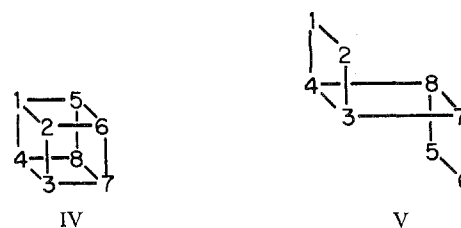The factors which determine whether a Cu_4X_4 (X = halogen) core will take up a "cubane" or a "step" configuration are clearly complex. We know that, in the solid state, $(PPh_3CuCl)_4$[1] and $(Et_3AsCuI)_4$[4,5] have a "cubane" structure, whereas $(PPh_3CuBr)_4$ and $(Ph_2PCH_2PPh_2)_2Cu_4I_4$ have the "step" structure. The stabilization of one form rather than the other must involve a combination of the following factors: (i) minimization of nonbonding X···X contacts within the molecule [this has been discussed above for the $(PPh_3CuBr)_4$ molecule]; (ii) relative stability of trigonally *vs.* tetrahedrally coordinated Cu(I); (iii) relative stability of two, as opposed to three, coordinated halogen atoms; (iv) steric and electronic properties of the substituents on copper (*e.g.*, phosphine or arsine ligand); (v) any restrictions imposed by chelating or bridging substituents on copper; (vi) crystal forces (molecular packing).

One interesting thought which emerges is that it might be possible to prepare both the "cubane" and the "step" isomers of some species. Indeed, it is not impossible that the two forms could interconvert (perhaps reversibly) in solution. The transformation from the "cubane" structure (IV) to the "step" structure (V) requires only a *net* breaking of two bonds (1-5 and 2-6) and the rotation of one face (5-6-7-8) through 180° about the 7-8 axis.

IV

V

Contribution from the Department of Chemistry, Southeast Missouri State University, Cape Girardeau, Missouri 63701

Determination of the Stability Constants for Equilibria Involving Copper(II) and Fluoride Ions in Aqueous Solutions[1]

SIDNEY GIFFORD,[2] WAYNE CHERRY, JOE JECMEN, and MIKE READNOUR*[3]

A fluoride specific ion electrode in conjunction with a reference electrode and millivolt meter has been used to determine equilibrium constants for the formation of complex ions between copper(II) ions and fluoride ions in aqueous solutions at 25°. Measurements were made at ionic strengths of 0.080 and 0.050. It was found that two equilibria are important, one involving the formation of CuF^+ and the other involving the formation of CuF_2. The values of the stability constants for CuF^+ and CuF_2 at 0.080 ionic strength are 7.4 ± 0.4 and 1 ± 1, respectively, and at 0.050 ionic strength these same values are 8.6 ± 0.9 and 7 ± 2.

Introduction

A number of ion-specific electrodes (sensitive to the activity of a certain ion) have been recently developed. These electrodes in conjunction with a suitable reference electrode and a voltmeter can be used to study equilibria involving complex ions. In this study, a fluoride specific ion electrode was utilized to examine the complex ion equilibria involving copper(II) ions and fluoride ions in aqueous solutions.

Three groups have previously looked at the equilibria between copper(II) ions and fluoride ions and in each case only one equilibrium was found to be important, that being

$$Cu^{2+}(aq) + F^-(aq) \rightleftarrows CuF^+(aq) \qquad (1)$$

Ahrland and Rosengren[4] used a potentiometric method and obtained a value of 9 ± 1 working at an ionic strength of 1 *M*

and 20°. A potentiometric method was also used by Connick and Paul[5] and they obtained a value of 5 ± 1 at an ionic strength of 0.5 *M* and at 25°. A value of 6.8 ± 0.5 was determined at 1.0 *M* ionic strength and 25° by Mesaric and Hume[6] using polarography.

The purpose of this research was to see if the fluoride specific ion electrode might be sensitive enough under the proper experimental conditions to detect the occurrence of further equilibria between copper(II) and fluoride ions beyond the one involving the formation of CuF^+ and, if so, to determine the equilibrium constants for those equilibria.

Experimental Section

The potential measurements were made with an Orion Model 94-09 fluoride specific ion electrode, an Orion Model 90-01 single-junction reference electrode, and an Orion Model 801 pH–millivolt meter. The temperature of the solutions was maintained at 25.0 ± 0.1° in a constant-temperature bath. The pH–millivolt meter was standardized with a standard fluoride solution each day that measurements were

(1) Presented in part at the Missouri Academy of Science Meeting, Cape Girardeau, Mo., April 1972.

(2) From the Masters thesis of S. G., Southeast Missouri State University, Jan 1972.

(3) To whom correspondence should be addressed.

(4) S. Ahrland and K. Rosengren, *Acta Chem. Scand.*, 10, 727 (1956).

(5) R. E. Connick and A. D. Paul, *J. Amer. Chem. Soc.*, 80, 2069 (1958).

(6) S. S. Mesaric and D. N. Hume, *Inorg. Chem.*, 2, 1063 (1963).

made. All solutions were prepared using distilled, deionized water and any solutions containing fluoride ions were stored in plastic containers.

The solutions were prepared using reagent grade chemicals. The sodium fluoride was dried in an oven at 120°, cooled, and then weighed. Sodium nitrate solutions were analyzed by flame emission and copper nitrate solutions were determined by electroanalysis. Nitric acid was analyzed by titrating it with sodium hydroxide, standardized with potassium acid phthalate.

The concentrations of all solutions were determined as molalities. This was done by weighing a known volume of the solution whose molar concentration had already been obtained. The required molalities for sodium fluoride were obtained by adding the proper weighed amount of dried NaF to a specific volume of weighed solution.

Theory and Results

The fluoride specific ion electrode is sensitive to the activity of fluoride ion and the Nernst equation describes the electrode potential behavior as a function of fluoride ion activity. The equation is

$$E = E_s - 59.16 \log a_{F^-} \tag{2}$$

where E is the measured total potential of the system, E_s is the portion of the total potential due to the choice of internal and external reference electrodes and internal solutions, and a_{F^-} is the activity of fluoride ion in the solution. If it is assumed that the activity coefficient of fluoride ion remains constant at constant ionic strength and if solutions of varying concentrations of fluoride ion are maintained at the same ionic strength, the Nernst equation can then be put in the form

$$E = \text{constant} - 59.16 \log m_{F^-} \tag{3}$$

Experiments carried out with the fluoride specific ion electrode by the Orion Co.[7] have shown that if the ionic strength is maintained within ±20%, the concentration measurements will be accurate to ±2% for fluoride concentrations up to 0.1 M. The ionic strengths in this work were maintained constant within ±10%.

Two series of solutions containing varying concentrations of fluoride ion but having the ionic strength held constant at 0.080 and 0.050 were prepared using sodium fluoride along with sodium nitrate to maintain the ionic strength of all the solutions at the chosen value. Potential measurements were made on each of these solutions and a graph was made of E vs. $-\log m_{F^-}$ at each ionic strength. The graphs were linear. Rather than take the fluoride concentrations directly from a graph, the best straight line was determined by the method of least squares and an equation which described the line was obtained. The equations were then used to calculate the fluoride ion concentrations in the remaining solutions. The data involved in these determinations and the equations obtained at the two ionic strengths are shown in Table I. The pH of all of the solutions was above 5. At a pH of 5 or above the amount of fluoride ion that is complexed by hydrogen ion is negligible.[8]
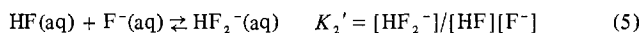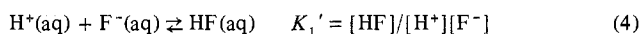
Solutions containing both Cu^{2+} and F^- were prepared using NaF and $Cu(NO_3)_2$ of known concentrations. At a pH of 5 or greater, copper(II) complexes with hydroxide ion to an appreciable extent.[9] Consequently the pH was kept below 5 in these solutions. However, at this low pH hydrogen ion complexes with fluoride. In order to account for the amount of fluoride complexed by hydrogen ion, two potential measurements were made on solutions containing

Table I. Potential Measurements on Solutions Containing Sodium Fluoride and Sodium Nitrate

$[NaNO_3]$, m	$[NaF]$, m	$[F^-]$, m	$-\log m_{F^-}$	E, mV
Ionic Strength 0.080 ± 0.000, Temp 25.00 ± 0.07°, $E = -186 - 59.6 \log m_{F^-}$				
0.0763	0.00367	0.00367	2.44	−41.2
0.0642	0.0158	0.0158	1.80	−78.4
0.0482	0.318	0.0318	1.50	−96.5
0.0000	0.0800	0.0800	1.10	−121.1
Ionic Strength 0.050 ± 0.000, Temp 25.00 ± 0.07°, $E = -189 - 60.2 \log m_{F^-}$				
0.0482	0.00183	0.00183	2.74	−24.4
0.0385	0.0115	0.0115	1.94	−71.8
0.0290	0.0210	0.0210	1.68	−87.9
0.00967	0.0403	0.0403	1.39	−105.1
0.0000	0.0500	0.0500	1.30	−110.9

HNO_3 and NaF at each of the two ionic strengths (0.080 and 0.050).

Previous studies[8] have shown that only two equilibria involving hydrogen and fluoride ions are important. These are

$$H^+(aq) + F^-(aq) \rightleftarrows HF(aq) \quad K_1' = [HF]/[H^+][F^-] \tag{4}$$

$$HF(aq) + F^-(aq) \rightleftarrows HF_2^-(aq) \quad K_2' = [HF_2^-]/[HF][F^-] \tag{5}$$

Bjerrum's method[10] was used to determine the values of K_1' and K_2'. $\bar{n}$, the average number of fluoride ions complexed by each hydrogen ion, was calculated by subtracting the concentration of uncomplexed fluoride ion (obtained from the standard graph in equation form) from the sodium fluoride concentration and dividing by the concentration of nitric acid. The concentrations of sodium fluoride and nitric acid as well as the data required to calculate $\bar{n}$ are shown along with the values of $\bar{n}$ in Table II. An expression for $\bar{n}$ can be put in the form

$$\bar{n} = \frac{K_1'[F^-] + 2K_1'K_2'[F^-]^2}{1 + K_1'[F^-] + K_1'K_2'[F^-]^2} \tag{6}$$

The only unknowns in this equation are K_1' and K_2' and so two measurements are all that are required to establish these values. The values determined for K_1' and K_2' at 0.080 ionic strength were 898 and 3.6, respectively, and the values at 0.050 ionic strength were 934 and 0.7.

Finally, two series of potential measurements were made at 0.080 and 0.050 ionic strengths on solutions containing sodium fluoride, copper nitrate, and nitric acid in order to determine the stability constants for copper(II)-fluoride complex ions. The concentrations of free fluoride in each solution were determined from the equations for the standard graphs prepared previously. The results of these measurements are shown in Table III. The concentrations of nitric acid were kept at such a level that the final pH of each solution was below 5.

In order to calculate the equilibrium constants, the concentrations of HF and HF_2^- were first determined. The two equilibrium expressions involving HF and HF_2^- can be written as

$$\frac{[HF]}{([HNO_3] - [HF] - [HF_2^-])[F^-]} = K_1' \tag{7}$$

$$[HF_2^-]/[HF][F^-] = K_2' \tag{8}$$

Since K_1' and K_2' have been obtained, the only unknowns are [HF] and $[HF_2^-]$. Therefore, they can be calculated by solving these two equations. Again, Bjerrum's method was

(7) "Instruction Manual Fluoride Electrode Model 94–09," Orion Research Inc., Cambridge, Mass., 1967.

(8) E. Baumann, *J. Inorg. Nucl. Chem.*, **31**, 3155 (1969).

(9) L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes," 2nd ed, Chemical Society, London, 1964, p 59.

(10) J. Bjerrum, "Metal Amine Formation in Aqueous Solutions," P. Haase and Son, Copenhagen, 1941.

Table II. Potential Measurements on Solutions Containing Sodium Fluoride and Nitric Acid

[HNO$_3$], m	[NaF], m	Ionic strength	[F$^-$], m	$-$log m_F-	E, mV	$\bar{n}$
Ionic Strength 0.080 ± 0.006, Temp 25.00 ± 0.07°						
0.0420	0.0805	0.0816	0.0350	1.46	$-$99.4	1.082
0.0842	0.0403	0.0853	0.000966	3.02	$-$6.4	0.467
Ionic Strength 0.050 ± 0.004, Temp 25.00 ± 0.10°						
0.0105	0.0500	0.0503	0.0395	1.40	$-$104.7	0.998
0.0526	0.0300	0.0539	0.00128	2.89	$-$15.2	0.546

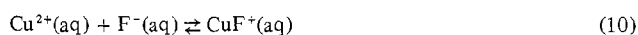**Table III.** Potential Measurements on Solutions Containing Sodium Fluoride, Copper Nitrate, and Nitric Acid

[HNO$_3$], m	[Cu(N-O$_3$)$_2$], m	[NaF], m	Ionic strength	[F$^-$], m	$-$log m_F-	E, mV	$\bar{n}$
Ionic Strength 0.080 ± 0.006, Temp 25.00 ± 0.07°							
0.00420	0.0208	0.0190	0.0779	0.0131	1.88	$-$74.0	0.0885
0.00315	0.0156	0.0335	0.0750	0.0274	1.56	$-$93.0.	0.179
0.00263	0.0130	0.0502	0.0826	0.0440	1.36	$-$105.3.	0.256
Ionic Strength 0.050 ± 0.001, Temp 25.00 ± 0.10°							
0.00402	0.0120	0.0160	0.0500	0.0111	1.96	$-$71.4	0.103
0.00301	0.00901	0.0270	0.0507	0.0223	1.65	$-$89.7	0.200
0.00201	0.00609	0.0355	0.0505	0.0317	1.50	$-$98.9	0.302

used to analyze the data. Once [HF] and [HF$_2$$^-$] have been determined, $\bar{n}$, the average number of fluoride ions complexed per copper(II) ion, can be calculated

$$\bar{n} = \frac{[\text{NaF}] - [\text{F}^-] - [\text{HF}] - 2[\text{HF}_2^-]}{[\text{Cu(NO}_3)_2]} \tag{9}$$

These values of $\bar{n}$ are shown in Table III.

Making use of Bjerrum's method, the approach was first of all to assume that only one equilibrium occurs. If that is true, then the equation describing that equilibrium will be

$$\text{Cu}^{2+}(\text{aq}) + \text{F}^-(\text{aq}) \rightleftarrows \text{CuF}^+(\text{aq}) \tag{10}$$

and the equilibrium constant, K_1, will be given by the equation

$$K_1 = [\text{CuF}^+]/[\text{Cu}^{2+}][\text{F}^-] \tag{11}$$
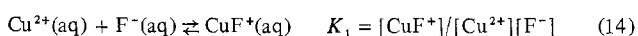
An expression for $\bar{n}$ can be obtained in the form

$$\bar{n} = [\text{CuF}^+]/([\text{Cu}^{2+}] + [\text{CuF}^+]) \tag{12}$$

The preceding equation can be rearranged and simplified to the form

$$\bar{n}/(1 - \bar{n}) = K_1[\text{F}^-] \tag{13}$$

A graph of $\bar{n}/(1 - \bar{n})$ vs. [F$^-$] should give a straight line whose slope is K_1 if the assumption that only one equilibrium is important is correct. Table IV shows the values of $\bar{n}/(1 - \bar{n})$ for each solution and the graphs of $\bar{n}/(1 - \bar{n})$ vs. [F$^-$] at each ionic strength are shown in Figure 1. It can be seen from Figure 1 that both graphs are curved instead of linear indicating that the assumption (that only one equilibrium is important) is false.

The next assumption that was made was that two equilibria were occurring. The two equilibria along with expressions for the equilibrium constants are
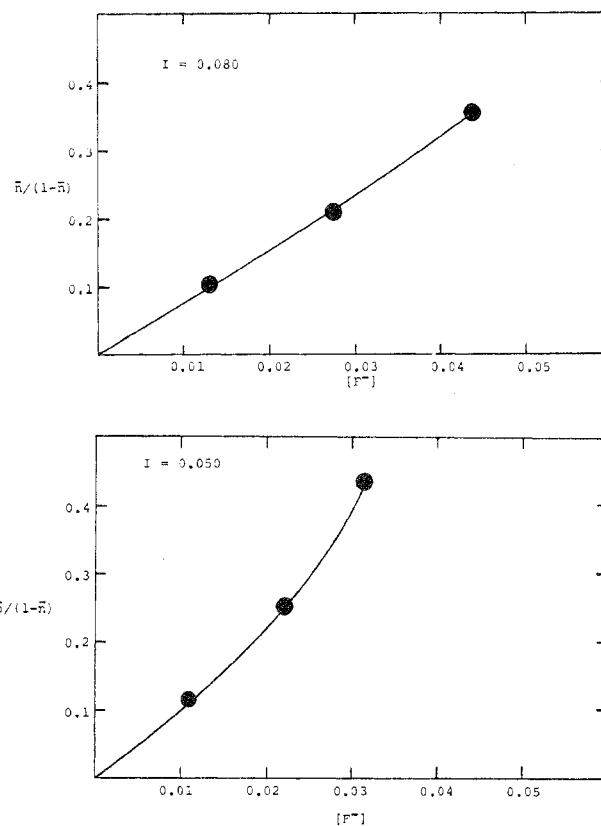
$$\text{Cu}^{2+}(\text{aq}) + \text{F}^-(\text{aq}) \rightleftarrows \text{CuF}^+(\text{aq}) \quad K_1 = [\text{CuF}^+]/[\text{Cu}^{2+}][\text{F}^-] \tag{14}$$

$$\text{CuF}^+(\text{aq}) + \text{F}^-(\text{aq}) \rightleftarrows \text{CuF}_2(\text{aq}) \quad K_2 = [\text{CuF}_2]/[\text{CuF}^+][\text{F}^-] \tag{15}$$

The equation for $\bar{n}$ in this case becomes

$$\bar{n} = \frac{[\text{CuF}^+] + 2[\text{CuF}_2]}{[\text{Cu}^{2+}] + [\text{CuF}^+] + [\text{CuF}_2]} \tag{16}$$

Table IV. Values of $\bar{n}/(1 - \bar{n})$, $\bar{n}/[\text{F}^-](1 - \bar{n})$ and $(2 - \bar{n})[\text{F}^-]/(1 - \bar{n})$ for Solutions Containing Sodium Fluoride, Copper Nitrate, and Nitric Acid

[F$^-$], m	$\bar{n}$	$\bar{n}/(1 - \bar{n})$	$\bar{n}/[\text{F}^-]\cdot$ $(1 - \bar{n})$	$(2 - \bar{n})[\text{F}^-]/$ $(1 - \bar{n})$
Ionic Strength 0.080				
0.0131	0.0885	0.0971	7.41	0.0275
0.0274	0.179	0.218	7.96	0.0608
0.0440	0.256	0.344	7.82	0.1031
Ionic Strength 0.050				
0.0111	0.103	0.114	10.3	0.0234
0.0223	0.200	0.250	11.2	0.0501
0.0317	0.302	0.435	13.6	0.0770

Figure 1. Graphs of $\bar{n}/(1 - \bar{n})$ vs. [F$^-$].

By substituting $K_1[\text{Cu}^{2+}][\text{F}^-]$ for [CuF$^+$] and $K_2[\text{CuF}^+]\cdot$[F$^-$] for [CuF$_2$], then rearranging and simplifying, the equation can be put in the form

$$\frac{\bar{n}}{[\text{F}^-](1 - \bar{n})} = K_1 + \frac{K_1 K_2(2 - \bar{n})[\text{F}^-]}{1 - \bar{n}} \tag{17}$$

Values for $\bar{n}/[\text{F}^-](1 - \bar{n})$ and $(2 - \bar{n})[\text{F}^-]/(1 - \bar{n})$ were calculated and the results are shown in Table IV. If the assumption that two equilibria are important is correct, a graph of $\bar{n}/[\text{F}^-](1 - \bar{n})$ vs. $(2 - \bar{n})[\text{F}^-]/(1 - \bar{n})$ will be a straight line with an intercept of K_1 and a slope $K_1 K_2$. The graphs at the two ionic strengths are shown in Figure 2. This time the graphs are linear, indicating that two equilibria are important. By the method of least squares, values for K_1 were determined from the intercepts of the lines and values of K_2 were obtained from the slopes. At an ionic strength of 0.080 the values of K_1 and K_2 were 7.4 ± 0.4 and 1 ± 1, respectively, and at an ionic strength of 0.050, the values of K_1 and K_2 were 8.6 ± 0.9 and 7 ± 2, respectively. The errors were determined from the standard deviations of the points from the least-squares fits to the straight lines.
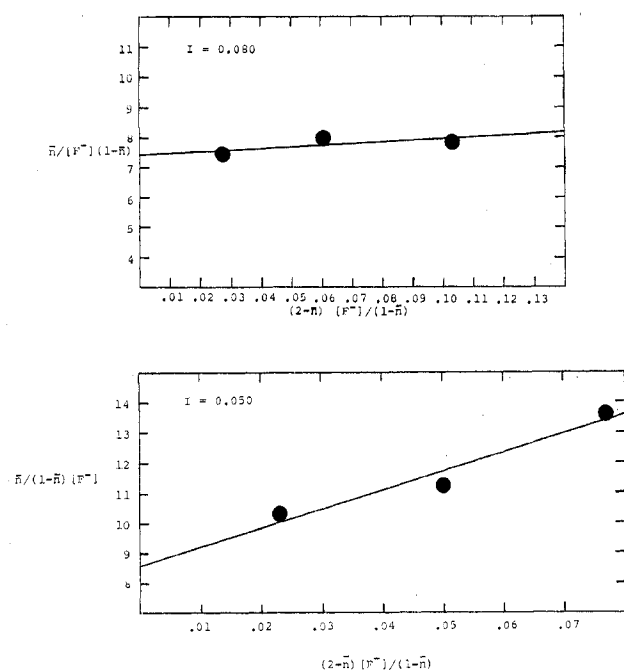
Figure 2. Graphs of $\bar{n}/(1 - \bar{n})[F^-]$ vs. $(2 - \bar{n})[F^-]/(1 - \bar{n})$.

The values of K_1 determined here compare favorably with those obtained by previous workers. It should be noted, however, that K_1 is highly dependent upon the ionic strength. The values of K_1 decrease with increasing ionic strength, which is what would be expected on the basis of Debye–Huckel theory.

The apparent reason that the previous workers on the copper–fluoride system did not observe the equilibrium involving the formation of CuF_2 is that their experiments were carried out at lower $\bar{n}$ values than were used here. For example, Connick and Paul carried out their experiments in such a way that the values of $\bar{n}$ were of the order of 0.002. A typical value of $\bar{n}$ in this work would be 0.2. When the values of $\bar{n}$ are very small, the concentrations of CuF_2 formed are so low that CuF_2 cannot be detected.

The copper(II) ions in aqueous solution are thought to have an octahedral geometry that is distorted along one axis. The solutions containing copper(II) ions in the presence of fluoride are blue just like those containing copper(II) in the absence of fluoride. Presumably, then, CuF^+ and CuF_2 have the distorted octahedral geometry also and could be represented as $[Cu(H_2O)_5F]^+$ and $[Cu(H_2O)_4F_2]$.

Registry No. Copper, 7440-50-8.

Contribution from the Department of Chemistry,
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Kinetics of Tetracyanonickelate(II) Reactions

WALTER C. CROUSE and DALE W. MARGERUM*

AIC30662W

Ammonia, diamines, and glycinate ion greatly accelerate the rate of decomposition of $Ni(CN)_4{}^{2-}$ in the presence of iodine as a scavenger for CN^-. The second-order rate constants (M^{-1} sec^{-1} at 25°, 0.1 M NaClO$_4$) for the nucleophilic reaction of these ligands with $Ni(CN)_4{}^{2-}$ are 120 for NH_3, 425 for ethylenediamine, 206 for 1,2-diaminopropane, 590 for 1,3-diaminopropane, and 54 for glycinate ion. The reactivities of N-methyl derivatives of ethylenediamine also fall within this range. The $Ni(CN)_4{}^{2-}$ complex dissociates in the presence of iodine, having a first-order rate constant of 4.8×10^{-4} sec^{-1}, independent of acidity from pH 3 to 8 and independent of iodine concentration. In the absence of iodine the acid dissociation rate of $Ni(CN)_T{}^{2-}$ has an inverse first-order dependence in CN_T (CN^- + HCN) above pH 2 and is pH dependent.

Introduction

The rate of dissociation of the $Ni(CN)_4{}^{2-}$ complex is slow in acidic solutions and is very dependent on the hydrogen ion concentration.[1] In basic solution the breakup of $Ni(CN)_4{}^{2-}$ can be forced by multidentate ligands such as aminopolycarboxylates and polyamines. The EDTA reaction is very slow and has a first-order dependence in $EDTA^{4-}$ and $Ni(CN)_4{}^{2-}$ concentrations, with an inverse first-order dependence in cyanide ion concentration.[2] Similar rate expressions are observed[3,4] for the reaction of eight other aminopolycarboxylates with $Ni(CN)_4{}^{2-}$. The behavior of triethylenetetramine (trien) is quite different in that it reacts much faster with $Ni(CN)_4{}^{2-}$ and exhibits no inverse cyanide ion dependence.[5] Preliminary studies[5] indicated that ethylenediamine (en) reacted in a manner similar to trien, but with a second-order rate constant of about 50 M^{-1} sec^{-1} compared to a rate constant of 310 M^{-1} sec^{-1} for trien. On the other hand, ammonia (in the presence of EDTA to force the reaction) was found to be many orders of magnitude less effective than en and had an apparent rate constant of only 9×10^{-4} M^{-1} sec^{-1}. The much greater reactivity of en and trien, compared to NH_3, suggested a possible kinetic chelate effect for the substitution reactions of the tetracyanonickelate(II) square-planar complex and the existence of a six-coordinate reactive intermediate. A six-coordinate activated complex was propsed for the reaction of a Pt(II) complex[6] and it is well known that Ni(II) forms six-coordinate species much more readily than does Pt(II).[7] The ring-closure reactions of monodentate-bonded

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

(2) D. W. Margerum, T. J. Bydalek, and J. J. Bishop, *J. Amer. Chem. Soc.*, 83, 1791 (1961).

(3) L. C. Coombs and D. W. Margerum, *Inorg. Chem.*, 9, 1711 (1970).

(4) L. C. Coombs, D. W. Margerum, and P. C. Nigam, *Inorg. Chem.*, 9, 2081 (1970).

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

(6) U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *Inorg. Chem.*, 4, 925 (1965).

(7) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, pp 395, 419.