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The Crystal Structure of Dipotassium Trimolybdate

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The structure of dipotassium trimolybdate is monoclinic with the following unit cell dimensions:
$a = 13.95$ Å, $b = 7.58$ Å, $c = 9.02$ Å, $\beta = 99.2°$.
The space group is $C2/c$.
The structure is built up by infinite trimolybdate chains interleaved by potassium ions. The coordination around molybdenum is mixed octahedral and tetrahedral with a strong tendency towards five-fold coordination on part of the tetrahedrally surrounded molybdenum atoms. The parameters have been refined using the least squares method.

In a review article by Lindqvist [1] on the crystal structures of several alkali isopolymolybdates some preliminary data are given for dipotassium trimolybdate. The unit cell dimensions and symmetry of this compound are given, as are also the positions of the molybdenum and potassium atoms. In order to examine the structure more closely a new investigation of this compound has been carried out, where the data reported by Lindqvist have been refined and the crystal structure determination completed.

Dipotassium trimolybdate was prepared by the dry method. An intimate mixture of potassium molybdate (Hopkins & Williams Ltd., England) and molybdenum trioxide (Analytical Reagent, Mallinckrodt Chemical Works, USA) was heated in a platinum crucible at 600°C for two weeks. The crystals obtained were white, needle-shaped and adhering strongly to each other in the needle direction.

Weissenberg data were taken rotating a single crystal around the needle axis, which was chosen as the c direction, using Cu$K\alpha$ radiation. The dimensions of the crystal used were 0.07 mm in the direction of the rotation axis, the cross section of the crystal being an approximately equilateral triangle with the side 0.03 mm. The layers $hk0$–$hk7$ were recorded using multiple film technique. The relative intensities were estimated visually by comparison with an intensity scale obtained by photographing a reflection with different exposure times.

All calculations including Lorentz-polarization correction, absorption correction,[2] Fourier summations [3] and least squares refinement were carried

out on a Facit EDB digital computer by means of programs assigned the numbers 6014, 6015, 6016, 6019, and 6023 in the World List of Crystallographic Computer Programs.[4] The least squares program makes use of the block diagonal matrix approximation with individual, isotropic temperature factors. Cruickshank's weighting function $w = (a + |F_0| + c|F_0|^2)^{-1}$ was used in the refinement. The total linear absorption coefficient $\mu = 411.6$ cm^{-1} used for the calculation of absorption factors was derived from the atomic absorption coefficients given in the *International Tables for X-Ray Crystallography*.[5] The atomic scattering curves [5,6] for Mo^{3+}, K^+, and O^- were used with the real part of the dispersion correction [5] applied. The scattering curve for Mo^{3+} was extrapolated from the ones calculated for Mo° and Mo^+.

A list of the observed and calculated structure factors may be obtained from this Institute on request.

DERIVATION OF THE STRUCTURE

The unit cell dimensions were determined by the method of least squares from a powder pattern recorded in a Guinier focusing camera using KCl as an internal standard. The unit cell which is monoclinic has the following dimensions

$a = 13.952$ Å	$\sigma(a) = \pm 0.009$ (13.95 Å)
$b = 7.757$ Å	$\sigma(b) = \pm 0.007$ (7.76 Å)
$c = 9.015$ Å	$\sigma(c) = \pm 0.011$ (9.01 Å)
$\beta = 99.18°$	$\sigma(\beta) = \pm 0.28°$ (99.1°)

where the constants within parentheses are those obtained by Lindqvist.

The systematically absent reflections were hkl with $h+k$ odd and $h0l$ with l odd. These conditions lead to the alternative space-groups Cc and $C2/c$. The assumption of space-group $C2/c$, which was also chosen by Lindqvist, was confirmed by the subsequent refinement, whereas later attempts to lower the symmetry to space-group Cc were unsuccessful. Initially all 469 of the independent reflections measured were made use of in the calculations. Only observed reflections were included.

The coordinates for the metal atom positions as determined by Lindqvist were submitted to a least squares refinement together with roughly estimated temperature factors. The discrepancy index

$$R = \frac{\sum |F_o(hkl) - F_c(hkl)|}{\sum |F_o(hkl)|}$$

was then 0.188, which indicated the correctness of these values. The final parameters (Table 2) are in good agreement with those obtained by Lindqvist. The oxygen positions were determined from a three-dimensional Fourier synthesis. Assuming space-group $C2/c$ the oxygens were placed in five eightfold positions. The least squares refinement made on these coordinates together with the refined metal atom parameters gave an R-factor of 0.098. There were, however, slight discrepancies in the temperature factors for the oxygen atoms. To account for these, attempts were made to split the eightfold posi-

Table 1. Analysis of the weighting scheme used in the last cycles of refinement of the structure of $K_2Mo_3O_{10}$.

Interval sin ϑ	Number of independent reflections	$\overline{w\,\Delta^2}$	Interval F_o	Number of independent reflections	$\overline{w\,\Delta^2}$
0–0.46	80	1.11	0–26	1	4.31
0.46–0.58	61	0.67	26–52	32	1.44
0.58–0.67	49	0.85	52–78	82	0.98
0.67–0.74	41	1.07	78–104	83	0.75
0.74–0.79	33	1.13	104–130	63	1.01
0.79–0.84	27	0.68	130–156	39	0.80
0.84–0.89	28	0.90	156–182	20	0.98
0.89–0.93	20	0.95	182–208	18	1.22
0.93–0.97	14	0.71	208–234	9	1.66
0.97–1.00	14	3.00	234–260	20	1.12

tions of the oxygen atoms into fourfold positions using the alternative space-group *Cc*. This procedure gave no indication as to the space-group symmetry being *Cc* nor did it diminish the anomalies in the temperature factors. The Weissenberg photographs of the highest layers showed a great variation in size and shape of the reflections, the low-angle reflections being much broader than the high-angle ones. This made the visual estimation comparatively difficult. After the *hk*6 and *hk*7 layers had been excluded from the further refinement, the temperature factors evened out considerably. Using the remaining 367 reflections a final least squares refinement was made. This was considered completed when the successive shifts were no higher than 5 % of the standard deviations. The *R*-factor was then down at 0.094. The final parameters as shown in Table 2 were arrived at after the two highest

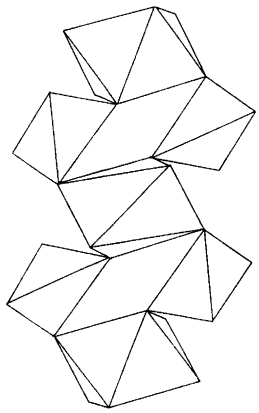

Fig. 1a. Part of a Mo_3O_{10} chain formed by MoO_4 tetrahedra and MoO_6 octahedra linked together by shared corners. The chains are running parallel to [001].

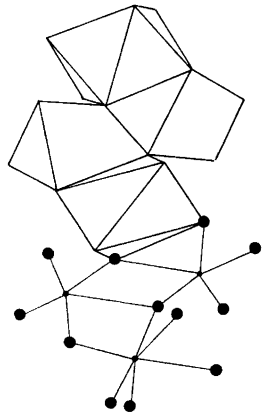

Fig. 1b. Part of a Mo_3O_{10} chain pictured as being composed by MoO_6 octahedra and MoO_5 trigonal bipyramids.

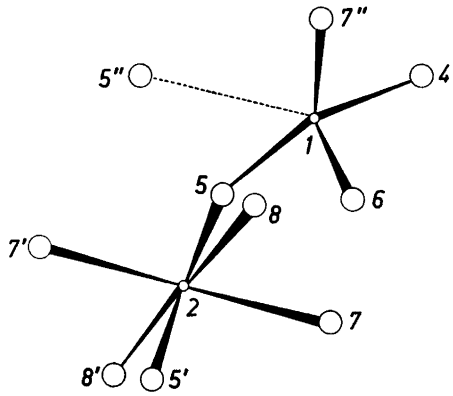

Fig. 2. Detail of Fig. 1 showing the two kinds of polyhedra.

layers had been omitted. The weight analysis used in the last cycles is given in Table 1. A three-dimensional full-difference synthesis computed over 1/4 of the unit cell at points spaced 0.3 Å apart along the x-axis and 0.2 Å apart along the y- and z-axes did not show maxima exceeding 1/5 or minima exceeding in absolute value 1/3 of the maximum oxygen peak height in the electron density function.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure of dipotassium trimolybdate is built up by parallel infinite chains consisting of two kinds of polyhedra. One way of visualizing the structure is given in Fig. 1a in which MoO_6 octahedra are linked together by pairs of MoO_4 tetrahedra, each octahedron sharing corners with four MoO_4 tetrahedra. (In Fig. 2 the corners 5, 5', 7, and 7' are shared by tetrahedra.) One MoO_6 octahedron and two MoO_4 tetrahedra compose one formula unit. The chains are interleaved by potassium ions which are surrounded each by six oxygens forming distorted octahedra. The K—O distances vary within the range 2.75—2.90 Å.

A notable feature of the structure is the tendency on part of the molybdenum towards five-fold coordination. The tetrahedrally surrounded molybdenum is a distance of only 2.08 Å apart from one of the non-shared corners of the neighbouring octahedron thus clearly forming a bond (the dotted distance 1—5" in Fig. 2). Accordingly this molybdenum atom can be regarded as the centre of a deformed trigonal bipyramid. This alternative way of describing the structure is shown in Fig. 1b. Here the chain is composed of alternating octahedra and pairs of trigonal bipyramids. Any MoO_6 octahedron in the chain is sharing corners (5 and 5' in Fig. 2) with two trigonal bipyramids and edges (5—7' and 5'—7 in Fig. 2) with two others. A pair of trigonal bipyramids connecting two octahedra also have a common edge (5—5" in Fig. 2), the length of which is 2.43 Å. The length of an edge between an octahedron and a trigonal bipyramid is 2.38 Å. The O—O distances of edges shared by the polyhedra being less than 2.5 Å make the shortest O—O separations in the structure, an observation which is in accordance with one of Pauling's rules.[7]

Table 2. The crystal structure of $K_2Mo_3O_{10}$ (monoclinic).

Space-group $C2/c$ (No. 15 of *International Tables*).
Cell content: 4 $K_2Mo_3O_{10}$.
8 Mo, 8 K and 40 O in 8(*f*): x,y,z $\bar{x},\bar{y},\bar{z}$ $\bar{x},y,\frac{1}{2}-z$; $x,\bar{y},\frac{1}{2}+z$ $(\frac{1}{2},\frac{1}{2},0)$
4 Mo in 4(*e*): $0,y,\frac{1}{4}$; $0,\bar{y},\frac{3}{4}$ $(\frac{1}{2},\frac{1}{2},0)$

Atom	$x \pm \sigma(x)$	$y \pm \sigma(y)$	$z \pm \sigma(z)$	$B \pm \sigma(B)$
Mo(1)	.10781 ± .00023	.07905 ± .00032	.51844 ± .00045	1.169 ± .045
Mo(2)	0	.69648 ± .00045	1/4	.972 ± .059
K(3)	.3160 ± .0007	.0957 ± .0010	.8444 ± .0014	2.26 ± .16
O(4)	.2047 ± .0021	.0513 ± .0034	.0757 ± .0040	2.26 ± .51
O(5)	.0253 ± .0024	.0946 ± .0034	.9056 ± .0040	2.75 ± .60
O(6)	.1394 ± .0026	.1865 ± .0038	.3771 ± .0046	3.38 ± .65
O(7)	.3766 ± .0018	.2599 ± .0028	.3211 ± .0036	1.25 ± .42
O(8)	.4445 ± .0022	.0622 ± .0034	.1125 ± .0040	2.43 ± .55

Both MoO_6 octahedra and MoO_4 tetrahedra (alternatively MoO_5 trigonal bipyramids) are much deformed as can be seen from the data in Table 3. The numbers assigned to the atoms which Table 3 is referring to are the same as given in Fig. 2.

Mixed polygonal chains are also characteristic of the sodium dimolybdate, the structure of which was determined by Lindqvist [8] and recently refined by the present author.[9] A comparison (Table 4) between the two structures shows that the octahedral oxygen atoms have the same tendency of forming two long, two intermediate, and two short bonds to the central atom. This is also the case in the structure of molybdenum trioxide as has been shown

Table 3. Interatomic distances and angles in $K_2Mo_3O_{10}$.

Mo—Mo (Å)	
1—1	3.216 ± .005
1—2	3.264 ± .004

Mo—O within octahedra (Å)	
2—5	2.14 ± .03
2—7	1.99 ± .03
2—8	1.71 ± .03

∠ O—Mo—O within octahedra (°)	
5—2—5′	81
5—2—7	88
5′—2—7	70
5—2—8	89
5′—2—8	161
7—2—7′	151
7—2—8	94
7′—2—8	103
8—2—8′	105

O—O within octahedra (Å)
2.38—2.91 (mean 2.72)

Mo—O within tetrahedra (Å)	
1—4	1.70 ± .03
1—5	1.95 ± .03
1—6	1.64 ± .04
1—7″	1.90 ± .03
and forming a fifth bond	
1—5	2.08 ± .03

∠ O—Mo—O within tetrahedra (°)	
4—1—5	97
4—1—6	104
4—1—7	100
5—1—6	99
5—1—7″	147
6—1—7″	104

O—O within tetrahedra (Å)
2.64—2.80 (mean 2.73)
with the exception of one long bond (5—7″ in Fig. 2) of 3.68 Å.

Table 4. Comparison of Mo—O distances in some related compounds (Å).

	$K_2Mo_3O_{10}$	$Na_2Mo_2O_7$	MoO_3
	(2.08)		
Mo—O within tetrahedra	1.95	1.79	—
(trigonal bipyramids)	1.90	1.79	—
	1.70	1.75	—
	1.64	1.71	—
Mo—O within octahedra	2.14	2.26	2.33
	2.14	2.26	2.25
	1.99	1.90	1.95
	1.99	1.90	1.95
	1.71	1.70	1.73
	1.71	1.70	1.67

by Kihlborg.[10] This is not, however, a general feature of MoO_6 octahedra. Other combinations are described by Kihlborg, *e.g.* in Mo_8O_{23} [11] where a 2+2+2 arrangement as well as 1+4+1 and 1+2+2+1 arrangements are found. In the two modifications of Mo_4O_{11} [11,12] there is a 3+3 arrangement, whereas the Mo—O distances within the tetrahedra of Mo_4O_{11} are similar to those of the disodium dimolybdate. The tetrahedra of the dipotassium trimolybdate, which can be regarded as an intermediate stage between tetrahedra and trigonal bipyramids, accordingly show a larger extent of distortion from the ideal tetrahedral configuration. If the fifth bond of 2.08 Å is also taken into account the variation of bond lengths greatly resembles that of an octahedron, the sixth bond being absent (2+2+1 arrangement). A similar kind of distorted tetrahedra is also found in a wolframate. The structure of europium wolframate, $Eu_2(WO_4)_3$, determined by Templeton and Zalkin,[13] contains WO_4 tetrahedra with W—O distances of 1.72—1.81 Å. An additional bond is formed with a fifth oxygen neighbour at 2.19 Å. If the coordination is considered to be fivefold, the coordination polyhedron is an irregular trigonal bipyramid, and pairs of these polyhedra share edges across centers of symmetry. The resemblance to the MoO_5 polyhedra as described above is apparent. Whether the wolframate $K_2W_3O_{10}$ which corresponds to the dipotassium trimolybdate also shows this kind of coordination is not known at present. The two compounds are not isomorphous. A single crystal structure investigation is in progress.

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