R = 3.8 to 4.1. An hour later, after evolving appreciable H_2, they are only a little greener. When the gas atmosphere is nitrogen the color immediately after mixing the $CoCl_2$ and KCN solutions is orange. Following an induction period, H_2 evolution commences and is accompanied by a color change from orange to green. There is no direct correlation between the amount of H_2 evolved and the amount of green material formed.

In the presence of a little acid and an atmosphere of either H_2 or N_2 the initial precipitate is buff colored, while in the presence of alkali it is a deep green. Within a range of low alkali concentrations the amount of green material that is formed appears to be proportional to the amount of alkali added. KCl cannot substitute even in part for KOH. Alternate additions of acid and alkali destroy and reconstitute the green compound, and it can be reformed from the hydrosulfite complex by adding alkali. Thus it is fairly stable and probably has a definite composition rather than being an adsorption complex at the surface of particles of cobaltous dicyanide. Descamps[6] considered it to be $K_2Co[Co(CN)_6]$.

Discussion

According to the published literature there are only two or three compounds of cobalt present in significant amount immediately after mixing KCN solution with $CoCl_2$ in an inert atmosphere, namely, cobaltous dicyanide, pentacyanocobaltate(II) ion and possibly hexacyanocobaltate(II) ion. The composition and structure of none of these is known with certainty. In the early literature there are claims for two distinct cobaltous cyanides, one a dihydrate[19] and the other a trihydrate.[20] The probable nature of the pentacyanide ion is discussed by Adamson[9] and of the hexacyanide ion by King and Winfield.[13]

After a short period of aging the mixture contains several new ionic species. Disappearance of the pentacyanide is accompanied by the formation of a series of ions which are not readily isolated and identified, since they are continually undergoing chemical change. We have studied them chiefly by means of their absorption spectra.[13]

After prolonged aging there is presumably equilibrium and a smaller number of species. This final product we have attempted to investigate only when cyanide is present in excess. The solution then contains hexacyanocobaltate(III) ion together with a smaller amount of an orange complex which is characterized by absorption bands at 267 and 285 mμ.[13]

It is reasonably certain that the complex directly responsible for H_2 evolution is not a previously described compound of cobalt. We are working on the hypothesis that it is formed as follows: $[Co^{II}(CN)_5]^{3-}$ becomes attached by a double bridge to another cobalt complex at the surface of a particle of cobaltous dicyanide, the second partner being either $[Co^{II}(CN)_5]^{3-}$ or part of the solid itself. Each bridging cyanide group is reduced to an imine with uptake of H^+, the necessary electrons being derived from the cobalt atoms.

When the rate of H_2 evolution is measured at 1 atmosphere pressure of H_2, it is found to be one-tenth as fast as in an atmosphere of argon. This is not evidence for the reversibility of the H_2 evolution, but is due to an initial uptake of H_2 with a resulting decrease in concentration of $[Co^{II}(CN)_5]^{3-}$ which is the source of the H_2-evolving complex. Mills, Weller and Wheeler[2] have made the interesting observation that with a concentrated solution of pentacyanocobaltate ion in an atmosphere of H_2 the paramagnetism disappears and the pressure change ceases after several minutes at room temperature, but the solution then catalyzes the exchange reaction between D_2 and water. Here we apparently have as part of the exchange process an H_2 evolution reaction which is due to the reversal of H_2 uptake, and which therefore yields as product a reduced cobalt complex that can again take up D_2. In the H_2 evolution process in argon which we have described, there is no prior uptake of H_2 and the evolution is irreversible since the product is an oxidized complex.

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[19] N. V. Sidgwick, "The Chemical Elements and their Compounds," Vol. II, Oxford University Press, Oxford, 1951, p. 1380.

[20] "Gmelins Handbuch der anorganischen Chemie," Vol. 58, part 2, Verlag Chemie, Berlin, 1932, p. 364.

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, TEXAS SOUTHERN UNIVERSITY]

Interaction of Rhodium(III) Solutions with 1,2,3-Benzotriazole[1]

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Methods for the synthesis of several coördination type compounds formed in the interaction of rhodium with 1,2,3-benzotriazole are described.

As a result of a recently initiated study of the reactions between the platinum elements and 1,2,3-benzotriazole the preparations of several palladium compounds have been reported.[2,3] It was observed, also, that a solution of rhodium(III) chloride when reacting with 1,2,3-benzotriazole yielded a precipitate.[4]

The purpose of the present study was to examine the precipitate obtained from the rhodium(III) chloride–1,2,3-benzotriazole system and to prepare and investigate precipitates from analogous sys-

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[1] This work was supported by a grant from the National Science Foundation.

[2] R. F. Wilson and L. E. Wilson, THIS JOURNAL, **77**, 6204 (1955).

[3] R. F. Wilson, L. E. Wilson and L. J. Baye, *ibid.*, **78**, 2370 (1956).

[4] R. F. Wilson and L. E. Wilson, *Anal. Chem.*, **28**, 93 (1956).

tems involving 1,2,3-benzotriazole and several other rhodium(III) salts.

Experimental

Materials and Preparation of Solutions.—A rhodium(III) chloride solution was prepared by dissolving a weighed amount of rhodium(III) chloride in a small amount of distilled water contained in a 250-ml. volumetric flask, adding 5 ml. of concentrated hydrochloric acid to prevent hydrolysis and diluting to volume with distilled water. Solutions of rhodium(III) nitrate and rhodium(III) sulfate were prepared using similar procedures. A rhodium(III) bromide solution was prepared by dissolving a weighed amount of rhodium(III) hydroxide in 20 ml. of 47% hydrobromic acid contained in a 50-ml. beaker. The solution was evaporated almost to dryness, quantitatively transferred to a 100-ml. volumetric flask and diluted to volume with distilled water.

Rhodium(III) chloride and rhodium(III) hydroxide were obtained from A. D. Mackay, Inc. The other rhodium(III) salts were obtained from K and K Laboratories.

A stock solution of 1,2,3-benzotriazole in 50% acetic acid was prepared according to the method of Wilson and Wilson.[2]

A stock hydriodic acid–benzotriazole solution was prepared by dissolving 2.5 g. of benzotriazole in 30 ml. of 47% hydriodic acid contained in a 100-ml. volumetric flask and diluting to volume, making the final solution 30% in hydriodic acid and 2.5% in 1,2,3-benzotriazole.

Analytical Methods.—The determinations of carbon, hydrogen and nitrogen content in the compounds reported under "Procedure" were performed in our laboratory and rechecked by Laboratory of Microchemistry, Tiedcke, N. J. Analyses of all other elements were carried out in our laboratory using conventional methods. All precipitates were collected using medium porosity sintered-glass crucibles.

Procedure.—Three samples, each containing 0.173 mmole of the stock rhodium(III) nitrate solution, were treated with sodium acetate to neutralize excess nitric acid. After adding 25 ml. of the acetic acid–1,2,3-benzotriazole solution, the mixture was heated at 90° for about two hours. The precipitates which were formed were washed several times with dilute acetic acid (1:100), and finally several times with warm distilled water. After drying the precipitates at 110° for two hours to constant weights, the following weights were obtained: 88.4, 88.6, 88.5 mg.; yield 100%. *Anal.* Calcd. for the rose colored precipitate: C, 42.28; H, 3.55; N, 24.66; Rh, 20.13. Found: C, 42.43; H, 3.67; N, 24.57; Rh, 20.01. The data correspond to the formula $Rh(C_6H_4NN_2)_3 \cdot 3H_2O$.

To three erlenmeyer flasks, each containing 5-ml. aliquots of the stock rhodium(III) nitrate solution, were added 6.5 g. of sodium acetate and 75 ml. of the stock hydriodic acid–1,2,3-benzotriazole solution. After heating just below boiling for about five minutes, dark brown precipitates were formed. The mixtures were then digested for about 1.5 hours. After standing at room temperature for three hours, the mixtures were filtered and the precipitates washed, dried and weighed in the usual manner. The following weights were obtained for the three precipitates: 140.2, 139.6, 139.8 mg.; yield 99.9%. *Anal.* Calcd.: C, 24.27; H, 1.53; N, 14.15; I, 42.73; Rh, 17.32. Found: C, 24.04; H, 1.38; N, 13.96; I, 42.75; Rh, 17.21. The data correspond to the formula $Rh(C_6H_4NHN_2)(C_6H_4NN_2)I_2$.

To three erlenmeyer flasks, each containing 10-ml. aliquots of the stock rhodium bromide solution, were added 6 g. of sodium acetate and 80 ml. of the stock acetic acid–1,2,3-benzotriazole solution. After heating at 90° for 15 min., light brown precipitates were formed. The mixtures were then digested for about 1.5 hr. After allowing to sit for three hours, the mixtures were filtered and the precipitates were washed, dried and weighed in the usual manner: 182.4, 181.6, 180.9 mg.; yield 100%. *Anal.* Calcd.: C, 34.92; H, 2.28; N, 20.36; Br, 25.83; Rh, 16.62. Found: C, 34.70; H, 2.41; N, 20.35; Br, 25.58; Rh, 16.38. The data correspond to the formula $Rh(C_6H_4NHN_2)_2(C_6H_4NN_2)Br_2$.

To three erlenmeyer flasks, each containing 10-ml. aliquots of the stock rhodium sulfate solution, were added 2 g. of sodium acetate and one milliliter of the stock 1,2,3-benzotriazole solution. Upon heating yellow precipitates formed and settled within two minutes. The mixtures were then digested for two hours and allowed to sit for an additional hour. The mixtures were then filtered and the precipitates were washed, dried and weighed in the usual manner. The following weights were obtained: 72.4, 71.8, 72.0 mg.; yield 100%. *Anal.* Calcd.: C, 35.14; H, 3.69; N, 20.49; Rh, 25.09. Found: C, 34.90; H, 3.52; N, 20.48; Rh, 25.23. The data correspond to the formula $Rh(H_2O)_3(OH)(C_6H_4NN_2)_2$.

Discussion

Elemental analyses and weight relations obtained in this study indicated that two rhodium substitution type compounds and two substitution coördination type compounds were produced. Similar palladium compounds were prepared by Wilson, Wilson and Baye.[3]

It was observed that the *p*H of the solutions was a deciding factor in the preparation of these compounds. In all preparations, the solutions were slightly acidic. Precipitation could not be effected in basic or strongly acidic solutions. Accordingly, the four compounds were soluble in strong bases and in warm, concentrated nitric, sulfuric or hydrochloric acid. Also, $Rh(C_6H_4NHN_2)_2(C_6H_4NN_2)Br_2$ was soluble in concentrated hydrobromic acid, and $Rh(C_6H_4NHN_2)(C_6H_4NN_2)I_2$ was soluble in concentrated hydriodic acid. All of the compounds were insoluble in water, acetic acid, ethyl alcohol and ether.

The absorption spectra for concentrated nitric acid solutions of the four compounds were different from the spectrum obtained from the corresponding concentration of rhodium nitrate dissolved in concentrated nitric acid. This difference in absorption spectra probably suggests that the rhodium ions remain coördinated by 1,2,3-benzotriazole in nitric acid medium.

In the preparation of $Rh(C_6H_4NN_2)_3 \cdot 3H_2O$, it was observed that rhodium was quantitatively precipitated. Moreover, elemental analyses and weight relations indicated that the previously reported precipitate of the rhodium(III) chloride–1,2,3-benzotriazole system[4] has the same formula. Chloride, bromide, nitrate and sulfate solutions of rhodium(III) when treated with the acetic acid–1,2,3-benzotriazole solution according to the method given under "Procedure" for the preparation of rhodium(III)–1,2,3-benzotriazole trihydrate always gave a compound corresponding to $Rh(C_6H_4NN_2)_3 \cdot 3H_2O$. The fact that this compound was formed irrespective of the several anions present suggests a gravimetric method for the determination of rhodium in the presence of certain anions. Further study will be directed toward this end at a later date.

Thermogravimetric analyses of $Rh(C_6H_4NN_2)_3 \cdot 3H_2O$ supported this proposed formula; however, pyrolysis data obtained from the other three compounds could not be interpreted readily.[5] From room temperature up to 120° the trihydrate is stable. Between 120 and 175°, this compound's change in weight corresponds to the loss of one molecule of water; its weight loss between 175 and 220° corresponds to two molecules of water.

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[5] Unpublished data.