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Reactions of Some Transition Metal Cyano Complexes with Molecular Hydrogen at Elevated Temperatures

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The reactions of a number of transition metal complexes with molecular hydrogen at moderately elevated temperatures have been studied with the following results. Potassium tetracyanonickelate(II) is reduced at 390° with the formation of the nickel(I) complex $K_4Ni_2(CN)_6$ and the liberation of hydrogen cyanide. Reduction of potassium octacyanomolybdate(IV) and potassium octacyanotungstate(IV) at 390° yields the hitherto unknown molybdenum(II) and tungsten(II) complexes, $K_4[Mo(CN)_6]$ and $K_4[W(CN)_6]$. Long extraction of these complexes in the open air with methanol converts them to $K_3[Mo(CN)_6]$ and $K_3[W(CN)_6]$, also previously unreported. At 420°, hydrogen converts potassium hexacyanomanganate(III) to a substance with the empirical formula $K_3Mn(CN)_5$. This material, which is insoluble in water and common organic solvents, has an infrared spectrum which indicates that it is polymeric. Potassium hexacyanocobaltate(III) absorbs appreciable quantities of hydrogen at 240°, but does not appear to undergo any reaction but a slight thermal decomposition. The hydrogen absorbed is released at 350°, leaving the starting material virtually unchanged.

In the extensive literature on the use of molecular hydrogen as a reducing agent there appears to be no report of the application of this reagent for the preparation, in the absence of solvent, of complexes containing transition metals in low, uncommon oxidation states. The most suitable complexes as starting materials would seem to be those in which the ligands could be removed as volatile compounds of hydrogen. Cyano complexes should be particularly appropriate since the cyanide group is an effective stabilizer of low oxidation states.

This paper describes the reactions at moderately elevated temperatures of molecular hydrogen with the following complexes: $K_2[Ni(CN)_4]$, $K_4[Mo(CN)_8]$, $K_4[W(CN)_8]$, $K_3[Mn(CN)_6]$, and $K_3[Co(CN)_6]$. In each instance, the reaction was carried out at a temperature below which any significant thermal decomposition of the complex occurred. Reduction of the central atom to a lower oxidation state, accompanied by the liberation of hydrogen cyanide, occurred with all the complexes except the cobalt compound.

Experimental

Materials.—Potassium tetracyanonickelate(II) was prepared according to the method of Fernelius and Burbage.[1] Potassium octacyanomolybdate(IV) 2-hydrate was made from molybdenum(VI) oxide according to the directions of Furman and Miller.[2] After a final washing of the compound with ethyl ether, the hydrate water was removed by drying at 110° under high vacuum. Potassium octacyanotungstate(IV) 2-hydrate, prepared as described by Heintz,[3] was also converted to the anhydrous compound by washing with ethyl ether and drying at 110° under high vacuum. Potassium hexacyanomanganate(III) was synthesized by the method of Lower and Fernelius[4] and purified as described by Christensen, Kleinberg, and Davidson.[5] Potassium hexacyanocobaltate(III) was made as described by Bigelow.[6] Tank hydrogen, of high purity, was obtained from Air Products and Chemicals, Inc. Just prior to passage over any particular complex, the hydrogen was passed through a tower containing ammoniacal copper(I) solution to remove oxygen, then through a tower containing small glass beads and concentrated sulfuric acid, and finally through two towers packed with sodium hydroxide pellets.

Reactions of Hydrogen with the Cyano Complexes. General Procedure.—The reaction chamber consisted of a Pyrex tube 9 cm. long and 2.2 cm. in outside diameter, each end of which was tapered and joined to Pyrex tubing 1 cm. in outside diameter and 17 cm. long. Two rows of diametrically opposite glass fingers about 2 mm. long and 1 cm. apart lined the inside of the chamber and served to crush any lumps formed and to mix the sample homogeneously during the course of reaction. The reaction tube was installed in a Pyrex tube 50 cm. long and 3 cm. in outside diameter on two Teflon bearings, in such a manner that it could be rotated magnetically.[7] The Pyrex tube containing the reaction chamber was fitted at each end with a one-hole stopper, one end being connected to the source of hydrogen and the other serving as the connection to four towers joined in series. The first tower served as a trap, the next two contained standardized acidified silver nitrate solution for the detection of hydrogen cyanide, and the fourth held standardized sodium hydroxide solution for the absorption of any cyanogen formed during reaction.

Heating was effected in a tubular Hevi-Duty electric multiple unit furnace, Type 70, which was hinged to permit convenient manipulation and observation. The temperature was measured with a chromel–alumel thermocouple and was controlled within a 3° range by means of a Wheelco Model 407 temperature controller with a Model 610 pilot amplifier. The furnace was calibrated over the temperature range 30–600° against known lattice transition and melting points of ammonium nitrate, silver nitrate, potassium dichromate, and sodium molybdate. The reaction assembly, with a thoroughly dried 2–3-g. sample of starting complex in the reaction chamber, was placed in the furnace in such a manner that both the hot junction of the thermocouple and the central portion of the sample were set in the middle of the furnace.

For each starting complex, preliminary experiments were carried out to find a temperature at which complete reaction could be carried out smoothly within a reasonable length of time without any appreciable thermal decomposition of the starting material. The preliminary runs were performed at each trial temperature first with hydrogen passing through the system and then on a new sample with nitrogen sweeping through the system. At

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[1] W. C. Fernelius and J. J. Burbage, *Inorg. Syn.*, **2**, 227 (1946).

[2] N. H. Furman and C. O. Miller, *ibid.*, **3**, 160 (1950).

[3] E. A. Heintz, *ibid.*, **7**, 142 (1963).

[4] J. A. Lower and W. C. Fernelius, *ibid.*, **2**, 213 (1946).

[5] V. J. Christensen, J. Kleinberg, and A. W. Davidson, *J. Am. Chem. Soc.*, **75**, 2495 (1953).

[6] J. H. Bigelow, *Inorg. Syn.*, **2**, 225 (1946).

[7] A complete description of the reaction tube and its manner of installation and utilization can be found in the Ph.D. thesis of Jin Sun Yoo, University of Kansas, 1964. The tube was designed by Mr. Curtis E. Uebele, who has submitted a paper on its construction to *J. Chem. Educ.* We express our thanks to Mr. Uebele for his invaluable assistance.

the temperatures finally chosen for actual study, no cyanogen was evolved from any sample. However, in most instances traces of hydrogen cyanide were liberated in the runs with nitrogen, as evidenced by the formation of a slight turbidity in the first silver nitrate tower. It is probable that the hydrogen cyanide arose through hydrolysis of the starting compound by traces of moisture in the nitrogen

In an actual run, the hydrogen flow rate from the glass tube (7-mm. inside diameter) dipping into the sulfuric acid drying tower was about one bubble per second. The hydrogen was permitted to pass through the reaction chamber at the appropriate temperature until no further silver cyanide precipitation was observed in the silver nitrate absorption towers, after the original solution in them had been replaced by fresh solution.

Reactions of Hydrogen with the Cyano Complexes. Specific Systems.—In the reduction of potassium tetracyanonickelate(II), the complex was first heated in a stream of hydrogen at 110° for 2–3 hr. to make certain that the system was dry. The temperature was then raised to 390° and maintained there until evolution of hydrogen cyanide ceased (about 6 hr.). The product was transferred to a drybox, where it was pulverized to a fine powder, then extracted with dimethylformamide (Spectro reagent, obtained from Matheson Coleman and Bell) until the extract was free of cyanide and nickel ions. (Dimethylformamide readily dissolves potassium cyanide and starting material but has little if any solvent action on the brick-red product.) The product was dried under vacuum, and chemical analyses, oxidation number determinations, magnetic susceptibility measurements, conductivity measurements, and infrared spectra were employed in its characterization. A measure of the hydrogen cyanide liberated in reaction was obtained by titration by the Volhard method of unconsumed silver nitrate in the absorption towers.

In the reaction between potassium octacyanomolybdate(IV) and hydrogen, the system was first swept out with nitrogen for about 3 hr. at 110° and then hydrogen was substituted for the nitrogen and the temperature raised slowly. At 330° hydrogen cyanide began to be evolved. When evolution of this gas ceased, the temperature was raised to 390° and maintained there until reaction was complete (8–10 hr.). The final product was green or black and attempts to find conditions which would yield either the green or black material preferentially were unsuccessful. The final product was extracted under a nitrogen atmosphere in a Soxhlet extractor with Spectroquality methanol (source Fisher Scientific Co.) until the extract contained no dissolved material. The product was characterized by the same types of procedures as described for the nickel-containing product.

In additional experiments, the green product was extracted with methanol in the presence of dry air. Two to three days was required before extraction of soluble material was completed. The residue left after extraction was characterized in the usual fashion.

The conditions for reaction between potassium octacyanotungstate(IV) and hydrogen were essentially identical with those described above for the molybdenum complex. The usual characterization procedures were applied to all products.

The extreme sensitivity of potassium hexacyanomanganate(III) necessitated special precautions in its handling. Samples were purified (see ref. 5) from time to time in order to keep them free from oxide formed by hydrolysis by absorbed moisture. Just prior to use, a sample was dried by pumping under high vacuum. After a sample was placed in the reaction chamber, the system was swept out with nitrogen at 110° for 3 hr. Then the nitrogen stream was replaced by one of hydrogen and the temperature was slowly raised to 420°, where it was maintained for about 10 hr. The brown product which had formed was extracted with dimethylformamide; this solvent removed unreacted starting material, but did not affect the reduction product. The final brown product was analyzed for potassium and manganese. Its magnetic moment and infrared spectrum were also determined.

When potassium hexacyanocobaltate(III) was heated in an atmosphere of hydrogen, no visible change occurred until the temperature reached 240°. At that point the yellow color of the starting material began to change to gray, but neither hydrogen cyanide nor cyanogen was evolved. To determine whether the starting material absorbed hydrogen at 240°, weighed samples were heated for periods of 24, 70, and 90 hr., respectively, under a hydrogen pressure of 1 atm. in a system designed to measure hydrogen uptake. This system consisted of a heating flask connected to a manometer and a large gas reservoir; all connections were of neoprene and were sealed with sealing wax to prevent leakage of hydrogen. In each experiment, a sample of complex was weighed into the heating flask, which contained a stirring bar. The flask was then mounted on a heating mantle over a magnetic stirrer. The system was closed, evacuated, and flushed thoroughly with hydrogen. After the internal pressure of the hydrogen had been adjusted to atmospheric pressure and the initial volume of hydrogen determined, the system was heated to 240° for the appropriate length of time. Then the heating mantle was removed, the system permitted to come to room temperature, and the volume of hydrogen left determined. A number of experiments were carried out at each temperature. Some of the products were examined by magnetic susceptibility measurements, chemical analysis, infrared spectra, and electron paramagnetic resonance. Others were heated for 3–4 hr. at 350° in an atmosphere of nitrogen and the volume of hydrogen evolved was measured. Prior to measurement, the gas was passed through towers containing acidified silver nitrate solution and sodium hydroxide solution, respectively, to remove any hydrogen cyanide and cyanogen formed during the heating process. (No significant quantities of these gases were liberated.) Chromatographic analysis showed that the gas which was collected was hydrogen.

Analytical Methods.[8]—Potassium was determined gravimetrically from acidic solution as the tetraphenylborate.[9] Nickel was analyzed for by the common dimethylglyoxime procedure.[10] Molybdenum was determined gravimetrically as lead molybdate[11] after the cyano complexes had been destroyed by heating with concentrated nitric acid. Tungsten was analyzed for as tungsten(VI) oxide[12] after the complexes had been decomposed by concentrated nitric and perchloric acids. Manganese was determined by the bismuthate procedure[13] after the complex had been decomposed by heating in sulfuric acid solution. Cobalt was determined by precipitation as dithiocyanatotetrapyridinecobalt[14] after the cyano complex had been destroyed by concentrated sulfuric acid. Two methods were commonly employed for the determination of cyanide in the various complexes: the procedure proposed by Williams[15] specifically for cyanide in ferrocyanide complexes and a modified semimicro method for nitrogen.[16] Results obtained by these procedures were sometimes inconsistent since accurate cyanide values are difficult to obtain for cyano complexes which are rather resistant to hydrolysis. Therefore, some of the samples were sent to the Microanalytical Laboratory, Oxford, England, for separate carbon and nitrogen analyses by combustion methods. These analyses showed unequivocally that cyanide was the only source of carbon and nitrogen in the compounds.

Oxidation State Determinations.—The oxidation state of nickel in the product obtained by reduction of potassium tetracyanonickelate(II) was determined by a method described previously.[17]

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[8] For detailed accounts of the analytical procedures the reader is referred to the Ph.D. thesis cited in ref. 7.

[9] K. Sporek and A. F. Williams, *Analyst*, **80**, 347 (1955).

[10] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd Ed., Macmillan Co., New York, N. Y., 1963, p. 689.

[11] N. H. Furman, "Scott's Standard Methods of Chemical Analysis," 6th Ed., D. Van Nostrand Company, Inc., New York, N. Y., 1963, p. 674.

[12] C. L. Wilson and D. W. Wilson, "Comprehensive Analytical Chemistry," Elsevier Publishing Co., New York, N. Y., 1962, p. 601.

[13] T. R. Cunningham and R. W. Coltman, *Ind. Eng. Chem.*, **16**, 58 (1924).

[14] G. Spacu and M. Schiau, *Acad. Rep. Populare Romine, Studii Cercetari Chim.*, **3**, 167 (1955).

[15] H. E. Williams, *J. Soc. Chem. Ind.* (London), **31**, 468 (1912).

[16] B. Jaselski and J. G. Lanese, *Anal. Chim. Acta*, **23**, 6 (1960).

[17] S. von Winbush, E. Griswold, and J. Kleinberg, *J. Am. Chem. Soc.*, **83**, 3197 (1961).

The oxidation state of molybdenum in each of the new cyano complexes obtained for this element was found by the procedure developed by Collenberg,[18] which involved oxidation of molybdenum to molybdate by ferric ion. The oxidation state of tungsten in each of its cyano complexes was determined by a modification of Collenberg's method for molybdenum. A 300-mg. sample was dissolved in deaerated water. To this solution there was added an excess of ferric alum and then of sulfuric acid, and the resulting blue solution was stirred under nitrogen for about 10 min. After this time the reduced iron was titrated potentiometrically with standardized potassium permanganate solution using a calomel electrode as reference and a platinum plate (1 cm.^{2}) as working electrode. In this procedure, tungsten is oxidized to the +5 state.

Magnetic Susceptibility Measurements.—These measurements were made by the Gouy method. The accuracy and reproducibility of the balance was checked by determining the susceptibility of $Hg[Co(SCN)_4]$ against water as the standard. The measurements were made at room temperature, approximately 25°.

Conductance Measurements.—All data were obtained with an Industrial Instruments Model RC-16B2 bridge with two conventional dip-type cells. Every measured resistance was corrected to 25° by the relation $R_{25} = R_t(1 + 0.025\Delta t)$, where R_{25} is the resistance at 25°, R_t is the measured resistance at temperature t, and Δt is the difference in temperature between 25° and the temperature of actual measurement. The cell constant was determined by measuring the resistance of a 0.01 M potassium chloride solution, whose specific conductivity is known to be 0.001413 ohm^{-1}/cm. at 25°.

Infrared Spectra.—These spectra were taken on all starting compounds and products in Nujol mulls on a Perkin-Elmer infrared spectrometer, Model 421.

Results and Discussion

Analytical results are given below in connection with each specific reaction system studied. For the new compounds obtained in this work, Table I presents the effective magnetic moments (in Bohr units) at approximately 25°, the molar conductances (in ohm^{-1}) of 0.001 M solutions at 25°, and the principal infrared absorption maxima (in cm.$^{-1}$) in the region 1950–2200 cm.$^{-1}$, with indications of their relative intensities.

TABLE I

MAGNETIC MOMENTS, MOLAR CONDUCTANCES, AND INFRARED ABSORPTION

Compound	μ_{eff}	Λ_m	Infrared peaks
$K_4Mo(CN)_6$	1.13	546, 489, 537	2073 m, 2055 s, 2035 m, 2010 s, 1960 s, br
$K_3Mo(CN)_6$	1.50	405, 408	2135 w, 2110 s, 2050 s
$K_4W(CN)_6$	0.94	595, 639	2098 m, 2080 s, 2050 m, 2010 s, 1990 m, 1950 s
$K_3W(CN)_6$	1.76	396, 408, 418	2099 s, 2041 m, 2023 s
$K_3Mn(CN)_5$	4.40	...	2178, s, 2090 s, 2060 s, 2040 s

Potassium Tetracyanonickelate(II) and Hydrogen.—The solid product obtained from this reaction is the long-known nickel(I) compound, $K_4Ni_2(CN)_6$. Like the known compound, the present product is brick-red in color and is diamagnetic. The three strong infrared bands observed at 2129, 2083, and 2055 cm.$^{-1}$ are in almost exact agreement with those previously reported[19] for $K_4Ni_2(CN)_6$. Confirmation is provided by the following analytical results, based on replicate analyses of three separate preparations. *Anal.* Calcd. for $K_4Ni_2(CN)_6$: K, 36.38; Ni, 27.31; CN, 36.31. Found: K, 37.18 ± 0.38; Ni, 26.86 ± 0.28; CN, 35.57 ± 0.42; oxidation number of Ni, 1.08 ± 0.01. Cyanide recovered from the HCN evolved during the reaction amounted to 10.71 ± 0.10% of the weight of the starting material, which is close to the 10.80% calculated for loss of one cyanide by $K_2Ni(CN)_4$ and indicates substantially complete conversion of the starting material in accordance with the reaction

$$2K_2Ni(CN)_4 + H_2 = K_4Ni_2(CN)_6 + 2HCN$$

Potassium Octacyanomolybdate(IV) and Hydrogen.—The dark green solid product which was usually obtained and the black product which occasionally resulted exhibited no significant difference from each other in composition, infrared spectrum, or magnetic character. The analytical results which follow are based on direct determinations of potassium and molybdenum on three separate preparations, but only on direct cyanide determination, the others being calculated by difference. The latter procedure appears to be justified by the absence of cyanogen evolution and the results of combustion analysis of the product, showing a 1:1 atomic ratio of C:N. Moreover the cyanide values by difference are in substantial agreement with the value directly determined. *Anal.* Calcd. for $K_4Mo(CN)_6$: K, 38.29; Mo, 23.49; CN, 38.22. Found: K, 37.85 ± 0.74; Mo, 23.60 ± 0.48; CN, 38.20 ± 0.12; oxidation number of Mo, 2.10 ± 0.11. The cyanide recovered from the evolved HCN was 10.61 ± 0.38% of the weight of starting material, just slightly less than the 11.30% calculated for loss of two cyanides by $K_4Mo(CN)_8$. The reaction which occurs under these conditions is thus

$$K_4Mo(CN)_8 + H_2 = K_4Mo(CN)_6 + 2HCN$$

yielding the hitherto unreported hexacyanomolybdate(II) compound.

The infrared spectrum of the product, as shown in Table I, exhibits a series of bands which represent a shift to lower frequencies as compared with $K_4Mo(CN)_8$, which absorbs mainly at 2132 (m), 2126 (m), and 2104 (s) cm.$^{-1}$. The direction of the shift is consistent with a reduction in the ratio of coordination number to oxidation number[20] in going from $K_4Mo(CN)_8$ to $K_4Mo(CN)_6$.

Aqueous solutions of the compound exhibited strong reducing power toward hydrogen peroxide, iodine, and silver ion. On standing, the solutions, initially green, changed to a reddish color and finally to yellow.

Prolonged extraction of the green $K_4Mo(CN)_6$ with methanol in dry air yielded a greenish brown solid which turned out to be a hexacyanomolybdenum(III) compound, as the following results show. *Anal.* Calcd. for $K_3Mo(CN)_6$: K, 31.76; Mo, 25.97; CN, 42.27. Found: K, 33.26 ± 0.28; Mo, 25.88 ± 0.42; CN, 41.44 ± 0.42; oxidation number of Mo, 2.93 ± 0.10. Molar conductance values given in

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[18] O. O. Collenberg, *Z. anorg. allgem. Chem.*, **121**, 308 (1922).

[19] M. F. A. El-Sayed and R. K. Sheline, *J. Am. Chem. Soc.*, **78**, 702 (1956).

[20] M. F. A. El-Sayed and R. K. Sheline, *J. Inorg. Nucl. Chem.*, **6**, 187 (1958).

Table I may be compared with the value 435 for $K_3Fe(CN)_6$. There can be little doubt that the product is the hexacyanomolybdate(III), $K_3Mo(CN)_6$, which appears not to have been previously reported.

Potassium Octacyanotungstate(IV) and Hydrogen.—As with the analogous molybdenum compound, both black and green products, apparently differing in no significant respect, were obtained in different runs. Analytical results from three preparations (only one direct cyanide determination; the others by difference) were as follows. *Anal.* Calcd. for $K_4W(CN)_6$: K, 31.51; W, 37.04; CN, 31.45. Found: K, 30.88 ± 0.74; W, 37.11 ± 0.03; CN, 31.68 ± 0.59; oxidation number of W, 1.98 ± 0.05. Cyanide recovered from the evolved HCN was 9.94 ± 0.16% of the starting compound, thus corresponding to the loss of two cyanides by $K_4W(CN)_8$ (calcd. 9.49). The principal infrared bands lie at lower frequencies than those of the parent compound.

The reaction between hydrogen and the octacyanotungstate(IV) compound, therefore, is entirely similar to that with the corresponding molybdenum compound

$$K_4W(CN)_8 + H_2 = K_4W(CN)_6 + 2HCN$$

The similarity extends even further. When the green $K_4W(CN)_8$ was subjected to long extraction with methanol in dry air, a brown product was afforded which analyzed as follows. *Anal.* Calcd. for $K_3W(CN)_6$: K, 25.65; W, 40.21; CN, 34.14. Found: K, 25.51 ± 1.33; W, 39.89 ± 0.27; CN, 34.60 ± 0.58; oxidation number of W, 3.08 ± 0.07. Oxidation of the tungsten(II) compound to give $K_3W(CN)_6$, analogous to the second reaction described above for the molybdenum system, has obviously occurred. Neither a hexacyanotungstate(II) nor a hexacyanotungstate(III) compound appear to have been reported before.

Potassium Hexacyanomanganate(III) and Hydrogen.—The cyanide evolved as HCN in this reaction came to only 6.50 ± 0.58% (calcd. for loss of one cyanide, 7.92), indicating incomplete conversion of the starting material. Analysis of the brown solid product which remained after dimethylformamide extraction to remove the unconverted hexacyanomanganate(III) gave the following results. *Anal.* Calcd. for $K_3Mn(CN)_5$: K, 38.80; Mn, 18.17; CN, 43.03. Found: K, 39.47 ± 0.29; Mn, 18.06 ± 0.26; CN, 42.47 ± 0.34.

The product is insoluble in water and in all the common organic solvents tried. An oxidation number determination could not be effected, but the analytical data clearly support the empirical formula $K_3Mn(CN)_5$. The effective magnetic moment of manganese is much higher than the value 2.18 which has been reported[21] for the hexacyanomangate(II) compound, $K_4Mn(CN)_6 \cdot 3H_2O$. It is, however, fairly close to the 4.22 B.M. value[21] observed for the compound commonly formulated as $K_2Mn[Mn(CN)_6]$. This last compound might be expected to have a spin-only moment corresponding roughly to three unpaired electrons. The value 4.40 found for $K_3Mn(CN)_5$ might then be taken as some indication of true five-coordination here. However, the possibility that the high value may arise from contamination with a small amount of highly paramagnetic oxide cannot be excluded. The insolubility of the compound strongly indicates the presence of a polymeric species, perhaps involving cyanide bridges. A strong infrared band observed at 2178 cm.$^{-1}$ might arise from such bridging groups.

Potassium Hexacyanocobaltate(III) and Hydrogen.—In the hydrogen uptake experiments conducted at 240° for periods of 24, 70, and 90 hr., the moles of hydrogen taken up per mole of $K_3Co(CN)_6$ were, respectively, 0.08, 0.09, and 0.10. Magnetic susceptibility measurements made using a coil current of 4.60 amp. corresponded to cobalt μ_{eff} values, respectively, of 2.53, 2.71, and 2.75. With a coil current of 6.60 amp., values of 1.88, 2.41, and 2.40 were obtained. The dependence on field strength suggests the presence of some ferromagnetic material, probably minute amounts of cobalt metal. When samples of the gray materials were heated at 350°, the amount of hydrogen recovered was the same as that taken up, within experimental error. Analysis of the gray material indicated no significant difference from $K_3Co(CN)_6$, nor did the infrared spectrum show any difference. It would appear that under the conditions employed here there is a small, probably physical, uptake of hydrogen, but no significant reaction.

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[21] N. Goldenberg, *Trans. Faraday Soc.*, **36**, 847 (1940).