Inorganica Chimica Acta, *99* (1985) 149–155

Mechanisms of Ligand Replacement in Square Planar Nickel(II) Complexes. II. Reaction of Cyanide with Nickel(II) Complexes of Two Methyl-substituted Ethylenediamine Ligands

JOANNE C. PLESKOWICZ and E. J. BILLO

Department of Chemistry, Boston College, Chestnut Hill, Mass. 02167, U.S.A.

Received June 26, 1984

Abstract

The kinetics of the reaction of cyanide with the square planar complexes $Ni(tetmeen)_2^{2+}$ and $Ni(ibn)_2^{2+}$ to form square planar $Ni(CN)_4^{2-}$ have been studied in aqueous solution at 25 °C, $I = 0.10$ ($NaClO_4$). The reactions of both complexes proceed via very stable mixed-ligand intermediates $NiL(CN)_2$. The spectra and stability constants of these intermediates are reported and discussed. The rates of formation of $NiL(CN)_2$ from NiL_2^{2+} or of $Ni(CN)_4^{2-}$ from $NiL(CN)_2$ are first order in nickel(II) complex and, depending on cyanide concentration, pH and ligand, can be either first or second order in cyanide. The order with respect to protons is either zero, one or two depending on conditions. A mechanism for the reactions is proposed.

Introduction

A previous report from our laboratory [1] examined the reaction of cyanide ion with a square planar nickel(II) complex of the bidentate ligand 1,5-diazacyclooctane (daco) (eqn. 1, L = daco). Cyanide ion is an ideal ligand for the examination

$$NiL_2^{2+} + 4CN^- \longrightarrow Ni(CN)_4^{2-} + 2L \qquad (1)$$

of substitution reactions of square planar nickel(II) complexes because (i) it is a monodentate ligand, permitting in favorable cases detection of the replacement of individual donor atoms, (ii) the molar absorptivity of $Ni(CN)_4^{2-}$ is large, permitting the observation of reaction rates at low concentrations, and (iii) $Ni(CN)_4^{2-}$ is very stable, so that the reactions go to completion even at very low concentrations.

In the second paper of this series we have examined the reaction of cyanide ion with nickel(II) complexes of two additional bidentate nitrogen ligands, namely 1,2-diamino-2-methylpropane (ibn) and 2,3-diamino-2,3-dimethylbutane (tetmeen). These two ligands stabilize square planar geometry in aqueous solution, presumably through steric interaction of the methyl substituents, preventing solvation in the axial positions [2, 3].

The reaction of cyanide ion with $Ni(daco)_2^{2+}$ was found to proceed via a stable square planar intermediate, $Ni(daco)(CN)_2$. We have examined the substitution kinetics of these additional complexes with bidentate ligands in order to ascertain whether similar mixed-ligand intermediates are formed. Furthermore, we hoped to determine the effect of varying axial steric hindrance on the rate of substitution.

Experimental

Reagents

Nickel(II) perchlorate hexahydrate was prepared from nickel carbonate and perchloric acid and was recrystallized twice from water. Solutions were standardized by EDTA titration. Sodium perchlorate was recrystallized twice from water. Solutions of sodium cyanide were standardized by titration with silver nitrate.

1,2-Diamino-2-methylpropane (Aldrich) was redistilled under reduced pressure. Ligand stock solutions were standardized by titration with acid. 2,3-Diamino-2,3-dimethylbutane dihydrochloride was synthesized [4]. Ligand stock solutions were standardized by titration with base. Sodium tetracyanonickelate(II) trihydrate was recrystallized from water. Buffer components (H_3BO_3, NaH_2PO_4, Na_2HPO_4 and NaOH) were reagent grade and were used without further purification.

NiL_2^{2+} solutions were prepared by mixing appropriate volumes of ligand and nickel(II) solutions.

Kinetic Measurements

Reaction rates were followed using the stopped-flow spectrophotometer described earlier [1]. Rates were run under *pseudo* first-order conditions (at least twenty-fold excess of cyanide ion). Rate cons-

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tants were calculated using a computer program which calculated the least-squares fit to the usual $\ln(A_t - A_\infty)$ *vs.* t line, and are the mean of two to four replicates, unless otherwise noted.

Rates were followed at 267 nm (formation of $Ni(CN)_4^{2-}$) or at 243 nm (formation and disappearance of $NiL(CN)_2$). The latter wavelength was used only in the case of L = tetmeen.

For measurements made at 243 nm, a computer program was written to calculate the observed rate constants k_I and k_{II} for the consecutive pseudo first-order sequence: $NiL_2^{2+} \rightarrow NiL(CN)_2 \rightarrow Ni(CN)_4^{2-}$. A pit-mapping search routine [5] was employed. The technique involved finding values of k_I and k_{II} that best approximated the experimental data in the sense that the sum of squares of errors between the experimental curve of *%T vs.* time and the calculated curve was a minimum. The calculated curve was obtained using estimates of k_I and k_{II}, molar absorptivities of NiL_2^{2+}, $NiL(CN)_2$ and $Ni(CN)_4^{2-}$ at 243 nm (5.0×10^2, 4.67×10^3, 7.5×10^2 M^{-1} cm^{-1} respectively) and the equations for two consecutive first order reactions [6]. Initial estimates of k_I and k_{II} were obtained from the stopped-flow photographs. A 5 × 5 matrix was defined, using values of k_I and k_{II} equal to 0.6, 0.8, 1.0, 1.2 and 1.4× the estimated values. The *%T vs.* t data and the error square sum were then calculated for each of the 25 combinations of k_I and k_{II}. The set of k_I and k_{II} which gave the smallest error square sum then became the new estimates, the incremental spacing of the grid was reduced by a factor of 10 and the procedure was repeated. If the new estimates defined a boundary point of the grid, the increments were not reduced. The calculations were continued until the error square sum reached a minimum.

All reactions were carried out at 25 °C and an ionic strength of 0.10 ($NaClO_4$). Measurements of pH were converted to $-\log[H^+]$ by subtracting 0.10 [7]. A log K_1^H value of 9.0 was used for HCN [8].

Results and Discussion

The Intermediate NiL(CN)₂

$Ni(tetmeen)_2^{2+}$ solutions do not exhibit any absorption bands in the wavelength range 220–300 nm. A band at 243 nm appears upon addition of cyanide ion; the intensity increases until $a = 2$ (a = mol cyanide added per mol of nickel complex). The characteristic spectrum of $Ni(CN)_4^{2-}$ (peaks at 267 nm, $\epsilon = 1.16 \times 10^4$ M^{-1} cm^{-1} and 285 nm, $\epsilon = 4.7 \times 10^3$ M^{-1} cm^{-1}) is not evident until after $a = 2$, whereupon the band at 243 nm decreases while those of $Ni(CN)_4^{2-}$ increase, and an isosbestic point is observed at 254 nm. Spectra of $Ni(ibn)_2^{2+}$ solutions exhibited similar behavior, the intermediate also absorbing at 243 nm. At $a = 2$ the formation of the intermediate appears to be quantitative, since mol ratio plots (A_{233} *vs.* mol CN^- added) show no detectable curvature. A band in the visible (370 nm, $\epsilon = 128$), characteristic of square planar nickel(II) complexes, parallels the appearance and disappearance of the band at 243 nm. These observations indicate the reaction sequence (4) and (5) (L = tetmeen, ibn):

$$\text{Reaction I: } NiL_2^{2+} + 2CN^- \longrightarrow NiL(CN)_2 + L \qquad (4)$$

$$\text{Reaction II: } NiL(CN)_2 + 2CN^- \longrightarrow Ni(CN)_4^{2-} + L \qquad (5)$$

The equilibrium constants for the formation of these mixed-ligand complexes were determined spectrophotometrically by addition of ligand to solutions of $Ni(CN)_4^{2-}$. The pH was maintained at 10.8 ± 0.1 to eliminate interference by protonation of CN^- or L. A decrease in absorbance at 267 nm and 285 nm and an increase in absorbance at 243 nm was observed. Using $\beta_{104} = [Ni(CN)_4^{2-}]/[Ni^{2+}][CN^-]^4 = 10^{30.5}$ [8] the equilibrium constant $\beta_{112} = [NiL(CN)_2]/[Ni^{2+}][L][CN^-]^2$ was calculated. For L = tetmeen, $\log\beta_{112} = 23.7 \pm 0.1$, for L = ibn, $\log\beta_{112} = 23.5 \pm 0.1$.

The extent to which mixed ligand complex formation is favored can be expressed by the quantity X, the equilibrium constant for reaction (4) [9]. For a purely statistical distribution $X = 4$ (log

$$MA_2 + MB_2 \rightleftharpoons 2MAB \qquad (4)$$

$X = 0.6$), and values of log X significantly greater than 0.6 indicate favorable formation of the mixed-ligand complex.

In the present case,

$$\log X = 2\log\beta_{112} - \log\beta_{120} - \log\beta_{104} \qquad (5)$$

where $\beta_{120} = [NiL_2^{2+}]/[Ni^{2+}][L]^2$. For L = tetmeen, log β_{120} = 14.7 [2] and thus log X = 2.2. For L = ibn, log β_{120} = 12.2 [2] and log X = 4.3. These log X values are much larger than the octahedral values observed for octahedral Ni(II) complexes, and indicate the large degree to which ternary complex formation is favored. It is interesting to note that log X is much larger for the ibn complex, although in general in increase in axially-directed substituents tends to favour the formation of square planar nickel(II) complexes. Mixed-ligand complex formation was not observed with cyanide and nickel(II)–ethylenediamine [10]. We also note that the λ_{max} of the intermediate, both in the visible and in the UV, and the formation constant, log β_{112}, are unaffected by a change in the degree of methyl substitution. λ_{max} might reasonably

TABLE I. Rate Data for Reaction of Cyanide with Ni(tetmeen)$_2^{2+}$.[a]

$-\log [H^+]$	$10^4 [CN^-]_T$, M	$k_{I obsd}$, sec^{-1}	$k_{II obsd}$, sec^{-1}
10.70	3.71	8.7	2.63
10.70	4.62	10.0	4.20
10.22	5.00	12.3	3.75
9.18	7.30	5.85 ± 0.03	2.97 ± 0.13
9.18	3.66	2.23	0.72
9.18	6.12	6.0	1.71
9.13	4.69	–	1.50
9.13	4.69	–	1.16
8.70	24.0	–	11.7
8.64	4.00	0.75	0.39
8.62	7.30	1.75	0.99
8.58	4.64	–	0.50 ± 0.03
8.58	3.66	0.62	0.23
8.57	4.69	–	0.40 ± 0.01
8.55	6.12	1.24	0.68
8.25	11.0	0.88	0.52
8.12	16.0	–	1.0
8.11	8.00	0.61	0.40
7.55	5.00	–	0.066
7.44	8.00	–	0.101
7.40	24.0	0.80	0.473
7.34	24.0	0.49	0.410
7.05	16.0	0.21	0.181
7.01	16.0	0.14	0.165
6.97	5.00	–	0.025
6.77	8.00	0.066	0.065
6.77	8.00	0.050	0.056
6.77	15.0	–	0.16
6.73	5.00	–	0.026
6.69	10.0	–	0.060
6.63	5.00	–	0.024
6.54	8.00	–	0.059
6.51	8.00	–	0.064
6.25	5.00	–	0.021

[a] 25.00 °C, $I = 0.10$ ($NaClO_4$).

be expected to be determined only by the ligand field strength of the four donor atoms in the plane (2-NH_2 and 2 CN^-) as is observed in the case of copper(II) complexes [11, 12].

Reaction of Cyanide Ion with Ni(tetmeen)$_2^{2+}$

The rate of formation of $Ni(CN)_4^{2-}$ from Ni(tetmeen)$_2^{2+}$ or from Ni(tetmeen)$(CN)_2$ was measured at 267 nm. Initial studies were performed at high pH, where all of the cyanide is in the form of CN^-. The results are shown in Fig. 1. A plot of log k_{obsd} *vs.* log $[CN^-]$ shows a second-order dependence on $[CN^-]$. (For 28 data points, the least squares slope was 1.91 ± 0.06, correlation coefficient 0.988.) The same rate constant is obtained whether the initial reactant is Ni(tetmeen)$_2^{2+}$ or Ni(tetmeen)$(CN)_2$, demonstrating that reaction I is faster than reaction II. The rate law is given by eqn. 9, where

$$d[Ni(CN)_4^{2-}]/dt = k_{II,o}[Ni(tetmeen)(CN)_2]\,[CN^-]_2 \quad (k_{II,o} = (1.4 \pm 0.5) \times 10^7\ M^{-2}\ sec^{-1}) \qquad (6)$$

Further studies beginning with Ni(tetmeen)$_2^{2+}$ and monitoring the reaction at 243 nm confirm that the rate of formation of Ni(tetmeen)$(CN)_2$ is faster than its rate of disappearance (Fig. 2 and Table I). The $k_{II,o}$ values obtained from these reactions were in good agreement with those measured at 267 nm. The $k_{I,o}$ values could only be obtained over a limited range of $[CN^-]$, from 4 to 8 × 10^{-4} M. At higher $[CN^-]$, the reaction was too fast, while at lower concentrations the transmittance change was too small (the complex concentration was decreased correspondingly to maintain an excess of cyanide). However, over the limited range of concentrations used, the reaction was found to be first-order in $[CN^-]$ (see Table I) with $k_{I,o} = (2.1 \pm 0.2) \times 10^4\ M^{-1}\ sec^{-1}$. (Because of the difference in

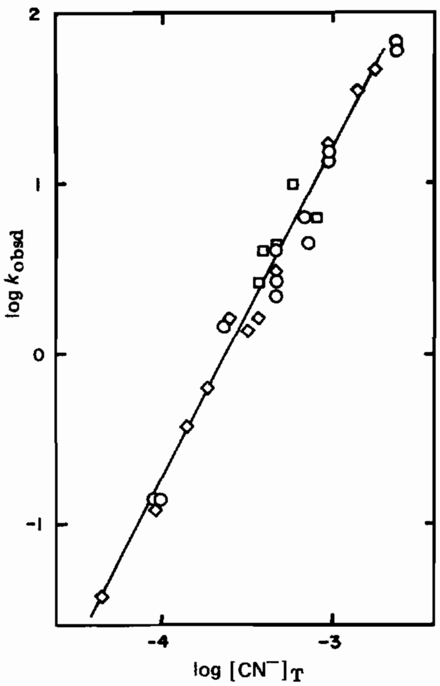

Fig. 1. Cyanide dependence of observed first-order rate constants at pH 10.8 ± 0.1, 25 °C, I = 0.10 ($NaClO_4$). ○) NiL_2^{2+} reactant, observation wavelength 267 nm; □) NiL_2^{2+}, 243 nm; ◇) $NiL(CN)_2$, 267 nm. L = tetmeen. The line is calculated from the rate constants in the text.

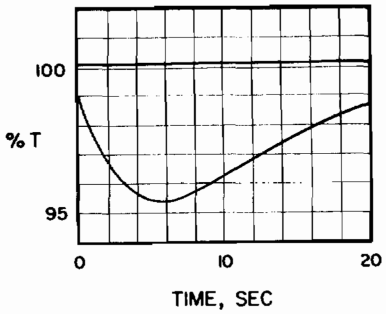

Fig. 2. Typical stopped-flow oscilloscope trace for reaction of cyanide with $Ni(tetmeen)_2^{2+}$, observation wavelength 243 nm. Initial concentrations: $[NiL_2^{2+}]$, 4.0×10^{-5}; $[CN^-]_t$, 1.60×10^{-3} M, Final pH, 7.15.

order dependence on cyanide, reaction II is expected to become faster than reaction I at cyanide concentrations greater than *ca.* 10^{-3} M.)

The mechanism proposed here for the reaction of cyanide with $Ni(tetmeen)_2^{2+}$ is similar to that proposed for the reaction of cyanide with $Ni(daco)_2^{2+}$ [1], and is summarized below:

Reaction I:

$$NiL_2^{2+} + CN^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NiL_2CN^+ \qquad (7)$$

$$NiL_2CN^+ + CN^- \xrightarrow{k_2} NiL(CN)_2 + L \qquad (8)$$

Reaction II:

$$NiL(CN)_2 + CN^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} NiL(CN)_3^- \qquad (9)$$

$$NiL(CN)_3^- + CN^- \xrightarrow{k_4} Ni(CN)_4^{2-} + L \qquad (10)$$

For reaction I (eqns. 7 and 8), assuming the steady-state condition for NiL_2CN^+, the rate law (11) is obtained. A similar rate law

$$k_I = \frac{k_1 k_2 [CN^-]^2}{k_{-1} + k_2 [CN^-]} \qquad (11)$$

can be written for reaction II (eqns. 9 and 10). These rate laws predict that at low $[CN^-]$ the observed rate will be second order in $[CN^-]$ and at sufficiently high $[CN^-]$ the reaction will become first order in $[CN^-]$. This was observed in the $Ni(daco)_2^{2+}$ system [1]. In the present work, for reaction II, there was no evidence for deviation from second-order in $[CN^-]$ kinetics, and the rate law can be written as $k_{II} = k_3 k_4 [CN^-]^2 / k_{-3}$. On the other hand, reaction I was first-order in $[CN^-]$ under the conditions used in this investigation, and the rate law (11) reduces to $k_I = k_1 [CN^-]$.

pH Dependence of the Reaction of Cyanide Ion with $Ni(tetmeen)_2^{2+}$

The hydrogen-ion dependence of the two reactions was also examined. Reaction II was examined in greater detail, from $-\log[H^+]$ = 10.7 down to 6.25. The pH profile of the reaction is shown in Fig. 3. The observed rate constant decreases below pH 10 as cyanide ion is protonated, but the order in cyanide ion remains two. Below pH 7 the slope of the pH profile is zero, indicating the involvement of two protons as well as two cyanide ions. The rate law can be written as

$$k_{II} = k_{II,o}[CN^-]^2 + k_{II,1}[CN^-][HCN] + k_{II,2}[HCN]^2 + k_d \qquad (12)$$

The rate constants evaluated from Fig. 3 are: $k_{II,o} = 1.6 \times 10^7$ M^{-2} sec^{-1}, $k_{II,1} = 2 \times 10^6$ M^{-2} sec^{-1}, $k_{II,2} = 6 \times 10^4$ M^{-2} sec^{-1}. A slightly better fit to the low-pH data points was obtained if a ligand-independent term, k_d = 0.010 sec^{-1}, was introduced. This term is considered to arise from the spontaneous dissociation of $Ni(tetmeen)CN_2$, and can be compared with the dissociation rate of $Ni(tetmeen)_2^{2+}$ measured by Wilkins (1.3×10^{-4} sec^{-1} at pH 6.9) [13] and the rate of acid dissociation of $Ni(tetmeen)(CN)_2$ measured in this laboratory: 5×10^{-2} M $HClO_4$, pH 1.37, k_{obsd} = 0.36 sec^{-1}; 5×10^{-3}

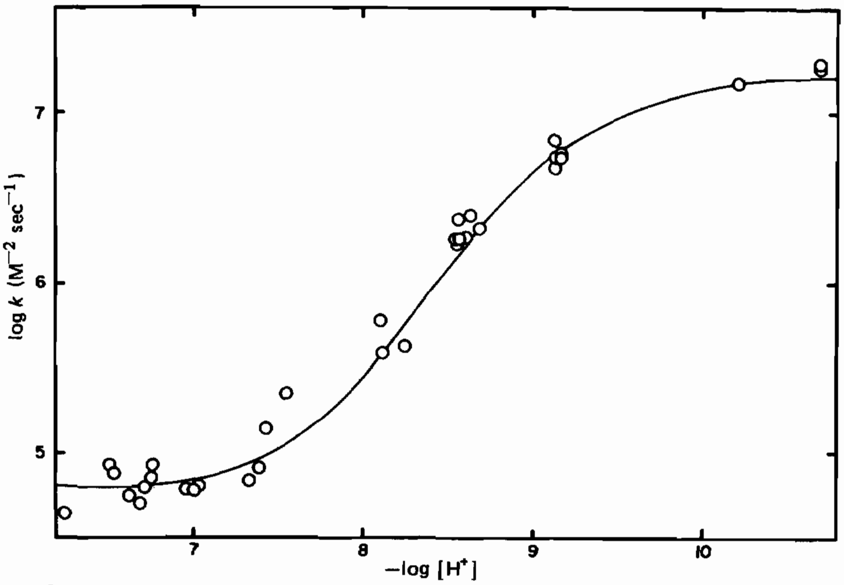

Fig. 3. Hydrogen-ion dependence of Reaction II. The line is calculated using the rate constants in the text.

M $HClO_4$, pH 2.32, k_{obsd} = 0.091 sec^{-1}; 5 × 10^{-2} M acetic acid, pH 3.07, k_{obsd} = 0.067 sec^{-1}. A crucial point in this discussion is the second order dependence on total cyanide at pH values below 7. The second-order dependence is well established at high pH (see Fig. 1) but at low pH, the observed rates are much lower and small contributions from other paths can affect the interpretation. The rate constants for data from −log (H^+) 6.2 to 7.0, where the rate constants are essentially independent of [H^+], were plotted *vs.* [CN^-] and *vs.* $[CN^-]^2$. The data (N = 12) conform well to a $[CN^-]_T^2$ dependence (correlation coefficient 0.989).

Two mechanisms have been proposed to account for proton dependence in substitution reactions involving displacement of a polydentate ligand. Catalini *et al.* [14] proposed a mechanism in which the free amino group, following displacement by the entering ligand X, is in proton equilibrium. Margerum *et al.* [15] proposed a concerted mechanism in which HCN acts as a nucleophile, displacing, and simultaneously transferring a proton to the polyamine nitrogen. In the previous study in this series [1] the rate law was found to be second order in total cyanide, but to involve only a single proton, even at relatively low pH. Although it was proposed that HCN was acting as a nucleophile at low pH, the data could also be explained by the mechanism of Catalini *et al.* [14]. In the present study the observation of a rate law which at low pH is second order in total cyanide and second order in [H^+] can only be explained by invoking HCN as a reactant. The mechanism may include protonation of the free amino group but must include at least one HCN reactant. The rate law (12) has been written assuming that the proton dependence arises solely from HCN participation.

The pH dependence of reaction I was investigated in lesser detail. Below pH 9, k_I decreases, but the decrease is not consistent with one caused by protonation of cyanide. From the data shown in Table I, a protonation constant of approximately 9.7 is indicated, consistent with a mechanism in which the free amino group in NiL_2CN^+ is in proton equlibrium. Below pH 8 there is evidence of participation by a second proton, while the reaction remains first order in total cyanide. In this low pH region the reaction must involve HCN as well as a protonated amino nitrogen.

Compare now the behavior of $Ni(daco)_2^{2+}$ and $Ni(tetmeen)_2^{2+}$ at low pH. In the former case a rate law term involving [HCN] [CN^-] was seen, but no term involving two protons was detected, even at pH 4.5. In the present study, reaction I appears to involve one HCN and one H^+, while reaction II is second order in total cyanide, second order in [H^+]. This difference in behavior may be the result of the rigid structure of daco, limiting the extent to which the dissociating nitrogen can move away from the metal ion. This has the effect of lowering the basicity of the nitrogen and lessening the possibility of protonation. The free terminal nitrogen of the more flexible tetmeen ligand can be protonated and, in combination with reaction of HCN, gives rise to rate law terms involving two protons.

Reaction of Cyanide Ion with $Ni(ibn)_2^{2+}$

$Ni(ibn)_2^{2+}$ in aqueous solution is a mixture of planar NiL_2^{2+} and octahedral $NiL_2(H_2O)_2^{2+}$. Under the conditions of our experiments (25 °C, I = 0.1 M

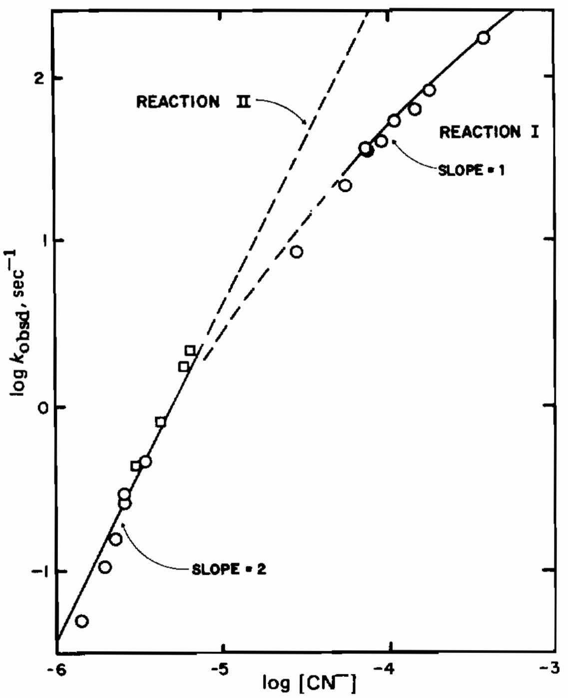

Fig. 4. Cyanide-ion dependence of observed first-order rate constants at 25 °C, $I = 0.10$ (NaClO$_4$). Final pH values ranged from 7.08 to 9.26. ○ NiL_2^{2+} reactant, □ $NiL(CN)_2$ reactant. L = ibn. The observation wavelength was 267 nm.

NaClO$_4$) the distribution is *ca.*, 40% planar and 60% octahedral [3, 16]. We saw no evidence of biphasic reaction with cyanide, suggesting that the planar–octahedral equilibrium is rapid, as has been seen for other systems of this type [17, 18]. We are thus limited in the extent to which we can discuss the mechanism of reaction of cyanide with $Ni(ibn)_2^{2+}$, since it is not clear which complex, NiL_2^{2+} or $NiL_2(H_2O)_2^{2+}$, reacts with cyanide.

As well, the rates of reaction of cyanide with $Ni(ibn)_2^{2+}$ were significantly faster than with $Ni(tetmeen)_2^{2+}$ and this limited the extent to which we could examine the rate law experimentally. Reactions at pH 11 were too fast for the stopped-flow method, and reactions were run at lower pH values. The following summarizes our experiments and observations on this system:

(i) At low [CN$^-$], rates determined using either NiL_2^{2+} or $NiL(CN)_2$ as reactant, and monitoring the appearance of $Ni(CN)_4^{2-}$, gave log k_{obsd} values which, when plotted *vs.* log[CN$^-$], fell on a single straight line with slope of 2. Thus reaction II is slower than reaction I, and the reaction is second order in [CN$^-$]. This could not be confirmed by following the reaction at 243 nm, as was done in the case of $Ni(tetmeen)_2^{2+}$. Due to the lower molar absorptivity of the intermediate, these experiments can only be carried out at relatively high concentrations of NiL_2^{2+} and CN$^-$.

(ii) Rates were determined at pH values of 9.32, 7.44 and 7.12; no difference was detectable in the rate constants measured at these different pH values when log k_{obsd} was plotted as a function of log[free cyanide ion] (Fig. 4). Thus there is no evidence for the occurrence of proton-containing terms in the rate law.

(iii) At high [CN$^-$], using NiL_2^{2+} as reactant, the rection was first-order in [CN$^-$]. Under the same conditions, reactions run using $NiL(CN)_2$ as reactant were too fast to observe, and reactions using NiL_2^{2+}, monitoring at 243 nm, showed no evidence for the formation and disappearance of the $NiL(CN)_2$ intermediate. Thus at high [CN$^-$] reaction I is slower than reaction II.

The data are summarized in Fig. 4. At low [CN$^-$] k_{obsd} is determined by reaction II; at high [CN$^-$] k_{obsd} is determined by reaction I, reaction II being much faster. It is reasonable to assume that reaction II remains second order in [CN$^-$] throughout the range of cyanide concentrations used, and this is shown as a broken line in Fig. 4. In the range of intermediate [CN$^-$], the rate-determining step shifts from reaction II to reaction I, as indicated by a broken line in the Figure. The rate laws and rate constants obtained from the data are shown in eqns. 13 and 14.

Reaction I:

$$d[Ni(CN)_4^{2-}]/dt = k_I[Ni(ibn)_2^{2+}][CN^-] \qquad (13)$$

where $k_I = 5.6 \times 10^5$ M^{-1} sec^{-1}.

Reaction II:

$$d[Ni(CN)_4^{2-}]/dt = k_{II}[Ni(ibn)(CN)_2][CN^-]^2 \qquad (14)$$

where $k_{II} = 4 \times 10^{10}$ M^{-2} sec^{-1}

As mentioned earlier, it was not possible to determine whether low-spin $Ni(ibn)_2^{2+}$ or high-spin $Ni(ibn)_2(H_2O)_2^{2+}$ was the actual reactant in eqn. 13.

Conclusions

Table II summarizes the results from this study with, for comparison, the corresponding rate constants for $Ni(daco)_2^{2+}$.

As expected, an increase in methyl substitution on the ethylenediamine backbone leads to a decrease in the rate of substitution by cyanide. However, this decrease in rate may be the result of either a decrease in the ability of cyanide to attack in an axial position or to a more rigid chelate ring, slowing the rate of dissociation of the ligand. If acid dissociation rates for the complexes are taken as a measure of chelate ring rigidity, then the daco complex (k_d = 3.3×10^{-6} sec^{-1} [1]) is much more rigid than the

TABLE II. Rate Constants for Nickel(II)–Diamine Complexes.[a]

	L = daco[b]	L = tetmeen[c]	L = ibn[c]
Reaction I:			
k_I, M^{-1} sec^{-1}	4.2×10^4	2.1×10^4	5.6×10^5
Form of rate law at low pH[d]	k[HCN] [CN^-]	see text	k[CN^-]
Reaction II:			
k_{II}, M^{-2} sec^{-1}	6.0×10^8	1.4×10^7	4×10^{10}
Form of rate law at low pH	k[CN^-]	k[HCN]^2	k[CN^-]^2

[a] At 25 °C, 0.10 M $NaClO_4$. [b] From reference [1]. [c] Present study. [d] *Ca.* pH 7.

tetmeen complex ($k_d = 1.3 \times 10^{-4}$ sec^{-1} [13]). The daco complex, however, reacts more rapidly with cyanide than does the tetmeen complex, suggesting that the axial positions in the daco complex are more accessible.

There are a number of similarities in the rate behavior of the three systems. First, all three complexes react by the same general scheme, in which a stable dicyano intermediate forms and decays. In each case also, reaction I is first order in cyanide, reaction II second order in cyanide. This indicates that addition of the fourth CN^- and concomitant loss of the diamine ligand is much faster than the reverse reaction, closure of the chelate ring with displacement of the cyanide, while when only one cyanide is bound (Reaction I) this is not true. This can be attributed to the labilizing effect of strong donors observed in the case of octahedral nickel(II) complexes [19] or to the operation of the *trans* effect in square planar nickel(II).

As indicated by Table II, there seems to be no pattern in the pH dependence of the reactions, with a different type of behavior being observed in nearly every case. Some differences can be understood on the basis of differences in ligand structure, but a fuller elucidation of these effects will require the study of further complexes.

Acknowledgement

The authors acknowledge the assistance of John A. Tyrell with some of the experiments.

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