Table 4(*a*). *Bond lengths and other interatomic distances with their standard deviations*

N(0) is the nitrogen atom in an adjacent molecule bonded to O(1) by H(0).

	Length	e.s.d.
O(1)–C(6)	1·31 Å	0·01 Å
O(2)–C(6)	1·21	0·01
C(6)–C(5)	1·54	0·01
C(5)–C(4)	1·53	0·01
C(4)–C(3)	1·50	0·01
C(3)–N	1·51	0·01
N–C(2)	1·49	0·01
C(2)–C(1′)	1·51	0·01
N–C(1)	1·47	0·01
C(1)–C(2′)	1·51	0·01
O(1)–N(0)	2·60	0·01
O(1)–H(0)	1·52	
H(0)–N(0)	1·11	

Table 4(*b*). *Bond angles with their standard deviations*

Angle	Value	e.s.d.
O(1)–C(6)–O(2)	125°	1°
O(2)–C(6)–C(5)	122	1
O(1)–C(6)–C(5)	113	1
C(6)–C(5)–C(4)	113	1
C(5)–C(4)–C(3)	110	1
C(4)–C(3)–N	112	1
C(2)–N–C(1)	110	1
C(3)–N–C(1)	114	1
N–C(2)–C(1′)	110	1
N–C(1)–C(2′)	111	1
C(6)–O(1)–N(0)	111	1
C(6)–O(1)–H(0)	105	
O(1)–H(0)–N(0)	163	
C(3)–N–C(2)	107	1

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The Crystal Structure of a Sodium Molybdenum Bronze

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The sodium molybdenum bronze of reported composition $Na_{0\cdot9}Mo_6O_{17}$ has a monoclinic structure with space group $C2/m$, $C2$ or Cm, and cell dimensions $a=9\cdot57$, $b=5\cdot50$, $c=12\cdot95$ Å, $\beta=90°$; and two formula units per unit cell. Crystals are always repeatedly twinned about the normals to (310) and $(3\bar{1}0)$, and the composite reciprocal lattice has trigonal symmetry $P\bar{3}m1$. The corresponding 'average structure', representing a disordered superposition of various domain arrangements, was solved by three-dimensional Patterson methods, and refined by differential Fourier techniques. It is a trigonally distorted perovskite structure, in which the sodium ions are ordered in one sixth of the voids left between the MoO_6 octahedra; and it requires either a ratio Mo:O = 0:18 or randomness in the distribution of 17 oxygen atoms over 18 sites. The further distortion of the true structure to monoclinic, though not fully soluble, is consistent with the ordered distribution of 34 oxygen atoms in the unit cell. The detailed environments of the atoms are discussed.

Introduction

A recent report by Wold, Kunnmann, Arnott & Ferretti (1964) describes what is probably the first synthesis of alkali-metal molybdenum bronzes. The success of this preparation is dependent upon both the reduction temperature and the molar ratio of alkali-metal molybdate to molybdic anhydride. The reduction was carried out at a platinum cathode in a melt of the above components.

The structures of the potassium molybdenum bronzes have been described (Graham, Stephenson, Wadsley & Wold, 1965). The present work concerns a sodium molybdenum bronze reported by Wold *et al.* to be within the composition range $Na_{0\cdot93}Mo_{5\cdot9}O_{17}$ to $Na_{0\cdot87}Mo_{5\cdot95}O_{17}$ and thus to approach the composition $NaMo_6O_{17}$; a three-dimensional structure analysis has been made.

Determination of the unit cell and twin relationships

Crystals of the sodium molybdenum bronze, which were apparently single, invariably gave Weissenberg photographs indicating twinning, as shown by the fact that at Bragg angles greater than 40° all spots other than 001 began to appear as doublets; the 001 spots were always sharp. If these spot splittings were ignored, the reflexions could be indexed by using a hexagonal lattice with cell dimensions $a=5{\cdot}51$, $c=12{\cdot}95$ Å. The splittings can be explained by the assumption that the true lattice is orthogonal, C-face-centred, with spacings d_{200} and d_{110} nearly equal, (actually $d_{110}/d_{200}=0{\cdot}997$), and that repeated twinning occurs with the normals to (310) and ($3\bar{1}0$) as twin axes. The overlapping reflexions of two components 1 and 2 are related by the index transform:

$$\begin{array}{ll} & \longrightarrow 2 \\ 1 & \boxed{\begin{matrix} \frac{1}{2} & \frac{3}{2} & 0 \\ \frac{1}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & -1 \end{matrix}} \end{array}$$

The intensities associated with the composite reciprocal lattice show the Laue symmetry $\bar{3}m$. This means that the individual components cannot have higher symmetry than $C2/m$ (in spite of the 90° angle). This can be seen from Fig. 1, where the symmetry elements are depicted for two orientations of a monoclinic lattice with identical d_{200} and d_{110} spacings twinned about the normal to (310). A limit of 0·25° can be set to the possible departure of β from 90°. This limit is based upon the very small horizontal splitting observed for $hh\,.\,l$ type reflexions recorded on Weissenberg photographs.

The pseudo-hexagonal nature of the lattice is evident from powder data. Photographs taken with a Guinier-type focusing camera showed broadening and eventual splitting of lines other than 001, which were sharp. This observation was also made by Wold (1964). The splittings could be indexed on the assumption of a monoclinic lattice whose approximate unit-cell dimensions were calculated from the dimensions of the trigonal cell. The latter values were obtained earlier, as a first approximation, from the composite reciprocal lattice. The exact dimensions of the monoclinic cell were obtained by a least-squares treatment of the powder data, and these values are given in Table 1, where the dimensions of the trigonal average cell are also given for comparison. Since, according to Wold, the empirical formula of the bronze approaches $NaMo_6O_7$, there is one formula unit per trigonal cell, or two per monoclinic cell.

Table 1. *Crystal data*

$Na_{0.93}Mo_6O_{17}$. Deep purple plates elongated along [010].
Monoclinic unit cell of true structure:
$a=9{\cdot}57$, $b=5{\cdot}50$, $c=12{\cdot}95$ Å, $\beta=90°$.
$U=684$ Å^3, $D_m=4{\cdot}17$, $D_x=4{\cdot}26$ g.cm^{-3}.
$Z=2$, Space group $C2/m$, $C2$ or Cm.
Hexagonal unit cell of 'average structure':
$a=5{\cdot}51$, $c=12{\cdot}95$ Å, $\gamma=120°$.
$U=342$ Å^3, $Z=1$.
Space group $P\bar{3}m1$, $P321$ or $P3m1$.
(All cell dimensions accurate to 0·5 %).

An examination of the single crystals using transmission optics was not possible owing to their intense colour and opacity. Petrographic methods utilizing polished specimens and reflexion microscopy revealed the presence of twinned domains, each approximately twelve microns across. It was not possible to tell whether each 'domain' was a true single (monoclinic) crystal or was itself pseudo-trigonally twinned but in a different optic orientation to its neighbour.

There appears to be a close similarity between this domain structure and that of the bronze of composition $Na_{0.75}WO_3$ which was examined by Atoji & Rundle (1960). Although the latter appeared to be cubic, the structure was actually tetragonal with c/a very close to 1: an apparently single crystal consisted of domains oriented in all three pseudo-cubic directions without any preferred distribution, so that the average structure over the crystal could be considered as isometric.

When crystals are twinned, the information gained from the intensity data is of limited value. Sometimes it is possible to isolate an untwinned fragment, *e.g.* $NaNbO_3$ (Wells & Megaw, 1961) or one twin can be ground from the twin plane, *e.g.* $GdFeO_3$ (Geller, 1956). Unfortunately, it appears practically impossible to obtain an untwinned fragment of the sodium molybdenum bronze, and the establishment of a relationship between the structure of the true monoclinic phase and the averaged trigonal phase seemed, at first sight, remote. An encouraging feature emerged when it was observed that those members of the doublets which

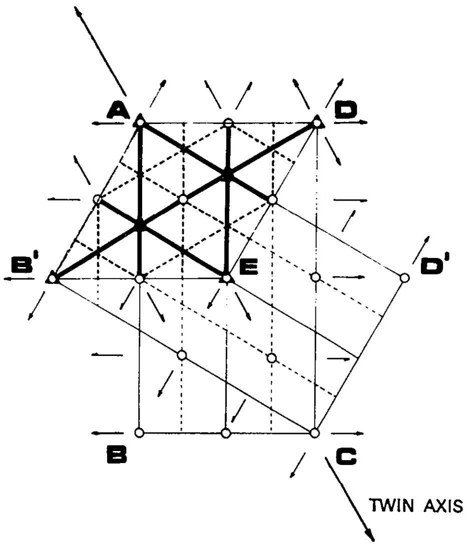

Fig. 1. Relationship of twinned monoclinic C-face-centred structure and trigonal structure, showing symmetry elements. $ABCD$, first orientation of monoclinic unit cell; $AB'CD'$, second orientation of monoclinic unit cell produced by twinning about AC, the (310) normal of the first; $AB'ED$, trigonal unit cell. (The third monoclinic orientation $B'BD'D$, produced by twinning about BD, the ($3\bar{1}0$) normal of the first, has been omitted for clarity except where it overlaps with the trigonal unit cell). The monoclinic β is 90°, and the c axis of both structures is normal to the paper.

are resolved have practically identical intensities. The true monoclinic cell thus has pseudo-trigonal symmetry, and the average structure should bear a close relationship to the true structure.

In the following discussion the average or statistical structure is first determined for the trigonal unit cell. (The intensities of doublet members of the composite reciprocal lattice were added together when spot splitting occurred.) This is followed by an attempt to define the structure of the monoclinic phase.

The determination of the statistical structure

The X-ray data were collected from one crystal which was approximately $0{\cdot}25 \times 0{\cdot}05 \times 0{\cdot}04$ mm in dimensions and elongated in the [010] direction.

Intensity data for the reciprocal lattice layers $k=$ 0, 1, 2–5 were recorded on multifilms with the equi-inclination Weissenberg technique. Data were collected over the whole sphere of Cu $K\alpha$, and intensities were estimated by eye against a standard scale prepared in the usual manner. Data reduction was effected by the ancillary programme for UTECOM (a DEUCE electronic digital computer) written by Sime (1961). The twofold axes and mirror planes relating rows of weighted reciprocal-lattice points by symmetry enabled many correlations to be made between different layers of the above intensity set. The interlayer scaling factors were then determined by the least-squares method of Dickerson (1959) and Rollett & Sparks (1960). The percentage standard deviation from the mean of scaled structure amplitudes of symmetry-related reflexions was approximately 8%.

There are no systematic absences in spectra (though there are systematic weaknesses mentioned later) and the possible space groups for the trigonal cell are $P\bar{3}m1$, $P32\bar{1}$ and $P3m1$. The last space group is unlikely since the atoms in point positions 3(d) or 6(e) have the same z coordinates and are, therefore, arranged in planes parallel to (001). This situation is rendered impossible by the magnitude of a.

A three-dimensional Patterson synthesis clearly indicated that the six molybdenum atoms occupied positions 2(c) and 2(d) of either of the space groups $P\bar{3}m1$ or $P32\bar{1}$. Phase angles of zero or π radians could be assigned to the observed data on the basis of the Mo contributions to the structure amplitudes, since no matter which space group is chosen, the Mo atoms have a centrosymmetric distribution with respect to the crystallographic axes. The resulting three-dimensional Fourier synthesis enabled the sodium atom to be placed in position 1(b) of either space-group, and the presence of peaks attributable to oxygen in the special positions 3(e) and 3(f) of space group $P\bar{3}m1$ suggested that this space group was correct. An analysis of intensity statistics, with the use of the full three-dimensional data, also favoured the centrosymmetric space-group $P\bar{3}m1$.

One can see from the list of observed reflexion amplitudes (Table 6) that the strong reflexions obey the relation $l=2n$, $h-k+\frac{1}{2}=3m$, at least for l small. The first condition means that the upper half of the cell is *approximately* the same as the lower; the second means that the molybdenum atoms are approximately in rhombohedral array, though with vertical displacements from the ideal positions which become important as l increases. This approximation to a rhombohedral array strongly suggests a relationship between the ideal perovskite structure and that of the sodium molybdenum bronze.

The coordinates of oxygen atoms in six-fold positions 6(i) of space-group $P\bar{3}m1$ were determined from further three-dimensional Fourier and difference Fourier syntheses. There are thus a total of 18 oxygen atoms in the unit cell, one more than the number arrived at by Wold on the basis of analytical figures. A randomness in the distribution of 17 oxygen atoms over 18 sites is therefore required, although a satisfactory agreement between observed and calculated peak heights (Table 2) was obtained by assuming full occupancy of the eighteen oxygen sites. This point will be discussed in detail at a later stage.

The positional coordinates and isotropic thermal parameters of atoms in the unit cell were refined by successive cycles of structure factors and differential syntheses. The scattering curves of Freeman (1962) for Na^+ and O^-, and Thomas–Fermi for Mo were obtained from *International Tables for X-ray Crystallography*, and a correction for the real component of the anomalous dispersion of Cu $K\alpha$ by molybdenum was made with the f' values given by Dauben & Templeton (1955). The estimated standard deviations in atomic positional parameters were calculated according to Cruickshank (1949). All calculations were carried out on a DEUCE machine with the programs of Rollett (1961) and Sime (1961). Refinement was continued un-

Table 2. *Atomic parameters for the sodium molybdenum bronze*

Space group $P\bar{3}m1$

		Peak heights	(e.Å^{-3})	Fractional coordinates			Standard deviations (Å)			
Atom	Point position	$\varrho(o)$	$\varrho(c)$	x/a	y/b	z/c	(x/a)	(y/b)	(z/c)	B(Å^2)
Na	1(b)	12·2	12·4	zero	zero	0·5000	0·0093	0·0120	0·0201	2·46
Mo(1)	2(d)	121·7	127·4	$\frac{1}{3}$	$\frac{2}{3}$	0·3883	0·0013	0·0010	0·0011	1·89
Mo(2)	2(d)	107·0	112·9	$\frac{1}{3}$	$\frac{2}{3}$	0·9245	0·0014	0·0012	0·0013	2·54
Mo(3)	2(c)	101·1	105·9	zero	zero	0·2327	0·0016	0·0012	0·0014	2·87
O(1)	6(i)	10·3	12·8	0·1350	0·8650	0·3558	0·02	0·03	0·02	2·95
O(2)	6(i)	10·3	10·5	0·1891	0·8109	0·8121	0·02	0·02	0·02	3·28
O(3)	3(f)	17·9	17·2	0·5000	zero	0·5000	0·02	0·02	0·02	2·95
O(4)	3(e)	16·7	15·9	0·5000	zero	zero	0·02	0·03	0·02	1·56

* Standard deviations calculated along directions parallel to the true monoclinic cell axes.

til the final shifts were less than the standard deviations in parameters.

During the refinement it was necessary to reduce the occupancy factor of the sodium site 1(*b*) from 93% to 60% in order to obtain a satisfactory agreement between observed and calculated peak heights. At first sight this seems to be in agreement with a higher oxygen content, since low figures for oxygen percentage composition would arise if the sodium content had been overestimated. However, there are five other positions within the unit cell which offer the same stereochemical environment to the sodium atom as it enjoys in space-group position 1(*b*). On the other hand, three-dimensional difference Fourier sections subsequently failed to reveal sodium atoms in any of these sites; an observation not surprising since the remaining 0·33 Na^+ distributed over five sites would hardly be detectable with a standard deviation in ϱ(obs) of 1·0 $e.A^{-3}$.

The final atomic parameters and their standard deviations are listed in Table 2. These parameters were used to calculate the final set of structure factors which are listed for comparison with *F*(obs.) in Table 6. There are many instances in which *F*(calc.) is much greater than *F*(obs.) and this is considered to be due to extinction. Such reflexions are marked with an asterisk. The overall *R* index using the observed reflexions and omitting those marked with an asterisk is 0·16. The temperature factors are surprisingly high, in particular for molybdenum. This is probably to be explained as an artefact of the averaging process since each peak in the Fourier map is a composite peak from the addition of three superposed single structures (blurred, perhaps, by distortions in twin boundary regions). Reliance on interatomic distances to an accuracy of better than $(B/8\pi^2)^{\frac{1}{2}}$ cannot be claimed, and standard deviations listed in Table 2 are probably very much underestimated.

Description and discussion of the average structure

The sodium molybdenum bronze has a distorted perovskite structure. The ideal perovskite structure for compounds of the type ABO_3 is cubic with octahedrally coordinated B cations, all octahedra identical and parallel and sharing corners with 12-coordinated A cations in the cages. The ideal structure might alternatively be described in terms of a rhombohedral lattice with a special value of 90° for the interaxial angle. Using hexagonal axes, one can give a matrix for transforming all edges and indices: $c_H=\sqrt{3}a_0$, $a_H=\sqrt{2}a_0$, where a_0 is the cubic cell edge.

For comparison with the bronze, the ideal structure (1) can be described in terms of a unit cell (2) with $c=2\sqrt{3}a_0$, $a=\sqrt{2}a_0$. The rhombohedral and hexagonal axes are oriented in the reverse setting, and the appropriate transformation matrix for direct lattice vectors and plane indices is

$$\begin{array}{cc} & R_{\text{hex}}\,(2) \\ R_{\text{rev}}\,(1) & \boxed{\begin{matrix} \frac{1}{3} & \frac{\bar{1}}{3} & \frac{1}{6} \\ \frac{1}{3} & \frac{2}{3} & \frac{1}{6} \\ \frac{\bar{2}}{3} & \frac{\bar{1}}{3} & \frac{1}{6} \end{matrix}} \end{array}$$

The resemblance between the ideal and actual cell dimensions and parameters is shown in Table 3, whilst a diagram (Fig. 2) giving projections of the ideal and actual structures on 0001 further illustrates the nature of the distortion.

The sodium ions are not statistically distributed over all available cage sites (empty sites are listed in Table 3), but are ordered at various levels. Parallel to [42$\bar{1}$] every sixth cage is occupied by the interstitial cation

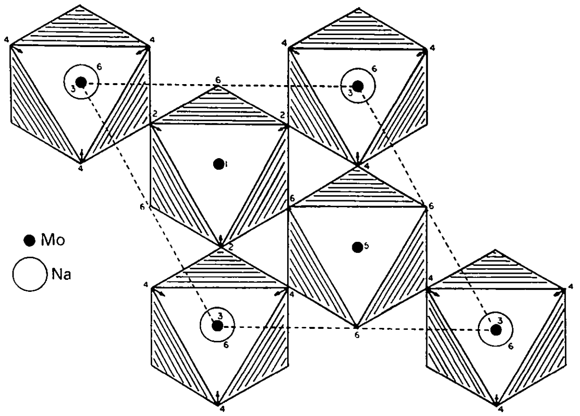

Fig. 2. Projections of the ideal and average structure on (0001). The directions and magnitudes of the deviations of oxygen atoms from the ideal positions are shown by arrows. The upper half of the cell has been omitted, and figures give approximate heights of atoms above (0001) in twelfths of c_H.

Table 3. *A comparison between ideal and actual cell dimensions and parameters for the 'average' structure*

		Actual	Ideal
Cell edge *a* (Å)		5·51	5·40 $(=\sqrt{2}\,a_0)$
Cell edge *c* (Å)		12·95	13·22 $(=\ 2\sqrt{3}\,a_0)$
Cell contents		$Na_{0.9}Mo_6O_{17}$	$Na_6Mo_6O_{18}$
Fractional atomic parameters	Na	0, 0, $\frac{1}{2}$	0, 0, $\frac{1}{2}$
	Mo(1)	$\frac{1}{3}$ $\frac{2}{3}$ 0·3883	$\frac{1}{3}$, $\frac{2}{3}$, 0·4166
	Mo(2)	$\frac{1}{3}$ $\frac{2}{3}$ 0·9245	$\frac{1}{3}$, $\frac{2}{3}$, 0·9167
	Mo(3)	0 0 0·2327	0, 0, 0·2500
	O(1)	0·1350 0·8650 0·3558	0·1667, 0·8333, 0·3333
	O(2)	0·1891 0·8109 0·814	0·1667, 0·8333, 0·8333
	O(3)	$\frac{1}{2}$ 0 $\frac{1}{2}$	$\frac{1}{2}$, 0, $\frac{1}{2}$
	O(4)	$\frac{1}{2}$ 0 0	$\frac{1}{2}$, 0, 0
	Na	vacant	000, $\frac{1}{3}\frac{2}{3}\frac{2}{3}$, $\frac{1}{3}\frac{2}{3}\frac{1}{6}$, $\frac{2}{3}\frac{1}{3}\frac{1}{3}$, $\frac{2}{3}\frac{1}{3}\frac{5}{6}$

whilst in each sheet parallel to $(10\bar{2})$ every sixth row of cages parallel to [010] is filled. Each sodium ion is surrounded by twelve oxygen atoms in the manner shown in Fig. 3. The approach distances (2·27 – 2·76 Å, e.s.d. 0·03 Å) indicate normal ionic interaction [2·25 – 2·78 (±5) according to the tabulation of Ondik & Smith (1962)].

There are three different types of octahedra centred on the three crystallographically distinct molybdenum atoms. Bond distances and angles for each type of octahedron are given in Table 4. The Mo-O bond distances vary between 1·87 and 2·15 Å (e.s.d. 0·02 Å) and variations of these magnitudes are observed in similar metal–oxygen bond distances in distorted perovskite structures such as tetragonal barium titanate (Megaw, 1957*a*). The distortion is an example of the 'off-centre effect' (Megaw, 1957*b*) – the displacement of the small molybdenum atom within its octahedron of oxygen atoms. The off-centre displacements occur towards the mid-point of a face, *i.e.* a three-corner displacement, and the magnitude of the displacement varies from 0·10 to 0·37 Å. Displacements of similar magnitude occur in the sodium, potassium and cadmium niobates – although the direction of the displacements may be towards the mid-point of an edge or towards the corner of an octahedron. The displacements are small when compared with topologically different oxides – undoubtedly because of the fairly homogeneous distribution of positive molybdenum ions throughout the crystal. In compounds such as K_xMoO_3 (Stephenson & Wadsley, 1965) and MoO_3 (Kihlborg, 1963*a*) where molybdenum–oxygen octahedra are sharing edges, as well as corners, to form infinite sheets, the coulombic repulsion experienced by the metal cations is quite asymmetric, and considerable variation in the metal–oxygen bond distance is observed.

If the octahedra associated with Mo(1), Mo(2) and Mo(3) are denoted by (1), (2) and (3) then the oxygen corner-sharing gives rise to approximately linear strings of octahedra in which the sequence is always (1)(3)(2)(2)(3)(1)(1)(3)(2)(2) *etc.* This differs from the conventional order of sequence of sites in cubic close-packing, *i.e.* (1)(3)(2)(1)(3)(2)(1) *etc.* These strings of octahedra are arranged parallel to each of three mutually perpendicular directions, and the sequence is the same in each string, no matter which direction is taken. The sodium ions are surrounded by six octahedra of the type (1) and two of the type (3).

The extent of the 'off-centre' distortion is most pronounced for Mo(1) and Mo(3) – the cations immediately surrounding the sodium ions. The displacements are in directions away from the sodium ions. Oxygen atoms of the type O(1) are noticeably displaced towards the sodium ions, and in the type (3) octahedra the angle subtended at Mo(3) by the symmetry-related O(1) atoms is 66°. The distance between these oxygen atoms is 2·23 ± 0·04 Å, which is low compared with short oxygen–oxygen distances found previously, *e.g.* 2·36 ± 0·04 Å (Wadsley, 1961). The difference is probably not significant, as the variance is high. It might be concluded that the distortions in the molybdenum–oxygen framework are influenced by the ordered sodium cations, but it should be noted that differences between the true structure and the average structure might seriously affect the above results.

The extent to which the molybdenum–oxygen framework can host the alkali metal depends upon the reduction of the presumably hexavalent molybdenum to

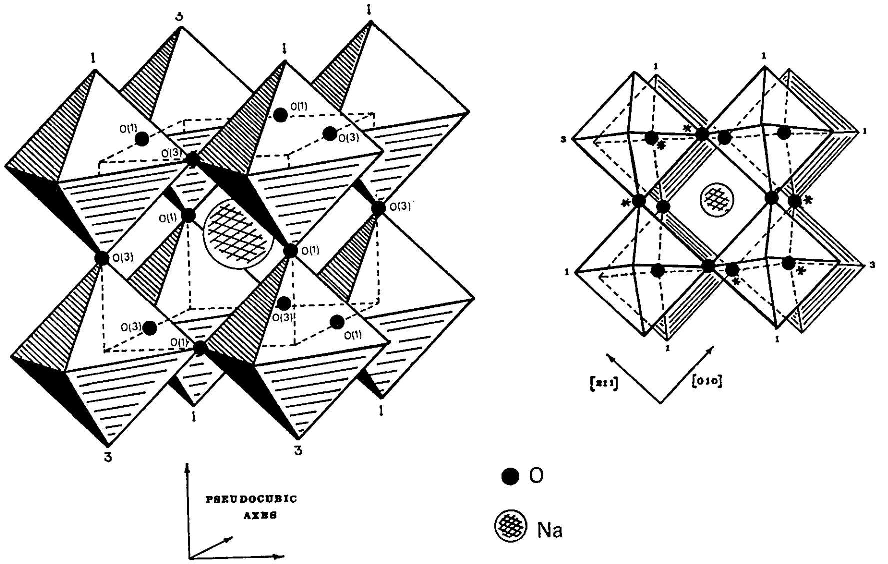

Fig. 3. Depictions of the twelvefold coordination of oxygen atoms about each sodium ion in the trigonal structure. Left: The packing of octahedra around the sodium ion viewed in clinographic projection with respect to the pseudocubic axes. The oxygen atoms of the type O(1) are those giving the short Na–O distances. Right: The environment of a sodium ion viewed perpendicular to $(10\bar{2})$. Octahedra of the type (1) and (3) surround the cation in the manner shown. Atoms marked with an asterisk give short Na–O distances.

Table 4. *Selected interatomic distances* (Å) *and angles* (°) *in the sodium molybdenum bronze*

The table refers to the trigonal 'average structure'.

The first symbol denotes the atom in accordance with Table 2; the second number denotes the following symmetry transformations of the parameters of Table 2:

1: $x, 2x, z$
2: $2\bar{x}, \bar{x}, z$
3: $\bar{x}, x, \bar{z}$
4: $x, 2\bar{x}, \bar{z}$
5: $2x, x, \bar{z}$
6: $x, 1-x, z$
7: $1-2x, 1-x, z$
8: $\bar{x}, 1-2x, \bar{z}$
9: $x, \bar{x}, z$

Following the distances and angles the first number in parentheses is the estimated standard deviation, and refers to the last place of the preceding number; the second number is the number of such distances or angles.

Mo(1) octahedron.

Mo(1)9–O(1)6	1·94(2) (3)	O(1)6–Mo(1)9–O(1)1	115·4(9) (1)
–O(3)9	2·15(1) (3)	O(1)6–Mo(1)9–O(3)1	77·6(9) (2)
O(1)6–O(1)1	3·28(4) (3)	O(3)9–Mo(1)9–O(3)1	79·7(9) (1)
–O(3)1	2·57(2) (3)	O(1)7–Mo(1)9–O(3)2	150·3(9) (1)
O(3)9–O(3)1	2·76(1) (3)	O(1)6– O(3)1–O(3)9	96·0(1) (4)
–O(1)1	2·57(2) (3)	O(1)6– O(1)1–O(3)9	84·0(1) (4)

Mo(2) octahedron.

Mo(2)5–O(2)3	2·00(2) (3)	O(2)3–Mo(2)5–O(2)8	73·1(9) (1)
–O(4)9	1·87(1) (3)	O(2)8–Mo(2)5–O(4)9	95·0(9) (2)
O(2)3–O(2)5	2·38(4) (3)	O(4)9–Mo(2)5–O(4)1	95·1(9) (1)
–O(4)1	2·86(2) (3)	O(2)5–Mo(2)5–O(4)5	165·0(9) (3)
O(4)9–O(4)1	2·76(2) (3)	O(2)3– O(2)8–O(4)9	94·0(1) (4)
		O(2)3– O(4)1–O(4)9	86·0(1) (4)

Mo(3) octahedron.

Mo(3)9–O(1)9	2·05(2) (3)	O(1)9–Mo(3)9–O(1)1	66·0(9) (1)
–O(2)3	1·90(2) (3)	O(1)1–Mo(3)9–O(2)3	86·5(9) (2)
O(1)9–O(1)1	2·23(4) (3)	O(2)3–Mo(3)9–O(2)4	111·1(9) (1)
–O(2)4	2·71(3) (3)	O(1)2–Mo(3)9–O(2)5	146·8(9) (1)
O(2)3–O(2)4	3·13(4) (3)	O(1)9– O(1)1–O(2)3	99·0(1) (4)
		O(1)1– O(2)3–O(2)4	81·0(1) (4)

Na cuboctahedron

Na,9–O(3)9	2·76(1) (6)
–O(1)1	2·27(3) (6)

Cation–cation

Mo(1)1–Mo(3)9	3·761(2) (3)
–Mo(1)5	4·296(2) (3)
Mo(2)5–Mo(3)9	3·772(2) (3)
–Mo(2)9	3·729(2) (3)
Mo(3)9–Mo(1)1	3·761(2) (3)
–Mo(2)5	3·772(2) (3)

Table 5. *Transformed coordinates of the atoms listed in Table* 2

Space group $C2/m$. $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0)^+$

Atom	Point position	Fractional coordinates *x/a*	*y/b*	*z/c*
Na	2(*c*)	zero	zero	½
Mo(1)	4(*i*)	⅔	zero	0·3883
Mo(2)	4(*i*)	⅔	zero	0·9245
Mo(3)	4(*i*)	zero	zero	0·2327
O(41)	2(*b*)	zero	½	zero
O(31)	2(*d*)	zero	½	½
O(42)	4(*e*)	¼	¼	zero
O(32)	4(*f*)	¼	¼	½
O(21)	4(*i*)	0·8109	zero	0·8121
O(11)	4(*i*)	0·8650	zero	0·3558
O(22)	8(*j*)	0·0946	0·1891	0·8121
O(12)	8(*j*)	0·0675	0·1350	0·3558

Mo^{5+}. Up to a point then the occupancy of the sodium 1(*b*) sites depends upon the demand of charge balance imposed by the distribution of Mo^{5+} and Mo^{6+} in the 2(*d*) and 2(*c*) positions.

Description and discussion of the monoclinic structure

The true unit cell of the sodium molybdenum bronze is monoclinic, with dimensions listed in Table 1. This unit cell contains twice the volume of the trigonal cell, and should therefore contain the unit $Na_{1\cdot20}Mo_{12}O_{36}$. As mentioned above, the oxygen content of the unit cell has been overestimated, since it is *not* possible to place 17 oxygen atoms in the trigonal unit cell. However, it *is* possible to place 34 oxygen atoms in the true monoclinic cell using the symmetry transformations of the space-group $C2/m$. It is difficult to see why the structure postulated for the trigonal cell should not, in fact, be the true structure, but a reduction in the number of oxygen atoms provides a possible explanation for this and the twinning phenomenon.

The transformed coordinates in the monoclinic symmetry for the atoms listed in Table 2 are shown in Table 5. The twelve oxygen atoms resulting from 6(*i*) of $P\bar{3}m1$ are broken down to eightfold 8(*j*) and fourfold 4(*i*) positions in $C2/m$. Although the *x* and *y* coordinates of both atoms in 8(*j*) are independent, the values listed for them in Table 5 are obviously related viz. *y* is twice *x*. There is also a relationship between the *y* of the 8(*j*) position and the *x* of the related 4(*i*) position. The interdependence of these parameters results from the twinning, since only the average positions of the oxygen atoms have been determined. The scheme adopted for the numbering of the oxygen atoms so

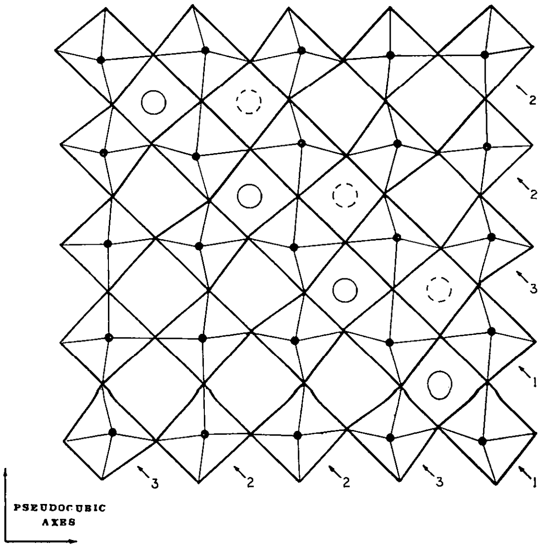

Fig. 4. A section, parallel to (10$\bar{2}$), through the molybdenum atoms in the trigonal structure showing the arrangement of the basal planes of one layer of octahedra. The dark circles represent molybdenum atoms, the large open circles sodium ions. The sodium ions are one half of an octahedral depth above (full circle) or below (broken circle) the section plane. Rows of octahedra of the type (1), (2) or (3) are indicated by arrows.

Table 6. *Observed reflexion amplitudes and calculated structure factors*

Within each group of constant h and k, the columns contain, from left to right: 1, $10F_o$ and $10F_c$. An asterisk indicates a reflexion probably affected by extinction.

0,0,ℓ

2	95	- 85
3	182	211
4	237	- 138
5	416	785 *
6	370	- 551 *
7	762	-1256 *
8	366	431
9	291	- 321
10	93	251 *
11	137	- 16
12	395	210
13	968	583
14	135	59
15	44	66
16	122	150

1,0,ℓ

16	205	-110
15	84	41
14	58	31
13	134	-157
12	133	122
11	870	-770
10	464	-436
9	156	-160
7	280	280
6	249	-233
5	569	734 *
4	695	1304 *
3	325	-368
2	182	197
1	146	157
0	94	93
-1	62	-109
-2	833	-2393 *
-3	415	-342
-4	241	220
-5	335	-347
-6	298	223
-7	461	-588
-8	576	695
-9	804	942
-10	201	-240
-11	187	203
-12	66	-74
-13	54	18
-14	104	64
-15	892	502
-16	167	-44

1,1,ℓ

15	71	50
14	93	-52
13	759	619
12	118	85
11	257	- 214
10	174	93
9	308	-294
8	293	246
7	690	-771
6	712	-1128 *
5	210	289
4	101	-214 *
3	75	188 *
2	65	-108 *
1	76	91
0	587	1668 *

2,0,ℓ

15	486	-490
14	201	84
13	160	141
12	55	59
11	160	191
10	127	-84
9	646	616
8	658	878 *
7	209	-172
6	129	336 *
5	178	-316 *
4	190	303 *
3	281	-566 *
2	493	-853 *
1	198	172
0	99	84
-1	121	-137
-2	139	222 *
-3	143	-164
-4	988	1974 *
-5	517	419
-6	238	-137
-7	275	264
-8	130	-53
-9	401	401
-10	161	-154
-11	857	-820
-12	168	202
-13	117	-128
-14	115	64
-15	80	61

2,1,ℓ

14	43	-50
13	114	-124
12	60	69
11	647	-614
10	304	-227
9	184	134
8	174	-199
7	230	250
6	233	-256
5	446	607 *
4	624	1113 *
5	253	-477 *
2	152	147
1	106	-102
0	49	-34
-1	106	213 *
-2	749	-1574 *
-3	344	-455 *
-4	231	232
-5	256	-286
-6	233	233
-7	295	-318
-8	400	402
-9	601	674
-10	140	-143
-11	158	158
-12	48	-29
-13	53	9
-14	83	7

2,2,ℓ

13	418	401
12	233	119
11	102	-50
10	119	176
9	260	-213
8	233	244
7	474	-586
6	377	-448
5	250	338
4	141	-67
3	157	112
2	64	31
1	63	47
0	742	1492 *

3,0,ℓ

14	105	-37
13	679	514
12	61	-2
11	211	-171
10	137	138
9	231	-259
8	237	240
7	559	-603
6	605	-958 *
5	164	384 *
4	133	-129
3	71	107
2	47	15
1	91	-116
0	581	1157 *
-1	79	239 *
-2	82	-92
-3	71	132
-4	121	-174 *
-5	127	94
-6	508	-742 *
-7	500	-502
-8	171	134
-9	206	-224
-10	118	54
-11	211	-191
-12	131	121
-13	604	487
-14	94	-70

3,1,ℓ

13	82	29
12	54	-56
11	144	141
10	134	-144
9	518	507
8	379	408
7	267	-272
6	169	133
5	217	-208
4	129	109
3	236	-240
2	560	-1034 *
1	87	24
0	60	-57
-1	87	-57
-2	124	92
-3	217	-218
-4	619	824 *
-5	352	337
-6	167	-159
-7	201	206
-8	158	-158
-9	156	164
-10	275	-233
-11	538	-512
-12	93	94
-13	82	-112

3,2,ℓ

11	487	-381
10	300	-225
9	163	116
8	124	-95
7	161	159
6	136	-95
5	325	250
4	525	549
3	171	-131
2	156-	128
1	98	-73
0	69	-17
-1	108	-36
-2	693	-841 *
-3	257	-94
-4	131	75
-5	204	-184
-6	186	126
-7	228	-274
-8	336	345
-9	460	446
-10	168	-151
-11	123	123

3,3,

8	144	102
7	427	-313
6	457	-349
5	169	155
4	188	-151
3	87	93
2	63	-48
1	127	-2
0	659	634

4,0,ℓ

11	549	-475
10	166	-86
9	299	200
8	191	150
7	224	193
6	186	-99
5	371	311
4	725	960 *
3	158	-171
2	140	199 *
1	61	-79
0	68	36
-1	122	139
-2	565	-670 *
-3	219	-243
-4	149	187
-5	140	-210
-6	172	247
-7	142	-144
-8	459	456
-9	495	425
-10	113	-64
-11	155	141

4,1,ℓ

10	100	48
9	193	-170
8	138	108
7	373	-342
6	443	-441
5	156	132
4	145	-154
3	87	97
2	66	-43
1	94	60
0	692	735
-1	115	-53
-2	66	-28
-3	112	101
-4	141	-132
-5	171	197
-6	489	-501
-7	402	-384
-8	170	139
-9	167	-167
-10	107	81

4,2,ℓ

7	123	-122
6	154	178
5	129	-132
4	105	109
3	177	-98
2	447	-451
1	112	82
0	65	31
-1	56	-51
-2	165	149
-3	167	-103
-4	565	549
-5	339	195
-6	129	-42
-7	194	134

5,0,ℓ

9	505	329
8	339	163
7	201	-159
6	164	159
5	181	-161
4	167	114
3	259	-200
2	705	-706
1	131	142
0	93	-37
-1	75	-57
-2	158	100
-3	207	-250
-4	595	521
-5	427	293
-6	170	-130
-7	151	151
-8	111	-129
-9	138	57

5,1,ℓ

5	277	154
4	452	430
3	151	-142
2	140	83
1	87	-30
0	124	-60
-1	133	70
-2	601	-477
-3	238	-134
-4	127	43
-5	154	-117

that the trigonal-monoclinic relationships are evident is as follows:

Trigonal	O(1)	O(2)	O(3)	O(4)
Monoclinic	O(11), O(12)	O(21), O(22)	O(31),O(32)	O(41),O(42)

The coordinates listed in Table 5 were calculated from Fourier maps in which each peak is a composite peak from the addition of three superposed single structures; the coordinates of the peak of one component lie somewhere within this composite, but not necessarily at its centre. An estimate of the spread is given by $(B/8\pi^2)^{\frac{1}{2}} \simeq 0{\cdot}15$ to 0·2 Å. Differences of about half this in atomic positions might be expected.

Either of the point positions 2(*d*) or 2(*b*) is void of oxygen. It seems that 2(*d*), *i.e.* O(31), is the most likely choice for the following reasons:

(*a*) The atom sequence along directions parallel to the two pseudo-hexagonal axes a_1 and a_2 will be –Na–O–Na–O–... *etc.* and –Na–space–Na–space– respectively. The greater concentration of atoms or electron density along a_1 rather than a_2 results in a_1 (5·52 Å) being slightly longer than a_2 (5·50 Å).

(*b*) The sodium ions occupy ordered 2(*c*) positions in lines which run parallel to the unique *b* axis of the monoclinic cell, and are separated from each other only by 2(*d*) positions. If these were not occupied by oxygen atoms, *tunnels* would be formed through the framework, and a partial disordering of sodium into 2(*d*) positions would explain why the occupancy factor for the 2(*c*) position is lower than that suggested by the analytical figures.

The choice of 2(*b*) as an oxygen void does not lend itself to any plausible argument. In support of the above argument (*b*) it is found that tunnel structures occur extensively in ternary oxides. The potassium tungsten bronzes (Magnéli, 1949), the compound $Na_{0\cdot3}WO_3$ (Hägg, 1935) and the tetragonal bronze $Ba_6Ti_2Nb_8O_{30}$ (Stephenson, 1965) all have structures in which the oxygen octahedra are joined together by corners in a framework containing four- and five-sided tunnels which run through the structure. The hexagonal tungsten bronzes, the ternary alkali titanates and the alkali-metal vanadium bronzes (Wadsley, 1964) are further examples of structures with an open metal–oxygen framework in which tunnels persist throughout the structure in one particular direction, and hold the alkali-metal cations in specifically ordered positions.

The monoclinic structure described above is, in effect, derived from the trigonal average 'structure' by the removal of oxygen from a close-packed structure. The Mo(1) atom to which the oxygen was formerly bonded will have five oxygen atoms grouped about it, which is not unlikely. The remaining molybdenum atoms in the sodium bronze each has a normal surround of six oxygens, whilst the sodium ions will have eight- or ten-fold coordination, depending on whether they are in positions 2(*d*) or 2(*c*).

A similar distortion is found in the case of $CaFeO_{2\cdot5}$ (Bertaut, Blum & Sagnières, 1959) where complete rows of oxygen atoms are regularly missing, and the accompanying movements of atoms remaining in the same planes impose tetrahedral coordination upon the iron atoms, whilst calcium has an eight- or nine-fold grouping, not twelvefold as in perovskite itself. Kihlborg (1963*b*) has discussed the structures of certain reduced molybdenum oxides, where the oxidation numbers for Mo are of the same order of magnitude as in the molybdenum bronze. In all cases there are considerable variations in bond distances, and the polyhedron can vary from a distorted octahedron to what may be considered to be virtually a tetrahedron.

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