CCCLXI.—*Co-ordination Compounds of Quinquevalent Molybdenum: Complex Thiocyanates.*

By ROBERT GILBERT JAMES and WILLIAM WARDLAW.

ONE of the most sensitive methods for the detection and estimation of small amounts of molybdenum is the so-called potassium thiocyana te reaction, based on the observation of Braun (*Z. anal. Chem.*, 1863, **2**, 36; 1867, **6**, 86) that a mineral acid solution of molybdenum

trioxide containing an alkali thiocyanate turns a deep red on the addition of a reducing agent such as zinc or stannous chloride. Even at the present time the constitution of the substance responsible for the red coloration is not known with certainty. It can, however, be almost quantitatively extracted from its aqueous solution by ether. Addition of pyridine or quinoline to the ethereal extract gives dark red oils which, on standing, or boiling with alcohol, yield brownish-red crystalline substances to which the formula $R_2Mo(OH)_2(CNS)_3$, where $R = C_5H_5N$ or C_9H_7N, was assigned (Rosenheim and Koss, *Z. anorg. Chem.*, 1906, **49**, 148; Sand and Burger, *Ber.*, 1906, **39**, 1761).

A more rational formulation on the basis of Werner's theory would be $R_2[MoO_2(CNS)_3]$, where $R = C_5H_6N$ or C_9H_8N, which suggests that possibly the red colour in the ethereal solution is due to the complex acid $H_2[MoO_2(CNS)_3]$. The isolation of this acid was attempted by Rosenheim and Koss (*loc. cit.*), who produced a deep red solution by boiling molybdenum trioxide with thiocyanic acid (10%) under reflux, and obtained from the filtrate by evaporation an almost black, hygroscopic residue of variable composition, but probably chiefly containing $Mo(OH)_2(CNS)_3$ (Abegg, " Handbuch," IV, 1, p. 541). By dissolving the pyridinium salt

$$(C_5H_6N)_2[MoO_2(CNS)_3]$$

in thiocyanic acid, Rosenheim and Koss obtained insoluble, dark green, rhombic crystals to which they gave the composition $Mo(OH)_2(CNS)_5H_2(C_5H_5N)_2$, which is better written as

$$(C_5H_6N)_2[MoO(CNS)_5],H_2O.$$

As the above summary indicates, our knowledge concerning thiocyanates of quinquevalent molybdenum is still far from complete, and in view of their interest in both analytical and theoretical chemistry, further investigation seemed desirable.

Salts of the Type $R_2[MoO_2(CNS)_3]$.—In the present investigation, the above method for the preparation of the complex pyridinium and quinolinium salts has been discarded in favour of the reaction between ammonium thiocyanate and salts of the type $R_2[MoOCl_5]$; Sand and Burger (*loc. cit.*) mentioned this method but gave no experimental details. In a previous communication (J., 1927, 2145) the preparation and properties of the green crystalline salts $R_2[MoOCl_5]$ were described, and it was shown from physico-chemical data that such salts undergo extensive decomposition in aqueous solution. Qualitative evidence of this decomposition is seen in the fact that these green salts dissolve in water giving brown acidic solutions from which it is impossible satisfactorily to obtain the original salt by recrystallisation. It is not unexpected, therefore, that in aqueous solution the reaction between ammonium thiocyanate and complex

salts of the type $R_2[MoOCl_5]$ does not give products in accordance with the equation: $5NH_4CNS + R_2[MoOCl_5] = R_2[MoO(CNS)_5] + 5NH_4Cl$, but yields instead insoluble substances of the type $R_2[MoO_2(CNS)_3]$. As shown later, salts of the type $R_2[MoO(CNS)_5]$ can only be produced in presence of excess of thiocyanic acid.

The formation of the compounds $R_2[MoO_2(CNS)_3]$ is additional evidence for the scheme of ionisation and hydrolysis mentioned in our previous communication:

$$R_2[MoOCl_5] + H_2O \rightleftharpoons R[MoOCl_4,H_2O] + RCl \quad . \quad (1)$$

$$R[MoOCl_4,H_2O] + H_2O \rightleftharpoons [MoOCl_3,2H_2O] + RCl \quad . \quad (2)$$

$$[MoOCl_3,2H_2O] + H_2O \rightleftharpoons [MoO(OH)Cl_2,2H_2O] + HCl \quad (3)$$

$$[MoO(OH)Cl_2,2H_2O] + H_2O \rightleftharpoons [MoO(OH)_2Cl,2H_2O] + HCl$$

$$\rightleftharpoons [MoO_2Cl,3H_2O] + HCl \quad . \quad . \quad (4)$$

$$[MoO_2Cl,3H_2O] + H_2O \rightleftharpoons [MoO_2OH,3H_2O] + HCl \quad . \quad (5)$$

When stage (4) is reached, in all probability the reaction in the presence of ammonium thiocyanate takes the following course:

$$[MoO_2Cl,3H_2O] + NH_4CNS \longrightarrow [MoO_2CNS,3H_2O] + NH_4Cl$$

$$2RCl + 2NH_4CNS \longrightarrow 2RCNS + 2NH_4Cl$$

$$2RCNS + [MoO_2CNS,3H_2O] \longrightarrow R_2[MoO_2(CNS)_3] + 3H_2O$$

In this way complex thiocyanates, where R = C_9H_8N, C_5H_6N, or Tl (ous), have been prepared.

The reaction between aqueous solutions of $(NH_4)_2[MoOCl_5]$ and ammonium thiocyanate may be expressed as follows:

$$[NH_4]_2[MoOCl_5] + 4H_2O \rightleftharpoons [MoO_2Cl,3H_2O] + 2NH_4Cl + 2HCl$$

$$2HCl + MoO_2Cl + 3NH_4CNS \rightleftharpoons H_2[MoO_2(CNS)_3] + 3NH_4Cl.$$

The *dihydrogen molybdenum dioxytrithiocyanate* has been thus prepared. It is extremely deliquescent, and exhibits a green lustre. A concentrated aqueous solution is purple-red, but on further dilution becomes red, orange, and finally yellow. The concentrated solutions yield purple precipitates with nitrates of silver and thallium, but the dilute yellow solutions give almost white precipitates consisting chiefly of thallous or silver thiocyanate. These reactions indicate that whilst in concentrated aqueous solution a complex acid is present, on dilution the complex anion undergoes hydrolysis and further ionisation.

Salts of the Type $R_4[Mo_2O_3(CNS)_8]$.—In view of the production of salts of the foregoing type, it was interesting to discover that when the green salts $[(CH_3)_3NH]_2MoOCl_5$ and $[(CH_3)_4N]_2MoOCl_5$ reacted with ammonium thiocyanate, the products were not reddish-brown compounds like the pyridinium and quinolinium derivatives

of the type $R_2[MoO_2(CNS)_3]$, but purple crystalline *substances* of the empirical formula $R_4[Mo_2O_3(CNS)_8]$. These octathiocyanates may be conveniently considered as bridge compounds having the constitution

$$R_4\left[\begin{matrix}(CNS)_3\\O\end{matrix}Mo<\begin{matrix}O\\CNS\end{matrix}\!\!\!\!\!\!\begin{matrix}\\CNS\end{matrix}>Mo\begin{matrix}(CNS)_3\\O\end{matrix}\right]$$

The basis for such a configuration will be demonstrated later.

Salts of the Type $R_2[MoO(CNS)_5]$.—Rosenheim and Koss (*loc. cit.*), who first discovered this series, describe the preparation of the one known derivative as follows : " When $(C_5H_5N)_2Mo(OH)_2(CNS)_3$ is dissolved in thiocyanic acid, or pyridinium thiocyanate is added directly to a solution of molybdic acid in aqueous thiocyanic acid, black, glittering, rhombic needles are obtained which are decomposed by water and dissolve in alcohol and in chloroform with a deep red colour." The composition $(C_5H_5N)_2H_2Mo(OH)_2(CNS)_5$ was ascribed to the crystals.

The above method was investigated, and after a suitable way of preparing thiocyanic acid had been established, a *pyridinium* compound was obtained of the composition $(C_5H_6N)_2[MoO(CNS)_5]$.

Quinolinium, *tetramethyl-* and *trimethyl-ammonium* salts of this type were also isolated, entirely analogous in formulation to the green complex chlorides $R_2[MoOCl_5]$. In their properties, however, salts of the two series exhibited marked contrasts; whilst the chlorides readily dissolved in water with considerable decomposition (the probable cause of their high solubility), the corresponding black thiocyanates were almost insoluble. In carefully dried alcohol the thiocyanates dissolved very readily, whereas the corresponding complex chlorides were almost insoluble in the cold. The formation of pentathiocyanates by the method described above takes place as follows :

$$[MoO_2(CNS)_3]R_2 + 2HCNS = [MoO(CNS)_5]R_2 + H_2O.$$

They can also be prepared by addition of the green chlorides to a boiling solution of thiocyanic acid, the thiocyanate crystallising immediately on cooling :

$$R_2[MoOCl_5] + 5HCNS \rightleftharpoons R_2[MoO(CNS)_5] + 5HCl.$$

This is a reversible reaction, for by treating the thiocyanate with hot concentrated hydrochloric acid, it is possible to obtain the pentachloride.

The preparation of the ditrimethylammonium and ditetramethylammonium members of the pentathiocyanate series involves the action of thiocyanic acid on the corresponding octathiocyanates,

and is therefore of special interest. The reaction can be represented as follows:

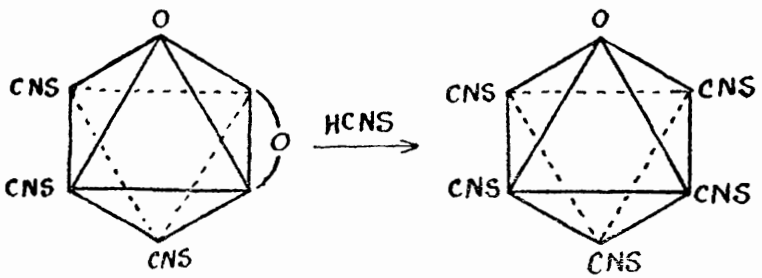
$$R_4\left[\begin{matrix}(CNS)_3\\O\end{matrix}Mo\begin{matrix}<\!\!\!-\!\!\!-O-\!\!\!-\!\!\!-\\CNS\quad CNS\end{matrix}>Mo\begin{matrix}(CNS)_3\\O\end{matrix}\right] + 2HCNS$$

$$\longrightarrow 2R_2\left[\begin{matrix}(CNS)_3\\O\end{matrix}Mo\begin{matrix}CNS\\CNS\end{matrix}\right] + H_2O$$

and also seems to indicate that the octathiocyanates possess a symmetrical structure.

The Co-ordination Number of Oxygen.

In a previous communication (J., 1927, 1087) it was mentioned that oxygen, contrary to the view of Werner, did not always occupy only one position in the co-ordination sphere, but that cases did arise in which this bivalent atom must be assigned two positions. A possible illustration of this fact is afforded by the co-ordination compounds of quinquevalent molybdenum. In the complex salts $R_2[MoOCl_5]$ and $R_2[MoO(CNS)_5]$, with oxygen occupying only one position in the co-ordination sphere, the molybdenum has a co-ordination number of six. With related complex substances of the type $R_2[MoO_2(CNS)_3]$ Werner's conclusions would lead to the molybdenum atom being assigned a co-ordination number of five. However, by the action of thiocyanic acid it is a simple matter to transform a salt of the type $R_2[MoO_2(CNS)_3]$ into the type $R_2[MoO(CNS)_5]$, where the molybdenum atom has a co-ordination number of six. It seems questionable whether this reaction involves the change of a five-point into a six-point system, and a more rational formulation would be to assign in both cases a co-ordination number of six to the molybdenum atom. It would then be necessary to consider one oxygen as occupying one position, and the other two positions, in the co-ordination sphere.



Such a configuration clearly demonstrates why one oxygen is reactive, and the other is not. It is also a matter of interest to find that neither in the case of the complex chlorides $R_2[MoOCl_5]$ nor in

that of the corresponding thiocyanates $R_2[MoO(CNS)_5]$ can the oxygen atom be displaced by the highest concentration of acid with the formation of such salts as $R_2[MoCl_7]$ or $R[MoCl_6]$.

It must be noted, however, that salts of the type $R_2[MoO_2(CNS)_3]$ may be represented as $R_4\left[\begin{matrix}(CNS)_3\\O\end{matrix}Mo\begin{matrix}O\\O\end{matrix}Mo\begin{matrix}(CNS)_3\\O\end{matrix}\right]$.

In a previous communication the importance of the effective atomic number of the molybdenum atom in determining the stability of its complex salts was emphasised. With the spatial configuration shown in the above diagram it will be seen that in salts of the type $R_2[MoO(CNS)_5]$ and $R_2[MoO_2(CNS)_3]$ the effective atomic number is 49. It is not surprising, therefore, that in aqueous solution these salts exhibit instability, in marked contrast to the great stability of the series $R_4Mo(CN)_8$, where the effective atomic number of the central atom is 54—that of the next inert gas.

Experimental.

Compounds of the Type $R_2[MoO_2(CNS)_3]$.

The green salts of the type $R_2[MoOCl_5]$ used in the following preparations were made by methods already detailed (J., 1927, 2145).

Dipyridinium Molybdenum Dioxytrithiocyanate.—10 C.c. of warm ammonium thiocyanate solution (containing 2·3 g.) were added to 30 c.c. of a warm, constantly stirred solution containing 4·5 g. of the salt $(C_5H_6N)_2[MoOCl_5]$. The bright reddish-brown crystals thus precipitated were washed with cold water and dried over phosphoric oxide in a vacuum. The compound melted at 181°, was soluble in acetone, and dissolved in boiling alcohol, giving a deep red solution.

Analysis. A hot ammoniacal solution of the substance was oxidised with hydrogen peroxide, and the molybdenum precipitated as sulphide (J., 1924, **125**, 1911), ignited, and weighed as the trioxide. The thiocyanate radical was determined by precipitation as silver thiocyanate from a cold, very dilute solution of the complex salt acidified with nitric acid. Nitrogen was estimated by Dumas's method (Found: Mo, 20·8; CNS, 37·6; N, 15·1; C, 33·9; H, 3·0. Calc. for $(C_5H_6N)_2[MoO_2(CNS)_3]$: Mo, 20·8; CNS, 37·7; N, 15·2; C, 33·8; H, 2·6%).

Diquinolinium Molybdenum Dioxytrithiocyanate.—25 C.c. of a solution containing 5·6 g. of the salt $(C_9H_8N)_2[MoOCl_5],H_2O$ were slowly poured with constant stirring into 15 c.c. of a warm, aqueous ammonium thiocyanate solution (containing 2·3 g.). This method gave a high yield of brownish-red crystals, which were washed and dried as previously described; they dissolved in boiling alcohol, but

were almost insoluble in water (Found: Mo, 17·1; CNS, 31·0; N, 12·5; C, 44·7; H, 3·36. Calc. for $(C_9H_8N)_2[MoO_2(CNS)_3]$: Mo, 17·1; CNS, 31·0; N, 12·5; C, 44·8; H, 2·85%).

Apart from their low solubility in water, the above-mentioned brownish-red complex thiocyanates $R_2[MoO_2(CNS)_3]$ closely resemble the copper-red pyridinium molybdenum dioxydichloride,

$$C_5H_6N[MoO_2Cl_2,H_2O],$$

previously described by the present authors (*loc. cit.*). Alcoholic hydrogen chloride converts all these red salts to the corresponding green complex chlorides $R_2[MoOCl_5]$, whilst on standing, their dilute aqueous solutions deposit light brown insoluble precipitates.

Treatment of $C_5H_6N[MoO_2Cl_2,H_2O]$ with ammonium thiocyanate, in an attempt to prepare $C_5H_6N[MoO_2(CNS)_2,H_2O]$, resulted in brownish-red crystals containing a high proportion of

$$(C_5H_6N)_2[MoO_2(CNS)_3].$$

Dihydrogen Molybdenum Dioxytrithiocyanate.—Hitherto no metallic salts of the type $R_2[MoO_2(CNS)_3]$ have been prepared. However, the addition of thallous or silver nitrate solution to a concentrated purple-red, aqueous solution of what is probably the complex acid $H_2[MoO_2(CNS)_3]$ gave rich purple precipitates. It proved extremely difficult to prepare pure specimens of these insoluble salts, owing to the simultaneous precipitation of thallous or silver thiocyanate, or even chloride. It seemed desirable, therefore, to find a method of preparing the acid, free from impurities, and also to attempt to determine its composition and constitution. The following method proved very satisfactory for the preparation of *dihydrogen molybdenum dioxytrithiocyanate*: To 15 c.c. of a solution of ammonium thiocyanate (4·6 g.) at 40° contained in a tap-funnel in an atmosphere of nitrogen, there were added 6·5 g. of the salt $(NH_4)_2[MoOCl_5]$, dissolved in 25 c.c. of warm water. The deep purple-red solution thus produced was agitated with 150 c.c. of ether, and the aqueous layer drawn off as completely as possible. About 2 c.c. of water were added to the ethereal extract remaining in the funnel, the mixture was agitated, and the aqueous layer completely withdrawn. By pressure of nitrogen, the ethereal solution was filtered into a flask which was evacuated to remove the ether. The product was a deep purple-red oil. The evacuated flask was heated on a water-bath, and the purple-red oil converted into an almost black solid which was kept in a vacuum over phosphoric oxide and solid potassium hydroxide (Found: Mo, 27·7; CNS, 52·5. Mo : CNS = 1 : 3·13. $H_2[MoO_2(CNS)_3],2H_2O$ requires Mo, 28·2; CNS, 51·2%). A solid of similar composition was obtained by keeping the oil for a long time over concentrated sulphuric acid.

In a modification of this method in which the flask containing the

solidified oil was connected with another flask containing concentrated sulphuric acid and the whole kept as highly evacuated as possible for a day, the solid *anhydrous acid* was obtained (Found : Mo, 31·2; CNS, 55·3; N, 14·3; Mo : CNS : N = 1 : 2·93 : 3·13. $H_2[MoO_2(CNS)_3]$ requires Mo, 31·6; CNS, 57·2; N, 13·8%).

Preparation of Dithallous Molybdenum Dioxytrithiocyanate.—The purple-red oil obtained as described above was mixed with 50 c.c. of water (the total volume of the mixture being *ca.* 55 c.c.), the solution warmed to 30°, and poured slowly with constant stirring into 50 c.c. of a saturated solution of thallous nitrate at 30°. The bluish-purple precipitate after being washed with water was dried in a vacuum over phosphoric oxide.

Analysis. To a weighed amount of the substance mixed with water, concentrated hydrochloric acid was added immediately with stirring, whereby the complex salt was partly decomposed with liberation of the free acid. The solution was now boiled to complete the decomposition of the salt. Some thallous chloride was precipitated, but with further dilution and boiling the precipitated chloride was wholly dissolved. To this boiling solution a slight excess of potassium iodide solution was added, and the precipitated thallium iodide was washed with very dilute potassium iodide solution, and finally with aqueous alcohol, and dried at 130—140°. The filtrate and washings were raised to boiling, treated with hydrogen peroxide, and the liberated iodine was boiled off. The resulting solution was made ammoniacal, boiled, and oxidised with more hydrogen peroxide until colourless, the molybdenum then being determined in the usual way (Found, for two samples : Mo, 13·4, 13·1; Tl, 55·9, 56·6; CNS, 24·0, 25·0; N, 6·0, 6·0. $Tl_2[MoO_2(CNS)_3,H_2O]$ requires Mo, 13·2; Tl, 56·0; CNS, 23·9; N, 5·8%).

The composition of this *thallium* salt varied slightly with variations in the method of preparation. For example, it is essential to pour the warmed purple-red solution of the complex acid into the thallium nitrate solution, and not *vice versa*. Moreover, the preparation of the purple-red solution must be carefully carried out in order to avoid oxidation or contamination with thiocyanic or hydrochloric acid.

Salts of the Type $R_4[Mo_2O_3(CNS)_8]$.

The preparations of the three substituted ammonium molybdenyl pentachlorides used below are described later (p. 2737).

Tetra-trimethylammonium Dimolybdenum Trioxyoctathiocyanate.—A solution of 4 g. of $[(CH_3)_3NH]_2[MoOCl_5],H_2O$ in 10 c.c. of water was poured into 10 c.c. of a warm, constantly stirred, aqueous solution of ammonium thiocyanate (3·1 g.). The copious purple crystalline precipitate was washed with water and dried in a vacuum

over phosphoric oxide (Found: Mo, 20·3, 20·35; CNS, 49·1; N, 17·9; C, 25·2; H, 4·25. $[(CH_3)_3NH]_4[Mo_2O_3(CNS)_8]$ requires Mo, 20·3; CNS, 49·2; N, 17·8; C, 25·4; H, 4·24%); it exhibits a green lustre and leaves a bluish-purple streak on unglazed porcelain. It is sparingly soluble in cold water, but more soluble in hot, owing to hydrolysis. Concentrated solutions are purple, but on dilution turn blood-red, then orange, and finally bright yellow. An interesting reaction of this complex thiocyanate is its decomposition with thallous nitrate: To a warm, blood-red, saturated solution of the octathiocyanate, there was added, drop by drop, a saturated aqueous solution of thallous nitrate. A purple or reddish-purple precipitate was obtained if care was taken to add insufficient thallous nitrate for complete precipitation, which was shown by the supernatant liquid remaining reddish-orange. After washing and drying in a vacuum over phosphoric oxide, this precipitate gave Mo, 12·8; Tl, 58·1; CNS, 24·1; Tl : CNS = 2 : 2·93, showing it to be an impure specimen of $Tl_2[MoO_2(CNS)_3,H_2O]$. The isolation of this thallium derivative indicates that the octathiocyanate undergoes hydrolysis in solution in such a way as to indicate a symmetrical structure for the octathiocyanate

$$R_4\left[\begin{matrix}(CNS)_3\\O\end{matrix}Mo\begin{matrix}<O>\\<CNS\ CNS>\end{matrix}Mo\begin{matrix}(CNS)_3\\O\end{matrix}\right] \xrightarrow{2H\cdot OH}$$

$$2R_2[MoO\cdot OH(CNS)_4] \longrightarrow 2R_2[MoO_2(CNS)_3] + 2HCNS.$$

The action of thiocyanic acid on the octathiocyanate furnishes additional evidence in favour of the above configuration.

Tetra-tetramethylammonium Dimolybdenum Trioxyoctathiocyanate.—Into 10 c.c. of a warm aqueous solution of ammonium thiocyanate (2·8 g.), there were slowly poured with constant stirring 10 c.c. of a solution containing 4 g. of $[(CH_3)_4N]_2MoOCl_5$. An excellent yield of a magenta salt was obtained, which was washed with water and dried in a vacuum over phosphoric oxide (Found: Mo, 19·3; CNS, 46·6; N, 16·9; C, 28·7; H, 4·92. $[(CH_3)_4N]_4[Mo_2O_3(CNS)_8]$ requires Mo, 19·2; CNS, 46·5; N, 16·8; C, 28·8; H, 4·80%). On standing, the filtrate deposited bluish-purple crystals, exhibiting a green lustre, which had the same empirical composition as the first yield (Found: Mo, 19·25; CNS, 46·6; N, 16·6%). The properties of this second complex octathiocyanate resemble those of the trimethylammonium analogue.

In order to determine whether a similar octathiocyanate could be obtained with the diethylammonium derivative, the salt $[(C_2H_5)_2NH_2]_2MoOCl_5$ was prepared, and its reaction with ammonium thiocyanate studied. It was found that an oil resulted from which no crystalline substance could be isolated.

Tetrapyridinium Dimolybdenum Trioxysulphatohexathiocyanate.—By treating the reddish-brown thiocyanate, previously formulated as $(C_5H_5N)_2Mo(OH)_2(CNS)_3$, with sulphuric acid, Sand and Burger (*loc. cit.*) obtained from the resulting deep purple-red solution dark green needles, to which they assigned the formula

$$Mo(OH)(SO_4)_{\frac{1}{2}}(CNS)_3(C_5H_5N)_2,$$

basing their deductions on the following analysis :

	Mo.	N.	Total S.	S as SO_4.
Calc.	19·47	14·19	22·72	3·25
Found	19·17	13·66	23·01	3·01

By repeating this experiment, with slight modifications, we have isolated a purple compound which appears to have the configuration

$$(C_5H_6N)_4\left[\begin{matrix}(CNS)_3\\O\end{matrix}Mo\begin{matrix}O\\SO_4\end{matrix}Mo\begin{matrix}(CNS)_3\\O\end{matrix}\right]$$

in which a relationship to the octathiocyanates

$$R_4\left[\begin{matrix}(CNS)_3\\O\end{matrix}Mo\begin{matrix}O\\CNS\end{matrix}\begin{matrix}O\\CNS\end{matrix}Mo\begin{matrix}(CNS)_3\\O\end{matrix}\right]$$

is readily apparent. Although the colour of this substance differs from that of the salt obtained by Sand and Burger, the two compounds are probably identical, for the analytical figures obtained by Sand and Burger for their substance agree very closely with those demanded by the formula ascribed to the purple compound.

Preparation. 9·0 G. of $(C_5H_6N)_2[MoOCl_5]$ in 40 c.c. of water were added to 25 c.c. of a warm solution containing ammonium thiocyanate (4·6 g.), and the precipitated thiocyanate

$$(C_5H_6N)_2[MoO_2(CNS)_3]$$

was dried, finely powdered, and treated with 150 c.c. of sulphuric acid (5*N*). On warming, a deep red solution resulted, and crystals gradually appeared on the surface of the liquid. Further warming caused the crystals to revert to a black oil, which later began to bubble. At this stage the well-shaken mixture was rapidly filtered, and the filtrate cooled, finally by ice-cold water. The crystals obtained were washed with sulphuric acid (5*N*), then with absolute alcohol, and finally dried in a vacuum over calcium chloride (Found : Mo, 19·1; CNS, 35·0; N, 13·9; SO_4, 9·72; C, 31·1; H, 2·50. Calc. for $(C_5H_6N)_4[Mo_2O_3(SO_4)(CNS)_6]$: Mo, 19·1; CNS, 34·7; N, 13·9; SO_4, 9·56; C, 31·1; H, 2·39%).

Properties. The bright purple crystalline compound was almost insoluble in alcohol, and sparingly soluble in cold water, but on continued contact the crystals slowly dissolved, producing a brown solution changing to yellow on dilution. If the action of sulphuric acid was continued beyond the stage specified above, dark brown,

crystalline substances were produced (Found: Mo : N = 1 : 9 and Mo : CNS : N = 1 : 2 : 4). It appears probable that in these compounds some of the thiocyanate groups in the original purple salt have been replaced by sulphate equivalents.

Inconclusive results were obtained from the action of hydrochloric acid on $(C_5H_6N)_2[MoO_2(CNS)_3]$ and of sulphuric and hydrochloric acids on $(C_9H_8N)_2[MoO_2(CNS)_3]$.

Salts of the Type $R_2[MoO(CNS)_5]$.

Thiocyanic Acid Solution.—To 200 c.c. of a well-cooled solution of potassium thiocyanate (100 g.), 180 c.c. of sulphuric acid (5*N*) were slowly added with constant stirring, and the mixture was distilled in a vacuum, the distillate (*ca.* 200 c.c.) being collected in a well-cooled receiver. As a yellow substance separates on standing or prolonged boiling, freshly distilled acid was used in the following experiments.

Dipyridinium Molybdenyl Pentathiocyanate.—Dipyridinium molybdenum dioxytrithiocyanate (4·0 g.) was added to 150 c.c. of boiling thiocyanic acid, the solution rapidly filtered, and the filtrate cooled in ice. The crystals obtained were washed with cold thiocyanic acid solution, and dried in a vacuum over solid potassium hydroxide and phosphoric oxide. The compound was greenish-black in colour, and made a red mark on unglazed porcelain (Found: Mo, 17·1; CNS, 51·7; N, 17·4; C, 31·8; H, 2·28. $(C_5H_6N)_2[MoO(CNS)_5]$ requires Mo, 17·1; CNS, 51·7; N, 17·4; C, 32·0; H, 2·14%).

Diquinolinium Molybdenyl Pentathiocyanate.—This was prepared as above from the corresponding diquinolinium salt (5·0 g.) and thiocyanic acid (180 c.c.), greenish-black crystals being obtained (Found: Mo, 14·5; N, 14·9; C, 41·7; H, 2·49.

$(C_9H_8N)_2[MoO(CNS)_5]$

requires Mo, 14·5; N, 14·8; C, 41·7; H, 2·42%).

Ditrimethylammonium Molybdenyl Pentathiocyanate.—Tetratrimethylammonium dimolybdenum trioxyoctathiocyanate, prepared from 4 g. of $[(CH_3)_3NH]_2[MoOCl_5],H_2O$, was treated as before with 75 c.c. of thiocyanic acid solution and yielded greenish-black crystals of the required *compound* (Found: Mo, 18·5; CNS, 55·7; N, 18·8; C, 25·1; H, 4·03. $[(CH_3)_3NH]_2[MoO(CNS)_5]$ requires Mo, 18·4; CNS, 55·6; N, 18·8; C, 25·25; H, 3·83%).

Ditetramethylammonium Molybdenyl Pentathiocyanate.—3·0 G. of $[(CH_3)_4N]_2MoOCl_5$ were converted into the octathiocyanate. The finely powdered product was treated with thiocyanic acid (100 c.c.), whereupon reddish-brown crystals separated, which were very sparingly soluble in water, but more soluble in alcohol and chloroform (Found: Mo, 16·96; N, 17·34; C, 27·75; H, 4·59.

$[(CH_3)_4N]_2[MoO(CNS)_5],H_2O$

requires Mo, 16·89; N, 17·26; C, 27·45; H, 4·58%). Treatment with aqueous alcohol gave a magenta-coloured precipitate, which was probably the octathiocyanate regenerated by hydrolysis.

Salts of the Type $R_2[MoOCl_5]$.

For the preparation and investigation of the octathiocyanates previously described, the following complex molybdenyl pentachlorides were required. The preparations detailed below, involving electrolytic reduction and the use of alcoholic hydrogen chloride, differ from the method employed by Nordenskjold (*Ber.*, 1901, **34**, 1572), and give high yields of the pure salt.

Ditrimethylammonium Molybdenyl Pentachloride.—This salt was prepared by an alternative method to that previously described (J., 1927, 2148). To 100 c.c. of a boiling solution of quinquevalent molybdenum (10 g. Mo) in alcoholic hydrogen chloride, obtained as described under dipyridinium molybdenyl pentachloride (*loc. cit.*), there was added trimethylammonium chloride (16 g.). The well-stirred mixture was boiled until clear, and yielded yellowish-green needles, which were recrystallised from alcoholic hydrogen chloride and dried over potassium hydroxide and phosphoric oxide in a vacuum (Found: Mo, 22·6; Cl, 41·7; N, 6·59; C, 17·0; H, 5·10. Calc. for $[(CH_3)_3NH]_2[MoOCl_5],H_2O$: Mo, 22·5; Cl, 41·5; N, 6·56; C, 16·9; H, 5·15%).

Bisdiethylammonium Molybdenyl Pentachloride.—This was prepared as detailed above, except that diethylamine (13 g.) was used, the resulting solution being evaporated under diminished pressure. On re-saturation with hydrogen chloride, a large yield of green needles was obtained; these were washed with alcoholic hydrogen chloride and dried as before (Found: Mo, 21·9; Cl, 40·5; N, 6·40; C, 21·9; H, 5·65. $[(C_2H_5)_2NH_2]_2[MoOCl_5]$ requires Mo, 22·0; Cl, 40·5; N, 6·20; C, 22·0; H, 5·49%).

Ditetramethylammonium Molybdenyl Pentachloride.—An interesting point in connexion with the preparation of this salt is that by a variation in the proportions of the reactants it is possible to isolate a salt of the type $R[MoOCl_4,H_2O]$, of which so far only one other example is known, *viz.*, $(CH_3)_3NH[MoOCl_4,H_2O]$, previously described by the present authors. 50 C.c. of an alcoholic hydrogen chloride solution of quinquevalent molybdenum (6·4 g.) were diluted with an equal volume of alcohol, raised to boiling, and tetramethylammonium chloride (10 g.) added. The resulting light green crystals were dissolved in 200 c.c. of hydrochloric acid (4*N*), the solution saturated with hydrogen chloride, and on evaporation and re-saturation with this gas, crops of crystals were obtained. The first yields consisted of the *pentachloride*, whilst the last fraction proved

to be pure *monotetramethylammonium molybdenyl tetrachloride*. The salts were recrystallised, if necessary, and dried as previously described (Found, for pentachloride: Mo, 21·9; Cl, 40·4; N, 6·4. $[(CH_3)_4N]_2MoOCl_5$ requires Mo, 22·0; Cl, 40·5; N, 6·4%. Found, for tetrachloride: Mo, 27·70, 27·60; Cl, 41·15, 41·31; N, 4·04. $(CH_3)_4N[MoOCl_4,H_2O]$ requires Mo, 27·76; Cl, 41·0; N, 4·05%).

Physico-chemical Measurements.

Throughout this communication the various complex salts have been formulated in accordance with the principles of Werner's co-ordination theory. Indirect evidence for such a formulation is obtained from the method of preparation of the salts and from their reactions, but confirmation may be obtained from determinations of molecular weights and molecular conductivities. The slight solubility of the complex salts in cold water, and their decomposition by hot water, renders determinations of molecular weight unsatisfactory by either cryoscopic or ebullioscopic methods in air-free water. However, molecular conductivities were determined at 25°:

	$(C_5H_6N)_2[MoO_2(CNS)_3]$.				$(C_9H_8N)_2[MoO_2(CNS)_3]$.			
v	262·8	525·6	1051	2102	1090	2180	4360	
μ	492	534	559	591	571	604	640	
	$[(CH_3)_3NH]_4[Mo_2O_3(CNS)_8]$.				$[(CH_3)_4N]_4[Mo_2O_3(CNS)_8]$.			
v	736·3	2945	5890	11,781	882·6	3530	7061	14,122
μ	1614	1860	1900	1960	1711	1871	1942	2036

	$(C_5H_6N)_4[Mo_2O_3(SO_4)(CNS)_6]$.				
v	623·9	1248	2496	4991	9982
μ	1504	1713	1820	1930	2010

	$(C_5H_6N)_2[MoO(CNS)_5]$.				$[(CH_3)_3NH]_2[MoO(CNS)_5]$.			
v	441	1764	3529	7058	422	1688	3376	6752
μ	1089	1286	1314	1360	1069	1272	1305	1324

It is clear from the appended figures that in no case do the complex salts behave in aqueous solution as typical electrolytes, but exhibit abnormally high molecular conductivities. Such behaviour is not unexpected in view of the series of colour changes which aqueous solutions of the salts undergo with increasing dilution. According to our views on hydrolysis and ionisation, at infinite dilution salts of the type $R_2[MoO_2(CNS)_3]$ should give undissociated $[MoO_2OH,2H_2O]$ together with six ions, *viz.*, $2R^{\cdot} + H^{\cdot} + 3CNS'$. The ionic velocities at 25° are $H^{\cdot} = 347$; $CNS' = 65·4$ (Landolt–Börnstein, "Tabellen," 1923, ii, 1104); $C_5H_6N^{\cdot} = 43·1$ (Lundén, *J. Chim. physique*, 1907, **5**, 592); $C_9H_8N^{\cdot} = 35·1$; $(CH_3)_3NH^{\cdot} = 47·0$; $(CH_3)_4N^{\cdot} = 43·6$ (Bredig, *Z. physikal. Chem.*, 1894, **13**, 228). If the proposed scheme is correct the pyridinium

salt should give a value for $\mu_{\infty}^{25^{\circ}}$ of 629, which is in good agreement with the experimental values. It is interesting to find that Sand and Burger, in determining the molecular conductivity of this salt, obtained $\mu = 564$ and 613 for $v = 700$ and 2803 respectively, and concluded that the substance behaved abnormally, although no explanation was advanced. A scheme for the ionisation and hydrolysis of salts of the type $R_2[MoO(CNS)_5]$, identical with that previously recorded for the complex salts $R_2[MoOCl_5]$ (*loc. cit.*), would result in the ions $2R^{\cdot} + 3H^{\cdot} + 5CNS'$ being present at infinite dilution in aqueous solution. This should give, for

$$(C_5H_6N)_2[MoO(CNS)_5]$$

$\mu_{\infty} = 1454$, and for $[(CH_3)_3NH]_2[MoO(CNS)_5]$ $\mu_{\infty} = 1462$. The close agreement between the experimental and theoretical values lends strong support to the view that the scheme of hydrolysis and ionisation is substantially correct. A similar scheme for the complex salts of the new type $R_4[Mo_2O_3(CNS)_8]$ would be $R_4[Mo_2O_3(CNS)_8] + H_2O = 2R_2[MoO_2(CNS)_3] + 2HCNS$, followed by the further hydrolysis and ionisation of the complex salt as before, whence there should result at infinite dilution the ions $4R^{\cdot} + 4H^{\cdot} + 8CNS'$. Where $R^{\cdot} = (CH_3)_3NH^{\cdot}$, the calculated value for $\mu_{\infty} = 2099$, and where $R^{\cdot} = (CH_3)_4N^{\cdot}$, $\mu_{\infty} = 2086$ at 25°. Similarly, for the complex salt $(C_5H_6N)_4[Mo_2O_3(SO_4)(CNS)_6]$, the presence of the ions $4C_5H_6N^{\cdot} + 4H^{\cdot} + SO_4'' + 6CNS'$ in solution at 25° would give a calculated value for μ_{∞} of 2111. Again the agreement between the theoretical and experimental results is very satisfactory and therefore the formulation of these series of salts on the basis of the co-ordination theory seems to afford a satisfactory explanation of their behaviour in aqueous solution.

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THE UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

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