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Ternary Complex Formation Kinetics Involving (Triethylenetetramine)nickel(II) and Bidentate Ligands

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The kinetics of ternary complex formation between Ni(trien)$^{2+}$ and 1,10-phenanthroline was studied at pH 7.1 and 7.5, covering a phen concentration range of $(1.5–6) \times 10^{-3}$ M, while that of Ni(trien)$^{2+}$ and glycine was studied over a pH range of 7.0–8.2, covering a glycine concentration range of $(5–50) \times 10^{-3}$ M. In both cases, the reaction is first order in Ni(trien)$^{2+}$ and is reversible. In the case of phenanthroline, the reaction is first order in phenanthroline with k_{NiT}^{phen} = 7.9×10^3 M^{-1} s^{-1}, which is 34 times less than that expected. The reverse rate constant is $k_b = 6.2$ s^{-1}, and the stability constant for the addition of phen to Ni(trien)$^{2+}$ is 1.3×10^3 M^{-1}. The decrease in stability and formation rate is felt to be due to the steric hindrance of coordinated trien. The reaction of Ni(trien)$^{2+}$ with glycine varies in order as a function of the glycine concentration, being first order at low glycine concentration and shifting toward a zero-order dependence at high glycine concentrations. A mechanism consistent with the kinetics involves a singly bonded (T–Ni–O–N) intermediate in rapid equilibrium with reactants, $K = 6.9 \times 10^2$ M^{-1}, coupled with a sluggish ring closure, $k_2 = 1.3 \times 10^2$ s^{-1}. The reverse rate constant is $k_b = 8.1$ s^{-1}, and the stability constant for the addition of gly to Ni(trien)$^{2+}$ is 1.1×10^4 M^{-1}. The type of dentate sites available for coordination coupled with a ligand that provides steric hindrance to ring closure is shown to profoundly affect the mechanism of ternary complex formation.

Introduction

The effect that a coordinated ligand has upon ternary complex formation has been studied for many nickel complexes.[1] Most attention has been focused upon the effect that the various types of donor atoms in the coordinated ligand have upon the formation reaction. In most of these cases, the complexed ligand is bi- or tridentate and the attacking ligand is monodentate. Thus three or four coordination sites are available for the attacking ligand with the result that little or no steric hindrance is present in the reaction. For example, a recent study[2] showed that the tridentate planar ligand TRI when complexed to nickel has no significant steric effect upon subsequent formation reactions with glycine or histidine.

The steric effect which a large multidentate ligand coordinated to a metal can have upon subsequent formation reactions has received little attention. A few systems of this type have been studied. Formation reactions between Ni(trien)$^{2+}$, Ni(tren)$^{2+}$, and Ni(NTA)$^-$ and PADA[3] all had formation rate constants which were lower than expected and which were explained as a ring-closure contribution brought on by steric hindrance. Other systems involved malonate reacting with Ni(trien)$^{2+}$[4] at a rate estimated to be $>10^7$ M^{-1} s^{-1}, 1,10-phenanthroline, bipyridine, and glycine all reacting with Ni(tren)$^{2+}$[5] at rates which appeared to be normal considering the effect of tren on the rate of water loss from nickel, and 5-nitrosalicylate reacting with Ni(trien)$^{2+}$, Ni(tren)$^{2+}$, and Ni(NTA)$^-$[6] at a normal rate. However, the reaction of glycine and alanine with Ni((pay)$_2$tn)$^{2+}$,[7] where (pay)$_2$tn is a tetradentate Schiff base which bonds to nickel in a square-planar fashion, showed a slow chelation step.

The present study was designed to investigate the effect of coordinated triethylenetetramine (trien) upon formation reactions of bidentate ligands. Two ligands were chosen, one with two strong donor sites, 1,10-phenanthroline (phen), and the other with one weak and one strong donor site, glycine. The effect of coordinated ligands upon the rate of water loss

Scheme I
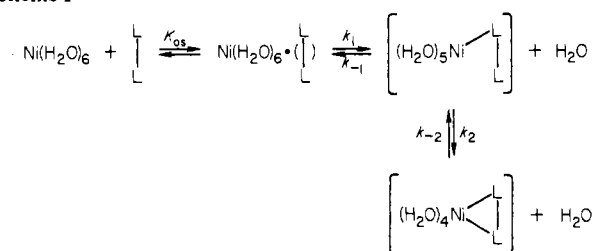
has been well documented.[1] Further, the mechanism through which bidentate ligands, in particular, amino acids, chelate to nickel has now been thoroughly studied and is well-known.[8] Thus a fairly detailed comparison of expected behavior with observed behavior can be made. In all formation reactions involving nickel, the Eigen–Tamm mechanism, illustrated in Scheme I, has been found to hold. The steady state has been applied to the singly bonded intermediate, resulting in eq 1.

$$k_{Ni}^{L-L} = K_{os}k_1k_2/(k_2 + k_{-1}) \qquad (1)$$

If ring closure is much faster than bond rupture of the singly bonded intermediate, then $k_2 \gg k_{-1}$ and the formation rate can be predicted as $K_{os}k_1$. Experimental values which are much lower than expected (at least a factor of 10) are felt to be due to $k_{-1} > k_2$ so that ring closure does contribute to the rate. If k_1 and k_{-1} were sufficiently fast and ring closure sufficiently slow, the steady state would not be applicable. In the present system, trien complexed to nickel is shown to exert just such an effect upon subsequent formation reactions but only for certain types of dentate sites on the attacking ligand.

Experimental Section

Reagents. trien was obtained as the disulfate from J. T. Baker Chemical Co. and recrystallized twice from hot water by the addition of methanol. It was standardized by a mole ratio plot against standard Ni(NO$_3$)$_2$ at 565 nm and pH 8.7. Ni(NO$_3$)$_2$ was standardized by titration with standard EDTA. Ni(trien)$^{2+}$ was prepared by adding a 5% molar excess of standard Ni(NO$_3$)$_2$ to a solution of trien and precipitating the excess nickel with base. The solution was stored at pH 6. The nickel and trien content were both analyzed and agreed to within 0.15%. Glycine and 1,10-phenanthroline were recrystallized before use. The buffer was *N*-(2-hydroxyethyl)piperazine-*N'*-2-ethanesulfonic acid (HEPES), a noncomplexing buffer, pK_a = 7.55.[9]

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(2) R. B. Jordan and B. E. Erno, *Inorg. Chem.*, **18**, 2895 (1979).
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(8) D. W. Margerum, G. C. Cayley, D. C. Weatherburn, and G. K. Pagenkopf in "Coordination Chemistry", A. E. Martell, Ed., American Chemical Society, Washington, D.C., 1978, ACS Monogr. No. 174, pp 33–43.
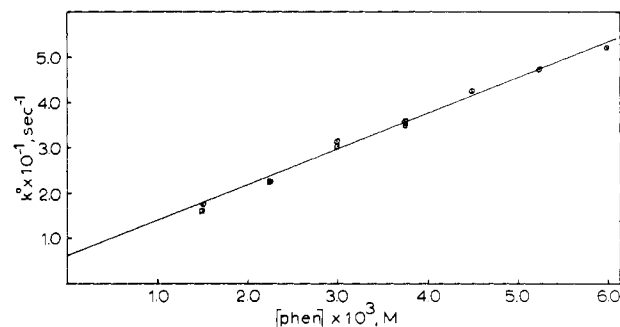
Table I. Experimental Values of the Rate Constants for the Reaction of Ni(trien)$^{2+}$ with 1,10-Phenanthroline and Glycine at 25 °C and $\mu = 0.1$

1,10-Phenanthroline^a

pH	10^3[phen], M	$k°$, s^{-1}	[buffer], M
7.49	1.50	17.2	0.010
7.47	2.24	22.6	0.010
7.48	2.99	31.7	0.010
7.47	3.74	35.9	0.010
7.46	4.49	42.5	0.010
7.46	5.23	47.5	0.010
7.46	5.98	51.8	0.010
7.12	1.49	16.0	0.000
7.11	2.24	22.4	0.000
7.13	2.98	30.4	0.000
7.14	3.72	34.9	0.000

Glycine^b

pH	10^4[NiT], M	10^2[gly], M	$k°$, s^{-1}
7.00	4.81	1.00	9.58
6.99	4.81	1.50	10.2
6.98	4.81	2.00	11.8
6.97	4.81	2.50	10.8
6.97	4.81	3.75	12.1
6.97	4.81	5.00	15.5
7.19	9.62	1.00	11.7
7.18	9.62	1.50	13.5
7.18	9.62	2.00	15.2
7.18	9.62	2.50	18.1
7.18	9.62	3.75	20.4
7.17	9.62	5.00	25.9
7.47	9.62	1.00	14.7
7.48	9.62	1.50	17.5
7.47	9.62	2.00	21.7
7.45	9.62	2.50	24.2
7.47	9.62	3.75	31.8
7.46	9.62	5.00	42.7
7.99	9.62	1.00	30.5
7.99	9.62	1.50	36.1
7.98	9.62	2.00	41.5
7.98	9.62	2.50	52.2
7.98	9.62	3.75	64.1
7.98	9.62	5.00	68.2
8.16	24.1	2.50	47.3
8.16	24.1	3.75	64.2
8.16	24.1	5.00	68.8
8.21	4.81	.50	26.2
8.20	4.81	1.00	37.6
8.19	4.81	1.50	35.0
8.20	4.81	2.00	53.1
8.22	4.81	2.50	59.5
8.21	4.81	3.75	76.2
8.21	4.81	5.00	80.7

^{a} All runs at 1.44×10^{-4} M Ni(trien)$^{2+}$. ^{b} All runs at 0.12 M buffer.

NaCl was used to control the ionic strength.

Kinetic and Equilibrium Measurements. All pH measurements were made on a Beckman Model 110 research pH meter. All spectra were taken on a Cary Model 14 spectrophotometer. Spectra of an equimolar mixture of Ni(trien)$^{2+}$ and phen matches that obtained by dissolving solid [Ni(trien)(phen)](ClO$_4$)$_2$ in water and indicates the reaction product to be Ni(trien)(phen)$^{2+}$. Although Ni(trien)(gly)$^+$ has not been isolated, this is no reason to believe that the spectral change seen when Ni(trien)$^{2+}$ and glycine are mixed is due to anything but the formation of Ni(trien)(gly)$^+$. Kinetic runs were made on an American Instrument Co. stopped-flow attached to a Schimadzu QV-50 spectrophotometer. Transmittance–time changes were stored in a Biomation Model 805 waveform recorder and displayed on a Sargent Model SR recorder. Reactions were followed at the wavelength yielding the largest difference in absorbance between product and reactant: 250 nm for Ni(trien)$^{2+}$ and glycine and 343 nm for Ni-

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Figure 1. Dependence of $k°$ upon [phen] for reaction of Ni(trien)$^{2+}$ and phen ($\mu = 0.1$ M, 25 °C): runs with buffer (O); runs without buffer (□). Solid line is least-squares best fit of the points.

Table II. Rate Constant and Equilibrium Constant Values for NiT–phen and NiT–gly Systems ($\mu = 0.1$ M, 25 °C)

k_b (phen system)	6.2 ± 2.0 s^{-1}
k_b (gly system)	8.7 ± 0.6 s^{-1} ^{a}
	7.6 ± 1.0 s^{-1} ^{b}
	8.1 ± 0.9 s^{-1} ^{c}
$k_{NiT}{}^{phen}$	$(7.9 \pm 0.6) \times 10^3$ M^{-1} s^{-1}
	2.7×10^5 M^{-1} s^{-1} ^{d}
K_1	$(6.9 \pm 2.6) \times 10^2$ M^{-1}
k_2	$(1.3 \pm 0.5) \times 10^2$ s^{-1}

^{a} pH 7.0. ^{b} pH 7.2. ^{c} pH 7.5. ^{d} Calculated value from eq 8.

(trien)$^{2+}$ and phen. Each reaction was repeated three to six times and the average rate constant reported. All reactions were run at 25.0 ± 0.1 °C and at $\mu = 0.1$ M. The pH of the reaction was measured by mixing equal volumes of reactants and monitoring the pH. The measured values agreed with those set for each reactant solution prior to mixing.

The very slow displacement of trien from Ni(trien)$^{2+}$ by phen[10] prevented any accurate absorbance measurements from being made on solutions whose phen/Ni(trien)$^{2+}$ ratio was >1. However the absorbance of solution containing a constant amount of Ni(trien)$^{2+}$ and variable excess amounts of both phen and glycine increased as a function of the excess ligand after correction was made for absorbance due to the ligand, indicating that the reactions did not go to completion.

Results

1,10-Phenanthroline. All reactions were carried out with at least a 10-fold excess of phen to Ni(trien)$^{2+}$ at pH 7.5 both with and without buffer. The ionic strength was held at 0.1. The data are shown in Table I. The reaction followed the rate expression

$$-d[\text{NiT}]/dt = k_{NiT}{}^L[\text{NiT}][\text{L}] - k_b[\text{NiTL}] \qquad (2)$$

with L = phen and T = trien. With the assumption that the phen concentration remains constant, eq 2 integrates to eq 3, where [NiTL]$_e$ and [NiT]$_0$ refer to equilibrium and initial concentrations, respectively.

$$k° = k_{NiT}{}^L[\text{L}] + k_b = \frac{-2.303}{t} \log \frac{[\text{NiTL}]_e - [\text{NiTL}]}{[\text{NiT}]_e - [\text{NiT}]_0} \qquad (3)$$

Reactions were run both with and without buffer present. A plot of the pseudo first-order rate constant, $k°$, vs. phen concentration is shown in Figure 1 and demonstrated linear behavior through a 4-fold increase in phen concentration. Further, the plot did reveal the presence of a phen-independent term, k_b, with a value of 6.2 s^{-1}. Since reactions without buffer fell on the same line as those containing buffer, the intercept does not represent a reaction involving buffer. Neither the stopped-flow trace nor the subsequent first-order plots shows

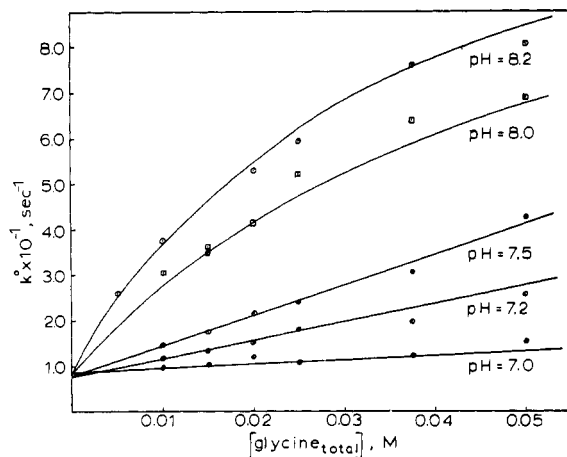(10) R. K. Steinhaus and J. A. Boersma, *Inorg. Chem.*, **11**, 1505 (1972).

Figure 2. Dependence of k° upon total glycine concentration at various pH values for reaction of Ni(trien)$^{2+}$ and glycine ($\mu = 0.1$ M, 25 °C). Solid lines at pH 7.0, 7.2 and 7.5 are least-squares best fits of the points; solid lines at pH 8.0 and 8.2 are calculated from eq 5.

Figure 3. Dependence of $k^{\circ\prime}$ upon glycinate ion concentration over pH range of 7.0–8.2 for reactions of Ni(trien)$^{2+}$ and glycine ($\mu = 0.1$ M, 25 °C). Solid line is calculated from eq 6.

any evidence of biphasic behavior. Thus the intercept must indicate a reversible reaction, and k° is correctly described by eq 3. Values of k_b and k_{NiT}^{phen} are given in Table II.

Glycine. All reactions were carried out with at least a 10-fold excess of glycine to Ni(trien)$^{2+}$ over a pH range from 6.9 to 8.2. The total glycine was varied over a 10-fold range from 5.0×10^{-3} to 5.0×10^{-2} M. The total buffer concentration was held constant at 0.12 M in all runs, but the ratio of buffer anion to acid form varied from 0.32 at pH 6.9 to 5.0 at pH 8.2. The data are shown in Table I. Under all conditions, the reactions followed the rate expression of eq 2. Plots of the observed pseudo-first-order rate constant, k°, against total glycine concentration at a constant pH are shown in Figure 2. The plots were linear up to pH 7.5. Higher pHs showed a curvature indicative of a shift from first-order to zero-order behavior in glycine as shown by the pH 8.0 and 8.2 curves of Figure 2. The intercepts of the plots at pHs less than 7.5, listed in Table II, were constant and gave an average value of 8.1 s^{-1}, which is independent of glycine, hydrogen, or hydroxide ion and buffer anion and protonated buffer. Plots above pH 7.5 appear to intercept at the same point. This value must represent a reaction involving only Ni(trien)$^{2+}$ and cannot involve Ni(T)(OH)$^+$ or Ni(TH)$^{3+}$ species since these would show a pH dependence. Again, as with the Ni(trien)$^{2+}$–phen system, no biphasic behavior was seen so that the intercepts indicate a reversible reaction with k° described by eq 4. The

$$k^\circ = k_{NiT}^{gly}[\text{gly}] + k_b \qquad (4)$$

average value of 8.1 s^{-1} was subtracted from k° for the glycine reactions. When this corrected value, $k^{\circ\prime}$, was plotted against the glycinate ion concentration with $K_a = 2.69 \times 10^{-10}$ for glycine, according to eq 5, all points covering all pHs and

$$k^{\circ\prime} = k_{NiT}^{gly}[\text{gly}] = k_{NiT}^{gly}\left(\frac{K_a[\text{glycine}]_{tot}}{K_a + [\text{H}]}\right) \qquad (5)$$

glycine concentrations studied fell on the same line. The plot, shown in Figure 3, has a definite curvature to it; nevertheless, all points appear to fit the line. Behavior such as this is represented by the rate expression shown in eq 6. Equation

$$k^{\circ\prime} = \frac{ab[\text{gly}]}{1 + a[\text{gly}]} \qquad (6)$$

6 can be rearranged to eq 7 and plotted as shown in Figure

$$\frac{1}{k^{\circ\prime}} = \frac{1}{ab[\text{gly}]} + \frac{1}{b} \qquad (7)$$
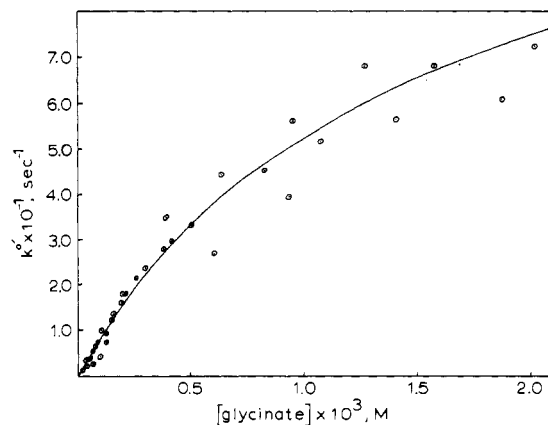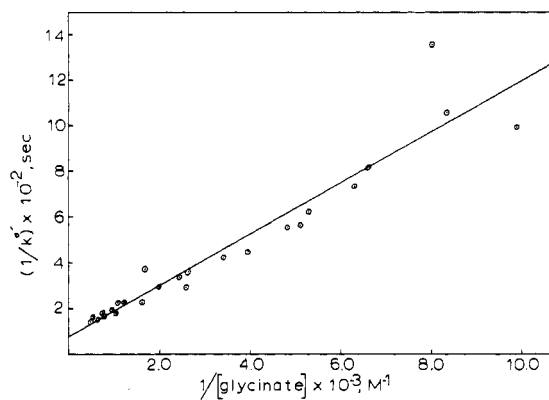

Figure 4. Resolution of $k^{\circ\prime}$ for reaction of Ni(trien)$^{2+}$ with glycine into terms a and b of eq 6. Plot covers glycinate ion concentration range of 1.0×10^{-4} to 2.1×10^{-3} M. Solid line is least-squares best fit of the data.

4. The plot covers the glycinate ion concentration range showing curvature in Figure 3 from 1.00×10^{-4} to 2.11×10^{-3} M. Values of a and b obtained from the plot are $a = 6.9 \times 10^2$ and $b = 1.3 \times 10^2$. Attempts were made to fit the data to other rate laws containing monoprotonated glycine without success. No reactive protonated terms were found.

Discussion

1,10-Phenanthroline. The Eigen–Tamm mechanism, Scheme I, has been used successfully as a model for predicting complexation formation rates for many systems. Differences seen by comparison of experimental formation rate constants to those predicted from the Eigen–Tamm mechanism are used to reveal the presence of other factors which affect the formation rate. The reaction between Ni(trien)$^{2+}$ and phen can be predicted with eq 8 which results from eq 1 with the as-

$$k_{NiT}^{phen} = K_{os}k_1(2/6) \qquad (8)$$

sumption that initial complex formation is rate limiting. The basicity of phen is far too low to allow for an ICB contribution[11] to the rate and the absence of aromatic rings in the coordinated ligand precludes the presence of stacking interactions.[12] The value of K_{os} was calculated to be 0.16 M^{-1},[13] and k_1 for Ni(trien)$^{2+}$, the rate of water loss of Ni(trien)$^{2+}$,

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(12) G. C. Cayley, D. W. Margerum, *J. Chem. Soc., Chem. Commun.*, 1002 (1974).
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Scheme II
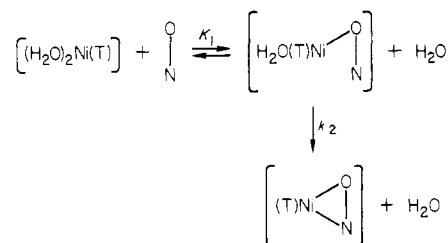
is 5×10^6 s^{-1}.[14] The factor of $^2/_6$ accounts for the number of available coordination sites on Ni(trien)$^{2+}$ relative to Ni-(H$_2$O)$_6^{2+}$. Equation 8 yields a value of 2.7×10^5 M^{-1} s^{-1}, which is 34 times larger than the observed value of $k_{\text{NiT}}^{\text{phen}}$. Both values are given in Table II.

trien clearly exerts a decelerating effect on the reaction. It has been suggested that ring closure contributes to the rate of formation between Ni(H$_2$O)$_6^{2+}$ and bipyridine.[15] Thus, Ni(trien)$^{2+}$ containing only two sites, both of which are considerably more hindered compared to those of Ni(H$_2$O)$_6^{2+}$, would be expected to show a considerably larger ring-closure contribution. On the other hand, the proximity for bonding to nickel of the second nitrogen of phen compared to that of bipyridine is greater and would lessen the ring-closure contribution of phen compared to bipyridine. This effect, however, should be small and can be approximated by the small difference seen in the rate of formation of Ni(phen)$^{2+}$ (k_f = 3.2 $\times 10^3$ M^{-1} s^{-1})[16] compared to Ni(bpy)$^{2+}$ (k_f = 1.6 $\times 10^3$ M^{-1} s^{-1}).[16] Thus the decelerating effect of trien on the reaction could be due to a ring-closure contribution or to a steric blocking of phen at the point of initial coordination. It is impossible to determine which effect causes the low rates observed in this study.

The stability constant for the addition of phen to Ni(trien)$^{2+}$ can be established as the ratio of $k_{\text{NiT}}^{\text{phen}}$ to k_b. This yields a value of 1.3×10^3, which can be compared to the stability constant for Ni(phen)$^{2+}$ of 4.0×10^8.[17] The huge drop in stability is further evidence of the effect coordinated trien has upon the formation reaction.

Glycine. The reaction between Ni(trien)$^{2+}$ and glycine varies in the order of glycine from first to zero, depending on the glycine concentration as shown in Figure 3. The rate law shown in eq 6 describes the curvature seen in the plot.

A mechanism consistent with eq 6 involves a rapid equilibrium between Ni(trien)$^{2+}$ and glycine followed by a slow ring closure of glycine. The mechanism is shown in Scheme II with glycine represented as O–N and trien as T. The mechanism by which amino acids coordinate to nickel has been thoroughly studied, resulting in the conclusion that the carbonyl group bonds first.[8] This will be shown later to be consistent with the present study.

A kinetic expression for Scheme II can be derived with the assumption that I is in equilibrium with Ni(trien)$^{2+}$ and glycine throughout the reaction. As stated earlier, there was no kinetic evidence for a reactive protonated form of glycine; none have been included in the mechanism. Equations 9–11 yield the kinetic expression given in eq 12 which is identical with eq 6.

Thus, $a = K_1$ and $b = k_2$. The values are listed in Table II.

$$K_1 = [\text{I}]/[\text{NiT}][\text{O–N}] \qquad (9)$$

$$[\text{NiT}_t] = [\text{NiT}] + [\text{I}] \qquad (10)$$

$$-d[\text{NiT}_t]/dt = k^{\circ\prime}[\text{NiT}_t] = k_2[\text{I}] \qquad (11)$$

$$k^{\circ\prime} = K_1 k_2[\text{O–N}]/(1 + K_1[\text{O–N}]) \qquad (12)$$

The presence of trien in the coordination sphere has a pronounced effect on the mechanism of the reaction involving glycine. The most obvious effect is the change in order dependence upon glycine concentration. This is a result of ring closure, measured by k_2, being considerably slowed down due to the steric hindrance of trien. At high glycine concentration, ring closure becomes rate limiting and can actually be measured. Since the carbonyl group of glycine bonds first, species I has a relatively labile nickel–oxygen bond which is made even weaker by the labilizing effect of the four trien nitrogens.[18] Thus, if $k_2 << k_{-1}$ coupled with K_1 = 6.9 $\times 10^2$ M^{-1}, showing the position of equilibria for species I to lie to the right, the steady state may no longer be applied to species I. Rather, a rapid equilibrium is established with considerable buildup of species I before the very sluggish ring closure can occur. Thus the steric hindrance which trien provides coupled with the labile initial bond to nickel results in the mechanism seen.

The value of K_1 should be similar to the stability constant of Ni(acetate)$^+$ (K = 5.0)[19] if the amine nitrogen on glycine is assumed not to affect the stability. However, the experimental K_1 value is 6.9 $\times 10^2$ or about 140 times larger than it should be. The value of K_1 consists of the terms shown in eq 13. The presence of the four trien nitrogens coordinated

$$K_1 = K_{\text{os}} k_{\text{Ni}}^{-\text{H}_2\text{O}}/k_{-1} \qquad (13)$$

to nickel increases the rate of water-bond rupture but should also have the same accelerating effect on acetate-bond rupture, k_{-1}, and cannot be the cause of the observed increase. The above comparison has ignored the presence of the amine nitrogen on glycine. It is suggested that the amine nitrogen, pK_a = 9.57, increases the stability of the species I through an ICB mechanism and thus increases the value of K_{os}. Hydrogen bonds can form with one of the two remaining water molecules coordinated to Ni(trien)$^{2+}$ or to the protons on either of the terminal nitrogens of trien. The mechanism by which amino acids coordinate to nickel assumes the presence of an ICB effect,[8] but due to the possible contribution of ring closure to the overall rate, its magnitude cannot be determined. The reaction of Ni(trien)$^{2+}$ and glycine allows an estimation of the effect. However, the presence of trien in the coordination sphere complicates the picture because hydrogen bonding may occur with the protons of trien instead of those of water. These bonds may be stronger than those formed with use of water protons because of the strength of the nickel–nitrogen bond compared to that of the nickel–oxygen bond. Thus the difference of 140 seen between K_1 and the stability constant of nickel acetate is an upper limit and may be larger than the ICB effect present when glycine reacts with Ni(H$_2$O)$_6^{2+}$.

The rate constant for the reaction of gly with Ni(trien)$^{2+}$ is given by $K_1 k_2$ = 9.0 $\times 10^4$ M^{-1} s^{-1}. This may be compared to the value of $k_{\text{gly}}^{\text{Ni}}$ = 2.2 $\times 10^4$ M^{-1} s^{-1}.[20] trien increases the rate of water loss of nickel by a factor of about 180[14] but occupies two-thirds of the available coordination sites. Thus gly should react about 60 times faster with Ni(trien)$^{2+}$ than with Ni(H$_2$O)$_6^{2+}$, yet an increase of only 4 is seen experimentally, again showing the steric effect of trien.

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Finally the stability constant for the addition of gly to Ni(trien)$^{2+}$ can be calculated as the ratio of $k_{gly}{}^{NiT}$ to k_b, which yields a value of 1.1×10^4. This must be compared to the stability constant of Ni(gly) of 6.03×10^5.[17] Although not as pronounced as the phen system, a significant decrease in stability is seen which must be due to the presence of trien.

It is interesting to note that the reaction between Ni(trien)$^{2+}$ and phen does not show an order dependence upon ligand concentration as glycine does. Ni(trien)$^{2+}$ provides the same amount of steric hindrance in both cases and molecular models show that the phen ring system does not interfere with chelation any more than the amine nitrogen of glycine. Yet eq 8, which assumes the steady-state approximation, can be used to describe the formation kinetics of the phen reaction. This means that k_{-1} is small compared to k_2 or of about the same size as k_2 such that species I does not build up in concentration. The opposite is true for the glycine reaction: k_{-1} is large compared to k_2. The reason for the different type of behavior is due to the difference in dissociation rates, k_{-1}, estimated by nickel–acetate and nickel–pyridine dissociation. The rate of nickel–acetate dissociation is 5×10^3 s^{-1} [21] while that of

nickel–pyridine is only 38 s^{-1},[22] a decrease in rate of 130 which is too great to be compensated for by a decrease in k_2 due to steric hindrance. The effect of trien in decreasing the rate of ring closure is not great enough to decrease k_2 to the point where it is less than k_{-1} when a stable dentate site bonds initially; however, it is great enough to drop k_2 well below k_{-1} when a labile one bonds first. Thus the type of dentate sites available or the attacking ligand help determine the mechanism of the formation reaction when ring closure is very sluggish.

It must be noted that if the amine end of glycine bonded to nickel first, the k_{-1} value would be sufficiently low so that ring closure would not be much smaller than k_{-1} and the equilibrium type of mechanism would not be seen. This study provides evidence which supports the conclusion that the carbonyl group of amino acids bonds first in complex formation.

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Hydroxyl Radical Reactions with the Nickel(II) Macrocyclic Complexes Ni^{II}CR, Ni^{II}(CR-2H), and Ni^{II}(CR+4H). Generation of Ligand Radicals and Nickel(III) Species

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Reactions of hydroxyl radicals with the three closely related nickel(II) macrocylic complexes Ni^{II}(CR-2H), Ni^{II}(CR)(H$_2$O)$_2$, and Ni^{II}(CR+4H) have been studied by pulse radiolysis. With use of spectral data from the Ni(III) forms of these complexes and the behavior of radiolytically generated intermediates toward O$_2$, it has been found that both Ni(III) species and ligand radicals may be produced. The reaction of Ni^{II}CR(H$_2$O)$_2$ with ·OH gives evidence for formation of ligand radical alone. By contrast ·OH attack on Ni^{II}(CR-2H) and Ni^{II}(CR+4H) produces Ni(III) intermediates as well as ligand radicals through competitive pathways. The generation of a Ni(III) intermediate appears to parallel the absence of solvent binding at axial positions in the parent Ni(II) complexes. Such behavior may be linked to steric effects and/or electronic considerations.

Introduction

Anion radicals (e.g., Br$_2^-$, Cl$_2^-$, (CNS)$_2^-$) generated by pulse radiolysis have been shown to be useful tools in the study of redox processes in macrocyclic complexes, particular attention being given to Ni(II) systems.[1-5] Such investigations have provided considerable information on the behavior of Ni(III) intermediates with regard to mechanisms of formation, ligand binding at axial positions, and product formation. The initial event in all such reactions with anion radicals is taken to be oxidative attack on the central metal atom. Subsequent behavior has been shown to depend on both the nature of the ligand and solution conditions.

The precursor to the anion radical is the hydroxyl radical, ·OH, generated directly by water radiolysis. This radical is a powerful oxidant toward metal ions; but, by contrast with anion radicals such as Br$_2^-$, has the potential for hydrogen abstraction or addition to the ligand. There are, to date, only a few reports in the literature regarding reactions of ·OH radical with nickel(II) macrocyclic complexes.[1-3] In those systems (Ni^{II}[Me$_6$[14]aneN$_4$], Ni^{II}[Me$_6$[14]-4,11-dieneN$_4$],

Ni^{II}[Me$_6$[14]-1,4,8,11-tetraeneN$_4$]) oxidation of the metal center leading to a Ni(III) intermediate was found to occur and no evidence for attack on the macrocyclic ring to generate Ni(II) ligand radicals was obtained.

We have now investigated reactions of ·OH radicals with a different series of closely related Ni(II) macrocyclic complexes (Ni^{II}(CR), Ni^{III}(CR+4H), and Ni^{II}(CR-2H))[5] and find that, by contrast with the earlier systems investigated, both Ni(III) species and ligand radical can be formed here.

CR+4H   CR   CR-2H
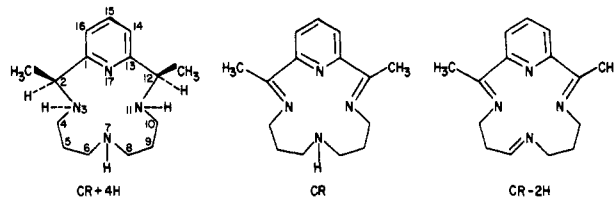
The choice of this present series of macrocyclic ligands is attractive not only because of the variation in degree of ring unsaturation but also because solvent bonding at the sites axial to the planar tetradentate ligand differs among members of this group.[6] The complex Ni^{II}(CR) is reported to be fully aquated, namely Ni^{II}(CR)(H$_2$O)$_2$ in octahedral configuration; by coontrast the CR-2H ligand complex is known to be free of axial water and exists in a square-planar configuration. The

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