Studies on the Composition and Properties of Less Familiar Metal Cyano Complexes. II. Composition of Copper Octacyano Molybdate and the Existence of the Redox System $Cu^{+}+Mo(CN)_8^{3-} \rightleftarrows Cu^{2+}+Mo(CN)_8^{4-}$

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In continuation to our studies on the composition of the complex molybdocyanides of heavy metals by electrometric methods (Part I, this Bulletin*), investigations were extended to the copper complexes. The study of such complexes, besides providing information regarding the composition of cupric molybdocyanide, opens a new aspect for further investigation, viz., the existence of redox potential in the system $Cu^{+}+Mo(CN)_8^{3-} \rightleftarrows Cu^{2+}+Mo(CN)_8^{4-}$. Little work has been done in this direction even for the well-known metal ferrocyanogen complexes and very few references are available in the literature on this aspect of the problem.

For the first time Davidson[1] in 1937 drew attention towards the existence of $Fe^{3+}+Fe(CN)_6^{4-} \rightleftarrows Fe(CN)_6^{3-}+Fe^{2+}$ couple in the slow formation of ferric-ferrocyanide while carrying out experiments on the iron blues. Very recently systematic studies on these lines have been carried out by Malik[2] for systems like $Cu^{+}+Fe(CN)_6^{3-} \rightleftarrows Fe(CN)_6^{4-}+Cu^{2+}$; $Mn^{3+}+Fe(CN)_6^{4-} \rightleftarrows Fe(CN)_6^{3-}+Mn^{2+}$; $Cr^{2+}+Fe(CN)_6^{3-} \rightleftarrows Cr^{3+}+Fe(CN)_6^{4-}$ etc., applying amperometric methods.

The present communication deals with two aspects of the problem of copper complexes of alkali cyanomolybdates: i) the composition of the freshly precipitated cupric molybdocyanide by electrometric methods and ii) the study of the cuprous chloride potassium molybdicyanide reaction employing a cuprous-cupric couple at the bright platinum electrode.

Experimental

Solutions of potassium molybdo- and molybdicyanide were prepared and standardized as given in Part I. Copper sulfate solution was prepared by dissolving a weighed amount of A. R. crystals of the salt in redistilled water and its concentration determined iodometrically[3]. Cuprous chloride[4] was prepared and a weighed amount of it dissolved in 1 M potassium chloride solution (acidified with a little hydrochloric acid). The solution was kept under a layer of paraffin to avoid oxidation. The concentration of the solution was determined by titrating against 0.1 M ammonium thiocyanate, using ferric alum[5] as the indicator.

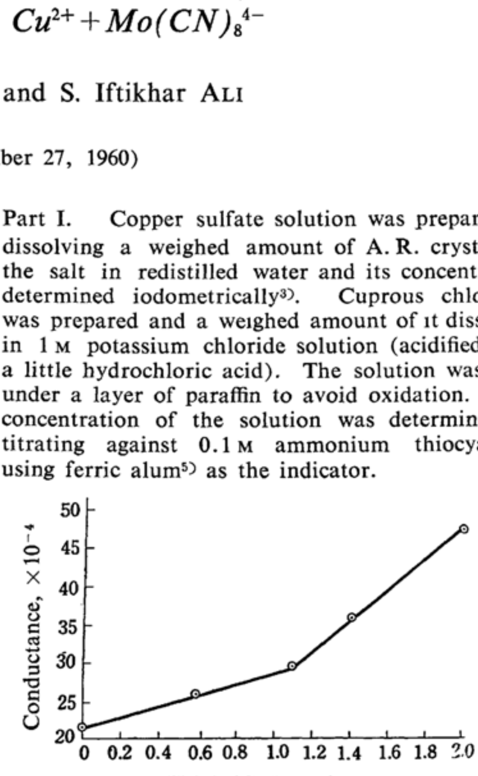

Fig. 1A. 40 cc. 0.0025 M $CuSO_4$ vs. $K_4Mo(CN)_8$ 0.05 M.

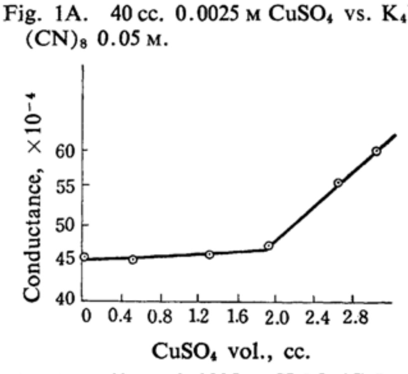

Fig. 1B. 40 cc. 0.0025 M $K_4Mo(CN)_8$ vs. 0.1 M $CuSO_4$.

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* Part I, This Bulletin, **34** 1306 (1961).

[1] D. Davidson, *J. Chem. Educ.*, **14**, 238 (1937).

[2] W. U. Malik, *J. Ind. Chem. Soc.*, in press.

[3] "Scott's Standard Method of Chemical Analysis", by Furman, Vol. I, Ed V, p. 368.

[4] Fernelius, "Inorganic Syntheses", Vol. II, p. 1.

[5] W. U. Malik and Co-workers, *Z. anorg. u. allgem. Chem.*, **299**, 322 (1959).

Conductometric, potentiometric and amperometric titrations between copper sulfate and potassium molybdocyanide were carried out as described earlier. Potentiometric titrations between cuprous chloride and potassium molybdicyanide were carried out, using $Cu^+ \rightleftarrows Cu^{2+}+e$ couple, obtained by dipping bright platinum electrode in a solution of cuprous chloride containing a little cupric chloride.

All the experiments were performed in the dark room and the vessels were also wrapped with black paper to avoid the decomposition of potassium molybdicyanide.

The results are summarized below. A few typical curves are shown in Figs. 1A, 1B, 2, 3A, 3B and 4A, 4B.

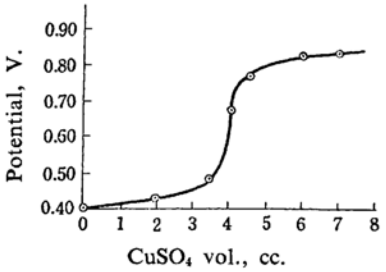

Fig. 2. 10 cc. 0.02 M $K_4Mo(CN)_8$ vs. 0.1 M $CuSO_4$.

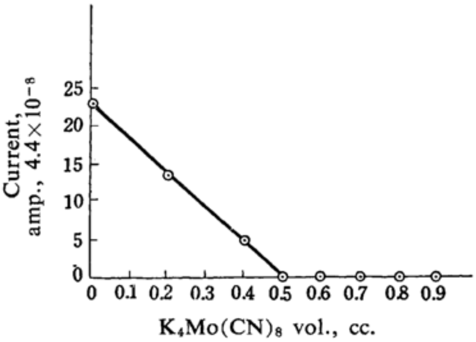

Fig. 3A. 20 cc. 0.005 M $CuSO_4$ vs. $K_4Mo(CN)_8$ 0.1 M.

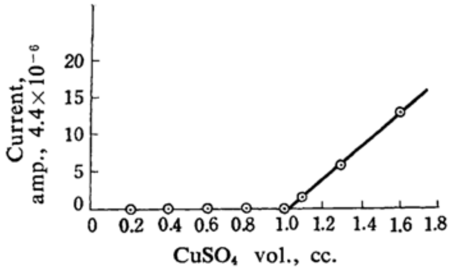

Fig. 3B. 20 cc. 0.0025 M $K_4Mo(CN)_8$ vs. 0.1 M $CuSO_4$.

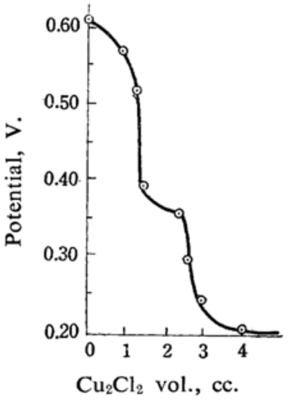

Fig. 4A. 5 cc. 0.0368 M $K_3Mo(CN)_8$ vs. 0.0794 M Cu_2Cl_2.

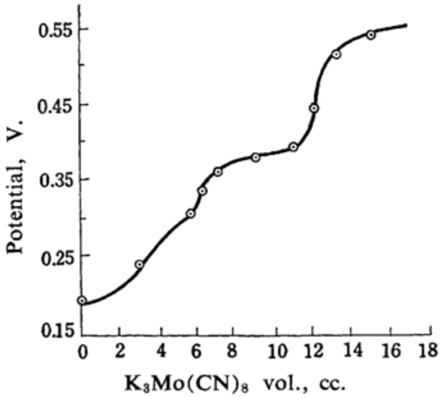

Fig. 4B. 5cc. 0.0619 M Cu_2Cl_2 vs. 0.046 M $K_3Mo(CN)_8$.

Results

TABLE I. CONDUCTOMETRIC TITRATIONS

Direct: Copper sulfate solution in the cell.

$CuSO_4$ in the cell Vol., cc.	Concn., M	Vol. of 0.05 M $K_4Mo(CN)_8$ from the curves, cc.	Ratio Cu^{2+} : $Mo(CN)_8{}^{4-}$
40	0.00075	0.3	2 : 1.0
40	0.00125	0.54	2 : 1.05
40	0.0020	0.84	2 : 1.05
40	0.0025	1.10	2 : 1.09

Reverse: Potassium molybdocyanide in the cell.

$K_4Mo(CN)_8$ Vol., cc.	Concn., M	Vol. of 0.1 M $CuSO_4$ from the curves, cc.	Ratio Cu^{2+} : $Mo(CN)_8{}^{4-}$
40	0.00075	0.54	2 : 1.1
40	0.00125	0.86	2 : 1.16
40	0.0020	1.48	2 : 1.08
40	0.0025	1.80	2 : 1.1

TABLE II. POTENTIOMETRIC TITRATIONS

Direct: Potassium molybdocyanide in the cell.

$K_4Mo(CN)_8$ Vol., cc.	$K_4Mo(CN)_8$ Concn., M	Vol. of 0.1 M $CuSO_4$ from the curves, cc.	Ratio $Cu_2^+ : Mo(CN)_8^{4-}$
10	0.02	3.9	2 : 1.02
10	0.0125	2.45	2 : 1.02
10	0.01	1.90	2 : 1.05

TABLE III. AMPEROMETRIC TITRATIONS

Direct: Copper Sulfate Soln. in the cell.

Voltage applied, −0.4 V. Temp., 30±0.1°C

copper sulphate Vol., cc.	copper sulphate Concn., M	Vol. of 0.1 M $K_4Mo(CN)_8$ from the curves, cc.	Ratio $Cu^{2+} : Mo(CN)_8^{4-}$
20	0.003	0.30	2 : 1
20	0.005	0.50	2 : 1
20	0.0075	0.72	2 : 1

Reverse: Potassium molybdocyanide in the cell.

$K_4Mo(CN)_8$ Vol., cc.	$K_4Mo(CN)_8$ Concn., M	Vol. of 0.1 M $CuSO_4$ from the curves, cc.	Ratio $Cu^{2+} : Mo(CN)_8^{4-}$
20	0.0015	0.6	2 : 1
20	0.0025	1.0	2 : 1
20	0.00375	1.46	2 : 1.02

TABLE IV. POTENTIOMETRIC TITRATIONS BETWEEN CUPROUS CHLORIDE AND POTASSIUM MOLYBDICYANIDE

Direct: Potassium molybdicyanide in the cell.

$K_3Mo(CN)_8$ Vol., cc.	$K_3Mo(CN)_8$ Concn.,	Vol. of 0.0794 M Cu_2Cl_2 from the curves, cc.		Ratio $Cu^+ : Mo(CN)_8^{3-}$	
5	0.0276	1.0	2.0	1.12 : 2	1.12 : 1
5	0.0368	1.3	2.6	1.12 : 2	1.12 : 1
5	0.046	1.6	3.2	1.10 : 2	1.12 : 1

Reverse: Cuprous chloride in the cell.

Cu_2Cl_2 Vol., cc.	Cu_2Cl_2 Concn., M	Vol. of 0.046 M $K_3Mo(CN)_8$ from the curves, cc.		Ratio $Cu^+ : Mo(CN)_8^{3-}$	
5	0.0397	3.8	7.7	1.13 : 1	1.13 : 2
5	0.0619	6.0	12.0	1.14 : 1	1.14 : 2
5	0.0794	7.2	14.4	1.19 : 1	1.19 : 2

Discussion

Conductometric titrations between copper sulfate and potassium molybdocyanide (Figs. 1A and 1B) give the ratio Cu^{2+} to $Mo(CN)_8^{4-}$ as 2 : 1. Potentiometric titrations carried out with copper sulfate solution in the cell did not give typical titration curves and there was a sharp rise in potential on the addition of even a small amount of molybdocyanide (containing a little molybdicyanide) from the burette. Titrations carried out in the reverse manner, viz., by adding copper sulfate solution to the molybdocyanide in the cell ($Mo(CN)_8^{4-} \rightleftarrows Mo\cdot(CN)_8^{3-} + e$ couple at the bright platinum electrode) gave very satisfactory results (Fig. 2) and here too a ratio of 2 : 1 was found to exist. However, both these methods gave a little more of potassium molybdocyanide than required by the stoichiometric equation: $2\cdot CuSO_4 + K_4Mo(CN)_8 = Cu_2Mo(CN)_8 + 2K_2SO_4$ for the formation of the complex. Here this may also be attributed to the adsorption of $Mo(CN)_8^{4-}$ by the freshly precipitated complex although the adsorption effect is not so marked as in the case of cobalt and nickel complexes (Part I). The behavior of copper molybdocyanide is also slightly different from those of cobalt and nickel molybdocyanides in as much as that the precipitate of the latter pass into colloidal solution more readily than the former. Amperometric titrations (Figs. 3A and 3B) both direct and reverse give the ratio 2 : 1, again pointing towards the formation of the complex $Cu_2Mo(CN)_8$.

Conductometric titrations as well as the amperometric titrations were unsuccessful in investigating the reaction between cuprous chloride and potassium molybdicyanide. In the latter suitable potential to be applied could not not be found while in the former sharp points of intersection at the equivalence point were not realized. However, potentiometric titrations at the $Cu^+ \rightleftarrows Cu^{2+}+e$ couple (Pt electrode dipped in a solution of cuprous chloride containing a little cupric chloride) gave typical titration curves with two sharp breaks (Figs. 4A and 4B). The values for the ratio $Cu^+ : Mo(CN)_8{}^{3-}$ being nearly 1 : 2 and 1 : 1 respectively.

Before assigning a particular formula to the complex formed by this reaction it is important to consider the oxidation reduction reaction : $Cu^+ + Mo(CN)_8{}^{3-} \rightleftarrows Cu^{2+} + Mo(CN)_8{}^{4-}$. Taking the redox potentials of $Mo(CN)_8{}^{4-} \rightleftarrows Mo(CN)_8{}^{3-} + e$ as -0.82 V. and that of $Cu^+ \rightleftarrows Cu^{2+} + e$ as -0.17 V., the equilibrium constant of the above mentioned redox reaction comes out to be 1.5×10^{12}. It means that during the interaction of cuprous chloride and potassium molybdicyanide, a large amount of cuprous is oxidized to the cupric state and the molybdicyanide is reduced to the molybdocyanide.

On the basis of the above explanation the reaction should take place in the following two steps.

$Cu_2Cl_2 + 2K_3Mo(CN)_8 + 2KCl = 2CuCl_2 + 2K_4 \cdot Mo(CN)_8$ followed by, $2CuCl_2 + 2K_4Mo(CN)_8 = 2K_2CuMo(CN)_8 + 2KCl$. The ratio 1 : 2 ($Cu^+ : Mo(CN)_8{}^{3-}$) found on the basis of potentiometric titration support the above mechanism since the overall reaction would be $Cu_2Cl_2 + 2K_3Mo(CN)_8 = 2K_2CuMo(CN)_8 + 2KCl$, giving the complex $K_2Cu^{II}Mo^{IV}(CN)_8$.

Whether an oxidation-reduction equilibrium ($K = 1.5 \times 10^{12}$) can completely hold good in the case of precipitation reactions is rather difficult to say. It is quite probable that some of the cuprous chloride is precipitated by potassium molybdicyanide before mutual oxidation reduction takes place and some cuprous molybdicyanide is also formed. Under these conditions a ratio of 1 : 1 for the reactants should be realized. This is what we actually get from the second break of the direct and the first break of the reverse titrations. To sum up it may be said that the products of interaction between cuprous chloride and potassium octacyanomolybdate(V) are predominantly $K_2Cu^{II}Mo^{IV}(CN)_8$ although a little amount of $KCu_2{}^{I}Mo^{V}(CN)_8$ is also formed.

Summary

The reaction between copper sulfate and potassium molybdocyanide was studied using conductometric, potentiometric and amperometric methods. The stoichiometric ratio of 2 : 1 for Cu^{2+} to $Mo(CN)_8{}^{4-}$ correspond to the formation of $Cu_2Mo(CN)_8$. The interaction of cuprous chloride and potassium molybdicyanide resulted in the formation of $K_2Cu^{II}Mo^{IV}(CN)_8$. Evidence for the existence of a redox potential in the system $Cu^+ + Mo(CN)_8{}^{3-} \rightleftarrows Cu^{2+} + Mo(CN)_8{}^{4-}$ could be obtained for the latter reaction on the basis of potentiometric titrations.

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