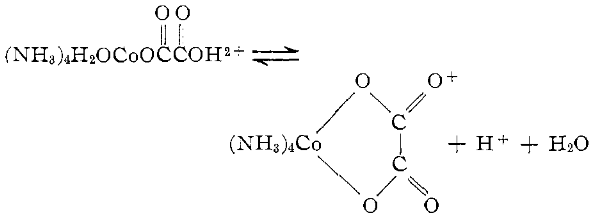
The Monodentate and Chelated Maleate Complexes of Cr(III).—A conspicuous feature of the behavior of the monodentate and chelated maleate complexes of Cr(III) is the relative thermodynamic stability of the monodentate species. Based on studies of the stabilities[39] of maleate complexes of labile cations, maleate has generally been regarded as a strongly chelating ligand. Most of the stability constants were measured, however, either without variation of pH or over such narrow ranges of pH that no test of the number of protons involved in the equilibrium was possible. Nonetheless, arguments based on the magnitude of the stability constants, in comparison with values for related ligands such as fumarate, do suggest a chelate effect.[40] All the measurements on labile systems, however, were made at much higher pH's than those reported for Cr(III). At pH's above 3, the acid range of most previous measurements, the dominant behavior of maleate may well be chelating.

A basis of comparison with the Cr(III) results is supplied by Andrade and Taube's[41] estimate of the driving force for ring closing in the *cis*-binoxalatotetraamminecobalt(III) ion. Their estimate is based on the collection of equilibrium data from several sources. It also involves the assumption that the affinity of *cis*-diaquotetraamminecobalt(III) for binoxalate to form the monodentate *cis*-binoxalatoaquotetraamminecobalt(III) complex is the same as the affinity of aquopentaamminecobalt(III) for binoxalate. The argument is reasonable, although not rigorous, and leads to an estimate of 10 as the equilibrium constant for ring closing (eq 2).


(2)

$$K = ((NH_3)_4CoC_2O_4^+)(H^+)/((NH_3)_4H_2OCoC_2O_4H^{2+}) \approx 10\ (\mu = 0,\ 25°).$$

To the extent that this estimate is valid, it offers perspective on the value of 0.06 measured for the maleate–chromium(III) system. Oxalate forms five-membered chelate rings with little strain. For maleate chelates, in contrast, the ring has seven members and the added rigidity imposed by the olefinic linkage.

Acknowledgment.—Financial support for this research by the National Science Foundation, both for fellowships for M. V. Olson, 1965–1969, and for Grant No. GP 5322, is gratefully acknowledged. Many of the stopped-flow rate measurements reported in Table V were made by Dr. Yasuo Yamamoto, Visiting Scholar from Osaka University, Osaka, Japan, Sept–Nov 1967.

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Mechanism of Tetracyanonickelate Formation from Mono(aminocarboxylate)nickel(II) Complexes

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The rate of formation of $Ni(CN)_4^{2-}$ is first order in nickel aminocarboxylate concentration and varies from first to third order in cyanide ion concentration, depending upon the level of the cyanide ion concentration and the nature of the aminocarboxylate ligand. Sexadentate, pentadentate, tetradentate, and tridentate ligands are compared and their rates of reaction (at the same cyanide ion concentration) vary by ratios as large as 10^8. Nevertheless, the reactions proceed by a similar mechanism. In each case three cyanide ions and a segment of the aminocarboxylate ligand are coordinated to nickel(II) in the rate-determining step. The observed variation in cyanide ion reaction order is caused by the relatively rapid formation of mixed cyanide–aminocarboxylate complexes. All the reverse reactions are first order in $Ni(CN)_4^{2-}$ concentration, first order in the aminocarboxylate ligand concentration, and inverse first order in cyanide ion concentration.

Introduction

Cyanide ion reacts with mono(aminocarboxylato)nickel(II) complexes, NiL^{2-n}, to give tetracyanonickelate ion and to displace the aminocarboxylate ligand (eq 1). The speed of the reaction is highly dependent upon the cyanide ion concentration and is inversely dependent on the stability constant of NiL^{2-n}.

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

In the present work the kinetics of the forward and reverse reactions for eq 1 are examined for six aminocarboxylates ($EDDA^{2-}$, NTA^{3-}, $EGTA^{4-}$, $HPDTA^{4-}$, $HEEDTA^{3-}$, and 1,2-$PDTA^{4-}$) and are compared with the behavior of four others (IDA^{2-}, $MIDA^{2-}$, $EDTA^{4-}$, and $CyDTA^{4-}$). Table I gives the struc-

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TABLE I

AMINOCARBOXYLATE LIGANDS AND THEIR STABILITY CONSTANTS WITH NICKEL(II)

		Log K_{NiL}	Ref
IDA^{2-}	$HN(CH_2COO)_2^{2-}$	8.26	*a*
$MIDA^{2-}$	$CH_3N(CH_2COO)_2^{2-}$	8.73	*b*
NTA^{3-}	$N(CH_2COO)_3^{3-}$	11.54	*c*
$EDDA^{2-}$	$(OOCCH_2)NHCH_2CH_2NH(CH_2COO)^{2-}$	13.5	*d*
$HEEDTA^{3-}$	$(HOCH_2CH_2)(OOCCH_2)NCH_2CH_2(CH_2COO)_2^{3-}$	17.0	*e*
$EDTA^{4-}$	$(OOCCH_2)_2NCH_2CH_2N(CH_2COO)_2^{4-}$	18.47	*f, g*
$EGTA^{4-}$	$(OOCCH_2)_2NCH_2CH_2OCH_2CH_2OCH_2CH_2N(CH_2COO)_2^{4-}$	13.6	*h*
$HPDTA^{4-}$	$(OOCCH_2)_2NCH_2CHOHCH_2N(CH_2COO)_2^{4-}$	16.45	*i*
1,2-$PDTA^{4-}$	$(OOCCH_2)_2NCH(CH_3)CH_2N(CH_2COO)_2^{4-}$	...	...
$CyDTA^{4-}$	$(OOCCH_2)_2N(C_6H_{10})N(CH_2COO)_2^{4-}$	21.4	*j*

[a] S. Chaberek and A. E. Martell, *J. Amer. Chem. Soc.*, **74**, 5052 (1952); 30°, $\mu = 0.1\ M$. [b] G. Schwarzenbach, B. Anderegg, W. Schneider, and H. Senn, *Helv. Chim. Acta*, **38**, 1147 (1955); 20°, $\mu = 0.1\ M$. [c] G. Schwarzenbach and R. Gut, *ibid.*, **34**, 1589 (1956); 20°, $\mu = 0.1\ M$. [d] S. Chaberek and A. E. Martell, *J. Amer. Chem. Soc.*, **74**, 6228 (1952); 30°, $\mu = 0.1\ M$. [e] S. Chaberek, Jr., and A. E. Martell, *ibid.*, **77**, 1477 (1955). [f] G. Schwarzenbach, R. Gut, and G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954); corrected to 25° ($\Delta H = -7.6$ kcal/mol),[g] $\mu = 0.1\ M$. [g] R. G. Charles, *J. Amer. Chem. Soc.*, **76**, 5854 (1954). [h] J. H. Holloway and C. N. Reilley, *Anal. Chem.*, **32**, 249 (1960); 25°, $\mu = 0.1\ M$. [i] This work; 25°, $\mu = 0.1\ M$. [j] D. W. Margerum, P. J. Menardi, and D. L. Janes, *Inorg. Chem.*, **6**, 283 (1967); 25°, $\mu = 0.1\ M$.

tures for these ligands and the stability constants for the NiL^{2-n} complexes.

The general reaction mechanism is the same as that found for nickel–EDTA[2] and for the monoiminodiacetate complexes of nickel.[3] Three cyanide ions are needed around nickel to bring about the rate-determining step in the reaction. The fourth cyanide ion adds rapidly and displaces the remaining segment, a glycinate group of the aminocarboxylate ligand.

Earlier work has shown that both CN^- and HCN may take part in the reactions to form mixed cyanide–aminocarboxylate complexes of nickel[4] and in the displacement of trien from nickel–trien.[5] In order to simplify the kinetics for comparative purposes all reactions were run at pH 10.8 ± 0.2 where CN^- is the predominant species. Under these conditions HCN did not contribute to the displacement of $EDTA^{4-}$ from nickel[2] and it is assumed that CN^- is also the kinetically reactive species with the other aminocarboxylate complexes.

Experimental Section

Ethylene glycol bis(aminoethyl)tetraacetic acid (EGTA, 98% minimum) and N-hydroxyethylethylenediaminetriacetic (HEEDTA, 98% minimum) were obtained from G. F. Smith Chemical Co. Nitrilotriacetatic acid (NTA) and 1,3-diamino-2-hydroxypropanetetraacetic acid (HPDTA) were obtained from Aldrich Chemical Co. Ethylenediamine-N,N′-diacetic acid (EDDA) and 1,2-diaminopropanetetraacetic acid (1,2-PDTA) were obtained from K & K Laboratories.

EGTA and 1,2-PDTA were recrystallized twice by dissolving the acid in hot water with the aid of NaOH and precipitated by adjusting the solution to pH 2 with dilute $HClO_4$. NTA and HPDTA were crystallized once by the above procedure and twice from water. HEEDTA and EDDA were purified by procedures described previously.[6] Microanalysis results for C, H, and N agreed with the theoretical composition for each ligand. The kinetic experiments themselves provided additional evidence of the purity of each ligand because small amounts of another aminocarboxylate as a contaminant are easily detected.

The nickel complexes were prepared by adding a slight excess of $Ni(ClO_4)_2$ to the ligand solution and removing the excess as $Ni(OH)_2$ at pH 11 by Millipore filtration. The solutions were diluted to 0.01 *M* and adjusted to pH 9 with dilute $HClO_4$ for storage. All solutions were standardized by addition of a 10-fold excess of NaCN at pH 11. After the formation of $Ni(CN)_4^{2-}$ was complete, the absorbance was measured at 267 nm (ϵ 1.16 × $10^4\ M^{-1}\ cm^{-1}$) and at 285 nm (ϵ 4.63 × $10^3\ M^{-1}\ cm^{-1}$) using suitable dilutions.

Solid $Na_2Ni(CN)_4$ was prepared for use in the reverse rate studies. Sodium cyanide solutions (0.10 *M*) were standardized by an argentimetric method just prior to use.

The pH of all reactions was maintained at 10.8 ± 0.2 using dilute NaOH. The ionic strength for the forward rates was adjusted to 0.10 *M* with $NaClO_4$. The ionic strength for the reverse rates ranged from 0.10 to 0.51 *M* as dictated by the ligand concentration needed.

All reactions were followed by monitoring the concentration of $Ni(CN)_4^{2-}$ at 267 mμ. Cary Model 14 and Model 16 spectrophotometers were used for the slow reactions. A Durrum-Gibson stopped-flow apparatus with Kel-F construction and a 2-cm cell was used for the more rapid reactions. A Tektronix 564 storage oscilloscope equipped with a Polaroid camera was used to record the stopped-flow data. The forward reactions were run with excess CN^- and all gave excellent first-order plots. Three to five runs were made for most reactions and rate constants are reported with the standard deviation found. The rate expression with excess CN^- present is given in eq 2 where x

$$\frac{d[Ni(CN)_4^{2-}]}{dt} = k_{obsd}[NiL(CN)_x^{2-n-x}] \qquad (2)$$

varies from 0 to 2 depending on the extent of mixed cyanide complex formation. The observed first-order rate constant was obtained from plots of ln ($A_\infty - A$) against time where A is the absorbance. The value of k_{obsd} is dependent on the free cyanide ion concentration as well as the nature of $NiL(CN)_x^{2-n-x}$. The rate of formation of $NiL(CN)_x$ is very rapid compared to the formation of $Ni(CN)_4^{2-}$ and there is a preequilibration of NiL, NiL(CN), and $NiL(CN)_2$.

Results

Kinetics of the Forward Reaction.—The rate of formation of $Ni(CN)_4^{2-}$ is first order in the concentration of NiL, where L is $EDDA^{2-}$, NTA^{3-}, $EGTA^{4-}$, $HPDTA^{4-}$, $HEEDTA^{3-}$, and 1,2-$PDTA^{4-}$. The observed first-order rate constants for each complex at

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[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] D. W. Margerum and L. I. Simandi, "Proceedings of the 9th International Conference on Coordination Chemistry," W. Schneider, Ed., Verlag Helvetica Chimica Acta, Basel, Switzerland, 1966, p 371.

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

[6] N. E. Jackobs and D. W. Margerum, *ibid.*, **6**, 2038 (1967).

TABLE II

KINETICS OF FORMATION OF $Ni(CN)_4^{2-}$ FROM MONO(AMINOCARBOXYLATE)NICKEL(II) COMPLEXES USING EXCESS CYANIDE ION AT 25.0°, $\mu = 0.1\ M$

$[CN^-]_T$, M	$[CN^-]_T/4[NiL]_i$	k_{obsd},[a] sec^{-1}
NiEDDA: $[NiL]_i = (0.053\text{–}7.6) \times 10^{-5}\ M$, pH 10.8 ± 0.2		
1.00×10^{-5}	5	$(6.3 \pm 0.6) \times 10^{-4}$
1.78×10^{-5}	8	$(4.1 \pm 0.2) \times 10^{-3}$
1.00×10^{-4}	4	$(2.0 \pm 0.2) \times 10^{-1}$
5.00×10^{-4}	22	5.2 ± 0.2
1.00×10^{-3}	43	$(1.69 \pm 0.05) \times 10$
2.00×10^{-3}	86	$(3.1 \pm 0.1) \times 10$
3.20×10^{-3}	11	$(5.4 \pm 0.4) \times 10$
8.00×10^{-3}	26	$(1.2 \pm 0.1) \times 10^2$
$NiNTA^-$: $[NiL]_i = (0.044\text{–}7.3) \times 10^{-5}\ M$, pH 10.8 ± 0.2		
1.77×10^{-5}	8	$(2.5 \pm 0.1) \times 10^{-4}$
2.00×10^{-5}	11	$(3.3 \pm 0.5) \times 10^{-4}$
3.53×10^{-5}	17	$(1.38 \pm 0.08) \times 10^{-3}$
5.30×10^{-5}	25	$(3.3 \pm 0.2) \times 10^{-3}$
1.76×10^{-4}	30	$(6.4 \pm 0.5) \times 10^{-2}$
2.93×10^{-4}	50	$(1.67 \pm 0.04) \times 10^{-1}$
4.11×10^{-4}	70	$(3.06 \pm 0.04) \times 10^{-1}$
5.86×10^{-4}	100	$(5.5 \pm 0.2) \times 10^{-1}$
1.74×10^{-3}	10	2.4 ± 0.1
1.80×10^{-3}	10	2.25 ± 0.09
2.93×10^{-3}	10	5.0 ± 0.4
5.22×10^{-3}	30	9.3 ± 0.2
5.39×10^{-3}	30	9.4 ± 0.2
8.70×10^{-3}	50	$(1.7 \pm 0.2) \times 10$
8.79×10^{-3}	30	$(1.99 \pm 0.04) \times 10$
1.22×10^{-2}	70	$(2.0 \pm 0.6) \times 10$
1.47×10^{-2}	50	$(3.58 \pm 0.04) \times 10$
1.80×10^{-2}	100	$(3.16 \pm 0.05) \times 10$
2.05×10^{-2}	70	$(4.84 \pm 0.05) \times 10$
2.64×10^{-2}	90	$(5.68 \pm 0.07) \times 10$
3.22×10^{-2}	110	$(5.82 \pm 0.09) \times 10$
$NiEGTA^{2-}$: $[NiL^{2-}]_i = (0.55\text{–}3.8) \times 10^{-5}\ M$, pH 10.8 ± 0.2		
5.02×10^{-5}	2	$(3.1 \pm 0.4) \times 10^{-4}$
2.01×10^{-4}	9	$(1.09 \pm 0.05) \times 10^{-3}$
5.02×10^{-4}	23	$(2.61 \pm 0.05) \times 10^{-3}$
1.00×10^{-3}	46	$(5.09 \pm 0.08) \times 10^{-3}$
7.17×10^{-3}	47	$(3.9 \pm 0.2) \times 10^{-2}$
1.43×10^{-2}	93	$(7.5 \pm 0.5) \times 10^{-2}$
2.87×10^{-2}	187	$(1.5 \pm 0.2) \times 10^{-1}$
4.30×10^{-2}	281	$(2.1 \pm 0.2) \times 10^{-1}$
$NiHPDTA^{2-}$: $[NiL^{2-}]_i = (0.67\text{–}4.5) \times 10^{-5}\ M$, pH 10.8 ± 0.2		
2.54×10^{-4}	10	$(1.72 \pm 0.02) \times 10^{-5}$
6.35×10^{-4}	24	$(1.34 \pm 0.03) \times 10^{-4}$
1.27×10^{-3}	47	$(7.63 \pm 0.07) \times 10^{-4}$
2.54×10^{-3}	95	$(3.23 \pm 0.02) \times 10^{-3}$
3.81×10^{-3}	142	$(6.25 \pm 0.04) \times 10^{-3}$
5.08×10^{-3}	97	$(9.9 \pm 0.2) \times 10^{-3}$
5.08×10^{-3}	28	$(1.00 \pm 0.03) \times 10^{-2}$
1.02×10^{-2}	56	$(2.07 \pm 0.04) \times 10^{-2}$
2.03×10^{-2}	112	$(4.09 \pm 0.09) \times 10^{-2}$
3.05×10^{-2}	168	$(5.68 \pm 0.08) \times 10^{-2}$
4.06×10^{-2}	223	$(7.0 \pm 0.1) \times 10^{-2}$
$NiHEEDTA^-$: $[NiL^-]_i = (0.05\text{–}1.0) \times 10^{-4}\ M$, pH 10.9 ± 0.1		
1.25×10^{-3}	54	$(6.2 \pm 0.2) \times 10^{-5}$
2.50×10^{-3}	108	$(2.5 \pm 0.2) \times 10^{-4}$
3.16×10^{-3}	60	$(4.30 \pm 0.04) \times 10^{-4}$
3.75×10^{-3}	166	$(5.5 \pm 0.2) \times 10^{-4}$
4.80×10^{-3}	53	$(9.03 \pm 0.01) \times 10^{-4}$
5.00×10^{-3}	208	$(9.99 \pm 0.03) \times 10^{-4}$
5.62×10^{-3}	106	$(1.35 \pm 0.02) \times 10^{-3}$
9.60×10^{-3}	106	$(3.59 \pm 0.01) \times 10^{-3}$
9.60×10^{-3}	140	$(3.6 \pm 0.1) \times 10^{-3}$
1.00×10^{-2}	189	$(3.97 \pm 0.06) \times 10^{-3}$
1.25×10^{-2}	520	$(5.33 \pm 0.04) \times 10^{-3}$
1.78×10^{-2}	337	$(1.17 \pm 0.01) \times 10^{-2}$
2.40×10^{-2}	324	$(2.3 \pm 0.3) \times 10^{-2}$
$Ni(1,2\text{-}PDTA)^{2-}$: $[NiL^{2-}]_i = 1.18 \times 10^{-5}\ M$, pH 11.0 ± 0.1		
1.78×10^{-2}	377	$(4.43 \pm 0.06) \times 10^{-6}$
3.16×10^{-2}	670	$(1.4 \pm 0.1) \times 10^{-5}$
5.62×10^{-2}	1191	$(4.53 \pm 0.02) \times 10^{-5}$
9.91×10^{-2}	2100	$(1.14 \pm 0.01) \times 10^{-4}$

[a] See eq 2.

various levels of excess cyanide ion are given in Table II. The effect of variation of the cyanide ion concentration (always in excess) can be seen in Figures 1 and 2 where the slopes of the plots of log k_{obsd} against log $[CN^-]_T$ give the order of the reaction in cyanide. (The term $[CN^-]_T$ refers to the concentration of added cyanide ion and includes the small fraction of HCN which is present at pH 10.8.) For the reactions of the $EDDA^{2-}$ and NTA^{3-} complexes the slopes approach 3 at $10^{-5}\ M$ CN^-. As the cyanide concentration increases, the slopes of the log–log plots for these complexes change to 2 and above $10^{-2}\ M$ cyanide the slopes are unity. The reactions of the other complexes show a first-order or second-order cyanide dependence. Data from earlier work[2] with $EDTA^{4-}$ are included in Figure 2 for comparison.

A variable dependence of the reaction rate on cyanide ion concentration was encountered previously with EDTA (at lower $[CN^-]_T$ than presented in Figure 2) and was shown to be the rapid preequilibrium between

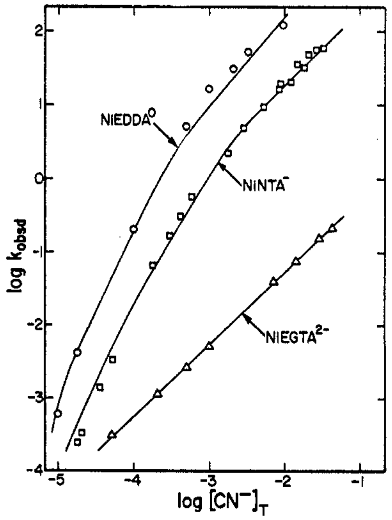

Figure 1.—Cyanide dependence of the observed forward rate constants in the NiEDDA, $NiNTA^-$, and $NiEGTA^{2-}$ systems at 25°, pH 10.8 ± 0.2, and $\mu = 0.1\ M$. (The solid line is calculated from the resolved rate constants.)

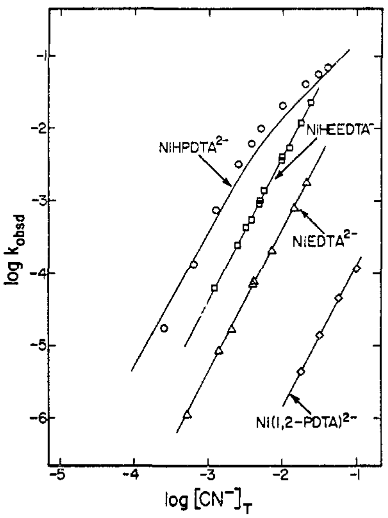

Figure 2.—Cyanide dependence of the observed forward rate constants in the NiHPDTA^{2-}, NiHEEDTA$^-$, NiEDTA^{2-}, and Ni(1,2-PDTA)$^{2-}$ systems at 25°, pH 10.8 ± 0.2, and μ = 0.1 M. (The solid line is calculated from the resolved rate constants.)

NiEDTA^{2-} and Ni(EDTA)(CN)$^{3-}$. Under the experimental conditions given in Table II (where the NiL concentration is usually very low) the absorbance of the Ni(CN)$_4^{2-}$ is so intense that small changes due to the formation of complexes of the general formula NiL(CN)$_x$ have little effect on the measured absorbance. Nevertheless, as the cyanide ion concentration increases, the reactant present immediately after mixing changes from NiL to NiL(CN) to NiL(CN)$_2$. Other experiments[4] have been used to measure the stability constants and kinetics of the monocyanide complexes of Ni(EDTA)$^{2-}$, Ni(HEEDTA)$^-$, and Ni(CyDTA)$^{2-}$. Biscyano complexes of Ni(IDA) and Ni(MIDA) were encountered[3] in the reactions of these ligands. Therefore, a simple explanation of the variable order in cyanide ion is that, as in the cases of EDTA, IDA, and MIDA, a total of three cyanide ions is needed in the rate-determining step and the observed order depends on how many of the three cyanides are already complexed to the nickel aminocarboxylate (eq 3). The slopes in Figures 1 and 2 are equal to 3 − x and approach 3 at low CN$^-$ when the reactant is primarily NiL and approach unity at high CN$^-$ when the reactant is primarily NiL(CN)$_2$. The kinetics of the reverse reaction are used to confirm this mechanism. Biscyanide species are formed with the nickel complexes of EDDA, NTA, EGTA, and HPDTA but only monocyanide complexes occur with HEEDTA, EDTA, and 1,2-PDTA at the cyanide ion concentration levels shown in Figure 2.

$$\text{rate} = k_{obsd}[\text{NiL(CN)}_x{}^{2-n-x}] = k_f[\text{NiL(CN)}_x{}^{2-n-x}][\text{CN}^-]^{3-x} \tag{3}$$

In the reactions of Ni(HEEDTA)$^-$, Ni(EDTA)$^{2-}$, and Ni(1,2-PDTA)$^{2-}$, where the forward rates are relatively slow and higher concentrations were used, a distinct color change from blue to violet was observed on the addition of cyanide ion before the solutions slowly changed to the yellow of Ni(CN)$_4^{2-}$. Spectrophotometrically the two peaks due to NiL in the visible region disappear upon the addition of CN$^-$ and two new peaks appear at lower wavelengths with a higher absorbance. With these complexes this is due to the formation of NiL(CN)$^{1-n}$. The other systems behave similarly and, although their reactions were too rapid to observe the formation of mixed complexes in spectrophotometric scans, extrapolation of stopped-flow data to the time of mixing showed initial absorbance changes. The stability constants in eq 4 and 5 are determined from the kinetic data from the forward and reverse reactions.

$$K_1 = \frac{[\text{NiL(CN)}^{1-n}]}{[\text{NiL}^{2-n}][\text{CN}^-]} \tag{4}$$

$$K_2 = \frac{[\text{NiL(CN)}_2{}^{n-}]}{[\text{NiL(CN)}^{1-n}][\text{CN}^-]} \tag{5}$$

Rate constants for the reaction of NiCyDTA^{2-} and CN$^-$ are not given because this reaction is extraordinarily slow. Thus, with [CN$^-$] = 10^{-2} M and [NiCyDTA^{2-}] = 10^{-3} M there was no evidence for any Ni(CN)$_4^{2-}$ after 2 months.[7] This corresponds to a k_{obsd} value less than 5×10^{-11} sec^{-1} at 10^{-2} M cyanide ion and means that the CyDTA reaction is at least seven orders of magnitude slower than the EDTA reaction.

Kinetics of the Reverse Reaction.—Dilute solutions of Ni(CN)$_4^{2-}$ react with excess free ligand by the rate expression in eq 6. Linear plots are obtained for eq 7,

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

$$(A_i - A) + A_i \ln (A/A_i) = -\frac{\epsilon l}{4} k'_{obsd}t \tag{7}$$

which is the integrated form of the rate expression where A_i is the initial absorbance, A is the absorbance at any time t, ϵl is the molar absorptivity times the cell path, and k'_{obsd} is $k_r[L^{n-}]$. Values for k'_{obsd} are given in Table III.

In every system studied, plots of absorbance against time for less than 6% of the reverse reaction yielded an intercept at the time of mixing which was slightly lower than the initial absorbance expected for the reactants. This indicates that there is an intermediate present in small concentrations which is in rapid equilibrium with Ni(CN)$_4^{2-}$. The same observation has been made with the iminodiacetate complexes and with EDTA. The intermediate is assumed to be Ni(CN)$_3$L$^{(n+1)-}$ in order to be consistent with the proposed mechanism.

The kinetics of the reverse reaction with 1,2-PDTA^{4-} was not studied because the stability constant of the complex with nickel is not known and the desired correlations could not be made.

Discussion

The reverse rate expression shows that before the rate-determining step one CN$^-$ is displaced from Ni(CN)$_4^{2-}$ and is in rapid equilibrium with an intermediate species (of small concentration) resulting from the addition of a large excess of L^{n-}, namely, Ni(CN)$_3$L$^{(n+1)-}$. This is consistent with the dependence shown

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[7] H. Hauer and D. W. Margerum, unpublished data.

TABLE III

KINETICS OF THE DECOMPOSITION OF $Ni(CN)_4^{2-}$ IN ITS REACTION WITH AMINOCARBOXYLATE LIGANDS, 25.0°

$EDDA^{2-}$: pH 10.6 ± 0.1, $\mu = 0.10$ M,
$[Ni(CN)_4^{2-}]_i = 6.75 \times 10^{-6}$ M

$10^3[EDDA^{2-}]$	$10^8k'_{obsd}$, M sec^{-1}	10^5k_r, sec^{-1}
2.44	6.38, 5.70, 5.70	2.61, 2.33, 2.33
1.22	3.12, 2.87, 3.04	2.55, 2.34, 2.49
	Av	2.4 ± 0.1

NTA^{3-}: pH 10.9 ± 0.1, $\mu = 0.51$ M,
$[Ni(CN)_4^{2-}]_i = 4.63 \times 10^{-6}$ M

$10^2[NTA^{3-}]$	$10^{10}k'_{obsd}$, M sec^{-1}	10^8k_r, sec^{-1}
8.47	10.16, 9.98, 9.49, 9.29	1.20, 1.18, 1.12, 1.10
4.27	4.55, 3.61, 5.98	1.07, 0.85, 1.40
	Av	1.1 ± 0.1

$EGTA^{4-}$: pH 10.8 ± 0.1, $\mu = 0.30$ M,
$[Ni(CN)_4^{2-}]_i = 1.14 \times 10^{-5}$ M

$10^2[EGTA^{4-}]$	$10^9k'_{obsd}$, M sec^{-1}	10^8k_r, sec^{-1}
2.54	1.99, 1.76, 1.62	7.84, 6.94, 6.39
1.52	1.20, 1.18	7.90, 7.73
1.01	0.714, 0.701	7.03, 6.91
	Av	7.3 ± 0.6

$HPDTA^{4-}$: pH 10.9 ± 0.1, $\mu = 0.27$ M,
$[Ni(CN)_4^{2-}]_i = 1.13 \times 10^{-5}$ M

$10^2[HPDTA^{4-}]$	$10^{10}k'_{obsd}$, M sec^{-1}	10^8k_r, sec^{-1}
2.31	5.89, 5.14, 4.88	2.55, 2.22, 2.11
1.16	3.01, 2.51, 2.54	2.60, 2.17, 2.20
	Av	2.3 ± 0.2

$HEEDTA^{3-}$: pH 10.9 ± 0.1, $\mu = 0.50$ M,
$[Ni(CN)_4^{2-}]_i = 5.00 \times 10^{-6}$ M

$10^2[HEEDTA^{3-}]$	$10^9k'_{obsd}$, M sec^{-1}	10^8k_r, sec^{-1}
4.90	3.89, 3.99	7.93, 8.14
4.90	3.64, 3.68	7.42, 7.50
2.45	1.74, 1.71	7.10, 6.96
	Av	7.5 ± 0.5

$NiLCN^{1-n}$ and $NiL(CN)_2^{n-}$ may be present in appreciable concentrations even at low cyanide ion concentrations. As noted earlier, there is evidence for small concentrations of $Ni(CN)_3L^{(n+1)-}$ at very high L^{n-} concentrations. In accord with this mechanism the forward reactions with a first-order cyanide dependence (slope = unity in Figures 1 and 2) give k_3 in eq 10, those with a second-order cyanide dependence give K_2k_3, and those with a third-order cyanide dependence give $K_1K_2k_3$. The reverse reaction measures $K_4^{-1}k_{-3}$.

Using $\log \beta_4 = 30.5$[8] for $Ni(CN)_4^{2-}$ and the $\log K_{NiL}$ values in Table I it is possible to calculate values for the stability constants of the mixed cyanide complexes (K_1 and K_2) from the kinetic data. Table IV summarizes the rate constants and stability constants determined for the aminocarboxylates in this and earlier studies.[2,8] The relative reactivities of the various aminocarboxylate complexes can be compared using the fourth-order rate constants given as $K_1K_2k_3$. The ratio of these rate constants for Ni(IDA) compared to those for $Ni(EDTA)^{2-}$ is 3.5×10^{11}. The $Ni(1,2\text{-}PDTA)^{2-}$ complex is more than 100 times slower in its reaction than $Ni(EDTA)^{2-}$. Kinetic data are not given for $Ni(CyDTA)^{2-}$ because it is essentially unreactive, being at least seven orders of magnitude slower to form $Ni(CN)_4^{2-}$ than the EDTA complex. Hence, there are enormous differences in kinetic reactivity. Figures 1 and 2 show that the k_{obsd} values at 10^{-2} M CN^- are 10^8 times greater for Ni(EDDA) than for $Ni(1,2\text{-}PDTA)^{2-}$.

All of the aminocarboxylate complexes which react with cyanide ion appear to follow the same mechanism for the forward reaction in eq 3 and is the same dependence observed for the EDTA, IDA, and MIDA complexes. The mechanism is given in eq 8–11, where

TABLE IV

RATE CONSTANTS FOR THE FORMATION AND DECOMPOSITION OF $Ni(CN)_4^{2-}$ AND STABILITY CONSTANTS OF MIXED CYANIDE–AMINOCARBOXYLATE COMPLEXES OF NICKEL(II) DETERMINED FROM THE KINETICS[a]

NiL^{2-n}	k_3, M^{-1} sec^{-1}	K_2k_3, M^{-2} sec^{-1}	$K_1K_2k_3$, M^{-3} sec^{-1}	$K_4^{-1}k_{-3}$, sec^{-1}	K_1, M^{-1}	K_2, M^{-1}	K_1K_2, M^{-2}
Ni(IDA)	$(5.0 \pm 0.2) \times 10^4$	...	8.1×10^{15}	$(4.7 \pm 0.3) \times 10^{-7}$	...	...	1.6×10^{11}
Ni(MIDA)	$(5.3 \pm 0.1) \times 10^4$	...	1.1×10^{15}	$(1.9 \pm 0.4) \times 10^{-7}$	...	...	2.1×10^{10}
Ni(EDDA)	$(1.6 \pm 0.1) \times 10^4$	$(2.1 \pm 0.1) \times 10^7$	2.4×10^{12}	$(2.4 \pm 0.1) \times 10^{-5}$	1.2×10^5	1.3×10^3	1.5×10^8
$Ni(NTA)^-$	$(2.0 \pm 0.3) \times 10^3$	$(1.9 \pm 0.1) \times 10^6$	1.0×10^{11}	$(1.1 \pm 0.1) \times 10^{-8}$	5.3×10^4	1.0×10^3	5.3×10^7
$Ni(EGTA)^{2-}$	5.2 ± 0.3	...	5.8×10^9	$(7.3 \pm 0.6) \times 10^{-8}$	...	...	1.1×10^9
$Ni(HPDTA)^{2-}$	1.70 ± 0.07	507 ± 5	2.6×10^6	$(2.3 \pm 0.2) \times 10^{-8}$	5.1×10^3	3.0×10^2	1.5×10^6
$Ni(HEEDTA)^-$	...	39.1 ± 0.5	2.4×10^6	$(7.5 \pm 0.5) \times 10^{-8}$	6.1×10^4	...	...
$Ni(EDTA)^{2-}$	...	4.0 ± 0.2	2.3×10^4	2.2×10^{-8}	5.8×10^3	...	...
$Ni(1,2\text{-}PDTA)^{2-}$	...	$(1.44 \pm 0.01) \times 10^{-2}$	...	...	...	...	...

[a] See the mechanism given in eq 8–11.

$$NiL^{2-n} + CN^- \overset{K_1}{\rightleftharpoons} NiLCN^{1-n} \quad \text{(rapid)} \qquad (8)$$

$$NiLCN^{1-n} + CN^- \overset{K_2}{\rightleftharpoons} NiL(CN)_2^{n-} \quad \text{(rapid)} \qquad (9)$$

$$NiL(CN)_2^{n-} + CN^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Ni(CN)_3L^{(n+1)-} \quad \text{(rate determining)} \qquad (10)$$

$$Ni(CN)_3L^{(n+1)-} + CN^- \overset{K_4}{\rightleftharpoons} Ni(CN)_4^{2-} + L^{n-} \quad \text{(rapid)} \qquad (11)$$

The reactions are given in eq 8–11 and in each case there are three cyanide ions around nickel in the rate-determining step. Although there was no reaction observed between CN^- and $Ni(CyDTA)^{2-}$, the reaction of cobalt(II)–CyDTA with cyanide ion also has three cyanide ions around cobalt in the rate-determining step.[9] On the other hand in the reactions of aquonickel(II) and (triethylenetetramine)nickel(II) four cyanide ions are needed around the metal in the rate-determining step. It appears that the critical step in

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

(9) J. P. Jones and D. W. Margerum, *ibid.*, **8**, 1486 (1969).

all the nickel systems is the conversion from an octahedral (or tetragonal) to a square-planar complex. Once the square-planar complex is formed, the substitution reactions are relatively labile if the entering group is a good nucleophile because the reaction follows an associative rather than a dissociative mechanism.[10] Although the proposed complex $Ni(CN)_3L^{(n+1)-}$ is not very stable relative to $Ni(CN)_4^{2-}$, it can react rapidly with another CN^- much as radiocyanide exchanges rapidly with $Ni(CN)_4^{2-}$.[11] Therefore, one role which the aminocarboxylate ligand can play is to give an intermediate species with only three cyanides the kinetic properties of a square-planar complex. Figure 3 depicts a possible structure for such an intermediate in which only one amine nitrogen remains coordinated to nickel and R represents the rest of the aminocarboxylate ligand. In the case of the Ni–trien complex it appears that the chelation of two amine nitrogens (without any carboxylate groups) may help to keep four cyanide ions around nickel in the kinetic step.[5] In terms of the reverse reaction the polyamines do not force the loss of the fourth CN^- before the rate-determining step but the negatively charged aminocarboxylates cause the loss of one CN^-. As a result the rate of trien reaction is many orders of magnitude faster than the rates of reaction of the aminocarboxylate ligands with $Ni(CN)_4^{2-}$. The trien reaction has a second-order rate constant of 310 M^{-1} sec^{-1} and the reaction does not have the inverse first-order dependence in cyanide ion which is found with the aminocarboxylate ligands.

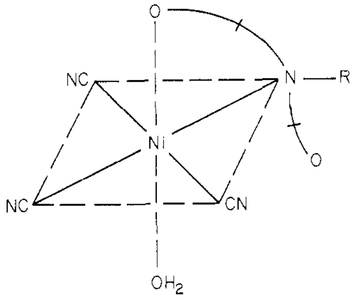

Figure 3.—Proposed structure of the $Ni(CN)_3L^{(n+1)-}$ intermediate.

There is an inverse relation between the values calculated for $K_1K_2k_3$ and the initial stability constant, K_{NiL}, of the aminocarboxylate complex. This can be understood if a common segment of the aminocarboxylate remains bonded in the rate-determining step and the rest of the ligand is unwrapped prior to that step. If the intermediate preceding that given in Figure 3 is represented by $NiL^*(CN)_3{}^{n-1}$ and if it reacts with the rate constant k_3^*, then eq 12–16 can be used.

$$\text{rate} = K_1K_2k_3[NiL^{2-n}][CN^-]^3 = k_3^*[NiL^*(CN)^{n-1}] \qquad (12)$$

$$K_1K_2k_3 = k_3^*\frac{[NiL^*(CN)^{n-1}]}{[NiL^{2-n}][CN^-]^3} = k_3K^* \qquad (13)$$

$$K^* = \frac{[NiL^*(CN)^{n-1}]}{[NiL^{*2-n}][CN^-]^3}\,\frac{[NiL^{*2-n}]}{[NiL^{2-n}]} = \frac{\beta_3{}^*K_{Ni(segment)}}{K_{NiL}} \qquad (14)$$

$$K_{Ni(segment)} = \frac{[NiL^{*2-n}]}{[Ni^{2+}][L^{n-2}]} \qquad (15)$$

$$\log K_1K_2k_3 = \log\,(k_3{}^*\beta_3{}^*K_{Ni(segment)}) - \log K_{NiL} \qquad (16)$$

Figure 4 is a plot of eq 16 for eight aminocarboxylate complexes. However the slope is −1.1 rather than −1.0. The above equations neglect the electrostatic repulsions which must exist between the R portion of the free aminocarboxylates and the rest of the complex. With EDTA the R group has a 2− charge which makes it harder for the last CN^- to approach than in the case of IDA. The arrows in Figure 4 show the effect of an electrostatic correction term (log K_{elec}) added to log $K_1K_2k_3$ to compensate for the different charges. The values for log K_{elec} are estimated using distances obtained from the center of the nickel atom to the center of the remote carboxylate groups.[12] With the exception of EDDA the corrected values give a good linear relationship with a slope of −0.90 ± 0.02. The electrostatic correction term is approximate and the data are probably overcorrected because the 0.1 M Na^+ in solution will have some specific association with the free aminocarboxylate groups. Hence the fit of eq 16 is adequate and the experimentally observed 10^{12}-fold range of reaction rate is accounted for in terms of the necessity of most of the aminocarboxylate ligand to unwrap from nickel in order to permit three cyanide ions to enter the coordination sphere.

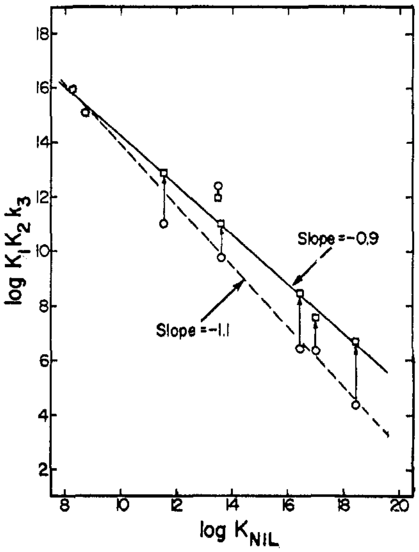

Figure 4.—Dependence of the forward rate constants on the stability constants of the nickel–aminocarboxylate complexes: O, experimentally determined $K_1K_2k_3$ values; □, rate constants corrected for electrostatic repulsion.

There are two exceptions to this general behavior. One is the CyDTA complex where the cyclohexane ring keeps all the carboxylate and amine groups close to nickel as long as one amine is coordinated. As a result the $NiCyDTA^{2-}$ reaction is much slower than with $NiEDTA^{2-}$. The other exception is the EDDA com-

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[10] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965, p 8.

[11] A. W. Adamson, J. P. Welker, and M. Volpe, *J. Amer. Chem. Soc.* **72**, 4030 (1950).

[12] T. J. Bydalek and D. W. Margerum, *Inorg. Chem.*, **2**, 678 (1963).

plex, which falls off the plots in Figure 4, but its different behavior is more obvious in comparison of the reverse rate constants ($K_4^{-1}k_{-3}$) in Table IV. The reaction of $EDDA^{2-}$ with $Ni(CN)_4{}^{2-}$ is more than 100 times faster than $MIDA^{2-}$. This suggests that $EDDA^{2-}$ may react in a manner similar to the polyamines in that two nitrogens may be bonded in the rate-determining step but electrostatic repulsion causes the loss of a cyanide ion as with the other aminocarboxylates.

The K_1 values (the stability constant of the $NiLCN^{1-n}$ complex) increase in a regular fashion as the electrostatic repulsion decreases between CN^- and NiL^{2-n}. From this trend in K_1 values the stability constant for $Ni(trien)(CN)^+$ would be expected to be much larger than its value of $1.6 \times 10^4\ M^{-1}$. It is apparent that there are factors in addition to the availability of a coordination site and electrostatics which govern the relative stability of the monocyanide complexes. The same point has been made concerning the mixed biscyano complexes (K_1K_2 values in Table IV) which are remarkably stable for IDA and MIDA.

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Base Adducts of Nickel Dithiophosphate

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The reaction of a variety of nitrogen bases with $Ni[S_2P(OC_2H_5)_2]_2$ is reported. Bases such as 2-picoline and diethylamine form monoadducts with association constants smaller than 10 l./mol, while pyridine, 3-picoline, and 4-picoline form diadducts in two successive steps. The values of K_1 are, respectively, 29, 21.8, and 31.6 l./mol in benzene, and K_2 is much larger (78, 68.7, and 215.7 l./mol, respectively). $Ni(dtp)_2$ adds 2 mol of pyridine in nitrobenzene with an enthalpy change of −16.8 kcal/mol. The five-coordinate adducts of 2-picoline and 2,6-lutidine are diamagnetic (by nmr) but the diethylamine and di-*n*-butylamine monoadducts are paramagnetic, though the electronic spectra of the two series of molecules are quite similar. The complicated temperature dependence of the contact shifts in the 2:1 adducts is also reported.

The great difference in reactivity toward nitrogen bases of three diamagnetic planar nickel complexes, each with an NiS_4 coordination sphere, has been of interest to us. Bis(diethyldithiocarbamato)nickel(II) does not readily[1-3] form an adduct with pyridine, while bis(ethylxanthato)nickel(II) readily adds two molecules of pyridine.[2,4] Behavior intermediate between those two extremes is exhibited by bis(diethyldithiophosphato)nickel(II), $Ni(dtp)_2$, which adds two molecules of pyridine in a stepwise fashion.[2] Several reports concerning the 1:1 adducts of secondary amines with $Ni(dtp)_2$ have appeared, with particular attention being placed on an assignment of the spectra.[1,5,6]

We felt that it would be worthwhile to investigate more carefully the nature of both the 1:1 and the 2:1 adducts of $Ni(dtp)_2$ with a variety of bases in solution. First we sought to determine the factors which affect the stoichiometry of the adducts formed. Second, we sought information on the nature of the five-coordinate complexes, particularly their structure and their magnetic properties in solution. Finally, we have tried to characterize better the six-coordinate (2:1) adducts.

Experimental Section

Solutions and Materials.—Bis(O,O′-diethyldithiophosphato)-nickel(II), $Ni[S_2P(OC_2H_5)_2]_2$, was prepared according to the method outlined in the literature.[7] Because of the instability of this compound and because of the presence of charge-transfer bands in the near-ultraviolet spectrum, the compound was recrystallized periodically and stored in the dark. By following this procedure no decomposition was observed. All nitrogen bases were twice distilled from Zn dust before use.

Optical spectra were recorded in spectroscopic grade benzene while nmr spectra were recorded in deuteriochloroform using TMS as the internal reference. Solution susceptibility measurements were run in a 15% (v/v) solution of TMS in $CHCl_3$.

Crystallization of the 1:1 adduct from solution was attempted in the diethylamine, dibutylamine, 2-picoline, and 2,6-lutidine systems. Decomposition occurred in all cases when the solutions containing the amines were evaporated except for 2,6-lutidine, which yielded a crystalline material. At present this substance is incompletely characterized, since elemental analysis of two different samples has yielded indeterminate results.

Apparatus.—Optical spectra were recorded on a Cary Model 14 spectrophotometer equipped with fluid thermostated sample cell holders. All spectra were recorded at 25 ± 0.1°.

A Varian A-60A spectrometer equipped with the Model V6057 variable-temperature accessory was used to record proton contact shifts and their temperature variation.

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[1] C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962).

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