

LXXVI.—*The Complex Chlorides of Tervalent Molybdenum.*

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By the addition of the appropriate alkali chloride to electrolytically reduced solutions of trivalent molybdenum, Chilesotti (*Atti R. Accad. Lincei*, 1903, [v], 12, ii, 67) isolated the salts K_3MoCl_6 and

$R_2MoCl_5 \cdot H_2O$, where $R = NH_4, Rb,$ and Cs . These represent two types of compounds common among trivalent elements. The conditions under which one or other type of salt could be obtained with certainty were not apparent to this investigator, but a recent research by Foerster and Fricke (*Z. angew. Chem.*, 1923, **36**, 458), in which they prepared R_3MoCl_6 and $R_2MoCl_5 \cdot H_2O$, where $R = NH_4, K, Rb,$ or Cs , indicates, as would be expected, that the principal factor is acid concentration. So far, only an examination of their general reactions has been attempted. In view of the fact that they can be considered as co-ordination compounds, $R_3[MoCl_6]$ and $R_2[MoCl_5 \cdot H_2O]$, in which molybdenum exhibits a co-ordination number of six, it seemed of interest to determine whether such a formulation was justified.

The results obtained from physico-chemical determinations confirmed the above formulations for the salts, and at the same time furnished information as to the stability of the complex anion and the varying changes which the compounds undergo in aqueous solution.

EXPERIMENTAL.

Tripotassium Molybdenum Hexachloride.—The method of preparation was that of Chilesotti (*loc. cit.*). 350 C.c. of a solution of molybdenum trioxide (35 g.) in 8*N*-hydrochloric acid were reduced to the trivalent condition, concentrated to 150 c.c. (33% $MoCl_3$) and saturated with hydrogen chloride. One-half to three-quarters of the theoretical amount of pure potassium chloride (30—40 g.) was added as a 10% solution in air-free water and the mixture concentrated at 70° under reduced pressure, until crystallisation commenced. The liquid was now filtered and the filtrate saturated with hydrogen chloride until cold, whereupon the double salt separated. The crystals were washed with concentrated hydrochloric acid, alcoholic hydrochloric acid, and finally with alcohol, and dried in a vacuum.

Analysis. The molybdenum was precipitated as sulphide (J., 1924, **125**, 1911), ignited, and weighed as the trioxide. The chloride in the filtrate and washings was estimated as silver chloride. The potassium was weighed as potassium sulphate (Found: Mo, 22.5; Cl, 50.2; K, 27.3. K_3MoCl_6 requires Mo, 22.5; Cl, 49.9; K, 27.5%).

Dipotassium Molybdenum Pentachloride.—This salt was isolated by Foerster and Fricke (*loc. cit.*) who, however, gave neither analyses nor details of preparation. The following method gave a satisfactory yield. 100 C.c. of the red solution containing trivalent molybdenum, prepared by the electrolysis of molybdenum trioxide (10 g. MoO_3) in 100 c.c. of 8*N*-hydrochloric acid, were added to

25 c.c. of a solution of potassium chloride (1 g.) and the mixture was concentrated in an air-free flask at 60—70° under reduced pressure to a volume of about 20 c.c. Air-free, absolute alcohol was now admitted and a bright brick-red crystalline precipitate separated, which, after filtration and washing with alcohol, was dried in a vacuum (Found: Mo, 26.0; Cl, 47.8. $K_2MoCl_5 \cdot H_2O$ requires Mo, 26.0; Cl, 48.0%). In attempting to isolate this compound from very dilute acid solutions, as suggested by Foerster and Fricke, an oxysalt was obtained (*q. v.*).

Triammonium Molybdenum Hexachloride.—Both Foerster and Fricke (*loc. cit.*) and Rosenheim and Li (*Ber.*, 1923, **56**, 2225) have prepared this salt, but in neither case were experimental details given. The formula assigned by Foerster and Fricke was $(NH_4)_3MoCl_6$, whilst the analyses of the other authors corresponded to $(NH_4)_3MoCl_6 \cdot 2.5H_2O$.

Preparation. 80 C.c. of the concentrated solution containing trivalent molybdenum (33% $MoCl_3$) were saturated with hydrogen chloride, added to a saturated aqueous solution of ammonium chloride (20 g.), and the mixture concentrated to the crystallising point. The diammonium molybdenum pentachloride thus formed was removed, and the filtrate again saturated with hydrogen chloride until cold. Small rose-coloured crystals separated which, after washing free from hydrochloric acid with aqueous alcohol, were dried in a vacuum.

Analysis. The molybdenum and chloride were estimated as above, and the ammonium by the distillation method. In this method, the ammoniacal distillate was titrated continuously against standard acid, using bromophenol-blue (0.04% solution) as indicator [Found: Mo, 25.2; Cl, 56.3; NH_4 , 14.1. $(NH_4)_3MoCl_6 \cdot H_2O$ requires Mo, 25.2; Cl, 55.9; NH_4 , 14.2%].

Diammonium Molybdenum Pentachloride.—This was prepared by the following method of Chilesotti: To 175 c.c. of the concentrated solution (33% $MoCl_3$) containing trivalent molybdenum, 25 g. of ammonium chloride as a 10% aqueous solution were added, and the mixture was concentrated at 70° under reduced pressure, until the salt crystallised as a bright brick-red compound [Found: Mo, 29.2; Cl, 54.4; NH_4 , 11.0. $(NH_4)_2MoCl_5 \cdot H_2O$ requires Mo, 29.3; Cl, 54.2; NH_4 , 11.0%].

Cæsium and Rubidium Salts.—These were prepared from solutions of the above salts by double decomposition with the alkali chlorides. They were also obtained by the addition of the corresponding alkali chlorides to the concentrated solution containing trivalent molybdenum and subsequent evaporation. Salts of the type R_3MoCl_6 were prepared in a similar manner from more concentrated

acid solutions (Found : Mo, 21.0; Cl, 38.6. $\text{Rb}_2\text{MoCl}_5 \cdot \text{H}_2\text{O}$ requires Mo, 20.8; Cl, 38.4%. For $\text{Cs}_2\text{MoCl}_5 \cdot \text{H}_2\text{O}$, found : Mo, 17.4; Cl, 32.1. Calc. : Mo, 17.2; Cl, 31.8%. For Rb_3MoCl_6 , found : Mo, 16.9; Cl, 37.4. Calc. : Mo, 17.0; Cl, 37.7%. For Cs_3MoCl_6 , found : Mo, 13.5; Cl, 29.9. Calc. : Mo, 13.6; Cl, 30.1%).

General Properties of the Complex Salts.—The salts of potassium and ammonium are extremely soluble even in cold water and give intensely red solutions. The salts of caesium are quite insoluble and those of rubidium nearly so. In alcohol and ether all are practically insoluble. The aqueous solutions have an acid reaction, due to hydrolysis, which is accelerated by warming and results ultimately in the precipitation of the hydroxide of molybdenum. All the salts have pronounced reducing properties.

Physico-chemical Measurements.

Molecular-weight Determinations.—The molecular weight was determined by the depression of the freezing point of air-free water. If $\text{K}_3[\text{MoCl}_6]$ represents the correct formulation for tripotassium molybdenum hexachloride, four ions should be present in solution, and the apparent molecular weight, when ionisation is complete, should be 106.6; whilst diammonium molybdenum pentachloride, represented by $(\text{NH}_4)_2[\text{MoCl}_5 \cdot \text{H}_2\text{O}]$, should yield three ions and give an apparent molecular weight of 109.2.

TABLE I.

G. of substance per 100 g. water.	Conc. in mols. per 1000 g. water.	Osmotic factor.	Apparent mol. wt.
Tripotassium molybdenum hexachloride.			
0.498	0.01170	3.86	110.3
0.829	0.01947	3.68	116.0
1.470	0.03453	3.54	120.5
3.045	0.07153	2.55	167.0
Diammonium molybdenum pentachloride.			
0.863	0.02635	3.10	105.6
1.484	0.04532	2.92	112.2
2.115	0.06460	2.81	116.8
5.391	0.1646	2.31	141.7

The results (Table I) furnish strong evidence in favour of the suggested formulations, although it was found that the substances underwent continuous hydrolysis in solution, as illustrated by the data (Table II) for a solution of tripotassium molybdenum hexachloride at a concentration of 0.07153 mol. per 1000 g. of water.

TABLE II.

Time after dissolving (mins.)	—	10	30	37	45	53	73	155
Apparent mol. wt. ...	167.0	158.2	146.8	146.0	142.7	139.8	135.5	117.3
Osmotic factor	2.55	2.70	2.91	2.92	2.99	3.05	3.18	3.64

After a considerable time, the hydroxide of molybdenum separated.

Molecular-conductivity Determinations.—Further evidence for the existence of these complex ions was obtained by determinations of the molecular conductivity. Whilst salts of the type R_3MoCl_6 gave results—immediately after dissolving—similar to those for a quaternary electrolyte, complexes of the type $R_2MoCl_5 \cdot H_2O$ were analogous to typical ternary electrolytes. Table III gives the values of μ for various dilutions at 1° when $t = 0$ min., and for comparison

TABLE III.

Dilution (litres per mol.)	K_3MoCl_6 .					$(NH_4)_3MoCl_6 \cdot H_2O$.		
	μ	15.67	58.97	95.84	153.3	222.0	48.11	66.44
	155	195	220	230	245	208	210	225
Dilution (litres per mol.)	$(NH_4)_2MoCl_5 \cdot H_2O$.					$K_2MoCl_5 \cdot H_2O$.		
	μ	16.37	33.76	54.96	101.4	251.3	21.19	58.31
	107	110	132	140	175	113	140	142

the values of the molecular conductivities at 1° of typical salts are given in Table IV.

TABLE IV.

Dilution (litres per mol.).	16.	32.	64.	128.	256.
KCl.	75.2	77.3	79.2	80.6	81.8
K_2SO_4 .				164	172
$K_3Fe(CN)_6$.	204.3	219.6	232.2	247.2	259.2
$K_3W(CN)_8$.	201.9	216.0	229.2	243.6	255.6
$K_4Fe(CN)_6$.				292	316

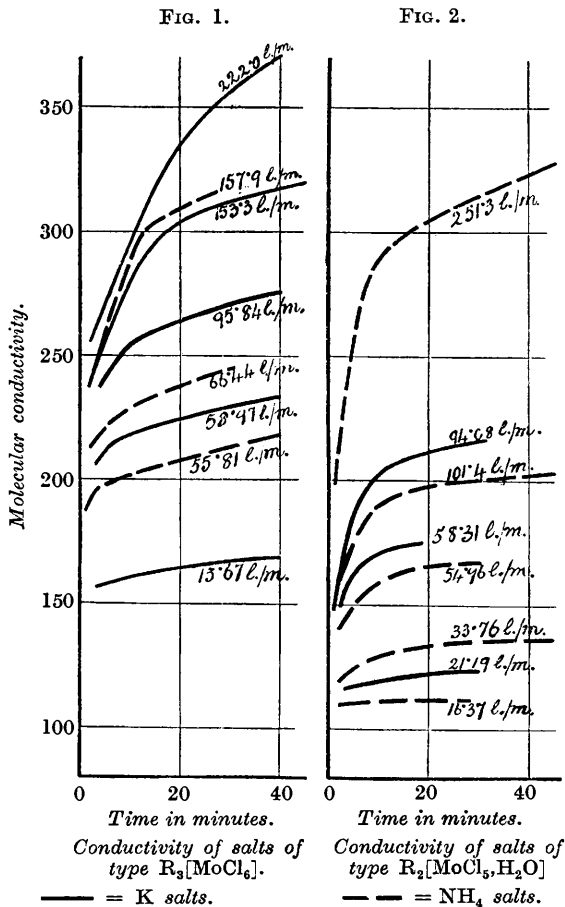
However, as was anticipated from the molecular-weight determinations, the conductivities increased with time, as is seen from Figs. 1 and 2, in which molecular conductivities are plotted against time for various dilutions (as litres per mol., indicated as l./m.) of the two types of salt.

Isolation of Double Salts of Molybdenyl Monochloride.

It was noticed, during the preparation of tripotassium molybdenum hexachloride and in attempts to prepare dipotassium molybdenum pentachloride, that solutions containing trivalent molybdenum of a low acid concentration, tended to give rise to molybdenyl monochloride, which had previously been isolated from solutions of high molybdenum content, by precipitation in acetone (J., 1924, **125**, 2372).

Preparation of Potassium Molybdenyl Dichloride.—350 C.c. of the green solution containing trivalent molybdenum (35 g. MoO_3) were concentrated to ca. 120 c.c. and re-electrolysed for an hour to ensure that all the molybdenum was trivalent. 250 C.c. of a 10% solution of potassium chloride were then added and the whole was

concentrated nearly to dryness under reduced pressure at 70°. The red salt formed was then removed and the filtrate treated with alcohol, whereby a bright yellow substance was precipitated. This was filtered, washed with alcohol, and dried in a vacuum. It was slowly soluble in water to a reddish-brown solution and after a time



the solid turned greenish-brown (Found: Mo, 36.0; Cl, 26.8; K, 14.3. $KMoOCl_2 \cdot 2.5H_2O$ requires Mo, 36.0; Cl, 26.6; K, 14.6%). The true hydrate is probably $KMoOCl_2 \cdot 3H_2O$.

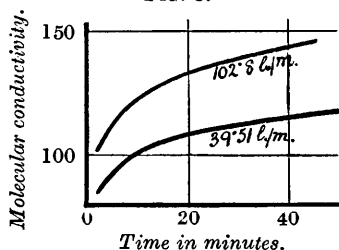
Valency. This was determined by titration with standard permanganate in the presence of manganous phosphate. The valency of the molybdenum is given by $(6 - 3w_1/w_2)$, where w_1 is the percentage of molybdenum calculated from the titration, assuming that

it is tervalent, and w_2 is the percentage of molybdenum found by gravimetric means. Here $w_1 = 35.56$ and $w_2 = 36.0$; hence the valency is 3.

Conductivity at 1°. The increase of molecular conductivity with time is illustrated in Fig. 3, with the same conventions as for Figs. 1 and 2. These results indicate, by analogy with potassium chloride (Table IV) that two ions are present in solution and that rapid hydrolysis occurs. Thus the new compound is shown to be $K[MoOCl_2, 3H_2O]$.

By similar treatment of the green solution with ammonium chloride, a slightly impure substance was obtained, which was probably $(NH_4)[Mo(OH)Cl_3, 2H_2O]$, and was shown to contain tervalent molybdenum.

FIG. 3.



Conductivity of $K[MoOCl_2, 3H_2O]$.

The Replacement of the Halogen Units in the Complex Salts.

Chilesotti (*Gazzetta*, 1905, **34**, ii, 493), by double decomposition of the tripotassium molybdenum hexachloride and potassium thiocyanate, has prepared the complex salt $K_3Mo(CNS)_6$, whilst, by the action

of hydrofluoric acid on the complex chlorides (Rosenheim and Li, *loc. cit.*), complex fluorides have been prepared. In view of the possibility of replacing the six chlorine atoms by three chelate groups such as the oxalato-, salicylato-, or phthalato-group the reactions between the complex chlorides and the alkali salts of oxalic, salicylic, and phthalic acids were investigated. In no case, however, was a complex salt obtained. Instead, the reactions yielded the co-ordination compounds $[Mo(OH)(OH \cdot C_6H_4 \cdot CO \cdot O)_2, H_2O]$ and $[Mo(OH)(O \cdot CO \cdot C_6H_4 \cdot CO \cdot O), 3H_2O]$ and an impure oxalate of the latter type.

Reaction with Sodium Salicylate.—A concentrated aqueous solution containing 2 g. (1 mol.) of diammonium molybdenum pentachloride and 1 g. (2 mols.) of sodium salicylate, was warmed to 70° in an atmosphere of nitrogen. The solution gradually darkened and finally became greenish-brown, a brown precipitate being formed. This was washed several times with air-free water in a nitrogen atmosphere and dried in a vacuum. The substance was dark-brown, insoluble in water, but soluble in alcohol giving a brown solution, and in alkaline hydroxides to a yellow solution.

The molybdenum was estimated by precipitation (as above) and also by direct ignition to the trioxide. The carbon and hydrogen

were estimated by combustion in oxygen [Found: Mo, 23.5; C, 41.5; H, 3.3. $\text{Mo}(\text{OH})(\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O})_2, \text{H}_2\text{O}$ requires Mo, 23.7; C, 41.5; H, 3.2%].

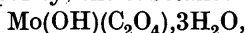
The same compound results from the reaction between sodium salicylate and the other complex chlorides.

The solubility of this substance in alkaline hydroxides indicates a probable acidic structure, which can be represented by the co-ordination formula $[\text{MoO}(\text{O}\cdot\text{OC}\cdot\text{C}_6\text{H}_4\cdot\text{OH})_2, \text{H}_2\text{O}]\text{H}$, in which the molybdenum has a co-ordination number of six.

Reaction with Disodium Phthalate.—By warming equimolecular proportions of the complex salt and disodium phthalate in concentrated solution, a brown phthalate was prepared of which the analysis indicates the constitution $\text{Mo}(\text{OH})[\text{C}_6\text{H}_4(\text{CO}\cdot\text{O})_2], 3\text{H}_2\text{O}$ (Found: Mo, 29.2; C, 29.1; H, 3.4. Calc.: Mo, 29.0; C, 29.0; H, 3.35%).

Like the salicylate, the new substance is insoluble in water and soluble in alkaline hydroxides, and probably has an acidic structure in accordance with the formulation $[\text{MoO}\cdot(\text{C}_6\text{H}_4(\text{CO}\cdot\text{O})_2), 3\text{H}_2\text{O}]\text{H}$.

Reaction with Ammonium Oxalate.—On warming a concentrated solution containing the complex salt and ammonium oxalate, the liquid turned brown and finally greenish-brown, but no insoluble compound was formed. The addition of the solution to alcohol resulted in the precipitation of a brown substance which, after freeing from ammonium chloride by washing with aqueous alcohol, gave analyses which showed that, although ammonium oxalate was still present as impurity, the substance was probably



identical with the oxyoxalate previously isolated (J., 1925, 127, 1311).

Reaction of the Complex Salts with Liquid Ammonia.

Attempts to replace the chlorine in the red salts by the NH_3 group proved unsuccessful, but it was shown that diammonium molybdenum pentachloride takes up ammonia to give an unstable monoammine, which may be written as $(\text{NH}_4)_2[\text{MoCl}_5, \text{NH}_3]\text{H}_2\text{O}$.

About 15 c.c. of liquid ammonia were added to 2–3 g. of the above complex chloride contained in a dry tube surrounded by ether and solid carbon dioxide. The reaction mixture was well stirred and the supernatant liquid then decanted off. The remaining solid was treated similarly with a further quantity of liquid ammonia to extract any ammonium chloride formed. After repeated washing with dry acetone to remove excess of ammonia, the solid mass was dried in an evacuated desiccator containing calcium chloride, and immediately analysed [Found: Mo, 26.7; Cl, 49.6; NH_4 , 15.1; Mo : NH_4 : Cl = 1 : 3.01 : 5.03. $(\text{NH}_4)_2\text{MoCl}_5, \text{NH}_3, \text{H}_2\text{O}$ requires

Mo, 27.9; Cl, 51.5; NH_4 , 15.7. $(\text{NH}_4)_2\text{MoCl}_5 \cdot \text{NH}_3 \cdot 2\text{H}_2\text{O}$ requires Mo, 26.5; Cl, 49.0; NH_4 , 14.9%. The true hydrate when freshly prepared is probably $(\text{NH}_4)_2[\text{MoCl}_5 \cdot \text{NH}_3] \cdot \text{H}_2\text{O}$.

This mauve-coloured ammine is extremely hygroscopic and undergoes rapid hydrolysis, ammonium chloride being liberated whilst the substance itself turns brown. It is readily soluble in water, producing a reddish-brown solution from which the hydroxide separates after a few minutes. It was therefore impossible to determine its molecular conductivity.

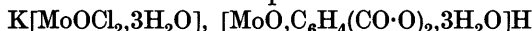
On treatment with concentrated hydrochloric acid, the ammine dissolved, producing a brilliant blue coloration. On dilution the solution turned green and finally pink, owing, in all probability, to the re-formation of the original red complex chloride, with liberation of ammonium chloride.

An attempt was made to isolate the blue substance by passing hydrogen chloride into the acid solution of the ammine, maintained at the low temperature of the mixture of solid carbon dioxide and ether. A greenish-blue substance was precipitated, which, after washing with alcohol to remove hydrochloric acid, turned greenish-grey. In water, it gave a greenish-blue solution, which rapidly turned pink. The analytical figures were not in agreement with any definite formula.

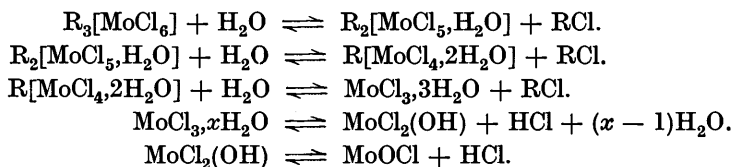
Liquid ammonia does not appear to react with the tripotassium molybdenum hexachloride, thus supporting the view that the ammonia replaces the molecule of water in diammonium molybdenum pentachloride.

Discussion.

The results of the physico-chemical measurements, together with the isolation of co-ordination compounds of the formulæ



and $[\text{MoO} \cdot (\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{O})_2 \cdot \text{H}_2\text{O}]\text{H}$, can be explained on the assumption that the complex salts undergo ionisation and hydrolysis in accordance with the following scheme :



The existence of the double salts R_3MoCl_6 and $\text{R}_2\text{MoCl}_5 \cdot \text{H}_2\text{O}$ is evidence of the presence of MoCl_3 ; the salicylato- and phthalato-compounds are derived from the intermediate $\text{MoCl}_2(\text{OH})$; whilst MoOCl and its complex salts have been isolated.

It is of interest to note, in the case of the complex chlorides R_3MoCl_6 , $R_2MoCl_5 \cdot H_2O$, and $KMoOCl_2 \cdot 3H_2O$, and also of the insoluble molybdenyl salicylate and phthalate, that the molybdenum atom is associated with 51 electrons, 3 less than the number required for an inert-gas structure. In this respect, molybdenum shows a close analogy to chromium in its complex salts.

Here is an excellent illustration of the fact that co-ordination compounds may be stable in cases where the central atom has not an inert-gas structure, provided that the associating units are regularly distributed. Nevertheless, the complex compounds of trivalent molybdenum do not exhibit the stability of the complex cyanides of quadrivalent molybdenum, $R_4[Mo(CN)_8]$, in which the central atom has an inert-gas structure.

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