The Crystal Structure of a Sodium Molybdenum Oxide, $Na_6Mo_{10}O_{33}$, Containing Cross-Linked Chains of Octahedra and Square Pyramids

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$Na_6Mo_{10}O_{33}$ crystallizes in the triclinic system with unit-cell dimensions $a = 8.049(4)$, $b = 12.180(6)$, $c = 7.576(4)$ Å, $\alpha = 99.96(9)$, $\beta = 100.74(1)$, $\gamma = 109.88(10)°$, and space group $P\bar{1}$ with $z = 1$. The structure was solved using Patterson and Fourier methods. Of the 3045 unique reflections measured by counter techniques 2758 with $I \geq 3\sigma(I)$ were used in the least-squares refinement of the model to a conventional R of 0.030 ($R_w = 0.034$). The structure of $Na_6Mo_{10}O_{33}$ consists of two different types of chains of molybdenum–oxygen polyhedra linked to one another approximately at right angles. One chain of edge- and corner-shared distorted MoO_6 octahedra is approximately parallel to [001] and the second chain, consisting of corner-shared pairs of octahedra edge-shared to pairs of edge-shared MoO_5 square pyramids (inverted with respect to one another), is approximately parallel to [100]. These linked chains form an infinite three-dimensional network in the interstices of which the sodium atoms are located. One of the chains of the $Na_6Mo_{10}O_{33}$ structure is the same as that found in $Ag_6Mo_{10}O_{33}$; the second chain, however, does not occur in $Ag_6Mo_{10}O_{33}$.

Introduction

Investigations by several groups in the past (*1, 2*) have indicated that in the $Na_2MoO_4–MoO_3$ system the 1 : 1 ($Na_2Mo_2O_7$), the 1 : 3 ($Na_2Mo_4O_{13}$), and the 1 : 4 ($Na_2Mo_5O_{16}$) compounds are formed. Caillet (*3*) reexamined the system and reported the existence of the 1 : 2 and 1 : 4 compounds only.

Miskin (*4*), using single-crystal techniques, showed that the only compound formed in the region 1 : 2 ($Na_2MoO_4 : MoO_3$) to 1 : 3 was the 3 : 7 composition, $Na_6Mo_{10}O_{33}$. As part of a general study of anhydrous polymolybdates we report here the structure of $Na_6Mo_{10}O_{33}$. A preliminary report was published elsewhere (*5*).

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Experimental

A suitable crystal fragment ($\sim 0.15 \times 0.125 \times 0.125$ mm) was chipped from the light silver-grey crystalline mass obtained by slowly cooling a melt formed by heating Na_2CO_3 and MoO_3 in the mole ratio 3 : 10 in open porcelain furnaceware in an electric furnace. Preliminary Weissenberg photography confirmed that the crystal was single, suitable for data collection, and belonged to the triclinic system. The crystal was mounted on a silica capillary using clear epoxy resin ("Resiweld") and the crystal data were obtained using a Philips PW 1100 computer-controlled diffractometer in a manner described earlier (*6*).

Crystal data. $Na_6Mo_{10}O_{33}$, $M = 1625.32$, triclinic, $a = 8.049(4)$, $b = 12.180(6)$, $c = 7.576(4)$ Å, $\alpha = 99.96(9)$, $\beta = 100.74(10)$, $\gamma = 109.88(10)°$. $V = 663.39$ Å^3, $D_m = 4.10(5)$

g cm^{-3} (by flotation), $z = 1$, $D_c = 4.07$ g cm^{-3}, $F(000) = 750$, $\mu(\text{Mo}K\alpha) = 43.6$ cm^{-1} ($\lambda = 0.7107$ Å). Space group $P\bar{1}$ (C_i^2), confirmed by successful refinement.

Intensity Measurements

Intensity measurements were made with the crystal described above using the diffractometer and Mo $K\alpha$ radiation monochromated with a flat graphite monochromator crystal. A unique data set was collected out to 2θ (Mo$K\alpha$) = 60° using the $\theta-2\theta$ scan technique with a symmetric scan range of $\pm(1.2 + 0.30 \tan \theta)$° in 2θ from the calculated Bragg angle, at a scan rate of 0.05° sec^{-1}. No reflection was sufficiently intense to require the insertion of an attenuation filter. Of the 3045 independent reflections measured 2758 were considered to be significantly above background ($I \geq 3\sigma(I)$) and only these were used during the refinement. Three standard reflections, measured at 2-hr intervals, showed no significant variation in intensity.

The data were processed in a manner described recently (6). Owing to the lack of clearly defined faces on the crystal a spherical absorption correction was applied. No correction was made for extinction. The atomic scattering factors used were for neutral atoms and were corrected for anomalous dispersion (7). All calculations were carried out on the Monash University Burroughs B6700 computer; the major program used was SHELX (8).

Structure Solution and Refinement

The solution to the structure was obtained by the "P1" method described by Abrahams (9) and used subsequently in this laboratory in the determination of other triclinic structures, e.g., Ag$_6$Mo$_{10}$O$_{33}$ (10) and K$_2$Mo$_4$O$_{13}$ (11).

In the solution obtained here, apart from the origin, the largest peak in the Patterson synthesis was at $(0, 0, \frac{1}{2})$, approximately 3.8 Å (corresponding to Mo–Mo vectors between corner-shared MoO$_6$ octahedra) from the origin.

A further three consistent molybdenum atom positions were located from the Patterson synthesis and these, together with a molybdenum atom on the origin, were used as the basis for structure factor calculations and Fourier syntheses in space group P1. The remaining six molybdenum atoms were located and a further structure factor calculation gave $R = 0.227$, where $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$.

At this stage a center of inversion was apparent and the space group was changed to $P\bar{1}$. All oxygen and sodium atoms were located in subsequent difference Fourier syntheses, and, following initial refinement with all thermal parameters isotropic and weighted data ($w = (\sigma^2(F))^{-1}$), the sodium and molybdenum atoms were assigned anisotropic thermal parameters.

Final refinement of all parameters resulted in $R = 0.030$ and $R_w = 0.034$, where $R_w = \Sigma(w^{\frac{1}{2}} \cdot ||F_o| - |F_c||)/\Sigma w^{\frac{1}{2}}|F_o|$. Final parameters and their estimated standard deviations are presented in Table I[1] and selected interatomic distances in Table II.

Description and Discussion of the Structure

The structure of Na$_6$Mo$_{10}$O$_{33}$ may be described as a three-dimensional framework

[1] For a table of observed and calculated structure factors see NAPS document No. 04025 for 16 pages of supplementary material. Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10163. Remit in advance in U.S. funds only for each NAPS Accession Number. Institutions may use purchase orders when ordering; however, there is a billing charge for this service. Make checks payable to Microfiche Publications. Photocopies are $5.00. Microfiche are $3.00. Outside the U.S. and Canada, postage is $3.00 for a photocopy or $1.50 for a fiche.

TABLE I

Final Atomic Parameters with Their Estimated Standard Deviations in Parentheses (Mo × 10^5, others × 10^4, U's × 10^4)

Atom	x/a	y/b	z/c	U^a
Na(1)	3,879(5)	2,338(3)	1,449(4)	
Na(2)	−1,246(3)	2,156(2)	1,049(3)	
Na(3)	−1,514(4)	2,390(2)	6,324(4)	
Mo(1)	40,856(5)	1,693(3)	71,161(5)	
Mo(2)	38,747(5)	31,908(3)	67,647(5)	
Mo(3)	27,799(5)	50,785(3)	95,081(5)	
Mo(4)	27,328(5)	50,055(3)	44,841(5)	
Mo(5)	1,032(5)	2,802(3)	71,906(5)	
O(1)	6,048(5)	788(3)	8,848(5)	180(7)
O(2)	3,257(5)	−1,331(3)	7,116(5)	175(7)
O(3)	6,579(4)	4,706(3)	7,814(4)	90(6)
O(4)	1,580(4)	2,318(3)	6,096(5)	148(6)
O(5)	4,887(4)	2,134(3)	6,725(5)	135(6)
O(6)	3,167(4)	4,802(3)	6,995(4)	97(6)
O(7)	4,143(4)	3,794(3)	9,391(4)	100(6)
O(8)	2,571(5)	6,404(3)	9,371(5)	181(7)
O(9)	611(4)	4,028(3)	9,013(5)	174(7)
O(10)	855(5)	3,732(3)	3,348(5)	175(7)
O(11)	4,370(4)	3,770(3)	4,633(4)	95(6)
O(12)	1,923(5)	6,116(3)	4,892(5)	201(7)
O(13)	¼	0	¼	156(8)
O(14)	−393(4)	1,371(3)	8,498(5)	153(6)
O(15)	−937(5)	−1,028(3)	7,786(5)	169(7)
O(16)	2,597(4)	746(3)	8,537(5)	127(6)
O(17)	−1,490(4)	88(3)	4,821(4)	109(6)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na(1)	905(12)	278(10)	246(10)	−1(9)	199(10)	−35(10)
Na(2)	151(8)	200(8)	162(8)	−14(7)	29(7)	69(7)
Na(3)	486(11)	221(9)	356(10)	58(8)	−158(9)	153(8)
Mo(1)	70(2)	93(2)	64(2)	24(1)	21(1)	38(1)
Mo(2)	84(2)	58(2)	58(2)	17(1)	29(2)	23(1)
Mo(3)	71(2)	97(2)	44(2)	16(2)	20(1)	41(2)
Mo(4)	62(2)	86(2)	52(2)	31(1)	23(2)	33(1)
Mo(5)	68(2)	115(2)	57(2)	26(2)	22(2)	42(2)

Note. The anisotropic thermal parameters ($Å^2$) are of the form exp $[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

[a] Anisotropic thermal parameters for sodium and molybdenum.

structure formed by the linking of two different types of chains of molybdenum–oxygen polyhedra linked to one another approximately at right angles (Fig. 1). One chain of edge- and corner-shared distorted MoO_6 octahedra (Mo(2), Mo(3), and Mo(4)) is almost parallel to [001] and is linked to the second chain by corner-sharing of octahedra both above and below the chain. The second chain, which comprises corner-shared pairs of octahedra (Mo(1))

edge-shared to pairs of edge-shared MoO_5 square pyramids (Mo(5)) that are inverted

TABLE II

Selected Interatomic Distances in $Na_6Mo_{10}O_{33}$(Å)

Mo(1)–O(1)	1.691(3)	Mo(2)–O(4)	1.711(3)
O(2)	1.719(4)	O(5)	1.741(4)
O(13)	1.893(1)	O(11)	1.926(4)
O(16)	1.970(4)	O(7)	1.942(3)
O(17)	2.206(3)	O(3)	2.211(4)
O(5)	2.344(4)	O(6)	2.211(3)
Mo(3)O(8)	1.697(4)	Mo(4)–O(12)	1.697(5)
O(9)	1.702(3)	O(10)	1.700(3)
O(3)	1.945(3)	O(6)	1.943(3)
O(6)	1.976(4)	O(3)	1.975(4)
O(7)	2.195(4)	O(11)	2.195(3)
O(7)	2.288(3)	O(11)	2.316(4)
Mo(5)–O(15)	1.710(4)	Na(1)–O(16)	2.450(4)
O(14)	1.721(4)	O(7)	2.539(5)
O(16)	1.911(3)	O(11)	2.596(4)
O(17)	1.927(3)	O(15)	2.598(5)
O(17)	2.124(4)	O(8)	2.986(5)
——O(4)	2.708(4)	O(2)	3.075(6)
		——O(6)	3.329(4)
		——O(14)	3.417(5)
Na(2)–O(10)	2.262(3)	Na(3)–O(12)	2.268(5)
O(14)	2.328(5)	O(14)	2.446(5)
O(1)	2.349(3)	O(9)	2.456(4)
O(8)	2.378(5)	O(4)	2.558(5)
O(2)	2.404(5)	O(2)	2.582(4)
O(15)	2.691(5)	O(17)	2.845(5)
O(9)	3.094(5)	O(5)	2.885(5)
——O(16)	3.416(4)	——O(13)	3.120(2)
		——O(1)	3.376(5)

Molybdenum–molybdenum distances

Mo–Mo edge-shared distances

Mo(5)–Mo(5)	3.2318(8)	Mo(2)–Mo(4)	3.2903(6)
Mo(1)–Mo(5)	3.2643(6)	Mo(2)–Mo(3)	3.3036(4)
Mo(2)–Mo(4)	3.2832(5)	Mo(3)–Mo(3)	3.5897(8)
Mo(2)–Mo(3)	3.2850(6)	Mo(4)–Mo(4)	3.5924(8)

Mo–Mo corner-shared distances

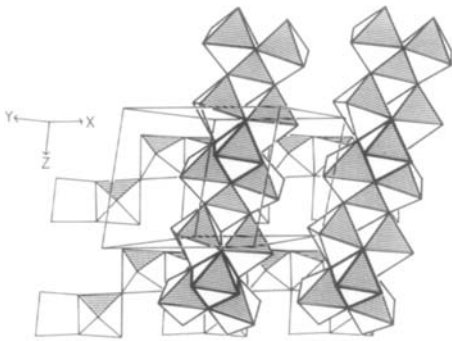| Mo(3)–Mo(4)	3.7846(6)	Mo(3)–Mo(4)	3.7931(6)
Mo(1)–Mo(1)	3.7858(8)	Mo(1)–Mo(2)	3.7935(6)

Mo–Mo shortest nonbonding interchain contact

Mo(2)–Mo(5) 3.9151(5)

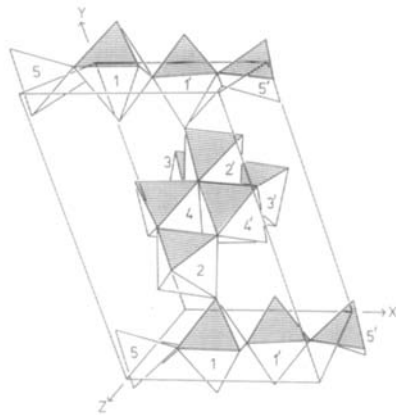FIG. 1. The structure of $Na_6Mo_{10}O_{33}$ showing the two sets of chains approximately parallel to [001] and [100].

FIG. 2. The structure of $Na_6Mo_{10}O_{33}$ drawn to show the linking of the two chains. Unprimed numbers are Mo atoms as in the parameter list, and primed numbers are symmetry-related Mo atoms.
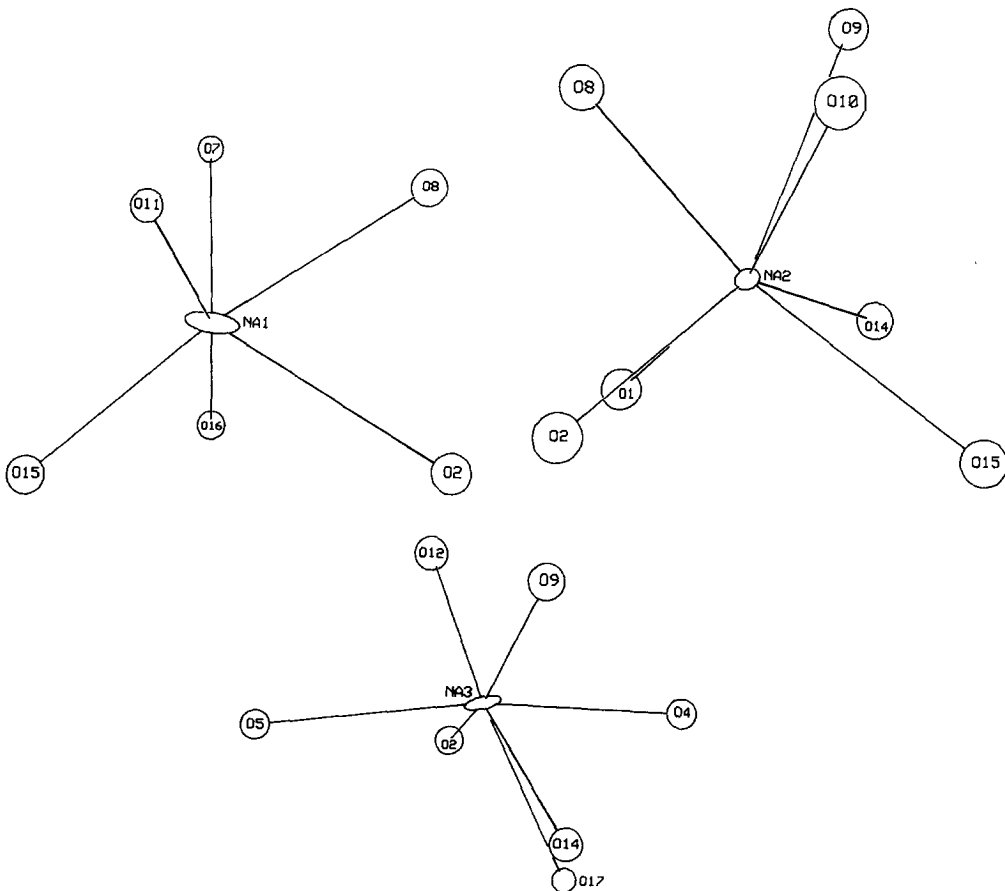

FIG. 3. The sodium ion coordination polyhedra for Na(1), Na(2), and Na(3).

with respect to one another, is approximately parallel to [100] (see Figs. 1 and 2).

The chain consisting of octahedra only is virtually identical to the chain in Ag$_6$ Mo$_{10}$O$_{33}$—a structure that may well have been anticipated to be isostructural with that described here—however, the second chain does not form in Ag$_6$Mo$_{10}$O$_{33}$; the corresponding octahedra remain as blocks of four edge-shared to one another and attached to the chains above and below thus forming infinite sheets.

Within the first chain the Mo–O distances range from 1.697(4) to 2.316(4) Å compared with those in the Ag$_6$Mo$_{10}$O$_{33}$ chain that range from 1.69(3) to 2.34(3) Å, typically exhibiting the two short, two medium, and two long Mo–O bonds frequently observed in molybdenum–oxygen octahedra. The Mo–O distances in the second chain range from 1.691(3) to 2.344(4) Å in the octahedron and 1.710(4) to 2.124(4) Å in the square pyramid that has a sixth oxygen in the direction that would give Mo(5) octahedral coordination but at 2.708(4) Å distance. In Ag$_6$Mo$_{10}$O$_{33}$ the range of Mo–O distances in the comparable octahedra is from 1.71(3) to 2.45(3) Å. The plane of best fit to the base of the Mo(5) square pyramid is given in Table III—Mo(5) is 0.4802(4) Å out of the plane toward the apical oxygen atom O(15).

The sodium ions occupy interchain interstices; Na(1) is six-coordinate and best approximates an irregular hexahedron (12), Na(2) is seven-coordinate and approximates a 7,11,6-polyhedron (12), and Na(3), also seven-coordinate, has a reasonably regular pentagonal bipyramidal coordination. The coordination polyhedra were identified using the method suggested by Johnson et al. (14), and are illustrated in Fig. 3.

The compound Ag$_6$Mo$_{10}$O$_{33}$ was tested for ionic conductivity (13) and was shown to behave as a normal ionic crystal and not as a solid electrolyte. The structure collapsed at the melting point as there is no cross-linking between the sheets to keep them apart. In Na$_6$Mo$_{10}$O$_{33}$, however, the structure is cross-linked and may, therefore, prove to be a more suitable candidate for ionic conductivity as perhaps indicated by the thermal parameters of the sodium ions—in particular Na(1).

TABLE III

EQUATION OF MEAN PLANE THROUGH THE BASE OF THE Mo(5) SQUARE PYRAMID AND THE DEVIATIONS (Å) OF ATOMS FROM IT

X, Y, Z are orthogonal coordinates and are related to the fractional coordinates x, y, z in the crystal sys- by the equation

$$\begin{pmatrix} 8.049000 & -4.141825 & -1.411807 \\ 0.000000 & 11.454156 & -1.903895 \\ 0.000000 & 0.000000 & 7.195676 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}$$

Plane. Mean plane through O(14), O(16), O(17), and O(17') ($-x$, $-y$, $1 - z$ from O(17)).

$$0.2026X + 0.9574Y - 0.2056Z + 1.7996 = 0$$

O(14)	0.074(4)	Mo(5)	−0.4802(4)
O(16)	−0.085(4)	O(15)	−2.188(4)
O(17)	−0.084(4)		
O(17')	0.095(4)		

Coordinates of the plane center of gravity:

−0.7299   −0.6806   4.8634

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