

1(17),2,13,15-tetraenenickel(II) Perchlorate,  $\text{Ni}(\text{CR} + 2\text{H})(\text{ClO}_4)_2$ .—This complex was prepared in two ways: (1) by air oxidation of  $\alpha$ -*meso*- $\text{Ni}(\text{CR} + 4\text{H})(\text{ClO}_4)_2$  and (2) by partial chemical reduction of  $\text{Ni}(\text{CR})(\text{ClO}_4)_2$ .

(1)  $\alpha$ -*meso*- $\text{Ni}(\text{CR} + 4\text{H})(\text{ClO}_4)_2$  (5 g) was dissolved in 250 ml of hot water. This solution was maintained at  $\sim 80^\circ$  for 20 hr while bubbling air through it. The solution was then evaporated to dryness on a rotary evaporator and the solid was then fractionally crystallized from methanol. The last crop of material contained  $\sim 0.3$  g of the desired product. This fraction was twice recrystallized from methanol. *Anal.* Calcd. for  $\text{NiC}_{15}\text{H}_{24}\text{N}_4(\text{ClO}_4)_2$ : C, 34.75; H, 4.63; N, 10.81. Found: C, 35.42; H, 4.72; N, 10.92.

(2)  $\text{Ni}(\text{CR})(\text{ClO}_4)_2$  (4 g) was dissolved in 50 ml of water at  $65^\circ$  and this solution was then treated with 80 mg of  $\text{NaBH}_4$  mixed with 20 mg of borax and heated for 30 min. The reaction mixture was then neutralized with perchloric acid and evaporated to near dryness. The resulting oil was fractionally crystallized from methanol, the more soluble fraction being the desired one. The yield was 25%. The infrared and nmr spectra of this compound are identical with those of the complex obtained by aerial oxidation of  $\text{Ni}(\text{CR} + 4\text{H})^{2+}$ .

Infrared spectra were obtained on Nujol mulls using a Perkin-Elmer 337 spectrophotometer. Nmr spectra were obtained on 10–15 wt % trifluoroacetic acid solutions using a Varian A-60 spectrometer. Chemical shift data are in ppm *vs.* internal TMS. Visible spectra were obtained on a Cary 14 spectrophotometer using 1-cm quartz cells. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

**Electrochemistry.**—Conventional polarography and cyclic voltammetry were performed with an Indiana Instrument and Chemical Corp. Controlled-Potential and Derivative Voltammeter, Model ORNL-1988A. A Hewlett-Packard/Moseley Division X-Y recorder was used to obtain permanent records of current-potential curves.

Electrochemical measurements in acetonitrile were carried out in a Vacuum Atmospheres Dri-Train with a nitrogen atmosphere. Experimental runs were made using a three-compartment H-type polarographic cell. A silver wire immersed in a 0.1 *M*  $\text{AgNO}_3$ - $\text{CH}_3\text{CN}$  solution was used as the reference electrode. A glass

capillary extending into the working electrode compartment made possible optimum placement of the working electrode with respect to the reference electrode. This minimized the solution resistance observed for the cyclic voltammetric studies. The rotating platinum wire electrode used was driven by a 600-rpm synchronous motor (Welch Scientific Co.). A stationary platinum wire electrode, 20 gauge and approximately 6 mm in length, was used for the cyclic voltammetry studies. Pretreatment involved washing with solvent and preanodizing at a small positive potential. Excellent reproducibility was obtained for a series of polarograms on the same compound. The platinum surface was periodically tested for constancy with standard compounds.

For the studies in methanol, a thermostated cylindrical cell served as the polarographic vessel and was connected through a salt bridge to an aqueous *sce* reference electrode. Nitrogen used to deaerate the solutions was obtained from Burdett Oxygen Co. (99.96% pure) and further purified by passing through a column packed with activated BASF catalyst to remove trace oxygen and then through a column packed with molecular sieves (5 Å) to remove the last traces of water. The dropping mercury electrode employed had a value of  $m^{2/3}t^{1/3} = 1.92 \text{ mg}^{2/3} \text{ sec}^{-1/3}$  at an applied potential of 0.0 V *vs.* *sce* and a mercury column height of 50 cm.

Spectroquality acetonitrile was obtained from Matheson Coleman and Bell (Spectroquality AX145) and was further purified for electrochemical use by the method described by Kuwana.<sup>15</sup> Polarographic grade tetraethylammonium perchlorate was purchased from Southwestern Analytical, Inc., and dried over  $\text{P}_4\text{O}_{10}$  *in vacuo* for 1 week before use. Methanol (Baker AC) was used without further purification.

Polarographic measurements were made, using millimolar concentrations of complex dissolved in the appropriate solvent, with 0.05 *M* tetraethylammonium perchlorate as supporting electrolyte.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
WAYNE STATE UNIVERSITY, DETROIT, MICHIGAN 48202

## Steric Effects in Chelation Kinetics. III. Reactions of Aquonickel(II) Ion with *N*-Alkyl-Substituted Ethylenediamines<sup>1</sup>

By T. S. TURAN AND D. B. RORABACHER\*<sup>2</sup>

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The formation and dissociation rates for the reaction of aquonickel(II) ion with several *N*-alkyl-substituted ethylenediamines have been studied at  $25^\circ$  and 0.1 *M* ionic strength over a pH range of 5.8–7.6 using stopped-flow techniques. The ligands studied (in order of decreasing formation rate constants) were *N,N*-diethyl-, *N,N'*-diethyl-, *N,N,N',N'*-tetramethyl-, *N,N,N',N'*-triethyl-, and *N,N,N',N'*-tetraethylethylenediamine. Protonation constants of the ligands and stability constants of the 1:1 Ni(II) complexes were also determined under the above conditions. Large differences in the formation rate constants are attributed to three contributing factors: steric hindrance by the substituted alkyl groups, changes in ligand conformation influenced by the alkyl groups, and (in the case of the unprotonated species) internal conjugate base effects. For highly substituted ligands, a shift in the rate-determining step to the point of second bond formation is implied. Differences in dissociation rate constants are assigned to a decreasing rate of second bond re-formation with increasing *N*-alkyl substitution and the possibility of a slight increase in the rates of bond ruptures as a result of steric strain. The pronounced differences in kinetic reactivity exhibited by Ni(II) ion toward primary, secondary, and tertiary nitrogen donor atoms are correlated to the reaction mechanisms of larger multidentate ligands.

### Introduction

In contrasting the kinetic behavior of unidentate and multidentate ligands, we have previously investi-

gated the kinetics of Ni(II) ion reacting with ammonia<sup>3</sup> and with higher polyamines<sup>4</sup> in aqueous solution. Whereas the rate constant for the former reaction has

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(2) To whom correspondence should be addressed.

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been shown to be in nearly perfect agreement with the predictions of the two-step "outer-sphere dissociative" mechanism,<sup>5,6</sup> the polyamine ligands appear to exhibit anomalously rapid formation rates.<sup>3</sup> To explain this rate enhancement, an *internal conjugate base* (ICB) mechanism has been postulated which is presumed to apply only to highly basic multidentate ligands.<sup>7</sup>

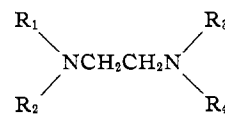
Although attempts at a quantitative comparison between ammonia and the related multidentate amines have been made,<sup>8</sup> a complete assignment of the differing kinetic behavior to the ICB effect must be considered somewhat tenuous due to a lack of kinetic information on the attendant steric and inductive effects resulting from alkyl substitution on the nitrogen donor atom. Since such effects are inherent in any multidentate ligand structure, we have undertaken a series of investigations designed to determine the magnitude of the kinetic consequences of such substitution.

In a recent study Rorabacher and Melendez-Cepeda reported the results of an investigation on the kinetics of Ni(II) ion reacting with a series of *N*-alkyl-substituted monoamines.<sup>8</sup> Although a distinct decrease in formation rate constant was observed paralleling increased alkyl substitution, the study was limited to monoamine ligands containing no more than three carbon atoms due to the apparent instability of unidentate complexes involving more highly substituted amines.

In the current study we have investigated the kinetics of aquonickel(II) ion reacting with a series of *N*-alkyl-substituted ethylenediamine ligands including *N,N*-diethylethylenediamine (*N,N*-DiEten), *N,N'*-diethylethylenediamine (*N,N'*-DiEten), *N,N,N'*-triethylethylenediamine (TriEten), *N,N,N',N'*-tetraethylethylenediamine (TeEten), and *N,N,N',N'*-tetramethylethylenediamine (TeMeen).

While the use of these bidentate ligands permits an examination of the kinetic effects of increased substitution on nitrogen donor atoms, interpretation of the data is complicated once again by the appearance of enhanced rates—attributed to ICB effects—and the possibility of variable conformations for the ligands. However, a comparison of rate constants for the unprotonated and monoprotonated ligand species, along with corresponding values estimated for ethylenediamine (en), reveals a uniform decrease in reactivity proceeding from primary to secondary to tertiary amine nitrogens. These results are correlated to previous mechanistic interpretations for the reactions of Ni(II) ion with the linear polyamines,<sup>4</sup> branched poly(amino alcohols),<sup>1,9</sup> and ligands related to ethylenediaminetetraacetate ion (EDTA).

The structural relationship between the ligands discussed in this work is illustrated as



en:  $R_1, R_2, R_3, R_4 = H$

TeMeen:  $R_1, R_2, R_3, R_4 = CH_3$

*N,N*-DiEten:  $R_1, R_2 = H; R_3, R_4 = CH_2CH_3$

*N,N'*-DiEten:  $R_1, R_3 = H; R_2, R_4 = CH_2CH_3$

TriEten:  $R_1 = H; R_2, R_3, R_4 = CH_2CH_3$

TeEten:  $R_1, R_2, R_3, R_4 = CH_2CH_3$

TKED:  $R_1, R_2, R_3, R_4 = CH_2CH_2OH$

THPED:  $R_1, R_2, R_3, R_4 = CH_2CH(OH)CH_3$

EDTA:  $R_1, R_2, R_3, R_4 = CH_2COO^-$

### Experimental Section

**Reagents.**—TeMeen, *N,N*-DiEten, and *N,N'*-DiEten were obtained from the J. T. Baker Chemical Co. while TeEten and TriEten were obtained from Eastman Organic Chemicals and Aldrich Chemical Co., respectively. These ligands were obtained as impure yellow liquids and purified by fractional distillation over BaO (*N,N*-DiEten, TriEten, and TeEten under vacuum to prevent decomposition). An F & M Model 700 gas chromatograph fitted with a 4 ft  $\times$  1/4 in. diameter column packed with 10% silicone rubber on 60–80 Chromosorb P was used to check the purity of the ligands. All distillations were found to be successful in eliminating detectable impurities. Solutions of the ligands were standardized by potentiometric acid–base titration. All solutions were prepared with doubly distilled deionized water.

Nickel perchlorate was prepared from NiCO<sub>3</sub> and HClO<sub>4</sub> and recrystallized; solutions were standardized by titration with EDTA. The sodium perchlorate (G. F. Smith Chemical Co.) used for ionic strength control was purified by dissolution in water, filtration, and recrystallization. All other chemicals were reagent grade and used without further purification.

**Kinetic and pH Measurements.**—The complex formation reactions of Ni(II) with the *N*-alkyl-substituted ethylenediamines were studied spectrophotometrically at 230 nm using either a Durrum stopped-flow spectrometer or an Aminco-Morrow stopped-flow attachment mounted on a Beckman DU-2 spectrophotometer as previously described.<sup>1</sup> All reactions were studied at 25.0  $\pm$  0.2° and 0.1 *M* ionic strength (NaClO<sub>4</sub>) with a borate–mannitol buffer used to maintain constant pH.

For all solutions, pH was measured using either a Radiometer Model TTT1c or a Sargent Model DR digital pH meter. Molar absorptivity values and stability constants were determined using a Beckman DU-2 spectrophotometer equipped with a 10-cm cell thermostated at 25.0  $\pm$  0.1°.

### Results

**Protonation Constants.**—The protonation constants of all ligands included in this work were determined by means of potentiometric titrations of acidified ligand solutions, thermostated at 25.0  $\pm$  0.1°, using standard NaOH solution as titrant. Mixed-mode constants, defined by the relationships

$$K_{H_1}^m = \frac{[HL^+]}{a_H[L]} \quad (1)$$

$$K_{H_2}^m = \frac{[H_2L^{2+}]}{a_H[HL^+]} \quad (2)$$

were then calculated using a modification of the Bjerrum  $\beta_H$  method as previously described.<sup>10</sup> The resultant values are listed in Table I along with available literature<sup>11–17</sup> values.

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(7) As originally postulated,<sup>3</sup> the ICB effect involves the formation of a hydrogen bond between a strongly basic donor atom (generally amine nitrogen) of a multidentate ligand and a water molecule coordinated to the metal ion resulting in a stabilization of the outer-sphere complex and a labilization of subsequent metal–water bond rupture, thereby permitting more rapid bonding of a second donor atom (from within the same ligand molecule) to the metal ion.

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TABLE I  
 MIXED-MODE PROTONATION CONSTANTS AND NICKEL COMPLEX STABILITY CONSTANTS  
 OF *N*-ALKYL-SUBSTITUTED ETHYLENEDIAMINES AT 25.0°

Ligand	Medium	Log $K_{H1}^m$	Log $K_{H2}^m$	Log $K_{NiL}$	Ref
<i>N,N</i> -DiEten	0.1 <i>M</i> NaClO <sub>4</sub>	9.90	6.85	4.57 (spectro) 4.80 (kinetic)	This work
	0.1 <i>M</i> NaClO <sub>4</sub>	9.98	6.79	...	11
	0.1 <i>M</i> KCl	10.02	7.07	...	12
<i>N,N'</i> -DiEten	0.1 <i>M</i> NaClO <sub>4</sub>	10.10	7.32	5.67 (spectro) 5.81 (kinetic)	This work
	0.1 <i>M</i> NaClO <sub>4</sub>	10.22	7.24	...	13
	0.5 <i>M</i> KNO <sub>3</sub>	10.46	7.70	5.62	14
	0.5 <i>M</i> KNO <sub>3</sub>	10.38	7.62	5.62	15
	0.1 <i>M</i> NaClO <sub>4</sub>	10.03	6.98	<3	This work
TriEten	0.1 <i>M</i> NaClO <sub>4</sub>	9.63	6.45	<1	This work
TeEten	0.1 <i>M</i> NaClO <sub>4</sub>	9.14	5.94	3.57 (spectro)	This work
TeMeen	0.1 <i>M</i> KNO <sub>3</sub>	9.14	5.90	...	16
	0.5 <i>M</i> KNO <sub>3</sub>	10.13	6.56	...	17
	?	9.34	6.26	4.1	15

**Stability Constants.**—With the possible exception of *N,N'*-DiEten, all complexes of these diamine ligands with Ni(II) ion were too weak to yield reliable stability constants using a titrimetric approach. Therefore, these constants were determined spectrophotometrically by measuring the absorbance of the nickel complex at 230 nm as a function of pH and solving simultaneously for the molar absorptivity value and the stability constant of the complex. The latter values are included in Table I.

**Kinetic Measurements.**—Under the conditions studied (pH 5.8–7.6) the kinetics of the complex formation reactions were found to obey the reversible mixed second- and first-order rate equation

$$-\frac{d[Ni^{2+}]}{dt} = k_f[Ni^{2+}][\Sigma L] - k_d[NiL^{2+}] \quad (3)$$

where  $k_f$  and  $k_d$  represent the observed formation and dissociation rate constants, respectively, and  $[\Sigma L]$  represents the total molar concentration of all species of uncomplexed ligand

$$[\Sigma L] = [L] + [HL^+] + [H_2L^{2+}] = C_L - [ML]$$

The resolution of the kinetic data was accomplished using the integrated form of eq 3 as previously described.<sup>9</sup> Simultaneous computer iteration to determine the best equilibrium concentrations consistent with the kinetic data made it possible to obtain useful data even for TeMeen under conditions of low pH where the reaction proceeded less than 1% toward completion.

The resulting values for  $k_f$  and  $k_d$  for the reactions with *N,N*-DiEten, *N,N'*-DiEten, and TeMeen are tabulated in Tables II–IV, respectively. All individual

 TABLE II  
 EXPERIMENTAL RATE CONSTANTS FOR THE REACTION  
 OF NICKEL ION WITH *N,N*-DiEten  
 (25.0°,  $\mu = 0.1 M$ ,  $[Ni^{2+}] = 5.32 \times 10^{-3} M$ )

pH	$10^3[N,N$ -DiEten],		$10^{-1}k_d$ , sec <sup>-1</sup>	pH	$10^3[N,N'$ -DiEten],		$10^{-1}k_d$ , sec <sup>-1</sup>
	<i>M</i>	$10^{-2}k_f$ , M <sup>-1</sup> sec <sup>-1</sup>			<i>M</i>	$10^{-2}k_f$ , M <sup>-1</sup> sec <sup>-1</sup>	
5.89	3.96	0.059	0.838	6.65	0.510	1.25	0.956
5.93	2.04	0.127	0.837	6.74	3.96	1.66	1.32
6.11 <sup>a</sup>	3.96	0.132	1.05	6.76	4.95	1.51	1.25
6.27	2.04	0.253	0.859	6.77	0.990	1.71	1.02
6.36 <sup>a</sup>	3.96	0.365	1.25	6.97	1.02	2.91	1.05
6.45	3.96	0.502	1.18	7.02	3.96	3.53	1.02
6.51	2.04	0.656	1.03	7.10	3.96	4.04	0.910
6.55 <sup>a</sup>	3.96	1.41	2.21	7.11	3.96	4.54	0.834
6.64	1.02	1.21	1.12	7.19	3.96	6.09	0.866
6.64	2.04	1.10	1.20	7.32	1.98	7.02	0.612
6.64 <sup>a</sup>	3.96	1.22	1.34				

<sup>a</sup>  $[Ni^{2+}] = 7.98 \times 10^{-3} M$ .

 TABLE III  
 EXPERIMENTAL RATE CONSTANTS FOR THE REACTION  
 OF NICKEL ION WITH *N,N'*-DiEten  
 (25.0°,  $\mu = 0.1 M$ ,  $[Ni^{2+}] = 1.064 \times 10^{-2} M$ )

pH	$10^3[N,N'$ -DiEten],		$10^3k_d$ , sec <sup>-1</sup>	pH	$10^3[N,N'$ -DiEten],		$10^3k_d$ , sec <sup>-1</sup>
	<i>M</i>	$k_f$ , M <sup>-1</sup> sec <sup>-1</sup>			<i>M</i>	$k_f$ , M <sup>-1</sup> sec <sup>-1</sup>	
5.81	4.31	0.0780	10.28	6.83 <sup>b</sup>	5.0	3.03	6.30
5.91	4.31	0.0903	9.42	6.90	2.16	3.98	6.58
6.03	4.31	0.180	9.68	6.97 <sup>a</sup>	4.31	4.47	6.57
6.17 <sup>a</sup>	2.16	0.348	9.46	6.97 <sup>a</sup>	1.08	5.05	5.47
6.27 <sup>a</sup>	2.16	0.498	9.47	6.98 <sup>a</sup>	0.539	5.13	5.05
6.34	4.31	0.653	9.63	7.04	2.16	5.66	5.08
6.47 <sup>a</sup>	2.16	1.25	9.27	7.29	2.16	10.7	3.72
6.66	4.31	1.99	9.08	7.60 <sup>a</sup>	2.16	21.4	1.34
6.82 <sup>a</sup>	2.16	3.43	6.99				

<sup>a</sup>  $[Ni^{2+}] = 5.33 \times 10^{-3} M$ . <sup>b</sup>  $[Ni^{2+}] = 5.67 \times 10^{-3} M$ .

 TABLE IV  
 EXPERIMENTAL RATE CONSTANTS FOR THE REACTION  
 OF NICKEL ION WITH TeMeen

Series I: 25.0°, $\mu = 0.1 M$ , $[Ni^{2+}] = 5.67 \times 10^{-3} M$				Series II: 25.0°, $\mu = 0.1 M$ , $[Ni^{2+}] = 1.064 \times 10^{-2} M$			
pH	$10^3[Te$ -Meen],		$k_d$ , sec <sup>-1</sup>	pH	$10^3[Te$ -Meen],		$k_d$ , sec <sup>-1</sup>
	<i>M</i>	$k_f$ , M <sup>-1</sup> sec <sup>-1</sup>			<i>M</i>	$k_f$ , M <sup>-1</sup> sec <sup>-1</sup>	
5.78	4.07	0.107	0.112	6.05	3.92	0.181	0.104
5.79	3.02	0.104	0.104	6.21 <sup>a</sup>	1.96	0.306	0.100
6.03	4.07	0.286	0.112	6.29 <sup>a</sup>	1.96	0.382	0.098
6.17	2.03	0.385	0.107	6.33	3.92	0.406	0.110
6.44	2.03	0.880	0.118	6.50 <sup>a</sup>	1.96	0.581	0.094
6.59	4.07	1.00	0.116	6.62	3.92	0.930	0.122
6.61	2.03	1.40	0.105	6.75	1.96	1.01	0.073
6.61	1.02	1.25	0.102	6.83 <sup>a</sup>	1.96	1.52	0.099
6.90	2.03	2.87	0.123	6.89	1.96	1.58	0.102
7.14	2.03	4.07	0.118	7.03	1.96	2.15	0.109
7.27	2.03	4.47	0.161	7.30	1.96	4.10	0.129
7.43	1.02	3.10	0.104				

<sup>a</sup>  $[Ni^{2+}] = 5.33 \times 10^{-3} M$ .

rate runs gave excellent integrated plots and, as expected, the formation rate constants increase in magnitude with increasing pH. In the singular case of TeMeen, two different series of kinetic runs, made at different times, yielded significantly different formation rate constant values at equivalent acidities. Although the results of the earlier study could not be reproduced, no cause could be established for this disagreement and the results of both series are reported in Table IV.

Since both the unprotonated and monoprotonated ligand species may react with Ni(II) eq 3 may be expanded to the form

$$-\frac{d[Ni^{2+}]}{dt} = k_{NiL}[Ni^{2+}][L] + k_{NiHL}[Ni^{2+}][HL^+] - k_{NiL}[NiL^{2+}] - k_{H^+NiL}[H^+][NiL^{2+}] \quad (4)$$

which, after combination with eq 3, yields

$$\frac{k_f[\Sigma L]}{[L]} = k_{Ni}^L + k_{Ni}^{HL}K_{H_1}^{m_0} \quad (5)$$

and

$$k_d = k^{NiL} + k_{H}^{NiL}[H^+] \quad (6)$$

Plots of eq 5 for *N,N*-DiEten, *N,N'*-DiEten, and TeMeen were linear over the entire pH range studied and the resolved formation rate constants thus obtained are listed in Table V.

TABLE V  
RESOLVED RATE CONSTANT VALUES FOR NICKEL(II)  
ION REACTIONS WITH *N*-ALKYL-SUBSTITUTED  
ETHYLENEDIAMINES (25.0°,  $\mu = 0.1 M$ )

Ligand	$k_{Ni}^L$ , $M^{-1} \text{ sec}^{-1}$	$k_{Ni}^{HL}$ , $M^{-1} \text{ sec}^{-1}$	$k_{NiL}$ , $\text{sec}^{-1}$	$k_{H}^{NiL}$ , $M^{-1} \text{ sec}^{-1}$
en	$\leq 4 \times 10^6$ <sup>a</sup>	$\sim 200$ <sup>a</sup>	0.005 <sup>b</sup>	...
<i>N,N</i> -DiEten	$3.4 \times 10^5$	123	5.4	$3.9 \times 10^7$
<i>N,N'</i> -DiEten	$9.7 \times 10^3$	8.0	0.015	$3.5 \times 10^5$
TriEten	<10	...	...	...
TeEten	$\sim 0$ (?) <sup>c</sup>	$\sim 0$ (?) <sup>c</sup>	...	...
TeMeen	$3.6 \times 10^2$ <sup>d</sup>	0.2	0.1 <sup>e</sup>	...

<sup>a</sup> D. B. Rorabacher and H. K. Stepien, unpublished results; J. C. Cassatt and R. G. Wilkins, *J. Amer. Chem. Soc.*, **90**, 6045 (1968), have reported an experimental value for  $k_{Ni}^{H_1}$  equal to  $6.2 \times 10^2 M^{-1} \text{ sec}^{-1}$  at 25° which appears to be too large since the contribution of unprotonated en to the total rate was not taken into account in resolving their data. <sup>b</sup> A. K. S. Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 3700 (1959). <sup>c</sup> No observable reaction (see text). <sup>d</sup> Average value obtained from series I ( $3.0 \times 10^2$ ) and series II ( $4.2 \times 10^2$ ). <sup>e</sup> Calculated from  $k_{Ni}^L$  and  $K_{NiL}$  values.

In resolving the dissociation rate constants using eq 6, excellent results were obtained for the *N,N'*-DiEten complex. For *N,N*-DiEten, however, only the data obtained at pH 6.75 and above were sufficiently reliable to be utilized. (At lower pH values the reaction did not proceed far enough to yield satisfactory  $k_d$  values.) The resulting value obtained for  $k_{NiL}$  is in excellent agreement with the values of  $k_{Ni}^L$  and  $K_{NiL}$ . In the case of TeMeen, the small extent of reaction observed resulted in dissociation rate data which were too erratic to be resolvable. Thus, the value for  $k_{NiL}$  given for this system in Table V is calculated from the formation rate constant,  $k_{Ni}^L$ , and the stability constant,  $K_{NiL}$ .

The stopped-flow kinetic study of Ni(II) reacting with TriEten proved unsuccessful since only a very small amount of reaction was detected and the resulting oscillographic traces were unreliable. Thus, it was only possible to place an upper limit on the formation rate constant for this system. Furthermore, there was some indication of a second reaction step but the data were not sufficiently precise to permit analysis of this behavior.

All attempts to observe complex formation between Ni(II) and TeEten were unsuccessful even at high reactant concentrations over time intervals as long as 1 month (more than  $10^5$  longer than the mean lifetimes observed for the other ligand reactions). The use of high temperatures only resulted in eventual decomposition of the ligand. Thus it is concluded that the formation of the Ni(TeEten)<sup>2+</sup> complex is thermodynamically unfavorable. Although it is inferred that the formation rate constant is very small, no limiting value can be established.

## Discussion

### Thermodynamic Evaluation of the Steric Effects.—

Although no previous comparative studies are to be found in the literature dealing definitively with the kinetic steric effects exhibited by the title ligands, several previous workers have made quantitative comparisons of their complex stability constants in attempting to assess the steric effects from a thermodynamic standpoint.<sup>12,14,15,18</sup> Thus, Leussing was able to conclude that inductive effects with these ligands were not significant while steric effects were exhibited more strongly with Ni(II) than with either Mn(II) or Zn(II).<sup>15</sup>

In a related approach, Basolo and Murmann determined values of the function  $\log K_{Ni}(\text{av})/\log K_{H_1}$ <sup>19</sup> for a series of *N*-monoalkyl<sup>18</sup> and *N,N'*-dialkylethylenediamines<sup>14</sup> and obtained a good correlation with the steric bulk of the substituents (Table VI). It should

TABLE VI  
THERMODYNAMIC STERIC EFFECTS AS A FUNCTION OF  
*N*-ALKYL AND *N,N'*-DIALKYL SUBSTITUTION OF  
ETHYLENEDIAMINE BASED ON LITERATURE  
VALUES (25°,  $\mu = 0.5 M$  (KNO<sub>3</sub>))

Substituent	$-\log K_{Ni}(\text{av})/\log K_{H_1}$		$-\log K_{NiL}/\log K_{H_1}$	
	N <sup>18</sup>	N,N' <sup>14</sup>	N	N,N'
H	0.63	0.63	0.75	0.75
Methyl	0.48	0.58	0.71	0.69
Ethyl	0.44	0.43	0.64	0.54
<i>n</i> -Propyl	0.43	0.34	0.64	0.54
<i>n</i> -Butyl	(0.47)	0.27	(0.65)	0.53
Isopropyl	0.27		0.49	

be noted that the foregoing function contains ligand-ligand steric interactions, arising within the 1:2 and 1:3 complexes,<sup>19</sup> as well as metal-ligand steric effects. The former interactions can be separated out, however, by utilizing only the stability constant for the 1:1 complex in this function, *i.e.*,  $\log K_{NiL}/\log K_{H_1}$ , as suggested in the monoamine study.<sup>8</sup>

When computed for Basolo and Murmann's data, the values of this latter function, as shown in Table VI, are seen to be considerably larger than those based on  $\log K_{Ni}(\text{av})$ . Furthermore, the decreasing trend with increasing chain length is seen to disappear for *n*-alkyl groups larger than ethyl, indicating that the increasing steric effects noted by Basolo and Murmann for these ligands are a result of ligand-ligand interactions only. Thus it appears that an increase in the chain length of *N*-substituted linear alkyl groups beyond two carbon atoms does not significantly affect metal-ligand interactions from either an equilibrium standpoint or (by correlation to other studies<sup>8</sup>) a kinetic standpoint. In combination with the observation from Table VI and the monoamine kinetic study that methyl groups exhibit less dramatic steric effects than ethyl groups, it is concluded that the latter substituents represent the optimal choice for a kinetic investigation of steric effects arising from increased *N*-substitution on the ethylenediamine moiety.

For comparative purposes, values for  $\log K_{NiL}/\log$

(18) F. Basolo and R. K. Murmann, *J. Amer. Chem. Soc.*, **74**, 5243 (1952).

(19) In this function  $\log K_{Ni}(\text{av})$  represents the average value of the logarithmic stability constants for the 1:1, 1:2, and 1:3 complexes and the use of this ratio presumes that the values for the first ligand protonation constant,  $K_{H_1}$ , are unaffected by steric effects and simply reflect the intrinsic basicities of the nitrogen donor atoms; *cf.* J. Bjerrum, *Chem. Rev.*, **46**, 381 (1950).

$K_{H1}$  calculated from the thermodynamic data obtained in this work are listed in Table VII. A continuing

TABLE VII  
THERMODYNAMIC STERIC EFFECTS CALCULATED FOR  
THE *N*-ALKYL-SUBSTITUTED ETHYLENEDIAMINES  
INCLUDED IN THIS WORK  
(25.0°,  $\mu = 0.1 M$  (NaClO<sub>4</sub>))

Ligand	Log $K_{NiL}$ / log $K_{H1}$	Ligand	Log $K_{NiL}$ / log $K_{H1}$
en	0.73 <sup>a</sup>	TeMeen	0.39
<i>N,N'</i> -DiEten	0.56 <sup>a</sup>	TriEten	<0.3
<i>N,N</i> -DiEten	0.46	TeEten	<0.1 <sup>b</sup>

<sup>a</sup> The small discrepancies between these values and the corresponding values in Table VI arise from the use of slightly different thermodynamic constants in the two studies. <sup>b</sup> This estimate is based on the inability to detect Ni(TeEten)<sup>2+</sup> spectrophotometrically from which it is concluded that the value of the complex stability constant,  $K_{NiL}$ , is less than 10.

dramatic decrease in this function is to be observed as the number of *N*-ethyl groups is increased.

**Specific Rate Equations.**—On the basis of earlier studies,<sup>4,6,20</sup> the nickel(II)–diamine reactions in aqueous solution are presumed to be bound in a stepwise fashion with the individual bonding steps being dissociative in nature.<sup>5</sup> On this basis the loss of a coordinated water molecule must precede the formation of each metal–donor atom bond and the short-lived nature of the five-coordinate intermediates dictates that the reactants must be adjacent at the time of metal–water bond rupture in order for reaction to occur.<sup>5</sup> Thus, the rate of initial bond formation is limited by the extent of ion pair (outer-sphere complex) formation.

Following the manner of Wilkins,<sup>6</sup> the reaction mechanism is represented schematically in Figure 1. As-

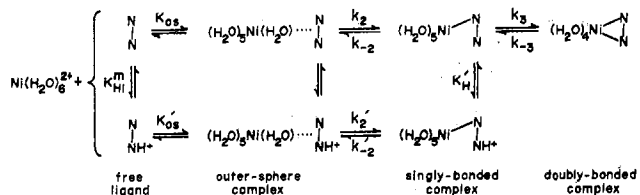


Figure 1.—Schematic representation of the reaction mechanism for aquonickel(II) ion reacting with a bidentate ligand such as the ethylenediamines. The diprotonated species is presumed to be unreactive.

suming that (i) outer-sphere complex formation and dissociation rates are much faster than the subsequent steps, (ii) the protonation equilibrium in the singly bonded complex ( $K_H'$ ) is rapidly established relative to the rate of nickel–nitrogen bond rupture ( $k_{-2}$ ), and (iii) the steady-state condition may be applied for the intermediates, the rate constants in eq 4 may be related to the stepwise rate constants as

$$k_{NiL} = \frac{K_{os}k_2k_3}{k_{-2} + k_3} \quad (7)$$

$$k_{NiHL} = \frac{K_{os}'k_2'k_3}{k_{-2}'K_H'[H^+] + k_3} \quad (8)$$

$$k^{NiL} = \frac{k_{-2}k_{-3}}{k_{-2} + k_3} \quad (9)$$

$$k_H^{NiL} = \frac{k_{-2}'k_{-3}K_H'}{k_{-2}'K_H'[H^+] + k_3} \quad (10)$$

where  $K_{os}$  represents the equilibrium constant for outer-sphere complex formation and  $K_H'$  is defined as the protonation constant for the singly bonded intermediate Ni–L<sup>2+</sup>

$$K_H' = \frac{[NiHL^{3+}]}{[H^+][Ni-L^{2+}]} \quad (11)$$

Under conditions where the first bond formation ( $K_{os}k_2$  or  $K_{os}'k_2'$ ) represents the rate-determining step, *i.e.*,  $k_{-2} \ll k_3 \gg k_{-2}'K_H'[H^+]$ , eq 7–10 simplify to

$$k_{NiL} = K_{os}k_2 \quad (7a)$$

$$k_{NiHL} = K_{os}'k_2' \quad (8a)$$

$$k^{NiL} = k_{-2}k_{-3}/k_3 \quad (9a)$$

$$k_H^{NiL} = K_H'k_{-2}'k_{-3}/k_3 \quad (10a)$$

where  $K_3 = k_3/k_{-3}$  represents the equilibrium constant for the formation of the second coordinate bond. (In the context of the dissociative mechanism, the rate constants  $k_2$  and  $k_2'$  represent the rate constant for metal–water bond rupture,  $k^{Ni-H_2O}$ , modified by any applicable statistical factors, such as those associated with steric hindrance.)

In the earlier polyamine study<sup>4</sup> it was concluded that, for aquonickel(II) ion reacting with the straight-chain polyamines,  $k_3 \approx 100k_{-2}$  and  $K_H \approx 10^6$ – $10^7$ ,<sup>5</sup> so that eq 7a–10a might be presumed to apply in the pH range included in this study. It was further suggested at that time, however, that “the substitution of groups on the polyamine chain could slow the formation rate of successive bonds by interfering with the rotation of the ligand molecule or hindering the closeness of approach to the metal ion such that later steps would become rate determining.” Although no previous examples of such behavior have been reported for non-cyclic ligands containing only strong donor atoms (except for those forming larger chelate rings),<sup>6</sup> sterically induced alterations in the values of  $k_{-2}$  and  $k_3$  could invalidate the use of eq 7a–10a for ligands more substituted than *N,N'*-DiEten (which corresponds structurally to the straight-chain polyamines).

As a first approximation, it has been assumed in the ensuing discussion that eq 7a–10a are applicable for the systems included in this study. The values of  $k_{-2}$ ,  $k_3$ , and  $K_H'$  thus generated are then used to test this assumption. For systems where these equations are not applicable, the values generated will, of course, be quantitatively incorrect, but the qualitative trends observed should still be valid.

**Steric Effects of Dissociation Kinetics.**—Previous investigations on the dissociation kinetics of *N*-alkyl-substituted ethylenediamine complexes of Ni(II) have been carried out by Ahmed and Wilkins in strongly acidic solutions.<sup>20–22</sup> Under these conditions  $k_3 < k_{-2}'K_H'[H^+]$  so that eq 10 simplifies to

$$k_H^{NiL} = k_{-3}/[H^+] \quad (10b)$$

where the  $[H^+]$  quantity cancels with the  $[H^+]$  quantity in the corresponding term in eq 4. Thus, the observed dissociation rate constant,  $k_d$ , becomes first order and is equal to  $k_{-3}$ . In this manner these authors obtained  $k_{-3}$  values for the Ni(II) complexes with en and TeMeen of 0.14 and 0.15, respectively, and concluded that *N*-substitution on en does not affect the

(21) A. K. S. Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 2895 (1960).

(22) R. G. Wilkins, *ibid.*, 4475 (1962).

(20) See ref b of Table V.

rate of dissociation but must be manifested only in the formation rate constants.<sup>22</sup>

Under the less acidic conditions used in this study, however, the values of the dissociation rate constant,  $k^{\text{NiL}}$ , observed for the en and TeMeen complexes differ by a factor of 20 and the values for the other diamine complexes also vary (Table V). Possible explanations for this behavior are examined below.

**Evidence for Unidentate Behavior by  $N,N$ -DiEten.**—Correlated to the apparent failure of the tertiary nitrogens in TeEten to coordinate with Ni(II) to a significant extent is the observation that the  $k^{\text{NiL}}$  value for Ni( $N,N$ -DiEten)<sup>2+</sup> (Table V) is essentially identical with the corresponding values for the 1:1 Ni(II) complexes with ammonia<sup>3</sup> and other unidentate amines.<sup>8</sup> This indicates that  $N,N$ -DiEten acts only as a unidentate ligand<sup>23</sup> although, allowing for uncertainties in the  $k^{\text{NiL}}$  values, a weak interaction between Ni(II) and the tertiary nitrogen of this ligand cannot be ruled out on this basis alone. (In fact, the reported dissociation rate constant for the Ni(II) complex with the unidentate 2-aminoethyltrimethylammonium ion has been reported to be 40 sec<sup>-1</sup> at 25° in highly acidic solutions<sup>24</sup> and it could be argued that Ni( $N,N$ -DiEten)<sup>2+</sup> should exhibit a similar value if interactions between Ni(II) and the tertiary nitrogen atom were negligible.)

Further support for the premise that  $N,N$ -DiEten acts only as a unidentate ligand, however, is obtained by comparing the  $k^{\text{NiL}}$  values for Ni(en)<sup>2+</sup> and Ni( $N,N$ -DiEten)<sup>2+</sup> complexes, where any steric strain associated with the  $k_{-2}$  values should be nearly equivalent.<sup>8</sup> The ratio of these values is  $1 \times 10^3$  (or  $2 \times 10^3$  if normalized by the appropriate statistical factor) which is almost exactly equal to the increase in stability constant values observed for nickel(II)-polyamine complexes with the addition of each chelate ring.<sup>4</sup> Thus it is apparent that the dissociation of Ni(en)<sup>2+</sup> involves breaking an additional chelate ring relative to the dissociation of Ni( $N,N$ -DiEten)<sup>2+</sup>, leading to the conclusion that the latter complex essentially contains a single coordinate bond (*i.e.*,  $K_3 \leq 1$ ). These arguments, coupled with the observations on TeEten, suggest the more generalized conclusion that *terminal tertiary nitrogen donor atoms do not form thermodynamically stable bonds with Ni(II) in aqueous solution* if the substituted groups are two or more carbons in length. (The designation *terminal* is used to signify a donor atom which does not contain more than one linkage to other donor atoms; thus the tertiary nitrogen donor atoms in EDTA, TKED, and THPED are not *terminal*.)

**Steric Effects upon Second-Bond Formation.**—The results of the monoamine study<sup>8</sup> indicate that  $k_{-2}$  values for all the ligands studied should be roughly equivalent (*cf.* ref 6). Assuming the unidenticity of  $N,N$ -DiEten, a comparison of the  $k^{\text{NiL}}$  value for this system with the corresponding values for the remaining ligand systems can be used to generate  $K_3$  values for all the complexes as indicated in the preceding paragraph. The resulting estimates for en,  $N,N'$ -DiEten, and TeMeen are  $1 \times 10^3$ , 360, and 54, respectively.

(23) In agreement with this observation, Jones, Billo, and Margerum were unable to determine the rate of NH<sub>3</sub> exchange on the Ni( $N,N$ -DiEten)<sup>2+</sup> complex due to the rapid competing exchange of  $N,N$ -DiEten: J. P. Jones, E. J. Billo, and D. W. Margerum, *J. Amer. Chem. Soc.*, **92**, 1875 (1970).

(24) G. A. Melsos and R. G. Wilkins, *J. Chem. Soc.*, 4208 (1962).

Even if  $N,N$ -DiEten were not unidentate, the trend in  $K_3$  values is valid, *i.e.*, en >  $N,N'$ -DiEten > TeMeen  $\gg$   $N,N$ -DiEten. This yields the conclusion that *increasing  $N$ -alkyl substitution leads to decreasing  $K_3$  values*.

The apparent equivalence of  $k_{-3}$  values observed for the en and TeMeen complexes by Ahmed and Wilkins coupled with the trend in  $K_3$  values implies a large steric factor for TeMeen relative to en in the formation of a second nickel-nitrogen bond, the estimated  $k_3$  values being 8.1 and  $1.4 \times 10^2$  sec<sup>-1</sup>, respectively. (The latter value compares favorably to previous estimates of  $2 \times 10^2$ <sup>4</sup> and  $9 \times 10^2$ .<sup>6</sup>) For  $N,N'$ -DiEten a  $k_3$  value of 54 sec<sup>-1</sup> is inferred if  $k_{-3}$  remains constant.

From a theoretical standpoint, the maximum value of  $k_3$  should be limited by the rate constant for Ni(II)-H<sub>2</sub>O bond rupture in the singly bonded intermediate,  $k_2^{\text{Ni-H}_2\text{O}}$ . Interpolating from the data of Jones, Billo, and Margerum,<sup>23</sup> the rate constant for metal-water bond rupture in a species containing one nitrogen donor atom in the inner coordination sphere should be approximately  $6 \times 10^4$  sec<sup>-1</sup>. If the smaller values actually observed for  $k_3$  were attributed to a rotational barrier associated with bringing the second nitrogen into a bonding position,<sup>4,20</sup> the same rotational barrier should also apply to the corresponding  $k_{-3}$  values.<sup>6</sup> As a result, this factor would cancel out and could not account for the apparent decrease in the  $K_3$  equilibrium values with increasing  $N$ -alkyl substitution. Thus, the variability in the  $k_3$  (and  $K_3$ ) values is attributed to either or both of the following effects: (1) The apparent trend in  $k_3$  values could arise from a statistical factor relating to steric blocking by the  $N$ -alkyl groups toward second-bond formation. (2) The apparent trend in  $k_3$  values could represent rotational barrier effects upon the second-bond formation process. In order to account for the trend in  $K_3$  values and the apparent constancy of  $k_{-3}$ , however, it would then have to be assumed that the corresponding rotational barrier effects upon  $k_{-3}$  are exactly compensated by an increase in the rate of nickel-nitrogen bond rupture as a result of steric strain caused by increasing  $N$ -alkyl substitution. Based on the results obtained with the unidentate amines, indicating that nickel-nitrogen bond rupture is little affected by  $N$ -alkyl substitution,<sup>8</sup> the first effect is assumed to be the greater. However, a definitive choice as to the actual source of the apparent differences in  $k_3$  values cannot be made solely on the basis of the information available.

**Sterically Induced Shift in the Rate-Determining Step.**—Based on the foregoing estimates and the results from the earlier polyamine study, the assumption that the first-bond formation is rate determining for the acid-independent path appears to be valid for the en and  $N,N'$ -DiEten complexes. For the TeMeen complex, estimates of  $k_{-2} \approx 5$  or  $10$  sec<sup>-1</sup><sup>3,8</sup> and  $k_3 \approx 8$  sec<sup>-1</sup> indicate that this system is at the crossover point and *a shift in the rate-determining step to the point of second-bond formation is inferred for more highly substituted diamines*. This conclusion is consistent with the qualitative kinetic observations on the TriEten system where a two-step reaction was indicated.

For the acid-dependent path, the position of the rate-determining step is pH dependent being influenced by the product  $K_{\text{H}}[\text{H}^+]$ . Assuming unidenticity for  $N,N$ -DiEten, the  $k_{\text{H}}^{\text{NiL}}$  value for this system may be

equated to  $K_H'k_{-2}'$  yielding  $K_H' = 10^6$ – $10^{6.9}$  (in good agreement with corresponding estimates for the polyamines<sup>4</sup>) depending on the value assumed for  $k_{-2}'$ . This indicates that  $K_H'[H^+]$  is in the range of 1–10 for the lowest pH values included in this study leading to the conclusion that the rate-determining step is still at the point of the first-bond formation for en and *N,N'*-DiEten but may have shifted to the point of second-bond formation for TeMeen, at least in the lower part of the pH range studied.

**Steric Effects on First-Bond Formation.**—Assuming that the rate-determining step occurs at the point of first-bond formation (a premise which may not be valid for TeMeen), the relative steric effects upon  $k_2$  and  $k_2'$  can be estimated from the experimental formation rate constants using eq 7a and 8a. Theoretical values of  $K_{os}$  and  $K_{os}'$  can be calculated from the equation<sup>8,9</sup>

$$K_{os} = \frac{4}{3} \pi a^3 N_A \times 10^{-3} \exp \left\{ \frac{Z_1 Z_2 e_0^2}{a' D k T} - \frac{Z_1 Z_2 e_0^2 \kappa}{D k T (1 + \kappa a')} \right\} \quad (12)$$

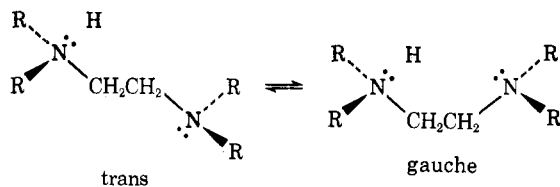
where

$$\kappa = \left( \frac{8 \pi N_A e_0^2 \mu}{1000 D k T} \right)^{1/2} \quad (13)$$

(for  $K_{os}$ ,  $Z_2 = 0$ ; for  $K_{os}'$ ,  $Z_2 = +1$ ). In these expressions  $\mu$  represents the ionic strength of the reaction solution and the other terms have been previously defined.<sup>3,6,9</sup>

In the current study several complicating factors affect such calculations. As noted earlier, an accelerative ICB effect has been proposed for the unprotonated diamine ligands which is presumed to increase the value of  $K_{os}$  (and  $k^{Ni-H_2O}$ ) relative to the theoretical value.<sup>3</sup> The relative contributions of the opposing ICB and steric effects incurred with the unprotonated species cannot be assessed at the present time.

For the monoprotonated ligand species, the ICB effect should be nonexistent<sup>1,9</sup> but a tendency for the proton to be shared between the two nitrogen donor atoms<sup>25</sup> (perhaps through a bridging water molecule) could result in a net conformational shift from the extended (trans) to a folded (gauche) conformation



The anticipated result would be an apparent increase in the steric hindrance exhibited by the monoprotonated ligand relative to the corresponding unprotonated species. Moreover, molecular models indicate that the trans ligand conformation of the diamines becomes less favorable as the extent of *N*-alkyl substitution increases due to increased *back-side* crowding, an effect which appears to be particularly severe for diamines substituted on both nitrogen donor atoms.

Recognizing that the applicable value for  $a'$  (the electrostatic repulsive distance in the reactive outer-

sphere complex<sup>9</sup>) should decrease as the conformational equilibrium shifts toward the gauche form, the use of a constant reference  $a'$  value in eq 12 permits an estimation of relative metal–ligand steric effects which include the relative electrostatic factors.

Using estimates of  $a$  and  $a'$  equal to 4 and 8 Å, respectively (representing the trans conformation), a  $K_{os}'$  value equal to 0.062 is calculated for 25° and 0.1 *M* ionic strength. Substituting this quantity into eq 8a and using a reference value of  $k_2' = k^{Ni-H_2O} = 2.7 \times 10^4 \text{ sec}^{-1}$ <sup>26</sup> yields a theoretical value for  $k_{Ni}^{HL}$  equal to  $1.7 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ .

Assigning this value to the reference  $k_0$  constant in the so-called organic substituent function<sup>1,3,9</sup>

$$E_s = \log (k/k_0) \quad (14)$$

the relative steric effects associated with the formation rate constants for the monoprotonated ligands may be estimated as listed in Table VIII.

TABLE VIII  
APPARENT STERIC FACTORS FOR AQUONICKEL(II)  
ION REACTING WITH *N*-ALKYL SUBSTITUTED  
ETHYLENEDIAMINES (25°,  $\mu = 0.1 \text{ M}$ )

Ligand	Log $k_{Ni}^{HL}$		$E_s$
	Theoret	Exptl	
Hen <sup>+</sup>	3.2	2.3	-0.9
H( <i>N,N</i> -DiEten) <sup>+</sup>	3.2	2.1	-1.1
H( <i>N,N'</i> -DiEten) <sup>+</sup>	3.2	0.9	-2.3
H(TeMeen) <sup>+</sup>	3.2	0.7	-3.9
en	3.9	5.6	1.7
<i>N,N</i> -DiEten	3.6 <sup>a</sup>	5.5	1.9
<i>N,N'</i> -DiEten	3.9	4.0	0.1
TeMeen	3.9	2.6	-1.3

<sup>a</sup> Only one nitrogen donor atom presumed reactive.

The 8-fold decrease in formation rate constant indicated by the  $E_s$  value for Hen<sup>+</sup> is in good agreement with the 5-fold and 7.5-fold decreases noted earlier for ethylamine and isopropylamine, respectively.<sup>3</sup> This implies that conformational changes induced by proton sharing are minimal for this ligand. Of additional special interest is the  $E_s$  value observed for H(*N,N*-DiEten)<sup>+</sup>. Despite the substitution of two ethyl groups on one nitrogen donor atom, this species reacts nearly as rapidly as Hen<sup>+</sup>. Furthermore, based on the previous conclusions regarding the nonreactivity of the tertiary nitrogen atom, it is concluded that only that isomer of H(*N,N*-DiEten)<sup>+</sup> which involves protonation on this donor atom can be significantly reactive. Thus, by correlation to Hen<sup>+</sup> it is inferred that *alkyl substitution at sites three or more atoms removed from the donor atom undergoing coordinate-bond formation has little effect upon the ligand reactivity*. This conclusion is consistent with the results of the monoamine study<sup>8</sup> and the conclusions reached earlier based on the comparison of equilibrium constants (Table VI).

To permit a relative comparison of the rate behavior exhibited by the unprotonated ligands, a theoretical model has been chosen in which each nitrogen on a diamine is regarded as an independent entity.<sup>9</sup> Thus, using the same parameters as applied earlier ( $a = 4$  Å,  $k^{Ni-H_2O} = 2.7 \times 10^4 \text{ sec}^{-1}$ ), a theoretical rate constant of  $8 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$  is calculated for  $k_{Ni}^L$  at 25°, *i.e.*, twice the value for Ni–NH<sub>3</sub>.<sup>3,8</sup> (Based on the earlier assumption that the tertiary nitrogen of

*N,N*-DiEten does not participate in initial bond formation, a lower theoretical rate constant value of  $4 \times 10^8 M^{-1} \text{sec}^{-1}$  is chosen for this ligand.)

Substituting these theoretical values into eq 14, substituent effects have been calculated for the unprotonated ligand species and tabulated in Table VIII. From this comparison it is immediately apparent that the rate constants for Ni(II) reacting with en and *N,N*-DiEten are much larger than the theoretical values. As discussed earlier, this rate enhancement is ascribed to an ICB effect. In the case of *N,N*-DiEten, this indicates that a sterically hindered nitrogen donor atom can promote the ICB mechanism even if it is too sterically blocked to bond significantly. In fact, assuming that steric effects cause an approximate 8-fold decrease in the formation rates of Ni(en)<sup>2+</sup> and Ni(*N,N*-DiEten)<sup>2+</sup>, the rate enhancements for these two ligands must be about 500-fold.

### Conclusions

From the combined results of this study and the previous study on *N*-alkyl-substituted monoamines,<sup>8</sup> a consistent trend emerges of decreasing nitrogen donor atom reactivity with increasing alkyl substitution. In the earlier study it was shown that ethyl substitution reduced the reactivity of ammonia by 5-fold at 25°. As inferred from the kinetic data for *N,N'*-DiEten (and the previous failure to observe a reaction between Ni(II) and diethylamine<sup>8</sup>), the substitution of a second ethyl group causes an additional decrease in nitrogen donor atom reactivity of 10- to 50-fold. The further decrease in reactivity resulting from substitution by a third ethyl group on a nitrogen donor atom appears to be extremely large as evidenced by the failure to observe any reaction between Ni(II) and tertiary nitrogen donor atoms in *N,N*-DiEten and TeEten. Thus the relative reactivities are clearly established for ethyl substitution:  $\text{NH}_3 > \text{RNH}_2 > \text{R}_2\text{NH} \gg \text{R}_3\text{N}$ .

A similar, but less distinct, trend is observed for methyl substitution, the Ni(II) formation rate constants for NH<sub>3</sub>, methylamine, and dimethylamine being in the ratio 14:4:1 at 25°,<sup>8</sup> and the slow, but observable, reaction of TeMeen with Ni(II) makes it apparent that trimethylamine would fit into this pattern.

Arguments presented in this paper support the contention that the rate of second-bond formation to complete a chelate ring is similarly decreased in the case

of the diamines by increasing *N*-alkyl substitution. The ultimate result is an apparent shift in the rate-determining step from the first- to the second-bond formation when the substituents become sufficiently large.

Based on the implications of the foregoing relative reactivities of substituted nitrogen donor atoms, several conclusions of mechanistic significance can be formulated governing the coordination reactions of large multidentate ligands. (1) In linear multidentate ligands such as the straight-chain polyamines, the terminal (primary) donor atoms are much more reactive than the internal (secondary) donor atoms to the extent that the reaction path involving first-coordinate-bond formation with a terminal donor atom represents the predominant reaction route. (2) For branched multidentate ligands such as EDTA and analogous ligands involving both primary and tertiary donor atoms, the reaction path involving first-coordinate-bond formation to a primary (terminal) donor atom predominates to such an extent that it represents the only kinetically significant route to the final complex ion even when the terminal donor atoms are so weak that the rate-determining step is shifted to the point of second-coordinate-bond formation.<sup>1,9</sup> (3) Extrapolation of these conclusions to ligands involving a high degree of steric hindrance, such as the macrocyclic ligands, suggests that these species will be very slow to react and, considering the large potential energy barriers to internal rotation, will probably involve a shift in the rate-determining step to the point of second bond formation even when all donor atoms may be classified as "strong." This conclusion is at least qualitatively upheld by experimental studies.<sup>27-29</sup>

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