Contribution from the Department of Chemistry, Boston
College, Chestnut Hill, Massachusetts 02167

Mechanisms of Ligand Replacement in Square-Planar Nickel(II) Complexes. I. Reaction of Cyanide with Bis(1,5-diazacyclooctane)nickel(II) Ion

E. J. BILLO

Received March 2, 1973

The kinetics of the reaction of cyanide with square-planar $Ni(daco)_2^{2+}$ (daco = 1,5-diazacyclooctane) to form square-planar $Ni(CN)_4^{2-}$ have been studied in aqueous solution at 25° using a stopped-flow technique. The reaction proceeds *via* a stable square-planar intermediate, $Ni(daco)(CN)_2$. At cyanide concentrations below 10^{-4} *M*, the rate of formation of $Ni(daco)(CN)_2$ from $Ni(daco)_2^{2+}$ and the rate of formation of $Ni(CN)_4^{2-}$ from $Ni(daco)(CN)_2$ are third-order reactions, first order in nickel complex and second order in cyanide. The rate constants are $2.8 \times 10^8\ M^{-2}\ \text{sec}^{-1}$ and $6.0 \times 10^8\ M^{-2}\ \text{sec}^{-1}$, respectively. At pH values below 8, the reactions are first-order in total cyanide. A mechanism for the reactions is proposed.

Introduction

Although the mechanism of ligand replacement in octahedral nickel(II) complexes is well established,[1] very little is known about substitution reactions of square-planar complexes of nickel(II). Octahedral complexes of nickel(II) are much more plentiful than are square-planar complexes. Many complexes which are square-planar in the crystalline state yield six-coordinate solvated complexes in donor solvents. However, several types of ligands form square-planar nickel(II) complexes even in aqueous solution. The ligands which tend to stabilize square-planar complexes in solution are[2] (i) those which produce a strong ligand field, *e.g.*, cyanide, (ii) those in which the donor atoms are held in a planar configuration, *e.g.*, cyclam, and (iii) those in which steric hindrance prevents solvation in the axial positions, *e.g.*, 1,1,-7,7-tetraethyldiethylenetriamine.

In the present study, some reactions of the square-planar complex $Ni(daco)_2^{2+}$ (daco = 1,5-diazacyclooctane) are examined. This complex is square planar as a result of shielding of the axial positions by methylene groups of the ligands.[3,4] Although the reactions of this complex with concentrated acids and with most ligands are unusually slow, its reaction with cyanide (eq 1) is extremely rapid. The cyanide dependence and pH dependence of the reaction and the observation of reaction intermediates permit the mechanism of the reaction to be examined in detail.

$$Ni(daco)_2^{2+} + 4CN^- \rightarrow Ni(CN)_4^{2-} + 2daco \qquad (1)$$

Experimental Section

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 using Murexide indicator. Sodium perchlorate was recrystallized twice from water; solutions were standardized by passage of an aliquot through a column of Dowex 50 followed by titration with standard sodium hydroxide. Solutions of sodium cyanide were standardized by titration with silver nitrate. Acetic acid, boric acid, NaH_2PO_4, and Na_2HPO_4 were reagent grade and were used without further purification.

1,5-Diazacyclooctane dihydrobromide was prepared according to the procedure of Buhle, *et al.*[5] The free diamine was obtained by reaction with saturated sodium hydroxide, separation of the organic layer, and vacuum distillation.

The nickel complex $Ni(daco)_2(ClO_4)_2$ was prepared in the following manner. Approximately equivalent amounts of nickel(II) perchlorate solution and diamine were mixed and the solution was filtered. Addition of 1 *M* perchloric acid to the yellow solution resulted in crystallization of the perchlorate, which was filtered, washed with a little water, and dried *in vacuo.* (*Warning. Perchlorate salts of similar complexes are known to be explosive. They are heat and pressure sensitive. Accordingly, only small amounts of this complex should be prepared and should be handled with care.*) The elemental analyses and visible spectrum (λ_{max} 442 nm, ϵ 113) agreed with those reported by Musker and Hussain[3] for the anhydrous complex. Several different samples were prepared in this way; they exhibited identical spectral and kinetic properties.

The complex $Ni(daco)(CN)_2$ was obtained by adding 2 equiv of 0.1 *M* NaCN to a weighed amount of $Ni(daco)_2(ClO_4)_2$. Upon warming, the yellow $Ni(daco)_2(ClO_4)_2$ dissolved; a tan solid separated when the solution was cooled.

Anal. (Dornis und Kolbe Mikroanalytisches Laboratorium, Mulheim, West Germany). Calcd for $Ni(C_6H_{14}N_2)(CN)_2$: C, 42.7; H, 6.3; N, 24.9. Found: C, 42.8; H, 5.9; N, 25.1.

Solutions of $Ni(daco)_2^{2+}$ were prepared by dissolving weighed amounts in water. Solutions of $Ni(daco)(CN)_2$ were prepared from $Ni(daco)_2^{2+}$ solutions by addition of the appropriate volume of cyanide solution or, in a few instances, by dissolving $Ni(daco)(CN)_2$.

Measurements. Rates were measured using a stopped-flow spectrophotometer based on the Sturtevant design.[6] The monochromator was a Beckman DU. The glass and Teflon flow system, four-jet tangential mixer, and 4-mm optical path cell were maintained at a constant temperature by means of water circulated from a thermostat. A Tektronix 564B storage oscilloscope with a Polaroid camera was used to record the data. A few of the slower reactions were followed using a Cary 14 spectrophotometer with thermostated cell holders. The reactions were run in excess cyanide and all gave pseudo-first-order rate plots. Rate constants reported are the average of two to four kinetic runs, except where noted.

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

Results

Dissociation Rate of $Ni(daco)_2^{2+}$. Dissociation of the complex in acid solution is extremely slow. The rate of disappearance of the absorption band at 442 nm (the characteristic band of square-planar NiN_4 chromophores) was followed; thus the measured rate is the rate of dissociation of the first ligand (eq 2).

$$Ni(daco)_2^{2+} \rightarrow Ni(daco)^{2+} + daco \qquad (2)$$

In dilute perchloric acid solutions the rate of dissociation is independent of acidity, $k_d = 3.3 \times 10^{-6}\ \text{sec}^{-1}$. In 1 *M* perchloric acid the rate is lower ($k_d = 1.5 \times 10^{-6}\ \text{sec}^{-1}$) which may be the result of decreasing hydrogen ion activity in this medium. In acetate buffers (Table I) the rate increases with increasing pH as a result of catalysis by acetate

---

(1) R. G. Wilkins, *Accounts Chem. Res.*, 3, 408 (1970).

(2) W. K. Musker, *Advan. Chem. Ser.*, No. 62, 469 (1966).

(3) W. K. Musker and M. S. Hussain, *Inorg. Chem.*, 5, 1416 (1966).

(4) D. J. Royer, V. H. Schievelbein, A. R. Kaljanaraman, and J. A. Bertrand, *Inorg. Chim. Acta*, 6, 307 (1972).

(5) E. L. Buhle, A. M. Moore, and F. G. Wiseloge, *J. Amer. Chem. Soc.*, 65, 29 (1943).

(6) J. M. Sturtevant in "Rapid Mixing and Sampling Techniques in Biochemistry," B. Chance, *et al.*, Ed., Academic Press, New York, N. Y., 1964, p 89.

(7) R. G. Bates, "Determination of pH," Wiley, New York, N. Y., 1964, p 74.

(8) G. B. Kolski and D. W. Margerum, *Inorg. Chem.*, 7, 2239 (1968).

Table I. Dissociation of $Ni(daco)_2{}^{2+}$ in Acetate Buffers[a]

$-\log [H^+]$	$10^6 k_{obsd}$, sec^{-1}	$-\log [H^+]$	$10^6 k_{obsd}$, sec^{-1}
3.20	3.37	4.89	7.07
4.05	4.50	5.44	8.41
4.46	5.75		

[a] $[Ni(daco)_2{}^{2+}] = 10^{-3}$ *M*, $[acetate]_T = 0.10$, $I = 0.10$ ($NaClO_4$), 25°.

ion. A plot of k_{obsd} *vs.* $[OAc^-]$ yielded an acetate-independent dissociation rate of 3.2×10^{-6} sec^{-1}, in excellent agreement with the values determined in perchloric acid solutions. Thus the dissociation is independent of acidity from pH 1 to at least pH 5.5. In basic solution (pH 9) using EDTA to force the reaction to completion, the rate appeared to be dissociation limited also. The observed rates ranged from 5 to 7×10^{-6} sec^{-1}, were independent of EDTA concentration, and increased slightly with increasing pH.

The Intermediate $Ni(daco)(CN)_2$. The spectrum of $Ni(daco)_2{}^{2+}$ exhibits an intense charge-transfer band at 238 nm (ϵ 1.1×10^4). The spectra of solutions of $Ni(daco)_2{}^{2+}$ containing added cyanide (Figure 1) exhibit a new band at 218 nm which increases in intensity until exactly 2 equiv of cyanide is added. Well-defined isosbestic points occur at 230 and 261 nm. No evidence of the characteristic spectrum of $Ni(CN)_4{}^{2-}$ (peaks at 267 and 285 nm) is evident until after the addition of two cyanides, whereupon the band at 218 nm decreases in intensity and a new isosbestic point is observed at 257 nm. A band in the visible spectrum (λ_{max} 373 nm, ϵ 145) also reaches maximum intensity when exactly 2 equiv of cyanide is added. This band is typical of square-planar nickel(II).

These observations are consistent with the formation of a square-planar intermediate, $Ni(daco)(CN)_2$. Isolation of a solid complex with the expected composition confirms the formulation of the intermediate as $Ni(daco)(CN)_2$. Insufficient material was available for determination of the magnetic susceptibility, but the visible spectrum indicates square-planar geometry.

The rate of dissociation of the mixed complex was investigated briefly. The rate of disappearance of the complex was measured at 218 nm. In dilute perchloric acid, pH 1.5, $k_{obsd} = 3.34 \times 10^{-4}$ sec^{-1}. In 1 *M* perchloric acid, $k_{obsd} = 5.5 \times 10^{-4}$ sec^{-1}. The rate of dissociation of the mixed complex is a factor of 100 greater than that of $Ni(daco)_2{}^{2+}$ at the same acidity, and a factor of 2-5 less than that of $Ni(CN)_4{}^{2-}$.[8]

Rates of Reaction with Cyanide. Existence of the intermediate $Ni(daco)(CN)_2$ suggests the reaction scheme (3) and (4). The rate of formation of $Ni(daco)(CN)_2$ from $Ni(daco)_2{}^{2+}$ was measured at 238 nm, the rate of formation of $Ni(CN)_4{}^{2-}$ from $Ni(daco)(CN)_2$ was measured at 218 nm or 267 nm, and the rate of formation of $Ni(CN)_4{}^{2-}$ from $Ni(daco)_2{}^{2+}$ (*vide infra*) was measured at 267 nm. The observed rates are shown in Table II.

$$\text{reaction I:}\quad Ni(daco)_2{}^{2+} + 2CN^- \rightarrow Ni(daco)(CN)_2 + daco \qquad (3)$$

$$\text{reaction II:}\quad Ni(daco)(CN)_2 + 2CN^- \rightarrow Ni(CN)_4{}^{2-} + daco \qquad (4)$$

Table II.

A. Cyanide Reactions with $Ni(daco)_2{}^{2+}$ at High pH[a]

$10^5[Ni(daco)_2{}^{2+}]$, *M*	$10^4[CN^-]$, *M*	Wavelength,[b] nm	k_{obsd}, sec^{-1}
0.10	0.12	267	0.025[c]
0.20	0.20	267	0.10 ± 0.01
1.00	0.50	267	0.49 ± 0.01
1.02	0.50	267	0.50 ± 0.01
0.58	0.90	238	2.23[c]
1.15	0.92	267	1.6 ± 0.1
1.02	1.00	267	1.8[c]
1.00	1.00	267	1.98 ± 0.07
0.58	1.01	267	2.3 ± 0.1
0.58	1.01	238	2.8 ± 0.1
0.58	1.01	238	2.84 ± 0.05
0.58	1.01	238	2.78 ± 0.03[d]
1.15	1.84	267	5.3 ± 0.2
1.15	1.84	267	5.2 ± 0.2
1.15	1.84	238	6.7[c]
1.00	2.00	267	5.8 ± 0.1
2.00	2.00	267	5.6 ± 0.2
2.90	4.50	267	15.5[c]
0.58	4.50	238	15.9 ± 0.2
2.06	4.85	238	19.4[c]
1.00	5.00	267	18 ± 2
2.00	5.00	267	19.3 ± 0.3
2.90	9.00	267	36[c]
0.58	9.00	238	40[c]
2.00	10.0	267	42 ± 2
3.20	10.0	267	46 ± 3
3.20	20.0	267	81 ± 3

B. Cyanide Reactions with $Ni(daco)(CN)_2$ at High pH[a]

$10^5[Ni(daco)(CN)_2]$, *M*	$10^4[CN^-]$	Wavelength,[b] nm	k_{obsd}, sec^{-1}
0.55	0.45	267	1.28 ± 0.04
0.55	0.90	267	5.1 ± 0.1
0.55	0.90	218	4.9[c]
2.70	0.90	267	4.9[c]
0.55	1.04	218	6.3 ± 0.2
2.88	2.25	267	22.9 ± 0.5
2.70	4.50	267	85 ± 5

[a] pH = 10.6 ± 0.3, $I = 0.10$ ($NaClO_4$), 25°. [b] Wavelength at which rates were measured. [c] Single determination. [d] pH 11.7.

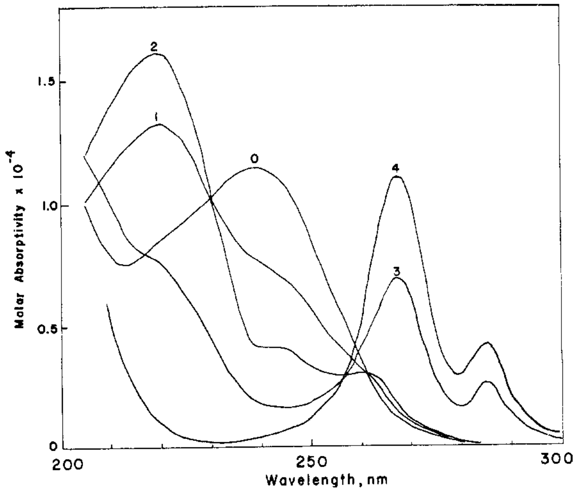

Figure 1. Effect of added cyanide on the ultraviolet spectrum of $Ni(daco)_2{}^{2+}$. The numbers on the curves refer to the number of moles of cyanide added per mole of $Ni(daco)_2{}^{2+}$.

A plot of log k_{obsd} as a function of log $[CN^-]$ (Figure 2) shows that at low cyanide concentrations (below 10^{-4} *M*) reaction I is a third-order reaction, first order in $Ni(daco)_2{}^{2+}$ and second order in cyanide (eq 5), where the subscript I, 2

$$\text{rate} = k_{I,2}[CN^-]^2[Ni(daco)_2{}^{2+}] \qquad (5)$$

refers to reaction I, second order in cyanide. Above 10^{-4} *M* cyanide, the reaction is first order in cyanide (eq 6). The

$$\text{rate} = k_{I,1}[CN^-][Ni(daco)_2{}^{2+}] \qquad (6)$$

rate of formation of $Ni(CN)_4{}^{2-}$ from $Ni(daco)(CN)_2$ is second order in cyanide concentration over the complete range of concentrations studied (eq 7).

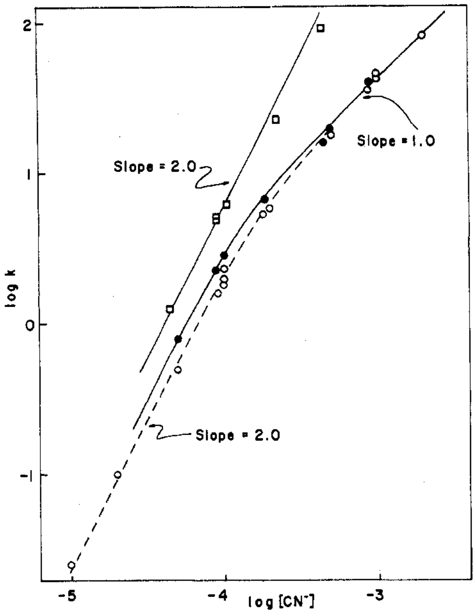

Figure 2. Order dependence of the observed first-order rate constants at pH 10.6 ± 0.3, 25.0°, and $I = 0.1$ ($NaClO_4$). The solid circles are for reaction I, the squares for reaction II, and the open circles for reaction III.

Table III. Hydrogen Ion Dependence of Reaction I[a]

$-\log [H^+]$[b]	$10^4 [CN^-]_T$, M	k_{obsd}, sec^{-1}	k_{obsd}, M^{-1} sec^{-1}
4.48	1.00	1.4×10^{-4} [c]	1.4
6.14	1.00	$(6.35 \pm 0.03) \times 10^{-3}$	63.5
6.42	4.85	0.068 ± 0.002	1.4×10^2
6.70	9.70	0.240 ± 0.001	2.5×10^2
6.87	1.92	0.055 ± 0.002	2.9×10^2
6.92	0.98	0.028 ± 0.002	2.9×10^2
6.93	1.00	0.034 ± 0.002	3.4×10^2
6.93	1.00	0.042 ± 0.001	4.2×10^2
6.96	2.00	0.097 ± 0.006	4.9×10^2
6.98	2.00	0.090 ± 0.004	4.5×10^2
7.04	4.80	0.197 ± 0.007	4.1×10^2
7.09	5.00	0.36 ± 0.02	7.2×10^2
7.13	5.00	0.345[c]	6.9×10^2
7.40	9.60	0.90 ± 0.03	9.4×10^2
7.43	1.00	0.089 ± 0.003	8.9×10^2
7.48	10.0	1.39 ± 0.10	1.4×10^3
7.49	10.0	1.87[c]	1.9×10^3
7.73	1.00	0.196 ± 0.006	2.0×10^3
8.45	4.85	7.5 ± 0.2	1.5×10^4
9.10	4.85	10.8[c]	2.2×10^4
9.52	4.85	15.5 ± 0.2	3.2×10^4
10.42	4.85	20.9 ± 0.4	4.3×10^4
10.84	4.85	19.4[c]	4.0×10^4

[a] $I = 0.10$ ($NaClO_4$), 25°, $[Ni(daco)_2{}^{2+}]_T = (0.58–2.06) \times 10^{-5}\ M$. [b] Buffers: acetate, 0.010 M; phosphate, 0.005 or 0.010 M; borate, 0.010 or 0.025 M; dilute NaOH. [c] Single determination.

Table IV. Hydrogen Ion Dependence of Reaction II[a]

$-\log [H^+]$[b]	$10^4 [CN^-]_T$, M	k_{obsd}, sec^{-1}	k_{obsd}, M^{-1} sec^{-1}
4.63	1.04	2.21×10^{-3} [c]	21
6.34	0.97	0.063[c]	6.5×10^2
6.51	1.04	0.123 ± 0.001	1.2×10^3
6.68	0.97	0.120 ± 0.005	1.2×10^3
6.84	0.96	0.175[c]	1.8×10^3
6.85	1.04	0.252[c]	2.4×10^3
6.87	1.94	0.345 ± 0.002	1.8×10^3
6.96	0.97	0.270 ± 0.005	2.8×10^3
7.01	1.04	0.316 ± 0.003	3.0×10^3
7.04	4.80	1.49 ± 0.01	3.1×10^3
7.05	2.08	0.719[c]	3.5×10^3
7.40	9.60	5.3 ± 0.2	5.5×10^3
7.99	1.04	1.88 ± 0.05	1.8×10^4

[a] $I = 0.10$ ($NaClO_4$), 25°, $[Ni(daco)(CN)_2] = 5 \times 10^{-6}\ M$. [b] Buffers: acetate, 0.010 M; phosphate, 0.005 or 0.010 M. [c] Single determination.

$$\text{rate} = k_{II,2} [CN^-]^2 [Ni(daco)(CN)_2] \quad (7)$$

For all reactions, the calculated initial absorbance and the calculated absorbance change were observed, indicating that $Ni(daco)_2{}^{2+}$ or $Ni(daco)(CN)_2$ were the actual reactants.

The values of the rate constants obtained are $k_{I,2} = 2.8 \times 10^8\ M^{-2}\ sec^{-1}$, $k_{I,1} = 4.2 \times 10^4\ M^{-1}\ sec^{-1}$, and $k_{II,2} = 6.0 \times 10^8\ M^{-2}\ sec^{-1}$.

Under pseudo-first-order conditions, the conversion of $Ni(daco)_2{}^{2+}$ to $Ni(CN)_4{}^{2-}$ occurs *via* two consecutive first-order reactions: $Ni(daco)_2{}^{2+} \rightarrow Ni(daco)(CN)_2 \rightarrow Ni(CN)_4{}^{2-}$. Although the rate of formation of $Ni(CN)_4{}^{2-}$ is not strictly a first-order process, and indeed a slight induction period was observed at 267 nm, the rate data corresponded well to first-order plots of $\ln (A_t - A_\infty)$ *vs.* t. Deviations from first-order behavior, as measured by the standard deviation of the slope of the least-squares line through the data points, were within acceptable limits.

The overall rate of formation of $Ni(CN)_4{}^{2-}$ from $Ni(daco)_2{}^{2+}$ can be estimated from the values of k_I and k_{II}. At cyanide concentrations lower than $10^{-4}\ M$, where both k_I and k_{II} are second-order in cyanide, $Ni(CN)_4{}^{2-}$ is formed by two consecutive pseudo-first-order reactions, the second reaction being 2.1 ± 0.1 times faster than the first. Under these conditions the overall rate of formation of $Ni(CN)_4{}^{2-}$, which will be designated by k_{III}, is somewhat slower than k_I, the rate of disappearance of $Ni(daco)_2{}^{2+}$. At higher cyanide concentrations, k_{II} is much faster than k_I and k_{III} becomes equal to k_I (see Figure 2). The dashed line in Figure 2 shows the estimated value of k_{III}. This value was estimated by calculating the concentrations of $Ni(daco)_2{}^{2+}$, $Ni(daco)(CN)_2$, and $Ni(CN)_4{}^{2-}$ as functions of time, using the equations for two consecutive first-order reactions[9] and pseudo-first-order rate constants obtained from Figure 2. The calculated concentrations of $Ni(CN)_4{}^{2-}$ were then fitted to a first-order equation.

pH Dependence of the Cyanide Reactions. The rate constants were measured in the range pH 5-12 using total cyanide concentrations, $[CN^-]_T = [CN^-] + [HCN]$, from 10^{-4} to $10^{-3}\ M$. No significant change in rates was observed when the concentration of the buffer (acetate, phosphate, or borate) was varied. The observed rates are given in Tables III and IV. Although the reaction of $Ni(daco)_2{}^{2+}$ with cyanide is second order in cyanide at $[CN^-] = 10^{-4}\ M$ at high pH, the reaction is first order in cyanide at lower pH. Similarly, the reaction of $Ni(daco)(CN)_2$ is first-order in total cyanide from pH 5 to pH 8, although the reaction is second order in cyanide at high pH.

The observed second-order rate constants, $k_{obsd}/[CN^-]_T$, for reaction I are listed in Table III and are plotted as a function of $-\log [H^+]$ in Figure 3. The decrease in the observed second-order rate constant below pH 10 parallels the decrease in free cyanide ion concentration. The rate expression for the data of Table III is $k_{obsd} = k_{I,1} [CN^-]$ (*i.e.*, eq 6) where $[CN^-] = [CN^-]_T/(1 + K^H[H^+])$ and K^H is the protonation constant of cyanide ion. The solid line drawn through the data points in Figure 3 is calculated from the above expression with $k_{I,1} = 4.2 \times 10^4\ M^{-1}\ sec^{-1}$ and $K^H = 10^{9.0}$.

Similarly, a plot of the second-order rate constants for reaction II indicates the rate expression $k_{obsd} = k_{II,1} [CN^-]$. A value of $3.0 \times 10^5\ M^{-1}\ sec^{-1}$ was obtained for $k_{II,1}$.

---

(9) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed., Wiley, New York, N. Y., 1961, p 166.

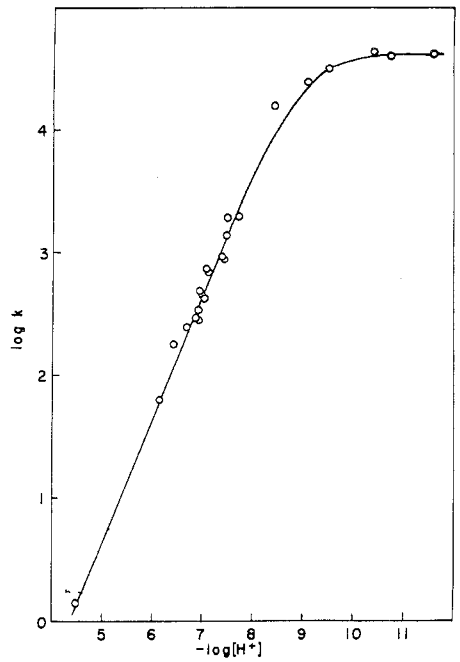

Figure 3. Hydrogen ion dependence of reaction I, first order in cyanide, at 25.0° and $I = 0.1$ ($NaClO_4$). The solid line is calculated using $k_{I,1} = 4.2 \times 10^4\ M^{-1}\ \mathrm{sec}^{-1}$ and $K^H = 1.0 \times 10^9$.

Discussion

Only a few mixed complexes of the type NiL(CN)$_2$ have been reported previously (L = dithiooxalate[10] or 1,10-phenanthroline[11]) and mixed complex formation was not observed with L = ethylenediamine.[12] However, we have observed very stable mixed complexes with L = 2-methyl-1,2-diaminopropane and 2,3-dimethyl-2,3-diaminobutane.[13]

The stability of the mixed complex Ni(daco)(CN)$_2$ is surprising. The mole ratio plot used to determine the stoichiometry of the complex showed no evidence of disproportionation, even though the complexes Ni(daco)$_2^{2+}$ and Ni(CN)$_4^{2-}$ are extremely stable[3,8] ($\beta_2 = 10^{18.7}$ for Ni(daco)$_2^{2+}$ and $\beta_4 = 10^{30.5}$ for Ni(CN)$_4^{2-}$). Assuming that a maximum of 5% dissociation might have been undetected, the β for Ni(daco)(CN)$_2$ must be greater than 10^{26}. This value is similar to formation constants for NiL(CN)$_2$ complexes with methyl-substituted ethylenediamines.[13]

The reaction of cyanide with square-planar Ni(daco)$_2^{2+}$ or Ni(daco)(CN)$_2$ proceeds by an associative mechanism, in agreement with the mechanism of substitution reactions of square-planar platinum(II). Equations 8-11 describe the proposed mechanism for the successive addition of cyanide and loss of daco.

$$\mathrm{Ni(daco)_2^{2+} + CN^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ni(daco)_2(CN)^+} \tag{8}$$

$$\mathrm{Ni(daco)_2(CN)^+ + CN^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Ni(daco)(CN)_2 + daco} \tag{9}$$

$$\mathrm{Ni(daco)(CN)_2 + CN^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Ni(daco)(CN)_3^-} \tag{10}$$

$$\mathrm{Ni(daco)(CN)_3^- + CN^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} Ni(CN)_4^{2-} + daco} \tag{11}$$

Assuming the steady-state approximation for Ni(daco)$_2$(CN)$^+$, the rate expression 12 is obtained for the reaction of two cyanides with Ni(daco)$_2^{2+}$.

$$k_{\mathrm{obsd}} = \frac{k_1k_2[\mathrm{CN}^-]^2}{k_{-1} + k_2[\mathrm{CN}^-]} \tag{12}$$

At low cyanide concentration (less than 10^{-4} *M*) $k_{-1} > k_2 \cdot [\mathrm{CN}^-]$ and the expression simplifies to $k_{\mathrm{obsd}} = k_1k_2[\mathrm{CN}^-]^{-2}/k_{-1}$; thus $k_{I,2} = k_1k_2/k_{-1}$. At higher cyanide concentration, $k_{-1} < k_2[\mathrm{CN}^-]$ and eq 12 reduces to $k_{\mathrm{obsd}} = k_1[\mathrm{CN}^-]$ from which $k_{I,1} = k_1$. Similarly, for the addition of two cyanides to Ni(daco)(CN)$_2$, the steady-state assumption yields $k_{II,2} = k_3k_4/k_{-3}$.

An alternative to the steady-state assumption is that the addition of the first cyanide (eq 8) is in rapid equilibrium. This assumption predicts the same second-order and first-order cyanide dependence. At low cyanide concentrations, the steady-state and equilibrium assumptions are equivalent. At high [CN$^-$] the equilibrium assumption requires that Ni(daco)$_2^{2+}$ is rapidly and completely converted to Ni(daco)$_2$(CN)$^+$ before the observed reaction. However, the initial absorbance of reactions at high [CN$^-$] corresponded exactly to the absorbance expected for Ni(daco)$_2^{2+}$, while Ni(daco)$_2$(CN)$^+$, either four- or five-coordinate, would be expected to have a much different spectrum. (Curtis[14] observed a spectral change, upon the addition of cyanide to nickel(II)-macrocylic tetramine complexes, from the yellow square-planar tetramine complex to a pink monocyanide adduct.)

The proposed sequence of reactions leading to Ni(daco)(CN)$_2$ is shown in Figure 4. A possible structure is shown for Ni(daco)$_2$(CN)$_2$, which may be either a reaction intermediate or the transition state in which daco leaves as the second cyanide adds. A similar mechanism was proposed by Pearson and Sweigart[15] for the reaction of cyanide with square-planar Ni(dto)$_2^{2-}$ (dto^{2-} = dithiooxalate). They also observed two consecutive third-order reactions (eq 13 and 14), with rate constants 4×10^7 and $1.2 \times 10^7\ M^{-2}\ \mathrm{sec}^{-1}$.

$$\mathrm{Ni(dto)_2^{2-} + 2CN^- \rightarrow Ni(dto)(CN)_2 + dto^{2-}} \tag{13}$$

$$\mathrm{Ni(dto)(CN)_2 + 2CN^- \rightarrow Ni(CN)_4^{2-} + dto^{2-}} \tag{14}$$

Kolski and Margerum[16] studied the reaction of cyanide with high-spin, octahedral Ni(trien)(H$_2$O)$_2^{2+}$ (trien = triethylenetetramine). The reaction is fourth-order in total cyanide and at low pH two HCN molecules are reactants. They suggested that the addition of cyanide might produce a square-planar intermediate, Ni(trien)(CN)$_2$; this complex could then react further by the characteristic associative mechanism of square-planar substitution reactions. In the present study, the existence of a stable intermediate and the observation of two consecutive reactions point out the similarity of the two mechanisms.

Previous studies[16,17] have shown that in reactions of cyanide with nickel(II) complexes, HCN is a reactant as well as CN$^-$. In the present study the change in reaction order, from second-order in cyanide at pH 11 to first-order in cyanide below pH 8, indicates that HCN must be a reactant in this system also. In order for reaction I to become first order in cyanide at low pH, reaction of HCN with the intermediate Ni(daco)$_2$(CN)$^+$ must be postulated (eq 15 and 16).

$$\mathrm{Ni(daco)_2^{2+} + CN^- \rightleftharpoons Ni(daco)_2(CN)^+} \tag{15}$$

---

[10] S. Kida, *Bull. Chem. Soc. Jap.*, 33, 1204 (1960).

[11] A. A. Schilt, *J. Amer. Chem. Soc.*, 81, 2966 (1959).

[12] S. Kida, *Bull. Chem. Soc. Jap.*, 32, 981 (1959).

[13] J. C. Pleskowicz and E. J. Billo, in preparation.

[14] Y. M. Curtis and N. F. Curtis, *Aust. J. Chem.*, 18, 1933 (1965).

[15] R. G. Pearson and D. A. Sweigart, *Inorg. Chem.*, 9, 1167 (1970).

[16] G. B. Kolski and D. W. Margerum, *Inorg. Chem.*, 8, 1125 (1969).

[17] G. K. Pagenkopf, *J. Coord. Chem.*, 2, 129 (1972).

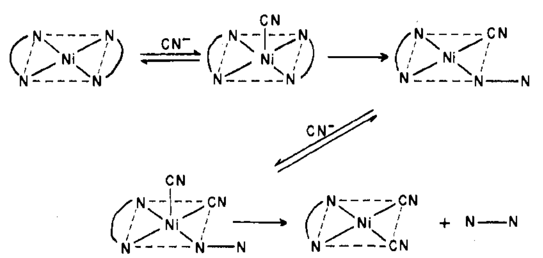

Figure 4. Mechanism of reaction I. Charges are omitted. Although the five-coordinate intermediates are shown with square-pyramidal geometry, their actual structures are unknown.

$$\mathrm{Ni(daco)_2(CN)^+ + HCN \rightarrow Ni(daco)(CN)_2 + hdaco^+} \qquad (16)$$

Inclusion of a rate constant for the reaction of HCN with $Ni(daco)_2(CN)^+$ in the steady-state approximation (eq 8 and 9) yields the rate expression

$$k_{\mathrm{obsd}} = \frac{k_1k_{2,0}[\mathrm{CN^-}]^2 + k_1k_2[\mathrm{CN^-}][\mathrm{HCN}]}{k_{-1} + k_{2,0}[\mathrm{CN^-}] + k_{2,1}[\mathrm{HCN}]} \qquad (17)$$

where $k_{2,0}$ and $k_{2,1}$ refer to reaction of CN^- and HCN, respectively. At relatively high $[CN^-]_T$ and low pH, $k_{2,1}\cdot$[HCN] is the dominant term in the denominator and eq 17 reduces to $k_{\mathrm{obsd}} = k_1[CN^-]$, in agreement with the observed kinetics.

A similar mechanism can be written for reaction II at low pH, leading to a rate expression similar to eq 17. Since at low pH reaction II is first order in total cyanide, while it is second order in cyanide at high pH, the rate constant $k_{4,1}$ (for reaction of HCN with $Ni(daco)(CN)_3^-$) must be significantly greater than $k_{4,0}$.

The rate constants determined in the present investigation are summarized in Table V. The ratio $k_{2,0}/k_{-1}$ permits the calculation of the cyanide concentration at which the observed reaction order changes from first to second order in cyanide. (When $k_{2,0}[CN^-]/k_{-1}$ is less than 1, the reaction is second order in cyanide; when it is greater than 1, the reaction is first order in cyanide.) Since $k_{2,0}/k_{-1} = 6.7 \times 10^3$, the change in reaction order for reaction I is calculated to occur in the vicinity of $[CN^-] = 1.5 \times 10^{-4}\,M$ (log $[CN^-] = -3.8$), in agreement with Figure 2. Similarly, since $k_{4,0}/k_{-3} = 2 \times 10^{-3}$, the change in reaction order for reaction II should occur at $[CN^-] = 5 \times 10^{-4}\,M$ (log $[CN] = -3.3$).

At low pH, where $[CN^-]_T$ = [HCN], reaction II is first order in total cyanide, even at $[CN^-]_T = 10^{-4}\,M$. Thus $k_{4,1}\cdot$[HCN]$/k_{-3}$ must be greater than 1 at this concentration, leading to the conclusion that $k_{4,1}/k_{4,0} > 5$.

For reaction I, the relative magnitudes of $k_{2,0}$ and $k_{2,1}$ can be estimated more precisely. At $-\log [H^+] = 9.15$, with $[Ni(daco)_2^{2+}] = 5.8 \times 10^{-6}\,M$ and $[CN^-]_T = 1.00 \times 10^{-4}\,M$, $k_{\mathrm{obsd}} = 1.79 \pm 0.01\ \mathrm{sec}^{-1}$. Using eq 17 with $k_1 = 4.2 \times 10^4\,M^{-1}\,\mathrm{sec}^{-1}$ and $k_{2,0}/k_{-1} = 6.7 \times 10^3$, the ratio $k_{2,1}/k_{2,0}$ = 1.3 is obtained. The third-order rate constant for the reaction of one HCN and one CN^- with $Ni(daco)_2^{2+}$, $k_1k_{2,1}/k_{-1}$, is therefore $3.6 \times 10^8\,M^{-2}\,\mathrm{sec}^{-1}$. This value is also obtained from a plot of the k_{obsd} values determined at $[CN^-]_T = 1.00 \times 10^{-4}\,M$, where the reaction is second-order in cyanide. A plot of these rates (taken from Table III and expressed as third-order rate constants) *vs.* $-\log [H^+]$ is shown in Figure 5. The solid line is calculated using $k_1k_{2,0}/k_{-1} = 2.8 \times 10^8\,M^{-2}\,\mathrm{sec}^{-1}$, $k_1k_{2,1}/k_{-1} = 3.6 \times 10^8\,M^{-2}\,\mathrm{sec}^{-1}$, and $K^{\mathrm{H}} = 10^{9.0}$ for HCN.

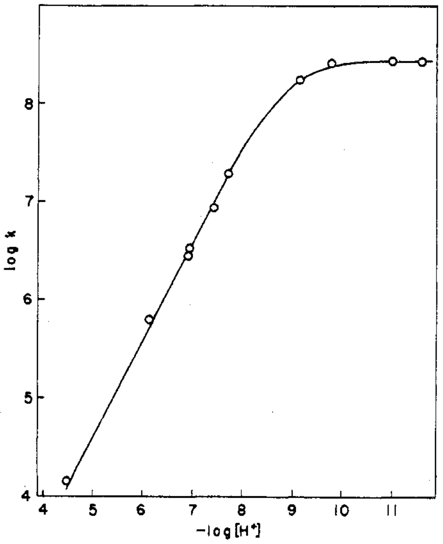

Figure 5. Hydrogen ion dependence of reaction I, second-order in cyanide, at 25.0° and $I = 0.1$ ($NaClO_4$). The solid line is calculated using $k_1k_{2,0}/k_{-1} = 2.8 \times 10^8\,M^{-2}\,\mathrm{sec}^{-1}$, $k_1k_{2,1}/k_{-1} = 3.6 \times 10^8\,M^{-2}\,\mathrm{sec}^{-1}$, and $K^{\mathrm{H}} = 1.0 \times 10^9$.

Table V. Summary of Rate Constants for Ni^{II}–daco Complexes[a]

$k_d = 3.3 \times 10^{-6}\ \mathrm{sec}^{-1}$	$k_d = 3.4 \times 10^{-4}\ \mathrm{sec}^{-1}$ [b]
$k_1 = 4.2 \times 10^4\,M^{-1}\,\mathrm{sec}^{-1}$	$k_3 = 3.0 \times 10^5\,M^{-1}\,\mathrm{sec}^{-1}$
$k_1k_{2,0}/k_{-1} = 2.8 \times 10^8\,M^{-2}\,\mathrm{sec}^{-1}$	$k_3k_{4,0}/k_{-3} = 6.0 \times 10^8\,M^{-2}\,\mathrm{sec}^{-1}$
$k_{2,0}/k_{-1} = 6.7 \times 10^3$	$k_{4,0}/k_{-3} = 2.0 \times 10^3$
$k_{2,1}/k_{2,0} = 1.3$	$k_{4,1}/k_{4,0} = > 5$
$k_1k_{2,1}/k_{-1} = 3.6 \times 10^8\,M^{-2}\,\mathrm{sec}^{-1}$	

[a] 25°, $I = 0.10$ ($NaClO_4$). [b] In dilute perchloric acid, $-\log [H^+] = 1.40$.

Although HCN is a much poorer nucleophile than CN^-, it is kinetically more effective. Intramolecular proton transfer from the attacking HCN to the leaving amine nitrogen facilitates the dissociation of the amine ligand. Similar intramolecular proton transfer was observed in the reactions of HCN with the nickel(II) complexes of triethylenetetramine[16] and ethylenediamine-*N,N′*-disuccinate.[17] If a reaction pathway involving two HCN molecules were possible, the slope of the pH profile (Figure 3) would tend toward zero at low pH. There is no evidence, even at pH 5, that the slope of the line is becoming less than 1.0. Thus even at very low cyanide concentrations, one cyanide ion is necessary for the reaction.

It is interesting to compare the reaction of $Ni(daco)_2^{2+}$ with another sterically hindered square-planar complex, $Pd(Et_4dien)Cl^+$.[18] The palladium(II) complex reacts with bromide or iodide about 10^5 times slower than does the unhindered complex, $Pd(dien)Cl^+$. The hindered complex does not react by the associative mechanism typical of square-planar reactions but by a dissociative mechanism. In the case of $Ni(daco)_2^{2+}$, steric shielding of the axial positions stabilizes the square-planar geometry but does not prevent ligand substitution by an associative mechanism. The greater tendency for square-planar nickel(II) to form five- or six-coordinate complexes, as well as the greater nucleophilicity of the cyanide ion, probably accounts for the difference.

Acknowledgment. Financial support for this research was provided in part by the Research Corporation. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Registry No. NaCN, 143-33-9; $Ni(daco)_2(ClO_4)_2$, 41685-76-1; $Ni(daco)(CN)_2$, 41685-77-2; $Ni(daco)_2^{2+}$, 41685-78-3; CN^-, 57-12-5; $Ni(CN)_4^{2-}$, 15453-80-2.

---

[18] W. H. Baddley and F. Basolo, *J. Amer. Chem. Soc.*, 86, 2075 (1964); 88, 2944 (1966).