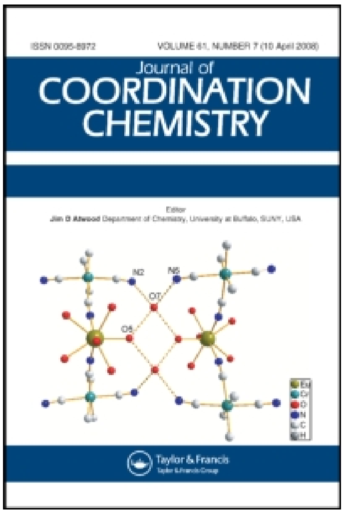

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KINETICS AND MECHANISM OF THE REACTION BETWEEN MONO ((ETHYLENEDIOXY) DIETHYLENEDINITRILO)-TETRAACETATODINICKELATE(II) AND CYANIDE ION

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The kinetics of ligand substitution at the binuclear nickel(II) chelate Ni_2L, where L is EGTA ((Ethylenedioxy)diethylenedinitrilo)tetraacetic acid with cyanide ion has been investigated spectrophotometrically. The reaction conditions were pH = 11.0 ± 0.1, $\mu = 0.1$ M ($NaClO_4$) and T = 25 ± 0.1°. The formation of $Ni(CN)_4^{2-}$ is first order in Ni_2L and first-order in cyanide over a large range of cyanide concentration, but below 10^{-3} M the reaction becomes zero order in cyanide. These results indicate the presence of a slow step in which Ni_2L dissociates to give NiL^{2-n} and $Ni^{2+}_{(aq)}$ at low cyanide concentrations and a cyanide assisted rapid dissociation of Ni_2L to produce $NiL(CN)_x^{2-n-x}$ and $Ni^{2+}_{(aq)}$ at higher cyanide concentrations. These species react with excess cyanide finally producing $Ni(CN)_4^{2-}$. On the other hand, reaction of $Ni(CN)_4^{2-}$ with EGTA is first-order in both reactants and inverse-order in cyanide. These results lead to a five step mechanism in which the fourth step has been identified as rate determining. The rate constants have been calculated and results compared with earlier work on binuculear complexes.

INTRODUCTION

A considerable amount of data is now available on the formation of tetracyanonickelate(II) complexes of aminocarboxylates[1–10] and polyamines[11–12] as well as $Ni^{2+}_{(aq)}$.[13–15] Cyanide ion reacts with mono(aminocarboxylato) complexes of Ni(II) to form the $Ni(CN)_4^{2-}$ complex and releasing the aminocarboxylate ligand according to (*1*). Kinetic and mechanistic studies on binuclear complexes of nickel(II) have attracted little attention.[16–18] We had occasion to reinvestigate the reaction between Ni_2TTHA and CN^- earlier reported by Stara and Kopanica[16] and to disprove their mechanism.[17] We also undertook the study of the $Ni_2DTPA\text{-}CN^-$[18] reaction to gain further understanding of the reaction pathway of binuclear complexes in substitution processes.

$$NiL^{2-n} + 4CN^- \rightleftharpoons Ni(CN)_4^{2-} + L^{n-} \qquad (1)$$

In this paper we report the kinetics and mechanism of the substitution of another binuclear complex of nickel(II), *viz* Ni_2EGTA, with cyanide ion in further support of the mechanism proposed previously.[18]

EXPERIMENTAL

EGTA was obtained through the courtesy of the Geigy Chemical Co. (Switzerland) and was recrystallized twice by dissolving the acid in hot water with the aid of sodium hydroxide and precipitating the same by adjusting the pH of the solution to 2 with dilute

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$HClO_4$. The recrystallized acid was dried in an oven at 110°. It was standardized by potentiometric titration against carbon dioxide-free NaOH solution. $Ni(ClO_4)_2$, supplied by Alpha Inorganics, was recrystallized before use. A stock solution of $Ni(ClO_4)_2$ was standardised against EDTA by a complexometric titration.[19] A solution of Ni_2EGTA was prepared by adding a slight excess of nickel ions (over the stoichiometric amount) and removing excess nickel as $Ni(OH)_2$ at pH 10 by millipore filtration using a 0.45 μm filter. The clear solution of Ni_2EGTA was standardised by the addition of a ten-fold excess of NaCN at pH 11.0. After allowing for complete conversion to $Ni(CN)_4^{2-}$, the absorbance was measured at 267 nm ($\epsilon_{Ni(CN)_4^{2-}} = 1.16 \times 10^4$ M^{-1} cm^{-1}) using suitable dilution. All other chemicals were of reagent grade and were used without further purification. All solutions were prepared in doubly distilled water.

All pH measurements were made using an Elico digital pH meter (model LI-120). A Toshniwal Spectrophotometer (model RL-02) was used for the study of slow reactions. A SF-3A stopped flow spectrophotometer from Hitech (England) coupled to a storage oscilloscope (model OS-768S) from ECIL (India) was used for the study of fast reactions.

RESULTS AND DISCUSSION

Kinetics of forward reaction of Ni_2L with cyanide.

Potentiometric titration data indicate that EGTA forms a mononuclear as well as a binuclear complex with nickel(II).[20] A computer calculation using the overall stability constant value for Ni_2EGTA and protonation constants of EGTA (the protonation constants for the ligand used in this study are $\log K_{HL} = 9.46$, $\log K_{H_2L} = 8.85$, $\log K_{H_3L} = 2.6$ and $\log K_{H_4L} = 2.00$. The stability constants of nickel complexes are $\log K_{NiL} = 13.6$, $\log K_{Ni} = 8.3$, $\log K_{NiL} = 6.0$ and $\log K_{NiL} = 4.9$, all at 20° and $\mu = 0.1$ M) shows that starting with a metal to ligand ratio of 2:1, the binuclear complex Ni_2EGTA is the predominent chemical species (80-85%) between pH 7.5 and 11.0. The forward reactions

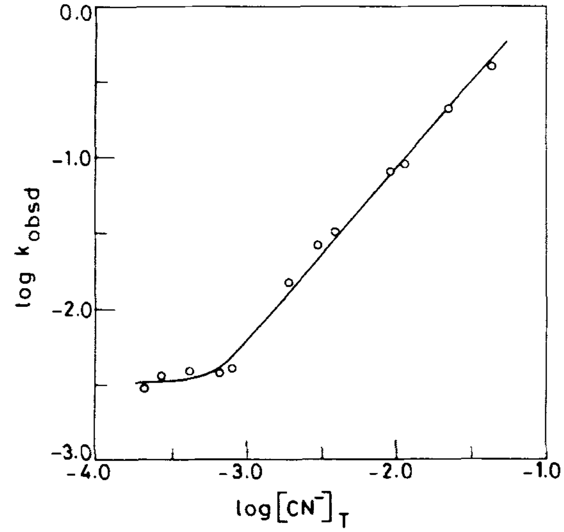


FIGURE 1 Cyanide dependence of the observed forward rate constants for the Ni_2EGTA system at 25 ± 0.1°, pH = 11.0 ± 0.2 and μ = 0.1 M.

were run at 25°, with pH = 11 ± 0.1 and $\mu = 0.1$ M ($NaClO_4$) in the presence of excess cyanide under pseudo-first-order conditions. The rate constants were evaluated from plots of log $(A_\infty - A_t)$ *vs* t. They were found to be first-order in Ni_2L and first order in cyanide over a wide range of cyanide concentrations. The observed pseudo-first-order rate constants are plotted as log k_{obsd} *vs* log $[CN^-]_T$ in Fig. 1; $[CN^-]_T$ includes cyanide present in all its forms. A very significant feature of this curve is that the plot tends toward zero-order dependence below 10^{-3}M cyanide concentration. The same trend was also found in the case of the reaction of cyanide with Ni_2TTHA and Ni_2DTPA in our earlier reported work.[17,18] The zero-order dependence on cyanide indicates the slow dissociation of Ni_2L complex according to (*2*).

$$Ni_2L^{4-n} \xrightarrow{k_d} NiL^{2-n} + Ni^{+2}_{(aquo)} \text{ (slow)} \qquad (2)$$

The experimental rate expression is formulated as in equation (*3*),

$$\text{Rate} = (k_d + k')\,[Ni_2L] = k_{obsd}\,[Ni_2L] \qquad (3)$$

where $k' = k_f[CN^-]^{3-x}$ and k_f is a composite rate constant made up of equilibrium constant and rate constant (*vide supra*).

It was also observed that when cyanide is added to the binuclear complex, in a concentration range where order with respect to cyanide is one, there is an instantaneous and large absorbance change on mixing. This is due to the formation of $Ni(CN)_4^{2-}$ and mixed complexes of the type $NiL(CN)_x$ according to equation (*4*). This, however, overweighs the slow formation of $Ni(CN)_4^{2-}$ according to equation (*2*). There is a region where order changes from zero to one correspondingly (Fig. 1).

$$Ni_2L^{4-n} + (x+4)CN^- \longrightarrow NiL(CN)_x^{2-n-x} + Ni(CN)_4^{2-} \qquad (4)$$

The species NiL and $NiL(CN)_x$ react further with excess cyanide finally forming $Ni(CN)_4^{2-}$. This means that in the presence of CN^-, the Ni_2L complex gives $NiL(CN)_x$ and $Ni^{+2}_{(aq)}$ and cyanide assists this dissociation. The subsequent steps are same as for the reactions of mono(aminocarboxylato)nickel(II) complexes with cyanide.[1-10]

Kinetics of the reverse reaction.

The reverse reaction was seen to proceed only in the presence of a large excess of ligand concentration. For this reason the ionic strength for the reverse rate studies was kept at 0.3 M instead of the usual 0.1 M. Only NiL is formed in the reverse reaction and there is no evidence for the formation of Ni_2L. The rate of the reverse reaction depends upon the first power of the concentrations of both $Ni(CN)_4^{2-}$ and the ligand. It also showed an inverse-first-order dependence in free cyanide. The rate expression was formulated as shown in (*5*)

$$-d[Ni(CN)_4^{2-}] \longrightarrow dt = k_r[Ni(CN)_4^{2-}]\,[L^{4-}]/[CN^-] \qquad (5)$$

The integrated form of this equation is (*6*),

$$(A_i - A_t) + A_i \ln A_t/A_i = -\epsilon l/4.\, k'_{obsd}t \qquad (6)$$

where A_i is the initial absorbance, A_t is the absorbance at time t, ϵ is the molar absorp-

TABLE I
Rate Constants for the Reaction of $Ni(CN)_4^{2-}$ with EGTA at 25°, $\mu = 0.3$ M ($NaClO_4$), pH = 11.0 ± 0.1, $[Ni(CN)_4^{2-}] = 2.6 \times 10^{-5}$ M.

10^2 [EGTA] M	$k'_{obsd} \times 10^{10}$ M s^{-1}	$k_r \times 10^8$ s^{-1}
0.25	1.82 ± 0.2	7.28 ± 0.4
0.50	3.8 ± 0.15	7.6 ± 0.3
1.00	7.2 ± 0.1	7.2 ± 0.1
1.20	7.5 ± 0.2	6.25 ± 0.15
		Av. 7.1 ± 0.5

tivity of $Ni(CN)_4^{2-}$, l is the path length and $k'_{obsd} = k_r [L^{4-}]$. A plot of the left hand side of (6) *vs* time gives straight lines, and slopes of these plots give k'_{obsd} and hence k_r. These values are given in Table I. A plot of k'_{obsd} *vs* [EGTA] is a straight line with a slope equal to k_r. The value of this constant is found to be $7.1 \pm 0.5 \times 10^{-8}$ S^{-1}.

Temperature dependence of forward and reverse reactions.

The temperature dependences of the rates of forward and reverse reactions were investigated over a temperature range of 25-50° and were found to obey the Arrhenius equation. The activation parameters for the forward reaction have been evaluated for situations where dependence in cyanide is zero and one respectively. These data are given in Table II.

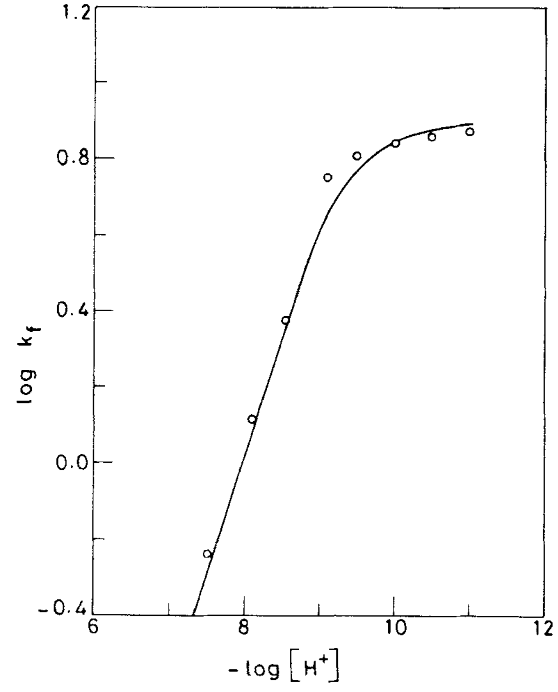


FIGURE 2 Effect of pH on the reaction of CN^- with Ni_2EGTA. The solid curve is calculated from resolved rate constants k_{CN} and k_{HCN}.

TABLE II
Activation Parameters for the Forward and Reverse Reactions.

Forward Reaction (pH = 11.0 ± 0.1 and $\mu = 0.1$ M ($NaClO_4$))	
Zero order dependence	First order dependence
($[CN^-] = 5.0 \times 10^{-4}$ M)	($[CN^-] = 1.11 \times 10^{-2}$ M)
$E_a = 40.2 \pm 1.4$ kJ Mol^{-1}	$E_a = 25.5 \pm 1.0$ kJ Mol^{-1}
$\Delta S^{\neq} = -127.2 \pm 3.0$ J K^{-1} Mol^{-1}	$\Delta S^{\neq} = -153.5 \pm 4.0$ J K^{-1} Mol^{-1}
$p_z = 1.58 \times 10^6$ cm^{-1}	$p_z = 8.5 \times 10^4$ cm^{-1}
Reverse reaction (pH = 11.0 ± 0.1 and $\mu = 0.3$ M ($NaClO_4$))	
$E_a = 88.3 \pm 1.32$ kJ Mol^{-1}	
$\Delta S^{\neq} = -94.1 \pm 2.0$ J K^{-1} Mol^{-1}	
$p_z = 7.9 \times 10^7$ cm^{-1}	

pH dependence of Ni_2L-CN^- reaction

The pH dependence of the forward reaction is shown in Figure 2 under the conditions where order dependence in cyanide is one. It is seen that the rate remains almost constant in the pH range 9.5 to 11 but it decreases below pH 9.0 as found in our earlier studies[17–18] of Ni_2TTHA and Ni_2DTPA. This is due to the formation of a less reactive species below pH 9.0. The initial linear portion of the plot of log k_f *vs* –log $[H^+]$, ($k_f = k_{obsd}/[CN^-]_T$), gives a slope equal to one. This value indicates that one HCN molecule is involved in addition to two cyanides below pH 9.0. A rate expression valid for the whole range of pH (7.5–11.0) is given in equation (*7*),

$$\text{rate} = d[Ni(CN)_4^{2-}]/dt = \{ k_{f(CN)}[CN^-] + k_{f(HCN)}[HCN] \} \; [NiL(CN)_2] \qquad (7)$$

where $k_{f(CN)}$ and $k_{f(HCN)}$ are the rate constants for CN^- and HCN reactions respectively.

The resolution of the rate constants was done using an expression derived earlier[18] and is reproduced below in (*8*),

$$k_f = \{ k_{f(CN)} + k_{f(HCN)} K_{HCN} [H^+] \} / \{ 1 + K_{HCN} [H^+] \} \qquad (8)$$

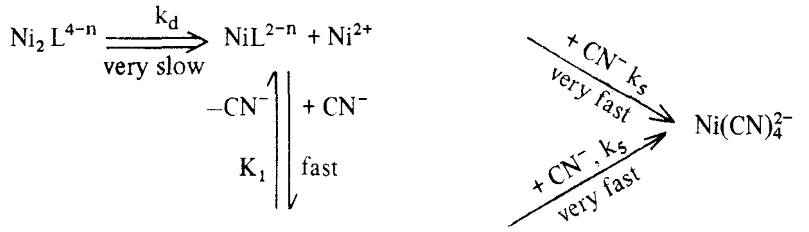
where K_{HCN} is the protonation constant for CN^- (log $K_{HCN} = 9.0$ at 25° and $\mu = 0.1$ M).

Below pH 9, one is negligible in comparison to $K_{HCN}[H^+]$ and equation (*8*) takes the form (*9*).

$$k_f = k_{f(CN)}/K_{HCN}[H^+] + k_{f(HCN)} \qquad (9)$$

A plot of k_f *vs* $1/[H^+]$ is a straight line (Fig. 3) and $k_{f(CN)}$ and $k_{f(HCN)}$ are evaluated respectively from the slope and intercept of this straight line. These are 7.8 M^{-1} s^{-1} and 0.35 M^{-1} s^{-1} respectively.

The initial part of reaction of cyanide with the binuclear chelate Ni_2EGTA proceeds *via* two paths, (*i*), a slow dissociation and (*ii*), a fast cyanide-assisted dissociation of Ni_2L. The following scheme (*10*)–(*14*) outlines the proposed mechanism on the basis of experimental results and is in line with the mechanism proposed by us earlier.[17,18]



(10)

$$Ni_2L^{4-n} + CN^- \underset{\text{fast}}{\overset{K_1'}{\rightleftharpoons}} NiL(CN)^{1-n} + Ni^{2+} \tag{11}$$

$$NiL(CN)^{1-n} + CN^- \underset{\text{fast}}{\overset{K_2}{\rightleftharpoons}} NiL(CN)_2^{n-} \tag{12}$$

$$NiL(CN)_2^{n-} + CN^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} NiL(CN)_3^{(n+1)-} \tag{13}$$

$$NiL(CN)_3^{(n+1)-} + CN^- \underset{\text{fast}}{\overset{K_4}{\rightleftharpoons}} Ni(CN)_4^{2-} + L^{n-} \tag{14}$$

The reverse reaction rate depends upon the concentrations of $Ni(CN)_4^{2-}$ and EGTA and is inversely proportional to the free cyanide concentration. A steady-state treatment of the intermediate species $NiL(CN)_3$, $NiL(CN)_2$, $NiL(CN)$ and NiL, and a consideration of dissociation of Ni_2L according to (*10*) give the combined rate expression (*15*)

$$\text{rate} = k_d[Ni_2L] + K_1' K_2 k_3 [CN^-]^3 [Ni_2L] \tag{15}$$

which is easily transformed to the experimental rate expression given in (*3*).

The above expression shows that a third-order dependence in cyanide would be expected if the reactant is Ni_2L. However, only a first-order dependence has been

TABLE III
Summary of the Rate Constants and Equilibrium Constants.

	Ni_2TTHA	Ni_2DTPA	Ni_2EGTA
$K_{Ni_2L}^{NiL}$	1.00×10^{13}	3.39×10^5	7.94×10^4
$\beta_{Ni_2L}^{Ni}$	2.51×10^{32} [d]	5.02×10^{25} [d]	3.16×10^{18} [d]
k_d s^{-1}	$1.63 \pm 0.03 \times 10^{-5}$	$1.40 \pm 0.05 \times 10^{-4}$	$3.9 \pm 0.4 \times 10^{-3}$
k_3 $M^{-1}s^{-1}$	–	$1.63 \pm 0.05 \times 10^{-1}$	8.1 ± 0.5
K_2k_3 $M^{-2}s^{-1}$	10.15 ± 1.40	–	–
k_{CN}	10.15[a]	1.77×10^{-1} [b]	7.80[b]
k_{HCN}	2.4[a]	8.60×10^{-2} [b]	3.5×10^{-1} [b]
K_4^{-1} k_{-3} s^{-1}	$3.08 \pm 0.17 \times 10^{-7}$ [c]	$4.78 \pm 0.6 \times 10^{-8}$ [c]	$7.1 \pm 0.5 \times 10^{-8}$

[a] $M^{-2}s^{-1}$; [b] $M^{-1}s^{-1}$; [c] from ref. 18; [d] ref. 21.

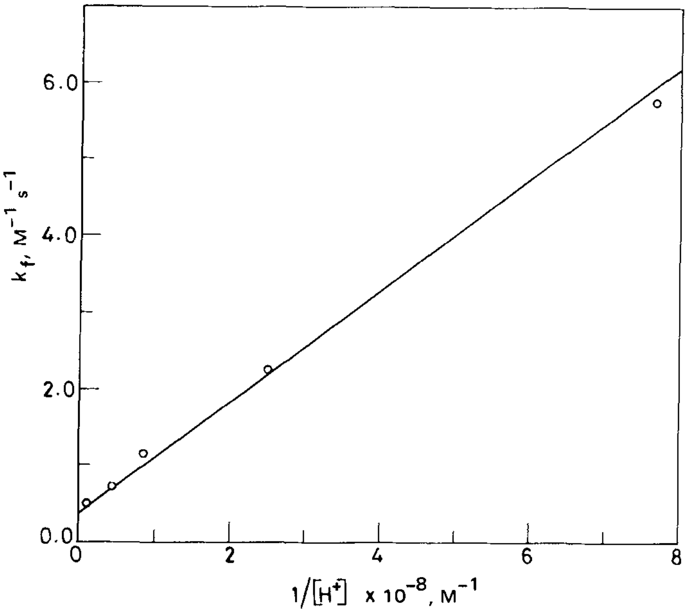


FIGURE 3 Resolution of rate constants for the reaction of Ni_2EGTA with cyanide.

observed in the present study (Figure 1) though a first-order dependence was observed for Ni_2DTPA and second-order for Ni_2TTHA reactions in an earlier investigation.[18] No third-order order dependence has been observed so far. These results are interpreted to mean that only $NiL(CN)_2$ and $NiL(CN)$ are reactants consistent with first- and second-order dependences in cyanide. Accordingly the rate expression (*15*) is rewritten as in (*16*)

$$\text{Rate} = k_d[Ni_2L] + k_f[CN^-]^{3-x}[NiL(CN)_x^{2-n-x}] \qquad (16)$$

where x may be 1 or 2 and k_f is K_2k_3 or k_3 respectively. In the case of substitutions of mononuclear complexes of aminocarboxylates it has been shown that x can be 0, 1 and 2 corresponding to the observed third-, second- and first-order dependence at low, medium and high concentrations of cyanide. The zero-order dependence in cyanide in the present case points to a cyanide-independent dissociation pathway for Ni_2L with a rate constant k_d.

In the pH range 7.5 to 9, the forward reaction predominantly occurs by a path that has one HCN and two CN^- molecules as reactants. A function α_{CN} is defined as $\alpha_{CN} = K_a/(K_a + [H^+])$, where K_a is the dissociation constant of HCN. When k_f/α_{CN} is plotted against α_{CN}, a straight line is obtained (Figure 4) which shows that one molecule of HCN is involved in the rate-determining step. The rate constants due to reactions of CN^- and HCN have been resolved and the solid line of Fig. 2 gives the calculated curve. The agreement between experimental points and calculated solid curve can be considered good.

Some arguments in support of the proposed mechanism have been discussed at length earlier.[18] They hold good in the present case as well, including those relating to the values of the activation parameters and to the pH dependence. The important reaction step in all the three systems investigated by us involves the cyanide assisted dissociation of the binuclear complex according to Eqn. (*11*) followed by its conversion from an octahedral to a square planar complex *via* a five-coordinate intermediate as proposed earlier.[1-4]

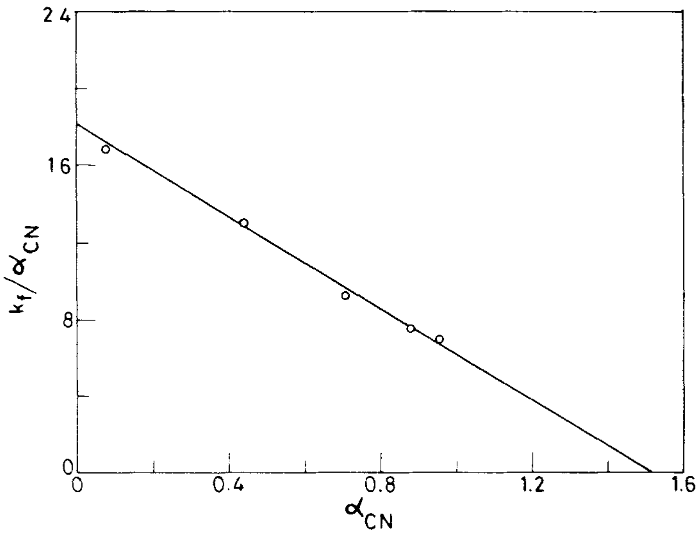


FIGURE 4 Determination of order in HCN for the Ni_2EGTA system. Plot of k_f/α_{CN} vs. α_{CN}, where $\alpha_{CN} = K_a/([H^+] + K_a)$ and K_a is the dissociation constant of HCN.

Three cyanides are required around the central nickel ion to bring about the rate determining step. The fourth cyanide adds rapidly displacing the remaining glycinate residue of the aminocarboxylate to give the product. At pH values lower than 9 however, HCN is also a reactant along with CN^- (in step *12*) and an intramolecular shift of a proton seems to take place from HCN. A similar proton transfer was also postulated in earlier studies.[1-5,18]

For the sake of comparison, the various rate constants and equilibrium constants evaluated for reactions of binuclear complexes of Ni(II) and TTHA, DTPA and EGTA with cyanide are tabulated in Table III. An interesting though not unexpected result is a linear correlation between log β_{Ni_2L} and log k_d (Figure 5). This shows that the rate of dissociation at low cyanide concentrations is inversely related to the overall stability of the binuclear complex. The generality of this relationship will be further tested in the future.

A consideration of structures of binuclear complexes may be in order in so much as the structures of Ni_2TTHA and Ni_2DTPA are known.[22] In each case one of the nickel atoms is surrounded identically by two amine nitrogens and three carboxylate oxygens. In the TTHA complex the second nickel atom is bonded to two amines and three carboxylate groups while in the DTPA complex it is linked to one amine and two carboxylate groups. The latter is expected to be more labile with respect to self-dissociation than the former. A correlation has been suggested[23] between electron donating abilities of multidentate ligands L in MAL type complexes and the dissociation rate for the loss of 5-nitrosalicyclic acid (M = nickel, A = 5-nitrosalicyclic acid and L = amino carboxylate or polyamine). Here we are dealing with the case of a part of the multidentate ligand itself leaving one of the metal ions in a binuclear complex. The electron donating abilities of the three ligands can be estimated assuming additivity of E_n's (electron-donor constants) of NH_3 and CH_3COOH (1.84 and 0.95 respectively). The E_n's for TTHA, DTPA and EGTA in the three binuclear complexes would be 13.06, 10.27 and 7.84 respectively. A log-log plot of E_n's *vs* $k_d^{Ni_2L}$, the dissociation constant of step (*10*) in the

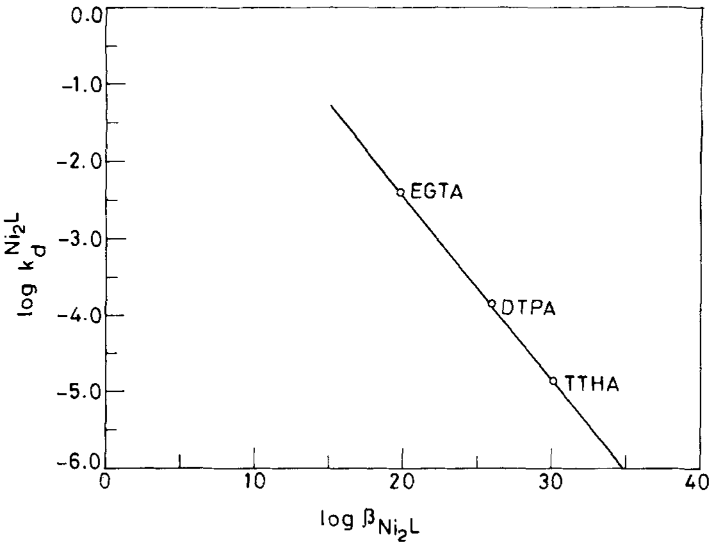


FIGURE 5 Correlation between dissociation rate constant $k_d^{Ni_2L}$ and overall stability constants of nickel aminocarboxylate complexes (β_{Ni_2L}).

scheme, is found to be linear with a negative slope. This trend indicates that the lability of the binuclear complexes toward self dissociation is inversely related to the E_n's of the complexed ligands. The same trend is also reflected in the inverse linear relationship between log $\beta^{Ni}_{Ni_2L}$ and log $k_d^{Ni_2L}$ in Figure 5.

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