

CCLXXXV. — *Co-ordination Compounds of Quinquevalent Molybdenum.*

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ONE important result of the application of electronic theories of valency to co-ordination compounds has been to indicate the relative stabilities of the systems within the co-ordination sphere. The marked stability of the ion $\text{Mo}(\text{CN})_8^{4-}$, present in an aqueous solution of the complex salt $\text{K}_4\text{Mo}(\text{CN})_8$, can be readily appreciated when it is seen that the effective atomic number of the molybdenum is 54—that of the next inert gas—and that the associating units are regularly distributed. The stability of complex salts is not, however, the same for all associated units, the order of decreasing stability being cyanides, fluorides, thiocyanates, chlorides, bromides, and iodides, and this third factor must always have consideration. In a recent investigation (this vol., p. 512) on the complex chlorides of trivalent molybdenum, such as K_3MoCl_6 and $\text{K}_2\text{MoCl}_5 \cdot \text{H}_2\text{O}$, it was shown that ionisation in dilute aqueous solution produced initially four and three ions, respectively, but that the complex ions were gradually decomposed. Here, the effective atomic number of the metallic atom is 51 and the decreased stability of the complex ion MoCl_6^{3-} , compared with that of the ion $\text{Mo}(\text{CN})_8^{4-}$, is due primarily to the smaller number of electrons associated with the molybdenum atom, but also to the replacement of the cyanide by the chloride radical. With the chlorides of quinquevalent molybdenum of the general formula $\text{R}_2[\text{MoOCl}_5]$, the effective atomic number of the central atom has fallen to 49, and this is reflected in the marked changes which occur when these green, crystalline substances are dissolved in water. They give, immediately, brown solutions with acid reactions, from which it is impossible to obtain the original salt satisfactorily by crystallisation. Although these facts are well known, no systematic examination of this decomposition has hitherto been attempted. In the present research,

this has been done, and not only has it yielded information as to the course of the reaction in aqueous solution, but it has resulted in the evolution of improved methods of preparation for the complex salts themselves, and in the isolation of new series of co-ordination compounds characteristic of the intermediate stages of the hydrolytic decomposition.

EXPERIMENTAL.

Chilesotti (*Z. Elektrochem.*, 1906, 12, 173) first showed that by electrolytic reduction of molybdenum trioxide, dissolved in hydrochloric acid of appropriate concentration, a solution containing quinquivalent molybdenum could be obtained if a platinised platinum cathode was used, whereas with a cathode of polished platinum, reduction to the trivalent state resulted. This observation has been utilised in the following preparations.

Molybdenum trioxide solution. Molybdenum trioxide (100 g.) was heated with 500 c.c. of hydrochloric acid (*d* 1.16) till dissolved; the solution was evaporated to 250 c.c., filtered, and made up to 500 c.c. with hydrochloric acid, and thus contained molybdenum trioxide (20%) in 9*N*-hydrochloric acid.

Salts of the Type $R_2[MoOCl_5]$.

Diammonium Molybdenyl Pentachloride.—Klason (*Ber.*, 1901, 34, 148) and Nordenskjold (*ibid.*, p. 1572) obtained this salt by reducing ammonium molybdate in concentrated hydrochloric acid with hydrogen iodide, whilst Foerster and Fricke (*Z. angew. Chem.*, 1923, 36, 458), using Chilesotti's results (*loc. cit.*), prepared it by the electrolytic reduction method, of which the following is a variation: 75 C.c. of the molybdenum trioxide solution, diluted with an equal volume of water, were placed in the cathode chamber of a diaphragm cell, of which the anode chamber contained hydrochloric acid (5*N*). A polished platinum electrode served as the anode, whilst the cathode was of platinised platinum, 5 cm. square. A current of 2.5 amp. was employed, and on electrolytic reduction to the quinquivalent stage, a reddish-brown cathode solution was obtained. This was concentrated to 50 c.c. under diminished pressure, 30 c.c. of ammonium chloride solution (containing 9 g.) were admitted, and the mixture was heated for about a minute. On saturating with hydrogen chloride and cooling, emerald-green crystals separated. These were recrystallised by dissolving in the minimum volume of water at *ca.* 80°, and saturating with hydrogen chloride until cold. The crystals were washed with concentrated hydrochloric acid and dried in a vacuum over solid potassium hydroxide.

Analysis. The molybdenum was precipitated as sulphide (*J.*, 1924, 125, 1911), ignited, and weighed as the trioxide, the chloride

in the filtrate and washings being estimated as silver chloride. The ammonia was determined by the distillation method, the ammoniacal distillate being titrated continuously against standard acid with bromophenol-blue as indicator [Found: Mo, 29.5; Cl, 54.4; NH_4 , 11.1. Calc. for $(\text{NH}_4)_2\text{MoOCl}_5$: Mo, 29.5; Cl, 54.5; NH_4 , 11.1%].

A New Electrolytic Method.—150 C.c. of the prepared molybdenum trioxide solution were placed in the cathode chamber of the diaphragm cell, the anode chamber containing ammonia (10*N*) and a small quantity of ammonium chloride. On electrolysis with a current density of 0.1 amp. per sq. cm. and continuous saturation of the cathode liquid with hydrogen chloride, the diammonium molybdenyl pentachloride separated in good yield. After being washed and dried, the crystals gave Mo, 29.3; Cl, 54.6; NH_4 , 11.1%.

Dirubidium Molybdenyl Pentachloride.—This salt was first prepared by Nordenskjold (*loc. cit.*) and later by Foerster and Fricke (*loc. cit.*). By the use of the first of the methods here described for the preparation of the ammonium salt, but adding 30 c.c. of a rubidium chloride solution (containing 14 g.), yellowish-green crystals were obtained, which were washed, dried, and recrystallised (Found: Mo, 20.9; Cl, 38.6; Rb, 36.9. Calc. for $\text{Rb}_2\text{MoOCl}_5$: Mo, 20.9; Cl, 38.5; Rb, 37.1%).

Dipotassium Molybdenyl Pentachloride.—The methods described by Nordenskjold and by Foerster and Fricke for the preparation of this salt were found always to give a product contaminated with potassium chloride. The following method gave an excellent yield of pure salt, which, being crystallised at a high temperature, was obtained free from the more soluble alkali chloride: 75 C.c. of molybdenum trioxide solution, diluted with 75 c.c. of water, were electrolytically reduced to the quinquevalent condition. The resulting solution was concentrated under diminished pressure to 50 c.c., 30 c.c. of potassium chloride solution (containing 6.5 g.) were added, and the solution was further concentrated to 70 c.c. The flask was now placed in a thermostat at 90°, and the solution saturated with hydrogen chloride. With the hydrogen chloride still passing through the solution, the temperature was lowered to 70°, whereupon the required green salt began to separate; the temperature of the thermostat was then altered to and maintained at 60° and a high yield of the complex salt was thus obtained. The dark green crystals were filtered through a hot filter, drained in a current of dry hydrogen chloride, and dried in a vacuum over solid potassium hydroxide and phosphoric oxide [Found: Mo, 25.8; Cl, 47.4; K, 20.9. Calc. for K_2MoOCl_5 : Mo, 26.1; Cl, 48.2;

K, 21.3%; the presence of a small amount of water of crystallisation ($0.25\text{H}_2\text{O}$) accounts for the slight difference].

Dipyridinium Molybdenyl Pentachloride.—The only method previously described for the preparation of this salt is that of Rosenheim and Koss (*Z. anorg. Chem.*, 1906, **49**, 148) and of Sand and Burger (*Ber.*, 1906, **39**, 1761), who obtained it by the action of hydrochloric acid on the complex compound $\text{Mo}(\text{OH})_2(\text{CNS})_3(\text{C}_5\text{H}_5\text{N})_2$. The following method gave an almost theoretical yield of pure salt: 150 c.c. of the molybdenum trioxide solution, reduced electrolytically to the quinquevalent stage, were evaporated on a water-bath under diminished pressure almost to dryness; alcohol, saturated with hydrogen chloride, was now admitted, and after warming and agitation, the reddish-brown mass dissolved producing an emerald-green solution (100 c.c.). This was cooled to room temperature, saturated with hydrogen chloride, and filtered if necessary; one half of the filtrate was utilised for the preparation of the pyridinium salt, and the other half for the quinolinium derivative. By the addition of alcohol saturated with hydrogen chloride, the 50 c.c. of solution were made up to 100 c.c., and to this water-cooled solution pyridine was added, drop by drop, with constant stirring till no more green precipitate separated (excess of pyridine gives a red solution). This was filtered and dissolved in alcoholic hydrogen chloride (2 vols. of alcohol, saturated with hydrogen chloride at room temperature, and 1 vol. of absolute alcohol). On concentrating this solution, yellowish-green crystals separated; these were filtered, washed with alcohol saturated with hydrogen chloride, and dried over potassium hydroxide and phosphoric oxide in a vacuum [Found: Mo, 21.4; Cl, 39.6; N, 6.2; C, 26.8; H, 2.7. Calc. for $(\text{C}_5\text{H}_5\text{N})_2\text{MoOCl}_5$: Mo, 21.4; Cl, 39.5; N, 6.2; C, 26.7; H, 2.7%].

Diquinolinium molybdenyl pentachloride was prepared by adding pure quinoline (18 g.) with constant stirring to the boiling molybdenum solution previously mentioned. On evaporation and crystallisation, a large amount of the required substance was obtained, which was recrystallised and dried as in the case of the pyridinium compound [Found: Mo, 16.9; Cl, 31.2; N, 5.0; C, 37.8; H, 3.3. $(\text{C}_9\text{H}_8\text{N})_2\text{MoOCl}_5 \cdot \text{H}_2\text{O}$ requires Mo, 16.9; Cl, 31.3; N, 4.9; C, 38.1; H, 3.2%].

Ditrimethylammonium Molybdenyl Pentachloride.—Nordenskjöld (*loc. cit.*) prepared this salt by employing hydrogen iodide as a reducing agent. Using the electrolytic reduction method under conditions to be described later, the present authors isolated the first chloride of the type $\text{R}[\text{MoOCl}_4 \cdot \text{H}_2\text{O}]$ as *monotrimethylammonium molybdenyl tetrachloride*, $\text{NMe}_3\text{H}[\text{MoOCl}_4 \cdot \text{H}_2\text{O}]$ (see below), and converted it into the ditrimethylammonium pentachloride by

dissolving it in alcoholic hydrogen chloride, evaporating to small bulk, saturating with hydrogen chloride, and allowing to crystallise. After recrystallisation, the light emerald-green crystals were washed with alcoholic hydrogen chloride and dried in a vacuum over solid potassium hydroxide and phosphoric oxide {Found: Mo, 23.5; Cl, 43.2; N, 6.9; C, 17.6; H, 5.1. Calc. for $[(\text{CH}_3)_3\text{NH}]_2\text{MoOCl}_5$: Mo, 23.5; Cl, 43.3; N, 6.8; C, 17.6; H, 4.9%}.

General Properties of the Complex Salts.—The salts described in this paper generally crystallise in the rhombic form and range in colour from dark green through shades of emerald-green to yellowish-green. The pyridinium salt exhibits a strong pleochroism and has a very high double refraction. When exposed to a moist atmosphere, these salts more or less rapidly turn reddish-brown, in which condition they are very susceptible to aerial oxidation, molybdenum blue being formed. The pyridinium and the ditrimethylammonium salts give a bright copper-red substance at one stage of these changes. The potassium and the substituted-ammonium salts are the most sensitive, and the quinolinium the least sensitive, to the action of moist air. All the complex salts are soluble in water, the concentrated solutions being reddish-brown, passing through orange to bright yellow on dilution. On saturation with hydrogen chloride, these aqueous solutions finally turn emerald-green and from sufficiently concentrated solutions the complex salts separate. Alcohol dissolves all these green salts, and from the solution of the alkali complex salts, alkali chlorides separate on heating. The pyridinium salt under these conditions yields a red precipitate which will be referred to in detail later. The addition of pyridine or quinoline to aqueous solutions of any of the complex salts gives a brown, insoluble precipitate.

Physico-chemical Measurements.

Molecular-weight Determinations.—The molecular weight was determined by the depression of the freezing point of air-free water.

The figures given on p. 2150 indicate that the complex salts $\text{R}_2[\text{MoOCl}_5]$ undergo extensive ionisation in aqueous solution, and instead of yielding the (theoretical) 3 ions, furnish 9 ions in the reddish-brown solutions of concentrations *ca.* 0.02—0.05 g.-mol. per litre, and 10—11 ions in the bright yellow solutions obtained by further dilution. Additional evidence for this ionisation in aqueous solution is afforded by determinations of molecular conductivity. Table II gives the value of μ at 0° for various dilutions v (as litres per mol.).

A satisfactory explanation of the high molecular conductivity and the exceptional osmotic factor is forthcoming if it be assumed

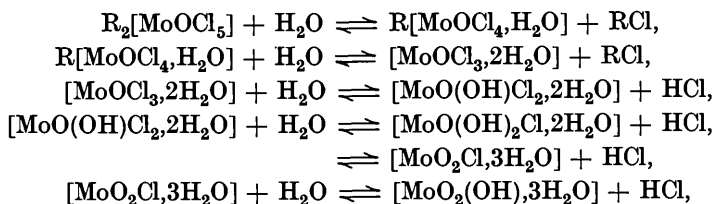
TABLE I.

G. of substance per 100 g. of water.	Conc. (mol. per 1000 g. water).	Osmotic factor.	Apparent mol. wt.
Diammonium molybdenyl pentachloride.			
1.675	0.0515	9.00	36.15
0.725	0.0223	9.03	36.02
0.278	0.0085	10.1	32.21
M for $(\text{NH}_4)_2\text{MoOCl}_5 = 325.3$.			
Dipotassium molybdenyl pentachloride.			
2.308	0.0628	8.89	41.34
0.765	0.0208	9.12	40.30
0.285	0.0077	10.1	36.39
M for $\text{K}_2\text{MoOCl}_5 = 367.5$.			
Dirubidium molybdenyl pentachloride.			
1.567	0.0340	8.88	51.82
0.853	0.0185	9.11	50.52
0.457	0.0099	9.42	48.85
M for $\text{Rb}_2\text{MoOCl}_5 = 460.2$.			
Dipyridinium molybdenyl pentachloride.			
1.640	0.0365	8.77	51.23
0.765	0.0170	9.00	49.92
0.417	0.0093	9.84	45.66
M for $(\text{C}_5\text{H}_5\text{N})_2\text{MoOCl}_5 = 449.3$.			
Diquinolinium molybdenyl pentachloride.			
1.150	0.0203	9.01	62.96
0.558	0.0098	9.89	57.35
0.269	0.0047	10.45	54.30
M for $(\text{C}_9\text{H}_8\text{N})_2\text{MoOCl}_5 \cdot \text{H}_2\text{O} = 567.3$.			

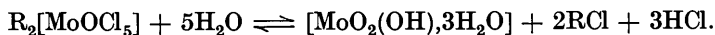
TABLE II.

	$(\text{NH}_4)_2\text{MoOCl}_5$.				$\text{Rb}_2\text{MoOCl}_5$.			
v	199.2	796.8	1593.6	3187.2	51.14	409.1	818.2	1636.4
μ	755.3	865.6	916.8	948	689	849	910	973
	K_2MoOCl_5 .				$[(\text{CH}_3)_2\text{NH}]_2\text{MoOCl}_5$.			
v	36.54	292.3	584.6	1169.3	59.76	239.0	478.1	1912.3
μ	676.6	834.3	897.3	954	644	757	836	935
	$(\text{C}_5\text{H}_5\text{N})_2\text{MoOCl}_5$.				$(\text{C}_9\text{H}_8\text{N})_2\text{MoOCl}_5$.			
v	54.7	437.5	875	1751	152	1216	2432	
μ	659.1	842.6	914.7	959	693	870	929	

that the complex ion MoOCl_5'' is unstable, and that ionisation and hydrolysis occur in accordance with the following scheme :



Whence, at infinite dilution :



In the first place, it is seen from such a scheme of ionisation that 10 ions should result at infinite dilution and that the osmotic factor should be 11. These theoretical deductions are in accordance with the experimental data. The ionic velocities at 0° deduced from the values at 18° (Landolt-Börnstein, "Tabellen," 1923, ii, 1104) are : H' = 227.6; Cl' = 40.0; Rb' = 41.5; NH₄' = 38.4. From the ammonium and rubidium salts, for example, which on the proposed scheme of ionisation should each yield at infinite dilution 2 metal (or ammonium), 3 hydrogen, and 5 chlorine ions, a molecular conductivity of 959.6 and 965.8, respectively, would be expected. Since, for the pyridinium ion an ionic velocity of 20 is obtained at 0° (Landin, *J. Chim. physique*, 1907, 5, 592), the value of μ_∞ for the pyridinium complex salt should be 923. Reference to the experimental values shows that they are in good agreement with these theoretical values. Additional confirmation of this scheme of ionisation for the complex salts is afforded by the isolation of the intermediate products R[MoOCl₄, H₂O], R[MoO₂Cl₂, 2H₂O], and an oxychloride, [Mo₂O₄(OH)Cl, 4H₂O], which may be considered as derived from the intermediate substances [MoO₂Cl, 3H₂O] and [MoO₂(OH), 3H₂O].

Salts of the Type R[MoOCl₄, H₂O].

Hitherto only bromides of this type of co-ordination compound have been isolated. The first chloride of this type, *monotrimethylammonium molybdenyl tetrachloride*, was obtained as follows :

75 C.c. of the molybdenum trioxide solution, electrolytically reduced to the quinquevalent stage, were concentrated on a water-bath under diminished pressure to 20—25 c.c. 30 C.c. of a solution of trimethylamine hydrochloride (11 g.) were now admitted by releasing the vacuum, and the mixture was heated to boiling under diminished pressure. The solution was then saturated with hydrogen chloride while it was being cooled, finally in a freezing-mixture, and the emerald-green crystals thus obtained were filtered, washed with

concentrated hydrochloric acid, and dried in a vacuum over solid potassium hydroxide and phosphoric oxide {Found: Mo, 28.8; Cl, 42.6; N, 4.24; C, 10.8; H, 3.67. $(\text{CH}_3)_3\text{NH}[\text{MoOCl}_4, \text{H}_2\text{O}]$ requires Mo, 28.9; Cl, 42.7; N, 4.22; C, 10.9; H, 3.62%}.

Molecular-weight Determinations.—The molecular weight was determined by the depression of the freezing point of air-free water.

G. of substance per 100 g. of water.	Conc. (mol. per 1000 g. water).	Osmotic factor.	Apparent mol. wt.
1.940	0.0585	6.97	47.60
0.787	0.0237	7.05	47.07
0.199	0.0060	8.07	41.13

$$M \text{ of } (\text{CH}_3)_3\text{NH}[\text{MoOCl}_4, \text{H}_2\text{O}] = 331.8.$$

Molecular Conductivities.

v	35.6	71.2	142.4	284.8	569.6	1139.2	2278.4	4556.8
μ	580	614	657	706	773	832	849	874

The calculated value for μ_∞ at 0° is *ca.* 880 on the scheme of ionisation and hydrolysis previously outlined, for there are produced 1 trimethylammonium, 4 chlorine, and 3 hydrogen ions, whilst the osmotic factor should be 9. The experimental results are clearly in accordance with the theoretical predictions.

Salts of the Type $[\text{MoO}_2\text{X}_2, 2\text{H}_2\text{O}]\text{R}$.

In the scheme of ionisation proposed for the complex salts of quinquevalent molybdenum, the co-ordination compound $[\text{MoO}_2\text{Cl}_2, 2\text{H}_2\text{O}]\text{H}$ was postulated as an intermediate product. Although this acid has not been isolated, its derivatives have been obtained in reactions involving the green complex salts.

Barium Oxalomolybdite.—Bailhache (*Bull. Soc. chim.*, 1903, 68, 161) prepared this compound by reducing ammonium molybdate in hydrochloric acid with red phosphorus, and formulated it as $\text{BaH}_2(\text{MoO})_2(\text{OH})_6(\text{C}_2\text{O}_4)_2, \text{H}_2\text{O}$. Viewed in the light of Werner's co-ordination theory, however, a more rational formulation and name for the substance are obtained if the molybdenum is assigned a co-ordination number of six. The new formula $\text{Ba}[\text{MoO}_2(\text{C}_2\text{O}_4), 2\text{H}_2\text{O}]_2, \text{H}_2\text{O}$ clearly shows the relationship to the co-ordination compound $\text{H}[\text{MoO}_2\text{Cl}_2, 2\text{H}_2\text{O}]$, and requires the name barium molybdenum dioxyoxalate. The probable correctness of this formulation and the importance of this salt can be appreciated from Bailhache's statement (*loc. cit.*) that it is produced when diammonium molybdenyl pentachloride is treated with oxalic acid and barium chloride. No details of the method were given, but experiments showed that the salt could be satisfactorily isolated by the following method:

30 C.c. of an aqueous solution of oxalic acid (1.2 g.) were added to 30 c.c. of a solution of diammonium molybdenyl pentachloride (3.5 g.), and the mixture was warmed. To the dark red solution produced, barium chloride (1.1 g.) in 60 c.c. of water was added, and on boiling, with constant stirring, a red, crystalline solid separated in good yield, which was washed with warm water and dried; it proved to be the required compound {Found: Ba, 20.8; Mo, 29.0; C, 7.28; H, 1.50. Calc. for $\text{Ba}[\text{MoO}_2(\text{C}_2\text{O}_4)_2, 2\text{H}_2\text{O}]_2, \text{H}_2\text{O}$: Ba, 20.8; Mo, 29.1; C, 7.25; H, 1.52%}.

Pyridinium Molybdenum Dioxychloride.—Sand and Burger (*loc. cit.*) noticed that when their green pyridinium molybdenyl pentachloride was boiled with alcohol, copper-red crystals separated on cooling. This compound contained Mo, 31.7; Cl, 23.68; N, 4.75; C, 22.05; H, 2.90%, and it was assigned the formula $\text{Mo}(\text{OH})_3\text{Cl}_2, \text{C}_5\text{H}_5\text{N}$, which requires Mo, 32.32; Cl, 23.09; N, 4.71; C, 20.20; H, 2.69%. Although the analytical figures do not show very close agreement with those demanded by theory, yet the empirical formula assigned to the substance by Sand and Burger has now been shown to be correct. It should be written, however, as $\text{C}_5\text{H}_5\text{N}[\text{MoO}_2\text{Cl}_2, \text{H}_2\text{O}]$, whereby it is characterised as the pyridinium salt of the acid $\text{H}[\text{MoO}_2\text{Cl}_2, 2\text{H}_2\text{O}]$. A pure product was obtained by the following method: Freshly prepared dipyridinium molybdenyl pentachloride was added to boiling alcohol (95%) until the solution turned dark red and further solid dissolved with difficulty. On filtering and allowing the clear liquid to cool, a light red substance separated which gave Mo:Cl = 1:2.1 and proved to be an impure product. This was removed, and the mother-liquor, on concentration to small bulk and cooling, gave copper-red needles, which were washed with alcohol (95%) and dried in a vacuum over phosphoric oxide. The water content of the crystals varied with different samples, whilst the colour deepened with increasing water content (Found: Mo, 33.88; Cl, 24.97; N, 4.93; C, 21.5; H, 2.34. Calc. for $\text{C}_5\text{H}_5\text{N}[\text{MoO}_2\text{Cl}_2], 0.25\text{H}_2\text{O}$: Mo, 33.88; Cl, 25.02; N, 4.94; C, 21.2; H, 2.29%). That this pyridinium salt and barium molybdenum dioxoxalate are similarly constituted is readily demonstrated as follows: 3 G. of pyridinium molybdenum dioxychloride in 50 c.c. of water were warmed with an aqueous solution of oxalic acid (1.2 g. in 30 c.c.). 1.1 G. of barium chloride in 60 c.c. of water were now added and the mixture was heated to boiling. The corresponding barium compound separated in good yield (Found: Ba, 21.4; Mo, 29.7. Calc. for $\text{Ba}[\text{MoO}_2(\text{C}_2\text{O}_4)_2, 2\text{H}_2\text{O}]_2$: Ba, 21.4; Mo, 29.9%). It will be noticed that the water content is less than that in the sample prepared from the green complex salt.

Molecular-weight Determinations.

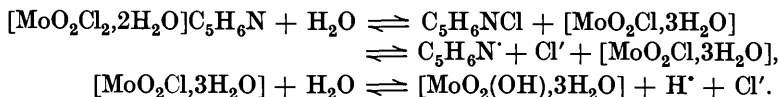
G. of substance per 100 g. of water.	Conc. (mol. per 1000 g. water).	Osmotic factor.	Apparent mol. wt.
2.489	0.0838	3.45	86.06
1.148	0.0387	3.73	79.60
0.692	0.0233	3.90	76.12
0.222	0.0075	4.82	61.60

$$M \text{ for } C_5H_6N[MoO_2Cl_2, H_2O] = 296.9.$$

Molecular Conductivity.—This was determined at 0° :

v	20.56	41.12	164.5	329	1316
μ	185	210.6	275.1	312.0	336.0

These two results find an adequate explanation on the assumption that in aqueous solution the pyridinium salt undergoes ionisation and hydrolysis in accordance with the scheme :



Hereby, in dilute solutions, an osmotic factor of 5 should be obtained, whilst conductivity measurements, due to a pyridinium ion, 2 chlorine ions, and 1 hydrogen ion, should give $\mu_\infty =$ approx. 327.6. The experimental results are in close agreement with the theoretical values and support the scheme of hydrolysis outlined above.

Dimolybdenum Tetraoxyhydroxychloride.—The isolation of this salt, $Mo_2O_4(OH)Cl$, formed an important link in the chain of evidence for the scheme of ionisation and hydrolysis proposed for the green complex salts.

Preparation. The reddish-brown solution of quinquevalent molybdenum, obtained by the electrolytic reduction of 150 c.c. of molybdic acid solution, was concentrated on a water-bath under diminished pressure until a dark, viscous mass was obtained. Pure, dry acetone was admitted in small portions with frequent shaking and warming, until the mass just dissolved, giving a deep brown solution. This was poured with constant stirring into a large volume of dry ether and a bulky reddish-brown precipitate separated, which was washed with dry ether and kept over solid potassium hydroxide in a vacuum [Found: Mo, 51.6; Cl, 9.54; Mo : Cl = 2 : 1. $Mo_2O_4(OH)Cl, 3.5H_2O$ requires Mo, 51.7; Cl, 9.55%].

Valency. A solution of the compound in dilute sulphuric acid was titrated with standard permanganate according to Reinhardt's method, and required t_1 c.c. A solution of the same concentration was passed through the reductor (J., 1923, 123, 969) and required

t_2 c.c. of permanganate. The valency is given by $(6 - 3t_1/t_2)$. Found: $t_1 = 7.58$ c.c.; $t_2 = 22.79$ c.c. Hence the molybdenum is quinquevalent.

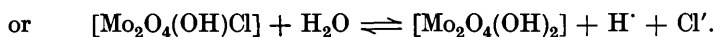
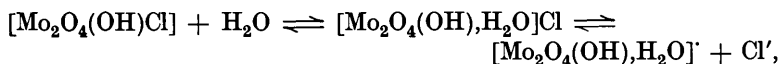
Properties. The new chloride is a reddish-brown powder, readily soluble in water and in alcohol, giving deep reddish-brown solutions which on dilution become bright yellow. The aqueous solution is acid to litmus and reduces solutions of silver salts. The brown aqueous or alcoholic solutions of the compound turn emerald-green on saturation with hydrogen chloride, and complex salts of the type R_2MoOCl_5 may be isolated from them. On heating, the chloride decomposes with evolution of hydrogen chloride.

Molecular-weight Determinations.—These were determined in air-free water.

G. of substance per 100 g. of water.	Conc. (mol. per 1000 g. water).	Osmotic factor.	Apparent mol. wt.
1.193	0.0314	1.85	205.7
0.656	0.0172	2.03	187.5
0.483	0.0127	2.41	157.9

$$M \text{ for } Mo_2O_4(OH)Cl, 4H_2O = 380.5.$$

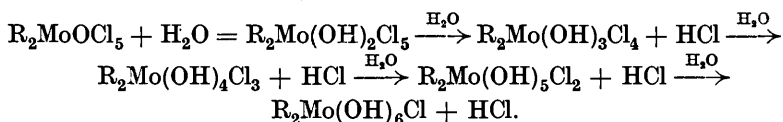
These results indicate that two ions are present in the more concentrated solutions and three individuals in the more dilute. This is satisfactorily explained by the progressive hydrolysis



Conclusions.

The results obtained from the determinations of molecular weights and molecular conductivities of a wide range of co-ordination compounds of the formula $R_2[MoOCl_5]$ leave little doubt that the scheme of hydrolysis and ionisation outlined in this paper substantially explains their behaviour in aqueous solution. It receives added support from the physico-chemical measurements made with compounds typical of the intermediate stages of the hydrolysis. Still more convincing proof of the correctness of the scheme is that it allows the formulation and characterisation of salts previously known, and derived from the green complex salts, but which had hitherto lacked systematisation. In a paper by Scagliarini (*Atti R. Accad. Lincei*, 1925, 1, 676), the isolation of two salts, formulated as $MoOCl_3, C_5H_5N$ and $2[(NH_4)_2\{Mo(\overset{OH}{\underset{Cl_3}{O}})_4\}] + C_6H_{12}N_4, HCl$, by

reactions involving the complex salt $(\text{NH}_4)_2[\text{MoOCl}_5]$ has been made the basis of the following scheme of hydrolytic decomposition :



Such a scheme does not adequately explain the physico-chemical results obtained in the present paper, nor does it elucidate the constitution of intermediate products, which are assigned co-ordination numbers of 7. The analyses quoted by Scagliarini (*loc. cit.*) for the compounds he isolated involve only determinations of molybdenum, chlorine, and nitrogen, and do not show very satisfactory agreement with the calculated values. Confirmation of the isolation of the salt $\text{MoOCl}_3 \cdot \text{C}_5\text{H}_5\text{N}$ would be of interest, for as yet MoOCl_3 has not been obtained.

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