Multicomponent Polyanions. 12. The Crystal Structure of Na$_6$Mo$_{18}$P$_2$O$_{62}$(H$_2$O)$_{24}$, a Compound Containing Sodiumcoordinated 18-Molybdodiphosphate Anions

ROLF STRANDBERG

Department of Inorganic Chemistry, University of Umeå, S-901 87 Umeå, Sweden

The crystal structure of Na$_6$Mo$_{18}$P$_2$O$_{62}$(H$_2$O)$_{24}$ has been determined from three-dimensional X-ray diffraction data collected with a PAILRED diffractometer using MoKα-radiation. The cell dimensions of the monoclinic ($C2/c$) unit cell are $a = 23.091(2)$ Å, b = 13.481(1) Å, $c = 23.157(2)$ Å and $\beta = 100.35(1)°$, and it contains four formula units. Final refinement by least squares methods using anisotropic vibrational parameters gave an R-value of 0.040, based on 7260 independent reflexions.

The structure consists of Mo$_{18}$P$_2$O$_{62}$$^{6-}$-groups linked together by direct sodium bridges (O – Na – O) in the y- and z-directions forming layers parallel with the yz-plane. The layers are held together by O – Na – H$_2$O – Na – O linkages.

The Mo – Mo distances vary between 3.35 and 3.39 Å for edge-sharing MoO$_6$-octahedra and increase to 3.66 – 3.84 Å for corner-sharing octahedra. The Mo – O distances fall in four ranges, 1.67 – 1.70, 1.75 – 2.14, 2.31 – 2.36, and 2.37 – 2.40 Å, depending on the coordination number of the coordinated oxygen atom.

In equilibrium analysis involving H$^+$, MoO$_4$$^{2-}$, and HPO$_4$$^{2-}$ a series of protonized enneamolybdomonophosphates, (H$^+$)$_{14}$(MoO$_4$$^{2-}$)$_9$(HPO$_4$$^{2-}$), (H$^+$)$_{15}$(MoO$_4$$^{2-}$)$_9$(HPO$_4$$^{2-}$), (H$^+$)$_{16}$(MoO$_4$$^{2-}$)$_9$-(HPO$_4$$^{2-}$), (H$^+$)$_{17}$(MoO$_4$$^{2-}$)$_9$(HPO$_4$$^{2-}$), have been reported.[1] These emf-investigations also indicate the presence of a dimer of the 17,9,1 complex in the most acidic part of the pH-range investigated. In connection with these studies two crystalline phases have been obtained, Na$_3$H$_6$Mo$_9$PO$_{34}$(H$_2$O)$_{12-13}$ and Na$_6$Mo$_{18}$P$_2$O$_{62}$-(H$_2$O)$_{24}$. The structure of the first has already been published [2,3] and the structure of the latter is the topic of the present report.

EXPERIMENTAL

Crystal preparation and analyses. In a typical preparation of the crystals, Na$_2$MoO$_4$.2H$_2$O and NaH$_2$PO$_4$.2H$_2$O were dissolved in HClO$_4$. The concentrations used were [MoO$_4$$^{2-}$]$_{tot}$ = 1.0 M, [HPO$_4$$^{2-}$]$_{tot}$ = 0.11 M and [HClO$_4$]$_{tot}$ = 1.78 M. After one or a few days of evaporation at a temperature of about 40 °C, yellow prismatic crystals were formed. The crystals are not stable in air and during the X-ray exposures they were sealed together with part of the mother liquor in a capillary of Lindemann glass. The contents of Na, Mo, and P were determined by elemental analyses (carried out at the Department of Analytical Chemistry, University of Umeå). (Found weight-%: Na 4.2, Mo 50.2, P 1.8, Calc.: Na 4.1, Mo 51.5, P 1.8). The water content of the crystal was determined by thermogravimetric analysis as well as by simply heating (400 °C) a very big crystal (weight about 1.4 g). The results found here were 13.7 weight-% H$_2$O (Calc. 12.9).

Crystal data and space group. Rotation photographs around [100], [010], and [001] and the corresponding Weissenberg photographs (zero, first and second layer lines) taken with CuKα-radiation showed that the crystals are monoclinic. This was confirmed from precession photographs. Accurate cell dimensions were determined with a Guinier-Hägg camera using Si as internal standard. The cell parameters and their corresponding standard deviations are: $a = 23.091 \pm 0.002$ Å, $b = 13.481 \pm 0.001$ Å, $c = 23.157 \pm 0.002$ Å and $\beta = 100.35° \pm 0.01°$.

The density of the crystals as determined by flotation in a bromoform-diiodomethane solution was $d = 3.10$ g/cm^3 ($d_{calc} = 3.14$). The systematic extinctions of reflexions were: hkl, $h + k = 2n + 1$ and $h0l$, $l = 2n + 1$. This is characteristic for the two space groups $C2/c$ and Cc.

Collection and reduction of intensity data. Three-dimensional intensity data were collected,

at 25 °C, with a Philips PAILRED linear diffractometer using Mo$K\alpha$-radiation. A crystal of approximate dimensions $0.34 \times 0.17 \times 0.09$ mm was mounted and rotated along the c-axis (parallel to the 0.34 mm-edge of the crystal). A total of 10 008 unique reflexions from the layers $hk0 - hk23$ were scanned. Data beyond a limit of sin $\theta = 0.5$ were left out. Reflexions with a relative statistical error of $\Delta I_o/I_o$ greater than 0.5 were omitted, the final data set thus consisting of 7260 reflexions. The intensities were corrected for Lorentz and polarization effects and a correction was applied for absorption.

Computer programs. The computer programs used were based on the programs given in Ref. 4. With the exception of ORTEP the programs have been modified for a CDC 3300 computer by Dr. Britt Hedman, University of Umeå.

CRYSTAL DATA

$Na_6Mo_{18}P_2O_{62}(H_2O)_{24}$ F.W. = 3351.1
Monoclinic $C2/c$ $V = 7091$ Å^3
$a = 23.091(2)$ Å $Z = 4$

$b = 13.481(1)$ Å $d_{calc} = 3.14$ g cm^{-3}
$c = 23.157(2)$ Å) $d_{exp} = 3.10$ g cm^{-3}
$\beta = 100.35(1)°$ $\mu = 32.3$ cm^{-1} (MoKα)

STRUCTURE DETERMINATION AND REFINEMENT

The three-dimensional Patterson synthesis showed extremely strong overlapping of cross-vectors and attempts to solve it failed at first. Direct methods were then applied but these gave no useful information. From the elemental analysis, giving the ratio Mo/P = 9, as well as from the observations during the crystallization experiments, a heteropolyanion with 18 Mo and 2 P was assumed. This anion, if isostructural with $P_2W_{18}O_{62}^{6-}$,[5] should in a Patterson synthesis give a rather high peak, at a distance of about 3.7 Å, arising from the Mo − Mo vectors between the two zigzag rings (see below). On the basis of these assumptions six eight-fold Mo-positions could be found from the Patterson

Table 1. The fractional atomic coordinates and in parentheses their estimated standard deviations (referring to the last decimal place given). For the oxygen atoms indexed O(ij) or OP(ij) the (ij) means that the atom is bonded to the molybdenum atoms i and j. When the oxygen atoms are denoted Aq(ij) they are water oxygens and (ij) means that the atom is bonded to the sodium ions i and j.

	X	Y	Z
Mo1	0.81547(3)	0.75392(5)	0.33590(3)
Mo2	0.76889(2)	0.55495(5)	0.25075(3)
Mo3	0.84482(3)	0.52146(5)	0.38865(3)
Mo4	0.97687(3)	0.82944(5)	0.35101(3)
Mo5	0.87845(3)	0.82859(5)	0.20815(3)
Mo6	0.85794(3)	0.61696(5)	0.13156(3)
Mo7	0.88073(3)	0.38408(5)	0.21357(3)
Mo8	0.97277(3)	0.38087(5)	0.34301(3)
Mo9	0.99616(3)	0.61496(5)	0.42462(3)
P	0.42110(7)	0.10940(12)	0.28119(8)
O(1)	0.2272(2)	0.1546(4)	0.6447(3)
O(13)	0.3118(2)	0.1616(4)	0.3937(3)
O(14)	0.1120(2)	0.2009(4)	0.6401(2)
O(15)	0.1738(2)	0.1982(4)	0.7459(2)
O(12)	0.2526(2)	0.1733(4)	0.2833(2)
OP(123)	0.3620(2)	0.1089(3)	0.3047(2)
O(2)	0.2005(2)	0.0136(4)	0.2224(3)
O(23)	0.2798(2)	0.0035(4)	0.8327(2)
O(26)	0.2952(2)	0.0998(4)	0.1873(2)
O(27)	0.3187(2)	0.0697(4)	0.7408(2)
O(3)	0.3242(3)	0.0216(5)	0.9499(3)
O(38)	0.3936(2)	0.0700(4)	0.8699(2)

O(39)	0.4196(2)	0.0951(4)	0.4270(2)
O(4)	0.0273(2)	0.0580(4)	0.6184(3)
O(45)	0.0607(2)	0.1485(4)	0.7266(2)
O(54')	0.0486(2)	0.1720(4)	0.8360(2)
O(49)	0.4939(2)	0.2561(4)	0.4232(2)
OP(49)	0.4673(2)	0.1624(3)	0.3261(2)
O(5)	0.1404(2)	0.0566(4)	0.8160(3)
O(56)	0.1583(2)	0.2442(4)	0.8589(2)
OP(56)	0.4107(2)	0.1640(3)	0.2219(2)
O(6)	0.3054(2)	0.0968(5)	0.0714(3)
O(67)	0.3771(2)	0.0137(4)	0.6577(2)
O(69')	0.4215(2)	0.1351(4)	0.1009(2)
O(7)	0.3533(2)	0.2126(4)	0.6716(3)
O(78)	0.4172(2)	0.1836(4)	0.7821(2)
O(78')	0.4645(2)	0.1347(4)	0.6894(2)
OP(78)	0.4385(2)	0.0014(3)	0.2736(2)
O(8)	0.4801(2)	0.2130(4)	0.8922(3)
O(89)	0.4966(2)	0.0106(4)	0.6097(2)
O(9)	0.4716(2)	0.0977(4)	0.0054(3)
Na1	0.2284(4)	0.0107(8)	− 0.0033(4)
Na2	0.0932(17)	0.1315(27)	0.0996(10)
Na3	0.1011(11)	0.2014(18)	0.4100(9)
Aq1(1)	0.2270(12)	0.1645(15)	0.9618(6)
Aq2(1)	0.1150(12)	0.0740(22)	0.9512(12)
Aq3(1)	0.2690(6)	0.1465(12)	0.5337(6)
Aq(12)	0.1733(6)	0.0269(12)	0.0840(7)
Aq(13)	0.1916(4)	0.0912(8)	0.4068(5)
Aq1(2)	0.3716(7)	0.2430(10)	0.9714(7)
Aq2(2)	0.0186(13)	0.1048(12)	0.0227(9)
Aq3(2)	0.0864(5)	0.1099(7)	0.2080(8)
Aq4(2)	0.2979(5)	0.2378(8)	0.8459(5)
Aq1(3)	0.0516(10)	0.1067(13)	0.3443(18)
Aq2(3)	0.3913(5)	0.1415(11)	0.5464(5)
Aq3(3)	0.1074(12)	0.1515(19)	0.5111(9)

Table 2. Final anisotropic thermal parameters ($\times 10^4$) and their estimated standard deviations ($\times 10^4$) in parentheses. The parameters are calculated according to the formula
$$\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})].$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo1	7(0)	22(0)	8(0)	1(0)	3(0)	−1(0)
Mo2	5(0)	24(0)	8(0)	−1(0)	2(0)	−0(0)
Mo3	8(0)	24(0)	8(0)	0(0)	3(0)	2(0)
Mo4	8(0)	17(0)	7(0)	−1(0)	2(0)	−2(0)
Mo5	7(0)	18(0)	7(0)	3(0)	2(0)	2(0)
Mo6	7(0)	24(0)	6(0)	1(0)	1(0)	−0(0)
Mo7	7(0)	18(0)	8(0)	−1(0)	1(0)	−1(0)
Mo8	7(0)	18(0)	8(0)	−0(0)	2(0)	2(0)
Mo9	8(0)	23(0)	5(0)	−1(0)	1(0)	1(0)
P	5(0)	15(1)	5(0)	0(0)	2(0)	0(0)
O(1)	8(1)	31(3)	11(1)	2(1)	3(1)	−3(1)
O(13)	8(1)	24(3)	10(1)	−1(1)	4(1)	1(1)
O(14)	7(1)	27(3)	6(1)	1(1)	2(1)	−2(1)
O(15)	7(1)	22(3)	7(1)	1(1)	3(1)	1(1)
O(12)	8(1)	26(3)	10(1)	3(1)	2(1)	1(1)
OP(123)	5(1)	20(2)	7(1)	−1(1)	2(1)	0(1)
O(2)	9(1)	34(3)	11(1)	−2(1)	2(1)	−0(1)
O(23)	8(1)	22(3)	7(1)	0(1)	3(1)	−0(1)
O(26)	5(1)	24(3)	9(1)	1(1)	2(1)	−1(1)
O(27)	7(1)	23(3)	8(1)	−1(1)	2(1)	−0(1)
O(3)	13(1)	39(3)	9(1)	1(2)	5(1)	−4(2)
O(38)	6(1)	19(2)	9(1)	2(1)	1(1)	−3(1)
O(39)	10(1)	24(3)	6(1)	1(1)	3(1)	1(1)
O(4)	11(1)	27(3)	11(1)	−2(1)	3(1)	−5(1)
O(45)	10(1)	28(3)	7(1)	1(1)	3(1)	1(1)
O(54′)	7(1)	25(3)	7(1)	2(1)	2(1)	0(1)
O(49)	11(1)	20(3)	6(1)	−2(1)	3(1)	−0(1)
OP(49)	7(1)	15(2)	5(1)	0(1)	1(1)	−0(1)
O(5)	12(1)	26(3)	11(1)	2(1)	5(1)	3(1)
O(56)	6(1)	29(3)	7(1)	4(1)	1(1)	4(1)
OP(56)	7(1)	17(2)	6(1)	1(1)	2(1)	3(1)
O(6)	9(1)	37(3)	10(1)	2(1)	−0(1)	−0(2)
O(67)	6(1)	16(2)	8(1)	−2(1)	1(1)	−1(1)
O(69′)	7(1)	25(3)	8(1)	2(1)	2(1)	−1(1)
O(7)	6(1)	25(3)	16(1)	3(1)	2(1)	8(2)
O(78)	8(1)	17(2)	10(1)	2(1)	4(1)	−3(1)
O(78′)	6(1)	21(3)	8(1)	2(1)	1(1)	−3(1)
OP(78)	5(1)	17(2)	5(1)	1(1)	0(1)	2(1)
O(8)	13(1)	26(3)	13(1)	0(1)	4(1)	−8(1)
O(89)	8(1)	23(3)	7(1)	1(1)	2(1)	2(1)
O(9)	12(1)	37(3)	7(1)	3(1)	1(1)	−3(1)
Na1	60(3)	172(9)	31(2)	4(4)	−0(2)	−16(3)
Na2	324(21)	560(54)	61(7)	185(28)	67(9)	33(14)
Na3	175(11)	349(26)	76(6)	95(14)	62(7)	32(10)
Aq1(1)	163(13)	219(19)	16(3)	149(14)	−13(5)	−8(6)
Aq2(1)	105(10)	371(35)	64(10)	132(16)	16(7)	22(14)
Aq3(1)	44(4)	176(15)	34(4)	10(6)	17(3)	−7(6)
Aq(12)	46(4)	165(15)	45(4)	21(6)	0(3)	43(6)
Aq(13)	22(2)	83(7)	28(3)	−9(3)	4(2)	−5(3)
Aq1(2)	60(5)	106(10)	41(4)	36(6)	7(3)	−9(5)
Aq2(2)	158(15)	108(12)	36(5)	−6(11)	13(7)	6(6)
Aq3(2)	27(3)	38(5)	90(7)	7(3)	−10(3)	−4(5)
Aq4(2)	33(3)	85(8)	38(3)	28(4)	−8(2)	3(4)
Aq1(3)	78(7)	119(13)	260(22)	60(8)	118(11)	90(14)
Aq2(3)	24(2)	175(13)	22(3)	8(4)	2(2)	−13(5)
Aq3(3)	116(12)	323(28)	32(5)	−8(15)	31(6)	−42(10)

synthesis. A least squares refinement at this stage gave a conventional R-value of 0.52. A Fourier synthesis based on these atoms gave the positions of the remaining Mo-atoms and the R-value decreased to 0.26. In a second Fourier synthesis the positions of the phosphorus and oxygen atoms belonging to the $Mo_{18}P_2O_{62}{}^{6-}$-group could be located. The positions of the sodium and water oxygen atoms, were finally obtained from numerous successive Fourier and difference Fourier syntheses.

The positional parameters and anisotropic temperature factors for the atoms were refined by full-matrix least squares methods, a final R-value of 0.040 being obtained, $R = \sum||F_o| - |F_c||/\sum|F_o|$. The atomic scattering factors used for molybdenum were those given for Mo^{3+} by Cromer and Waber,[6] for phosphorus those given for P by Hanson, Herman, Lea and Skillman,[7] and for sodium and oxygen the values for Na^+ and O^- in International Tables. Account was taken of the real part of the dispersion correction. A weighting scheme according to Cruickshank was applied:

$\omega = 1/(a + |F_o| + c|F_o|^2 + d|F_o|^3)$ where the values of the constants were $a = 600$, $c = 0.0001$ and $d = 0$.

Final atomic coordinates, vibrational parameters, and corresponding standard deviations are given in Tables 1 and 2. The structure factor table is available from the author on request. The difference Fourier synthesis based on the listed parameters showed no anomalies. No attempts were made to locate hydrogen atoms.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure is built up from $Mo_{18}P_2O_{62}{}^{6-}$-anions, Na^+-ions and H_2O-molecules. Two of the Na^+-ions act as links in $O-Na-O$-bridges between adjacent groups and in this way layers parallel to the yz-plane are formed. The third Na^+-ion connects these layers by $O-Na-H_2O-Na-O$ linkages.

The $Mo_{18}P_2O_{62}{}^{6-}$-group. This group consists of two enneamolybdomonophosphate groups joined together by the sharing of six oxygen atoms. A detailed description of the Mo_9PO_{34}-group has been given in an earlier paper [2] and will only be outlined briefly here. It consists of

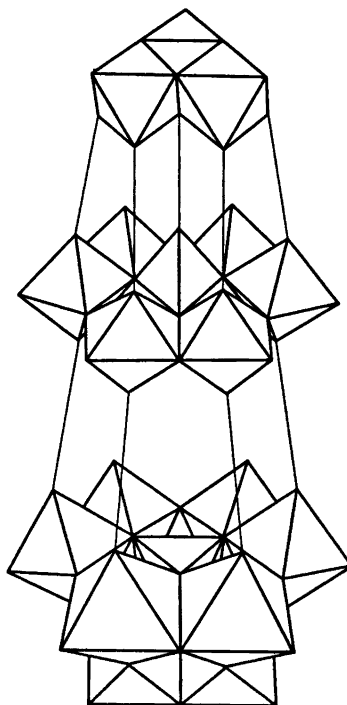*Fig. 1.* The coupling of the eighteen MoO_6-octahedra and the two PO_4-tetrahedra in the $Mo_{18}P_2O_{62}{}^{6-}$-group. For clarity the figure is idealized.

a central PO_4-tetrahedron sharing corners with nine MoO_6-octahedra. Three of these octahedra form a compact group by sharing edges and the remaining six octahedra form a zigzag ring by alternately sharing edges and corners (Fig. 1). The six MoO_6-octahedra forming the ring have one unshared oxygen each pointing in approximately the same direction (perpendicular to the plane of the ring). On forming the $Mo_{18}P_2O_{62}{}^{6-}$-group, these oxygens are shared with the corresponding oxygens from another Mo_9PO_{34}-group as outlined in Fig. 1. Eighteen of the oxygen atoms in the group are unshared, one per octahedron. The symmetry in the group is a two-fold rotation axis (parallel to the b-axis) but the deviations from the symmetry $\bar{6}$ are rather small. Distances and angles between the Mo and P atoms in the group are given in Table 3. The $Mo-Mo$ distances vary between 3.35 and 3.39 Å in edge-sharing MoO_6-octahedra. There is a significant difference between these distances in the compact group (3.386 − 3.388 Å)

Table 3. Distances (Å) and angles (degrees) within the $Mo_{18}P_2O_{62}{}^{6-}$-group. The designation of the atoms is explained in Table 1. The estimated standard deviations, given in parentheses, refer to the last decimal place given.

Mo, P					
Mo1 – Mo2	3.388(1)		P – Mo1	3.530(2)	
Mo1 – Mo3	3.387(1)		P – Mo2	3.535(2)	
Mo1 – Mo4	3.818(1)		P – Mo3	3.503(2)	
Mo1 – Mo5	3.664(1)		P – Mo4	3.510(2)	
Mo2 – Mo3	3.386(1)		P – Mo5	3.459(2)	
Mo2 – Mo6	3.819(1)		P – Mo6	3.511(2)	
Mo2 – Mo7	3.676(1)		P – Mo7	3.467(2)	
Mo3 – Mo8	3.816(1)		P – Mo8	3.514(2)	
Mo3 – Mo9	3.667(1)		P – Mo9	3.460(2)	
Mo4 – Mo9	3.345(1)		P – P	4.154(3)	
Mo4 – Mo5	3.662(1)		Mo1 – Mo2 – Mo3	60.01(2)	
Mo4 – Mo5'	3.832(1)		Mo2 – Mo3 – Mo1	60.02(2)	
Mo5 – Mo6	3.348(1)		Mo3 – Mo1 – Mo2	59.96(2)	
Mo6 – Mo7	3.658(1)		Mo4 – Mo5 – Mo6	119.15(2)	
Mo6 – Mo9'	3.823(1)		Mo5 – Mo6 – Mo7	117.57(3)	
Mo7 – Mo8	3.349(1)		Mo6 – Mo7 – Mo8	119.00(2)	
Mo7 – Mo8'	3.841(1)		Mo7 – Mo8 – Mo9	117.46(2)	
Mo8 – Mo9	3.668(1)		Mo8 – Mo9 – Mo4	119.16(3)	
			Mo9 – Mo4 – Mo5	117.51(2)	

MoO₆-octahedra

	O(1)	O(13)	O(12)	O(14)	O(15)	OP(123)
Mo1	1.689(5)	1.841(6)	2.034(5)	1.775(5)	2.057(5)	2.404(5)
O(1)		2.730(8)	2.846(8)	2.717(7)	2.898(8)	
OP(123)		2.636(7)	2.633(7)	2.879(7)	2.911(7)	
O(12)		2.678(8)			2.599(7)	
O(14)		2.764(7)			2.603(7)	
O(1) – Mo1-		101.2(3)	99.3(2)	103.3(2)	100.9(2)	
OP(123) – Mo1-		75.5(2)	72.3(2)	85.7(2)	81.1(2)	
O(12) – Mo1-		87.3(2)			78.9(2)	
O(14) – Mo1-		99.7(2)			85.2(2)	

	O(2)	O(26)	O(12)	O(27)	O(23)	OP(123)
Mo2	1.691(5)	1.793(5)	1.832(5)	2.073(5)	2.027(5)	2.398(4)
O(2)		2.725(7)	2.732(8)	2.910(7)	2.872(8)	
OP(123)		2.878(7)	2.633(7)	2.907(7)	2.599(7)	
O(12)		2.771(8)			2.669(7)	
O(27)		2.610(7)			2.610(8)	
O(2) – Mo(2)-		102.9(3)	101.6(3)	100.8(2)	100.8(3)	
OP(123) – Mo2-		85.4(2)	75.7(2)	80.8(2)	71.4(2)	
O(12) – Mo2-		99.7(2)			87.4(2)	
O(27) – Mo2-		84.6(2)			79.1(2)	

	O(3)	O(13)	O(23)	O(39)	O(38)	OP(123)
Mo3	1.679(6)	2.048(5)	1.829(5)	2.051(5)	1.775(5)	2.366(5)
O(3)		2.781(8)	2.735(8)	2.833(8)	2.737(8)	
OP(123)		2.636(7)	2.599(7)	2.910(7)	2.869(7)	
O(23)		2.668(7)			2.763(7)	
O(39)		2.627(7)			2.603(7)	
O(3) – Mo3-		96.1(3)	102.4(3)	98.4(3)	104.8(3)	
OP(123) – Mo3-		72.9(2)	75.3(2)	82.1(2)	86.4(2)	
O(23) – Mo3-		86.8(2)			100.1(2)	
O(39) – Mo3-		79.7(2)			85.4(2)	

Table 3. Continued.

	O(4)	O(45)	O(14)	O(54')	O(49)	OP(49)
Mo4	1.684(6)	1.874(6)	2.138(5)	1.752(5)	1.922(5)	2.325(5)
O(4)		2.768(8)	2.726(7)	2.685(7)	2.698(8)	
OP(49)		2.850(7)	2.806(7)	2.898(7)	2.557(7)	
O(14)		2.601(7)			2.680(7)	
O(54')		2.617(8)			2.744(7)	
O(4)−Mo4-		102.0(3)	90.2(2)	102.8(3)	96.7(3)	
OP(49)−Mo4-		84.8(2)	77.8(2)	89.5(2)	73.3(2)	
O(14)−Mo4-		80.5(2)			82.4(2)	
O(54')−Mo4-		95.9(2)			96.5(2)	

	O(5)	O(56)	O(15)	O(54')	O(45)	OP(56)
Mo5	1.676(6)	1.902(5)	1.784(5)	2.122(5)	1.894(5)	2.344(5)
O(5)		2.721(8)	2.707(8)	2.735(7)	2.799(8)	
OP(56)		2.549(7)	2.888(7)	2.833(7)	2.823(7)	
O(15)		2.775(7)			2.655(7)	
O(54')		2.677(7)			2.693(7)	
O(5)−Mo5-		98.8(3)	102.9(3)	91.4(2)	103.1(3)	
OP(56)−Mo5-		72.9(2)	87.7(2)	78.6(2)	82.8(2)	
O(15)−Mo5-		97.6(2)			92.4(2)	
O(54')−Mo5-		83.2(2)			81.1(2)	

	O(6)	O(67)	O(26)	O(69')	O(56)	OP(56)
Mo6	1.697(6)	1.889(5)	2.119(5)	1.758(5)	1.929(5)	2.311(5)
O(6)		2.787(8)	2.736(8)	2.695(7)	2.723(8)	
OP(56)		2.852(7)	2.780(7)	2.884(7)	2.549(7)	
O(26)		2.619(7)			2.671(7)	
O(69')		2.699(7)			2.743(7)	
O(6)−Mo6-		101.9(3)	90.9(2)	102.5(3)	97.1(3)	
OP(56)−Mo6-		84.9(2)	77.6(2)	89.2(2)	73.3(2)	
O(26)−Mo6-		81.4(2)			82.4(2)	
O(69')−Mo6-		95.4(2)			96.0(2)	

	O(7)	O(67)	O(27)	O(78')	O(78)	OP(78)
Mo7	1.680(6)	1.882(5)	1.778(5)	2.123(5)	1.891(5)	2.356(5)
O(7)		2.767(7)	2.716(8)	2.736(7)	2.741(8)	
OP(78)		2.810(7)	2.897(7)	2.820(7)	2.556(7)	
O(27)		2.652(7)			2.767(7)	
O(78')		2.595(7)			2.661(7)	
O(7)−Mo7-		101.8(3)	103.5(2)	91.3(2)	100.1(3)	
OP(78)−Mo7-		82.2(2)	87.8(2)	77.8(2)	73.1(2)	
O(27)−Mo7-		92.8(2)			87.8(2)	
O(78')−Mo7-		80.5(2)			82.8(2)	

	O(8)	O(78)	O(38)	O(78')	O(89)	OP(78)
Mo8	1.690(6)	1.934(5)	2.140(5)	1.759(5)	1.887(5)	2.322(5)
O(8)		2.727(8)	2.757(7)	2.681(8)	2.783(8)	
OP(78)		2.556(7)	2.794(7)	2.820(7)	2.848(7)	
OP(38)		2.679(7)			2.620(7)	
O(78')		2.661(7)			2.691(7)	
O(8)−Mo8-		97.3(3)	91.3(2)	102.0(3)	102.0(3)	
OP(78)−Mo8-		73.2(2)	77.4(2)	89.6(2)	84.5(2)	
O(38)−Mo8-		82.1(2)			80.9(2)	
O(78')−Mo8-		97.2(2)			95.1(2)	

Table 3. Continued.

	O(9)	O(49)	O(39)	O(69')	O(89)	OP(49)
Mo9	1.674(6)	1.903(5)	1.799(5)	2.108(5)	1.891(5)	2.348(5)
O(9)		2.729(8)	2.710(8)	2.721(8)	2.794(8)	
OP(49)		2.557(7)	2.903(7)	2.834(7)	2.810(7)	
O(39)		2.778(7)			2.663(7)	
O(69')		2.680(7)			2.605(7)	
O(9) – Mo9-		99.3(3)	102.6(3)	91.3(2)	103.1(3)	
OP(49) – Mo9-		73.1(2)	87.8(2)	78.8(2)	82.3(2)	
O(39) – Mo9-		97.2(2)			92.4(2)	
O(69') – Mo9-		83.7(2)			81.1(2)	

PO_4-tetrahedron

	OP(49)	OP(56)	OP(78)	OP(123)
P	1.528(5)	1.538(5)	1.528(5)	1.557(5)
OP(49)		2.530(7)	2.517(6)	2.499(6)
OP(56)			2.525(7)	2.504(7)
OP(78)				2.489(6)
OP(49) – P-		111.2(3)	110.9(3)	108.2(3)
OP(56) – P-			110.8(3)	108.0(3)
OP(78) – P-				107.5(3)

and in the ring of six MoO_6-octahedra (3.345 – 3.349 Å). A similar difference was also found in the structure of $Na_3H_6Mo_9PO_{34}(H_2O)_{12-13}$. In corner-sharing there are four different types of Mo – Mo distance:

(i) 3.66 – 3.67 Å in the zigzag rings;
(ii) 3.66 – 3.68 Å between the Mo-atoms in the compact group and three of the Mo-atoms in the zigzag ring;
(iii) 3.82 Å between the Mo-atoms in the compact group and the remaining three Mo-atoms in the zigzag ring;
(iv) 3.82 – 3.84 Å between the two zigzag rings.

The Mo – P distances vary between 3.46 and 3.54 Å while the P – P distance is 4.15 Å. A stereoscopic view of the $Mo_{18}P_2O_{62}{}^{6-}$-group is given in Fig. 2.
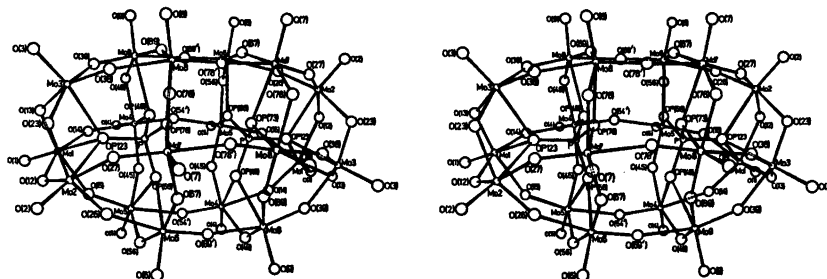
The MoO_6-octahedra. The MoO_6-octahedra are somewhat distorted from an ideal octahedron and the Mo-O distances can be divided into four groups according to the number of atoms that the oxygen atoms is coordinated to:

(i) Coordinated to one Mo-atom; the distances vary between 1.67 and 1.70 Å;
(ii) coordinated to two Mo-atoms; the distances vary between 1.75 and 2.14 Å;
(iii) coordinated to P and to two Mo-atoms; the distances vary between 2.31 and 2.36 Å;
(iv) coordinated to P and to three Mo-atoms; the distances vary between 2.37 and 2.40 Å.

This trend of increasing distances with increasing coordination numbers has also been found in other structures.[3,4]

As mentioned above, the six MoO_6-octahedra

Fig. 2. Stereoscopic view of the $Mo_{18}P_2O_{62}{}^{6-}$-group.

forming a ring in the Mo_9PO_{34}-group have one unshared oxygen each with the $Mo-O$ direction approximately perpendicular to the plane of the ring. In the structure of $Na_3H_6Mo_9PO_{34} \cdot (H_2O)_{12-13}$ the distances from the Mo-atoms to these oxygens were alternately short and long. The short distance given was 1.70 Å, which is a normal distance for $Mo-O$ (unshared), while the long distance was 2.21 Å, the lengthening being ascribed to protonization of the oxygen atom (if two protons are attached we have a Mo-coordinated water molecule). In the $Mo_{18}\text{-}P_2O_{62}$-group these distances are still alternately short and long but the difference is reduced and the mean values found here are 1.76 and 2.12 Å, respectively. In the dimerization reaction of the two Mo_9PO_{34} groups the oxygens with short $Mo-O$ distances in one group approach the oxygens with long distances in the other group and vice versa. The six $Mo-Mo$ distances are practically equal (3.82 − 3.84 Å).

The sodium ions and water molecules. In the structure there are three kinds of crystallographically different sodium ions, Na1, Na2, and Na3. Each of these ions is always coordinated to two $Mo_{18}P_2O_{62}^{6-}$-oxygens, Na1 and Na2 to oxygens in two different groups, and Na3 to oxygens in one and the same group

Table 4. Sodium − oxygen distances (Å). The designation of the atoms is explained in Table 1. The estimated standard deviations are given in parentheses and refer to the last decimal place given.

Na1 − Aq1(1)	2.22(2)
Na1 − Aq2(1)	2.78(3)
Na1 − Aq3(1)	2.41(2)
Na1 − Aq(12)	2.58(2)
Na1 − Aq(13)	2.51(1)
Na1 − O(3)	2.64(1)
Na1 − O(6)	2.53(1)
Na2 − Aq1(2)	2.59(4)
Na2 − Aq2(2)	2.27(4)
Na2 − Aq3(2)	2.56(3)
Na2 − Aq4(2)	3.14(4)
Na2 − Aq(12)	2.40(4)
Na2 − O(4)	3.05(4)
Na2 − O(8)	2.72(4)
Na3 − Aq1(3)	2.15(4)
Na3 − Aq2(3)	2.34(3)
Na3 − Aq3(3)	2.42(3)
Na3 − Aq(13)	2.57(3)
Na3 − O(7)	2.60(2)
Na3 − O(8)	2.98(3)

(Table 4). The $O-Na1-O$ bridges connect symmetry related groups in the z-direction and in this way a zigzag chain is formed. These chains are then connected by $O-Na2-O$ bridges in the y-direction thus forming infinite layers parallel to the yz-plane. Finally the layers are coupled by $O-Na3-H_2O-Na1-O$-linkages. In all there are ten Na^+-ions coordinated to the group but since eight of these are shared between two groups this implies that the charge has been neutralized by the coordinated Na^+-ions.

Besides bonding to two group-oxygens each sodium ion is also surrounded by water oxygen atoms. In earlier determinations of similar structures the Na^+-ions have always coordinated six oxygen atoms but in this investigation seven coordination is also found.

Na3 has the ordinary octahedral oxygen coordination, while the seven oxygen atoms around Na1 and Na2 form no distinct polyhedron. Two of the water oxygens, Aq(13) and Aq(12) are shared between two Na^+-ions. All water molecules are sodium coordinated.

The PO_4-tetrahedron. It can be seen from the distances and angles in Table 3 that the PO_4-tetrahedron is not far from regular. The $P-O$ distances are in the range 1.53 − 1.56 Å and the different $O-P-O$ angles vary between 108 and 111°. It can also be seen that the oxygen OP(123), which is coordinated to three Mo-atoms gives the longest distance and is one of the oxygen atoms in the smallest angles. The values given above and the values of the $O-O$ distances (2.49 − 2.53 Å) agree well with distances found in other compounds containing phosphate groups.

REFERENCES

1. Pettersson, L. *Chem. Scr. Accepted for publication.*

2. Strandberg, R. *Acta Chem. Scand. A 28* (1974) 217.
3. d'Amour, H. and Allmann, R. *Naturwissen-schaften 61* (1974) 31.
4. Hedman, B. *Acta Chem. Scand. 27* (1973) 3335.
5. Dawson, B. *Acta Crystallogr. 6* (1953) 113.
6. Cromer, D. T. and Waber, J. T. *Acta Crystallogr. 18* (1965) 104.
7. Hanson, H. P., Herman, F., Lea, J. D. and Skillman, S. *Acta Crystallogr. 17* (1964) 1040.