The Crystal Structure of the Yellow Molybdic Acid,

$MoO_3 \cdot 2H_2O$

On the Existence of an H_4O^{2+} Ion

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This study of the yellow molybdic acid $MoO_3 \cdot 2H_2O$ is a part of the series of investigations on polymolybdates, carried out at this institute. $MoO_3 \cdot 2H_2O$ is of special interest as a limiting compound in the series from normal molybdates to MoO_3 and its hydrates.

CRYSTALS

Crystals of $MoO_3 \cdot 2H_2O$ may be obtained mainly in three different ways. Thus it is formed after prolonged standing of HNO_3 solution of ammonium molybdate, which is used in the analysis of phosphorous. This product and that obtained by Rosenheim's[1] method are not pure, but contain small amounts of ammonium polymolybdates, as we have shown by powder photographs. A very pure acid is formed by the procedure described by Carpéni[2].

For this investigation a prismatic crystal was selected. Rotation and Weissenberg photographs were taken with Cu-K radiation around the a-axis $(h = 0\text{—}4)$. The Weissenberg photographs indicated orthorhombic symmetry. The crystals have earlier been described as monoclinic[3] with $a:b:c = 1.0950:1:1.0664$ and $\beta = 90°\ 41'$ (cf. Groth[4]). The small difference of $41'$ from $90°$ is very difficult to measure on single crystal photographs, but the symmetry of the intensities was obviously in agreement with an orthorhombic crystal. In order to get further information we also investigated powder photographs with Cr-K radiation in focusing cameras. The results are given in Table 1. Evidently the crystals are monoclinic, but it is not easy to detect any measurable differences in the intensities of hkl and $h\bar{k}l$. The cell dimen-
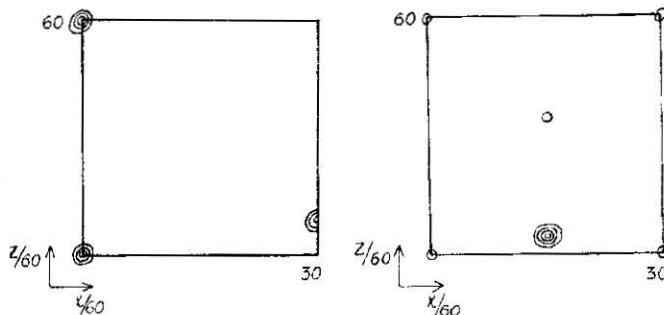
Fig. 1. $P(x, 0, z)$.

Fig. 2. $\varrho\ (x, 0, z)$.

sions are $a = 3.77$ Å, $b = 6.91$ Å, $c = 7.34$ Å, and $\beta = 90°\ 40'$, (corresponding to $a:b:c = 1.09:1:1.06$ in the notation of Groth[4]). The density 3.124[3] requires 2.02 formula units of $MoO_3 \cdot 2H_2O$ in the cell. No $hk0$ reflections could be detected for h odd. Such a lack is, however, not typical for any monoclinic space-group, but must be due to the nearly orthorhombic structure. The only possible space-groups are $C_2^1\text{—}P\ 2$, $C_s^1\text{—}P\ m$ and $C_{2h}^1\text{—}P\ 2/m$. The crystallographic measurements[3,4] make the space-group $C_{2h}^1\text{—}P\ 2/m$ most probable.

The intensities were estimated visually and the values multiplied by $\cos^2 \mu \cdot \sin \Upsilon/(1 + \cos^2 2\Theta)$[5]. The absorption and temperature factors were neglected.

MOLYBDENUM POSITIONS

The positions of two Mo atoms in the unit cell are to be determined. They can be placed in two of the eight single-fold general positions $1(a)\text{—}1(h)$ or in one of the six two-fold positions $2(i)\text{—}2(n)$. $2(i)\text{—}2(l)$ should require a maximum in $P(0, y, 0)$ and $2(m)\text{—}2(n)$ in $P(x, 0, z)$. These cuts were therefore calculated. $P(0, y, 0)$ has only one maximum for $y = 0$, so the positions $2(i)\text{—}2(l)$ cannot be occupied by Mo atoms. In addition to the maximum in $(0, 0, 0)$, $P(x, 0, z)$ (Fig. 1) has one other maximum in $(30/60, 0, 8.5/60)$. As the coordinates for the general positions are $2(m):(x, 0, z)\ (\bar{x}, 0, z)$ and $2(n):(x, \frac{1}{2}, z)\ (\bar{x}, \frac{1}{2}, \bar{z})$ the values $(30/60, 8.5/60)$ must correspond to $(2\,x_{Mo}, 2\,z_{Mo})$ giving $x_{Mo} = 15/60$ and $z_{Mo} = 4.25/60$. These parameters can easily be verified by a comparison with the intensities obtained. The lack of detect-
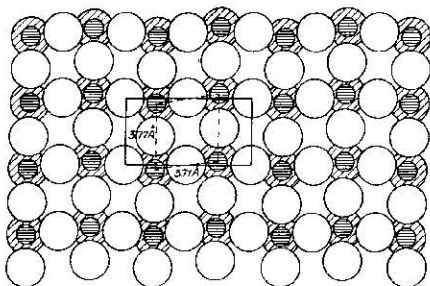
Fig. 3. MoO$_4^{2-}$ layer.

{Large circles = oxygen atoms
{Small circles = molybdenum atoms
The oxygen atoms nearest to the spectator are omitted to show the underlying metal atoms.

able reflections $hk0$ for h odd is thus caused by $x_{Mo} = 15/60$. Of course the choice between $2(m)$ and $2(n)$ is quite arbitrary, and the two Mo atoms are placed in $2(m)$: $(x, 0, z)$ $(x, 0, \bar{z})$ with $x = 15/60$ and $z = 4.25/60$. The signs of all F (hkl) could then easily be determined and ϱ $(x, 0, z)$ was calculated (Fig. 2). The Mo parameters definitely obtained are $x = 0.25$ and $z = 0.07$.

OXYGEN POSITIONS. MOLYBDENUM-OXYGEN COORDINATION

The Mo atoms in the planes $y = 0$ form distorted squares with the sides 3.71 Å and 3.77 Å. (Fig. 3). These distances agree very well with Mo—Mo and W—W distances obtained earlier for MoO$_6$ or WO$_6$ octahedra sharing corners [6-8]. As the zig-zag Mo—Mo strings are also found in WO$_3$[6], the structure may be built up of MoO$_6$ octahedra, which share corners. As a matter of fact oxygen maxima corresponding to such a structure occur in ϱ $(x, 0, z)$ (Fig. 2), although they are diffuse. It is not possible to fix the positions of these oxygen atoms more accurately by any method, so they have been placed halfway between neighbouring Mo atoms. The other two oxygen atoms may be situated at suitable distances on each side of the Mo atoms. It seems most reasonable to give these Mo—O distances values between 1.8 and 2.0 Å (the other Mo—O are about 1.86 Å and 1.89 Å). The parameters of the oxygen atoms will then be:

1 O in 1(a)	0, 0, 0	
1 O in 1(d)	0.5, 0, 0	
2 O in 2(m)	$(x, 0, z)$ with $x = 0.25$ and $z = 0.57$	
4 O in 4(o)	(x, y, z) with $x = 0.25$, $y = 0.27$, $z = 0.07$	

This part of the structure is thus built up of parallel layers of MoO$_6$ octahedra sharing corners (Fig. 3). The formula of each layer is MoO$_4^{2-}$. The problem then remains of placing the additional oxygen atoms required by the formula MoO$_3 \cdot 2H_2O$. As the layers are identical, their unshared oxygen atoms are opposed to each other. If these atoms are given the distance 1.9 Å from Mo, their mutual distance is 3.1 Å, a little more than what corresponds to contact. The only space available for an ion with a radius larger than 1 Å is in the interstice between the eight oxygen atoms already placed in the cell, that is in 1(f): 0 $\frac{1}{2}$ $\frac{1}{2}$ and 1(h): $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$. As a matter of fact maxima corresponding to these positions are found in ϱ $(x, \frac{1}{2}, z)$. The distances from such a central oxygen atom to its oxygen neighbours will then be ~ 2.9 Å to four of them and ~ 3.2 Å to the other four.

The structure finally obtained has a very great resemblance to the structure of BaUO$_4$[9]. The UO$_4^{2-}$ ion forms layers very similar to those of MoO$_4^{2-}$ and the Ba^{2+} ions are in contact with eight oxygen atoms, four of which are a little nearer to Ba^{2+}. In the determination of the structure of BaUO$_4$, space considerations were used to fix the positions of the oxygen atoms, so that the octahedral coordination is unequivocally correct.

EXISTENCE OF AN H$_4$O^{2+} ION

The great resemblance with BaUO$_4$ indicates immediately the possible existence of H$_4$O^{2+} ions in the crystal. However, such an ion has not been described previously, and other ways to distribute the four hydrogen atoms must be considered. Two of them may definitely be placed close to the central oxygen atom, forming H$_2$O, while the distribution of the other two must be discussed. At first it seems probable that they are attached to the MoO$_4^{2-}$ layers, for example as hydroxyl bridges, giving H$_2$MoO$_4 \cdot$ H$_2$O. Such a structure is a typical layer structure, having only neutral water molecules between the repelling layers. (Two oxygen atoms from different layers are pair by pair nearly in contact as described above.) In the habits of the crystals there are, however, no signs of cleavage, and the crystals have even been obtained as pseudo cubes (cf. Schulten[3]). This physical evidence seems to exclude definitely the H$_2$MoO$_4 \cdot$ H$_2$O structure theory. Another possibility would be to place the hydrogens between the repelling

Table 1. *Powder photographs of* $MoO_3 \cdot 2H_2O$. *Cr-K_α-radiation.*

hkl	$10^4 \sin^2 \Theta$		I
	calc.	obs.	obs.
001	0919	0918	v st
200	0970	0973	st
020	1096	1095	v st
011	1193	1193	st
210	1244	1245	v st
111	1424		v w
11$\bar{1}$	1447	1435	diffuse
201	1866	1865	v st
20$\bar{1}$	1912	1911	v st
021	2015	2016	st
220	2086	2066	st
211	2140	2138	w
21$\bar{1}$	2186	2184	w
121	2250	2245	v w
030	2466	2470	v st

oxygens. Their distances (in any case larger than 3 Å) are, however, much too large to correspond to a hydrogen bond of this type, joining only two oxygen atoms. (Evans [10] gives the value 2.54 Å).

One explanation is that there are hydroxyl bridges in only one direction in the MoO_4^{2-} layers giving central H_3O^+ ions. Such an assumption cannot be definitely excluded, but there is no evidence in favour of this unsymmetrical distribution of the hydrogen atoms, (cf. especially the analogy with $BaUO_4$).

All the hydrogen atoms may thus in some way be attached to the central oxygen atom. Then the question arises whether there are hydroxyl bonds between this central oxygen atom and its oxygen neighbours, or if there really exists an H_4O^{2+} ion. The distances are a little too large to be in agreement with earlier data on the hydroxyl bond length. (Evans [10] gives 2.7—2.8 Å.) The coordination of the oxygen atoms is, however, contradictory to the assumption of hydroxyl bonds, which requires a tetrahedral arrangement of oxygen around a central oxygen atom. Undoubtedly four of the oxygen atoms are nearer to the central atom than the others (2.9 and 3.2 Å), but the same distortion is found in $BaUO_4$ [9] (2.7 and 3.0 Å), where no hydroxyl bond can exist. Consequently, we find the existence of an H_4O^{2+} ion to be the most reasonable explanation of all known facts. (The existence of H_3O^+ ion in

H_3OClO_4 [11] has been established earlier by analogy with NH_4ClO_4). Of course a large amount of energy is required to attach an additional H^+ to H_3O^+. In this structure, however, there is a large gain of electrostatic energy, when an H_4O^{2+} ion is placed between the MoO_4^{2-} layers, which may be sufficient to explain its existence. Probably it can be considered as a rotating tetrahedral H_4O^{2+} ion (cf. NH_4^+). The acid will be written H_4OMoO_4. Possibly the yellow colour of the acid, unique among the molybdates, may be attributed to the H_4O^{2+} ion.

RELATIONS TO THE MOLYBDATES

The molybdates of well known structure with which a comparison can be made are the normal waterfree molybdates (e. g. $BaMoO_4$) [12] and the paramolybdates containing the ion $Mo_7O_{24}^{6-}$, described in two recent papers [13, 14]. If we formulate the molybdic acid as H_4OMoO_4 it seems to be analogous to such compounds as $BaMoO_4$. The structure is, however, quite different, containing MoO_4^{2-} layers instead of discrete tetrahedral MoO_4^{2-} ions. This discrepancy is explained by the fact that H_4OMoO_4 is formed from highly acid solutions, where MoO_6 octahedra in some way sharing corners probably preexist (v. infra). The waterfree molybdates on the other hand often crystallise from solutions with pH > 7, which may contain tetrahedral MoO_4^{2-} ions [2]. (It must be mentioned in this connection that the structure of no hydrated normal molybdate is known.)

A comparison with the $Mo_7O_{24}^{6-}$ ion, which is rather compact and built up by MoO_6 octahedra preferentially sharing edges does not give any new relations. The equilibrium study by Byé [15, 16] on the system $Na_2O \cdot MoO_3$—H_2O reveals, however, some interesting facts, which may be combined with the knowledge of the two structures. Byé states, that in the highly acid region the polymolybdates are the stable compounds, and he indicates $MoO_3 \cdot H_2O$, $MoO_3 \cdot 2H_2O$ and MoO_3 as metastable. Of these three compounds the structure of MoO_3 is also known [6]. It contains zigzag rows of MoO_6 octahedra, which are coupled together by edges. These rows form layers by sharing corners. Transformations evidently take place rather easily in the solution which makes it possible for these two different compounds to be formed from very similar solutions. The transformation may have proceeded one step further to complexes with MoO_6 preferentially sharing edges, when the stable polymolybdates are formed, which probably in some way are derivatives of the paramolybdates. The most unstable compound is $MoO_3 \cdot H_2O$, which also may be built up by MoO_6 octahedra which share corners in some way. It is also interesting to study the relations to the tungstates. In WO_3 [6] there is a three-dimensional net-work of WO_6 octahedra sharing corners. If this fact indicates that the

WO_6 octahedra have less tendency to share edges than the MoO_6 octahedra, it would also explain why there are only octatungstates but no deca- or higher tungstates described in the literature (cf. the great number of deca- and 16-molybdates).

These large ions of different kinds readily account for the high molecular weights obtained by diffusion [17] and dialysis [18] methods in very acid solutions, and for the polydispersity pointed out by Lamm [19]. A contradiction seems to arise in relation to the freezing point investigations [20,21], which indicate the existence of ions with 4 Mo atoms. It is, however, not possible to determine the molecular weights at high concentrations with freezing point methods, and probably the large ions are disaggregated to smaller complexes on dilution.

RELATIONS TO THE MOLYBDENYL ION

The reason why we also wish to direct attention to the solutions on the acid side of MoO_3 is in connection with a theory on oxygen bridgings put forward in a recent paper [22]. Electrochemical measurements combined with earlier crystal chemical data on several Bi compounds have led to the conclusion that in solutions on the acid side of $Bi(OH)_3$, there exist polynuclear complexes $Bi_nO_{n-1}^{(n+2)+}$, or $(BiO)_n^{n+}$. Such complexes are built up by Bi—O—Bi strings or as two-dimensional $(BiO)_n^{n+}$ sheets. It seems possible to apply similar discussions to acidified molybdic acid solutions, where there should be polynuclear complexes such as (MoO_{2n}^{2n+}) sheets. Of course such a theory must be verified by electrochemical measurements or X-ray investigations of molybdenum solutions, but it seems very probable.

SUMMARY

The crystal structure of $MoO_3 \cdot 2H_2O$ has been determined. It contains MoO_4^{2-} layers built up by MoO_6 octahedra, which share corners in two directions. In the interstices between the oxygen atoms of the parallel layers there are probably H_4O^{2+} ions, the existence of which has been discussed. The structure gives an answer to the main questions about the ionic conditions in very acid molybdate solutions, and it may also throw some light on the constitution of molybdenyl ions.

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