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Binuclear Complex Ions. III. Formation of Peroxo and Cyano Bridged Complexes by Oxidation of the Pentacyano Complex of Cobalt(II)¹⁻³

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The binuclear ions $[(\text{NC})_5\text{Co}^{\text{III}}\text{OOCo}^{\text{III}}(\text{CN})_5]^{-6}$ and $[(\text{NC})_5\text{Fe}^{\text{II}}\text{CNC}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_5]^{-6}$ have been prepared by oxidation of the pentacyano complex of Co(II) with O_2 and $\text{Fe}(\text{CN})_6^{-3}$, respectively. The one electron oxidation of these binuclear ions yields $[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}^{\text{IV}}(\text{CN})_5]^{-5}$ and $[(\text{NC})_5\text{Fe}^{\text{II}}\text{CNC}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_5]^{-5}$. Oxidation of the pentacyano complex of Co(II) with H_2O_2 , $\text{S}_2\text{O}_8^{--}$ and $[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}^{\text{III}}(\text{CN})_5]^{-6}$ yields $(\text{NC})_5\text{CoOH}_2^{--}$ as the major product in each instance. Only $\text{Cr}(\text{CN})_6^{-3}$ appears to be formed in the oxidation of the Cr(II) cyanide complex with either oxygen or hydrogen peroxide. $(\text{NC})_5\text{CoOH}_2^{--}$ undergoes spontaneous polymerization in solution and in the solid state. The mechanism of formation of the various complex ions is discussed in terms of outer sphere and bridged activated complexes.

Introduction

In recent years, Taube and his co-workers have emphasized the importance of the information which may be obtained when a complex ion which is labile with respect to ligand substitution is converted by oxidation to a complex ion which is inert with respect to such substitution. For an oxidation-reduction system which possesses such properties, the composition and geometry of the activated complex may be obtained, under favorable circumstances, by mere examination of the coordination sphere of the oxidized product.⁴

This approach has now been applied to the reactions of the pentacyano complex of Co(II) with a variety of oxidizing agents, and the results obtained provide evidence for paths in which the oxidant enters the coordination sphere of Co(II) and is found in the Co(III) product and paths in which

the oxidant does not become a part of the coordination sphere of the Co(III) product.

During the course of the present work, Adamson⁵ has established that oxidation of the pentacyano complex of Co(II) with bromine, iodine and chlorine produces, under some conditions, the ions $(\text{NC})_5\text{CoBr}^{-3}$, $(\text{NC})_5\text{CoI}^{-3}$ and possibly $(\text{NC})_5\text{CoCl}^{-3}$.

In the present work it has been established that in the oxidation of the pentacyano complex of Co(II) by oxygen or $\text{Fe}(\text{CN})_6^{-3}$, the oxidant is captured in the coordination sphere of Co with formation of the binuclear ions $[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}^{\text{III}}(\text{CN})_5]^{-6}$ and $[(\text{NC})_5\text{Fe}^{\text{II}}\text{CNC}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_5]^{-6}$, respectively. Some of the properties of $[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}^{\text{III}}(\text{CN})_5]^{-6}$ are reported, in particular its one electron oxidation to produce the binuclear complex $[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}^{\text{IV}}(\text{CN})_5]^{-5}$ containing Co in the formal oxidation states III and IV, thus extending our limited knowledge of binuclear peroxo complexes of Co(III, III) and Co(III, IV). The ion $[(\text{NC})_5\text{Fe}^{\text{II}}\text{CNC}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_5]^{-6}$ provides an interesting example of an inert bridged chemical complex having the same composition and geometry as the bridged activated complex for the reaction. It represents also an instance of an inert binuclear complex containing two different octahedrally substituted metal ions, a type of com-

(1) This work was supported by the Office of Naval Research and the Atomic Energy Commission. It is based in part on a dissertation submitted by A. Haim to the Graduate School of the University of Southern California in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

(2) (a) Paper I, L. R. Thompson and W. K. Wilmarth, *J. Phys. Chem.*, **56**, 5 (1952). (b) Paper II, W. K. Wilmarth, H. Graff and S. T. Gustin, *THIS JOURNAL*, **78**, 2683 (1956).

(3) Reported in part at the 131st Meeting of the American Chemical Society held in Miami, Florida, in April, 1957.

(4) A recent review of this subject by H. Taube has appeared in "Advances in Inorganic Chemistry and Radiochemistry," Vol. 1, Academic Press, Inc., New York, N. Y., 1959, Chap. 1.

(5) A. W. Adamson, *THIS JOURNAL*, **78**, 4260 (1956).

pound which hitherto has not been definitely characterized in aqueous solution.⁶

In the oxidation of the pentacyano complex of Co(II) by peroxydisulfate or $[(\text{NC})_5\text{Co}^{\text{II}}\text{OOC}^{\text{II}}(\text{CN})_5]^{-6}$, the oxidant is not captured in the coordination sphere of the Co(III) product, and the product of both reactions is the mononuclear ion $(\text{NC})_5\text{CoOH}_2^{-}$. The reaction with hydrogen peroxide also yields $(\text{NC})_5\text{CoOH}_2^{-}$, but in the absence of oxygen labelling experiments it cannot be ascertained whether the oxidant enters the coordination sphere of Co(II).

In a preliminary report,³ some of the results presented in this paper were given an alternate and incorrect interpretation. The revised interpretation given here will be justified in the experiments and discussion presented below.

Experimental

Instruments.—Absorption spectra were obtained with a Cary Model 14PM Recording Spectrophotometer. A Beckmann Model G pH meter was used for pH measurements. Current-voltage curves were obtained with a Sargent-Heyrovsky Model XII Polarograph. The technique described by Laitinen and Kivalo⁷ was followed, except for the use of a normal calomel electrode. The dropping mercury electrode had a column height of 69 cm, a drop time of 3.47 sec. and a value of 2.12 for $m^{2/3}t^{1/3}$. All solutions for polarographic investigation contained 0.01% gelatin and were deaerated by bubbling oxygen-free nitrogen for 15 min. prior to recording the polarogram. The polarographic cell and the reference electrode were kept in a thermostat at $25 \pm 0.1^\circ$.

Analysis.—Methods of analysis for C, H and N in the various cyanide complexes considered in this paper were developed by Mr. William J. Schenck, microanalyst in this department. To obtain complete combustion in the C and H analyses, it was necessary to mix the sample with potassium dichromate and raise the combustion temperature to 1050–1100°. For the N analysis it was necessary to mix the sample with copper oxide. In our later work, when Mr. Schenck's services were no longer available, the analyses of C, H and N were discontinued, since the results obtained from commercial analysts, who presumably did not take the above precautions, were irreproducible and internally inconsistent with respect to C and N.

Oxidation of the Pentacyano Complex of Co(II) with $\text{Fe}(\text{CN})_6^{-3}$.—The oxidation of 0.2 M Co(II) chloride in 1 M potassium cyanide was carried out in a nitrogen atmosphere at 0° by adding, with stirring, an equal volume of 0.2 M potassium ferricyanide. Visual observation suggested that the reaction was complete in the two minutes required to mix the solutions. Addition of ethanol to 80% in volume precipitated a mixture of 18% potassium ferrocyanide and 82% $\text{K}_6[(\text{NC})_5\text{Fe}^{\text{II}}\text{CNC}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_5]$, the composition being determined by various analytical procedures and eventual separation of the two complex ions by fractional precipitation of the barium salts. The yield, expressed in terms of $\text{K}_6[(\text{NC})_5\text{Fe}^{\text{II}}\text{CNC}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_5]$, was 66%.

Iron was analyzed spectrophotometrically according to Bastian, Weberling and Palilla⁸ after decomposition of the complexes with hot concentrated perchloric acid. Cobalt was determined according to Laitinen and Burdett⁹ after

(6) H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954), suggested that the reaction between Cr(II) and $\text{Fe}(\text{CN})_6^{-3}$ occurs via a bridged activated complex with the cyanide bridge persisting in the insoluble product. They also suggested that the intermediate green color observed in the reaction of IrCl_4^- with Cr(II) is due to the binuclear complex $(\text{H}_2\text{O})_2\text{CrClIrCl}_5$. W. H. Sphiman, S. C. Foti and W. Simon, *Anal. Chem.*, **27**, 1240 (1955), postulated the formation of a binuclear $(\text{Fe}^{\text{II}}, \text{Co}^{\text{III}})$ complex in the presence of nitroso-R salt.

(7) H. A. Laitinen and P. Kivalo, *THIS JOURNAL*, **75**, 2198 (1953).

(8) R. Bastian, R. Weberling and F. Palilla, *Anal. Chem.*, **28**, 459 (1956).

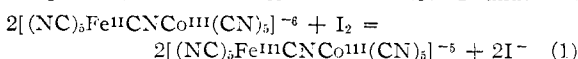
(9) H. A. Laitinen and I. W. Burdett, *ibid.*, **23**, 1269 (1951).

decomposition of the complexes with perchloric acid and separation of iron by the basic acetate method.¹⁰

The fractional precipitation referred to above was achieved by dissolving 3.2 g. of the mixture of $\text{K}_4[\text{Fe}(\text{CN})_6]$ and $\text{K}_6[(\text{NC})_5\text{Fe}^{\text{II}}\text{CNC}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_5]$ in 5 ml. of water and adding 5 ml. of 3 M barium chloride. After cooling to 0° the precipitate of $\text{Ba}_2[\text{Fe}(\text{CN})_6] \cdot 6\text{H}_2\text{O}$, which amounted to 0.7 g., was filtered out and air dried. 30 ml. of ethanol was added to the solution and 3.4 g. of $\text{Ba}_3[(\text{NC})_5\text{Fe}^{\text{II}}\text{CNC}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_5] \cdot 16\text{H}_2\text{O}$ was obtained.

Anal. Calcd. for $\text{Ba}_2[\text{Fe}(\text{CN})_6] \cdot 6\text{H}_2\text{O}$: Fe, 9.38; Co, 0.0. Found: Fe, 9.1; Co, 0.9. Calcd. for $\text{Ba}_3[(\text{NC})_5\text{Fe}^{\text{II}}\text{CNC}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_5] \cdot 16\text{H}_2\text{O}$: Co, 5.30; Fe, 5.01. Found: Co, 5.25; Fe, 5.03.

A sample of $\text{Ba}_3[(\text{NC})_5\text{Fe}^{\text{II}}\text{CNC}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_5] \cdot 16\text{H}_2\text{O}$ was treated with an excess of iodine; after 15 minutes the excess iodine was titrated with thiosulfate, using starch as indicator. Equivalent weight of $\text{Ba}_3[(\text{NC})_5\text{Fe}^{\text{II}}\text{CNC}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_5] \cdot 16\text{H}_2\text{O}$ calculated for reaction 1: 1101.3. Found: 1130.



The one electron oxidation product of $[(\text{NC})_5\text{Fe}^{\text{II}}\text{CNC}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_5]^{-6}$ was not isolated but was spectrophotometrically identified in solution as $[(\text{NC})_5\text{Fe}^{\text{III}}\text{CNC}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_5]^{-5}$ since it could be reversibly reduced to $[(\text{NC})_5\text{Fe}^{\text{II}}\text{CNC}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_5]^{-6}$ with sulfite, as shown in Fig. 1.

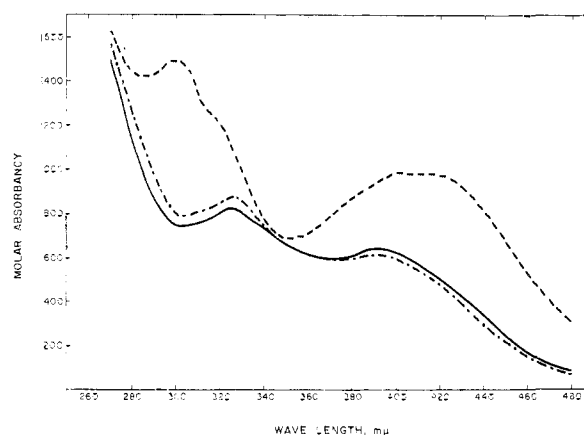


Fig. 1.—, $[(\text{NC})_5\text{Fe}^{\text{II}}\text{CNC}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_5]^{-6}$; - - -, $[(\text{NC})_5\text{Fe}^{\text{III}}\text{CNC}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_5]^{-5}$; - · - ·, $[(\text{NC})_5\text{Fe}^{\text{III}}\text{CNC}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_5]^{-5}$ after reduction with sulfite.

Further evidence to support the binuclear structure was obtained by comparing the spectrum of a solution of $[(\text{NC})_5\text{Fe}^{\text{II}}\text{CNC}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_5]^{-6}$, after being heated at 80° for 8 hr., with the spectrum calculated for quantitative hydrolysis to $\text{Fe}(\text{CN})_6^{-4}$ and $(\text{NC})_5\text{CoOH}_2^{-}$. The agreement was better than 9% for all wave lengths between 440 and 289 μ .

It was found that the yield of $\text{Fe}(\text{CN})_6^{-4}$ mentioned above, which is accompanied probably by an equivalent amount of $(\text{NC})_5\text{CoOH}_2^{-}$, was somewhat variable. In an experiment carried out apparently under the same conditions described above, 80% of $\text{K}_6[(\text{NC})_5\text{Fe}^{\text{II}}\text{CNC}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_5]$ and an estimated 10% of $\text{K}_4[\text{Fe}(\text{CN})_6]$ were obtained. When the reaction was carried out at 25° and 0.1 M concentrations of Co(II) and $\text{Fe}(\text{CN})_6^{-3}$, the resulting solution displayed an absorption spectrum which agreed within 6%, for all wave lengths between 480 and 280 μ , with the spectrum of pure $[(\text{NC})_5\text{Fe}^{\text{II}}\text{CNC}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_5]^{-6}$, a result which indicates that the yield of $\text{Fe}(\text{CN})_6^{-4}$ probably was smaller than 10%. The variation in the experimental conditions that would maximize the yield of $[(\text{NC})_5\text{Fe}^{\text{II}}\text{CNC}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_5]^{-6}$, and correspondingly minimize the yields of $\text{Fe}(\text{CN})_6^{-4}$ and $(\text{NC})_5\text{CoOH}_2^{-}$, or *vice versa*, was not systematically investigated.

Hume and Kolthoff¹¹ presented polarographic evidence indicating that when 0.004 M Co(II) in 1 M potassium cyanide

(10) W. W. Scott, "Standard Methods of Chemical Analysis," Vol. I, 5th Ed., D. Van Nostrand Company, Inc., New York, N. Y., 1939, p. 558.

(11) D. N. Hume and I. M. Kolthoff, *THIS JOURNAL*, **71**, 867 (1949).

is oxidized with 0.1 *M* $K_3[Fe(CN)_6]$, the reaction products are $(NC)_5CoOH_2^{--}$ and $Fe(CN)_6^{-4}$. The half-wave potential for the product of the oxidation was -1.4 v. vs. s.c.e. in agreement with the value -1.45 which they determined for $(NC)_5CoOH_2^{--}$.

The possibility that $(NC)_5CoOH_2^{--}$ and $[(NC)_5Fe^{II}CNCo^{III}(CN)_5]^{-6}$ had somewhat similar polarographic behavior prompted a polarographic examination of $[(NC)_5Fe^{II}CNCo^{III}(CN)_5]^{-6}$. In 1 *M* potassium cyanide as supporting electrolyte, it yielded a polarographic wave with $E_{1/2} = -1.62$ v. vs. s.c.e. (no correction for *rI* drop across the cell) and $i_d/(cm^2/s^{1/2}) = 2.14$. For $(NC)_5CoOH_2^{--}$, the corresponding values obtained in the present work were -1.42 and 2.33 , respectively. When 0.004 *M* Co(II) in 1 *M* potassium cyanide was oxidized with 0.1 *M* $Fe(CN)_6^{-3}$ (the conditions employed by Hume and Kolthoff) and the $Fe(CN)_6^{-3}$ was rapidly added (20 seconds, the time required to deliver the content of the pipet) to the Co(II) solution, polarographic examination of the resulting solution yielded the values $E_{1/2} = -1.63$ and $i_d/(cm^2/s^{1/2}) = 2.20$. In an experiment designed to duplicate the conditions employed by Hume and Kolthoff more closely, the $Fe(CN)_6^{-3}$ was added to the Co(II) solution in four portions, with a 2 minute wait before each addition. $E_{1/2}$ was again -1.63 , but $i_d/(cm^2/s^{1/2}) = 2.51$.

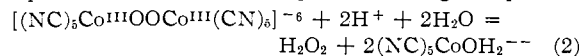
An estimate of the equilibrium constant of reaction 5, the one electron oxidation of $[(NC)_5Fe^{II}CNCo^{III}(CN)_5]^{-6}$ by $Fe(CN)_6^{-3}$ was obtained spectrophotometrically by comparing the spectrum of a solution containing stoichiometric amounts of the reactants with the spectra expected for no reaction and for complete reaction. The value 0.1 obtained from small differences between optical densities, gives only the order of magnitude of the equilibrium constant.

Preparation of $K_6[(NC)_5Co^{III}OOC Co^{III}(CN)_5] \cdot H_2O$.—When oxygen was rapidly bubbled through a solution 0.4 *M* in Co(II) chloride or nitrate and 2.1 *M* in potassium cyanide at 0°, the reddish brown color¹² immediately changed to a darker brown indicating a rapid oxygenation reaction. After bubbling oxygen through the solution for a period of five to ten minutes, a time probably in excess for complete oxygenation, the brown crystalline compound $K_6[(NC)_5Co^{III}OOC Co^{III}(CN)_5] \cdot H_2O$ was obtained by adding to the solution an equal volume of ethanol cooled to 0°. To induce crystallization and avoid formation of an oil, it was necessary to scratch the walls of the beaker with a glass stirring rod. The solid then was filtered out, washed with ethanol and diethyl ether and dried in a vacuum desiccator over sulfuric acid. The yield of $K_6[(NC)_5Co^{III}OOC Co^{III}(CN)_5] \cdot H_2O$ was 60%, but it was evident from the color of the mother liquor that precipitation of the highly soluble salt was far from complete.

Anal. Calcd. for $K_6[(NC)_5Co^{III}OOC Co^{III}(CN)_5] \cdot H_2O$: C, 18.12; N, 21.14; H, 0.30; Co, 17.79. Found: C, 18.06, 18.10; N, 21.00, 21.16; H, 0.44, 0.30; Co, 17.60, 17.75.

The barium salt of $[(NC)_5Co^{III}OOC Co^{III}(CN)_5]^{-6}$ was obtained as a dark orange powder when barium cyanide was used instead of potassium cyanide in the preparation described above. The yield calculated on the basis of the formula $Ba_3[(NC)_5Co^{III}OOC Co^{III}(CN)_5] \cdot 3H_2O$ was 85%. The formula of the barium salt was assigned by iodometric analysis of the peroxide content as described below, the state of hydration being uncertain by one water molecule.

The presence of a peroxo ligand in the complex $K_6[(NC)_5Co^{III}OOC Co^{III}(CN)_5] \cdot H_2O$ was best demonstrated by the formation of hydrogen peroxide upon acidification of an aqueous solution of the complex, according to equation 2.



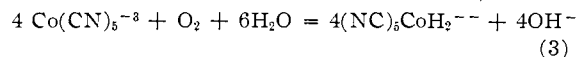
Evidence for the formation of $(NC)_5CoOH_2^{--}$ will be considered below. Hydrogen peroxide was detected by qualitative tests with dichromate ion. In quantitative studies, excess iodide ion was added to an acidified solution of $K_6[(NC)_5Co^{III}OOC Co^{III}(CN)_5] \cdot H_2O$ and the iodine formed was titrated with thiosulfate, using starch as indicator. As expected from equation 2, 0.97 ± 0.03 mole of iodine

(12) The color of Co(II) cyanide solutions was found to be dependent upon concentration and temperature. Solutions 0.1 *M* in Co(II) and 0.5 *M* in cyanide were reddish brown at 0° and olive green at 25°; solutions 0.1 *M* in Co(II) and 5.0 *M* in cyanide were also reddish brown at 0° but yellowish green at 25°.

was formed for each mole of $K_6[(NC)_5Co^{III}OOC Co^{III}(CN)_5] \cdot H_2O$.

Smith, Kleinberg and Griswold¹³ have reported that $K_8-[(NC)_5CoOH] \cdot H_2O$ was formed upon air oxidation of moist $K_8Co(CN)_5$. Various observations presented in their paper led us to suspect that the product was really $K_6[(NC)_5Co^{III}OOC Co^{III}(CN)_5] \cdot H_2O$, which differs insignificantly in analysis from the postulated $K_8[(NC)_5CoOH] \cdot H_2O$. A repetition of the Smith, Kleinberg and Griswold experiment yielded a product which was identified as $K_6[(NC)_5Co^{III}OOC Co^{III}(CN)_5] \cdot H_2O$ by iodometric peroxide analysis, spectrophotometry, acid-base titration and a comparison of its X-ray powder pattern with that of a sample of $K_6[(NC)_5Co^{III}OOC Co^{III}(CN)_5] \cdot H_2O$ prepared by oxygenation of an aqueous solution of the pentacyano complex of Co(II).

Stoichiometry of the Reaction Between the Pentacyano Complex of Co(II) and Oxygen.—The 60% yield of $K_6-[(NC)_5Co^{III}OOC Co^{III}(CN)_5] \cdot H_2O$ is not an accurate indication of the reaction stoichiometry, as indicated above. A more accurate estimation of the yield of $[(NC)_5Co^{III}OOC Co^{III}(CN)_5]^{-6}$ was obtained by oxygenation of the pentacyano complex of Co(II), followed by acidification, and iodometric analysis of the hydrogen peroxide formed. All measurements were carried out at a cyanide to Co(II) ratio of 5 and a Co(II) concentration of 0.1 *M*. At 0° and with rapid bubbling of oxygen or air through the solution, the yields of $[(NC)_5Co^{III}OOC Co^{III}(CN)_5]^{-6}$ were 90 and 86%, respectively. When the reaction was carried out at 25°, the yields were 68 and 62%, respectively, with rapid bubbling of oxygen and air. When the reaction was carried out with air at 25°, using a gas buret designed to regulate the rate of admission of air to the Co(II) solution, the yield of $[(NC)_5Co^{III}OOC Co^{III}(CN)_5]^{-6}$ was decreased to 0% by slow admission of air. Under these conditions, the total gas absorption corresponded to that required for quantitative formation of $(NC)_5CoOH_2^{--}$ according to equation 3 but only to one-half of that required for production of $[(NC)_5Co^{III}OOC Co^{III}(CN)_5]^{-6}$ according to equation 6 given below. Spectrophotometric analysis of the



resulting solution indicated that $(NC)_5CoOH_2^{--}$ was the sole product under these conditions of intentionally slow oxygenation.

Acid-base Properties of $[(NC)_5Co^{III}OOC Co^{III}(CN)_5]^{-6}$.—Aqueous solutions of $[(NC)_5Co^{III}OOC Co^{III}(CN)_5]^{-6}$ were found to be alkaline, suggesting that the complex is the conjugate base of a rather weak acid. When pH titrations of $[(NC)_5Co^{III}OOC Co^{III}(CN)_5]^{-6}$ were rapidly carried out at room temperature or lower and no more than about 0.90 equivalents of acid per mole of complex was added, one proton was added reversibly to the complex, as evidenced by the reversibility of back titrations with alkali. Under these conditions, reaction 2 described above occurred to a negligible extent. The *pK* of the conjugate acid of $[(NC)_5Co^{III}OOC Co^{III}(CN)_5]^{-6}$, measured as the pH after addition of 0.5 equivalent of acid per mole of complex, was 10.5.

When more than about 0.90 equivalent of acid was added to a solution of $[(NC)_5Co^{III}OOC Co^{III}(CN)_5]^{-6}$, the rate of decomposition according to reaction 2 became so rapid that it was impossible to carry out a reversible titration, even at 0°. The pH measured immediately after adding a portion of acid drifted to higher values at an initial rate of one pH unit per minute and then much slower, indicating irreversible consumption of acid.¹⁴ After addition of

(13) L. C. Smith, J. Kleinberg and E. Griswold, *J. Am. Chem. Soc.*, **75**, 449 (1953).

(14) Smith, Kleinberg and Griswold¹³ reported that titration with acid of the compound which they formulated as $(NC)_5CoOH^{-3}$ and which we have correctly identified as $[(NC)_5Co^{III}OOC Co^{III}(CN)_5]^{-6}$, yielded a titration curve with two inflection points. As shown above, only about 0.9 equivalent of acid can be added reversibly to one mole of $[(NC)_5Co^{III}OOC Co^{III}(CN)_5]^{-6}$; further addition of acid results in hydrolysis according to equation 2. A possible explanation for the results of Smith, Kleinberg and Griswold can be found in the extreme rapidity of the hydrolysis of $[(NC)_5Co^{III}OOC Co^{III}(CN)_5]^{-6}$. The acid added to the solution of $[(NC)_5Co^{III}OOC Co^{III}(CN)_5]^{-6}$ is rapidly consumed, with the plausible consequence that the pH versus added acid curve closely resembles a pH titration curve.

2.0 equivalents of acid per mole of complex there was no further drift in pH, a result to be anticipated if all $[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}^{\text{IV}}(\text{CN})_5]^{-6}$ had been converted to hydrogen peroxide and $(\text{NC})_5\text{CoOH}_2^{-}$ according to reaction 2.

Evidence supporting reaction 2 includes the iodometric determination of hydrogen peroxide described above and the identification of $(\text{NC})_5\text{CoOH}_2^{-}$ as the other reaction product by spectroscopic studies and by isolation and analysis of its poorly soluble silver salt.

The spectroscopic studies were complicated by the presence of 2–3% of μ -peroxododecacyanodicobaltate (III, IV), $[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}^{\text{IV}}(\text{CN})_5]^{-5}$, whose preparation and properties are described below. Extremely small quantities of $[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}^{\text{IV}}(\text{CN})_5]^{-5}$ could readily be detected in solutions of $(\text{NC})_5\text{CoOH}_2^{-}$, because at 310 $m\mu$ $[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}^{\text{IV}}(\text{CN})_5]^{-5}$ has a molar absorptivity of 6,800 whereas the corresponding value for $(\text{NC})_5\text{CoOH}_2^{-}$ is only 100.¹⁵ $[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}^{\text{IV}}(\text{CN})_5]^{-5}$ was easily removed from $(\text{NC})_5\text{CoOH}_2^{-}$ by fractional precipitation with silver ion, $[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}^{\text{IV}}(\text{CN})_5]^{-5}$ precipitating completely when silver nitrate solution was added in amounts sufficient to precipitate only 10% of the total cobalt. To obtain solutions of $(\text{NC})_5\text{CoOH}_2^{-}$ of known concentration it was convenient, after removal of $[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}^{\text{IV}}(\text{CN})_5]^{-5}$, to precipitate the poorly soluble $\text{Ag}_2[(\text{NC})_5\text{CoOH}_2]$ and then to return the ion $(\text{NC})_5\text{CoOH}_2^{-}$ to solution by trituration of the freshly precipitated moist $\text{Ag}_2[(\text{NC})_5\text{CoOH}_2]$ with a slight excess of sodium bromide solution. By weighing the amount of silver bromide formed it was possible to calculate the amount of $(\text{NC})_5\text{CoOH}_2^{-}$ that went into solution in the trituration reaction. The absorption spectra of solutions prepared in this manner, shown in Fig. 2, agreed quantitatively with the spectrum reported for $(\text{NC})_5\text{CoOH}_2^{-}$ by Adamson and Sporer,¹⁶ which was obtained by photolytic aquation of $(\text{NC})_5\text{CoCl}^{-3}$, $(\text{NC})_5\text{CoBr}^{-3}$, $(\text{NC})_5\text{CoI}^{-3}$ and $\text{Co}(\text{CN})_5^{-3}$. The same spectrum was obtained in the present work by thermal aquation of $(\text{NC})_5\text{CoBr}^{-3}$, $(\text{NC})_5\text{CoI}^{-3}$, $(\text{NC})_5\text{CoS}_2\text{O}_3^{-4}$ ¹⁷ and $(\text{NC})_5\text{CoN}_3^{-3}$.¹⁸

Smith, Kleinberg and Griswold¹³ reported that $(\text{NC})_5\text{CoOH}_2^{-}$, which they prepared following the method of Rây and Dutt,¹⁷ displays an absorption maximum at 350 $m\mu$, in disagreement with the value 380 $m\mu$ reported by Adamson and Sporer¹⁶ and in the present work. The probable reason for this disagreement will be given below where it will be shown that the absorption maximum at 350 $m\mu$ corresponds to a polymeric Co(III) pentacyanide which is formed by spontaneous polymerization of $(\text{NC})_5\text{CoOH}_2^{-}$ under the conditions of the Rây and Dutt¹⁷ preparation.

Preparation and Properties of $[(\text{NC})_5\text{Co}^{\text{III}}\text{O}-\text{O}-\text{Co}^{\text{IV}}(\text{CN})_5]^{-6}$.—When a 0.15 M solution of $[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}^{\text{IV}}(\text{CN})_5]^{-6}$ was added to a slight excess of bromine dissolved in 0.1 M potassium hydroxide, the one-electron oxidation of the complex ion proceeded rapidly at 0°, as evidenced by the change in color of the solution from red brown to deep red. Addition of ethanol to 70% in volume caused the separation of a red oil which was removed by filtration when it solidified after standing in contact with the solution for a period of 2 hr. at 0°. The solid, which was washed with ethanol, diethyl ether and then air-dried, was obtained in only 60% yield, assuming the formula given below. However, the hypobromite oxidation of $[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}^{\text{IV}}(\text{CN})_5]^{-6}$ may well have been essentially quantitative, since the separation of the red oil was obviously an inefficient process.

Anal. Calcd. for $\text{K}_5[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}^{\text{IV}}(\text{CN})_5] \cdot 5\text{H}_2\text{O}$: Co, 17.0. Found: Co, 17.2.

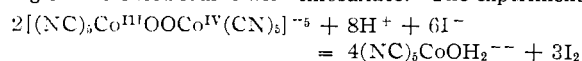
(15) Acidified solutions of $[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}^{\text{IV}}(\text{CN})_5]^{-6}$ displayed two absorption maxima, one at 380 $m\mu$ with molar absorptivity varying between 260 and 280, and another at 310 $m\mu$ with molar absorptivity varying between 120 and 300. $\text{Co}(\text{CN})_5^{-3}$ has an absorption maximum at 310 $m\mu$ with molar absorptivity 207. The absorption maximum at 310 $m\mu$ present in acidified solutions of $[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}^{\text{IV}}(\text{CN})_5]^{-6}$ cannot therefore be caused by $\text{Co}(\text{CN})_5^{-3}$, as postulated by Smith, Griswold and Kleinberg.¹³

(16) A. W. Adamson and A. H. Sporer, *THIS JOURNAL*, **80**, 3865 (1958).

(17) P. R. Rây and N. K. Dutt, *Z. anorg. u. allgem. Chem.*, **234**, 65 (1937).

(18) $(\text{NC})_5\text{CoN}_3^{-3}$ was prepared by reaction of $[(\text{NH}_3)_5\text{CoN}_3]\text{Cl}_2$, M. Linhard and H. Tlygare, *ibid.*, **262**, 328 (1950), with potassium cyanide, a trace of Co(II) being present as a catalyst.⁵

The oxidation states of the cobalt atoms in $\text{K}_5[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}^{\text{IV}}(\text{CN})_5] \cdot 5\text{H}_2\text{O}$ were established by reducing the complex with excess iodide in acid solution and titrating the liberated iodine with thiosulfate. The experimental



value of 1.42 moles of iodine produced per mole of complex is significantly lower than the theoretical value of 1.50, suggesting that the complex contained some impurities. This result is not surprising considering that the complex was separated as an oil. $(\text{NC})_5\text{CoOH}_2^{-}$, the other product of the reaction, was quantitatively identified by spectrophotometry.

The molar magnetic susceptibility of $\text{K}_5[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}^{\text{IV}}(\text{CN})_5] \cdot 5\text{H}_2\text{O}$ measured in 0.10 M solution using the Gouy technique was 1060×10^{-6} e.s.u.

In exploratory experiments it was found that a variety of oxidants could be used instead of hypobromite in the preparation of $[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}^{\text{IV}}(\text{CN})_5]^{-6}$. Visual observations suggested that rapid reaction occurred in solution at room temperature when hypochlorite, peroxydisulfate, iodine, hydrogen peroxide or ferricyanide was added to a solution of $[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}^{\text{IV}}(\text{CN})_5]^{-6}$. Oxidation also occurred slowly and incompletely when the hygroscopic solid $\text{K}_5[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}^{\text{IV}}(\text{CN})_5] \cdot \text{H}_2\text{O}$ was exposed to moist air.

Preliminary polarographic examination of 0.001 M solutions of $\text{K}_5[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}^{\text{IV}}(\text{CN})_5] \cdot 5\text{H}_2\text{O}$ in 0.4 M NaClO_4 as supporting electrolyte indicated the presence of two waves at -0.12 and -1.55 v. vs. s.c.e., the latter wave being about 6 times higher than the first one. This is the expected result if the first wave corresponds to reduction of Co^{IV} to Co^{III} and the second wave to the simultaneous reduction of Co^{III} to Co^{I} and O_2^{-} to $2\text{H}_2\text{O}$.

Formation of $(\text{NC})_5\text{CoOH}_2^{-}$ by Reaction of the Pentacyano Complex of Co(II) with H_2O_2 , $\text{S}_2\text{O}_8^{--}$ and $[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}^{\text{IV}}(\text{CN})_5]^{-6}$.— $(\text{NC})_5\text{CoOH}_2^{-}$ was produced in almost quantitative yields when solutions of H_2O_2 , $\text{S}_2\text{O}_8^{--}$ or $[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}^{\text{IV}}(\text{CN})_5]^{-6}$ were added, under vacuum in order to avoid air oxidation, to well stirred solutions 0.1 M in Co(II) and 0.5 M in potassium cyanide at 0°. In all instances the reactants were present in stoichiometric amounts, the number of moles of Co(II) being twice that of the peroxide under consideration. Visual observation of color changes seemed to indicate that the reactions were complete upon mixing the reactants. The spectra of the resulting solutions, obtained within 10 minutes of mixing, agreed within 5% with the spectrum calculated, assuming quantitative formation of $(\text{NC})_5\text{CoOH}_2^{-}$, except in the region 340 to 280 $m\mu$, where $(\text{NC})_5\text{CoOH}_2^{-}$ has a low absorption shallow minimum and traces of strongly absorbing impurities are readily detected. In this wave length region the absorbance of the solutions exceeded the calculated values by not more than 10%. For the reaction with $\text{S}_2\text{O}_8^{--}$, free sulfate after reaction was determined as BaSO_4 and was found to be within 5% of that expected if no sulfate complexes were formed.

Properties of $\text{Ag}_2[(\text{NC})_5\text{CoOH}_2]$ and Preparation of Polymeric Cobalt(III) Pentacyanide.—In agreement with earlier observations by Rây and Dutt¹⁷ it was found that when freshly precipitated moist $\text{Ag}_2[(\text{NC})_5\text{CoOH}_2]$ prepared in the manner described above was dried in a vacuum desiccator over sulfuric acid, it underwent a continuous loss of weight until the completely anhydrous state $\text{Ag}_2\text{Co}(\text{CN})_5$ was reached.

Anal. Calcd. for $\text{Ag}_2\text{Co}(\text{CN})_5$: Co, 14.56; Ag, 53.41. Found: Co, 14.71; Ag, 53.24.

A complete analysis was performed before complete dehydration had occurred: calcd. for $\text{Ag}_2\text{Co}(\text{CN})_5 \cdot 1/2 \text{H}_2\text{O}$: Co, 14.24; C, 14.51; N, 16.93; H, 0.24; Ag, 52.14. Found: Co, 14.34; C, 14.99; N, 17.22; H, 0.34; Ag, 52.05. The significance of this analysis does not lie in the extent of hydration, but in the establishment of the Co:Ag:C:N ratios.

Rây and Dutt¹⁷ stated that the color of $\text{Ag}_2\text{Co}(\text{CN})_5$ is blue. In our experience, the change in color upon dehydration of $\text{Ag}_2[(\text{NC})_5\text{CoOH}_2]$ to $\text{Ag}_2\text{Co}(\text{CN})_5$ was from yellow to greenish yellow.¹⁹ In some cases complete dehydration

(19) Upon heating $\text{Ag}_2[(\text{NC})_5\text{CoOH}_2]$ at 190° for 2 hr., a blue color developed; however, there was extensive decomposition with evolution of cyanogen.

could not be achieved rapidly at room temperature; however, heating at 100° for thirty minutes readily yielded the greenish yellow $\text{Ag}_2\text{Co}(\text{CN})_6$. For the corresponding sodium salt, dehydration to the greenish yellow $\text{Na}_2\text{Co}(\text{CN})_6$ could only be achieved by heating at 100° for 2 hr.

Upon exposure of $\text{Ag}_2\text{Co}(\text{CN})_6$ to moist air there was a color change from greenish yellow to yellow and an increase in weight, presumably due to absorption of water. The composition of the hydrated product after constant weight had been reached was $\text{Ag}_2\text{Co}(\text{CN})_6 \cdot 1.4 \pm 0.1\text{H}_2\text{O}$, a product which could be dehydrated back to $\text{Ag}_2\text{Co}(\text{CN})_6$. A somewhat surprising result was obtained when either of the two latter solids was triturated with sodium bromide solution, as described above. The solution obtained after separating the silver bromide formed contained no free cyanide and displayed the absorption spectrum shown in Fig. 2, with a maximum occurring at 350 $m\mu$, and not at 380 $m\mu$ as expected for $(\text{NC})_5\text{CoOH}_2^{--}$. In order to identify the complex responsible for the absorption maximum at 350 $m\mu$, it was precipitated as the insoluble silver salt.

Anal. Calcd. for $\text{Ag}_2\text{Co}(\text{CN})_6 \cdot \text{H}_2\text{O}$: Co, 13.94; C, 14.20; N, 16.56; H, 0.48; Ag, 51.30. Found: Co, 13.68; C, 14.17; N, 16.55; H, 0.32; Ag, 51.36. Here again the significance of the analysis does not lie in the extent of hydration, since the complex could be dehydrated to $\text{Ag}_2\text{Co}(\text{CN})_6$, but in the fact that it serves to demonstrate that the ratios Co:Ag:CN are 1:2:5.

The polymerization of $(\text{NC})_5\text{CoOH}_2^{--}$ could also be achieved upon heating a 0.5 *M* solution at 80° for 2 hr., the reaction taking place with no change in *pH*. It also was found that upon standing for 48 hr. in a closed weighing bottle, $\text{Ag}_2[(\text{NC})_5\text{CoOH}_2]$ underwent polymerization.

The polymeric pentacyanide did not exhibit any acidic properties in solution, its absorption spectrum being unchanged between 0.01 *N* HCl and 10 *N* NaOH.

Oxidation of Cr(II)-Cyanide Complex by O_2 and H_2O_2 .—Cr(II) solutions, prepared by reduction of Cr(III) with amalgamated zinc, were added to an excess of potassium cyanide. The resulting bright red solution, 0.1 *M* in Cr(II), 0.05 *M* in Zn(II) and 5 *M* in cyanide, was oxidized by rapid bubbling of oxygen for 5 to 10 minutes at 0°. Addition of ethanol to 70% in volume yielded a yellow precipitate of $\text{K}_3[\text{Cr}(\text{CN})_6]$ contaminated by $\text{K}_2[\text{Zn}(\text{CN})_4]$. Upon recrystallization from water, 76% yield of pure $\text{K}_3[\text{Cr}(\text{CN})_6]$ was obtained. Cr was analyzed for by decomposition of the complex with sulfuric acid, then oxidation in alkaline solution with hydrogen peroxide and iodometric determination of the chromate formed.

Anal. Calcd. for $\text{K}_3[\text{Cr}(\text{CN})_6]$: Cr, 15.98; C, 22.14; N, 25.83. Found: Cr, 16.04, 15.88; C, 21.96, 22.38; N, 26.00, 25.70.

Under the same conditions, oxidation with hydrogen peroxide yielded 78% of $\text{K}_3[\text{Cr}(\text{CN})_6]$.

Results and Discussion

Much of the following discussion deals with the products formed by oxidation of the Co(II) cyanide complex present in solutions where the ratio (CN^-) to (Co^{II}) equals 5. A variety of studies^{11,20-24} indicate that the dominant species in such solutions is a pentacyanide, but there is no evidence regarding the state of hydration or polymerization of cobalt(II) pentacyanide. In the absence of such evidence, the formula $\text{Co}(\text{CN})_5^{-3}$ will be used to simplify the presentation of our results. However, the following discussion and equations readily could be reformulated using the formula $(\text{NC})_5\text{CoOH}_2^{-3}$ or even a dimeric form of $\text{Co}(\text{CN})_5^{-3}$ without a major change in viewpoint,

(20) A. W. Adamson, *THIS JOURNAL*, **73**, 5710 (1951).

(21) N. Kelso King and M. E. Winfield, *ibid.*, **80**, 2060 (1958).

(22) G. A. Mills, S. Weller and A. Wheeler, *J. Phys. Chem.*, **63**, 403 (1959).

(23) W. P. Griffith and G. Wilkinson, *J. Chem. Soc.*, 2757 (1959).

(24) Complications because of aging of Co(II) cyanide solutions²¹⁻²³ were avoided in our experiments by the use of freshly prepared solutions.

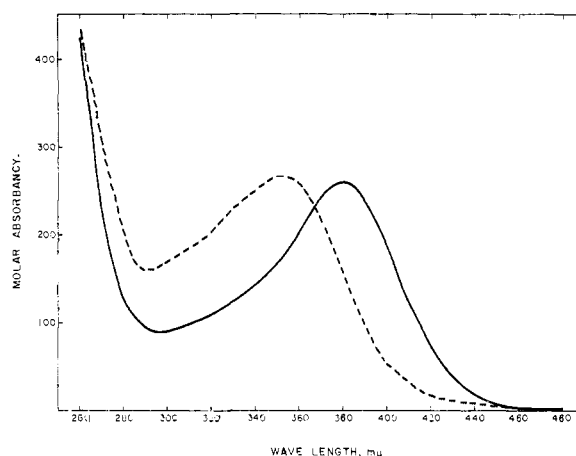
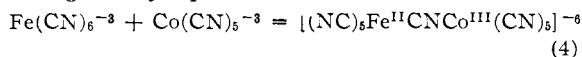


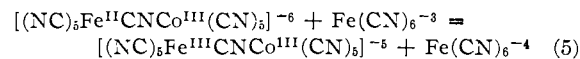
Fig. 2.— —, $(\text{NC})_5\text{CoOH}_2^{--}$; ---, polymeric Co(III) pentacyanide.

since our main interest lies not in the structural nature of the reactant but in the chemical composition and geometry of the activated complexes which generate the products found in the various reactions considered in this paper.

From the mechanistic viewpoint the simplest of the reactions under consideration would seem to be that given by equation 4



The isolation of the binuclear ion as a major product demonstrates that the reaction occurs *via* a bridged-activated complex,⁴ with a cyano ligand bonded to both Fe(III) and Co(II) at the transition state. The simultaneous formation of small and somewhat variable amounts of $\text{Fe}(\text{CN})_6^{-4}$, presumably accompanied by equal amounts of $(\text{NC})_5\text{CoOH}_2^{--}$, may imply a second reaction path taking place *via* an outer sphere activated complex.⁴ However, there is another obvious path for formation of $\text{Fe}(\text{CN})_6^{-4}$ during the reaction. As $\text{Co}(\text{CN})_5^{-3}$ and $\text{Fe}(\text{CN})_6^{-3}$ are mixed, appreciable amounts of $[(\text{NC})_5\text{Fe}^{\text{III}}\text{CNC}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_5]^{-5}$ may be formed in reaction 5, a process having an equilibrium constant of the order of 0.1.



In the latter stages of reaction, $\text{Fe}(\text{CN})_6^{-3}$ and $[(\text{NC})_5\text{Fe}^{\text{III}}\text{CNC}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_5]^{-5}$ would compete for $\text{Co}(\text{CN})_5^{-3}$, with the latter oxidant perhaps forming $(\text{NC})_5\text{CoOH}_2^{--}$ as well as the trinuclear ion mentioned below.

The preparation and characterization of the inert (with respect to hydrolysis) $[(\text{NC})_5\text{Fe}^{\text{III}}\text{CNC}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_5]^{-5}$ provided an opportunity to carry out exploratory studies of the reduction of this species with $\text{Co}(\text{CN})_5^{-3}$. One possible path, considered above, would yield the products $(\text{NC})_5\text{CoOH}_2^{--}$ and $[(\text{NC})_5\text{Fe}^{\text{II}}\text{CNC}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_5]^{-6}$; another possible path would yield the trinuclear product $[\text{Fe}^{\text{II}}(\text{CN})_6 \cdot 2\text{Co}^{\text{III}}(\text{CN})_5]^{-8}$. Our studies do suggest that the trinuclear ion is formed in yields of perhaps 50%, but it has not yet been possible to isolate a pure salt of the complex. It may be noted that, in principle, continuous repeti-

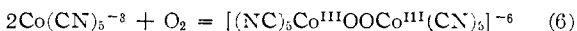
TABLE I
SOME PROPERTIES OF Co(III,III) PEROXO COMPLEXES

	$[(\text{NC})_5\text{CoOOC}(\text{CN})_5]^{-3}$	$[(\text{H}_2\text{N})_5\text{CoOOC}(\text{NH}_2)_5]^{+4}$	$\left[\begin{array}{c} \text{H}_2 \\ \diagup \quad \diagdown \\ (\text{en})_2\text{Co} \quad \text{Co}(\text{en}) \\ \diagdown \quad \diagup \\ \text{OO} \end{array} \right]^{-3}$
E^1	$-0.12 > E^3 > -0.34$	-1.0	-1.0
pK (base)	3.5	...	13
Decomposition	Co(III) + H ₂ O ₂ in acid solution	Rapid formation of Co(II) and O ₂ at all pH	Unreactive; decomposition products unknown

tion of the oxidation of Fe(II) followed by reduction with $\text{Co}(\text{CN})_5^{-3}$ provides a method, which has apparently not been exploited in other systems, to build up inorganic polymers.

Hume and Kolthoff¹¹ have presented reasonably convincing evidence that the reaction of $\text{Fe}(\text{CN})_6^{-3}$ with $\text{Co}(\text{CN})_5^{-3}$ yielded only $\text{Fe}(\text{CN})_6^{-4}$ and $(\text{NC})_5\text{CoOH}_2^{-}$, products which we obtained, under presumably identical conditions, in very small yield. At present we have no satisfactory explanation for this discrepancy. In attempting to devise a possible explanation, it was thought that when $\text{Fe}(\text{CN})_6^{-3}$ is added slowly to a $\text{Co}(\text{CN})_5^{-3}$ solution, the excess $\text{Co}(\text{CN})_5^{-3}$ might catalyze the hydrolysis of the initial product, $[(\text{NC})_5\text{Fe}^{\text{II}}\text{CNC}(\text{CN})_5]^{-6}$, by electron transfer between the cobalt ions through an outer sphere activated complex. However, our experiments indicate that this interesting reaction does not occur at an appreciable rate at room temperature; if electron transfer occurs, it must proceed through a bridged activated complex, with no net chemical change.

In the formation of $[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}(\text{CN})_5]^{-6}$, the ion $\text{Co}(\text{CN})_5^{-3}$ again captures the oxidant in its coordination sphere.

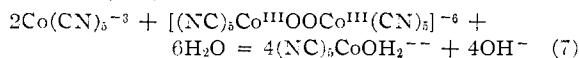


Reaction 6 obviously may proceed stepwise, perhaps with the formation of $(\text{NC})_5\text{CoO}_2^{-3}$ as a reactive intermediate, but the nature of the product clearly establishes that the Co(II) ions and the oxygen molecule are in actual contact whenever electron transfer occurs. In considering the possible generality of processes like reaction 6, it is of interest to note the recently reported²³ preparation of $[(\text{NC})_5\text{CoC}_2\text{H}_2\text{Co}(\text{CN})_5]^{-6}$ by reaction of $\text{Co}(\text{CN})_5^{-3}$ and acetylene.

It is of interest to compare the properties of the decacyano peroxo complexes with those of the corresponding ammonia and ethylenediamine derivatives. To facilitate comparison of the rather different behavior of the three well characterized Co(III, III) peroxo complexes, some of the pertinent information is summarized in Table I. The negatively charged Co(III, III) cyano complex is evidently a much better reducing agent and stronger base than the positively charged ammine complexes. The cyano complex hydrolyzes very rapidly in acid solution, even at 0°, to yield hydrogen peroxide. By contrast, the decammine complex decomposes by rapid loss of oxygen in an internal disproportionation reaction. The ethylenediamine complex is very inert, presumably because of a stabilization arising, in some poorly understood manner, from the presence of the second bridging ligand.

The three Co(III, IV) complexes obtained by one electron oxidation of the Co(III, III) complexes of Table I display paramagnetism corresponding to one unpaired electron per binuclear unit, as expected. Recently,²⁵ e.p.r. measurements have yielded some information about the location of the odd electron in these molecules, but the interpretation seems to remain somewhat uncertain, especially in solutions of low acidity. None of the three Co(III, IV) complexes shows appreciable basic properties, and all are relatively inert with respect to loss of either oxygen or hydrogen peroxide. This decreased reactivity may possibly be associated with a resonance stabilization of the Co(III, IV) oxidation state in which the odd electron is delocalized and free to move over a considerable portion of the molecule.²⁶

$[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}(\text{CN})_5]^{-6}$ is the major product of reaction 6 only when the oxygenation is rapidly carried out to completion. By contrast, when the oxygen is admitted slowly to the $\text{Co}(\text{CN})_5^{-3}$ solution, $(\text{NC})_5\text{CoOH}_2^{-}$ is formed in essentially quantitative yield. This change in stoichiometry becomes readily understandable when it is recognized that $[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}(\text{CN})_5]^{-6}$ reacts rapidly with $\text{Co}(\text{CN})_5^{-3}$.



Presumably, reaction 6 is always the initial step in the oxygenation, but $[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}(\text{CN})_5]^{-6}$ subsequently is destroyed in reaction 7, unless reaction 6 is rapidly carried to completion.

Reaction 7 is formally analogous to the oxidation of $\text{Co}(\text{CN})_5^{-3}$ by hydrogen peroxide or by peroxydisulfate ion: in each of the three systems, a peroxide oxidant converts $\text{Co}(\text{CN})_5^{-3}$ to $(\text{NC})_5\text{CoOH}_2^{-}$. The detailed mechanisms of these rather complicated processes are not known, although it might reasonably be supposed that the two-electron reduction of the peroxide proceeds stepwise, as it does in the Fe(II) hydrogen peroxide reaction.²⁷ Despite this uncertainty regarding mechanism, it would seem that the complete absence of Co(III) sulfato complexes in the peroxydisulfate oxidation does provide reasonably good evidence that in the initial electron transfer the peroxydisulfate ion does not enter the coordination sphere of Co(II). To be sure, it may be argued that a readily hydrolyzable sulfato complex is a precursor of the $(\text{NC})_5\text{CoOH}_2^{-}$ product; however, such

(25) E. A. V. Ebsworth and J. A. Weil, *J. Phys. Chem.*, **63**, 1890 (1959).

(26) $[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}(\text{CN})_5]^{-6}$ is under e.p.r. examination by Mr. Concetto R. Giuliano at the California Institute of Technology.

(27) W. G. Barb, J. H. Baxendale, P. George and K. R. Hargrave, *Trans. Faraday Soc.*, **47**, 462 (1951).

an alternative is rendered rather unlikely by the experimental restriction that the hydrolysis must be complete in less than ten minutes at 0°. Reduction of $[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}^{\text{III}}(\text{CN})_5]^{-6}$ by $\text{Co}(\text{CN})_5^{-3}$ might be expected to produce binuclear ions such as $[(\text{NC})_5\text{CoOHCo}(\text{CN})_5]^{-5}$ or $[(\text{NC})_5\text{CoNCCo}(\text{CN})_4\text{OH}_2]^{-4}$ if initial electron transfer in reaction 7 involved a bridged activated complex. Again it must be concluded that if such binuclear ions are formed, they must hydrolyze within 10 minutes at 0°, a restriction which makes their formation rather unlikely. Therefore it is reasonable to suggest that reaction 7 occurs *via* an outer sphere activated complex.

In addition to the experiments at a (CN^-) to (Co^{II}) ratio of five, some oxygenation studies were carried out in 5.0 *M* cyanide solution where $(\text{CN}^-)/(\text{Co}^{\text{II}})$ was 50. Under these extreme conditions $[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}^{\text{III}}(\text{CN})_5]^{-6}$ was still the major product, but $\text{Co}(\text{CN})_5^{-3}$ also was formed in approximately 25% yield. Obviously there are a number of reaction paths which might produce $\text{Co}(\text{CN})_5^{-3}$ as a minor product, and speculation with regard to its origin is not profitable at the present time. However, it is of interest to note that when 0.1 *M* Cr(II) in 5.0 *M* cyanide was oxidized with oxygen, $\text{Cr}(\text{CN})_6^{-3}$ was the major and perhaps only reaction product. The absence of significant amounts of oxygen-containing Cr(III) products strongly suggests that a binuclear Cr(III) peroxo complex is not a reaction intermediate in this system. Oxidation of Cr(II) by hydrogen peroxide under the same conditions also produced $\text{Cr}(\text{CN})_6^{-3}$. Again oxygen atoms are not permanently trapped in the coordination sphere of the Cr(III) product, and it may be concluded either that the oxidant does not contact the Cr(II) ion or that electron transfer proceeds through an activated complex with coordination number 7, $[(\text{NC})_5\text{Cr-oxidant}]^{-4}$, from which the oxidant is expelled as the Cr(III) ion assumes its conventional coordination number 6. The rapid oxygenation of Cr(II) in cyanide solution gains in interest when it is compared with that of Cr(II) in ammoniacal solution,²⁹ a rapid reaction in which the oxidant is incorporated in the product, $[(\text{NH}_3)_5\text{CrOHCr}(\text{NH}_3)_5]^{+5}$, and with that of aqueous Cr(II), a rapid reaction that forms a binuclear product.³⁰ The ligands in the three systems differ in what may loosely be called conducting properties: flow of electrons from Cr(II) would presumably be efficient through a cyanide coordination sphere but somewhat restricted through a water or ammonia coordination sphere. However, in addition to the relative conducting properties of the ligands, other factors must be responsible for the difference in behavior between the cyanide system on one hand and the ammine and aqueous systems on the other. The Cr(II) cyanide complex, like $\text{Cr}(\text{CN})_6^{-3}$, is an

(28) Attempts to study the hydrolysis of $(\text{NC})_5\text{CoSO}_4^{-4}$ have thus far been unsuccessful because of our inability to prepare the complex. No reaction occurred between 1 *M* SO_4^{--} and 0.02 *M* $(\text{NC})_5\text{CoOH}_2^{-}$ during 10 hr. at 80°. The reaction between $(\text{NH}_3)_5\text{CoSO}_4^{+}$ and KCN yielded some $\text{Co}(\text{CN})_5^{-3}$ and other unidentified products, but no $(\text{NC})_5\text{CoSO}_4^{-4}$ was found.

(29) T. B. Joyner and W. K. Wilmarth, unpublished results.

(30) M. Ardon and R. A. Plane, *THIS JOURNAL*, **81**, 3197 (1959).

inner orbital complex,³¹ presumably free from serious Franck-Condon restrictions prohibiting electron transfer. By contrast, the water and ammonia Cr(II) complexes are of the outer orbital type,³¹ possibly having the geometry of a tetragonal bipyramid quite unlike that of the inner orbital octahedral Cr(III) complex: electron transfer is therefore difficult, but rapid reaction is achieved with oxygen entering the coordination sphere of Cr.³²

The anhydrous material $\text{Ag}_2\text{Co}(\text{CN})_5$ obtained upon dehydration of $\text{Ag}_2[(\text{NC})_5\text{CoOH}_2]$ was considered by Rây and Dutt¹⁷ as an unusual example of a pentacoordinated Co(III) complex. However, such an assumption is not necessary since the conventional coordination number 6 of Co(III) may be satisfied by means of cyano bridges between Co atoms. This formulation becomes even more attractive when it is realized that trituration of $\text{Ag}_2\text{Co}(\text{CN})_5$, or its hydrate $\text{Ag}_2\text{Co}(\text{CN})_5 \cdot 1.5\text{H}_2\text{O}$, with sodium bromide yields a solution containing a cobalt(III) pentacyanide isomeric with $\text{Co}(\text{CN})_5\text{OH}_2^{-}$. Since geometrical isomerism is not possible for an octahedral complex of the type MA_5B ,³³ polymerization isomerism is indicated.³⁴ A polymerization through water bridging according to the formulation $[(\text{NC})_5\text{CoH}_2\text{OCo}(\text{CN})_5]^{-4}$ is rejected since it requires a tetraoordinated oxygen atom in the bridge in order to maintain the charge-2 for every $\text{Co}(\text{CN})_5$ unit. Therefore, the polymerization must be achieved through cyanide bridges between cobalt atoms. The latter conclusion is supported by infrared studies to be published elsewhere. Unfortunately our results do not allow a distinction between various plausible structures for the polymeric Co(III) pentacyanide: a binuclear unit $[(\text{NC})_5\text{CoNCCo}(\text{CN})_4\text{OH}_2]^{-4}$, a cyclic tetramer analogous to $[(\text{C}_3\text{H}_7)_2\text{AuCN}]_4$ ³⁵ or a long chain polymer. The change in color, from greenish yellow to yellow, that occurs upon hydration of $\text{Ag}_2\text{Co}(\text{CN})_5$ might be taken as indicative of an important structural change, such as the coordination of water to Co(III). However, the change in color, although readily detected, is sufficiently small to be accounted for by simple hydration of the solid structure. The absence of change in the absorption spectrum of the polymeric Co(III) pentacyanide from 0.01 *N* HCl to 10 *N* NaOH might be taken as indicative that a Co(III)-OH₂ bond is not present in the polymeric complex. However, in the absence of reliable means of predicting acid strength, there is no firm basis to rule out the possibility that

(31) D. N. Hume and H. W. Stone, *ibid.*, **63**, 1200 (1941).

(32) A. W. Adamson, *Rec. trav. chim.*, **75**, 809 (1956).

(33) An isomerism in terms of cyanide and isocyanide structures may be ruled out on the grounds that the isomerization occurs spontaneously and would therefore imply that the isocyanide complex is more stable than the cyanide complex.

(34) Rây and Dutt¹⁷ and P. R. Rây and T. Gupta Chaudhuri, *Z. anorg. u. allgem. Chem.*, **220**, 154 (1934), concluded, from calculations of molecular weights from freezing point depression measurements, that $\text{K}_2[(\text{NC})_5\text{CoOH}_2]$ is monomeric and that $\text{K}[(\text{NC})_4\text{Co}(\text{OH})_2]$ is polymeric. However, an examination of the two papers by Rây and co-workers indicates that the authors neglected to consider ionization of the salts in their calculation of molecular weights. Recalculation of the molecular weights using the correct expression does not seem profitable because of uncertainty in activity coefficients.

(35) R. F. Philips and H. M. Powell, *Proc. Roy. Soc. (London)*, **A173**, 147 (1939).

an acid such as $[(\text{NC})_5\text{CoNCCo}(\text{CN})_4\text{OH}_2]^{-4}$ is very much weaker than $(\text{NC})_5\text{CoOH}_2^{--}$ with a pK of 11.

In an earlier and incorrect interpretation³ of parts of the present work, it was reported that the acid hydrolysis of $[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}(\text{CN})_5]^{-6}$ produced the polymeric Co(III) pentacyanide discussed above. The error arose because at that time it was thought that rehydration of Ag_2Co -

$(\text{CN})_5$ produced the ion $(\text{NC})_5\text{CoOH}_2^{--}$, a circumstance which resulted in the mistaken identification of the polymeric Co(III) pentacyanide as $(\text{NC})_5\text{CoOH}_2^{--}$ and *vice versa*. In addition, the species which was shown later to be $[(\text{NC})_5\text{Co}^{\text{III}}\text{OOC}(\text{CN})_5]^{-5}$ had then been isolated in only trace quantities and tentatively identified, again incorrectly, as an isomer of the polymeric Co(III) pentacyanide.

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Binuclear Complex Ions. IV. An Investigation of the Mechanism of Oxygenation of the Chromium(II) Ion in Ammoniacal Solution Using O^{18} Labelled Oxygen¹

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A study has been made of the extent of the labelling of the bridging oxygen atom of the $[(\text{H}_3\text{N})_5\text{Cr}-\text{O}-\text{Cr}(\text{NH}_3)_5]^{+4}$ ion, formed by oxygenation of the Cr(II) ion in ammoniacal solution. Under all conditions the labelling was extensive but never complete. The percentage labelling varied only over the range 40-70% despite an 80° variation in reaction temperature and a considerable variation in pH and Cr(II) concentration. On the basis of these results and other available information, it is possible to deduce a plausible path for the oxygenation process. In this mechanism the binuclear $[(\text{H}_3\text{N})_5\text{Cr}-\text{O}_2-\text{Cr}(\text{NH}_3)_5]^{+4}$ ion and a Cr(IV) complex, the $[(\text{H}_3\text{N})_5\text{Cr}(\text{OH})]^{+3}$ ion, both play important roles as transient intermediates in the over-all reaction.

Introduction

It was first reported by Jorgensen in 1882 that oxygenation of the Cr(II) ion in ammoniacal solution produced the interesting binuclear $[(\text{H}_3\text{N})_5\text{Cr}-\text{O}-\text{Cr}(\text{NH}_3)_5]^{+4}$ ion, a species which he named the rhodo ion.³ Although the rhodo ion is a major product of the reaction under favorable circumstances, all experience indicates that other unidentified substances are always formed in rather appreciable amounts. In these circumstances, product analysis alone does not yield any very definite information about the reaction mechanism. The present study represents an attempt to devise an experimental approach that would identify the reaction paths producing the rhodo ion, despite the presence of the troublesome and uncontrolled side reactions. In brief, the procedure involves a tracer study using O^{18} labelled molecular oxygen in the oxygenation, followed by analysis of the O^{18} content of the oxygen atoms in the bridging position of the rhodo ion.

Experimental

Oxygenation Techniques.—The Cr(III) solutions were prepared either by dissolving the common green, reagent grade $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ in water or by treating a solution of reagent grade ammonium dichromate with a slight excess of hydrogen peroxide, with the excess hydrogen peroxide being destroyed by boiling after the reaction was complete. The reduction of the Cr(III) ion to the Cr(II) oxidation state was carried out by adjusting the acidity to 2.0 *M* with hydrochloric acid and then adding an excess of amalgamated zinc. This and subsequent operations were carried out in a nitrogen atmosphere using an all glass apparatus designed to protect the Cr(II) solutions from air oxygenation. After reduction to the Cr(II) state was complete, the solutions were separated from the zinc by transfer through a stopcock into a

portion of the apparatus containing either ammonium chloride or ammonium bromide dissolved in concentrated aqueous ammonia. In this operation, the large excess of ammonia served to neutralize the hydrochloric acid and to convert the Cr(II) ion to the ammonia complex, while the presence of the ammonium salt decreased the basicity, thus preventing the precipitation of basic Cr(II) compounds except in a few experiments carried out at -50° and referred to below.

Labelled oxygen used in the oxygenation was prepared by electrolysis of water obtained from the Stuart Oxygen Co. which contained approximately 1.4% H_2O^{18} . The electrolysis was carried out in a simple H-cell, using platinum electrodes and added sodium sulfate electrolyte. At a current of 0.5 ampere it was necessary to cool the cell by immersing it in a bath. The oxygen was collected at the anode by water displacement in storage bulbs which could be attached by ground joints to the reaction vessel containing the ammoniacal Cr(II) solutions.

In a typical oxygenation experiment the initial concentrations of the reagents were: ammonia, 19.0 molal; ammonium bromide, 3.3 molal; chloride ion arising from the added hydrochloric acid, 0.7 molal; Cr(II), 0.01-0.18 molal; zinc ion formed in the reduction, about one half the concentration of the Cr(II). Other reagents added in some experiments were present at the concentrations indicated. Before oxygenation, each solution was frozen by cooling to -80° , the nitrogen removed by evacuation first at -80° and then for a short period (approximately 10 sec.) after the solid had been melted. The solution then was adjusted to any desired temperature with a liquid bath and the labelled oxygen admitted by opening the stopcock to the oxygen storage vessel. To increase the rate of solution of the oxygen, the solution was stirred by manual agitation of the entire reaction vessel. As the oxygenation proceeded, the basic rhodo bromide precipitated. After reaction was complete the color of the solution indicated that only very minor amounts of the rhodo ion could have remained unprecipitated.

To be sure that the oxygenation was complete before exposure to laboratory air, two methods of procedure were developed, with the duplication of results in the two procedures indicating the absence of errors in each. In the first method, the oxygenation was carried out for fifteen minutes, a period which should have been more than sufficient to complete the reaction.⁴ At this point, a small amount of

(4) In experiments where efficient agitation is achieved by bubbling air through the solution, the reactions seem to be complete within one minute at 0° .

(1) This work was supported in part by the Office of Naval Research.

(2) Based on a dissertation submitted by Taylor B. Joyner in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Southern California.

(3) S. M. Jorgensen, *J. prakt. Chem.*, **25**, 321, 308 (1882).