[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Reduction of Potassium Cyanopalladate(II) by Potassium in Liquid Ammonia; A Zerovalent Compound of Palladium[1]

BY JOSEPH J. BURBAGE AND W. CONARD FERNELIUS[2]

Eastes and Burgess[3] have recently made some very interesting observations on the reduction of complex cyanides by solutions of metals in liquid ammonia. Although the complex ions of cadmium, copper(I), silver and zinc are reduced directly to the free metals, the cyanonickelate (II) ion exhibits the following reactions

$Ni(CN)_4^{=}$ in excess: $Ni(CN)_4^{=} + e^- \longrightarrow Ni(CN)_3^{=} + CN^-$

Na, K or Ca in excess: $Ni(CN)_4^{=} + 2e^- \longrightarrow Ni(CN)_4^{==}$

Salts of the tricyanonickelate(I) ions have been obtained previously in aqueous solution[4,5] but salts of the tetracyanonickelate(0)[6] ion have been obtained only in liquid ammonia solution.

The ease with which these unusual nickel compounds can be prepared in liquid ammonia encourages the search for other compounds of similar character. The results of a study of the reduction of potassium cyanopalladate(II) by potassium in liquid ammonia are presented in this paper. The palladium complex was chosen because it has been shown that reduction in aqueous solution by potassium amalgam furnishes a clear, colorless solution free from colloidal metals which possesses strong reducing properties.[7] As yet the compound responsible for these characteristics has not been isolated.

Preparation of Potassium Cyanopalladate(II).—This compound was prepared according to the method of Rössler,[8] purified by recrystallization, and heated at 200° to obtain the anhydrous salt. It was moderately soluble in liquid ammonia.

Techniques.—The reactions at 0° were carried out in Faraday tubes using the familiar technique developed by Franklin.[9] Reactions at −33° to establish reacting ratios were carried out in a modified form of the apparatus described by Johnson and Fernelius.[10] Approximately 0.5 g. of the salt was dissolved in 100 ml. of liquid ammonia. Small cubes of potassium metal about one-eighth inch on a side were added singly and reacted immediately upon going into solution.

Potassium Cyanopalladate(II) and Potassium at −33°.—After three or four pieces of potassium had been added, very fine white crystals were observed in the solution. They continued to form with further additions of potassium. After the formation of an appreciable precipitate, it was evident that the crystals possessed a light yellowish tint. Any of the precipitate which happened to cling to the wall of the container above the surface of the liquid ammonia turned an intense yellow. When more liquid ammonia was condensed into the reacting flask this intense yellow substance redissolved and the entire precipitate present regained its homogeneous light yellowish-white color. When an amount of potassium slightly in excess of two equivalents was added to the system the solution turned bluish-green throughout and metallic palladium began to plate out on the walls of the containing vessel. There was no visible evidence to indicate that the character of the precipitate varied at any point throughout the reaction. No more than 1 ml. of hydrogen was liberated in any run. The following reacting ratios were found:

Moles of $K_2Pd(CN)_4$	Moles K	Ratio of $K_2Pd(CN)_4$ to K
0.00286	0.00661	1:2.31
.00226	.00512	1:2.26
.00198	.00401	1:2.02
.00172	.00354	1:2.06
.00262	.00543	1:2.07
.00219	.00459	1:2.09
.00305	.00620	1:2.03

Potassium Cyanopalladate(II) and Potassium at 0°.—Upon adding successive portions of potassium solution to one of the cyanopalladate, the dark blue color disappeared immediately and a yellowish-white precipitate formed. For the initial additions of small amounts of potassium, the precipitate dissolved rapidly upon shaking but further additions produced a permanent crystalline precipitate which settled readily. After the addition of two equivalents of potassium the solution acquired a permanent greenish-blue color, indicating that the reaction was complete. Because of the moderate solubility of the precipitate it was freed of impurities by washing either with small amounts of ammonia at 0° or by larger quantities at −33°. The addition of only one equivalent of potassium produced the same precipitate as that obtained with two equivalents.

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[1] From a thesis (1942) presented by Joseph J. Burbage for the Degree of Master of Science. Presented before the Division of Physical and Inorganic Chemistry at the Buffalo meeting of the American Chemical Society, September, 1942.

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[3] J. W. Eastes and W. M. Burgess, THIS JOURNAL, **64**, 1187–1189, 2715–2716 (1942).

[4] J. Belucci and R. Corelli, *Atti acad. Lincei*, **22**, I, 603–608, 703–708 (1913); *Gazz. chim. ital.*, **43**, II, 569–586 (1913); *Z. anorg. Chem.*, **86**, 88–104 (1914).

[5] J. Belucci, *Gazz. chim. ital.*, **49**, II, 70–91, 285–293 (1919).

[6] The name potassium tetracyanonickelate(0) is consistent with the recommendations of the Report of the International Committee for the Reform of Inorganic Chemical Nomenclature [THIS JOURNAL, **63**, 889–897 (1941)]. Because of the absence of a character for zero in the Roman system of notation, the conventional 0 is used.

[7] W. Manchot and H. Schmid, *Ber.*, **63B**, 2782–2786 (1930); **64B**, 2672–2677 (1931).

[8] H. Rössler, *Z. Chem.*, **9**, 175 (1866).

[9] E. C. Franklin, "The Nitrogen System of Compounds," Reinhold Publishing Corp., New York, N. Y., 1935, pp. 317–330.

[10] W. C. Johnson and W. C. Fernelius, *J. Chem. Ed.*, **6**, 444–447 (1929).

When an amount of potassium in excess of two equivalents was added, a heavy, dark green mass formed in the reaction tube and a mirror of metallic palladium deposited on the walls of the tube. Upon treatment with water prior to analysis the compound underwent immediate solution forming a clear solution momentarily, after which appreciable quantities of hydrogen and hydrogen cyanide gases were evolved with the subsequent deposition of palladium metal. Approximately one-third of the total palladium settled out, while the other two-thirds remained in solution in the form of the cyanide. Part of the palladium was weighed as the free metal and the remainder precipitated and weighed as the dimethylglyoximate. The potassium was determined as sulfate.

Anal. Calcd. for $K_4Pd(CN)_4$: K, 42.60; Pd, 29.06. Found (in separate runs): (1) Pd, 29.06; (2) K, 41.37; Pd, 29.00; (3)* K, 40.57; Pd, 28.76; (4) K, 42.32; Pd, 28.75; (5) K, 42.09; Pd, 29.16. The values marked (*) are for the precipitate formed by the addition of only one equivalent of potassium.

Potassium Cyanonickelate(II) and Potassium.—Ordinarily upon the addition of small amounts of potassium to a solution of $K_2Ni(CN)_4$, at 0 and −33°, red $K_2Ni(CN)_3$ precipitated until one equivalent of potassium had been added and then was transformed rather rapidly into yellow $K_4Ni(CN)_4$ upon the further addition of potassium. At 0°, agitation speeded the second stage of the reaction, but it always took place upon standing. However, on a few occasions at −33° a definite end-point was reached at the $K_2Ni(CN)_3$ stage and the blue color of a slight amount of unreacted potassium persisted without any indication of the formation of $K_4Ni(CN)_4$. Such runs were abandoned after four hours.

Thermal Stability of $K_4Pd(CN)_4$, $K_2Ni(CN)_3$, and $K_4Ni(CN_4)$.—Potassium tetracyanopalladate(0), $K_4Pd(CN)_4$, was stable for at least six hours when left in liquid ammonia at 0°, at least twelve hours in liquid ammonia at −33°, and approximately two hours in an ammonia atmosphere at room temperature. It was stable enough in a partial vacuum at −33° to allow the ammonia gas to be pumped off so that a pure sample might be weighed within the closed tube. Slight heating greatly increased the rate of decomposition.

Potassium tricyanonickelate(I), $K_2Ni(CN)_3$, was completely stable in liquid ammonia and in an ammonia atmosphere at room temperature. A pure sample of the compound was heated to 200° in a sealed tube with no visible change.

The compound $K_4Ni(CN)_4$ was completely stable in liquid ammonia and in an ammonia atmosphere at room temperature. When a sample of the compound was heated in an evacuated sealed tube, it began to turn green at 160° and with further increase in temperature rapidly became dark green.

Reactions of $K_4Pd(CN)_4$.—Addition of ammonium bromide to $K_4Pd(CN)_4$, at −33 and at 0°, caused the precipitate to dissolve. After the addition of 2–3 equivalents of ammonium bromide, a precipitate of a different character began to form, which proved to be potassium bromide. This potassium bromide continued to form until four equivalents of ammonium bromide had been added. Decantation of the solution and subsequent evaporation of the liquid ammonia brought about decomposition of the solute with the formation of free palladium when the solution became concentrated.

When silver iodide (less than an equivalent) was added to $K_4Pd(CN)_4$ in liquid ammonia at −33°, the solution immediately became brown and then gradually darkened until it became a dark purple, almost black. Upon evaporation of the ammonia all of the silver was recovered as the free metal along with much free palladium.

When mercuric iodide (less than an equivalent) was added to $K_4Pd(CN)_4$ in liquid ammonia at −33°, the solution turned bluish-green immediately and then gradually became very black. After a time black particles settled out leaving a brown solution. After evaporation of the ammonia, a palladium amalgam containing all of the mercury was obtained.

The color of a solution of azobenzene in contact with $K_4Pd(CN)_4$ at −33° gradually became lighter but the reaction was slow. After vigorous agitation for two hours, standing overnight, and evaporation of the ammonia, the light yellow residue was washed out with water and extracted with ether. To a portion of the ether extract were added ethyl alcohol, sodium hydroxide, and benzoyl chloride. Yellowish white crystals formed which after recrystallization melted at 126° (N,N′-diphenylbenzhydrazide melts at 126°).

Reactions of $K_4Ni(CN)_4$ and $K_2Ni(CN)_3$.—When $K_4Ni(CN)_4$ was treated with ammonium bromide at −33° the precipitate became more crystalline but otherwise there was no change. Solutions of silver iodide and mercuric iodide were reduced completely to the respective metals which in contrast to $K_4Pd(CN)_4$ were not contaminated with nickel. The product of reaction between azobenzene and $K_4Ni(CN)_4$ gave a benzoyl derivative, m. p. 125.5° (the quantity available was too small for recrystallization). Ammonium bromide was without effect on $K_2Ni(CN)_3$ at −33°.

Potassium Cyanoplatinate(II) and Potassium.—Preliminary study of this reaction indicated the existence of a more highly reduced compound than $K_2Pt(CN)_4$.[11] The complete characterization of the product formed in liquid ammonia at 0 and −33° was handicapped by the relative insolubility of $K_2Pt(CN)_4$ and the marked evolution of hydrogen ($2K + 2NH_3 \rightarrow 2KNH_2 + H_2$). The reacting ratios of $K:K_2Pt(CN)_4$ at −33° were greater than 2 even when correction was made for evolved hydrogen. However, on adding potassium to a solution of $K_2Pt(CN)_4 + 5KNH_2$, very little gas was evolved and the reacting ratio was 2.057:1. At 0°, addition of a potassium solution to one of $K_2Pt(CN)_4$ produced a white precipitate (intermediate brown coloration) which after washing was analyzed: K, 31.3; Pt, 43.05. Calcd. for $K_4Pt(CN)_4$: K, 34.32; Pt, 42.84.

Potassium Cyanochromate(III) and Potassium Cyanocobaltate(III) and Potassium.[12]—Both $K_3Cr(CN)_6$ and $K_3Co(CN)_6$ reacted with potassium in liquid ammonia but neither the reacting ratios at −33° nor the analytical composition of the brown precipitates at room temperature were consistent. Large quantities of hydrogen were liberated.

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[11] W. Manchot and G. Lehman, *Ber.*, **63B**, 2775–2782 (1930).

[12] J. H. Bigelow, Thesis, The Ohio State University, 1939.

Discussion

The experiments described here show that liquid ammonia solutions of potassium and potassium tetracyanopalladate(II) react in the ratio of 2:1 to form moderately soluble potassium tetracyanopalladate(0) which is more soluble and less stable than the corresponding compound of nickel. Both cyanopalladate(0) and the cyanonickelate(0) reduce azobenzene to hydrazobenzene and silver and mercuric ions to the metals. Ammonium cyanopalladate(0) exists in ammonia solution but has not been isolated. In contrast to nickel, palladium appears to form no compound of the type of $K_2Pd(CN)_3$. At least the composition of the precipitate is the same throughout the precipitation. It seems likely that Manchot and Schmid actually prepared a solution of $K_4Pd(CN)_4$ and not $K_2Pd(CN)_3$ as they supposed.

Experience in this Laboratory has not confirmed the experience of Eastes and Burgess in their inability to prepare $K_4Ni(CN)_4$ by the action of potassium on solutions of $K_2Ni(CN)_4$. Only occasionally did the reduction stop at the $K_2Ni(CN)_3$ stage. A possible cause of these apparent inconsistencies may lie in the physical character of the initial precipitate. Since the reaction $K_2Ni(CN)_3 + K + KCN \rightarrow K_4Ni(CN)_4$ requires the reaction of two soluble materials with a precipitate, a firm coating of more insoluble material over the surface may well block further action.

It is interesting to note that in the compounds $K_4Ni(CN)_4$ and $K_4Pd(CN)_4$ the central atom of the complex ion exhibits an *effective atomic number* (E. A. N.) equal to that of the rare gas at the end of the period in which the element is placed in the periodic classification: *i. e.*, E. A. N. of Ni in $Ni(CN)_4^{==} = 36$ (Kr); E. A. N. of Pd in $Pd(CN)_4^{==} = 54$ (Xe). Hence, these complex ions are to be compared to the known carbonyl of nickel, $Ni(CO)_4$, and the expected carbonyl of palladium, $Pd(CO)_4$. The difference lies in the fact that the CN^- ion, although isoelectronic with the CO molecule, carries with it a negative charge which must be balanced by a corresponding charge on a positive ion. Hence, the same pattern of combination leads to a neutral molecule in the one case, $Ni(CO)_4$, and to a complex ion in the other, $Ni(CN)_4^{==}$ (or $Pd(CN)_4^{==}$).[13]

Summary

1. Potassium tetracyanopalladate(0), $K_4Pd(CN)_4$, has been prepared by the reaction between potassium and potassium cyanopalladate(II) in liquid ammonia solution.

2. Some of the properties of $K_4Pd(CN)_4$ have been determined and compared with those of $K_4Ni(CN)_4$.

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[13] For a discussion of the relation between E. A. N. and stability of complex ions see A. A. Blanchard, *Chem. Rev.*, **26**, 409–422 (1940), *Science*, **94**, 311–317 (1941)

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Methods for Resolution of Enantiomorphs. III. Chromatographic Adsorption[1a,b]

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The separation of diastereoisomers by rectification by Bailey and Hass[1] suggested that other counter-current processes might be attempted. A partial separation by counter-current liquid–liquid extraction has been accomplished by Shapiro and Newton.[1b] That diastereoisomers differ in their adsorbability was demonstrated by Fischgold and Ammon[3] without the use of Tswett columns. Stoll and Hofman[4] were able to resolve isolysergic acid by chromatographic adsorption of the *d*-isopropanolamide on columns of alumina. Jamison and Turner[5] have recently reported a small separation of the *l*-menthyl *dl*-mandelates by selective adsorption on alumina.

The methods of chromatographic adsorption have also been used to resolve stereoisomers. The first separation of that kind was claimed by Winterstein and Stein.[6] Cook and others[7] were able to separate *cis*- and *trans*-azobenzene on

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[1] (a) Original manuscript received August 22, 1942. (b) Abstracted from the M.S. thesis of H. H. Jaffé. Previous papers of this series were by M. E. Bailey and H. B. Hass, THIS JOURNAL, **63**, 1969 (1941), and by E. Shapiro and R. F. Newton, *ibid.*, **65**, 777 (1943).

[2] McCoy Research Fellow, 1941–1942.

[3] A. Fischgold and R. Ammon, *Biochem. Z.*, **234**, 39 (1931).

[4] A. Stoll and A. Hofman, *Z. physiol. Chem.*, **251**, 155 (1938).

[5] M. M. Jamison and E. E. Turner, *J. Chem. Soc.*, 611 (1942).

[6] A. Winterstein and G. Stein, *Z. physiol. Chem.*, **220**, 247 (1933).

[7] (a) A. H. Cook, *J. Chem. Soc.*, 876 (1938); (b) L. Zechmeister, O. Frehden and P. Fischer-Jörgensen, *Naturwissenschaften*, **26**, 496 (1938)