

X-RAY STRUCTURAL INVESTIGATION OF  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$   
CRYSTALS

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An x-ray structural investigation of  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  crystals was performed. The lattice parameters are:  $a = 13.823 \pm 0.004$ ,  $b = 10.562 \pm 0.003$ ,  $c = 8.514 \pm 0.002$  Å,  $N = 8$ . The space group is  $Pcab$ . The structure is built up of  $\text{MoO}_4^{2-}$  anions connected together by a system of hydrogen bonds in a continuous chain. The mean Mo-O distance is 1.76 Å, and the angle O-Mo-O is  $109.5^\circ$ .

It is known from the available structural data on the oxidic compounds of molybdenum that the distance between the oxygen atoms in  $\text{MoO}_6$  octahedra is, as a rule, maintained within quite narrow limits. A shift of a molybdenum atom from the central point of a polyhedron is the chief external expression of distortions characteristic of such octahedra. These shifts, which reflect the complex picture of the  $\sigma$ - and  $\pi$ -valence interactions, lead to unequivalence in the lengths of the Mo-O bonds [1].

The shift of molybdenum from the center of an octahedron takes place in a quite definite manner. Thus, for example, one of the types of distortions is accomplished as a result of the possibility of localization of three  $\pi$ -bonds in the octahedron in three cis-disposed molybdenum-ligand contacts. The transition from this polyhedron, intermediate between an octahedron and a tetrahedron, to a purely tetrahedral coordination is accompanied by a redistribution of the  $\pi$ -interaction in all four ligands [1].

The molybdenum atom has tetrahedral coordination only in its highest oxidation state (speaking about the solid phase). Actually, such a coordination is achieved in certain complex oxides  $\alpha$ - and  $\beta$ - $\text{Mo}_4\text{O}_{11}$ ,  $\text{Mo}_{18}\text{O}_{52}$  [2], in sodium dimolybdate [3], and in a large group of orthomolybdates [4-14]. None of the simple and complex orthomolybdates whose structure has been studied contains water molecules in its composition.

We were interested in the structure of  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  crystals mainly because of their compositional similarity with crystals of  $\text{K}_2\text{OsO}_4 \cdot 2\text{H}_2\text{O}$ , in which water molecules enter the inner sphere of the complex with the formation of an octahedral configuration from atoms of oxygen surrounding an atom of osmium [15].

On the other hand, the picture is different for the complex  $\text{K}_2[\text{OsO}_3(\text{NO}_2)_2] \cdot 3\text{H}_2\text{O}$ , in which entrance of the water molecules into the inner sphere was also assumed for forming octahedral coordination [16, 17]: octahedral coordination is managed as a result of anion dimerization [18].

It is possible that the tendency toward octahedral coordination in oxidic compounds of osmium is determined by the trans-stabilization of the  $\pi$ -bonds, whereas for oxidic compounds of molybdenum, it is characterized by cis-stabilization of the  $\pi$ -bonds [1].

TABLE 1

	Coordinates and errors						$B_j, \text{Å}^2$	$\sigma(B_j)$	$\rho, \text{el}/\text{Å}^3$
	$x$	$\sigma(x)$	$y$	$\sigma(y)$	$z$	$\sigma(z)$			
Mo	0,4767	0,0002	0,1983	0,0002	0,5153	0,0007	0,98	0,03	107,5
Na <sub>1</sub>	0,3526	0,0009	0,449	0,001	0,742	0,003	1,4	0,2	16,8
Na <sub>2</sub>	0,415	0,001	0,504	0,001	0,333	0,003	1,3	0,2	16,1
O <sub>1</sub>	0,391	0,002	0,148	0,002	0,361	0,004	2,1	0,6	9,5
O <sub>2</sub>	0,459	0,001	0,359	0,002	0,552	0,005	1,0	0,3	12,0
O <sub>3</sub>	0,596	0,001	0,179	0,002	0,445	0,005	1,5	0,4	10,3
O <sub>4</sub>	0,462	0,002	0,106	0,002	0,675	0,005	2,1	0,5	9,6
(H <sub>2</sub> O) <sub>1</sub>	0,701	0,001	0,407	0,002	0,463	0,005	1,8	0,4	11,7
(H <sub>2</sub> O) <sub>2</sub>	0,297	0,001	0,357	0,002	0,227	0,005	1,4	0,5	9,4

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TABLE 2. Interatomic Distances (Å) and Valence Angles (°) [ $\sigma(\text{Mo}-\text{O}) = 0.03$ ,  $\sigma(\text{Na}-\text{O}) = 0.04$ ,  $\sigma(\text{O}-\text{O}) = 0.04$  Å,  $\alpha(\text{O}-\text{Mo}-\text{O}) = 1.5^\circ$ ,  $\alpha(\text{O}-\text{H}_2\text{O}-\text{O}) = 2.0^\circ$ ]

Mo—O <sub>1</sub>	1,85	Na <sub>1</sub> —O <sub>2</sub>	2,39
O <sub>2</sub>	1,74	O <sub>3</sub>	2,31
O <sub>3</sub>	1,77	O <sub>4</sub>	2,35
O <sub>4</sub>	1,68	(H <sub>2</sub> O) <sub>1</sub>	2,43
		(H <sub>2</sub> O) <sub>2</sub>	2,29
Na <sub>2</sub> —O <sub>1</sub>	2,27	O <sub>1</sub> —O <sub>2</sub>	2,91
O <sub>2</sub>	2,49	O <sub>3</sub>	2,95
O <sub>3</sub>	2,47	O <sub>4</sub>	2,89
O <sub>4</sub>	2,47	O <sub>2</sub> —O <sub>3</sub>	2,83
(H <sub>2</sub> O) <sub>1</sub>	2,55	O <sub>4</sub>	2,87
(H <sub>2</sub> O) <sub>2</sub>	2,42	O <sub>3</sub> —O <sub>4</sub>	2,80
(H <sub>2</sub> O) <sub>1</sub> —O <sub>1</sub> '	2,81	(H <sub>2</sub> O) <sub>2</sub> —O <sub>1</sub> '	2,80
O <sub>3</sub>	2,82	O <sub>3</sub> '	2,84
O <sub>1</sub> —Mo—O <sub>2</sub>	108,4		
O <sub>2</sub> —Mo—O <sub>3</sub>	109,1	O <sub>3</sub> —(H <sub>2</sub> O) <sub>1</sub> —O <sub>1</sub> '	106,7
O <sub>1</sub> —Mo—O <sub>4</sub>	109,3	O <sub>1</sub> —(H <sub>2</sub> O) <sub>2</sub> —O <sub>3</sub> '	90,0
O <sub>2</sub> —Mo—O <sub>3</sub>	107,8		
O <sub>2</sub> —Mo—O <sub>4</sub>	113,6		
O <sub>3</sub> —Mo—O <sub>4</sub>	108,6		

Therefore, the difference in the direction of the stabilizing effect of the  $\pi$ -bonds in complex compounds of osmium and molybdenum must evidently be manifested also in a different geometry of the anions in crystals of  $\text{K}_2\text{OsO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ .

Crystals of  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  are formed from aqueous solutions in the form of thin transparent and very brittle plates. A commercial sample (TU 4-03-48) was used for the investigation.

The crystals belong to the space group  $\text{Pcab}$ . The lattice parameters, accurately measured on a DRON-1 diffractometer with a single crystal attachment, agree well with those previously given in [19]:  $a = 13.823 \pm 0.004$ ,  $b = 10.562 \pm 0.003$ ,  $c = 8.514 \pm 0.002$  Å,  $d_{\text{meas}} = 2.56 \text{ g/cm}^3$ ,  $N = 8$ ,  $\mu(\text{Mo}, \text{K}\alpha) = 21.7 \text{ cm}^{-1}$ ,  $F(000) = 880$ . The experimental data were obtained in KFOR with unfiltered molybdenum radiation. Five hundred and ninety-nine separate non-null reflections were recorded (maximum  $\sin \vartheta/\lambda = 1.05$ ). The intensities of the reflections were determined visually. Since we could not get spherical crystals, the absorption was disregarded.

The structural investigation was started with the analysis of the three-dimensional distribution of the Patterson function. Final interpretation of the structure was made using the method of successive approximations. Refinement of the MNK structure was started with  $R = 0.238$ . For the refinement, we used the weight system, which considers the reliability of the determination of the reflection intensities (the maximum value of the blackening mark is equal to 100):

$$15 < I_{hkl} < 100, \quad w = 1, \quad I_{hkl} < 15, \quad w = I/15, \quad I_{hkl} > 100, \quad w = \frac{300 - I}{200}$$

Refinement of the coordinates of all atoms, of the individual isotropic temperature corrections, and also of the general and layer coefficients of the reduction to the absolute scale led to a final  $R = 0.114$ .

Table 1 presents the values of the atomic coordinates, the individual isotropic temperature coefficients, the errors of their determination, and the peak heights of the electron density. Table 2 presents the interatomic distances and the valence angles. Figure 1 shows the structure in projection on the  $xOz$  plane.

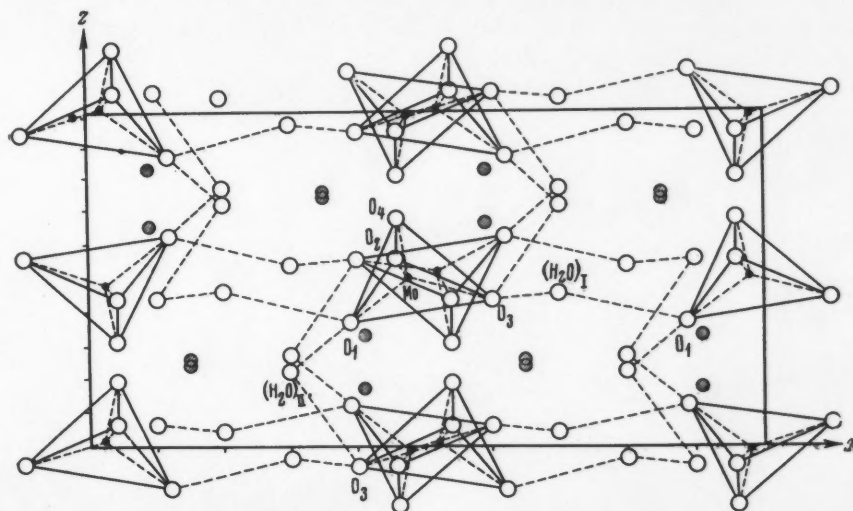


Fig. 1

TABLE 3

NaCo <sub>7</sub> (MoO <sub>4</sub> ) <sub>3</sub> [14]		α-MnMoO <sub>4</sub> [9]		Na <sub>2</sub> MoO <sub>4</sub> ·2H <sub>2</sub> O	Na <sub>2</sub> Mo <sub>2</sub> O <sub>7</sub> [3]		K <sub>2</sub> Mo <sub>2</sub> O <sub>10</sub> [20]		MoO <sub>3</sub> [21]
1,726	1,760	1,731	1,724	1,68	1,70 <sub>8</sub>	1,68 <sub>4</sub>	1,64	1,71	1,67
1,751	1,760	1,731	1,724	1,74	1,75 <sub>2</sub>	1,66 <sub>4</sub>	1,70	1,71	1,73
1,773	1,761	1,795	1,738	1,77	1,78 <sub>4</sub>	1,90	1,90	1,99	1,95
1,811	1,817	1,795	1,851	1,85	1,78 <sub>4</sub>	1,90	1,95	1,99	1,95
						2,26 <sub>7</sub>	2,08	2,14	2,25
						2,26 <sub>7</sub>		2,14	2,25

It is evident from Fig. 1 that the water molecules do not enter the inner sphere of the complex. The MoO<sub>4</sub><sup>2-</sup> anions form hydrogen bonds with the water molecules, as a result of which continuous chains MoO<sub>4</sub><sup>2-</sup>-H<sub>2</sub>O-MoO<sub>4</sub><sup>2-</sup>... are formed.

A comparison of the Mo-O bond lengths in MoO<sub>4</sub> tetrahedra, MoO<sub>5</sub> pentahedra, and MoO<sub>6</sub> octahedra given in Table 3 indicates the extent of the gradation from the tetrahedral to the distorted octahedral configuration, emphasizing the same deep analogy in the electronic structures of the molybdenum complexes.

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