Studies on the Composition and Properties of Less Familiar Metal Cyano Complexes. I. Composition of Nickel and Cobalt Octacyanomolybdates by Electrometric Methods

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The chemical literature abounds in references on the properties and composition of metal complexes of alkali ferro- and ferricyanides but very little attention appears to have been paid to the study of the metal complexes of alkali octacyanomolybdates. The only work worth mentioning is that of Wardlaw and co-workers[1] who carried out studies on the metal complexes of silver, thallium, copper, etc. by the method of chemical analysis. It is a well known fact that the physical methods have got certain advantages over the methods of chemical analysis in as far as that they not only provide precise information of the composition of the freshly precipitated complex but are able to eliminate the errors which might creep in during the washing and drying of precipitate possessing adsorptive and hydrolytic properties. Attention to this point was drawn by Bhattacharya[2] on the basis of the work carried out by him and his students on metal ferro- and ferricyanides. Since the metal complexes of alkali octacyanomolybdates appear to belong to the class of metal ferrocyano complexes, it was thought worthwhile to employ physical methods for the elucidation of their composition.

The present communication deals with our studies on the nickel and cobalt complexes of potassium octacyanomolybdate employing conductometric, potentiometric and amperometric methods. Moreover these complexes have not so far been studied and are likely to open a new field for the physico-chemical studies on metal cyano complexes.

Experimental

The method recommended by Fieser[3] was followed for the preparation of potassium octacyanomolybdate. All chemicals, molybdenum(VI) oxide, potassium thiocyanate, pyridine and potassium cyanide, used were A. R. samples. The crystallized product (golden yellow in color) was dried over calcium chloride in a vaccum dessicator. It was dissolved in water twice distilled by a all-glass apparatus and its concentration was determined by titrating potentiometrically against the potassium permanganate solution of a known concentration. Potassium octacyanomolybdate(V) was prepared by the method

1) W. Wardlaw and co-workers, *J. Chem. Soc.*, **1927**, 2981.

2) A. K. Bhattacharya, "Proc. Symp. Coordination Compounds, Part I", National Academy of Science, India (1959), p. 139.

3) L. F. Fieser, *J. Am. Chem. Soc.*, **52**, 5204 (1930).

recommended by Kolthoff[4] and standardized potentiometrically against potassium ferrocyanide.

Nickel and cobalt chlorides of A. R. grade were used for preparing their solutions and their concentrations were estimated gravimetrically after precipitating as nickel dimethylglyoxime and cobalt ammonium phosphate respectively.

Conductometric titrations were done with the help of Cambridge conductivity bridge (No. L-350140) with a bridge type conductivity cell (No. L-355234 and cell constant 0.36). Potentiometric titrations were performed with Tinsley potentiometer (Type 338713) with a lamp and scale arrangement. The indicator electrode was the $K_4Mo(CN)_8 \rightleftarrows K_3Mo(CN)_8 + e$ couple obtained by dipping a bright platinum electrode in a solution of potassium octacyanomolybdate(IV) containing a little potassium octacyanomolybdate(V).

In order to carry out amperometric studies, the constant potential to be applied during the course of titrations was first of all determined, taking in the polarographic cell 1 cc. of 0.1 M salt solution in 0.1 M potassium chloride as supporting electrolyte, 0.0003% sodium methyl red for nickel(II) and 0.01% gelatin for cobalt(II) as maximum suppressor, the total volume made up to 20 cc. The current was measured with Fischer Elecdropode in conjunction with Multiflex galvanometer (type MGF 2, sensitivity 1 : 10), in the external circuit. Polarograms were drawn and from the plateau the potentials to be applied for the amperometric titrations were found out. The potential applied during the course

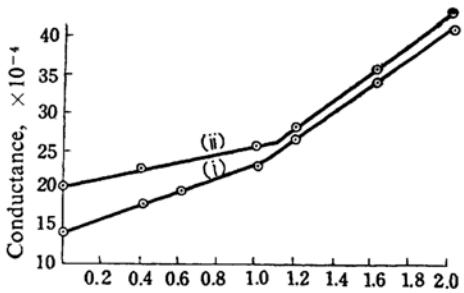

Fig. 1A. 40 cc., 0.0025 M (i) $NiCl_2$ and (ii) $CoCl_2$ vs. 0.05 M $K_4Mo(CN)_8$.

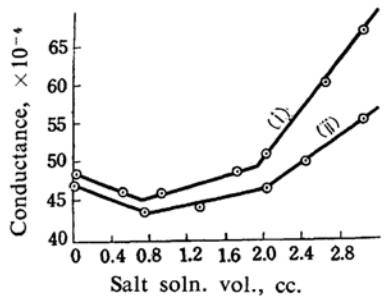

Fig. 1B. 40 cc. $K_4Mo(CN)_8$ 0.0025 M vs. 0.1 M (i) $NiCl_2$ and (ii) $CoCl_2$.

4) I. M. Kolthoff and W. J. Tomsicek, *J. Phys. Chem.*, **40**, 247 (1936).

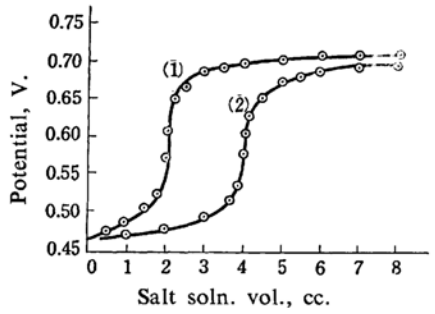

Fig. 2A. Curve (1), 10cc. 0.01 M $K_4Mo(CN)_8$ vs. 0.1 M $NiCl_2$. Curve (2), 10 cc. 0.02 M $K_4Mo(CN)_8$ vs. 0.1 M $CoCl_2$.

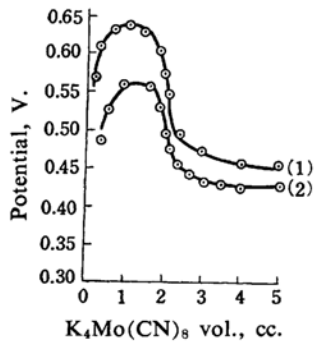

Fig. 2B. 10 cc. 0.02 M (1) $NiCl_2$ and (2) $CoCl_2$ vs. 0.05 M $K_4Mo(CN)_8$.

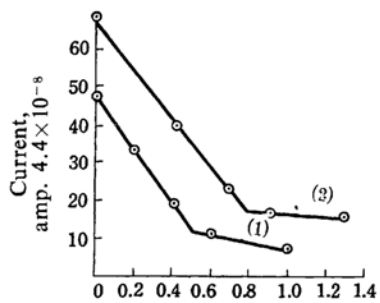

Fig. 3A. 20 cc. (1) 0.005 M $NiCl_2$ and (2) 0.0075 M $CoCl_2$ vs. 0.1 M $K_4Mo(CN)_8$.

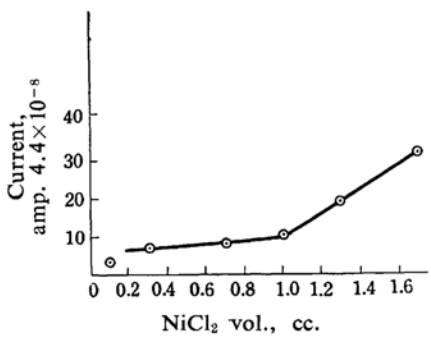

Fig. 3B. 20 cc., 0.0025 M $K_4Mo(CN)_8$ vs. 0.1 M $NiCl_2$.

of titrations for nickel(II) and cobalt(II), being −1.2 and −1.4 V. respectively. Electrodes used were the dropping mercury electrode and the S.C.E. Pure nitrogen was passed in order to maintain the inert atmosphere. All measurements were made at 30±0.1°C. Both direct (salt solution in the cell) and reverse ($K_4Mo(CN)_8$ in the cell) titrations were performed with different concentrations of the reactants.

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

Results

TABLE I. CONDUCTOMETRIC TITRATIONS

Direct: Salt soln. in the cell.

Salt Soln. in the cell Vol., cc.	Concn., M	Vol. of 0.05 M $K_4Mo(CN)_8$ from the curves, cc. $NiCl_2$	$CoCl_2$	Ratio Ni^{2+}: $Mo(CN)_8^{4-}$	Co^{2+}: $Mo(CN)_8^{4-}$
40	0.00075	0.4	0.38	2 : 1.25	2 : 1.1
40	0.00125	0.53	0.55	2 : 1.05	2 : 1.08
40	0·0020	0.90	1.0	2 : 1.09	2 : 1.1
40	0.0025	0.98	1.08	2 : 1.0	2 : 1.08

Reverse: Potassium molybdocyanide in the cell.

$K_4Mo(CN)_8$ in the cell Vol., cc.	Concn., M	Vol. of 0.1 M salt soln. from the curves, cc. $NiCl_2$		$CoCl_2$		Ratio Ni^{2+}: $Mo(CN)_8^{4-}$	Co^{2+} : $Mo(CN)_8^{4-}$
40	0.0020	0.6	1.32	0.7	1.6	1 : 1.3 ; 2 : 1.04	1 : 1.3 ; 2 : 1
40	0.0025	0.76	1.85	0.88	2.0	1 : 1.2 ; 2 : 1.08	1 : 1.1 ; 2 : 1

TABLE II. POTENTIOMETRIC TITRATIONS

Direct: Potassium molybdocyanide in the cell.

$K_4Mo(CN)_8$ Vol., cc.	Concn., M	Vol. of salt soln. from the curves, cc. $NiCl_2$	$CoCl_2$	Ratio Ni^{2+}: $Mo(CN)_8^{4-}$	Co^{2+}: $Mo(CN)_8^{4-}$
10	0.02	3.8	4.1	2 : 1.05	2.05 : 1
10	0.0125	2.4	2.6	2 : 1.04	2.01 : 1
10	0.01	2.0	2.1	2 : 1.0	2.0 : 1

Reverse: Salt soln. in the cell.

Salt soln. in the cell Vol., cc.	Concn., M	Vol. of 0.05 M $K_4Mo(CN)_8$ from the curves, cc. $NiCl_2$	$CoCl_2$	Ratio Ni^{2+}: $Mo(CN)_8^{4-}$	Co^{2+}: $Mo(CN)_8^{4-}$
10	0.02	2.15	2.0	2 : 1.07	2 : 1.0
10	0.0125	1.3	1.7	2 : 1.04	2 : 0.87
10	0.01	1.0	1.0	2 : 1.0	2 : 1.0

TABLE III. AMPEROMETRIC TITRATIONS

Direct: Salt soln. in the cell.

Salt solution Vol., cc.	Cocn., M	Vol. of 0.1 M $K_4Mo(CN)_8$ from the curves, cc, $NiCl_2$	$CoCl_2$	Ratio Ni^{2+}: $Mo(CN)_8^{4-}$	Co^{2+}: $Mo(CN)_8^{4-}$
20	0.005	0.53	0.54	2 : 1.01	2 : 1.08
20	0.0075	0.77	0.77	2 : 1.02	2 : 1.02

Reverse: $K_4Mo(CN)_8$ in the cell.

$K_4Mo(CN)_8$ Vol., cc.	Concn., M	Vol. of 0.1 M $NiCl_2$ from the curves, cc.	Ratio Ni^{2+} : $Mo(CN)_8^{4-}$
20	0.0025	1.0	2 : 1
20	0.0030	1.2	2 : 1
20	0.00375	1.5	2 : 1

Discussion

The reaction between nickel chloride/cobalt chloride and potassium molybdocyanide may be represented by the following stoichiometric equations:

$$MCl_2 + K_4Mo(CN)_8 = K_2MMo(CN)_8 + 2KCl \quad (1)$$

$$3MCl_2 + 2K_4Mo(CN)_8 = K_2M_3(Mo(CN)_8)_2 + 6KCl \quad (2)$$

$$2MCl_2 + K_4Mo(CN)_8 = M_2Mo(CN)_8 + 4KCl \quad (3)$$

$$MCl_2 + xK_4Mo(CN)_8 = K_2MMo(CN)_8 \cdot (x-1)K_4Mo(CN)_8 + 2KCl \quad (4)$$

(adsorption complex)

The results on conductometric, potentiometric and amperometric titrations summarized in the foregoing paragraph give a ratio of $2M^{2+}$: $1Mo(CN)_8^{4-}$ pointing towards the formation of the complex $M_2Mo(CN)_8$ (M being Ni/Co) in accordance with Eq. 3 given above. Further, a ratio of 1 : 1 for the reactants is also found in the case of conductometric titration when the metal salt is added to the potassium molybdocyanide in the conductivity cell. For this ratio the complex formed would have the composition $K_2MMo(CN)_8$.

The combining ratios (both 2 : 1 and 1 : 1) show a slight discrepancy from the stoichiometric equations. For almost all the different concentrations of the reactants employed for these titrations, the amount of potassium molybdocyanide required is larger than the theoretical values. This behavior can well be explained by assuming that the freshly precipitated complexes have got the property of adsorbing $Mo(CN)_8^{4-}$ ion. An indirect proof of the adsorptive capacity of the complexes was forthcoming from our preliminary experiments. There it was found that the green precipitate of nickel molybdocyanide can be transformed into a stable sol when nickel chloride is added to a little excess of potassium molybdocyanide. However, mixing in the reverse order ($K_4Mo(CN)_8$ to $NiCl_2$) resulted in a thick precipitate rather than a sol. A similar behavior was found with cobalt molybdocyanide which could be obtained in the form of a stable orange colored sol by using excess of potassium molybdocyanide.

The potentiometric studies need a special mention here. We observed that potentiometric titrations for this precipitation reaction can be successfully performed by employing a $Mo(CN)_8^{4-} \rightleftarrows Mo(CN)_8^{3-} + e$ couple at bright platinum electrode. Typical curves (Fig. 2A) are obtained when the metal solution is added to the solution of potassium molybdocyanide containing a little potassium molybdicyanide. But in the case of reverse titrations (Fig. 2B) the curves are of a different nature, the e. m. f. increasing in the initial stages before showing a downward slope. This behavior points towards the fact that the molybdo-molybdicyanide couple attains equilibrium condition when an optimum amount of the reagent is present in the titrating cell. When sufficient amount of molybdocyanide has been added from the burette the curves have got the typical nature.

Amperometric titrations carried out with potassium molybdocyanide in the polarographic cell are different in shape than those which should be obtained on theoretical considerations, for such titrations (reducible ions added to non-reducible ions in the cell). The current increases appreciably on adding the titrant (Fig. 3B) and this is more so for Co^{2+} solution (results not given). It was thought that the increase in current might be due to the formation of some intermediate soluble complex. The products of interactions at different stages in this region were taken separately and polarograms drawn. The $E_{1/2}$ in each case corresponded to the $E_{1/2}$ of Ni^{2+} (−1.1 V.) and Co^{2+} (−1.2 V.) thereby showing the non-existence of a soluble complex in between. Titrations with the metal solution in the cell (Fig. 3A) were of the same nature as required on theoretical grounds. It is quite likely that the colloidal nature of the solution in the former case influence the performance of the dropping mercury electrode and typical curves are not obtained there.

Summary

The composition of the freshly precipitated nickel and cobalt cyano molybdates was determined using conductometric, potentiometric and amperometric methods. The nickel compound is green in color and its composition may be represented as $Ni_2Mo(CN)_8$. The orange precipitate of the cobalt cyano molybdate has also got the composition $Co_2Mo(CN)_8$. Reverse conductometric titration (salt solution added to molybdocyanide) give evidence of the complexes $K_2NiMo(CN)_8$ and $K_2CoMo(CN)_8$. These titrations provide information of the adsorption of $Mo(CN)_8^{4-}$ ions by the freshly precipitated complex. Both the compounds show tendency to pass into the colloidal state when the salt solution is added to excess of potassium octacyano molybdate.

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