

A Refinement of the Crystal Structure of Disodium Dimolybdate

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The structure of disodium dimolybdate previously determined by Lindqvist has been refined down to an *R*-factor of 0.10. Although Lindqvist's investigation did not permit a discussion of bond lengths, his description of the structure has been proved to be correct. Interatomic distances with standard deviations are given as well as a discussion of the structure.

Extensive investigations dealing with the crystal structures of binary and complex oxides containing molybdenum and wolfram as well as with the structures of related oxide glasses have been carried out at this Institute. This research program has recently been extended to include investigations of isopolymolybdates and isopolywolframates of the alkali metals. The purpose of these studies is to contribute to the detailed information necessary to elucidate the structural behaviour of molybdenum and tungsten in the crystalline and vitreous state.

The result of a crystal structure determination of disodium dimolybdate was published by Lindqvist¹ in 1950. The structure is described as built up by infinite chains formed by MoO₆ octahedra sharing corners within the chains. MoO₄ tetrahedra are bridging adjacent MoO₆ groups. In the structure determination the oxygen atoms were placed on spatial grounds. Later Lindqvist published an additional note² on the structure where the positions of some of the light atoms were shifted to some extent by use of the Buerger minimum function. As the data did not permit a refinement with modern methods and the atomic positions were still uncertain, the present author thought it worth while to refine this structure on basis of newly recorded data.

EXPERIMENTAL

Disodium dimolybdate was prepared by heating an intimate mixture of sodium molybdate ("Baker's Analyzed", J. T. Baker Chemical Co., USA) and molybdenum trioxide (Analytical Reagent, Mallinckrodt Chemical Works, USA) at 700°C in a platinum crucible for two weeks. White rod-shaped crystals were obtained. The single crystal

chosen for the recording of Weissenberg data had the dimensions 0.2 mm (in the direction chosen as a axis) \times 0.05 mm (b direction) \times 0.05 mm (c direction). The crystal was mounted with the rotation axis in the needle direction. The layers $0kl-4kl$ were recorded using $\text{CuK}\alpha$ radiation and multiple film technique. The intensities of the 384 independent reflections were estimated visually by comparison with an intensity scale. The calculations, including Lorentz-polarization correction, absorption correction,³ Fourier summations,⁴ and least squares refinement, were performed by means of programs listed in the *World List of Crystallographic Computer Programs*.⁵ The least squares program makes use of the block diagonal matrix approximation with individual isotropic temperature factors. A total linear absorption coefficient $\mu = 347.4 \text{ cm}^{-1}$ was used in the calculation of absorption factors. This value was derived from the atomic absorption coefficients given in the *International Tables of Crystallography*.⁶ From this source were also taken the atomic scattering curves for Mo^0 and Mo^+ used to extrapolate the curve for Mo^{3+} , the atomic scattering curves for Na^+ and O^- as well as the real part of the dispersion correction which was applied to the scattering curves of Na^+ and Mo^{3+} .

REFINEMENT OF THE STRUCTURE PARAMETERS

The Weissenberg photographs showed orthorhombic symmetry. The systematic extinction conditions are hkl with $h+k$ odd, $h0l$ with l odd and $hk0$ with h odd. No observation was made which contradicted the assumption of the space group being $Cmca$ as was also made by Lindqvist. From a Guinier powder pattern recorded using $\text{CuK}\alpha_1$ radiation and potassium chloride as an internal standard, the unit cell dimensions (given in Table 1) were calculated by means of the least squares method.

Table 1. The structure of $\text{Na}_2\text{Mo}_2\text{O}_7$ (Lindqvist's parameters within brackets). Space group: $Cmca$ (No. 64 of *International Tables*). Unit cell dimensions: $a = 7.164 \pm 0.006 \text{ \AA}$, $b = 11.837 \pm 0.004$, $c = 14.713 \pm 0.002$. Cell content: $8 \text{ Na}_2\text{Mo}_2\text{O}_7$.

Atom	Position	$x \pm \sigma(x)$	$y \pm \sigma(y)$	$z \pm \sigma(z)$	$B \pm \sigma(B) \text{ \AA}^2$
Mo(1)	8(e)	1/4	$0.0818 \pm 0.0002(0.08)$	1/4	0.581 ± 0.036
Mo(2)	8(f)	0	$0.2463 \pm 0.0002(0.25)$	$0.0846 \pm 0.0002(0.08)$	0.719 ± 0.042
Na(3)	8(f)	0	$0.3175 \pm 0.0014(0.31)$	$0.3436 \pm 0.0011(0.36)$	1.93 ± 0.30
Na(4)	8(d)	$0.2492 \pm 0.0035(0.25)$	0	0	1.38 ± 0.23
O(5)	16(g)	$0.2000 \pm 0.0032(0.18)$	$0.2301 \pm 0.0015(0.22)$	$0.1556 \pm 0.0012(0.17)$	1.37 ± 0.34
O(6)	16(g)	$0.1950 \pm 0.0031(0.18)$	$0.4944 \pm 0.0015(0.48)$	$0.3363 \pm 0.0013(0.33)$	1.41 ± 0.36
O(7)	8(f)	0	$0.3582 \pm 0.0025(0.37)$	$0.5003 \pm 0.0019(0.52)$	1.66 ± 0.55
O(8)	8(f)	0	$0.1209 \pm 0.0020(0.11)$	$0.2793 \pm 0.0016(0.28)$	0.67 ± 0.42
O(9)	8(f)	0	$0.3753 \pm 0.0024(0.38)$	$0.0326 \pm 0.0019(0.02)$	1.51 ± 0.53

The starting point of the refinement was the molybdenum positions arrived at by Lindqvist. For the sake of completeness rather than from any doubt as to the correctness of the positions of the light atoms, these were derived from a three-dimensional difference Fourier synthesis. This was calculated at points spaced 0.4 \AA , 0.3 \AA , and 0.4 \AA apart in the directions of the a , b , and c axes, respectively. The coordinates of all the atoms together with roughly

Table 2. Analysis of the weighting scheme used in the last cycles of refinement.

Interval $\sin \theta$	Number of independent reflections	$\overline{w \Delta^2}$ (normalized)	Interval F_{obs}	Number of independent reflections	$\overline{w \Delta^2}$ (normalized)
0-0.46	72	1.94	25-50	40	0.40
0.46-0.58	60	0.76	50-75	54	1.05
0.58-0.67	40	0.94	75-100	48	0.82
0.67-0.74	42	0.82	100-125	43	0.80
0.74-0.79	33	0.70	125-150	59	0.93
0.79-0.84	32	0.51	150-175	42	0.77
0.84-0.89	28	0.35	175-200	28	0.99
0.89-0.93	31	0.35	200-225	28	1.47
0.93-0.97	28	0.67	225-250	40	2.00
0.97-1.00	16	2.87			

estimated temperature factors were then used for a least squares refinement. The refinement was considered completed when all the shifts were below 5 % of the standard deviations at which point the discrepancy index $R = \sum |F_o(hkl) - F_c(hkl)| / \sum |F_o(hkl)|$ was 0.100. Hughes' weighting function $w = 1/h^2 |F_o, \min|^2$ for $|F_o| \leq |F_o, \min|$ and $w = 1/|F_o|^2$ for $|F_o| \geq h|F_o, \min|$ with the parameter h given the value 4 was used in the refinement. The weight analysis obtained in the last cycles is given in Table 2. A comparison between observed and calculated structure factors is presented in Table 3. Only observed reflections were included in the refinement. Reflections marked with an asterisk were not used in the refinement but are included in the reliability index. Those and other strong reflections could possibly suffer from extinction as a comparison between the F_o and F_c listed in Table 3 may indicate.

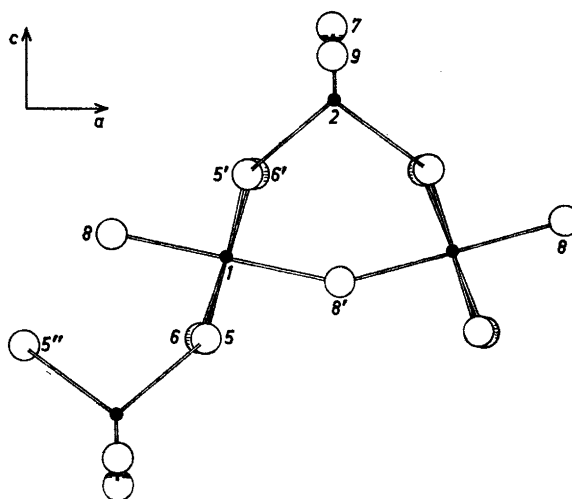


Fig. 1. Part of a dimolybdate chain showing the oxygen coordination around molybdenum. The b axis is perpendicular to the plane of the paper and the chains run parallel to the a axis.

DISCUSSION

As was expected, the coordinates obtained in the refinement are in good agreement with those previously reported by Lindqvist.² The parameters are listed in Table 1. The arrangement of the MoO_6 octahedra and MoO_4 tetrahedra into chains is shown in Fig. 1. The atoms in Fig. 1 are assigned numbers consistent with those given in Tables 1 and 4. As can be seen from Table 4 the tetrahedra are slightly distorted and the octahedra considerably more so, a fact which seems reasonable considering the relatively small size of hexavalent molybdenum. Notable is the splitting of the Mo—O distances within the octahedra into two long, two intermediate, and two short bonds, as is also the case with the octahedral arrangement in some other hexavalent molybdenum compounds, *e.g.* molybdenum trioxide⁷ and dipotassium trimolybdate.⁸

Table 4. Interatomic distances and angles in $\text{Na}_2\text{Mo}_2\text{O}_7$.

		<i>Octahedron</i>	
	Mo—O		\angle O—Mo—O
1—5 = 1—5'	$2.267 \pm 0.018 \text{ \AA}$	5—1—5'	79°
1—6 = 1—6'	1.684 ± 0.019	5—1—6	89
1—8 = 1—8'	1.900 ± 0.008	5—1—6'	167
		5—1—8	79
O—O mean 2.72 Å		5—1—8'	80
		6—1—6'	104
		6—1—8	96
		6—1—8'	101
		8—1—8'	152
		<i>Tetrahedron</i>	
	Mo—O		\angle O—Mo—O
2—5 = 2—5"	$1.784 \pm 0.021 \text{ \AA}$	5—2—5"	107°
2—7	1.752 ± 0.029	5—2—7	110
2—9	1.708 ± 0.028	5—2—9	111
		7—2—9	108
O—O mean 2.87 Å			
	<i>Na—O (octahedral arrangement)</i>		
	Na(3)—O mean	2.45 Å	
	Na(4)—O mean	2.42	

According to investigations by Kihlberg of several higher molybdenum oxides⁹ the Mo—Mo separations for MoO_6 octahedra sharing corners fall within the range 3.60—4.05 Å. For an octahedron and a tetrahedron connected by a shared corner the Mo—Mo separations were found to be 3.50—3.86 Å. The corresponding distances in the disodium dimolybdate are 3.58 Å and 3.60 Å.

The influence of the alkali metal cation on the stability of anions of isopolyacids has been discussed by several authors: the lower the polarizing effect of the alkali metal ion the more complex the anion that can be stably associated with it. In connection with this Lindqvist pointed out the possibility that transition from octahedral to tetrahedral coordination around molybdenum is favoured by the presence of small polarizing cations.¹⁰ A com-

parison between the disodium dimolybdate and dipotassium trimolybdate agrees with this assumption. Whereas the fourfold coordination around molybdenum in the disodium dimolybdate is distinctly tetrahedral, the corresponding coordination polyhedron in the dipotassium trimolybdate⁸ represents a transitional stage between a tetrahedron and a trigonal bipyramid.

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