chromite were bright green by transmitted light.

Precautions to be Observed.—Appreciable attack of the platinum crucibles was observed when the concentration of sought compound to PbO or Bi_2O_3 was too high. Dilute solutions, such as the ratio 1:6 used, produced little or no attack. Furnace linings should be new or uncontaminated by previous runs with other solvents. The presence of certain volatile substances in the muffle have been known to cause reduction of the PbO with subsequent loss of the crucible due to the alloying of Pt and Pb.

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Halogenopentacyano Compounds of Cobalt(III)

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The new compounds $K_3Co(CN)_5Br$ and $K_3Co(CN)_5I$ are described. They may be prepared either by the action of the appropriate halogen on aqueous pentacyanocobaltate(III) ion or by that of potassium cyanide on the appropriate aqueous halogenopentamminecobaltate(III) species. Possible mechanisms are discussed.

The number of known cyano complexes of Co(III) is quite limited, in contrast to the extensive family of complex ammines. The species $Co(CN)_6^{-3}$ is, of course, well known, and the following mixed cyano complexes have been reported: $K_2Co(CN)_5(H_2O)$,[1] $KCo(CN)_4(H_2O)_2$[2] and $K_4Co(CN)_5(S_2O_3)$.[1] The existence in aqueous solution of the ion $Co(CN)_4(OH)_2^{-3}$ has been postulated,[3] but the evidence is not unambiguous. Finally, a binuclear complex containing five cyanides per cobalt appears to result from the air oxidation of $Co(CN)_5^{-3}$.[4]

No mixed halogenocyano complexes of Co(III) are known, nor, indeed, do there appear to be any known for any other central metal ion. In what follows the properties of the new compounds $K_3Co(CN)_5Br$ and $K_3Co(CN)_5I$ will be described, along with evidence for the probable existence of $K_3Co(CN)_5Cl$, and a discussion of the rather interesting reactions whereby these species may be prepared.

Experimental

Preparation of $K_3Co(CN)_5Br$ by the Ray and Dutt reaction.—[1,5] Twenty-one grams of potassium bromopentamminocobaltate(III) was added, with stirring, to an aqueous solution of 24 g. of potassium cyanide, giving a dark reddish-yellow solution which evolved ammonia copiously. Addition of alcohol to about 75% by volume gave a voluminous cream colored precipitate which was filtered off, washed with alcohol and ether, and dried in a vacuum desiccator.

The product was analyzed for potassium by the chloroplatinate method,[6] for cobalt by the α-nitroso-β-naphthol method[7] (after evaporation with hydrochloric acid to decompose the complex), and for bromide by an adaptation of a method reported by Kamm.[8] One quarter of a gram of the complex was refluxed with 35 cc. of absolute ethanol and 3.5 g. of metallic sodium was added gradually. After about two hours, the solution was cooled, and 50 cc. of water added. The solution was then acidified with nitric acid and the bromide present determined by the Volhard method. Found for K, 30.5 ± 0.4%; Co, 15.7 ± 0.1%; Br, 19.4 ± 0.05%. Calcd. for $K_3Co(CN)_5Br$: K, 30.4; Co, 15.3; Br, 20.7. Calcd., assuming 6.3% $K_2CO(CN)_5(H_2O)$ impurity: K, 30.2; Co, 15.6; Br, 19.4.

The compound is very soluble in water and insoluble in organic solvents; as with $Co(CN)_6^{-3}$, insoluble salts are formed with a number of transition metal ions. The dry potassium salt is light brown in color, and, in aqueous solution gives an absorption maximum at 393 mμ with an extinction coefficient of 163.

Rate Studies.—Qualitative rate data were obtained for the above reaction by adding aqueous potassium bromopentamminecobaltate(III) to solutions of potassium cyanide buffered to the desired *p*H by either acetate or phosphate buffer. Qualitative rates were obtained either by noting the rate of color change or, in some cases, from a spectrophotometric measurement of the optical density.

Preparations by the Reaction of Halogen with $Co(CN)_5^{-3}$.—The procedure for the preparation of the bromide was as follows. A solution of 20 g. of cobalt(II) nitrate hexahydrate in 150 cc. of water was deaerated by bubbling nitrogen through it, and cooled to *ca.* 5°. Solid potassium cyanide was then added slowly, in amount sufficient to give a clear solution (a slight excess over five cyanides per cobalt). This solution was then added rapidly to one containing a small excess of bromine, and the product was isolated by alcohol precipitation as described above. The $K_3Co(CN)_5Br$ product was analyzed for cobalt by the method of Cartledge and Nichols[9] (after sulfuric acid digestion), for potassium by a flame spectrophotometer, and for bromide, as before. *Anal.* Calcd. for $K_3Co(CN)_5Br$: K, 30.3; Co, 15.3; Br, 20.7. Found: K, 28.5; Co, 15.8; Br, 21.9. The analyses suggest the presence of an impurity such as $CoBr_2$, but no satisfactory method was found to purify the product further.

The procedure for the preparation of $K_3Co(CN)_5I$ was similar to that above, except that aqueous potassium triiodide was employed instead of bromine water. Analyses were likewise by the same procedures as above. *Anal.* Calcd. for $K_3Co(CN)_5I$; K, 27.3; Co, 13.6; I, 29.3. Found: K, 25.9; Co, 14.0; I, 29.8. The product was reddish brown in color, its solubility characteristics were similar to those of $K_3Co(CN)_5Br$, and its aqueous solution showed a shallow absorption maximum at 495 mμ, with an extinction coefficient of 95, followed by an intense band in the near ultraviolet.

The course of the reaction with aqueous chloride as oxi-

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(1) P. R. Ray, *J. Ind. Chem. Soc.*, 327 (1927); P. R. Ray and N. K. Dutt, *Z. anorg. allgem. Chem.*, **234**, 65 (1937).

(2) P. R. Ray and T. Guptuchanduri, *ibid.*, **220**, 154 (1934).

(3) L. C. Smith, J. Kleinberg and E. Griswold, THIS JOURNAL, **75**, 449 (1953).

(4) W. K. Wilmarth, private communication.

(5) This work was done in part by J. M. Grunlund.

(6) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Analysis," The Macmillan Co., New York, N. Y., 1936, p. 390.

(7) I. M. Kolthoff and E. B. Sandell, ref. 6, p. 77.

(8) O. Kamm, "Qualitative Organic Analysis," John Wiley and Sons, New York, N. Y., 2nd Ed., p. 199.

(9) G. H. Cartledge and P. M. Nichols, *Ind. Eng. Chem., Anal. Ed.*, **13**, 20 (1941).

dant was less clean cut. On carrying out the above type of procedure, a light yellow solid was obtained. It contained only about half of the theoretical amount of chloride, although the potassium and cobalt analyses were correct. Chloride, in this course, was estimated from the specific activity of a preparation containing radiochlorine, since neither the Volhard nor other methods attempted proved satisfactory. It seems likely that some $K_3Co(CN)_5Cl$ was obtained, but mixed with considerable $K_3Co(CN)_6$ impurity. A similar product may also be obtained by a Ray and Dutt type reaction, *i.e.*, addition of potassium cyanide to aqueous $Co(NH_3)_5Cl^{+2}$. The compound gave an absorption maximum at 370 mμ, with an apparent extinction coefficient of 160, and a shoulder at 320 mμ, probably due to $K_3Co(CN)_6$.

For all three cases above, it was important that the solution of $Co(CN)_5^{-3}$ be added *to* one containing a *slight excess* of halogen. Deviation from either of the italicized specifications led to insoluble, polymeric products.

Results and Discussion

Ray and Dutt[1] reported the preparation of $K_4Co(CN)_5(S_2O_3)$ by the reaction of potassium cyanide with the corresponding pentammine, and the analogous type of reaction employed here was

$$Co(NH_3)_5X^{+2} + 5CN^- = Co(CN)_5X^{-3} + 5NH_3 \quad (1)$$

where **X** denotes a halogen atom. The mechanism cannot involve the displacement and subsequent reentry of the halogen. The halogenopentacyano complexes are unstable toward aquation,[10] yet the product of reaction (1) is entirely specific for the halogen present in $Co(NH_3)_5\mathbf{X}^{+2}$ even though other halide ions are present in excess in the mixture. Since any Co(II) impurity would form $Co(CN)_5^{-3}$,[11] catalysis by an atom transfer process is a possibility[12]

$$Co(CN)_5^{-3} + Co(NH_3)_5X^{+2} = Co(CN)_5X^{-3} + Co(NH_3)_5^{+2} \quad (2)$$

$$Co(NH_3)_5^{+2} + 5CN^- = Co(CN)_5^{-3} + 5NH_3 \text{ (fast)} \quad (3)$$

For the case of **X** = Br, reaction (1) is immeasurably fast in alkaline solution, with 0.002 M $Co(NH_3)_5Br^{+2}$ and 0.1 *M* potassium cyanide. There is a strong *p*H dependence; in buffered solutions containing the above concentrations of reactants, the time of half reaction was less than one minute at $(H^+) = 1.1 \times 10^{-7}$, *ca.* one minute at $(H^+) = 1.4 \times 10^{-7}$, and *ca.* five minutes at $(H^+) = 3.0 \times 10^{-7}$. At a *p*H of five, the rate was quite slow.

Under conditions such that the half-life was a few minutes, there was definite catalysis if the solution of complex was made *ca.* 0.001 *M* in cobalt(II) nitrate prior to the addition of potassium cyanide. However, the life of $Co(CN)_5^{-3}$ in small concentrations is short because of a rapid air oxidation, and, in acid media, also because of oxidation by solvent. Thus if cobalt(II) nitrate was added to the *potassium cyanide solution* prior to its addition to that of the complex, there was no catalysis. Moreover, in the first mentioned test of added Co(II) impurity, the initial catalysis due to the momentary presence of $Co(CN)_5^{-3}$ was followed by a period of slow further reaction. It thus appears that while reactions (2) and (3) may account for the rapid reaction in basic solution, some other path is also involved. Evidently, kinetic studies would be of interest.

The nature of the reaction of aqueous halogens with $Co(CN)_5^{-3}$ is also unusual. The net process, given by reaction (4), has the same character of specificity as does reaction (1) in that if the oxidation were by electron transfer, the expected product would be $Co(CN)_5(H_2O)^{-2}$. It seems clear that in this as well as in other cases where a Co(II) species is oxidized,[13] oxidation and coördination of the oxidizing agent occurs in a single act. A possible mechanism for (4) would be

$$Co(CN)_5^{-3} + {}^1/_2X_2 = Co(CN)_5X^{-3} \quad (4)$$

$$Co(CN)_5^{-3} + X_2 = Co(CN)_5X^{-3} + X \text{ (or } Co(CN)_5X_2^{-3}) \quad (5)$$

$$Co(CN)_5^{-3} + X \text{ (or } Co(CN)_5X_2^{-3}) = Co(CN)_5X^{-3} \text{ (or } 2Co(CN)_5X^{-3}) \quad (6)$$

The poor yield when **X** = Cl may be due to an energetic difficulty with reaction (5) stemming from the high Cl–Cl bond energy.

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[10] See A. W. Adamson and F. Basolo, *Acta Chem. Scand.*, **9**, 1261 (1955); R. G. Pearson, R. E. Meeker and F. Basolo, THIS JOURNAL, **78**, 709 (1956).

[11] A. W. Adamson, *ibid.*, **73**, 5710 (1951).

[12] The author is indebted to Dr. H. Taube for this suggestion.

[13] See A. W. Adamson, *Rec. trav. chim. Pays Bas*, in press.