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Further Studies on Transition Metal–Cyano Complexes in Molten Potassium Cyanide

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The reactions of elemental iron, chromium, silver, copper, cobalt, titanium, vanadium, and molybdenum with mercury(II) cyanide in molten (except for the iron system) potassium cyanide have been investigated. In every case but with chromium, the molar ratio of metal to mercury(II) cyanide was approximately 2:1. Iron, chromium, silver, copper, and cobalt reacted to give as main products small yields of the following cyano complexes: $K_4Fe(CN)_6$ (*ca.* 20%), $K_3Cr(CN)_6$ (*ca.* 5%), $KAg(CN)_2$ (*ca.* 10%), $K_2Cu(CN)_3$ and $K_3Cu(CN)_4$ (*ca.* 20–25% combined), and $K_3Co(CN)_5$ (*ca.* 12–16%). The last product, which is tan, can also be obtained from the reaction between cobalt(II) cyanide and molten potassium cyanide or by heating the well-known violet compound of the same empirical formula. Whereas the latter is diamagnetic and presumably dimeric, the tan compound is paramagnetic, the magnetic moment (*ca.* 2 BM) strongly indicating monomeric character. Titanium, vanadium, and molybdenum do not appear to react with mercury(II) cyanide in molten potassium cyanide, although a small amount of a water-soluble brown-black solid is produced in each case. The same solid, as shown by infrared spectra, is obtained when potassium cyanide and mercury(II) cyanide are heated to about 600°. Although the dark brown solid has not been completely characterized, chemical analysis and the infrared spectrum together suggest that it contains a polymeric CN anion.

In previous papers,[1,2] we described novel methods for the preparation of cyano complexes of transition metals in molten potassium cyanide. Two main types of reactions were carried out in the melt: (a) direct oxidation of metal (Ni, Mn, Pd) by mercury(II) cyanide and (b) oxidation of potassium cyanide by a transition metal (Ni, Mn, Mo, Pd) cyano complex. Unusual cyano complexes of these metals were made and characterized. Investigation of the first class of reaction has now been extended to a number of other transition metals—Fe, Cr, Ag, Cu, Co, Ti, V, and Mo—and this paper deals with the results obtained.

Experimental Section

Materials.—Potassium cyanide, granular reagent grade with an assay of 99.1% KCN, was obtained from the J. T. Baker Chemical Co. and purified in the following manner. The substance was dried *in vacuo* for 12 hr and then gradually heated to a molten condition at 650° under a continuous stream of nitrogen. The material was then cooled to room temperature, during which time small particles of a black carbonaceous material settled to the bottom. The potassium cyanide was separated from the black material, powdered, analyzed, and stored in a drybox. The KCN assay, based on cyanide analysis, was greater than 99.5%. Mercury(II) cyanide, Baker Analyzed reagent with an assay of 100%, was dried under vacuum at 200° for 12 hr and stored in a drybox. Iron powder, supplied by the Mallinckrodt Chemical Co., was treated with hydrogen at 400° to reduce any surface coating of oxide. The product was found to have an iron content of 99.3%. Chromium powder of at least 99% purity was obtained from the Fisher Scientific Co. and used without further purification. The silver metal employed was Fisher Certified precipitated powder. Copper, J. T. Baker purified powder containing less than 98% of the metal, was treated with hydrogen at 400° until the purity of the metal was greater than 99.1%. Cobalt metal, Fisher Certified reagent powder, had a stated purity of 99.2% and was used without further treatment. Titanium powder, 99.9% pure from Alfa Inorganics, Inc., molybdenum powder, 99.9% pure from Matheson Coleman & Bell, and granular vanadium, 99.56% pure from Alfa Inorganics, Inc., were also used without further purification. The purple, presumably dimeric, form of potassium pentacyanocobaltate(II) was made according to the directions of Adamson.[3] *Anal.* Calcd for $K_3Co(CN)_5$: Co, 19.24. Found: Co, 19.06 ± 0.02 (oxidation state of cobalt, 1.99 ± 0.02). Cobalt(II) cyanide was prepared by the slow addition of potassium cyanide to a very dilute solution of cobalt(II) chloride. The light brown precipitate was air dried and then heated under dry nitrogen for 12 hr at 260–280° to remove water of hydration. Since analysis indicated the presence of water in the product, it was further dehydrated on a vacuum line by heating for 10 hr at 260° with continuous pumping. The cobalt content of the final product was consistent with the formula $Co(CN)_2 \cdot 0.19H_2O$. Methanol and ethanol, obtained as commercial grade solvents, were converted to the anhydrous condition by distillation from magnesium metal and a trace of iodine. N,N-Dimethylformamide, Baker Analyzed reagent, was passed through 4A molecular sieves and then distilled *in vacuo*. The same compound supplied by Fisher Scientific Co. as reagent material with a water content of 0.08% was used without further treatment. Acetonitrile was obtained from the J. T. Baker Chemical Co. and was distilled from calcium hydride. The addition of a small quantity of potassium cyanide to the distillation pot was found advantageous since it apparently reacted with impurities which catalyzed polymerization of the solvent. Liquid ammonia of anhydrous grade was purchased from the Spencer Chemical Co. and used directly from the tank.

Analytical Procedures.—Potassium was determined gravimetrically by precipitation from acidic solution as the tetraphenylborate.[4] Ferrocyanide ion was analyzed for by titrating the sample in dilute sulfuric acid with standard potassium permanganate solution using iron(II) 1,10-phenanthroline as indicator.[5] For the determination of chromium, the sample was decomposed with a mixture of concentrated sulfuric and perchloric acids (5:2 by volume) to oxidize the metal to the +6 oxidation state. The chromium content was then found by the standard iodometric method. In the analysis for silver, the sample was decomposed by concentrated nitric acid and the diluted solution was titrated with standardized potassium thiocyanate in the presence of iron(III) nitrate as indicator. Copper was deter-

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

[2] W. L. Magnuson, E. Griswold, and J. Kleinberg, *Inorg. Chem.*, **3**, 88 (1964).

[3] A. W. Adamson, *J. Am. Chem. Soc.*, **73**, 5710 (1951).

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

[5] I. M. Kolthoff and R. Belcher, "Volumetric Analysis," Vol. III, Interscience Publishers, New York, N. Y., 1957, p 1153.

mined by a standard iodometric procedure after the sample had been decomposed with concentrated nitric acid and boiled to near dryness, and the metal was converted to the copper(II)–ammine complex.[6] The determination of cobalt was effected by a gravimetric method utilizing the formation of the insoluble compound, dithiocyanatotetrapyridinecobalt(II),[7] following decomposition of the sample by concentrated sulfuric acid. The percentage of cyanide in a sample was ordinarily calculated from nitrogen values found by a modified Kjeldahl procedure.[8] In a few instances, additional data on cyanide content were obtained by microanalysis for carbon and nitrogen performed by Pascher Mikroanalytisches Laboratory, Bonn, Germany, or by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. The oxidation state of cobalt in the cyano complex solated was found by oxidation of the complex to the hexacyanocobaltate(III) ion with an excess of a standardized solution of potassium ferricyanide and iodometric determination of unreacted oxidant.[9]

Infrared Spectra.—Such spectra were taken on all products in Nujol mulls or KBr pellets on a Perkin-Elmer infrared spectrometer, Model 421.

Magnetic Susceptibility Measurements.—These measurements were made at room temperature, *ca.* 25°, by the Gouy method, using the susceptibility of $Hg[Co(NCS)_4]$ as a standard.

X-Ray Patterns.—As part of the characterization of the cyano complex obtained in the cobalt system, X-ray powder patterns were obtained for a number of compounds on a diffraction unit manufactured by Philips Electronics Instruments, with which a Debye–Scherrer powder camera of 5.7-cm radius was used. The sample was loaded into a 0.2-mm capillary tube and sealed with a flame to exclude moisture and oxygen during the 8-hr exposure time. Copper Kα radiation with a wavelength of 1.54050 Å was used. The *d*-spacing values were calculated from the lines on the photographic film with the use of data from published tables.[10]

The Reaction Involving Iron, Mercury(II) Cyanide, and Potassium Cyanide.—In a typical experiment, 1 g of iron powder, 2 g of mercury(II) cyanide, and 2 g of potassium cyanide (approximate molar ratio 2:1:4) were intimately mixed and transferred to a Pyrex reaction vessel which consisted of a piece of tubing 80 mm long and 22 mm in i.d., which was closed at one end and open at the other end where it was sealed to another tube 180 mm in length and 7 mm in i.d. The vessel was placed in a hinged Hevi-Duty electric multiple-unit furnace, 33 cm long with a bore 30 mm in diameter, so that a portion of the narrow part of the vessel protruded from the furnace. It was then evacuated to a pressure of less than 0.05 mm and heated at 100° for at least 1 hr with continuous pumping, the temperature being regulated by means of a Wheelco indicating controller with Pilot amplifier. The reaction vessel was sealed with the use of a hand torch and the temperature of the reaction mixture was gradually raised to 550° and maintained there for 1 hr. During the course of heating, elemental mercury distilled from the hot zone of the reactants into that part of the reaction tube which was outside the furnace. The reaction mixture apparently did not form a free-flowing melt and at 550° it was a dark gray solid mass. The reaction vessel was permitted to cool to room temperature and the contents then were transferred to a drybox and powdered. Unreacted potassium cyanide was removed from the solid by extraction with anhydrous ethanol for 36 hr. The gray-black solid remaining on the extraction thimble was dried *in vacuo* at room temperature and then dissolved in deaerated water. The solution was filtered in a nitrogen atmosphere and ethanol was added to the filtrate to precipitate a white material. The latter was collected, dried under vacuum for several hours at 100°, cooled, and analyzed.

The Chromium–Mercury(II) Cyanide–Potassium Cyanide System.—To a reaction vessel similar to that described above, there was added a mixture of chromium (2 g), mercury(II) cyanide (3.5 g), and potassium cyanide (8.5 g), corresponding to a molar ratio of 2.75:1:10. The mixture was heated in the electric furnace at 150° for at least 1 hr with continuous pumping and the reaction vessel was sealed. The temperature was then gradually raised to 620°, during which operation the contents of the tube slowly changed to a dark brown-red melt containing pockets of solid material, and mercury deposited in that part of the reaction vessel which was outside the furnace. After a heating period of 5 hr at 620°, the reaction mixture was allowed to cool to room temperature and was transferred to a drybox and powdered. It was then extracted with anhydrous ethanol for several days in a Soxhlet extractor. The material remaining on the extraction thimble was dried under vacuum at room temperature and subjected to extraction with liquid ammonia. Although the liquid ammonia extract was a yellowish brown, the solid residue obtained after the ammonia was allowed to boil off was light tan. This material was dried *in vacuo* at 50° for several hours, cooled, and analyzed.

Reaction Involving Silver, Mercury(II) Cyanide, and Potassium Cyanide.—A powdered mixture of 1.5 g of silver metal, 2 g of mercury(II) cyanide, and 2 g of potassium cyanide (molar ratio 2:1:4) was added to a specially designed Pyrex reaction tube (see ref 9, p 32), equipped with a glass well for the collection of mercury and a 28/12 standard taper ball joint for attachment to a vacuum line. The reaction tube was placed in the electric furnace so that the well was just outside the furnace, after which the tube was attached to the vacuum line and heated at 100° for 2 hr with continuous pumping. The stopcock leading to the vacuum was closed and the reaction mixture was gradually heated to 350°, where vigorous frothing of the mixture occurred and the system had the appearance of a black melt. The temperature was kept at 350° for 1 hr, and after the reaction mixture was cooled to room temperature, it was transferred to a drybox and powdered. It was then extracted with acetonitrile at room temperature. The solvent was removed from the extract by heating under reduced pressure on a hot water bath, leaving a white solid with a yellow tinge. After being dried *in vacuo* at 100° for several hours, the solid was analyzed.

Copper–Mercury(II) Cyanide–Potassium Cyanide.—One gram of copper, 2 g of mercury(II) cyanide, and 2 g of potassium cyanide (molar ratio 2:1:4) were mixed thoroughly and the mixture was transferred to a vessel like that described for the iron reaction. The system was evacuated, heated with pumping to 100°, and kept at this temperature for several hours. The reaction vessel was then sealed, and the temperature was raised slowly to 550°, where it was maintained for 30 min. The dark brown melt which had formed was allowed to solidify by cooling. The solid was transferred to a drybox and powdered. It was then extracted with anhydrous ethanol for 36–46 hr to remove potassium cyanide. The light brown solid remaining after the extraction with ethanol was dried under vacuum and subjected to extraction with liquid ammonia. The light beige solid which was left after extraction was dried at 100° *in vacuo* for several hours and analyzed. A brown residue was obtained from the liquid ammonia solution upon evaporation of the solvent. This was also dried under vacuum at 100° and analyzed.

Cobalt–Mercury(II) Cyanide–Potassium Cyanide.—To a Pyrex reaction tube like that employed for the silver system, there was added, in a typical experiment, an intimate mixture of 0.91 g of cobalt powder, 2.0 g of mercury(II) cyanide, and 3.1 g of potassium cyanide (molar ratio 2:1:6). The tube was attached to a vacuum line and evacuated to a pressure of less than 10^{-3} Torr. The reaction mixture was then heated to 150° for several hours with continuous pumping. The system was then closed off to the pumping unit and the temperature was gradually raised. At about 560° the reaction mixture became a dark brown melt.

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(6) G. Ayres, "Quantitative Analysis," Harper Brothers, New York, N. Y., 1958, p 463.

(7) A Vogel, "Quantitative Chemical Analysis," 3rd ed, Longmans, Green and Co., London, 1961, p 531.

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

(9) Detailed directions for all of the analytical procedures cited above and for the preparative experiments to be described below may be found in the Ph.D. thesis of Jesse G. Reinstein, University of Kansas, 1969.

(10) "Tables for the Conversion of X-Ray Diffraction Angles to Interplanar Spacing," National Bureau of Standards Applied Mathematics Series, Monograph 10, U. S. Government Printing Office, Washington, D. C., 1950.

The temperature was kept in the 560–580° range for 5 hr, after which the melt was permitted to solidify. The brown solid was powdered in a drybox and placed in a filtration apparatus which consisted of a fine fritted disk (20-mm porosity) sealed into the center of a Pyrex tube 300 mm in length and 22 mm in i.d., closed at one end. The filtration tube was then placed in an electric furnace, 13 cm long and with a bore 28 mm in diameter. The system was evacuated and heated gradually with continued pumping to 560–580°. When the solid had become molten, a positive pressure of dry nitrogen was introduced above the melt, causing the liquid to flow through the filter disk. The filtrate on solidification retained its brown color, although in some areas there were tiny spots of gray material. The solid which remained on the disk was dark gray and was shown to contain metallic cobalt. The brown solid filtrate was powdered (light tan) and subjected to a Soxhlet extraction *in vacuo* with N,N-dimethylformamide for 2–4 days. The solid remaining in the extraction thimble was then extracted with liquid ammonia and the light tan solid which remained undissolved by the ammonia was dried under vacuum at room temperature for several hours. The magnetic susceptibility of the substance was determined and a chemical analysis was performed.

Reaction of Cobalt(II) Cyanide with Potassium Cyanide.—Six grams of potassium cyanide and 2 g of cobalt(II) cyanide (approximate molar ratio 5.1:1) were ground together in a drybox and then placed in a reaction tube which, except for the absence of a well for the collection of mercury, was like that used for the silver system. The reaction tube was evacuated to a pressure of 10^{-3} Torr and while pumping was continued, the temperature was raised slowly to 260–280° and kept there for 3 hr. The reaction tube was then closed off from the pumping unit and the temperature increased to 530° and was maintained there for 1 hr (at 480°, the solid reactant mixture changed to a dark brown melt). The brown solid resulting from cooling the melt was powdered, placed in the filtration apparatus described above, heated to 530°, and filtered. The tan product which came through the filter was extracted first with N,N-dimethylformamide and then with liquid ammonia. The solid left after the extraction was dried under vacuum at 50°, after which it was analyzed and its magnetic susceptibility was measured.

Thermal Treatment of Purple Potassium Pentacyanocobaltate(II).—This compound was heated under vacuum at 230° for 15–20 min. The purple starting material was transformed into a tan product; there was no gas evolution during the heating process. The magnetic susceptibility, infrared spectrum, and X-ray powder pattern of the tan material were determined.

Reaction of Titanium, Vanadium, or Molybdenum with Mercury(II) Cyanide and Potassium Cyanide.—Reaction of each of these metals with mercury(II) cyanide and potassium cyanide (molar ratio 2:1:6) at 600° under vacuum produced a brown material and was accompanied by evolution of cyanogen. Each product was extracted with ethanol to remove unreacted potassium cyanide and an infrared spectrum was run on the undissolved portion.

The Mercury(II) Cyanide–Potassium Cyanide System.—In a typical experiment, a mixture of 8 g of mercury(II) cyanide and 6 g of potassium cyanide, corresponding to an approximate molar ratio of 1:3, was placed in a reaction tube like that used for the silver reaction. The tube was attached to a vacuum line and the system evacuated and then closed to the pumping system. The temperature of the reaction mixture was raised gradually and the evolution of a gas (cyanogen) was observed at 250°. At 450° the pressure within the reaction volume of about 2 l. was approximately 300 mm. At 500–520° the pressure within the system began to decrease and the mixture was quite dark. The temperature was increased to 590–600° and kept there for 12 hr. After a 10-hr passage of time, the pressure in the system had decreased to 10–20 mm. On completion of heating, the reaction mixture, which never did melt, was cooled to room temperature, powdered, and extracted with ethanol to remove potassium cyanide. The brown-black solid remaining after extraction was treated with a stream of nitrogen to remove ethanol and then dissolved in 150 ml of water. The solution was filtered and ethanol was added to the filtrate until a dark brown solid was precipitated. The latter was collected on a sintered-glass crucible of fine porosity, dried under vacuum at 100°, and analyzed.

Results and Discussion

The Iron System.—The white solid isolated from reaction involving iron, mercury(II) cyanide, and potassium cyanide proved to be potassium ferrocyanide. *Anal.* Calcd for $K_4Fe(CN)_6$: K, 42.46; $Fe(CN)_6^{4-}$, 57.53. Found: K, 41.67 ± 0.28; $Fe(CN)_6^{4-}$, 57.62 ± 0.25. The infrared spectrum showed absorption bands at 2092 (s), 2079 (vs), 2060 (vs), 2042 (vs), and 2028 cm^{-1} (vs), in excellent agreement with the absorptions reported in the literature.[11] The yield of complex was about 20% based on the amount of iron reactant.

The Chromium System.—The chromium-containing product in this system was potassium hexacyanochromate(III) (yield, *ca.* 5% based on chromium starting material). *Anal.* Calcd for $K_3Cr(CN)_6$: K, 36.10; Cr, 16.10. Found: K, 35.76 ± 0.30; Cr, 15.53 ± 0.25. The material isolated exhibited infrared absorption bands at 2170 (s) and 2130 cm^{-1} (vs), in addition to a series of broad and intense bands with maxima at 1620, 1520, and 1400 cm^{-1}. A sample of pure potassium hexacyanochromate(III) had a single absorption band at 2130 cm^{-1} (vs). It is evident that the complex isolated from reaction among chromium metal, mercury(II) cyanide, and potassium cyanide was contaminated with a small amount of impurity. The maxima in the absorption bands in the 1620–1400-cm^{-1} region are similar to those found in the product of reaction between mercury(II) cyanide and potassium cyanide, the results of which are described later. It is worth noting that strong heating of potassium hexacyanochromate(III) caused the appearance of a sharp band at 2170 cm^{-1}, the original band at 2130 cm^{-1} still being present.

The Silver System.—Extraction of the solidified melt with acetonitrile after reaction of silver, mercury(II) cyanide, and potassium cyanide and removal of the solvent gave a white solid which proved to be potassium dicyanoargentate(I) (yield, *ca.* 10%). *Anal.* Calcd for $KAg(CN)_2$: K, 19.65; Ag, 54.20; CN, 26.14. Found: K, 19.48 ± 0.04; Ag, 53.46 ± 0.17; CN, 25.68 ± 0.15. The infrared spectrum had absorption bands at 2140 (vs) and 2094 cm^{-1} (w); reported[12] for $KAg(CN)_2$, 2139 cm^{-1}.

There is some evidence that a small amount of potassium tetracyanoargentate(I) was also formed in the reaction. The solid left after extraction with acetonitrile had infrared absorption bands at 2170 (w),[13] 2140 (mw), 2094 (vs), and 2091 cm^{-1} (s). Potas-

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(11) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1966.

(12) L. Jones and R. Penneman, *J. Chem. Phys.*, **22**, 965 (1954).

(13) The solidified melts of all the systems studied showed a weak band at 2170 cm^{-1}, which ordinarily could be removed by extraction with solvents in which potassium cyanide is soluble, *e.g.*, ethanol. This absorption band is believed to be due to some thermally stable product arising from potassium cyanide. A likely candidate is potassium cyanate which could result from reaction of traces of moisture with the cyanide. The cyanate is reported to have an absorption band at 2165 cm^{-1}.[11]

sium tetracyanoargentate(I) is reported to show infrared bands at 2097 (s) and 2091 cm^{-1} (m).[12] Attempts to purify the product remaining after acetonitrile extraction were unsuccessful.

The Copper System.—Two cyano complexes of copper—potassium tricyanocuprate(I) and potassium tetracyanocuprate(I)—in a combined yield of 20–25% were generally isolated from the Cu–Hg(CN)$_2$–KCN system. The former compound was obtained as a brown material from the liquid ammonia extract, the solidified melt having been previously extracted with anhydrous ethanol to remove potassium cyanide. The tetracyano complex made up the light beige liquid ammonia insoluble material. *Anal.* Calcd for $K_2Cu(CN)_3$: K, 35.58; Cu, 28.91; CN, 35.50. Found: K, 34.60 ± 0.50; Cu, 28.12 ± 0.13; CN, 34.83 ± 0.64. Calcd for $K_3Cu(CN)_4$: K, 41.18; Cu, 22.30; CN, 36.52. Found: K, 40.60 ± 0.60; Cu, 21.91 ± 0.12; CN, 35.59 ± 0.50.

The beige color of the tetracyano complex isolated indicates that it is contaminated with traces of impurity since it is known that copper(I) forms a colorless $K_3Cu(CN)_4$ complex with cyanide ion. This is borne out by the infrared spectrum of the material which showed the following absorption bands: 2080 (vs), 2042 (m), and 2033 cm^{-1} (vw). The same compound prepared by reaction of copper(I) cyanide with potassium cyanide in aqueous solution, according to the directions of Jones,[14] is a white material which gave absorption maxima at 2094, 2081, and 2075 cm^{-1} in agreement with the literature values.

The brown material which analyzed as the tricyano complex is probably also impure. This substance had major absorption bands at 2109 (s) and 2080 cm^{-1} (vs) and a weak one at 2042 cm^{-1}. Attempts to repeat a reported preparation[15] of the tricyano complex, in order to have material for comparison with the product isolated from the Cu–Hg(CN)$_2$–KCN system, were unsuccessful. It should also be pointed out that in one or two instances only the tetracyano complex could be isolated from the reaction in molten potassium cyanide.

The Cobalt Systems.—The most interesting results were obtained in these systems. The light tan material (yield, 12–16%) isolated from reaction between cobalt metal, mercury(II) cyanide, and potassium cyanide at 560–580° had the empirical formula $K_3Co(CN)_5$. *Anal.* Calcd for $K_3Co(CN)_5$: K, 38.29; Co, 19.24; CN, 42.47. Found: K, 37.52 ± 0.05; Co, 18.90 ± 0.10; CN, 42.01 ± 0.20 (oxidation state, 2.13 ± 0.01). The compound showed major bands in the infrared spectrum at 2129 (s), 2077 (vs), and 2042 cm^{-1} (w). In some preparations additional bands at 2120 and 2110 cm^{-1} were present. Magnetic susceptibility measurements showed it to be ferromagnetic, but such behavior was not unexpected since the compound was contaminated with traces of cobalt metal which could not be removed.

The same tan compound was obtained in about 30% yield from the reaction between cobalt(II) cyanide and an excess of potassium cyanide *in vacuo* at 530°. *Anal.* Found: K, 37.75 ± 0.30; Co, 19.14 ± 0.14; CN, 41.75 ± 0.07 (empirical formula, $K_{2.97}Co(CN)_{4.95}$) (oxidation state, 2.09 ± 0.03). The infrared spectrum was identical (major bands at 2129, 2077, and 2042 cm^{-1}; additional bands at 2120 and 2110 cm^{-1} in one synthesis) with that of the product isolated from the Co–Hg(CN)$_2$–KCN system and the material was also ferromagnetic owing to the presence of traces of free metal.

The question arises as to the relationship between the tan compound of empirical formula $K_3Co(CN)_5$ isolated in this investigation and the well-known purple substance of similar composition, which is often referred to as Adamson's compound and is obtained from reaction between cobalt(II) salts and potassium cyanide in aqueous solution.[3,16]

The infrared spectrum of the purple compound is reported to have absorption bands at 2133 (vs), 2090 (vs), and 2079 cm^{-1} (vs).[17] The same substance prepared in our laboratory showed bands at 2128 (s), 2120 (s), 2110 (s), and 2079 cm^{-1} (vs). (We can offer no explanation for the observed discrepancy in the spectrum of the purple compound.) Thus, except for an absorption band at 2042 cm^{-1} in the tan compound, it and the purple material have very similar infrared spectra. The purple compound is diamagnetic and this fact is believed to be due to interaction between two cobalt(II) atoms, each with an unpaired electron, to form the dimer $K_6Co_2(CN)_{10}$. Magnetic measurements on the tan compound prepared by the two methods cited above were of little value since the material contained traces of the ferromagnetic metal, probably formed by some decomposition at the high temperatures used for reaction.

A third method of preparation—the heating of the diamagnetic purple compound for a short time under vacuum at 230°—gave the tan material apparently free of contamination by metal. The product obtained by this method showed infrared absorption bands at 2128 (s), 2076 (vs), and 2042 cm^{-1} (w). The product was paramagnetic, the molar susceptibilities (on the basis of the formula $K_3Co(CN)_5$) for two different preparations being 2064×10^{-6} and 1832×10^{-6} cgs emu/mol. These values correspond to effective magnetic moments of 2.22 and 2.09 BM, respectively, and are somewhat higher than the spin-only moment of 1.73 BM expected for a low-spin cobalt(II) complex. Nevertheless they show unequivocally the presence of one unpaired electron and therefore indicate that the tan compound is a mononuclear species. It should be noted that the tan substance did not revert to the purple material even on long standing at room temperature.

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(14) L. Jones, *J. Chem. Phys.*, **29**, 463 (1958).

(15) F. Gallais, *Bull. Soc. Chim. France*, [5] **12**, 657 (1945).

(16) Adamson's compound generally contains some bound potassium cyanide, *e.g.*, $K_3Co(CN)_5 \cdot 0.17KCN$.

(17) W. P. Griffith and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **7**, 296 (1958).

Additional proof that the tan and purple compounds differ in structure comes from their substantially different X-ray powder patterns. The tan compound exhibits strong *d*-value spacings at 3.779, 3.066, 2.937, 2.761, and 2.164 Å, whereas for Adamson's compound strong lines are found at 4.304, 3.847, 3.068, and 2.687 Å. There is also little similarity in the *d* spacings of the tan compound and those of potassium hexacyanocobaltate(III).

Reaction of Titanium, Vanadium, or Molybdenum with Mercury(II) Cyanide and Potassium Cyanide.—After reaction at 600° and removal of excess potassium cyanide by extraction with ethanol, the brown products in all three cases gave infrared spectra which were essentially identical with those of each other and with that exhibited by the product formed on reaction of mercury(II) cyanide with molten potassium cyanide. The transition metals undergo no reaction.

The Mercury(II) Cyanide–Potassium Cyanide System.—The brown-black water-soluble material obtained from reaction of these substances at about 600° gave for four separate experiments the following analyses for potassium and nitrogen (Kjeldahl): K, 23.70 ± 0.30; N, 36.76; K, 23.85 ± 0.49; N, 36.68; K, 24.19 ± 0.23; N, 37.08 ± 0.59; and K, 23.55 ± 0.12; N, 36.73 ± 0.10. No mercury was present in the brown substance. These data would appear to show that the same compound was formed in each case. On the reasonable assumptions that the nitrogen is part of a grouping arising from the interaction of cyanide ion with cyanogen formed from the decomposition of mercury(II) cyanide and that the product contains nitrogen and carbon in a 1:1 correspondence, the ratio of potassium to CN is 1:4.32 ± 0.03. The content of potassium and CN based on Kjeldahl nitrogen analysis accounts for 92–94% of the material.

Commercial analysis of one sample gave the following values: C, 33.02; N, 34.39; H, 1.39. The C:N ratio of 1.12:1 indicates perhaps that the product contains a small amount of free carbon resulting from some thermal decomposition of the product. If it is assumed that the small percentage of hydrogen results from the presence of water, the elemental analysis accounts for essentially all of the product. The infrared spectrum of the brown-black solid showed strong absorptions at 2146, 1620, 1540, 1400, and 1375 cm^{-1} and a weak band at 810 cm^{-1}.

An insight into the possible structure of the dark brown solid isolated from the reaction of mercury(II) cyanide with potassium cyanide can be obtained from a paper concerned with the anionic polymerization of cyanogen.[18] Polymerization of the latter substance was effected in tetrahydrofuran by the addition of lithium naphthalene, monolithium benzophenone, or butyllithium. The black substance formed in each instance was soluble both in water and in polar organic solvents such as methanol and ethanol. Evidence indicated that the black materials contained linear polycyanoazapolyene anions of molecular weight in the range 200–500. The substances showed strong infrared absorption bands at 2200 and 1600 cm^{-1} (b), the former being attributed to terminal $-C{\equiv}N$ groups and latter to conjugated-chain $-C{=}N-$ groups. The presence of absorption bands at 2146 and 1620 cm^{-1} in our compound can also be attributed to terminal and conjugated-chain CN groups, respectively. This combined with the analytical data offers good evidence for the presence of a polymeric CN anion in the product reaction.

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(18) J. Peska, M. Benes, and O. Wichterle, *Collection Czech. Chem. Commun.*, **31**, 243 (1966).