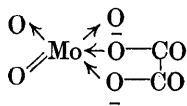


CCXXXVI.—*The Structures of the Oxalates of Sexavalent Molybdenum.*

By HENRY MILLS SPITTLE and WILLIAM WARDLAW.

WHEN a boiling aqueous solution of oxalic acid or a normal or acid oxalate is treated with molybdenum trioxide, salts of the type  $\text{MoO}_3, \text{R}_2\text{C}_2\text{O}_4, x\text{H}_2\text{O}$  are obtained. These are stable substances which can be recrystallised from water unchanged in composition. Physicochemical measurements have indicated that the molybdenum and the oxalate radical are present as a complex ion and that the substances are ternary electrolytes (Rosenheim and Bertheim, *Z. anorg. Chem.*, 1903, **34**, 436). An insight into the constitution of these substances is obtained by applying the electronic theory of valency. In all probability the molecule of molybdenum trioxide is represented as  $\text{O} \leftarrow \underset{\text{O}}{\text{Mo}} \rightarrow \text{O}$ , for X-ray analysis has disclosed that

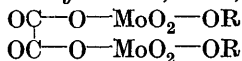
in  $\text{Ag}_2[\text{MoO}_4]$  the associated oxygen atoms are tetrahedrally distributed round the central molybdenum atom (Wyckoff, *J. Amer. Chem. Soc.*, 1922, **44**, 1994). The co-ordination of a molecule of



oxalic acid then takes place in accordance with the annexed scheme, whereby a five-membered ring is formed and molybdenum has a covalency of six. If, however, excess of molybdenum trioxide is used in the preparation, then it is possible to

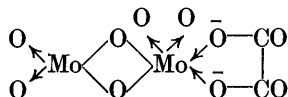
isolate the acid  $(\text{MoO}_3)_2, \text{H}_2\text{C}_2\text{O}_4, 2.5\text{H}_2\text{O}$  and a series of salts  $(\text{MoO}_3)_2, \text{R}_2\text{C}_2\text{O}_4, x\text{H}_2\text{O}$ . The members of this series are relatively unstable, their cold aqueous solutions slowly depositing molybdenum trioxide. To these substances Rosenheim (*Z. anorg. Chem.*, 1893,

**4**, 361; 1899, **21**, 15) gave the configuration

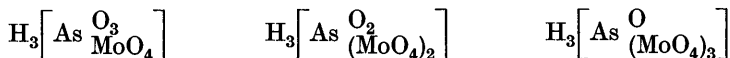


accounting for their instability by the reasoning that "a compound which contains two strongly acidic  $\text{MoO}_2$  residues with the oxalic acid residue cannot be very stable." It is much more probable,

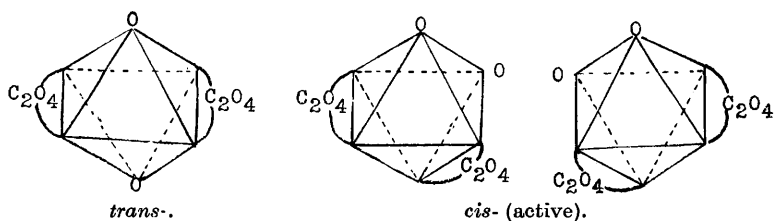
however, that the additional molecule of trioxide forms the group  $\text{MoO}_4$  and that the complex oxalate has the configuration



This replacement of oxygen atoms by the group  $\text{MoO}_4$  is clearly seen in the co-ordination compounds



The isolation of these two series of compounds might lead one to infer that the reaction between molybdenum trioxide and oxalic acid was invariably one of molecular addition. That this is not so, has been demonstrated by the present research. It has been shown that, when a saturated aqueous solution of molybdenum trioxide (1 mol.) in oxalic acid (2—3 mols.) is treated with suitable bases, a new series of *oxyoxalates* of sexavalent molybdenum can be obtained of the general formula  $\text{R}_2[\text{MoO}_2(\text{C}_2\text{O}_4)_2]$ , where  $\text{R} = \text{C}_9\text{H}_8\text{N}$ ,  $\text{C}_{10}\text{H}_{10}\text{N}$ ,  $\text{C}_{21}\text{H}_{23}\text{N}_2\text{O}_2$ . These substances are of special interest, for, from the space diagrams, it can be seen that they may occur in three forms, two of which should be optical isomerides.



After the preparation of the *strychnine* derivative, attempts were made to resolve it into two optically active forms, but with no positive results.

#### EXPERIMENTAL.

*Molybdenum Trioxide Solution.*—Hydrated molybdenum trioxide (4 g. of  $\text{MoO}_3 \cdot \text{H}_2\text{O}$ ) was heated with 60 c.c. of a solution of oxalic acid (14 g.) till dissolved. After filtration and cooling, water was added in quantity sufficient to keep the oxalic acid in solution. This solution (solution A) was prepared as required.

For precipitation of double molybdenum oxyoxalates from solution A, it was necessary to find a base giving a double molybdenum oxyoxalate more insoluble than either the corresponding oxalate or oxalic acid. Owing to the inability to use alkali or alkaline-earth

salts, advantage was taken of the knowledge that some organic bases, notably pyridine and quinoline, form well-defined, stable, normally hydrated, complex salts with molybdenum compounds. Pyridine failed to give any precipitate with solution A in water or in 95% water-alcohol. Quinoline and quinaldine, though possessing soluble oxalates, had relatively insoluble double oxalates, and later, during the investigation on the optical properties of this series of salts, strychnine and brucine were found to have similar properties. Amongst other bases investigated, no suitable example was discovered.

*Diquinolinium Molybdenum Dioxydioxalate.*—To solution A, pure quinoline, in quantity insufficient to cause precipitation of all the molybdenum, was added slowly with constant stirring. The white, nearly insoluble, crystalline solid precipitated was dried in a vacuum over calcium chloride, after washing with cold water {Found: Mo, 17.1;  $C_2O_4$ , 31.1; N, 5.0.  $(C_9H_8N)_2[MoO_2(C_2O_4)_2]$  requires Mo, 17.0;  $C_2O_4$ , 31.2; N, 5.0%}. The substance was quite stable and could be recrystallised unchanged from water or from a concentrated solution of molybdenum trioxide in oxalic acid (Found: Mo, 17.0;  $C_2O_4$ , 31.1%).

*Quinaldinium Molybdenum Oxyoxalates.*—Pure quinaldine (1—2 g.) was added slowly with constant stirring to solution A (40 c.c.). At first no precipitation occurred, but after some minutes' standing, a small amount of an oil separated and slowly solidified. Agitation accelerated the rate of crystallisation. The product, after collection, was washed with cold water and dried over calcium chloride in a vacuum (Found: Mo, 23.8;  $C_2O_4$ , 22.9%; Mo :  $C_2O_4$  = 1.00 : 1.05). The solid was therefore a mixture, consisting probably of compounds with Mo :  $C_2O_4$  ratios of 1 : 1 (95%) and 1 : 2 (5%).

The precipitation from similar solutions of molybdenum trioxide in oxalic acid, of molybdenum oxalates with Mo :  $C_2O_4$  ratios of 1 : 2 and 1 : 1 (impure) by quinoline and quinaldine respectively, indicated the existence of an equilibrium in the solution. The precipitation and stability of quinolinium molybdenum dioxydioxalate is evidently due to its insolubility, whilst the mixture of salts obtained with quinaldine indicated that two salts of similar solubility occur. To prepare these in a pure state, the effect of mass action was used.

*Quinaldinium Hydrogen Molybdenum Trioxymonoxalate.*—The mixture of quinaldinium salts (4—5 g.) resulting from treatment of solution A with quinaldine was recrystallised twice from separate quantities (40 c.c.) of solution A. The white crystalline solid, which separated in excellent yield, was washed with cold water and dried over calcium chloride in a vacuum {Found: Mo, 24.2;  $C_2O_4$ , 22.3;

N, 3.5.  $(C_{10}H_{10}N)H[MoO_3 \cdot C_2O_4 \cdot H_2O]$  requires Mo, 24.3;  $C_2O_4$ , 22.3; N, 3.5%}.

The formation of this *salt* is in accordance with the lowering of the ionic concentration of quinaldine in the recrystallising medium. In agreement with the above formula the salt shows acid reactions. The solubility is much higher than that of the quinolinium salt, and the temperature coefficient of solubility extremely high.

*Diquinaldinium Molybdenum Trioxymonoxalate*.—The above acid quinaldinium salt (2.5 g.) in water (10 c.c.) was heated with excess quinaldine under reflux for 2 hours. The filtrate from undissolved quinaldine was concentrated to a thick syrup over phosphoric oxide in a vacuum till crystallisation commenced. Treatment with dry acetone induced crystallisation, and the solid, after being washed with acetone, was dried over calcium chloride in a vacuum. Analysis of several samples showed that in each case mixtures of normal and acid salts were present, and a pure normal salt has not yet been obtained.

*Diquinaldinium Molybdenum Dioxydioxalate*.—For preparation of this salt it is necessary to increase the ionic concentrations of quinaldinium oxalate relative to the molybdenum concentration. To a solution of quinaldine (4 g.) and oxalic acid (6 g.) in water (3 c.c.), solution A (20 c.c.) was added slowly with rapid stirring. The white *solid*, which separated slowly in granular crystals quite distinct from the flakes of the acid salt, was washed with cold water and dried in a vacuum over calcium chloride {Found : Mo, 15.8;  $C_2O_4$ , 28.8; N, 4.6.  $(C_{10}H_{10}N)_2[MoO_2(C_2O_4)_2] \cdot H_2O$  requires Mo, 15.7;  $C_2O_4$ , 28.8; N, 4.6%}.

The extra molecule of water was quite loosely held and was removed by drying over phosphoric oxide in a vacuum for 24 hours {Found : Mo, 16.1%. Mo :  $C_2O_4$  : N = 1.00 : 1.99 : 2.00.

$(C_{10}H_{10}N)_2[MoO_2(C_2O_4)_2]$   
requires Mo, 16.2%}.

To verify further the equilibrium existing between solutions of the two quinaldinium molybdenum oxyoxalates, a pure sample of diquinaldinium molybdenum dioxydioxalate was converted to quinaldinium hydrogen molybdenum trioxymonoxalate by a double recrystallisation from solution A (Found : Mo, 24.3;  $C_2O_4$ , 22.4. Calc. : Mo, 24.3;  $C_2O_4$ , 22.3%}.

*Distrychnine Molybdenum Dioxydioxalate*.—Strychnine oxalate solution (strychnine, 7 g.; oxalic acid, 4 g.; water, 100 c.c.) was slowly added to molybdenum trioxide solution (50 c.c.) containing hydrated molybdenum trioxide (5 g.) and oxalic acid (10 g.). The resulting white precipitate, which at first was somewhat viscid, changed to a granular condition on digestion with hot water. It

was washed with cold water, and dried in a vacuum over calcium chloride {Found : Mo, 9·8; C<sub>2</sub>O<sub>4</sub>, 18·0; N, 5·7.

(C<sub>21</sub>H<sub>23</sub>O<sub>2</sub>N<sub>2</sub>)<sub>2</sub>[MoO<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>]  
requires Mo, 9·8; C<sub>2</sub>O<sub>4</sub>, 18·1; N, 5·8%}. The substance was quite stable and could be recrystallised unchanged from water or solution A.

*Brucine Molybdenum Oxyoxalates.*—Brucine molybdenum oxyoxalates, prepared either by the addition of a deficiency of brucine oxalate to solution A or by addition of a deficiency of solution A to brucine oxalate solution, appear to be mixtures of two or more of the four possible compounds.

*Analytical Methods.*—Molybdenum was estimated by direct ignition to the trioxide at 350°, and nitrogen by the method of Dumas. With quinolinium and quinaldinium salts, oxalate was estimated by titration with standard potassium permanganate after removal of the organic base by steam distillation from alkaline solution. With strychnine and brucine derivatives the following method was used. A solution of the salt (0·5 g.) was treated with ammonia solution (*d* 0·880; 25 c.c.); after filtration from precipitated organic base, excess of calcium chloride was added, and the precipitated calcium oxalate was washed, and titrated with standard potassium permanganate.

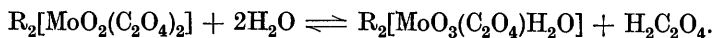
*General Properties.*—The complex oxalates investigated were all colourless crystalline substances. The examples prepared were necessarily fairly insoluble in water, but were soluble in concentrated hydrochloric acid. By the action of hydrogen sulphide on aqueous solutions or suspensions of the oxalates, molybdenum trisulphide was formed.

*Molecular-conductivity Determinations.*—Investigation of the constitution of solutions of the complex oxalates was made by means of conductivity determinations. Owing to their insolubility, it was necessary to measure the conductivity with high accuracy, and a modified conductivity bridge was used (Angell, Drew, and Wardlaw, J., 1930, 367). The values of  $\mu$  obtained at 18° are shown below :

|  | $v =$ | 1555. | 2043. | 2217. | 2582. | 2772. |
|--|-------|-------|-------|-------|-------|-------|
| (A) (C <sub>10</sub> H <sub>10</sub> N)H[MoO <sub>3</sub> (C <sub>2</sub> O <sub>4</sub> )H <sub>2</sub> O] ...              | 299·4 |       |       | 318·4 |       |       |
| (B) (C <sub>9</sub> H <sub>8</sub> N) <sub>2</sub> [MoO <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ] .....   |       | 389·7 |       |       | 403·7 |       |
| (C) (C <sub>10</sub> H <sub>10</sub> N) <sub>2</sub> [MoO <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ] ..... |       |       |       |       |       | 407·0 |

The values obtained for salt (A) compare well with those given by Rosenheim (*Z. anorg. Chem.*, 1896, **11**, 225) for other salts of the type RH[MoO<sub>3</sub>(C<sub>2</sub>O<sub>4</sub>)H<sub>2</sub>O]. Similar values are recorded for acid salts of certain dibasic acids. Hydrolysis does not occur to any great extent, since the oxalic acid liberated by such a process would greatly increase the molecular conductivity.

With salts (B) and (C) the higher conductivities obtained are in accordance with the hydrolysis of the complex acid into oxalic acid and the monoxalate :



The authors wish to express their thanks to the Department of Scientific and Industrial Research for the award of a grant to one of them (H. M. S.).

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[Received, May 11th, 1931.]

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