preparation procedure and for many valuable discussions. Linguistic corrections have been made by Dr Kenneth Wing. This work is part of a programme financially supported by the Swedish National Science Research Council.

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Multicomponent Polyanions.
16. The Molecular and Crystal Structure of Na$_6$Mo$_5$P$_2$O$_{23}$(H$_2$O)$_{14}$, a Compound Containing Sodium-Coordinated Pentamolybdodiphosphate Anions

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The crystal structure of Na$_6$Mo$_5$P$_2$O$_{23}$(H$_2$O)$_{14}$ has been determined from three-dimensional X-ray diffraction data collected with a Pailred diffractometer using Mo $K\alpha$ radiation. The crystals are orthorhombic with space group $P2_12_12_1$, cell dimensions $a = 15\cdot8304$ (9), $b = 19\cdot876$ (1), $c = 10\cdot6828$ (6) Å and $Z = 4$. Full-matrix least-squares refinements of positional and anisotropic thermal parameters based on 6171 independent reflexions resulted in a final R value of $0\cdot024$. The Mo$_5$P$_2$O$_{23}^{6-}$ anion consists of a ring formed by five MoO$_6$ octahedra with one PO$_4$ tetrahedron attached to each side of the ring. The Mo–Mo distances vary between $3\cdot355$ and $3\cdot377$ Å for edge-sharing octahedra and the distance is $3\cdot6604$ (4) Å when a corner is shared. In each octahedron the Mo–O distances are distributed with two distances in each of the three ranges $1\cdot70$–$1\cdot73$, $1\cdot90$–$1\cdot95$ and $2\cdot17$–$2\cdot39$ Å depending on coordination number. The P–O distances vary between $1\cdot50$ and $1\cdot57$ Å. The anions are held together in a three-dimensional framework by O–Na–O and O–Na–H$_2$O–Na–O linkages as well as by hydrogen bonds. Four of the Na ions are surrounded by six, and two Na ions by five, anion O or water O atoms, in distorted octahedral, trigonal prismatic and square pyramidal arrangements. The Na–O distances are in the range $2\cdot32$–$2\cdot83$ Å.

Introduction

Aqueous equilibria between H$^+$, MoO$_4^{2-}$ and HPO$_4^{2-}$ in a $3\cdot0$ M Na(ClO$_4$) medium have been investigated by potentiometric, spectrophotometric and Raman methods (Pettersson, 1974, 1975). The EMF measurements covered the range $1\cdot5 < -\log[\text{H}^+] < 9$. Least-squares analyses of the data indicated the formation of two series of complexes: $(\text{H}^+)_p(\text{MoO}_4^{2-})_5(\text{HPO}_4^{2-})_2$ with $p = 8$, 9 and 10, and $(\text{H}^+)_p(\text{MoO}_4^{2-})_9(\text{HPO}_4^{2-})$ with $p = 14$, 15, 16 and 17. At the ratio $[\text{MoO}_4^{2-}]/[\text{HPO}_4^{2-}] = 2\cdot5$ the $(p,5,2)$ complexes were totally dominant.

Crystallization experiments were carried out parallel with these investigations. A number of phases containing the complexes were obtained and have been or are being investigated by X-ray structure determination methods (Table 1). The identity between the complexes in solution and those in crystals has been confirmed by large-angle X-ray scattering methods (Johansson, Pettersson & Ingri, 1974).

This paper presents the crystal structure of Na$_6$Mo$_5$P$_2$O$_{23}$(H$_2$O)$_{14}$ (A), corresponding to the $(\text{H}^+)_8(\text{MoO}_4^{2-})_5(\text{HPO}_4^{2-})_2$ complex. Another phase containing this complex, Na$_6$Mo$_5$P$_2$O$_{23}$(H$_2$O)$_{13}$ (B), has

Table 1. *Chemical formula, complex composition and crystallographic data for the phases obtained in the aqueous* H^+–MoO_4^{2-}–HPO_4^{2-} *system*

Formula	Complex composition (p,q,r)	Crystal system	Cell dimensions (Å, °)	Space group	Density, D_m (g cm⁻³)	Z	Reference
$Na_6Mo_5P_2O_{23}(H_2O)_{13}$	(8,5,2)	Orthorhombic	$a = 15.423$ $b = 16.896$ $c = 12.394$	$Pbcn$	2.62	4	1
$Na_6Mo_5P_2O_{23}(H_2O)_{14}$	(8,5,2)	Orthorhombic	$a = 15.8304$ $b = 19.876$ $c = 10.6828$	$P2_12_12_1$	2.56	4	2
$Na_5HMo_5P_2O_{23}(H_2O)_{7-9}$	(9,5,2)	Triclinic	$a = 10.448$ $\alpha = 89.85$ $b = 18.656$ $\beta = 108.74$ $c = 8.318$ $\gamma = 101.30$	$P\bar{1}$	2.66	2	3
$Na_4H_2Mo_5P_2O_{23}(H_2O)_{10}$	(10,5,2)	Monoclinic	$a = 26.388$ $b = 13.661$ $\beta = 91.37$ $c = 8.041$	$P2_1/n$	2.71	4	4
$Na_3H_6Mo_9PO_{34}(H_2O)_{12-13}$	(17,9,1)	Hexagonal	$a = 14.248$ $c = 10.83$	$P6_3$	3.04	2	5
$Na_6Mo_{18}P_2O_{62}(H_2O)_{24}$	(34,18,2)*	Monoclinic	$a = 23.091$ $b = 13.481$ $\beta = 100.35$ $c = 23.157$	$C2/c$	3.10	4	6
$H_3Mo_{12}PO_{40}(H_2O)_{29-31}$	(23,12,1)	Tetragonal	$a = 16.473$ $c = 23.336$	$I4_1/amd$	2.42	4	7

References: (1) Strandberg (1973). (2) Present paper. (3) Hedman & Strandberg (1977). (4) Hedman (1973). (5) Strandberg (1974). (6) Strandberg (1975a). (7) Strandberg (1975b).
* Dimer of (17,9,1).

been investigated by Strandberg (1973). The structures contain identical heteropolyanions but differ in the arrangement of Na ions and water molecules.

Experimental

Crystal preparation, analyses and data

The crystals were grown by slow evaporation at room temperature of aqueous solutions prepared from 24·68 g $Na_2MoO_4.2H_2O$, 6·37 g $NaH_2PO_4.2H_2O$, 10·52 ml of concentrated (11·64 M) $HClO_4$ (*i.e.* a molar ratio of H^+:MoO_4^{2-}:HPO_4^{2-} = 8:5:2) and water to make the total volume 50 ml. Colourless crystals were formed within a week. The *B* phase is also obtained from solutions of the same composition, but transforms in solution to (*A*) with time. The two phases are distinguished by their crystal forms, (*A*) being tabular needle-like and (*B*) spherical. Upon exposure to air the crystals slowly decompose and those which were subjected to X-ray investigation were therefore sealed in a capillary of Lindemann glass. Elemental analysis of the crystals (Department of Analytical Chemistry, University of Umeå) gave: Mo 36·8, P 4·6 and Na 10·8 wt%; calculated Mo 36·9, P 4·8 and Na 10·6 wt%. The water content was determined by thermo-balance analysis to be 19·4 wt% (calculated 19·4 wt%).

From Weissenberg photographs the crystals were found to be orthorhombic with systematic extinctions $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; and $00l$, $l = 2n + 1$

Table 2. *Crystal data for* $Na_6Mo_5P_2O_{23}(H_2O)_{14}$

Orthorhombic, space group $P2_12_12_1$

$a = 15.8304$ (9) Å	FW 1299·79
$b = 19.876$ (1)	$D_x = 2.57$ g cm⁻³
$c = 10.6828$ (6)	$D_m = 2.56$ (1)
$V = 3361.3$ (6) Å³	μ(Mo $K\alpha$) = 20·60 cm⁻¹
$Z = 4$	

which are consistent only with space group $P2_12_12_1$. Accurate unit-cell parameters were determined from X-ray powder photographs taken with a Guinier–Hägg camera using Cu $K\alpha_1$ radiation (λ = 1·54051 Å). With the data from three independent exposures, two with $Pb(NO_3)_2$ {a[$Pb(NO_3)_2$] = 7·85750 Å, 25 °C} and one with Si {a[Si] = 5·43088 Å, 25 °C} used as the internal standard, cell parameters were refined by least-squares methods (Werner, 1969) and the results weighted together. The density of the crystals was independently determined from flotation in bromoform/carbon tetrachloride and from pycnometry with xylene as the medium. Complete crystal data are given in Table 2.

Data collection and reduction

Three-dimensional X-ray diffraction data were collected with a Philips Pailred diffractometer at 25 °C. Mo $K\alpha$ radiation (λ = 0·71069 Å) monochromatized with a graphite monochromator was used and measurements made with a scan speed of 1° min⁻¹. Back-

ground was recorded for 40 s at both ends of the scan interval. The approximate dimensions of the crystal used were $0.32 \times 0.16 \times 0.28$ mm, with c parallel to the 0.28 mm edge. 12728 hkl and $h\bar{k}l$ reflexions from layers $hk0-hk15$ were measured $[(\sin \theta_{max})/\lambda = 0.818$ Å$^{-1}]$. After primary data reduction and computation of the $\sigma(I)$ (Hedman, 1977), reflexions with $I < 2\sigma(I)$ were omitted as they were considered unobserved, leaving 11785 reflexions. The intensities and the $\sigma(I)$ were corrected for Lp and absorption effects. With the $6 \times 8 \times 8$ Gaussian grid applied the transmission factor varied from 0.531 to 0.726 $[\mu(\text{Mo } K\alpha) = 20.60$ cm$^{-1}]$. The hkl and $h\bar{k}l$ reflexions were then weighted together giving a unique set of 6171 reflexions.

Structure determination and refinement

From a Patterson synthesis the Mo atomic positions were located, and routine heavy-atom methods yielded the positions of the remaining non-hydrogen atoms. For the water O atom Aq(13) two distinct peaks appeared in the electron density maps with too short an internal distance (~ 1.0 Å) to be considered as two separate atoms and with lower peak heights than the other water O atoms. Refinements of either position

diverged and the water molecule was therefore assumed to be distributed statistically over both positions with the sum of their occupancy factors restricted to 1.0. Full-matrix least-squares refinements with isotropic temperature factors gave an R value of 0.055. As the data were severely affected by extinction, an isotropic extinction parameter (Coppens & Hamilton, 1970) was included, which significantly improved the refinement. The refined value of the extinction parameter g' is 6.62 (10). With anisotropic temperature factors the refinements converged at $R = 0.024$ ($R_w = 0.028$), R and R_w being defined as $R = \Sigma \|F_o| - |F_c\|/\Sigma |F_o|$ and $R_w = [\Sigma w_i(|F_o| - |F_c|)^2/\Sigma w_i|F_o|^2]^{1/2}$ with $\Sigma w_i(|F_o| - |F_c|)^2$ being the function minimized. A weighting scheme, $w = 1/\sigma^2(F_o)$, was applied in which $\sigma^2(F_o)$ was modified to $\sigma^2(F_o) = \sigma^2(F_o) + (0.014F_o)^2$. In the final cycle the parameter shifts were less than 0.3σ. As the refinements must be divided into four blocks because of the low core memory capacity of the computer, the standard deviations may be somewhat underestimated. Computed F_c values for the previously omitted reflexions were all shown to be lower than or of the same magnitude as the threshold value. A final difference Fourier synthesis showed no anomalies. Mo^{3+}, P, O$^-$ (anion oxygen atoms), Na$^+$ and O scattering factors were used and account was taken of the real part of

Table 3. *Fractional atomic coordinates* ($\times 10^4$; *for* Mo *and* P $\times 10^5$)

Estimated standard deviations are given in parentheses. For the oxygen atoms O(i), O(ij), OP(i) and OP(ij) the index indicates that the atom is bonded to molybdenum atoms i or i and j, and P indicates that it is also bonded to a phosphorus atom. Aq(i) and Aq(ij) are coordinated to sodium ions i or i and j.

	x	y	z		x	y	z
Mo(1)	68177 (2)	13888 (2)	21158 (3)	O(5)	5304 (2)	34 (2)	−533 (3)
Mo(2)	58100 (2)	18695 (2)	47547 (3)	O'(5)	5826 (2)	1270 (2)	−1249 (2)
Mo(3)	37700 (2)	14392 (2)	44672 (3)	OP1	5470 (2)	−256 (1)	2786 (2)
Mo(4)	34586 (2)	11964 (2)	11021 (3)	OP2	5250 (2)	2975 (1)	1995 (3)
Mo(5)	53953 (2)	8403 (2)	−55 (3)	Na(1)	6736 (1)	−432 (1)	1613 (2)
P(1)	51318 (5)	4427 (4)	29951 (7)	Na(2)	2092 (1)	668 (1)	6871 (2)
P(2)	49548 (5)	22513 (4)	19645 (8)	Na(3)	5109 (1)	3807 (1)	5497 (2)
O(1)	7596 (2)	919 (2)	2815 (3)	Na(4)	272 (2)	1041 (1)	1293 (2)
O'(1)	7364 (2)	1894 (2)	1090 (3)	Na(5)	3136 (1)	3037 (1)	797 (2)
O(12)	6579 (2)	2048 (1)	3371 (2)	Na(6)	6513 (1)	3074 (1)	831 (2)
O(15)	6385 (2)	705 (1)	1014 (3)	Aq(1)	7938 (3)	−98 (2)	276 (4)
OP(12)	5859 (2)	921 (1)	3422 (2)	Aq(13a)*	3568 (7)	3682 (5)	4733 (11)
OP(15)	5615 (2)	1817 (1)	1251 (2)	Aq(13b)*	3950 (4)	3508 (3)	4038 (6)
O(2)	6500 (2)	1476 (2)	5746 (3)	Aq(15)	2565 (2)	4134 (2)	1594 (3)
O'(2)	5753 (2)	2668 (1)	5315 (3)	Aq(2)	3363 (3)	348 (2)	7927 (5)
O(23)	4786 (2)	1491 (2)	5472 (2)	Aq(23)	710 (2)	998 (2)	6481 (3)
OP(23)	4837 (2)	1983 (1)	3331 (2)	Aq(26)	2360 (2)	1787 (1)	7389 (3)
O(3)	3154 (2)	931 (2)	5371 (3)	Aq(34)	4269 (2)	3506 (2)	7264 (4)
O'(3)	3362 (2)	2226 (2)	4760 (3)	Aq'(34)	1251 (3)	1001 (2)	3071 (4)
OP(3)	4427 (2)	477 (1)	3970 (3)	Aq(4)	−182 (4)	−120 (2)	1538 (4)
O(34)	3270 (2)	1321 (1)	2838 (2)	Aq(45)	4347 (2)	3758 (2)	424 (3)
O(4)	3047 (2)	397 (1)	950 (3)	Aq(46)	876 (2)	2171 (2)	1116 (4)
O'(4)	2682 (2)	1672 (1)	431 (3)	Aq'(46)	6375 (3)	4317 (2)	361 (5)
OP(4)	4104 (2)	2178 (1)	1320 (2)	Aq(5)	2283 (2)	2642 (2)	2532 (3)
O(45)	4253 (2)	1161 (1)	−282 (2)	Aq1	4146 (3)	2087 (2)	7746 (3)
OP(45)	4726 (2)	709 (1)	1752 (2)				

* The occupancy factors for Aq(13a) and Aq(13b) were refined to 0.363 (13) and 0.637 (13) respectively.

the anomalous dispersion (*International Tables for X-ray Crystallography*, 1974). The computer programs used have been described by Antti (1976). The computations were performed with the CD 3300 and CD CYBER 172 computers at the University of Umeå. Final atomic positional parameters are given in Table 3.*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32642 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
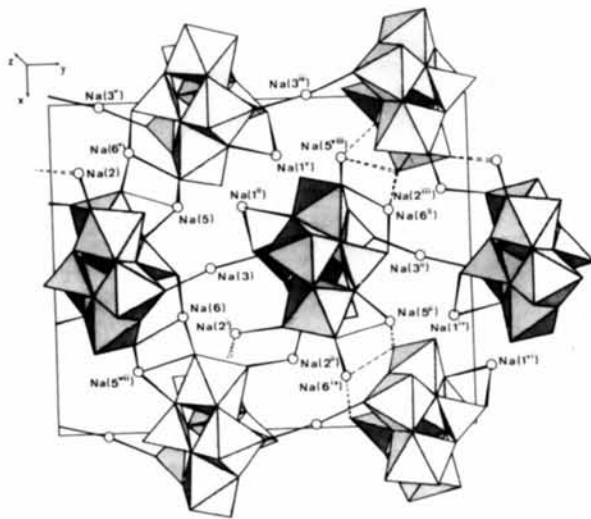
Description and discussion of the structure

The crystal structure consists of $Mo_5P_2O_{23}^{6-}$ anions joined in a three-dimensional framework by Na^+ ions and water molecules in electrostatic force links O—Na—O and O—Na—H_2O—Na—O as well as by numerous hydrogen bonds. The anion pentagonal rings are approximately parallel to (010) with O—Na—O links preferentially in the [010] and diagonal directions and O—Na—H_2O—Na—O links in the [100] and [001] directions (Figs. 1 and 2).

The $Mo_5P_2O_{23}^{6-}$ anion

The anion consists of five MoO_6 octahedra forming a ring by sharing edges in all connexions, except one in which a corner is shared [O(34)]. Two PO_4 tetrahedra are connected one to each side of the ring with three of
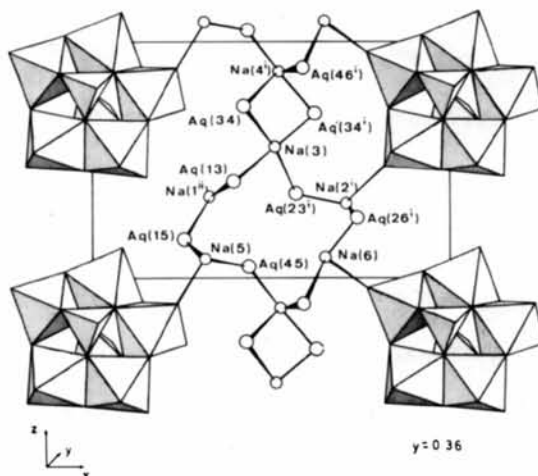

Fig. 1. The O—Na—O links in the structure projected on the *xy* plane. Average *z* values are 0·25 and −0·25 for anions drawn with heavy and thin lines respectively. Symmetry operations: (i) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; (ii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $\frac{1}{2} - x, 1 - y, -\frac{1}{2} + z$; (iv) $x, 1 + y, z$; (v) $-\frac{1}{2} + x, \frac{1}{2} - y, -z$; (vi) $\frac{3}{2} - x, 1 - y, -\frac{1}{2} + z$; (vii) $\frac{1}{2} + x, \frac{1}{2} - y, -z$; (viii) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$; (ix) $\frac{3}{2} - x, 1 - y, \frac{1}{2} + z$. Broken lines represent bonds to anions on $1 + z$ compared with the anion drawn.

Fig. 2. Selected O—Na—H_2O—Na—O links as projected on the *xz* plane. The projection is restricted to atoms within $y \sim 0.2$–0.55. Symmetry operations as in Fig. 1.

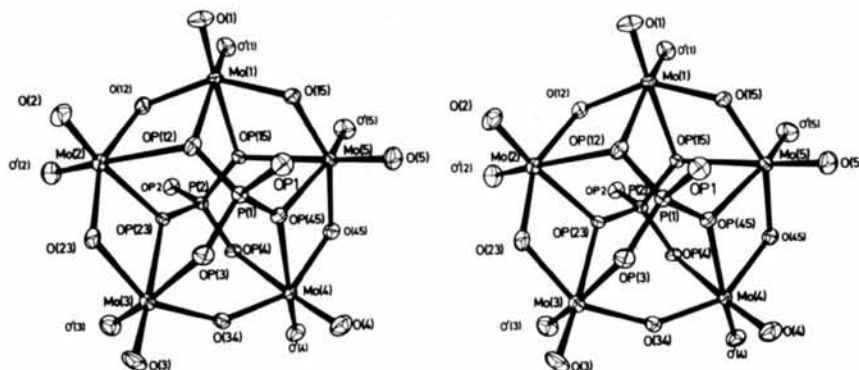Fig. 3. A stereoscopic view of the $Mo_5P_2O_{23}^{6-}$ anion. The thermal ellipsoids are scaled to include 50% probability (*ORTEP*; Johnson, 1965).

Table 4. *Distances* (Å) *and angles* (°) *within the* $Mo_5P_2O_{23}^{6-}$ *anion in* $Na_6Mo_5P_2O_{23}(H_2O)_{14}$ *(A)*

Selected values from the $Mo_5P_2O_{23}^{6-}$ anion in $Na_6Mo_5P_2O_{23}(H_2O)_{13}$ (*B*) and the $H_2Mo_5P_2O_{23}^{4-}$ anion in $Na_4H_2Mo_5P_2O_{23}(H_2O)_{10}$ (*C*) have been included for comparison. Estimated standard deviations are given in parentheses.

		A	B	C
Mo(1)–Mo(2)		3·3771 (4)	3·364 (1)	3·375 (1)
Mo(1)–Mo(5)		3·3755 (4)	3·364 (1)	3·405 (1)
Mo(2)–Mo(3)		3·3548 (5)	3·356 (1)	3·389 (1)
Mo(4)–Mo(5)		3·3617 (4)	3·356 (1)	3·391 (1)
Mo(3)–Mo(4)		3·6604 (4)	3·647 (2)	3·681 (1)
Mo(1)–Mo(3)		5·4403 (5)	5·459 (2)	5·507 (1)
Mo(1)–Mo(4)		5·4403 (5)	5·459 (2)	5·520 (1)
Mo(2)–Mo(5)		5·5204 (5)	5·493 (2)	5·526 (1)
Mo(2)–Mo(4)		5·5563 (4)	5·566 (1)	5·608 (1)
Mo(3)–Mo(5)		5·5557 (5)	5·566 (1)	5·609 (1)
Mo(2)–Mo(1)–Mo(5)		109·67 (1)	109·44 (5)	109·19 (3)
Mo(3)–Mo(2)–Mo(1)		107·83 (1)	108·63 (4)	109·00 (3)
Mo(4)–Mo(3)–Mo(2)		104·67 (1)	105·18 (3)	104·89 (3)
Mo(5)–Mo(4)–Mo(3)		104·51 (1)	105·18 (3)	104·89 (3)
Mo(1)–Mo(5)–Mo(4)		107·71 (1)	108·63 (4)	108·63 (3)

P(1)–Mo(1)	3·3972 (9)	P(2)–Mo(1)	3·4149 (9)
P(1)–Mo(2)	3·5676 (8)	P(2)–Mo(2)	3·3606 (8)
P(1)–Mo(3)	3·3231 (9)	P(2)–Mo(3)	3·6430 (8)
P(1)–Mo(4)	3·6538 (9)	P(2)–Mo(4)	3·2947 (8)
P(1)–Mo(5)	3·3277 (8)	P(2)–Mo(5)	3·5748 (8)
		P(1)–P(2)	3·7700 (11)

their four O atoms in common with different MoO_6 octahedra and with the fourth O atom extending away from the ring (Fig. 3). The Mo–Mo distances between edge-sharing octahedra vary between 3·355–3·377 Å and the distance is 3·6604 (4) Å when a corner is shared. The distances across the ring lie in the range 5·440–5·556 Å. As can be seen from Table 4, the distances correspond more closely to the values found in (*B*) than to those of the $H_2Mo_5P_2O_{23}^{4-}$ anion in $Na_4H_2Mo_5P_2O_{23}(H_2O)_{10}$ (Hedman, 1973).

The MoO_6 octahedra are distorted with the characteristic 2 + 2 + 2 distribution of Mo–O distances in the following three ranges: (i) 1·70–1·73 Å, O atom coordinated to one Mo atom only, (ii) 1·90–1·95 Å, O atom coordinated to two Mo atoms, (iii) 2·17–2·39 Å, O atom coordinated to P and to one or two Mo atoms. O atoms in group (i) are always in the *cis* position relative to one another with an atom of group (iii) in the *trans* position, while O atoms of group (ii) are in the *trans* position relative to one another. This is accompanied by an increase in the O–Mo–O angle from the ideal value when atoms of groups (i) and/or (ii) only are involved, and a corresponding decrease when at least one atom of group (iii) is present. The distortions result from the variation in π-bond character of the Mo–O bonds.

Table 4 *(cont.)*

	O(1)	O'(1)	O(12)	O(15)	OP(12)	OP(15)
Mo(1)	1·717 (3)	1·720 (3)	1·912 (2)	1·924 (3)	2·262 (3)	2·281 (3)
O(1)		2·700 (4)	2·825 (4)	2·749 (4)	2·825 (4)	
OP(15)		2·779 (4)	2·769 (4)	2·537 (3)	2·949 (4)	
O(12)		2·752 (4)			2·515 (3)	
O(15)		2·827 (4)			2·738 (4)	
O(1)–Mo(1)–		103·6 (2)	102·1 (1)	97·9 (1)	89·4 (1)	
OP(15)–Mo(1)–		86·8 (1)	82·2 (1)	73·7 (1)	81·0 (1)	
O(12)–Mo(1)–		98·4 (1)			73·6 (1)	
O(15)–Mo(1)–		101·6 (1)			81·3 (1)	

	O(2)	O (2)	O(12)	O(23)	OP(12)	OP(23)
Mo(2)	1·711 (3)	1·698 (3)	1·948 (3)	1·944 (3)	2·364 (3)	2·176 (2)
O(2)		2·688 (4)	2·784 (4)	2·729 (4)	2·900 (4)	
OP(23)		2·907 (4)	2·761 (4)	2·489 (4)	2·661 (4)	
O(12)		2·746 (4)			2·515 (3)	
O(23)		2·800 (4)			2·994 (4)	
O(2)–Mo(2)–		104·1 (1)	98·9 (1)	96·4 (1)	89·2 (1)	
OP(23)–Mo(2)–		96·4 (1)	83·9 (1)	74·1 (1)	71·6 (1)	
O(12)–Mo(2)–		97·5 (1)			70·6 (1)	
O(23)–Mo(2)–		100·3 (1)			87·5 (1)	

	O(3)	O'(3)	O(23)	O(34)	OP(3)	OP(23)
Mo(3)	1·703 (3)	1·720 (3)	1·937 (3)	1·926 (2)	2·240 (3)	2·344 (3)
O(3)		2·675 (4)	2·815 (4)	2·820 (4)	2·666 (4)	
OP(23)		2·832 (4)	2·489 (4)	2·858 (4)	3·138 (4)	
O(23)		2·792 (4)			2·639 (4)	
O(34)		2·733 (4)			2·761 (4)	
O(3)–Mo(3)–		102·8 (2)	101·1 (1)	101·8 (1)	83·9 (1)	
OP(23)–Mo(3)–		86·9 (1)	70·4 (1)	83·4 (1)	86·3 (1)	
O(23)–Mo(3)–		99·4 (1)			78·0 (1)	
O(34)–Mo(3)–		96·9 (2)			82·6 (1)	

Table 4 (cont.)

	O(4)	O'(4)	O(34)	O(45)	OP(4)	OP(45)
Mo(4)	1·725 (3)	1·708 (3)	1·895 (3)	1·943 (2)	2·215 (3)	2·334 (2)
O(4)		2·657 (4)	2·750 (4)	2·772 (4)		2·862 (4)
OP(4)		2·643 (4)	2·698 (4)	2·660 (4)		3·116 (4)
O(34)		2·823 (4)				2·852 (4)
O(45)		2·793 (4)				2·468 (3)
O(4)–Mo(4)–		101·4 (2)	98·8 (1)	98·0 (1)		88·3 (1)
OP(4)–Mo(4)–		83·6 (1)	81·7 (1)	79·3 (1)		86·4 (1)
O(34)–Mo(4)–		103·0 (1)				84·2 (1)
O(45)–Mo(4)–		99·6 (1)				69·8 (1)

	O(5)	O'(5)	O(15)	O(45)	OP(15)	OP(45)
Mo(5)	1·704 (3)	1·720 (3)	1·928 (3)	1·940 (3)	2·385 (3)	2·172 (3)
O(5)		2·702 (4)	2·728 (4)	2·802 (4)		2·932 (4)
OP(15)		2·903 (4)	2·537 (3)	3·005 (4)		2·667 (4)
O(15)		2·809 (4)				2·743 (4)
O(45)		2·704 (4)				2·468 (3)
O(5)–Mo(5)–		104·2 (2)	97·2 (1)	100·3 (1)		97·6 (1)
OP(15)–Mo(5)–		88·5 (1)	71·2 (1)	87·4 (1)		71·5 (1)
O(15)–Mo(5)–		100·6 (1)				83·8 (1)
O(45)–Mo(5)–		95·1 (1)				73·5 (1)

	OP1	OP(3)	OP(12)	OP(45)
P(1)	1·504 (3)	1·528 (3)	1·560 (3)	1·567 (2)
OP1		2·539 (4)	2·511 (3)	2·506 (4)
OP(3)			2·502 (4)	2·459 (4)
OP(12)				2·564 (4)
OP1–P(1)–		113·7 (2)	110·1 (2)	109·4 (2)
OP(3)–P(1)–			108·2 (1)	105·2 (2)
OP(12)–P(1)–				110·1 (2)

	OP2	OP(4)	OP(15)	OP(23)
P(2)	1·513 (3)	1·519 (3)	1·555 (3)	1·565 (3)
OP2		2·513 (4)	2·504 (4)	2·521 (4)
OP(4)			2·498 (4)	2·472 (3)
OP(15)				2·561 (3)
OP2–P(2)–		112·0 (2)	109·4 (2)	109·9 (2)
OP(4)–P(2)–			108·7 (1)	106·5 (2)
OP(15)–P(2)–				110·3 (2)

The PO_4 tetrahedra are less distorted with mean P–O distances 1·51 Å (unshared O), 1·52 Å (O shared with one Mo atom) and 1·56 Å (O shared with two Mo atoms). When the anion is protonized, as in $Na_4H_2Mo_5P_2O_{23}(H_2O)_{10}$, the protons are attached to OP1 and OP2 converting the shortest P–O distances in this structure to the longest ones. Distances and angles within the anions are given in Table 4.

The sodium–oxygen arrangement

The Na–O connexions, O–Na–O, between the anions include only four of the six crystallographically different Na^+ ions. The arrangement is described schematically in Fig. 1. Of the other two Na^+ ions, Na(1) is attached to only one anion and takes part in O–Na–H_2O–Na–O links (Figs. 1 and 2), while Na(4) is unattached and surrounded by water O atoms only. Eight of the twelve unshared and two of the shared [O(15),OP(4)] anion O atoms are in contact with Na^+ ions (Fig. 4). The remaining four unshared O atoms [O(1),O(2),O'(3),O'(5)] each have two water molecules at hydrogen-bond distances.

Of the six Na^+ ions, three are surrounded by six O atoms in a distorted octahedral arrangement, Na(4) by six water O atoms (Aq), Na(3) by four Aq and two anion O atoms and Na(6) by three Aq and three O. Na(5) shows trigonal prismatic coordination of three Aq and three O. Na(1) and Na(2) are five-coordinated with distorted square pyramids of three Aq and two O each, but both ions have a sixth neighbour atom at a greater distance opposite the pyramidal base, viz O(5) at 3·355 (4) Å and Aq'(46) at 3·167 (6) Å respectively. Since many of the O atoms are coordinated to two Na^+ ions, the distorted polyhedra are connected by sharing edges and corners as indicated in Fig. 5. The Na–O distances (Table 5) vary between 2·32 and 2·58 Å with two exceptions. When an anion O atom is coordinated to two Na^+ ions, one Na–O distance is
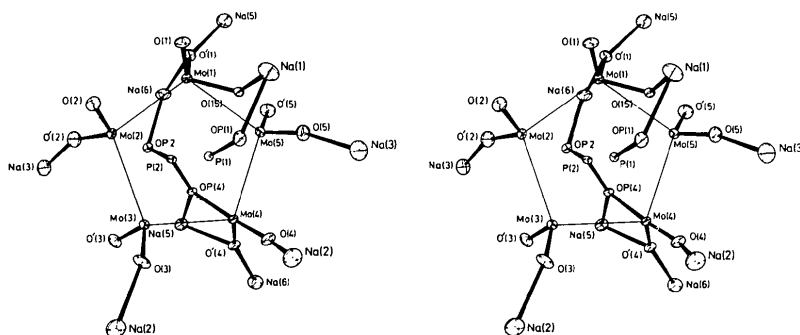
Fig. 4. Stereoscopic view of the Na coordination to the $Mo_5P_2O_{23}^{6-}$ anion (for clarity most Mo-shared O atoms have been omitted). The thermal ellipsoids are scaled to include 50% probability.

increased. Thus Na(5)—O'(4) is 2·834 (3) Å and Na(6)—O'(1) is 2·719 (4) Å. The Na—Na distances are in the range 3·45–4·45 Å.

From a comparison of the Na—O arrangement in the two structures (A) and (B), the following main differences may be noted. (i) In (B) all Na^+ ions are coordinated to the anions, while in (A) one Na^+ ion is surrounded by water O atoms only. (ii) For both structures four Na^+ ions take part in direct links O—Na—O, while (A) has one and (B) two Na^+ ions attached only to one anion. (iii) The Na^+ ions in (B) all show octahedral coordination of two O and four Aq each, while in (A) there are several coordination configurations with different numbers of coordinated O atoms. The Na—O distances are quite comparable however, and there appears to be no significant difference between distances to anion O and water O atoms.
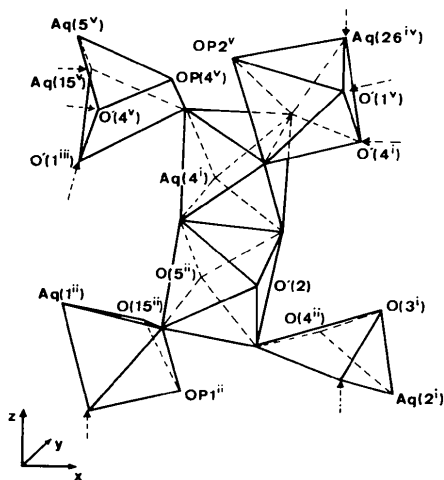

Fig. 5. The smallest unit necessary to describe the arrangement of the Na—O polyhedra. Missing atom labels are to be found in Fig. 2 by superimposing the figures. The arrows indicate atoms shared with other symmetry-related units. Symmetry operations: (i) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; (ii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, 2 - z$; (v) $x, y, 1 + z$.

Table 5. *Sodium—oxygen distances* (Å)

The superscripts refer to the following symmetry operations:

(i)	$1 - x$,	$-\frac{1}{2} + y$, $\frac{1}{2} - z$
(ii)	$\frac{1}{2} - x$,	$-y$, $\frac{1}{2} + z$
(iii)	$\frac{1}{2} + x$,	$\frac{1}{2} - y$, $1 - z$
(iv)	$1 - x$,	$\frac{1}{2} + y$, $\frac{1}{2} - z$
(v)	$-\frac{1}{2} + x$,	$\frac{1}{2} - y$, $-z$
(vi)	$-\frac{1}{2} + x$,	$\frac{1}{2} - y$, $1 - z$
(vii)	$\frac{1}{2} + x$,	$\frac{1}{2} - y$, $-z$

Na(1)—Aq(13a^i)	2·324 (11)*		Na(4)—Aq(45^v)	2·381 (4)
Aq(15^i)	2·374 (4)		Aq(34^{vi})	2·390 (4)
OP1	2·390 (3)		Aq(4)	2·432 (5)
O(15)	2·414 (3)		Aq(46)	2·447 (4)
Aq(1)	2·470 (5)		Aq'(34)	2·452 (5)
Aq(13b^i)	2·470 (6)*		Aq'(46^v)	2·584 (5)
Na(2)—Aq(23)	2·321 (4)		Na(5)—OP(4)	2·362 (3)
Aq(26)	2·330 (4)		O'(1^v)	2·362 (4)
O(4^{ii})	2·345 (3)		Aq(5)	2·424 (4)
O(3)	2·381 (4)		Aq(45)	2·427 (4)
Aq(2)	2·394 (6)		Aq(15)	2·509 (4)
			O'(4)	2·834 (3)
Na(3)—Aq(23^{iii})	2·349 (4)			
Aq(34)	2·385 (4)		Na(6)—Aq(26^{iii})	2·343 (4)
Aq'(34^{iii})	2·399 (5)		O'(4^{vii})	2·345 (3)
Aq(13b)	2·479 (7)*		OP2	2·363 (3)
O'(2)	2·491 (4)		Aq(46^{vii})	2·363 (4)
O(5^{iv})	2·526 (3)		Aq'(46)	2·530 (4)
Aq(13a)	2·583 (12)*		O'(1)	2·719 (4)

* Aq(13) is disordered over two positions, see text.

A 'free' water molecule

Aq1 is the only water molecule uncoordinated to Na. It acts as a hydrogen-bond donor to O(23) and

Table 6. *Some selected hydrogen-bond distances* (Å)

The superscripts refer to the following symmetry operations:

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

Aq1—Aq(34)	2·873 (5)	Aq(13a)—O'(3)	2·913 (11)
Aq(26)	2·915 (5)	O(1^{ii})	3·140 (12)
O(23)	2·886 (4)	Aq(13b)—O'(3)	2·821 (6)
O(45^i)	2·803 (4)	OP2	3·181 (7)

O(45^i), *i.e.* binds different anions in the [001] direction. It is also an acceptor of hydrogen bonds from Aq(26) and Aq(34). The coordination of O atoms around Aq(1) is tetrahedral with distances as given in Table 6.

The disordered water molecule

Aq(13) is, as previously mentioned, disordered over two positions with occupancy factors 0·363 (13) and 0·637 (13) for positions *a* and *b* respectively. A possible explanation for this is the formation of different weak hydrogen bonds for the two positions, in which Aq(13) acts as a donor, see Table 6. Na(1) and Na(3) complete a tetrahedral arrangement of atoms around Aq(13) in both the *a* and *b* positions.

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Multicomponent Polyanions.
17. The Crystal Structure of Na₄Mo₁₂GeO₄₀(H₂O)₈, a Compound Containing Sodium-Coordinated Dodecamolybdogermanate Anions

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The crystal structure of Na$_4$Mo$_{12}$GeO$_{40}$(H$_2$O)$_8$ has been determined from three-dimensional X-ray diffraction data collected with a Pailred diffractometer using Mo $K\alpha$ radiation. There are two formula units in the triclinic ($P\bar{1}$) unit cell and the cell parameters are $a = 14\cdot421$ (1), $b = 13\cdot187$ (1), $c = 11\cdot596$ (1) Å, $\alpha = 114\cdot31$ (1), $\beta = 103\cdot88$ (1) and $\gamma = 76\cdot45$ (1)°. The structure was refined by least-squares methods using anisotropic vibrational parameters to a final R value of 0·029 based on 9988 independent reflexions. The structure is built up of Mo$_{12}$GeO$_{40}^{4-}$ groups linked together by Na$^+$ and water molecules in a three-dimensional framework. The heteropolyanion has the well known Keggin structure (α isomer). The Mo–Mo distances within the group vary between 3·32 and 3·38 Å when the MoO$_6$ octahedra are sharing edges and increase to 3·70–3·78 Å when only a corner is shared. As would be expected from previous investigations, the Mo–O distances depend on the O coordination number. The four groups of Mo–O distances observed have mean values of 1·69, 1·82, 2·05 and 2·29 Å.

Introduction

The present crystal structure study forms part of a research project in progress in this department aimed at elucidating the equilibria and structures of three-component polyanion complexes present in aqueous solutions. One of the systems studied contains the reacting components H$^+$, MoO$_4^{2-}$ and Ge(OH)$_4$. The