

Multicomponent Polyanions. 54. Crystal Structure of Tetracaesium Monohydrogen Phosphato(phosphito)pentamolybdate Dihydrate, $\text{Cs}_4[\text{H}(\text{HP})\text{PMo}_5\text{O}_{22}] \cdot 2\text{H}_2\text{O}$

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The crystal structure of tetracaesium monohydrogen phosphato(phosphito)pentamolybdate dihydrate was determined by single-crystal X-ray diffraction. The compound crystallises in the triclinic space group $P1$, $a=10.284(2)$, $b=10.791(2)$ and $c=13.047(3)$ Å, $\alpha=109.34(2)$, $\beta=99.92(2)$ and $\gamma=102.85(2)^\circ$, $V=1283.4(5)$ Å³ and $Z=2$. The final R -values are $R=0.066$, $wR=0.039$ and $S=1.3667$. The $\text{H}(\text{HP})\text{PMo}_5\text{O}_{22}^{4-}$ anion has common features with the Strandberg X_2M_5 -type heteropolyanion. The five MoO_6 octahedra form a five-membered ring by one corner-sharing and four edge-sharing connections, and the tripodal phosphate and phosphite ligands protrude from each side of this ring in opposite directions. This is the first example of the structure of the heteropolyoxometalate having both P^{III} and P^{V} as heteroatoms.

The transition metals in groups five and six, such as V, Mo and W, are well known to form isopolyoxometalates (isopolyanions) by dehydrative condensation of the monooxoanions. By involving a third element, e.g. P or Si, so-called heteropolyoxometalates (heteropolyanions) are formed.¹ There are several common structures for heteropolyanions, and some typical examples are illustrated in Fig. 1.^{2–5}

In an equilibrium analysis of the $\text{H}^+ - \text{MoO}_4^{2-} - (\text{HP})\text{O}_3^{2-} - \text{HPO}_4^{2-}$ system (in 0.600 M NaCl medium at 298 K), a novel heteropoly species with a composition of molybdate/phosphite/phosphate = 5/1/1 was found to be formed, and its structure was proposed to be similar to the Strandberg X_2M_5 -type heteropolyanion⁴ (Fig. 1). The result of the equilibrium analysis will be published elsewhere.⁶ To confirm the proposed structure of this 5/1/1 species, attempts were made to isolate it in a crystalline phase. Suitable crystals for single-crystal X-ray diffraction were obtained using caesium as the counterion, and a structure determination was subsequently carried out.

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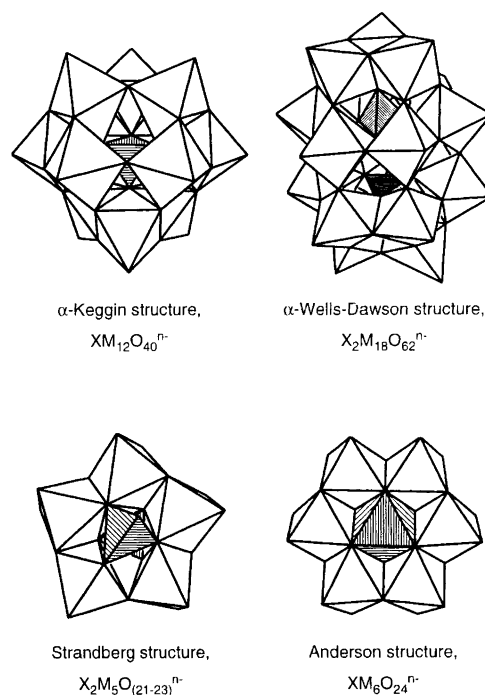


Fig. 1. Examples of the structures of four common heteropolyoxoanions, as polyhedral representations. The hetero-groups are depicted as hatched polyhedra.

Experimental

Chemicals. All reagents used were commercially available and used without further purification: $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (E. Merck, p.a.), $\text{H}_2(\text{HP})\text{O}_3$ (Aldrich, 99%), $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ (E. Merck, p.a.), NaCl (E. Merck, p.a.), hydrochloric acid (E. Merck, p.a.) and CsCl (Aldrich, GR).

Preparation. The crystal was prepared as follows. Aqueous stock solutions of 1.5 M sodium molybdate (3.3 ml), 0.625 M phosphorous acid (3.2 ml) and 0.230 M disodium hydrogenphosphate (4.9 ml), and 0.15 g NaCl were mixed with water to give a 25 ml solution of 0.20 M molybdate, 0.080 M phosphite, 0.045 M phosphate ($\text{Mo}_{\text{tot}}/\text{P}_{\text{tot}}=1.6$) and 0.6 M Na^+ . The sodium chloride was added in order to give the same ionic medium as in the equilibrium analysis of the four-component system. The pH was adjusted to 3.5 with concentrated hydrochloric acid. Then 3.0 ml of an aqueous 2.4 M CsCl solution was added and the resulting

mixture was left to stand at room temperature. Colourless tabular or prismatic crystals appeared within a few days.

The molar ratio of molybdate/phosphite/phosphate = 200/80/45 was chosen according to the equilibrium model calculated with the SOLGASWATER program,⁷ using the formation constants obtained in the equilibrium analysis study in 0.600 M $\text{Na}(\text{Cl})$ ionic medium. The $\text{Na}(\text{Cl})$ notation implies the Na^+ concentration is kept constant, while the Cl^- concentration is allowed to vary. If the phosphite and phosphate were mixed in a 1/1 ratio, as in the formula of the complex obtained, the distribution of the species in the aqueous solution would be as in Fig. 2a (molybdate 200 mM, phosphite and phosphate 62.5 mM each). Under this condition the target complex $\text{H}_x(\text{HP})\text{PMo}_5\text{O}_{22}^{(5-x)-}$ [abbreviated as $(\text{HP})\text{PMo}_5$] has approximately the same strength as the $\text{H}_x\text{P}_2\text{Mo}_5\text{O}_{23}^{(6-x)-}$ (abbreviated as P_2Mo_5) complex, indicating that the product of the crystallisation could be a mixture of $(\text{HP})\text{PMo}_5$ and P_2Mo_5 . Hence the conditions required to give the maximum amount of

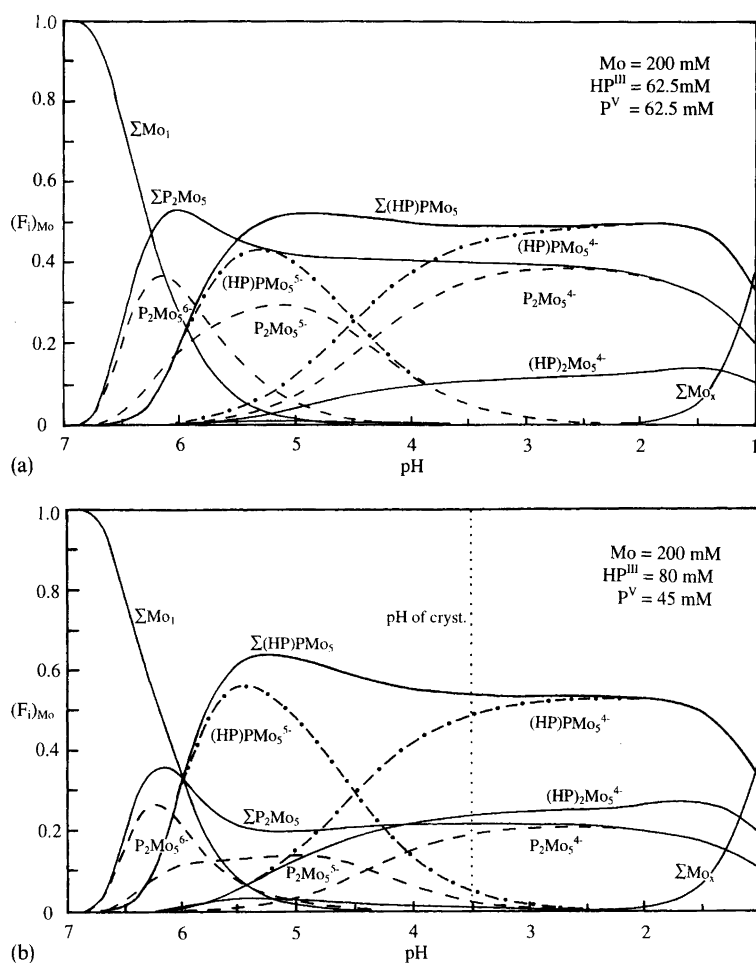


Fig. 2. Diagrams showing the distribution of molybdate as a function of pH. $(F_i)_{\text{Mo}}$ is defined as the ratio between Mo in a given species and Mo_{tot} in the solution. $\text{Mo}_{\text{tot}}/\text{P}_{\text{tot}}=1.6$. (a) $\text{HP}^{\text{III}}/\text{P}^{\text{V}}=1$; (b) $\text{HP}^{\text{III}}/\text{P}^{\text{V}}=1.78$. Full lines represent the sum of species with the same nuclearity, differing only in their number of protons. Dashed/dotted lines represent individual species.

(HP)PMo5 were found by changing the (HP)/P ratio ($\text{Mo}_{\text{tot}}/\text{P}_{\text{tot}}=1.6$). The ratio molybdate/phosphite/phosphate = 200/80/45 mM (Fig. 2b) appeared to give the maximum amount of the (HP)PMo5 complex and was therefore used for the crystallisation work. The monoprotonated species $\text{H}(\text{HP})\text{PMo}_5\text{O}_{22}^{4-}$ is predominant at pH 3.5, where the crystals were obtained.

Intensity measurement. A single crystal with dimensions $0.3 \times 0.25 \times 0.1 \text{ mm}^3$ was used for intensity measurements on a SYNTEX R3 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. The experimental details are summarised in Table 1.

Calculations. The intensity data were corrected for L_p and empirical absorption based on psi-scans. The cell parameters were calculated by least-squares refinement with 25 reflections $15.6 < 2\theta < 29.8^\circ$, with programs supplied with the diffractometer system.

Calculations for the structure determination were carried out with the Xtal3.2 program package.⁸ The five molybdenum atoms were located by direct methods, and the rest of the non-H atoms were determined by successive Fourier and difference Fourier syntheses. Extinction correction was made by applying the formalism of Zachariasen. Scattering factors used for refinements were those of Mo^{3+} , P^0 , O^- , O^0 (water) and Cs^0 and anomalous dispersion was considered.⁹ Of the total 7537 reflections, 7141 with $I > 3.0\sigma(I)$ were used in the calculations. All the atoms found were refined assuming anisotropic displacements. The full-matrix refinement with 317 parameters gave $R=0.066$, $wR=0.039$ and $S=1.366$. Details from calculations are listed in Table 1.

Structure description and discussion

The structure of the anion is shown in Fig. 3. The fractional coordinates and equivalent displacement parameters are given in Table 2, and distances and angles within the anion are listed in Table 3. The features of the polyanion show the typical Strandberg X2M5-type structure,⁴ where five distorted MoO_6 octahedra are joined via four shared edges and one shared corner, giving a five-membered ring to which the two phosphate moieties are attached on opposite sides by sharing three oxygens. In the X2M5 structure, the X units are usually related by a true- or a pseudo-twofold symmetry axis through the polyanion. In this case, however, this symmetry axis is not present, since the two X groups are not equivalent (one phosphate and one phosphite).

The MoO_6 octahedra are very distorted and in several cases three groups of octahedral Mo–O distances can be distinguished in polyoxyanions.¹ Terminal oxygens are involved in the shortest Mo–O bonds, whereas oxygens shared by two or three metal atoms are involved in

Table 1. Crystal and experimental data for $\text{Cs}_4[\text{H}(\text{HP})\text{PMo}_5\text{O}_{22}] \cdot 2\text{H}_2\text{O}$

Formula	$\text{H}_6\text{O}_{24}\text{Cs}_4\text{Mo}_5\text{P}_2$
M_r	1463.3
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
$a/\text{\AA}$	10.284(2)
$b/\text{\AA}$	10.791(2)
$c/\text{\AA}$	13.047(3)
$\alpha/^\circ$	109.34(2)
$\beta/^\circ$	99.92(2)
$\gamma/^\circ$	102.85(2)
$V/\text{\AA}^3$	1283.4(5)
Z	2
$D_c/\text{Mg m}^{-3}$	3.786
$\mu(\text{Mo } K\alpha)/\text{mm}^{-1}$	8.19
$F(000)$	1330
Crystal colour	Colourless
Crystal size/mm	$0.3 \times 0.25 \times 0.1$
Temperature/K	293
No. of reflns. for cell determination (2θ -range/ $^\circ$)	25 ($15.6 < 2\theta < 29.8$)
Scan mode	θ - 2θ
2θ range/ $^\circ$	$4.2 < 2\theta < 60.1$
hkl range	$-14 \leq h \leq 14$ $-15 \leq k \leq 14$ $0 \leq l \leq 18$
2θ scan speed/ $^\circ \text{ min}^{-1}$	1.0–11.7
Total no. of reflns. measured	8350
Total no. of independent reflns.	7537
Test reflns. (deviation %)	0 –3 1 (2.1); 2 4 3 (3.0); 5 –4 5 (5.8)
R_{int}	0.015
Refinement on	F
No. of observed independent reflns. [$I > 3.0\sigma(I)$]	7141
No. parameters refined	317
Weights calcd. according to	$w = 1/[\sigma^2 + 69 + 0.23F$ $-(2.1 \times 10^2) \sin \theta$ $+ (1.8 \times 10^{-3})F^2$ $- 1.0F \sin \theta$ $+ (1.9 \times 10^2) \sin^2 \theta]$
R (R_w)	0.066 (0.039)
S	1.366
Extinction coefficient	697
$(\Delta/\sigma)_{\text{max}}$	0.002
Min/max. resid. electron density/ $e \text{ \AA}^{-3}$	–3.16/4.81

longer Mo–O bonds, those shared by three metal atoms being the longest. In the present structure, there are 10 terminal bonds, which fall in the range 1.702(7)–1.74(1) \AA . The Mo–O bonds involving doubly shared oxygens, 10 in total, are between 1.80(1)–1.953(8) \AA . For the third group of eight bonds, where the oxygens are shared between two molybdenums and one phosphorus, the bonds are considerably longer, between 2.220(8) and 2.447(6) \AA (Table 3).

The differences of the P–O bonds are relatively small. The terminal bond of the phosphate group is, however, distinctly longer than bonds to the shared oxygens, which is in accordance with the expected protonation of this oxygen. Comparisons between protonated and unprotonated terminal oxygens in phosphate groups have

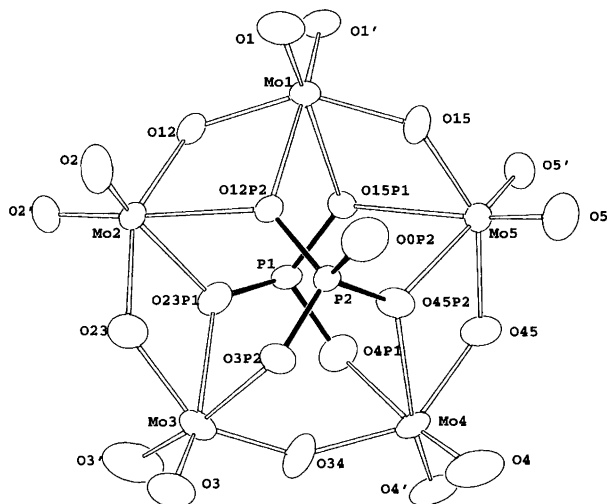


Fig. 3. The structure of the $\text{H(HP)PMo}_5\text{O}_{22}^{4-}$ anion, with atomic labelling. Thermal ellipsoids drawn at the 50% probability level.

revealed that in the former, the distances are considerably longer than in the latter, where the terminal P–O distance is the shortest of the four P–O bonds.¹⁰ The O–P–O (non-terminal oxygen) angles in the phosphate group vary between 107.1 and 113.3°, whereas the corresponding angles of the phosphite group are more similar: 111.7–112.6°. The rather small angle O12P2–P2–O0P2 [102.8(4)°] could possibly be caused by a weak hydrogen bond interaction between O1aq and O12P2 (Table 4). Distances and angles of the phosphite group do not differ significantly in comparison with the diphosphito-pentamolybdate anion.¹¹

The four structurally independent caesium cations coordinate irregularly to anion oxygens as well as to the two water molecules. In Fig. 4, the caesium–oxygen distances shorter than 3.6 Å are depicted; eight for Cs1 and Cs2, and nine for Cs3 and Cs4. However, there are still some slightly longer distances, which can be regarded as caesium–oxygen bonds. Since there is no distinct limit in the coordination sphere of the caesium ions, and since

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters with e.s.d.'s in parentheses.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$U_{\text{eq}}^a/\text{\AA}^2$
Cs1	0.78893(6)	0.82646(6)	0.02621(5)	0.0358(2)
Cs2	0.46737(7)	0.25340(6)	0.35909(6)	0.0414(2)
Cs3	0.74034(7)	0.6831(1)	0.30656(6)	0.0599(3)
Cs4	0.9592(1)	0.28093(9)	0.27486(6)	0.0589(3)
Mo1	0.35565(6)	0.62279(6)	0.07307(5)	0.0243(2)
Mo2	0.21421(7)	0.88054(6)	0.08994(5)	0.0240(2)
Mo3	0.11892(7)	0.97660(7)	0.34010(6)	0.0314(2)
Mo4	0.13515(8)	0.71018(9)	0.44208(5)	0.0318(2)
Mo5	0.33029(7)	0.53209(6)	0.29533(5)	0.0251(2)
P1	0.0574(2)	0.6210(2)	0.1641(1)	0.0203(4)
P2	0.4056(2)	0.8710(2)	0.3394(1)	0.0201(5)
O12	0.2266(8)	0.7040(7)	0.0104(4)	0.033(2)
O15	0.4321(6)	0.5826(8)	0.1964(6)	0.034(2)
O23	0.198(1)	1.0169(9)	0.2251(7)	0.050(3)
O34	0.094(2)	0.861(1)	0.4123(6)	0.064(5)
O45	0.187(1)	0.547(1)	0.3756(7)	0.045(3)
O1	0.5050(8)	0.7019(9)	0.0483(8)	0.045(3)
O1'	0.2951(9)	0.4639(7)	−0.0333(6)	0.040(2)
O2	0.3541(8)	0.9884(8)	0.0764(8)	0.043(3)
O2'	0.0811(8)	0.8779(8)	−0.0108(6)	0.037(2)
O3	0.1767(9)	1.1418(8)	0.4363(7)	0.046(2)
O3'	−0.053(1)	0.960(1)	0.2812(9)	0.064(4)
O4	0.2464(9)	0.780(1)	0.5738(7)	0.058(3)
O4'	−0.0154(8)	0.6348(9)	0.4656(5)	0.045(3)
O5	0.4711(9)	0.5445(8)	0.3937(6)	0.042(2)
O5'	0.2599(7)	0.3580(6)	0.2227(5)	0.032(2)
O15P1	0.1825(5)	0.5660(6)	0.1536(4)	0.024(2)
O23P1	0.0913(8)	0.7708(7)	0.1751(5)	0.035(2)
O4P1	−0.0009(7)	0.5989(8)	0.2569(6)	0.039(2)
O0P2	0.565(1)	0.909(1)	0.3783(7)	0.052(3)
O12P2	0.3778(6)	0.8348(6)	0.2141(4)	0.026(2)
O3P2	0.3552(8)	0.9918(7)	0.3966(5)	0.034(2)
O45P2	0.337(1)	0.7528(6)	0.3697(6)	0.041(3)
O1aq	0.658(1)	1.029(2)	0.193(1)	0.083(6)
O2aq	0.629(3)	0.289(3)	0.181(2)	0.12(1)

$$^a U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

Table 3. Selected interatomic distances (in Å) and bond angles (in °) within the H(HP)PMo₅O₂₂⁴⁻ anion.

Mo1–Mo2	3.377(1)	Mo3–O3	1.702(7)
Mo1–Mo6	3.379(1)	Mo3–O3'	1.74(1)
Mo2–Mo3	3.464(1)	Mo3–O23	1.95(1)
Mo3–Mo4	3.568(1)	Mo3–O34	1.80(1)
Mo4–Mo5	3.462(1)	Mo3–O23–P1	2.447(6)
P1–Mo1	3.473(2)	Mo3–O3p2	2.366(8)
P2–Mo1	3.481(2)	Mo4–O4	1.706(8)
P1–Mo2	3.421(2)	Mo4–O4'	1.709(9)
P2–Mo2	3.547(2)	Mo4–O34	1.91(1)
P1–Mo3	3.603(2)	Mo4–O45	1.92(1)
P2–Mo3	3.389(2)	Mo4–O4P1	2.324(6)
P1–Mo4	3.327(2)	Mo4–O45P2	2.44(1)
P2–Mo4	3.636(2)	Mo5–O5	1.709(8)
P1–Mo5	3.516(2)	Mo5–O5'	1.712(5)
P2–Mo5	3.391(2)	Mo5–O15	1.933(8)
Mo1–O1	1.722(9)	Mo5–O45	1.95(1)
Mo1–O1'	1.704(6)	Mo5–O15P1	2.364(6)
Mo1–O12	1.953(8)	Mo5–O45P2	2.33(7)
Mo1–O15	1.891(9)	P2–O12P2	1.507(6)
Mo1–O15P1	2.289(6)	P2–O3P2	1.521(8)
Mo1–O12P2	2.346(6)	P2–O45P2	1.519(8)
Mo2–O2	1.713(9)	P2–OP2	1.55(1)
Mo2–O2'	1.715(8)	P1–O15P1	1.540(6)
Mo2–O12	1.888(7)	P1–O4P1	1.504(9)
Mo2–O23	1.949(9)	P1–O23P1	1.527(7)
Mo2–O23P1	2.220(8)		
Mo2–O12P2	2.379(6)		
O12P2–P2–O3P2	111.8(4)	O15P1–P1–O4P1	111.8(4)
O12P2–O45P2	113.3(4)	O15P12–P1–O23P1	111.7(4)
O12P2–O0P2	102.8(4)	O4P1–P1–O23P1	112.6(4)
O3P2–P2–O45P2	107.1(5)	O45P2–P2–O0P2	110.9(6)
O3P2–P2–O0P2	111.1(5)		

Table 4. Selected Cs–O distances (in Å) and possible hydrogen Oaq–O bonds (in Å)

Cs1–O1	3.035(9)	Cs3–O15	3.026(6)
Cs1–O1 ⁱ	3.097(8)	Cs3–O34 ⁱⁱⁱ	3.49(1)
Cs1–O2 ⁱⁱ	3.22(1)	Cs3–O0P2	3.33(1)
Cs1–O2 ⁱⁱⁱ	3.260(9)	Cs3–O4P1 ⁱⁱⁱ	3.099(9)
Cs2–O2 ⁱⁱⁱⁱ	3.083(9)	Cs4–O2 ⁱ	3.203(7)
Cs1–O3 ^{viii}	3.12(1)	Cs4–O3 ^{viii}	3.47(2)
Cs1–O5 ⁱ	3.078(6)	Cs4–O4 ^v	3.24(1)
Cs1–O1aq	3.24(2)	Cs4–O4 ^{iv}	3.111(7)
Cs2–O3 ^{iv}	3.41(1)	Cs4–O5 ⁱⁱⁱⁱ	3.267(8)
Cs2–O4 ^v	3.06(1)	Cs4–O45 ⁱⁱⁱ	2.986(8)
Cs2–O5	3.012(9)	Cs4–O4P1 ⁱⁱⁱ	3.45(1)
Cs2–O5 ^v	3.095(6)	Cs4–O1aq ^{vii}	3.36(1)
Cs2–O5'	3.176(8)	Cs4–O2aq	3.44(3)
Cs2–O23 ^{iv}	3.079(9)	O1aq–O4 ^{vi}	2.89(1)
Cs2–O3P2 ^{iv}	3.033(8)	O1aq–O0P2	3.28(2)
Cs2–O2aq	3.15(3)	O1aq–O1P2	3.28(2)
Cs3–O1 ⁱ	3.302(7)	O1aq–O1	3.26(2)
Cs3–O3 ⁱⁱ	3.106(7)	O1aq–O2	3.10(2)
Cs3–O3 ⁱⁱⁱ	3.41(1)	O2aq–O12 ⁱ	3.13(3)
Cs3–O4 ⁱⁱⁱ	3.224(9)	O2aq–O1 ⁱ	3.11(3)
Cs3–O15	3.401(9)	O2aq–O1aq ^{iv}	2.94(4)

Symmetry operations: ⁱ1–x, 1–y, –z; ⁱⁱ1–x, 2–y, –z; ⁱⁱⁱ1+x, y, z; ^{iv}x, –1+y, z; ^v1–x, 1–y, 1–z; ^{vi}1–x, 2–y, 1–z; ^{vii}x, 1+y, z; ^{viii}1+x, –1+y, z.

the caesium–oxygen coordination structure is rather complex, the limit of 3.6 Å was applied in Fig. 4 and in Table 4. In Fig. 5 the packing of the anions is shown,

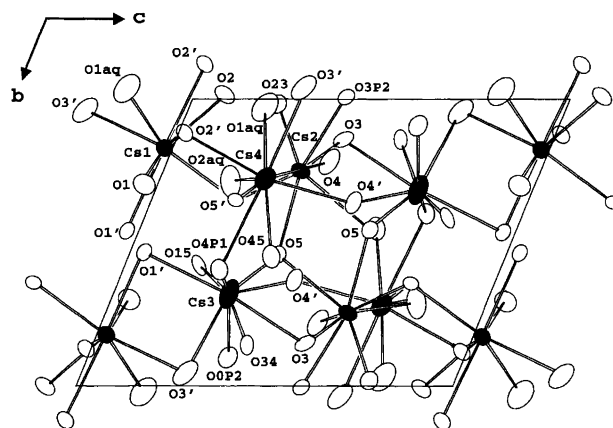


Fig. 4. A perspective view of the Cs coordination along the a-axis.

together with the positions of the four caesium ions and the two water molecules. The two O–O distances shorter than 3.0 Å (Table 4), O1aq–O2aq (2.94 Å) and O1aq–O4 (2.89 Å) indicate the presence of hydrogen bonds and are shown with dashed lines in the figure. Listed in Table 4 are five additional distances between the water molecules and anion oxygens, ranging from 3.0 to 3.3 Å. The distances possibly indicate weak hydrogen-bond interactions.

To conclude, the structure of the H(HP)PMo₅O₂₂⁴⁻

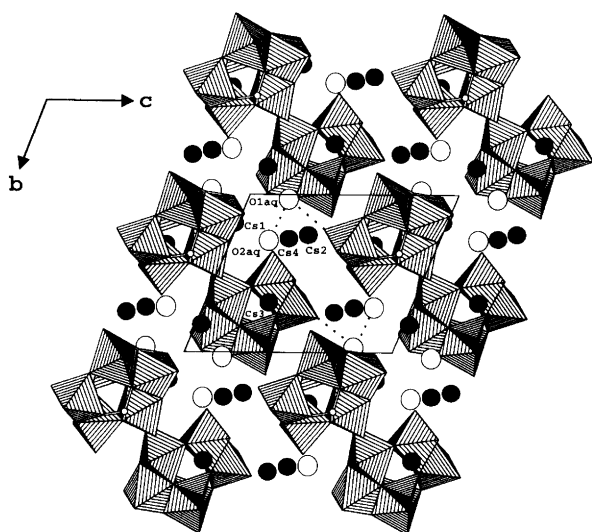


Fig. 5. A packing diagram of $\text{Cs}_4[\text{H}(\text{HP})\text{PMo}_5\text{O}_{22}] \cdot 2\text{H}_2\text{O}$. The polyanion is represented by a polyhedral model. Filled and unfilled large circles show the caesium cations and the oxygen atoms of the crystal water, respectively. The dotted lines indicate the presence of hydrogen bonds.

anion, as determined in the present X-ray diffraction investigation, represents the first example of a mixed heterophosphorus-containing polyoxometalate having the Strandberg structure. This anion is also the predominant species in the solution from which the crystals

precipitated (c.f. Fig. 2b), and this corroborates the assumption that the $(\text{H}^+)_{10}(\text{MoO}_4^{2-})_5((\text{HP})\text{O}_3^{2-})(\text{HPO}_4^{2-})$ species determined in the equilibrium analysis⁶ has the formula $\text{H}(\text{HP})\text{PMo}_5\text{O}_{22}^{4-}$.

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