ing modes, respectively. With the disappearance of bands at 3310 and 2080 cm^{-1} of the free base V, compound VI_a shows a band at 3010 cm^{-1} assigned to the =C—H stretching mode. This assignment is confirmed by the comparison with the corresponding band (2250 cm^{-1}) of the deuterated complex VI_d. Compound VI_a also shows other bands at 1575 and 675 cm^{-1} assigned to the C=C and C—Cl stretching modes, respectively. The nmr spectra of IV_a and VI_a are also consistent with the structures. The ethynyl proton of the free base V appears at τ 7.85 (in CCl_4) besides other peaks at τ 8.65 (singlet, $(CH_3)_2C$) and τ 7.80 (singlet, $(CH_3)_2N$), whereas VI_a (in $CDCl_3$) shows three singlet signals at τ 8.57, 7.28, and 4.18 in the ratio 6:6:1. They are assigned to C-methyl protons, N-methyl protons, and the C_1-vinyl proton, respectively. The spectrum of IV_a (in CH_2Cl_2) consists of singlets at τ 7.26 and 7.16 (N-methyl protons, wt 6), a singlet at τ 6.41 (methylene protons, wt 2), and multiplets at τ 2.80–3.12 (phenyl protons, wt 5).

Although the infrared bands at 670 cm^{-1} of IV_a and 675 cm^{-1} of VI_a are attributed to the C–Cl stretching mode, these assignments are not reliable. To clarify the presence of a chlorine atom bonded to a carbon atom, IV_a and VI_a are converted to acetato-bridged complexes. When IV_a and VI_a are treated with excess silver acetate in benzene, compounds IV_b and VI_b are obtained, respectively. The infrared spectra of both IV_b and VI_b show bands at 1555 and 1430 cm^{-1} which are ionic acetate carbon–oxygen stretching frequencies. The nmr spectra of IV_b and VI_b show singlets at τ 8.83 and 8.06, respectively, which integrate one acetate group per two N-methyl groups. Molecular weight measurements and elemental analyses also show these are dimeric and one chlorine atom is present per one palladium atom. Only one of the chlorines can be replaced by an acetate group with silver acetate, and this suggests the residual one is not bonded to palladium atom.

Although the direction of addition cannot be decided from the above data alone, we prefer the proposed one on the analogy of the oxy adducts by Cope.[2]

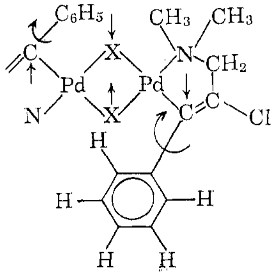

Figure 2.

Chloro-bridged dimers IV_a and VI_a are readily split by pyridine to give monomeric species IV_c and VI_c, respectively.

It will be noted that N-methyls of IV_a appear as two singlets in the nmr spectrum whereas that of VI_a appears as one signal. A possible explanation of this is the steric hindrance caused by the phenyl group. Because of the steric interference of the phenyl group with the μ-chlorine atom, the latter is lifted up (or let down) and the former is let down (or lifted up) with some rotation of the ring. Thus the σ symmetry of the molecule is broken, making the two methyls nonequivalent (Figure 2). This effect also appears in the case of the acetato complex IV_b, where N-methyl groups appear as two singlets (ν_{diff} = 0.25 ppm) and methylene protons as four-line AB pattern (ν_{diff} = 0.68 ppm, J = 15 Hz). Moreover, for the rotation of the phenyl ring, the acetate methyl is placed above the ring, and the signal appears at τ 8.83 which is 0.77 ppm higher than that of VI_b. Being monomeric, pyridine adduct IV_c is much released from the steric restriction, and N-methyls appear as one signal.

CONTRIBUTION FROM THE ISTITUTO CHIMICA GENERALE,
II SEZIONE, THE UNIVERSITY, PADUA, ITALY

Five-Coordinated Low-Spin Complexes of Cobalt(II) with Tertiary and Ditertiary Phosphines

BY P. RIGO, M. BRESSAN, AND A. TURCO

Received January 22, 1968

Cobalt(II) gives with tertiary phosphines a number of tetrahedral high-spin complexes $Co(PR_3)_2X_2$ but does not form low-spin five-coordinated complexes $Co(PR_3)_3X_2$ (X^- = Cl^-, Br^-, I^-, NCO^-).[1] However, such complexes can be easily formed when X^- = NCS^-.[2] The peculiar role of the NCS^- ion in determining the stability of the tris(phosphine) complexes has been attributed to ligand-field effects and it has been suggested that other strong anionic ligands should enhance the ability of cobalt(II) to give this type of five-coordination.

Nickel(II) can form $Ni(PR_3)_3X_2$ complexes when X^- = CN^- (and not when X^- = Cl^-, Br^-, NCO^-, NCS^-),[3] and this suggested that the hitherto unknown corresponding complexes of cobalt(II) could also be prepared. To obtain such complexes may be difficult because the large affinity of cobalt(II) for CN^- may prevent binding of other ligands. Thus, mixed cyano complexes of cobalt(II) have not been reported to date (neglecting $[Co(CN)_5(H_2O)]^{3-}$). We report the preparation of five-coordinated complexes formed by $Co(CN)_2$ with tertiary and ditertiary phosphines and by $Co(CNS)_2$ with ditertiary phosphines. The new complexes with tertiary phosphines have the composition $Co(PR_3)_3(CN)_2$ (PR_3 = $P(C_2H_5)_2C_6H_5$, $PC_2H_5(C_6H_5)_2$).

---

[1] The only known exception is $Co(C_{14}H_{13}P)_3X_2$ ($C_{14}H_{13}$ = 2-phenylisophosphindoline), the stability of which is related to the peculiar stereochemistry of the phosphine.

[2] T. Boschi, M. Nicolini, and A. Turco, *Coord. Chem. Rev.*, **1**, 269 (1966).

[3] P. Rigo, C. Pecile, and A. Turco, *Inorg. Chem.*, **6**, 1636 (1967).

Those with ditertiary phosphines have the unusual composition $Co(diphosphine)_{1.5}X_2$ ($X^- = CN^-$ and NCS^-; diphosphine = 1,3-bis(diphenylphosphino)propane and 1,4-bis(diphenylphosphino)butane).

Experimental Section

Apparatus.—All preparative work and handling of compounds was carried out under an atmosphere of dry nitrogen or argon. Solvents were dried by standard methods and distilled under nitrogen just prior to use. Magnetic susceptibilities were measured using the standard Gouy method at room temperature and were corrected for the diamagnetism of the ligands. Electronic spectra were recorded on an Optica CF4NI spectrophotometer. Infrared spectra were measured on a Perkin-Elmer 257 grating spectrometer. The molecular weights were measured at 25° using a Mechrolab 301A osmometer or at about −32° cryoscopically in $C_2H_4Cl_2$.

Starting Materials.—The tertiary phosphines and tertiary phosphine–cobalt halide complexes were prepared by standard methods of the literature.

The ditertiary phosphine 1,3-bis(diphenylphosphino)propane (dpp) was prepared by the method of Van Hecke and Horrocks.[4]

1,4-Bis(diphenylphosphino)butane (dpb).—The ligand was prepared by treating $P(C_6H_5)_2K$ with $BrCH_2CH_2CH_2CH_2Br$ in dioxane.

$Co(P(C_2H_5)_2C_6H_5)_3(CN)_2$.—The compound $Co(P(C_2H_5)_2C_6H_5)_2Cl_2$ (10 mmol) was dissolved in 70 ml of 1:1 ethanol–methylene chloride to which was added $P(C_2H_5)_2C_6H_5$ (15 mmol). The green solution was passed through a column of an anionic resin (Dowex 1 × 4, 50–100 mesh) in CN^- form. The resulting dark red solution was reduced in volume and treated with *n*-hexane. The small dark red crystals obtained were dried *in vacuo* and stored under argon; dec pt 110–113°; magnetic moment $\mu = 2.0$ BM. *Anal.* Calcd for $Co(P(C_2H_5)_2C_6H_5)_3(CN)_2$: C, 63.05; H, 7.44; N, 4.59; mol wt, 610. Found: C, 61.25; H, 7.50; N, 4.67; mol wt at −32°, 560.

$Co(P(C_6H_5)_2C_2H_5)_3(CN)_2$.—This was prepared in a manner similar to that used for the previous compound. Red crystals were obtained; dec pt 108–110°; magnetic moment $\mu = 2.0$ BM. *Anal.* Calcd for $Co(P(C_6H_5)_2C_2H_5)_3(CN)_2$: C, 70.12; H, 6.01; N, 3.71. Found: C, 69.0; H, 6.26; N, 3.98.

$Co[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2]_{1.5}(CN)_2$.—A solution of dibromo-[1,3-bis(diphenylphosphino)propane]cobalt(II) (2 mmol) and ligand dpp (4 mmol) in 50 ml of methylene chloride was passed through the anionic resin in CN^- form. The resulting pink-red solution was reduced in volume. Pink-red crystals were obtained on addition of *n*-hexane and were washed with *n*-hexane and dried *in vacuo*; magnetic moment $\mu = 2.3$ BM. *Anal.* Calcd for $Co[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2]_{1.5}(CN)_2$: C, 69.95; H, 5.38; N, 3.85; mol wt for the dimeric formula, 1459. Found: C, 67.83; H, 5.40; N, 3.85; mol wt in CH_2Cl_2 at 25°, 1180.

$Co[(C_6H_5)_2P(CH_2)_4P(C_6H_5)_2]_{1.5}(CN)_2$.—This was obtained from the corresponding thiocyanate complex $Co(dpb)_{1.5}(NCS)_2$ (1 mmol) dissolved in 50 ml of methylene chloride and treated with the same anionic resin in CN^- form. The pink-red solution was evaporated to dryness, and the pink-red crystals were washed several times with acetone and dried *in vacuo;* Magnetic moment $\mu = 2.40$ BM. *Anal.* Calcd for $Co[(C_6H_5)_2P(CH_2)_4P(C_6H)_2]_{1.5}(CN)_2$: C, 70.39; H, 5.63; N, 3.73. Found: C, 69.93; H, 5.62; N, 3.77.

$Co[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2]_{1.5}(NCS)_2$.—The ligand dpp (4 mmol) was dissolved in 50 ml of ethanol, and cobalt(II) thiocyanate (2 mmol) in 10 ml of ethanol was added dropwise. The brown crystals that formed were filtered, washed with ethanol and *n*-hexane, and dried *in vacuo;* measured magnetic moment $\mu = 2.7$ BM. *Anal.* Calcd for $Co[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2]_{1.5}(NCS)_2$: C, 64.31; H, 4.95; N, 3.53. Found: C, 63.07; H, 4.70; N, 3.42.

$Co[(C_6H_5)_2P(CH_2)_4P(C_6H_5)_2]_{1.5}(NCS)_2$.—Cobalt(II) thiocyanate (2 mmol) dissolved in 20 ml of acetone was added to dpb (4 mmol) in 50 ml of 2:1 acetone–ethylene chloride. The brown crystals that precipitated were washed with acetone and dried *in vacuo;* magnetic moment $\mu = 2.2$ BM. *Anal.* Calcd for $Co[(C_6H_5)_2P(CH_2)_4P(C_6H_5)_2]_{1.5}(NCS)_2$: C, 64.85; H, 5.20; N, 3.44. Found: C, 63.88; H, 5.53; N, 3.45.

Results

The Complexes $Co(PR_3)_3(CN)_2$ and $Co(diphosphine)_{1.5}(CN)_2$.—When an anionic resin in the CN^- form was treated with blue-green solutions of $Co(PR_3)_2X_2$ ($X^- = Cl^-, Br^-$) and free phosphine in CH_2Cl_2, red solutions were obtained, containing the five-coordinated complexes $Co(PR_3)_3(CN)_2$. Only the complexes with $P(C_2H_5)_2C_6H_5$ and $PC_2H_5(C_6H_5)_2$ were isolated in the solid state. Those with $P(C_2H_5)_3$, $P(C_3H_7)_3$, and $P(C_4H_9)_3$ are also formed in solution, as shown by the visible spectra, but are difficult to isolate owing to their high solubility. The value of the magnetic moment of solid $Co(P(C_2H_5)_2C_6H_5)_3(CN)_2$ and $Co(PC_2H_5(C_6H_5)_2)_3(CN)_2$ (2.0 BM) is typical of other five-coordinate low-spin complexes of cobalt(II). The visible spectra (Figure 1) of $Co(P(C_2H_5)_2C_6H_5)_3(CN)_2$ in ethanol in the presence of phosphine are coincident with the reflectance spectra and show a band at 20,400 cm^{-1} (ϵ_{molar} in solution, about 1050). The spectrum of $Co(PC_2H_5(C_6H_5)_2)_3(CN)_2$ is very similar to that of $Co(P(C_2H_5)_2$-

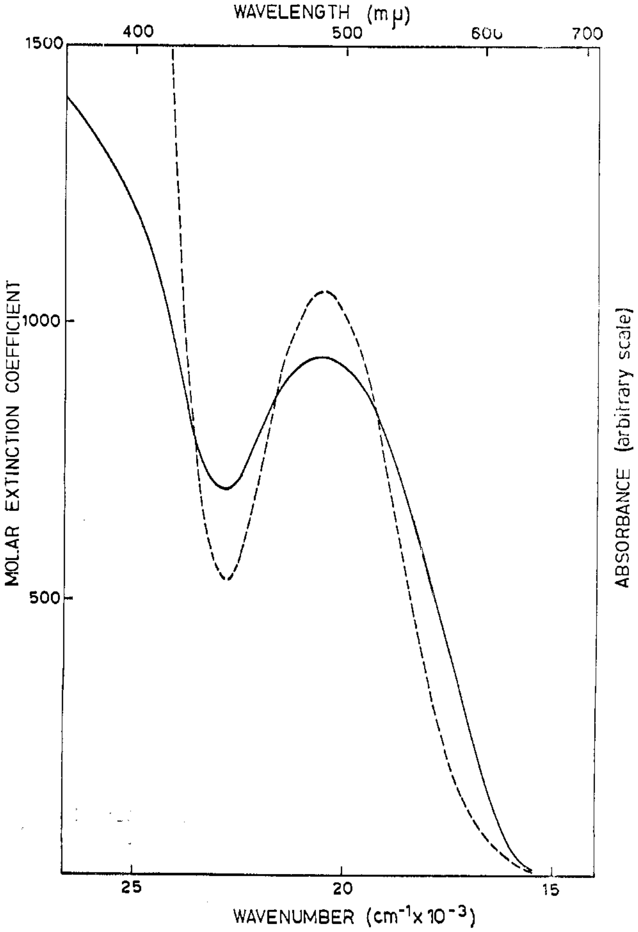

Figure 1.—Absorption and reflectance spectra of $Co(P(C_2H_5)_2C_6H_5)_3(CN)_2$: ----, 5.4×10^{-3} *M* complex in C_2H_5OH containing 3.7×10^{-2} *M* $P(C_2H_5)_2C_6H_5$; ———, reflectance spectrum.

---

(4) G. R. Van Hecke and W. D. Horrocks, Jr., *Inorg. Chem.*, **5**, 1960 (1966).

$C_6H_5)_3(CN)_2$ but the value of ϵ_{max} at 20,400 cm^{-1} is lower (about 720), as is also found for the bands of the corresponding complexes of nickel(II).[5] The infrared spectrum in Nujol mull has a strong band at 2080 cm^{-1} and a much weaker band at 2098 cm^{-1}. The latter band is still present in the spectra in CH_2Cl_2 solution as a weak shoulder (intensity ratio with the band at 2080 cm^{-1}, 1:5). It might be attributed to a combination tone, or alternatively it might indicate that the two CN^- groups are not perfectly aligned along a NC–Co–CN axis. The band at 2080 cm^{-1} is attributed to nonbridging CN groups.[6] Finally the compound is monomeric and slightly dissociated in freezing $C_2H_4Cl_2$ (calcd mol wt, 610; found, 560).

These data show that the complex is a true five-coordinated compound, in which the metal atom is bound to three phosphorus atoms and to two CN^- groups. Both complexes are stable in ethanol or methanol in the presence of excess phosphine. If no phosphine is added, the solution slowly turns to yellow and the band around 20,400 cm^{-1} slowly disappears. The change is more rapid for $Co(PC_2H_5(C_6H_5)_2)_3(CN)_2$. The final visible spectra display only the tail of the charge-transfer ultraviolet bands. Dilute solutions in $C_2H_4Cl_2$ and in benzene slowly become green. The fact that the five-coordinate compound is stable in the presence of excess phosphine indicates that a dissociative process of the type $Co(PR_3)_3(CN)_2 \rightleftarrows Co(PR_3)_2(CN)_2 + PR_3$ is primarily responsible for the formation of the yellow and green species. Attempts to isolate the yellow and the green compounds have not been successful and only impure products with erratic composition have been obtained.

Using the ditertiary phosphines dpp (dpp = 1,3-bis(diphenylphosphino)propane) and dpb (dpb = 1,4-bis(diphenylphosphino)butane), pink-red solids were obtained which analyze as $Co(dpp)_{1.5}(CN)_2$ and $Co(dpb)_{1.5}(CN)_2$, respectively. The magnetic moments of the compounds are in the range 2.3–2.4 BM. The infrared spectra in Nujol mulls of both compounds show a strong band at about 2080 cm^{-1} and a band of medium intensity at about 2090 cm^{-1} which can be attributed to the CN stretching. These values rule out the existence of Co–CN–Co bridges and consequently the possibility that cobalt is six-coordinated.

The molecular weight found for $Co(dpp)_{1.5}(CN)_2$ in CH_2Cl_2 is 1150 suggesting that the compound is dimeric (expected molecular weight, 1450) and dissociated in this solvent. The previously known complexes of Ni(II) and Co(II) with dpp show that this phosphine acts as a chelating ligand in planar or tetrahedral structures.[4,7] On the other hand the stoichiometry $Co(dpp)_{1.5}(CN)_2$, as well as the fact that the compound is dimeric, requires that at least one diphosphine molecule acts as a bridge between two different cobalt atoms. Hence the most reasonable structure for this compound can be represented as $(CN)_2(dpp)Co(dpp)Co(dpp)(CN)_2$, wherein two dpp ligands are chelating and one is acting as a bridge between two cobalt atoms. The visible spectra of this compound and that of $Co(dpb)_{1.5}(CN)_2$ are quite similar to the spectrum of the monomeric $Co(P(C_2H_5)_2C_6H_5)_3(CN)_2$ except that the band at 20,400 cm^{-1} is shifted to 19,600 cm^{-1}.

The solubility of $Co(dpb)_{1.5}(CN)_2$ is too low to allow the determination of the molecular weight. In view of the similarity of the infrared and visible spectra with those of $Co(dpp)_{1.5}(CN)_2$ it is safe to conclude that the structure of this compound is probably similar to that of $Co(dpp)_{1.5}(CN)_2$. In fact the length of the alkyl chain still permits dpb to act as a chelating agent.

Thiocyanate Complexes with dpp and dpb.—The reaction of $Co(CNS)_2$ with tertiary phosphines yields the five-coordinated complexes $Co(PR_3)_3(NCS)_2$.[2] Using the ditertiary phosphines dpp and dpb we have obtained complexes with the composition Co(diphosphine)$_{1.5}$(NCS)$_2$. These complexes dissociate in several solvents into free phosphine and a tetrahedral compound of cobalt(II).[8] Thus refluxing a solution of $Co(dpb)_{1.5}(NCS)_2$ in boiling $C_2H_4Cl_2$ produces the tetrahedral compound $Co(dpb)(NCS)_2$ already described by Sacconi.[9]

The spectra in Nujol of the solid compounds have a strong band at 2080 cm^{-1} assigned to the CN stretching vibration of the SCN group and do not have absorption bands in the 2130–2160 cm^{-1} region. These data indicate that Co–NCS–Co bridges are practically absent and therefore the cobalt atoms are five-coordinated.

The direct determination of the molecular weight is practically impossible for these complexes because they are stable only in solutions containing a great excess of phosphine. Hence the molecular structure can be deduced only from the composition and the demonstrated five-coordination. It is probably similar to that of the corresponding cyanides.

Discussion

The ability of both nickel(II) and cobalt(II) to give $M(PR_3)_3X_2$ complexes appears to be controlled by the nature of the anionic ligand X. In fact using either tertiary or ditertiary phosphines such complexes are not obtainable when $X^- = Cl^-, Br^-, I^-$, or another weak ligand.[10] The presence of a strong ligand such as CN^- is necessary in the case of nickel(II), whereas a weaker ligand such as NCS^- is sufficient in the case of cobalt(II). This seems to suggest that the tendency of cobalt(II) to give this type of coordination is greater than that of nickel(II).

The reason why secondary phosphines give the tris complexe s$M(PH(C_6H_5)_2)_3X_2$ even when $X^- = Br^-$ or I^- has been discussed elsewhere.[3] With tertiary phosphines, the entropy change on going from four- to five-

---

(5) P. Rigo and A. Turco, unpublished results.

(6) D. A. Dows, A. Haim, and W. K. Wilmarth, *J. Inorg. Nucl. Chem.*, **21**, 33 (1961).

(7) W. D. Horrocks, Jr., G. R. Van Hecke, and D. D. Hall, *Inorg. Chem.*, **6**, 694 (1967).

(8) The easy decomposition into tetrahedral high-spin species (which have magnetic moments of about 4.5 BM) explains the somewhat high value (2.7 BM) found for the magnetic moment of $Co(dpp)_{1.5}(NCS)_2$ in the solid state.

(9) L. Sacconi, Abstracts, National Meeting on Coordination Compounds of the Italian Council for Research, Rome, April 1967.

(10) See ref 8 and references therein.

coordination certainly becomes less favorable for the addition of a third phosphine molecule. Therefore stronger bonds are required in order to increase the stability of the complexes $Co(PR_3)_3X_2$. These are probably the factors which demand the presence of a good anionic ligand (either in σ or π, or in the $\sigma + \pi$ sense) in the five-coordinated compounds. However it appears that once the ligand field requirements are satisfied, the tendency to five-coordination becomes the ruling factor, and coordination of three phosphorus atoms can be achieved, with the rather unusual stoichiometry reported here, even with ditertiary phosphines.

Acknowledgment.—We thank the Italian Council for Research (CNR, Rome) for support of this investigation.

CONTRIBUTION NO. 2247 FROM THE INSTITUTE FOR
ATOMIC RESEARCH AND THE DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA 50010

A Kinetic Study of the Decomposition of Pentacyanocobaltate(II) Ion in Perchloric Acid Solution[1]

BY JAMES H. ESPENSON AND J. ROBERT PIPAL

Received January 25, 1968

Solutions of cobalt(II) containing cyanide ion are known to contain the species $Co(CN)_5{}^{3-}$, provided the ratio CN/Co, R, is ≥ 5. The structure, reactions, and optical and esr spectra of this ion have been subjects of a large number of studies[2-10] which have recently been reviewed.[11,12] Structural evidence based largely on esr data[9,10] established that the complex has a square-pyramidal configuration with C_{4v} symmetry. The complex has been suggested[10] to be a six-coordinate species $Co(CN)_5OH_2{}^{3-}$ largely on the similarity of its spectrum with those of CoL_5OH_2 with L = CH_3NC and C_6H_5NC. Aside from this evidence, all of the reactions of the complex are most easily formulated as belonging to a five-coordinate $Co(CN)_5{}^{3-}$ ion.[2,4-6] This reactive species may be the predominant species, or a coordinated water molecule may be removed prior to reaction. We shall represent the ion as $Co(CN)_5{}^{3-}$, intending no comment on the question of five- or six-coordination.

Our particular interest in this ion arose in the course of kinetic studies on the mechanism of reduction of substituted cobalt(III) complexes $Co(CN)_5X^{3-}$ by V^{2+} in strongly acidic solution,[13] where it appeared that $Co(CN)_5{}^{3-}$ was generated as an intermediate. In acid solution, such an intermediate would presumably decompose to $Co_{aq}{}^{2+}$ and HCN (eq 1). To the best of

$$Co(CN)_5{}^{3-} + 5H^+ = Co_{aq}{}^{2+} + 5HCN \tag{1}$$

our knowledge, the complex has not been examined previously under such conditions.

We have carried out kinetic studies on the decomposition of the known complex $Co(CN)_5{}^{3-}$ in perchloric acid.

Experimental Section

Materials.—Reagent grade materials, cobalt(II) perchlorate, sodium and potassium cyanide, and perchloric acid, were used without further purification. Lithium perchlorate, used to maintain ionic strength, was prepared from the carbonate and was recrystallized twice before use. Stock solutions were analyzed by standard volumetric or spectrophotometric methods. All solutions were prepared in conductance water, obtained by a double redistillation of laboratory-distilled water from alkaline permanganate in a tin-lined Barnstead still.

Solutions of pentacyanocobaltate(II) ion were prepared by mixing solutions of cobalt(II) perchlorate and sodium or potassium cyanide, often containing added lithium perchlorate. The complex was prepared with $R \geq 5.2$. These solutions were prepared and handled under an inert atmosphere. Our early work used nitrogen which had been purified of traces of oxygen by passage through two to four scrubbing solutions of acidified chromium(II) perchlorate in contact with amalgamated zinc. Most kinetic runs were, however, carried out under high-purity argon to avoid the reaction of the complex with the traces of hydrogen (eq 2) possibly generated from the reaction of zinc with perchloric acid. Presumably the hydrido complex decomposes rapidly in acid solution (eq 3), although this point was not checked. No rate differences were noted between runs in nitrogen or argon atmospheres.

$$Co(CN)_5{}^{3-} + 0.5H_2 = Co(CN)_5H^{3-} \tag{2}$$

$$Co(CN)_5H^{3-} + H^+ + H_2O = Co(CN)_5OH_2{}^{2-} + H_2 \tag{3}$$

Rate Procedures.—The rate of reaction 1 was studied by stopped-flow spectrophotometry using the apparatus previously described.[14] Most studies were carried out at wavelengths in the ultraviolet region using as the light source either a conventional Beckman deuterium lamp or a quartz iodide lamp (General Electric 1959), the latter powered by a Sorenson supply (QRC 40-8A) operated at 28-V dc.

Results and Interpretation

Reaction Kinetics.—The visible and ultraviolet spectra of solutions of pentacyanocobaltate(II) prepared with careful exclusion of oxygen and hydrogen were in essential agreement with published results.[3] Addition of perchloric acid to dilute solutions, $\leq 10^{-3}$ M, again with careful exclusion of oxygen, produced $Co_{aq}{}^{2+}$ in quantitative yield in accord with eq 1.[15] The

[1] Work performed in the Ames Laboratory under the auspices of the U. S. Atomic Energy Commission.

[2] A. Haim and W. K. Wilmarth, *J. Am. Chem. Soc.*, **83**, 509 (1961).

[3] N. K. King and M. E. Winfield, *ibid.*, **83**, 3366 (1961).

[4] J. P. Candlin, J. Halpern, and S. Nakamura, *ibid.*, **85**, 2517 (1963).

[5] J. Halpern and S. Nakamura, *ibid.*, **87**, 3002 (1965).

[6] J. Halpern and P. J. Maher, *ibid.*, **87**, 5361 (1965).

[7] M. G. Burnett, P. J. Connolly, and C. Kemball, *J. Chem. Soc., A*, 800 (1967).

[8] J. Kwiatek and J. K. Seyler, *J. Organometal. Chem.* (Amsterdam), **3**, 421 (1965).

[9] J. J. Alexander and H. B. Gray, *J. Am. Chem. Soc.*, **89**, 3356 (1967).

[10] J. M. Pratt and R. J. P. Williams, *J. Chem. Soc., A*, 1291 (1967).

[11] J. Halpern, *Chem. Eng. News*, 68 (Oct 31, 1966).

[12] B. M. Chadwick and A. G. Sharpe, *Advan. Inorg. Chem. Radiochem.*, **8**, 83 (1966).

[13] J. H. Espenson, Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, p O-107.

[14] D. W. Carlyle and J. H. Espenson, *Inorg. Chem.*, **6**, 1370 (1967).

[15] The yield of Co^{2+} was verified by spectrophotometric analysis as the thiocyanate complex in 50 vol % acetone. Were a cobalt(III) species such as $Co(CN)_5OH_2{}^{2-}$ also formed, the analysis for Co^{2+} would have been low.