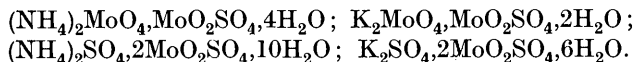


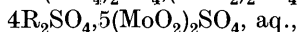
CXCVI.—*The Constitution of the Sulphates of Molybdenum.*

By FRANK HAROLD NICHOLLS, HAROLD SAENGER, and  
WILLIAM WARDLAW.

OUR knowledge of the chemistry of molybdenum is still far from complete, as shown by the paucity of the information available on the sulphates of that metal. The literature discloses that a compound  $\text{MoO}_2\text{SO}_4$  has been isolated from a solution of the trioxide in concentrated sulphuric acid and that complex salts are known:

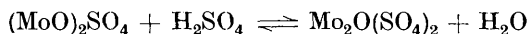


In the case of molybdenum with valencies of five and three, oxy-sulphates  $\text{Mo}_2\text{O}_3(\text{SO}_4)_2$  and  $\text{Mo}_2\text{O}(\text{SO}_4)_2, x\text{H}_2\text{O}$ , where  $x = 5$  or  $6$ , are recorded. We have investigated the sulphates of quinquevalent and trivalent molybdenum and have been unable to confirm the existence of a substance  $\text{Mo}_2\text{O}_3(\text{SO}_4)_2$ . New *compounds* of quinquevalent molybdenum  $(\text{NH}_4)_2\text{SO}_4, (\text{MoO}_2)_2\text{SO}_4, 2\text{H}_2\text{O}$  and



where  $\text{R} = \text{C}_5\text{H}_6\text{N}$ , have been isolated, and new salts of trivalent molybdenum of the type  $\text{R}_2\text{SO}_4, 2\text{Mo}_2\text{O}(\text{SO}_4)_2, 6\text{H}_2\text{O}$ , where  $\text{R} = \text{NH}_4, \text{K}, \text{Rb}$ , have been obtained. It will be noticed that no normal sulphate of molybdenum has been prepared but that throughout the series oxysulphates are always obtained.

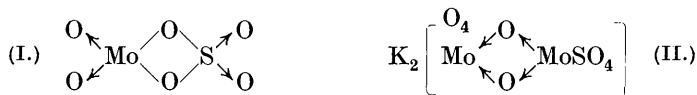
The presence of the molybdenyl radical  $\text{MoO}_2^{\cdot\cdot}$  and  $\text{MoO}_2^{\cdot}$  in compounds of molybdenum with valencies of six and five is especially noteworthy and one might have anticipated the isolation of derivatives of trivalent molybdenum of the form  $(\text{MoO})_2\text{SO}_4$ . The radical  $\text{MoO}^{\cdot}$  is undoubtedly present in such salts as  $\text{MoOR}$  where  $\text{R} = \text{Cl}, \text{Br}, \text{F}$ , etc. In the case of the sulphates, however, it appears that certain equilibria exist of the type



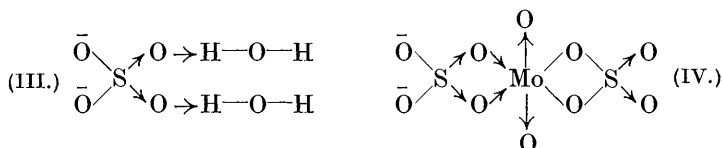
and that under the experimental conditions the isolation of the  $\text{Mo}_2\text{O}(\text{SO}_4)_2$  is favoured.

A most interesting series of structures can be deduced for the complex sulphates when they are formulated in accordance with the principles elaborated by Sidgwick ("Electronic Theory of Valency").

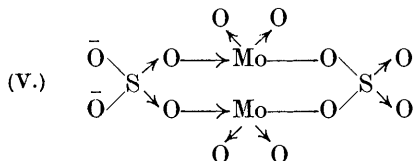
The sulphate of sexavalent molybdenum in all probability has the configuration (I), and when it combines with potassium molybdate



the compound (II) must be formed. The presence of two or four molecules of water of crystallisation follows readily from the association of water with the sulphate radical, as in (III). The existence

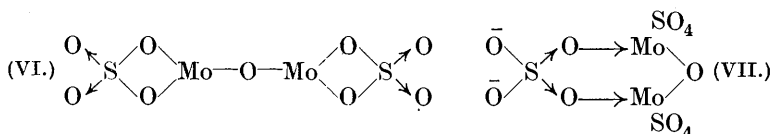


of  $\text{K}_2\text{MoO}_4, \text{MoO}_2\text{SO}_4, 2\text{H}_2\text{O}$  agrees with this theory. It is obvious that the complex sulphate  $\text{K}_2\text{SO}_4, 2\text{MoO}_2\text{SO}_4, 6\text{H}_2\text{O}$  cannot be similarly constituted, for that would involve assigning a covalency of eight to sulphur—a supposition disproved by experimental evidence. Here, there seems little doubt that the co-ordination is through the oxygen atoms of the sulphate, as in (IV). The molybdenum has now a covalency of six, the co-ordination of two molecules of molybdenyl sulphate with the potassium sulphate is simply explained without recourse to a higher covalency for sulphur than four, and the hydration of the salt is also satisfactorily indicated. A similar scheme is applicable to the sulphates of quinquevalent molybdenum,  $(\text{NH}_4)_2\text{SO}_4, (\text{MoO}_2)_2\text{SO}_4, 2\text{H}_2\text{O}$ , except that an eight-membered ring must be postulated (V).



For the salts of trivalent molybdenum,  $\text{R}_2\text{SO}_4, 2\text{Mo}_2\text{O}(\text{SO}_4)_2, 6\text{H}_2\text{O}$ , the configuration is eminently satisfactory. If the oxysulphate is written as in (VI), then co-ordination with the  $\text{R}_2\text{SO}_4$  will involve

the formation of stable six-membered rings (VII). As each sulphate radical is capable of associating with one or two molecules of water, the presence of the water of crystallisation is readily explained.

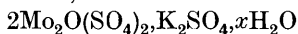


That the sulphate is present in a complex ion is proved by the fact that in the cold it is not precipitated by barium chloride.

#### EXPERIMENTAL.

The procedure adopted for the preparation of the complex oxysulphates of trivalent molybdenum was similar to that used for the isolation of the simple oxysulphate,  $\text{Mo}_2\text{O}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (J., 1924, **125**, 1911), except that acetone was replaced by air-free alcohol as precipitant. The alkali sulphate was added to the reduced solution before concentration. The first products isolated contained much free alkali sulphate as impurity, but by using about one-third of the theoretical quantity of alkali sulphate pure products could be obtained. Four samples of the complex ammonium salt gave ratios Mo, 1;  $\text{SO}_4$ , 1.256, 1.243, 1.257, 1.253. These indicated the composition  $2\text{Mo}_2\text{O}(\text{SO}_4)_2 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot x\text{H}_2\text{O}$  for the complex salt. Complete analysis of further samples gave Mo, 36.98, 36.82;  $\text{SO}_4$ , 45.97, 46.29;  $\text{NH}_4$ , 3.47, 3.50.  $2\text{Mo}_2\text{O}(\text{SO}_4)_2 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  requires Mo, 36.91;  $\text{SO}_4$ , 46.16;  $\text{NH}_4$ , 3.47%. This *complex salt* has all the characteristic properties of the oxysulphate from which it is derived. It is green and hygroscopic. Its aqueous solution is green when freshly prepared but rapidly oxidises and hydrolyses on standing. The salt possesses marked reducing properties and, like the parent body, gives a precipitate with barium chloride solution or with lead acetate in acetic acid solution only on heating, indicating the existence of the sulphate radical as a constituent of a complex ion.

In addition to the ammonium derivative the *potassium* and *rubidium* complex salts have been prepared. The results obtained indicate complete analogy with the foregoing ammonium salt [Found, for potassium salt, Mo : K = 1 : 0.2033.



requires Mo : K = 1 : 0.2037. Found for rubidium salt, Mo : Rb = 1 : 0.4467.  $2\text{Mo}_2\text{O}(\text{SO}_4)_2 \cdot \text{Rb}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$  requires Mo : Rb = 1 : 0.4450].

Potassium and rubidium were estimated in identical manner. To avoid the presence of large quantities of ammonium chloride in those samples in which it was proposed to estimate the alkali metal

present, the molybdenum was removed by precipitation with hydrogen sulphide; the acidity of the solution was  $N/5$ , and two precipitations sufficed for complete removal. The filtrate from the above was evaporated to about 10 c.c., transferred to a platinum crucible, and the alkali metal estimated as sulphate in the usual way.

*Compounds of Quinquevalent Molybdenum.*—The procedure adopted for the preparation of the complex oxysulphates of quinquevalent molybdenum was similar to that used for the isolation of the complex oxysulphates of tervalent molybdenum, except that in this case the solution of molybdic acid was only reduced to the quinquevalent stage, platinised platinum electrodes replacing those of polished platinum. The valency was tested by withdrawing a known amount of the brown solution and following the procedure of Wardlaw and Sylvester (J., 1923, **123**, 969).

For isolation of the *pyridinium* complex oxysulphate the reduced solution was not concentrated, but instead 2—2.5 c.c. of pyridine were added to and well shaken with 25 c.c. of the reduced solution before pouring into excess air-free alcohol [Found, in two samples : Mo, 30.71, 31.08; SO<sub>4</sub>, 28.95, 28.95; N, 3.66, 3.66.

$4(\text{C}_5\text{H}_6\text{N})_2\text{SO}_4 \cdot 5(\text{MoO}_2)_2\text{SO}_4 \cdot 16\text{H}_2\text{O}$   
requires Mo, 31.24; SO<sub>4</sub>, 28.13; N, 3.65%].

The complex salt is apricot-coloured and slightly hygroscopic. It is soluble in water, forming a brown solution which is rapidly oxidised and hydrolysed on standing. In concentrated hydrochloric acid the salt forms a vivid green solution, typical of solutions containing the salts of molybdenum, R<sub>2</sub>[MoOCl<sub>5</sub>]. Like sulphates of tervalent molybdenum, the new salt gives a precipitate with barium chloride or with lead acetate in acetic acid solution only on heating.

In the case of the *ammonium* complex oxysulphate, ammonium sulphate (1.8 g.) was added to 200 c.c. of the reduced solution before concentration, and the same method of procedure was then followed as for the tervalent compounds [Found, in two samples : Mo, 36.53, 36.59; SO<sub>4</sub>, 37.44, 37.38; NH<sub>4</sub>, 6.93, 6.88.

$(\text{NH}_4)_2\text{SO}_4 \cdot (\text{MoO}_2)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$   
requires Mo, 36.91; SO<sub>4</sub>, 36.93; NH<sub>4</sub>, 6.94%]. The properties of this salt are similar to those of the pyridinium complex salt but it is deeper in colour.

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