

Crystal Structure Studies on Anhydrous Sodium Molybdates and Tungstates

INGVAR LINDQVIST

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

In a thorough thermal investigation of the systems $\text{Na}_2\text{MoO}_4\text{—MoO}_3$ and $\text{Na}_2\text{WO}_4\text{—WO}_3$, Hoermann¹ has established the existence of *i. a.* Na_2MoO_4 , $\text{Na}_2\text{Mo}_2\text{O}_7$, Na_2WO_4 and $\text{Na}_2\text{W}_2\text{O}_7$, the crystal structures of which will be given in this paper. All crystals have been obtained from melts in accordance with Hoermann¹.

SODIUM MOLYBDATE AND TUNGSTATE

These two compounds (in the notation of Hoermann¹, the isotropic δ -phases), which are isomorphous, have been studied by powder photographs obtained with monochromatized Cu—K_α radiation. Both compounds were easily shown to be regular with a cube edge of $a = 8.99 \text{ \AA}$. Na_2MoO_4 and Na_2WO_4 , thus seem to be isomorphous with Ag_2MoO_4 , which has a spinel structure² with $a = 9.26 \text{ \AA}$. In agreement with Ag_2MoO_4 only hkl with h , k and l all odd or all even appear on the photographs. A calculation of $I(hkl)$, for Na_2WO_4 under this assumption gives values in agreement with the observed ones (Table 1).

Na_2MoO_4 and Na_2WO_4 thus have a spinel structure quite as Ag_2MoO_4 , while Li_2MoO_4 has a phenacite structure³. This fact may give a new insight in the morphotropy of A_2BX_4 structures, which has been discussed by Goldschmidt⁴. (A review is given by Evans⁵.) The theory has been put forward, that the transition from phenacite to spinel structure is brought about by the polarizing power of Ag^+ . As Na_2MoO_4 also has a spinel structure and Na^+ undoubtedly has a smaller polarizing power than Li^+ , this is obviously not correct. The most natural way to treat this problem seems to be a consideration of the ionic radii. Ag^+ and Na^+ have larger ionic radii than Li^+ , and therefore may require a 6-fold octahedral coordination instead of the 4-fold

tetrahedral in the phenacite structure. This type of spinel structure A_2BX_4 , where A has a larger ionic radius than B, appears more natural than the classical one with $B > A$, although B has a lower oxygen coordination. The spinel structure should thus be considered as related to the olivine structure (*cf.* 5), both having the same types of coordination around A and B. The olivine structure gives, however, a more well defined MoO_4^{2-} ion, while the spinel structure has more double oxide character.

With an idealized spinel structure ($x_o = 3/8$) the Mo—O (W—O) distances will be 2.0 Å, Na—O = 2.3 Å and O—O = 3.2 Å.

Table 1. Powder photograph of Na_2WO_4 taken with $CuK\alpha$ radiation.

<i>h k l</i>	$\sin^2\theta$		intensities		<i>h k l</i>	$\sin^2\theta$		intensities	
	obs.	calc.	obs.	calc.		obs.	calc.	obs.	calc.
1 1 1	0.0219	0.0219	v st	193	5 3 1	0.2568	0.2566	m	54
2 0 0	0.0587	0.0586	v st	209	6 0 0)	—	—	—	0
2 2 0	—	—	—	0	4 4 2)	—	—	—	0
3 1 1	0.0799	0.0806	v st	135	6 2 0	0.2933	0.2933	m	53
2 2 2	—	—	—	1	5 3 3	0.3145	0.3152	w	31
4 0 0	0.1165	0.1173	v w	16	6 2 2	—	—	—	1
3 3 1	0.1387	0.1393	m	59	4 4 4	0.3510	0.3518	v w	5
4 2 0	—	—	—	0	7 1 1)	0.3733	0.3738	w	38
4 2 2	0.1760	0.1759	v st	104	5 5 1)	—	—	—	0
5 1 1)	0.1981	0.1979	st	71	6 4 0	0.4104	0.4105	st	88
3 3 3)	0.2347	0.2346	st	79	6 4 2	0.4104	0.4105	st	88
4 4 0	0.2347	0.2346	st	79	7 3 1)	0.4321	0.4323	st	79
					5 5 3)				

SODIUM DIMOLYBDATE AND DITUNGSTATE

Unit cell. Space group

The crystal structure of these two isomorphous compounds, which have identical unit dimensions, has been determined from an X-ray crystallographic investigation of a needle-shaped dimolybdate single crystal. Rotation and Weissenberg photographs were taken around the *a*-axis with *Cu-K* radiation. The crystal was found to be orthorhombic with $a = 7.17$ Å, $b = 11.83$ Å and $c = 14.70$ Å. The density is 3.6, corresponding to eight formula units $Na_2Mo_2O_7$ in the cell. Reflections $h k l$ are missing if $h + k$ is odd, $h k 0$ if h or k is odd,

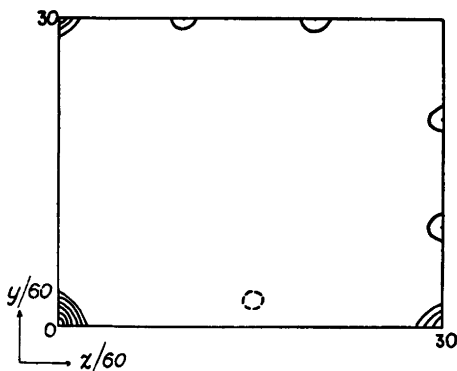


Fig. 1. Patterson function $P(0, y, z)$ of the sodium dimolybdate.

$h \ 0 \ l$ if h or l is odd, and $0 \ k \ l$ if k is odd. As an investigation with a dynamic method showed no signs of piezo-electricity, the most probable space group is $D_{2h}^{18}-Cmca$. The $|F|$ values were calculated from the estimated intensities according to Lu⁶.

Molybdenum and sodium positions

The first problem is to determine the positions of 16 Mo atoms in the unit cell. The coordinates of the general position (16 g), which indicates the most interesting Patterson cuts $P(x, y, z)$ to calculate, are the following:

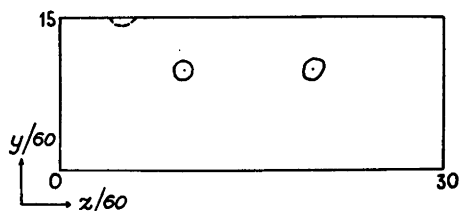
$$\begin{aligned} &(x, y, z) \quad (x, \bar{y}, \bar{z}) \quad (x, \frac{1}{2} + y, \frac{1}{2} - z) \quad (x, \frac{1}{2} - y, \frac{1}{2} + z) \\ &(\bar{x}, \bar{y}, \bar{z}) \quad (\bar{x}, y, z) \quad (\bar{x}, \frac{1}{2} - y, \frac{1}{2} + z) \quad (\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z) \\ &(\frac{1}{2} + x, \frac{1}{2} + y, z) \quad (\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}) \quad (\frac{1}{2} + x, y, \frac{1}{2} - z) \quad (\frac{1}{2} + x, \bar{y}, \frac{1}{2} + z) \\ &(\frac{1}{2} - x, \frac{1}{2} - y, \bar{z}) \quad (\frac{1}{2} - x, \frac{1}{2} + y, z) \quad (\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z) \quad (\frac{1}{2} - x, y, \frac{1}{2} - z) \end{aligned}$$

$P(0, y, z)$ will give all equivalent Mo—Mo vectors $[2 y_{Mo}, 2 z_{Mo}]$, $[\frac{1}{2}, \frac{1}{2} - 2 z_{Mo}]$, and $[\frac{1}{2} - 2 y_{Mo}, \frac{1}{2}]$, (cf. the more complete discussion in ref. 7), and was therefore calculated. (Fig. 1.)

The two largest maxima have the (y, z) coordinates $(0, \frac{1}{2})$ and $(\frac{1}{2}, 0)$. Then there are four maxima at $(1/6, 1/2)$, $(1/3, 1/2)$, $(1/2, 1/6)$, and $(1/2, 1/3)$. Finally there is one still smaller maximum at $(1/12, 1/4)$.

The three maxima $(y, \frac{1}{2})$ may correspond to $y_{Mo} = 1/12, 1/6$ or $1/4$ (in $0 \leq y \leq 1/4$) and the three maxima $(1/2, z)$ to $z_{Mo} = 1/12, 1/6$ or $1/4$ (in $0 \leq z \leq 1/4$). These two triplets can be combined to give the following $[2y_{Mo}, 2z_{Mo}]$ values: $(1/6, 1/6)$ $(1/6, 1/3)$ $(1/6, 1/2)$ $(1/3, 1/6)$ $(1/3, 1/3)$ $(1/3, 1/2)$ $(1/2, 1/6)$ $(1/2, 1/3)$ and $(1/2, 1/2)$, of which $(1/6, 1/2)$ $(1/3, 1/2)$ $(1/2, 1/6)$ and $(1/2, 1/3)$

Fig. 2. Patterson function $P(\frac{1}{4}, y, z)$ of the sodium dimolybdate.



are found in $P(0, y, z)$. The only combinations possible are evidently $y_{\text{Mo}} = 1/12$ or $1/6$ with $z_{\text{Mo}} = 1/4$, and $y_{\text{Mo}} = 1/4$ with $z_{\text{Mo}} = 1/12$ or $1/6$, which may correspond to positions 8 (e) and 8 (f):

- 8 (e): $(1/4, y, 1/4) (3/4, \bar{y}, 3/4) (3/4, y, 1/4) (1/4, \bar{y}, 3/4)$
 $(3/4, \frac{1}{2} + y, 1/4) (1/4, \frac{1}{2} - y, 3/4) (1/4, \frac{1}{2} + y, 1/4) (3/4, \frac{1}{2} - y, 3/4)$
 with $y = 1/12$ or $1/6$
- 8 (f): $(0, y, z) (0, \bar{y}, \bar{z}) (\frac{1}{2}, y, \frac{1}{2} - z) (\frac{1}{2}, \bar{y}, \frac{1}{2} + z)$
 $(\frac{1}{2}, \frac{1}{2} + y, z) (\frac{1}{2}, \frac{1}{2} - y, \bar{z}) (0, \frac{1}{2} + y, \frac{1}{2} - z) (0, \frac{1}{2} - y, \frac{1}{2} + z)$
 with $y = 1/4$ and $z = 1/12$ or $1/6$.

In order to confirm this assumption and to get a choice between the two alternatives for each position, $P(1/4, y, z)$ was calculated (Fig. 2). The largest maxima obtained are situated at $(1/6, 1/6)$ and $(1/6, 1/3)$. Besides there is a smaller maximum at $(1/4, 1/12)$.

In the following discussion we treat the interatomic vectors between Mo atoms in $x = 0$ and $x = 1/4$. In $x = 0$ there are four Mo atoms in 8 (f), having the (y, z) coordinates $(1/4, 1/12) (3/4, 11/12) (3/4, 5/12) (1/4, 7/12)$ or $(1/4, 1/6) (3/4, 5/6) (3/4, 1/3) (1/4, 2/3)$ and in $x = 1/4$ there are four Mo atoms in 8 (e): $(1/12, 1/4) (11/12, 3/4) (5/12, 3/4) (7/12, 1/4)$ or $(1/6, 1/4) (5/6, 3/4) (1/3, 3/4) (2/3, 1/4)$.

The sets derived from $(1/4, 1/12)$ in $x = 0$ and $(1/12, 1/4)$ in $x = 1/4$ should give the following maxima in $P(1/4, y, z)$: $(1/6, 1/6) (1/6, 1/3)$ quite in agreement with the results obtained.

$(1/4, 1/12)$ and $(1/6, 1/4)$ should require *e. g.* $(1/12, 1/6)$ which is not obtained,

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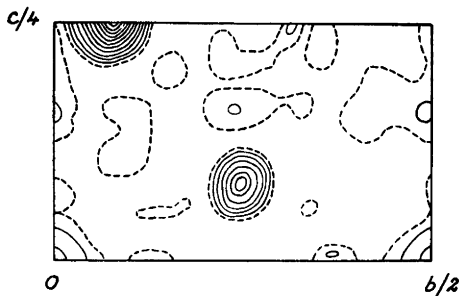


Fig. 3. Electron density projection $\rho(y, z)$ of the sodium dimolybdate.

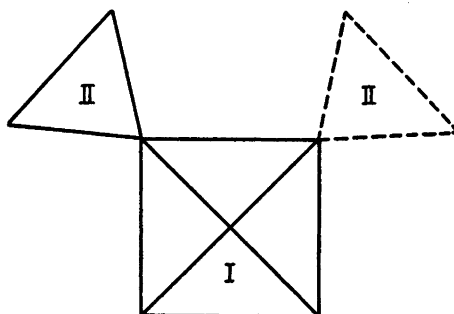
A calculation of the electron density projection $\rho(y, z)$ definitely confirmed that the Mo atoms are placed in 8 (e) with $y = 1/12$, and in 8 (f) with $y = 1/4$ and $z = 1/12$. (Fig. 3.)

On the electron density projection map, $\rho(y, z)$, there appeared some small maxima (with a height of about $1/10$ of the Mo peaks), which possibly could be interpreted as Na or O atoms. To test the reliability of $\rho(y, z)$, a new $\rho(y, z)$ was calculated from the theoretical intensities of only those reflections which were used in the actual $\rho(y, z)$ summation. It then was evident that almost all the small maxima were due to termination effects of a type also found by Magnéli⁸. The only clearly real maximum was situated at (0, 0). Three-dimensional electron density calculations $\rho(0, y, z)$ and $\rho(\frac{1}{4}, y, z)$ confirmed the Mo positions, but indicated that there was not any chance to determine the Na and O positions in this way.

In $P(0, y, z)$ and $P(\frac{1}{4}, y, z)$, however, there remain to interpret two obvious peaks at $(0, 1/12, 1/4)$ and $(1/4, 1/4, 1/12)$, corresponding to $(0, \pm 1/12, \pm 1/4)$ and $(\pm 1/4, \pm 1/4, \pm 1/12)$ if care is taken of the whole cell. If now the vector $[0, 1/12, 1/4]$ is added to the Mo position $(0, 1/4, 1/12)$, the point $(0, 1/3, 1/3)$ is reached. The vector $[\bar{1}/4, 1/4, 1/12]$ added to the Mo position $(1/4, 1/12, 1/4)$ will also give $(0, 1/3, 1/3)$. In the same way $[1/4, \bar{1}/4, \bar{1}/12]$ added to $(0, 1/4, 1/12)$ will give $(1/4, 0, 0)$, which point is also reached by adding $[0, \bar{1}/12, \bar{1}/4]$ to $(1/4, 1/12, 1/4)$. Just that point was found in $\rho(y, z)$. The two vectors cannot be combined with the Mo atoms to give any other new point. If the Na atoms are placed in 8 (d) with $x = 1/4$ and in 8 (f) with $y = 1/3$ and $z = 1/3$, the multiplicity of the Mo—Na vectors accounts for the appearance of the peaks in $P(x, y, z)$. The correctness of this assumption is confirmed below.

Fig. 4. The Structure of $\text{Mo}_2\text{O}_7^{2-}$.

- I: MoO_6 octahedra forming chains perpendicular to the plane of the figure.
 II: MoO_4 tetrahedra sharing corners with each of two MoO_6 octahedra in the chain, with Mo in the planes $x = 0$ (full lines) and $x = 0.5$ (dotted lines).



Oxygen positions. Crystal structure

In some other crystal structure studies on polymolybdates, the oxygen coordination has been worked out by considering the Mo-Mo distances corresponding to MoO_6 octahedra sharing edges or corners^{7,9,10}. The Mo-Mo distances in $\text{Na}_2\text{Mo}_2\text{O}_7$ were therefore calculated. The Mo atoms in 8 (e) (I in fig. 4, dotted circles in fig. 5) are placed in straight lines parallel to the a -axis (\perp the bc plane) with a distance of $1/2 a = 3.62 \text{ \AA}$. Each Mo_I atom has two Mo_{II} neighbours from 8 (f) (II in fig. 4, full drawn circles in fig. 5), 3.63 \AA apart. Distances of this magnitude are found as corresponding to $\text{MoO}_6(\text{WO}_6)$ octahedra sharing corners in infinite zig-zag chains in several compounds: 3.69 \AA in MoO_3 ⁽¹¹⁾, 3.64 \AA in WO_3 ⁽¹¹⁾, 3.71 \AA in $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ ⁽⁹⁾. It may also correspond to MoO_6 octahedra and MoO_4 tetrahedra sharing corners: 3.73 — 3.79 \AA in Mo_4O_{11} ⁽¹²⁾. Finally it might correspond to MoO_4 tetrahedra sharing corners: Mo-O is 1.8 \AA in some normal molybdates containing MoO_4 complexes.

The problem of the oxygen coordination around Mo can now be approached from this point of view, investigating all possibilities in agreement with the Mo-Mo distances obtained. At first we regard the infinite 3.62 \AA Mo-Mo chain in the direction of the a -axis. If all these distances correspond to Mo-O-Mo, it is easy to see that MoO_4 tetrahedra cannot build up the straight chains. A sharing of corners within groups of each two MoO_4 tetrahedra should in itself give Mo_2O_7 complexes, making it impossible to get a coordination around Mo_{II} giving the net formula $\text{Mo}_2\text{O}_7^{2-}$ for the compound. Finally one has the possibility of Mo_2O_7 complexes being formed by couples of Mo_IO_4 and Mo_{II}O_4 tetrahedra. This implies that there is no sharing of oxygen between the Mo_I atoms in the chain. Due to the mirror plane in $x = 0$, however, every Mo-O polyhedron around Mo_{II} must share oxygens with two Mo_I polyhedra (in $x = 0.25$ and $x = 0.75$), which definitely excludes the possibility of having

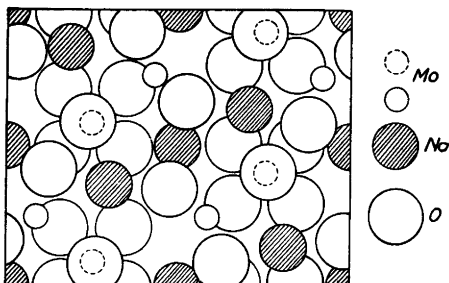


Fig. 5. Structure of sodium dimolybdate showing atoms with $x = 0$ (upper layer) and $x = 0.25$ (lower layer). The hidden atoms in the lower layer are denoted by dotted circles.

tetrahedra in I. (Tetrahedra in I and tetrahedra in II will give Mo_2O_6 , tetrahedra in I and octahedra in II will give $\text{Mo}_2\text{O}_8^{4-}$.) It can thus be stated that there are MoO_6 octahedra in I. Further it seems most reasonable to assume that there are infinite Mo-O-Mo chains in the direction of the a -axis in agreement with earlier data on interatomic distances, *v. supra*. (If the octahedra shared edges in the chain direction they would be extremely distorted.) The only possibility to obtain a formula $\text{Mo}_2\text{O}_7^{2-}$ is then to place MoO_4 tetrahedra in 8 (*f*) (II), sharing corners with each of two MoO_6 octahedra in the chain (Fig. 4 and 6). This structure requires some distortion of the MoO_6 octahedra in order to get reasonable O—O distances, so the four oxygens in the plane of Mo_I can not be placed in $x = 0.25$ but in $x = 0.21$ and 0.29 .

If we consider the sodium positions earlier arrived at as correct we can attack the problem in another way. Putting the Mo-O distances to at least 1.7 Å and Na-O to at least 2.3 Å, and taking care of the symmetry of the space group, the space available for oxygen atoms can be investigated. Such an investigation gives only two possible arrangements for the oxygen atoms, one of which is in agreement with the structure in Fig. 4. (The other arrangement corresponds to a 90° rotation of the MoO_6 octahedra, but gives no possible coordination around Mo_{II} .) After adjustments of the O and Na parameters in order to get the most reasonable interatomic distances, the structure shown in fig. 5 was obtained. The parameters are:

8 Mo_I	in 8(<i>e</i>) :	$x = 0.25$	$y = 0.08$	$z = 0.25$
8 Mo_{II}	in 8(<i>f</i>) :	$x = 0.00$	$y = 0.25$	$z = 0.08$
8 Na_I	in 8(<i>d</i>) :	$x = 0.25$	$y = 0.00$	$z = 0.00$
8 Na_{II}	in 8(<i>f</i>) :	$x = 0.00$	$y = 0.36$	$z = 0.30$
16 O_I	in 16(<i>g</i>) :	$x = 0.21$	$y = 0.21$	$z = 0.16$
16 O_{II}	in 16(<i>g</i>) :	$x = 0.21$	$y = 0.49$	$z = 0.34$
8 O_{III}	in 8(<i>f</i>) :	$x = 0.00$	$y = 0.08$	$z = 0.27$
8 O_{IV}	in 8(<i>f</i>) :	$x = 0.00$	$y = 0.41$	$z = 0.13$
8 O_V	in 8(<i>f</i>) :	$x = 0.00$	$y = 0.35$	$z = 0.49$

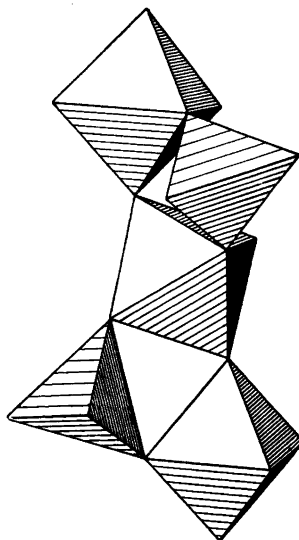


Fig. 6. Part of the infinite dimolybdate or ditungstate chain $\text{Mo}_2\text{O}_7^{2-}$ or $\text{W}_2\text{O}_7^{2-}$. Idealized drawing with regular polyhedra.

Each Mo_VI atom is surrounded by 6 oxygen atoms at the distances 1.80 Å, 1.81 Å and 2.06 Å; each Mo_IV atom has four oxygen neighbours, 1.78 Å and 1.93 Å apart.

The sodium atoms each have six oxygen neighbours (distorted octahedra) at distances of 2.4—2.6 Å. The O—O distances vary between 2.4 and 3.6 Å (cf. 2.7—3.5 Å in $\text{MoO}_3^{(11)}$ and 3.2 Å in Na_2MoO_4).

Discussion of the structure

The ion $\text{Mo}_2\text{O}_7^{2-}$ ($\text{W}_2\text{O}_7^{2-}$) is evidently not a discrete ion built up by double tetrahedra, but it is an infinite complex ion forming chains in the crystals parallel with the a -axis. This is in agreement with the physical evidence that this compound always crystallizes as long needles with the a -axis in the needle direction. The structure of one chain is shown in fig. 4 and 6, where it is seen how the tetrahedra are attached to the chain of octahedra.

A comparison of this structure with the discrete $\text{Mo}_7\text{O}_{24}^{6-}$ and $\text{Mo}_8\text{O}_{26}^{4-}$ ions found in crystals obtained from water solutions ^{7, 10}, clearly shows the quite different states of molybdates in melts and water solutions.

In an earlier paper ⁷, it has been proposed that in the molybdates crystallizing from melts, the ratio Mo:O determines whether the coordination around Mo is tetrahedral (as for Mo:O = 1 : 4) or octahedral (as for Mo:O = 1 : 3). This salt (with Mo:O = 1 : 3.5) is evidently a limiting case as it contains both tetrahedra and octahedra.

It is also interesting to compare the molybdates and tungstates with complex oxygen salts of related elements. The structure of *e.g.* $\text{K}_2\text{Cr}_2\text{O}_7$ has not been determined, but as it crystallizes from acid water solutions of chromates, where probably $\text{Cr}_2\text{O}_7^{2-}$ ions exist, it seems reasonable to assume that the dichromates contain discrete $\text{Cr}_2\text{O}_7^{2-}$ ions built up as double tetrahedra. If we on the other hand consider the uranates, it is known that even normal uranates, *e.g.* BaUO_4 , contain UO_6 octahedra forming two-dimensional infinite UO_4^{2-} ions¹³.

SUMMARY

Na_2MoO_4 and Na_2WO_4 have been shown to have spinel structure. The crystal structure of $\text{Na}_2\text{Mo}_2\text{O}_7$ and $\text{Na}_2\text{W}_2\text{O}_7$ has been determined. It is built up by infinite $\text{Mo}_2\text{O}_7^{2-}$ ions, formed by MoO_4 tetrahedra, each sharing two oxygens with a chain of MoO_6 octahedra sharing corners.

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