.694 (4)
Mo2—O2'	1.714 (4)	Mo6—O16P	2.346 (3)
Mo2—O2 _{aq}	2.384 (4)	P—O16P	1.537 (3)
Mo2—O23P	2.332 (3)	P—O23P	1.538 (3)
Mo3—O23	1.914 (3)	P—O45P	1.538 (3)
Mo3—O34	1.902 (3)	P—C1	1.782 (4)
Mo3—O3	1.709 (4)	C1—C2	1.397 (7)
Mo3—O3'	1.707 (4)	C1—C6	1.393 (7)
Mo3—O34 _{aq}	2.506 (4)	C2—C3	1.40 (1)
Mo3—O23P	2.294 (3)	C3—C4	1.39 (1)
Mo4—O34	1.909 (4)	C4—C5	1.39 (1)
Mo4—O45	1.921 (4)	C5—C6	1.391 (8)
Mo4—O4	1.703 (4)	N2—C12	1.42 (2)
Mo4—O4'	1.709 (5)	N2—C22	1.49 (2)
Mo4—O34 _{aq}	2.634 (3)	N2—C32	1.45 (3)
Mo4—O45P	2.243 (3)	N1—C11	1.49 (1)
Mo5—O45	1.916 (3)	N1—C21	1.49 (1)
Mo5—O56	1.866 (3)	N1—C31	1.48 (1)
O16P—P—O23P	110.6 (2)	O16P—P—C1	110.6 (2)
O16P—P—O45P	108.6 (2)	O23P—P—C1	109.6 (2)
O23P—P—O45P	111.6 (2)	O45P—P—C1	105.8 (2)
C2—C1—C6	120.1 (4)	C3—C4—C5	120.8 (7)
C1—C2—C3	119.8 (6)	C4—C5—C6	119.5 (6)
C2—C3—C4	119.5 (7)	C1—C6—C5	120.2 (5)

Symmetry code: (i) $1 - x, -y, 1 - z$.

3. Results and discussion

The structure consists of $(\text{C}_6\text{H}_5\text{P})_2\text{Mo}_{12}\text{O}_{42}(\text{H}_2\text{O})_6^{4-}$ anions, $\text{NH}(\text{CH}_3)^{3+}$ cations and water molecules. The atomic positions and equivalent displacement parameters are given in Table 2. An ORTEPII (Johnson, 1971) view of the polyanion with atomic labeling is shown in Fig. 3(a) and a polyhedral representation with the same orientation in Fig. 3(b). Selected bond lengths and angles in the anion are compiled in Table 3. The anion can be described as being built up from two $(\text{C}_6\text{H}_5\text{P})\text{Mo}_6\text{O}_{23}(\text{H}_2\text{O})_3$ units linked by four common O atoms: O5, O5', O5ⁱ and O5'ⁱ (see Fig. 3a and Table 3). The unit can be divided into two parts of edge-sharing molybdenum octahedra. The first part consists of four octahedra (Mo2–Mo5) and the second part of two octahedra (Mo1 and Mo6). These two parts are in turn joined through two corner-sharing O atoms (O12 and O56), forming a bent Mo₆ ring, which is stabilized by the coordination of the phosphorus in the phenylphosphonate group.

Three groups of distances are commonly found in the MoO₆ octahedra: Mo—O(terminal), Mo—O(Mo) and Mo—O(P) with values of *ca.* 1.7, 1.9 and 2.3 Å, respectively, which are in agreement with earlier results for $(\text{C}_6\text{H}_5\text{P})_2\text{Mo}_5\text{O}_{21}^{4-}$ in Fig. 1 (Lyxell & Strandberg,

1988). However, a fourth group of distances, falling in the range 2.34–2.63 Å, can be distinguished in this study. These distances are suggested to be Mo—OH₂ bonds and bonds from dehydrative condensation (Mo1—O5ⁱ and Mo6—O5'ⁱ) of the two monomeric Mo₆PhP units. In the phenylphosphonate group three O atoms (O16P, O23P and O45P) and one C atom (C1) coordinate to phosphorus, making an elongated tetrahedron which ligates to the Mo₆ ring as a tripodal ligand with very well defined P—O distances of 1.538 (3) Å. The phenyl group is also very regular. There are two independent $\text{NH}(\text{CH}_3)^{3+}$ cations [(I) and (II)], depending on the

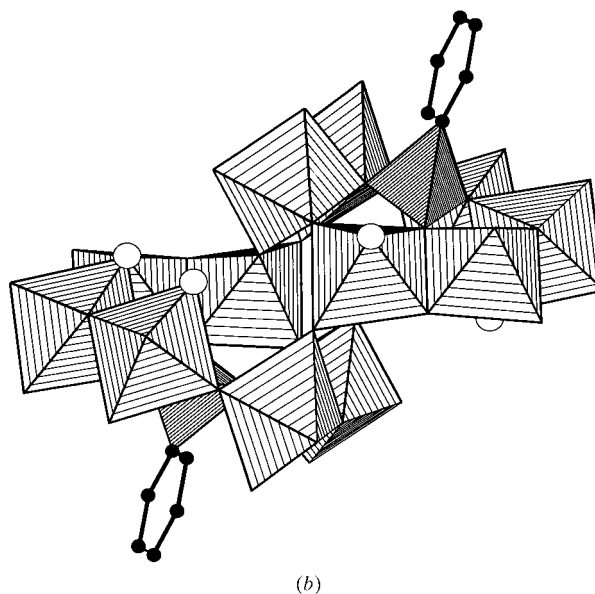
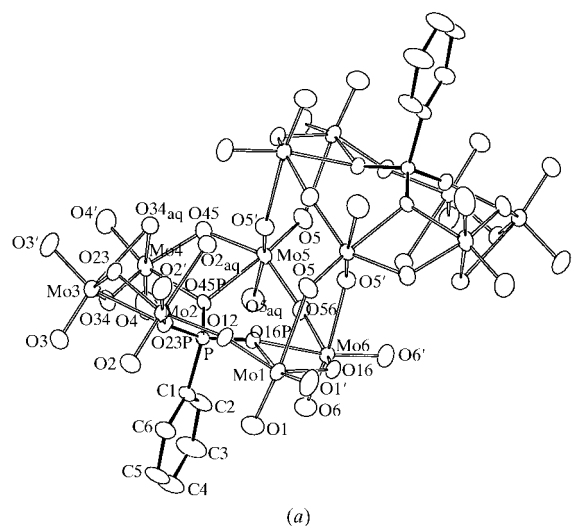


Fig. 3. (a) An ORTEP view of the $\{(\text{C}_6\text{H}_5\text{P})\text{Mo}_6\text{O}_{21}(\text{H}_2\text{O})_3\}_2$ polyanion, with atomic labeling. The thermal ellipsoids are scaled to include 50% probability. (b) A polyhedral representation of the $\{(\text{C}_6\text{H}_5\text{P})\text{Mo}_6\text{O}_{21}(\text{H}_2\text{O})_3\}_2$ polyanion. The open circles show the water molecules.

Table 4. Bond distances (\AA) and angles ($^\circ$) in the $\text{NH}(\text{CH}_3)^{3+}$ cation and distances (\AA) between the anion and the cation within 300\AA

Type (I)		Type (II)	
N1—C11	1.49 (1)	N2—C12	1.42 (2)
N1—C21	1.49 (1)	N2—C22	1.49 (2)
N1—C31	1.48 (1)	N2—C32	1.45 (3)
C11—N1—C21	112.2 (7)	C12—N2—C22	111 (2)
C11—N1—C31	109.5 (8)	C12—N2—C32	117 (2)
C21—N1—C31	112.6 (9)	C22—N2—C32	104 (2)
N1—O1 ⁱ	2.826 (7)	N2—O3 ⁱⁱ	2.816 (9)

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $2 - x, 1 - y, 1 - z$.

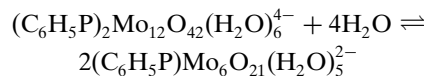
coordination of the cation to its environment. As seen in Table 4, the type (I) cation has a more regular form than type (II), which is highly distorted. Type (II) is more affected by the O atoms of the surrounding anions.

A packing diagram of the compound is shown in Fig. 4. The anions form layers parallel to (001). The type (I) cation lies in the space between two layers, while the type (II) cation is located almost inside the layer. Plausible hydrogen bonds between the cation and anion are listed in Table 4. The whole structure is stabilized in the layer by hydrogen bonds bridging between the water molecule (O1_w) and neighboring anions. Two distances are especially short around the water molecule, O1_w...O5_{aq} 2.699 (8) \AA and O1_w...O3 2.867 (7) \AA , and they are indicated by dashed lines in Fig. 4.

The monomeric Mo₆PhP unit represents a new type of six-membered heteropolymolybdate. There are three other types of six-membered polyanion structures with tetrahedrally coordinated heteropolyatoms reported. The *first type* has a flat ring of six edge-sharing MoO₆ octahedra, with the tetrahedra capped on each side of the ring, e.g. (AsO₄)₂Mo₆O₁₈⁶⁻, see Fig. 5(a) (Hedman, 1980). The *second type* has a noncoplanar six-membered ring consisting of alternate corner- and edge-sharing MoO₆ octahedra, with the tetrahedron connected to the edge-sharing MoO₆ octahedra, e.g. CH₃AsO₃-Mo₆O₁₈(H₂O)₆²⁻, see Fig. 5(b) (Matsumoto, 1979). A *third type* of MoO₆ six-membered ring arrangement has been found in the (C₆H₅AsO₃)₂Mo₆O₁₈(H₂O)₄⁴⁻ anion, see Fig. 5(c) (Matsumoto, 1978). Another anion structure, in which this bent Mo₆ ring can be identified, is that of TeMo₈O₂₉(H₂O)₄⁴⁻. However, in this structure the bis-octahedral part contains one penta-coordinated molybdenum (Ichida & Yagasaki, 1991).

In the equilibrium analysis study of the H⁺-MoO₄²⁻- (C₆H₅P)O₃²⁻ system (Mo_{tot} ≤ 80 mM in 0.600 M Na⁺ medium) no species corresponding to the dimeric structure found in this study could be established. However, a complex with the composition Mo₆PhP²⁻, i.e. the same Mo/PhP ratio (and half the charge of the dimeric compound), was found as a major species. As described above, the anion can be considered to consist of two Mo₆PhP units (Fig. 5d). If this monomeric unit is

present as discrete anions in aqueous solution, it would be expected to have the formula (C₆H₅P)Mo₆O₂₁(H₂O)₅²⁻ and be formed according to the decondensation reaction below.



The crystal structure of the monomeric unit has been successfully used as a model for the Mo₆PhP species in a LAXS investigation of a concentrated aqueous solution (Lyxell *et al.*, 1998). Even in this concentrated solution (Mo = 1.5 M) no dimers could be identified. The dimeric anion found in this structure investigation is probably formed in the crystallization process, where the influence of the organic cation present may be important.

Considering the three-component system H⁺-MoO₄²⁻-(C₆H₅P)O₃²⁻, the only remaining species to be structurally established was the Mo₇PhP complex. An earlier observation of a rapid exchange between the Mo₆PhP and the Mo₇PhP complexes on the ³¹P NMR time scale indicated a close structural relationship between these complexes (Yagasaki *et al.*, 1987). Consequently, an attempt to 'construct' the Mo₇PhP structure from the Mo₆PhP monomer was made by capping a MoO₄ tetrahedron to the ring, opposite to the phosphate tetrahedron. However, this failed due to steric mismatch. In the Mo₆PhP complex the O—O distances in the 4MoO₆ group [O5'—O2_{aq} 3.477 (5), O5'—O3_{aq} 3.224 (5) and O2_{aq}—O3_{aq} 3.041 (5) \AA] are too long to fit an additional MoO₄ tetrahedron with an

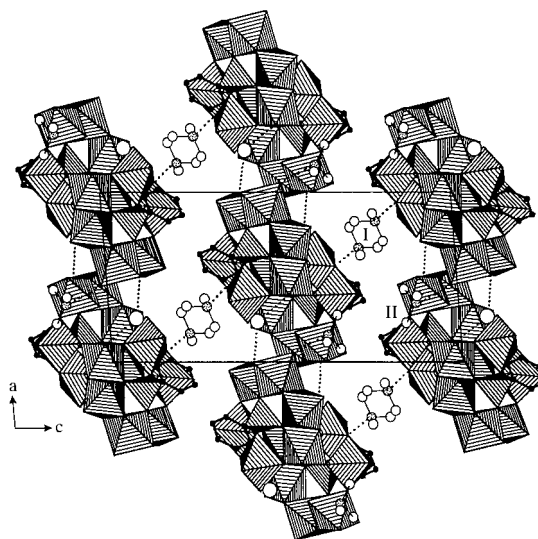


Fig. 4. A packing diagram of $[\text{NH}(\text{CH}_3)_3]_4\{[(\text{C}_6\text{H}_5\text{P})\text{Mo}_6\text{O}_{21}(\text{H}_2\text{O})_3]_2\} \cdot 2\text{H}_2\text{O}$. The polyanion is represented by a polyhedral model. Large unfilled circles show the water molecules, and unfilled and shaded small circles display the C and N atoms in the trimethylammonium cation. The presence of hydrogen bonds is indicated by dotted lines.

average O—O distance of 2.89 Å (Matsumoto *et al.*, 1975). On the other hand, a comparison between the present monomer and the third type mentioned above (Fig. 5c) shows that the only structural difference, except for the additional tetrahedron, is within the group of the two octahedra (2MoO_6) connected by corner-sharing with the other group of four octahedra (4MoO_6). In the monomeric unit found in the present study (Fig. 5d), these two octahedra are edge-sharing, while in the Matsumoto structure (Fig. 5c) the two octahedra are face-sharing. This circumstance causes a contraction of the 4MoO_6 group, resulting in shorter distances between the facial O atoms in the 4MoO_6 group. The corresponding O—O distances in the tripodal $\text{C}_6\text{H}_5\text{AsO}_3$ tetrahedron (Matsumoto, 1978) are in the range 2.69–2.83 Å and are compatible with the distances found in the MoO_4 tetrahedron. A plausible structure for the Mo_7PhP species was thus constructed from the *third type*. When applied to the overall structural model, in

the LAXS investigation of the concentrated aqueous solutions, it was evident that this proposed Mo_7PhP structure was in accordance with the experimental LAXS data.

4. Conclusions

The monomeric unit obtained in the present single crystal investigation has been shown to be a key structure in the process of deducing the aqueous solution structures of both the $\text{Mo}_6\text{PhP}^{2-}$ and $\text{Mo}_7\text{PhP}^{4-}$ species found in a previous equilibrium study. A basic piece of information was that these species gave rise to a single ^{31}P NMR resonance due to rapid exchange on the NMR time scale. This indicated a close structural relationship between the two species, a relationship that was found between the present monomeric unit and a previously determined species in a related system. The formulae $(\text{C}_6\text{H}_5\text{P})\text{Mo}_6\text{O}_{21}(\text{H}_2\text{O})_5^{2-}$ and $(\text{C}_6\text{H}_5\text{P})\text{Mo}_7\text{O}_{24}(\text{H}_2\text{O})^{4-}$

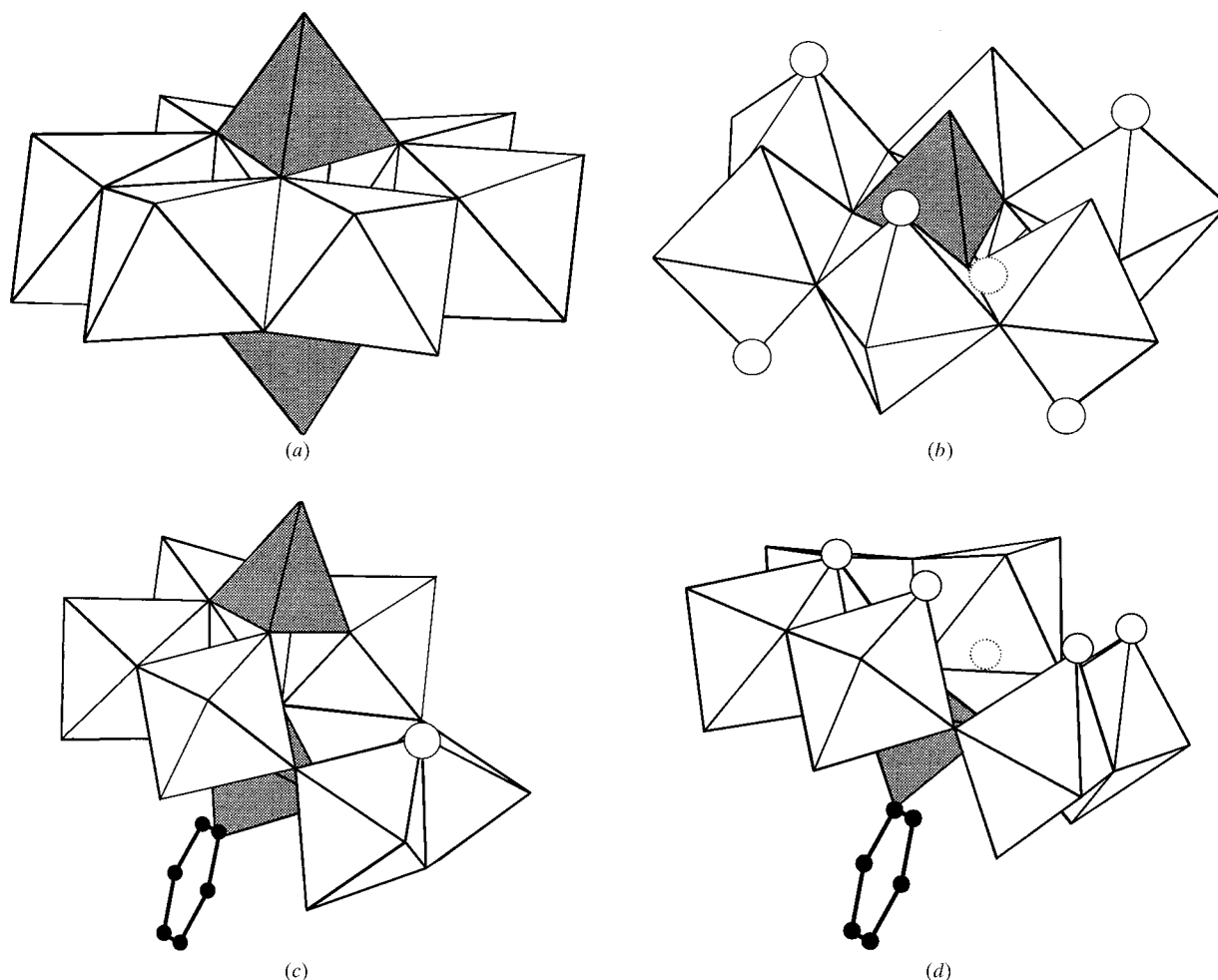


Fig. 5. Polyhedral representations of different types of six-membered heteropolymolybdates with tetrahedrally coordinated heteroatoms. The open circles show the water molecules. (a) $(\text{AsO}_4)_2\text{Mo}_6\text{O}_{18}^{6-}$, (b) $(\text{CH}_3\text{AsO}_3)\text{Mo}_6\text{O}_{18}(\text{H}_2\text{O})_6^{2-}$, (c) $(\text{C}_6\text{H}_5\text{AsO}_3)_2\text{Mo}_6\text{O}_{18}(\text{H}_2\text{O})^{4-}$ (upper benzene ring missing) and (d) $(\text{C}_6\text{H}_5\text{PO}_3)\text{Mo}_6\text{O}_{18}(\text{H}_2\text{O})_5^{2-}$.

with structures shown in Figs. 5(c) and 5(d) are in accordance with data from a recent LAXS investigation of concentrated aqueous molybdophenylphosphonate solutions.

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