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### Ternary Complex Formation Kinetics. 3. Reaction of (Ethylenediamine-*N,N'*-diacetato)nickel(II) with Ethylenediamine, Bipyridine, 1,10-Phenanthroline, Glycine, and Sarcosine

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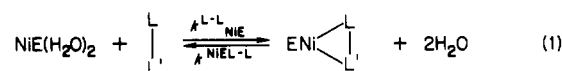
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The kinetics of ternary complex formation between Ni(EDDA) and ethylenediamine, bipyridine, 1,10-phenanthroline, glycine, and sarcosine were studied. All reactions were first order in NiEDDA. The reaction of ethylenediamine with NiEDDA was studied over the pH range 6.8–8.8 and was resolved into the terms  $k^{\text{en}}_{\text{NiEDDA}} = 3.75 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  and  $k^{\text{Hen}}_{\text{NiEDDA}} = 9.77 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ . The data show only a small steric factor to be present as en reacts with NiEDDA; however, the formation rate is about 15 times lower than predicted. Two pathways with virtually identical rates can explain the slow formation rate. One involves a slower ring closure due to coordination angle distortion of the open sites of the nickel coordination sphere while the other involves a slow isomerization of NiEDDA to relieve coordination angle distortion. The two paths are indistinguishable. The reactions of bpy and phen with NiEDDA are described by  $k^{\text{bpy}}_{\text{NiEDDA}} = 5.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  and  $k^{\text{phen}}_{\text{NiEDDA}} = 4.3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ . The formation rates agree well with a rate based on the rapid dissociation of an acetate arm prior to coordination of the aromatic ligand. Stability constants for the mixed complex substantiate incomplete coordination of EDDA. The reactions of Gly and sar were studied over the pH range 6.8–9.1. The reaction order in both amino acids varied from 1 to 0 as the ligand concentration increased. The mechanism involves a singly bonded EDDA–Ni–O–N intermediate in rapid equilibrium with reactants followed by isomerization of NiEDDA to relieve coordination angle distortion, thus allowing chelation of the amino acid. The magnitude of the equilibrium constant governing the formation of EDDA–Ni–O–N is due to the ICB effect.

#### Introduction

Several recent studies have been reported<sup>1–7</sup> involving formation reactions between a bidentate ligand and a metal ion already coordinated to a multidentate ligand. The ternary complex that is formed could have all the coordination sites on the metal occupied by ligands if complete coordination occurred without dissociation of the already coordinated ligand. Two of these studies revealed some interesting features in the mechanism that depend upon both the coordinated ligand and the attacking ligand. The reactions of Ni(trien)<sup>2+</sup> with 1,10-phenanthroline (phen)<sup>2</sup> and bipyridine (bpy)<sup>1</sup> were shown to result in a product having only three of the trien nitrogens coordinated to nickel as a result of severe steric hindrance.<sup>1</sup> The reaction of phen and bpy with Ni(en)<sub>2</sub><sup>2+</sup> shows the same behavior while their reactions with Ni(dien)<sup>2+</sup> appears normal.<sup>8</sup> The reaction of Ni(trien)<sup>2+</sup> with ethylene diamine (en)<sup>1</sup> was shown to have a rate-determining ring-closure step as a result of coordination angle distortion (CAD) in the nickel coordination sphere that was due to coordinated trien. The reaction of en with Ni(en)<sub>2</sub><sup>2+</sup>,<sup>9</sup> which has steric hindrance identical with that of the Ni(trien)<sup>2+</sup>–en system, does not show this effect. The reaction of glycine (Gly)<sup>2</sup> and sarcosine (sar)<sup>1</sup> with Ni(trien)<sup>2+</sup> shows an equilibrium-governed mechanism as opposed to a steady-state behavior for the singly bonded NiT–O–N species, followed by a sluggish ring closure that is sensitive to the substituent on the amino acid nitrogen.

We report here on the mechanism of phen, bpy, en, Gly, and sar reacting with NiEDDA. The general mechanism is shown in eq 1, where L–L' represents the bidentate ligand and NiE



represents NiEDDA. Coordination of EDDA to nickel instead

**Table I.** Stability Constants and Protonation Association Constants for Ni–EDDA–phen and Ni–EDDA–bpy Mixtures (25.0 °C,  $\mu = 0.1 \text{ M}$ )

Stability Constants	
$K^{\text{Ni}}_{\text{NiEDDA}} = 4.47 \times 10^{13}, \text{ M}^{-1}$	$K^{\text{Ni}}_{\text{NiHEDDA}} = (9.99 \pm 0.21) \times 10^9, \text{ M}^{-1}$
$K^{\text{Ni}}_{\text{Ni(en)}} = 3.98 \times 10^8, \text{ M}^{-1}$	$K^{\text{Ni}}_{\text{Ni(bpy)}} = 2.51 \times 10^7, \text{ M}^{-1}$
$K^{\text{Ni}}_{\text{Ni(phen)}_2} = 5.01 \times 10^{16}, \text{ M}^{-2}$	$K^{\text{Ni}}_{\text{Ni(bpy)}_2} = 7.08 \times 10^{13}, \text{ M}^{-2}$
$K^{\text{Ni}}_{\text{Ni(phen)}_3} = 2.00 \times 10^{24}, \text{ M}^{-3}$	$K^{\text{Ni}}_{\text{Ni(bpy)}_3} = 1.45 \times 10^{20}, \text{ M}^{-3}$
$K^{\text{Ni}}_{\text{Ni(EDDA)(phen)}} = (3.06 \bullet) \times 10^{18}, \text{ M}^{-2}$	$K^{\text{Ni}}_{\text{Ni(EDDA)(bpy)}} = (1.65 \bullet) \times 10^{18}, \text{ M}^{-2}$
$K^{\text{Ni}}_{\text{Ni(HEDDA)(phen)}} = (1.53 \bullet) \times 10^{16}, \text{ M}^{-1}$	$K^{\text{Ni}}_{\text{Ni(HEDDA)(bpy)}} = (2.10 \pm 0.000) \times 10^{17}, \text{ M}^{-1}$
Proton Dissociation Constants, M	
$K_{\text{Hphen}} = 1.17 \times 10^{-5}, \text{ a}$	$K_{\text{Hbpy}} = 3.80 \times 10^{-5}, \text{ a}$
$K_{\text{HEDDA}} = 3.16 \times 10^{-10}, \text{ a}$	$K_{\text{EDDA}}^{\text{H}_2\text{EDDA}} = 7.57 \times 10^{-17}, \text{ a}$

<sup>a</sup> Values taken from ref 12 at 25 °C,  $\mu = 0.1 \text{ M}$ . <sup>b</sup> This work.

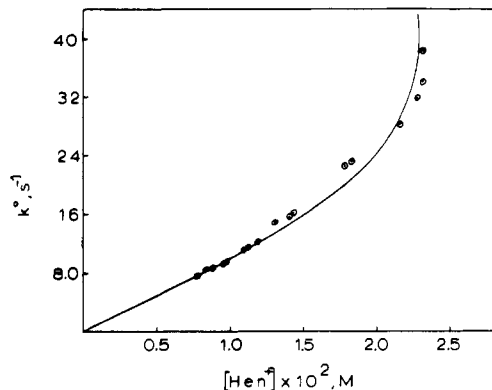
of trien results in a complex with a slower rate of water loss<sup>10,11</sup> that may effect the equilibrium step in the amino acid mechanism. EDDA also results in a less hindered complex because carboxyl group dentate sites have no hydrogens on either of the last two atoms in the chelate ring whereas the last two atoms in the amine chelate ring have four hydrogens. Finally, the use of EDDA results in a complex having relatively labile terminal dentate sites compared to Ni(trien)<sup>2+</sup>.

#### Experimental Section

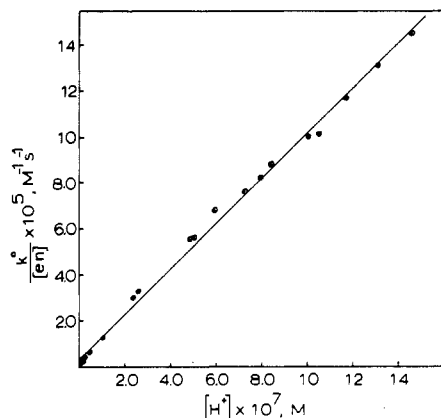
**Reagents.** Reagent grade EDDA was recrystallized twice from a hot aqueous solution with methanol. NiEDDA was prepared and standardized following the procedure used for Ni(trien)<sup>2+</sup>.<sup>2</sup> Carbonate-free sodium hydroxide was prepared and standardized against primary standard potassium acid phthalate. Ethylenediamine was distilled and standardized by a potentiometric titration against standard HCl. Bipyridine and 1,10-phenanthroline were used without further purification and standardized by weight. Glycine and sarcosine were recrystallized from a water–methanol solution and standardized by weight. The buffers used were HEPES, *N*-(2-hydroxymethyl)piperazine-*N'*-ethanesulfonic acid ( $\text{p}K_{\text{a}} = 7.75$ ), TAPS, [[tris(hydroxymethyl)methyl]amino]propane ( $\text{p}K_{\text{a}} = 8.4$ ), and an equimolar mixture of sodium tetraborate and boric acid whose pH was adjusted through the addition of manitol. NaCl was used to control the ionic strength in both the kinetic and potentiometric experiments.

**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: 254 nm for en, 305 nm for bpy, 343 nm for phen, 240 nm for Gly, 242 nm

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**Figure 1.** Dependence of  $k^\circ$  upon  $[\text{Hen}^+]$  for the reaction of NiEDDA and ethylenediamine ( $\mu = 0.1 \text{ M}$ ,  $25^\circ \text{C}$ ). Solid line is constructed from resolved rate constants.



**Figure 2.** Resolution of  $k^\circ$  for the reaction of NiEDDA and ethylenediamine into  $k^{\text{en}}_{\text{NiEDDA}}$  and  $k^{\text{Hen}}_{\text{NiEDDA}}$  terms ( $\mu = 0.1 \text{ M}$ ,  $25^\circ \text{C}$ ). Solid line is least-squares best fit of the points.

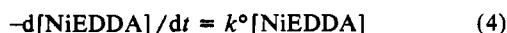
for *sar*. Potentiometric and pH measurements were carried out on a Beckman Model 110 research pH meter. Potentiometric titrations were performed in a four-neck round-bottom flask containing measured amounts of  $\text{Ni}(\text{NO}_3)_2$  ( $9.90 \times 10^{-4} \text{ M}$ ),  $\text{H}_2\text{EDDA}$  ( $1.00 \times 10^{-3} \text{ M}$ ),  $\text{NaCl}$ , and either phen ( $1.01 \times 10^{-3} \text{ M}$ ) or bpy ( $9.99 \times 10^{-4} \text{ M}$ ). Deionized, double-distilled water was used. All experiments were done at  $25.0 \pm 0.1^\circ \text{C}$  and  $\mu = 0.1 \text{ M}$  and covered a pH range from 3 to 10. The pH meter was standardized at both pH 4.01 and 6.86 before each titration and checked after the titration. A  $\text{N}_2$  blanket was maintained over the solution during the titration. Stability constants for the reactions defined by eq 2 and 3 with L as phen or bpy were calculated by computer



using an iterative curve-fitting program. The best fit to the data was obtained by including a term for a monoprotonated complex,  $\text{NiHEDDA}^+$ , a species that had previously been unreported. The values are listed in Table I. Kinetic measurements were performed as previously described.<sup>2</sup> All reactions were run at  $25.0 \pm 0.1^\circ \text{C}$  and  $\mu = 0.1 \text{ M}$ . Each rate constant is the average of at least three individual runs.

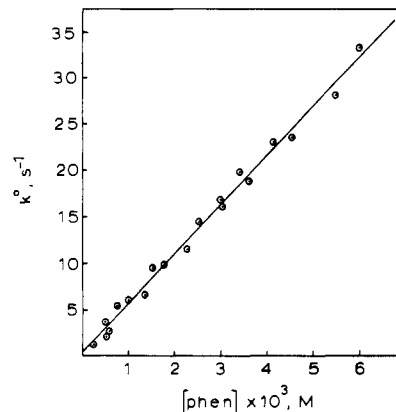
## Results

**Ethylenediamine.** The reactions of NiEDDA and en were run with a 20-fold excess of en ( $t = \text{total}$ ) over a pH range of 6.8–8.5. This variation in pH at constant en, caused the  $\text{Hen}^+$  concentration to vary between  $7.6 \times 10^{-3}$  and  $2.3 \times 10^{-2} \text{ M}$  while the en concentration varied between  $5.2 \times 10^{-6}$  and  $1.0 \times 10^{-3} \text{ M}$ . Both TAPS and HEPES were used as buffers. The data are listed in Table II. The reactions followed eq 4. The pseudo-first-order

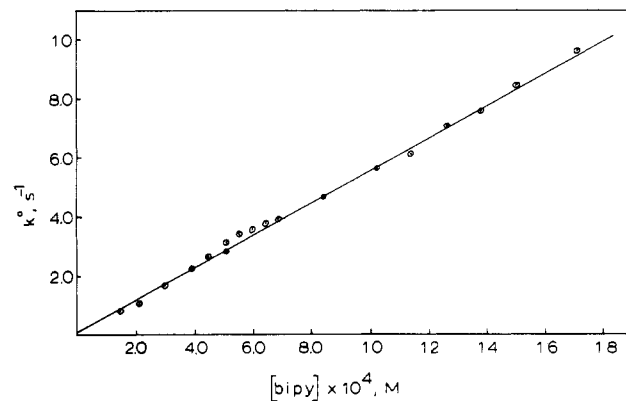


rate constant,  $k^\circ$ , was plotted vs. the  $\text{Hen}^+$  concentration according to eq 5 as shown in Figure 1. An obvious curvature suggested

$$k^\circ = k^{\text{Hen}}_{\text{NiEDDA}}[\text{Hen}^+] \quad (5)$$



**Figure 3.** Dependence of  $k^\circ$  upon [phen] for reaction of NiEDDA and phen ( $\mu = 0.1 \text{ M}$ ,  $25^\circ \text{C}$ ). Solid line is least-squares best fit of the points.



**Figure 4.** Dependence of  $k^\circ$  upon [bpy] for reaction of NiEDDA and bpy ( $\mu = 0.1 \text{ M}$ ,  $25^\circ \text{C}$ ). Solid line is least-squares best fit of the points.

the presence of another reactive form of en whose concentration increases at higher pH values. The pseudo-first-order rate constant can be written in terms of  $\text{Hen}^+$  and en as shown in eq 6. This

$$k^\circ = k^{\text{Hen}}_{\text{NiEDDA}}[\text{Hen}^+] + k^{\text{en}}_{\text{NiEDDA}}[\text{en}] \quad (6)$$

$$\frac{k^\circ}{[\text{en}]} = k^{\text{Hen}}_{\text{NiEDDA}} \frac{[\text{H}^+]}{K_{a2}} + k^{\text{en}}_{\text{NiEDDA}} \quad (7)$$

may be rearranged to eq 7, which is suitable for resolution of the data by plotting  $k^\circ/[\text{en}]$  vs.  $[\text{H}^+]$  where  $K_{a2} = [\text{H}^+][\text{en}]/[\text{Hen}^+] = 1.2 \times 10^{-10}$ . Figure 2 shows a least-squares plot of eq 7, which yields values of  $k^{\text{en}}_{\text{NiEDDA}}$  and  $k^{\text{Hen}}_{\text{NiEDDA}}$ . The values are listed in Table III.

**Bipyridine and 1,10-Phenanthroline.** The reactions of phen and bpy with NiEDDA were carried out with at least a 10-fold excess of ligand over the nickel complex. The data are shown in Table II. Both HEPES and the borate–boric acid buffers were used. Under these conditions, phen and bpy are both thermodynamically able to displace EDDA, forming  $\text{Ni}(\text{phen})_3^{2+}$  and  $\text{Ni}(\text{bpy})_3^{2+}$ . However, this displacement is very sluggish in the case of phen (displacement proceeds to the extent of 0.07% during the length of time needed for 10 half-lives of the ternary complex formation under the most favorable conditions).<sup>13</sup> The same is also assumed to be true for bpy so that displacement does not interfere with the formation reactions. The reactions of both ligands followed eq 4. Plots of  $k^\circ$ , the pseudo-first-order rate constant, vs. ligand concentration, shown in Figures 3 and 4 for bpy and phen, re-

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

(11) Calculated from  $k^{-\text{H}_2\text{O}} = 6/2(k_{12}/K_{a2})$  with  $K_{a2} = 0.16 \text{ M}^{-1}$  and  $k_{12}$  from ref 14.

(12) Martell, A. E.; Smith, R. M. "Critical Stability Constants"; Plenum Press: New York, 1979; Vol. 1 and 2.

(13) Steinhaus, R. K. *Inorg. Chim. Acta* **1982**, *63*, 1.

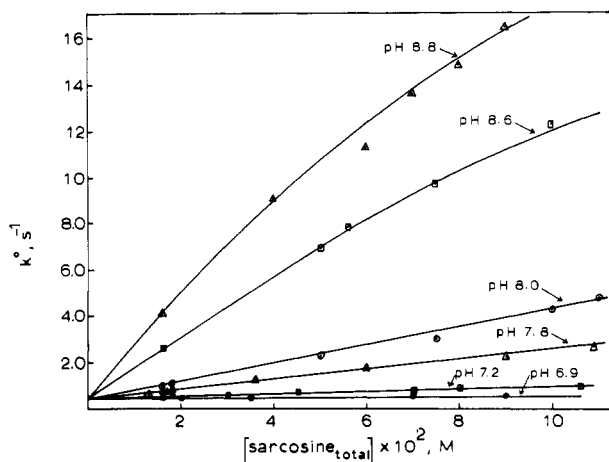


Figure 5. Dependence of  $k^o$  upon total sarcosine concentration at constant pH for reaction of sarcosine with NiEDDA ( $\mu = 0.1$  M,  $25^\circ\text{C}$ ). Solid lines are calculated from eq 8.

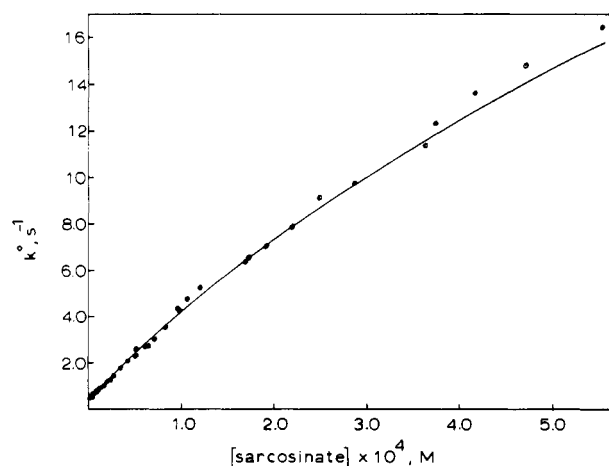


Figure 6. Dependence of  $k^o$  upon sarcosinate ion concentration over pH range 6.8–9.1 for the reaction of NiEDDA and sarcosine ( $\mu = 0.1$  M,  $25^\circ\text{C}$ ). Solid line is calculated from eq 8.

spectively, revealed a linear dependence in ligand concentration.

**Glycine and Sarcosine.** The reactions of Gly and sar with NiEDDA were carried out with at least a 10-fold excess of ligand over the nickel complex in the pH range 6.8–9.1. TAPS and HEPES were both used as buffers. The data are listed in Table II. The reactions followed eq 4. Kinetically, both ligands behaved in an identical fashion, allowing the rate constants to be resolved in the same manner for both systems. Plots of  $k^o$  vs. total ligand concentration, at constant pH, shown in Figure 5 for sar, revealed (1) a nonzero intercept, (2) first-order behavior in total ligand concentration at low pH (up to pH 7.5 for Gly and 8.0 for sar), and (3) a shift from first-order to zero-order behavior in total ligand concentration at high pH. This type of behavior is identical with that seen in the reactions of Ni(trien)<sup>2+</sup> with Gly<sup>2</sup> and sar.<sup>1</sup> The nonzero intercept obtained from least-squares plots of the linear portion of the data indicates a reversible reaction whose dissociation rate constant,  $k^{\text{Ni(EDDA)(L)}}$ , is given by the intercept. The values are listed in Table IV for both Gly and sar. Plots of  $k^o$  vs. ligand anion, shown for sar in Figure 6, indicate that all the reactions in the pH range 6.8–9.1, covering a variety of total ligand concentrations and thus a variety of protonated ligand concentrations, fit the same line. This shows that the only reactive form of either amino acid is the unprotonated anion. The curve appears linear at low ligand concentration but shifts to a zero-order dependence in ligand at higher concentrations. Equation 8 can

$$k^o - k^{\text{Ni(EDDA)(L)}} = k^{o'} = \frac{ab[L^-]}{1 + b[L^-]} \quad (8)$$

be used to describe and resolve the data. Here,  $L^-$  represents the

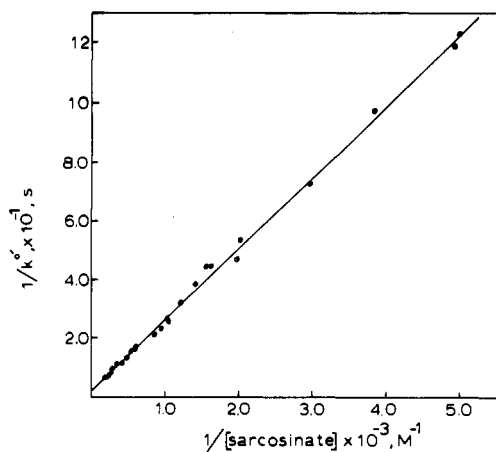
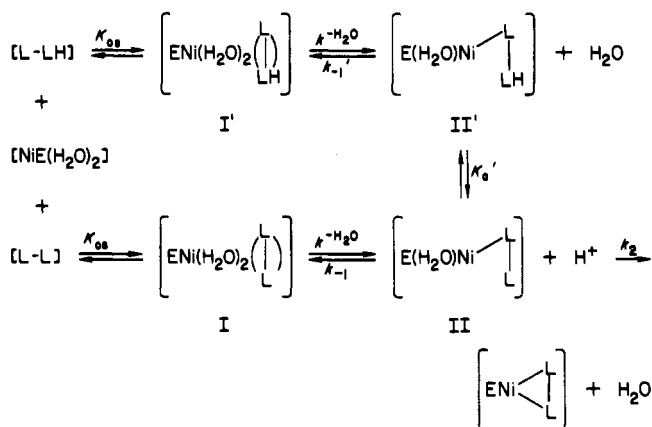


Figure 7. Resolution of  $k^o$  into terms  $a$  and  $b$  of eq 9 for reaction of NiEDDA and sarcosine ( $\mu = 0.1$  M,  $25^\circ\text{C}$ ). Solid line is least-squares best fit of the data.

#### Scheme I



glycinate or sarcosinate concentration. Rearrangement of eq 8 to eq 9 permits calculation of  $a$  and  $b$  from a plot of the left-hand

$$\frac{1}{k^{o'}} = \frac{1}{ab[L^-]} + \frac{1}{b} \quad (9)$$

side of eq 9 vs.  $1/[L^-]$ . The plot for the sar system is shown in Figure 7, and values of  $a$  and  $b$  are given in Table IV.

#### Discussion

The vast majority of metal–ligand formation reactions, including ternary complex formation, may be successfully described by the Eigen–Tamm mechanism.<sup>14</sup> Scheme I illustrates this mechanism with both a protonated and unprotonated pathway where E represents EDDA and L–L a bidentate ligand. Equations 10 and 11 are derived from the above mechanism assuming (1)  $K_{os}$  to

$$k^{\text{L}_{\text{NiEDDA}}} = \frac{2}{6} \frac{K_{os} k^{-\text{H}_2\text{O}} k_2}{k_{-1} + k_2} \quad (10)$$

$$k^{\text{HL}_{\text{NiEDDA}}} = \frac{2}{6} \frac{K_{os} k^{-\text{H}_2\text{O}} k_2}{k_{-1}' K_{\text{H}'} [\text{H}^+] + k_2} \quad (11)$$

represent a rapid equilibrium, (2) steady-state behavior in both the monocoordinated intermediates, and (3) a rapid proton equilibria. The factor of  $2/6$  accounts for the number of available coordination sites on NiEDDA relative to  $\text{Ni(H}_2\text{O)}_6^{2+}$ . Values of  $K_{os}$  may be calculated from a modification of the Fuoss equation<sup>15</sup> and are listed in Table V for the different charge combinations used in the study. The value of  $k^{-\text{H}_2\text{O}}$  for NiEDDA

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

**Table II.** Experimental Values of the Rate Constants for the Reaction of NiEDDA with Ethylenediamine, Bipyridine, 1,10-Phenanthroline, Glycine, and Sarcosine at 25 °C,  $\mu = 0.1$  M

Ethylenediamine <sup>a</sup>							
pH	$k^\circ$ , s <sup>-1</sup>	pH	$k^\circ$ , s <sup>-1</sup>	pH	$k^\circ$ , s <sup>-1</sup>		
6.72	7.62	7.03	12.37	7.91	28.22		
6.77	8.40	7.12	14.93	8.21 <sup>d</sup>	31.95		
6.82	8.72	7.19	15.64	8.50 <sup>d</sup>	38.49		
6.87	9.23	7.21	16.32	8.53 <sup>d</sup>	34.06		
6.89	9.69	7.48	22.66	8.53 <sup>b,d</sup>	47.27		
6.97	11.36	7.52	23.26	8.75 <sup>c,d</sup>	53.42		
6.99	11.64						
Bipyridine <sup>e</sup>							
pH	10 <sup>4</sup> [bpy], M	$k^\circ$ , s <sup>-1</sup>	pH	10 <sup>4</sup> [bpy], M	$k^\circ$ , s <sup>-1</sup>		
8.10 <sup>f</sup>	1.50	0.811	8.01	6.45	3.79		
8.01	2.10	1.06	8.01	6.90	3.91		
8.10 <sup>f</sup>	3.00	1.66	7.99	8.40	4.68		
8.01	3.90	2.22	7.50 <sup>f</sup>	10.2	5.63		
8.10 <sup>f</sup>	4.50	2.65	7.99	11.4	6.08		
8.01	5.10	2.78	8.00	12.6	7.04		
7.50 <sup>f</sup>	5.10	3.11	7.98	13.8	7.57		
8.01	5.55	3.40	7.91	15.0	8.43		
8.01	6.00	3.58	7.99	17.1	9.64		
1,10-Phenanthroline <sup>e</sup>							
pH	10 <sup>3</sup> [phen], M	$k^\circ$ , s <sup>-1</sup>	pH	10 <sup>3</sup> [phen], M	$k^\circ$ , s <sup>-1</sup>		
8.00	0.25	1.11	8.00 <sup>f</sup>	3.00	16.4		
7.99	0.51	3.68	7.50 <sup>f</sup>	3.00	16.8		
8.02	0.52	2.18	7.98	3.39	19.4		
8.00	0.61	3.24	8.00	3.60	18.8		
8.00	0.75	5.63	8.00	4.11	23.0		
8.01	0.99	6.09	8.00	4.50	23.4		
8.00	1.35	6.58	8.00	5.00	28.1		
8.49	1.51 <sup>f</sup>	9.51	8.01	5.47	28.0		
8.01	1.76	11.6	8.00	6.00	33.4		
8.01	2.51	14.5					
Glycine <sup>e</sup>							
pH	10 <sup>2</sup> [Gly], M	$k^\circ$ , s <sup>-1</sup>	pH	10 <sup>2</sup> [Gly], M	$k^\circ$ , s <sup>-1</sup>		
6.83	1.30	0.646	7.50	1.30	1.29		
6.85	1.60	0.610	7.51	3.20	2.57		
6.83	3.20	0.862	7.51	5.00	3.63		
6.83	5.00	1.10	7.52	7.50	4.83		
6.83	7.50	1.40	7.50	10.0	6.16		
6.83	10.0	1.77	7.64	1.60	1.94		
7.02	2.00	0.850	7.77	1.30	2.11		
7.02	5.00	1.66	7.78	3.20	4.66		
7.02	7.00	2.14	7.78	5.00	6.39		
7.01	10.0	2.82	7.78	7.50	8.76		
7.19	1.30	0.894	7.78	10.0	9.94		
7.22	1.60	0.903	7.81	1.60	2.75		
7.23	3.20	1.84	7.83	1.60	2.57		
7.22	5.00	2.31	8.01	1.60	3.92		
7.23	7.50	3.14	8.23	1.60	5.93		
7.23	10.0	3.94					
Sarcosine <sup>h</sup>							
pH	10 <sup>3</sup> [NiEDDA], M	10 <sup>2</sup> [sar], M	$k^\circ$ , s <sup>-1</sup>	pH	10 <sup>3</sup> [NiEDDA], M	10 <sup>2</sup> [sar], M	$k^\circ$ , s <sup>-1</sup>
6.86	1.28	2.00	0.470	7.97	1.28	7.50	3.00
6.85	1.28	3.50	0.470	7.97	1.28	10.0	4.32
6.86	1.28	7.00	0.540	7.98	1.28	11.0	4.75
6.85	1.28	9.00	0.580	8.01	1.12	1.60	0.917
7.22	1.12	1.60	0.413	8.16	1.12	1.60	1.23
7.21	1.28	1.80	0.532	8.21	1.12	1.60	1.44
7.21	1.28	3.00	0.534	8.39	1.12	3.40	3.53
7.21	1.28	4.50	0.705	8.42	1.12	1.60	2.07
7.21	1.28	7.00	0.773	8.61	1.12	1.60	2.67
7.21	1.28	8.00	0.883	8.59	1.12	5.00	7.00
7.21	1.28	10.6	1.01	8.60	1.12	5.60	7.84
7.42	1.12	1.60	0.443	8.59	1.12	7.50	9.72
7.62	1.12	1.60	0.531	8.58	1.12	10.0	12.3
7.76	1.28	1.30	0.587	8.81	1.12	1.60	4.16
7.81	1.12	1.60	0.740	8.81	1.12	4.00	9.09
7.81	1.16	1.70	0.770	8.79	1.35	6.00	11.3
7.75	1.28	1.80	0.826	8.79	1.35	7.00	13.6
7.74	1.28	3.60	1.25	8.79	1.35	8.00	14.8

Table II (Continued)

				Sarcosine <sup>a</sup>			
pH	10 <sup>3</sup> [NiEDDA], M	10 <sup>2</sup> [sar], M	k <sup>o</sup> , s <sup>-1</sup>	pH	10 <sup>3</sup> [NiEDDA], M	10 <sup>2</sup> [sar], M	k <sup>o</sup> , s <sup>-1</sup>
7.74	1.28	6.00	1.79	8.81	1.35	9.00	16.4
7.74	1.28	9.00	2.55	8.89	1.12	1.60	5.21
7.74	1.28	10.9	2.68	9.03	1.12	1.60	6.32
7.99	1.28	1.80	1.07	9.07	1.12	1.70	6.48
7.99	1.28	5.00	2.28				

<sup>a</sup>All runs at [NiEDDA] = 1.38 × 10<sup>-3</sup> M; [en]<sub>t</sub> = 2.5 × 10<sup>-2</sup> M; HEPES buffer at 0.5 M or as noted in footnotes. <sup>b</sup>[en]<sub>t</sub> = 5.01 × 10<sup>-2</sup> M. <sup>c</sup>[en]<sub>t</sub> = 5.99 × 10<sup>-2</sup> M. <sup>d</sup>TAPS buffer at 0.05 M. <sup>e</sup>All runs at [NiEDDA] = 1.51 × 10<sup>-5</sup> M; HEPES buffer at 0.005 M or as noted in footnote. <sup>f</sup>Borate/boric acid buffer used, 0.1 M in each; pH adjusted to desired value with manitol. <sup>g</sup>All runs at [NiEDDA] = 1.12 × 10<sup>-3</sup> M; HEPES buffer at 0.1 M used through pH 7.81; TAPS buffer at 0.1 M used after pH 7.81. <sup>h</sup>HEPES buffer at 0.05 M used through pH 7.74; TAPS buffer at 0.05 M used at pH 7.99 and above.

Table III. Rate Constants (M<sup>-1</sup> s<sup>-1</sup>) for the Reaction of NiEDDA with Ethylenediamine, Bipyridine, and 1,10-Phenanthroline at 25 °C, μ = 0.1 M

	exptl	pred
k <sup>en</sup> <sub>NiEDDA</sub>	(3.75 ± 1.1) × 10 <sup>4</sup>	5.6 × 10 <sup>5</sup>
k <sup>Hen</sup> <sub>NiEDDA</sub>	(9.77 ± 0.16) × 10 <sup>2</sup>	5.9 × 10 <sup>3</sup>
k <sup>bpy</sup> <sub>NiEDDA</sub>	(5.5 ± 0.08) × 10 <sup>3</sup>	5.9 × 10 <sup>3</sup>
k <sup>phen</sup> <sub>NiEDDA</sub>	(4.3 ± 0.15) × 10 <sup>3</sup>	5.9 × 10 <sup>3</sup>

Table IV. Rate and Equilibrium Constants for the Reactions of NiEDDA and Ni(trien)<sup>2+</sup> with Glycine and Sarcosine at 25 °C and μ = 0.1 M

	NiEDDA		Ni(trien) <sup>2+</sup>	
	Gly	Sar	Gly <sup>a</sup>	Sar <sup>b</sup>
a = K <sub>1</sub> , M <sup>-1</sup>	(1.93 ± 0.34) × 10 <sup>2</sup>	(9.3 ± 2.1) × 10 <sup>1</sup>	690	430
b = k <sub>2</sub> , s <sup>-1</sup>	(4.4 ± 0.8) × 10 <sup>1</sup>	(4.4 ± 1.0) × 10 <sup>1</sup>	130	68
k <sup>Ni(L)(amino acid)</sup> , s <sup>-1</sup>	(4.5 ± 0.6) × 10 <sup>-1</sup>	(4.1 ± 0.6) × 10 <sup>-1</sup>	8.1	17.7

<sup>a</sup>Reference 2. <sup>b</sup>Reference 1.

Table V. Values of K<sub>os</sub> for Various Combinations of Charged Reactants Calculated at 25 °C by the Modified Fuoss Equation<sup>15</sup>

reactant cge combin	a, Å	a', Å	K <sub>os</sub> , M <sup>-1</sup>
2+,0 and 1-,0	4		0.16
2+,1+	4	6.5	0.044

is 1.1 × 10<sup>5</sup> s<sup>-1</sup>.<sup>10,11</sup> If it is now assumed that k<sub>2</sub> > k<sub>-1</sub> or k<sub>2</sub> > k<sub>-1</sub>K<sub>H</sub><sup>+</sup>[H<sup>+</sup>], then k<sup>L</sup><sub>NiEDDA</sub> and k<sup>HL</sup><sub>NiEDDA</sub> may be predicted from eq 12.

$$k^{\text{HL}}_{\text{NiEDDA}} = k^{\text{L}}_{\text{NiEDDA}} = \frac{2}{6}K_{\text{os}}^{-\text{H}_2\text{O}} \quad (12)$$

**Ni(EDDA)(en).** The kinetic data for the reaction between NiEDDA and en were resolved into terms involving free en and monoprotonated en, with no reverse rate constant being found. Figure 2, a plot of eq 6, shows that in the pH range studied there is no complex dependence upon hydrogen ion such as required by eq 11. Thus, for the Hen<sup>+</sup> pathway, k<sub>2</sub> > k<sub>-1</sub>K<sub>H</sub><sup>+</sup>[H<sup>+</sup>] in the pH range of 6.8–8.5 and eq 12 may be used to calculate the value of k<sup>Hen</sup><sub>NiEDDA</sub>. The value is calculated to be 5.9 × 10<sup>3</sup> M<sup>-1</sup> s<sup>-1</sup> and is to be compared to the experimental value of k<sup>Hen</sup><sub>NiEDDA</sub> = 977 M<sup>-1</sup> s<sup>-1</sup> from Table III.

The predicted value of k<sup>Hen</sup><sub>NiEDDA</sub> is a factor of 6 higher than the experimental value and is a measure of the steric interaction present during initial coordination to nickel.<sup>16</sup> It has been estimated that an intramolecularly hydrogen-bonded form of Hen<sup>+</sup> slows the formation reaction of Hen<sup>+</sup> down by a factor of 3.<sup>17</sup> Thus, the actual steric factor of en and Hen<sup>+</sup> reacting with NiEDDA is only 2. This may be compared to the steric factor of 14 found in the reaction of en and Hen<sup>+</sup> with Ni(trien)<sup>2+</sup>.<sup>1</sup> The

two carboxyl groups of EDDA coordinated to nickel leave far more room near the open coordination sites than the two terminal en segments of trien due to the lack of protons on the carboxyl groups. Thus, it is consistent with molecular structure that the steric factor is much less with coordinated EDDA than with coordinated trien.

The reaction of en with NiEDDA will involve an ICB effect.<sup>14</sup> A clear estimation of the magnitude of this factor is obtained by comparing the formation rate of en and tmen<sup>+</sup> (N,N,N-trimethylethylenediammonium ion) with a nickel, using a correction factor to account for the charge difference. This results in a value of 190,<sup>1</sup> which is consistent with other estimates of the ICB effect for the reaction of en with nickel.<sup>17,18</sup> Equation 12 may now be used to predict k<sup>en</sup><sub>NiEDDA</sub> by including a steric factor of 2 and an ICB factor of 190. The predicted value of k<sup>en</sup><sub>NiEDDA</sub> is 5.6 × 10<sup>5</sup> M<sup>-1</sup> s<sup>-1</sup>, and comparison to the experimental value of 3.75 × 10<sup>4</sup> M<sup>-1</sup> s<sup>-1</sup> from Table III shows the predicted value to be 15 times higher. The difference between the two values indicates that ring closure is not rapid as required by 12.

If it is assumed that ring closure is rate limiting, use of eq 10 allows calculation of k<sub>2</sub>. The term k<sub>-1</sub>, dissociation of monocoordinated en from NiEDDA, is obtained from the corresponding value for the dissociation of monocoordinated en from Ni(en)<sub>2</sub><sup>2+</sup>,<sup>9</sup> correcting for the difference in rates of water loss between NiEDDA and Ni(en)<sub>2</sub><sup>2+</sup>.<sup>19</sup> Thus, k<sub>-1</sub> is 2.6 × 10<sup>3</sup> s<sup>-1</sup>, and eq 10, using the experimental value of k<sup>en</sup><sub>NiEDDA</sub> and incorporating a steric factor of 2 and an ICB factor of 190, gives k<sub>2</sub> = 1.9 × 10<sup>2</sup> s<sup>-1</sup>.

An upper limiting value of k<sub>2</sub> may be approximated by the rate of water loss of the Ni(EDDA)(-N-N) species divided by a rotational barrier (estimated to be 44<sup>20</sup>) needed to bring en into position for ring closure. The rate of water loss of the Ni(EDDA)(-N-N) species will be faster than that of NiEDDA by a factor of about 10<sup>21</sup> due to the additional nitrogen coordinated to nickel. Thus, the upper limit of k<sub>2</sub> is about 3 × 10<sup>4</sup> s<sup>-1</sup>, which is 150 times faster than the value of k<sub>2</sub> calculated from eq 10.

Comparison of k<sub>2</sub>, the ring-closure rate, occurring during the addition of en to NiEDDA with the k<sub>2</sub> value for the addition of en to Ni(trien)<sup>2+</sup> shows that, in both cases, the coordinated ligand lowers the ring-closure rate to about the same extent. The value of k<sub>2</sub> from experimental data in the Ni(trien)(en)<sup>2+</sup> system was 240 times less than the upper limit for that system,<sup>1</sup> and the k<sub>2</sub> value in the NiEDDA-en system is about 150 times less than the upper limit. The explanation for the decreased rate of ring closure of en on Ni(trien)<sup>2+</sup> was a coordination angle distortion (CAD) caused by the middle chelate ring on trien coordinated in a cis-α-octahedral configuration. The middle chelate ring of Ni(trien)<sup>2+</sup> has a bond angle of about 82° for the Ni-Ni-N group and causes

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(19) 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.

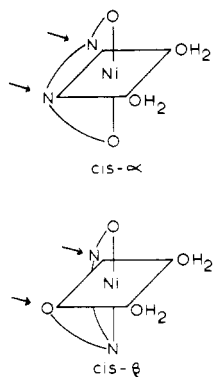
(20) Margerum, D. W.; Rorabacher, D. B.; Clarke, J. F. G. *Inorg. Chem.* **1963**, *2*, 667.

(21) Coordination of NH<sub>3</sub> to Ni(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> appears to increase the rate of water loss of Ni(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> by about a factor of 10;<sup>22</sup> k<sup>-H<sub>2</sub>O</sup><sub>Ni(H<sub>2</sub>O)<sub>6</sub></sub> = 2.7 × 10<sup>4</sup> s<sup>-1</sup> and k<sup>-H<sub>2</sub>O</sup><sub>Ni(H<sub>2</sub>O)<sub>5</sub>(NH<sub>3</sub>)</sub> = 2.5 × 10<sup>5</sup> s<sup>-1</sup>.

(22) 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 112.

(16) Rorabacher, D. B.; Melendez-Cepeda, C. A. *J. Am. Chem. Soc.* **1971**, *93*, 6071.

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



**Figure 8.** Cis- $\alpha$ -octahedral (A) and cis- $\beta$ -octahedral (B) configurations of NiEDDA. Arrows indicate ligand segments directly behind open coordination sites.

the "bite angle" between the two open coordination sites on nickel ( $\text{H}_2\text{O}-\text{Ni}-\text{H}_2\text{O}$ ) to be about  $92.5^\circ$ .<sup>23</sup> Crystallographic studies show that en and en segments of polyamines coordinated to nickel require about  $82^\circ$ .<sup>23,24</sup> Thus, severe strain is placed on en as it undergoes ring closure because the coordination sites are too far apart.

Although no crystallographic data are available for NiEDDA, the crystal structures of NiEDDD<sup>25</sup> and NiEDTA<sup>26</sup> show that, in the square plane of the octahedra, the middle chelate rings involving the S-Ni-S and N-Ni-N groups have bond angles of  $87.1$  and  $86.5^\circ$ , with the angle involving the opposite two positions and nickel being  $96.2$  and  $95.4^\circ$ , respectively. It is logical to assume that EDDA coordinated to nickel in a cis- $\alpha$ -octahedral configuration would also cause about a  $95$ – $96^\circ$  bite angle to be available to en and, thus, that the CAD effect will be present and slow down ring closure. Thus, two different ligands, trien and EDDA, coordinated to nickel yield tetradentate complexes each with different rates of water loss and each showing different amounts of steric hinderance toward en. Nevertheless, both coordinated ligands decelerate the ring closure of en to about the same extent. The common factor is the distortion in the square plane of the octahedra, which causes a large bite angle and thus slows the rate of ring closure.

The above discussion has assumed that NiEDDA is coordinated in a cis- $\alpha$ -octahedral configuration. It has been shown that isomerization of  $\text{Ni}(\text{trien})^{2+}$  from a cis- $\alpha$ -octahedral configuration to a cis- $\beta$ -octahedral configuration would relieve the CAD effect since the two open coordination sites in the cis- $\beta$ -octahedral configuration are no longer opposite a  $-\text{NCH}_2\text{CH}_2\text{N}-$  group as they are in a cis- $\alpha$ -octahedral configuration. This is shown in Figure 8. However, isomerization also predicts formation rates for  $\text{Ni}(\text{trien})^{2+}$  species that were lower than the experimentally observed rates.<sup>1</sup> Thus, isomerization is not an experimentally observed pathway for the formation of  $\text{Ni}(\text{trien})(\text{en})^{2+}$ . However, NiEDDA has relatively labile terminal acetate arms compared to the terminal en segments of  $\text{Ni}(\text{trien})^{2+}$  and will isomerize to a cis- $\beta$ -octahedral configuration more readily than  $\text{Ni}(\text{trien})^{2+}$ . Isomerization may represent a pathway for the reaction of en with EDDA and is shown in Scheme II with a rate-determining dissociation of an acetate arm of EDDA after initial coordination of en. This would allow ring closure of en on NiEDDA with no CAD effect. The free acetate arm of EDDA would then coordinate in a cis- $\beta$ -octahedral configuration.

Assuming a steady state in species I of this mechanism, eq 13 can be derived and used to predict  $k^{\text{en}}_{\text{NiEDDA}}$ . All the values on

$$k^{\text{en}}_{\text{NiEDDA}} = \frac{2}{6} \frac{K_{\text{os}} k^{-\text{H}_2\text{O}} (190/2) k_d}{k_{-1} + k_d} \quad (13)$$

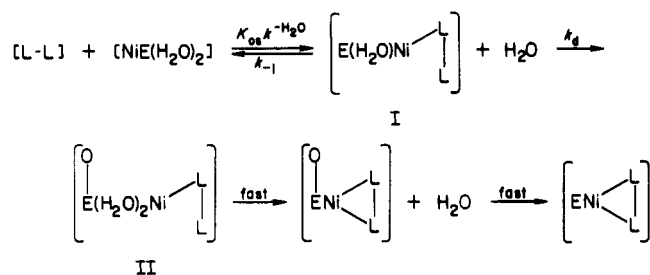
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#### Scheme II



the right-hand side of eq 13 except  $k_d$  are known. The factor of  $190/2$  represents the ICB effect (190) and the steric hinderance (2). A value for  $k_d$ , the dissociation of an acetate arm of EDDA from  $\text{Ni}(\text{EDDA})(-\text{N}-\text{N})$ , can be estimated from (1) the stability difference between NiEDMA ( $\log 10.44$ )<sup>12</sup> and NiEDDA ( $\log 13.65$ )<sup>12</sup> which represents the stability of an acetate chelate ring on NiEDDA, and (2) the rate of formation of an acetate chelate ring, which can be approximated by the rate of water loss of NiEDDA corrected for (1) the effect of the en nitrogen in the coordination sphere (a factor of 10),<sup>21</sup> (2) rotation around a carbon-carbonyl carbon bond in the acetate arm (a factor of 3),<sup>27</sup> and (3) the electrostatic attraction between the free acetate arm and the nickel complex (a factor of 3).<sup>28</sup> Thus, the value of  $k_d$  is  $7 \times 10^2 \text{ s}^{-1}$ . Using this value in eq 13 gives a predicted value of  $k^{\text{en}}_{\text{NiEDDA}}$  of  $1.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , which is only about three times faster than the observed value of  $3.75 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . The close agreement between the experimental value of  $k^{\text{en}}_{\text{NiEDDA}}$  and that predicted from eq 13 means that the mechanism of Scheme II is as likely a pathway as rate-limiting ring closure (Scheme I, eq 10).

Two pathways may therefore exist for the addition of en to NiEDDA: rate-limiting ring closure due to the CAD effect and an isomerization of NiEDDA. Both explain the slower rate of formation, and both are consistent with the experimental data and with other similar systems. At this point, it is impossible to determine which of the two predominates.

**Ni(EDDA)(bpy) and Ni(EDDA)(phen).** The reaction of both bpy and phen with NiEDDA can be predicted from eq 12. The predicted value of  $k^{\text{L}}_{\text{NiEDDA}}$  for both ligands is  $5.9 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ , which is very similar to the observed values for bpy and phen as shown in Table III. The very slight differences seen between the calculated and observed values would indicate (1) that there is no steric hindrance between EDDA and either aromatic ligand, (2) that  $k_2 > k_{-1}$  in eq 9, and (3) that coordinated EDDA does not influence the formation rate. However, molecular models do show that complete coordination of either aromatic ligand to a tetraacoordinated NiEDDA species is impossible just as it was with  $\text{Ni}(\text{trien})^{2+}$ .<sup>1</sup> The sources of this severe steric interaction are protons in the  $-\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2-$  group common to both trien and EDDA and the protons on carbons 2 and 9 of the aromatic ligands.

In order to completely coordinate phen and bpy to  $\text{Ni}(\text{trien})^{2+}$ , a terminal nitrogen of trien had to dissociate. Even then, molecular models showed a significant amount of steric interaction to be present. The stability constants for the addition of the aromatic ligands to  $\text{Ni}(\text{trien})^{2+}$  were orders of magnitude less than the stability for the addition of either aromatic to nickel but are consistent with addition to a tricoordinated  $\text{Ni}(\text{trien})^{2+}$  species. Also, the formation rate constants predicted from a mechanism involving dissociation of a trien nitrogen of  $\text{Ni}(\text{trien})^{2+}$  prior to aromatic ligand coordination are consistent with the experimental data.

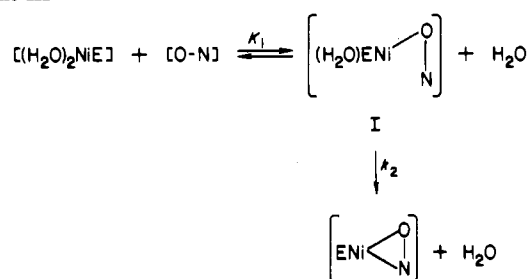
In the present system, the only pieces of evidence as to whether or not an acetate arm has dissociated from NiEDDA, prior to coordination of the aromatic ligand, are the stability constants

(27) Rorabacher, D. B.; Margerum, D. W. *Inorg. Chem.* **1964**, *3*, 382.

(28) The electrostatic attraction of the free acetate arm for the complex can be calculated from the following equation:<sup>29</sup>  $E_d = Z_1 Z_2 e^2 / Dr_{ab} = 2.3 RT \log K_d$  with  $r_{ab} = 6 \text{ \AA}$  estimated from molecular models.

(29) Bydalek, T. J.; Margerum, D. W. *Inorg. Chem.* **1963**, *2*, 678.

## Scheme III



for the addition of either aromatic ligand to NiEDDA, as shown in eq 14. These stability constants may be calculated from the



values found in Table I and have log values of 4.56 and 4.84 for bpy and phen, respectively. The addition of bpy and phen to  $\text{Ni(H}_2\text{O)}_6^{2+}$  gives  $\log K_{\text{stab}}$  values of 7.4 and 8.5, respectively,<sup>12</sup> both of which are orders of magnitude larger than the observed values. However, a decrease in stability due to acetate dissociation, calculated to be 3.2 log units from the ratio of stability constants of NiEDDA ( $\log K = 13.64$ )<sup>12</sup> and NiEDMA ( $\log K = 10.44$ ),<sup>12</sup> coupled with the increase in stability due to coordination of the aromatic ligand, will give stability constants for the formation of ternary complexes of 4.2 and 5.3 log units. These values are quite close to the experimental values and show that EDDA is only tricoordinated in the ternary complex.

The forward rate constant, however, may not appear to reflect the dissociation of an acetate arm because the process may be of the same order of magnitude as the rate of formation. A mechanism for a pathway involving coordination of an aromatic ligand to NiEDDA would consist of initial coordination of the ligand to NiEDDA followed by dissociation of an acetate arm and then ligand ring closure. This is similar to Scheme II except that the dissociated acetate arm remains uncoordinated in the final product due to steric restraints. Assuming a steady state for species I of Scheme II with  $k_d$  as the rate-determining step, followed by a rapid ring closure, eq 13 can be used to predict  $k^{\text{L}}_{\text{NiEDDA}}$ . The ICB effect is not present since neither of the aromatic ligands are basic enough to react through an ICB mechanism.<sup>14</sup> The value of  $k_d$ , the dissociation of an acetate arm, is only  $71.4 \text{ s}^{-1}$ , which is a factor of 10 less than the  $k_d$  value of  $\text{Ni(EDDA)(-N-N)}$  due to the lack of coordinated aliphatic nitrogen. Coordinated aromatic nitrogens appear not to affect the rate of water loss of nickel species. The value of  $k_{-1}$  for the  $\text{Ni(EDDA)(aromatic ligand)}$  systems in Scheme II is approximated by the dissociation of  $\text{Ni(pyridine)}$ ,  $38 \text{ s}^{-1}$ ,<sup>30</sup> corrected by the ratio of rates of water loss between NiEDDA and  $\text{Ni(H}_2\text{O)}_6^{2+}$  which gives  $k_{-1} = 155 \text{ s}^{-1}$ . Thus, eq 13 predicts  $k^{\text{L}}_{\text{NiEDDA}}$  to be  $1.9 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ , which is very close to the experimental values of  $k^{\text{L}}_{\text{NiEDDA}}$  for phen and bpy shown in Table III. Although both eq 12 and 13 predict rate constants that are very similar to the experimental values, it is the low value of the stability constant for the addition of the aromatic ligand to NiEDDA that shows that the correct pathway is Scheme II. Consideration of only the forward rate constant does not reveal the existence of the dissociative pathway.

**Ni(EDDA)(Gly) and Ni(EDDA)(sar).** The reaction of both Gly and sar with NiEDDA showed kinetic behavior identical with that found for the reaction of Gly<sup>2</sup> and sar<sup>1</sup> with  $\text{Ni(trien)}^{2+}$ . Thus, the mechanism used for the  $\text{Ni(trien)}$ -amino acid reactions may be used for the NiEDDA-amino acid reactions and is shown in Scheme III. Equation 15 is derived from this mechanism and

$$k^{\text{L}}_{\text{NiEDDA}} = \frac{K_1 k_2 [\text{L}^-]}{1 + k_2 [\text{L}^-]} \quad (15)$$

is identical with eq 8. The values of  $a$  and  $b$  from eq 8, shown in Table IV, are equal to  $K_1$  and  $k_2$ , respectively. Corresponding values for the reaction of  $\text{Ni(trien)}^{2+}$  with Gly and sar are also listed in Table IV.

The magnitude of the  $K_1$  values for the Gly and sar reactions with  $\text{Ni(trien)}^{2+}$  compared to  $K_{\text{stab}}$  for  $\text{Ni(OAc)}^+$ , which equals 5,<sup>31</sup> was attributed to an ICB effect resulting from the amine nitrogen on the amino acids. The magnitude of the ICB effect is directly related to the ligand basicity.<sup>18</sup> The ICB effect of en reacting with nickel is 190 whereas the ratio of  $K^{\text{Ni(trien)(gly)}^+}_1$  to  $K_{\text{stab}}^{\text{(OAc)}^+}$  is 140 and is a measure of the ICB effect of Gly as it reacts with  $\text{Ni(trien)}^{2+}$ . The above values are reasonable and consistent, considering the  $\text{p}K_a$  value of en which is 9.89<sup>12</sup> and that of Gly which is 9.57.<sup>12</sup>

The  $K_1$  values for the Gly and sar reactions with NiEDDA involve a neutral species reacting with a 1- ion and, thus, cannot be compared directly to either the stability constant of  $\text{NiOAc}^+$  or the  $K_1$  values of  $\text{Ni(trien)}^{2+}$ -amino acid systems, both of which involve the interaction of 2+ and 1- species. Further, EDDA provides less steric hindrance to an incoming ligand than trien does. The effect of charge may be estimated by using the ratio of  $K_{\text{os}}$  values for a 2+, 1- reaction to a 0, 1- reaction. The values in Table V give a ratio of 12. The steric hindrance that coordinated EDDA presents to an incoming ligand is also different from that of coordinated trien. The steric factor for the reaction of  $\text{Hen}^+$  with  $\text{Ni(trien)}^{2+}$  was 14 while that of  $\text{Hen}^+$  reacting with NiEDDA was only 2. The steric interaction of an acetate will be different from that for a primary amine, and no estimation of the actual value is possible except to state that less hindrance is to be expected as amino acids coordinate to NiEDDA compared to  $\text{Ni(trien)}^{2+}$ . Thus, the  $K_1$  values for the Gly and sar reactions with NiEDDA should be decreased by about 12 and increased by an unknown amount, corresponding to the lesser steric interaction of EDDA relative to trien that makes the overall decrease less than 12. The ratio of  $K_1$  for  $\text{Ni(trien)(Gly)}^+$  to  $\text{Ni(EDDA)(Gly)}^-$  shows a decrease of 3.6 while that for the  $K_1$  values of  $\text{Ni(trien)(sar)}^+$  to  $\text{Ni(EDDA)(sar)}^-$  shows a decrease of 4.6. These ratios seem very reasonable in light of the electrostatic and steric effects that are present.

Finally, the  $K_1$  value of  $\text{Ni(EDDA)(sar)}^-$  is less than the corresponding  $K_1$  value for  $\text{Ni(EDDA)(Gly)}^-$ , which is consistent with the  $\text{Ni(trien)}^{2+}$  system. The difference is again attributed to the *N*-methyl group interfering with the ICB hydrogen-bonding process.

The value of  $k_2$  in Scheme II is a measure of ring closure of the amino acids on NiEDDA. The  $k_2$  values for the reaction of  $\text{Ni(trien)}^{2+}$  with both Gly and sar showed ring closure to be slow due to the CAD effect and were consistent with the ring-closure rate of en on  $\text{Ni(trien)}^{2+}$ . Further, the *N*-methyl group of sar was seen to lower the rate of ring closure relative to Gly because of increased steric hindrance. However, Table IV shows the  $k_2$  values for the reactions of NiEDDA with Gly and with sar to have identical values.

If the  $b$  term of eq 8 represents amino acid ring closure, then  $k_2$  for the NiEDDA system should be less than  $k_2$  for the  $\text{Ni(trien)}^{2+}$  systems as a result of the difference in rates of water loss of  $\text{Ni(EDDA)(-O-N)}^-$  compared to  $\text{Ni(trien)(-O-N)}^+$  but would be increased as a result of a lesser amount of steric hindrance due to coordinated acetate groups compared to coordinated en segments. The rate of water loss ratio for  $\text{Ni(trien)(-O-N)}^+$  and  $\text{Ni(EDDA)(-O-N)}^-$  is given by the ratio  $k^{-\text{H}_2\text{O}}_{\text{Ni(trien)}}/k^{-\text{H}_2\text{O}}_{\text{Ni(EDDA)}} = 45$ . The difference in steric hindrance is not known but would be sizable. Thus, the  $k_2$  values for the NiEDDA systems should be somewhat less than 45 times smaller than the  $k_2$  values of the  $\text{Ni(trien)}^{2+}$  system. The actual ratios of  $k^{\text{Ni(trien)(amino acid)}}_2/k^{\text{Ni(EDDA)(amino acid)}}_2$  are only 3 and 1.5 for Gly and sar, respectively, which shows that the  $k_2$  values of the NiEDDA system are larger than expected compared to the  $\text{Ni(trien)}^{2+}$  system. Thus, a mechanism involving rate-limiting ring closure of the amino acid ligands does not fit the data.

Ring closure of the amino acids requires a coordination angle or bite angle of about  $81^\circ$  as seen from the crystal structure of bis(glycinato)bis(imidazole)nickel(II).<sup>32</sup> NiEDDA, however,

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provides a bite angle of 95–96° as discussed earlier, which causes a CAD effect. Isomerization of NiEDDA from cis- $\alpha$ -octahedral to cis- $\beta$ -octahedral to relieve the CAD effect, like the reaction of NiEDDA with en, may be used to explain the slow rate of formation. The  $b$  term of eq 8 then represents  $k_d$ , the dissociation of an acetate arm of Ni(EDDA)(-O-N)<sup>-</sup>. The dissociation of an acetate arm from Ni(EDDA)(-N-N) having a monocoordinated en species was estimated to be  $7 \times 10^2 \text{ s}^{-1}$ . The  $k_d$  value for the dissociation of an acetate arm from Ni(EDDA)(-O-N)<sup>-</sup> having an amino acid coordinated through the acetate group will differ from  $k_d$  of Ni(EDDA)(-N-N) due to (1) the added negative charge of the coordinated acetate from the amino acid and (2) the coordination of an oxygen of the amino acid instead of a nitrogen of en. Thus, the factors of 3.1 due to charge and of 10 due to coordinated nitrogen do not apply, and  $k_d$  for the NiEDDA-amino acid systems is  $23 \text{ s}^{-1}$ . This is very close to the observed value of  $44 \text{ s}^{-1}$  seen for both systems. Further, a dissociation mechanism would predict identical  $k_d$  values for both amino acids reacting with NiEDDA, which is what is experimentally seen. The conclusion is that the NiEDDA reaction with amino acids proceeds through an isomerization mechanism.

### Conclusions

The rate of formation of a ternary complex in which all metal coordination sites could be occupied by multidentate ligands in-

volves a combination of many factors. The amount of steric hindrance that occurs as a ligand attacks an already coordinated metal varies considerably, depending on the size and geometry of the attacking ligand and the coordinated ligand. Protons on atoms in the chelate rings adjacent to open coordination sites severely limit the room at those sites as is seen by comparing the rate of reaction of Ni(trien)<sup>2+</sup> and NiEDDA with attacking ligands. These steric requirements may cause dissociation of an arm of the coordinated ligand in order to accommodate the attacking ligand. bpy and phen are examples of this. Thus, in some instances, there may not be enough room for complete coordination of all sites on the metal.

Further, dissociation of the coordinated ligand may not be apparent from a consideration of only the formation rate constant. Dissociation of a chelate ring can be rapid enough to not influence the formation rate, as it is with EDDA, or it may be slower than a formation reaction, as it is with Ni(trien)<sup>2+</sup>. The stability of the ternary complex provides evidence for this.

Finally, the coordinated ligand appears to be able to decrease ring closure of the attacking ligand through distortion of the metal coordination sphere. This CAD effect may be revealed through isomerization of the complex, which, in some cases, can occur at a rate comparable to ring closure.

The complicated and variable nature of these effects has prompted the current study of other similar systems.

**Registry No.** en, 107-15-3; bpy, 366-18-7; phen, 66-71-7; gly, 56-40-6; sar, 107-97-1.

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## Chemical Reduction of Bis[bis(diphenylphosphino)ethane]rhodium(1+), [Rh(dppe)<sub>2</sub>]<sup>+</sup>. Characterization of Rh(dppe)<sub>2</sub><sup>0</sup> and Rh(dppe)<sub>2</sub><sup>-</sup>

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The reduction of bis[bis(diphenylphosphino)ethane]rhodium(1+), [Rh(dppe)<sub>2</sub>]<sup>+</sup>, has been reexamined, employing a purely chemical approach. The reduction is found to proceed in two discrete single-electron steps, with initial formation of Rh(dppe)<sub>2</sub><sup>0</sup>, followed by reduction to Rh(dppe)<sub>2</sub><sup>-</sup>. In dry benzene, Rh(dppe)<sub>2</sub><sup>+</sup> is reduced with 1 equiv of sodium naphthalenide (NaNp) to yield an extremely air-sensitive solution that shows a strong EPR signal with coupling to four equivalent phosphorus atoms, assigned to Rh(dppe)<sub>2</sub><sup>0</sup>. Further reduction with NaNp yields Rh(dppe)<sub>2</sub><sup>-</sup>, characterized by NMR and by chemical quenching experiments. The fully reduced species Rh(dppe)<sub>2</sub><sup>-</sup> reacts with proton sources by acid-base chemistry to produce RhH(dppe)<sub>2</sub>, while Rh(dppe)<sub>2</sub><sup>0</sup> is inert to reaction with MeOH, CH<sub>3</sub>CN, cumene, and triphenylmethane. A kinetic barrier to H atom transfer exists as shown by the lack of reaction between Rh(dppe)<sub>2</sub><sup>0</sup> and Ph<sub>3</sub>CH and between RhH(dppe)<sub>2</sub> and Ph<sub>3</sub>C· radical. Through variation of solvent and temperature conditions, the intermediate d<sup>9</sup> Rh(0) species is found to be in equilibrium with Rh(dppe)<sub>2</sub><sup>+</sup> and Rh(dppe)<sub>2</sub><sup>-</sup>. In toluene, the Rh(dppe)<sub>2</sub><sup>0</sup> species is found to be fluxional on the EPR time scale.

### Introduction

The electrochemical behavior of square-planar (dppe)<sub>2</sub> complexes (dppe = 1,2-bis(diphenylphosphino)ethane) of Rh and Ir has been studied by a number of research groups.<sup>1-4</sup> There is general agreement that the electrolysis of M(dppe)<sub>2</sub><sup>+</sup> in CH<sub>3</sub>CN results in the formation of the metal hydride species MH(dppe)<sub>2</sub> and the overall passage of two electrons.

Pilloni et al.<sup>1</sup> first proposed that the electrochemical reduction of the Rh(I) and Ir(I) complexes proceeds by a single two-electron reduction to the anion M(dppe)<sub>2</sub><sup>-</sup>, followed by proton abstraction from the solvent to give the hydride product. Later work by Ginsberg et al.<sup>2</sup> and Eisenberg et al.<sup>3</sup> contrasted this report. These

groups proposed that the path by which hydride is formed involves one-electron reduction of M(dppe)<sub>2</sub><sup>+</sup> to the d<sup>9</sup> intermediate M(dppe)<sub>2</sub><sup>0</sup>, followed by hydrogen atom abstraction from the solvent and subsequent reduction of the solvent radical. The viability of a d<sup>9</sup> M(0) species received support from reports by Keim<sup>5</sup> describing the electrochemical preparation of Rh(0) complexes and by Hanzlik<sup>6</sup> reporting one-electron reductions of other Rh(I) and Ir(I) chelates.

Although agreement exists on the formation of the metal hydride MH(dppe)<sub>2</sub> and the passage of two electrons in the electrolysis as determined by coulometry, there is fundamental disagreement on the mechanism of hydride formation. Pilloni et al.<sup>1,4</sup> favor a single two-electron EC mechanism, while Ginsberg et al.<sup>2</sup> and Eisenberg et al.<sup>3</sup> envision the reduction proceeding via an ECE mechanism with one-electron steps for hydride formation.

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