CX.—*Complex Oxalates of Quadrivalent Molybdenum.*

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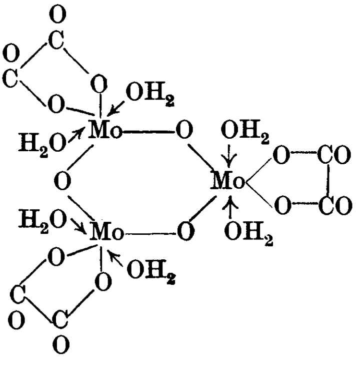
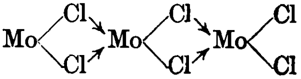
Although molybdenum readily forms a wide range of oxalates, in which the metal has valencies of six, five, four, and three, yet in no case has a normal oxalate been isolated : this is in accordance with the well-known tendency of this element to form oxy-salts. The close relationship existing between the oxalates is shown in the case of the sexa- and quinque-valent derivatives by their co-ordination formulæ, $[MoO_3(C_2O_4),xH_2O](H_2, HR, \text{ or } R_2)$ and $[MoO_2(C_2O_4),yH_2O](H \text{ or } R)$ (J., 1928, 2742). Knowledge of the oxalates of molybdenum in its lower valency states is still, however, very limited, since there have been isolated but one oxalate, $MoO(C_2O_4),3H_2O$, of quadrivalent molybdenum, and only two of tervalent molybdenum, the soluble $Mo_2O(C_2O_4)_2,6H_2O$ and the insoluble $Mo_4O_3(C_2O_4)_3,12H_2O$ (Wardlaw and Parker, J., 1925, **127**, 1311). By analogy with the co-ordination formulæ used above, it appeared (*loc. cit.*) that the oxalate $MoO(C_2O_4),3H_2O$ could be more adequately formulated as the acid $H_2[MoO_2(C_2O_4),2H_2O]$, especially in the light of its pronounced acidic properties.

With a view to decide this question, further investigation of the oxalates of quadrivalent molybdenum has been undertaken. In addition to the preparation of molybdenyl oxalate, $MoO(C_2O_4),3H_2O$, and a study of its hydrolytic products, new complex *salts* of the general formula $R_2[Mo_3O_4(C_2O_4)_3,5H_2O]$, where $R = K, NH_4$, or C_5H_6N, have been obtained.

The interesting result emerges from this investigation that, contrary to the original hypothesis, the oxalate $MoO(C_2O_4),3H_2O$ is not satisfactorily formulated as the dibasic acid $H_2[MoO_2(C_2O_4),2H_2O]$ with a co-ordination number of six, but rather as the compound $H_2[Mo_3O_4(C_2O_4)_3,xH_2O]$ containing a polynuclear complex of three molybdenum atoms. This is supported by the conductivity data, which indicate that the complex oxalates are ternary electrolytes. Amongst the compounds of molybdenum the occurrence of such complexes is not exceptional. The un-ionised acid, $Mo_3O_3(C_2O_4)_3,6H_2O$, corresponding to the salts mentioned above can be conveniently formulated as shown in the annexed figure. In this formula



each atom of molybdenum carries one oxalato-group and two water molecules, and the three molybdenum and three oxygen atoms form a symmetrical 6-membered ring. Such a configuration does not appear improbable in view of the great stability of the new compounds. Ionisation can take place by means of the reaction $\mathrm{Mo{\leftarrow}OH_2 = [Mo{-}O{-}H]' + H^{\bullet}}$. The only point left unexplained is why such a compound can ionise as far as a dibasic acid and no further. It seems comparable with the behaviour of Mo_3Cl_6, in which the peculiar reactivity of two chlorine atoms is still unexplained, although the formula  $\mathrm{Mo}\!<\!\substack{\mathrm{Cl}\searrow\\ \mathrm{Cl}\nearrow}\!\mathrm{Mo}\!<\!\substack{\mathrm{Cl}\searrow\\ \mathrm{Cl}\nearrow}\!\mathrm{Mo}\!<\!\substack{\mathrm{Cl}\\ \mathrm{Cl}}$ would account for this property.

The possibility that the metallic atoms may be linked by oxalate radicals rather than by oxygen atoms has been considered, but this leads to a co-ordination number of five for the molybdenum; only by using the oxygen atoms as linkages can a co-ordination **number** of six be assigned to the metal.

For the oxalates of quinque- and ter-valent molybdenum similar polynuclear complexes, $R_2\left[X(C_2O_4)OMo{<}\substack{O\\O}{>}MoO(C_2O_4)X\right]$, where $X = C_5H_5N$ or H_2O, and $[3H_2O,(C_2O_4)Mo{-}O{-}Mo(C_2O_4),3H_2O]$, have already been suggested. This tendency of molybdenum to form complex substances containing large numbers of the metal atoms is also seen when molybdenyl oxalate is hydrolysed. Products have been isolated of the empirical formulæ $Mo_5O_6(C_2O_4)_4$ and $Mo_4O_5(C_2O_4)_3$. They appear analogous to the insoluble tervalent oxyoxalate $Mo_4O_3(C_2O_4)_3$, which has been shown to give $Mo_4O_5(C_2O_4)_3$ on atmospheric oxidation. Thus a close relationship is now apparent throughout the whole range of the oxalates of molybdenum.

The isolation of an *ammonium salt* of the type

$$R_2[Mo_3O_4(C_2O_4)_3,5H_2O],1{\cdot}5C_2H_5{\cdot}OH$$

might be adduced as evidence that the complex salts contain a minimum of six molybdenum atoms. In the absence of further convincing evidence in this direction, however, there seems no reason for assigning a more complicated structure to the complex salts.

EXPERIMENTAL.

The simplest method of preparation for the oxalates involves the electrolytic reduction of an acid solution of molybdic acid. This problem is complicated, however, in the case of the oxalates, by the electrolytic reduction of oxalic acid itself, although Chilesotti (*Z. Elektrochem.*, 1906, **12**, 146) states that in oxalic acid solutions of molybdic acid this side reaction has only a very slight influence.

It was found, however, that solutions of tervalent molybdenum thus produced, after oxidation to the quadrivalent state, yielded impure molybdenum oxalates. Accordingly, in the present research, this electrolytic method was discarded in favour of one previously described by Wardlaw and Parker (*loc. cit.*), in which molybdenum trihydroxide, precipitated by addition of ammonia to an electrolytically reduced solution of molybdic acid in sulphuric acid, was dissolved in oxalic acid.

For the preparation of molybdenum trihydroxide the details given in previous communications (J., 1924, **125**, 1910; 1925, **127**, 1311) were followed, but special measures were adopted to remove, as completely as possible, ammonia and ammonium salts. Over a period of 2—3 months, the hydroxide (20 g.) was washed 6 or 7 times with 5 l. of boiling air-free water, by decantation, in an atmosphere of nitrogen. The time required for the settling of the hydroxide was not appreciably affected by the addition of electrolytes, in the form of small quantities of oxalic acid, or a solution of tervalent molybdenum oxyoxalate. The hydroxide, suspended in the smallest possible quantity of water, was then forced on to crystals of oxalic acid (50 g.), just covered with water to displace air, and the mixture heated to give a clear solution. If the brown solution thus produced was boiled in an atmosphere of nitrogen for a considerable period, the brown insoluble tervalent oxyoxalate $Mo_4O_3(C_2O_4)_3,12H_2O$ separated, provided the solution was not concentrated below 150 c.c., and water was added at intervals to make up for that lost by evaporation. On the other hand, by rapid concentration of the solution to 120 c.c., in absence of air, the formation of this insoluble oxalate was avoided, and a deep brown solution resulted, which was cooled, filtered to remove separated oxalic acid, and oxidised at room temperature by the passage of a current of air (free from ammonia). A bright red solution containing quadrivalent molybdenum was obtained (Solution A). It was found undesirable to concentrate this, as boiling caused a colour change to reddish-brown, and the solution so produced did not yield the required product $MoO(C_2O_4),xH_2O$. By addition of the unconcentrated bright red solution to acetone, however, a pinkish-red precipitate of the above composition was obtained, identical in properties with the substance already described (*loc. cit.*).

Salts of the Type $R_2[Mo_3O_4(C_2O_4)_3,5H_2O]$.

For the preparation of this series of complex oxalates, alcohol was added to Solution A. No molybdenyl oxalate was precipitated, but a clear blood-red solution resulted, from which the various complex oxalates described below were obtained by addition of the appropriate base.

Dipyridinium Trimolybdenumtetroxytrioxalate.—To the clear red solution produced by the addition of Solution A (20 c.c.) to alcohol (1000 c.c.), pure pyridine, in sufficient quantity to precipitate 75% of the molybdenum, was added slowly with constant stirring. The bluish-pink flocculent precipitate was collected, washed with alcohol, and dried over calcium chloride in a vacuum {Found: Mo, 33·6; C_2O_4, 30·7; N, 3·26; C, 21·9; H, 2·64. $(C_5H_6N)_2[Mo_3O_4(C_2O_4)_3,5H_2O]$ requires Mo, 33·3; C_2O_4, 30·5; N, 3·24; C, 22·1; H, 2·56%}. In order to determine whether the salt as originally precipitated, and before being dried over calcium chloride in a vacuum, contained associated alcohol, a freshly precipitated sample was air-dried on a porous plate and analysed. Alcohol was thereby shown to be absent. Estimation of valency proved that the molybdenum was quadrivalent.

Analysis. Molybdenum was estimated by direct ignition to the trioxide, or by precipitation as trisulphide and ignition to trioxide (J., 1924, **125**, 1911). Nitrogen was estimated by the method of Dumas, and oxalate as previously described for the oxalates of quinquevalent molybdenum (J., 1928, 2742). In the present research the ignition to trioxide of the $Mo(OH)_4$ obtained during the estimation of oxalate was not found to be satisfactory for the estimation of molybdenum (see p. 796).

Dipotassium Trimolybdenumtetroxytrioxalate.—For the preparation of this salt the method used was similar to that for the pyridinium compound, potassium hydroxide (20%) being added slowly instead of pyridine, in sufficient quantity to precipitate only half the molybdenum present. The product resembled the pyridinium compound in appearance and properties {Found: Mo, 36·7; C_2O_4, 33·4; K, 9·8. $K_2[Mo_3O_4(C_2O_4)_3,5H_2O]$ requires Mo, 36·7; C_2O_4, 33·6; K, 10·0%}.

Diammonium Trimolybdenumtetroxytrioxalate.—Treatment of the clear red liquid produced by the addition of Solution A (10 c.c.) to alcohol (500 c.c.) with ammonia solution (3*N*) in sufficient quantity to precipitate half the molybdenum, resulted in the separation of a bluish-pink precipitate similar to the pyridinium and potassium salts. After being washed with alcohol and dried over calcium chloride in a vacuum, this compound was found by analysis usually to contain a small amount of ammonium oxalate. All the oxalates described above have been precipitated in an amorphous condition. In addition, the ammonium salt has been obtained in the form of purplish-red crystals containing both water and alcohol of crystallisation. For the preparation of this salt, a portion of Solution A (containing 2 g. Mo) was carefully concentrated on the water-bath to 10 c.c. and dissolved in alcohol (500 c.c.); ammonium oxalate (0·5 g.) was then added in the form of crystals or fine powder. In the latter case the mixture was mechanically agitated for some weeks, and the resulting purplish-red crystals were collected and washed with alcohol. In the former case, after a suitable period, the unchanged crystals of ammonium oxalate were separated from the required red crystals by hand picking. In both cases it was found advisable to re-agitate the product for some days with a freshly prepared alcoholic solution of molybdenyl oxalate, after which the crystals were washed with alcohol and dried in a vacuum over calcium chloride {Found : Mo, 35·5; C_2O_4, 32·7; NH_4, 4·5; C, 13·4; H, 3·5. $(NH_4)_2\,[Mo_3O_4(C_2O_4)_3,5H_2O],1{\cdot}5C_2H_6O$ requires Mo, 35·5; (C_2O_4), 32·6; NH_4, 4·5; C, 13·3; H, 3·4%}. An exactly similar salt slowly separated from an alcoholic solution of molybdenyl oxalate, to which ammonia or ammonium oxalate solution had been added until there was a faint permanent precipitate. By treatment of alcoholic molybdenyl oxalate solutions with potassium or sodium oxalate or hydroxide solution in a similar manner, very small quantities of crystalline compounds separated, similar in appearance to the ammonium salt described above.

Attempts to make sodium and barium salts, by addition of sodium or barium hydroxide to an alcoholic solution of molybdenyl oxalate, yielded mixtures containing the required salt with the free metallic oxalate.

General Properties.—With the exception of the crystalline ammonium salt, the complex oxalates described above are bluish-pink amorphous solids. They are all very soluble in water, forming bright red solutions, but are insoluble in alcohol or acetone. Addition of alkalis or ammonium oxalate to aqueous solutions of the complex salts gives a blue coloration, but the red colour is restored by the addition of any acid, even acetic. The oxalate ion cannot be detected in aqueous solutions by the usual ionic reactions, nor is molybdenum hydroxide immediately precipitated by the action of alkalis in the cold. Hot potassium hydroxide solution, however, gives a black flocculent precipitate of molybdenum hydroxide, although some of the molybdenum may remain in the solution as the alkali molybdate. If the hydroxide is precipitated by means of sodium hydroxide, it can be obtained in a light green form. Solutions of the complex oxalates possess marked reducing properties, silver nitrate being reduced to metallic silver on boiling. On the addition of lead acetate solution to an aqueous solution of any of the salts, a voluminous bluish-pink precipitate is formed the colour of which changes on warming to brown.

Molecular-conductivity Determinations.—To decide whether the complex salts $R_2[Mo_3O_4(C_2O_4)_3,5H_2O]$ are correctly formulated as ternary electrolytes, determinations of molecular conductivity were carried out. Experiments at 0° indicated that the molecular conductivity of aqueous solutions of the complex oxalates did not change with time. This is in accordance with the qualitative observation that in such aqueous solutions neither the oxalate radical nor the molybdenum can be detected by ionic reactions in the cold. The molecular conductivities for dilute solutions at 0° are as follows :

$(NH_4)_2[Mo_3O_4(C_2O_4)_3,5H_2O],1{\cdot}5C_2H_5{\cdot}OH.$

v	92·7	139·1	208·6	312·9
μ	105·1	124·9	132·0	137·8

$(C_5H_6N)_2[Mo_3O_4(C_2O_4)_3,5H_2O].$

v	71·3	142·6	285·2	570·5	1141
μ	73·6	87·0	101·0	115·9	129·4

It is interesting to note that the lower molecular conductivity of the pyridinium salt is in accordance with the ionic velocities of the pyridinium and ammonium ions, which at 0° are respectively 20 (Lundén, *J. Chim. physique*, 1907, **5**, 592) and 38·4 (Landolt–Börnstein Tabellen, 1923, II, 1104). Moreover, the values for both salts are in agreement with those given by typical ternary electrolytes (J., 1927, 516), although, as would be expected, the large complex anion decreases the values of the molecular conductivity.

Hydrolysis of Molybdenyl Oxalate.

It has already been mentioned that addition of Solution A to acetone yields pinkish-red molybdenyl oxalate with the empirical formula $MoO(C_2O_4),xH_2O$. If, however, Solution A is concentrated by boiling before being added to acetone, a purple product results, of empirical formula $Mo_5O_6(C_2O_4)_4$, and containing both acetone and water. By extraction with aqueous alcohol at room temperature, this compound yields a brown residue of empirical formula $Mo_4O_5(C_2O_4)_3$. These reactions indicate that from molybdenyl oxalate by the action of aqueous acetone or alcohol, various polynuclear molybdenum complexes can be obtained. The probable reactions occurring can be symbolised as follows :

$$(a)\quad 5MoO(C_2O_4) + H_2O \rightleftharpoons Mo_5O_6(C_2O_4)_4 + H_2C_2O_4,$$

$$(b)\quad Mo_5O_6(C_2O_4)_4 \rightleftharpoons Mo_4O_5(C_2O_4)_3 + MoO(C_2O_4),$$

or

$$4Mo_5O_6(C_2O_4)_4 + H_2O \rightleftharpoons 5Mo_4O_5(C_2O_4)_3 + H_2C_2O_4.$$

It is interesting to note that the brown product $Mo_4O_5(C_2O_4)_3$ can also be obtained by atmospheric oxidation of a suspension of the insoluble tervalent oxyoxalate, $Mo_4O_3(C_2O_4)_3,12H_2O$, in aqueous or oxalic acid solution.

Pentamolybdenum Hexaoxytetroxalate.—A portion of Solution A (12 g. Mo in 120 c.c.) was concentrated to 40 c.c. by rapid boiling, cooled, filtered from the deposited oxalic acid, and added to acetone (400 c.c.). The dark red oil which separated was treated with dry acetone till granular, collected, and dried over calcium chloride in a vacuum. The *compound* tends to retain acetone, even after long drying, and hence analyses are calculated as molecular ratios [Found: (*a*) Mo, 39·1; C_2O_4, 29·1%; Mo : C_2O_4 = 4·95 : 4·00. (*b*) Mo, 39·0; C_2O_4, 28·8%; Mo : C_2O_4 = 4·98 : 4·00]; it is a purplish-brown crystalline solid, readily soluble in water to a red solution, but insoluble in acetone or alcohol.

Tetramolybdenum Pentoxytrioxalate.—This *compound* can be formed by the addition of the above $Mo_5O_6(C_2O_4)_4$ (1—2 g.) to a mixture of water (8 c.c.) and alcohol (52 c.c.); after shaking and filtration, the resulting brown solid is washed with alcohol and dried over calcium chloride in a vacuum (Found: Mo : C_2O_4 = 4·02 : 3·00, 4·01 : 3·00). A better method for the preparation of this compound is as follows: To a suspension of the insoluble tervalent oxalate (5 g.) in water (30 c.c.), oxalic acid (1 g.) was added. Air (free from ammonia) was drawn through the mixture for 3—4 weeks, and the resulting red solution, without being heated, was filtered and added to acetone (500 c.c.). The light brown precipitate was collected, washed with acetone, and dried in a vacuum over calcium chloride [Found: Mo, 42·1; C_2O_4, 28·8; Mo : C_2O_4 = 4·02 : 3·00. $Mo_4O_5(C_2O_4)_3,10H_2O$ requires Mo, 42·3; C_2O_4, 29·1%]. This compound was proved to contain quadrivalent molybdenum by the usual method of valency determination. As indicated by equations (*a*) and (*b*), it should be possible to convert the above compounds into molybdenyl oxalate, by treatment with appropriate concentrations of oxalic acid. This has been shown to be the case by the following experiment.

Oxalic acid, in slight excess of the theoretical amount, was added to an aqueous solution of either of the above complex molybdenum oxalates. After evaporation to dryness in a vacuum at 50°, the excess oxalic acid was extracted by dry acetone, and the resulting purplish-brown solid dried over calcium chloride in a vacuum [Found: (*a*) Mo, 39·2; C_2O_4, 36·3; Mo : C_2O_4 = 1·00 : 1·01; (*b*) Mo, 39·6; C_2O_4, 36·6; Mo : C_2O_4 = 1·00 : 1·01. Calc. for $MoO(C_2O_4),3H_2O$: Mo, 37·8; C_2O_4, 34·7. Calc. for $MoO(C_2O_4),2H_2O$: Mo, 40·7; C_2O_4, 37·3%]. If too great an excess of oxalic acid is used, the water of crystallisation remaining in the dried mixture of molybdenyl oxalate and oxalic acid forms aqueous acetone, which hydrolyses the product.

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