CCCXCVII.—*The Complex Cyanides of Molybdenum.*

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SPECIAL interest is attached to the complex cyanides of molybdenum and tungsten, $R_4Mo(CN)_8$ and $R_4W(CN)_8$, for few cyanides of quadrivalent elements exist, and complex cyanides are known only in isolated cases. Moreover, these complex salts represent well-substantiated examples of a co-ordination number of 8, and the exceptional stability of the complex ions $[Mo(CN)_8]''''$ and $[W(CN)_8]''''$ finds a satisfactory explanation in the modern electronic theory of valency. Undoubtedly this marked stability is intimately associated with the fact that the cyanide units are regularly distributed round a central metallic atom, of which the effective atomic number—in the case of molybdenum, 54, and of tungsten, 86—is that of the next higher inert gas.

The abnormal behaviour of these complex cyanides on oxidation with acid permanganate has been the subject of much theoretical speculation. Unlike the majority of compounds containing molybdenum and tungsten, which on oxidation with acid permanganate are converted into the sexavalent condition, these complex cyanides pass only to the quinquevalent state. In order to dispel any doubt as to the correctness of formulating the complex tungsten cyanide, $K_4W(CN)_8$, as a derivative of quadrivalent tungsten, Olsson (*Ber.*, 1914, **47**, 917; *Z. anorg. Chem.*, 1914, **88**, 49) showed that on complete oxidation with ammoniacal silver salt solution, two atoms of silver separated for each molecule of the salt oxidised. Further convincing proof of the extent of oxidation by acid permanganate was the isolation of compounds of the type $R_3W(CN)_8$ from the oxidised solution of $K_4W(CN)_8$. Olsson was unsuccessful, however, in isolating the corresponding molybdenum type, $R_3Mo(CN)_8$. By taking special precautions, this has now been done, and not only have salts of this series been prepared, but also the complex *acid* $H_3Mo(CN)_8,3H_2O$ has been isolated. It is also hoped to show that a satisfactory explanation of the abnormal oxidation by acid permanganate is forthcoming from a consideration of the electronic theory of valency.

In researches on the complex cyanides of the type $R_4Mo(CN)_8$, Rosenheim and his co-workers (*Z. anorg. Chem.*, 1909, **65**, 166; 1907, **54**, 97) prepared derivatives where R was replaced by equivalent proportions of cadmium, thallium (univalent), manganese, pyridinium, and the ammines of silver, copper, and nickel. The methods of preparation and the compositions of the silver, copper, thallous, and ammino-silver compounds have been re-examined, confirming Rosenheim's data, whilst the isolation of the new insoluble, dark green *ammino-copper* salt, $[Cu(NH_3)_3]_2Mo(CN)_8$, and the dark blue, soluble *complex salt*, $[Cu\ en_2]_2Mo(CN)_8$, affords interesting examples of copper exhibiting co-ordination numbers of 3 and 4. In addition, a study of the so-called red and blue cyanides of quadrivalent molybdenum has been made, and a bright brick-red, insoluble compound, which is probably the complex acid $H[MoO_2(CN)_2,2H_2O]$, has been prepared by the action of concentrated nitric acid on $K_4Mo(CN)_8$.

EXPERIMENTAL.

Salts of the Type $R_4[Mo(CN)_8]$.—From the reaction of potassium cyanide with the complex chloride of tervalent molybdenum, K_3MoCl_6, Chilesotti (*Gazzetta*, 1904, **34**, ii, 493) obtained a yellow, crystalline salt of the composition $K_4Mo(CN)_8,2H_2O$, in which he assumed that the molybdenum was quadrivalent. The same compound was isolated later by Rosenheim and Koss (*Z. anorg. Chem.*, 1906, **49**, 148) from the interaction of a derivative of quinquevalent molybdenum, $(NH_4)_2[MoOCl_5]$ or $Mo(OH)_2(CNS)_3(C_5H_5N)_2$, and potassium cyanide. Conductivity data (*ibid.*, 1907, **54**, 97) established that the ionisation was in accordance with the formula $K_4[Mo(CN)_8]$, whilst Collenberg (*ibid.*, 1922, **121**, 298) has confirmed Olsson's results, which indicated the quadrivalency of the central atom.

Tetrapotassium Molybdenum Octacyanide.—The method of Chilesotti (*loc. cit.*) was used. One part by weight of K_3MoCl_6 and 2 parts of potassium cyanide were intimately mixed and 6 parts of water added in small portions, during about 2 hours. The solution was raised to boiling point and concentrated on a water-bath, whereby yellow crystals were obtained. These were separated from the mother-liquor and extracted with small quantities of hot water, and the solution was filtered and allowed to crystallise. Further purification was obtained by redissolution in a little water and precipitation by alcohol with rapid stirring. The small, golden-yellow crystals thus prepared were very pure.

Analysis. It was found necessary to destroy the complex anion completely before the molybdenum could be precipitated quantitatively. The general method used was to digest the compound with boiling concentrated sulphuric acid for some time, dilute the mixture, make it alkaline with ammonia, and then add colourless ammonium sulphide solution and acid as previously described (J., 1924, **125**, 1911). Unfortunately, large quantities of ammonium sulphate have to be eliminated in the potassium estimation [Found : Mo, 19·2; K, 31·2; C, 19·3; N, 22·8. Calc. for $K_4Mo(CN)_8,2H_2O$: Mo, 19·4; K, 31·5; C, 19·4; N, 22·6%].

The compound, which is readily soluble in water, producing a yellow, slightly alkaline solution, is decomposed neither by dilute acids nor by alkalis. Concentrated sulphuric acid is required to effect complete decomposition. It is light-sensitive (Collenberg, *Z. anorg. Chem.*, 1924, **136**, 245), but not to such an extent as the analogous compound of quinquevalent molybdenum. A detailed account of its properties is given by Chilesotti (*loc. cit.*).

Tetrasilver Molybdenum Octacyanide.—Silver nitrate solution was added to a solution of $K_4Mo(CN)_8$, and the yellow silver salt which separated was washed with water and dried in a vacuum desiccator [Found : Ag, 58·3; Mo, 12·9. Calc. for $Ag_4Mo(CN)_8$: Ag, 58·7; Mo, 13·0%]. On being warmed with ammonia (*d* 0·88), this silver salt dissolved, and concentration of the solution over sulphuric acid yielded a yellow, crystalline compound insoluble in water. This was kept over concentrated sulphuric acid until free from the smell of ammonia [Found: Ag, 54·5; Mo, 12·1; NH_3, 6·3. Calc. for $Ag_4(NH_3)_3Mo(CN)_8$: Ag, 54·8; Mo, 12·2; NH_3, 6·4%].

Tetrathallous Molybdenum Octacyanide.—This salt was prepared by adding the theoretical amount of a solution of thallous nitrate to a concentrated solution of $K_4Mo(CN)_8$, evaporating the mixture to small bulk, filtering, and allowing the salt to crystallise. The orange-yellow crystals obtained were washed with water and dried on a filter-paper.

Analysis. The substance was boiled with concentrated sulphuric acid until the solution was nearly colourless. On diluting it, making it alkaline with ammonia, and adding colourless ammonium sulphide solution, thallous sulphide was precipitated, which was washed with ammonium sulphide solution and filtered off. Molybdenum was estimated in the usual way in the filtrate and washings. The thallous sulphide was dissolved in dilute nitric acid, the solution evaporated to dryness, and potassium iodide added to an aqueous solution of the residue, precipitating thallous iodide, which was washed by decantation with potassium iodide solution, collected, and treated with alcohol to remove any potassium iodide [Found: Tl, 72·3; Mo, 8·6. Calc. for $Tl_4Mo(CN)_8$: Tl, 72·8; Mo, 8·5%].

The compositions of this salt and of the corresponding silver salt indicate that water of crystallisation, which is present in many of these complex cyanides, is not an essential constituent of the co-ordination complex.

Dicupric Molybdenum Octacyanide.—This was prepared by double decomposition of the potassium complex cyanide with copper sulphate solution. The precipitate was coagulated by boiling, washed with water, and dried in a vacuum desiccator; it was then dark purple.

Analysis. The substance was heated with concentrated sulphuric acid until a nearly colourless solution resulted; this was diluted and made just alkaline with sodium hydroxide, excess of sodium sulphide solution added, and the whole boiled for a few minutes to ensure all the molybdenum being present as the soluble thiomolybdate. The precipitated copper sulphide was filtered off, washed with sodium sulphide solution, then with hydrogen sulphide water, dried, and gently ignited. The residue, after being moistened with pure nitric acid and reheated, was weighed as copper oxide. The molybdenum in the filtrate and washings was precipitated as sulphide by the addition of dilute sulphuric acid, filtered off, and ignited to trioxide [Found: Mo, 22·1; Cu, 29·7. Calc. for $Cu_2Mo(CN)_8$: Mo, 22·3; Cu, 29·5%].

Hexamminodicupric Molybdenum Octacyanide.—By treatment of the above copper salt with concentrated ammonia solution, Rosenheim (*Z. anorg. Chem.*, 1907, **54**, 97) obtained a dark green ammino-compound to which he assigned the formula $Cu_2(NH_3)_4Mo(CN)_8,7H_2O$. By the use of a similar method, a new *ammino-copper* derivative has been obtained. On addition of ammonia (*d* 0·88) to the purple $Cu_2Mo(CN)_8$, the colour changed to bright green. On warming, the solid dissolved, producing a dark green solution from which, after filtration and standing over sulphuric acid, dark green crystals separated, which were insoluble in water but could be recrystallised from ammonia solution (*ca.* 10*N*). The substance was washed with water and dried in a vacuum over sulphuric acid, whereupon the colour became a lighter green {Found : Mo, 17·8; Cu, 24·1; NH_3, 19·4. $[Cu(NH_3)_3]_2Mo(CN)_8$ requires Mo, 18·0; Cu, 23·9; NH_3, 19·1%}. Treatment with acid removes the ammonia and precipitates the purple $Cu_2Mo(CN)_8$.

Tetraethylenediaminodicupric Molybdenum Octacyanide.—The purple $Cu_2Mo(CN)_8$ (1 mol.) was mixed with ethylenediamine hydrate (4 mols.) and well shaken. A blue substance formed immediately and was recrystallised from water, in which it gave a deep bluish-purple solution. After being dried over sulphuric acid, the new salt was deep blue, readily soluble in warm water, and easily decomposed by dilute acids, $Cu_2Mo(CN)_8$ being precipitated {Found : Cu, 18·8; Mo, 14·3; N, 33·5. $[Cu(en)_2]_2Mo(CN)_8$ requires Cu, 19·0; Mo, 14·3; N, 33·4%}.

Conductivity measurements at 25° indicated, as would be expected from the formula, a maximum of 3 ions in very dilute solutions.

Dilution (litres per mol.)	155	310	620	1240
μ	78·5	104·3	134·4	166·2

For comparison, the values of the molecular conductivities of typical salts at 25° are given :

Dilution (litres per mol.)	128	256	512	1024
NaCl	113	115	117	118
K_2SO_4	246	257	265	273

In the more concentrated solutions, the molecular conductivity is even less than that required for a typical binary electrolyte, but at higher dilutions, although less than that demanded by a ternary electrolyte, it exceeds that of the binary electrolyte.

In the complex kations containing copper, it is possible to assign to the copper co-ordination numbers of 2, 3, and 4, but with the silver salt $[Ag_4(NH_3)_3]Mo(CN)_8$ it is difficult to discern any satisfactory co-ordination number for the silver atom.

Salts of the Type $R_3Mo(CN)_8$.—In attempting to isolate salts of this type, Olsson (*Ber.*, 1914, **47**, 917) added silver nitrate solution to a solution of $K_4Mo(CN)_8$ which had been as fully oxidised as possible with acid permanganate. Thereby he obtained a reddish-brown precipitate obviously different from the yellow $Ag_4Mo(CN)_8$. By decomposition with potassium chloride solution, this reddish-brown silver salt gave a yellow liquid which could no longer be oxidised by permanganate. From this solution, green crystals of a copper salt were obtained, again distinct from the purple $Cu_2Mo(CN)_8$. The yellow liquid readily decomposed on warming or on exposure to light, yielding molybdic acid, hydrocyanic acid, and $K_4Mo(CN)_8$, and probably contained the salt $K_3Mo(CN)_8$. It appeared that this potassium salt could be satisfactorily isolated only in the absence of light.

Trisilver Molybdenum Octacyanide.—A solution of $K_4Mo(CN)_8$ was oxidised with acid permanganate until a faint pink colour remained. Excess of silver nitrate was then added, the resulting reddish-brown precipitate was washed repeatedly by decantation with water, and then dried in a vacuum. This substance was contaminated with manganese dioxide from the decomposition of the permanganate in the presence of the silver ions; by working with dilute solutions of both $K_4Mo(CN)_8$ and permanganate, however, the amount of dioxide produced was small. The reddish-brown precipitate was triturated with a little potassium chloride solution (insufficient for complete decomposition), and the yellow solution was filtered and again treated with silver nitrate solution. Any slight amount of chloride in the yellow solution is precipitated by the silver nitrate before the reddish-brown silver complex cyanide. Therefore, silver nitrate solution was carefully added until a faint brown precipitate was obtained, the solution again filtered, and the pure reddish-brown salt obtained by the addition of excess silver nitrate solution to the filtrate. The compound was washed with cold water and dried in a vacuum over phosphoric oxide.

Analysis. The silver was estimated as chloride by boiling the compound with concentrated sulphuric acid, diluting the solution, and adding either dilute hydrochloric acid or potassium chloride solution. The molybdenum was estimated in the usual way [Found: Ag, 51·3; Mo, 15·2; N, 17·6. $Ag_3Mo(CN)_8$ requires Ag, 51·6; Mo, 15·2; N, 17·7%].

Tripotassium Molybdenum Octacyanide. — The silver salt, $Ag_3Mo(CN)_8$, was triturated with insufficient potassium chloride solution for complete decomposition. The filtered yellow solution, which contained no chloride, was concentrated in a vacuum desiccator over phosphoric oxide, whereupon yellow needles were obtained. These operations were carried out in a dark room with a red light, and the solid was preserved in a desiccator covered with black paper. In daylight, the yellow crystals turned reddish-brown [Found: Mo, 22·4; N, 26·4; K, 28·2. $K_3Mo(CN)_8$ requires Mo, 22·8; N, 26·6; K, 27·8%]. Because of its sensitivity to light, conductivity measurements were not carried out on the new complex cyanide. By addition of copper sulphate solution to the yellow solution of the new salt, a grass-green precipitate was obtained, which, after a few minutes' exposure to light, turned purple.

Trihydrogen Molybdenum Octacyanide.—The yellow solution, produced by triturating the complex silver salt with a little dilute hydrochloric acid and filtering, was saturated with hydrogen chloride at the temperature of an ice–salt mixture. A reddish-orange substance separated, which was possibly an addition compound of hydrogen chloride with the required complex acid. This was filtered off and dried in a vacuum over potassium hydroxide and phosphoric oxide, and thereby became orange-coloured and free from hydrogen chloride. The new solid gave a yellow, aqueous solution, from which silver and copper salts precipitated the characteristically coloured complex cyanides of quinquevalent molybdenum. The same compound is obtained if the yellow solution is concentrated in a vacuum over potassium hydroxide and phosphoric oxide, without saturation with hydrogen chloride. In either case, all operations must be conducted in the absence of light. The new *acid* is extremely deliquescent [Found: Mo, 26·7; N, 31·1. $H_3Mo(CN)_8,3H_2O$ requires Mo, 26·6; N, 31·0%].

In order to confirm the constitution of the substance and to demonstrate its freedom from hydrogen chloride, a solution of the complex acid was treated with silver nitrate solution, all the molybdenum being thereby precipitated as $Ag_3Mo(CN)_8$. This precipitate was washed free from silver nitrate, and excess of potassium chloride solution added. The $Ag_3Mo(CN)_8$ was thereby converted quantitatively into silver chloride, which was washed and weighed. Any hydrogen chloride in the original substance would also have been precipitated as silver chloride. 0·2164 G. of the new acid, containing 26·7% of Mo, gave 0·2606 g. of AgCl; hence Mo : AgCl = 1 : 3·02, proving also the absence of hydrogen chloride from the complex acid.

The Abnormal Oxidation of the Complex Cyanides.

On the basis of the electronic theory of valency, an explanation is now available of the abnormal behaviour of the complex cyanides of molybdenum on oxidation with acid permanganate. Estimation of the valency of the molybdenum in $K_4Mo(CN)_8$ through titration with acid permanganate involves the consumption of only one equivalent of oxygen for each molecule of salt oxidised, from which one would conclude that the molybdenum was quinquevalent, since the usual end-product would be expected to contain sexavalent molybdenum. This, however, does not agree with the formula of the compound, in which the molybdenum must be quadrivalent. That, by complete oxidation with acid permanganate, the molybdenum in $K_4Mo(CN)_8$ is oxidised from the quadrivalent to the quinquevalent condition, is now clearly shown by the isolation of the complex salts $R_3Mo(CN)_8$ from the fully oxidised solution of $K_4Mo(CN)_8$. Ephraim ("Inorganic Chemistry," English transl., 1926, p. 280), commenting on this exceptional oxidation, says: "It is not easy to see the explanation of this anomaly, but it is possible that the metal atom is surrounded by voluminous radicles which are fairly firmly attached." A much more satisfactory explanation is forthcoming from a consideration of the effective atomic number of the central atom in the various complex salts involved in the preparation of the complex cyanides. The salt $K_4Mo(CN)_8$ is normally prepared by the interaction of potassium cyanide with complex compounds of either tervalent or quinquevalent molybdenum. In the former case the reaction may be conveniently formulated as $K_3MoCl_6 + 8KCN + \frac{1}{2}H_2O + \frac{1}{2}O(\text{air}) = K_4Mo(CN)_8 + 6KCl + KOH$. The instability of the intermediate $K_3Mo(CN)_6$—a salt as yet unisolated—which reverts to the stable $K_4Mo(CN)_8$, can be readily appreciated when it is seen that the effective atomic number of the molybdenum is only 51, whereas in the stable compound it is 54. In the preparation from the complex chlorides of quinquevalent molybdenum, R_2MoOCl_5, the importance of the effective atomic number of the molybdenum in $K_4Mo(CN)_8$ is again emphasised. The reaction may be considered as occurring in the following stages:

$$K_2MoOCl_5 + 5KCN = K_2MoO(CN)_5 + 5KCl$$
$$K_2MoO(CN)_5 + 3KCN + H_2O = K_3Mo(CN)_8 + 2KOH$$
$$2K_3Mo(CN)_8 + 2KOH = 2K_4Mo(CN)_8 + H_2O + \tfrac{1}{2}O_2$$
$$[\text{compare } 2K_3Fe(CN)_6 + 2KOH = 2K_4Fe(CN)_6 + H_2O + \tfrac{1}{2}O_2]$$

The instability of the salt $K_2MoO(CN)_5$ follows as a consequence of the low effective atomic number, *viz.*, 49, of the molybdenum atom, whilst the formation of $K_4Mo(CN)_8$ from $K_3Mo(CN)_8$ involves a change of an effective atomic number of 53 to 54—a clear proof of the influence of an inert-gas structure in determining chemical stability. The inability to oxidise $K_4Mo(CN)_8$ to the salt $K_2Mo(CN)_8$ of sexavalent molybdenum, with an effective atomic number of 52, is not surprising in view of the experimental evidence that $K_3Mo(CN)_8$ functions as an oxidising agent in order to revert to the more stable $K_4Mo(CN)_8$. This change, as has been previously mentioned, is readily brought about by light or by the action of heat. Further evidence of the instability of the system $[Mo(CN)_8]'''$ is seen in the rapidity with which, in light, the green complex salt $Cu_3[Mo(CN)_8]_2$ reverts to the purple $Cu_2[Mo(CN)_8]$. Oxidation to the sexavalent condition is realised only by complete decomposition of the complex anion. When the complex salt $K_4Mo(CN)_8$ is oxidised by ammoniacal silver nitrate, the molybdenum is converted into the trioxide.

The Red and the Blue Cyanides of Quadrivalent Molybdenum.

Just as the yellow cyanide, $K_4Mo(CN)_8$, results from the reaction of potassium cyanide with salts of tervalent and quinquevalent molybdenum, so by adjusting the proportion of the reactants so that 1 g.-mol. of the salt of quinquevalent molybdenum reacts with 4 g.-mols. of potassium cyanide, a red cyanide is obtained, which may be formulated as either $[Mo(OH)_4(CN)_4]K_4,xH_2O$ or $[MoO_2(CN)_4]K_4,(x + 2)H_2O$. Moreover, by use of excess potassium cyanide the red will revert to the yellow salt in accordance with the equations

$$[Mo(OH)_4(CN)_4]R_4 + 4RCN = [Mo(CN)_8]R_4 + 4ROH,$$
$$[MoO_2(CN)_4]R_4 + 4RCN = [Mo(CN)_8]R_4 + 2R_2O.$$

By strong dehydration over sulphuric acid, or by cautious heating, these red cyanides become blue; their aqueous solutions also are blue. Addition of potassium hydroxide in sufficient concentration to the blue aqueous solution results in the reprecipitation of the red cyanide. The addition of alcohol to the blue aqueous solution causes the precipitation of a blue solid, which, after being dissolved in water and reprecipitated several times, has a composition for which various formulæ have been proposed. Two in particular may be noted: $MoO_2,4KCN,5H_2O$ and $Mo(OH)_2(CN)_2,3KCN$. These show the quadrivalency of the molybdenum, but indicate the possibility that quite different blue complex cyanides exist. With the object of investigating the reasons for these striking colour changes, samples of the red and the blue cyanides were prepared and examined.

The Red Cyanides.—By the reduction of an acid solution of molybdenum trioxide with potassium iodide, removal of the excess iodine, and subsequent treatment with potassium cyanide and hydroxide, Heide and Hofmann (*Z. anorg. Chem.*, 1896, **12**, 277) obtained red crystals to which they assigned the formula

$$4KCN,MoO_2,10H_2O.$$

Rosenheim, Garfunkel, and Kohn (*ibid.*, 1910, **65**, 166) obtained a similar compound by treating $(NH_4)_2MoOCl_5$ or

$$Mo(OH)_2(CNS)_3(C_5H_5N)_2$$

—salts of quinquevalent molybdenum—with potassium cyanide, and subsequently adding potassium hydroxide. The method used by the present authors followed that of Péchard (*Compt. rend.*, 1894, **118**, 804), who dissolved molybdenum pentoxide in potassium cyanide solution, and precipitated the red crystals by the addition of solid potassium hydroxide to the blue solution.

300 C.c. of a solution of molybdenum trioxide (10%) in hydrochloric acid (3*N*) were electrolysed in a diaphragm cell for 2 hours (1 amp.; 8 volts) and concentrated at *ca.* 70° to a very small bulk. On careful addition of very concentrated potassium hydroxide solution, the brown hydroxide of quinquevalent molybdenum was obtained. On addition of the theoretical amount of potassium cyanide (54 g.) as a saturated solution, the hydroxide slowly dissolved, producing a blue solution, which was filtered and concentrated under diminished pressure at *ca.* 70° to a small bulk (30—40 c.c.). Red crystals were deposited on addition of solid potassium hydroxide to this blue solution. By means of a little water and then alcohol, the crystals were freed from potassium hydroxide. They are stable towards dilute mineral acids, but appear to be decomposed by organic acids, such as salicylic or oxalic acid, although no definite compounds could be obtained. In the presence of concentrated potassium hydroxide, the crystals exhibit a bright red colour, but as the hydroxide is removed the colour becomes bluish-red.

Analysis. An aqueous solution of the substance was oxidised with hydrogen peroxide and made alkaline with ammonia, and colourless ammonium sulphide was added. Addition of dilute sulphuric acid precipitated the molybdenum as sulphide, which was ignited and weighed as trioxide. The potassium in the filtrate was weighed as sulphate {Found : Mo, 19·3; K, 31·1; C, 9·9; H, 2·4; N, 11·5. Calc. for $K_4[Mo(OH)_4(CN)_4],4H_2O$: Mo, 19·3; K, 31·4; C, 9·6; H, 2·4; N, 11·3%}.

Even when the crystals did not contain any free potassium hydroxide, their aqueous solution gave an alkaline reaction with phenolphthalein, suggesting hydrolysis. This view is supported by the conductivity data, which indicate that, even at 1°, more than 5 ions are present in dilute solutions. The table gives the value of μ for various dilutions v (as litres per mol.).

v	23·5	47	94	188
μ	275·6	298·4	320·6	342·3

(compare this vol., p. 516, Table IV, for conductivities of typical salts at 1°).

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. water.	Conc. (mol. per 1000 g. water).	Osmotic factor.	Apparent mol. wt.
0·7136	0·01440	5·16	96·2
1·517	0·03560	5·06	97·9
2·636	0·05314	4·85	102·6

These results indicate the correctness of a formulation which requires 5 ions, but they also show that slow hydrolysis takes place in dilute aqueous solution.

The Blue Cyanides.—An aqueous solution of the red cyanide was treated with alcohol, whereby a blue precipitate resulted. The mother-liquor was alkaline to phenolphthalein, indicating that by the conversion of the red into the blue cyanide, potassium hydroxide was removed. The blue solid was redissolved in water and re-precipitated with alcohol; these operations were repeated until the mother-liquor from the precipitation was no longer alkaline. Thereby a blue substance was obtained {Found: Mo, 22·5; K, 28·0; C, 11·5; N, 13·1. $K_3[Mo(OH)_3(CN)_4,H_2O],2H_2O$ requires Mo, 22·7; K, 27·8; C, 11·3; N, 13·3%}.

The aqueous solution of this compound was alkaline to phenolphthalein, and with potassium cyanide yielded the yellow $K_4Mo(CN)_8$. The blue substance was prepared several times by the above method and always had the same composition. The formulation given above was in accordance with the results of molecular-weight and conductivity determinations, which indicated that 4 ions were present in solution but that gradual hydrolysis also took place.

Molecular-weight Determinations.

G. of substance per 100 g. water.	Conc. (mol. per 1000 g. water).	Osmotic factor.	Apparent mol. wt.
0·6618	0·01554	4·25	99·3
1·235	0·02898	4·23	99·7

Molecular-conductivity Determinations, at 1°.

v	35·5	71	142	284
μ	198·8	215·5	232·8	250·0

The Relationship of the Red and the Blue Cyanides.—The fact that the red cyanide becomes blue on dehydration and yet yields a blue aqueous solution seems to depend on the equilibrium

$$K_4[Mo(OH)_4(CN)_4],4H_2O \rightleftharpoons K_3[Mo(OH)_3(CN)_4,H_2O],2H_2O + KOH + H_2O.$$

It was noticed that the red colour of the complex cyanide is attained only in the presence of concentrated potassium hydroxide, and that on removal of this free alkali the pure complex salt becomes bluish-violet. It appears probable, therefore, that on dehydration and on dissolution in water, a decomposition takes place in accordance with the above equation. A co-ordination number of 8 for the molybdenum atom in the red cyanides seems indicated by the fact that on cautious dehydration over sulphuric acid or at 100° they retain 2 mols. of the associated water, suggesting the formula $R_4[MoO_2(CN)_4,2H_2O]$aq. or $R_4[Mo(OH)_4(CN)_4]$aq.

Brick-red, Insoluble Molybdenum Cyanide.—Chilesotti (*Gazzetta*, 1904, **34**, ii, 493) noticed that the oxidation of the yellow quadrivalent cyanide by means of concentrated nitric acid resulted in the separation of a brick-red, insoluble compound, which he did not further examine.

When $K_4Mo(CN)_8$ was heated with even dilute nitric acid (*ca.* 6*N*) in a test-tube, this compound was obtained pure, but when the experiment was made in an open dish, varying amounts of molybdic acid were formed. The brick-red compound was washed with cold water, in which it was but slightly soluble, and dried in a desiccator over sulphuric acid.

Analysis. The substance was heated with pure sulphuric acid until the solution was colourless, and the molybdenum precipitated as previously described {Found : Mo, 43·8; N, 12·8; C, 11·0; H, 1·8. $H[MoO_2(CN)_2,2H_2O]$ requires Mo, 44·2; N, 12·9; C, 11·0; H, 2·3%}.

Valency. A solution of the substance in dilute aqueous ammonia was made acid with sulphuric acid and titrated with permanganate. On the assumption that the molybdenum in the compound has a valency of 5, the theoretical content of molybdenum calculated from the titration is 44·8%. By gravimetric means it was found to be 43·8%. Hence the molybdenum is quinquevalent.

The solid is soluble in hot water, giving a yellow solution. It is much more readily soluble in ammonia or alkalis, suggesting an acidic structure. In view of this, it is probably correctly formulated as above.

This new derivative is of interest as indicating that on oxidation the quinquevalent molybdenum still persists as a complex anion, but that on oxidation to the sexavalent state complete disruption of the complex ion takes place, a fact which is in complete agreement with the theoretical considerations previously advanced to explain the abnormal oxidation of the yellow complex cyanides.

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 (W. R. B.), and to the Chemical Society and the University of Birmingham Research Committee for grants in aid of this investigation.

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[*Received, October* 15*th*, 1927.]