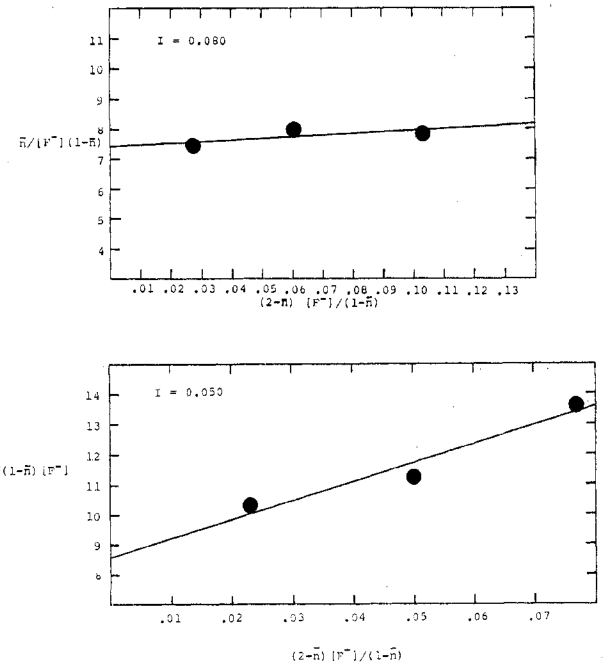

Figure 2. Graphs of $\bar{n}/(1-\bar{n})[F^-]$ *vs.* $(2-\bar{n})[F^-]/(1-\bar{n})$.

The values of K_1 determined here compare favorably with those obtained by previous workers. It should be noted, however, that K_1 is highly dependent upon the ionic strength. The values of K_1 decrease with increasing ionic strength, which is what would be expected on the basis of Debye-Huckel theory.

The apparent reason that the previous workers on the copper-fluoride system did not observe the equilibrium involving the formation of CuF_2 is that their experiments were carried out at lower $\bar{n}$ values than were used here. For example, Connick and Paul carried out their experiments in such a way that the values of $\bar{n}$ were of the order of 0.002. A typical value of $\bar{n}$ in this work would be 0.2. When the values of $\bar{n}$ are very small, the concentrations of CuF_2 formed are so low that CuF_2 cannot be detected.

The copper(II) ions in aqueous solution are thought to have an octahedral geometry that is distorted along one axis. The solutions containing copper(II) ions in the presence of fluoride are blue just like those containing copper(II) in the absence of fluoride. Presumably, then, CuF^+ and CuF_2 have the distorted octahedral geometry also and could be represented as $[Cu(H_2O)_5F]^+$ and $[Cu(H_2O)_4F_2]$.

Registry No. Copper, 7440-50-8.

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Kinetics of Tetracyanonickelate(II) Reactions

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Received September 11, 1973 AIC30662W

Ammonia, diamines, and glycinate ion greatly accelerate the rate of decomposition of $Ni(CN)_4{}^{2-}$ in the presence of iodine as a scavenger for CN^-. The second-order rate constants (M^{-1} sec^{-1} at 25°, 0.1 M $NaClO_4$) for the nucleophilic reaction of these ligands with $Ni(CN)_4{}^{2-}$ are 120 for NH_3, 425 for ethylenediamine, 206 for 1,2-diaminopropane, 590 for 1,3-diaminopropane, and 54 for glycinate ion. The reactivities of *N*-methyl derivatives of ethylenediamine also fall within this range. The $Ni(CN)_4{}^{2-}$ complex dissociates in the presence of iodine, having a first-order rate constant of 4.8×10^{-4} sec^{-1}, independent of acidity from pH 3 to 8 and independent of iodine concentration. In the absence of iodine the acid dissociation rate of $Ni(CN)_4{}^{2-}$ has an inverse first-order dependence in CN_T ($CN^- + HCN$) above pH 2 and is pH dependent.

Introduction

The rate of dissociation of the $Ni(CN)_4{}^{2-}$ complex is slow in acidic solutions and is very dependent on the hydrogen ion concentration.[1] In basic solution the breakup of $Ni(CN)_4{}^{2-}$ can be forced by multidentate ligands such as aminopolycarboxylates and polyamines. The EDTA reaction is very slow and has a first-order dependence in $EDTA^{4-}$ and $Ni(CN)_4{}^{2-}$ concentrations, with an inverse first-order dependence in cyanide ion concentration.[2] Similar rate expressions are observed[3,4] for the reaction of eight other aminopolycarboxylates with $Ni(CN)_4{}^{2-}$. The behavior of triethylenetetramine (trien) is quite different in that it reacts much faster with $Ni(CN)_4{}^{2-}$ and exhibits no inverse cyanide ion dependence.[5] Preliminary studies[5] indicated that ethylenediamine (en) reacted in a manner similar to trien, but with a second-order rate constant of about 50 M^{-1} sec^{-1} compared to a rate constant of 310 M^{-1} sec^{-1} for trien. On the other hand, ammonia (in the presence of EDTA to force the reaction) was found to be many orders of magnitude less effective than en and had an apparent rate constant of only 9×10^{-4} M^{-1} sec^{-1}. The much greater reactivity of en and trien, compared to NH_3, suggested a possible kinetic chelate effect for the substitution reactions of the tetracyanonickelate(II) square-planar complex and the existence of a six-coordinate reactive intermediate. A six-coordinate activated complex was propsed for the reaction of a Pt(II) complex[6] and it is well known that Ni(II) forms six-coordinate species much more readily than does Pt(II).[7] The ring-closure reactions of monodentate-bonded

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ethylenediamine on Pt(II) are relatively rapid and this has been termed a kinetic chelate effect.[8] The present study was undertaken to learn more about the relative reactivities of ammonia and bidentate amines with $Ni(CN)_4^{2-}$ to see if chelation has a large effect on the rate of displacement of cyanide ion.

Tetracyanonickelate(II) is a very strong complex ($\log \beta_4 = 30.5$)[1] and in order to displace cyanide ion from it a strong nickel-complexing agent or a rapid scavenger for cyanide ion is needed. It is possible to force the reaction with EDTA and to observe catalysis by ammonia and by ethylenediamine, but reversibility is a serious interference as the cyanide ion is released. A scavenger for cyanide ion was sought to avoid this difficulty. Iodine proved to be effective because it reacts very rapidly with CN^- and relatively fast with HCN.[9] The iodine reaction with $Ni(CN)_4^{2-}$ is slow and catalysis of the decomposition of $Ni(CN)_4^{2-}$ by ammonia and other complexing agents can be studied without the difficulties of reversibility.

Experimental Section

Crystalline $Na_2Ni(CN)_4 \cdot 3H_2O$ was prepared from the reaction of NaCN and $Ni(ClO_4)_2$ in water. The reaction mixture was boiled and concentrated. The product was recrystallized from water. Solution concentrations were checked using a molar absorptivity of 1.16×10^4 M^{-1} cm^{-1} at 267 nm. The diamine ligands were reagent grade. They were distilled and the purity of each was confirmed by gas chromatographic analysis. Standard solutions were prepared by weighing out the freshly distilled diamine. Iodine solutions were prepared just before use by mixing a standard solution of KIO_3 with NaI and acidifying with $HClO_4$. The ionic strength was maintained at 0.10 *M* (except where noted) using $NaClO_4$, twice recrystallized.

Dissociation rates of $Ni(CN)_4^{2-}$ were followed spectrophotometrically (Cary 14). Most of the reactions were followed to completion but in some cases the method of initial rates was used. The loss of absorbance of $Ni(CN)_4^{2-}$ was observed at 285 and 267 nm when iodine was not present. The loss of I_3^- was followed at 390, 380, and 352 nm and in a few cases the disappearance of both $Ni(CN)_4^{2-}$ and I_3^- was followed at 285 nm. When iodine was added at high pH, the reactions were observed by the disappearance of $Ni(CN)_4^{2-}$ at 285 nm. The molar absorptivities used are given in Table I and are in agreement with previously determined values.[1,3,4,10,11] The molar absorptivities of all other species were negligible by comparison.

The kinetic data for the reactions of $Ni(CN)_4^{2-}$ with amines and with glycinate ion were obtained using a Durrum-Gibson stopped-flow spectrophotometer with 2.0-cm cell path. Data were reduced using an on-line digital computer (Hewlett-Packard 2115A), interfaced to the stopped-flow instrument as described elsewhere.[12] Using this system, data can be taken at a rate of 1 point/msec. A least-squares analysis of the conformance of the data to a programmed rate law can be obtained within 1 min of the completion of the experiment. After on-line analysis, data from all stopped-flow experiments were recorded on punched paper tape, for possible later off-line calculations. These reactions were run under pseudo-first-order conditions and each rate constant is the average of four to eight kinetic runs. The standard deviations were calculated from the deviation of the individual rate constants from the mean.

A cyanide ion electrode (Orion Model 94-06) was used in conjunction with a calomel reference electrode containing NaCl to monitor the release of CN^- in a few experiments. These measurements and the pH values were taken with an Instrumentation Laboratory Model 245 pH meter. The specific ion electrode gave a linear calibration curve from 10^{-6} to 10^{-3} *M* cyanide ion, but higher concentrations (>0.01 *M*) of ethylenediamine interfered. Cyanide solutions were standardized argentimetrically.

For the kinetic studies in the presence of iodine and below pH 8.0 the total iodine concentration ($[I_2]_T = [I_2] + [I_3^-]$) was calculated for each absorbance reading using a value of 710 M^{-1} for the triiodide ion equilibrium constant ($K_{I_3} = [I_3^-]/[I_2][I^-]$).[13,14] This calculation takes into account the variable I^- concentration during the reaction. The iodine reacts with cyanide ion to form ICN and the $Ni(CN)_4^{2-}$ concentration is calculated from eq 1, where *a* is the

$$[Ni(CN)_4^{2-}] = (4a - b + [I_2]_T)/4 \qquad (1)$$

initial $Ni(CN)_4^{2-}$ concentration and *b* is the initial total iodine concentration. Plots of ln $[Ni(CN)_4^{2-}]$ *vs.* time were linear and gave slopes equal to k_{obsd} in accord with the first-order rate expression in eq 2. This lack of dependence upon iodine concentration was

$$-d[Ni(CN)_4^{2-}]/dt = k_{obsd}[Ni(CN)_4^{2-}] \qquad (2)$$

observed even when the $Ni(CN)_4^{2-}$ concentration was in stoichiometric excess compared to the total iodine concentration. For reactions run in the absence of iodine the $Ni(CN)_4^{2-}$ concentration was measured directly from its absorbance and the rate expression in eq 2 also was valid.

Table I. Molar Absorptivities Used in the Kinetics Studies

Species	λ, nm	ε, M^{-1} cm^{-1}	Species	λ, nm	ε, M^{-1} cm^{-1}
I_3^-	390	1.00×10^4	IO^-	350	53
	380	1.44×10^4		285	185
	352	2.64×10^4	$Ni(CN)_4^{2-}$	380	5.8×10
	285	4.0×10^4		352	2.16×10^2
I_2	390	115		285	4.63×10^3
	380	62		267	1.16×10^4
	352	20			
	285	100			

Results and Discussion

Iodine as a Scavenger for Cyanide Ion. The reaction between iodine and cyanide ion to form iodine monocyanide (eq 3) is thermodynamically very favorable, having an

$$I_2 + CN^- \overset{k_3}{\rightleftarrows} ICN + I^- \qquad (3)$$

equilibrium constant K_3 equal to $10^{8.8}$ according to Gauguin[15] or equal to $10^{9.3}$ from Smith's data.[9] The latter study of the HCN reaction (eq 4) gave $K_4 = 1.6$ *M* (at an ionic strength

$$I_2 + HCN \overset{k_4}{\rightleftarrows} ICN + I^- + H^+ \qquad (4)$$

of 0.20 *M*, 25.1°) and K_3 is calculated using a pK_a value of 9.1 for HCN. The rate constants for reactions 3 and 4 are $k_3K_a = 6.1$ sec^{-1} and $k_4 = 65$ M^{-1} sec^{-1}. If a pK_a value of 9.0 is used for HCN (taken from Anderegg's value[16] of 9.14 at 0.10 *M* $NaNO_3$ and 20° and corrected to 25° using $\Delta H° = 10.3$ kcal/mol[17]), a rate constant of 6.1×10^9 M^{-1} sec^{-1} is obtained for reaction 3. The reaction of triiodide ion with cyanide ion (eq 5) also is rapid ($k_5 = 10^9$ M^{-1} sec^{-1})[9] and the

$$I_3^- + CN^- \overset{k_5}{\rightleftarrows} ICN + 2I^- \qquad (5)$$

iodine–triiodide equilibrium (eq 6) is rapidly established

$$I_2 + I^- \overset{k_6}{\rightleftarrows} I_3^- \qquad (6)$$

with k_6 equal to 2×10^9 M^{-1} sec^{-1}.[18] Thus, iodine is capable of rapidly scavenging cyanide ion and of reducing its concentration to a sufficiently low level to permit the complete dissociation of $Ni(CN)_4^{2-}$.

In the present work it was necessary to have a scavenger

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for CN^- at high pH, where iodine is hydrolyzed. The equilibrium constant for the formation of hypoiodous acid (eq 7)

$$I_2 + H_2O \underset{k_{-7}}{\overset{k_7}{\rightleftarrows}} HOI + H^+ + I^- \qquad (7)$$

has been measured and two values have been reported for K_7 at 25.0° and an ionic strength of 0.01 *M*: 5.4×10^{-13} M^2 [19] and 4.5×10^{-13} M^2.[13] The equilibrium constant K_8 for the reaction with hydroxide ion (eq 8) has a value of

$$I_2 + OH^- \rightleftarrows HOI + I^- \qquad (8)$$

50 at 20° and an ionic strength of 0.1 *M*. The kinetics of reaction 7 have been studied by Eigen and Kustin[20] by relaxation methods, and they gave a value of 3.0 sec^{-1} for the forward rate constant, k_7, and a value of 4.4×10^{12} M^{-2} sec^{-1} for the reverse rate constant, k_{-7}. Chia[11] reported a value of $K_9 = 196$ for the base hydrolysis of I_3^- (eq 9) to

$$I_3^- + 2OH^- \rightleftarrows IO^- + 2I^- + 2H_2O \qquad (9)$$

form hypoiodite ion and a pK_a value of 10.64 for HOI. In the present study the I^- concentration was usually 4×10^{-4} *M* which gave a crossover between total iodine ($I_2 + I_3^-$) and HOI (observed by the large spectral changes) in the vicinity of pH 9.

The direct reaction between hypoiodite ion and cyanide ion (eq 10) has not been studied previously, but the equilibrium constant, K_{10}, calculated from the above data has a value of 2×10^4 to 2×10^5 *M*, depending upon which of the other constants are chosen. We examined reaction 10 by stopped-flow methods using equal concentrations of reactants (from 5×10^{-5} to 5×10^{-4} *M*) at pH 11.8, 25.0°, with an ionic strength of 0.01-0.1 *M* $NaClO_4$. In all instances there were very rapid absorbance changes and the reactions were too fast to measure indicating that k_{10} is greater than 10^7 M^{-1} sec^{-1}. We have not proved that the product of the reaction between IO^- and CN^- is ICN but the spectral changes support this assumption and the reaction products are very rapidly reconverted to iodine and HCN when the solution is acidified. Furthermore, in the presence of hypoiodite ion the CN^- concentration level is sufficiently reduced to cause the dissociation of $Ni(CN)_4^{2-}$, in agreement with the estimated values for K_{10}.

$$IO^- + CN^- + H_2O \overset{k_{10}}{\rightleftarrows} ICN + 2OH^- \qquad (10)$$

The disproportionation of hypoiodite ion (eq 11) is of concern when iodine is used in basic solutions. The kinetics of this reaction have been studied extensively in highly alkaline solutions.[21-24] The rate law proposed by Li and White[23] is given in eq 12 (M^{-1} sec^{-1}) and we extended and confirmed

$$3IO^- \rightarrow IO_3^- + 2I^- \qquad (11)$$

$$-d[IO^-]/dt = 0.05[IO^-]^2 + 1.7[IO^-]^2[I^-]/[OH^-] \qquad (12)$$

this rate expression at pH 12 using 10^{-4} to 10^{-3} *M* initial hypoiodite and 3×10^{-4} to 3×10^{-3} *M* I^- at 25°. The rate of disproportionation of the hypoiodite ion is slow compared to the ligand substitution reactions of $Ni(CN)_4^{2-}$ and does not interfere when hypoiodite ion is used as a scavenger for cyanide ion. However, in the absence of ligand catalysts for $Ni(CN)_4^{2-}$ at high pH (*i.e.*, pH 12) the disproportionation rate can become significant.

Kinetics of Dissociation of $Ni(CN)_4^{2-}$ in the Presence and Absence of Iodine. The reaction of iodine with $Ni(CN)_4^{2-}$ was investigated in both acidic and basic solutions. The overall stoichiometry of the reaction, given by eq 13 (neglecting triiodide and hydrolyzed species), was confirmed by spectral measurements. Each reaction rate observed was first order in $Ni(CN)_4^{2-}$ concentration and independent of the I_2 concentration. Table II gives the observed first-order rate constant (eq 2) from pH 2.5 to 8.0 with variable $[I_2]_T$ and $[I^-]_T$ (=$[I^-] + [I_3^-]$). When the $Ni(CN)_4^{2-}$ was in stoichiometric excess, all of the iodine was consumed. At the lower pH values the $Ni(CN)_4^{2-}$ complex will tend to dissociate due to HCN formation.[1] The HCN must be converted to ICN in order to follow the reaction by the disappearance of I_3^-. Under the conditions given in Table II, the [ICN]/[HCN] ratio using eq 4 and 6 is always greater than 50 and becomes as large as 10^7. The k_{obsd} values are approximately constant and equal to 4.8×10^{-4} sec^{-1} from pH 3.3 to 8.0. A dependence on the hydrogen ion concentration is observed below pH 3 (Figure 1) and therefore these data are not used in calculating the average value for k_{obsd}.

$$Ni(CN)_4^{2-} + 4I_2 \rightarrow Ni^{2+} + 4ICN + 4I^- \qquad (13)$$

No dependence on iodine or iodide ion concentration is observed. The rapid formation of a strong 1:1 complex between $Ni(CN)_4^{2-}$ and I_2 or I_3^- could explain the kinetics; however, this can be ruled out because a formation constant greater than 10^5 M^{-1} would be required. In concentrated cyanide ion solutions $Ni(CN)_4^{2-}$ will add a fifth cyanide to form $Ni(CN)_5^{3-}$, but the formation constant is very small (0.2-1.1 M^{-1}, 23 and 25°, ionic strength 1-4 *M*).[25-29] Weak 1:1 complexes are formed with SCN^-, I^-, and Br^- [25,28] but high ligand (X^-) concentrations are required to give the $Ni(CN)_4X^{3-}$ complexes. There are no spectral shifts of the I_2 absorption band when it is mixed with $Ni(CN)_4^{2-}$ or with excess concentrations of $Pd(CN)_4^{2-}$ or $Co(CN)_6^{3-}$.[30] Therefore I_2 does appear to react as either a nucleophile or an electrophile with the metal-cyanide complexes. The I_2 concentrations in the present study are below 10^{-4} *M* in many cases and the formation of appreciable concentrations of a 1:1 complex between iodine and $Ni(CN)_4^{2-}$ is extremely unlikely.

The zero-order dependence in iodine observed in individual reactions suggests that the iodine is behaving as a scavenger for CN^- and HCN after the dissociation of $Ni(CN)_4^{2-}$ in accord with eq 14-16. If the value of $k_3'[I_2]_T$ is large com-

$$Ni(CN)_4^{2-} \underset{k_{34}}{\overset{k_{43}}{\rightleftarrows}} Ni(CN)_3^- + CN_T \qquad (14)$$

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Table II. Observed Rate Constants for the Dissociation of $Ni(CN)_4^{2-}$ in the Presence of Iodine at 25.0°

pH	$10^5 \times$ $[Ni(CN)_4^{2-}]$, *M*	$10^4 \times$ $[I_2]_T$, *M*	$10^4[I^-]_T$, *M*	$10^4 k_{obsd}$,[a] sec^{-1}
2.47	3.47	0.99	4.35	4.67 ± 0.03[b]
2.63	3.44	9.06	34.8	6.13 ± 0.04[b]
3.33	3.40	1.02	4.2	5.24 ± 0.03[b]
5.21	3.47	0.97	4.2	4.95 ± 0.04[c]
5.70	3.14	3.00	4.0	4.58 ± 0.02[b]
6.10	3.14	3.00	4.0	4.69 ± 0.02[b]
6.23	3.37	1.02	10.4	4.69 ± 0.01[c]
6.40	3.14	3.00	4.0	4.96 ± 0.02[b]
6.43	3.22	0.35	4.2	4.76 ± 0.07[c]
6.81	3.44	0.97	102	4.5± 0.2[c]
6.89	3.47	1.01	4.2	5.06 ± 0.01[c]
6.97	3.47	0.39	4.2	4.68 ± 0.06[c]
7.98	3.45	1.00	4.2	5.15 ± 0.02[c]

[a] The standard deviations given for individual runs. The average for all runs above pH 3 is (4.8 ± 0.2) × 10^{-4} sec^{-1}. [b] $\mu = 0.1$ *M*. [c] $\mu = 0.01$ *M*.

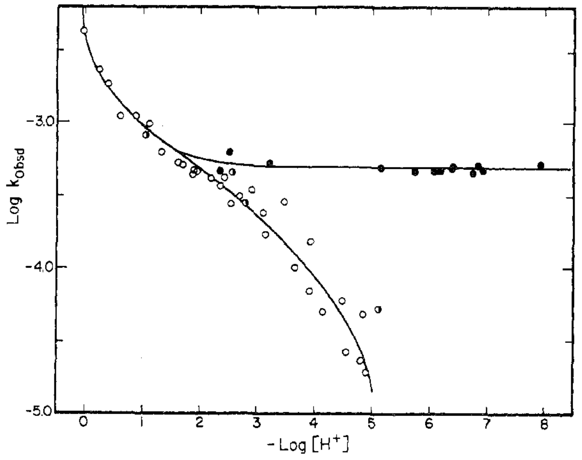

Figure 1. Plot of the observed rate constants for the dissociation of $Ni(CN)_4^{2-}$ in the presence and absence of iodine as a function of hydrogen ion concentration at 25.0°: iodine present as scavenger for cyanide (●); no scavenger present, this work (◑) and ref 1 (○).

$$Ni(CN)_3^- \underset{k_{03}}{\overset{k_{30}}{\rightleftarrows}} Ni^{2+} + 3CN_T \tag{15}$$

$$CN_T + [I_2]_T \xrightarrow{k_3'} ICN + I^- \tag{16}$$

pared to the value of $k_{34}[Ni(CN)_3^-]$, then k_{obsd} is equal to k_{43} (provided that k_{30} is greater than k_{43}). The concentration of CN_T will be very small because of the I_2 reaction.

The lack of pH dependence for k_{obsd} was a surprise in view of earlier studies[1] where acid had been used to force the dissociation of $Ni(CN)_4^{2-}$. Figure 1 compares the dissociation rate constants found in the presence and absence of iodine. The iodine method of following the reaction was not possible below pH 2 because of the requirement that [ICN]/[HCN] be large. Near pH 2 the same rate constants are found by the two methods, but above pH 2 the dissociation rate constant in the presence of iodine is much faster. Most of the acid dissociation rate constants in Figure 1 were taken from the work of Kolski and Margerum[1] but four additional runs were made (Table III) in an attempt to minimize the effect of the overall reaction reversibility on the evaluation of the rate constants. Initial rates were used in these runs to determine k_{obsd} but the rate plot for run 4 in Table III appears to be affected by the reversibility of the system even in the first 2% of the reaction.

Table III. Observed First-Order Rate Constants for the Acid Dissociation of $[Ni(CN)_4^{2-}]$ (No I_2) at 25.0°, $\mu = 0.1$ *M*

Run	pH	$10^5 \times$ $[Ni(CN)_4^{2-}]$, *M*	% reacn used for 1st-order plots	$10^4 k_{obsd}$,[a] sec^{-1}
1	1.17	0.460	90	8.10 ± 0.01[b]
2	2.69	0.460	45	4.49 ± 0.01[b,c]
3	2.88	2.08	18	2.73 ± 0.05[d]
4	5.22	3.46	2	0.53[d,e]

[a] The standard deviations given are for individual runs. [b] At 267 nm. [c] $\mu = 0.15$ *M*. [d] At 285 nm. [e] At 0.01 *M* (HOAc + NaOAc).

The difference between the rate constants measured in the presence and absence of iodine must be due to iodine reacting at an earlier stage in the dissociation mechanism than is the case for the acid dissociation. One possibility is that in the latter case the loss of $Ni(CN)_3^-$ is the rate-determining step above pH 2 whereas the dissociation of $Ni(CN)_4^{2-}$ itself is measured by the reaction in the presence of iodine.

A dissociation rate constant, k_d, is defined for the acid dissociation reactions in the absence of iodine from eq 17. A

$$-d[Ni(CN)_4^{2-}]/dt = k_d[Ni(CN)_4^{2-}] \quad (\text{no } I_2) \tag{17}$$

steady-state approximation in $Ni(CN)_3^-$ using eq 14 and 15 leads to eq 18 where the individual rate constants k_{43}, k_{34},

$$k_d = \frac{k_{43}k_{30}}{k_{34}[CN_T] + k_{30}} \tag{18}$$

and k_{30} may vary with acidity. In order for k_d to become much smaller than k_{43} above pH 2 it is necessary for $k_{34} \cdot [CN_T]$ to become much greater than k_{30}. Thus, at pH 5 the rate expression for the dissociation is given by eq 19

$$-\frac{d[Ni(CN)_4^{2-}]}{dt} = k'\frac{[Ni(CN)_4^{2-}]}{[CN_T]} \tag{19}$$

where $k' = k_{43}k_{30}/k_{34}$. Integrating this expression gives eq 20 where x is $[Ni(CN)_4^{2-}]$ at any time, a is $[Ni(CN)_4^{2-}]_{initial}$,

$$4x - (b + 4a)\ln x = k't + 4a - (b + 4a)\ln a \tag{20}$$

and b is $[CN_T]_{initial}$. Under the conditions used for run 4 in the acid dissociation reactions, $b \ll 4a$ and eq 20 can be simplified to eq 21. Figure 2 is a plot of run 4 using eq 21

$$x - a(\ln x) = (k'/4)t + a - a(\ln a) \tag{21}$$

and gives an excellent fit for the period of time the reaction was followed (22% completion). The value of k' is 1.4 × 10^{-10} *M* sec^{-1} and assigning a value of 5 × 10^{-4} sec^{-1} to k_{43} (from the I_2 studies) gives k_{30}/k_{34} = 2.8 × 10^{-7} *M* at pH 5.2. The postulate used to give eq 19 was that $k_{34}[CN_T] \gg$ 2.8 × 10^{-7} *M* for this situation. This postulate is satisfied when 2% of the $Ni(CN)_4^{2-}$ is dissociated. The rate constants also predict that the initial rate method is not suitable to determine k_{43} at this pH in the absence of iodine as a scavenger. Therefore the lower curve in Figure 1 does not give k_{43}, but rather is a composite of constants as given in eq 18. This is the reason that above pH 3 there is no pH dependence for the dissociation rate constant in the presence of iodine while there is a pH dependence in the absence of iodine.

The conditions used for run 3 had an appreciable level of CN_T (b = 5.04 × 10^{-5} *M*) before the rate data were collected. These data are recalculated using eq 20 and are plotted in Figure 3. An excellent fit was obtained for the period the reaction was followed (54% completion) and gave a k' value of 1.88 × 10^{-8} *M* sec^{-1} and a k_{30}/k_{34} ratio of 3.8 × 10^{-5} *M*

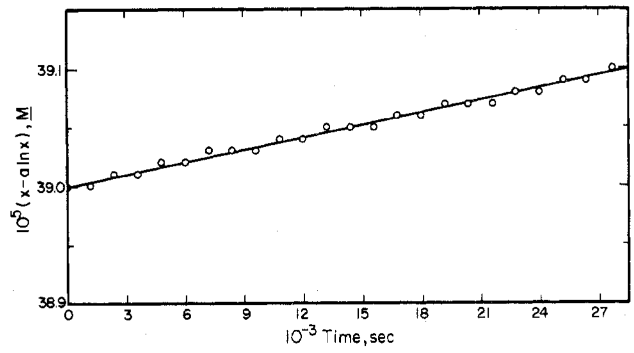

Figure 2. Rate plot of run 4 of Table III using eq 21.

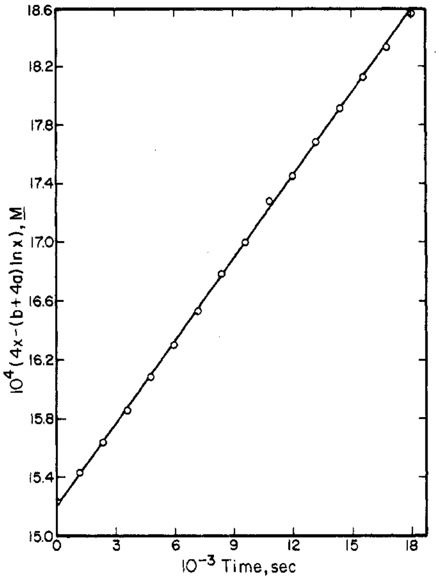

Figure 3. Rate plot of run 3 of Table III using eq 20.

at pH 2.88. The k_{30}/k_{34} ratio increased with hydrogen ion concentration. This would be expected because k_{34} would decrease with acidity if the actual reactant for the k_{34} step were CN^- rather than CN_T. It is also possible for k_{30} to increase with acidity in this pH range (2.8-5.2). Although k_{43} is apparently not affected by $[H^+]$ above pH 3, it definitely increases below pH 2 (see Figure 1) and the k_d value becomes equal to k_{43} because $k_{30} >> k_{34}[CN_T]$. Simple first-order rate plots are obtained for the dissociation rates below pH 2 (even in the absence of iodine).

Kinetics of the Dissociation of $Ni(CN)_4^{2-}$ in the Presence of Hypoiodite Ion. The observed dissociation rate constant of $Ni(CN)_4^{2-}$ is somewhat larger at pH 12 in the presence of hypoiodite ion than in the presence of iodine and equals 1.7×10^{-3} sec^{-1} for 10^{-4} *M* IO^- concentration. The apparent rate constant increases at higher IO^- concentration as the rate of disproportionation of IO^- to IO_3^- becomes significant. The two concurrent reactions (eq 22 and 23) could

$$Ni(CN)_4^{2-} + 4IO^- + 4H_2O \rightarrow Ni^{2+} + 4ICN + 8OH^- \qquad (22)$$

$$2IO^- \rightleftarrows IO_2^- + I^- \xrightarrow{+IO^-} IO_3^- \qquad (23)$$

not be differentiated because both IO^- and $Ni(CN)_4^{2-}$ absorb at 285 nm so that k_{obsd} is actually the sum of two rate constants and the increase in k_{obsd} may be due to this rather than to an IO^- reaction with $Ni(CN)_4^{2-}$.

Kinetics of the Substitution Reactions of Ethylenediamine, Substituted Ethylenediamines, Glycinate Ion, and Ammonia with $Ni(CN)_4^{2-}$ Utilizing Iodine as Scavenger for Cyanide. In the reaction of $Ni(CN)_4^{2-}$ with ammonia, the diamines, and glycinate ion, reversibility is removed by use of iodine as scavenger for cyanide ion. The reaction with iodine is not only much faster than the dissociation of $Ni(CN)_4^{2-}$, but it also is faster than the substitution reactions of interest. The values of the observed rate constants and the corresponding second-order rate constants for the substitution reactions of ethylenediamine, methyl-substituted ethylenediamines, 1,2-diaminopropane (pn), 1,3-diaminopropane (trimethylenediamine, tn), ammonia, and glycinate ion with $Ni(CN)_4^{2-}$ (eq 24) appear in Table IV. In the presence of iodine the

$$Ni(CN)_4^{2-} + L \overset{k_{11}}{\rightleftarrows} NiL(CN)_{4-x} + xCN^- \qquad (24)$$

subsequent breakup of $NiL(CN)_{4-x}$ is rapid. The first-order k_{obsd} values for the dissociation of $Ni(CN)_4^{2-}$ increase by factors of 10^4-10^5 in the presence of the various ligands (L) and the dissociation rates have a first-order dependence on L. Thus, nucleophilic attack by these ligands on $Ni(CN)_4^{2-}$ greatly accelerates the release of CN^-. Although ammonia is a much poorer catalyst than ethylenediamine for the reaction of $Ni(CN)_4^{2-}$ with $EDTA^{4-}$,[5] it is almost as good a nucleophile as en in the present case. The different behavior is due to the great importance of removing the released cyanide ion which can suppress the EDTA reaction. The conclusion is that chelation is not critical in the initial nucleophilic attack of amines on $Ni(CN)_4^{2-}$ and that ammonia accelerates the release of CN^- from the nickel ion almost as effectively as the polyamines. Chelation is important if CN^- is not scavenged, but the earlier postulate[5] that the reaction of polyamines and $Ni(CN)_4^{2-}$ proceeds through a six-coordinate transition state, with chelation of the polyamine occurring as the first CN^- is released, is no longer necessary. A five-coordinate transition state with only one amine group entering the nickel coordination sphere before or during the loss of CN^- is adequate to explain the kinetic behavior. The k_{11} values do vary somewhat with the nature of the amine. The smaller value for the glycinate ion can be attributed to electrostatic repulsion. There is a fivefold increase in k_{11} for trimethylenediamine (tn) compared to ammonia but some of the other diamines do not react much faster than ammonia. These variations are interesting but they cannot be assigned to a kinetic chelate effect and are probably due to a combination of other factors including changes in outer-sphere association, basicity, and possibly some steric hindrance.

The ammonia substitution reaction with $Ni(CN)_4^{2-}$ cannot be observed without iodine or another scavenger. On the other hand, it is possible to displace cyanide ion from nickel ion with excess ethylenediamine or excess glycine. The direct displacement reaction with triethylenetetramine is relatively straightforward[5] but the corresponding reactions with glycinate ion and ethylenediamine have complex kinetics with evidence of several reaction steps. In order to confirm the results for the ethylenediamine reaction in the presence of iodine, the reaction also was studied using only the diamine to cause the dissociation of $Ni(CN)_4^{2-}$.

Reactions between Ethylenediamine and $Ni(CN)_4^{2-}$ in the Absence of Iodine. Two rates are observed when excess ethylenediamine reacts with $Ni(CN)_4^{2-}$. The faster reaction corresponds to the rate expected from the studies using iodine while the slower reaction is in accord with the previously reported rate constant of 50 M^{-1} sec^{-1} for ethylenediamine.[5] Nevertheless the ultraviolet spectral changes show that both reactions are measuring the disappearance of $Ni(CN)_4^{2-}$.

Table IV. Rate Constants for the Reaction of L with $\mathrm{Ni(CN)_4^{2-}}$ Utilizing I_2 as Scavenger for $\mathrm{CN^-}$ at $[\mathrm{Ni(CN)_4^{2-}}]_i = 3.47 \times 10^{-5}$ M, $[I_2]_{Ti} = (1.0\text{–}1.2) \times 10^{-4}$ M, pH 11.91 ± 0.09, 25.0 ± 0.1°, $\mu = 0.10$ M ($\mathrm{NaClO_4}$), and λ 285 nm

L	[L], M	k_{obsd}, $\mathrm{sec^{-1}}$	k_{11}, M^{-1} $\mathrm{sec^{-1}}$
en	5.00×10^{-2}	21.3 ± 0.2	426
en	5.00×10^{-3}	2.16 ± 0.04	432
en	5.00×10^{-3}	2.11 ± 0.04	422
pn	9.60×10^{-2}	19.5 ± 0.4	203
pn	4.80×10^{-2}	10.0 ± 0.2	208
tn	7.5×10^{-2}	44 ± 3	590
N-Meen	5.00×10^{-2}	10.3 ± 0.3	206
N,N-diMeen	2.52×10^{-1}	27.0 ± 0.3	107
N,N-diMeen	5.04×10^{-2}	6.96 ± 0.05	138
N,N'-diMeen	6.6×10^{-2}	9 ± 1	140
NH_3	2.5×10^{-1}	30 ± 1	120
NH_3	2.5×10^{-1}	29 ± 1	120
NH_3	2.5×10^{-1}	29 ± 1	120
NH_3	1.08×10^{-1}	13.0 ± 0.1	120
$\mathrm{gly^-}$	5.00×10^{-2}	2.71 ± 0.03	54.2

Initial rate methods were employed to evaluate the rate constant for the first reaction. The observed values for the initial first-order rate constant, k_i, are given in Table V and $k_i/[\mathrm{en}]$ gives an average value for k_{11} equal to 423 M^{-1} $\mathrm{sec^{-1}}$ which is consistent with the studies where iodine is present. Above 0.1 M en the reactions are so fast that it is difficult to measure the initial rate without interference from the second reaction (or from the released $\mathrm{CN^-}$) and these data are not used in the average value for k_{11}.

The agreement of the two sets of k_{11} values (with and without I_2) indicates that $\mathrm{CN^-}$ is being released in the initial reaction with excess en just as it is with lower en concentrations in the presence of iodine. This was further confirmed by the use of a cyanide ion electrode in conjunction with ultraviolet spectral scans which showed that the initial rapid loss of absorbance on the addition of ethylenediamine was accompanied by a rapid increase in $\mathrm{CN^-}$ concentration. Furthermore, if extra $\mathrm{CN^-}$ ($>5 \times 10^{-4}$ M) is first added to $\mathrm{Ni(CN)_4^{2-}}$, then the addition of en has no effect on the spectrum indicating that there is no $\mathrm{Ni(CN)_4(en)^{2-}}$ mixed complex. Other spectral studies[31] have shown no evidence of mixed en and $\mathrm{CN^-}$ complexes such as $\mathrm{Ni(en)(CN)_2}$ or $\mathrm{Ni(en)_2(CN)_2}$ in equilibrium mixtures, but, of course, they could be present as transient kinetic species. Although two distinct rate processes appear to be present in the reaction of en with $\mathrm{Ni(CN)_4^{2-}}$, the absorbance changes for both reactions are caused by the disappearance of $\mathrm{Ni(CN)_4^{2-}}$. This was confirmed by observing the reactions at the absorbance peaks of $\mathrm{Ni(CN)_4^{2-}}$ (310, 285, and 267 nm) and at the absorbance minima between these peaks. Hence, $\mathrm{Ni(CN)_4^{2-}}$ could be serving as an indicator for the second reaction. The addition of small amounts of free $\mathrm{CN^-}$ eliminates the faster reaction but not the slower reaction while larger amounts of free $\mathrm{CN^-}$ prevent both reactions from occurring.

A puzzling aspect of the kinetics for the slower reaction is that good first-order rate plots are obtained for sizable portions of the reaction. The continued release of $\mathrm{CN^-}$ from the breakup of $\mathrm{Ni(CN)_4^{2-}}$ would be expected to suppress the second rate as well as the first if the reaction sequence involved any of the steps (25)–(29). The extent of

$$\mathrm{Ni(CN)_4^{2-}} + \mathrm{en} \underset{k_{-11}}{\overset{k_{11}}{\rightleftharpoons}} \mathrm{Ni(en)(CN)_3^-} + \mathrm{CN^-} \tag{25}$$

$$\mathrm{Ni(en)(CN)_3^-} \overset{k_{22}}{\rightleftharpoons} \mathrm{Ni(en)(CN)_2} + \mathrm{CN^-} \tag{26}$$

Table V. Initial Rate Data for the $\mathrm{Ni(CN)_4^{2-}}$ Reaction with Ethylenediamine, at $[\mathrm{Ni(CN)_4^{2-}}]_i = 5.0 \times 10^{-6}$ M, 25.0 ± 0.1°, pH 11.96 ± 0.05, $\mu = 0.10$ M ($\mathrm{NaClO_4}$), and λ 267 nm

[en], M	k_i, $\mathrm{sec^{-1}}$	k_{11}, M^{-1} $\mathrm{sec^{-1}}$	[en], M	k_i, $\mathrm{sec^{-1}}$	k_{11}, M^{-1} $\mathrm{sec^{-1}}$
5.00×10^{-3}	2.0 ± 0.1	400	5.00×10^{-2}	22 ± 2	440
1.00×10^{-2}	4.3 ± 0.1	430	0.100	44 ± 2	440
1.00×10^{-2}	4.1 ± 0.2	410	0.200	74 ± 2	370
2.00×10^{-2}	8.4 ± 0.1	420	0.400	125 ± 3	312
2.00×10^{-2}	8.4 ± 0.1	420			

Table VI. Observed First-Order and Resolved Second-Order Rate Constants for the Second Step in the Reaction of $\mathrm{Ni(CN)_4^{2-}}$ with Ethylenediamine at $[\mathrm{Ni(CN)_4^{2-}}] = 9.8 \times 10^{-6}$ M, 25.0 ± 0.1°, $\mu = 0.50$ M ($\mathrm{NaClO_4}$), and λ 267.5 nm

$[\mathrm{en}]_T$, M	[en],[a] M	pH	k_{obsd}, $\mathrm{sec^{-1}}$	k,[b] M^{-1} $\mathrm{sec^{-1}}$
0.160	0.123	10.51	5.21 ± 0.08	42.4
0.160	0.145	10.99	6.68 ± 0.10	46.1[c]
0.160	0.154	11.40	7.21 ± 0.03	46.8
0.202	0.157	10.54	7.41 ± 0.07	47.2
0.202	0.185	11.03	9.44 ± 0.05	51.0
0.202	0.194	11.38	10.64 ± 0.05	54.8
0.319	0.294	11.05	16.7 ± 0.3	56.8

[a] $[\mathrm{en}]_T$ corrected for pH using log $K_{\mathrm{Hen}} = 9.98$: A. Vacca and D. Arenare, *J. Phys. Chem.*, 71, 1495 (1967); P. Paoletti, R. Barbucci, A. Vacca, and A. Dei, *J. Chem. Soc. A*, 319 (1971). [b] $k = k_{\mathrm{obsd}}/[\mathrm{en}]$. [c] One of the runs under these conditions is plotted in Figures 4 and 5.

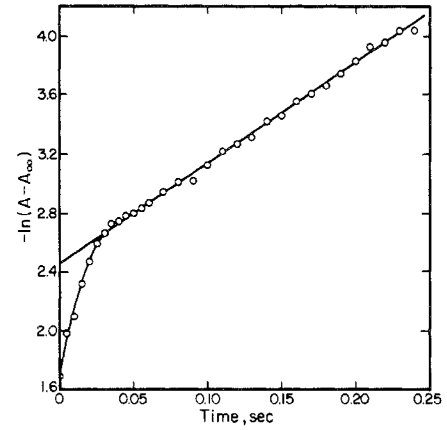

Figure 4. Pseudo-first-order rate plot for the slower reaction between ethylenediamine and $\mathrm{Ni(CN)_4^{2-}}$, indicating the presence of two reactions (Table VI).

$$\mathrm{Ni(en)(CN)_2} + \mathrm{en} \rightleftharpoons \mathrm{Ni(en)_2(CN)_2} \tag{27}$$

$$\mathrm{Ni(en)_2(CN)_2} \rightleftharpoons \mathrm{Ni(en)_2CN^+} + \mathrm{CN^-} \tag{28}$$

$$\mathrm{Ni(en)_2CN^+} + \mathrm{en} \rightleftharpoons \mathrm{Ni(en)_3^{2+}} + \mathrm{CN^-} \tag{29}$$

the absorbance change for the fast reaction was measured as a function of en concentration and $\mathrm{CN^-}$ concentration and this suggests that species such as $\mathrm{Ni(en)(CN)_2}$, present in appreciable concentrations, are reacting in the slower reaction. A preequilibration with $\mathrm{Ni(CN)_4^{2-}}$ will permit the latter to act as an indicator for the reaction, but any $\mathrm{CN^-}$ released should cause the slower reaction to deviate from a first-order dependence in $\mathrm{Ni(CN)_4^{2-}}$. It may be that some of the intermediate mixed complexes are strong enough to act as $\mathrm{CN^-}$ buffers and that this helps to maintain an approximately constant $\mathrm{CN^-}$ concentration during the slower reaction. Figure 4 shows a first-order plot of the second reaction and Table VI gives the observed rate constants as a function of the en concentration. The second reaction depends on the en concentration and gives a second-order rate constant in the vicinity of 50 M^{-1} $\mathrm{sec^{-1}}$, but there is a noticeable trend to-

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(31) S. Kida, *Bull. Chem. Soc. Jap.*, 32, 981 (1959).

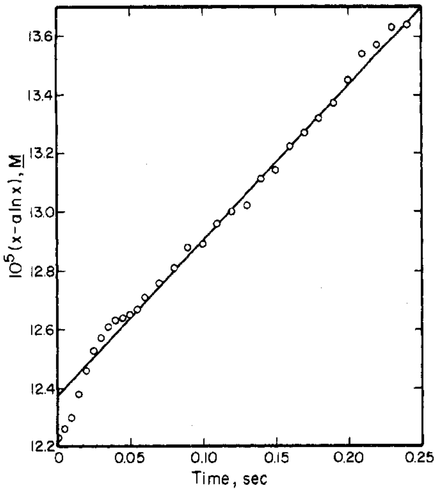

Figure 5. Rate plot for the same reaction given in Figure 4 using eq 32, where CN^- suppresses the rate.

ward larger values as the free en concentration increases.

A second explanation for the kinetics observed is that the slower reaction is actually the cyanide suppression of the faster reaction (k_{11}). Initially en reacts with $Ni(CN)_4^{2-}$ to form product, but as the reaction proceeds, there is an appreciable buildup of CN^- which suppresses the faster reaction. The overall observed rate of the reaction is significantly reduced and it is observed kinetically as the second reaction. The CN^- suppression operates through the series of reactions given by eq 26-29. A steady-state approximation in $Ni(en)(CN)_3^-$ using eq 25 and 26 leads to eq 30. As the cyanide

$$-\frac{d[Ni(CN)_4^{2-}]}{dt} = \frac{k_{11}k_{22}[en][Ni(CN)_4^{2-}]}{k_{22} + k_{-11}[CN^-]} \tag{30}$$

concentration builds up, $k_{-11}[CN^-]$ is assumed to become greater than k_{22} so that eq 30 reduces to eq 31, where $k'' = k_{11}k_{22}[en]/k_{-11}$.

$$-dx/dt = k''x/2(a - x) \tag{31}$$

Figure 5, a plot of the integrated form of this expression (eq 32) [where x is $[Ni(CN)_4^{2-}]$, a is $[Ni(CN)_4^{2-}]_i$, and $2(a - x)$ is $[CN^-]$], is also linear for the same portion of the reaction as is Figure 4 (same run). The initial curvature observed in Figure 5 would be expected due to the fact that $k_{-11}[CN^-]$ is not greater than k_{22} until an appreciable quantity of CN^- is present. Note that this derivation also assumes that only two CN^- are released during the observed reaction. An average value of $(1.7 \pm 0.3) \times 10^{-6}\ M^{-1}$ is obtained for the k_{22}/k_{-11} ratio for the runs in Table VI.

$$x - a(\ln x) = \frac{k''t}{2} + a(1 - \ln a) \tag{32}$$

More study would be needed to resolve the exact reaction pathway but the results prove that the initial rate of reaction of en with $Ni(CN)_4^{2-}$ is the same in the presence and absence of iodine. Furthermore, because the iodine reaction fails to detect a second reaction, it is clear that the slower reaction is related to the released CN^-. Thus, the reaction in eq 27 cannot be slower than the reaction in eq 25 but the rate process could be slower in the presence of CN^-.

Table VII. Summary of Second-Order Rate Constants Measured for the Reaction between L and $Ni(CN)_4^{2-}$ at 25.0°

L	k_{11}, M^{-1} sec^{-1}	L	k_{11}, M^{-1} sec^{-1}
trien	310^{a,b}	tn	590^{d}
Htrien$^+$	295^{a,b}	*N*-Meen	206^{d}
H_2trien^{2+}	14^{a,b}	*N,N'*-diMeen	140^{d}
en	423^{b,c}	*N,N*-diMeen	125^{d}
en	427^{d}	NH_3	120^{d}
pn	206^{d}	gly$^-$	54^{d}

[a] Reference 5. [b] Measured in the absence of iodine. [c] From initial rate data. [d] Measured in the presence of iodine.

Conclusions

Iodine and hypoiodite ion can be used as scavengers for cyanide ion in order to measure the dissociation rate constant of $Ni(CN)_4^{2-}$, giving $k_{43} = 4.8 \times 10^{-4}$ sec^{-1}. The dissociation rate is independent of acidity above pH 3, but the loss of cyanide ion is greatly accelerated by amine ligands. Second-order rate constants for these ligands are summarized in Table VII. Ammonia is somewhat less effective as a nucleophile than ethylenediamine or trimethylenediamine but its reactivity is of the same order of magnitude when iodine is the scavenger for CN^-, while this was not the case when EDTA was used as the scavenger for nickel ion. As a result it is concluded that chelation by the incoming nucleophile is not necessary to displace rapidly a cyanide ion from $Ni(CN)_4^{2-}$ and that this complex undergoes substitution reactions with five-coordinate transition states.

The acid dissociation kinetics of $Ni(CN)_4^{2-}$ (in the absence of iodine) has the first CN^- (or HCN) loss as the rate-determining step below pH 2 but above pH 2 and with increasing $[CN_T]$ the rate-determining step tends to shift to the breakup of $Ni(CN)_3^-$. If this is the case, then the kinetics of formation of $Ni(CN)_4^{2-}$ should have no more than third-order dependence in $[CN_T]$ above pH 2 rather than a fourth-order dependence.[1] It is sometimes difficult to distinguish between higher orders of rate dependence and this is under additional study.

Acknowledgments. This investigation was supported by a David Ross Grant (W. C. C.) from the Purdue Research Foundation and by National Science Foundation Grant GP 14781 X. The assistance of Dr. D. A. Bennett in obtaining some of the results in Table II is appreciated.

Registry No. $Ni(CN)_4^{2-}$, 15453-80-2; I_2, 7553-56-2; IO^-, 15065-65-3; en, 107-15-3; pn, 78-90-0; tn, 109-76-2; *N*-Meen, 109-81-9; *N,N*-diMeen, 108-00-9; *N,N'*-diMeen, 110-70-3; NH_3, 7664-41-7; gly, 56-40-6.