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Multicomponent Polyanions. 19. The Molecular and Crystal Structure of Na₅HMo₅P₂O₂₃(H₂O)₁₁, a Superstructure with Sodium-Coordinated Monohydrogenpentamolybdodiphosphate Anions

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Abstract

The crystal structure of $Na_5HMo_5P_2O_{23}(H_2O)_{11}$ has been determined from three-dimensional X-ray diffraction data collected with a Pailred diffractometer using Mo $K\alpha$ radiation. The crystals are triclinic, $P\bar{1}$, with four formula units in a cell of dimensions $a = 19\cdot470\,(5)$, $b = 20\cdot865\,(5)$, $c = 8\cdot352\,(2)$ Å, $\alpha = 70\cdot10\,(1)$, $\beta = 99\cdot86\,(1)$ and $\gamma = 110\cdot63\,(3)°$. The structure contains $HMo_5P_2O_{23}^{5-}$ anions consisting of a ring of five MoO_6 octahedra with two PO_4 tetrahedra, one attached to each side of the ring. In the anion, which is a member of a series of protonated pentamolybdodiphosphate anions, the H atom is bonded to one of the unshared phosphate oxygens. The Na^+ ions are directly coordinated to the anions and join these in a three-dimensional framework through $O-Na-O$ and $O-Na-H_2O-Na-O$ bridges. The coordination of anion and water oxygens around Na^+ is octahedral, square pyramidal or irregularly seven-fold. Because of systematic vacancies at the site of one of the Na^+ ions, accompanied by a change in water positions, the structure is a superstructure containing a subcell with b halved (10·432 Å). An 'average' structure based on this subcell has been refined with full-matrix least-squares refinement methods. The final R value, based on 6182 independent reflexions, is 0·036.

Introduction

Aqueous equilibria of the form

$$pH^+ + qMoO_4^{2-} + rHPO_4^{2-} \rightleftharpoons (H^+)_p(MoO_4^{2-})_q(HPO_4^{2-})_r$$
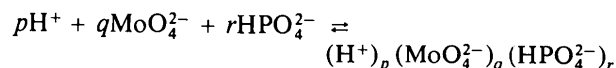
have been studied using potentiometric, spectrophotometric and Raman methods [298 K, 3·0 M Na(ClO₄) medium; Pettersson, 1974, 1975]. The investigations established the formation of two series of complexes which, in (p,q,r) notation, are $(p,5,2)$ with $p = 8, 9$ and 10 (dominant at Mo/P ratios ~2·5), and $(p,9,1)$ with $p = 14, 15, 16$ and 17 (dominant at Mo/P ratios ~9). In crystallization experiments performed parallel with these investigations it was possible to obtain crystals containing each member of the $(p,5,2)$ series. They were all subjected to X-ray structure determinations in order to investigate how the protonation occurs and what influence, if any, protonation has on the structure of the complex. The complexes were shown to consist of the anions $Mo_5P_2O_{23}^{6-}$ ($p = 8$), $HMo_5P_2O_{23}^{5-}$ ($p = 9$) and $H_2Mo_5P_2O_{23}^{4-}$ ($p = 10$), which are equivalent to the complex formulae given above except for five water molecules which cannot be determined from aqueous equilibrium analyses. The $(8,5,2)$ complex has been described in $Na_6Mo_5P_2O_{23}(H_2O)_{13}$ (Strandberg, 1973) and $Na_6Mo_5P_2O_{23}(H_2O)_{14}$ (Hedman, 1977a), and the $(10,5,2)$ complex in $Na_4H_2Mo_5P_2O_{23}(H_2O)_{10}$ (Hed-

man, 1973). The present X-ray structure analysis of the (9,5,2) complex in $Na_5HMo_5P_2O_{23}(H_2O)_{11}$ completes the investigation of the members in this proton series of complexes.

Experimental

Crystal preparations, analyses and data

The crystals were grown by the slow evaporation at room temperature of an aqueous solution of 21·47 g $Na_2MoO_4.2H_2O$, 4·90 g $Na_2HPO_4.H_2O$, 10·67 ml of concentrated (11·64 M) $HClO_4$ (*i.e.* a molar ratio of $H^+:MoO_4^{2-}:HPO_4^{2-} = 9:5:2$) and water to make the total volume 50 ml. After a few days colourless tabular crystals were formed. The crystals decompose quickly in air and were therefore sealed in a Lindemann-glass capillary together with a portion of the mother liquor during the X-ray exposures. Elemental analyses of the crystals (Department of Analytical Chemistry, University of Umeå) gave Mo 39·6, P 5·02 and Na 9·39 wt% compared with the calculated Mo 39·2, P 5·06 and Na 9·39 wt%. Thermobalance analysis of the water content gave 17·1 wt% (calculated 16·2 wt%).

Preliminary Weissenberg and precession photographs indicated triclinic symmetry and the space group $P\bar{1}$ was established in the structure determination. The appearance of very weak reflexions on the films revealed the presence of a superstructure. The effect on the originally reported unit cell (Pettersson, 1975; Hedman 1977a) is a doubling of the a and b parameters giving a C-centred lattice. A reorientation of the axes was made in order to obtain a primitive lattice and, with the new axes, the subcell is found by halving the b parameter ($b = 20·865$ Å). Accurate unit-cell parameters were determined from least-squares refinements (Werner, 1969) of powder data collected with a Guinier–Hägg camera. Si was used as the internal standard $[a(Si) = 5·43088$ Å, 298 K] and the radiation was Cu $K\alpha_1$ ($\lambda = 1·54051$ Å). The density of the crystals was determined by flotation in bromoform/carbon tetrachloride. Crystal data are given in Table 1.

Table 1. *Crystal data for* $Na_5HMo_5P_2O_{23}(H_2O)_{11}$

Triclinic, space group $P\bar{1}$

$a = 19·470 (5)$ Å*	FW 1223·8
$b = 20·865 (5)$	$V = 2980·7$ Å³
$c = 8·352 (2)$	$Z = 4$
$\alpha = 70·10 (1)°$	$D_x = 2·73$ Mg m⁻³
$\beta = 99·86 (1)$	$D_m = 2·69$
$\gamma = 110·63 (3)$	$\mu(Mo\ K\alpha) = 2·296$ mm⁻¹

* Throughout this paper, numbers in parentheses represent the estimated standard deviations and refer to the last decimal place.

Data collection and reduction

Three-dimensional X-ray diffraction data were collected with a Philips Pailred diffractometer (Mo $K\alpha$ radiation, $\lambda = 0·71069$ Å, graphite monochromator) at 298 K. The measurements were made using a scan speed of 1° min⁻¹ and the background was measured for 40 s at the beginning and end of the scan interval. Weak reflexions, including those caused by the superstructure, were scanned twice. Because of the instability of the crystals, a complete data set could only be obtained by using two crystals of approximate dimensions 0·27 × 0·11 × 0·48 mm (I) and 0·20 × 0·18 × 0·35 mm (II) with **c** parallel to the 0·48 (0·35) mm edges [for I (II) respectively]. For crystals (I) and (II) 5177 (6330) reflexions were measured of which 1617 (3093) were superstructure reflexions. The $hk0$–$hk9$ layers were measured out to $(\sin \theta)/\lambda = 0·674$ (0·694) Å⁻¹. In the primary reduction (Hedman, 1977b) the reflexions with $I < 2\sigma(I)$ were considered to be unobserved and were omitted, leaving 4423 (4563) reflexions of which 1177 (1627) were caused by the superstructure. The intensities and the $\sigma(I)$ were corrected for Lp and absorption effects using an 8 × 4 × 12 (6 × 6 × 12) grid. The transmission factor varied from 0·546 to 0·795 (0·623 to 0·713), $\mu(Mo\ K\alpha) = 2·296$ mm⁻¹. The $hk0$ reflexions were then used to compute a preliminary scale factor between the data sets.

Structure determination and refinement

The structure was solved with data set (I) neglecting the superstructure, *i.e.* with $b = 10·432$ Å and reflexions with k odd removed and k halved for the others. The Mo atoms were located from a Patterson synthesis and, using routine heavy-atom methods, the remaining non-hydrogen atoms were found. With four Na atoms in position $2(i)$ and the fifth in $1(d)$, 4·5 of the 5 Na atoms indicated by chemical analyses were accounted for. The remaining Na atom, Na(3), was distinguished from the water oxygens by geometrical considerations, and its low Fourier peak height confirmed the expected occupancy factor of $\frac{1}{2}$, giving a total of five Na atoms. In the subsequent refinements the isotropic temperature factors for the four water oxygens coordinated to Na(3) were considerably higher than for the other water oxygens. A difference Fourier synthesis with these atoms removed showed elongations of their peaks in different directions. The superstructure was therefore considered to arise from an ordered distribution of the Na(3) vacancies, with the atom present at y but absent at $y + \frac{1}{2}$ in the cell with $b = 20·865$ Å. This is accompanied by changes in the positions of four coordinated water molecules. Each of these water O positions was therefore separated into two independent positions according to the Fourier peak elongations and

treated as separate atoms with an occupancy factor of $\frac{1}{2}$.

This 'average structure' was refined by full-matrix least-squares refinement methods based on the 6182 subcell reflexions from data sets (I) and (II). To allow an adjustment of the data sets, separate scale factors were varied in the final refinement of positional and isotropic thermal parameters. Anisotropic thermal parameters were applied for all atoms except for the 'split' water oxygens, for which high correlations between some of the positional and thermal parameters made this impossible. The refinements converged with a final R value of 0.036 ($R_w = 0.051$); R and R_w being defined as $R = \sum ||F_o| - |F_c||/\sum |F_o|$ and $R_w = [\sum w_i(|F_o| - |F_c|)^2/\sum w_i|F_o|^2]^{1/2}$, the function $\sum w_i(|F_o| - |F_c|)^2$ being minimized. A weighting scheme, $w = 1/\sigma^2(F_o)$, was applied in which $\sigma^2(F_o)$ was modified according to $\sigma^2(F_o) = \sigma^2(F_o) + (0.009F_o)^2$. The parameter shifts were less than 0.1σ in the final refinement cycle. Because of the large number of parameters the refinements had to be divided into four overlapping blocks and the estimated standard deviations may, therefore, be somewhat underestimated. No H atoms were located in a final difference Fourier synthesis. Mo^{3+}, P, O^- (anion oxygens), Na^+ and O scattering factors were used and the real and imaginary parts of the anomalous dispersion were taken into account (*International Tables for X-ray Crystallography*, 1974). The computer programs used have been described by Antti (1976) and were run on a CD Cyber 172 computer at the University of Umeå. Final atomic parameters are given in Table 2.*

After the refinements, the F_c values were computed for the superstructure reflexions by combining two subcells, one with and one without Na(3), to a cell with $b = 20.865$ Å. The agreement between F_o and F_c for the stronger superstructure reflexions was good but for some of the weakest reflexions large deviations were found. However, these deviations were of the same magnitude as those of the weakest substructure reflexions. This computation thus supports the explanation of the superstructure.

Description and discussion of the structure

The structure consists of $HMo_5P_2O_{23}^{5-}$ anions, Na^+ ions and water molecules. The $HMo_5P_2O_{23}^{5-}$ anions, which are oriented with their pentagon of Mo atoms approximately parallel to (001), are connected in a three-

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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 33980 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional atomic coordinates* ($\times 10^4$; *for* Mo *and* P $\times 10^5$) *referring to the subcell with* $b = 10.432$ Å

For atoms O(i), O(ij), OP(i) and OP(ij) the index indicates that the atom is bonded to Mo atoms i or i and j, and P indicates that it is also bonded to a P atom. Aq(i) and Aq(ij) are coordinated to sodium ions i or i and j. Aq atoms marked with asterisks are part of the superstructure and are in position (a) when Na(3) is present and in position (b) when Na(3) is absent (see text). Their occupancy factors are $\frac{1}{2}$.

	x	y	z
Mo(1)	71090 (2)	−28743 (4)	80062 (6)
Mo(2)	89086 (2)	−10818 (4)	84673 (5)
Mo(3)	91358 (2)	23510 (4)	79160 (5)
Mo(4)	73302 (2)	27778 (4)	61392 (5)
Mo(5)	61433 (2)	−5412 (4)	68610 (5)
P(1)	76280 (6)	−198 (12)	97424 (14)
P(2)	78503 (6)	4502 (13)	52062 (14)
O(1)	7115 (2)	−4177 (4)	9894 (5)
O'(1)	6667 (2)	−3798 (5)	6599 (5)
O(12)	8096 (2)	−2315 (4)	7413 (5)
O(15)	6369 (2)	−2219 (4)	8366 (5)
OP(12)	7838 (2)	−1244 (4)	9515 (4)
OP(15)	7155 (2)	−772 (4)	5878 (4)
O(2)	9007 (2)	−2353 (4)	327 (5)
O'(2)	9560 (2)	−925 (4)	7238 (5)
O(23)	9360 (2)	624 (4)	9146 (4)
OP(23)	8490 (2)	572 (4)	6585 (4)
O(3)	9608 (2)	3420 (4)	9178 (4)
O'(3)	9697 (2)	3008 (4)	6241 (4)
OP(3)	8318 (2)	1237 (4)	9873 (4)
O(34)	8380 (2)	3160 (4)	6831 (4)
O(4)	7098 (2)	3280 (4)	7647 (5)
O'(4)	7365 (2)	4198 (4)	4380 (5)
OP(4)	7700 (2)	1855 (4)	4503 (4)
O(45)	6427 (2)	1459 (4)	5597 (4)
OP(45)	7156 (2)	558 (4)	8147 (4)
O(5)	5510 (2)	−633 (4)	8091 (5)
O'(5)	5644 (2)	−1167 (4)	5238 (5)
OP1	7218 (2)	−542 (4)	1341 (4)
OP2	8118 (2)	131 (4)	3775 (4)
Na(1)	$\frac{1}{2}$	0	0
Na(2)	6633 (1)	3160 (3)	199 (3)
Na(3)	6103 (4)	4909 (6)	2853 (9)
Na(4)	7984 (1)	6508 (3)	2351 (3)
Na(5)	9113 (1)	4915 (3)	876 (3)
Na(6)	9204 (1)	857 (3)	2213 (3)
Aq(12)	6134 (3)	420 (6)	1648 (6)
Aq'(12)	5474 (3)	2636 (6)	−1385 (6)
Aq(23a)*	5899 (6)	2721 (13)	2425 (14)
Aq(23b)*	5893 (8)	3008 (16)	2466 (18)
Aq(25)	7902 (2)	3198 (4)	1096 (5)
Aq(3a)*	5189 (8)	4024 (16)	4888 (18)
Aq(3b)*	5410 (7)	3913 (14)	5009 (16)
Aq'(3a)*	5351 (6)	5900 (12)	569 (14)
Aq'(3b)*	5493 (6)	6158 (11)	953 (13)
Aq(34a)*	7044 (5)	6845 (10)	3318 (11)
Aq(34b)*	6794 (6)	6582 (12)	3029 (13)
Aq(45)	8884 (2)	5188 (5)	3446 (5)
Aq(46)	8956 (4)	8285 (6)	3683 (7)
Aq(5)	8839 (2)	5686 (4)	−2127 (5)
Aq(56)	9646 (2)	3078 (5)	2832 (5)

dimensional framework by O—Na—O and O—Na—H$_2$O—Na—O bridges, as well as by numerous hydrogen bonds.

The $HMo_5P_2O_{23}^{5-}$ anion

The anion consists of five MoO_6 octahedra and two PO_4 tetrahedra. The octahedra form a ring by sharing four edges and one corner as shown in Fig. 1. The tetrahedra are attached, one on each side of the ring, by each having three oxygens in common with Mo atoms and the unshared oxygen protruding from the ring. The H atom is attached to one of these unshared oxygens, OP2.

As can be seen in Table 3, the Mo—Mo distances vary between 3·33 and 3·38 Å for octahedra sharing edges and increase to 3·691 (1) Å when a corner is shared [Mo(3)—Mo(4)]. Cross distances within the ring lie in the range 5·44–5·61 Å. Apart from the H atoms the anion has the same structural arrangement as the $Mo_5P_2O_{23}^{6-}$ (Strandberg, 1973; Hedman 1977a) and $H_2Mo_5P_2O_{23}^{4-}$ (Hedman, 1973) anions. As can be seen from the comparison of their Mo—Mo, Mo—P and P—P distances given in Table 3, no radical change is induced in the structure by protonation/deprotonation. The only trend appears to be a decreased P—P distance accompanied by a minor expansion of the pentagonal ring of Mo atoms in the direction defined by Mo(1)—O(34).

All MoO_6 octahedra are systematically distorted from ideal values (cf. Table 3). The Mo—O distances are divided into three different groups with mean values of 1·70, 1·92 and 2·29 Å for unshared oxygens, oxygens shared between two Mo atoms, and oxygens coordinated to P as well as to one or two Mo atoms respectively. Every octahedron contains two oxygens of each type. Unshared oxygens are in cis positions relative to one another with oxygens of the longest distance in trans positions. The oxygens with intermediate distances are situated in trans positions relative to one another. The O—Mo—O angles are larger for atoms with short interatomic distances and vice versa. This systematic variation of Mo—O distances and O—Mo—O angles is generally found for octahedral 2 + 2 + 2 coordination of oxygens around Mo (Schröder, 1975) and reflects the variation in the π-bond contribution in the Mo—O bonds.

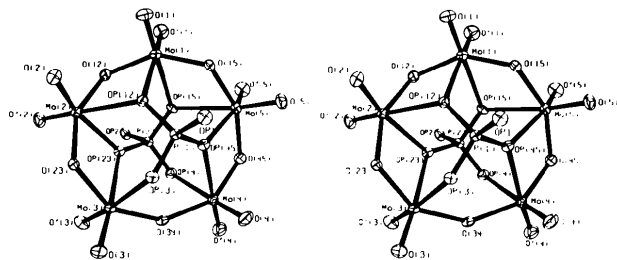In the PO_4 tetrahedra the P—OP1/OP2 distances are of particular interest (cf. Table 3). In the $Mo_5P_2O_{23}^{6-}$

Fig. 1. A stereoscopic view of the $HMo_5P_2O_{23}^{5-}$ anion. The thermal ellipsoids are scaled to include 50% probability (ORTEP II, Johnson, 1976).

anion this distance is the shortest P—O distance in each tetrahedron [1·504 (3), 1·513 (3) Å], while it is the longest in the $H_2Mo_5P_2O_{23}^{4-}$ anion [1·564 (8), 1·565 (8) Å] (Hedman, 1977a; Hedman, 1973). For the $HMo_5P_2O_{23}^{5-}$ anion the P—OP1 and P—OP2 distances are 1·510 (4) and 1·556 (4) Å respectively. The increased distances are caused by the attachment of a H atom to these oxygens. Similar differences for the P—O and P—OH bond lengths are observed in, for example, the structures of $(NH_4)_5HMo_5P_2O_{23}.3H_2O$ (Fischer, Ricard & Toledano, 1974), $Na_2HPO_4.2H_2O$ (Bartl, Catti & Ferraris, 1976) and $H_3PO_4.\frac{1}{2}H_2O$ (Dickens, Prince, Schroeder & Jordan, 1974). In the present structure the anion H takes part in a short hydrogen bond, OP2—H···OP1' [2·565 (5) Å], to a second anion. In this way the anions are linked by hydrogen bonds to form a continuous chain extended in the z direction. The PO_4 tetrahedra are slightly distorted, mainly as a result of having one or two Mo atoms coordinated to three of the oxygens, but also by this attachment of an H atom. The overall mean P—O distances in the four $Na_{6-x}H_xMo_5P_2O_{23}(H_2O)_y$ structures $(x = 0–2)$ are for tetrahedra with H attached: 1·56, 1·50 and 1·54 Å for P—O(H), P—O—Mo and $P-O\langle^{Mo}_{Mo}$ coordination, respectively, but 1·51, 1·53 and 1·56 Å for the nonprotonated tetrahedra. Thus, not

Table 3. Distances (Å) and angles (°) within the $HMo_5P_2O_{23}^{5-}$ anion

Some corresponding values from the $Mo_5P_2O_{23}^{6-}$ anion in $Na_6Mo_5P_2O_{23}(H_2O)_{14}$ and the $H_2Mo_5P_2O_{23}^{4-}$ anion in $Na_4H_2Mo_5P_2O_{23}(H_2O)_{10}$ are included for comparison.

	$HMo_5P_2O_{23}^{5-}$	$Mo_5P_2O_{23}^{6-}$	$H_2Mo_5P_2O_{23}^{4-}$
Mo(1)—Mo(2)	3·366 (1)	3·3771 (4)	3·375 (1)
Mo(1)—Mo(5)	3·376 (1)	3·3755 (4)	3·405 (1)
Mo(2)—Mo(3)	3·326 (1)	3·3548 (5)	3·389 (1)
Mo(4)—Mo(5)	3·333 (1)	3·3617 (4)	3·391 (1)
Mo(3)—Mo(4)	3·691 (1)	3·6604 (4)	3·681 (1)
Mo(1)—Mo(3)	5·473 (2)	5·4403 (5)	5·507 (1)
Mo(1)—Mo(4)	5·437 (1)	5·4403 (5)	5·520 (1)
Mo(2)—Mo(5)	5·501 (2)	5·5204 (5)	5·526 (1)
Mo(2)—Mo(4)	5·548 (2)	5·5563 (4)	5·608 (1)
Mo(3)—Mo(5)	5·612 (2)	5·5557 (5)	5·609 (1)
Mo(2)—Mo(1)—Mo(5)	109·33 (3)	109·67 (1)	109·19 (3)
Mo(3)—Mo(2)—Mo(1)	109·73 (3)	107·83 (1)	109·00 (3)
Mo(4)—Mo(3)—Mo(2)	104·36 (3)	104·67 (1)	104·89 (3)
Mo(5)—Mo(4)—Mo(3)	105·93 (3)	104·51 (1)	104·89 (3)
Mo(1)—Mo(5)—Mo(4)	108·27 (2)	107·71 (1)	108·63 (3)
P(1)—Mo(1)	3·508 (1)	3·3972 (9)	3·461 (3)
P(1)—Mo(2)	3·498 (1)	3·5676 (8)	3·521 (3)
P(1)—Mo(3)	3·303 (2)	3·3231 (9)	3·303 (3)
P(1)—Mo(4)	3·539 (1)	3·6538 (9)	3·602 (3)
P(1)—Mo(5)	3·442 (1)	3·3277 (8)	3·401 (3)
P(2)—Mo(1)	3·419 (2)	3·4149 (9)	3·482 (3)
P(2)—Mo(2)	3·414 (1)	3·3606 (8)	3·409 (3)
P(2)—Mo(3)	3·597 (2)	3·6430 (8)	3·606 (3)
P(2)—Mo(4)	3·289 (1)	3·2947 (8)	3·306 (3)
P(2)—Mo(5)	3·493 (2)	3·5748 (8)	3·534 (3)
P(1)—P(2)	3·732 (2)	3·7700 (11)	3·712 (4)

Table 3 (cont.)

	O(1)	O'(1)	O(12)	O(15)	OP(12)	OP(15)
Mo(1)	1·697 (4)	1·700 (4)	1·903 (4)	1·902 (4)	2·375 (3)	2·289 (3)
O(1)		2·678 (6)	2·778 (6)	2·756 (5)	2·811 (5)	
OP(15)		2·832 (5)	2·732 (5)	2·503 (5)	3·049 (5)	
O(12)		2·762 (6)			2·573 (5)	
O(15)		2·802 (6)			2·795 (5)	
O(1)–Mo(1)–		104·1 (2)	100·9 (2)	99·8 (2)	85·6 (2)	
OP(15)–Mo(1)–		89·2 (2)	80·8 (1)	72·7 (1)	81·6 (1)	
O(12)–Mo(1)–		100·0 (2)			73·0 (1)	
O(15)–Mo(1)–		102·0 (2)			80·8 (1)	

	O(2)	O'(2)	O(12)	O(23)	OP(12)	OP(23)
Mo(2)	1·698 (4)	1·696 (4)	1·948 (4)	1·917 (4)	2·328 (3)	2·195 (3)
O(2)		2·691 (6)	2·752 (5)	2·781 (5)	2·788 (5)	
OP(23)		2·898 (5)	2·698 (5)	2·493 (5)	2·721 (5)	
O(12)		2·708 (5)			2·573 (5)	
O(23)		2·777 (5)			2·917 (5)	
O(2)–Mo(2)–		104·9 (2)	97·8 (2)	100·4 (2)	86·2 (2)	
OP(23)–Mo(2)–		95·5 (2)	81·0 (1)	74·3 (1)	73·9 (1)	
O(12)–Mo(2)–		95·8 (2)			73·4 (1)	
O(23)–Mo(2)–		100·3 (2)			86·3 (1)	

	O(3)	O'(3)	O(23)	O(34)	OP(3)	OP(23)
Mo(3)	1·716 (4)	1·722 (4)	1·906 (3)	1·897 (3)	2·203 (3)	2·354 (3)
O(3)		2·673 (5)	2·792 (5)	2·817 (5)	2·721 (5)	
OP(23)		2·754 (5)	2·493 (5)	2·860 (5)	3·148 (4)	
O(23)		2·791 (5)			2·549 (5)	
O(34)		2·760 (5)			2·638 (5)	
O(3)–Mo(3)–		102·1 (2)	100·7 (2)	102·4 (2)	87·0 (2)	
OP(23)–Mo(3)–		83·5 (1)	70·8 (1)	83·8 (1)	87·3 (1)	
O(23)–Mo(3)–		100·5 (2)			76·3 (1)	
O(34)–Mo(3)–		99·3 (2)			79·7 (1)	

	O(4)	O'(4)	O(34)	O(45)	OP(4)	OP(45)
Mo(4)	1·696 (4)	1·685 (4)	1·961 (4)	1·907 (4)	2·244 (3)	2·300 (3)
O(4)		2·643 (6)	2·752 (5)	2·819 (5)	2·767 (5)	
OP(4)		2·711 (5)	2·653 (5)	2·637 (5)	3·083 (5)	
O(34)		2·807 (5)			2·926 (5)	
O(45)		2·742 (5)			2·445 (5)	
O(4)–Mo(4)–		102·8 (2)	97·3 (2)	102·8 (2)	86·3 (2)	
OP(4)–Mo(4)–		86·0 (2)	77·9 (1)	78·4 (1)	85·5 (1)	
O(34)–Mo(4)–		100·4 (2)			86·4 (1)	
O(45)–Mo(4)–		99·3 (2)			70·4 (1)	

	O(5)	O'(5)	O(15)	O(45)	OP(15)	OP(45)
Mo(5)	1·695 (4)	1·707 (4)	1·921 (4)	1·914 (4)	2·374 (3)	2·208 (3)
O(5)		2·698 (5)	2·674 (5)	2·779 (5)	3·001 (5)	
OP(15)		2·805 (5)	2·503 (5)	3·053 (5)	2·702 (5)	
O(15)		2·810 (5)			2·717 (5)	
O(45)		2·717 (6)			2·445 (5)	
O(5)–Mo(5)–		105·0 (2)	95·2 (2)	100·6 (2)	99·7 (2)	
OP(15)–Mo(5)–		85·2 (2)	70·4 (1)	90·2 (1)	72·2 (1)	
O(15)–Mo(5)–		101·4 (2)			82·0 (1)	
O(45)–Mo(5)–		97·1 (2)			72·4 (1)	

	OP1	OP(3)	OP(12)	OP(45)		OP2	OP(4)	OP(15)	OP(23)
P(1)	1·510 (4)	1·530 (4)	1·547 (4)	1·551 (3)	P(2)	1·556 (4)	1·494 (5)	1·527 (4)	1·547 (3)
OP1		2·467 (5)	2·516 (5)	2·521 (5)	OP2		2·492 (5)	2·499 (5)	2·483 (5)
OP(3)			2·527 (5)	2·479 (5)	OP(4)			2·486 (5)	2·476 (5)
OP(12)				2·525 (5)	OP(15)				2·558 (5)
OP1–P(1)–		108·4 (2)	110·8 (2)	110·8 (2)	OP2–P(2)–		109·6 (2)	108·4 (2)	106·4 (2)
OP(3)–P(1)–			110·5 (2)	107·1 (2)	OP(4)–P(2)–			110·7 (2)	109·0 (2)
OP(12)–P(1)–				109·2 (2)	OP(15)–P(2)–				112·7 (2)

only has a larger number of coordinated Mo atoms increased the P—O distance, but also the attachment of the H atom induced a decrease of the remaining P—O distances owing to its elongation of the P—OH bond. These tetrahedra are thus more distorted than in some of the orthophosphates; for example, in $(NH_4)_3PO_4.3H_2O$ with d(P—O) 1·533–1·541 Å (Mootz & Wunderlich, 1970).

Large-angle X-ray scattering studies of aqueous solutions containing predominantly the (8,5,2), (9,5,2) and (10,5,2) complexes have shown their structure to be identical with that of the $Mo_5P_2O_{23}$ group (Johansson, Pettersson & Ingri, 1974). It may thus be concluded that these complexes are the anions $Mo_5P_2O_{23}^{6-}$, $HMo_5P_2O_{23}^{5-}$ and $H_2Mo_5P_2O_{23}^{4-}$, with the structures described, and that the three members of this proton series differ by the successive attachment of H atoms to the unshared phosphate oxygens.

The O—Na—O bridges and the Na^+ coordination around the anions

There are six crystallographically different Na^+ ions in the structure. They are all coordinated to anion oxygens and, with the exception of Na(3), all form electrostatic O—Na—O bridges. Na(1), being in a special position, coordinates O(5) in two anions. Na(2) forms bridges O(4)—Na(2)—O(1)′ while Na(4) is attached to O(1), O(2) and OP(12) in one anion bridging to O′(4) in another. Three anions are connected via Na(5), which coordinates O(2), O(3) and O(3)′. Na(6) also connects three anions via O(3), OP(3) and O(23) in one anion and O′(2) and OP2, respectively, in the other two. These bridges join the anions to a framework mainly in the [010] and [001] directions (as shown in Figs. 2 and 3), with Na(1) providing the only link in the [100] direction.

The Na^+ ions are in this way coordinated to eight of the twelve unshared and to three of the shared anion oxygens, as shown in Fig. 4. The remaining unshared oxygens [O′(1),O′(3),O′(5),OP1] each have two water molecules at hydrogen-bond distances. Na(3) takes no
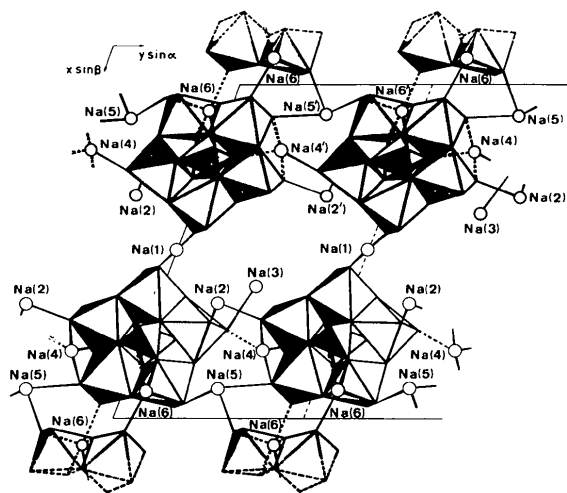

Fig. 2. The O—Na—O bridges in the structure projected along the z axis. Average z values are 0·25 and −0·25 for anions drawn with heavy and thin lines respectively. The subcell is indicated by a broken line. Broken double lines represent bonds to anions on z ± 1 compared with the anions drawn. The prime indicates the symmetry operation $\bar{x},\bar{y},\bar{z}$.
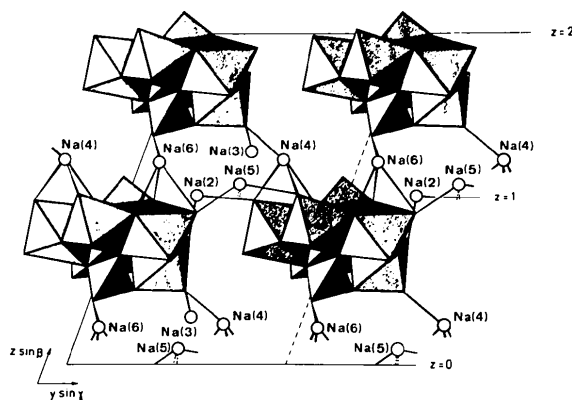

Fig. 3. The O—Na—O bridges [except for Na(1)] in the structure projected along the x axis. The projection is restricted to atoms within x ~ 0·5–1·0. The subcell is indicated by a broken line.

part in O—Na—O bridging, being coordinated to only one anion (cf. Figs. 2 and 3). In addition, this atom is only present at every second anion because of the superstructure (see below).

The sodium–oxygen arrangement

In addition to binding to anion oxygens each Na^+ ion coordinates water O atoms. Generally, Na^+ ions coordinate six O atoms but, in this structure, five and seven coordination are also found. Na(1) and Na(2) are thus octahedrally coordinated by six oxygens, while the coordination of five oxygens around Na(3) is square pyramidal [a sixth oxygen, O(1), is 3·104 (8) Å away]. For the seven-coordinated Na(4), Na(5) and Na(6) atoms, the coordination is irregular and may be described as 'capped octahedral' or 'capped trigonal prismatic'. With the exception of Aq(3), Aq′(3) and Aq(5) all water molecules are coordinated to two Na^+ ions (if the superstructure is neglected; see below). Together with the multiply coordinated anion oxygens (Fig. 4) this implies that the Na—O polyhedra are connected by sharing edges and corners. The Na—Na distances are in the range 3·48–4·53 Å.
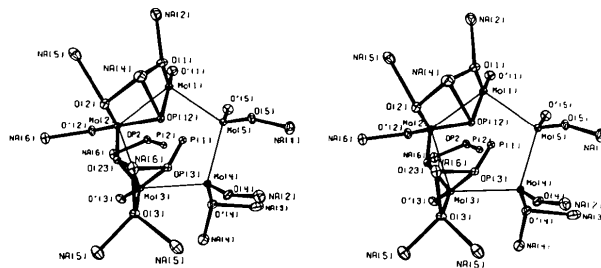

Fig. 4. A stereoscopic view of the Na^+ coordination to the $HMo_5P_2O_{23}^{5-}$ anion (for clarity most Mo-shared O atoms have been omitted). Na(3) is present only for every second anion because of the superstructure (see text). The thermal ellipsoids are scaled to include 50% probability.

Table 4. *Sodium–oxygen distances* (Å)

Waters with (*a*) or (*b*) in their notation are part of the super-structure, and are in position (*a*) when Na(3) is present and in position (*b*) when Na(3) is absent (see text). Distances to the vacant 'Na(3)' position are included.

The superscripts refer to the following symmetry operations:

(i)	$x,$	$y,$	$z - 1$	(iv)	$2 - x,$ $1 - y,$ $1 - z$
(ii)	$x,$	$1 + y,$	$z - 1$	(v)	$x,$ $y - 1,$ z
(iii)	$x,$	$1 + y,$	z	(vi)	$2 - x,$ $-y,$ $1 - z.$

Na(1)–Aq(12)	2·376 (5)	Na(5)–Aq(5)	2·386 (5)
O(5^i)	2·384 (4)	Aq(45)	2·391 (5)
Aq'(12)	2·482 (5)	Aq(25)	2·397 (5)
		Aq(56)	2·472 (5)
Na(2)–Aq(23a)	2·361 (12)	O(3^{iv})	2·481 (5)
Aq'(12)	2·396 (6)	O(2^{iii})	2·805 (5)
O(4^i)	2·404 (5)	O(3^i)	2·901 (4)
Aq(25)	2·448 (5)		
Aq(23b)	2·500 (14)	Na(6)–O'(2^{vi})	2·351 (4)
O(1^{ii})	2·535 (5)	Aq(56)	2·374 (5)
Aq(12)	2·583 (6)	OP(3^i)	2·399 (4)
		OP2	2·427 (4)
Na(3)–Aq(34a)	2·296 (11)	Aq(46^v)	2·447 (6)
Aq(23a)	2·315 (14)	O(23^i)	2·730 (4)
Aq'(3a)	2·371 (13)	O(3^i)	2·963 (4)
Aq(3a)	2·392 (16)		
O'(4)	2·789 (8)	'Na(3)'–Aq(34b)	1·825 (13)
		Aq(23b)	2·006 (16)
Na(4)–Aq(34a)	2·297 (10)	Aq'(3b)	2·160 (12)
O'(4)	2·450 (5)	Aq(3b)	2·171 (15)
Aq(45)	2·470 (5)		
Aq(34b)	2·509 (12)		
O(2^{ii})	2·522 (5)		
Aq(46)	2·543 (7)		
O(1^{ii})	2·557 (5)		
OP(12^{ii})	2·766 (4)		

The Na–O distances vary between 2·30 and 2·96 Å, but with only six distances exceeding 2·58 Å (Table 4). These longer distances occur (probably because of repulsion effects) when two or three Na$^+$ ions coordinate the same anion oxygen, or when Mo-shared oxygens are brought into coordination simultaneously with their unshared oxygen neighbours.

The superstructure

The superstructure, which causes a doubling of the cell parameter b (20·865 Å), is a result of the Na(3) atom being absent in every second subcell (*cf.* Figs. 2 and 3). At the vacancy the water molecules corresponding to those coordinated to Na(3) change their positions slightly (0·32–0·53 Å). The distances between these water molecules and the former Na(3) site

['Na(3)'] decrease by 0·21 to 0·47 Å and new Aq–Aq distances [2·80(2) and 2·99(2) Å compared with 3·49(2) and 3·99(2) Å] indicate a rearrangement to form hydrogen bonds through the previous Na—O polyhedron. This is accompanied by a corresponding increase in the Na—O distances for the other Na$^+$ ions coordinating the affected water molecules. It seems likely that this arrangement also causes minor positional changes for other atoms. There were, however, no such indications in the refinements on the temperature factors, for example. A refinement based on a cell with $b = 20·865$ Å and a doubled asymmetric unit was considered unrealistic in view of the number of parameters to be varied in relation to the additional chemical information obtained from the weak superstructure reflexions.

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