

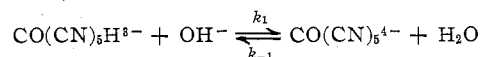
CONTRIBUTION No. 4089 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA 91109

## Reactions of Hydridopentacyanocobaltate(III) and Pentacyanocobaltate(II) with Mercury(II) to Form Complexes of the Type $(\text{NC})_5\text{CoHgX}^{3-}$ and $(\text{NC})_5\text{CoHgCo}(\text{CN})_5^{6-}$

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The stoichiometry and kinetics of the reaction between  $\text{Co}(\text{CN})_5\text{H}^{3-}$  and  $\text{HgX}_2$  ( $\text{X}^- = \text{CN}^-, \text{OH}^-$ ) have been investigated. The products of the reaction are two new complexes,  $(\text{NC})_5\text{CoHgX}^{3-}$  and  $(\text{NC})_5\text{CoHgCo}(\text{CN})_5^{6-}$ , whose spectra are reported. The kinetic measurements produced a value for the forward rate constant of the reaction



$k_1 = (9.7 \pm 0.8) \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$  at  $24^\circ$ , and an equilibrium constant for the reaction,  $K = 10^{-6} \text{ M}^{-1}$ .

The electrochemistry of pentacyanocobaltate(II) at mercury electrodes is complicated by an extensive and unusually strong adsorption of the reactant on the electrode surface.<sup>1</sup> The remarkable strength of the interaction between the cobalt(II) cyanide complex and the mercury surface lead us to examine the homogeneous reactions that occur when  $\text{Co}(\text{CN})_5^{3-}$  or  $\text{Co}(\text{CN})_5\text{H}^{3-}$  are exposed to complexes of Hg(II). Two relatively stable new complexes containing cobalt-mercury bonds were produced by these reactions. The novelty of these complexes and the possibility that they might be involved in the strong adsorption of cobalt-cyanide complexes on mercury electrodes prompted us to investigate the stoichiometry and kinetics of the reactions by which they are formed. The results of these studies are the basis of this report.

### Experimental Section

**Reagents.**—Reagent grade chemicals were used without further purification. Solutions of  $\text{Co}(\text{CN})_5^{3-}$  were prepared just before they were used by mixing deaerated solutions of  $\text{Co}(\text{NO}_3)_2$  with stoichiometric quantities of NaCN dissolved in deaerated water. Deaeration was accomplished with prepurified nitrogen which was further purified by passing it through a washing tower containing V(II) followed by another containing Cr(II).

Solutions of  $\text{Co}(\text{CN})_5\text{H}^{3-}$  were prepared either by treating  $\text{Co}(\text{CN})_5^{3-}$  with excess hydrogen gas<sup>2</sup> or by reducing solutions of  $\text{Co}(\text{CN})_5\text{Cl}^{3-}$  (prepared according to ref 3) electrochemically at a mercury pool electrode. For all the quantitative kinetic measurements the electrochemical preparation was employed. The solutions resulting from the electrochemical preparation were analyzed for  $\text{Co}(\text{CN})_5\text{H}^{3-}$  spectrophotometrically at 305 nm.<sup>2</sup>

A stock solution of 8 F NaClO<sub>4</sub> was prepared by neutralizing 60% HClO<sub>4</sub> with solid Na<sub>2</sub>CO<sub>3</sub>. After heating overnight on a steam bath and filtering off the siliceous residue, the solution was freed of CO<sub>2</sub> by making it slightly acidic and passing nitrogen gas through it.

Moderately pure solid samples of  $\text{K}_6[\text{HgCo}_2(\text{CN})_{10}] \cdot x\text{H}_2\text{O}$  were isolated by the following procedure. A 60-ml sample of a 1 F KOH solution containing 7.3 g (0.11 mol) of KCN was deaerated with hydrogen gas. A 20-ml amount of a deaerated 1 F

CoCl<sub>2</sub> solution was added and the mixture was stirred by passing hydrogen gas through it. The initially dark green solution became pale green after ca. 1 hr at which point 2.5 g (0.01 mol) of solid Hg(CN)<sub>2</sub> was added. As the Hg(CN)<sub>2</sub> dissolved, the solution turned yellowish orange. A 70-ml sample of deaerated absolute ethanol was added to the solution which caused a reddish orange oil to separate. The oil was transferred with a hypodermic syringe to ca. 10 ml of deaerated absolute ethanol whereupon a yellow solid formed. The solid was crushed, washed several times with ethanol, and then with dry ether. It was dried in a vacuum desiccator. Attempts to recrystallize the salt from aqueous solutions were thwarted by apparent decomposition of the complex.

The solid changes color slowly upon exposure to air. Dissolution of the solid in air-free water yielded a spectrum identical with that obtained by treating Hg(CN)<sub>2</sub> with an excess of  $\text{Co}(\text{CN})_5\text{H}^{3-}$ . Elementary analyses of solid samples resulting from the procedure described gave typical Co:Hg:C:N molar ratios of 2.00:0.95:10.4:10.6.

The reducing equivalents in the solid sample were assayed by means of Andrews titrations<sup>4</sup> of weighed portions. The results corresponded to 4 reducing equiv/mol of sample having a molecular weight given by the formula  $\text{K}_6[\text{HgCo}_2(\text{CN})_{10}] \cdot 4\text{H}_2\text{O}$ . Inasmuch as the conditions of the Andrews titration ensure that the final oxidation states of the mercury and cobalt are Hg(II) and Co(III), the results obtained correspond to initial oxidation states of either Hg(II) and Co(I) or Hg(0) and Co(II).

A solid sample of what appeared to be  $\text{K}_6[\text{CdCo}_2(\text{CN})_{10}] \cdot x\text{H}_2\text{O}$  was obtained by a similar procedure in which Cd(NO<sub>3</sub>)<sub>2</sub> was substituted for Hg(CN)<sub>2</sub>.

**Apparatus.**—Electronic spectra were recorded with a Cary 14 spectrophotometer or taken manually with a Beckmann Model DU spectrophotometer with a Gilford Model 220 absorbance indicator attachment. All kinetic runs were performed manually with the latter instrument. A Cary Model 14 CMRI recording spectrophotometer was employed to obtain spectra at low temperatures and infrared spectra were obtained with a Perkin-Elmer Model 225 spectrophotometer. Magnetic susceptibilities were measured with a Princeton Applied Research Model FM-1 vibrating-sample magnetometer. An Orion Model 94-06 cyanide-sensitive electrode was used to monitor cyanide activities in some solutions.

**Procedure for Kinetic Measurements.**—The rates of the reaction between  $\text{Co}(\text{CN})_5\text{H}^{3-}$  and Hg(CN)<sub>2</sub> were followed spectrophotometrically. Alkaline solutions containing measured quantities of Hg(CN)<sub>2</sub> were adjusted to an ionic strength of 0.5 with NaClO<sub>4</sub> and deaerated with nitrogen. An aliquot of an air-free

\* To whom correspondence should be addressed.

(1) H. S. Lim and F. C. Anson, experiments to be submitted for publication.

(2) N. K. King and M. E. Winfield, *J. Amer. Chem. Soc.*, **83**, 3366 (1961).(3) R. Grassi, A. Haim, and W. K. Wilmarth, *Inorg. Chem.*, **6**, 237 (1967).

(4) I. M. Kolthoff and R. Belcher, "Volumetric Analysis," Vol. III, Interscience, New York, N. Y., 1957, pp 451-469.

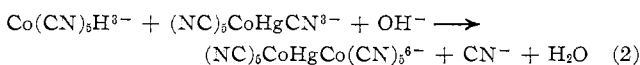
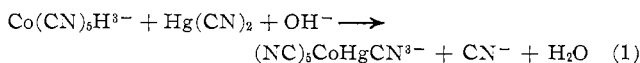
solution of  $\text{Co}(\text{CN})_5\text{H}^{3-}$  was added under nitrogen by means of a syringe and the mixture stirred briefly with nitrogen. An aliquot of this mixture was transferred without exposure to air to a spectrophotometer cell which was then placed in the thermostated cell compartment. The absorbances of the reaction products at 274 and 362 nm were then recorded manually using a 0.5 *F*  $\text{NaClO}_4$  solution as a blank. The small absorbance of  $\text{Co}(\text{CN})_5\text{H}^{3-}$  at 274 nm was corrected for.

The absorbance-time data were analyzed by conventional least-squares fitting to appropriate kinetic equations. The equations used and the assumptions involved are given in the Results and Discussion.

### Results and Discussion

When small increments of  $\text{Hg}(\text{CN})_2$  are added to alkaline solutions containing an excess of  $\text{Co}(\text{CN})_5\text{H}^{3-}$ , an intense absorption band develops with a maximum at *ca.* 274 nm. This band reaches a maximum intensity some time (depending on the concentrations employed) after the reagents are mixed and then begins to decrease in intensity. At the same time, a new band begins to develop at 362 nm. After the spectrum has become stable, the band at 274 nm is absent and the band at 362 nm is found to obey Beer's law with respect to the amount of  $\text{Hg}(\text{CN})_2$  added (excess  $\text{Co}(\text{CN})_5\text{H}^{3-}$  being present). At 25° and  $\mu = 1.0$  ( $\text{NaClO}_4$ ), the molar absorbance of the band at 362 nm is  $52,000 \text{ cm}^{-1} M^{-1}$ .

If the experiment is carried out with more nearly equal concentrations of  $\text{Co}(\text{CN})_5\text{H}^{3-}$  and  $\text{Hg}(\text{CN})_2$ , the band at 362 nm reaches a maximum absorbance with a ratio of  $\text{Hg}(\text{CN})_2$  to  $\text{Co}(\text{CN})_5\text{H}^{3-}$  of 0.5. When this ratio becomes larger than 0.5, the band that develops initially at 274 nm does not disappear completely when the spectrum has become stable and a corresponding decrease in the absorbance at 362 nm is observed. At ratios greater than *ca.* 1.2 no band develops at 362 nm and the band at 274 nm reaches a maximum absorbance which is stable on further standing. The molar absorbance at 274 nm under these conditions amounts to *ca.*  $20,000 \text{ cm}^{-1} M^{-1}$  based on the concentration of  $\text{Co}(\text{CN})_5\text{H}^{3-}$ . Figure 1 shows how the bands at 274 and 362 nm change during the period before the spectrum stabilizes. An isosbestic point is observed at *ca.* 300 nm. Figure 2 summarizes the behavior observed at both wavelengths and is consistent with the set of overall reactions



with the bands at 274 and 362 nm corresponding, respectively, to the ions  $(\text{NC})_5\text{CoHgCN}^{3-}$  and  $(\text{NC})_5\text{CoHgCo}(\text{CN})_6^{6-}$ .

**Properties of  $(\text{NC})_5\text{CoHgCo}(\text{CN})_6^{6-}$ .**—The proposed composition of the complex is supported by the stoichiometry of the reactions leading to its formation (Figure 2). The same complex results if  $\text{Hg}(\text{ClO}_4)_2$  rather than  $\text{Hg}(\text{CN})_2$  is treated with  $\text{Co}(\text{CN})_5\text{H}^{3-}$ , showing that the cyanide ligands originally attached to  $\text{Hg}(\text{II})$  are not essential for the complex to be formed. Addition of large excesses of chloride or bromide ions to

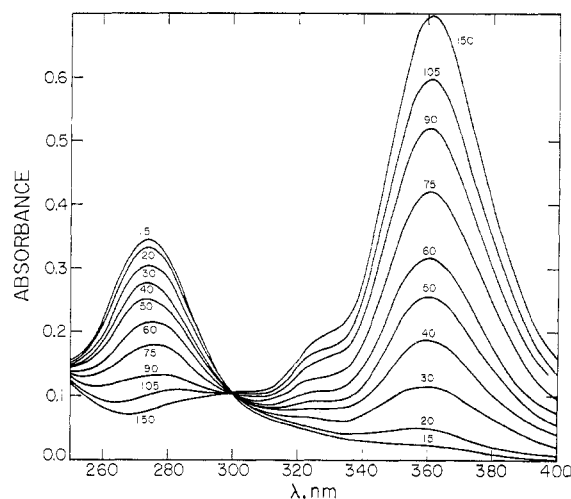


Figure 1.—Time dependence of the spectra of solutions containing  $\text{Co}(\text{CN})_5\text{H}^{3-}$  and  $\text{Hg}(\text{CN})_2$ . The numbers on each curve are the time in minutes since the two reagents were mixed. The maximum absorbance at 274 nm was attained after 15 min. Initial conditions:  $[\text{Co}(\text{CN})_5\text{H}^{3-}] = 9 \times 10^{-5} M$ ,  $[\text{Hg}(\text{CN})_2] = 1.5 \times 10^{-5} M$ , pH 12, and  $[\text{NaClO}_4] = 1 M$ .

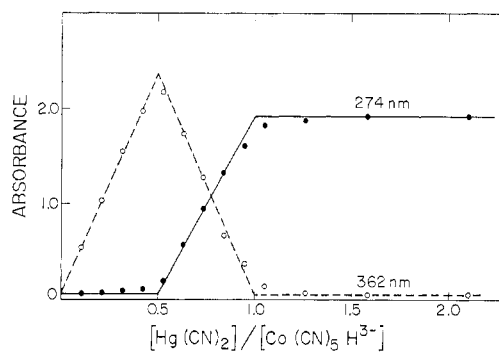


Figure 2.—Equilibrium absorbance of systematic mixtures of  $\text{Co}(\text{CN})_5\text{H}^{3-}$  and  $\text{Hg}(\text{CN})_2$  at 274 and 362 nm. The lines are calculated on the basis of the stoichiometry of reactions 1 and 2. The points are experimentally observed values. Initial conditions:  $[\text{Co}(\text{CN})_5\text{H}^{3-}] = 9 \times 10^{-5} M$  and  $[\text{NaClO}_4] = [\text{NaOH}] = 0.5 M$ .

the reaction mixture does not change the final spectrum obtained, indicating that no readily accessible coordination position is available on the  $\text{Hg}(\text{II})$  ion once the two mercury-cobalt bonds are formed. The release of free cyanide as the complex is formed according to reactions 1 and 2 was confirmed polarographically. An anodic cyanide wave develops when  $\text{Hg}(\text{CN})_2$  is used to form the complex, but no corresponding wave appears when  $\text{Hg}(\text{ClO}_4)_2$  is used. The magnetic susceptibility of the potassium salt of the complex ion was measured and showed the salt to be diamagnetic. These facts and the high value of the molar absorbance at 362 nm support the presence of the proposed metal-metal bonded configuration. Additional evidence is provided by the effect of lowering the temperature on the position of the absorption band. A solution of the complex in 10 *M*  $\text{LiCl}$  has its absorption maximum at 357 nm at 298°K and the band appears similar to that attributed to  $\sigma \rightarrow \sigma^*$  transitions in carbonyl complexes containing

metal-metal bonds.<sup>5</sup> This maximum is shifted to 347 nm when the temperature is lowered to 77°K. Such shifts to the blue at lower temperatures have been correlated with the presence of metal-metal bonding in several other complexes.<sup>5</sup>

The position and intensity of the absorption band obtained with the mercury(II) (and cadmium(II)) complexes are also nicely matched by those of two similar complexes which have been concluded to possess metal-metal bonds (Table I). A similar matching of bands occurs in the ir spectra in the cyanide stretch region.

TABLE I  
SPECTRAL PROPERTIES OF SOME METAL-BRIDGED  
COMPLEXES OF PENTACYANOCOBALTATE

Metal	$\lambda_{\max}$ , nm	$\epsilon$ , $\text{cm}^{-1} M^{-1}$	Ref
Cd	348	Ca. 30,000	a
Hg <sup>b</sup>	362	52,000	a
Tl(I)	389	57,000	c
SnCl <sub>2</sub>	405	Ca. 10,000	d

<sup>a</sup> This study. <sup>b</sup> Other absorption maxima observed with this complex are  $\epsilon_{325} \sim 11,000$  (sh),  $\epsilon_{300} \sim 5000$ , and  $\epsilon_{230} \sim 12,000 \text{ cm}^{-1} M^{-1}$ . <sup>c</sup> E. C. Crouch and J. M. Pratt, *Chem. Commun.*, 1243 (1969). <sup>d</sup> A. A. Vlček and F. Basolo, *Inorg. Chem.*, **5**, 156 (1966).

TABLE II<sup>a</sup>

A. Infrared Spectra of Some Cyanocobaltate Complexes in the Cyanide Stretch Region in KBr Disk (in  $\text{cm}^{-1}$ )

		Ref
Potassium salt of HgCo <sub>2</sub> (CN) <sub>10</sub> <sup>6-</sup>	2128 s, 2099 m, 2072 s, br, ca. 2035, w, sh	b
Potassium salt of CdCo <sub>2</sub> (CN) <sub>10</sub> <sup>6-</sup>	2128 m, 2090 m, 2062 s, br, 2050 sh	b
K <sub>4</sub> H <sub>2</sub> [Co(CN) <sub>10</sub> ]·4H <sub>2</sub> O <sup>c</sup>	2127 s, 2099 m, 2077 s, br, ca. 2040 w, sh	b
K <sub>6</sub> [Co(CN) <sub>10</sub> ]	2133 s, 2090 s, 2079 s	d

B. Infrared Spectra of Manganese-Carbonyl Complexes in the Carbonyl Stretch Region in KBr Disk (in  $\text{cm}^{-1}$ )

		Ref
Hg[Mn <sub>2</sub> (CO) <sub>10</sub> ]	2067 s, 2008 s, sh, 1975 vs	e
Mn <sub>2</sub> (CO) <sub>10</sub>	2060 m, 2014 vs, 1989 s	e

<sup>a</sup> Abbreviations: s, strong; m, medium; w, weak; vs, very strong; br, broad; sh, shoulder. <sup>b</sup> Data from this study. <sup>c</sup> Prepared according to the procedure of R. Nast, H. Ruppert-Mesche, and M. Helbig-Neubauer, *Z. Anorg. Allg. Chem.*, **312**, 314 (1961). <sup>d</sup> W. P. Griffith and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **7**, 295 (1958). <sup>e</sup> W. Hieber and W. Schropp, Jr., *Chem. Ber.*, **93**, 455 (1960).

Table IIA compares the infrared spectra obtained with potassium salts of the mercury(II) and cadmium(II) complexes with those of two binuclear cobalt complexes known to contain cobalt-cobalt bonds. The close similarity of the cyanide stretching frequencies among these four complexes supports the structures proposed for the mercury(II) and cadmium(II) complexes. Further support results from the additional comparison (Table IIB) with the spectra of dimanganese decacarbonyl and its mercury derivative, which is known to contain two mercury-manganese bonds.<sup>6</sup>

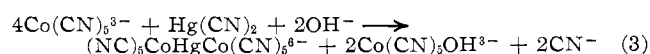
**The XHgCo(CN)<sub>5</sub><sup>3-</sup> Complex.**—Efforts to isolate a salt of this complex anion (with X<sup>-</sup> = CN<sup>-</sup> or OH<sup>-</sup>)

were unsuccessful. Nevertheless, the evidence for its existence is strong. Mixtures of Hg(CN)<sub>2</sub> and Co(CN)<sub>5</sub>H<sup>3-</sup> having mercury to cobalt ratios of 1.0 develop a strong absorption band at 274 nm which gradually increases in intensity until a final absorption is reached which is quite stable. If additional Co(CN)<sub>5</sub>H<sup>3-</sup> is added, however, the band at 274 nm decreases in intensity as the new band, attributed to (NC)<sub>5</sub>CoHgCo(CN)<sub>5</sub><sup>6-</sup>, develops at 362 nm (Figures 1 and 2). The stoichiometry of the reaction leading to the species which absorbs at 274 nm is consistent with its being NCHgCo(CN)<sub>5</sub><sup>3-</sup> and this configuration seems quite likely because of its similarity to the analogous iso-electronic carbonyl complexes XHgMn(CO)<sub>5</sub>, where X = Cl, Br, and I.<sup>6</sup> Added evidence for the proposed structure of the complex is the fact that species giving very similar spectra in the region from 274 to 290 nm are also produced when Co(CN)<sub>5</sub>H<sup>3-</sup> is treated with equal or greater quantities of CH<sub>3</sub>HgOH, C<sub>6</sub>H<sub>5</sub>HgOH, or Hg(OH)<sub>2</sub> (obtained by adding Hg(ClO<sub>4</sub>)<sub>2</sub> to the alkaline reaction solution). The complex resulting from CH<sub>3</sub>HgOH persists for some time even in the presence of excess Co(CN)<sub>5</sub>H<sup>3-</sup> while with C<sub>6</sub>H<sub>5</sub>HgOH formation of (NC)<sub>5</sub>CoHgCo(CN)<sub>5</sub><sup>6-</sup> occurs less slowly. (The fate of the methyl and phenyl groups during the second stage of these reactions was not investigated.) A number of closely analogous carbonyl complexes have been described.<sup>7,8</sup>

**Reaction of Co(CN)<sub>5</sub><sup>3-</sup> with Hg(CN)<sub>2</sub>.**—Both NCHgCo(CN)<sub>5</sub><sup>3-</sup> and (NC)<sub>5</sub>CoHgCl(CN)<sub>5</sub><sup>6-</sup> are also formed if Co(CN)<sub>5</sub><sup>3-</sup> and Hg(CN)<sub>2</sub> are allowed to react in alkaline solutions, but the rate of the reaction is much smaller than when Co(CN)<sub>5</sub>H<sup>3-</sup> is used. The band due to NCHgCo(CN)<sub>5</sub><sup>3-</sup> that develops at 274 nm is not as simple to follow because of the sizable absorption of Co(CN)<sub>5</sub><sup>3-</sup> at this wavelength.<sup>9</sup> However, the band at 362 nm, due to (NC)<sub>5</sub>CoHgCo(CN)<sub>5</sub><sup>6-</sup>, is readily observed and it reaches a maximum absorption when the ratio of reactants, Hg(CN)<sub>2</sub>:Co(CN)<sub>5</sub><sup>3-</sup>, is 0.2 or less. With ratios greater than 0.2, the absorption at 362 nm never achieves stability while with lower ratios, e.g., 0.1, the absorption at 362 nm remains at its maximum value for several days.

During the growth of the absorption at 362 nm the total absorption at 280 nm, where Co(CN)<sub>5</sub><sup>3-</sup> has an absorption maximum and where NCHgCo(CN)<sub>5</sub><sup>3-</sup> also absorbs strongly, decreases. When the absorption at 362 nm attains its maximum stable value, the absorption at 280 nm is smaller than its initial value corresponding to the concentration of Co(CN)<sub>5</sub><sup>3-</sup> present before any reactions occurred. This decrease in absorption at 280 nm corresponds to the consumption of ca. 4 mol of Co(CN)<sub>5</sub><sup>3-</sup> for each mole of Hg(CN)<sub>2</sub> used.

These observations can be accommodated by the overall reaction



(5) R. A. Levenson, Thesis, Columbia University, 1970; R. A. Levenson and H. B. Gray, to be submitted for publication.

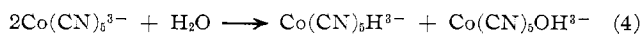
(6) W. Hieber and W. Schropp, Jr., *Chem. Ber.*, **93**, 455 (1960).

(7) M. C. Baird, *Progr. Inorg. Chem.*, **9**, 1 (1968).

(8) W. Jehn, *Z. Chem.*, **9**, 170 (1969).

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

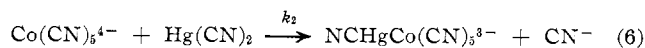
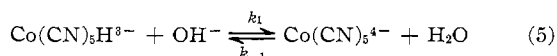
It seems likely that the slower rate and different stoichiometry obtained with  $\text{Co}(\text{CN})_5^{3-}$  result because of the need for an initial disproportionation reaction<sup>2,10,11</sup>



to generate the  $\text{Co}(\text{CN})_5\text{H}^{3-}$  which enters into the reaction scheme given by reactions 1 and 2. The much more complex kinetics which result when  $\text{Co}(\text{CN})_5^{3-}$  is employed caused us to concentrate our studies on cases where  $\text{Co}(\text{CN})_5\text{H}^{3-}$  was the reactant. It may, however, prove useful to know that the same products can result with either cobalt complex as a reactant, especially in electrochemical studies of cobalt cyanide complexes at mercury electrodes.<sup>1</sup> One unsuccessful attempt was made to observe a reaction between metallic mercury and  $\text{Co}(\text{CN})_5^{3-}$ . An 80-ml sample of a 1 mM  $\text{Co}(\text{CN})_5^{3-}$  solution (pH  $\sim 11$ ) was stirred over a 12-cm<sup>2</sup> mercury pool. The spectrum of the resulting solution indicated that the characteristic absorption of  $\text{Co}(\text{CN})_5^{3-}$  at 280 nm had declined to ca. half of its initial value after 30 min while a new, rather weak band was formed at 360–380 nm. However, after 14 hr of reaction the extinction at 362 nm corresponded to less than 1% of the  $\text{Co}(\text{CN})_5^{3-}$  having been converted to  $(\text{NC})_5\text{CoHgCo}(\text{CN})_5^{6-}$ . This system was not investigated further.

Cadmium(II) is able to take the role of mercury(II) in the reaction with  $\text{Co}(\text{CN})_5\text{H}^{3-}$ . The infrared and ultraviolet spectrum of the resulting complex is very similar to that of the mercury(II) complex (Tables I and IIA).

**Kinetics of the Reaction between  $\text{Co}(\text{CN})_5\text{H}^{3-}$  and  $\text{Hg}(\text{CN})_2$ .**—The stoichiometry of the first stage of the reaction between  $\text{Co}(\text{CN})_5\text{H}^{3-}$  and  $\text{Hg}(\text{CN})_2$  is as shown in reaction 1. The rate of the reaction is low enough to be conveniently followed spectrophotometrically at pH values between 11 and 12 if the reactant concentrations are in the range  $10^{-5}$ – $10^{-4}M$ . The formation of  $\text{NCHgCo}(\text{CN})_5^{3-}$  proceeds considerably faster than does its subsequent conversion to  $(\text{NC})_5\text{CoHgCo}(\text{CN})_5^{6-}$  so that the first stage of the reaction can be followed by monitoring the absorbance at 274 nm before significant consumption of the binuclear complex occurs. Kinetic runs were carried out with comparable concentrations of  $\text{Co}(\text{CN})_5\text{H}^{3-}$  and  $\text{Hg}(\text{CN})_2$  but with a much larger and therefore essentially constant concentration of hydroxide ion. Analysis of the resulting rate data according to the simple second-order kinetic equation showed that they deviated significantly from simple second-order kinetics in that the calculated rate constant displayed a systematic dependence upon the initial concentration of mercuric cyanide, Table III. The deviations were in the direction to be expected if the rate-determining step were preceded by quasi-reversible formation of a reactive intermediate. A likely mechanism for the reaction suggested by these results is



where  $\text{Co}(\text{CN})_5^{4-}$  is the reactive intermediate and reaction 6 is irreversible. Applying the steady-state approximation<sup>12</sup> to the concentration of  $\text{Co}(\text{CN})_5^{4-}$  leads to the rate equation

$$\frac{dP}{dt} = \frac{k_2 k_1 [\text{OH}^-] [\text{Co}(\text{CN})_5\text{H}^{3-}] [\text{Hg}(\text{CN})_2]}{k_{-1} + k_2 [\text{Hg}(\text{CN})_2]} \quad (7)$$

where  $P$  is the concentration of the product of the reaction,  $\text{NCHgCo}(\text{CN})_5^{3-}$ . Integration of eq 7 leads to

$$\frac{1}{A-B} \ln \left[ \frac{B(A-P)}{A(B-P)} \right] + \frac{k_2}{k_{-1}} \ln \left[ \frac{A}{A-P} \right] = \frac{k_2 k_1}{k_{-1}} [\text{OH}^-] t \quad (8)$$

where  $A$  and  $B$  are the initial concentrations of  $\text{Co}(\text{CN})_5\text{H}^{3-}$  and  $\text{Hg}(\text{CN})_2$ , respectively. When eq 8 was used to analyze the rate data, the apparent dependence of the rate constant on the initial concentration of  $\text{Hg}(\text{CN})_2$  (Table III) disappeared, Figure 3.

TABLE III  
KINETIC DATA ANALYZED ACCORDING TO THE SIMPLE SECOND-ORDER RATE EQUATION  $d[\text{PRODUCT}]/dt = k'[\text{OH}^-][\text{Co}(\text{CN})_5\text{H}^{3-}][\text{Hg}(\text{CN})_2]$  WITH  $[\text{OH}^-] = \text{CONSTANT}$

pH	Initial concn $\times 10^5, M$		$10^{-3}k', M^{-2} \text{sec}^{-1}$
	$\text{Co}(\text{CN})_5\text{H}^{3-}$	$\text{Hg}(\text{CN})_2$	
11.40	18.8	1.0	2.24
11.40	18.8	2.0	1.96
11.44	18.8	5.0	1.23
11.44	18.8	10	0.745
11.34	9.4	5.0	1.18
11.64	3.76	5.0	1.12
11.27	9.4	4.0	1.23

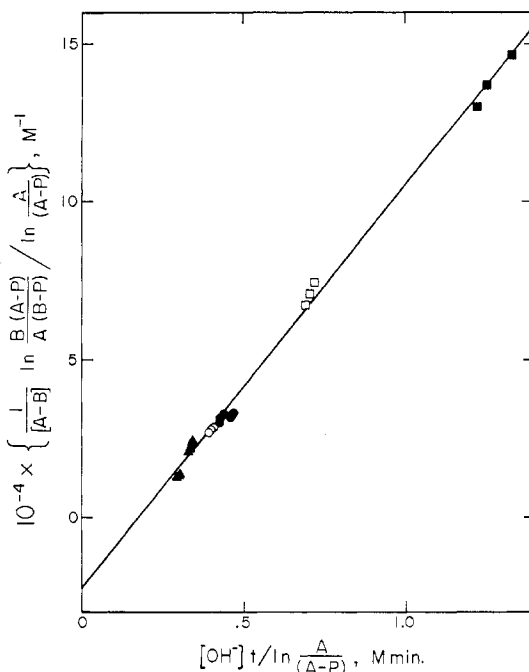


Figure 3.—Kinetic data analyzed according to eq 8. The solid line, calculated by least-squares fitting of the data, corresponds to  $k_2/k_{-1} = (2.18 \pm 0.11) \times 10^4 M^{-1}$  and  $k_2 k_1/k_{-1} = (2.12 \pm 0.03) \times 10^3 \text{sec}^{-1} M^{-1}$ . The plotted points correspond to initial  $\text{Hg}(\text{CN})_2$  concentrations:  $\blacksquare$ ,  $10^{-5} M$ ;  $\square$ ,  $2 \times 10^{-5} M$ ;  $\bullet$ ,  $4 \times 10^{-5} M$ ;  $\circ$ ,  $5 \times 10^{-5} M$ ;  $\blacktriangle$ ,  $10^{-4} M$ . The initial concentrations of  $\text{Co}(\text{CN})_5\text{H}^{3-}$  were in the range  $(4\text{--}19) \times 10^{-5} M$  and the pH was between 11.3 and 11.6;  $\mu = 0.5$  ( $\text{NaClO}_4$ ) at  $24.0^\circ$ .

(10) B. DeVries, *J. Catal.*, **1**, 489 (1962).

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

(12) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Wiley, New York, N. Y., 1953, p 179.

The order of the reaction with respect to hydroxide was determined by measuring the rate under second-order conditions at a series of constant concentrations of hydroxide ion. The results, plotted in Figure 4, confirm a first-order hydroxide dependence.

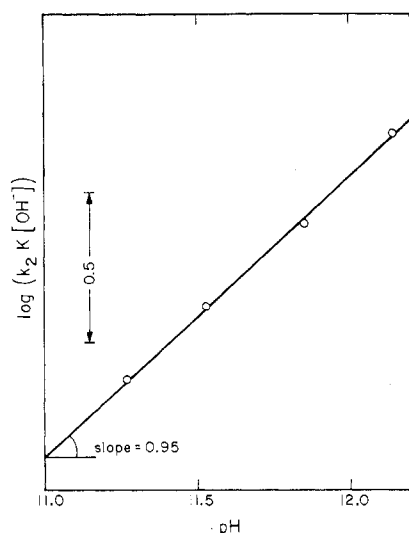


Figure 4.—pH dependence of the reaction rate. Initial conditions:  $[\text{Co}(\text{CN})_5\text{H}^{3-}] = 9 \times 10^{-5} \text{ M}$ ,  $[\text{Hg}(\text{CN})_2] = 4 \times 10^{-5} \text{ M}$ ;  $\mu = 0.5$  ( $\text{NaClO}_4$ );  $24^\circ$ . The ordinate values were obtained from analysis according to eq 8 with  $k_2/k_{-1}$  set equal to  $2.18 \times 10^4 \text{ M}^{-1}$ .

The slope and intercept of the least-squares line shown in Figure 3 yield the following values of the kinetic parameters:  $k_2/k_{-1} = (2.18 \pm 0.11) \times 10^4 \text{ M}^{-1}$  and  $k_2k_1/k_{-1} = k_2K = (2.12 \pm 0.03) \times 10^3 \text{ sec}^{-1} \text{ M}^{-2}$ , where  $K$  is the equilibrium constant for reaction 5.

Equation 7 predicts that the reaction rate should become zero order with respect to the concentration of  $\text{Hg}(\text{CN})_2$  when  $k_{-1} \ll k_2[\text{Hg}(\text{CN})_2]$ . The value of  $k_2/k_{-1}$  obtained from the kinetic data is  $2.2 \times 10^4 \text{ M}^{-1}$  so that the necessary condition for apparent zero-order dependence on  $\text{Hg}(\text{CN})_2$  becomes  $[\text{Hg}(\text{CN})_2] \gg 4.6 \times 10^{-5} \text{ M}$ . To test this prediction, kinetic runs were carried out with much larger concentrations of  $\text{Hg}(\text{CN})_2$ . Under these conditions, the reaction became pseudo first order and the first-order rate constants obtained at various concentrations of  $\text{Hg}(\text{CN})_2$  are summarized in Table IV. Contrary to the expectations based on eq 7,

TABLE IV  
FIRST-ORDER RATE CONSTANTS OBTAINED  
AT HIGH CONCENTRATIONS OF  $\text{Hg}(\text{CN})_2$

Initial concn, <sup>a</sup> mM		$[\text{Hg}(\text{CN})_2]/[\text{OH}^-]$	$10^{-3}k_{\text{obsd}}/[\text{OH}^-]$ , $\text{M}^{-1} \text{sec}^{-1}$
$\text{Hg}(\text{CN})_2$	$\text{OH}^-$		
4.0	5.76	0.695	$1.06 \pm 0.003$
10	6.16	1.62	$1.10 \pm 0.005$
40	5.76	6.95	$1.66 \pm 0.007$
70	5.37	13.05	$2.24 \pm 0.010$
100	5.01	19.95	$2.96 \pm 0.015$

<sup>a</sup> The initial concentration of  $\text{Co}(\text{CN})_5\text{H}^{3-}$  was  $9.8 \times 10^{-5} \text{ M}$  in each case.

the reaction rate continues to depend upon the concentration of  $\text{Hg}(\text{CN})_2$  up to concentrations of  $\text{Hg}(\text{CN})_2$  as

high as  $0.1 \text{ M}$ . It follows that eq 7 does not give an adequate account of the observed kinetics at high concentrations of  $\text{Hg}(\text{CN})_2$ . To explain the observed behavior, a second reaction pathway leading to the same product is needed. A good possibility<sup>13</sup> is



in which the hydrido complex reacts directly with  $\text{Hg}(\text{CN})_2$ . Hanzlick and Vlček have proposed an analogous direct reaction of  $\text{Co}(\text{CN})_5\text{H}^{3-}$  with benzoquinone.<sup>14</sup>

If the parallel reaction pathway indicated by reaction 9 is considered along with reactions 5 and 6, the rate law becomes

$$\frac{dP}{dt} = [\text{Co}(\text{CN})_5\text{H}^{3-}][\text{Hg}(\text{CN})_2] \left( \frac{k_1k_2[\text{OH}^-]}{k_{-1} + k_2[\text{Hg}(\text{CN})_2]} + k_3 \right) \quad (10)$$

For all of the cases listed in Table IV the condition  $[\text{Hg}(\text{CN})_2] \gg 4.6 \times 10^{-5} \text{ M}$  is met, so that eq 10 simplifies to

$$\frac{dP}{dt} = \left( k_1 + k_3 \frac{[\text{Hg}(\text{CN})_2]}{[\text{OH}^-]} \right) [\text{OH}^-][\text{Co}(\text{CN})_5\text{H}^{3-}] \quad (11)$$

Pseudo-first-order rate constants,  $k_{\text{obsd}}$ , were evaluated and divided by  $[\text{OH}^-]$ . Table IV lists the resulting values of  $k_{\text{obsd}}/[\text{OH}^-]$ , which can be identified with the first term in eq 11.

$$\frac{k_{\text{obsd}}}{[\text{OH}^-]} = k_1 + k_3 \frac{[\text{Hg}(\text{CN})_2]}{[\text{OH}^-]} \quad (12)$$

Plots of  $k_{\text{obsd}}/[\text{OH}^-]$  vs.  $[\text{Hg}(\text{CN})_2]/[\text{OH}^-]$  were linear and produced the following values for the rate constants:  $k_1 = (9.6 \pm 0.2) \times 10^{-2} \text{ M}^{-1} \text{sec}^{-1}$  and  $k_3 = (9.9 \pm 0.2) \times 10^{-3} \text{ M}^{-1} \text{sec}^{-1}$ . This value of  $k_1$  agrees well with the value obtained from the ratio of the slope to the intercept of the line in Figure 3 ( $k_1 = (9.7 \pm 0.8) \times 10^{-2} \text{ M}^{-1} \text{sec}^{-1}$ ). The value of  $k_3$  is small enough to ensure that reaction 9 made no significant contribution to the kinetics observed with the lower concentrations of  $\text{Hg}(\text{CN})_2$  employed in the experiments used to obtain the kinetic parameters from Figure 3.

**Free Cyanide Ion Dependence.**—A few kinetic runs were performed in solutions to which more than five cyanide ions per cobalt(II) ion were added. The rate of reaction was decreased by free cyanide in the way to be expected if  $\text{Hg}(\text{CN})_2$  were much more reactive than  $\text{Hg}(\text{CN})_4^{2-}$  and somewhat more reactive than  $\text{Hg}(\text{CN})_3^-$ . A more quantitative evaluation was not attempted because of the uncertainties in the reported values of the mercury(II) cyanide complex equilibrium constants.

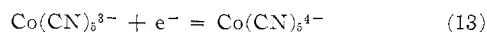
**Comparison with Other Results.**—The value of  $k_1$  resulting from this study is  $k_1 = (9.6 \pm 0.8) \times 10^{-2} \text{ M}^{-1} \text{sec}^{-1}$  at  $24^\circ$ . Recent pulse radiolysis experiments gave a value of  $10^{+5} \text{ sec}^{-1}$  for  $k_{-1}$ .<sup>15</sup> The equilibrium constant for reaction 5 is therefore calculated to be  $k = 10^{-6} \text{ M}^{-1}$ . Hanzlick and Vlček have estimated this

(13) J. Halpern and L. Y. Wong, *J. Amer. Chem. Soc.*, **90**, 6665 (1968).

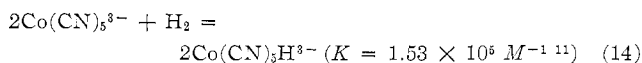
(14) J. Hanzlick and A. A. Vlček, *Inorg. Chem.*, **8**, 669 (1969).

(15) G. D. Venerable, II, E. J. Hart, and J. Halpern, *J. Amer. Chem. Soc.*, **91**, 7538 (1969).

constant to be *ca.*  $10^{-4} M^{-1}$  on the basis of unpublished polarographic data<sup>14</sup> but the experimental data they cited cannot be used to estimate this constant unless a value for the standard potential of reaction 13 is known. In strongly alkaline solutions of  $\text{Co}(\text{CN})_5\text{H}^{3-}$



an anodic polarographic wave<sup>16</sup> commencing at  $-1.2$  V *vs.* sce has been attributed to the reverse of reaction 13 but the thermodynamic reversibility of the wave has not been established. If the known equilibrium constant for



is combined with the ionization constant of water and the calculated value of  $K = 10^{-6} M^{-1}$  for reaction 5, the standard potential for reaction 13 is calculated to be  $-1.27$  V *vs.* sce. This value is not incompatible with the meager polarographic data presently available.<sup>16</sup>

Combining the value of  $k_2/k_{-1}$  obtained from Figure 3 with the pulse radiolysis value<sup>15</sup> of  $k_{-1} = 10^5 \text{ sec}^{-1}$  yields  $k_2 = 2 \times 10^9 M^{-1} \text{ sec}^{-1}$ , a value reflecting the high reactivity of  $\text{Co}(\text{CN})_5^{4-}$  as pointed out by Hanzlik and Vlček.<sup>14</sup> These authors estimated a minimum value for the second-order rate constant for the reaction

(16) J. Hanzlik and A. A. Vlček, *Chem. Commun.*, 47 (1969).

between  $\text{Co}(\text{CN})_5^{4-}$  and *p*-benzoquinone to be *ca.*  $10^9 M^{-1} \text{ sec}^{-1}$  at  $0^\circ$ . This constant increases to  $10^{11} M^{-1}$  if the equilibrium constant for reaction 5 obtained from this study ( $K = 10^{-6} M^{-1}$ ) is substituted for the estimated value ( $K = 10^{-4} M^{-1}$ ) used by Hanzlik and Vlček.<sup>14</sup> This value for the rate constant is uncomfortably large and it seems likely that Hanzlik and Vlček's assumption that reaction 5 proceeded rapidly enough to maintain equilibrium during their measurements caused them to derive an erroneously large rate constant from their data. The value of  $k_{-1}$  reported by Venerable, Hart, and Halpern<sup>15</sup> is too low by a factor of  $10^2$ – $10^3$  to permit the assumption of fast equilibrium for reaction 5 when the  $\text{Co}(\text{CN})_5^{4-}$  being generated is exposed to substrates with which it reacts as rapidly as it does with benzoquinone or mercuric cyanide.<sup>17</sup>

**Acknowledgment.**—We are indebted to Professor H. B. Gray, R. Levenson, and Y. S. Sohn for helpful discussions and assistance in obtaining the low-temperature spectra and magnetic measurements. This work was supported by the National Science Foundation.

(17) NOTE ADDED IN PROOF.—There is also a discrepancy between the value reported here for  $k_1$  and the much larger value that would be needed to accommodate the pH dependence reported by Hanzlik and Vlček with the benzoquinone system.<sup>14</sup> The erroneous assumption of preequilibrium for reaction 5 cannot account for this discrepancy. It remains to be explained.

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## Reactions of Coordinated Ligands. XXI. Nitric Acid Oxidation of 1,4,4,10,12,12-Hexamethyl-1,5,9,13-tetraazacyclohexadeca-1,9-dienickel(II) Perchlorate

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Oxidative dehydrogenation of the title compound, prepared by the condensation of acetone with  $\text{Ni}(\text{tm})_2^{2+}$  (tm = trimethylenediamine), produces two new complexes with three and four imines, respectively. The structures of these new complexes have been established by physical and chemical methods. From the structures of these products the hitherto unknown arrangement of imine donors in the starting material has been determined as *trans*. Nmr spectral studies indicate these complexes have very stable chelate ring conformations in acidic and nonbasic solvents. In basic solvents there is a base-catalyzed process for ring conformation interconversion.

### Introduction

It has been found recently that some Ni(II) complexes of cyclic ligands containing secondary amine donors may be chemically oxidized to forms containing a higher degree of unsaturation in the ligand than was previously present.<sup>1,2</sup> Examples are shown in reactions 1–3. Subsequent to Curtis' report on the preparation of I and II by the condensation of acetone with

$\text{Ni}(\text{en})_3^{2+}$ ,<sup>3</sup> he and his coworkers reported a similar reaction of  $\text{Ni}(\text{tm})_3^{2+}$  (tm = trimethylenediamine) with acetone.<sup>4,5</sup> This complex was reported to have limited stability toward acid or base hydrolysis<sup>4</sup> and to be destroyed under oxidative conditions.<sup>5</sup> The stereochemistry of the product from this reaction was not determined.<sup>6</sup> We have succeeded in oxidizing this com-

(3) N. F. Curtis and D. A. House, *Chem. Ind. (London)*, **42**, 1708 (1961); N. F. Curtis and M. M. Blight, *J. Chem. Soc.*, 3016 (1962).

(4) D. A. House and N. F. Curtis, *J. Amer. Chem. Soc.*, **86**, 223 (1964).

(5) N. F. Curtis, *Coord. Chem. Rev.*, **3**, 1 (1968).

(6) This reaction could also lead to isomers analogous to I and II. At present we have evidence for the existence of only one of these isomers; *vide infra*.

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(1) N. F. Curtis, *Chem. Commun.*, 881 (1966).

(2) E. G. Vassian and R. K. Murmann, *Inorg. Chem.*, **6**, 2043 (1967).