CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE
UNIVERSITY OF KANSAS, LAWRENCE, KANSAS

Reactions of Some Transition Metal Cyano Complexes in Molten Potassium Cyanide

BY W. L. MAGNUSON, ERNEST GRISWOLD, AND JACOB KLEINBERG

Received July 19, 1963

The reaction between potassium hexacyanomanganate(III) and potassium cyanide in a molar ratio of 1:10 under vacuum at 650° leads to the formation of a dark green cyano complex which contains both manganese(II) and manganese(III). The product has the empirical formula $K_{1.52}Mn(CN)_{3.72}$. Cyanogen is evolved from the melt during the period of heating. When metallic manganese, mercury(II) cyanide, and potassium cyanide in a 2:1:10 molar ratio are heated at 650° in an evacuated tube, mercury metal and $KMn(CN)_3$ are produced. The same manganese complex results when $K_4[Mn(CN)_6]$ is heated with excess KCN. When $KMn(CN)_3$ is heated with excess KCN, little, if any, reaction occurs. Extraction of an unheated mixture of $KMn(CN)_3$ and excess KCN with liquid ammonia, as well as similar extraction of any of the cooled melts from the above reactions, yields products which appear to contain a small proportion of $K_4[Mn(CN)_6]$ mixed with $KMn(CN)_3$. Potassium octacyanomolybdate(IV) undergoes thermal decomposition at 550° under vacuum in the presence of potassium cyanide with the evolution of cyanogen and the formation of potassium pentacyanomolybdate(III), $K_2Mo(CN)_5$. The molar conductivity of the product in aqueous solution is consistent with the dissociation into three ions. The magnetic moment of the product is not consistent, however, with the value expected for a complex containing molybdenum(III). The dark red melt obtained when metallic palladium, mercury(II) cyanide, and potassium cyanide in a 1:1:6 molar ratio are heated to 550° under vacuum is identical with the melt obtained when potassium tetracyanopalladate(II) and potassium cyanide in a 1:4 molar ratio are heated under the same experimental conditions. Likewise, these melts are identical with the one formed when palladium(II) cyanide and potassium cyanide in a molar ratio of 1:6 are heated under the same conditions. The melts solidify on cooling to give identical orange-yellow solids which contain four cyanide stretching frequencies in their infrared spectra. One peak is attributed to potassium cyanide and a doublet is assigned to potassium tetracyanopalladate(II). It is proposed that the fourth cyanide stretching frequency is due to cyanides which serve as bridging groups.

In a previous communication,[1] we described the preparation of cyano complexes of nickel(0) and nickel(I) by some unusual reactions in molten potassium cyanide as solvent. Potassium tetracyanonickelate(0), $K_4[Ni(CN)_4]$, was obtained by reduction of potassium tetracyanonickelate(II) with cyanide ion from the fused solvent and also by the reaction between metallic nickel, mercury(II) cyanide, and the solvent. Potassium tetracyanonickelate(I), $K_3[Ni(CN)_4]$, was formed by the interaction of metallic nickel, the nickel(II) complex, and molten solvent.

The present paper reports on the behavior of some cyano complexes of manganese, molybdenum, and palladium in molten potassium cyanide. Specifically, this paper deals with the behavior of the following systems in the molten solvent: (a) potassium hexacyanomanganate(III), $K_3[Mn(CN)_6]$; (b) manganese metal and mercury(II) cyanide; (c) potassium tricyanomanganate(II), $KMn(CN)_3$; (d) potassium hexacyanomanganate(II), $K_4[Mn(CN)_6]$; (e) potassium octacyanomolybdate(IV), $K_4[Mo(CN)_8]$; (f) potassium tetracyanopalladate(II), $K_2[Pd(CN)_4]$; (g) palladium metal and mercury(II) cyanide; and (h) palladium(II) cyanide.

Experimental

Materials.—The manganese metal employed was "Fisher Certified" Reagent, 99.93% pure, with a specified maximum iron content of 0.005%. Palladium metal was obtained by reduction of palladium(II) chloride with an aqueous solution of hydrazine sulfate. The precipitated metal was collected and dried at 200° under a high vacuum. Mercury(II) cyanide of C.P. quality was obtained from the Fisher Scientific Company and used without further purification. Potassium cyanide, Baker Analyzed Reagent with a cited purity of 99.1%, was dried at 300° for 3 days prior to use. Potassium hexacyanomanganate(III) was prepared according to the method of Lower and Fernelius[2] and potassium octacyanomolybdate(IV) 2-hydrate by the method described by Furman and Miller.[3] A final washing of the latter complex with ethyl ether, followed by drying at 110° under high vacuum, yielded the anhydrous compound. Sodium tetraphenylborate, Puriss, was employed as obtained from the Aldrich Chemical Company. Potassium tricyanomanganate(II) and potassium hexacyanomanganate(II) were prepared according to the method of Straus.[4] The latter complex was dried at 100° *in vacuo* to remove water of hydration. Potassium tetracyanopalladate(II) was obtained by the directions of Bigelow.[5] The addition of potassium cyanide to an acidic solution of palladium(II) chloride gave a precipitate of yellow hydrous palladium(II) cyanide. Drying of the latter material at 100° *in vacuo* yielded the anhydrous compound. The C^{14}-labeled potassium cyanide was purchased from Volk Radiochemical Company. The activity was 0.05 mcurie per sample. Prior to its being mixed with inactive potassium cyanide, the radioactive material was dried at 300° *in vacuo*. Liquid ammonia, used as an extractive solvent in the experiments with the manganese systems studied, was condensed on metallic sodium before being used.

Analytical Methods.[6]—Potassium was determined gravimetrically by precipitation from acidic solution as the tetraphenylborate.[7] Manganese was analyzed for by the bismuthate proce-

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

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

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

[4] P. Straus, *Z. anorg. allgem. Chem.*, **9**, 6 (1895).

[5] J. H. Bigelow, *Inorg. Syn.*, **2**, 245 (1946).

[6] For detailed accounts of the analytical procedures the reader is referred to W. L. Magnuson, Ph.D. Thesis, University of Kansas, 1963.

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

dure,[8] after the particular complex had been decomposed by heating in sulfuric acid solution. Cyano complexes of molybdenum were prepared for analysis of the metal in the following manner. A 200-mg. sample of the complex was treated with 10 ml. of concentrated nitric acid and the suspension was heated until the evolution of nitrogen(IV) oxide ceased. This treatment yielded a red-brown precipitate. The reaction mixture was diluted to 100 ml. and made basic by the addition of ammonia water to dissolve the precipitate. Then 15 ml. of 30% hydrogen peroxide was added in small portions and the solution was heated almost to boiling for 2 hr. to convert the molybdenum to molybdate. The solution was cooled, made slightly acidic with concentrated acetic acid, and the molybdenum determined as lead molybdate as described by Scott.[9] The cyanide content of most of the complexes was calculated from nitrogen values obtained by a modified semimicro Kjeldahl procedure.[10] In a number of instances, the cyanide content was determined from nitrogen analysis performed by the Schwarzkopf Microanalytical Laboratory, Woodside 77, New York. For cyano complexes which are rather resistant to hydrolysis, accurate cyanide values are difficult to obtain. A variety of methods gave variable and generally low results.

Determination of Oxidation State of Molybdenum.—The oxidation state of the molybdenum obtained in the reaction between potassium octacyanomolybdate(IV) and molten potassium cyanide was determined by the method developed by Collenberg[11] and later applied to the complex $K_4[Mo(CN)_7H_2O]$ by Young.[12] Approxmiately 200 mg. of the complex isolated from the reaction was poured into a hot solution of iron(III) ammonium sulfate which contained a small amount of mercury(II) sulfate. The solution and the flask containing it had been flushed previously with nitrogen in order to remove oxygen. The hot iron(III) ammonium sulfate oxidized molybdenum to molybdate, generating ferrous ions in the process. The solution was acidified with 5 ml. of concentrated sulfuric acid and the ferrous ion titrated with standard potassium permanganate solution. From a measure of the quantity of ferrous ion present and the molybdenum content of the sample, the initial oxidation state of the molybdenum could be calculated.

Magnetic Susceptibility Measurements.—These measurements were made by the Gouy method. For measurements on solids a single compartment cell was employed, and the accuracy and reproducibility of the balance was checked by determining the susceptibility of $Hg[Co(SCN)_4]$ against water as the standard. In measurements on aqueous solutions of the product isolated from reaction of potassium octacyanomolybdate(IV) with molten potassium cyanide, a slightly modified version of the double compartment cell recommended by Selwood[13] was used. This cell was checked with the use of a 2.000 M nickel(II) chloride solution.

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

Reaction between Potassium Hexacyanomanganate(III) and Potassium Cyanide.—In a typical experiment, 3.28 g. (0.01 mole) of potassium hexacyanomanganate(III) and 6.50 g. of potassium cyanide (0.1 mole) were intimately mixed in a drybox and the mixture transferred to a Pyrex tube 25 cm. in length and 20 mm. in o.d. At one end of the tube there was sealed an 18/9 standard taper ball joint. The tube was connected to a vacuum line through this joint and the system was evacuated to a pressure of 10 μ. The tube was then heated in a tubular furnace (maintained in a hood) to 650° for 30 min. The temperature of the furnace was controlled by means of a Wheelco indicating controller with Pilot amplifier. A trap which had been inserted in the vacuum line and immersed in liquid nitrogen was used to collect the gas which escaped from the melt during the heating period. This gas was identified as cyanogen. When heating had been completed, the furnace was removed and the molten material in the reaction tube permitted to cool to room temperature. The tube was then sealed near the ball joint and placed in the drybox.

The reaction mixture was powdered and transferred to a filter tube which contained a 10-mm. sintered glass disk in the center and was equipped with a stopcock near the top and one near the bottom, the latter being fitted to a 18/9 ball joint for connection to the vacuum line. The filter tube was placed on the line and the pressure inside reduced to 10 μ. The contents of the tube were heated to the point where they were just molten. Nitrogen, which was bled into the tube through the top stopcock, assisted in the filtration of the melt through the disk and into the lower compartment of the filter tube. In this manner, solid products of decomposition in the melt remained on the disk. When filtration was complete, the filter tube was allowed to cool to room temperature and was then transferred to the drybox. The filtrate, which was a dark green solid, was removed, ground, and transferred to an extraction apparatus adapted for use with liquid ammonia. Approximately 60 ml. of the anhydrous solvent was condensed into the extractor, which contained a Teflon-covered magnetic stirring bar. The mixture was stirred thoroughly and the solvent removed by means of an aspirator. Extraction in this fashion was continued until no solid residue remained in the filter flask of the extractor after evaporation of the liquid ammonia filtrate. The dark green solid which remained on the extraction disk was removed and dried *in vacuo*. The yield was about 1.4 g. Potassium, manganese, and nitrogen analyses were performed on the solid.

Reaction between Manganese Metal, Mercury(II) Cyanide, and Potassium Cyanide.—In a typical run, a mixture of 1.50 g. (0.027 g.-atom) of manganese metal, 3.45 g. (0.014 mole) of mercury (II) cyanide, and 8.50 g. (0.13 mole) of potassium cyanide were heated for 24 hr. at 650° in an evacuated tube 15 cm. in length and 20 mm. in o.d., on the end of which was sealed a tube 4 cm. long and 6 mm. in o.d. During the heating process the smaller tube stuck outside the furnace and served as a trap for the collection of metallic mercury which distilled out of the reaction mixture. Upon completion of heating, the molten material in the reaction vessel was allowed to solidify and the compartment containing the mercury was sealed off and the metal weighed. The tube containing solid material was transferred to the drybox, and the contents were removed and powdered and then filtered, extracted, and analyzed as described for the product of the previous reaction. The product obtained after filtration and extraction was light green in color and weighed 0.45 g.

Fusion of Potassium Tricyanomanganate(II) with Potassium Cyanide.—In a typical experiment, 1.73 g. (0.01 mole) of the complex and 6.50 g. (0.10 mole) of potassium cyanide were mixed thoroughly and the mixture was transferred to a Pyrex tube 20 cm. long and 20 mm. in o.d. The tube was attached to the vacuum line, which contained a gas collection trap cooled in liquid nitrogen. The system was swept out with nitrogen and the pressure reduced to 10 μ. The tube and its contents were then heated to 150° for 2 hr., after which the temperature was gradually increased. At 550° the mixture began to melt to a dull green liquid and the temperature was increased to 575°, where it was maintained for 4 hr. No gas was evolved from the melt. At the end of this time, the tube was permitted to cool to room temperature and was sealed off. The contents were powdered, extracted, and analyzed in the usual manner.

Reaction of Potassium Hexacyanomanganate(II) in Molten Potassium Cyanide.—In a typical experiment, 3.67 g. (0.01 mole) of freshly prepared potassium hexacyanomanganate(II) and 6.50 g. (0.10 mole) of potassium cyanide were intimately mixed and heated on a vacuum line as described above, except that the maximum temperature of heating was 550° rather than 575°. The color of the melt was dull green. After the heating period, the melt was allowed to cool and the solid transferred to a filter

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

[9] W. W. Scott, "Standard Methods of Chemical Analysis," Vol. I, 5th Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1934, p. 589.

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

[11] O. O. Collenberg, *Z. anorg. allgem. Chem.*, **121**, 310 (1922).

[12] R. C. Young, *J. Am. Chem. Soc.*, **54**, 1402 (1932).

[13] P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943, p. 151.

tube. The temperature of the tube was raised to melt the solid and the melt was filtered as described previously. Essentially no residue remained on the filter disk. The dark green solid filtrate was extracted in the usual fashion and analyzed. Approximately 1.7 g. of green solid was isolated.

Reaction between Potassium Octacyanomolybdate(IV) and Molten Potassium Cyanide.—In a typical run, a mixture of 4.60 g. (0.01 mole) of potassium octacyanomolybdate(IV) and 6.50 g. (0.10 mole) of potassium cyanide was transferred in the drybox to a Pyrex tube 20 cm. long and 20 mm. in o.d., to which was sealed an 18/9 ball joint. The tube was connected to the vacuum line (containing a trap cooled by liquid nitrogen) through the joint and the system was evacuated to a pressure of $10\ \mu$. The contents of the tube were heated to 550° for 10–20 min. by means of the tube furnace. The tube, now containing a red-brown melt, was cooled to room temperature and the contents were transferred to a beaker containing 50 ml. of oxygen-free water. The resulting suspension was filtered in a stream of nitrogen and the red filtrate was chilled. Addition, with stirring, of 150 ml. of ethanol to the chilled filtrate yielded a dark red oil. The supernatant liquid was decanted and an additional 50 ml. of ethanol was poured on the oil. Continued stirring and chilling of the oil converted it to a dark red crystalline solid which was collected by filtration and washed with ethanol and ethyl ether. The product was then dried at 100° under high vacuum. To remove any potassium cyanide present, the solid was extracted with anhydrous methanol in a Soxhlet extractor for 48 hr. After extraction, the product was dried *in vacuo* at 100°. Approximately 1 g. of product was obtained. It was analyzed for potassium, molybdenum, and nitrogen, and the oxidation state of the molybdenum was determined. Infrared examination of the product in Nujol showed the absence of water or bound hydroxyl groups. Once the empirical formula of the product had been established by analysis, the molar conductivity of 0.001 M aqueous solutions was determined.

During the course of reaction at 550° a gas identified as cyanogen was evolved and was collected in the cold trap.

Behavior of Potassium Tetracyanopalladate(II) in Molten Potassium Cyanide.—Usually 2.88 g. (0.01 mole) of the complex and 2.60 (0.04 mole) of potassium cyanide were employed. An intimate mixture of these substances was added to a 250-ml. round-bottomed flask with a 24/40 standard taper joint; sealed into the side of the flask was a stopcock fitted with a ball joint for connection to the vacuum line. A glass-covered bar magnet was placed in the flask for stirring purposes. The flask was connected to the vacuum line, and the system was flushed with nitrogen and then evacuated to a pressure of $10\ \mu$. The flask was heated to 550° by means of a heating mantle for periods of from 10 min. to 1 hr. At temperatures near 550°, the solid mixture was converted to a dark red melt, but no gas was collected in the liquid nitrogen trap in the vacuum line. Upon removal of the heating mantle, the melt solidified to a yellow-orange solid. When the solid was transferred to a filter tube and melted and filtered, essentially no residue remained on the filter disk. The absence of cyanogen evolution and of carbonaceous material on the filter disk showed that no decomposition had occurred during the course of heating and that the palladium(II) had not been reduced.

Attempts to separate the components of the product mixture by means of various solvents—liquid ammonia, glycerol, monobutyl ethylene ether, lithium chloride–potassium chloride eutectic, dioxane, nitromethane, diethyl ethylene ether—were unsuccessful. The mixture either dissolved completely or was insoluble.

Reaction between Palladium Metal, Mercury(II) Cyanide, and Potassium Cyanide.—In a typical experiment, a mixture of 1.06 g. (0.01 g.-atom) of palladium, 2.53 g. (0.01 mole) of mercury(II) cyanide, and 3.90 g. (0.06 mole) of potassium cyanide was transferred to a Pyrex tube 20 cm. long and 18 mm. in o.d., to which was sealed a small tube for collection of mercury. The reaction tube was evacuated, sealed, and placed in a tube furnace so that the small tube extended outside the furnace. The temperature of the furnace was raised to 550° and so maintained for varying periods of time up to a maximum of 24 hr. Upon termination of heating, the compartment containing the distilled mercury was sealed off, and the large compartment was cooled and transferred to the drybox. The yellow-orange contents were powdered and filtered in the usual manner while molten. Attempts to separate the components of the yellow-orange solidified filtrate by use of the extractants cited previously were not successful.

Reaction of Palladium(II) Cyanide with Molten Potassium Cyanide.—A mixture of 1.58 g. (0.01 mole) of the palladium compound and 3.90 g. (0.06 mole) of potassium cyanide in an appropriate Pyrex tube was heated in the usual manner on a vacuum line for 15 min. at 550°. A red melt was formed, but no gas was evolved. The familiar yellow-orange solid was obtained from the red melt.

Exchange Studies.—It has been noted that cyanogen was evolved in the reaction of potassium hexacyanomanganate(III) and also of potassium octacyanomolybdate(IV) with molten potassium cyanide. Attempts were made to determine the origin of the cyanogen in exchange studies in which these reactions were carried out with potassium cyanide labeled with C^{14}.

The reactions were effected as described previously. Sodium hydroxide solution was added to the frozen cyanogen which had collected in the cold trap in the vacuum line. The resulting solution of sodium cyanide and sodium cyanate was removed from the trap and treated with nitric acid and silver nitrate solution. In this manner, one-half of the cyanogen was lost by hydrolysis of the cyanate to ammonium ion and the other half was precipitated as silver cyanide. The silver cyanide was filtered onto a small filter paper, washed thoroughly with water and then with acetone, and air dried. The activity of 0.150 g. of this material was then measured.

The solid products obtained from the reaction were decomposed (the manganese materials by sulfuric acid and the molybdenum product by concentrated nitric acid) to liberate cyanide ion; the latter was converted to silver cyanide and the activity of 0.150 g. measured. The potassium cyanide extracted by means of liquid ammonia from the filtrate of the reaction of the manganese complex was also converted to silver cyanide, and the activity of 0.150 g. of the latter compound was measured.

Results and Discussion

Manganese Systems.—When potassium hexacyanomanganate(III), $K_3[Mn(CN)_6]$, was heated with a large excess of potassium cyanide at 650° in a vacuum system, cyanogen was evolved and a green material remained. After filtration of the molten green material and repeated extraction of the solidified filtrate with liquid ammonia, the dark green solid product remaining had the empirical formula $K_{1.52}Mn(CN)_{3.72}$, as is shown by the analytical results in part (a) of Table I. (In this table, each set of percentages represents the results of replicate analyses on a separate preparation.)

The gram-magnetic susceptibility, $41\text{–}42 \times 10^{-6}$, is much higher than that of the manganese(III) starting material ($\chi_g = 13.48 \times 10^{-6}$ for $K_3[Mn(CN)_6]$[14]). It is, in fact, not far below the value 44.11×10^{-6} reported[14] for potassium tricyanomanganate(II), commonly written $KMn(CN)_3$ though probably better formulated as $K_2Mn[Mn(CN)_6]$. The magnetic susceptibility, together with the average oxidation number +2.20 for manganese given by the empirical formula, indicates that approximately 80% of the manganese in the green product is present in the dipositive state. Here, as in the reaction of potassium tetra-

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(14) N. Goldenberg, *Trans. Faraday Soc.*, **36**, 847 (1940).

cyanonickelate(II) in molten potassium cyanide,[1] reduction has been effected by cyanide.

The presence of some manganese(III) and the excess of potassium and cyanide over that corresponding to the formula $KMn(CN)_3$ raised the question of whether some of the starting materials might have remained simply mixed in the green product, in spite of the fact that both are soluble in liquid ammonia and should have been extracted. To answer this question, the X-ray powder pattern of the product was compared with the patterns of the starting materials and potassium tricyanomanganate(II); the infrared spectrum was similarly compared.

The X-ray powder pattern of the material denoted by the empirical formula $K_{1.52}Mn(CN)_{3.72}$ is very similar in all respects to that of potassium tricyanomanganate(II). With the exception of a few very weak lines, the strong and weak lines of the two materials correspond very closely. On the other hand, the pattern is distinctly different from that of either starting material, and there was no indication of the presence of either free potassium cyanide or potassium hexacyanomanganate(III) in the green product.

The infrared spectrum, likewise, showed no absorption peaks corresponding to those of $K_3[Mn(CN)_6]$ (2117, 2126, and 2148 cm.$^{-1}$) or to that of potassium cyanide (2080 cm.$^{-1}$). Instead, a single peak with a maximum at 2057 cm.$^{-1}$ was observed in the usual region of cyanide stretching frequencies. This is essentially the same as the single peak at 2060 cm.$^{-1}$ exhibited by both $KMn(CN)_3$ and $K_4[Mn(CN)_6]$.

Although no detailed structure can at present be proposed for $K_{1.52}Mn(CN)_{3.72}$, it seems clear from the evidence that all of the cyanides must be equivalent and must be coordinated to manganese(II). Moreover, the predominant structural features of the material must be very similar to those of potassium tricyanomanganate(II).

In the hope that cyano compounds containing manganese in an oxidation state lower than +2 might be produced, three other series of experiments were conducted. In the first of these, a mixture of mercury(II) cyanide, manganese metal, and potassium cyanide was heated as previously described. After filtration and liquid ammonia extraction, the residual light green material gave the analytical results and magnetic susceptibility shown in part (b) of Table I. The mercury(II) cyanide was quantitatively converted to mercury metal in each run, but only about one-tenth of the manganese metal was consumed. No cyanomanganate(III) was found in the liquid ammonia extract. The X-ray powder pattern of the product was practically identical with that of $KMn(CN)_3$, and the gram-magnetic susceptibilities are almost the same. The infrared spectrum showed only one absorption peak in the cyanide region with a maximum at 2058 cm.$^{-1}$. The peak characteristic of free potassium cyanide at 2080 cm.$^{-1}$ was absent. The product thus is predominantly $KMn(CN)_3$, probably mixed with a small amount of $K_4[Mn(CN)_6]$.

TABLE I

ANALYSIS OF PRODUCTS FROM REACTIONS INVOLVING MANGANESE

		Molar ratios		Gram-magnetic susceptibility
K, %	Mn, %	K/Mn	CN/Mn[a]	$\chi_g \times 10^6$
(a) $K_3[Mn(CN)_6]$ + KCN				
28.09 ± 0.21	26.00 ± 0.01	1.53	3.74	...
27.86 ± 0.30	26.15 ± 0.05	1.53	3.75	42.06
28.25 ± 0.08	26.63 ± 0.13	1.50	3.70	40.78
28.06 ± 0.16	26.35 ± 0.01	1.50	3.69	41.76
Mean empirical formula $K_{1.52}Mn(CN)_{3.72}$				
(b) $Hg(CN)_2$ + Mn + KCN				
24.83 ± 0.18	29.75 ± 0.06	1.16	3.22	44.47
24.98 ± 0.08	29.79 ± 0.11	1.16	3.21	46.90
24.91 ± 0.09	29.86 ± 0.08	1.17	3.20	43.44
24.31 ± 0.13	30.70 ± 0.01	1.11	3.09	...
Mean empirical formula $K_{1.15}Mn(CN)_{3.18}$				
(c) $KMn(CN)_3$ + KCN				
24.29 ± 0.27	30.43 ± 0.11	1.14	3.15	
23.81 ± 0.09	30.07 ± 0.03	1.15	3.23	
23.63 ± 0.07	31.13 ± 0.08	1.08	3.10	
24.59 ± 0.10	30.08 ± 0.04	1.17	3.18	
Mean empirical formula $K_{1.14}Mn(CN)_{3.16}$				
(d) $K_4[Mn(CN)_6]$ + KCN				
25.27 ± 0.10	29.73 ± 0.15	1.19	3.19	
25.33 ± 0.09	29.53 ± 0.22	1.19	3.22	
Mean empirical formula $K_{1.19}Mn(CN)_{3.20}$				

[a] Cyanide by difference. Calculation in this manner is justified. A variety of experiments showed that the only source of nitrogen in the compounds was cyanide.

Essentially the same product was obtained, after liquid ammonia extraction of the cooled melt, when $KMn(CN)_3$ was heated with an excess of KCN and also when $K_4[Mn(CN)_6]$ was heated with excess of KCN. This is indicated by the analytical results given in Table I, parts (c) and (d), and was confirmed by the infrared absorption spectrum and color.

When an unheated 1:10 mixture of $K_4[Mn(CN)_6]$ and KCN was repeatedly extracted with liquid ammonia, the residue was found to be unchanged $K_4[Mn(CN)_6]$. On the other hand, a similar mixture of $KMn(CN)_3$ and KCN yielded, after liquid ammonia extraction, a residue of average empirical formula $K_{1.22}Mn(CN)_{3.22}$, indicating probable formation of some $K_4[Mn(CN)_6]$ during the extraction. It is quite possible that each of the three elevated-temperature processes just described yields $KMn(CN)_3$ as the only manganese-containing product. Whether a small proportion of $K_4[Mn(CN)_6]$ is then formed during the extraction or was present in the original melt cannot be decided from this evidence. In any case, the only oxidation state of manganese exhibited in the products from any of these three reactions is +2.

Molybdenum Systems.—A mixture of potassium octacyanomolybdate(IV), $K_4[Mo(CN)_8]$, with potassium cyanide, when heated as described, yielded a red crystalline molybdenum-containing product. Two somewhat different procedures were employed in isolating the red material from the original melt. In one, an aqueous solution of the melt was treated, after filtration, with ethanol, and the resulting precipitate was extracted with methanol. In the other, the melt was extracted directly with methanol, no water being used at all.

Analyses of three separate preparations by each procedure gave the following results. *Anal.* Calcd. for $K_2Mo(CN)_5$: K, 25.71; Mo, 31.54. Found: (a) Water-extracted products: K, 26.16 ± 0.05; Mo, 31.80 ± 0.19; oxidation no. of Mo, 3.05 ± 0.03. (b) Methanol-extracted product: K, 27.09 ± 0.37; Mo, 30.40 ± 0.71; oxidation no. of Mo, 3.04 ± 0.05. Although they may be of slightly different purity, the two products are undoubtedly the same, indicating that the material does not react readily with water.

The analytical results and the oxidation number determinations clearly point to the formulation of this red crystalline substance as potassium pentacyanomolybdate(III), $K_2Mo(CN)_5$. This compound has not been previously reported. The molar conductance, based on this formula, of three different preparations in 0.001 M aqueous solutions was found to be 253, 259, and 270 ohm^{-1}. These values are reasonable for a unibivalent salt. The infrared spectrum of the compound in Nujol mulls exhibited a number of bands in the cyanide region. Frequencies of the maxima and relative intensities of these bands for both this compound and potassium octacyanomolybdate(IV) were as follows: $K_2Mo(CN)_5$: 2157 (w), 2143 (w), 2131 (s), 2120 (vs), and 2111 (s); $K_4[Mo(CN)_8]$: 2139 (w), 2131 (w), 2126 (s), and 2108 (vs). It has been pointed out[15] that the cyanide stretching frequencies in cyano complexes show a dependency on the ratio of oxidation number of the metal to coordination number, becoming higher as this ratio increases. The somewhat higher frequencies observed for the new compound over those of the octacyanomolybdate(IV) are qualitatively consistent, at least, with its formulation as pentacyanomolybdate(III). Magnetic susceptibility measurements gave effective moments of 0.57 and 0.59 Bohr magneton in the solid compound and 0.87 in aqueous solution. These values are much lower than the moments 3.70–3.80 reported[16] for a number of six-coordinated complexes of molybdenum(III) and lower than the 1.75 reported for seven-coordinated $K_4Mo(CN)_7 \cdot 2H_2O$. They suggest the possibility of metal–metal bonding in the compound. A definite conclusion on this point, however, must await more detailed structural and magnetic studies.

Palladium Systems.—The yellow-orange solid produced in all three of the reactions (see Experimental section) involving a cyanide of palladium or palladium metal exhibited essentially the same appearance and the same solubility behavior throughout. It dissolved in water without the evolution of gas to give a colorless solution. The absence of gas evolution indicates the absence of any strongly reducing species, such as potassium tetracyanopalladate(0), $K_4[Pd(CN)_4]$,[17] in the product. Thus, the reactions of nickel metal, mercury(II) cyanide, and potassium cyanide and of potassium tetracyanonicketate(II) with potassium cyanide to give $K_4[Ni(CN)_4]$ at elevated temperatures[1] do not have their counterparts in the corresponding palladium systems.

The infrared spectra of these products all showed the same four peaks in the cyanide region, but with variations in relative intensity, as would be expected for mixtures of differing composition. The maxima occurred at 2080, 2135, 2141, and 2180 $cm.^{-1}$. The 2080 $cm.^{-1}$ band is characteristic of free potassium cyanide and is attributed to its presence. The 2135–2141 $cm.^{-1}$ doublet is exhibited by pure $K_2[Pd(CN)_4]$, and, presumably, is characteristic of terminal cyanides coordinated to palladium(II). The 2180 $cm.^{-1}$ band has not been hitherto reported for cyanide compounds of palladium. The ratio of the intensity of this band to that of the 2135 $cm.^{-1}$ band varied from one product to another and showed a significant relation to the length of time the mixture had been heated. For example, palladium(II) cyanide and potassium cyanide were heated at 550° for about 15 min. In that time the peak at 2207 $cm.^{-1}$, displayed (together with the KCN band at 2080 $cm.^{-1}$) by the unheated mixture and attributed to the extensively bridged $Pd(CN)_2$, had disappeared, and the 2135–2141 $cm.^{-1}$ doublet had become quite intense. The 2180 $cm.^{-1}$ band was also present, but the ratio of its intensity to that of the 2135 $cm.^{-1}$ band was low—about 1:10. On the other hand, the mixture of palladium, mercury(II) cyanide, and potassium cyanide was heated at 550° for about 6 hr., after which the corresponding ratio was found to be approximately 1:4. When the heating period was extended to 12 hr., the ratio increased to 1:3, which was the highest attained.

It seems probable that the 2180 $cm.^{-1}$ band appearing in these products can best be assigned to a cyanide which is serving as a bridge group between two palladium atoms, since bridging cyano groups appear to have higher stretching frequencies than do terminal groups.[18] One may postulate that $K_2[Pd(CN)_4]$ (present as a starting material or formed from the other reactants used) undergoes a condensation reaction at elevated temperatures to form a colored compound containing both cyano bridge groups and terminal groups. Since attempts to isolate the compound from the product mixtures have thus far been unsuccessful, no formulation for it can be given. It is conceivable that it may be simply the dipalladate, $K_2[Pd_2(CN)_6]$, analogous to the hexachlorodipalladate(II), $[(C_2H_5)_4N]_2[Pd_2Cl_6]$, which has been reported.[19] The disappearance of color when the yellow-orange solid is dissolved in water probably results from a reversal of the condensation reaction, the colored compound reacting with excess cyanide present in the mixture to form the colorless tetracyanopalladate(II) ion.

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Role of Potassium Cyanide.—The role of potassium cyanide in the reactions described above is a matter of considerable interest. The reduction of $K_3[Mn(CN)_6]$ and of $K_4[Mo(CN)_8]$, with attendant evolution of cyanogen, may be represented by the following equations (making a slight modification in the empirical formula of the manganese product).

$$4K_3[Mn(CN)_6] = 4K_{1.50}Mn(CN)_{3.75} + 1.5(CN)_2 + 6KCN$$

$$K_4[Mo(CN)_8] = K_2Mo(CN)_5 + 0.5(CN)_2 + 2KCN$$

Obviously, the stoichiometry of these reactions does not require potassium cyanide as a reactant, but as a product, instead. Cyanogen, too, is indicated to be a direct product of the reduction decomposition of the original cyano compound.

In an attempt to gain some insight into the mechanism of the reductions, runs were conducted in which C^{14}-labeled potassium cyanide was used. Examination of the products showed the C^{14} activity to be about uniformly distributed among the three products in each case. Therefore, whether the cyanogen originates, in part at least, from the potassium cyanide in the course of reduction of the metal compound, or from decomposition of the cyano complex subsequent to exchange of C^{14}-labeled cyanide between potassium cyanide and the complex, cannot be determined from this evidence. A sample of unlabeled $K_{1.52}Mn(CN)_{3.72}$ was found to exchange readily at the experimental temperature; presumably, $K_3[Mn(CN)_6]$ would behave similarly.

Since potassium cyanide appears as a product in the above equations, it seemed worthwhile to see whether or not these starting compounds would behave in the same manner as before if they were heated under the same conditions but in the absence of added potassium cyanide. When $K_3[Mn(CN)_6]$ was heated without potassium cyanide in this way, extensive carbonization occurred, and none of the green compound denoted by $K_{1.52}Mn(CN)_{3.72}$ could be isolated. Similar treatment of $K_4[Mo(CN)_8]$ also resulted in much decomposition, with formation of carbon and a metallic mirror. When the heating period was limited to 10 min., a small amount of $K_2Mo(CN)_5$ could be isolated; after 1 hr., none could be obtained. If $K_2[Pd(CN)_4]$ reacts to give condensed products containing cyano bridge groups, as postulated, potassium cyanide should be a product of this reaction, also. When $K_2[Pd(CN)_4]$ was heated without potassium cyanide, however, extensive decomposition occurred here, too, and the 2180 cm.$^{-1}$ band could not be detected in the infrared spectrum of the products.

It is clear that potassium cyanide plays a most important role in stabilizing the various cyano complex products described here and, therefore, in determining the course of reaction when cyanometallate compounds or their precursors are subjected to elevated temperatures.

Acknowledgment.—The authors gratefully acknowledge their indebtedness to the Atomic Energy Commission for financial support of this work and to the Stauffer Chemical Company for a fellowship held by W. L. M. during part of the time.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ARIZONA, TUCSON, ARIZONA

The Influence of Metal Chelation on the Structure of Certain Hydroxyquinaldinic Acids

BY SASWATI P. BAG, QUINTUS FERNANDO, AND HENRY FREISER

Received May 25, 1963

The acid dissociation constants and stepwise metal chelate formation constants of 4-hydroxyquinaldinic acid and 4,8-dihydroxyquinaldinic acid have been determined in 50% v./v. aqueous dioxane at 25°. Metal chelation was found to have an acid-strengthening effect on the 4-hydroxy group far in excess of that which could be attributed to a shift in the keto–enol equilibrium involving this group. Factors that contribute to this effect include the nature of the chelate ring, its position relative to the dissociating group, and the nature of the metal ion.

One of the useful techniques of evaluating the influence of metal ion chelation on the physical and chemical properties of a ligand is the measurement of the change in pK_a of an appropriate acidic or basic substituent suitably located on the ligand.[1,2] The phenolic group, whose pK_a is significantly higher than the pH range in which most metal chelation occurs, has been shown to be of value in this type of investigation.[2,3] Of course, the phenolic group can itself in certain types of compounds influence the properties of the ligand. In compounds such as 4-hydroxypyridine, the phenolic group interacting through keto–enol tautomerism exerts a profound influence on the coordinating properties of the nitrogen atom. In the case of 2,6-dicarboxy-4-hydroxypyridine, for example, the presence of the hydroxy group results in a tautomeric change to the pyridone. Instead of being a disadvantage, however, such a tautomeric transforma-

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