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Ternary Complex Formation Kinetics. 2. Reaction of (Triethylenetetramine)nickel(II) with Ethylenediamine, Bipyridine, and Sarcosine

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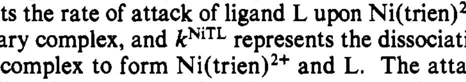
The kinetics of ternary complex formation between Ni(trien)$^{2+}$ and ethylenediamine, bipyridine, and sarcosine were studied. All reactions were first order in Ni(trien)$^{2+}$ and reversible. The reaction with ethylenediamine was resolved into the terms $k^{en}{}_{NiT}$ = 2.67 × 10^4 M^{-1} s^{-1}, $k^{Hen}{}_{NiT}$ = 1.77 × 10^3 M^{-1} s^{-1}, and k^{NiTen} = 8.62 s^{-1}. Ring closure was rate determining in the en pathway but not in the Hen$^+$ pathway through the pH range studied of 6.9–9.0. The rate constant for the step involving ring closure of en on Ni(trien)$^{2+}$ is 240 times less than the corresponding value for en on Ni(en)$_2{}^{2+}$ and is due to a conformation angle distortion (CAD) involving the "bite angle" of the two open coordination sites on Ni(trien)$^{2+}$. Linking together two en units as in trien causes the CAD effect. The reaction of bipyridine with Ni(trien)$^{2+}$ is described by $k^{bpy}{}_{NiT}$ = 7.6 × 10^3 M^{-1} s^{-1} and k^{NiTbpy} = 1.8 × 10^{-1} s^{-1}. The formation reaction is 36 times slower than expected. Comparison to the reaction of phenanthroline on Ni(trien)$^{2+}$ and bipyridine and phenanthroline on Ni(en)$_2{}^{2+}$ and on Ni(dien)$^{2+}$ shows that steric hindrance causes one of the trien nitrogens to dissociate prior to ring closure of the aromatic ligand and is the reason for the low formation rate. A kinetic expression for this mechanism is consistent with the experimental data. The mechanism of the reaction of sarcosine with Ni(trien)$^{2+}$ is identical with that of glycine and Ni(trien)$^{2+}$. The reaction order in sarcosine varies from first at low sarcosine concentration to zero at high sarcosine concentration. The mechanism involves a singly bonded T–Ni–O–N intermediate in rapid equilibrium with reactants, K_1 = 430 M^{-1}, followed by a sluggish ring closure, k_2 = 68 s^{-1}. The *N*-methyl group on sarcosine slows down ring closure of sarcosine on Ni(trien)$^{2+}$ compared to the same step involving glycine.

Introduction

Although considerable work has been done on the stability of ternary complexes, relatively little attention has been focused on the effect that a large multidentate ligand coordinated to a metal can have upon subsequent formation reactions with bidentate ligands. A few systems involving the reaction of bidentate ligands with tetradentate nickel complexes[1–6] and one with a tridentate nickel complex[7] have been reported. One of these was a recent report on the kinetics of ternary complex formation involving Ni(trien)$^{2+}$ and the bidentate ligands glycine (Gly) and 1,10-phenanthroline (phen).[1] The reaction involving phen was first order in phen, followed the Eigen–Tamm mechanism, and showed a formation rate 34 times lower than expected, thus demonstrating a significant amount of steric hindrance due to either coordinated trien, phen, or both. The reaction involving Gly showed a shift in Gly order from first to zero as the Gly concentration increased and followed a mechanism having a singly bonded intermediate involving the Gly oxygen that was in equilibrium with reactants, followed by a rate-determining ring closure. The formation rate was about 15 times less than expected. The shift in mechanism from steady state to equilibrium and ring closure and the lower than expected rate of formation are brought on by coordinated trien and the type of dentate site available on the incoming ligand.

We report here on the mechanism of three other bidentate ligands, bipyridine (bpy), ethylenediamine (en), and sarcosine (sar), reacting with Ni(trien)$^{2+}$, (triethylenetetramine)nickel(II). The general reaction is shown in eq 1, with L–L′ representing any



$$NiT(H_2O)_2{}^{2+} + \underset{L'}{\overset{L}{|}} \underset{k^{NiTL}}{\overset{k^{L-L}{}_{NiT}}{\rightleftharpoons}} TNi\langle\underset{L'}{\overset{L}{|}} + 2H_2O \quad (1)$$

bidentate ligand and T representing trien. The rate constant $k^L{}_{NiT}$ represents the rate of attack of ligand L upon Ni(trien)$^{2+}$ to form the ternary complex, and k^{NiTL} represents the dissociation of the ternary complex to form Ni(trien)$^{2+}$ and L. The attacking bidentate ligands, bpy and en, both have two strong donar sites like phen; yet, unlike phen, both are flexible, with en having tetrahedral nitrogens as opposed to the planar sites on phen and bpy. sar has a more hindered nitrogen than Gly, thus allowing an evaluation of the significance of steric hindrance during ring closure as a result of the *N*-methyl group. Comparison of rate constants obtained for the individual steps of the formation reaction of these bidentate ligands with Ni(trien)$^{2+}$ to the rate constants for Gly and phen reacting with Ni(trien)$^{2+}$ and the related systems of en, phen, and bpy reacting with Ni(en)$_2{}^{2+}$ [8] reveals that coordinated trien causes a deceleration of the formation rate. These lower rates are due to a variety of interactions and effects involving coordinated trien and the attacking bidentate ligands.

Experimental Section

Reagents. Ni(trien)$^{2+}$ was prepared as reported elsewhere.[1] Ethylenediamine was distilled and standardized by a potentiometric titration against standard HCl. Sarcosine was recrystalized from a methanol–water solvent, and bipyridine was used without further purification. Both were standardized by weight. The buffers used were HEPES, *N*-(2-hydroxyethyl)piperazine-*N*′-ethanesulfonic acid (pK_a = 7.75), and TAPS, [[tris(hydroxymethyl)methyl]amino]propane (pK_a = 8.4). Experiments with a related system (NiEDDA and the same bidentate ligands) showed the reaction to be independent of buffer concentration at constant pH.[9] NaCl was used to control the ionic strength.

Kinetic and Equilibrium Measurements. Spectrophotometric measurements were made on a Cary Model 14 spectrophotometer and were used to select the following wavelengths for monitoring the reactions: 305 nm for bpy, 254 nm for en, 242 nm for sar. Potentiometric and pH measurements were made on a Beckman Model 110 research pH meter. Kinetic measurements were performed as previously described.[1] Each reaction was repeated three to six times, and the average rate constant reported. All reactions were run at 25 ± 0.1 °C and at μ = 0.1 M.

Results

Ethylenediamine. Reactions were carried out with at least a 17-fold excess of en$_t$ (t = total) over Ni(trien)$^{2+}$ and covered a pH range of 6.9–9.0. Both HEPES and TAPS were used as buffers. Throughout this pH range, the Hen$^+$ concentration underwent a 2.6-fold change and the en concentration a 260-fold change. The data are listed in Table I and followed the rate expression shown in eq 2 with L = en$_t$ and T = trien. With the

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

assumption that L$_t$ remains constant, eq 2 integrates to eq 3 where

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

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[1] Steinhuas, R. K.; Lee, B. I. *Inorg. Chem.* **1982**, *21*, 1829.
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[9] Steinhaus, R. K.; Kolopajlo, L. H., submitted for publication.

0020-1669/85/1324-1839$01.50/0

Table I. Experimental Values of the Rate Constants for the Reaction of $Ni(trien)^{2+}$ with Bipyridine, Sarcosine, and Ethylenediamine (25 °C, μ = 0.1 M, 0.05 M HEPES Buffer Unless Noted)

Ethylenediamine

pH	10^2[en], M	10^3[NiT], M	$k°$, s^{-1}
6.90	2.95	1.51	29.80
6.92	2.45	1.35	25.90
6.94	2.95	1.51	30.00
7.06	2.95	1.51	35.00
7.16	2.95	1.51	40.80
7.21	2.45	1.24	33.30
7.31	2.45	1.35	36.70
7.31	2.95	1.51	42.00
7.51	2.95	1.51	47.90
7.70	2.95	1.35	53.60
7.78	2.45	1.41	54.00
7.97[a]	2.45	1.39	59.60
7.98	2.95	1.50	64.30
8.33[a]	2.95	1.50	73.90
8.50[a]	2.45	1.24	76.40
8.61[a]	2.45	1.24	82.80
8.71[a]	2.45	1.24	73.80
8.81[a]	2.45	1.24	79.20
8.90[a]	2.45	1.24	87.00
9.00[a]	2.45	1.24	91.10

Bipyridine

pH[b]	10^4[bpy], M	10^5[NiT], M	$k°$, s^{-1}
7.41	1.80	1.67	1.50
7.98	3.00	1.67	2.20
7.90	3.00	1.67	2.36
7.39	4.44	1.67	3.45
7.40	6.15	1.67	4.72
7.98	7.50	1.67	5.81
7.41	9.00	1.67	7.35
8.00	11.10	1.67	9.00
8.00	14.10	1.67	11.20
7.99	17.10	1.67	13.30
8.01	20.10	1.67	15.00

Sarcosine

pH	10^2[sar], M	10^3[NiT], M	k°, s^{-1}
7.20	2.20	1.51	18.30
6.89	6.00	1.77	19.10
7.20	4.00	1.51	20.20
6.89	10.00	1.77	20.20
7.18	4.00	1.51	20.90
7.18	8.00	1.51	21.40
7.19	7.95	1.51	22.20
7.19	10.00	1.51	20.80
7.18	10.00	1.51	20.90
7.50	5.00	1.51	23.70
7.50	8.00	1.51	23.30
7.50	10.00	1.51	25.10
7.89[a]	3.50	1.15	27.40
7.90[a]	5.50	1.15	30.10
7.89[a]	8.00	1.15	40.40
8.31[a]	5.00	1.15	37.10
8.32[a]	6.00	1.15	43.80
8.61[a]	3.50	1.15	40.80
8.61[a]	4.50	1.15	49.70
8.61[a]	5.50	1.15	51.10
8.63[a]	6.52	1.15	56.20
8.82[a]	5.00	1.15	50.30

[a] 0.05 M TAPS buffer. [b] 0.01 M HEPES buffer.

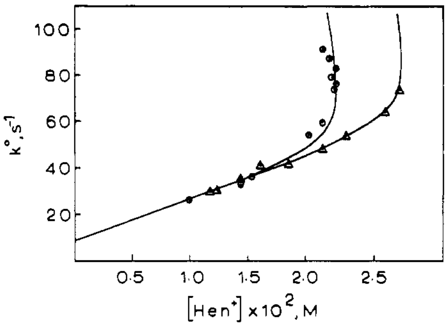

Figure 1. Dependence of $k°$ upon $[Hen^+]$ for the reaction of $Ni(trien)^{2+}$ and ethylenediamine (μ = 0.1 M, 25 °C). Circles represent en_t = 0.0245 M and triangles represent en_t = 0.0295 M. Solid line is constructed from resolved rate constants.

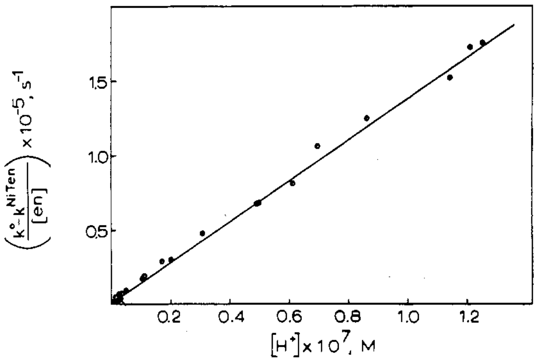

Figure 2. Fit of resolved rate constants to experimental points showing linear behavior in hydrogen ion (μ = 0.1 M, 25 °C).

Table II. Rate Constants for the Reaction of $Ni(trien)^{2+}$ with Ethylenediamine (25 °C, μ = 0.1 M)

	exptl	predctd
$k^{en}{}_{NiT}$, M^{-1} s^{-1}	$(2.67 \pm 1.23) \times 10^4$	4×10^{6}[a]
$k^{Hen}{}_{NiT}$, M^{-1} s^{-1}	$(1.77 \pm 0.13) \times 10^3$	7×10^{4}[b]
k^{NiTen}, s^{-1}	8.62 ± 1.43	

[a] Predicted from eq 11 including ICB effect of 193 and steric factor of 14. [b] Predicted from eq 11.

$[NiTL]_e$ and $[NiT]_0$ refer to equilibrium and initial concentrations, respectively. A plot of $k°$, the observed pseudo-first-order rate constant, vs. the Hen^+ concentration for two constant en_t concentrations is shown in Figure 1. The plot has a nonzero intercept and, at low pH values where the en concentration is small, appears linear, showing $k°$ to be independent of the en concentrations. At higher pH values where the en concentration becomes significant, $k°$ becomes dependent on both the Hen^+ and en concentrations. Thus, the pseudo-first-order rate constant of eq 3 can be written as the sum of two formation terms involving the two reactive forms of en as well as reverse rate constants for each pathway as shown in eq 4. Multiple linear regression analysis

$$k° = k^{en}{}_{NiT}[en] + k^{Hen}{}_{NiT}[Hen^+] + k^{Ni(T)(en)} + k^{H}{}_{Ni(T)(en)}[H^+] \quad (4)$$

of eq 4, cast in the form shown in eq 5 with $K_{a2} = [H^+][en]/$

$$\frac{k°}{[en]} = k^{en}{}_{NiT} + k^{Hen}{}_{NiT}\frac{[H^+]}{K_{a2}} + \frac{k^{Ni(T)(en)}}{[en]} + k^{H}{}_{Ni(T)(en)}\frac{[H^+]}{[en]} \quad (5)$$

$[Hen^+] = 1.29 \times 10^{-10}$,[10] showed $k°$ was fit best by including only the first three terms of eq 5. The term representing proton-assisted dissociation of $Ni(trien)(en)^{2+}$, $k^{H}{}_{Ni(T)(en)}$, had a negative value and is statistically unreliable, having a relative standard deviation of 60%. Regression analysis of eq 5 using only the first three terms on the right side yielded the values of $k^{Ni(T)(en)}$, $k^{en}{}_{NiT}$ and $k^{Hen}{}_{NiT}$ listed in Table II. A plot of $(k°/[en]) - (k^{Ni(T)(en)}/[en])$ vs. $[H^+]$, using the resolved rate constants to construct the solid line, is shown in Figure 2. The plot shows that the resolved rate constants describe the data accurately, and the linear behavior over the entire pH range shows that the $k^{Hen}{}_{NiT}$ term did not have a complex dependence upon hydrogen ion.

Bipyridine. All reactions were carried out with at least a 10-fold excess of bpy to $Ni(trien)^{2+}$ at pH 7.4 and 8.0 with HEPES as

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[10] Martell, A. E.; Smith, R. M. "Critical Stability Constants"; Plenum Press: New York, 1979; Vol. 1 and 2.

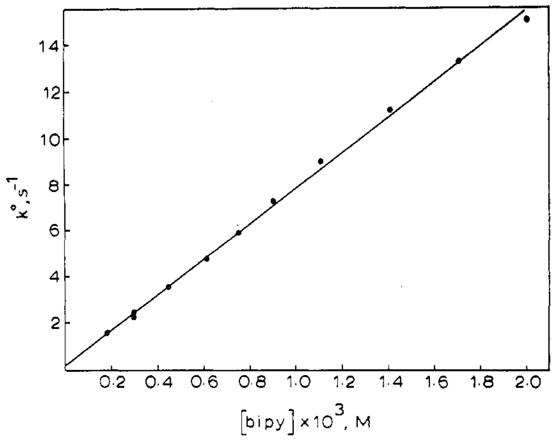

Figure 3. Dependence of k° upon bpy for reaction of $Ni(trien)^{2+}$ and bpy ($\mu = 0.1$ M, 25 °C). Solid line is least-squares best fit of the points.

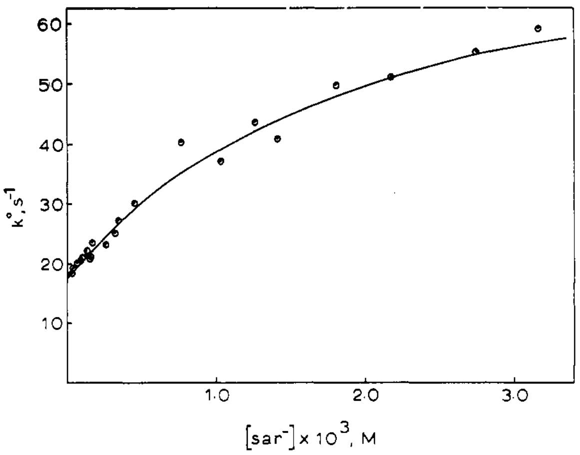

Figure 4. Dependence of k° upon sarcosinate ion concentration over pH range 6.9–8.8 for reaction of $Ni(trien)^{2+}$ and sarcosine ($\mu = 0.1$ M, 25 °C). Solid line is calculated from eq 8.

Table III. Rate Constants for the Reaction of Bipyridine and Phenanthroline with Nickel Polyamine Complexes (25 °C, $\mu = 0.1$ M)

	bipyridine	phenanthroline
k^{L}_{NiT}, $M^{-1}\ s^{-1}$	$(7.6 \pm 0.1) \times 10^3$	$8.2 \times 10^{3\,a}$
k^{L}_{NiT}, $M^{-1}\ s^{-1}$	$3 \times 10^{5\,b}$	$3 \times 10^{5\,b}$
$k^{L}_{Ni(en)_2}$, $M^{-1}\ s^{-1}$	$8.4 \times 10^{3\,c}$	$9.3 \times 10^{3\,c}$
$k^{L}_{Ni(en)_2}$, $M^{-1}\ s^{-1}$	$3 \times 10^{5\,b}$	$3 \times 10^{5\,b}$
$k^{L}_{Ni(dien)}$, $M^{-1}\ s^{-1}$	$1.1 \times 10^{4\,c}$	$2.3 \times 10^{4\,c}$
$k^{L}_{Ni(dien)}$, $M^{-1}\ s^{-1}$	$8 \times 10^{4\,b}$	$8 \times 10^{4\,c}$
k^{NiTL}, s^{-1}	$(1.8 \pm 1.7) \times 10^{-1}$	5.3^{a}

[a] Reference 1. [b] Predicted from eq 11. [c] Reference 23.

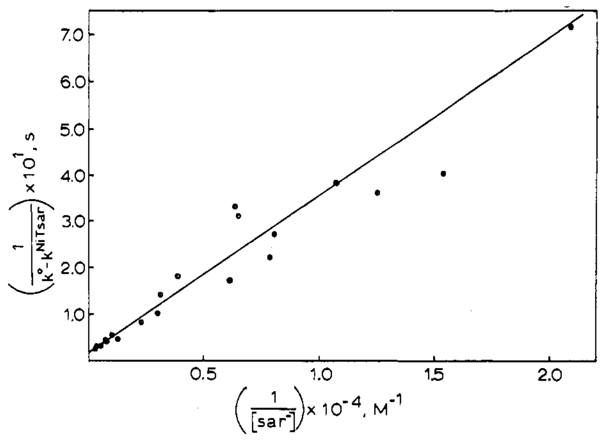

Figure 5. Resolution of k° for reaction of $Ni(trien)^{2+}$ and sarcosine into terms *a* and *b* of eq 8. Solid line is least-squares best fit of the data.

Table IV. Rate Constants for the Reaction of $Ni(trien)^{2+}$ with Sarcosine and Glycine (25 °C, $\mu = 0.1$ M)

	sarcosine	glycine[a]		sarcosine	glycine[a]
$a = K_1$, M^{-1}	430	690	k^{NiTL}, s^{-1}	17.7	8.1
$b = k_2$, s^{-1}	68	130			

[a] Reference 1.

the buffer. The data are given in Table I and followed eq 2 with L = bpy. A plot of k°, the pseudo-first-order rate constant, vs. the bpy concentration is shown in Figure 3 and revealed a linear dependence upon ligand concentration and a nonzero intercept. The resolved rate constants are listed in Table III.

Sarcosine. Reactions were carried out with at least a 10-fold excess of sar_t throughout the pH range 6.9–8.8. The data are listed in Table I and followed eq 2. A plot of k° vs. sarcosinate ion concentration, calculated with $K_a = 1.02 \times 10^{-10}$[10] shown in Figure 4, revealed a nonzero intercept and a shift in the order of the reaction with respect to sarcosinate ion as a function of the sarcosinate ion concentration. The behavior is identical with that seen for the $Ni(trien)^{2+}$ reaction with glycine.[1] Attempts to resolve the $Ni(trien)^{2+}$–sarcosine data into a set of terms involving a reactive protonated form of sarcosine using eq 3 as a model were unsuccessful. The nonlinear dependence of k° seen in Figure 4 is not due to reactive protonated and unprotonated forms of sarcosine.[11] The plot of k° vs. sarcosinate ion concentration (Figure 4) has points from many different total sarcosine concentrations, all of which fit the same plot. A reactive protonated form would cause values obtained from experiments with large total sarcosine concentrations to have larger contributions, due to the protonated form, than k° values obtained from experiments with small total sarcosine concentrations.

The k° value of eq 2 is described by eq 6. At low sarcosinate concentrations, the data appear linear and points covering the

$$k^\circ = k^{sar}_{NiT}[sar] + k^{Ni(T)(sar)} \qquad (6)$$

sarcosinate concentration range from 3.25×10^{-5} to 1.27×10^{-4} M were analyzed by simple least squares to give an intercept of 17.7 s^{-1}. As with the reaction of $Ni(trien)^{2+}$ and glycine, data covering the entire sarconsinate ion concentration range were then analyzed according to eq 7 with $k^{Ni(T)(sar)} = 17.7\ s^{-1}$. Equation

$$k^{\circ\prime} = k^\circ - k^{Ni(T)(sar)} = \frac{ab[sar]}{1 + a[sar]} \qquad (7)$$

7 can be rearranged to the linear form of eq 8. A plot of eq 8 is shown in Figure 5 with a least-squares analysis of the data, yielding values of *a* and *b* from the slope and intercept that are given in Table IV.

$$\frac{1}{k^{\circ\prime}} = \frac{1}{ab[sar]} + \frac{1}{b} \qquad (8)$$

Discussion

The Eigen–Tamm mechanism has been used as the basis for describing and predicting complexation formation rates for numerous systems provided first-order behavior in ligand is seen throughout the concentration range from which the rate constants are obtained.[12] The complexation reactions for the attack of both en and bpy on $Ni(trien)^{2+}$ follow this type of behavior as shown in Scheme I.

The upper pathway involves a reactive protonated ligand that is not present in the reactions involving bpy. If the usual assumptions are made that (1) outer-sphere formation and dissociation reactions are rapid compared to subsequent steps, (2) the

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(11) Margerum, D. W.; Cayley, C. W.; Weatherburn, D. C.; Pagenkopf, G. K. "Coordination Chemistry"; Martell, A. E., Ed.; American Chemical Society: Washington, DC, 1978; ACS Monogr. No. 174, pp 38–42.

(12) Margerum, D. W.; Cayley, C. W.; Watherburn, D. C.; Pagenkopf, G. K. "Coordination Chemistry"; Martell, A. E., Ed.; American Chemical Society: Washington, DC, 1978; ACS Monogr. No. 174, pp 26–30.

Scheme I

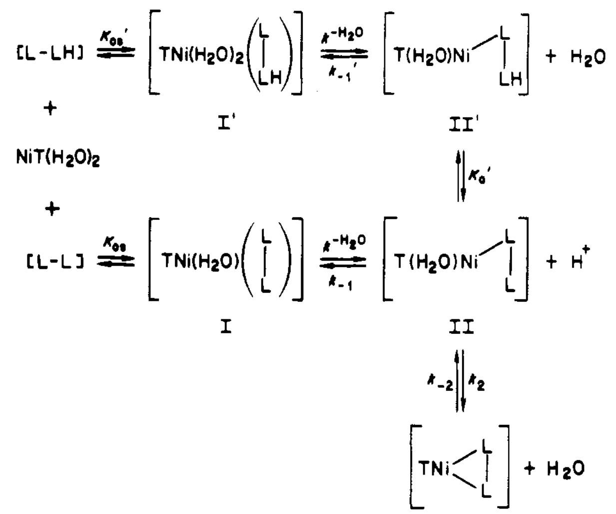

Table V. Values of K_{os} for Various Combinations of Charged Reactants Calculated at 25 °C by Using the Modified Fuoss Equation[13]

react charge combin	a,[a] Å	a',[b] Å	K_{os}, M^{-1}
2+, 1+	4	6.5	0.044
2+, 0	4		0.16

[a] Center to center distance of closest approach between metal ion and reactive site on ligand in outer-sphere complex; value taken from ref 11. [b] Center to center distance between charge site on metal ion and ligand in outer-sphere complex, value taken from ref 13.

steady-state approximation is applied to the singly bonded intermediates II and II′, and (3) the protonation equilibrium is rapid compared to other steps, then formation rate expressions can be written for the two forward pathways as shown in eq 9 and 10

$$k^{L}{}_{NiT} = \frac{2}{6}\,\frac{K_{os}k^{-H_2O}k_2}{k_{-1} + k_2} \tag{9}$$

$$k^{HL}{}_{NiT} = \frac{2}{6}\,\frac{K_{os}k^{-H_2O}k_2}{k_{-1}K_H'[H^+] + k_2} \tag{10}$$

where L and HL represent the unprotonated and protonated forms of the bidentate ligand. Scheme I defines the stepwise rate constants used in eq 9 and 10 as well as K_H'. The factor of $^2/_6$ accounts for the number of available coordination sites on Ni(trien)$^{2+}$ relative to Ni(H$_2$O)$_6^{2+}$ and assumes the sites to be equivalent. Values of K_{os} may be calculated from a modification of the Fuoss equation[13] and are listed in Table V for the different charge combinations used in this study. The value of k^{-H_2O} for Ni(trien)$^{2+}$ is 5 × 10^6 s^{-1}.[14] Steric factors[15] and the internal conjugate base (ICB) effect[16] must be included in eq 9 and 10 when appropriate.

If it is assumed that the initial bond formation is rate determining, that is, ring closure is fast so that $k_2 > k_{-1}$ or $k_2 > k_{-1}K_H'[H^+]$, eq 9 and 10 simplify to eq 11 and the formation rate constants may be predicted from calculated values of K_{os} and independent measurements of k^{-H_2O}.

$$k^{L}{}_{NiT} = {}^2/_6 K_{os}k^{-H_2O} \tag{11}$$

Ni(trien)$^{2+}$–Ethylenediamine. For the reaction of Hen$^+$ with Ni(trien)$^{2+}$, either eq 10 or 11 could be used to predict $k^{Hen}{}_{NiT}$, depending upon the relative sizes of k_2 and $k_{-1}K_H'[H^+]$. Figure 2, a plot of eq 4, shows the data to be a linear function of [H$^+$] throughout the pH range studied and thus gives a value of $k^{Hen}{}_{NiT}$ from the slope that is independent of [H$^+$]. Equation 10 substituted into eq 4 for $k^{Hen}{}_{NiT}$ would not yield a linear plot of the data. Thus, eq 11 must represent $k^{Hen}{}_{NiT}$ in the pH range 6.9–9.0, and the rate-determining step occurs before ring closure.

Equation 11 predicts a value of $k^{Hen}{}_{NiT}$, shown in Table II, which is 41 times larger than that observed. This difference is attributed to steric factors present during the initial coordination of Hen$^+$ to Ni(trien)$^{2+}$.[15] It has been estimated that an intramolecularly hydrogen bonded form of Hen$^+$ slows down the reaction of Hen$^+$ with nickel by a factor of 3.[17] Thus, the actual steric factor of Hen$^+$ reacting with Ni(trien)$^{2+}$ is only 14. This value is also applicable to the reaction of en with Ni(trien)$^{2+}$ since the unprotonated end of Hen$^+$ is the initial reaction site.

For the reaction of en with Ni(trien)$^{2+}$, either eq 9 or 11 could be used to predict $K^{en}{}_{NiT}$, depending upon the relative sizes of k_2 and k_{-1}. In both cases, however, an ICB effect factor must be included since reactions involving en and nickel proceed at an accelerated rate due to an internal conjugate base mechanism.[18]

Equation 11, incorporating an accelerating ICB factor of 190 and a retarding steric factor of 14, predicts a value of $k^{en}{}_{NiT}$, shown in Table II, which is about 140 times larger than the experimentally observed value. Thus, eq 11 is inappropriate, and the initial bond formation of en to Ni(trien)$^{2+}$ is not rate determining.

If ternary complex formation follows Scheme I with k_2 as the rate-determining step, eq 9 may be used to describe the formation reaction. The ring-closure rate constant, k_2, can be calculated from eq 9, the experimental value of $k^{en}{}_{NiT}$, and the value of k_{-1} which is the dissociation of monocoordinated en from Ni(trien)(en)$^{2+}$.[20] Equation 9, incorporating ICB and steric factors, gives the value of k_2 to be 9 × 10^2 s^{-1}.

The value of en ring closure as en reacts with Ni(en)$_2^{2+}$ has been measured to be 2.2 × 10^5 s^{-1},[8] which is 240 times faster than k_2 calculated from eq 10 for the reaction of en with Ni(trien)$^{2+}$. An explanation for this difference is found in the ethylene linkage which ties the two en segments of trien together. The crystal structure of *cis-α*-(triethylenetetramine)(isothiocyanato)nickel(II)[21] shows that the bond angle formed between the two NCS$^-$ ligands and nickel is 92.7°. Further, the crystal structure of Ni(en)$_3^{2+}$[22] reveals that the bond angle between the en nitrogens and nickel is 81.9°. Finally, the bond angle between the terminal en segments of trien and nickel is 81.2°.[21] The conclusion is that en requires a bond angle of about 82° when coordinated to nickel. Coordination of trien to nickel forces a bite angle of 92.7° on Ni(trien)$^{2+}$ involving the two open coordination sites. This has no effect on initial coordination of en but imposes considerable strain an en undergoes ring closure in Ni(trien)$^{2+}$ and is offered as the explanation for the seemingly anomalous behavior of Ni(trien)$^{2+}$ compared to Ni(en)$_2^{2+}$.

The above discussion has assumed that Ni(trien)$^{2+}$ is in a cis-α-octahedral configuration. If a cis-β-octahedral configuration were adopted, there should be no CAD effect because there is no linkage connecting the two coordination sites together opposite the two open sites. However, molecular models show that relative to the cis-α form, the cis-β form (1) involves more crowding of

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(13) Lin, C.; Rorabacher, D. B. *Inorg. Chem.* **1973**, *12*, 2402.

(14) Margerum, D. W.; Cayley, C. W.; Weatherburn, D. C.; Pagenkopf, G. K. "Coordination Chemistry"; Martell, A. E., Ed.; American Chemical Society: Washington, DC, 1978; ACS Monogr. No. 174, p 133.

(15) Rorabacher, D. B.; Melendez-Cepeda, C. A. *J. Am. Chem. Soc.* **1972**, *93*, 6071.

(16) Rorabacher, D. B. *Inorg. Chem.* **1966**, *5*, 1891.

(17) Taylor, R. W.; Stepien, H. K.; Rorabacher, D. B. *Inorg. Chem.* **1974**, *13*, 1282.

(18) The magnitude of the ICB effect present as en reacts Ni(trien)$^{2+}$ may be estimated from the ratio of rates of $k^{en}{}_{Ni}$ to $k^{tmen}{}_{Ni}$, corrected for a charge difference with K_{os} values. Tmen$^+$ reacts without any ICB contribution[15] and with the same steric restraint as en. The ICB value thus obtained is 190 and is consistent with other estimates of the ICB effect for en reacting with nickel.[15,19]

(19) Turan, T. S. *Inorg. Chem.* **1974**, *13*, 1584.

(20) The value of k_{-1} can be approximated by the rate constant for the corresponding step in the reaction of en with Ni(en)$_2^{2+}$, which is similar in all respects to the present system except that the two coordinated en molecules of Ni(en)$_2^{2+}$ are not tied together with an ethylene backbone. Thus, k_{-1} = 1.2 × 10^5 s^{-1}.

(21) Clausen, A.; Hazell, A. *Acta Chem. Scand.* **1970**, *24*, 2811.

(22) Mazher-Ul-Hague; Caughlin, C. N.; Emerson, K. *Inorg. Chem.* **1970**, *9*, 2421.

the protons on two of the three chelate rings as well as more crowding of the protons on the terminal nitrogen atoms and (2) shows a decrease in the space available to the coordinated water molecules. The fact that Ni(trien)(NCS)$_2$ exists in a cis-α configuration[21] would indicate that this form is the least hindered.

An alternate pathway that could also explain the formation rate involves isomerization of Ni(trien)$^{2+}$ from cis-α to cis-β to relieve the CAD effect. This process would occur after initial bonding of en to Ni(trien)$^{2+}$ because there is no reason to isomerize to the less stable cis-β form prior to coordination of en. This type of mechanism, however, predicts a value of $k^{\mathrm{en}}{}_{\mathrm{NiT}}$ that is about 60 times lower than the experimentally observed value. Thus, an isomerization pathway cannot account for the slow rate of formation of Ni(trien)(en)$^{2+}$ relative to Ni(en)$_3^{2+}$ with the conclusion that the CAD effect must be the cause of the slow ring closure.

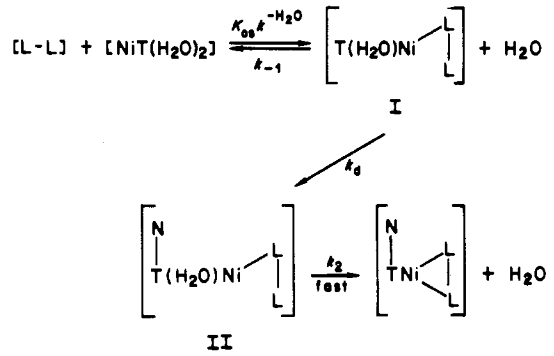
Ni(trien)$^{2+}$–Bipyridine. The reaction of bipyridine with Ni(trien)$^{2+}$ was found to be reversible, and data were resolved into the forward and reverse rate constants shown in Table III. This behavior is identical with that shown for the reaction between phen and Ni(trien)$^{2+}$.[1] Evaluation of the effect of coordinated trien on the formation reaction is obtained by comparing the experimental value of $k^{\mathrm{bpy}}{}_{\mathrm{NiT}}$ with a predicted value.

Equation 11 may be used to predict a value for $k^{\mathrm{bpy}}{}_{\mathrm{NiT}}$, assuming $k_2 > k_{-1}$. There is no ICB effect during the reaction of bpy with nickel; thus, eq 11 predicts a $k^{\mathrm{bpy}}{}_{\mathrm{NiT}}$ value, shown in Table III, that is 36 times larger than the experimentally observed value. Further, the experimental values of phen and bpy reacting both with Ni(trien)$^{2+}$ and with Ni(en)$_2^{2+}$[23] are almost identical, and the predicted values for all of those reactions are about 30–36 times larger than the experimentally observed values. Thus, the decelerating effect of trien is the same as that of two coordinated en molecules when phen and bpy are the attacking ligands.

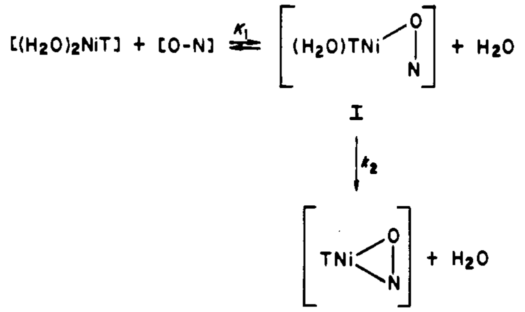
The Ni(en)$_2^{2+}$ complex, however, will not have a CAD effect because the two en ligands are not tied together on the nickel. The almost identical amounts of decerlation in the two systems must therefore be due to steric hindrance. Molecular models indicate that as either aromatic ligand coordinates to Ni(trien)$^{2+}$, a severe amount of steric interaction occurs between the protons on carbons 2 and 9 of the aromatic ligands and protons both on the secondary nitrogen atoms in the equatorial plane on Ni(trien)$^{2+}$ and on the carbon atoms in the terminal ethylenediamine chelate rings that are α to the secondary nitrogens. A cis-α configuration was assumed. These identical steric interactions are also present in Ni(en)$_2^{2+}$. Further, molecular models show that ring closure of the aromatic ligands is an impossibility, assuming all four nitrogens of trien or of both en molecules remain coordinated. Molecular models show that a nitrogen of coordinated trien or of one of the coordinated en ligands must dissociate from nickel in order to accommodate phen or bpy. Even after dissociation of a coordinated nitrogen, considerable twisting of the aromatic ligand must occur in order to effect ring closure. This is relatively easy for the flexible bpy but quite difficult for the rigid phen.

Evidence for a dissociated nitrogen is found in the stability constants for the addition of phen or bpy to Ni(trien)$^{2+}$ calculated from the experimental rate constant ratio $k^{\mathrm{L}}{}_{\mathrm{NiT}}/k^{\mathrm{NiTL}}$. These constants, which measure the stability gained as phen or bpy reacts with Ni(trien)$^{2+}$, show a gain of only 3.2 and 4.3 log units for the addition of phen and bpy, respectively, to Ni(trien)$^{2+}$. The addition of phen or bpy to nickel should add 8.5 and 7.14 log units, respectively.[10] However, the loss of stability equal to one chelate ring in going from a four-coordinate to a three-coordinate Ni(trien)$^{2+}$ species drops the stability by 3.3 log units, calculated from the difference in stability between Ni(trien)$^{2+}$ and Ni(dien)$^{2+}$. Thus, the overall gain of stability would be 5.2 log units for phen and 3.8 log unis for bpy. These values are much closer to the observed gain and indicate the presence of an uncoordinated arm of trien. Further, the observed stability gain of 3.2 log units for phen is still 2 log units lower than expected and reflects the twist strain placed upon phen in order to effect ring closure. The observed stability gain of 4.3 log units for bpy, compared to an expected gain of 3.8 log units, is quite good and demonstrates the flexible nature of bpy.

Scheme II



Scheme III



A mechanism that involves a partially dissociated trien species and is consistent with the observed rate constants, is shown in Scheme II, with L representing phen or bpy. In this mechanism, the dissociation of a trien nitrogen cannot occur before Ni(trien)$^{2+}$ reacts with the incoming ligand because of the observed order dependence in aromatic ligand and the fact the $k_{\mathrm{d}} < K_{\mathrm{os}}k^{-\mathrm{H_2O}}$. Equation 12 results by assuming steady-state behavior in species

$$k^{\mathrm{L}}{}_{\mathrm{NiT}} = \frac{2}{6}\,\frac{K_{\mathrm{os}}k^{-\mathrm{H_2O}}k_{\mathrm{d}}}{k_{-1} + k_{\mathrm{d}}} \tag{12}$$

I with k_{d} as the rate-determining step, followed by a rapid ring closure. The value of $k^{\mathrm{L}}{}_{\mathrm{NiT}}$ may be predicted from eq 12[24] and is 6×10^2 M^{-1} s^{-1}. This is a factor of about 10 less than the experimental values of $k^{\mathrm{L}}{}_{\mathrm{NiT}}$ for bpy and phen, respectively, and demonstrates that the mechanism is reasonably consistent with the observed kinetic data.

Final evidence for this mechanism is found in the formation reactions of phen and bpy with Ni(dien)$^{2+}$.[23] The rate constants for these reactions are listed in Table III and are only 2 and 6 times less than the predicted values for phen and bpy, respectively, from eq 11 with a statistical factor of $^3/_6$ to account for the number of open coordination sites. There seems to be little steric hindrance as phen and bpy react with Ni(dien)$^{2+}$, and it can be concluded that more than three polyamine nitrogens coordinated to nickel cause severe enough steric hindrance to be experienced by an aromatic bidentate ligand when coordinating to the nickel complex that polyamine dissociation must occur until there are only three nitrogens coordinated.

Ni(trien)(sar)$^+$. The reaction of sarcosine with Ni(trien)$^{2+}$ varies in the order of sarcosinate ion from first to zero, depending upon the sarcosinate ion concentration. This is identical with the reaction of Gly with Ni(trien)$^{2+}$.[1] The proposed mechanism, which is consistent with this type of behavior, is a modified Eigen–Tamm mechanism shown in Scheme III where the amino acid coordinates

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(23) Melvin, W. S.; Rablen, D. B.; Gordon, G. *Inorg. Chem.* **1972**, *11*, 488.

(24) The value of k_{-1} for eq 12 is obtained from the rate of dissociation of Ni(py)$^{2+}$,[25] corrected for the rate of water loss difference between Ni(trien)$^{2+}$ and Ni(H$_2$O)$_6^{2+}$. Thus, k_{-1} is 7.00×10^3 s^{-1}. The value of k_{d} is approximated by the dissociation rate constant for the first nickel–nitrogen bond of Ni(trien)$^{2+}$ which is 15 s^{-1}.[26]

(25) Melson, G. A.; Wilkins, R. G. *J. Chem. Soc.* **1962**, 4208.

(26) Melson, G. A.; Wilkins, R. G. *J. Chem. Soc.* **1962**, 2662.

initially through the oxygen and the monocoordinated species, I, is in equilibrium with reactants. Species I then undergoes a slow ring closure to form products. Equation 13 is derived from this mechanism and has the same form as eq 7. Thus, $K_1 = 430\ \mathrm{M}^{-1}$ and $k_2 = 68\ \mathrm{s}^{-1}$. The values are listed in Table IV along with the corresponding values for the reaction of Gly with Ni(trien)$^{2+}$.

$$k^\circ = \frac{K_1k_2[\mathrm{O{-}N}]}{1 + K_1[\mathrm{O{-}N}]} \tag{13}$$

The K_1 value for the reaction of sar with Ni(trien)$^{2+}$ is about 1.5 times lower than that for the reaction of Gly with Ni(trien)$^{2+}$. The large value of K_1 for the reaction of Gly with Ni(trien)$^{2+}$ (690 M^{-1}) relative to the stability constant of nickel acetate (5 M^{-1})[27] has been attributed to the ICB effect as a result of the amine nitrogen present in Gly.[1] Further, the ratio 690/5 = 138 agrees well with the estimate of the ICB effect of 190 obtained from the ratio of $k^{\mathrm{en}}{}_{\mathrm{Ni}}/k^{\mathrm{tmen}}{}_{\mathrm{Ni}}$. The p$K_a$ of glycine and en differ by only 0.2 log unit[10] so the comparison is reasonable. Sarcosine has a pK_a[10] of about 0.4 log unit larger than Gly, but the *N*-methyl group on sarcosine may hinder both the hydrogen bonding and the rotation of hydrogen-bonded sarcosine into position for coordination to nickel through the carboxyl group. Thus, the slight decrease seen in comparing K_1 for the reaction of Gly with Ni(trien)$^{2+}$ to K_1 for the reaction of sar with Ni(trien)$^{2+}$ is not unreasonable.

The value of $k_2 = 68\ \mathrm{s}^{-1}$ for ring closure of sar on Ni(trien)$^{2+}$ is about a factor of 2 less than that seen for Gly on Ni(trien)$^{2+}$ and shows that the *N*-methyl group does not cause much hindrance in bringing the nitrogen into the proper position for bonding to nickel. The likely presence of an ICB effect in the formation of Ni(Gly)$^+$ from $\mathrm{Ni(H_2O)_6}^{2+}$ and Gly prevents calculation of a ring-closure rate constant for that system. The only comparison that can be made is to the ring closure of en on Ni(trien)$^{2+}$. This value was found to be 900 s^{-1} and is 13 times faster than ring closure of sar and 7 times faster than ring closure of Gly.

The rate of ring closure of either amino acid on Ni(trien)$^{2+}$ would differ from that of en on Ni(trien)$^{2+}$ in that (1) the amino acid ligands must rotate around a carboxyl group and en around a carbon–carbon bond and (2) the initial bonding of en causes coordination of a nitrogen to nickel, which has been shown to accelerate the rate of water loss whereas the initial coordination of the amino acids causes coordination of a carboxyl group which does not appear to have much effect on water loss rates.[28,29] Thus, en ring closure should be faster than amino acid ring closure by an amount roughly equal to the accelerating effect of a coordinated nitrogen, which is about a factor of 10.[30] This is in excellent agreement with the 13- and 7-fold drop in ring-closure rate seen for Gly and sar on Ni(trien)$^{2+}$ compared to en on Ni(trien)$^{2+}$.

It has been suggested that the en ring-closure rate on Ni(trien)$^{2+}$ is lower than expected due to the CAD effect. Since Gly and sar have ring-closure rates that are reasonable compared to Ni(trien)(en)$^{2+}$, ring closure of Gly and sar must also be affected by the CAD effect. The crystal structure of bis(glycinato)bis(imidazole)nickel(II)[31] reveals the N–Ni–O bond angle in the coordinated Gly units to be 80.4°. This value is quite similar to the bond angle required by the other bidentate ligands studied and suggests that Gly and sar have abnormally low rates of ring closure as a result of the CAD effect of coordinated trien.

Conclusions. Coordinated tetradentate ligands are shown to affect the subsequent rate of formation with bidentate ligands in several ways: (1) Steric effects are present during initial coordination of the ligand but are not sizable. (2) Ring closure of the bidentate ligand may be slowed down through the CAD effect if the coordinated ligands do not partially dissociate or isomerize. Steric hindrance resulting from interaction between the coordinated ligand and the attacking bidentate ligand also appears to lower ring closure as in the case of Gly and sar. (3) Complete coordination involving all six sites on nickel appears impossible when aromatic ligands are involved. The formation reaction appears to proceed with partial dissociation of the coordinated ligand necessary in order to accomodate the incoming aromatic bidentate ligand. (4) The position of the rate-determining step can be shifted from initial coordination of the bidentate ligand to ring closure provided the CAD effect due to the coordinated ligand or steric effects are great enough. (5) The type of dentate site available for coordination can cause a shift from Eigen–Tamm steady-state behavior to an equilibrium-governed formation mechanism. Obviously, the choice of coordinated ligand and of attacking ligand will influence which of these effects predominate or are present. Other systems are currently under study in which these effects may be further tested and substantiated.

Registry No. en, 107-15-3; bpy, 366-18-7; sar, 107-97-1.

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(29) Jones, J. P.; Billo, E. J.; Margerum, D. W. *J. Am. Chem. Soc.* **1970**, *92*, 1875.

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