# Kinetics of Ligand Substitution Reactions. 1. A Reinvestigation of the Reaction of Nickel(II) Triethylenetetraminehexaacetate with Cyanide Ion

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The kinetics and mechanism of reaction between NiTTHA (where TTHA is triethylenetetraminehexaacetic acid) and cyanide ion at pH 11.0, 25 °C, and  $\mu = 0.1$  M (NaClO<sub>4</sub>) has been reinvestigated. The results are found to be different from those reported by Stara and Kopanica for this reaction, but are in line with results obtained for other aminocarboxylates. The reverse reaction was seen to be suppressed by free cyanide ions which was not accounted for by these workers in their mechanism. A rate expression reflecting this dependence has been proposed. The results obtained in the present work fit a four-step mechanism proposed earlier. The pH dependence of the forward and reverse rates has been investigated and interpreted in terms of the reactivities of CN<sup>-</sup> and HCN for forward rate and L<sup>n-</sup>, HL<sup>(n+1)-</sup>, and H<sub>2</sub>L<sup>(n+2)-</sup> for reverse rate, respectively. The stability constants of mixed ligand complexes, viz., NiL(CN)<sup>1-n</sup>, NiL(CN)<sub>2</sub><sup>n-</sup>, and also NaL<sup>5-</sup> have been calculated from kinetic data.

# Introduction

Stara and Kopanica<sup>1</sup> have reported their results on the rates of the following substitution reaction at pH 10.6, 24 °C, and  $\mu = 0.1$  M (NaClO<sub>4</sub>)

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

where L is triethylenetetraminehexaacetic acid. The mechanism proposed by them was shown to be unacceptable on grounds discussed in our earlier communication.<sup>2</sup> Later we checked on some of their experimental results under their reported conditions and failed to reproduce them. This prompted us to reinvestigate the rate data and in the present communication we wish to report our findings on the same. Our data fit the mechanism proposed earlier.<sup>3-9</sup> Formation of mixed ligand complexes of the type NiL(CN)<sub>x</sub><sup>2-n-x</sup> where x may be 1 or 2 was verified as in the case of some other aminocarboxylates.<sup>3-9</sup> Three cyanides are needed around the central nickel ion to bring about the rate-determining step. The fourth cyanide adds rapidly and displaces the remaining glycinate segment. The reverse reaction was found to be suppressed by free cyanide ions. The reverse rate law proposed by Stara and Kopanica<sup>1</sup> has been modified accordingly. The pH dependence of rates on forward rate reveals that HCN and  $CN^-$  are reactants in the pH range 7.5–9.5, a conclusion reached in previous investigations also.<sup>3,4,8–11</sup> In the reverse reaction it was found that L<sup>6-</sup>, HL<sup>5-</sup>, and H<sub>2</sub>L<sup>4-</sup> are reactants in the pH range 8-11.5.

### **Experimental Section**

Apparatus and Reagents. The apparatus and instruments used in the investigation have been described in our earlier communications.<sup>3,4</sup> The H<sub>6</sub>L solution was prepared from triethylenetetraminehexaacetic acid (Sigma Chemicals) and standardized by visual titration with standard zinc<sup>12</sup> solution and also by potentiometric titrations. Nickel perchlorate and sodium cyanide solutions were standardized as in our earlier work.<sup>3,4</sup> Na<sub>2</sub>Ni(CN)<sub>4</sub> was prepared for use in reverse reaction by adding stoichiometric amounts of Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and sodium cyanide in aqueous solution. The procedure for preparation of solution of NiTTHA<sup>4–</sup> was the same as reported in our earlier work<sup>3,4</sup> for other Ni–aminocarboxylate complexes. The stock solution of NiTTHA<sup>4–</sup> so obtained was standardized

TABLE I: Protonation and Equilibrium Constants (log Values) of TTHA and Ni(II) TTHA Complexes<sup>14,15</sup> at 25 °C and  $\mu = 0.1$  M

o una p	0.1 1.1			
$K_{\rm HL}$	10.19	K <sub>H<sub>6</sub>L</sub>	2.42	
$K_{\mathrm{H_2L}}$	9.40	K <sub>NiL</sub>	18.8	
$K_{\mathrm{H_{3}L}}$	6.16	$K_{ m NiHL}^{ m NiL}$	9.11	
$K_{H_4L}$	4.16	$K_{ m NiH_{-L}}^{ m NiHL}$	4.86	
$K_{H_5L}$	2.95	$K_{\mathrm{NiH_{3L}^{2}L}}^{\mathrm{NiH_{2L}^{2}L}}$	2.74	
	$ \frac{K_{\rm HL}}{K_{\rm H_2L}} $ $ \frac{K_{\rm H_3L}}{K_{\rm H_4L}} $ $ \frac{K_{\rm H_5L}}{K_{\rm H_5L}} $	$\begin{array}{c} K_{\rm HL} & 10.19 \\ K_{\rm H_2L} & 9.40 \\ K_{\rm H_3L} & 6.16 \\ K_{\rm H_4L} & 4.16 \\ K_{\rm H_5L} & 2.95 \end{array}$	$\begin{array}{c c} K_{\rm HL} & 10.19 & K_{\rm H_6L} \\ K_{\rm H_2L} & 9.40 & K_{\rm NiL} \\ K_{\rm H_3L} & 6.16 & K_{\rm NiHL}^{\rm NiL} \\ K_{\rm H_4L} & 4.16 & K_{\rm NiH,1L}^{\rm NiHL} \\ K_{\rm H_3L} & 2.95 & K_{\rm NiH,1L}^{\rm NiH,1L} \end{array}$	$\begin{array}{c c} K_{\rm HL} & 10.19 & K_{\rm H_6L} & 2.42 \\ \hline K_{\rm H_2L} & 9.40 & K_{\rm NiL} & 18.8 \\ \hline K_{\rm H_3L} & 6.16 & K_{\rm NiHL}^{\rm NiH} & 9.11 \\ \hline K_{\rm H_4L} & 4.16 & K_{\rm NiH_2L}^{\rm NiH} & 4.86 \\ \hline K_{\rm H_3L} & 2.95 & K_{\rm NiH_2L}^{\rm NiH_2L} & 2.74 \\ \end{array}$

by adding excess sodium cyanide and measuring its absorbance at 267 nm ( $\epsilon = 1.16 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) and at 285 nm ( $\epsilon = 4.63 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ).

Kinetic Runs. The experimental procedure adopted has been described in our earlier papers.<sup>3,4</sup> The rates of forward and reverse reactions were measured by spectrophotometric determination of the tetracyanonickelate concentration at 267 and 285 nm. The forward reactions were run in the presence of excess cyanide and gave excellent pseudo-first-order plots (log  $(A_{\infty} - A_t)$  vs. time, where A denotes absorbance). The reverse reaction was run in the presence of excess TTHA at 25 ± 0.1 °C,  $\mu =$ 0.5 M (NaClO<sub>4</sub>), and pH 11.0. The pH values were corrected to -log [H<sup>+</sup>] by subtracting 0.11 from recorded pH readings.<sup>13</sup>

The dependence of the forward rate on pH shows that cyanide as well as HCN are reactants in the working pH range (7.5–11.5). In order to interpret these results a  $pK_a$  value of  $9.0^{3.4}$  was used for HCN.

#### Results

Kinetics of the Forward Reaction of Mononuclear Nickel(II) Chelate with Cyanide. By using the respective stability constants of nickel(II) complexes of TTHA

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$$K_{\text{NiL}} = \frac{[\text{NiL}]}{[\text{Ni}^{2+}][\text{L}]} = 10^{18.8}$$

$$K_{\text{Ni}_{2}\text{L}} = \frac{[\text{Ni}_{2}\text{L}]}{[\text{Ni}^{2+}]^{2}[\text{L}]} = 10^{32.4}$$
(ref 14)

and the  $pK_a$  of TTHA<sup>15</sup> given in Table I we performed a computer calculation with a program given by Perrin and Sayce<sup>16</sup> to obtain the relative amounts of NiL and Ni<sub>2</sub>L present in the mixture. It was concluded therefrom that, in a solution having a molar ratio of nickel to ligand of 1:1,

Kinetics of Ligand Substitution Reactions



Figure 1. Species distribution of TTHA and NITTHA systems as a function of pH.

TABLE II: Cyanide Dependence of the Observed Forward Rate Constant for the Reaction of NiL<sup>4-</sup> Complex with Cyanide Ion at pH 11.0,  $\mu = 0.1$  M (NaClO<sub>4</sub>), and t = 25 °C

[CN <sup>-</sup> ] <sub>T</sub> , M	[NiTTHA], M	$k_{\rm obsd}, s^{-1}$	$k_{f} = k_{obsd} / [CN^{-}]^{x}$
$\begin{array}{c} 2.25 \times 10^{-4} \\ 4.50 \times 10^{-4} \\ 7.50 \times 10^{-4} \\ 9.00 \times 10^{-4} \\ 1.50 \times 10^{-3} \\ 1.80 \times 10^{-3} \\ 2.25 \times 10^{-3} \\ 2.25 \times 10^{-3} \\ 2.25 \times 10^{-3} \\ 3.00 \times 10^{-3} \\ 4.50 \times 10^{-3} \\ 4.50 \times 10^{-3} \\ 6.00 \times 10^{-3} \end{array}$	$7.25 \times 10^{-5}  7.25 \times 10^{-5}  6.40 \times 10^{-5}  6.40 \times 10^{-5}  7.25 \times 10^{-5}  6.40 \times 10^{-5}  7.25 \times 10^{-5}  7.25 \times 10^{-5}  7.45 \times 10^{-5}  7.00 \times 10^{-5}  8.00 \times 10^{-5}  8.10 \times 10^{-5} $	$\begin{array}{c} 6.12 \times 10^{-6} \\ 2.05 \times 10^{-5} \\ 8.23 \times 10^{-5} \\ 1.01 \times 10^{-4} \\ 1.63 \times 10^{-4} \\ 2.75 \times 10^{-4} \\ 3.00 \times 10^{-4} \\ 3.35 \times 10^{-4} \\ 3.91 \times 10^{-4} \\ 3.91 \times 10^{-4} \\ 5.75 \times 10^{-4} \\ 6.10 \times 10^{-4} \\ 6.10 \times 10^{-4} \end{array}$	$\begin{array}{c} 1.20 \times 10^2 \\ 1.01 \times 10^2 \\ 1.46 \times 10^2 \\ 1.24 \times 10^2 \\ 1.30 \times 10^2 \\ 1.38 \times 10^{-1} \\ 1.52 \times 10^{-1} \\ 1.66 \times 10^{-1} \\ 1.61 \times 10^{-1} \\ 1.24 \times 10^{-1} \\ 1.23 \times 10^{-1} \\ 1.27 \times 10^{-1} \\ 1.35 \times 10^{-1} \\ 1.43 \times 10^{-1} \end{array}$
$9.00 \times 10^{-3} 9.00 \times 10^{-3} 1.80 \times 10^{-2}$	$7.50 \times 10^{-5}$ 9.50 × 10^{-5} 1.00 × 10^{-4}	$\begin{array}{c} 1.40 \times 10^{-3} \\ 1.25 \times 10^{-3} \\ 2.79 \times 10^{-3} \end{array}$	$\begin{array}{c} 1.55 \times 10^{-1} \\ 1.38 \times 10^{-1} \\ 1.50 \times 10^{-1} \end{array}$

the binuclear complex predominates below pH 6.0 while the mononuclear complex is the predominant species above this pH (Figure 1). So under conditions of this investigation the mono complex is the principal species in solution. On mixing NiTTHA with a large excess of cyanide, a small but instantaneous change in absorbance was observed by us as well as by Stara and Kopanica<sup>1</sup> which was considered to be due to formation of a mixed ligand intermediate NiL(CN)<sup>1-n</sup>. In the present investigation the observed first-order dependence on cyanide concentration indicates the formation of NiL(CN)<sub>2</sub><sup>n-</sup> also. The stability constants of the mono and bis cyano complexes have been defined earlier.<sup>3,4</sup> The decrease in nickel chelate concentration or increase in Ni(CN)<sub>4</sub><sup>2-</sup> concentration was calculated according the equation

$$[Ni(CN)_{4}^{2-}] = \frac{A_t - A_0}{l\{\epsilon_{Ni(CN)_{4}^{2-}} - \epsilon_0\}}$$
(2)

where  $\epsilon_{\text{Ni}(\text{CN})_4^{2-}}$  and  $\epsilon_0$  are the molar absorbances of Ni-(CN)<sub>4</sub><sup>2-</sup> and NiTTHA<sup>4-</sup>, respectively,  $A_t$  is the absorbance due to all complexing species,  $A_0$  the absorbance at zero time, and *l* the path length. The results of these measurements showed a linear dependence of log [NiTTHA] vs. time, thus indicating first-order dependence on [NiT-THA]. The observed forward rate constants  $k_{obsd}$  are compiled in Table II. Stara and Kopanica<sup>1</sup> have reported only a third-order dependence in [CN<sup>-</sup>]<sub>T</sub> while in the same concentration range of CN<sup>-</sup> we have observed a variable order dependence, i.e., second order at lower cyanide concentration and first order at higher cyanide concen-



**Figure 2.** Cyanide dependence of the observed forward rate constants in the NITTHA<sup>4-</sup> system at  $t = 25 \pm 0.1$  °C; pH 11.0  $\pm$  0.2, and  $\mu = 0.1$  M: (O) data obtained by us, (D) data reported by Stara and Kopanica (ref 1). Solid line calculated from rate law.

tration (Figure 2). However, third-order dependence was not observed by us probably because at still smaller concentrations where it might have been observed the rate is very slow. As discussed earlier<sup>3-7</sup> a simple explanation of variable order dependence on cyanide concentration is that a total of three cyanide ions are required in the rate-determining step and the observed order depends upon how many of the three cyanides are already complexed to NiTTHA<sup>4-</sup>. Thus

$$d[Ni(CN)_{4}^{2^{-}}]/dt = k_{obsd}[NiL(CN)_{x}^{2-n-x}] = k_{f}[NiL(CN)_{x}^{2-n-x}][CN^{-}]^{3-x} (3)$$

The slope of log  $k_{obsd}$  vs. log  $[CN^-]_T$  is found to be 3 - x where x changes from 1 to 2 in the present case as the cyanide concentration varies from low to high.

Determination of Stability Constant of Monocyano Mixed Ligand Complex. There was spectrophotometric and kinetic evidence for the formation of a mixed ligand complex NiL(CN) in the forward reaction on mixing NiTTHA with large excess of cyanide. The stability constant of the NiL(CN) complex was determined spectrophotometrically by the mole ratio method (as applied by Margerum et al.<sup>7</sup> for the NiEDTA-CN<sup>-</sup> system) at 244 nm. It was found that on mixing a very small amount of  $CN^{-}$  (~1.20 × 10<sup>-4</sup> M) with a large excess of NiTTHA  $(\sim 2.5 \times 10^{-3} \text{ M})$  a new peak appears at 244 nm and the peaks at 267 and 285 nm due to  $Ni(CN)_4^{2-}$  disappeared. Assuming that there is no formation of other intermediates or Ni(CN)42-, we determined the  $\varepsilon_{\rm NiL(CN)}$  to be 1420 at 244 nm. The concentration of NiL(CN) was calculated from the expression

$$[NiL(CN)] = \frac{A - A_{NiL}}{l\{\epsilon_{NiL(CN)} - \epsilon_{NiL}\}}$$
(4)

where  $\epsilon_{NiL(CN)}$  and  $\epsilon_{NiL}$  are the molar absorbances of NiL-(CN) and NiL, respectively.

$$[NiL]_{f} = [NiL]_{T} - [NiL(CN)]$$
(5)

# 142 The Journal of Physical Chemistry, Vol. 84, No. 2, 1980

$$[CN^{-}]_{f} = [CN^{-}]_{T} - [NiL(CN)]$$
 (6)

where the subscript f denotes equilibrium concentrations

$$K_{\rm NiL(CN)} = \frac{[\rm NiL(CN)]}{[\rm NiL]_f[\rm CN^-]_f}$$
(7)

The value of  $K_{\rm NiL(CN)}$  found by this method is  $1.10 \times 10^3$  M<sup>-1</sup> while the value by the kinetic method discussed earlier<sup>3</sup> is  $1.20 \times 10^3$  M<sup>-1</sup>. The good agreement gives credence to the latter method.

Kinetics of the Reverse Reaction. The stability constant of NiTTHA<sup>4-</sup> is significantly less (log  $K_{\rm NiTTHA} = 18.8$ )<sup>14</sup> in comparison to the stability constant of Ni(CN)<sub>4</sub><sup>2-</sup> (log  $\beta_4 = 30.5$ ).<sup>11</sup> However, the reverse reaction can be made to proceed in the presence of a large excess of TTHA. The rate of the reverse reaction depends linearly on the concentration of both Ni(CN)<sub>4</sub><sup>2-</sup> and TTHA and is found to be suppressed by CN<sup>-</sup>. Stara and Kopanica<sup>1</sup> gave the following rate law for the reverse reaction:

$$-d[\text{Ni}(\text{CN})_4^{2-}]/dt = k_r[\text{Ni}(\text{CN})_4^{2-}][\text{L}^{6-}]$$
(8)

which is not correct because it does not include the cyanide dependence term which is responsible for suppressing the rate. Our experimental data on reverse rate do not obey eq  $8.^2$  The correct rate expression as derived earlier<sup>3</sup> also is

$$-d[Ni(CN)_{4}^{2-}]/dt = k_{r}[Ni(CN)_{4}^{2-}][L^{6-}]/[CN^{-}]$$
(9)

The integrated form of this equation is

$$(A_{i} - A_{t}) + A_{i} \ln \frac{A_{t}}{A_{i}} = -\frac{\epsilon_{l}}{4} k'_{obsd} t$$
(10)

where  $A_i$  and  $A_t$  are absorbances at t = 0 and t = t;  $\epsilon$  is the molar absorbancy of  $Ni(CN)_4^{2-}$  at the wavelength at which the reaction is followed. We found that the reverse rate data fit in eq 10 excellently. The  $k'_{obsd}$  values were calculated by plotting the left-hand side of eq 10 vs. time, where  $k'_{obsd} = k_r[L^{6-}]$  (Table III, Figure 3). A plot of  $k'_{obsd}$ vs. TTHA (not given) is a straight line with a slope which gives the value of  $k_r$  equal to  $2.19 \times 10^{-7}$  s<sup>-1</sup> and a nonzero intercept equal to  $2.5 \times 10^{-10}$  s<sup>-1</sup>. The latter corresponds to the very slow dissociation of  $Ni(CN)_4^{2-}$  unaffected by CN<sup>-</sup>. As in case of other aminocarboxylates<sup>3-7</sup> a definite decrease in absorbance was noticed immediately on mixing solutions of Ni(CN)<sub>4</sub><sup>2-</sup> and TTHA. This again indicates the formation of some intermediate present in rapid equilibrium prior to the rate-determining step. This intermediate is assumed to be  $NiL(CN)_3^{(n+1)-}$  in order to be consistent with reverse and forward rate results.

Temperature Dependence of Forward and Reverse Reactions. The forward and reverse rates were measured in the temperature range 25–50 °C and were found to follow the Arrhenius equation. The activation parameters have been calculated and are given in Table IV. The activation parameters are determined under conditions where the observed rate constant depends on both  $[CN^-]$ and  $[CN^-]^2$ . As a result they may have a complex dependence on  $[CN^-]$ .

Dependence of Forward and Reverse Rates on pH. The pH dependence of the forward rate is given in Figure 4. It is seen that in the pH range 9.5–11.5 the rate remains constant, but it decreases below pH 9.0 as in our earlier studies.<sup>3,4</sup> This is due to formation of the less reactive species HCN. The slope of log  $k_f$  vs. –log [H<sup>+</sup>] was found to be equal to one ( $k_f = k_{obsd}/[CN^-]_T^2$ ), while Stara and Kopanica<sup>1</sup> reported that it was two under similar conditions. The slope of one indicates that one HCN is involved

TABLE III: Reverse Rate Constants for the Reaction of Ni(CN)<sub>4</sub><sup>2-</sup> with H<sub>6</sub>L at pH 11.0,  $\mu = 0.5$  M (NaClO<sub>4</sub>), t = 25 °C, [Ni(CN)<sub>4</sub><sup>2-</sup>] =  $6.0 \times 10^{-5}$  M<sup>a</sup>

expt no.	10 <sup>3</sup> [TTHA <sup>6-</sup> ], M	$10^{10}k'_{obsd}, M s^{-1}$	
1	1.56	6.00	
2	2.09	7.01	
3	3.13	10.00	
4	4.18	12.20	
5	4.18	13.00	•
6	6.25	16.70	
7	12.50	30.00	

 $^{a}$  All kinetic runs have been carried out at  $\lambda_{max}$  = 285 nm.

 TABLE IV:
 Temperature Effect on the Forward and

 Reverse Reaction of the NiTTHA-CN<sup>-</sup> System

(i) forward reaction <sup>a</sup>		(ii) reverse reaction <sup><math>b</math></sup>	
temp, °C	$\frac{10^4 k_{\text{obsd}}}{\text{s}^{-1}},$	temp, °C	$\frac{10^{\circ}k'_{\text{obsd}}}{\text{M s}^{-1}},$
$\begin{array}{c} 25 \pm 0.1 \\ 30 \pm 0.1 \\ 35 \pm 0.1 \\ 40 \pm 0.1 \end{array}$	$2.60 \\ 3.70 \\ 4.62 \\ 7.13$	$\begin{array}{c} 25 \pm 0.1 \\ 30 \pm 0.1 \\ 35 \pm 0.1 \\ 40 \pm 0.1 \\ 45 \pm 0.1 \end{array}$	$     \begin{array}{r}       1.33 \\       1.88 \\       2.58 \\       4.21 \\       7.80 \\     \end{array} $
	Kinetic Pa	rameters	

remetic r arameters			
$E_{a} = 12.30 \text{ kcal}$	$E_{\rm a} = 17.06 \; {\rm kcal}$		
$\Delta H^{*} = 11.71$ kcal	$\Delta H^{\pm} = 16.47$ kcal		
$\Delta S^{\mp} = -22.88$ eu	$\Delta S^{\mp} = -32.75$ eu		
$pZ = 6.00 \times 10^7 \text{ cm}^{-1}$	$pZ = 4.09 \times 10^5 \text{ cm}^{-1}$		
$pZ = 6.00 \times 10^7 \text{ cm}^{-1}$	$pZ = 4.09 \times 10^5 \text{ cm}$		

<sup>*a*</sup> [NiTTHA] = 7.06 × 10<sup>-5</sup> M, [CN<sup>-</sup>]<sub>T</sub> = 1.80 × 10<sup>-3</sup> M, pH 11.0;  $\mu$  = 0.1 M (NaClO<sub>4</sub>). <sup>*b*</sup> [Ni(CN)<sub>4</sub><sup>2-</sup>] = 4.00 × 10<sup>-5</sup> M; [TTHA<sup>6-</sup>] = 4.18 × 10<sup>-3</sup> M; pH 11.0;  $\mu$  = 0.5 M (NaClO<sub>4</sub>).



**Figure 3.** Inverse first-order plot for the reaction of Ni(CN)<sub>4</sub><sup>2-</sup> with TTHA<sup>6-</sup>. (Plot of eq 10). All kinetic runs have been carried out at 285 nm where  $\epsilon = 4.63 \times 10^3$  M<sup>-1</sup> cm<sup>-1</sup>.

in addition to two cyanides in the forward reaction. One interesting observation is that below pH 7.5 the rate deviates from the expected value. This appears to be due to a decrease in concentration of NiL(CN) below this pH due to depletion of  $CN^-$  following its conversion to HCN.



**Figure 4.** Plot of log  $k_{obst}$  vs. –log [H<sup>+</sup>] for the forward reaction. The solid curve is the calculated curve from  $K_2k_3$ ,  $K_2k_3'$ , and  $pK_a$  of HCN.



**Figure 5.** pH profile of rate constants for TTHA substitution of Ni(CN)<sub>4</sub><sup>2-</sup>. The points correspond to experimental values at t = 25 °C,  $\mu = 0.5$  M (NaClO<sub>4</sub>). The solid line corresponds to the best fitting line calculated from resolved rate constants of eq 14.

A rate expression consistent with these observations for the entire pH range from 7.0 to 11.5 is given as

rate = 
$$d[Ni(CN)_4^{2-}]/dt = {K_2k_3[CN^-]^2 + K_2k'_3[CN^-][HCN]}[NiL(CN)]$$
 (11)

The values of  $K_2k_3$  and  $K_2k'_3$  are 124 and 16.7 M<sup>-2</sup> s<sup>-1</sup>, respectively, at t = 25 °C and  $\mu = 0.1$  M (NaClO<sub>4</sub>). The effect of pH on the reverse reaction was also investigated in the pH range 8.0–11.0. It was observed that the rate of reaction decreases up to pH 9.5 and then increases (Figure 5). This is attributed to the formation of HL, H<sub>2</sub>L,

TABLE V:Conditional Reverse Rate Constants of the<br/>Substitution Reaction on Variation of Sodium<br/>Ion Concentration $^a$ 

${k'_{obsd}}, \ { m M~s^{-1}}$	$k_{r(L,NaL)}, s^{-1}$	$rac{k_{r(L)}}{[k_{r(L)} - k_{r(L,NaL)}]}$
$4.09 \times 10^{-9}$	$4.90 \times 10^{-7}$	
$3.28 imes10^{-9}$	$3.93 \times 10^{-7}$	5.05
$2.90 imes10^{-9}$	$3.47 imes10^{-7}$	3.42
$2.30 imes10^{-9}$	$2.75  imes 10^{-7}$	2.28
$2.00 \times 10^{-9}$	$2.39 \times 10^{-7}$	2.05
	<i>k</i> ' <sub>obsd</sub> , M s <sup>-1</sup> 4.09 × 10 <sup>-9</sup> 3.28 × 10 <sup>-9</sup> 2.90 × 10 <sup>-9</sup> 2.30 × 10 <sup>-9</sup> 2.00 × 10 <sup>-9</sup>	$\begin{array}{c} k'_{\rm obsd}, \\ Ms^{-1} \\ \hline \\ 4.09 \times 10^{-9} \\ 3.28 \times 10^{-9} \\ 2.90 \times 10^{-9} \\ 2.30 \times 10^{-9} \\ 2.00 \times 10^{-9} \\ 2.00 \times 10^{-9} \\ 2.39 \times 10^{-7} \\ \end{array}$

<sup>a</sup> [Ni(CN)<sub>4</sub><sup>2-</sup>] =  $3.50 \times 10^{-5}$  M, [TTHA<sup>6-</sup>] =  $8.35 \times 10^{-3}$  M;  $\mu = 0.5$  M, pH 11.0, t = 25 °C. <sup>b</sup>  $k_{r(L,NaL)} = k'_{obsd}/[TTHA]_{T}$ .

 $H_3L$ ,...,etc. It is possible to deduce the hydrogen ion dependence of the reverse reaction by the following expression:

$$k_{\rm r}[{\rm L}]_{\rm T} = k_{\rm L}[{\rm L}^{6-}] + k_{\rm HL}[{\rm HL}^{5-}] + k_{\rm H_{2}L}[{\rm H}_{2}{\rm L}^{4-}] + k_{\rm H_{2}L}[{\rm H}_{3}{\rm L}^{3-}] + \dots (12)$$

where  $[L]_T = [L^{6-}] + [HL^{5-}] + [H_2L^{4-}] + [H_3L^{3-}] + \dots$ The species distribution of TTHA at various pH values

was calculated with an IBM 7044 computer by using a computer program developed by Perrin and Sayce,<sup>16</sup> and is given in Figure 1. It was found that the concentrations of species involving more than two protons are not more than 1% and can be ignored. Equation 12 therefore takes the form

$$k_{\rm r}\{[{\rm L}^{6-}] + [{\rm HL}^{5-}] + [{\rm H}_{2}{\rm L}^{4-}]\} = k_{\rm L}[{\rm L}^{6-}] + k_{\rm HL}[{\rm HL}^{5-}] + k_{\rm HaL}[{\rm H}_{2}{\rm L}^{4-}]$$
(13)

This may be transformed to

$$k_{\rm r} \left\{ 1 + \frac{[{\rm H}^+]}{K_{\rm HL}} + \frac{[{\rm H}^+]^2}{K_{\rm HL}K_{\rm H_2L}} \right\} = k_{\rm L} + k_{\rm HL} \frac{[{\rm H}^+]}{K_{\rm HL}} + \frac{[{\rm H}^+]^2}{K_{\rm HL}K_{\rm H_2L}}$$
(14)

where  $K_{\rm HL}$  and  $K_{\rm H_2L}$  are the sixth and fifth dissociation constants of TTHA. Expression 14 is not a simple expression. The plot of log  $k'_{\rm obsd}$  vs. pH gives a curve shown in Figure 5. The solid curve shown has been calculated on the basis of the values of  $k_{\rm L}$ ,  $k_{\rm HL}$ ,  $k_{\rm H_2L}$ , and  $pK_{\rm a}$  of TTHA. The resolved rate constants  $k_{\rm L}$ ,  $k_{\rm HL}$ , and  $k_{\rm H_2L}$  are  $4.00 \times 10^{-7}$ ,  $1.00 \times 10^{-7}$ , and  $1.25 \times 10^{-7}$  M<sup>-1</sup> s<sup>-1</sup>, respectively. From these values one can easily infer that L<sup>6-</sup> and H<sub>2</sub>L are more reactive in comparison to HL. This type of observations were also reported by Carr and Danielson<sup>17</sup> for the 1,2-PDTA reaction with Ni–EDTA and by Huber<sup>18</sup> for the CDTA reaction with Ni–EDTA.

Effect of Na<sup>+</sup> Concentration on the Reverse Reaction. Calculation of the Stability Constant of NaL<sup>5-</sup> from Kinetic Data. As described in our earlier communications<sup>3,4</sup> the rate of reaction of Ni(CN)<sub>4</sub><sup>2-</sup> with aminocarboxylates is affected by the presence of sodium ions which are used for ionic strength maintenance. No data were available for the pK<sub>a</sub>'s of TTHA in different media or the stability constant of the NaTTHA<sup>5-</sup> complex. Only pK<sub>a</sub>'s in KNO<sub>3</sub> have been reported in the literature.<sup>15</sup> The reverse reactions were carried out in the presence of varying concentration of NaClO<sub>4</sub> by using KNO<sub>3</sub> for ionic strength control. It was observed that the reaction rate of TTHA with Ni(CN)<sub>4</sub><sup>2-</sup> decreases with an increase in [Na<sup>+</sup>]. This is due to formation of NaL<sup>5-</sup>, which is less reactive than L<sup>6-</sup>.

The conditional rate constants for the reverse rates were calculated according to a method discussed in an earlier study<sup>4</sup> and their values for a sodium ion concentration varying from 0.1 to 0.5 M are presented in Table V.



Figure 6. Resolution of rate constants  $k_{\rm r(L)}, \, k_{\rm r(NaL)},$  and calculation of  $K_{\rm NaL}.$  Plot of eq 15.

TABLE VI:Summary of Rate and EquilibriumConstants Calculated from Kinetic Data

$k_{3}, M^{-1} s^{-1}$	$(1.39 \pm 0.05) \times 10^{-1}$
$K_2 k_3, M^{-2} s^{-1}$	$(1.24 \pm 0.06) \times 10^2$
$K_{1}K_{2}k_{3}, M^{-3} s^{-1}$	$1.10 \times 10^{\circ}$
$K_4^{-1}k_{-3}$ , s <sup>-1</sup> (NaClO <sub>4</sub> )	$2.19 \times 10^{-7}$
$K_{1}, M^{-1}$	$8.87 \times 10^{2}$
$K_{2}, M^{-1}$	$8.92 \times 10^{2}$
$K_1 K_2, M^{-2}$	$7.91 \times 10^{\circ}$
$k_{r(1)}, s^{-1}$	$4.00 \times 10^{-7}$
$k_{r(HL)}, s^{-1}$	$1.00 \times 10^{-7}$
$k_{r(H_{o}L)}, s^{-1}$	$1.25  imes 10^{-7}$
$k_{r(NaL)}/k_{r(L)}$	0.43
$K_{\rm NaL}, M^{-1}$	10.00

Denoting the conditional rate constants of the substitution reaction by uncomplexed  $L^{6-}$  and weakly complexed NaL<sup>5-</sup> by  $k_{r(L)}$  and  $k_{r(NaL)}$ , respectively, the  $K_{NaL}$  was calculated from eq 15 which was derived earlier.<sup>4</sup>

$$\frac{k_{\rm r(L)}}{k_{\rm r(L)} - k_{\rm r(L,NaL)}} = \left[1 - \frac{k_{\rm r(NaL)}}{k_{\rm r(L)}}\right]^{-1} \left[1 + \frac{1}{K_{\rm NaL}C_{\rm Na^+}}\right]$$
(15)

A plot of the left-hand side of above equation vs.  $1/C_{\rm Na^+}$  gives a straight line (Figure 6, Table V). From the intercept and slope of this straight line  $k_{\rm r(NaL)}/k_{\rm r(L)}$  and  $K_{\rm NaL}$  have been obtained. These results have been included in Table VI.

#### Discussion

The reaction between NiTTHA and cyanide ion had been investigated earlier by Stara and Kopanica.<sup>1</sup> The fallacies in the mechanism proposed by them have been discussed at length in one of our earlier communications.<sup>2</sup> Later, our investigations showed that even their experimental data were not reproducible. For example, we found a variable order dependence of one and two on cyanide concentration whereas they had reported only third-order dependence under similar conditions. Further, failure to incorporate inverse cyanide dependence in the reverse rate expression led them to an erroneous conclusion that this was a four-step reaction with the fourth step as the rate-



Figure 7. Proposed structure of NiHL3-.

determining one. Our results, however, fit in the mechanism proposed<sup>5</sup> and confirmed<sup>3,4</sup> for about a dozen aminocarboxylate reactions studied so far including TTHA. This mechanism is reproduced as follows:

$$\operatorname{NiL}^{2-n} + \operatorname{CN}^{-} \xrightarrow{K_1} \operatorname{NiL}(\operatorname{CN})^{1-n}$$
 (rapid) (16)

$$NiL(CN)^{1-n} + CN^{-} \underset{\longleftarrow}{\overset{K_{2}}{\longleftarrow}} NiL(CN)_{2}^{n-} \quad (rapid) \quad (17)$$

$$NiL(CN)_{2}^{n-} + CN^{-} \frac{k_{3}}{k_{-3}} NiL(CN)_{3}^{(n+1)-}$$
 (rds) (18)

$$\operatorname{NiL}(\operatorname{CN})_{3}^{(n+1)^{-}} + \operatorname{CN}^{-} \xrightarrow{K_{4}} \operatorname{Ni}(\operatorname{CN})_{4}^{2^{-}} + \operatorname{L}^{n^{-}}$$
(rapid) (19)

On the basis of this mechanism the following expression had been derived in an earlier communication<sup>3</sup>

$$K_1 K_2 k_3 = K_4^{-1} k_{-3} \beta_4 / K_{\rm NiL}$$
(20)

where  $\beta_4$  is the stability constant of Ni(CN)<sub>4</sub><sup>2-</sup>. A plot of log  $K_1K_2k_3$  vs. log  $K_{\rm NiL}$  gave a straight line with a slope equal to -1 as predicted by eq 20 for as many as 12 aminocarboxylates<sup>3</sup> and TTHA also fits admirably on this plot. This undeniably supports the idea that the same mechanism is applicable to TTHA also. The close agreement in the stability constant of NiL(CN) determined by the kinetic method assuming the above mechanism and value calculated by mole ratio method lends further support to our contention.

The pH dependence of forward and reverse rates over a wide range reflects some interesting features about reactivities of various chemical species present in the reaction mixture. The rate of forward reaction decreases linearly with increase in  $[H^+]$  with a slope of one (Figure 4). This shows that HCN is also a reactant below pH 9.0 in addition to cyanide ion. It is believed that an intramolecular transfer of a proton occurs from HCN to the more basic nitrogen atom of the attached ligand. The chance of its being transferred to the sufficiently acidic carboxylic groups is small. This type of proton transfer was visualized in some earlier studies.<sup>3,4,8,10</sup> It is known from the species distribution of the NiTTHA system (Figure 1) that NiL converts mostly to NiHL at a pH below 8.0. Yet no deviation is observed from the expected slope below pH 8.0 (Figure 4). One would conclude from this that the reactivities of NiL and NiHL are comparable. This is not unexpected when one considers the possible structure of NiHL if we assume that this is similar to the structure of CuHL proposed by Martell<sup>14</sup> (Figure 7). Since the proton is far removed from the actual binding sites where substitution occurs the rate of substitution remains same for NiL and NiHL. At low pH values the main reactant becomes NiHL instead of NiL and in the third step HCN is a reactant instead of CN<sup>-</sup>. The other two steps may be rewritten bearing electroneutrality and stoichiometry in mind.

As seen in Figure 5 the observed rate constant  $k'_{obsd}$ shows a minimum at pH 9.0. This is due to the formation of protonated forms of the ligand viz., HL, H<sub>2</sub>L, etc., H<sub>2</sub>L being the predominant species below and close to pH 8.0 (Figure 1).

Between pH 8.0 and 9.0, an alternative path for the third and fourth steps may be included as shown in the mechanism:

$$\operatorname{NiHL}(\operatorname{CN})_{3}^{n-} \xrightarrow{+\operatorname{CN}^{-}:K_{4}} \operatorname{Ni}(\operatorname{CN})_{4}^{2-} + \operatorname{HL}^{1-n}_{I}$$

NiHL(CN),1-n

+ (

$$-\operatorname{HCN}: h_{3'} \bigvee + \operatorname{HCN}: h_{3'} \\ \operatorname{NiH}_{2}L(\operatorname{CN})_{3}^{1-n} \xrightarrow{+\operatorname{CN}^{-}: K_{4'}}_{-\operatorname{CN}^{-}} \operatorname{Ni}(\operatorname{CN})_{4}^{2-} + \operatorname{H}_{2}L^{2-n} \\ \operatorname{II}$$

The reverse rate constants corresponding to L<sup>6-</sup>, HL<sup>5-</sup>, and H<sub>2</sub>L<sup>4-</sup> have been resolved from the kinetic data and are given in Table VI. It is interesting to note that  $k_{\rm L} >$  $k_{\text{H}_{oL}} > k_{\text{HL}}$ . This order accounts for the upward trend in reverse rate constant below pH 9.5 (Figure 5).

The proposed mechanism can be easily justified for TTHA on the basis of the structure of the NiTTHA complex (Figure 7). The first cyanide displaces the weakly bound water molecule in a very fast step forming NiL(CN), while the substitution by the other two cyanides is relatively slow. The third step is the rate-determining one in which the octahedral complex is transformed to square planar (or tetragonal) configuration, with one glycinate segment still holding on to the central nickel ion. The fourth cyanide adds rapidly displacing this segment and finally forming Ni(CN)<sub>4</sub><sup>2-</sup>.

An interesting comparison can be made between the forward rate constants of the NiTTHA reaction with those of its lower analog NiDTPA.

(i) The value of  $K_1K_2k_3$  is higher for the NiTTHA reaction than for the NiDTPA reaction which has been shown<sup>3,4</sup> to be due to the inverse dependence of  $K_1K_2k_3$ on the stability constants of NiL ( $K_{\text{NiTTHA}} = 10^{18.8}$ ;  $K_{\text{NiDTPA}} = 10^{20.2}$ ).<sup>14,25</sup>

(ii) The value of  $K_2k_3$  is higher for the NiTTHA reaction than for the NiDTPA reaction which is due to the lower value of the overall stability constants for the NiL(CN) mixed complex for TTHA ( $\beta_{111} = 10^{20.93}$  for Ni(TTHA)-(CN),  $\beta_{111} = 10^{22.43}$  for Ni(DTPA)(CN)).

(iii) The value of  $k_3$  is lower for the NiTTHA reaction than for the NiDTPA reaction which is due to the higher overall stability constant for the NiL(CN)<sub>2</sub> mixed complex for TTHA ( $\beta_{112} = 10^{24.88}$  for Ni(TTHA)(CN)<sub>2</sub>;  $\beta_{112} = 10^{23.56}$ for  $Ni(DTPA)(CN)_2$ ).

It was also found that the reverse rate decreases as the sodium ion concentration in the medium increases. A similar observation has been made for reverse reactions of many aminocarboxylate systems in the presence of sodium ions. The general result is that the reverse rate is inversely proportional to  $K_{\rm NaL},$  the stability constant of the sodium ion complex of the corresponding aminocarboxylate. This dependence is shown in Figure 8. This relationship can be used to advantage to predict the rates of reaction between Ni(CN)42- and a given amino-



Figure 8. Correlation of reverse rate constants with stability constants of sodium complexes of aminocarboxylates ( $K_{NaL}$ ).

carboxylate in the presence of Na<sup>+</sup> under a given set of conditions from a knowledge of stability constant of the NaL complex or vice versa. To the best of our knowledge such a relationship has not been recognized before.

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