be mentioned. They estimated theoretically an activation energy of 18,000 cal./g. mole for the racemization of 2,2'-dibromo-4,4'-dicarboxybiphenyl. It is unfortunate that this value cannot be compared with experimental data for this compound.

Salt Lake City, Utah Received May 4, 1951

[Contribution from the Lab. Prod. Mineral, Ministerio da Agricultura, Rio de Janeiro]

Salts of Tetracyanopalladic(II) Acid

By F. Feigl and G. B. Heisig[1]

Tetracyanopalladic(II) acid forms insoluble salts of silver and copper and of their amines. It also forms normal salts of benzidine, β-naphthoquinoline and oxine, and the acid salt of nitron. On heating aqueous solutions of the benzidine, β-naphthoquinolinium salts, hydrocyanic acid is lost and the corresponding diammine is formed.

It is well known that palladium(II) cyanide dissolves in an excess of cyanide ions and that tetracyanopalladate(II) ion is formed. We found that by acidifying such a solution with a mineral acid there is no immediate precipitation of palladium(II) cyanide according to the equation

$$\mathrm{Pd(CN)_4^{=} + H^+ \rightleftarrows Pd(CN)_2 + 2HCN}$$

The time required for the precipitation depends on the temperature and on the concentration of the cyanide ion in the solution. Tetracyanopalladic(II) acid, $H_2[Pd(CN)_4]$, is stable only in the presence of an excess of hydrocyanic acid. An acid having this formula should form insoluble salts with inorganic and organic cations.

The general method of preparing salts of this acid is to add a solution of the compound which gives the appropriate cation to a slightly acid, neutral or alkaline solution containing the tetracyanopalladate(II) ion. Thus by adding solutions of copper(II) sulfate and silver nitrate to a solution containing the tetracyanopalladate(II) ion, the corresponding salts precipitated. By adding a solution of copper(II) tetrammine sulfate or silver diammine nitrate to solutions containing the tetracyanopalladate(II) ion, impure diammines of copper and silver tetracyanopalladate(II) precipitated. From their hydrochloric acid solutions the salts of the following organic bases were precipitated: benzidine, β-naphthoquinoline, nitron and β-hydroxyquinoline (oxine). Aqueous suspensions of the salts of benzidine and β-naphthoquinoline when heated lose hydrogen cyanide according to the general equation

$$\mathrm{Bz_2H_2[Pd(CN)_4] \rightleftarrows [PdBz_2(CN)_2] + 2HCN}$$

and diammines of palladium(II) cyanide were formed. Hydrocyanic acid was lost almost quantitatively from crystals of β-naphthoquinolinium tetracyanopalladate(II).

Experimental

A solution of potassium tetracyanopalladate(II) was prepared by adding potassium cyanide to freshly prepared palladium(II) cyanide until all was dissolved. Just before it was to be used, an acid solution of tetracyanopalladate(II) ion was prepared by adding a slight excess of dilute hydrochloric, sulfuric or acetic acid to a cold solution of the potassium salt. The palladium cyanide was prepared by treating 0.01 mole of palladium(II) chloride with 0.02 mole of mercuric cyanide and allowing the mixture to stand overnight. The cream-colored precipitate, palladium(II) cyanide, was washed by decantation four or five times, filtered and washed with hot water.

A solution of crystals of potassium tetracyanopalladate(II)[2] was used to prepare the copper and silver salts.

Metals and Metal Ammine Salts of Tetracyanopalladic(II) Acid. Copper(II) Tetracyanopalladate(II), $CuPd(CN)_4$.—Blue copper(II) tetracyanopalladate(II) was prepared by adding a solution of copper sulfate to a solution of the crystals of $K_2Pd(CN)_4$. The residue obtained by ignition was 68.0%. The calculated value is 67.8%. The salt contained 19.9% of nitrogen and the calculated value is 20.4%.

Copper(II) Diamminetetracyanopalladate(II) $[Cu(NH_3)_2][Pd(CN)_4]$.—This salt was prepared by adding a solution of copper(II) tetrammine nitrate to a solution of potassium tetracyanopalladate(II). A blue copper salt precipitated and was crystallized from hot water containing a little ammonia. The dried salt was ignited. The ratio $\frac{\mathrm{Pd + CuO}}{\mathrm{wt.\ of\ sample}} \times 100$ was 60.0. The value calculated from the formula $[Cu(NH_3)_2][Pd(CN)_4]$ is 60.5. Analysis of the product from another experiment gave the ratio $\frac{\mathrm{Pd + CuO}}{\mathrm{wt.\ of\ sample}} = 61.7$. The per cent. of carbon was 15.1, hydrogen 2.6 and that of nitrogen 28.8. The percentages calculated for the diammine are 15.6, 2.0 and 27.3, respectively.

Silver Tetracyanopalladate(II) $Ag_2[Pd(CN)_4]$.—Silver tetracyanopalladate(II) was prepared by adding a slight excess of silver ions to a solution of the crystals of potassium tetracyanopalladate(II). The ratio of $\frac{\mathrm{Pd + Ag}}{\mathrm{wt.\ of\ sample}} \times 100$ was 75.5. The calculated value is 75.6.

Silver Diamminetetracyanopalladate(II) $[Ag(NH_3)_2]_2[Pd(CN)_4]$.—The white crystalline precipitate obtained by adding an ammoniacal solution of silver nitrate to a solution of potassium tetracyanopalladate(II) after recrystallization from hot, dilute ammonia was ignited. The ratio $\frac{\mathrm{Pd + Ag}}{\mathrm{wt\ of\ sample}} \times 100$ was 71.8. The value calculated for silver diamminetetracyanopalladate(II), $Ag_2[Pd(CN)_4]$ is 75.6. The product was, therefore, a mixture of the two salts. Since the diammines of silver are unstable and lose ammonia the suspension of the product was heated until no more ammonia was evolved. Ignition of the white residue gave a ratio of $\frac{\mathrm{Pd + Ag}}{\mathrm{wt.\ of\ sample}} \times 100$ of 76.3, showing that the mixture had been changed to silver tetracyanopalladate(II), $Ag_2[Pd(CN)_4]$.

Organic Salts of Tetracyanopalladic(II) Acid.—These salts were obtained by mixing dilute hydrochloric acid solutions of the respective bases with solutions of tetracyanopalladic(II) acid, $H_2[Pd(CN)_4]$. The pure salts were obtained by crystallization from hot water. The dry salts were analyzed by weighing the palladium obtained upon igniting the salts.

Benzidiniumtetracyanopalladate(II) $BzH_2[Pd(CN)_4]$.—When the precipitate formed by the reaction of the hydrochloric acid solutions of tetracyanopalladic(II) acid and benzidine (Bz) was recrystallized from hot water, a residue

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(1) On sabbatical leave from the University of Minnesota, Minneapolis, Minnesota.

(2) W. C. Fernelius, *et al.*, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Company, Inc., New York, N. Y., 1946, p. 245.

remained. On cooling the hot filtered solution, a white crystalline product was obtained which contained 26.9% of palladium. The value calculated for $BzH_2[Pd(CN)_4]$ is 26.8%. Since the residue might be a decomposition product of the salt, an aqueous solution of the recrystallized product, $BzH_2[Pd(CN)_4]$ was heated. Hydrogen cyanide was evolved and an insoluble product was obtained. Its palladium content was 30.8% corresponding to the value 31.2% calculated for dicyanobenzidinepalladium, $[BzPd(CN)_2]$.

β-Naphthoquinoliniumtetracyanopalladate(II) $Nq_2H_2[Pd(CN)_4]$.—The white crystalline precipitate obtained by mixing a hydrochloric acid solution of the base with tetracyanopalladic(II) acid was filtered, washed with water, alcohol and ether and dried at 50°. It contained 19.0% of palladium, 63.1% of carbon and 3.8% of hydrogen. The corresponding values calculated for $Nq_2H_2Pd(CN)_4$ are 18.7, 63.1 and 3.5%. The salt lost hydrocyanic acid on standing forming nearly pure dicyanodinaphthoquinoline palladium which contained 21.4% of palladium. The calculated value is 20.6%.

Oxiniumtetracyanopalladate(II) $Ox_2H_2[Pd(CN)_4]$.—This yellow crystalline product, obtained by the general method, was not decomposed by hot water. It contained 21.0% of palladium. The value calculated for $Ox_2H_2[Pd(CN)_4]$ is 21.3%. The solid salt had a strong yellow fluorescence in ultraviolet light.

Nitroniumtetracyanopalladate(II) $NtH_2[Pd(CN)_4]$.—This white crystalline product which is not decomposed by hot water, was obtained by the general method. The amount of palladium in the compound was 20.8%. The value calculated for $NtH_2[Pd(CN)_4]$ is 20.3%.

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[CONTRIBUTION FROM THE LAB. PROD. MINERAL, MINISTERIO DA AGRICULTURA, RIO DE JANEIRO]

Coördination of Organic Bases with Palladium(II) Cyanide

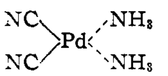
BY F. FEIGL AND G. B. HEISIG[1]

Palladium(II) cyanide coördinates ammonia and many organic nitrogen bases such as pyridine, ethylenediammine, quinoline, α,α'-dipyridyl, o-phenanthroline, benzidine, oxine, diphenylamine, "tetrabase" forming crystalline compounds which are homologs of the diammine, β-naphthoquinone forming a homolog of the monoamine. The reaction is one between a Lewis acid and base, respectively. Many amines including alkaloids in neutral or acid solutions coördinate with palladium(II) cyanide forming adsorption complexes (lakes). In the case of acid-base indicators the colors of the lakes are essentially the same as those of the acid solutions of the indicators. An explanation is proposed which is based on resonance and the Lewis theory of acids and bases. The colored oxidation products of uncolored amines form lakes with palladium(II) cyanide. These lakes are obtained by adding palladium(II) cyanide to the slightly colored, acidified hydrogen peroxide solutions of the amines. Two explanations for the formation of these lakes are offered. Examples of the analytical use of the lakes of acid-base indicators with palladium(II) cyanide are described.

Many analytical textbooks state that palladium(II) cyanide dissolves in ammonia, but the product formed is not mentioned. A search of the literature showed that in 1841 Fehling[2] isolated a white crystalline product whose empirical formula is $Pd(CN)_2 \cdot 2NH_3$. This compound is somewhat soluble in hot water and ammonia. From the standpoint of coördination chemistry and modern concepts of chemical bonds[3] palladium(II) should have a coördination number of 4. Therefore, the product may be an electrolyte—formula I—or a non-electrolyte—formula II

$[Pd(NH_3)_4][Pd(CN)_4]$

I

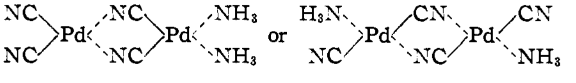


$$\begin{matrix} NC & & NH_3 \\ & Pd & \\ NC & & NH_3 \end{matrix}$$

II

We prepared the diammine by warming a suspension of palladium(II) cyanide in an excess of ammonia. The palladium(II) cyanide first dissolves and then a white crystalline product which contains 55.3% of palladium, 12.3% of carbon and 3.1% hydrogen, precipitates. The calculated values for $[Pd(NH_3)_2(CN)_2]$ are 55.3, 12.4 and 3.1%, respectively. Since palladium(II) sulfide is not precipitated from the hot aqueous solution by ammonium sulfide, tetrammine palladium(II) ions are not present. The absence of cyanide ions in the aqueous solution was shown by the non-precipitation of silver cyanide on the addition of silver nitrate. These facts eliminate formula I; therefore, formula II is the correct one.

The diammine reacts with 0.1 N acetic acid-forming a white crystalline product which contained 60.5% of palladium. This value corresponds to 60.7% of palladium calculated for the monammine. The product is not palladium(II) cyanide, for it does not form palladium sulfide when moistened with ammonium sulfide. Since palladium has a coördination number of four and not three as given by the formula $PdNH_3(CN)_2$, it is probable that the formula should be twice the simple one. In this case the compound can be thought of as an addition compound of palladium(II) cyanide and its diammine. The empirical formula is $Pd(CN)_2 \cdot [Pd(NH_3)_2(CN)_2]$ and the coördination formulas are



$$\begin{matrix} NC & & NC & & NH_3 \\ & Pd & & Pd & \\ NC & & NC & & NH_3 \end{matrix} \quad \text{or} \quad \begin{matrix} H_3N & & CN & & CN \\ & Pd & & Pd & \\ NC & & NC & & NH_3 \end{matrix}$$

Homologs of the monammines have analogous formulas.

We also found that an addition reaction took place between a suspension palladium(II) cyanide and amines dissolved in water or organic solvents. The products were crystalline organic homologs of dicyanodiamminepalladium(II) or microscopically amorphous adsorption complexes although in a few cases both types of products formed simultaneously. The lakes, adsorption complexes, formed by the action of palladium(II) cyanide

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[1] On sabbatical leave from the University of Minnesota, Minneapolis, Minn.

[2] R. Fehling, *Ann.*, **39**, 119 (1841).

[3] L. Pauling, "The Nature of the Chemical Bond," Ithaca, N. Y., 1940, p. 99.