ity of the bonding properties of the SCN bridging groups in the former and the $-\mathrm{C{\equiv}N}$: and $\begin{matrix}\mathrm{C}\\ \mathrm{C}\end{matrix}\!\!>\!\mathrm{O}$: groups in the latter. From the value for the QS it is inferred that the two alkyl groups still occupy *trans*-octahedral positions, but the present data do not permit any conclusions to be drawn concerning the *cis* or *trans* arrangement of the two SCN groups relative to the two solvent molecules. Moreover the observed similarity in the frozen-solution parameters for acetonitrile solutions (crystalline) and MTF solutions (glassy) lends added support to the assumption that the Mössbauer parameters reflect the nature of the metal–ligand bonding rather than structural features imposed by the nature of the surrounding matrix.

Acknowledgments.—The authors are indebted to Professor H. A. Schugar for a number of fruitful discussions concerning the interpretation of the data and to Dr. S. Chandra and Mr. Y. Goscinny for their contributions to the experimental portions of this research. We are also indebted to Dr. D. Z. Denney, not only for her assistance in obtaining the 100-MHz nmr data and the low-temperature proton spectra, but also for her insight and helpfulness in the interpretation of these results. We are grateful to Mr. T. Moyer and Mr. B. A. Bennett for their assistance in the synthetic aspects of this work and their initial Mössbauer results on $(CH_3)_3SnCN$ and $(CH_3)_2Sn(SCN)_2$. This work was supported in part by the U. S. Atomic Energy Commission (Document NYO-2472-57), the Petroleum Research Fund administered by the American Chemical Society, and the Research Council of Rutgers University. This support is gratefully acknowledged.

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Kinetics of Interconversion of Triethylenetetraminenickel(II) and Tetracyanonickelate(II)

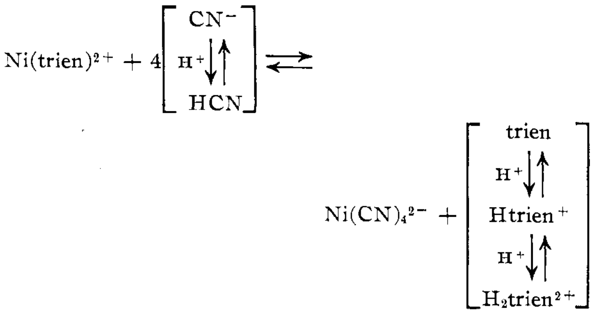
BY GERALD B. KOLSKI AND DALE W. MARGERUM[1]

Received December 9, 1968

Fifth-order kinetics are observed in the rate of formation of $Ni(CN)_4^{2-}$ from $Ni(trien)^{2+}$ and cyanide. The reaction is first order in $Ni(trien)^{2+}$ and fourth order in total cyanide ($CN^- + HCN$) from pH 5 to 12. As is the case with the aquonickel ion, HCN is a reactant as well as CN^-. From pH 5 to 7.5 the rate expression for the formation of $Ni(CN)_4^{2-}$ is $k_{2,2}[\mathrm{Ni(trien)^{2+}}][\mathrm{CN^-}]^2[\mathrm{HCN}]^2$, where $k_{2,2} = 4.0 \times 10^{18}\ M^{-4}\ \mathrm{sec}^{-1}$. This rate constant is more than twice as large as the corresponding constant for the reaction of CN^- and HCN with $Ni(H_2O)_6^{2+}$. This is extraordinary considering the fact that the strongly coordinated trien molecule must be displaced from nickel, a process which is extremely slow without the assistance of cyanide. At higher pH the reaction becomes fourth order in CN^- with $k_4 = 10^{18}\ M^{-4}\ \mathrm{sec}^{-1}$. In the reverse reaction the disappearance of $Ni(CN)_4^{2-}$ in the presence of trien is first order in each reactant, confirming the forward kinetics.

Introduction

The formation of tetracyanonickelate(II) ion from aquonickel ion has recently been shown[2] to be a relatively fast reaction with a fourth-order dependence in total cyanide, where both CN^- and HCN may be reactants. The reaction of aminocarboxylatonickelate complexes (NiL^{2-}) to form $NiL(CN)^{3-}$ also are rapid and can proceed *via* HCN.[3] However, the complete displacement of ethylenediaminetetraacetate ion from nickel is slow and requires only three cyanide ions around nickel in the rate-determining step, followed by rapid addition of a fourth cyanide ion to give tetracyanonickelate(II).[4]



$$\mathrm{Ni(trien)^{2+}} + 4\begin{bmatrix}\mathrm{CN^-}\\ \mathrm{H^+}\downarrow\uparrow\\ \mathrm{HCN}\end{bmatrix} \rightleftharpoons \mathrm{Ni(CN)_4^{2-}} + \begin{bmatrix}\mathrm{trien}\\ \mathrm{H^+}\downarrow\uparrow\\ \mathrm{Htrien^+}\\ \mathrm{H^+}\downarrow\uparrow\\ \mathrm{H_2trien^{2+}}\end{bmatrix} \qquad (1)$$

In the present work the reaction in eq 1, where trien is triethylenetetramine, is studied in both forward and reverse directions. Once again HCN is found to be an important reactant. The reaction is fourth order in total cyanide in a manner similar to aquonickel rather than following the behavior of the EDTA complex. An astonishing observation is that from pH 5 to 8 the nickel–trien complex reacts faster to form $Ni(CN)_4^{2-}$ than does the aquonickel ion. One reason why this behavior is surprising is that the dissociation of nickel–trien is known to be very slow at pH 4–7,[5] and using formation rate data the half-life calculated for the dis-

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[1] Correspondence to be addressed to this author.

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sociation at pH 8.2 (in the absence of cyanide) is 8.7 years.[6] That cyanide should help speed the unwrapping of trien from nickel is to be expected, but we find it novel that at pH 8 the formation of $Ni(CN)_4^{2-}$ is faster with nickel–trien than with aquonickel.

Experimental Section

Triethylenetetramine was regenerated from trien·$2H_2SO_4$ (Baker Chemical Co.) by reaction with sodium hydroxide. The regenerated trien was distilled under reduced pressure and the higher boiling fractions were shown by gas chromatography to contain no detectable impurities. The column was 25% SE-30 on 60–80 mesh silanized Chromosorb. Solutions of trien were standardized by the mole ratio method with standard copper. Nickel–trien solutions were prepared by the addition of a slight excess of nickel perchlorate to the trien solution followed by the precipitation of the excess nickel as nickel hydroxide at pH 10. The solution was standardized by the mole ratio method with standard cyanide. Cyanide and $Ni(CN)_4^{2-}$ solutions were prepared and standardized as reported previously.[2]

A pK_a value of 9.0 was used for HCN to fit[2] best the conditions of 0.10 *M* ionic strength (maintained with $NaClO_4$) and 25.0° and all pH values were corrected to give $-\log\ [H^+]$ by subtracting 0.11 from the pH readings given with NBS buffers.

The rates of formation and dissociation of $Ni(CN)_4^{2-}$ were measured at 267 mμ using a Durrum–Gibson stopped-flow apparatus with a 2.0-cm observation cell. Oscilloscope time scans as fast as 50 msec/cm were used.

Equilibrium constants used in this work for the protonation constants of trien were from Schwarzenbach's values[7] corrected to 25.0° from other temperature studies:[8] $\log K_{\mathrm{Htrien}^+} = 9.81$, $\log K_{\mathrm{H_2trien}^{2+}} = 9.09$, $\log K_{\mathrm{H_3trien}^{3+}} = 6.56$. The stability constant for nickel–trien[9] is $\log K_1 = 14.1$ and for tetracyanonickelate[2] is $\log \beta_4 = 30.5$. The $Ni(trien)(OH)^+$ complex has been shown not to form in the pH range of this study.[10]

Resolution of rate constants for the pH profile studies in the formation and dissociation rate studies were performed by use of a linear regression analysis program for the IBM 7094.

Results

Reaction Order in the Formation of $Ni(CN)_4^{2-}$.—The forward reaction in eq 1 is first order in nickel–trien and it is fourth order in total uncomplexed cyanide, $[CN_T] = [CN^-] + [HCN]$. (See eq 2.) With a large

$$\frac{d[Ni(CN)_4^{2-}]}{dt} = k_f[Ni(trien)^{2+}][CN_T]^4 \qquad (2)$$

excess of cyanide present at pH 6.65 the reactions are first order in $Ni(trien)^{2+}$ and Table I shows that the observed first-order rate constant, k_{obsd}, is independent of the initial concentration of nickel–trien but is very dependent upon the cyanide concentration. The data give an order dependence in $[CN_T]$ of 3.92 ± 0.06. The rate constant calculated for fourth-order cyanide dependence, $k_f = k_{obsd}/[CN_T]^4$, is given in the fourth column of Table I.

TABLE I

FORMATION RATE CONSTANT CALCULATED FOR A FOURTH-ORDER DEPENDENCE IN TOTAL CYANIDE AT pH 6.65 ± 0.10, 25.0°, AND $\mu = 0.1\ M$ ($NaClO_4$)

$10^4[CN_T]$, *M*	$10^6[Ni(trien)^{2+}]$, *M*	k_{obsd},[a] sec^{-1}	$10^{-14}(k_{obsd}/[CN_T]^4)$, $M^{-4}\ sec^{-1}$
1.02	1.96	0.012	1.11
1.02	2.80	0.013	1.20
1.02	5.60	0.014	1.29
	Av	0.013 ± 0.001	
2.04	1.96	0.20	1.15
2.04	2.80	0.22	1.27
2.04	5.60	0.18	1.04
	Av	0.020 ± 0.02	
3.06	1.96	0.97	1.11
3.06	2.80	1.03	1.17
3.06	5.60	1.00	1.14
	Av	1.00 ± 0.03	1.18 ± 0.13 for 20 runs

[a] All values are an average of two or three runs.

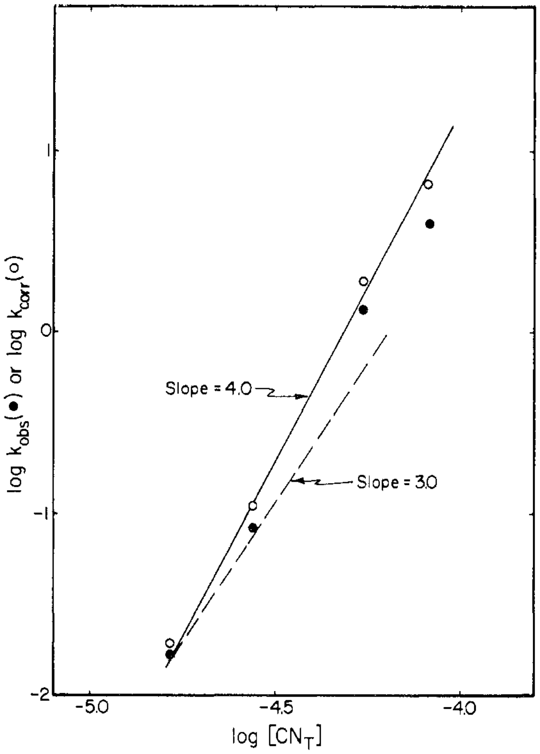

Figure 1.—Order dependence of the observed first-order rate constant on total cyanide at pH 9.0 ± 0.1, 25.0°, $\mu = 0.1\ M$ ($NaClO_4$), $[Ni(trien)^{2+}]_i = (1.12\text{–}8.40) \times 10^{-6}\ M$, and $[CN_T]_i = (1.59\text{–}8.10) \times 10^{-5}\ M$. The solid points are k_{obsd} and the open circles are corrected for $Ni(trien)(CN)^+$ formation. The values for k_{cor} are approximately equal to $k_{obsd}\ (1 + K'_{NiTCN}\cdot[CN_T])$.

At higher pH the rate of formation of $Ni(CN)_4^{2-}$ becomes so fast that it is difficult to use excess cyanide to determine the reaction order. However, the data in Figure 1 show the order dependence at pH 9.0 using very low concentrations of $Ni(trien)^{2+}$ and a 10–25-fold excess of cyanide. The observed values appear to have less than a fourth-order $[CN_T]$ dependence under these conditions. As seen in the next section this is due to partial formation of $Ni(trien)(CN)^+$ at higher concentrations of CN^-. When correction is made for the $Ni(trien)(CN)^+$ formation, the corrected first-order rate constant, k_{cor}, gives a fourth-order dependence in $[CN_T]$.

Suppression of the Rate of $Ni(CN)_4^{2-}$ Formation Using Excess $Ni(trien)^{2+}$.—As the concentration of nickel–trien (in excess over cyanide) is increased above 10^{-4} *M* at pH 9, the rate of formation of $Ni(CN)_4^{2-}$

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(6) M. R. James and D. W. Margerum, unpublished data.

(7) G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 974 (1950).

(8) H. B. Jonassen, R. B. LeBlanc, A. W. Meibohm, and R. M. Rogan, *J. Am. Chem. Soc.*, **72**, 2403 (1950).

(9) C. N. Reilley and R. W. Schmid, *J. Elisha Mitchell Sci. Soc.*, **73**, 279 (1957).

(10) D. C. Weatherburn and D. W. Margerum, work in progress.

decreases sharply. This behavior is understandable because rapid formation of mixed cyanide complexes has been found with $NiEDTA^{2-}$ to give $NiEDTA(CN)^{3-}$ and similar reactions occur with other aminocarboxylatonickel complexes. Therefore, a complex such as $Ni(trien)(CN)^+$ is to be expected. The formation of $Ni(trien)(CN)^+$ is undoubtedly the first step in the reaction path leading to $Ni(CN)_4^{2-}$ but its formation decreases the concentration of free cyanide present in the solution and hence removes the cyanide needed to form $Ni(CN)_4^{2-}$. Therefore the reaction velocity decreases as the nickel–trien concentration increases as seen in Figure 2.

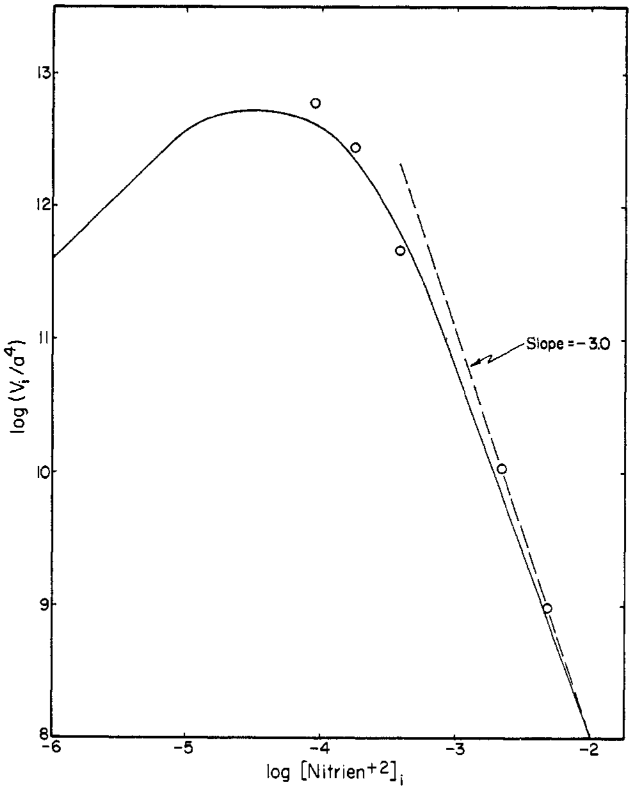

Figure 2.—Effect of $Ni(trien)^{2+}$ concentration in excess of $[CN_T]$ on the initial velocity of the formation of tetracyanonickelate(II) at pH 9.0 ± 0.2, 25.0°, $\mu = 0.1$ M ($NaClO_4$), and $[CN_T]_i = 8.0 \times 10^{-6}$ to 1.99×10^{-3} M. The solid line is generated by using $K'_{NiTCN} = 8.0 \times 10^3$ M^{-1} and $k' = 8.4 \times 10^{13}$ M^{-3} sec^{-1}.

The initial reaction velocity, V_i, is given by eq 3, assuming that the reaction proceeds by the $Ni(trien)(CN)^+$ complex which now needs only three additional

$$V_i = d[Ni(CN)_4^{2-}]_i/dt = k'[Ni(trien)(CN)^+]_i[CN_T]_i^3 \quad (3)$$

cyanides to reach the rate-determining step. The value of $[CN_T]$ equals the cyanide added, a, minus the concentration of $Ni(trien)(CN)^+$

$$[CN_T] = a - [Ni(trien)(CN)^+] \quad (4)$$

and

$$K'_{NiTCN} = \frac{[Ni(trien)(CN)^+]}{[Ni(trien)^{2+}][CN_T]} \quad (5)$$

so that a combination of eq 3–5 gives

$$V_i = k'K'_{NiTCN}[Ni(trien)^{2+}]_i\left(\frac{a}{1 + K'_{NiTCN}[Ni(trien)^{2+}]_i}\right)^4 \quad (6)$$

The function V_i/a^4 is plotted against the $[Ni(trien)^{2+}]_i$ in logarithmic form in Figure 2. If the nickel–trien concentration is in sufficiently large excess to make $K'_{NiTCN}[Ni(trien)^{2+}]_i \gg 1$, eq 6 simplifies to eq 7. At

$$V_i/a^4 = k'(K'_{NiTCN}[Ni(trien)^{2+}]_i)^{-3} \quad (7)$$

high concentrations of $Ni(trien)^{2+}$ the reaction velocity decreases by many orders of magnitude and the slope of the plot in Figure 2 approaches −3. This is in agreement with the assumptions made leading to eq 7. The solid line in Figure 2 is calculated from eq 6 using $K'_{NiTCN} = 8.0 \times 10^3$ M^{-1} and $k' = k_f/K'_{NiTCN} = 8.4 \times 10^{13}$ M^{-3} sec^{-1}. The k_f value used is taken from kinetic data at pH 9.0 when $[CN_T] > 4[Ni(trien)^{2+}]$ and both concentrations are very small.

As defined in eq 5 the value of K'_{NiTCN} will change with pH. If the constant is expressed in terms of cyanide ion rather than $[CN_T]$, the stability constant K_{NiTCN} (without a prime) is 1.6×10^4 M^{-1}.

pH Dependence of the Formation Rate.—The rate of the forward reaction in eq 1 is studied from pH 5 to 12. An integrated form of eq 2, similar to the one used previously for the aquonickel ion reaction,[2] should give the value of k_f when the total cyanide concentration is not in sufficient excess to use pseudo-first-order plots. This is given in eq 8 where $\alpha = [CN_T]_i - [Ni(trien)^{2+}]_i$.

$$\frac{1}{3\alpha}\left\{-\frac{1}{[CN_T]^3} + \frac{3}{2\alpha}\left[-\frac{1}{[CN_T]^2} - \frac{2}{\alpha}\left(\frac{1}{[CN_T]} + \frac{1}{\alpha}\log\frac{[Ni(trien)^{2+}]}{[CN_T]}\right)\right]\right\} = k_ft + c \quad (8)$$

At low cyanide ion concentrations plots of eq 8 consistently fit the kinetic data better than plots for other reaction orders. Table II gives the apparent k_f values assuming negligible formation of $Ni(trien)(CN)^+$. However, at higher pH even the lowest cyanide ion concentrations cause some conversion of $Ni(trien)^{2+}$ to $Ni(trien)(CN)^+$ and therefore some correction is necessary. Using eq 3, 4, 5, and 9 leads to eq 10 if the squared

$$[Ni(trien)_T] = [Ni(trien)^{2+}] + [Ni(trien)(CN)^+] \quad (9)$$

terms of $[Ni(trien)(CN)^+]$ are neglected. The latter approximation involves less than 1% error in the values used from eq 10 to correct $k_{f(app)}$. Therefore, the initial

$$\frac{V_i}{[Ni(trien)_T]a^4} = k_{f(app)} = \frac{k_f(1 + aK'_{NiTCN})^3}{\{1 + K'_{NiTCN}(a + [Ni(trien)_T])\}^4} \quad (10)$$

slopes of plots of eq 8 are used to give $k_{f(app)}$ in Table II. The corrected k_f values obtained from eq 10 are given in the fifth column of Table II and are the values plotted in Figure 3.

As the hydrogen ion concentration is increased below pH 8, the value of k_f decreases. In Figure 3 if hydrocyanic acid were not a reactant, the slope of the plot would become 4.0. Instead, a slope of 2.0 is found be-

Table II

Rate Constants for the Formation of Tetracyanonickelate(II) from Nickel–trien at 25.0° and μ = 0.1 M ($NaClO_4$)

−Log [H⁺]	10^6[Ni(trien)$_T$], M	10^5 × [CN$_T$], M	$k_{f(app)}$, M^{-4} sec^{-1}	k_f, M^{-4} sec^{-1}
5.20	11.20	45.50	2.1×10^{11}	2.1×10^{11}
5.55	11.20	45.50	$(7.0, 9.5) \times 10^{11}$	$(7.0, 9.5) \times 10^{11}$
5.78	5.60	48.00	$(2.5, 1.6, 3.6, 2.9) \times 10^{12}$	$(2.5, 1.6, 3.6, 2.9) \times 10^{12}$
6.10	11.20	45.50	$(3.2, 3.4) \times 10^{12}$	$(3.2, 3.4) \times 10^{12}$
6.31	5.60	22.70	5.0×10^{13}	5.0×10^{13}
6.72	5.60	22.70	$(1.3, 1.1) \times 10^{14}$	$(1.3, 1.1) \times 10^{14}$
7.48	2.80	2.54	6.6×10^{15}	6.7×10^{15}
7.62	5.60	22.70	2.7×10^{15}	3.2×10^{15}
8.23	2.80	2.54	5.0×10^{16}	5.4×10^{16}
8.65	2.80	2.54	$(1.3, 1.3) \times 10^{17}$	1.5×10^{17}
8.85	2.80	2.54	4.0×10^{17}	5.0×10^{17}
8.87	2.80	2.54	$(4.0, 4.0) \times 10^{17}$	5.0×10^{17}
8.92	4.48	4.44	3.8×10^{17}	5.5×10^{17}
9.28	2.80	2.54	$(5.6, 5.6) \times 10^{17}$	7.8×10^{17}
9.60	4.48	4.44	3.5×10^{17}	6.3×10^{17}
10.43	2.80	2.73	3.6×10^{17}	5.1×10^{17}
10.48	2.80	2.54	$(5.5, 5.5) \times 10^{17}$	8.7×10^{17}
10.64	2.80	2.54	$(5.0, 5.0) \times 10^{17}$	7.9×10^{17}
10.81	2.80	2.54	$(6.8, 6.8) \times 10^{17}$	1.1×10^{17}
10.98	2.80	2.54	$(4.9, 4.9) \times 10^{17}$	7.8×10^{17}
11.18	2.80	2.54	$(4.0, 4.0) \times 10^{17}$	6.4×10^{17}

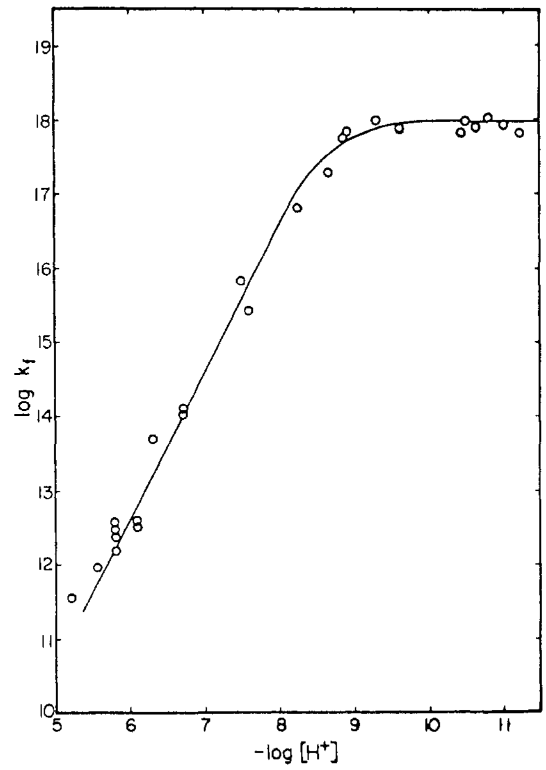

Figure 3.—Hydrogen ion dependence of the fifth-order formation rate constant at 25.0° and μ = 0.1 M ($NaClO_4$). The solid line is calculated from $k_{2,2} = 4.0 \times 10^{18}$ M^{-4} sec^{-1}, $k_{3,1}$ = 5×10^{18} M^{-4} sec^{-1}, and $k_4 = 10^{18}$ M^{-4} sec^{-1}.

low pH 8. This is the same type of behavior observed with aquonickel ion[2] and indicates the rate expression

$$\frac{d[Ni(CN)_4^{2-}]}{dt} = k_{2,2}[Ni(trien)^{2+}][CN^-]^2[HCN]^2 \qquad (11)$$

The value of $k_{2,2}$ is 4.0×10^{18} M^{-4} sec^{-1} for $Ni(trien)^{2+}$ whereas the corresponding rate constant for the aquonickel ion is 1.6×10^{13} M^{-4} sec^{-1}. The k_f values level off above pH 10 in accord with a rate equal to $k_4[Ni(trien)^{2+}][CN^-]^4$, where k_4 is 1.0×10^{18} M^{-4} sec^{-1}.

Kinetics of $Ni(CN)_4^{2-}$ Dissociation in the Presence of trien.—The disappearance of $Ni(CN)_4^{2-}$ is greatly accelerated by trien in comparison to the much slower reactions of $Ni(CN)_4^{2-}$ with EDTA or with perchloric acid. A large excess of trien is needed to force the dissociation reaction and the dissociation rate is pseudo first order in $Ni(CN)_4^{2-}$ under these conditions. The observed first-order constant, k_d, equals k_r[trien$_T$] as

$$\frac{-d[Ni(CN)_4^{2-}]}{dt} = k_r[Ni(CN)_4^{2-}][trien_T] \qquad (12)$$

seen in Table III. There is no contribution from the solvent dissociation rate. This agrees with the extremely small values found for the dissociation rate of $Ni(CN)_4^{2-}$ at low acidities.[2]

Table III

Effect of trien Concentration on the Decomposition of Tetracyanonickelate at 25.0°, μ = 0.1 M ($NaClO_4$), and pH 8.90 ± 0.03

10^3[trien$_T$], M	10^5[$Ni(CN)_4^{2-}$], M	k_d, sec^{-1}	k_r, M^{-1} sec^{-1}
2.36	2.08	0.44	186
2.36	4.11	0.39	165
2.36	6.24	0.32	136
4.71	2.08	0.74	157
4.71	4.11	0.71	151
4.71	6.24	0.67	142
4.71	8.32	0.67	142
4.71	10.40	0.92	195
4.71	12.50	0.67	142
9.42	2.08	1.36	144
9.42	4.11	1.52	161
9.42	6.24	1.52	161
9.42	8.32	1.70	180
9.42	10.40	1.80	191
9.42	12.50	1.59	169
14.10	2.08	2.44	173
14.10	4.11	2.44	173
14.10	6.24	2.19	155
14.10	8.32	2.40	170
14.10	10.40	2.63	186
14.10	12.50	1.66	118

The reaction rate in eq 12 is studied from pH 7 to 12 (Table IV). The value of k_r decreases as the acidity increases as seen in Figure 4. In this pH range trien is present in various protonated forms while the $Ni(CN)_4^{2-}$ does not add a proton until pH 5. The rate constants needed to fit the data are given in eq 13

$$k_r[trien_T] = k_{trien}[trien] + k_{Htrien}[Htrien^+] + k_{H_2trien}[H_2trien^{2+}] \qquad (13)$$

where [trien$_T$] = [trien] + [$Htrien^+$] + [H_2trien^{2+}] + [H_3trien^{3+}]. The rapid decrease in k_r below pH 10 is due first to the formation of H_2trien^{2+} which is less reactive than trien and $Htrien^+$ and second to the formation of H_3trien^{3+} which does not contribute significantly to the rate under the conditions used. The solid line in Figure 4 is calculated from the best fit of the rate constants in eq 13 where k_{trien} = 310 M^{-1} sec^{-1}, k_{Htrien} = 295 M^{-1} sec^{-1}, and k_{H_2trien} = 14 M^{-1} sec^{-1}.

TABLE IV

HYDROGEN ION DEPENDENCE OF THE RATE CONSTANT FOR trien ATTACK ON TETRACYANONICKELATE(II) AT 25.0° AND μ = 0.1 M (NaClO$_4$)

−Log [H$^+$]	10^5[Ni(CN)$_4^{2-}$], M	10^3[trien$_T$], M	k_r, M^{-1} sec^{-1}
11.63	10.00	30.60	318
11.55	2.08	4.71	285
11.55	2.08	4.71	310
11.55	2.08	4.71	285
11.47	10.00	23.60	308
11.42	2.08	4.71	310
11.42	2.08	4.71	280
11.20	2.08	4.71	301
11.20	2.08	4.71	280
11.00	2.08	4.71	294
11.00	2.08	4.71	289
10.80	2.08	4.71	289
10.80	2.08	4.71	294
10.65	2.08	4.71	280
10.65	2.08	4.71	297
10.61	6.23	9.42	379
10.26	6.23	9.42	310
9.81	6.23	9.42	274
9.27	6.23	9.42	169
8.90	2.08	4.71	104
8.90	2.08	4.71	117
8.53	2.08	4.71	62
8.26	2.08	4.71	46
7.91	2.08	4.71	33
7.91	2.08	4.71	33
7.30	2.08	4.71	1.7

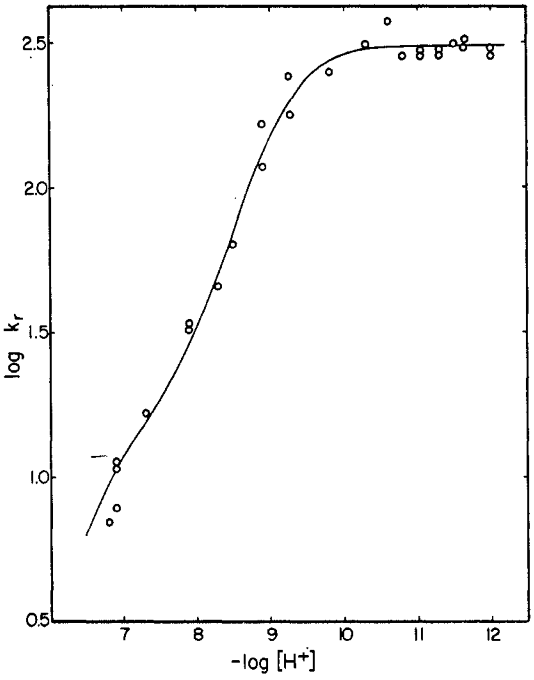

Figure 4.—Hydrogen ion dependence of the second-order rate constant for trien attack on tetracyanonickelate(II) at 25.0° and μ = 0.1 M (NaClO$_4$). k_{trien} = 310 M^{-1} sec^{-1}, k_{Htrien} = 295 M^{-1} sec^{-1}, and $k_{\text{H}_2\text{trien}}$ = 14 M^{-1} sec^{-1} were used to generate the solid line.

Discussion

The formation and dissociation kinetics agree with a mechanism in which four cyanides, trien, and nickel are present during the rate-determining step. There are from zero to two protons also present depending on the pH. The reactions given in eq 14–16 are needed to fit both the forward and reverse kinetics. The rate constants are summarized in Table V. The ratios of the forward and reverse rate constants for eq 14–16 give values of 2.9 × 10^{17}, 1.7 × 10^{16}, and 3.2 × 10^{15} M^{-3}, compared to values of 2.0 × 10^{17}, 1.0 × 10^{17}, and 2.5 × 10^{16} M^{-3}, calculated from equilibrium constants of Ni(trien)$^{2+}$ and Ni(CN)$_4^{2-}$ and the protonation constants for CN$^-$ and trien. There is excellent agreement between the equilibrium constant for eq 14 as determined kinetically and the value calculated from the stability constants. However, the agreement for eq 15 and 16 is not as good. The disagreement is a little greater than the range of uncertainty expected for the combination of stability constants.

$$\text{Ni(trien)}^{2+} + 2\text{CN}^- + 2\text{HCN} \rightleftarrows \text{Ni(CN)}_4^{2-} + \text{H}_2\text{trien}^{2+} \quad (14)$$

$$\text{Ni(trien)}^{2+} + 3\text{CN}^- + \text{HCN} \rightleftarrows \text{Ni(CN)}_4^{2-} + \text{Htrien}^+ \quad (15)$$

$$\text{Ni(trien)}^{2+} + 4\text{CN}^- \rightleftarrows \text{Ni(CN)}_4^{2-} + \text{trien} \quad (16)$$

TABLE V

CONSTANTS AT μ = 0.1 M (NaClO$_4$) AND 25.0°

Formation Rate Constants, k_{ij}, M^{-4} sec^{-1} (i = CN, j = HCN)

Ni(trien)$^{2+}$	Ni(H$_2$O)$_6^{2+}$
$k_{2,2} = 4.0 \times 10^{18}$	$k_{2,2} = 1.6 \times 10^{18}$
$k_{3,1} = 5 \times 10^{18}$	$k_{3,1} \cong 4 \times 10^{19}$
$k_4 = 1 \times 10^{18}$	$k_4 \cong 6 \times 10^{19}$

Dissociation of Ni(CN)$_4^{2-}$ with Polyamines and Ammonia (Rate Constants, M^{-1} sec^{-1})

$k_{\text{trien}} = 310$	$k_{\text{en}} = 50$
$k_{\text{Htrien}} = 295$	$k_{\text{NH}_3} \cong 9 \times 10^{-4}$
$k_{\text{H}_2\text{trien}} = 14$	

Stability Constant for Ni(trien)(CN)$^+$, M^{-1}

$K_{\text{Ni(trien)(CN)}^+} = 1.6 \times 10^4$

trien has an enormous labilizing effect on the dissociation of Ni(CN)$_4^{2-}$. The aqueous dissociation rate constant is calculated to be 2 × 10^{-11} sec^{-1} at high pH, and even the strongly acid-assisted reaction at pH 5 has an observed rate constant of only $10^{-4.8}$ sec^{-1}. By comparison, 0.01 M trien at pH 9 gives an observed dissociation rate constant of 1.6 sec^{-1}. The trien reaction obviously proceeds by an associative mechanism. A few reactions run with ethylenediamine (0.266 M at pH 11.56) show it to be an effective nucleophile for the attack on Ni(CN)$_4^{2-}$ with rate constants about one-sixth that of trien. On the other hand, ammonia (in the presence of EDTA to force the reaction) is many orders of magnitude less effective (see Table V). Chelation with at least two nitrogen donors apparently speeds the dissociation of cyanide, but all four cyanides are present before the rate-determining step. This suggests a mechanism in which the polyamine attacks the Ni(CN)$_4^{2-}$ complex in the typical associative manner of square-planar substitution reactions.[11,12] This leads to a five-coordinate intermediate such as I (trigonal bi-

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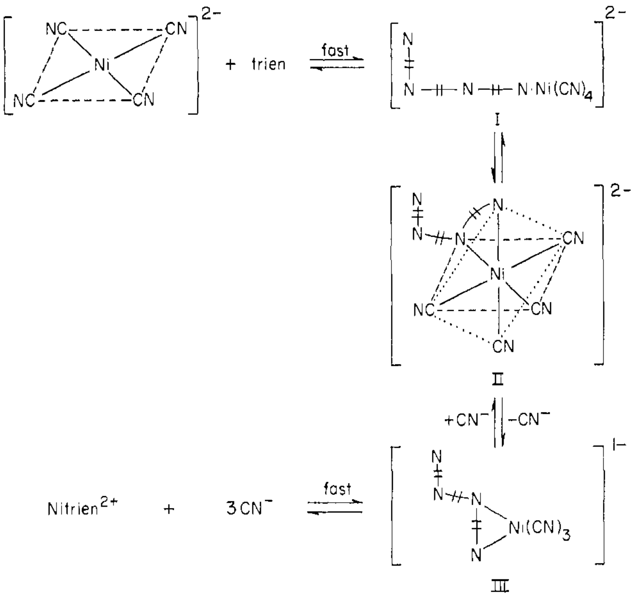
[11] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967, p 379.

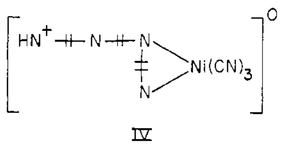
[12] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965, p 18.



pyramid or square pyramid), which weakens the cyanide bonding. It is proposed that the coordination number (to nitrogen and cyanide) then expands from 5 to 6 to give a structure such as II, which either may be a reaction intermediate preceding the rate-determining loss of cyanide or may be the transition state with a nitrogen chelate forming as the cyanide ion leaves. The drawing of structure II is intended to indicate the possibility that the complex may be predominently square planar with the plane defined by either the dashed or the dotted line.

Looking at the formation reaction by this mechanism, a fourth cyanide cannot enter the coordination sphere of nickel until trien becomes bidentate as in structure III, which may be five- or six-coordinate with H_2O as the sixth ligand. The rate-determining step for the formation would be somewhere between structures III and I as in the dissociation mechanism.

In this mechanism it is easy to see why the $k_{3,1}$ rate constant is larger than the k_4 constant for the formation reaction. At least one proton initially assigned to HCN would be expected to transfer to the more basic site of the free terminal nitrogen of the polyamine as in structure IV. This will assist the displacement of trien



IV

and give stronger bonding to the cyanides and therefore speed the reaction. The ratios of the rate constants for $Ni(trien)^{2+}$ compared to Ni_{aq}^{2+} are: $k_{2,2}$, 2.5; $k_{3,1}$, $\lesssim 0.13$; k_4, $\cong 0.016$. Hence it appears that two protons can be transferred from two HCN molecules in the transition state to the trien molecule. This is in agreement with the relative acidities expected for coordinated HCN ($\log K_H = 5.4$ in $HNi(CN)_4^-$ and $\log K_{2H} = 4.5$ in $H_2Ni(CN)_4$) compared to the $\log K_H$ values expected for coordinated trien (one $\log K_H \cong 10$; the other $\log K_H$ is between 6 and 8).

It is more difficult to understand why the reactions of nickel–trien with cyanide are as fast as they are compared to the aquonickel reaction with cyanide. trien must lose the coordination of at least two nitrogen donors before the rate-determining step if a maximum coordination number of 6 is permitted for nickel. (Even if a higher coordination number were postulated in order to keep trien tridentate and have four cyanides present in the rate-determining step, such a mechanism would require a rather marvelous and heretofore unknown type of rearrangement. Hence this possibility is discarded.) The stability constants for nickel–trien and for mononickel–en indicate a loss of $10^{6.8}$ in stability in going from the tetradentate to the bidentate complex. Because a corresponding energy change is not required in the reaction of aquonickel ion with cyanide, the latter reaction might be expected to be 2,000,000 times faster. Actually aquonickel ion reacts only about 60 times faster than nickel–trien to form $Ni(CN)_4^{2-}$.

There are possible explanations which seem worthwhile to postulate. In both reactions the initial high-spin complexes ($Ni(trien)^{2+}$ and Ni_{aq}^{2+}) are converted to the low-spin $Ni(CN)_4^{2-}$ complex. Nitrogen is a stronger field ligand than oxygen and tends to stabilize the low-spin state in the reaction intermediates. It may be that two amine nitrogen bonds from trien will stabilize the addition of cyanide to nickel (or *vice versa* the cyanides will stabilize the amine bonds). This would be the case if intermediates with two or more cyanides give a square-planar or a five-coordinate complex with stronger nickel–nitrogen bonds and stronger nickel–cyanide bonds than is the case with the octahedral form of the complex. Thus, III could be five-coordinate or could be predominantly square-planar with one nitrogen and three cyanides in a plane. Alternatively, two nitrogens and two cyanides could be in a plane. In the formation reaction either structure could precede structure II. The latter may have one or two nitrogens in a predominantly square-planar configuration. There is no doubt about the enhanced stability of the bonds in the square-planar form of the complex. For example, it has been shown[2] that the addition of the fourth cyanide ion to $Ni(CN)_3^-$ to give $Ni(CN)_4^{2-}$ must have a stability constant greater than 10^{14}.

The suggested enhancement of thermodynamic stability in the mixed cyanide complexes can explain the high speed of the nickel–trien reaction only if it does not lead to kinetically more stable complexes. This may appear to be a contradiction but in reality it is not because the speed and mechanism of square-planar substitution reactions are quite different from those of octahedral substitutions.[11,12] Thus, the first-order dissociation constant of CN^- in the octahedral complex $NiEDTA(CN)^{3-}$ to give $NiEDTA^{2-}$ and CN^- is only 3.1×10^{-3} sec^{-1} [3] ($t_{1/2} = 224$ sec) while the attack of trien on the square-planar $Ni(CN)_4^{2-}$ complex has a pseudo-first-order constant of 1.6 sec^{-1} at 10^{-2} M trien and pH 9, yet the stability constant for CN^- in $NiEDTA(CN)^{3-}$ is 4×10^3 M compared to the much larger value of $K_4 > 10^{14}$ M for $Ni(CN)_4^{2-}$. The difference is, of course, in the associative path of the square-planar substitution reactions. In the present case, once intermediates such as III form, they must react readily to add cyanide and break the nickel–nitrogen bonds to trien.

Lack of more detailed knowledge of the kinetic behavior of labile octahedral to square-planar reactions forces a somewhat speculative discussion. This is an interesting area for additional investigation. The fact remains that from pH 5 to 7.5 cyanide reacts 2.5 times faster with nickel–trien than it does with aquonickel to form tetracyanonickelate(II).

Acknowledgment.—This investigation was supported by PHS Research Grant No. GM 12152 from the National Institute of General Medical Sciences, NIH, and by National Science Foundation Grant No. GP 6725X.

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The Preparation and Optical and Electron Spin Resonance Spectra of Some Chloro(methanol) Complexes of Titanium(III)

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Received October 11, 1968

Several new chloro complexes of titanium(III) have been isolated: $H[TiCl_4(C_4H_{10}O)]$, $TiCl_3(CH_3OH)_3$, $(C_5H_6N)TiCl_4$, $(C_5H_6N)[TiCl_4(CH_3OH)_2]$, and $(C_5H_6N)_2[TiCl_5(CH_3OH)]$. These new compounds have been characterized and magnetic susceptibilities and optical spectra are reported. Esr spectra have been determined for these and previously reported[1] compounds of similar types. Three of the complexes, $[TiCl(CH_3OH)_5]Cl_2$, $TiCl_3(CH_3OH)_3$, and $(C_5H_6N)_2[TiCl_5(CH_3OH)_2]$, exhibited axial symmetry. No esr signals could be observed for the hexachlorotitanate(III), for the octachlorotitanate(III), or for $(C_5H_6N)_2[TiCl_5(CH_3OH)]$. Three distinct g's were observed for the other compounds. The nature of species present in methanol solutions of titanium(III) is discussed as are the electronic spectra of such species.

In a continuation of previous work[1] on solutions of titanium(III) in methanol solutions, we have prepared some new compounds, characterized them, and applied esr measurements to all of the series of compounds which gave esr signals.

Experimental Section

Materials and Experimental Techniques.—Solvents were purified as described in a previous study.[1] All other chemicals were reagent grade and were used without further purification. All operations were carried out as before under nitrogen, mainly by use of Schlenk-tube techniques. Nitrogen was purified by passing it through columns filled with BTS catalyst (BASF), calcium chloride, and magnesium perchlorate.

$H[TiCl_4(C_4H_{10}O)]$.—A 7.7-g sample of $TiCl_3$ was added to 50 ml of anhydrous ether saturated with HCl. The mixture was stirred vigorously for 1 day and was then resaturated with HCl. The resulting yellow-brown compound, which was slightly soluble in ether, was filtered and washed with dry ether (12.6 g). *Anal.* Calcd for $TiCl_4C_4H_{11}O$: Ti, 18.1; Cl, 53.8. Found: Ti (vol), 17.75; Ti (grav), 18.3; Cl, 52.8.

$TiCl_3(CH_3OH)$.—A 6.6-g sample of $TiCl_4HC_4H_{10}$ was added to a mixture of 50 ml of dry benzene and 3.0 ml of methanol. After being stirred for 1 day, the solution was filtered and its volume was reduced under reduced pressure. Pale blue crystals separated (4.8 g). They were filtered and washed with benzene and petroleum ether (bp 37.5–46.8) and were dried under vacuum. If the reaction is carried out with $TiCl_3$ and methanol in benzene, 1 week of vigorous stirring is required before the product is obtained. *Anal.* Calcd for $TiCl_3C_3H_{12}O_3$: Ti, 19.14; Cl, 42.49. Found: Ti (vol), 18.93; Ti (grav), 19.12; Cl, 42.36.

$TiCl_4(C_5H_6N)$.—A 7.7-g sample of $TiCl_3$ was added to a mixture of 4.0 ml of pyridine in 50 ml of anhydrous ether which was saturated with HCl. After 1 day of vigorous stirring the resulting pea green powder (13.5 g) was filtered and dried. *Anal.* Calcd for $TiCl_4C_5H_6N$: Ti, 17.75; Cl, 52.56; $C_5H_6N^+$, 29.69. Found: Ti (vol), 16.87; Ti (grav), 17.12; Cl, 51.98; $C_5H_6N^+$, 30.07.

$(C_5H_6N)[TiCl_4(CH_3OH)_2]$.—A 6.8-g sample of $(C_5H_6N)TiCl_4$ was added to a mixture of 2.0 ml of anhydrous methanol in 50 ml of anhydrous ether. After being stirred for 1 day, the turquoise product (8.4 g) was filtered, washed with ether, and dried *in vacuo*. *Anal.* Calcd for $TiCl_4C_7H_{14}O_2N$: Ti, 14.44; Cl, 42.73; $C_5H_6N^+$, 24.14. Found: Ti (vol), 14.22; Ti (grav), 14.31; Cl, 42.75; $C_5H_6N^+$, 24.33.

$(C_5H_6N)_2[TiCl_5(CH_3OH)]$.—A 7.7-g sample of $TiCl_3$ was added to a mixture of 8.0 ml of pyridine and 2.0 ml of methanol in 50 ml of anhydrous ether or chloroform saturated with HCl. After 1 day of vigorous stirring, the yellow product (20 g) was filtered, washed with chloroform and ether, and dried under vacuum. *Anal.* Calcd for $TiCl_5C_{11}H_{16}ON_2$: Ti, 11.47; Cl, 42.48; $C_5H_6N^+$, 38.38. Found: Ti (vol), 11.23; Ti (grav), 11.39; Cl, 42.24; $C_5H_6N^+$, 38.18.

Attempts to Prepare a Monomeric Titanium(III)–Chloro(methoxo) Complex.—From the behavior of tungsten(V)–,[2] molybdenum(V)–,[3] and niobium(IV)–chloro[4] compounds one could anticipate the formation of titanium(III)–chloro(methoxo) complexes by the reaction of higher titanium(III)–chloro complexes with methanol with elimination of HCl.

When methanol was added to a yellow suspension of $(C_5H_6N)_4H[TiCl_8]$ in chloroform, a green precipitate was obtained and proved to be $(C_5H_6N)_2[TiCl_5(CH_3OH)_2]$. This suspension was then

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