[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS]

The Preparation and Some Properties of Potassium Hydroxopentacyanocobaltate(III)

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RECEIVED JULY 14, 1952

Potassium hydroxopentacyanocobaltate(III) is prepared by air oxidation of moist solid potassium pentacyanocobaltate (II). The solid is diamagnetic. In solution it shows a reddish-brown color, but undergoes rather rapid change. Titration curves and spectrophotometric data indicate that one reaction occurring early after solution is $2[Co(CN)_5(OH)]^{\equiv} = [Co(CN)_4(OH)_2]^{\equiv} + [Co(CN)_6]^{\equiv}$. Evidence has also been obtained that the hydroxopentacyano complex is formed as an intermediate prior to actual reduction in the action of potassium amalgam upon aqueous potassium hexacyanocobaltate(III).

Comparatively few pentacyanocobaltate(III) complexes have been isolated.[1] In connection with the preparation of some aquopentacyanocobaltate(III) compounds, Rây and Dutt[2] mention the formation of a hydroxopentacyanocobaltate(III) complex in solution. The formation of this complex as a reddish-brown colored intermediate in the production of hexacyanocobaltate(III) ion by oxidation of cobalt(II) salts in excess aqueous cyanide has also been postulated.[3] In neither case, however, was its preparation described.

This paper describes the preparation of potassium hydroxopentacyanocobaltate(III), and reports some properties of the compound, especially some involving its behavior in aqueous solution. Observations are also included which indicate that this compound is formed in solution as an intermediate product in the course of the reduction of potassium hexacyanocobaltate(III) by means of potassium amalgam.

Experimental

Preparation of Potassium Hydroxopentacyanocobaltate (III).—A solution containing 20 g. of cobalt(II) nitrate hexahydrate in 100 ml. of water was boiled to expel oxygen, then chilled in an ice-bath, and a concentrated solution of potassium cyanide was added dropwise until the precipitate which first formed had redissolved. To the resulting olive-green solution, cold 95% ethanol was added, producing a copious precipitate of violet crystals which were quickly collected on a sintered-glass filter. These operations were all carried out in an oxygen-free nitrogen atmosphere. Determination of the Co:CN ratio in the violet compound showed it to be 1:5. This result, together with the appearance of the material and mode of formation, indicated it to be the cyanocobaltate(II) compound which Adamson[4] has shown to be $K_3Co(CN)_5$.

Air was next drawn through the moist violet colored solid on the filter until it had assumed a uniform brown color. The brown solid product was washed with ethanol and with ether, then dried in a vacuum desiccator over sulfuric acid or magnesium perchlorate, and used without further treatment. Some attempts to recrystallize the material by dissolving it in water and quickly adding cold ethanol yielded a solid which showed no significant difference in composition. In some of these attempts a dark brown oily liquid which did not crystallize readily was obtained.

Methods of Analysis. (a) **Cobalt.**—The sample was fumed with sulfuric acid to decompose the complex and to destroy the cyanide. Cobalt was then determined by electrolytic deposition.[5]

(b) **Potassium.**—After treatment of the sample with sulfuric acid as in (a) and removal of cobalt(II) by sulfide precipitation, potassium was determined as sulfate.

(c) **Cyanide.**—It was not possible to titrate the cyanide directly by the method of Deniges.[6] Moreover liberation and distillation of free hydrogen cyanide by means of sulfuric acid, with subsequent determination of the collected cyanide, was unsatisfactory as was to be expected, inasmuch as Bassett and Corbet[7] have shown that when either potassium hexacyanoferrate(III) or hexacyanocobaltate(III) is boiled with sulfuric acid only a part of the cyanide is evolved as hydrogen cyanide, the remainder undergoing hydrolysis. However, since hydrolysis of the hydrogen cyanide yields an equivalent amount of ammonium salt, the following method was employed. The sample was boiled with sulfuric acid, initially 1.5–2.5 *M*, until the solution had become clear and deep blue in color. The hydrogen cyanide liberated in this step was collected in 0.1–0.5 *M* potassium hydroxide, and the cyanide then determined with standard silver nitrate using an iodide end-point.[8] The sulfuric acid solution containing ammonium salt resulting from the hydrolysis of part of the cyanide was then made alkaline, the ammonia distilled into cold saturated boric acid solution and titrated using brom cresol green–methyl red indicator. From the results of the two steps together the amount of cyanide initially present was computed.

To test the suitability of the methods outlined above, samples of $K_3Co(CN)_6$ were analyzed. The results indicated a water content of about 3% in the preparation used, but gave the ratios 3.03:1.00:5.98 for K:Co:CN.

(d) **Hydroxide.**—Solutions of the brown solid were found to be alkaline to phenolphthalein. Samples were therefore titrated with standard sulfuric acid both potentiometrically and with indicators. The total alkalinity was calculated as hydroxide. Certain unexpected features of the titration are discussed in a later section.

Results of analyses of several different preparations of the brown solid are given in Table I.

TABLE I

ANALYSIS OF THE COMPLEX[a]

	Weight, % K	Co	CN	OH
Found	33.8	16.37	37.50	4.85
	34.0	16.43	37.65	4.95
	34.9	16.78	37.80	5.02
		17.55		
		17.95		
Av.	34.2	17.02	37.65	4.94
Ionic ratios	3.03	1.00	5.01	1.01
Wt. % calcd. for				
$K_3[Co(CN)_5(OH)]$	36.28	18.23	40.23	5.26
$K_3[Co(CN)_5(OH)]\cdot H_2O$	34.36	17.27	38.11	4.98
$K_3[Co(CN)_5(OH)]\cdot 2H_2O$	32.64	16.40	36.20	4.73

[a] Data in the same horizontal row do not necessarily refer to the same preparation.

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[1] N. V. Sidgwick, "The Chemical Elements and their Compounds," Oxford University Press, London, 1950, p. 1398.

[2] P. R. Rây and N. K. Dutt, *Z. anorg. allgem. Chem.*, **234**, 65 (1937).

[3] R. Uzel and B. Ježek, *Collection Czechoslov. Chem. Communs.*, **7**, 497 (1935).

[4] A. W. Adamson, THIS JOURNAL, **73**, 5710 (1951).

[5] N. H. Furman, Editor, "Scott's Standard Methods of Analysis," Vol. I, 5th ed., D. Van Nostrand Co., Inc., New York, N. Y., 1925, p. 315.

[6] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," Revised ed., The Macmillan Co., New York, N. Y., 1946, p. 479.

[7] H. Bassett and A. S. Corbet, *J. Chem. Soc.*, **125**, 1358 (1924).

[8] Kolthoff and Sandell, ref. 6, p. 574.

The compound is rather hygroscopic so the water content may be expected to vary somewhat with the different preparations. The ionic ratios, together with the actual percentages indicate the compound to be hydrated potassium hydroxopentacyanocobaltate(III), and the averages correspond fairly closely to the formulation $K_3[Co(CN)_5(OH)]\cdot H_2O$.

The magnetic susceptibility of the solid compound was determined using a Gouy balance, and the value $\chi_g = -0.064 \times 10^{-6}$ c.g.s. unit at 25° was obtained.

Properties of Aqueous Solutions of Potassium Hydroxopentacyanocobaltate(III).—When the solid was dissolved in water it at first produced a dark reddish-brown solution which, however, became progressively lighter upon standing. In the course of perhaps a half-hour the color was distinctly yellow and it eventually faded to a pale yellow color which was retained for several weeks. These observations make it clear that the original complex is not very stable in solution, but must undergo rather rapid change. The solutions gave no test for free cyanide ion with ammoniacal copper(II) sulfate, even when allowed to stand overnight with this reagent, nor did they show any reducing action toward ammoniacal silver nitrate. Upon being boiled, the solutions slowly deposited a black precipitate which contained cobalt but no cyanide. In view of the composition and color of this product and the circumstances under which it was formed it was very probably hydrous cobalt(III) oxide. The residual solution possessed the pale yellow color characteristic of hexacyanocobaltate(III) ion.

Titration with Acid.—Preliminary titrations with 0.1 *N* sulfuric acid showed the existence of a phenolphthalein end-point and a separate methyl red end-point. Potentiometric titrations were then carried out, using a glass electrode with a Beckman model G *p*H meter. The results were not at all what would be expected from the titration of a simple monohydroxo complex. Instead, two distinct breaks in the curve were obtained: the first occurring when one-half equivalent of acid per atom of cobalt had been added, the second at one equivalent of acid per atom of cobalt. These results strongly suggest that a species is being titrated which contains two equivalents of basic group per cobalt atom, but that only half of the total cobalt is present in this species.

The titration data may be readily interpreted if it is assumed that when the hydroxopentacyano complex dissolves the following reaction ensues

$$2[Co(CN)_5(OH)]^{\equiv} = [Co(CN)_4(OH)_2]^{\equiv} + [Co(CN)_6]^{\equiv} \quad (1)$$

Thus a dihydroxocomplex would be expected to give a titration curve of the type obtained, with the first break corresponding to one-half equivalent of hydroxyl per atom of total cobalt. Moreover, such a reaction as this is at least qualitatively in accord with the visual evidence that a change is occurring. In view of the change in color described above, it seemed of interest to investigate the solutions spectrophotometrically.

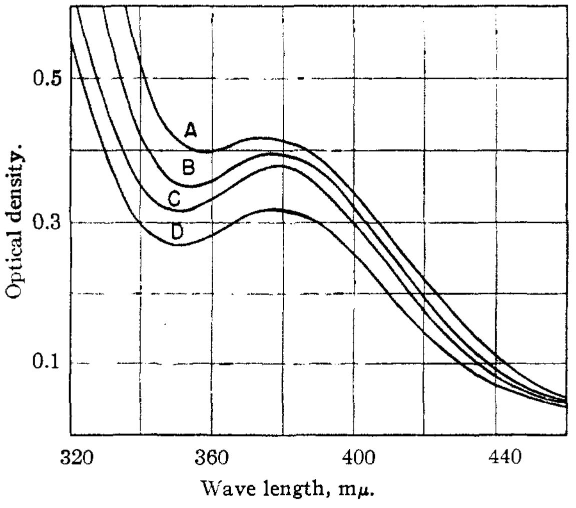

Fig. 1.—Absorption spectra of $K_3[Co(CN)_5(OH)]\cdot H_2O$ solutions: A, 20 min.; B, 2.5 hr.; C, 1 day; D, 4 days after preparation of the solution; 7.0×10^{-5} g. cobalt per ml.; cell length, 1.00 cm.; 20°; optical density = log (100/% transmission).

Spectrophotometric Studies.—A Beckman model DU spectrophotometer was used in this work, a tungsten light source being employed above 320 mμ and a hydrogen discharge tube in the range 240–320 mμ. Measurements were made in 1-cm. quartz cells at 20°. Solutions contained 7.0 × 10^{-5} g. of cobalt per ml. in all the studies reported. No absorption above 500 mμ was found for any of the compounds studied.

The results, while they do not afford conclusive proof of the reaction postulated above, appear nevertheless to be consistent with this interpretation. Figure 1 shows the absorption curves of aqueous solutions of potassium hydroxopentacyanocobaltate(III) at various intervals of time after preparation of the solution. An absorption peak occurs at 380 mμ, and it will be noted that, although the intensity of absorption decreases as the solution ages, the location of the peak remains constant. Strong general absorption below about 340 mμ is also shown by these solutions.

After treatment with acid, the solutions still show an absorption peak at 380 mμ (Fig. 2). Moreover after complete neutralization with acid an additional peak at 310 mμ appears. This is especially significant since the hexacyanocobaltate(III) complex shows an absorption peak at 308 mμ.[9] Presumably its presence before acidification is obscured by the strong absorption below 340 mμ by the dihydroxo complex. Incidentally, use of perchloric instead of sulfuric acid gave essentially the same results.

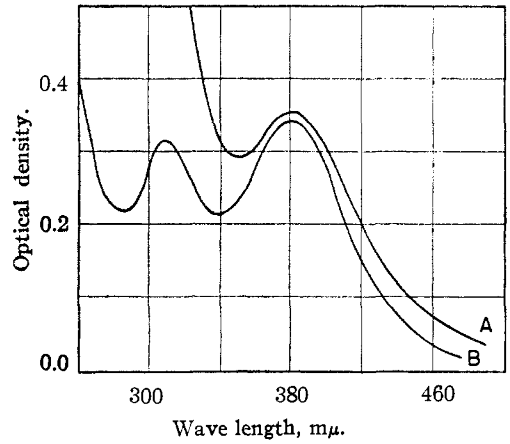

Fig. 2.—Absorption spectra of solutions of $K_3[Co(CN)_5(OH)]\cdot H_2O$ after addition of: A, one-half equivalent of sulfuric acid; B, one equivalent of sulfuric acid per mole of cobalt; 7.0×10^{-5} g. cobalt per ml.; cell length, 1.00 cm.; 20°; optical density = log (100/% transmission).

Since acidification of a dihydroxo complex should yield the corresponding diaquo compound, potassium diaquotetracyanocobaltate(III) was prepared according to the method of Rây and Guptachaudhuri,[10] and spectrophotometric curves were determined on solutions of this compound for comparison, with results shown in Fig. 3. A peak at about 380 mμ is clearly shown both in acidic and in basic solution. Below 320 mμ continued strong absorption was observed with no indication of a maximum. However, in order to get the solid compound as prepared into solution it was found necessary to add small amounts of sodium hydroxide or nitric acid. Under these conditions the absolute values of optical density represented in Fig. 3, especially in the shorter wave length region, are not very significant That none of the peaks observed can be attributed to the presence of the aquopentacyano complex was shown by the fact that solutions of potassium aquopentacyanocobaltate(III) prepared according to the method of Rây and Dutt,[2] were found to have an absorption peak at 350 mμ, both in

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[9] L. Szegö and P. Ostinelli, *Gazz. chim. ital.*, **60**, 946 (1930).

[10] P. R. Rây and I. Guptachaudhuri, *Z. anorg. u. allgem. Chem.*, **220**, 154 (1934).

neutral and in alkaline solution, but gave none at 310 or 380 mμ.

When a solution of potassium hydroxopentacyanocobaltate(III) was heated just below boiling with excess potassium cyanide, it was found that the absorption maximum at 380 mμ characteristic of these solutions disappeared, and that the resulting curve corresponded simply to that of a mixture of potassium cyanide and $K_3Co(CN)_6$, with the peak at 310 mμ plainly evident.

A pronounced characteristic of solutions of the cyanocobaltate(III) complexes studied was the change in intensity of absorption with time which they showed, as indicated in Fig. 1, for example. Similar studies were made on acidified solutions of the original complex, and both of the characteristic peaks shown in Fig. 2 were found to diminish rather rapidly, especially at first. Solutions of potassium hexacyanocobaltate(III) either in neutral or in acid solutions were likewise found to exhibit a progressive decrease in absorption in the 310 mμ region with age. The reaction responsible for the observed change in absorption in this case may well be retarded or prevented in the presence of excess cyanide, inasmuch as Adamson, Welker and Volpe[11] have shown that hexacyanocobaltate(III) in the presence of equimolar concentrations of radiocyanide shows no exchange of cyanide even after 190 hours. In the present experiment, however, no free cyanide was present in the solution at the beginning. Although the evidence discussed above indicates that reaction (1) occurs probably very soon after the hydroxopentacyano complex is dissolved, it must be borne in mind that other reactions undoubtedly ensue, and that the system is not a particularly simple one.

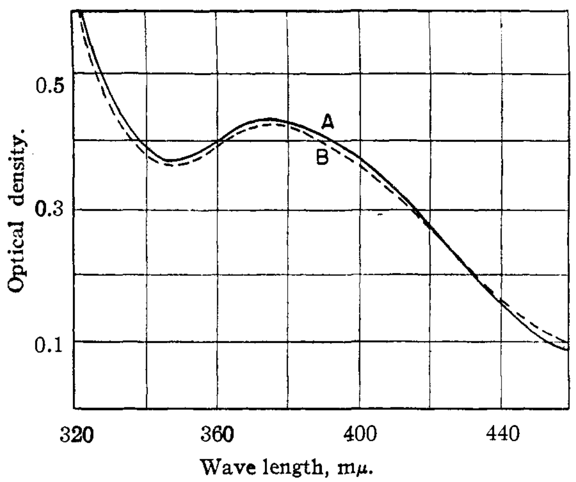

Fig. 3.—Absorption spectra of $K[Co(CN)_4(H_2O)_2]$ in: A, basic solution; B, acidic solution; 7.0×10^{-5} g. cobalt per ml.; cell length, 1.00 cm.; 20°; optical density = log (100/% transmission).

Miscellaneous Observations.—In the course of some experiments on the reduction of aqueous potassium hexacyanocobaltate(III) with potassium amalgam (3%), no visible change was observed for the first 10 or 15 minutes after which time the solution became reddish-brown in color and then changed to olive-green upon further reaction with the amalgam. The reddish-brown color could be restored by shaking the olive-green solution with air, but the green color returned when the solution was again allowed to stand over the amalgam. These changes could be carried out repeatedly. Both the red-brown solution and the green one gave tests for free cyanide with ammoniacal copper(II) sulfate. Upon decanting the olive-green solution and adding cold 95% ethanol to it, violet crystals of potassium pentacyanocobaltate(II) were obtained. These observations strongly indicate that, in the treatment of aqueous hexacyanocobaltate(III) with potassium amalgam, the replacement of a cyanide group in the complex precedes its reduction to pentacyanocobaltate(II). It is of interest to note in this connection that Hume and Kolthoff[12] found potassium hexacyanocobaltate(III) in the presence of excess potassium cyanide as supporting electrolyte not to be reducible at the dropping mercury electrode.

It seems worthwhile to point out also that the reddish-brown solution which appears in the course of the preparation of potassium hexacyanocobaltate(III) from cobalt(II) salts should very probably not be ascribed to the presence of $K_4Co(CN)_6$ as has been assumed,[13] but instead contains at least one cobalt(III) complex having fewer than six cyanide groups coördinated to the cobalt atom.

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[11] A. W. Adamson, J. P. Welker and M. Volpe, THIS JOURNAL, **72**, 4030 (1950).

[12] D. N. Hume and I. M. Kolthoff, *ibid.*, **71**, 867 (1949).

[13] J. H. Bigelow, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 225.

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Studies on Coördination Compounds. I. A Method for Determining Thermodynamic Equilibrium Constants in Mixed Solvents[1,2]

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RECEIVED MAY 2, 1952

In the past "*p*H" titrations in partially non-aqueous solvents have been made in order to determine the stability of coordination compounds. The interpretation of such data has been reconsidered with the object of obtaining thermodynamic stability constants. It is assumed that the activity coefficient of electrolytic solutes in these solvents is determined solely by the solvent composition and the ionic concentration. Experimental substantiation of the assumption is given and the method of calculating thermodynamic stability constants is discussed.

Several years ago Bjerrum introduced[3] the technique of determining the stability of metal ammines by a potentiometric titration in which a glass electrode was used to determine the hydrogen ion concentration during the formation reaction. The ease with which individual equilibrium constants for the *n* successive, reversible, step-reactions of the formation of a complex MA_n[4] could be determined led to the application of the method to other agents.

The stability of complexes with polydentate

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[1] A portion of a thesis presented by L. G. Van Uitert in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1952.

[2] For tables of data from which Figs. 1–4 were plotted order Document 3663 from American Documentation Institute, % Library of Congress, Washington 25, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

[3] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Sons, Copenhagen, 1941.

[4] M designates a metal ion; A, a complexing ligand.