Multicomponent Polyanions. 18. A Neutron Diffraction Study of Na$_3$Mo$_9$PO$_{31}$(OH$_2$)$_3$.12—13H$_2$O, a Compound Containing 9-Molybdomonophosphate Anions with Molybdenum-coordinated Water Molecules*

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A single crystal neutron diffraction study of Na$_3$Mo$_9$PO$_{31}$(OH$_2$)$_3$.12–13H$_2$O has been made. Full-matrix least-squares refinements based on 1175 independent reflexions resulted in an R-value of 0.091. The structure contains the Mo$_9$PO$_{31}$(OH$_2$)$_3^{3-}$ anion, which is an end member in a proton-series of 9:1-molybdophosphates.

The results of the investigation show that the hydrogen atoms are attached in pairs to Mo-coordinated oxygens of the heteropolyanion. Thus three Mo atoms formally coordinate one water molecule each. This arrangement excludes the possibility of the presence of H$_3$O$^+$ in the structure. The other members of the proton-series are obtained by step-wise emission of one hydrogen per water molecule.

The anions are held together in a three-dimensional framework by hydrogen bonds involving anion and water hydrogen atoms and by O–Na–O links. Large diameter channels along 0,0,z penetrate the framework. These channels are filled with water molecules, most of which are non-structural, giving the crystal a zeolitic character. The hydrogen bonding within the framework is described, and the partly occupied positions found for the water in the channels are given. The total amount of water located accounts for approximately 5 of the 12 to 13 H$_2$O indicated by the formula.

Aqueous equilibrium studies of the H$^+$ – MoO$_4^{2-}$ – HPO$_4^{2-}$ system have shown that (H$^+$)$_p$(MoO$_4^{2-}$)$_q$-

(HPO$_4^{2-}$), complexes are formed. In solutions with [MoO$_4^{2-}$]/[HPO$_4^{2-}$] ~9 a series of complexes with composition (p,9,1), where $p=14$, 15, 16 and 17, dominates.[1,2] In crystallization experiments performed parallel with the equilibrium studies only one crystalline (p,9,1) phase was obtained, Na$_3$H$_6$Mo$_9$PO$_{34}$(H$_2$O)$_{12-13}$. This phase, corresponding to the (17,9,1) complex, was investigated by X-ray methods.[3] The structure was shown to consist of 9-molybdomonophosphate anions connected by Na$^+$ ions. No water molecules could be located with certainty.

In the X-ray investigation, three of the Mo–O distances (crystallographically equivalent) were found to be extremely long, 2.21(1)* Å, for a terminal O atom, i.e. an atom coordinated to only one Mo atom (expected value 1.69–1.73 Å[4,5]). The oxygens were therefore assumed to be protonized with the six hydrogens in the formula situated either as two H$^+$ on each of the three oxygens, or as one H$^+$ on each of the three oxygens and the remaining H$^+$ as H$_3$O$^+$ ions within the structure. The existence of six H$_3$O$^+$ was considered unlikely.

For proton-series of hetero- and isopolyanions of this kind, the presence of oxonium ions has often been assumed, e.g. in H$_3$Mo$_{12}$PO$_{40}$(H$_2$O)$_{29-31}$ (broad-line ^{1}H NMR spectra,[6] single crystal X-ray diffraction[7]). Recently H$_5$O$_2^+$ ions were located in a neutron diffraction study of H$_3$W$_{12}$PO$_{40}$(H$_2$O)$_6$.[8]

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* A preliminary report of this work was presented at the ECM-4, Oxford, 1977 (PII.81).

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

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However, hydrogens have also been found attached to the anions, for example those attached to O atoms shared between Mo and Cr in $Na_3CrMo_6O_{24}H_6 \cdot 8H_2O$[9] or to O atoms coordinated to P in $Na_4H_2Mo_5P_2O_{23}(H_2O)_{10}$.[4]

The present neutron diffraction study was undertaken primarily to determine the positions of the six hydrogens in "$H_6Mo_9PO_{34}^{3-}$" in an attempt to understand how deprotonation occurs when p changes from 17 to 14 in the proton-series. An additional aim of the study was to investigate to what extent the crystal water is ordered or present in a non-structural way in channels. An independent X-ray structure determination of this crystalline phase has been reported,[10,11] but no further information on the hydrogens or crystal water was obtained.

CRYSTAL DATA[3]

$Na_3Mo_9PO_{31}(OH_2)_3 \cdot xH_2O$, $x = 12 - 13$: F.W. = 1729.6 ($x = 12$), space group $P6_3$ (No. 173), $a = 14.248(1)$ Å, $c = 10.83(1)$ Å, $V = 1904.0$ Å^3, $Z = 2$, $D_m = 3.038(3)$ g cm^{-3}, $D_x = 3.02$ ($x = 12$); 3.05 ($x = 13$) g cm^{-3}, μ(neutrons = 0.85 cm^{-1} (determined experimentally).

EXPERIMENTAL

Yellowish single crystals with a hexagonal prismatic form were grown from an aqueous solution by slow evaporation at room temperature. The composition of the solution was as reported previously[3] except that an addition of 10 % ethanol was made in order to avoid the initial formation of a large number of small crystals. The crystal used in the data collection had six boundary faces of the form $\{10\bar{1}0\}$. It was bounded at one end by a small cap and at the other by a rough face which were approximated to $(000\bar{1})$ and (0001), respectively. The crystal volume was 10.3 mm^3. The crystal was sealed in a thin-walled quartz glass tube to prevent it from losing water.

The neutron diffraction data were collected at the Swedish Atomic Energy R2 reactor in Studsvik, using a computer-controlled Hilger & Watts four-circle diffractometer at ~20 °C. The experimental arrangement has been described previously.[12] The flux at the specimen was 1.26×10^6 n cm^{-2} s^{-1} and the wavelength 1.210 Å. Reflexions with all three indices ≥ 0 (1/12 of reciprocal space) and out to $(\sin \theta)/\lambda = 0.693$ Å^{-1} were measured using an $\omega - 2\theta$ step-scan technique. The fluctuations observed in

the intensities of the three standard reflexions monitored at regular intervals throughout the data collection were random and negligible. The values of I and $\sigma_o(I)$ (calculation based on counting statistics) were corrected for Lorentz and absorption effects. The linear absorption coefficient, μ, was determined experimentally to be 0.85 cm^{-1}, which corresponds to a value of 26 barns for the incoherent scattering cross-section for hydrogen. The transmission factor varied from 0.83 to 0.88. Of the 2253 reflexions measured in all, 1862 were unique. Of these, only 1175 reflexions had $F_o^2 \geq 2\sigma_c(F_o^2)$ and 956 reflexions had $F_o^2 \geq 3\sigma_c(F_o^2)$. This may be attributed to the high level of background caused by the large incoherent scattering contribution from the hydrogen atoms.

STRUCTURE REFINEMENT

A three-dimensional difference Fourier synthesis based on the anion Mo, P and O parameters obtained in the X-ray study revealed the positions of the anion H atoms, the Na$^+$ ion and the water O atoms O(Aq1) and O(Aq2), (Figs. 3, 4). In a difference Fourier synthesis with these atoms included, two rather weak minima around each of O(Aq1) and O(Aq2) were interpreted as hydrogens. They were included in the refinement, one at a time, and each caused a significant improvement seen as a reduction in the R-value.[13,14] Unusually high temperature factors and comparatively low amplitudes of the difference Fourier maxima/minima for all atoms in these two water molecules indicated partial vacancies, and the occupancy factors were therefore refined. During the refinements, the hydrogens approached the O position even when the H occupancy factor was varied separately from the O factor. Since the geometries of the water molecules and the bonding situation around them as given from the Fourier synthesis were considered quite reasonable, the H atoms were constrained to give the O – H distances and H – O – H angles found in the synthesis. The H temperature factors were in each molecule constrained to the same values as those for the O atom.

Two additional, partly occupied water O positions were located in the Fourier maps, but their H atoms could not be found. These O atoms were included with isotropic temperature factors. In all, the water found accounts for ~5 of the 12 – 13 crystal water molecules indicated by water analysis and density measurements.[3] The effect of the remaining non-structural water on the intensities

and, hence, on the positional and thermal parameters is difficult to estimate. The largest discrepancies between F_o and F_c were found for weak reflexions and for reflexions at high $(\sin \theta)/\lambda$. Therefore, no comparison will be made between the positional and thermal parameters obtained in the X-ray structure investigation and those obtained in the neutron refinements.

The structure was refined using full-matrix least-squares methods minimizing the function $\Sigma w_i(|F_o|-|F_c|)^2$. Due to the low core memory capacity of the computer, the final refinements were divided into two extensively overlapping blocks. A weighting scheme was applied in which the weights were modified according to $w^{-1}=\sigma^2(F_o)+(0.04F_o)^2$. The presence of extinction was tested both by inclusion of one isotropic extinction parameter and by inclusion of six anisotropic (type I or II) extinction parameters in the refinements *ad modum* Coppens and Hamilton,[15] but no indication of extinction effects was discovered. Final refinements based on the 1175 reflexions with $F_o^2 \geq 2\sigma_c(F_o^2)$ converged with R-values $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|=0.091$ and $R_w=[\Sigma w_i(|F_o|-|F_c|)^2/\Sigma w_i|F_o|^2]^{1/2}=0.100$. The R-value based on reflexions with $F_o^2 \geq 3\sigma_c(F_o^2)$ is 0.079.

In the final cycle the parameter shifts were less than 0.1σ.

The coherent scattering amplitudes used were $\bar{b}_{Mo}=0.660$, $\bar{b}_P=0.510$, $\bar{b}_O=0.575$, $\bar{b}_{Na}=0.351$ and $\bar{b}_H=-0.372$ $(10^{-12}$ cm).[16] Data ·reduction was performed with the programs STUKC and DATAPH on the IBM 1800 and IBM 370/155 computers at the University of Uppsala.[17] All other computations were made with previously described programs[18] on the CD 3300 and CD CYBER 172 computers at the University of Umeå. Final atomic positional and thermal parameters are presented in Table 1. A list of observed and calculated structure factors may be obtained from the author on request.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The $Mo_9PO_{31}(OH_2)_3^{3-}$ anion. The anion is shown in Figs. 1 and 2, and a detailed description of the arrangement of the Mo, P and O atoms may be found in Ref. 3. With the exception of a few minor individual discrepancies, the dimensions of the

Table 1. Fractional atomic coordinates ($\times 10^4$), occupancy factors (for statistically disordered atoms), anisotropic thermal parameters ($\times 10^4$) and, for two water oxygens, isotropic temperature factors ($\mathring{A}^2$). The expression for the anisotropic temperature factor is $\exp[-(\beta_{11}h^2+...+2\beta_{12}hk+...)]$. For the anion O atoms, numbers within parentheses in the symbol denote the Mo atom(s) to which it is bonded.

	x	y	z	occupancy	β_{11}/B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo1	7571(4)	4917(4)	1ᵃ		22(3)	23(3)	22(3)	13(2)	-1(3)	0(3)
Mo2	7200(5)	5996(4)	3215(6)		31(3)	23(3)	44(4)	16(3)	2(4)	-5(4)
Mo3	4646(4)	4020(4)	2638(6)		25(3)	32(3)	24(4)	18(3)	5(3)	-4(3)
P	2/3	1/3	2750(11)		22(4)	22(4)	14(8)	11(2)	0	0
O(1)	8270(5)	5906(6)	-1062(7)		26(4)	33(4)	35(5)	12(3)	0(4)	8(4)
O(11')	7896(5)	3768(5)	- 688(6)		33(4)	24(4)	23(4)	14(3)	5(4)	1(3)
OP(11'1")	2/3	1/3	1310(11)		21(3)	21(3)	25(9)	11(2)	0	0
O(12)	7315(6)	5590(5)	1215(8)		37(4)	26(4)	35(5)	18(3)	6(4)	0(4)
O(13)	8880(5)	5144(5)	1076(7)		26(4)	31(4)	27(5)	14(3)	-3(4)	-3(4)
O1(2)	7741(7)	7322(6)	2830(9)		53(5)	28(4)	65(8)	23(4)	-4(5)	-14(5)
O2(2)	7058(7)	5973(7)	4783(8)		57(6)	55(6)	38(6)	27(5)	-3(5)	-25(5)
O1(23)	8516(5)	5895(6)	3213(7)		25(4)	35(4)	41(5)	19(3)	1(4)	-5(4)
O2(23)	5714(5)	5499(5)	2719(7)		31(4)	29(4)	38(5)	19(3)	0(4)	-2(4)
OP(23)	6300(5)	4117(5)	3195(7)		28(4)	25(3)	29(4)	15(3)	-3(4)	-4(4)
O1(3)	3527(6)	4123(7)	2467(8)		29(4)	55(5)	46(6)	30(4)	4(4)	-7(5)
O2(3)	4611(7)	4260(7)	4671(8)		48(5)	51(6)	35(6)	34(5)	0(4)	-6(5)
H1[O2(3)]	4752(17)	4961(15)	4995(19)		104(17)	72(12)	91(17)	56(13)	-30(15)	-43(13)
H2[O2(3)]	4731(30)	3873(25)	5281(20)		238(40)	153(27)	59(16)	143(30)	-4(21)	2(18)
Na	3390(29)	1716(22)	6753(26)		167(32)	86(18)	124(26)	69(21)	12(24)	8(18)
O(Aq1)	5097(24)	3303(17)	6432(17)	0.67(6)	257(37)	133(20)	93(20)	125(22)	75(18)	58(14)
H1(Aq1)ᵇ	5357(24)	3691(17)	7191(17)	0.67(6)						
H2(Aq1)ᵇ	5367(24)	2801(17)	6391(17)	0.67(6)						
O(Aq2)	2491(16)	2221(20)	5220(18)	0.44(4)	76(15)	121(22)	74(18)	73(16)	12(14)	25(15)
H1(Aq2)ᵇ	2980(16)	2757(20)	4675(18)	0.44(4)						
H2(Aq2)ᵇ	2230(16)	2497(20)	5855(18)	0.44(4)						
O(Aq3)	1793(37)	-250(36)	5830(46)	0.27(4)	4.4(8)					
O(Aq4)	1797(34)	303(35)	7326(43)	0.37(4)	6.1(8)					

a, Arbitrarily fixed.

b, Atomic, occupancy and thermal parameters constrained to those of the corresponding oxygen atom; see text.

anion calculated from the neutron data parameters (Table 2) do not differ significantly from those obtained in the X-ray study.[3] The hydrogens are attached in pairs to a single O atom, [O2(3)], in every second octahedron in the ring of six octahedra in the anion, cf. Figs. 1 and 2. This coordination of water molecules to Mo atoms induces a non-planar arrangement of the Mo2 and Mo3 atoms in the ring, with 'water-free' Mo2 displaced ~ 0.62 Å outside the Mo3 atoms. The Mo$-$OH$_2$ distance is 2.232(11) Å, which may be compared to the Mo$-$OH$_2$ distances found in $MoO_3.2H_2O^{19}$ [2.274(2), 2.276(2), 2.290(2) and 2.294(2) Å] and α-$MoO_3.H_2O^{20}$ [2.346(7) Å]. In the coordinated water molecules the O$-$H distances are 0.98(2) and 0.93(3) Å with an H$-$O$-$H angle of 110(2)°, i.e. the expected values for ordinary water molecules.[21]
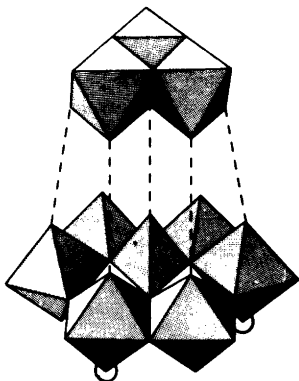

Fig. 1. The $Mo_9PO_{31}(OH_2)_3^{3-}$ anion depicted using idealized polyhedra. The rings denote the positions for two of the three water molecules.
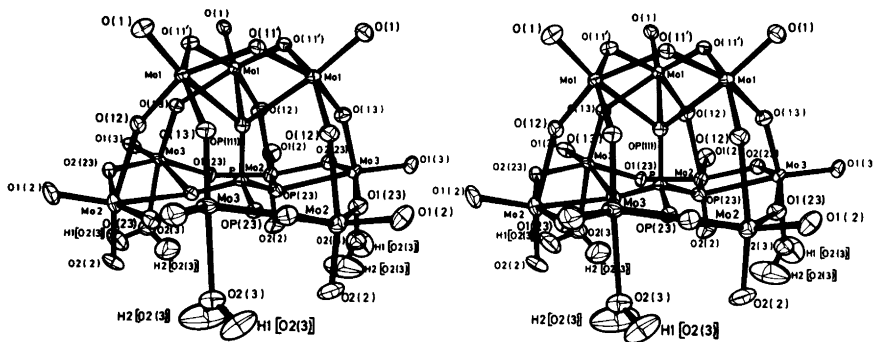
As mentioned above, the equilibrium studies established the series of (17,9,1), (16,9,1), (15,9,1) and (14,9,1) complexes.[1] However, crystals could be obtained for only the (17,9,1) complex. For the others large-angle X-ray scattering measurements were made. Solutions containing predominantly the (16,9,1) or (15,9,1) complexes were investigated for both the $H^+ - MoO_4^{2-} - HPO_4^{2-}$ system[22] and the analogous $H^+ - MoO_4^{2-} - HAsO_4^{2-}$ system,[23,24] while the (14,9,1) complex was investigated only for the latter system. The investigations clearly showed that the basic anion structure (Mo, P/As and O atoms) for the complexes is the same as that in the $Mo_9PO_{31}(OH_2)_3^{3-}$ anion with minor changes in the dimensions. Since the six hydrogens have been shown in the present study to be attached to the anion, it may be concluded that three of them are emitted one by one to obtain (16,9,1), (15,9,1) and (14,9,1), which have five, four and three hydrogens, respectively. Further removal of hydrogens appears to destabilize the anion which decomposes forming pentamolybdodiphosphates and heptamolybdates.[1]

The dimerization in solution[1] according to $2Mo_9PO_{31}(OH_2)_3^{3-} \rightleftharpoons Mo_{18}P_2O_{62}^{6-} + 6H_2O$ causes a removal of the Mo-coordinated water molecules. The structure of the dimer has been determined in X-ray investigations of $Na_6Mo_{18}P_2O_{62}(H_2O)_{24}^{25}$ and $Na_4H_2Mo_{18}P_2O_{62}.nH_2O, n \sim 20.^{11}$ In the latter investigation the presence of two H_3O^+ ions was suggested. There is, however, great similarity in the two structures, most of the cell and atomic parameters being the same within statistical errors except for one Na and two water O atoms, which are missing in the latter determination. It is therefore suggested that this phase is the same as the one in Ref. 25.

Fig. 2. A stereoscopic view of the $Mo_9PO_{31}(OH_2)_3^{3-}$ anion. The thermal ellipsoids are scaled to include 50 % probability.[29]

Table 2. Distances (Å) and angles (°) within the $Mo_9PO_{31}(OH_2)_3^{3-}$ anion. The superscipts refer to the following symmetry operations: (^{I}) $1-y,x-y,z$; (^{II}) $1+y-x,1-x,z$.

	Neutron	X-ray		Neutron	X-ray
Mo1 – Mo1^{II}	3.396(9)	3.411(1)	Mo1^{II} – Mo1 – Mo2	116.46(10)	116.50(4)
Mo1 – Mo2	3.946(8)	3.933(3)	Mo1^I – Mo1 – Mo3^{II}	118.00(12)	118.00(4)
Mo1 – Mo3^{II}	3.680(7)	3.690(3)	Mo3 – Mo2 – Mo3^{II}	116.84(22)	117.23(4)
Mo2 – Mo3	3.362(8)	3.364(1)	Mo2 – Mo3 – Mo2^I	117.01(22)	117.04(4)
Mo2 – Mo3^{II}	3.696(8)	3.703(1)			
P – Mo1	3.565(11)	3.564(11)			
P – Mo2	3.513(6)	3.516(2)			
P – Mo3	3.475(5)	3.486(1)			
Mo1 – O(1)	1.703(8)	1.713(9)	Mo3 – O1(3)	1.684(9)	1.697(9)
– O(11')	2.052(8)	2.080(7)	– O2(3)	2.232(11)	2.213(10)
– O(11')^I	1.821(8)	1.826(8)	– O(13)^I	1.799(10)	1.813(9)
– O(12)	1.770(8)	1.778(8)	– O1(23)^I	1.849(9)	1.825(8)
– O(13)	2.082(8)	2.075(8)	– O2(23)	1.886(8)	1.886(7)
– OP(11'1")	2.419(8)	2.419(9)	– OP(23)	2.369(9)	2.375(7)
Mo2 – O1(2)	1.697(9)	1.708(9)	P – OP(11'1")	1.560(17)	1.567(20)
– O2(2)	1.709(11)	1.695(12)	– OP(23)	1.528(7)	1.532(8)
– O(12)	2.268(11)	2.258(9)			
– O1(23)	1.952(9)	1.971(7)	O2(3) – H1[O2(3)]	0.98(2)	
– O2(23)	1.942(9)	1.942(8)	– H2[O2(3)]	0.93(3)	
– OP(23)	2.319(8)	2.312(7)			

Hydrogen bonding in the crystal structure. The anions are connected to a framework, illustrated in Fig. 3, through electrostatic O – Na – O links and hydrogen bonds O2(3) – H1[O2(3)]...O(13)^{II}. The framework contains cavities located between anions which are one unit cell apart in the z-direction. The cavities are filled with Aq1 molecules hydrogen bonded to O2(3). There are no O atoms available as possible acceptors within hydrogen bond distances from O(Aq1). The hydrogens are, however,
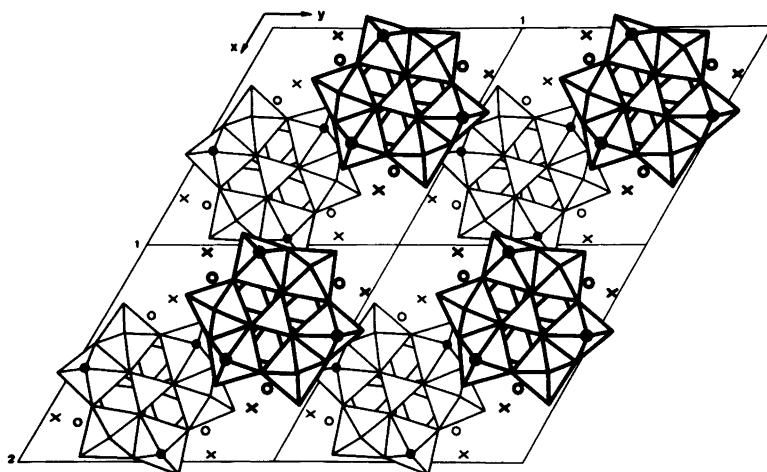

Fig. 3. The framework of anions around the 0,0,z channels. The anions are drawn as linked polyhedra. Filled circles = Mo-coordinated waters; open circles = Na$^+$ ions; crosses = Aq2 waters; thin lines = atoms at z; heavy lines = atoms at z + 1/2.
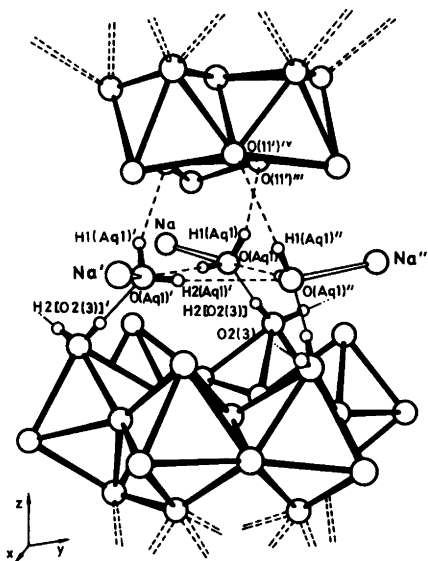
Fig. 4. The arrangement of Aq1 waters in the cavities between anions one unit cell apart along z. The anions are drawn as linked polyhedra. Thin full lines = hydrogen bonds; single dashed lines = direction to nearest neighbour O atom for H(Aq1). The superscripts refer to the following symmetry operations: (^{I}) $1-y,x-y,z$; (^{II}) $1+y-x,1-x,z$; (^{III}) $1-y$, $x-y,1+z$; (^{IV}) $x,y,1+z$.

directed towards O(11′), 3.44(2) Å, and towards the O atom of a symmetry-related Aq1 molecule,
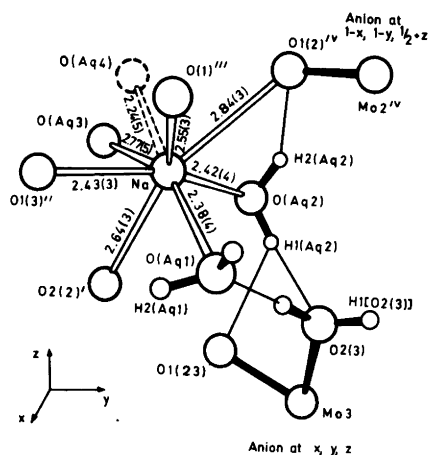

Fig. 5. The sodium-oxygen arrangement with bond distances (Å), and hydrogen bonds involving Aq2. (Aq3 and Aq4 are not present simultaneously; see text.) The superscripts refer to the following symmetry operations: (^{I}) $1-y,x-y,z$; (^{II}) $y,y-x$, $1/2+z$; (^{III}) $1-y,x—y,1+z$; (^{IV}) $1-x,1-y,1/2+z$.

3.84(5) Å away, *cf.* Fig. 4. The presence of an Na$^+$ ion in the opposite direction completes a tetrahedral coordination around O(Aq1). The occupancy factor for Aq1 is 0.67(6), *i.e.* ~two molecules are present around the three-fold axis. This is probably caused by the lack of hydrogen bond acceptors and

Table 3. Distances (Å) and angles (°) within the hydrogen bond system. Values for the atoms closest to O(Aq1) have also been included despite the fact that they exceed the hydrogen bond range. The geometry of Aq1 and Aq2 has been constrained; see text. The superscripts refer to the following symmetry operations: (^{I}) $1-y,x-y,z$; (^{II}) $y,1+y-x,1/2+z$; (^{III}) $1-y,x-y,1+z$; (^{IV}) $1-x,1-y,1/2+z$.

	H1−O	O−H2	H1−H2	∠H1−O−H2
H1[O2(3)]−O2(3)−H2[O2(3)]	0.98(2)	0.93(3)	1.57(4)	110(2)
H1(Aq1)−O(Aq1)−H2(Aq1)	0.96(3)	0.97(3)	1.54(3)	107(3)
H1(Aq2)−O(Aq2)−H2(Aq2)	0.94(3)	0.96(3)	1.59(3)	114(3)

	H···O	O···O	∠O−H···O
O2(3)−H1[O2(3)]···O(13)^{II}	2.02(2)	2.98(1)	165(2)
O2(3)−H2[O2(3)]···O(Aq1)	1.71(4)	2.63(2)	173(3)
O(Aq1)−H1(Aq1)···O(11′)^{III}	2.54(2)	3.44(2)	157(2)
O(Aq1)−H2(Aq1)···O(Aq1)^I	2.89(4)	3.84(5)	165(3)
O(Aq2)−H1(Aq2)···O1(23)^i	2.33(2)	3.00(2)	128(2)
O(Aq2)−H1(Aq2)···O2(3)	2.24(2)	3.02(2)	140(2)
O(Aq2)−H2(Aq2)···O1(2)^{IV}	2.15(2)	2.96(2)	141(2)

might explain the observed variation in the cell parameter c.[3]

Additional hydrogen bonds in the framework are formed via the Aq2 molecules. They are situated in the outermost part of channels through the framework around $0,0,z$ (Fig. 3) and are also coordinated to Na^+. The atomic positions are only partly occupied and the waters probably enter the channels in a statistical way as non-structural water. Also rotational behaviour of the Aq2 molecule might be induced by non-structural channel water giving a variety of possible hydrogen bond acceptors. The hydrogen positions found indicate for H1(Aq2) a bifurcated hydrogen bond to O2(3) and O1(23)^I, and for H2(Aq2) a bond to O1(2)^{IV}. The Aq2 molecules in this way connect adjacent anions in the z-direction in the manner shown schematically to the right in Fig. 5. Hydrogen bond distances and angles are given in Table 3.

The sodium-oxygen arrangement. The Na^+ ion coordinates seven O atoms, of which four are anion and three are water O atoms. The anion oxygens are donated by four different anions which implies that there are several different $O-Na-O$ links in the framework. The water positions are all partly occupied. In addition the O(Aq3)$-$O(Aq4) distance is too short (1.80 Å) for the molecules to be present simultaneously. The resulting coordination around Na^+, assuming full occupation on Aq1, Aq2 and one of Aq3 or Aq4, is irregular with the $Na-O$ distances varying between 2.24 and 2.84 Å, cf. Fig. 5.

The channel. The channel is limited by atoms such as O(1), O1(3), O(12) and O1(23) forming an approximate cylinder along $0,0,z$ with a diameter of ~ 10.6 Å. The channel passages are narrower, however, at the two z-levels in each cell where the O1(2) oxygens protrude into the channel, cf. Fig. 3. Here the $O-O$ distance is ~ 6.3 Å, with the diameter of a circle through the O positions of ~ 7.3 Å. If the average radius of an O atom is considered to be approximately 1.4 Å,[26] the open passage in the channel would have a cross-section of ~ 48 Å^2 and, at the narrow section, ≥ 16 Å^2, the inequality sign being used as there is additional space outside the circle.

A rough estimation of the channel volume would then give $\sim 22-24$ Å^3/water molecule for the ~ 20 channel waters in each unit cell. This may be compared to a value of ~ 25 Å^3 for the water and Na^+ in the zeolite phillipsite[27] and to $\sim 32-33$ Å^3 for ice structures, for example. In phillipsite the channel

cross-sections are ~ 9 and 12 Å^2, and it might be assumed that the wider channel in the present structure allows a more dense packing of water.

As mentioned above, most of the water in the channel is non-structural. Indications for three partly occupied water positions were found, but for two, O(Aq3) and O(Aq4), only the presence of one at a time is possible due to the short internal distance. In thermobalance analyses the loss of water upon heating was seen to first occur in three steps, while the temperature was increased to ~ 115 °C in which a total of ~ 10.2 H$_2$O were emitted (probably channel water). An additional ~ 2.4 H$_2$O was gradually emitted with a further increase of temperature to ~ 250 °C. At 400 °C the samples retained their hexagonal prismatic form and yellowish colour but displayed large cracks along z. At ~ 700 °C they decomposed rather quickly.

This type of channel containing non-structural water has also been reported for other structures containing large, compact heteropolyanions, e.g. in $H_3Mo_{12}PO_{40}(H_2O)_{29-31}$[7] and $(NH_4)_7Na_2-[H_2GaW_{11}O_{40}].15H_2O$.[28]

REFERENCES

1. Pettersson, L. *Chem. Scr.* 7 (1975) 145.
2. Pettersson, L. *Equilibrium and Structure Studies of Aqueous Three Component Polyanion Complexes Formed in the Systems $H^+-MoO_4^{2-}-HPO_4^{2-}$, $H^+-MoO_4^{2-}-HAsO_4^{2-}$ and $H^+-MoO_4^{2-}-(D-)mannitol$,* Diss., University of Umeå, Umeå 1974.
3. Strandberg, R. *Acta Chem. Scand. A 28* (1974) 217.
4. Hedman, B. *Acta Chem. Scand. 27* (1973) 3335.
5. Hedman, B. *Acta Crystallogr. B 33* (1977) 3083.
6. Wada, T. *C. R. Acad. Sci. Ser. C 259* (1964) 553.

7. Strandberg, R. *Acta Chem. Scand. A 29* (1975) 359.
8. Brown, G. M., Noe-Spirlet, M.-R., Busing, W. R. and Levy, H. A. *Acta Crystallogr. B 33* (1977) 1038.
9. Perloff, A. *Inorg. Chem. 9* (1970) 2228.
10. d'Amour, H. and Allman, R. *Naturwissenschaften 61* (1974) 31.
11. d'Amour, H. *Acta Crystallogr. B 32* (1976) 729.
12. Tellgren, R., Ramanujam, P. S. and Liminga, R. *Ferroelectrics 6* (1974) 191.
13. Hamilton, W. C. *Acta Crystallogr. 18* (1965) 502.
14. Pawley, G. S. *Acta Crystallogr. A 26* (1970) 691.
15. Coppens, P. and Hamilton, W. C. *Acta Crystallogr. A 26* (1970) 71.
16. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. IV, pp. 270 – 271.
17. Lundgren, J.-O. *Crystallographic Computer Programs*, UUIC-B13-4-03, Institute of Chemistry, University of Uppsala, Uppsala 1976.
18. Antti, B.-M. *Acta Chem. Scand. A 30* (1976) 24.
19. Åsbrink, S. and Brandt, B. G. *Chem. Scr. 1* (1971) 169.
20. Böschen, I. and Krebs, B. *Acta Crystallogr. B 30* (1974) 1795.
21. Ferraris, G. and Franchini-Angela, M. *Acta Crystallogr. B 28* (1972) 3572.
22. Johansson, G., Pettersson, L. and Ingri, N. *Acta Chem. Scand. A 32* (1978) 407.
23. Pettersson, L. *Acta Chem. Scand. A 29* (1975) 677.
24. Johansson, G., Pettersson, L. and Ingri, N. *Acta Chem. Scand. Submitted for publication.*
25. Strandberg, R. *Acta Chem. Scand. A 29* (1975) 350.
26. Pauling, L. *The Nature of the Chemical Bond*, Cornell University Press, New York 1960.
27. Steinfink, H. *Acta Crystallogr. 15* (1962) 644.
28. Evans, H. T., Jr. In Dunitz, J. D. and Ibers, J. A., Eds., *Perspectives in Structural Chemistry*, Wiley, New York 1971, Vol. IV, Chapter 1.
29. Johnson, C. K. *ORTEP-II*, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge 1976.