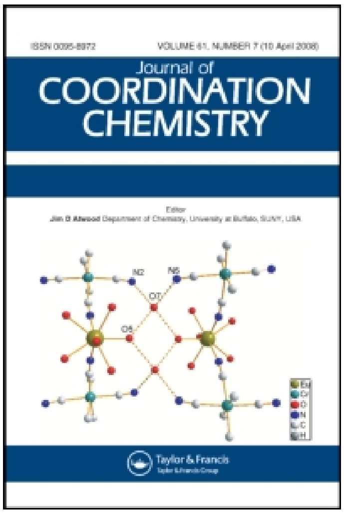

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KINETICS OF THE REACTION BETWEEN CYANIDE AND N,N′-ETHYLENEDIAMINEDISUCCINATONICKEL(II)

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Fourth order kinetics are observed in rate of formation of $Ni(CN)_4^{2-}$ from *N,N′*-ethylenediaminedisuccinatonickel (II), ($NiEDDS^{2-}$). The reaction is first order in $NiEDDS^{2-}$ and third order in total cyanide ($CN^- + HCN$) over a $-\log[H^+]$ range of 7.5 to 11.0 The rate of formation of $Ni(CN)_4^{2-}$ is equal to $(K_1K_2k_{3,0}[CN^-]^3 + K_1K_2k_{2,1}[CN^-]^2[HCN])[NiEDDS^{2-}]$ where $K_1K_2k_{3,0} = 2.0 \times 10^7 M^{-3}\ sec^{-1}$ and $K_1K_2k_{2,1} = 1.1 \times 10^7 M^{-3}\ sec^{-1}$. The reverse reaction is first order in $Ni(CN)_4^{2-}$, first order in EDDS and inverse order in cyanide ion concentration, confirming the forward kinetics. The kinetic results indicate that all six donor sites of EDDS are coordinated to the nickel atom.

INTRODUTION

The complete displacement of ethylenediaminetetraacetate ion from nickel(II) by cyanide ion is slow and requires that three cyanide ions be present in the rate-determining step. The fourth cyanide then adds to form tetracyanonickelate(II).[1] A similar mechanism is also observed for the reactions of cyanide ion with monoiminodiacetate[2] and other mono(aminocarboxylate) complexes of nickel(II).[3] The rates of these reactions are very dependent upon the total cyanide concentration and inversely proportional to the stability of the aminocarboxylatenickel(II) complex.

The reactions of cyanide ion with aquonickel ion[4] and triethylenetetraminenickel(II)[5] are first order in nickel complex and fourth order in total cyanide. In these reactions both cyanide and hydrogen cyanide are reactants. Hydrogen cyanide also has been observed as a reactant in the formation of mixed cyanide-aminocarboxylate complexes of nickel(II).[6]

The present study examines the kinetics of the forward and reverse reactions of cyanide with *N,N′*-ethylenediaminedisuccinatonickel(II), ($NiEDDS^{2-}$).

$$NiEDDS^{2-} \times 4CN^- \rightleftharpoons Ni(CN)_4^{2-} + EDDS^{4-} \qquad (1)$$

EDDS is isoelectronic with EDTA and has two amine and four carboxylate donors. However, there are several major differences: EDDS has secondary rather than tertiary nitrogens and the carboxylate segments of EDDS may be divided into two groups, one of which forms five-membered chelate rings and the other forms six-membered chelate rings upon complexation.

The forward reaction is first order in $NiEDDS^{2-}$ and third order in total cyanide. There is kinetic evidence for the formation of weak mixed complexes and hydrogen cyanide is a reactant. The reverse reaction is first order in $Ni(CN)_4^{2-}$, $EDDS^{4-}$ and inversely proportional to the free cyanide concentration. These kinetic observations indicate that all six of the EDDS donors are coordinated to nickel(II) and that hydrogen cyanide reacts through a mechanism probably involving intramolecular proton-transfer.

EXPERIMENTAL SECTION

The tetraacid form of EDDS was prepared by a previously reported method.[7, 8] To avoid precipitation of a chloride salt the ligand was recrystallized by dissolving in sodium hydroxide solution and reprecipitating through the addition of nitric acid. Microanalysis and potentiometric titration agreed with the theoretical composition of the ligand. Potentiometric titration was used to standardize the EDDS stock solutions. Nickel(II) perchlorate stock solution was prepared from twice recrystallized $Ni(ClO_4)_2$ and standardized by EDTA titration.[9] Sodium cyanide solutions (0.1 *M*) were standardized by the argentimetric method.[10] Twice recrystallized sodium perchlorate was used for ionic strength control. Boric acid-sodium borate and tris(hydroxymethyl)aminomethane were used for hydrogen ion control in their respective buffer regions.

The rates of formation of $Ni(CN)_4{}^{2-}$ were measured spectrophotometrically at 267 nm ($\epsilon = 1.16 \times 10^4$ M^{-1} cm^{-1}) and 285 nm ($\epsilon = 4.63 \times 10^3$ M^{-1} cm^{-1}). A typical reaction involved the preparation of a solution 1×10^{-5} M in $NiEDDS^{2-}$, 0.10 M in $NaClO_4$ and of desired *p*H. A small volume of standard NaCN was added by syringe to the nickel complex solution. A Cary Model 14 spectrophotometer was used to record the absorbance values. The forward reactions were run in the presence of excess CN^- and all gave pseudo first-order rate plots. The reverse reactions were studied in a similar manner with $Ni(CN)_4{}^{2-}$ concentration about 1×10^{-5} M and EDDS in large excess. All reactions were at 25.0°C and the *p*H values were corrected to $-\log[H^+]$ by subtracting 0.11 from the *p*H reading.[11]

A pK_a value of 9.0 was used for HCN which was calculated from a value of 9.14[12] in 0.10 M ($NaNO_3$) and at 20°C with correction to 25.0° using $\Delta H = 10.3$ kcal/mole.[13] The value of pK_a for $H(EDDS)^{3-}$ is 10.3[14] in 0.10 M ($NaClO_4$) and at 25.0°C. This value was determined from potentiometric titration data using the $\bar{p}$ method.[15] All reported rate constants are the average of at least three kinetic runs.

RESULTS

Kinetics of the forward reaction

The forward reaction shown in Eq. 1 is first order in $NiEDDS^{2-}$ complex and third order in total cyanide,

$$\text{rate} = \frac{d[Ni(CN)_4{}^{2-}]}{dt} = k_f[NiEDDS^{2-}][CN_T]^3 \quad (2)$$

where $[CN_T] = [CN^-] + [HCN]$. With a sizeable excess of cyanide present pseudo-first order kinetics are observed and $k_{obs} = k_f[CN_T]^3$, Eq. 3.

$$\text{rate} = \frac{d[Ni(CN)_4{}^{2-}]}{dt} = k_{obs}[NiEDDS^{2-}] \quad (3)$$

TABLE I

Cyanide dependence on the observed forward rate constant, T = 25.0°, μ = 0.10 M ($NaClO_4$)

$[CN_T]$ $\times 10^4, M$	$[NiEDDS^{2-}]$ $\times 10^6, M$	$-\log[H^+]$	k_{obs}, sec^{-1}
8.04	9.61	10.53	7.86×10^{-3}
6.09	9.61	10.51	3.51×10^{-3}
4.08	9.61	10.56	9.96×10^{-4}
2.03	9.61	10.41	1.26×10^{-4}
4.08	4.80	10.55	9.12×10^{-4}

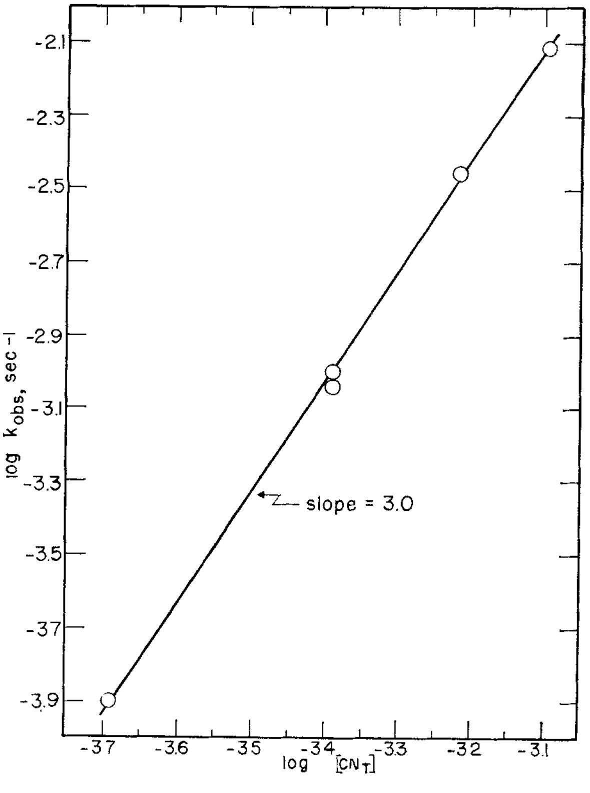

FIGURE 1 Order dependence of the observed first-order rate constant on total cyanide concentration. $-\log[H]^+ = 10.5 \pm .1$, $T = 25.0°$, $\mu = 0.1$ M($NaClO_4$), $[NiEDDS^{2-}] = (4.8\text{–}9.6) \times 10^{-6}$ M.

Table I lists the observed rate constants under varying concentrations of total cyanide and nickel complex. A plot of log k_{obs} as a function of log $[CN_T]$ is shown in Figure 1. The slope of this plot is 3.0. Numerous attempts to spectrophotometrically observe any mixed cyanide-$NiEDDS^{2-}$ complexes were unsuccessful, and it is concluded that the concetrations of such complexes must be

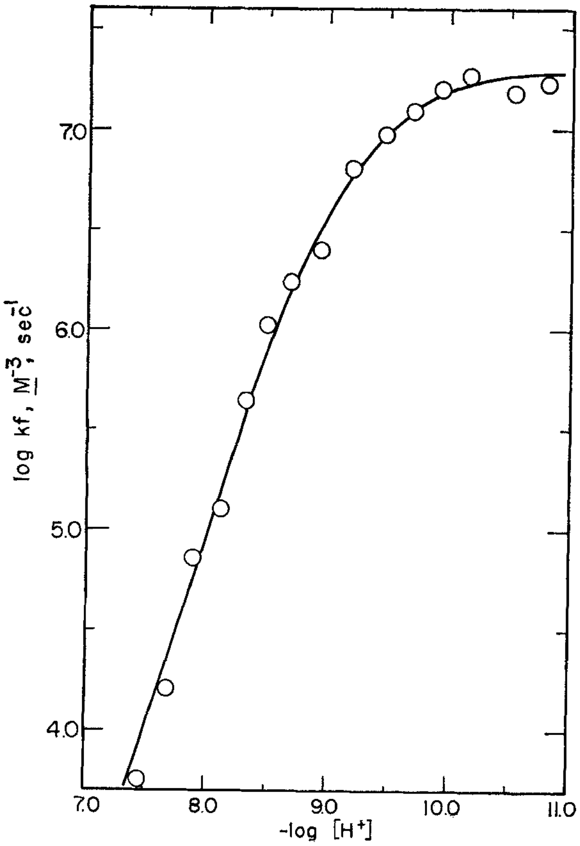

FIGURE 2 Hydrogen ion dependence of the reaction of cyanide with $NiEDDS^{2-}$. $T = 25.0°$, $\mu = 0.10\ M(NaClO_4)$. The solid line is calculated using $K_1K_2k_{3,0} = 2.0 \times 10^7\ M^{-3}$, sec^{-1} and $K_1K_2k_{2,1} = 1.1 \times 10^7\ M^{-3}$, sec^{-1}.

TABLE II

Hydrogen ion dependence on the forward rate constant, k

$[NiEDDS^-] = 9.5 \times 10^{-6}\ M$, $T = 25.0°$,
$\mu = 0.10\ M\ (NaClO_4)$, $k_f = k_{obs}/[CN_T]^3$

$-\log[H^+]$	$[CN_T] \times 10^{+4}, M$	k_{obs}, sec^{-1}	k_f, M^{-3}, sec^{-1}	$\log k_f$
9.93	8.08	1.31×10^{-3}	2.49×10^6	6.40
7.90	7.38	2.89×10^{-5}	7.20×10^4	4.86
9.21	8.08	3.25×10^{-3}	6.17×10^6	6.79
9.46	8.08	5.09×10^{-3}	9.65×10^6	6.98
9.70	8.08	7.04×10^{-3}	1.33×10^7	7.12
9.92	8.08	8.18×10^{-3}	1.55×10^7	7.19
10.19	8.08	9.72×10^{-3}	1.84×10^7	7.27
10.81	8.08	8.90×10^{-3}	1.69×10^7	7.23
8.69	7.94	8.73×10^{-4}	1.74×10^6	6.24
8.51	7.94	5.24×10^{-4}	1.05×10^6	6.02
8.34	7.94	2.26×10^{-4}	4.52×10^5	5.66
7.46	7.80	2.64×10^{-6}	5.46×10^3	3.75
8.13	8.08	6.73×10^{-5}	1.25×10^5	5.11
7.69	7.94	8.14×10^{-6}	1.62×10^4	4.21
10.53	8.04	7.86×10^{-3}	1.51×10^7	7.18

extremely low. The rate of the forward reaction shown in Eq. 1 was studied over the *p*H range of 7.5 to 11.0. As the hydrogen ion concentration is increased below *p*H 10, the values of k_f decrease (Figure 2). A slope of three would be expected in the *p*H region of 8 if hydrocyanic acid was not a reactant. However a slope of two is observed for the log k_f *vs* —log[H^+] plot; $k_f = k_{obs}/[CN_T]^3$. This is consistent with one molecule of HCN and two molecules of CN^- being reactants in this *p*H range. The rate expression for the *p*H range 7.5 to 11.0 is shown in Eq. 4. The value of $K_1K_2k_{3,0}$ is 2.0×10^7 M^{-3} sec^{-1} and $K_1K_2k_{2,1}$ equals

$$\text{rate} = \frac{d[Ni(CN)_4{}^{2-}]}{dt} = (K_1K_2k_{3,0}[CN^-]^3 + K_1K_2k_{2,1}[CN^-]^2[HCN])[NiEDDS^{2-}] \quad (4)$$

$1.1 \times 10^7\ M^{-3}\ sec^{-1}$. The solid line in Figure 2 represents the theoretical value calculated from

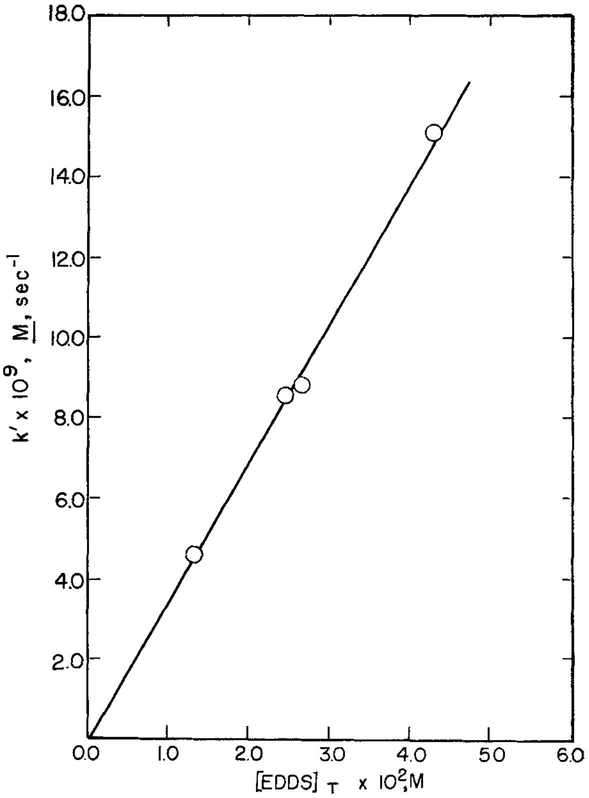

FIGURE 3 Effect of EDDS concentration on the reaction of EDDS with $Ni(CN)_4{}^{2-}$ (see Eq. 6). $[Ni^{2+}]_T = 1.13 \times 10^{-5}\ M$, $[CN]_T = 4.96 \times 10^{-5}\ M$, $-\log[H^+] = 10.6 \pm .1$, $T = 25.0°C$ and $\mu = 0.10\ M\ (NaClO_4)$.

$-\log[H^+]$, pK_a of HCN and the above rate constants. Table II lists the experimental data for the pH profile.

Kinetics of the reverse reaction

The stability of $NiEDDS^{2-}$ is significantly less (log $K_{NiEDDS} = 16.7$ *vide infra*) than $Ni(CN)_4^{2-}$ (log $\beta_4 = 30.5^4$). However, using dilute concentrations of $Ni(CN)_4^{2-}$ and a fairly high concentration of $EDDS^{4-}$ it is possible to measure the reverse reaction (Eq. 1). The rate of disappearance of $Ni(CN)_4^{2-}$ under these conditions does not obey a simple rate equation, and is dependent upon the $Ni(CN)_4^{2-}$ and $EDDS^{2-}$ concentrations and inversely proportional to the free cyanide concentration. The data fits the following rate equation.

$$\frac{-d[Ni(CN)_4^{2-}]}{dt} = \frac{k_r[Ni(CN)_4^{2-}][EDDS^{2-}]}{[CN^-]} \quad (5)$$

The integrated rate expression is shown in Eq. 5 where $[CN_T]$ is the total cyanide concentration and $k' = k_r[EDDS^{2-}]$. The subscripts i and t refer to initial concentration and concentration at time t, respectively. A plot of k' *vs* $[EDDS]_T$ is shown in Figure 3. From the slope of Figure 3, k_r is equal to $3.4 \times 10^{-7}\ sec^{-1}$.

$$[CN_T] \ln\left\{\frac{[Ni(CN)_4^{2-}]_i}{[Ni(CN)_4^{2-}]_t}\right\} + 4\{[Ni(CN)_4^{2-}]_t - [Ni(CN)_4^{2-}]_i\} = k't \quad (6)$$

DISCUSSION

The combination of the forward and reverse rate equations for the reaction of $NiEDDS^{2-}$ with cyanide ion results in the mechanism presented in Eqs. 7–9.

$$NiEDDS^{2-} + 2CN^- \xrightleftharpoons{K_1K_2} NiEDDS(CN)_2^{4-} \qquad \text{(rapid)} \qquad (7)$$

$$NiEDDS(CN)_2^{4-} + CN^- \xrightleftharpoons[k_{-3,0}]{k_{3,0}} NiEDDS(CN)_3^{5-} \qquad \text{rate determining} \qquad (8)$$

$$NiEDDS(CN)_3^{5-} + CN^- \xrightleftharpoons[\text{rapid}]{K_4} Ni(CN)_4^{2-} + EDDS^{4-} \qquad (9)$$

The forward reaction proceeds through the rapid pre-equilibrium addition of two molecules of cyanide prior to the rate-determining step which occurs when the third cyanide ion adds to the complex. The formation constants for the mixed complexes $NiEDDS(CN)^{3-}$ and $NiEDDS(CN)_2^{4-}$ are K_1 and K_2 respectively. At the concentration levels used in this study there is no evidence for a significant concentration of these proposed mixed complex species. However, this does not mean that they are not present as reactive intermediates. If complete formation of either $NiEDDS(CN)^{3-}$ or $NiEDDS(CN)_2^{4-}$ had occurred, the order dependence in cyanide for the forward reaction would be less than three. The forward rate constant k_f is equal to $K_1K_2k_{3}{}'_{0}$.

In the pH range of 7.5 to 9 the forward reaction is predominately carried by a path that has one HCN and two CN^- molecules as reactants. This reaction path differs from the one outlined in Eqs. 7–9 in that HCN replaces CN^- in Eq. 8. HCN transfers its proton to the most basic site of EDDS in the step shown in Eq.10. The reaction mechanism is described in Figure 4. For the benefit of clarity proposed structures are shown but it

$$NiEDDS(CN)_2^{4-} + HCN \xrightleftharpoons[k_{-2,1}]{k_{2,1}} NiHEDDS(CN)_3^{4-} \qquad \text{rate determining} \qquad (10)$$

$$NiEDDS(CN)_3^{4-} + CN^- \rightleftharpoons Ni(CN)_4^{2-} + HEDDS^{3-} \qquad (11)$$

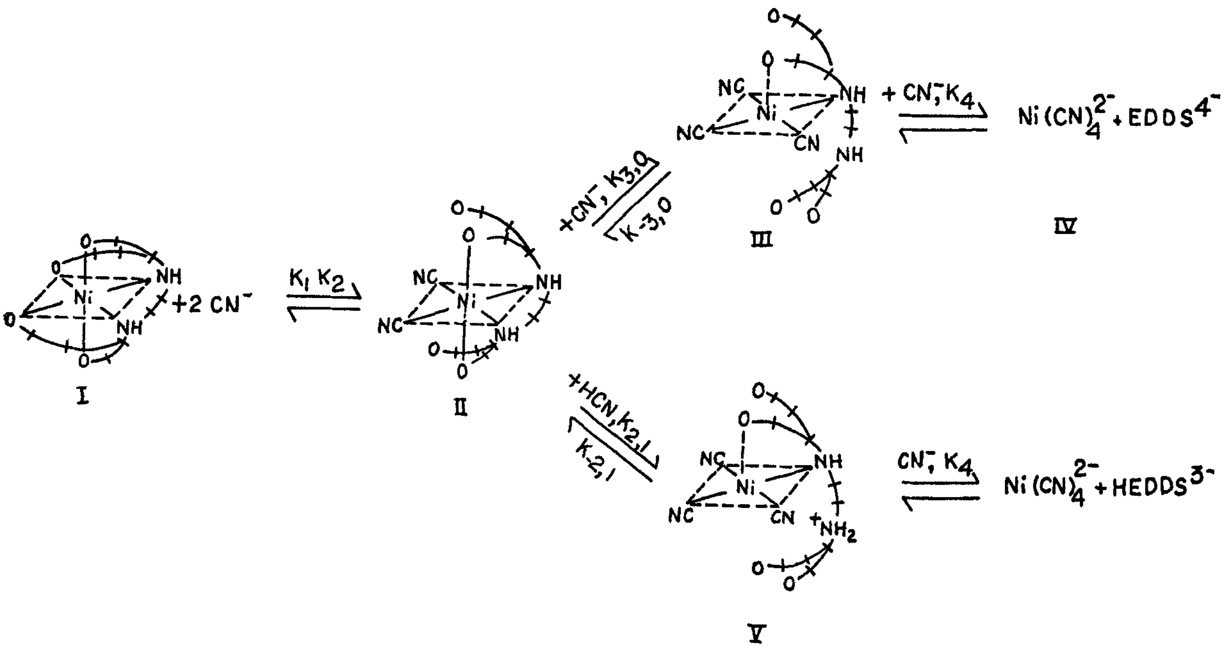

FIGURE 4 Proposed mechanism for the reaction of Nickel-EDDS with Cyanide.

must be emphasized that the actual structures are not known for any of these intermediates.

Previous studies[1,2,3] involving the reactions between nickel(II)aminocarboxylate complexes and cyanide ion also have three cyanide ions and the aminocarboxylate ligand present in the rate-determining step. A similar mechanism is consistent with the data for the present system. The path I → II → III → IV in Figure 4 has the rate-determining step at the addition of the third cyanide and the concurrent breakage of one nickel-nitrogen bond. This grouping of donors is sufficient to cause a high ligand field and convert the nickel from octahedral to square planar coordination. Once the square planar configuration is assumed the substitution reactions can proceed through an associative process which is faster than the preceeding steps[16] and thus the fourth cyanide is not involved in the rate-determining step of the forward reaction.

The actual structure of $NiEDDS^{2-}$ is not known, however a recent crystallographic study of the $CoEDDS^{1-}$ complex[17] indicates that the six-membered chelate rings are in the plane described by the cobalt and the two nitrogen atoms. The other two five-membered chelate rings would have orientation toward the axial coordination sites. A similar arrangement of chelate rings has been assumed for the nickel complex in Figure 4. The crystal structure of $CoEDDS^{1-}$ also indicates that all six donor groups are coordinated. The strain associated with the equatorial five-membered carboxylate rings[18] of $CoEDTA^{1-}$ is thus absent in $CoEDDS^{1-}$. This same type of behavior is evidenced for the nickel complexes through the observation that $NiEDTA^{2-}$ readily forms the $NiEDTA(CN)^{3-}$ mixed complex[6] whereas $NiEDDS^{2-}$ has no apparent tendency to form mixed complexes of comparable stability.

Coordination of the six donor sites of EDDS would reduce the thermodynamic feasibility of forming such mixed complexes.

The two most basic sites in the EDDS molecule are the amine nitrogens. When the first nickel-nitrogen bond cleaves, the uncoordinated nitrogen will pick up a hydrogen if the *p*H of the reaction is less than or slightly greater than the *p*K of the nitrogen. The pK_a value for $H(EDDS)^{3-}$ is 10.3. This value may change somewhat when the other nitrogen atom is coordinated to nickel but probably not very much. When HCN reacts the proton is transferred to the uncoordinated nitrogen, step II → V, and thus facilitates the unwrapping of EDDS from nickel. It is possible that the proton could be transferred to one of the carboxylate groups, however, this would be nonproductive since the carboxylate groups are acidic and the proton would rapidly be transferred to the solvent. Also the existence of such a path would predict an order greater than one for HCN.

In the reaction of cyanide with triethylenetetraminenickel(II) a more pronounced effect is observed when HCN is a reactant than that encountered in the $NiEDDS^{2-}$ system. The rate constants for the reactions with $Ni(trien)^{2+}$, where HCN is a reactant, are actually greater than the corresponding constant for the rate carried completely by CN^-. Apparently the intramolecular proton transfer is more effective in labelizing the trien than it is $EDDS^{4-}$. However this may result from the fact that the carboxylate groups don't protonate in these *p*H regions.

The relative reactivities of various aminocarboxylate complexes can be compared by using the fourth order rate constants $K_1K_2k_{3,0}$. The rate constants are listed in Table III. There is an inverse relationship between K_{NiL} and the fourth order rate constant $K_1K_2k_{3}{}'_{0}$ for all the systems except $NiEDDS^{2-}$ where the rate constant is greater than that predicted for the corresponding stability. It is not surprising that $NiEDDS^{2-}$ does not fit this model since EDDS coordination involves six-membered rings. All the other ligands have five-membered chelate rings.

TABLE III

Rate constants for the reaction of cyanide ion with aminocarboxylate complexes of nickel(II)[a]

Complex	$K_1K_2K_{3,0}$ M^{-3}, sec^{-1}	$K_4{}^1k_{-3,0}$ sec^{-1}	log K_{NiL}	Ref.
Ni(IDA)	8.1×10^{15}	4.7×10^{-7}	8.26	2
Ni(MIDA)	1.1×10^{15}	1.9×10^{-7}	8.73	2
$Ni(NTA)^{1-}$	1.0×10^{11}	1.1×10^{-8}	11.54	3
$Ni(EGTA)^{2-}$	5.8×10^{9}	7.3×10^{-8}	13.6	3
$NiEDDS^{2-}$	2.0×10^{7}	3.4×10^{-7}	16.7	this work
$Ni(HPDTA)^{2-}$	2.6×10^{6}	2.3×10^{-8}	16.4	3
$Ni(HEEDTA)^{1-}$	2.4×10^{6}	7.5×10^{-8}	17.0	3
$Ni(EDTA)^{2-}$	2.3×10^{4}	2.2×10^{-8}	18.5	1,3

[a] IDA = $HN(CH_2COO)_2{}^{2-}$;
MIDA = $CH_3N(CH_2COO)_2{}^{2-}$; NTA = $N(CH_2COO)_3{}^{3-}$;
EGTA = $(OOCCH_2)_2NCH_2CH_2OCH_2CH_2OCH_2CH_2N(CH_2COO)_2{}^{4-}$;
HPDTA = $(OOCCH_2)_2NCH_2CHOHCH_2-N(CH_2COO)_2{}^{4-}$;
HEEDTA = $(HOCH_2CH_2)(OOCCH_2)NCH_2CH_2(CH_2COO)_2{}^{3-}$;
EDTA = $(OOCCH_2)_2NCH_2CH_2N(CH_2COO)_2{}^{4-}$.

The kinetics of the reaction of EDDS with $Ni(CN)_4{}^{2-}$ are consistent with the mechanism shown in Eqs. 7–9. The rate-determining step occurs when the second cyanide ion dissociates. This is accompanied by coordination of the second nitrogen of the ethylene-diamine backbone of EDDS. The reverse rate constant $k_r = K_4{}^{-1}k_{-3,0}$ and equals 3.4×10^{-7} sec^{-1}. Analysis of the $K_4{}^{-1}k_{-3,0}$ values listed in Table III indicates that the degree of substitution of the nitrogen atoms is a contributing factor in determining the magnitude of the reverse rate constants. The two ligands with secondary nitrogens, IDA and EDDS, react significantly faster than the ligands with tertiary nitrogens. One could also argue that the lability of EDDS in the forward reaction is due to the presence of the six-membered chelate rings, however the data is not conclusive and apparently the presence of six-membered chelate rings and secondary nitrogens contribute to the lability.

The stability constant for NiEDDS can be predicted using the stability constant for $Ni(CN)_4{}^{2-}$ and the observed rate constants. From Eq. 1

$$\frac{[EDDS^{4-}][Ni(CN)_4{}^{2-}]}{[NiEDDS^{2-}][CN^-]^4}=\frac{\beta_4(Ni(CN)_4)^{2-}}{K_{NiEDDS}{}^{2-}}=K \qquad (12)$$

and

$$K=\frac{k_f}{k_r}=\frac{K_1K_2k_{3,0}}{K_4{}^{-1}k_{-3,0}} \qquad (13)$$

With log $\beta_4 = 30.5$ a value of log K_{NiEDDS} is calculated to be 16.7

The fourth-order kinetics observed in this work does not imply this order of molecularity and intermediate species must precede the rate-determining step. Their concentrations were not high enough to be observed spectrophotometrically in these studies.

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