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Thermodynamics of Metal Cyanide Coordination. VIII.
A Calorimetric Study of Co^{2+}–CN^- Interaction[1a]

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Values of $\Delta H°$ for the reactions $Co^{2+} + 5CN^- = Co(CN)_5{}^{3-}$ and $2Co(CN)_5{}^{3-} + H_3O^+ = Co(CN)_5(H_2O)^{2-} + Co(CN)_5H^{3-}$ have been calorimetrically determined to be −61.5 ± 0.5 and −32.0 ± 0.5 kcal/mol of $Co(CN)_5{}^{3-}$, respectively. The $\Delta H°$ values are examined and discussed in terms of the oxidation of $Co(CN)_5{}^{3-}$ and of the reaction of $Co(CN)_5{}^{3-}$ with $H_2(g)$. The increase in $\Delta H°$ of approximately 20 kcal/mol per step in going from $Fe(CN)_6{}^{4-}$ to $Co(CN)_5{}^{3-}$ to $Ni(CN)_4{}^{2-}$ is discussed in light of the increase in the number of electrons in the e_g subshell and the change in $\Delta H°$ per metal–cyanide bond in this series.

Introduction

The reaction between $Co(CN)_5{}^{3-}$ and $H_2(g)$[2-4] (eq 1) and the reaction of $Co(CN)_5{}^{3-}$ with water[4,5] (eq 2) have

$$2Co(CN)_5{}^{3-} + H_2(g) = 2Co(CN)_5H^{3-} \qquad (1)$$

$$2Co(CN)_5{}^{3-} + H_2O = Co(CN)_5H^{3-} + Co(CN)_5OH^{3-} \qquad (2)$$

recently been studied. These studies have established the kinetic and thermodynamic relationships for reaction 1 and the stoichiometry and spectral properties for the products of reaction 2.

To the best of our knowledge no thermodynamic studies dealing with the reaction of $Co(CN)_5{}^{3-}$ with water (eq 2) have been reported, probably because the nature of the reaction was poorly understood. A ΔH value of −74.4 kcal/mol has been reported[6] for the formation of $Co(CN)_5{}^{3-}$ from its constituent aqueous ions (eq 3), but the results of this study are questionable

$$Co^{2+} + 5CN^- = Co(CN)_5{}^{3-} \qquad (3)$$

since other reactions (see Results and Discussion sections) were probably occurring in the calorimeter under the given experimental conditions.

In this paper are reported $\Delta H°$ values for reactions 3 and 4. Reaction 4 is a modification of reaction 2 with

$$2Co(CN)_5{}^{3-} + H_3O^+ = Co(CN)_5H_2O^{2-} + Co(CN)_5H^{3-} \qquad (4)$$

the protonation of $Co(CN)_5OH^{3-}$ included.

Experimental Section

Materials.—A stock solution of $Co(ClO_4)_2$ was prepared by dissolving recrystallized reagent grade $Co(ClO_4)_2$ (Amend Drug and Chemical Co.) in oxygen-free, glass-distilled water and was standardized using sodium anthranilate. Subsequent $Co(ClO_4)_2$ solutions used in this study were prepared by diluting portions of this stock solution with deoxygenated, glass-distilled water.

The NaCN solutions were prepared just prior to use with reagent grade NaCN (Baker) and glass-distilled, deoxygenated water and were standardized by a modified Liebig procedure.[7]

Procedures. (1) **General.**—The calorimetric equipment used in this study has been described.[8] The procedure was essentially that used previously[8] with the additional precaution of flushing the calorimeter with oxygen-free nitrogen for several minutes prior to introducing the solutions.

In most of the calorimetric determinations, a 10-ml volume of an NaCN solution (0.5–0.05 *M*) was added to 200 ml of a $Co(ClO_4)_2$ solution (3×10^{-3} to 3×10^{-4} *M*). This procedure required that the over-all measured heat be corrected for the heat of dilution of the NaCN solution. These corrections were taken from previously determined values.[9] In those cases where a 10-ml volume of $Co(ClO_4)_2$ solution was added to 200 ml of a NaCN solution, separate determinations were made to correct for the heat of dilution of $Co(ClO_4)_2$. The heat of dilution of the 200-ml solution of either NaCN or $Co(ClO_4)_2$ was measured and found to be negligible. The ΔH values at a given $Co(CN)_5{}^{3-}$ *concentration were found to be independent of the order of mixing.*

The calorimetric determinations were corrected for thermal effects due to HCN formation using literature[10] p*K* and $\Delta H°$ values for HCN dissociation.

(2) **Reaction of CN^- with Co^{2+}.**—The reaction of CN^- with Co^{2+} was studied calorimetrically under four different sets of conditions: (a) at a CN^-/Co^{2+} molar ratio of 5/1, (b) at a CN^-/Co^{2+} molar ratio of 10/1, (c) at CN^-/Co^{2+} and OH^-/Co^{2+} molar ratios of 5/1, and (d) at a CN^-/Co^{2+} molar ratio of 5/1 with 1 mol of $HClO_4$ added per mole of Co^{2+}.

It was found experimentally that following the initial formation of $Co(CN)_5{}^{3-}$ the presence of NaOH, condition c, significantly retarded the subsequent reaction of $Co(CN)_5{}^{3-}$ with water (eq 2), making meaningful and reproducible calorimetric measurements possible for the formation of $Co(CN)_5{}^{3-}$ from Co^{2+} and CN^-. The NaOH was added to the 10 ml of NaCN solution in a concentration such that the NaOH concentration was about 1×10^{-3} *M* in the final 210 ml of solution in the calorimeter. Corrections were applied for the heat of dilution[11] of the NaOH solution as well as for thermal effects[10] arising from the change in HCN concentration due to the presence of NaOH.

(3) **Reaction of $Co(CN)_5{}^{3-}$ with H_2O.**—A spectrophotometric study at 970 mμ of $Co(CN)_5{}^{3-}$ kinetics carried out in this laboratory indicates that the addition of $HClO_4$ to a $Co(CN)_5{}^{3-}$ solution results in a marked increase in the rate of disappearance of the

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[11] "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

$Co(CN)_5^{3-}$. Thus, addition of $HClO_4$ made it possible to make calorimetric measurements with equilibrium times of less than 3 min for the reaction of $Co(CN)_5^{3-}$ with water. This reaction, described above under condition d, was carried out by mixing 200 ml of an NaCN solution with a 10-ml volume of $Co(ClO_4)_2$ containing 1 equiv of $HClO_4$. The added $HClO_4$ ensured that the $Co(CN)_5OH^{3-}$ species was completely protonated.[12]

Thus, when the solutions were mixed in the calorimeter, two chemical reactions occurred. First, $Co(CN)_5^{3-}$ formed rapidly from its constituent ions, and, second, the $Co(CN)_5^{3-}$ reacted at a slower rate with water, the rate depending upon the pH. The over-all reaction which occurred in the calorimeter with 1 equiv of $HClO_4$ added was the sum of eq 3 and 4 and can be represented by eq 5. The over-all heat change measured in the calorimeter

$$Co^{2+} + 5CN^- + {}^1/_2H_3O^+ = {}^1/_2Co(CN)_5H_2O^{2-} + {}^1/_2Co(CN)_5H^{3-} \quad (5)$$

also corresponds to the ΔH value for reaction 5. The absorbance, measured using a Beckman DU spectrophotometer at 380 and 970 mμ, of solutions similar to those used in the calorimetric measurements indicated that reaction 5 was completed in less than 3 min, the time interval for the calorimetric measurements.

The decomposition[13] of $Co(CN)_5^{3-}$ by $HClO_4$ to form Co^{2+} and HCN was precluded by using only small amounts of acid (such that the final solution pH was never less than 6) to catalyze the reaction of $Co(CN)_5^{3-}$ with H_2O, reaction 4. The increase in absorption with time at 380 mμ corresponding to an increase in the concentration of $Co(CN)_5OH^{3-}$ [3,5,14] provided evidence that reaction 4 was indeed occurring. However, it was observed that increasing the initial amount of $HClO_4$ or buffering the solution at a pH <6 caused decomposition of $Co(CN)_5^{3-}$ to occur with evolution of HCN in agreement with the observation of Espenson and Pipal.[13]

The possibility that some of the $Co(CN)_5H^{3-}$ decomposed by the reverse path of reaction 1 during the calorimetric measurements was ruled out in view of the rate data of Burnett, Connolly, and Kemball[3] and those of DeVries[4] which indicate that no significant amount of $Co(CN)_5H^{3-}$ would have decomposed under the experimental conditions existing in the calorimetric determinations.

TABLE I
CALORIMETRIC DATA FOR THE INTERACTION OF CN^- WITH Co^{2+}

Initial $[Co^{2+}]$, mmol	Q_{DI}, cal[a]	Q_{cor}, cal[b]	ΔH, kcal/mol of initial Co(II)[c]
(a) Initial Molar Ratio $CN^-/Co^{2+} = 5/1$			
0.5651	−0.131	−34.420	−60.68 ± 0.09
0.4462	−0.180	−27.520	−61.27 ± 0.05
0.3718	−0.185	−22.605	−60.30 ± 0.05
0.2972	−0.191	−18.548	−61.77 ± 0.10
0.2231	−0.180	−14.356	−63.54 ± 0.13
0.1487	−0.147	−9.768	−64.70 ± 0.14
0.1189	−0.050	−8.244	−68.92 ± 0.17
0.08919	−0.070	−6.510	−72.21 ± 0.18
0.07431	−0.050	−5.552	−74.04 ± 1.37
0.06538	+0.010	−4.858	−74.46 ± 0.20
0.06241	+0.010	−4.649	−74.65 ± 0.46
0.05943	+0.010	−4.302	−72.56 ± 1.30
0.03571	+0.040	−2.552	−72.58 ± 0.55
(b) Initial Molar Ratio $CN^-/Co^{2+} = 10/1$			
0.5950	+0.660	−36.372	−62.24 ± 0.03
0.4463	−0.040	−28.094	−62.86 ± 0.01
0.2975	−0.135	−19.461	−64.96 ± 0.08
0.2232	−0.040	−14.884	−66.51 ± 0.65
0.1487	−0.191	−10.633	−70.22 ± 0.03
0.07434	−0.147	−5.756	−75.45 ± 0.15
0.06547	−0.040	−5.063	−76.72 ± 0.28
0.05943	−0.030	−4.531	−75.74 ± 0.56
0.02970	+0.030	−2.177	−74.31 ± 0.35
(c) Initial Molar Ratios: $CN^-/Co^{2+} = OH^-/CO^{2+} = 5/1$			
0.4462	−0.35	−27.440	−60.71 ± 0.09
0.2230	−0.05	−13.762	−61.49 ± 0.44
0.1487	0.00	−9.174	−61.69 ± 1.35
0.1189	−0.200	−7.244	−59.24 ± 0.16
0.08925	−0.090	−5.071	−55.81 ± 1.02
0.07436	−0.080	−4.075	−53.72 ± 1.05
0.05947	−0.060	−3.261	−53.83 ± 0.67
(d) Initial Molar Ratios: $CN^-/Co^{2+} = 5/1$, $H^+/Co^{2+} = 1/1$			
0.1832	−0.030	−17.236	−93.92 ± 0.12
0.09182	+0.010	−8.533	−93.04 ± 0.05

[a] Q_{DI} is the heat resulting from the dilution of the NaCN solution and the interaction of CN^- with H^+. [b] Q_{cor} is the total heat liberated in the calorimeter corrected for all extraneous energy terms (*i.e.*, heat of stirring, etc.). The values given are in each case averages of at least three determinations. [c] The uncertainties are standard deviations based on at least three determinations.

Results

The calorimetric data for runs under conditions a–d discussed in the Experimental Section are presented in Table I. In each case, except d, the initial $Co(ClO_4)_2$ concentration was varied from 3×10^{-3} to 4×10^{-4} *M*.

Formation of $Co(CN)_5^{3-}$.—In Figure 1 is presented a plot of the ΔH values in Table I for the reaction of Co^{2+} with CN^- *vs.* the initial $Co(ClO_4)_2$ concentration. The data plotted in Figure 1 show that at initial Co(II) concentrations below 1.5×10^{-3} *M* the ΔH value becomes significantly more negative as the total cobalt concentration decreases for conditions a and b. Under condition c, however, this effect is removed by the presence of excess NaOH, which inhibits the further exothermic reaction of the newly formed $Co(CN)_5^{3-}$, reaction 4. If the best line defining the lower curve in Figure 1 between initial $Co(ClO_4)_2$ concentrations of 3×10^{-3} and 0.7×10^{-3} *M* is extrapolated (dashed line, Figure 1) to zero $Co(CN)_5^{3-}$ concentration, a $\Delta H°$ value of −61.5 ± 0.5 kcal/mol is obtained for the formation of $Co(CN)_5^{3-}$ by reaction 3. The reason for the decrease in the $-\Delta H$ values at $Co(ClO_4)_2$ concentrations below 7×10^{-4} *M* is unknown.

The presence of excess CN^-, condition b, has an interesting effect on the ΔH value for the formation of $Co(CN)_5^{3-}$ as seen in the upper curve of Figure 1 which parallels that obtained under condition a but with the ΔH values more negative by approximately 2 kcal/mol. Possible reasons for this effect are presented in the Discussion.

The calorimetric runs carried out under condition d involving addition of $HClO_4$ resulted in a large exothermic ΔH value of −93.5 ± 0.5 kcal/mol which can be assigned to reaction 5. Since the enthalpy change for this reaction is the sum of the ΔH values for the formation of $Co(CN)_5^{3-}$ and the reaction of $Co(CN)_5^{3-}$ with H_3O^+, one obtains $\Delta H_4 = \Delta H_5 - \Delta H_3 = (-93.5 + 61.5)$ kcal/mol = −32.0 kcal/mol of $Co(CN)_5^{3-}$ for the reaction of $Co(CN)_5^{3-}$ with H_3O^+, reaction 4.

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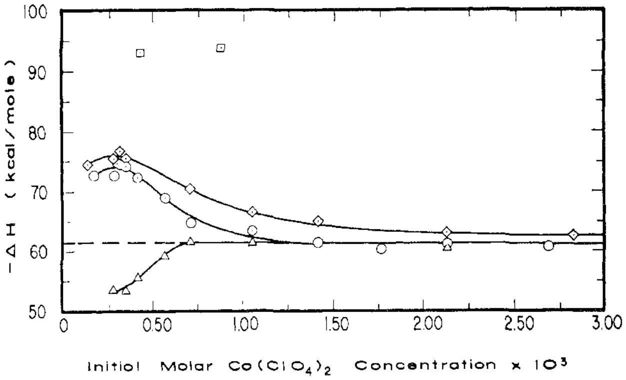

Figure 1.—Plot of initial molar $Co(ClO_4)_2$ concentration *vs.* $-\Delta H$ for the Co^{2+}–CN^- interaction. Conditions: (a) initial molar CN^-/Co^{2+} ratio = 5/1, ○; (b) initial molar CN^-/Co^{2+} ratio = 10/1, ◇; (c) initial molar ratios: $CN^-/Co^{2+} = OH^-/Co^{2+}$ = 5/1, △; (d) initial molar ratios: CN^-/Co^{2+} = 5/1, H^+/Co^{2+} = 1, □.

Discussion

The results from the earlier calorimetric study of the Co^{2+}–CN^- system by Guzzetta and Hadley[6] cannot be usefully compared to those of the present study because these workers used excess KCN (1.0 *M*) and did not specify the initial acid concentration in their 0.4 *M* $CoSO_4$ solution. Also, their results were obtained in much more concentrated solutions than those used in the present study.

The fact that the upper curve in Figure 1 which is drawn through data points obtained under condition b parallels that drawn through data points obtained under condition a suggests an interaction between $Co(CN)_5^{3-}$ and the excess NaCN present under condition b. Any appreciable interaction of $Co(CN)_5^{3-}$ with CN^- appears unlikely in view of the low equilibrium constant values, 10^{-1} to 10^{-4} [15] and <<1,[16] estimated for the reaction $Co(CN)_5^{3-} + CN^- = Co(CN)_6^{4-}$ On the other hand, Pratt and Williams[16] report weak interactions between M^+ (M = Rb, K, Na, Li) and $Co(CN)_5^{3-}$. A *K* value of 3.5 is reported by these authors for the reaction $Rb^+ + Co(CN)_5^{3-} = RbCo(CN)_5^{2-}$. No *K* values are given in the case of Na^+, but interactions somewhat weaker than in the case of Rb^+ are indicated. Also, log *K* values of 2.35 ± 0.02 and 1.46 ± 0.02 and ΔH values of 1.0 ± 0.3 and 0.5 ± 0.5 kcal/mol have been reported[17] for the interaction of K^+ with $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$, respectively. Thus, it appears likely that the upper curve in Figure 1 is the result of an interaction between Na^+ and $Co(CN)_5^{3-}$; however, further experimentation is desirable to resolve the question.

Recently, a $\Delta H°$ value of −11.2 kcal/mol of $H_2(g)$ was reported[4] for reaction 1. The combination of half this $\Delta H°$ value with that for reaction 4 gives an interesting thermochemical result, reaction 6. Reaction 6

$$Co(CN)_5^{3-} + H_3O^+ = {}^1/_2H_2(g) + Co(CN)_5H_2O^{2-}$$
$$(\Delta H° = -58.4 \text{ kcal/mol of } Co(CN)_5^{3-}) \quad (6)$$

is simply the oxidation of $Co(CN)_5^{3-}$ by an acidic solution to form $H_2(g)$ and $Co(CN)_5H_2O^{2-}$. It is now informative to compare the $\Delta H°$ value for reaction 6 with that[18] for reaction 7. The oxidation of $Co(CN)_5^{3-}$ is

$$Fe(CN)_6^{4-} + H_3O^+ = Fe(CN)_6^{3-} + {}^1/_2H_2(g) + H_2O$$
$$(\Delta H° = +26.7 \text{ kcal/mol of } Fe(CN)_6^{4-}) \quad (7)$$

seen to be a much more favorable process enthalpywise than is the oxidation of $Fe(CN)_6^{4-}$. This can be understood by considering the change in ligand field stabilization energy ($\Delta LFSE = LFSE_{products} - LFSE_{reactants}$) in going from the +2 to the +3 metal ion complexes. Using available $10Dq$ values for $Fe(CN)_6^{4-}$ (33,800 cm^{-1}),[19] $Fe(CN)_6^{3-}$ (35,000 cm^{-1}),[19] and $Co(CN)_5^{3-}$ (33,000 cm^{-1})[20] and calculating a $10Dq$ value of 32,100 cm^{-1} for $Co(CN)_5H_2O^{2-}$ by assuming it to be the weighted average of the $10Dq$ value of $Co(CN)_6^{3-}$ (34,800 cm^{-1})[19] and $Co(H_2O)_6^{3+}$ (18,600 cm^{-1})[21] (average environment rule), the values of ΔLFSE for reactions 6 and 7 are found to be −50 and +32 kcal/mol, respectively, compared with measured $\Delta H°$ values of −58.4 and +26.7 kcal/mol for these same reactions. Thus, the powerful reducing ability of the $Co(CN)_5^{3-}$ ion parallels the large negative enthalpy change when the antibonding a_1 (d_{z^2}) electron is lost from the C_{4v} $Co(CN)_5^{3-}$ ion[20] thereby forming the more stable $Co(CN)_5H_2O^{2-}$ ion.

Combination of the $\Delta H°$ value for reaction 6 with half of that for the reverse of reaction 1, 5.6 kcal/mol, results in a $\Delta H°$ value for reaction 8 of −52.8 kcal/mol.

$$Co(CN)_5H^{3-} + H_3O^+ = Co(CN)_5H_2O^{2-} + H_2 \quad (8)$$

If the $Co(CN)_5H^{3-}$ ion is considered to be a hydridopentacyanocobaltate(III) ion,[14] then the $\Delta H°$ value for reaction 8 can be visualized as the sum of the $\Delta H°$ values for a hypothetical two-step reaction. The first step is the replacement of a hydride ion by a water molecule and the second step is the subsequent reaction of the hydride ion with a hydrogen ion to form $H_2(g)$. Since the ΔH value for the aquation reaction of a substituted $Co(CN)_5X^{3-}$ complex is likely to be small, the $\Delta H°$ value for reaction 8 should reflect primarily the reaction between the hydride ion and the proton to form $H_2(g)$.

Earlier papers from this laboratory have reported $\Delta H°$ values for the formation of $Fe(CN)_6^{4-}$ [22] and $Ni(CN)_4^{2-}$ [23] from their respective aqueous ions. These complex ions together with $Co(CN)_5^{3-}$ form an interesting series in which the $Fe(CN)_6^{4-}$ ion is octahedral, the $Co(CN)_5^{3-}$ ion is likelys quare-pyramidal with a water molecule occupying the axial position,[16] and the

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$Ni(CN)_4^{2-}$ ion is square planar. The relationship in this series between the change in structure and the appearance of electrons in the e_g subshell has been discussed.[16] It is now of interest to examine the effect of these electrons on the $\Delta H°$ values for the formation of these complexes from their respective aqueous ions. The $\Delta H°$ values of −85.77, −61.5, and −43.2 kcal/mol show an increase of 24.3 kcal/mol between $Fe(CN)_6^{4-}$ and $Co(CN)_5^{3-}$ and 18.3 kcal/mol between $Co(CN)_5^{3-}$ and $Ni(CN)_4^{2-}$. These successive increases in $\Delta H°$ cannot be accounted for by the decreased number of CN^- per M^{2+} bonds alone. This is seen by dividing the $\Delta H°$ value in each case by the number of CN^- per M^{2+}. One thus obtains −14.3, −12.3, and −10.8 kcal per metal–cyanide bond for $Fe(CN)_6^{3-}$, $Co(CN)_5^{3-}$, and $Ni(CN)_4^{2-}$, respectively. Two questions now arise. First, why does the $\Delta H°$ value per bond decrease in the series and, second, why are the $\Delta H°$ values per bond only approximately half the differences in the $\Delta H°$ values per mole in the series? The decrease in the $-\Delta H°$ value per bond suggests that the successive addition of electrons to the e_g subshell has a labilizing effect on the metal–cyanide bonds as suggested by Pratt and Williams.[16] The second question indicates that additional factors play a role in increasing the $\Delta H°$ values per mole in the series. Such energy quantities as ligand field stabilization energies of the complexes and metal ions involved, pairing energies of the metal ions, π bonding, and relative hydration energies are undoubtedly important. Since the magnitudes of most of these terms are unknown for these species in aqueous solution, further interpretation is not attempted here.

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Kinetics of Formation and Dissociation of Tetracyanonickelate(II) Ion

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The rate of formation of $Ni(CN)_4^{2-}$ is a fifth-order reaction, first order in nickel and fourth order in total cyanide; HCN is a reactant as well as CN^-. From pH 5.5 to 7.5 the rate expression is $k_{2,2}[Ni^{2+}][CN^-]^2[HCN]^2$ where $k_{2,2}$ equals 1.6×10^{18} M^{-4} sec^{-1} at 25.0°, $\mu = 0.1$ M ($NaClO_4$). Above pH 7.5 the reaction order in CN^- is greater than 2 and the reaction order in HCN is less than 2, but the total cyanide dependence remains fourth order. The kinetics of dissociation of $Ni(CN)_4^{2-}$ in acid (10^{-5} to 2 M $HClO_4$) indicate the presence of several protonated species including $HNi(CN)_4^-$, $H_2Ni(CN)_4$, and $H_3Ni(CN)_4^+$. Equilibrium studies from pH 4 to 5 confirm the first two acid species with protonation constants $K_H = 2.5 \times 10^5$ M^{-1} and $K_{2H} = 3.0 \times 10^4$ M^{-1}; K_{3H} is estimated to be 400 M^{-1} from the kinetic data. The log β_4 value for $Ni(CN)_4^{2-}$ is 30.5.

Introduction

Stepwise stability constants for cyanide complexes of nickel are not known because the tetracyano complex is so stable that it forms preferentially when nickel(II) and cyanide ion are mixed. Even solid $Ni(CN)_2$ has been shown to consist of Ni^{2+} and $Ni(CN)_4^{2-}$ ions.[2-4] The log β_4 value is approximately 30 rather than the often quoted estimate of 22.[5] The magnitude of the constant is well established from a wide variety of determinations which have included toxicity,[6] spectrophotometric,[7] kinetic,[8] and potentiometric studies.[9] There are some variations in the β_4 value because of differences in ionic strength but there are additional disagreements which we believe can be attributed to the presence of protonated forms of the complex in some studies.

The overwhelming stability of the diamagnetic $Ni(CN)_4^{2-}$ complex compared to lesser cyanide ion complexes with nickel accounts in good measure for the kinetic behavior reported in this work. Four cyanide ions are needed both thermodynamically and kinetically to give the stable diamagnetic square-planar complex. Intermediate species such as $NiCN^+$, $Ni(CN)_2$, and $Ni(CN)_3^-$ are not observed, although they can be assumed to be present as reaction intermediates. An unusually high reaction order results—fifth order overall. Despite the high reaction order the speed of the reaction is great even at low concentrations and stopped-flow methods were used to follow the rate of formation. The kinetics of the formation reaction are extremely interesting for another reason, namely, that hydrocyanic acid is a reactant as well as cyanide ion. Earlier work has shown the important kinetic role of HCN in the formation of mixed cyanide complexes of aminocarboxylate complexes of nickel.[10] The importance

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