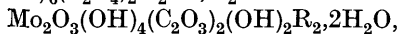


CCCLXIII.—*Complex Oxalates of Quinquevalent Molybdenum.*

By HENRY MILLS SPITTLE and WILLIAM WARDLAW.

SOME years ago Bailhache (*Bull. Soc. chim.*, 1903, **29**, 161; 1905, **33**, 439) prepared and investigated three crystalline complex oxalates of quinquevalent molybdenum, to which he assigned the formulæ $\text{Mo}_2\text{O}_2(\text{OH})_6(\text{C}_2\text{O}_4)_2\text{H}_2\text{Ba}, \text{H}_2\text{O}$ and



where R = K or NH_4 . Such a formulation gives no indication of the relationship, structure, or reactions of these compounds, which therefore seemed to afford an opportunity for testing the value of Werner's co-ordination theory in elucidating the structure of chemical compounds, for by applying the principles of that theory, it was possible to consider these substances as members of a series

of the general formula $R[\text{MoO}_2(\text{C}_2\text{O}_4)_x\text{H}_2\text{O}]$ where $R = \text{K}, (\text{NH}_4), \frac{1}{2}\text{Ba}$, etc.

In order to determine whether such a hypothesis was justifiable, and to investigate further the chemistry of molybdenum, we have prepared new members of the series, including the complex *acid* and *pyridinium* and *quinolinium* salts, and have submitted all these compounds to a physico-chemical examination.

EXPERIMENTAL.

In a previous communication (J., 1927, 2145) the preparation of salts of the type $\text{R}_2[\text{MoOCl}_5]$ was described. It has been found that when concentrated solutions of the pyridinium and quinolinium derivatives of this series are treated with oxalic acid, red solutions are obtained from which yellow solids separate. These substances have been shown to be complex oxalates. When the potassium and ammonium complex chlorides are similarly treated, red solutions are obtained, but owing to their high solubility, the resulting products are not precipitated.

Quinolinium Molybdenum Dioxoxalate.—This new salt was prepared by adding 30 c.c. of a warm aqueous solution of oxalic acid (1.2 g.) to 30 c.c. of a solution containing 5.6 g. of $(\text{C}_9\text{H}_8\text{N})_2[\text{MoOCl}_5]\cdot\text{H}_2\text{O}$, boiling the solution, filtering it hot, and cooling it; a bright yellowish-brown powder was thus obtained, which, after being washed with cold water and recrystallised from hot water, was dried in a vacuum over calcium chloride.

Analysis. The molybdenum was estimated by ignition of the compound to the trioxide, or by precipitation as trisulphide (J., 1924, 125, 1911) and oxidation to trioxide, which was weighed. The nitrogen was determined by the method of Dumas, and the oxalate by the following process: To 200 c.c. of a boiling aqueous solution of the complex salt (0.3 g.), 5 c.c. of potassium hydroxide solution (20%) were added. The precipitated hydroxide was removed, and the colourless filtrate concentrated to about 30 c.c. One c.c. of nitric acid (5*N*) was now added, and after boiling for about 2 minutes, the solution was acidified with sulphuric acid and titrated with standard potassium permanganate {Found: Mo, 26.3; C_2O_4 , 24.3; N, 3.9. $(\text{C}_9\text{H}_8\text{N})_2[\text{MoO}_2(\text{C}_2\text{O}_4)_x\text{H}_2\text{O}]$ requires Mo, 26.4; C_2O_4 , 24.2; N, 3.85%}.

The formation of this salt is in accordance with the scheme of hydrolysis and ionisation previously proposed (*loc. cit.*) for the complex chlorides $\text{R}_2[\text{MoOCl}_5]$.

Complex Pyridinium Molybdenum Oxyoxalates.—50 C.c. of a warm aqueous solution of oxalic acid (4.8 g.) were added to 50 c.c. of a solution of $(\text{C}_5\text{H}_6\text{N})_2[\text{MoOCl}_5]$ (18.4 g.) and the mixture was heated.

There separated on cooling an orange-yellow powder, which was washed with cold water and dried in a vacuum over calcium chloride {Found: Mo, 31.6; C_2O_4 , 29.0; N, 3.5; C, 22.6*; H, 2.5*; Mo : C_2O_4 : N : C : H = 4 : 4 : 3 : 23 : 30. $(C_5H_6N)_3H[Mo_4O_8(C_2O_4)_4 \cdot 6H_2O]$ or $(C_5H_6N)_3[Mo_4O_7(OH)(C_2O_4)_4 \cdot 6H_2O]$ requires Mo, 31.6; C_2O_4 , 29.0; N, 3.5; C, 22.7; H, 2.6%; Mo : C_2O_4 : N : C : H = 4 : 4 : 3 : 23 : 31}. The presence of quinquivalent molybdenum in this compound was confirmed by a valency determination.

In an attempt to prepare a normal salt from the above pyridinium salt, 1—2 g. of this compound were gently boiled under reflux with about 20 c.c. of pyridine. After removal of the pyridine by decantation, the operation was repeated on the product, and after drying in a vacuum over concentrated sulphuric acid until free from pyridine, the final product was a pale yellow powder, soluble in water {Found: Mo, 25.4; C_2O_4 , 23.3; N, 7.4. $(C_5H_6N)[MoO_2(C_2O_4) \cdot C_5H_5N]$ requires Mo, 25.6; C_2O_4 , 23.5; N, 7.5%}. Valency determinations indicated that quinquivalent molybdenum was present.

Treatment of the quinolinium complex oxalate with quinoline did not result in the replacement of the water molecule owing to the oxidation of the molybdenum.

Barium Molybdenum Dioxoxalate.—For the preparation of this compound (barium oxalomolybdate), Bailhache (*loc. cit.*) used two methods. The second method, which he considered preferable, involved the reduction of a hydrochloric acid solution of ammonium molybdate by red phosphorus, and addition of ammonium oxalate and barium chloride to the solution of quinquivalent molybdenum obtained. It was found, however, that this method yielded an impure salt containing a small amount of phosphate, and it was discarded in favour of the following method: 300 c.c. of an aqueous solution of oxalic acid (12 g.) were added to 300 c.c. of a solution of $(NH_4)_2[MoOCl_5]$ (35 g.) and the mixture was warmed. To the blood-red solution produced, barium chloride (11 g.) in 600 c.c. of water was added, and on heating to about 70° , a red, crystalline solid separated, which was collected hot, washed with hot water, and dried over calcium chloride in a vacuum {Found: Mo, 29.0; Ba, 20.8; C_2O_4 , 26.6. Calc. for $Ba[MoO_2(C_2O_4)]_2 \cdot 5H_2O$: Mo, 29.1; Ba, 20.8; C_2O_4 , 26.7%}. An equally satisfactory product was obtained by use of the pyridinium and quinolinium derivatives of the series $R_2[MoOCl_5]$.

The very soluble ammonium and potassium and the less soluble pyridinium and quinolinium compounds can readily be prepared by double decomposition of this insoluble barium salt with the appropriate sulphate.

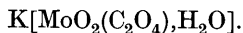
* Microanalysis.

Potassium Molybdenum Dioxyoxalate.—A satisfactory yield of this substance was obtained by the following method used by Bailhache, who, however, gave no experimental details. To 30 c.c. of a boiling aqueous solution of potassium sulphate (1.7 g.), barium molybdenum dioxyoxalate (7.0 g.) was added, and, after the mixture had been boiled for some minutes in a current of nitrogen, the insoluble sulphate was removed by filtration. If the filtrate was concentrated over phosphoric oxide at room temperature, tufts of golden needles were obtained, sometimes associated with red crystals. The yellow were separated from the red crystals by hand-picking and dried on a porous plate (Found: Mo, 30.3; C₂O₄, 27.8; K, 12.2. K[MoO₂(C₂O₄),3.5H₂O] requires Mo, 30.2; C₂O₄, 27.7; K, 12.3%).

The red crystals (Found: Mo, 32.0; C₂O₄, 29.3. Calc. for K[MoO₂(C₂O₄),2.5H₂O]: Mo, 32.0; C₂O₄, 29.3%) proved to be the less hydrated compound analysed by Bailhache. This red form separates in a pure condition from a very concentrated solution of the potassium complex oxalate (prepared as described) which has been slowly cooled and inoculated with a red crystal.

By drying over sulphuric acid in a vacuum, either form loses water and produces a yellow powder of the empirical formula K[MoO₂(C₂O₄),1.5H₂O] (Found: Mo, 34.0; C₂O₄, 31.4. Calc.: Mo, 34.0; C₂O₄, 31.2%).

On concentration of a solution of any of these hydrated salts at 100° in a vacuum, a red solid results (Found: Mo, 35.4; Mo : C₂O₄ = 1.00 : 1.00. K[MoO₂(C₂O₄),H₂O] requires Mo, 35.2%); this was formulated by Bailhache (*loc. cit.*) as Mo₂O₅(C₂O₃)₂(OH)₂K₂, which may be rewritten as K[MoO₂(C₂O₄),0.5H₂O]. In no case, however, have the present authors been able to obtain a substance with a lower water content than that demanded by



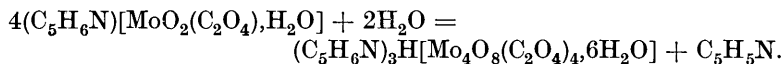
Ammonium Molybdenum Dioxyoxalate.—This salt was prepared by double decomposition of ammonium sulphate (1.3 g.) and barium molybdenum dioxyoxalate (7.5 g.). The preparation should be carried out in an atmosphere of nitrogen, for an aqueous solution of this salt oxidises more readily than a solution of the potassium derivative. The salt in the form of tufts of golden needles could not be isolated in sufficient quantity for analysis. By methods similar to those described for the isolation of the red crystals of the potassium salt, there were obtained orange crystals of the empirical formula (NH₄)[MoO₂(C₂O₄),2.5H₂O] (Found: Mo, 34.4; C₂O₄, 31.6; NH₄, 6.5. Calc.: Mo, 34.4; C₂O₄, 31.5; NH₄, 6.5%). On drying this salt over sulphuric acid in a vacuum, a yellow powder was obtained (Found: Mo, 36.6; C₂O₄, 33.6; NH₄, 6.9. Calc. for

$(\text{NH}_4)[\text{MoO}_2(\text{C}_2\text{O}_4), 1.5\text{H}_2\text{O}]$: Mo, 36.8; C_2O_4 , 33.7; NH_4 , 6.9%. When a solution of this ammonium salt was evaporated to dryness in a vacuum at 100° , a brittle red crust was obtained similar in composition to the potassium analogue {Found: Mo, 38.0; $\text{Mo} : \text{C}_2\text{O}_4 : \text{NH}_4 = 1.00 : 1.00 : 1.01$. $(\text{NH}_4)[\text{MoO}_2(\text{C}_2\text{O}_4), \text{H}_2\text{O}]$ requires Mo, 38.1%}.

Quinolinium Molybdenum Dioxyoxalate.—Barium molybdenum dioxyoxalate (7.0 g.) was added to quinolinium sulphate (3.5 g.) dissolved in 60 c.c. of boiling water. After being boiled for some minutes in an atmosphere of nitrogen, the liquid was filtered hot, and the bright yellowish-brown crystals which separated were washed with cold water and dried in a vacuum over calcium chloride {Found: Mo, 26.2; C_2O_4 , 24.2; N, 3.85; C, 35.7*; H, 2.65*. Calc. for $(\text{C}_9\text{H}_8\text{N})[\text{MoO}_2(\text{C}_2\text{O}_4), \text{H}_2\text{O}]$: Mo, 26.4; C_2O_4 , 24.2; N, 3.85; C, 36.3; H, 2.8%}.

Complex Pyridinium Molybdenum Oxyoxalates.—By analogy with the potassium, ammonium, and quinolinium salts, a pyridinium salt of the type $(\text{C}_5\text{H}_6\text{N})[\text{MoO}_2(\text{C}_2\text{O}_4), x\text{H}_2\text{O}]$ should be formed by interaction of pyridinium sulphate with barium molybdenum dioxyoxalate. In the preparation of a pyridinium salt from the pyridinium complex chloride $(\text{C}_5\text{H}_6\text{N})_2[\text{MoOCl}_5]$, however, a normal salt was not obtained (p. 2744). The following method yields a normal salt provided that the details are carefully observed. To 15 c.c. of boiling water, pyridinium sulphate (1.2 g.) and then barium molybdenum dioxyoxalate (3.5 g.) were quickly added. After boiling for 1 minute, the liquid was immediately filtered hot. The deep chrome-yellow powder, which separated from the filtrate on rapid cooling, was dried in a vacuum over calcium chloride {Found: Mo, 30.6; C_2O_4 , 28.1; N, 4.4. $(\text{C}_5\text{H}_6\text{N})[\text{MoO}_2(\text{C}_2\text{O}_4), \text{H}_2\text{O}]$ requires Mo, 30.6; C_2O_4 , 28.0; N, 4.5%}.

This normal salt is rapidly decomposed on boiling with water, and a yellow solid of varying composition separates from the aqueous solution on cooling. If, however, the pyridine is removed from the reaction, the acid salt is formed in accordance with the equation



For the preparation of this acid salt, the same reaction mixture that was used for the preparation of the normal salt was subjected to steam distillation in an atmosphere of nitrogen for about an hour to remove any liberated pyridine. The residual solution was filtered hot after concentration to about 10 c.c., and the orange-yellow powder which separated on cooling was washed with cold

* Microanalysis.

water and dried in a vacuum over calcium chloride {Found : Mo, 31.6; C_2O_4 , 28.8; N, 3.5. Calc. for $(C_5H_6N)_3H[Mo_4O_8(C_2O_4)_4, 6H_2O]$: Mo, 31.6; C_2O_4 , 29.0; N, 3.5%}. It appears from the results of the above experiment that complex pyridinium salts with a ratio C_5H_5N : Mo of less than 3 : 4 do not exist.

In order to determine whether the molecule of water present in the normal salt could be replaced as in the case of the acid pyridinium salt, the normal salt was treated with pyridine as previously described. The product had the same empirical formula and properties as that obtained from the acid pyridinium salt {Found : Mo, 25.4; C_2O_4 , 23.5; N, 7.5. Calc. for $(C_5H_6N)[MoO_2(C_2O_4)(C_5H_5N)]$: Mo, 25.6; C_2O_4 , 23.5; N, 7.5%}.

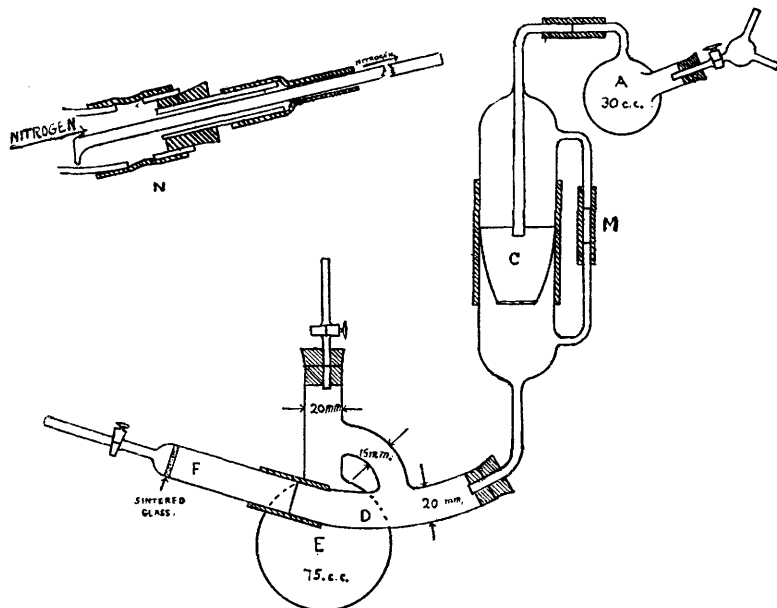
An Oxyoxalate of Quinquevalent Molybdenum.—The complex oxalates so far mentioned have been considered as derivatives of a hypothetical acid, $H[MoO_2(C_2O_4)_x, xH_2O]$. Such an acid should be formed initially when the insoluble barium salt $Ba[MoO_2(C_2O_4)]_2, 5H_2O$ is treated with dilute sulphuric acid. By warming this mixture a red supernatant liquid was obtained. Titrations with standard potassium permanganate, however, showed that in the solution the molybdenum was not quinquevalent, but had been partly oxidised. It was necessary, therefore, to conduct the whole preparation in an atmosphere from which air was rigidly excluded, and the following method proved satisfactory for the isolation of a substance with the empirical formula $Mo_2O_3(C_2O_4)_2, 4H_2O$.

Into *A* (Fig. 1), which consisted of a 30 c.c. flask fitted with a side tube, were introduced barium molybdenum dioxo-oxalate (4.0 g.) and water (7 c.c.). The whole apparatus was evacuated, tested to prove absence of air-leaks, and filled with nitrogen; 2 c.c. of sulphuric acid (5*N*) were then added to the liquid in *A*. With a slow stream of nitrogen passing through the apparatus from *F* to *A*, the reaction mixture was gradually raised to boiling point on a water-bath; this heating should occupy about an hour, for if the mixture is boiled quickly, hydrolysed products result. After gently boiling for 5 minutes, the red liquid formed was decanted into the filtering apparatus, *C*, by rotating the flask *A* : *C* consisted of a Gooch crucible, containing a perforated plate between two filter-papers, fitted into the modified adapter. By applying suction at *F*, the liquid was drawn into *C*, and by closing *M* it was filtered into *D*, which should hold about 12 c.c. of liquid. After this filtration, the apparatus was disconnected at *D*, the open end of *D* immediately closed with a solid rubber bung, and *DEF* evacuated. The liquid was concentrated at 30—35° to about 2 c.c. by means of the phosphoric oxide contained in the flask *E* of 75 c.c. capacity. Nitrogen was admitted into *DEF*, and from the liquid a bright

orange-yellow solid slowly separated. The mixture was then transferred to the filter *F*, by means of the device *N*, a rapid stream of nitrogen being passed through the apparatus to avoid oxidation. After the liquid had been filtered in nitrogen, the vessel *F* and its contents were rapidly transferred to a nitrogen-filled desiccator and dried over sulphuric acid in a vacuum.

The pale yellow substance thus obtained [Found: Mo, 39.4; C_2O_4 , 36.3. $Mo_2O_3(C_2O_4)_2 \cdot 4H_2O$ requires Mo, 39.4; C_2O_4 , 36.1%], which corresponds to the parent *acid*, was insoluble in cold water

FIG. 1.



or in cold concentrated hydrochloric or nitric acid, and was stable in air. In hot water it dissolved with oxidation, and in warm hydrochloric acid a green solution was produced. Red solutions resulted from treatment with dilute ammonia or alkalis. Cold water in which the solid was suspended reacted acid. Valency determinations proved that the molybdenum was quinquevalent.

Valency of the Molybdenum.—In the presence of the oxalic acid the ordinary method (J., 1923, **123**, 969) for the determination of valency was not available, and estimations were therefore carried out by the following method. A weighed quantity of the substance, dissolved in air-free sulphuric acid ($2N$), was titrated in the cold in a nitrogen atmosphere with standard potassium permanganate. When colourless, the solution was heated to 70° , and the titration

continued until a permanent pink colour was obtained. This reading gave the amount of permanganate necessary to oxidise the molybdenum to the sexavalent state and to decompose the oxalate radical. The permanganate required for the latter purpose was estimated independently by the method already described (p. 2743). By difference the amount of permanganate required to oxidise the molybdenum to the sexavalent condition was obtained, and since 1 c.c. of *N*-permanganate = 0.096 g. Mo^v, the percentage of molybdenum present in the salt can be deduced. When this agrees with the results obtained by gravimetric analysis, the molybdenum is quinquevalent.

Koppel and Goldmann (*Z. anorg. Chem.*, 1903, **36**, 281) have made an interesting observation with regard to the valency titrations for the quadrivalent vanadium oxyoxalates. They found that the amount of permanganate required was less than that demanded by theory, and observed that quadrivalent vanadium oxyoxalate could not be prepared; it therefore seems probable that this compound undergoes atmospheric oxidation in a similar manner to the analogous molybdenum oxyoxalate.

General Properties.—The complex oxalates in the dry condition are stable in air, but their aqueous solutions very slowly oxidise. Concentrated aqueous solutions are blood-red, but on dilution become brownish-yellow to yellow. The substances are insoluble in such organic solvents as alcohol, ether, and benzene. Concentrated hydrochloric acid decomposes the oxalates, yielding green solutions of the complex chlorides $R_2[MoOCl_5]$, and a green solution is also obtained by the action of concentrated sulphuric acid. A red solution results from the reaction between the complex oxalates and thiocyanic acid.

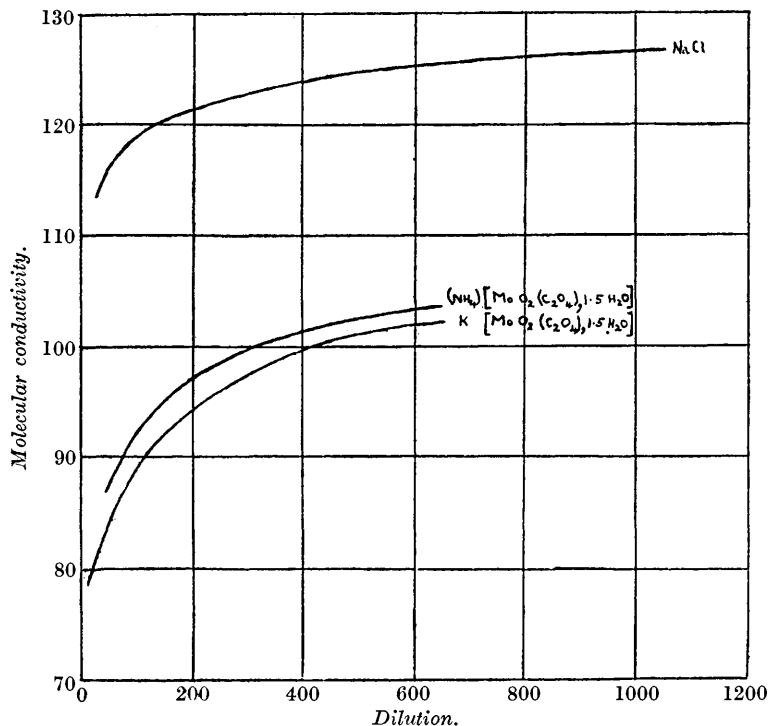
Physico-chemical Measurements.

To decide whether formulæ based on Werner's co-ordination theory are applicable to these complex oxalates, determinations of their molecular weights and molecular conductivities were carried out.

Molecular-weight Determinations.—The molecular weights, as determined by the depression of the freezing point of air-free water, are shown in Table I. If the formula $K[MoO_2(C_2O_4) \cdot 1.5H_2O]$ is assigned to the potassium salt, the apparent molecular weight when ionisation is complete should be 141. The results obtained in dilute solution are in accordance with this deduction, but the apparent molecular weights in concentrated solutions, which are even greater than that demanded by the un-ionised molecule, indicate that polymerisation is taking place with the formation of such molecules as $K_2[Mo_2O_4(C_2O_4)_2 \cdot 3H_2O]$. The fact that the

Chem., 1902, **31**, 42) on the catalytic oxidation of the complex niobium oxalates by platinised platinum electrodes. On treating an aqueous solution of potassium molybdenum dioxyoxalate with platinum-black, and estimating both valency and oxalate by means of standard potassium permanganate at intervals of several days, it was found that oxidation of the molybdenum to the hexavalent state took place and was accompanied by decolorisation of the solution.

FIG. 3.



It was therefore necessary to determine the conductivity by taking time curves for the conductivity at each dilution (see *J.*, 1927, 515), and deducing the initial conductivities from these. Table II gives the values of μ for various dilutions (v litres per mol.) at 25° at zero time, and for comparison the values of molecular conductivities at 25° of typical salts (Noyes and Falk, *J. Amer. Chem. Soc.*, 1912, **34**, 454) are given in Table III.

In dilute solutions the molecular conductivities are similar to those of a typical binary electrolyte (Fig. 3) and support the formulation $\text{R}[\text{MoO}_2(\text{C}_2\text{O}_4)_x\text{H}_2\text{O}]$ for the molybdenum dioxyoxalates

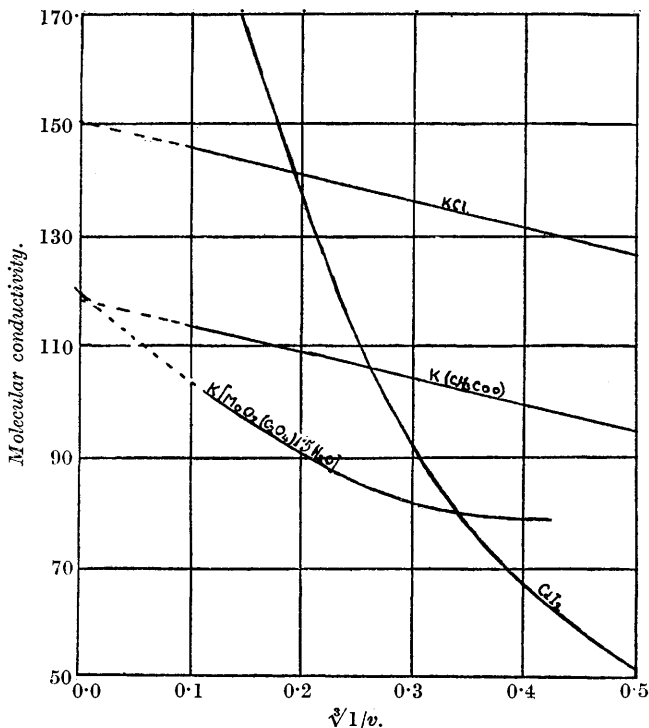
TABLE II.

K[MoO ₂ (C ₂ O ₄),1.5H ₂ O].						
v	15.3	34.7	103.7	175.8	391.8	613.2
μ	79.3	81.6	89.4	92.4	99.4	101.6
(NH ₄)[MoO ₂ (C ₂ O ₄),1.5H ₂ O].						
v	54.4	77.8	178.2	271.3	618.0	
μ	88.0	90.2	96.3	98.9	103.2	

TABLE III.

v	20	50	100	200	500	1000	∞
NaCl	111.8	116.1	118.8	121.0	123.05	124.1	127
KCl	133.3	138.5	141.4	143.95	146.55	—	150.6

FIG. 4.



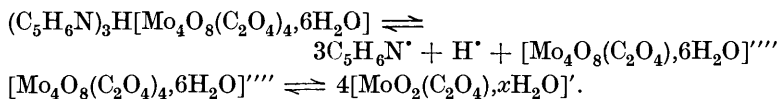
investigated above. The Ostwald-Walden rule does not apply in the case of these complex oxalates, for $\frac{1}{\sqrt{v}}(\lambda_{1024} - \lambda_{32})$ has a value of approximately 2 for both salts. This may be due to the polymerisation that takes place in their concentrated solutions. Russ (*loc. cit.*) obtained similar results with the complex niobium oxalates. A further indication that these molybdenum dioxyoxalates behave abnormally is afforded by the graphs obtained by plotting $\sqrt[3]{1/v}$

against μ . Binary electrolytes in dilute solutions, unlike ternary electrolytes, give straight lines, but the complex oxalates give a curve (Fig. 4) agreeing with the idea that polymerisation to a more complex electrolyte takes place in solutions of higher concentration. Cadmium iodide, which is known to undergo extensive polymerisation in solution, is included for comparison.

Complex Pyridinium Molybdenum Oxyoxalate.—From the analytical data an empirical formula $(C_5H_6N)_3H[Mo_4O_8(C_2O_4)_4,6H_2O]$ or $(C_5H_6N)_3[Mo_4O_7(OH)(C_2O_4)_4,6H_2O]$ was assigned to this orange-yellow compound. It was impossible, however, without further data finally to decide as to the constitution of this salt, although the fact that in aqueous solution it reacts acid to litmus and bromophenol-blue favours the first formula. Determinations of molecular weight by the depression of the freezing point of water indicated that in dilute solutions considerable ionisation occurred—owing to the comparative insolubility of the compound it was possible to determine molecular weights and conductivities only over a limited range of concentrations :

G. of substance per 100 g. water.	Conc. (mols. per 1000 g. water).	Apparent mol. wt.	Osmotic factor.
0.506	0.00417	184	6.59
1.049	0.00864	195	6.22
1.684	0.01388	198	6.12

It is obvious from the results that, although primary ionisation may take place in accordance with the first formula, further decomposition of the complex anion must occur, for with such a formulation, the complex salt even at infinite dilution should yield a maximum of five ions by primary ionisation, and give an apparent molecular weight of 243, whereas the osmotic factor suggests that at least seven ions are present at the concentrations used. It may be inferred, therefore, that in all probability the complex anion undergoes decomposition, possibly in accordance with the following scheme :



Taylor (*Z. physikal. Chem.*, 1898, **27**, 361) obtained an osmotic factor of 5.92 for sodium mellitate, $Na_6C_{12}O_{12}$, in 0.00181*M* concentration.

If such a scheme operates, it should be possible to deduce the value of μ_∞ for this complex salt. Since μ_∞ for both $K[MoO_2(C_2O_4),1.5H_2O]$ and $(NH_4)[MoO_2(C_2O_4),1.5H_2O]$ is approximately 120, it follows that the ionic mobility of the complex ion

$[\text{MoO}_2(\text{C}_2\text{O}_4)_x\text{H}_2\text{O}]'$ is approximately 46, the values of the ionic mobilities of the potassium and ammonium ions being 74.4 and 74.0 respectively at 25°. The possibility that there might be an error in the value of this ionic mobility due to the hydrolysis

$\text{R}[\text{MoO}_2(\text{C}_2\text{O}_4)_x\text{H}_2\text{O}] + \text{H}_2\text{O} \rightleftharpoons \text{ROH} + \text{H}[\text{MoO}_2(\text{C}_2\text{O}_4)_x\text{H}_2\text{O}]$ analogous to that of potassium cyanide, was disproved by the fact that the solutions of the complex oxalates, unlike those of potassium cyanide, do not give an alkaline reaction.

The above scheme indicates that μ_∞ for the complex pyridinium molybdenum oxyoxalate should be given by the sum of the ionic mobilities of $3\text{C}_5\text{H}_6\text{N}^+ + \text{H}^+ + 4[\text{MoO}_2(\text{C}_2\text{O}_4)_x\text{H}_2\text{O}]'$, which is 660, whereas the following experimental data lead to a value of 570 :

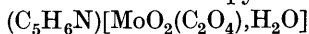
v	65.13	151.6	196.9	719.9	2043.0
μ	419.7	452.8	464.5	503.1	521.0

Although no satisfactory explanation of the discrepancy between the two values for μ_∞ is apparent, it seems that an experimental value of this magnitude can only be explained by the supposition that a hydrogen ion is formed by this salt on solution, and that the constitution of this salt can be adequately expressed by the co-ordination formula $(\text{C}_5\text{H}_6\text{N})_3\text{H}[\text{Mo}_4\text{O}_8(\text{C}_2\text{O}_4)_4, 6\text{H}_2\text{O}]$. The graph (Fig. 5) obtained with the acid pyridinium salt when $\sqrt[3]{I/v}$ is plotted against μ is a straight line, but this may be accounted for by the very small range of concentrations over which the conductivities could be determined.

Discussion of Results.

Molybdenum oxyoxalate, $\text{Mo}_2\text{O}_3(\text{C}_2\text{O}_4)_2, 4\text{H}_2\text{O}$, is an interesting example of a compound which is unstable and very reactive in solution, but far less reactive in the solid state, thus typifying the properties of polymerisable substances. Although from analytical data the above formula was assigned to this substance, yet a consideration of its markedly acidic properties and its method of preparation makes it clear that it is more adequately represented by the co-ordination formula $\text{H}[\text{MoO}_2(\text{C}_2\text{O}_4)_x, 1.5\text{H}_2\text{O}]$. It thus becomes the parent acid of this series of complex oxalates.

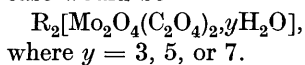
With the exception of the acid pyridinium salt, the compounds of this series dealt with in this communication can be represented by the general formula $\text{R}[\text{MoO}_2(\text{C}_2\text{O}_4)_x\text{H}_2\text{O}]$, where $x = 1, 1.5, 2.5,$ or 3.5 . Of these four groups of hydrates, the first appears to be the most general, and the suggestion that this is the normal one is strengthened by the fact that when the pyridinium salt



is boiled with pyridine, a salt $(\text{C}_5\text{H}_6\text{N})[\text{MoO}_2(\text{C}_2\text{O}_4)_x, \text{C}_5\text{H}_5\text{N}]$, con-

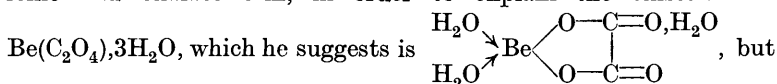
taining only one co-ordinated pyridine molecule, is produced. On Werner's theory these compounds apparently possess a co-ordination number of five, instead of the usual six for molybdenum compounds. This anomaly affords additional evidence for the theory of polymerisation put forward in the physicochemical section, for by considering two of the co-ordinating groups as bridge groups, the polymerised salts can be represented as six-point systems.

This theory of polymerisation is also needed to explain the existence of the acid pyridinium salt; moreover, it is necessary in the case of the higher hydrates, all of which can only be represented rationally by a formula which in the simplest case would be



The large number of water molecules (5 or 7) in the higher hydrates of such a series is very difficult to explain, since the normal co-ordination number of six is exceeded. Such hydrated forms are only obtained in the crystalline state, and the extra molecules of water are only loosely held. Sidgwick (J., 1926, 1301) put forward

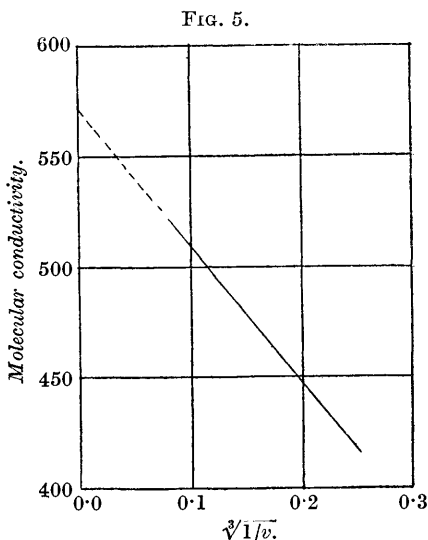
a theory of the monohydration of the oxalate group both in the ionic and oxalato-form, in order to explain the existence of



this theory does not fully explain the hydrates of these complex oxalates.

Barbieri (*Rend. Atti Accad. Lincei*, 1916, 775) has described the preparation of another series of oxalates of quinquevalent molybdenum of the general formula $R_4[Mo_2O_4(C_2O_4)_3 \cdot 2H_2O]$, where $R = K$ or NH_4 . These have not been investigated in the present research, but it may be noted that they contain two molybdenum atoms and have a co-ordination number of six.

In his papers on the series of complex oxalates, Bailhache (*loc. cit.*) suggests for the potassium, ammonium, and barium salts the



name "oxalomolybdites," but it is felt that the use of the name "dioxyoxalates" would be more in accordance with modern nomenclature.

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.), and to the Chemical Society and Messrs. Brunner Mond and Co., Ltd., for grants in aid of this investigation.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

[Received, August 2nd, 1928.]
