

Multicomponent Polyaniions.

15. The Molecular and Crystal Structure of $\text{Na}[\text{Mo}_2\text{O}_5\{\text{O}_3(\text{OH})\text{C}_6\text{H}_8(\text{OH})_2\}]\cdot 2\text{H}_2\text{O}$, a Protonized Mannitolatodimolybdate Complex

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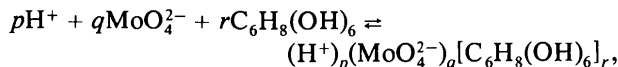
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The crystal structure of $\text{Na}[\text{Mo}_2\text{O}_5\{\text{O}_3(\text{OH})\text{C}_6\text{H}_8(\text{OH})_2\}]\cdot 2\text{H}_2\text{O}$ has been determined and refined from three-dimensional X-ray diffraction data collected using a Pailred linear diffractometer. The crystals are monoclinic, space group $P2_1$, with cell dimensions $a = 12.2342$ (6), $b = 6.9008$ (4), $c = 8.3845$ (5) Å and $\beta = 99.740$ (6)°; the unit cell contains two formula units. Full matrix least-squares refinement based on 4327 independent reflexions resulted in a final R value of 0.023. Positional and thermal parameters for all H atoms were included in the refinements. The $[\text{Mo}_2\text{O}_5\{\text{O}_3(\text{OH})\text{C}_6\text{H}_8(\text{OH})_2\}]^-$ anion, which is a complex formed by H^+ , MoO_4^{2-} and D-mannitol $[\text{C}_6\text{H}_8(\text{OH})_6]$, consists of two MoO_6 octahedra sharing a face, with four O atoms donated by the mannitolato chain (which acts as a tetradentate ligand). On one of these O atoms, the H atom from the OH group remains and constitutes the proton of the complex. The Mo–Mo distance is 3.1435 (3) Å, and the Mo–O distances fall into one of four ranges with mean values of 1.71, 1.94, 2.14 and 2.47 Å, depending on the coordination number. The anions are hydrogen-bonded by the proton as well as by one of the two water molecules to form layers parallel to (100). The layers are strengthened by Na^+ ions, which are octahedrally coordinated by O atoms from different anions and water molecules. Hydrogen bonds between the second water molecule and an OH group of the uncoordinated part of the mannitolato chain form a helix along [010] holding the layers together.

Introduction

Investigation of aqueous equilibria of the type



where $\text{C}_6\text{H}_8(\text{OH})_6$ is D-mannitol, has shown that complexes (2,2,1) and (3,2,1) are formed [(p,q,r) notation; Pettersson, 1972]. Potentiometric, polarimetric and spectrophotometric measurements were made over the range $1 < -\log[\text{H}^+] < 9$. Parallel to this investigation, crystallization experiments were carried out using molar ratios of H^+ , MoO_4^{2-} and $\text{C}_6\text{H}_8(\text{OH})_6$, corresponding to the complex composition ($p,2,1$), with $p = 2, 2.5, 3, 3.5$ and 4. Sodium was used as the cation in each case. Only one crystalline phase was obtained, corresponding to the (3,2,1) complex, no matter which of the solutions were used. The crystal structure of the (3,2,1) phase is the subject of the present paper.

Preliminary structural results based on a film data set have been reported previously (Hedman, 1974), but the phase was erroneously reported as a (4,2,1) complex. Cell parameters (orthorhombic, $a = 8.23$, $b = 12.32$, $c = 6.86$ Å) of a crystal corresponding to a (4,2,1) complex were reported by Shaw, Daniels & Sawyer (1967), but no structural information was given.

Experimental

In preparing the crystals, $\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$ and recrystallized D-mannitol $[\text{C}_6\text{H}_8(\text{OH})_6]$ were dissolved in water, and HClO_4 was added to give total concentrations of molybdenum(VI), D-mannitol and perchloric acid of 0.6, 0.3 and 0.9 *M* respectively. After several days of slow evaporation at room temperature, colourless acicular [010] crystals were formed in a thistle-like arrangement. The Na, Mo and C contents were determined by elemental analyses (Department of Analytical Chemistry, University of Umeå). The composition found (Na 4.5, Mo 37.8 and C 13.9 wt%) agrees well with the calculated composition (Na 4.5, Mo 37.6 and C 14.1 wt% respectively). The amount of water of crystallization was determined by thermobalance analysis and found to be 7.5% (7.1% calculated).

Preliminary Weissenberg photographs showed the crystal system to be monoclinic with systematic extinctions ($0k0$, $k = 2n + 1$) consistent with space groups $P2_1$ and $P2_1/m$. The fact that D-mannitol is optically active excludes the possibility of space group $P2_1/m$. Accurate unit-cell dimensions were determined from X-ray powder photographs taken with a Guinier–Hägg camera using $\text{Cu } K\alpha_1$ radiation ($\lambda = 1.54051$ Å), with $\text{Pb}(\text{NO}_3)_2$ as the internal standard $\{a[\text{Pb}(\text{NO}_3)_2] = 7.8575$ Å, $25^\circ\text{C}\}$. From exposures of three indepen-

Table 1. *Crystal data for*
 $\text{Na}[\text{Mo}_2\text{O}_5\{\text{O}_3(\text{OH})\text{C}_6\text{H}_8(\text{OH})_2\}].2\text{H}_2\text{O}$

$a = 12.2342$ (6) Å	FW 510.05
$b = 6.9008$ (4)	$Z = 2$
$c = 8.3845$ (5)	$D_m = 2.40$ (1) g cm ⁻³
$\beta = 99.740$ (6)°	$D_x = 2.43$
$V = 697.7$ (1) Å ³	$\mu(\text{Mo } K\alpha) = 18.511$ cm ⁻¹
Space group $P2_1$	

dent samples, cell parameters were refined using a least-squares program (Werner, 1969) and the results were weighted and combined. The density of the crystals was determined by flotation in a bromoform/carbon tetrachloride solution. Complete crystal data are given in Table 1.

Two intensity data sets were collected. Initially equi-inclination Weissenberg film methods were used. Preliminary results with further experimental details have been published previously (Hedman, 1974). In the present investigation three-dimensional X-ray diffraction data were collected at 25°C using a Philips Pailred linear diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) monochromatized with a graphite crystal. The crystal dimensions were $0.12 \times 0.22 \times 0.13$ mm. The 0.22 mm edge coincided with the [010] direction, which was also used as the rotation axis. 4864 $h\bar{k}l$ and hkl reflexions from the layers $h0l-h\bar{1}\bar{2}l$ up to $(\sin \theta)/\lambda = 0.940$ Å⁻¹ were measured with gradually increasing scan intervals for higher layers. The scan speed used was 1° min⁻¹ and background was measured for 40 s at both the beginning and end of each interval. The net intensity (I) was computed as $I = \text{TI}/n - (t_f/t_B)(B1 + B2)$, where TI is the total intensity, n is the number of times the reflexion was scanned (reflexions with $\text{TI} \leq 4000$ counts were remeasured as many as three times), t_f/t_B is the time factor between reflexion and background measurements, and $B1$ and $B2$ are the background intensities. The statistical error $\sigma(I)$ for each of the reflexions was computed according to the formula $\sigma(I) = [\text{TI}/n^2 + (t_f/t_B)^2(B1 + B2)]^{1/2}$. Reflexions with $I < 2\sigma(I)$ were eliminated, leaving a data set of 4336 unique reflexions for the refinements.

Two monitor reflexions together with two selected reflexions from the layer in question were measured before and after reflexions from the layer were measured. There was a gradual decrease in intensity of about 9% from $h0l$ to $h\bar{1}\bar{2}l$ and a separate scale factor for each layer was therefore applied. The intensities and their standard deviations were corrected for Lorentz, polarization and absorption effects. With the $6 \times 12 \times 6$ Gaussian grid applied, the transmission factor varied between 0.789 and 0.835 [$\mu(\text{Mo } K\alpha) = 18.511$ cm⁻¹].

Structure determination and refinement

The atomic parameters obtained from the investigation based on the film data set (Hedman, 1974) were used as

starting values in the refinement of the diffractometer data. Full-matrix least-squares refinement using isotropic temperature factors resulted in an R value of 0.083, but with the temperature factor of one of the assumed water O atoms negative. This atom was deduced to be a Na⁺ ion, which was confirmed from elemental analyses and from a titration of a solution prepared from the crystals. Final isotropic refinements, including refinement of the individual scale factors, converged with $R = 0.076$. Introduction of anisotropic temperature factors caused R to decrease to 0.026. In a subsequent difference Fourier synthesis based on reflexions with $(\sin \theta)/\lambda \leq 0.5$ Å⁻¹ all H atoms could be located. Their positional and isotropic thermal parameters were refined on a subset of data with $(\sin \theta)/\lambda \leq 0.64$ Å⁻¹ (Cu sphere), since at high $(\sin \theta)/\lambda$ values the contribution of the H scattering factor is comparatively low. Final refinements converged with $R = 0.023$ ($R_w = 0.028$), where $R = \sum |F_o| - |F_c| / \sum |F_o|$ and $R_w = [\sum w_i (|F_o| - |F_c|)^2 / \sum w_i |F_o|^2]^{1/2}$, the function minimized being $\sum w_i (|F_o| - |F_c|)^2$. A weighting scheme $w = 1/\sigma^2(F_o)$ was applied where $\sigma^2(F_o)$ was modified according to $\sigma^2(F_o) = \sigma^2(F_o) + (0.015F_o)^2$. As nine of the strong reflexions showed F_c values 10–13% greater than F_o , an isotropic extinction refinement (Coppens & Hamilton, 1970) was attempted but gave no significant improvement of the results, and these reflexions were instead excluded from the refinements. They are marked with an asterisk in the list of structure factors.* In the final cycle all parameter shifts were less than 0.15σ . Because of the low core memory capacity of the computer, the refinements had to be divided into three blocks; this may have caused the standard deviations to be somewhat underestimated. F_c values were computed for the previously omitted reflexions [with $I < 2\sigma(I)$] and were lower than the threshold value, except in the case of some 20 reflexions for which F_c was a maximum of twice the threshold value.

The atomic scattering factors used for Mo³⁺, O⁻ (for Mo-coordinated O atoms), O, Na⁺ and C were those given by *International Tables for X-ray Crystallography* (1974, pp. 71–98) and for H those given by Stewart, Davidson & Simpson (1965). The real and imaginary parts of the anomalous-dispersion effects were taken into account (*International Tables for X-ray Crystallography*, 1974, p. 80). The correct absolute configuration of the complex was confirmed by R -factor ratio tests at the 0.995 level (Hamilton, 1965; Pawley, 1970). The computer programs used in this investigation have been described by Antti (1976). The computations were

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32626 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Fractional atomic coordinates ($\times 10^4$; for Mo $\times 10^5$) for the non-hydrogen atoms

The estimated standard deviations are given in parentheses.

	x	y	z
Mo(1)	16026 (1)	36952 (4)	72633 (2)
Mo(2)	16010 (1)	36400*	35140 (2)
O(1)	402 (2)	4311 (4)	7968 (3)
O(2)	2122 (2)	1864 (4)	8509 (3)
O(3)	962 (1)	2447 (2)	5254 (2)
O(4)	425 (2)	4383 (4)	2247 (2)
O(5)	2042 (2)	1682 (4)	2561 (2)
O(6)	1089 (2)	6287 (3)	5264 (2)
O(7)	2502 (2)	5923 (3)	8004 (2)
O(8)	2796 (1)	3887 (2)	5641 (2)
O(9)	2534 (2)	5735 (3)	3039 (2)
O(10)	5525 (2)	5428 (3)	4440 (2)
O(11)	5149 (2)	7035 (4)	1477 (3)
C(1)	1814 (2)	7916 (3)	5746 (3)
C(2)	2844 (2)	7052 (3)	6726 (3)
C(3)	3454 (2)	5622 (3)	5790 (2)
C(4)	3567 (2)	6178 (3)	4051 (2)
C(5)	4485 (2)	4994 (3)	3470 (2)
C(6)	4543 (3)	5324 (4)	1683 (3)
Na	531 (1)	926 (2)	131 (1)
Aq(1)	1340 (2)	7756 (3)	309 (2)
Aq(2)	3962 (2)	353 (5)	1181 (3)

* Arbitrarily fixed.

performed with a CD 3300 computer at the University of Umeå. Final atomic positional and H thermal parameters are given in Tables 2 and 3.

Description and discussion of the structure

The crystal structure consists of $[\text{Mo}_2\text{O}_5\{\text{O}_3(\text{OH})\text{C}_6\text{H}_8(\text{OH})_2\}]^-$ anions hydrogen-bonded by the proton of the complex and by water molecules to form layers parallel to (100). Connexions within the layers are strengthened by O-coordinated Na^+ ions between the anions. Between the layers, hydrogen bonds involving

Table 3. Fractional atomic coordinates ($\times 10^3$) and isotropic thermal parameters for the hydrogen atoms

The estimated standard deviations are given in parentheses.

	x	y	z	$B(\text{Å}^2)$
H(C1)	148 (3)	875 (7)	625 (4)	1.5 (6)
H'(C1)	203 (3)	856 (9)	484 (4)	2.3 (7)
H(C2)	330 (3)	805 (5)	710 (4)	0.8 (6)
H(C3)	410 (3)	535 (6)	644 (4)	0.8 (6)
H(C4)	376 (3)	741 (6)	398 (4)	1.0 (6)
H(C5)	436 (3)	352 (8)	381 (4)	2.3 (7)
H(C6)	382 (4)	543 (7)	103 (5)	2.9 (9)
H'(C6)	496 (4)	416 (7)	116 (4)	2.2 (8)
H(O6)	56 (4)	649 (10)	513 (6)	4.3 (12)
H(O10)	579 (7)	637 (15)	410 (8)	8.6 (21)
H(O11)	472 (3)	798 (7)	143 (5)	2.5 (9)
H(Aq1)	184 (4)	751 (8)	117 (5)	2.8 (9)
H'(Aq1)	169 (4)	751 (9)	-27 (6)	3.7 (10)
H(Aq2)	338 (4)	38 (9)	145 (6)	4.2 (12)
H'(Aq2)	394 (5)	91 (11)	32 (7)	5.5 (13)

water molecules and an OH group of the uncoordinated part of the mannitolato chain form a helix in the [010] direction holding the layers together.

The $[\text{Mo}_2\text{O}_5\{\text{O}_3(\text{OH})\text{C}_6\text{H}_8(\text{OH})_2\}]^-$ complex

The Mo atoms are octahedrally coordinated by six O atoms, three of which are shared in a common face (Fig. 1), giving an Mo_2O_9 group with an Mo—Mo distance of 3.1435 (3) Å. Four of the O atoms are donated by four adjacent C atoms in the mannitolato chain, which acts as a tetradentate ligand. On one of these O atoms the H atom from the OH group has remained and constitutes the proton of the complex. It is unusual for MoO_6 octahedra to share faces (compared with edge or corner sharing) and this has previously been reported only in the structures of $(\text{NH}_4)_2\text{H}_6(\text{CeMo}_{12}\text{O}_{42}) \cdot 12\text{H}_2\text{O}$ (Dexter & Silverton, 1968) and $(\text{NH}_4)_2[\text{Mo}_2\text{O}_5(\text{C}_6\text{H}_4\text{O}_2)_2]$ (Atovmyan, Tkachev & Shishova, 1972). The distorted MoO_6 octahedra show typical dimensions for Mo^{VI} com-

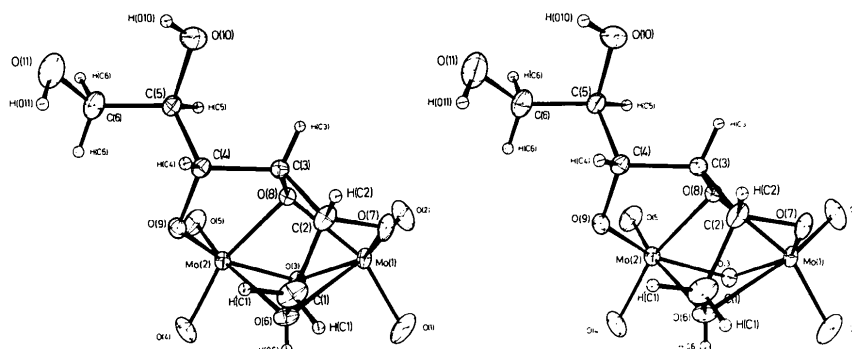


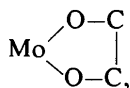
Fig. 1. Stereoscopic illustration of the $[\text{Mo}_2\text{O}_5\{\text{O}_3(\text{OH})\text{C}_6\text{H}_8(\text{OH})_2\}]^-$ anion, with thermal ellipsoids scaled to include 50% probability (ORTEP, Johnson, 1965).

Table 4. *Interatomic distances (Å) and bond angles (°) within the MoO₆ octahedra in the anion complex, with estimated standard deviations in parentheses*

	Mo(1)—Mo(2)	3.1435 (3)		Mo(1)—O(3)—Mo(2)	107.98 (7)	
				Mo(1)—O(6)—Mo(2)	78.89 (5)	
				Mo(1)—O(8)—Mo(2)	94.67 (5)	
	O(1)	O(2)	O(3)	O(6)	O(7)	O(8)
Mo(1)	1.727 (3)	1.693 (3)	1.936 (2)	2.459 (2)	1.931 (2)	2.162 (1)
O(1)		2.676 (4)	2.798 (3)	2.889 (3)	2.795 (3)	
O(8)		3.014 (3)	2.425 (2)	2.643 (2)	2.505 (2)	
O(2)			2.883 (3)		2.882 (3)	
O(6)			2.654 (3)		2.643 (2)	
O(1)—Mo(1)—		103.00 (11)	99.48 (9)	85.40 (9)	99.51 (10)	
O(8)—Mo(1)—		102.18 (9)	72.33 (5)	69.42 (5)	75.23 (6)	
O(2)—Mo(1)—			105.02 (9)		105.19 (10)	
O(6)—Mo(1)—			73.21 (6)		72.91 (6)	
	O(4)	O(5)	O(3)	O(6)	O(8)	O(9)
Mo(2)	1.716 (2)	1.703 (2)	1.950 (1)	2.489 (2)	2.113 (1)	1.925 (2)
O(4)		2.698 (4)	2.830 (3)	2.844 (3)		2.718 (3)
O(8)		3.005 (3)	2.425 (2)	2.643 (2)		2.500 (2)
O(5)			2.851 (3)			2.875 (3)
O(6)			2.654 (3)			2.805 (2)
O(4)—Mo(2)—		104.19 (11)	100.90 (8)	82.96 (9)		96.41 (9)
O(8)—Mo(2)—		103.36 (8)	73.18 (5)	69.56 (5)		76.36 (6)
O(5)—Mo(2)—			102.40 (8)			104.66 (9)
O(6)—Mo(2)—			72.31 (6)			77.76 (6)

pounds, with increasing distances for increasing coordination number (CN) of the O atom (Hedman, 1973; Strandberg, 1975) (see Table 4). Thus the mean Mo—O distances are 1.71 Å (CN 1), 1.94 Å (CN 2) and 2.14 Å (CN 3), reflecting the decrease in π -bond character of the Mo—O bonds. The Mo—O(6) distances (CN 4) are comparatively long, 2.459 (2) and 2.489 (2) Å, since O(6) is coordinated to two Mo atoms as well as being covalently bonded to C(1) and to H(O6), with which it takes part in a strong hydrogen bond. It should also be noted that in both octahedra, O atoms with CN 1 are in *cis* positions relative to one another and that they have an atom of CN 3 or 4 in the *trans* position, whereas O atoms with CN 2 are in *trans* positions relative to one another. Probably as a result of repulsion effects, the O—Mo—O angles are large between atoms involved in short Mo—O bonds, and *vice versa*.

In the chelate, three puckered five-membered rings,



are found, two of which show δ and one λ conformation, as defined by IUPAC (1970). The degree of puckering is indicated in Table 5 as the distances of the C atoms from the least-squares planes defined by the Mo and O atoms. The deviations of the rings from ideal twofold symmetry are due to the polydentate function of the ligand.

Table 5. *Conformation of the three puckered five-membered rings in the complex and the deviation (Å) of the carbon atoms from the least-squares O—Mo—O planes*

Ring	Conformation	Deviation
Mo(1)—O(6)—C(1)—C(2)—O(7)	λ	C(1) 0.099 (3) C(2) 0.773 (3)
Mo(1)—O(7)—C(2)—C(3)—O(8)	δ	C(2) 0.785 (3) C(3) 0.212 (2)
Mo(2)—O(8)—C(3)—C(4)—O(9)	δ	C(3) 0.311 (2) C(4) -0.229 (2)

The mannitolato ligand

In D-mannitol the conformation of the molecule viewed along the C—C bonds, from C(1)—C(2) to C(5)—C(6), is *gauche, trans, gauche, trans, gauche*, while in the chelate it has transformed to *gauche, gauche, gauche, trans, gauche*. The dihedral angles are given in Fig. 2. Of the C—C distances, C(1)—C(2) is significantly shorter [1.506 (3) Å] than the others (Table 6), though not significantly shorter than the values in the K form of D-mannitol (mean 1.519 Å) (Kim, Jeffrey & Rosenstein, 1968). Chelate formation also affects the C—C—C angles, such that \angle C(2)—C(3)—C(4) is 117.1 (2)° and \angle C(3)—C(4)—C(5) is 110.9 (2)° while the others agree well with the mean value in D-mannitol of 113.4° (Kim *et al.*, 1968). The O—C—C angles are significantly decreased from the average value of 110.2° in D-

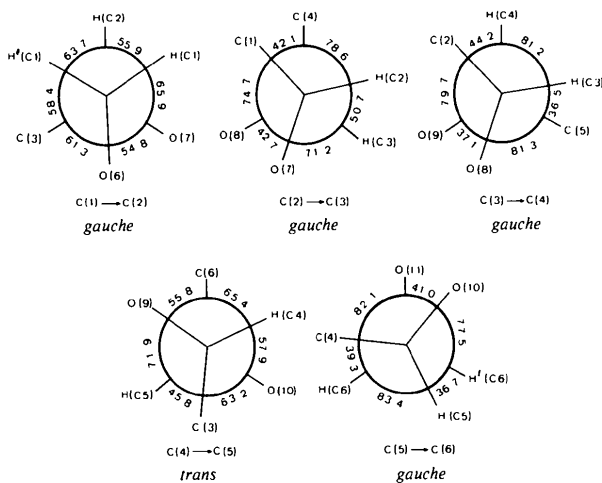


Fig. 2. The dihedral angles of the C—C bonds in the mannitolato ligand, shown in Newman projections.

mannitol, while the C—O distances appear to be slightly increased.

The uncoordinated part of the ligand shows an intramolecular O(10)—H(O10)···O(11) hydrogen bond with a bond length of 2.688 (3) Å. \angle O—H···O is small [115 (6)°] as the hydrogen bond is bifurcated [to O(8ⁱⁱ)]. Bond distances involving H atoms are of the accuracy expected from X-ray investigations (Table 6).

Hydrogen bonding in the crystal structure

The complexes are hydrogen-bonded to form layers parallel to (100) (see Fig. 3). In the [010] direction,

complexes related by a 2₁ axis are connected by short [2.599 (2) Å] O(6)—H(O6)···O(3ⁱ) hydrogen bonds, *i.e.* *via* the proton of the complex. The layer formation is completed by one of the water molecules forming hydrogen bonds, Aq(1)—H(Aq1)···O(9) and Aq(1)—H'(Aq1)···O(7^{iv}) binding along [001].

A helical arrangement of hydrogen bonds involving the terminal OH group and the second water molecule is formed between the layers, *viz* Aq(2)—H'(Aq2)···O(11^v) and O(11)—H(O11)···Aq(2ⁱⁱⁱ) (see Fig. 4). The connexion is further strengthened by Aq(2)—H(Aq2)···O(5) hydrogen bonds to the complex.

Table 6. *Interatomic distances (Å) and bond angles (°) in the mannitolato ligand of the complex, with estimated standard deviations in parentheses*

C(1)—C(2)	1.506 (3)	C(1)—H(C1)	0.86 (4)
C(2)—C(3)	1.531 (3)	C(1)—H'(C1)	0.95 (4)
C(3)—C(4)	1.536 (3)	C(2)—H(C2)	0.91 (3)
C(4)—C(5)	1.533 (3)	C(3)—H(C3)	0.91 (3)
C(5)—C(6)	1.529 (3)	C(4)—H(C4)	0.88 (4)
C(1)—O(6)	1.447 (3)	C(5)—H(C5)	1.07 (5)
C(2)—O(7)	1.443 (3)	C(6)—H(C6)	0.97 (5)
C(3)—O(8)	1.436 (3)	C(6)—H'(C6)	1.08 (5)
C(4)—O(9)	1.432 (3)	O(6)—H(O6)	0.65 (5)
C(5)—O(10)	1.421 (3)	O(10)—H(O10)	0.80 (9)
C(6)—O(11)	1.420 (4)	O(11)—H(O11)	0.83 (5)
C(1)—C(2)—C(3)	114.3 (2)	O(8)—C(3)—C(2)	105.5 (2)
C(2)—C(3)—C(4)	117.1 (2)	O(8)—C(3)—C(4)	105.4 (2)
C(3)—C(4)—C(5)	110.9 (2)	O(9)—C(4)—C(3)	107.3 (2)
C(4)—C(5)—C(6)	113.0 (2)	O(9)—C(4)—C(5)	108.6 (2)
O(6)—C(1)—C(2)	105.2 (2)	O(10)—C(5)—C(4)	109.8 (2)
O(7)—C(2)—C(1)	107.3 (2)	O(10)—C(5)—C(6)	110.1 (2)
O(7)—C(2)—C(3)	105.1 (2)	O(11)—C(6)—C(5)	110.8 (2)

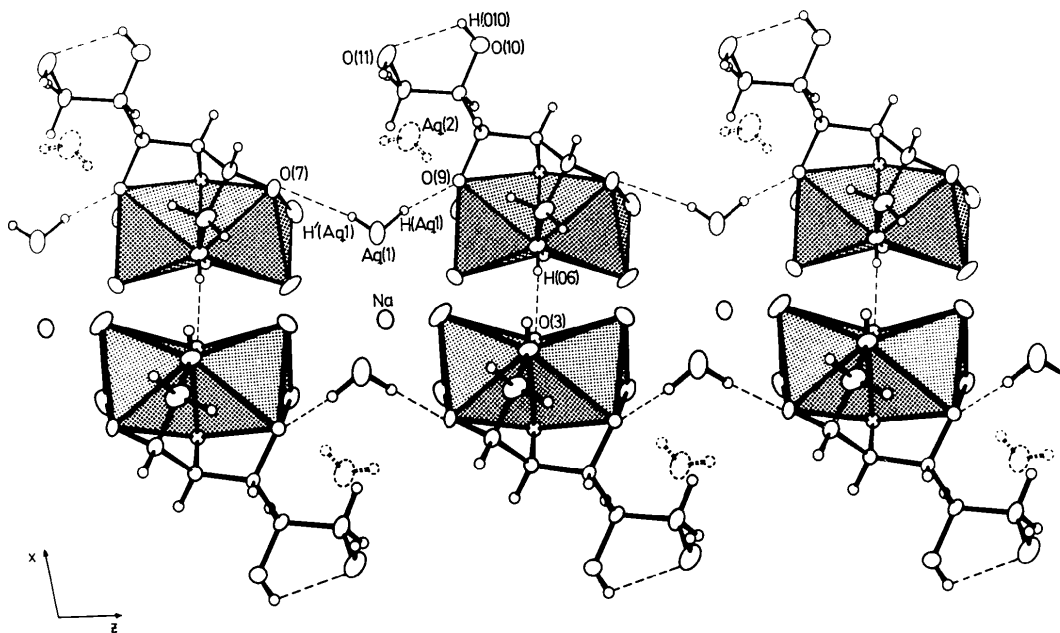


Fig. 3. Hydrogen bonds within the layers parallel to (100). The MoO₆ units are drawn as octahedra at y (fine lines) and $y + \frac{1}{2}$ (heavy lines).

In the structure there are two additional weak hydrogen bonds, $\text{Aq}(2)\text{--H}'(\text{Aq}2)\cdots\text{O}(2^{\text{iv}})$ and $\text{O}(10)\text{--H}(\text{O}10)\cdots\text{O}(8^{\text{ii}})$. The bonds are bifurcated,

both with O(11) as the other acceptor. As can be seen from Table 7, two of the $\text{O--H}\cdots\text{O}$ angles for bifurcated bonds deviate appreciably from linearity.

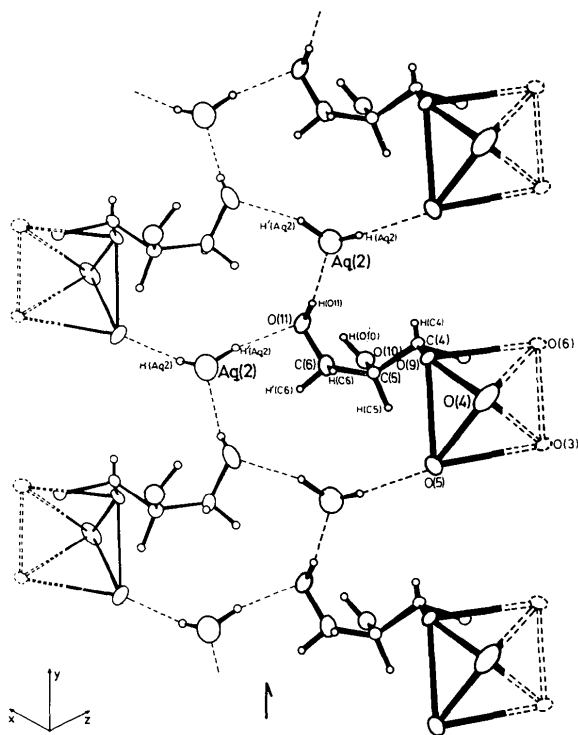


Fig. 4. Hydrogen bonds between the layers forming a helix in the [010] direction. The fragmental MoO_6 units are drawn as octahedra with coordinates x, z (heavy lines) and $1-x, z$ (fine lines).

Table 7. Distances (\AA) and angles ($^\circ$) in the hydrogen-bond system, with estimated standard deviations in parentheses

The superscripts refer to the following symmetry operations:

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

$\text{Aq}(1)\text{--H}(\text{Aq}1)$	0.88 (4)	$\text{Aq}(2)\text{--H}(\text{Aq}2)$	0.78 (5)
$\text{Aq}(1)\text{--H}'(\text{Aq}1)$	0.72 (5)	$\text{Aq}(2)\text{--H}'(\text{Aq}2)$	0.82 (6)

$\text{O--H}\cdots\text{O}$	$\text{O}\cdots\text{O}$	$\angle\text{O--H}\cdots\text{H}$
$\text{O}(6)\text{--H}(\text{O}6)\cdots\text{O}(3^{\text{i}})$	2.599 (2)	173 (8)
$\text{O}(10)\text{--H}(\text{O}10)\cdots\text{O}(11)$	2.688 (3)	115 (6)
$\text{O}(10)\text{--H}(\text{O}10)\cdots\text{O}(8^{\text{ii}})$	3.158 (3)	151 (6)
$\text{O}(11)\text{--H}(\text{O}11)\cdots\text{Aq}(2^{\text{iii}})$	2.701 (4)	170 (4)
$\text{Aq}(1)\text{--H}(\text{Aq}1)\cdots\text{O}(9)$	2.861 (2)	152 (5)
$\text{Aq}(1)\text{--H}'(\text{Aq}1)\cdots\text{O}(7^{\text{iv}})$	2.878 (3)	163 (6)
$\text{Aq}(2)\text{--H}(\text{Aq}2)\cdots\text{O}(5)$	2.936 (4)	155 (6)
$\text{Aq}(2)\text{--H}'(\text{Aq}2)\cdots\text{O}(11^{\text{v}})$	2.884 (4)	148 (6)
$\text{Aq}(2)\text{--H}'(\text{Aq}2)\cdots\text{O}(2^{\text{iv}})$	3.077 (4)	122 (5)

The sodium–oxygen arrangement

The Na^+ ion is octahedrally surrounded by six O atoms and connects complexes within the layers by electrostatic forces. In the octahedron four complexes contribute with one terminal O atom each, while two symmetry-related water O atoms complete the arrangement. As can be seen from Fig. 5, the Na--O distances lie in the range 2.38–2.64 \AA with O--Na--O angles varying from 76.8 to 121.3 $^\circ$, *i.e.* the octahedron is severely distorted. Because of the 2_1 symmetry, a chain of NaO_6 octahedra sharing corners [Aq(1)] is formed with its axis in the [010] direction (see Fig. 5). The strong connexions in the [010] direction (hydrogen bonds, electrostatic effects) appear clearly in the crystal habit with strong elongation along [010].

I wish to thank Professor Nils Ingri for much valuable advice, for his great interest and for all the facilities placed at my disposal. I also wish to express my gratitude to Dr Lage Pettersson for the crystal-

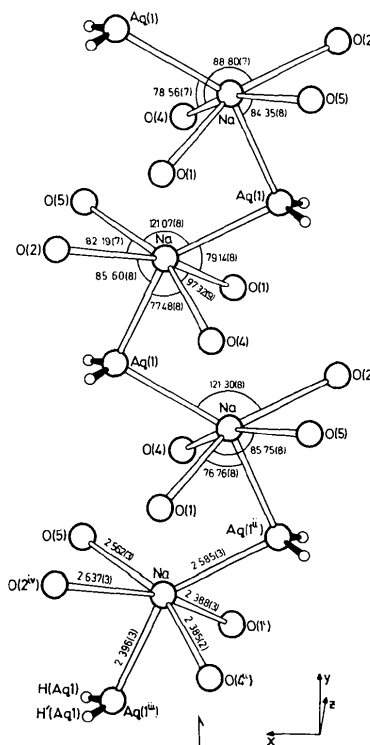


Fig. 5. The NaO_6 octahedra forming a chain in the [010] direction. Distances (\AA) and angles ($^\circ$) are given with estimated standard deviations in parentheses. The superscripts refer to the following symmetry operations: (i) $-x, -\frac{1}{2} + y, 1 - z$; (ii) $-x, -\frac{1}{2} + y, -z$; (iii) $x, -1 + y, z$; (iv) $x, y, -1 + z$.

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Multicomponent Poly-anions.

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

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The crystal structure of $\text{Na}_6\text{Mo}_5\text{P}_2\text{O}_{23}(\text{H}_2\text{O})_{14}$ 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 $a = 15.8304$ (9), $b = 19.876$ (1), $c = 10.6828$ (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 0.024. The $\text{Mo}_5\text{P}_2\text{O}_{23}^{5-}$ 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 3.355 and 3.377 Å for edge-sharing octahedra and the distance is 3.6604 (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 1.70–1.73, 1.90–1.95 and 2.17–2.39 Å depending on coordination number. The P–O distances vary between 1.50 and 1.57 Å. The anions are held together in a three-dimensional framework by O–Na–O and O–Na– H_2O –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 2.32–2.83 Å.

Introduction

Aqueous equilibria between H^+ , MoO_4^{2-} and HPO_4^{2-} in a 3.0 M $\text{Na}(\text{ClO}_4)$ medium have been investigated by potentiometric, spectrophotometric and Raman methods (Pettersson, 1974, 1975). The EMF measurements covered the range $1.5 < -\log[\text{H}^+] < 9$. 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 $[\text{MoO}_4^{2-}]/[\text{HPO}_4^{2-}] = 2.5$ 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 $\text{Na}_6\text{Mo}_5\text{P}_2\text{O}_{23}(\text{H}_2\text{O})_{14}$ (A), corresponding to the $(\text{H}^+)_8(\text{MoO}_4^{2-})_5(\text{HPO}_4^{2-})_2$ complex. Another phase containing this complex, $\text{Na}_6\text{Mo}_5\text{P}_2\text{O}_{23}(\text{H}_2\text{O})_{13}$ (B), has