

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

New Routes to Cyano Complexes of Nickel(0) and Nickel(I)

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Cyano complexes of nickel(0) and nickel(I) have been obtained by reactions carried out in molten potassium cyanide. When metallic nickel, mercury(II) cyanide and potassium cyanide in the respective molar proportions of 2:1:6 are heated together at 500° *in vacuo*, the major products are elementary mercury, potassium tetracyanonickelate(II) and potassium tetracyanonickelate(0), $K_4[Ni(CN)_4]$. About one-quarter to one-third of the nickel remains unconverted, and a small amount of a paramagnetic nickel(I) compound is produced also. It is suggested that $K_4[Ni(CN)_4]$ arises from disproportionation of $K_4[Ni_2(CN)_8]$ in the presence of potassium cyanide. The nickel(0) complex has also been obtained by reaction between potassium tetracyanonickelate(II) and potassium cyanide at 480°. The paramagnetic nickel(I) complex, $K_3[Ni(CN)_4]$, has been obtained in 50–80% yield by reaction between elementary nickel, potassium tetracyanonickelate(II) and potassium cyanide in the respective molar proportions of 1:1:4 at 450–480°.

Recent communications from this Laboratory^{1,2} have described a novel method for the preparation of gallium dihalides and indium mono- and dihalides, namely, by reaction of mercury(I) or mercury(II) halides with the appropriate metal at elevated temperatures. The work presented in the current report was initiated in an attempt to extend the type of reaction just cited to the preparation of compounds containing transition elements in low oxidation states. Specifically, it was hoped to prepare cyano complexes of nickel(I) by oxidation of nickel metal with mercury(II) cyanide in the presence of potassium cyanide as complexing agent, at temperatures where the latter reagent was molten. When it was observed that reaction at 500° between metallic nickel, mercury(II) cyanide and potassium cyanide in the molar ratios 2:1:5 gave potassium tetracyanonickelate(0) and potassium tetracyanonickelate(II), rather than nickel(I) complexes, as the major nickel-containing products, attempts were made to elucidate the mechanism of reaction. Experiments carried out in this direction led to the discovery of two additional novel reactions, one yielding potassium tetracyanonickelate(0) by oxidation of molten potassium cyanide by potassium tetracyanonickelate(II) at 480° and the other leading to the formation of potassium tetracyanonickelate(I), by the interaction of elementary nickel, potassium tetracyanonickelate(II) and potassium cyanide at 450–480°.

Experimental

Materials.—The nickel employed was obtained from Amend Drug Company and was in the form of a powder described as hydrogen reduced, cobalt free, and C.P. mercury(II) cyanide of C.P. quality was supplied by the Fisher Scientific Company and was used without further purification. The material had a chloride ion content of 0.07%. The potassium cyanide used was Baker Analyzed Reagent, 99.8%. Prior to use the compound was gradually brought to a temperature of 550° under a high vacuum and maintained at this temperature for several hours. When so treated, the compound could be fused without the appearance of carbon. *N,N*-Dimethylformamide, which was employed as an extractive solvent, was of spectroquality and was purchased from Matheson, Coleman and Bell. Potassium tetracyanonickelate(II) was prepared according to the method of Fernelius and Burbage.³ The

salt was recrystallized from water several times in order to ensure the absence of potassium cyanide. It then was sucked dry by means of a water aspirator, dried at 120° for several hours, powdered and finally dried by heating under a high vacuum. Potassium hexacyanodinitrate(I) was made by the reduction of potassium tetracyanonickelate(II) by means of potassium metal in liquid ammonia.⁴ Sodium tetraphenylborate, *puriss.*, was used as obtained from the Aldrich Chemical Company. Prior to use, solutions of the reagent were filtered.

Reaction between Nickel, Mercury(II) Cyanide and Potassium Cyanide.—The apparatus employed consisted of an 8 in. long, 10 mm. i.d. Pyrex tube divided into compartments by a fritted glass disk of coarse porosity, centrally located. At the end of one compartment an 18/9 standard taper ball joint was sealed. That portion of the tube which comprised the other compartment served as the site of reaction. It was constricted near the opening and had sealed onto it, about three-fourths of the way down, a Pyrex tube, 6 mm. in i. d., which extended well beyond the constriction. This narrow tube was sealed at the end and served as a trap for elementary mercury as it distilled from the reaction mixture.

To the reaction compartment there was added successive portions of nickel, mercury(II) cyanide and potassium cyanide in the molar ratio 2:1:6 and the tube was quickly sealed off at the constriction. In a typical experiment the following weights of materials were used: nickel, 0.7899 g.; mercury(II) cyanide, 1.7673 g.; potassium cyanide, 2.6314 g. The apparatus was heated gently (110–120°), while being continuously evacuated through the ball joint. (A heating tape wrapped around the tube served as the source of heat.) The tape was wrapped tightly around that portion of the tube containing the potassium cyanide but only loosely around the part with the mercury(II) cyanide. This arrangement was necessary to keep the latter compound from subliming appreciably. The gentle heating was continued for 2–4 hr. and the apparatus was sealed off above the ball joint. The reactants were then mixed intimately by shaking and the apparatus was placed horizontally in a tubular furnace in a hood. The temperature of the furnace was controlled by a Wheelco Indicating Controller with Pilot Amplifier. The apparatus was so arranged that the end of the tube for collecting mercury (see above) extended well outside the end of the furnace, while the rest of the apparatus was completely in the furnace. The temperature of the furnace was adjusted to 500° and maintained at that point overnight. At this temperature, the contents of the reaction compartment soon appear to be almost completely molten.

As reaction proceeded, mercury distilled into the trap located outside the furnace. When reaction was complete the furnace was cooled, the apparatus removed from the furnace and the tube containing the mercury sealed off and removed. (Completion of reaction was indicated by the absence of gas pressure in the mercury collection tube when a spot on it was heated with the pin-point flame of a hand torch.) After the mercury had been removed, the apparatus was replaced in the furnace, the furnace inclined at an angle of 60° to the hood floor and the temperature brought up to 500°. That portion of the product which became liquid was permitted to filter through the sintered glass disk into the

(1) R. C. Carlston, E. Griswold and J. Kleinberg, *J. Am. Chem. Soc.*, **80**, 1532 (1958).

(2) R. J. Clark, E. Griswold and J. Kleinberg, *ibid.*, **80**, 4764 (1958).

(3) W. C. Fernelius and J. J. Burbage, *Inorg. Syntheses*, **2**, 227 (1946).

(4) W. M. Burgess and J. W. Eastes, *ibid.*, **5**, 197 (1957).

lower compartment. When filtration was complete, the furnace was cooled and the reaction apparatus placed in a dry box. The portion containing the material which had filtered through the disk was broken off from the rest of the apparatus, the contents removed, powdered and placed in a weighing bottle. It is important to note that no nickel metal ever was observed in the filtrate. A small amount of solid remained on the sintered glass disk. Nickel metal invariably was present in the solid, and at times it was pyrophoric.

The solid filtrate was extracted with spectroquality N,N-dimethylformamide in a nitrogen atmosphere by means of a Soxhlet extractor, until the extract gave no test for Ni^{2+} and CN^- ions.⁶ When extraction was complete, the brick red solid in the Soxhlet thimble was analyzed for potassium, cyanide and nickel; the oxidation number of the nickel in the solution was found from its nickel content and reducing power. The reducing power was determined by measuring the volume of hydrogen liberated when a weighed sample of the solid was treated with an acidic aqueous solution containing potassium cyanide. (The nickel is oxidized to the dipositive state by the hydrogen ion in solution.) The solution remaining after such treatment was analyzed for nickel by its precipitation with dimethylglyoxime. A separate sample of the extracted solid was used for potassium and cyanide analysis. Potassium was determined by precipitation from acidic solution as potassium tetraphenylborate,⁶ and cyanide was analyzed for by precipitation as $\text{Ag}[\text{Ag}(\text{CN})_2]$.⁷ The magnetic susceptibility of the solid which had been extracted was determined by the Gouy method at a field strength of 2400 gauss.

The solid material remaining on the sintered glass disk of the original reaction vessel also was extracted with dimethylformamide and analyzed as above. It was shown to be mainly elementary nickel.

The Thermal Decomposition of Tetrapotassium Hexacyanodinitrnickelate(I).—The thermal behavior of potassium hexacyanodinitrnickelate(I), $\text{K}_4[\text{Ni}_2(\text{CN})_6]$, was studied both in the presence and absence of potassium cyanide. Experiments were carried out in which the molar ratio of potassium cyanide to $\text{K}_4[\text{Ni}_2(\text{CN})_6]$ varied from 0:1 to 35:1.

The apparatus employed was similar to the one described above, except that no trap for collection of mercury was necessary. The $\text{K}_4[\text{Ni}_2(\text{CN})_6]$ or an intimate mixture of this compound and potassium cyanide was heated at the melting point in the evacuated reaction tube for about 20 min. by means of a hand torch. The apparatus was then sealed off above the ball joint and liquid material was permitted to filter through the sintered glass disk, heat being applied as necessary.

After filtration was complete the dark red filtrate and solid remaining on the sintered disk were cooled and extracted and analyzed as described above.

Oxidation of Potassium Cyanide by Potassium Tetracyanonickelate(II).—The apparatus for carrying out this reaction consisted of a 250-ml. round bottom flask fitted with a 24/40 standard taper joint, above which was sealed a number 2 standard taper stopcock to permit evacuation and sealing. A glass encased magnetic bar was placed in the flask to effect stirring, and the bottom of the flask was covered by a Glas-col heating mantle, under which was a Fisher magnetic stirrer.

The flask was evacuated, baked out by heating under vacuum and placed in a dry box. Anhydrous potassium cyanide and potassium tetracyanonickelate(II), intimately ground together in the molar ratio 2:1, were added to the flask. (In a typical run 3.00 of the cyanide and 4.82 g. of the nickel complex were used.) The flask was then re-evacuated and heated gradually to 480° where the mixture was molten. The temperature was determined and controlled by a Wheelco Indicating Controller with the use of an iron-constantan thermocouple on the heating mantle.

Stirring was begun as soon as the reaction mixture was molten. A gas which was continuously evolved was collected in a trap cooled by means of a Dry Ice-acetone bath and was shown to be cyanogen. After about 20 min., the rate of gas evolution decreased sharply. Heating for several hours at 480° with continuous pumping did not cause the evolution of any appreciable additional gas. The flask was permitted to cool slowly to room temperature and the brick-red colored contents were extracted and analyzed as described previously.

Reaction between Nickel, Potassium Tetracyanonickelate(II) and Potassium Cyanide.—The apparatus for this reaction was constructed in the following manner. A piece of Pyrex tubing, 18 cm. long and 10 mm. i.d., with a fritted glass disk of coarse porosity sealed into the center, had attached to one end a number 2 standard taper stopcock with an 18/9 ball joint. Sealed onto the other end was another piece of Pyrex tubing, about 13 cm. long and 20 mm. i.d., with an 18/9 standard taper ball joint attached. Evacuation of the apparatus could be carried out by use of a stopcock-bearing unit which could be fitted to this ball joint.

After the apparatus had been dried by heating, it was evacuated and transferred to a dry box. Here, that part consisting of the tubing 20 mm. i.d. was charged with an intimate mixture of nickel powder, potassium tetracyanonickelate(II) and potassium cyanide in the molar ratios 1:1:4. (The total weight of reactants varied from 5 to 10 g.) The apparatus was removed from the dry box, evacuated and sealed off above the ball joint attached to the tubing of 20 mm. i.d. Then the apparatus was evacuated through the stopcock attached to the tubing of 10 mm. i.d.

The tube and its contents were heated gently with a hand torch until the mixture was just above its melting point. (The melting point range on similar mixtures, 450–480°, had been determined previously by controlling the temperature of a tubular furnace placed around the tube containing the mixture. Temperature control was effected by means of a Wheelco Indicating Controller with Pilot Amplifier. The furnace was lowered so that the mixture could be observed after it had been heated at a particular temperature for a short time. The temperature was raised by 50° increments until melting occurred.) It was necessary that the mixture be heated neither too rapidly nor at too high a temperature. Too rapid heating caused the material to rise to the fritted glass disk; heating at too high temperature resulted in low yields of the desired product. Heating was continued with the reaction mixture just molten until gas (cyanogen) evolution subsided (15–20 min.). At this point, the system was allowed to cool and the tubing of 10 mm. i.d. was sealed off just below the stopcock.

The apparatus was then placed horizontally in a tubular furnace (in a hood) with the tubing of 10 mm. i.d. at the cooler end. The furnace temperature was raised to 500°, and the product was gravity filtered by inclining the furnace at an angle of about 60° to the hood floor. It required about 4 or 5 hr. for the filtration process.

When filtration was complete, the furnace was allowed to cool and the filtrate was extracted and analyzed in the usual manner.

Results and Discussion

In Tables I–IV there are summarized the analytical data obtained on the significant products from the various types of reactions described in the Experimental section.

The data of Table I show unequivocally that when metallic nickel, mercury(II) cyanide and potassium cyanide in the respective molar proportions of 2:1:6 are heated at 500°, the major product in the filtrate of the reaction, after extraction with N,N-dimethylformamide, is potassium tetracyanonickelate(0), $\text{K}_4[\text{Ni}(\text{CN})_4]$. That this is not the only product is shown by the values of the oxidation number of the nickel and the slight paramagnetism of the material. The paramagnetism cannot be attributed to contamination of the nickel(0) complex by potassium tetracyanonickelate(II), since this substance is diamagnetic. Neither

(5) Experimental details for the extraction can be found in the Ph.D. thesis of S. von Winbush, University of Kansas, 1960. Preliminary experiments had shown that whereas potassium cyanide and $\text{K}_2[\text{Ni}(\text{CN})_4]$ were soluble in hot dimethylformamide, $\text{K}_4[\text{Ni}(\text{CN})_4]$ was insoluble and $\text{K}_4[\text{Ni}_2(\text{CN})_6]$ underwent disproportionation to nickel metal, $\text{K}_4[\text{Ni}(\text{CN})_4]$ and $\text{K}_2[\text{Ni}(\text{CN})_4]$.

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

(7) F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, 9th Ed., John Wiley and Sons, Inc., New York, N. Y., 1947.

TABLE I

ANALYSIS OF RESIDUE AFTER EXTRACTION OF FILTRATE FROM REACTION BETWEEN Ni, Hg(CN)₂ AND KCN (MOLAR RATIOS 2:1:6)

Oxidation no. of Ni	Ni, %	CN, %	K, %	Atomic ratios		Empirical formula (from analysis)
				CN/Ni	K/Ni	
0.11 ± 0.01	17.99 ± 0.09	33.39 ± 0.37	48.62 ± 0.20	4.19	4.07	K _{4.07} Ni(CN) _{4.19}
.12 ± 0.2	18.56 ± .08	32.65 ± .34	49.70 ± .41	4.06	3.94	K _{3.94} Ni(CN) _{4.06}
.25	19.10 ± .13	32.41 ± .20	48.20 ± .28	3.83	3.75	K _{3.75} Ni(CN) _{3.83}
.17	18.82 ± .10	33.40 ± .24	47.85 ± .30	4.07	3.81	K _{3.81} Ni(CN) _{4.07}

TABLE II

THERMAL DECOMPOSITION OF K₄[Ni₂(CN)₆]

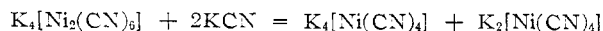
Initial ratio KCN/ K ₄ [Ni ₂ (CN) ₆]	Conversion to Ni metal, %	Analysis of product after DMF extraction		
		Oxidation no. of Ni	CN/Ni	K/ Ni
0.00	100			
1.43	71			
1.21	54			
5.00	36	0.18		
9.13	48	.21	3.92	3.56
35.40	43	.33	3.71	3.38

can it be attributed to contamination by potassium hexacyanodinitrate(I), K₄[Ni₂(CN)₆], inasmuch as this substance is also diamagnetic. It is our belief that the paramagnetism is due to the presence of a small amount of a thermally stable nickel(I) complex, probably potassium tetracyanonickelate(I), K₃[Ni(CN)₄], which can be formed in a manner to be described below.

In reaction between nickel, mercury(II) cyanide and potassium cyanide, the mercury compound invariably was reduced quantitatively to free mercury. Anywhere from one-quarter to one-third of the nickel was recovered unconverted, even though there was sufficient mercury(II) cyanide present in the reaction mixture to convert all of the nickel to the monovalent state. About 20–25% of the nickel was found as K₄[Ni(CN)₄] and approximately 50% as K₂[Ni(CN)₄], the latter being soluble in the N,N-dimethylformamide used as extractant.

It was hoped that the reaction would yield a nickel(I)-cyano complex as the major product. The fact that K₄[Ni(CN)₄] was formed as the major lower valent nickel complex is striking and surprising, since conversion of free nickel to this compound occurs under oxidizing conditions. The question arises as to the mechanism of formation of the nickel(0) complex. That the product could not arise from direct union of finely divided nickel and potassium cyanide was shown by the lack of reaction between these two substances at temperatures up to 650°. It might be visualized that in the presence of potassium cyanide, mercury(II) cyanide oxidizes some of the nickel to K₂[Ni(CN)₄] and that this complex is reduced by the metal to the nickel(0) complex. However, this mechanism is ruled out by the fact that at temperatures up to 500° virtually no nickel dissolves in K₂[Ni(CN)₄].

Another possible mechanism is that K₄[Ni₂(CN)₆] is formed as an initial product and that this compound, in the presence of potassium cyanide, undergoes disproportionation to K₄[Ni(CN)₄] and K₂[Ni(CN)₄].



Such a mechanism is consistent with the observations on the thermal decomposition of K₄[Ni₂(CN)₆] in the presence of potassium cyanide. As the data of Table II show, the product left after filtration and extraction of the filtrate contained nickel in an average oxidation number significantly lower than one but somewhat greater than 0, a fact which can be explained only by the formation of appreciable quantities of a nickel(0) complex. Moreover, nickel metal, in considerable amount, was invariably formed in the decomposition. It is to be recalled that from one-quarter to one-third of the nickel was recovered unconverted in the reaction between nickel, mercury(II) cyanide and potassium cyanide, although the second reagent was present in sufficient quantity to convert all of the nickel to the monovalent state. It is entirely conceivable that all of the nickel was originally consumed by the formation of K₄[Ni₂(CN)₆] but was partially regenerated on decomposition of the latter substance. Both nickel(II) and cyanide were found in the material extracted with N,N-dimethylformamide from the filtrate after the thermal decomposition of K₄[Ni₂(CN)₆] in the presence of potassium cyanide. Thus, all of the major products found in the reaction between nickel, mercury(II) cyanide and potassium cyanide were also obtained when K₄[Ni₂(CN)₆] was decomposed thermally in the presence of potassium cyanide. Finally, the residue from extraction of the filtrate after the thermal decomposition of K₄[Ni₂(CN)₆] was paramagnetic. This can only be attributed to the presence of some stable nickel(I)-cyanide complex which contaminates the K₄[Ni(CN)₄], the major lower valent nickel complex formed. The K₄[Ni(CN)₄] isolated from reaction between nickel, mercury(II) cyanide and potassium cyanide was similarly contaminated.

The reaction between potassium cyanide and potassium tetracyanonickelate(II) at 480° has no counterpart in ordinary solution chemistry. The data of Table III, along with the diamagnetism of the material, show beyond doubt that the brick-red substance left after extraction of the filtered product with N,N-dimethylformamide is potassium tetracyanonickelate(0), K₄[Ni(CN)₄]. That this product was formed by oxidation of potassium cyanide by the nickel(II) complex was demonstrated by the identification of cyanogen as the gas evolved during reaction. The highest conversion of K₂[Ni(CN)₄] to K₄[Ni(CN)₄] obtained was 21%, even when the reaction was carried out in the presence of a large excess of potassium cyanide. That K₄[Ni(CN)₄] possesses high thermal stability was shown by the fact that no elementary nickel was observed even when the reaction was effected at temperatures approaching 600°.

TABLE III
ANALYSIS OF RESIDUE AFTER EXTRACTION OF FILTRATE FROM REACTION BETWEEN KCN AND $K_2[Ni(CN)_4]$
(Molar ratio 2:1)

Oxidation no. of Ni	Ni, %	CN, %	K, %	Atomic ratios		Empirical formula
				K/CN	CN/Ni	
0.05	18.50 \pm 0.12	32.07 \pm 0.21	3.92
0.02	18.48 \pm 0.02	32.54 \pm 0.30	48.83 \pm 0.32	3.96	3.97	$K_{3.96}Ni(CN)_{3.97}$

TABLE IV
ANALYSIS OF RESIDUE AFTER EXTRACTION OF FILTRATE FROM REACTION BETWEEN Ni, $K_2[Ni(CN)_4]$ AND KCN
(Molar ratios 1:14)

Oxidation no. of Ni	Ni, %	CN, %	K, %	Atomic ratios		Empirical formula
				CN/Ni	K/Ni	
1.07	21.23 \pm 0.09
1.07	21.60 \pm .02	36.71 \pm .43	41.49 \pm .13	3.84	2.88	$K_{2.88}Ni(CN)_{3.84}$
1.16	21.61 \pm .00	37.56 \pm .52	42.30 \pm .21	3.93	2.93	$K_{2.93}Ni(CN)_{3.93}$

Another novel reaction is the one at 450–480° between nickel, potassium tetracyanonickelate(II) and potassium cyanide in the molar ratios 1:1:4. As the data of Table IV indicate, the lower valent nickel complex obtained from this reaction is potassium tetracyanonickelate(I), $K_3[Ni(CN)_4]$. This ox-blood red substance was isolated in 50–80% yield. It would be expected that this compound would be paramagnetic, with a spin-only moment of about 1.73 Bohr magnetons corresponding to one unpaired electron. Our product was paramagnetic, but the moment found varied in the range of 2.98–3.32 Bohr magnetons. No definite explanation

can be offered for the high moment obtained, but it is conceivable that traces of elementary nickel, which is ferromagnetic, were present in the product. The fact that $K_3[Ni(CN)_4]$ is stable at 480°, whereas $K_4[Ni_2(CN)_6]$ undergoes disproportionation, strongly suggests that it is the material which contaminates the $K_4[Ni(CN)_4]$ formed in the reaction between nickel, mercury(II) cyanide and potassium cyanide.

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF THE DIAMOND ALKALI COMPANY, PAINESVILLE, OHIO]

Organic Derivatives of Chromium, Molybdenum and Tungsten Carbonyls

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The reaction of the Group VIB metal hexacarbonyls and arene-metal tricarbonyls with trivalent Group VA ligands has been studied. Fifteen compounds described by the generic formula $(R_3A)_xM(CO)_{6-x}$ have been prepared. Correlations have been drawn between the position of the metal carbonyl stretching frequency in the infrared spectrum and the number and type of the substituting ligand.

We have previously reported¹ the preparation of compounds formed by the reaction of trivalent Group VA compounds (such as tertiary phosphines and phosphites) with carbonyl compounds of Group VIB metals. The products, obtained in high yield, were stable, non-volatile, monomeric compounds described by the generic formula $(R_3A)_xM(CO)_{6-x}$ where R_3A is a trialkyl or triaryl phosphine, phosphite, arsine or stibine; M is chromium, molybdenum or tungsten; and x is 1, 2 or 3, depending on the substituting ligand and the reaction conditions employed. We now wish to describe some additional compounds of this type, together with details concerning the preparation and infrared spectra of all of the reported compounds.

Until recent years the only substituted carbonyl compounds of the Group VIB metals which had been reported were those in which nitrogen served

as the donor atom.² This is in contrast with other transition elements, particularly those of Group VIII, for which a variety of compounds containing other donor atoms has been described [e.g., bis-(triphenylphosphine)-nickel dicarbonyl³ and triphenylphosphinemanganese tetracarbonyl⁴]. However, in addition to our earlier report,¹ several investigators recently have described substituted carbonyl compounds of the Group VIB metals in which the ligand donor atoms are phosphorus, arsenic or antimony.^{5–11}

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