INORGANIC COMPOUNDS

Two Original Infinite Chains in the New Caesium Tetramolybdate Compound Cs$_2$Mo$_4$O$_{13}$

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Abstract

Although dicaesium tetramolybdate, Cs$_2$Mo$_4$O$_{13}$, is a member of the molybdate family, its structure deviates from those of other tetramolybdates. It crystallizes in the monoclinic system with an a parameter six times greater than those of the other tetramolybdates. The structure comprises two different infinite chains of $[Mo_4O_{13}]_n^{2-}$, which propagate along the [001] direction. One contains blocks made up of two MoO$_6$ octahedra sharing a face, which is unusual in molybdate compounds. The asymmetric unit of the other chain consists of a set of two MoO$_6$ octahedra, one MoO$_5$ square pyramid and one MoO$_4$ tetrahedron sharing edges and corners.

Comment

The polymolybdate compounds of univalent ions with general formula $A_2Mo_nO_{3n+1}$ were studied extensively in the 1970's. Table 3 reports the cell parameters of the known structures. Studies have shown that the structures of these compounds depend on the number of Mo atoms, n and the size of the counter ion, the potassium compounds being taken as structural models. With $n = 1$, the structure contains isolated MoO$_4$ ions of tetrahedral shape. The compounds with $n = 2$ comprise infinite chains built of blocks of two octahedra sharing an edge, each block being connected through corners by two tetrahedra. The building block of the chain of the $n = 3$ compounds consists of two trigonal bipyramids connected by an octahedron, each polyhedron sharing edges. With $n = 4$, the chain starts to widen. It comprises two blocks of two octahedra sharing edges in a plane. Each double block shares an edge with each of two others, situated above and below. When n is greater than 4, only compounds with n odd and prepared with heavy alkaline atoms are known. Their structures consist of double sheets of MoO$_6$ octahedra sharing edges. The $n = 4$ compounds have been observed with all alkaline atoms except caesium.

In the course of our study of the pyrochlore compound CsMo$_2$O$_6$, crystals of Cs$_2$Mo$_4$O$_{13}$ were obtained after oxidation during the process. In contrast to the conclusions of Gatehouse & Miskin (1975), both the cell parameters and space group indicate that the obtained caesium compound is not isomorphous with the corresponding potassium and rubidium compounds (Table 3). Fig. 1 shows a stereoview of the structure along the [001] direction. It reveals that Cs$_2$Mo$_4$O$_{13}$ consists of isolated infinite chains which develop along [001]. The Cs ions situated around the chains give cohesion to the structure. Two kinds of chains, A and B, are observed instead of one in other compounds. The arrangement of the chains, $A,B,B,A,B,B,...$ with a shift of $\frac{1}{2}$ in the [010] direction for every chain, provides an explanation as to why the a parameter is about six times that observed in other tetramolybdates (Table 3). As in the potassium compound, the width of the chains seems to include two MoO$_6$ octahedra, but the similarity stops there.
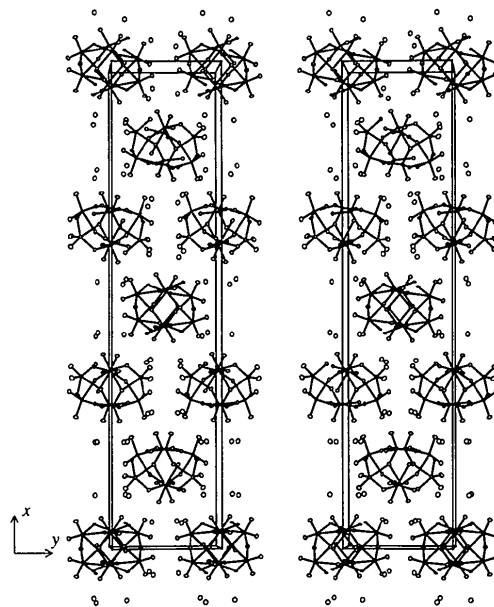

Fig. 1. Stereoview of the contents of the cell along the [001] direction.

A view of chain A is given in Fig. 2. It reveals that the asymmetric unit of the chain comprises two MoO$_6$ octahedra, Mo(1)O$_6$ and Mo(2)O$_6$, sharing the O(1), O(2), O(3) face. The two-octahedra block is reproduced by an inversion centre, which implys that the O(2)–O(2^{ii}) edge is shared, forming a four-MoO$_6$ block. This large block is 'pulled up' by the screw axis such that the replicated block comes above the initial block, sharing atoms O(3) and O(6). It should be noted that

for the face-sharing $Mo(1)O_6$ and $Mo(2)O_6$ octahedra, the distance between their centres, 2.363 Å, is too small to hold the Mo ions at their centres. Repulsion between the Mo ions results in an $Mo(1)\cdots Mo(2)$ distance of 3.167 Å. As a result, the distances of the Mo ion to atoms O(1), O(2) and O(3) of the common face are the longest Mo—O distances in both octahedra (Table 2).
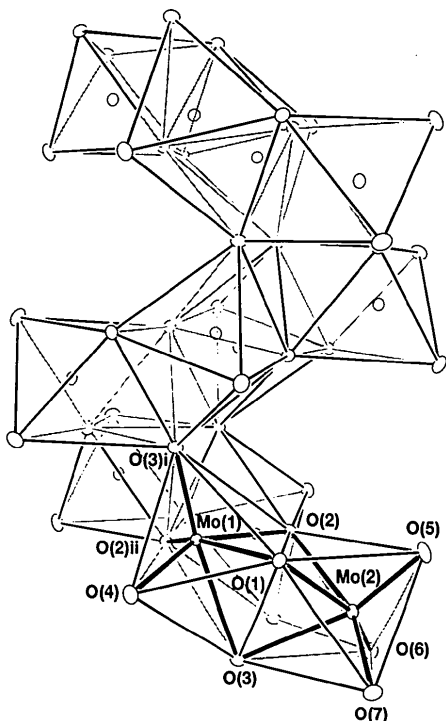
(trigonal bipyramidal), Mo(6) 5.87 (square pyramidal) and 6.00 (octahedral). As Mo is expected to be in oxidation state 6, such values allow the maximum coordination number for both atoms. This deformation of the coordination polyhedra has been observed in other metal oxide compounds (Galy, 1992). We have chosen and presented the first hypothesis, two octahedra, one tetrahedron and a square pyramid, in Fig. 3.
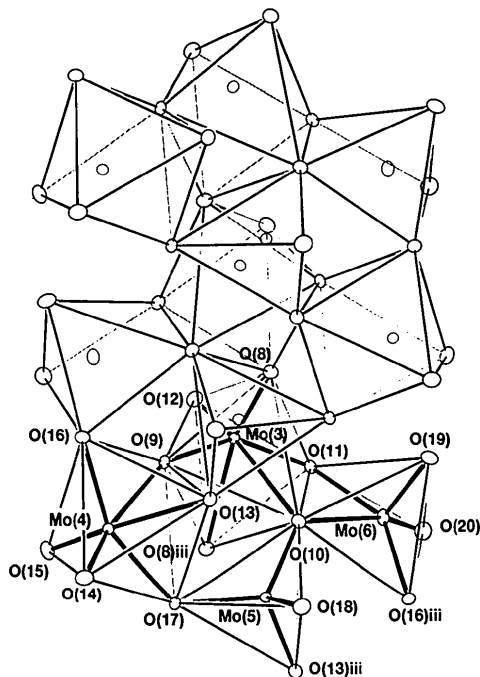

Fig. 2. View of the A chain with the labelling of the atoms. Ellipsoids are drawn at the 75% probability level. The symmetry operations are given in Table 2.

Fig. 3. View of the B chain with the labelling of the atoms. Ellipsoids are drawn at the 75% probability level. The symmetry operations are given in Table 2.

The description of the B chain, depicted in Fig. 3, raises the question of the determination of the Mo coordination number. If we assume that Mo—O bonding distances are shorter than 2.5 Å, then the asymmetric unit comprises two octahedra, $Mo(3)O_6$ and $Mo(4)O_6$, one tetrahedron, $Mo(5)O_4$, and one square pyramid, $Mo(6)O_5$. If we increase the Mo—O bonding distance to 2.7 Å, then it consists of three octahedra and one trigonal bipyramid, $Mo(5)O_5$ (Table 2). The O—Mo—O angles around the Mo(5) and Mo(6) atoms are in agreement with tetrahedral and square-pyramidal surroundings. The shifts of the Mo atoms out of the basal planes of the polyhedra (Table 4) show that the Mo(4) site is octahedral, the Mo(3) and Mo(6) sites are square pyramidal and the Mo(5) site is tetrahedral. The use of the empirical formula $V = \Sigma\exp[(1.907-d_i)/0.37]$ of Brown & Altermatt (1985), which allows determination of the valency of atoms from bond lengths, leads to the following valencies: Mo(5) 5.75 (tetrahedral) and 5.93

The $Mo(3)O_6$ octahedra constitute the spine of the chain, and are each connected to the $Mo(4)O_6$, $Mo(5)O_4$ and $Mo(6)O_5$ polyhedra. The $Mo(3)O_6$ and $Mo(6)O_5$ polyhedra share the O(10)–O(11) edge. The O(10) atom is also shared with the $Mo(5)O_4$ tetrahedron. The $Mo(4)O_6$ octahedron ties the $Mo(3)O_6$ and $Mo(5)O_4$ polyhedra through the O(9) and O(17) corners, respectively. This set is reproduced by the glide plane to form a symmetric block which is connected to the initial one by atoms O(8), O(13), O(16) and O(9), if the distance Mo(6)—O(9) is not considered too long. The basal plane of $Mo(6)O_6$ is nearly parallel to that of $Mo(3)O_6$, forming an angle of 13.0 (2)°, while that of $Mo(4)O_6$ makes an angle of 48.9 (1)°.

The Mo—O distances concur with the conclusions of Gatehouse & Miskin (1975), who presented the same type of variation as observed in other polymolybdate compounds. The distances vary with the type of O-atom environment. The longest Mo—O bonds occur with O

atoms of a face shared by two adjacent polyhedra [average 2.19 (22) Å]. The distances then decrease for O atoms of edges [2.17 (20) Å], corners [1.94 (23) Å] and terminal O atoms [1.704 (8) Å]. A similar correlation is observed between the Mo—O distances and the number of metal atoms linked to an O atom. With an O atom bonded to three, two or one Mo atom, the corresponding average distances decrease from 2.16 (26), through 1.99 (23) to 1.704 (8) Å, respectively. This illustrates that the Mo atoms lie in distorted polyhedra.

The Cs atoms are bonded to the O atoms of the chains by ionic interactions. Each Cs(1) atom, which connects two B chains, is surrounded by 13 O atoms, with Cs—O distances ranging from 3.068 to 3.686 (7) Å. Cs(2) atoms, each surrounded by 11 O atoms [Cs—O 3.013 (7)–3.589 (6) Å] and atoms Cs(3), also each surrounded by 11 O atoms [Cs—O 3.084 (8)–3.822 (7) Å], join the chains A and B. Examination of the Cs—O range and the corresponding average Cs—O distances [Cs(1)—O 3.34 (17), Cs(2)—O 3.25 (17), Cs(3)—O 3.39 (28) Å] reveals that for the most part, the bonds lie in the range 3.0–3.4 Å, which is consistent with the values found in the caesium penta- and heptamolybdates (Gatehouse & Miskin, 1975). Each CsO_n polyhedron shares at least four O atoms with other oxygenated caesium polyhedra. The shortest Cs$\cdots$Cs distances are observed between Cs(1) and Cs(1^{iv}) [4.793 (3) Å], and Cs(2) and Cs(2^{iv}) [4.739 (3) Å]; all other distances are greater than 5 Å.

This structure determination confirms the infinite-chain shape of the tetramolybdate compounds. The main difference with this structure is the presence of two types of chain, the first comprising MoO_6 octahedra sharing faces and corners and the second built from a set of MoO_4 tetrahedra, MoO_5 square pyramids and MoO_6 octahedra sharing edges and corners.

Experimental

Colourless single crystals of $Cs_2Mo_4O_{13}$ were obtained by heating a well ground mixture of Cs_2CO_3, MoO_3 and MoO_2 (1:3:1) at 900 K for 12 h. The specific mass was determined in water by pycnometry.

Crystal data

$Cs_2Mo_4O_{13}$
$M_r = 857.56$
Monoclinic
$C2/c$
$a = 45.92\,(5)$ Å
$b = 10.418\,(3)$ Å
$c = 7.923\,(8)$ Å
$\beta = 92.94\,(5)°$
$V = 3785\,(3)$ Å^3
$Z = 12$
$D_x = 4.52$ Mg m^{-3}
$D_m = 4.45\,(5)$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.24–16.16°$
$\mu = 9.63$ mm^{-1}
$T = 293$ K
Elongated plate
$0.32 \times 0.12 \times 0.06$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction:
by integration from crystal shape
$T_{min} = 0.308$, $T_{max} = 0.582$
12 923 measured reflections
7731 independent reflections

8116 observed reflections
[$I > \sigma(I)$]
$R_{int} = 0.020$
$\theta_{max} = 40.0°$
$h = -82 \rightarrow 82$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 14$
3 standard reflections
frequency: 120 min
intensity decay: 2.9%

Refinement

Refinement on F^2
$R(F) = 0.066$
$wR(F^2) = 0.160$
$S = 1.161$
7144 reflections
259 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0915P)^2 + 12.24P]$
$P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{max} = 0.0001$

$\Delta\rho_{max} = 2.07$ e Å^{-3}
$\Delta\rho_{min} = -2.51$ e Å^{-3}
Extinction correction:
SHELXL93 (Sheldrick, 1993)
Extinction coefficient: 0.00019
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
Cs(1)	0.28038 (1)	0.37051 (6)	0.29115 (8)	1.99 (1)
Cs(2)	0.05376 (1)	0.62486 (6)	−0.08755 (8)	1.79 (1)
Cs(3)	0.10990 (1)	0.14694 (6)	−0.07698 (9)	2.07 (1)
Mo(1)	0.03417 (1)	−0.01863 (6)	0.07235 (9)	0.94 (1)
Mo(2)	0.02811 (2)	0.26444 (6)	−0.07069 (9)	1.09 (1)
Mo(3)	0.13049 (2)	0.49412 (6)	0.13403 (9)	1.01 (1)
Mo(4)	0.19344 (2)	0.23231 (6)	0.13562 (9)	1.08 (1)
Mo(5)	0.20475 (2)	0.52548 (6)	−0.03243 (9)	1.01 (1)
Mo(6)	0.14555 (2)	0.77883 (7)	−0.0573 (1)	1.38 (2)
O(1)	0.0494 (1)	0.1509 (5)	0.0852 (8)	1.1 (1)
O(2)	−0.0035 (1)	0.1187 (6)	0.0211 (8)	1.3 (1)
O(3)	0.0333 (1)	0.0591 (6)	−0.2118 (8)	1.3 (1)
O(4)	0.0641 (2)	−0.0990 (6)	0.0111 (9)	1.6 (1)
O(5)	0.0193 (2)	0.3857 (6)	0.060 (1)	1.9 (1)
O(6)	0	0.2817 (9)	−1/4	1.6 (2)
O(7)	0.0570 (2)	0.3234 (7)	−0.1736 (9)	1.85 (9)
O(8)	0.1343 (2)	0.5631 (7)	0.3349 (9)	1.7 (2)
O(9)	0.1529 (2)	0.3508 (6)	0.1598 (8)	1.4 (1)
O(10)	0.1736 (2)	0.6016 (6)	0.0521 (8)	1.5 (1)
O(11)	0.1201 (1)	0.6478 (6)	0.0009 (9)	1.4 (1)
O(12)	0.0962 (1)	0.4289 (7)	0.1247 (9)	1.7 (2)
O(13)	0.2073 (2)	0.4187 (6)	0.2569 (9)	1.5 (1)
O(14)	0.2286 (2)	0.1779 (7)	0.145 (1)	2.2 (1)
O(15)	0.1756 (2)	0.1196 (7)	0.014 (1)	2.1 (1)
O(16)	0.1833 (1)	0.1894 (6)	0.3569 (8)	1.4 (1)
O(17)	0.2007 (1)	0.3536 (5)	−0.0546 (8)	1.2 (1)
O(18)	0.2368 (2)	0.5799 (7)	0.064 (1)	2.0 (1)
O(19)	0.1497 (2)	0.8650 (7)	0.124 (1)	2.4 (1)
O(20)	0.1236 (2)	0.8705 (7)	−0.187 (1)	2.3 (1)

Table 2. *Selected geometric parameters* (Å, °)

Mo(1)—O(4)	1.701 (7)	Mo(4)—O(15)	1.701 (7)
O(3^i)$\cdots$O(4)	2.706 (9)	O(14)$\cdots$O(15)	2.67 (1)
Mo(1)—O(3^i)	1.764 (7)	Mo(4)—O(14)	1.711 (7)
O(2^{ii})$\cdots$O(4)	2.790 (9)	O(16)$\cdots$O(15)	2.81 (1)
O(2^{ii})$\cdots$O(3^i)	2.813 (9)	O(16)$\cdots$O(14)	2.74 (1)
Mo(1)—O(2^{ii})	1.875 (6)	Mo(4)—O(16)	1.891 (6)

Atoms	Å	Atoms	Å
O(1)···O(4)	2.761 (8)	O(17)···O(15)	2.763 (9)
O(1)···O(3^{i})	2.836 (8)	O(17)···O(14)	2.699 (9)
O(1)···O(2^{ii})	3.585 (8)	O(17)···O(16)	3.803 (9)
Mo(1)—O(1)	1.900 (6)	Mo(4)—O(17)	2.007 (6)
O(2)···O(4)	3.847 (9)	O(13)···O(15)	3.903 (9)
O(2)···O(3^{i})	3.222 (8)	O(13)···O(14)	2.85 (1)
O(2)···O(2^{ii})	2.52 (1)	O(13)···O(16)	2.764 (9)
O(2)···O(1)	2.475 (9)	O(13)···O(17)	2.562 (9)
Mo(1)—O(2)	2.264 (6)	Mo(4)—O(13)	2.244 (6)
O(3)···O(4)	2.751 (9)	O(9)···O(15)	2.889 (6)
O(3)···O(3^{i})	4.148 (5)	O(9)···O(14)	3.92 (1)
O(3)···O(2^{ii})	2.793 (8)	O(9)···O(16)	2.642 (8)
O(3)···O(1)	2.610 (8)	O(9)···O(17)	2.844 (9)
O(3)···O(2)	2.689 (9)	O(9)···O(13)	2.670 (9)
Mo(1)—O(3)	2.390 (7)	Mo(4)—O(9)	2.250 (6)
Mo(2)—O(5)	1.695 (7)	Mo(5)—O(18)	1.717 (7)
O(7)···O(5)	2.68 (1)	O(13^{iii})···O(18)	2.723 (9)
Mo(2)—O(7)	1.707 (8)	Mo(5)—O(13^{iii})	1.776 (7)
O(6)···O(5)	2.784 (8)	O(10)···O(18)	2.91 (1)
O(6)···O(7)	2.690 (7)	O(10)···O(13^{iii})	2.88 (1)
Mo(2)—O(6)	1.877 (2)	O(10)···O(10)	1.796 (7)
O(1)···O(5)	2.811 (9)	O(17)···O(18)	3.003 (9)
O(1)···O(7)	2.763 (9)	O(17)···O(13)	2.828 (8)
O(1)···O(6)	3.663 (7)	O(17)···O(10)	3.008 (8)
Mo(2)—O(1)	1.937 (6)	Mo(5)—O(17)	1.808 (5)
O(2)···O(5)	2.981 (9)	O(13)···O(18)	2.68 (1)
O(2)···O(7)	3.884 (9)	O(13)···O(13^{iii})	4.307 (7)
O(2)···O(6)	2.749 (8)	O(13)···O(10)	2.897 (9)
O(2)···O(1)	2.475 (8)	O(13)···O(17)	2.562 (9)
Mo(2)—O(2)	2.247 (6)	Mo(5)—O(13)	2.545 (7)
O(3)···O(5)	4.094 (9)	Mo(6)—O(20)	1.695 (8)
O(3)···O(7)	2.971 (9)	O(19)···O(20)	2.68 (1)
O(3)···O(6)	2.785 (9)	Mo(6)—O(19)	1.696 (8)
O(3)···O(1)	2.610 (8)	O(11)···O(20)	2.77 (1)
O(3)···O(2)	2.639 (8)	O(11)···O(19)	2.79 (1)
Mo(2)—O(3)	2.431 (6)	Mo(6)—O(11)	1.871 (6)
Mo(3)—O(12)	1.711 (6)	O(16^{iii})···O(20)	2.81 (1)
O(8)···O(12)	2.733 (9)	O(16^{iii})···O(19)	2.74 (1)
Mo(3)—O(8)	1.746 (7)	O(16^{iii})···O(11)	3.599 (9)
O(9)···O(12)	2.727 (9)	Mo(6)—O(16^{iii})	1.923 (9)
O(9)···O(8)	2.771 (9)	O(10)···O(20)	4.03 (1)
Mo(3)—O(9)	1.819 (6)	O(10)···O(19)	3.02 (1)
O(11)···O(12)	2.734 (9)	O(10)···O(11)	2.517 (9)
O(11)···O(8)	2.832 (9)	O(10)···O(16^{iii})	2.721 (9)
O(11)···O(16)	3.638 (8)	Mo(6)—O(10)	2.388 (6)
Mo(3)—O(11)	1.963 (6)	O(9^{iii})···O(20)	2.96 (1)
O(10)···O(12)	4.050 (9)	O(9^{iii})···O(19)	4.32 (1)
O(10)···O(8)	2.98 (1)	O(9^{iii})···O(11)	3.163 (9)
O(10)···O(9)	2.923 (8)	O(9^{iii})···O(10)	2.642 (8)
O(10)···O(11)	2.517 (9)	O(9^{iii})···O(10)	3.240 (9)
Mo(3)—O(10)	2.393 (7)	Mo(6)···O(9^{iii})	2.653 (7)
O(8^{iii})···O(12)	2.96 (1)	Mo(1)···Mo(2)	3.167 (1)
O(8^{iii})···O(8)	4.174 (5)	Mo(4)···Mo(6^{iv})	3.366 (2)
O(8^{iii})···O(9)	2.816 (9)	Mo(1)···Mo(1^{ii})	3.307 (3)
O(8^{iii})···O(11)	2.659 (9)	Mo(4)···Mo(5)	3.383 (1)
O(8^{iii})···O(10)	2.973 (9)	Mo(3)···Mo(6)	3.419 (1)
Mo(3)—O(8^{iii})	2.458 (7)		

Angle	°	Angle	°
O(4)—Mo(1)—O(3^{i})	102.7 (3)	O(7)—Mo(2)—O(6)	97.1 (2)
O(4)—Mo(1)—O(2^{ii})	102.4 (3)	O(7)—Mo(2)—O(1)	98.4 (3)
O(4)—Mo(1)—O(1)	99.9 (2)	O(7)—Mo(2)—O(2)	158.2 (2)
O(4)—Mo(1)—O(2)	151.7 (2)	O(7)—Mo(2)—O(3)	90.0 (2)
O(4)—Mo(1)—O(3)	82.6 (2)	O(6)—Mo(2)—O(1)	147.6 (3)
O(3^{i})—Mo(1)—O(2^{ii})	101.2 (2)	O(6)—Mo(2)—O(2)	83.1 (2)
O(3^{i})—Mo(1)—O(1)	101.4 (2)	O(6)—Mo(2)—O(3)	79.4 (2)
O(3^{i})—Mo(1)—O(2)	105.5 (2)	O(1)—Mo(2)—O(2)	72.1 (2)
O(3^{i})—Mo(1)—O(3)	173.6 (1)	O(1)—Mo(2)—O(3)	72.3 (2)
O(2^{ii})—Mo(1)—O(1)	143.6 (2)	O(2)—Mo(2)—O(3)	68.5 (2)
O(2^{ii})—Mo(1)—O(2)	74.3 (2)	O(12)—Mo(3)—O(8)	104.4 (3)
O(2^{ii})—Mo(1)—O(3)	80.8 (2)	O(12)—Mo(3)—O(9)	101.1 (3)
O(1)—Mo(1)—O(2)	72.3 (2)	O(12)—Mo(3)—O(11)	95.9 (2)
O(1)—Mo(1)—O(3)	73.9 (2)	O(12)—Mo(3)—O(10)	160.9 (2)
O(2)—Mo(1)—O(3)	69.0 (2)	O(12)—Mo(3)—O(8^{iii})	88.4 (2)
O(5)—Mo(2)—O(7)	103.8 (3)	O(8)—Mo(3)—O(9)	101.9 (3)
O(5)—Mo(2)—O(6)	102.3 (3)	O(8)—Mo(3)—O(11)	99.4 (2)
O(5)—Mo(2)—O(1)	101.2 (3)	O(8)—Mo(3)—O(10)	90.6 (2)
O(5)—Mo(2)—O(2)	97.3 (3)	O(8)—Mo(3)—O(8^{iii})	165.8 (2)
O(5)—Mo(2)—O(3)	165.5 (2)	O(9)—Mo(3)—O(11)	148.2 (2)
O(11)—Mo(3)—O(8^{iii})	72.9 (2)	O(9)—Mo(3)—O(10)	86.7 (2)
O(10)—Mo(3)—O(8^{iii})	75.6 (2)	O(9)—Mo(3)—O(8^{iii})	80.8 (2)
O(15)—Mo(4)—O(14)	102.8 (4)	O(11)—Mo(3)—O(10)	69.7 (2)
O(15)—Mo(4)—O(16)	103.1 (3)	O(18)—Mo(5)—O(13)	75.3 (3)
O(15)—Mo(4)—O(17)	95.9 (3)	O(13^{iii})—Mo(5)—O(10)	107.3 (3)
O(15)—Mo(4)—O(13)	163.1 (3)	O(13^{iii})—Mo(5)—O(17)	104.1 (2)
O(15)—Mo(4)—O(9)	92.9 (3)	O(13^{iii})—Mo(5)—O(13)	170.7 (2)
O(14)—Mo(4)—O(16)	99.2 (3)	O(10)—Mo(5)—O(17)	113.1 (2)
O(14)—Mo(4)—O(17)	92.7 (3)	O(10)—Mo(5)—O(13)	81.7 (2)
O(14)—Mo(4)—O(13)	91.3 (3)	O(17)—Mo(5)—O(3)	69.7 (2)
O(14)—Mo(4)—O(9)	164.1 (3)	O(20)—Mo(6)—O(19)	104.6 (3)
O(16)—Mo(4)—O(17)	154.5 (2)	O(20)—Mo(6)—O(11)	101.6 (3)
O(16)—Mo(4)—O(13)	83.4 (2)	O(20)—Mo(6)—O(16^{iii})	101.9 (3)
O(16)—Mo(4)—O(9)	78.7 (2)	O(20)—Mo(6)—O(10)	161.3 (3)
O(17)—Mo(4)—O(13)	73.8 (2)	O(20)—Mo(6)—O(9^{iii})	82.6 (3)
O(17)—Mo(4)—O(9)	83.6 (2)	O(19)—Mo(6)—O(11)	102.7 (3)
O(13)—Mo(4)—O(9)	72.9 (2)	O(19)—Mo(6)—O(16^{iii})	98.4 (3)
O(18)—Mo(5)—O(13^{iii})	102.3 (3)	O(19)—Mo(6)—O(10)	93.8 (3)
O(18)—Mo(5)—O(10)	111.6 (3)	O(19)—Mo(6)—O(9^{iii})	166.2 (3)
O(18)—Mo(5)—O(17)	116.8 (3)	O(11)—Mo(6)—O(16^{iii})	143.1 (2)
		O(11)—Mo(6)—O(10)	71.3 (2)
		O(11)—Mo(6)—O(9^{iii})	86.9 (2)
		O(16)—Mo(6)—O(10)	77.4 (2)
		O(16)—Mo(6)—O(7)	68.4 (2)
		O(10)—Mo(6)—O(9^{iii})	79.8 (2)

Symmetry codes: (i) $x, -y, \frac{1}{2} + z$; (ii) $-x, -y, -z$; (iii) $x, 1 - y, z - \frac{1}{2}$; (iv) $x, 1 - y, \frac{1}{2} + z$.

Table 3. Crystallographic data for univalent-metal poly-molybdates (Å, °)

	a	b	c	α	β	γ	Volume (Å^3)	Space group
K_2MoO_4[a]	12.348	6.081	7.538	90	115.74	90	509	$C2/m$
Rb_2MoO_4[b]	12.821	6.253	7.842	90	115.64	90	566	$C2/m$
Cs_2MoO_4[c]	11.608	6.562	8.510	90	90	90	648	$Pnma$
$Na_2Mo_2O_7$[d]	7.164	11.837	14.714	90	90	90	1248	$Cmca$
$K_2Mo_2O_7$[e]	7.51	7.24	6.95	92	112	82.5	347	$P\bar{1}$
$K_2Mo_3O_{10}$[f,g]	13.952	7.757	9.015	90	99.18	90	963	$C2/c$
$Cs_2Mo_3O_{10}$[g]	14.55	8.43	9.52	90	90.99	90	1153	$C2/c$
$Rb_2Mo_3O_{10}$[h]	14.14	8.085	9.151	90	98.4	90	1035	$C2/c$
$Li_2Mo_4O_{13}$[i]	8.578	11.450	8.225	109.24	96.04	95.95	750	$P\bar{1}$
$K_2Mo_4O_{13}$[j]	8.352	10.024	7.972	102.75	109.8	107.14	560	$P\bar{1}$
$Rb_2Mo_4O_{13}$[j]	8.41	10.274	8.24	103.71	109.7	107.19	593	$P\bar{1}$
$Cs_2Mo_4O_{13}$[k]	45.92	10.418	7.923	90	92.94	90	3784	$C2/c$
$Tl_2Mo_4O_{13}$[l]	7.583	15.409	18.789	90	90	90	2195	$Pbca$
$Cs_2Mo_5O_{16}$[m]	21.44	5.559	14.338	90	98.647	90	1437	$C2/c$
$Cs_2Mo_7O_{22}$[m]	20.512	5.526	19.460	90	125.20	90	1802	$C2/c$
$Rb_2Mo_7O_{22}$[m]	20.73	5.553	18.56	90	120.79	90	1836	$C2/c$
$Tl_2Mo_7O_{22}$[n]	21.54	5.537	18.91	90	122.71	90	1898	$C2/c$

References: (a) Gatehouse & Leverett (1969); (b) Kools, Koster & Rieck (1970); (c) Gonschorek & Hahn (1973); (d) Lindqvist (1950); Seleborg (1967); (e) Magarill & Klevtsova (1971); (f) Seleborg (1966); (g) Gatehouse & Leverett (1968); (h) Foerster, Kreusler & Fuchs (1985); (i) Gatehouse & Miskin (1974); (j) Gatehouse & Leverett (1971); (k) present work; (l) Toledano & Touboul (1978); (m) Gatehouse & Miskin (1975); (n) Toledano, Touboul & Herpin (1976).

Table 4. Distances (Å) of Mo atoms to the main O-atom planes

Mo(1)	O(1),O(2),O(2^{ii}),O(4)	0.409 (6)
Mo(2)	O(1),O(2),O(5),O(7)	0.38 (5)
Mo(3)	O(9),O(10),O(11),O(12)	0.33 (3)
Mo(4)	O(9),O(13),O(14),O(15)	0.08 (1)
Mo(5)	O(10),O(17),O(18)	−0.45 (2)
Mo(6)	O(10),O(11),O(16^{iii}),O(20)	0.35 (3)

Symmetry codes: (ii) $-x, -y, -z$; (iii) $x, 1 - y, z - \frac{1}{2}$.

Heavy atoms (Cs and some Mo) were located by the Patterson technique; other atoms were found from a series of refinements and Fourier summations. Anisotropic displacement parameters were assigned to all atoms. At this step, it appeared that *SHELX*76 (Sheldrick, 1976) and the absorption correction

program *DIFABS* (Walker & Stuart, 1983) did not operate well with the data. The versions we used do not correctly handle indices over 50. So absorption corrections were performed using a modified version of *DATAP* (Coppens, Lieserowitz & Rabinovich, 1965) and the structure was refined using *SHELXL*93 (Sheldrick, 1993).

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1993). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *CADAK* (Savariault, 1991a). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *OR-TEP*II (Johnson, 1976). Software used to prepare material for publication: *TABPUB* (Savariault, 1991b).

References

Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* **B41**, 244–247.
Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035–1041.
Enraf–Nonius (1993). *CAD-4-EXPRESS*. Version 5.1. Enraf–Nonius, Delft, The Netherlands.
Foerster, A., Kreusler, H. U. & Fuchs, J. (1985). *Z. Naturforsch. Teil B*, **40**, 1139–1148.
Galy, J. (1992). *J. Solid State Chem.* **100**, 229–245.
Gatehouse, B. M. & Leverett, P. (1968). *J. Chem. Soc. A*, pp. 1398–1405.
Gatehouse, B. M. & Leverett, P. (1969). *J. Chem. Soc. A*, pp. 849–854.
Gatehouse, B. M. & Leverett, P. (1971). *J. Chem. Soc. A*, pp. 2107–2112.
Gatehouse, B. M. & Miskin, B. K. (1974). *J. Solid State Chem.* **9**, 247–254.
Gatehouse, B. M. & Miskin, B. K. (1975). *Acta Cryst.* **B31**, 1293–1299.
Gonschorek, W. & Hahn, T. (1973). *Z. Kristallogr.* **138**, 167–176.
Hoekstra, H. R. (1973). *Inorg. Nucl. Chem. Lett.* **9**, 1291–1301.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kools, F. X. N. M., Koster, A. S. & Rieck, G. D. (1970). *Acta Cryst.* **B26**, 1974–1977.
Lindqvist, I. (1950). *Acta Chem. Scand.* **4**, 1066–1074.
Magarill, S. A. & Klevtsova, R. F. (1971). *Kristallografiya*, **16**, 742–745.
Salmon, R. & Caillet, P. (1969). *Bull. Soc. Chim. Fr.* **5**, 1569–1573.
Savariault, J. M. (1991a). *CADAK. Programme de Réduction des Données du CAD-4*. CEMES, France.
Savariault, J. M. (1991b). *TABPUB. Programme de Présentation des Tableaux pour Structure Cristalline*. CEMES, France.
Seleborg, M. (1966). *Acta Chem. Scand.* **20**, 2195–2201.
Seleborg, M. (1967). *Acta Chem. Scand.* **21**, 499–504.
Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.
Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing 3*, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–179. Oxford Univ. Press.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.
Toledano, P. & Touboul, M. (1978). *Acta Cryst.* **B34**, 3547–3551.
Toledano, P., Touboul, M. & Herpin, P. (1976). *Acta Cryst.* **B32**, 1859–1863.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

NbAs₂

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Abstract

The structure of niobium diarsenide, $NbAs_2$, has been determined by single-crystal X-ray diffraction; it was found to crystallize with the $OsGe_2$ structure type.

Comment

The lattice parameters as well as the possible space groups of $NbAs_2$ were first reported in 1964 (Saini, Calvert & Taylor, 1964). A second study using the Guinier technique was performed in 1964 (Furuseth & Kjekshus, 1964a,b). In further investigations (Furuseth & Kjekshus, 1965), the crystal structure was solved in space group $C2$ using integrated intensities from Weissenberg photographs. Problems occurring during the refinement procedure were attributed to absorption effects. It was suggested by Pearson (1967, 1972) that $OsGe_2$ may be of the $NbAs_2$ type. A reinvestigation of a number of structures crystallizing with either the $OsGe_2$ or $NbAs_2$ structures showed that $C2/m$ gives the best refinement results (Calvert, 1992). These structures may be classified in $C2/m$ with $OsGe_2$ as the prototype structure (Calvert, 1992). Very recently, single crystals of $NbSb_2$ were reported to crystallize in space group $C2/m$ with the $OsGe_2$ structure type (Rehr & Kauzlarich, 1994). To confirm that $NbAs_2$ also crystallizes with the $OsGe_2$ structure type, we refined our single-crystal data in both $C2/m$ and $C2$. The final $R(F)$ and $wR(F)$ values were slightly lower for the $C2/m$ refinement (3.03 and 2.88%) compared with those of the $C2$ refinement (3.13 and 3.12%). The positional parameters differ from those reported by Furuseth & Kjekshus (1964b, 1965). Consequently, the bond distances (Table 2) are also different from the values given in the previous contributions (Furuseth & Kjekshus, 1964b, 1965).

The Nb atom is in a triangular prism of six As atoms. Two other As atoms and one Nb atom lie outside the rectangular faces. Outside each of the triangular faces two, more distant, Nb atoms are located. Each As1 atom has a distorted square-pyramidal environment of five Nb atoms. One close As1 atom is located across the base of the pyramid. Each As2 atom is coordinated to three other As2 and three Nb atoms. The arrangement of the