(1.50 mmol) was loaded into an addition funnel. The funnel was placed on the reaction flask and the nickel complex was quickly washed into the rapidly stirred slurry with 10 ml of THF. A deep red-orange solution formed. The mixture was stirred at room temperature for 1 hr. The flask was opened to the air and stirring was continued for 12 hr. The solution was filtered and stripped onto ~1 g of silica gel. This was mounted on a 1.25 in. × 8 in. column and eluted with hexane–CH_2Cl_2. The one orange band that eluted was identified by ^1H and ^{11}B nmr spectra as 0.068 g of pure II (0.27 mmol, 18%). Washing the column with CH_3CN gave 0.319 g of a red compound identified as $[(\eta\text{-}C_5H_5)_2Ni]^+B_9CH_{10}^-$.

Isomerization of $(\eta\text{-}C_5H_5)Ni(\eta\text{-}7\text{-}B_{10}CH_{11})$. In a typical rearrangement, 0.177 g of $(\eta\text{-}C_5H_5)Ni(\eta\text{-}7\text{-}B_{10}CH_{11})$ (II) (0.693 mmol) was weighed into a 10-ml Pyrex flask. This was fitted to a 12 mm × 500 mm Vycor tube attached to a vacuum line. A 200-mm segment of the lower portion of this tube was wrapped with asbestos insulation and nichrome heating wire. The system was evacuated (10^{-5} mm) and the heated section was raised to 450° (monitored by a chromel-alumel thermocouple). The Pyrex bulb was slowly heated to ~200° with an air heat gun to sublime II slowly into the hot zone. The volatile products collected on the cool unwrapped upper portion of the Vycor tube. After cooling, the system was filled with N_2 and opened; the products were washed out with CH_2Cl_2. Filtration collected some black metallic flakes (Ni metal). The orange filtrate was stripped unto 1 g of silica gel and eluted on a 1 in. × 12 in. silica gel column using hexane–CH_2Cl_2.

Three products eluted. The first band (R_f 73, R_f(hexane) 100) was recrystallized from hexane–CH_2Cl_2 to give 0.057 g (0.223 mmol, 32%) of long yellow needles of $(\eta\text{-}C_5H_5)Ni(\eta\text{-}1\text{-}B_{10}CH_{11})$ (IV). The second band (R_f 54) was recrystallized from hexane–CH_2Cl_2 to give 0.089 g (0.349 mmol, 50%) of yellow-orange plates of $(\eta\text{-}C_5H_5)Ni(\eta\text{-}2\text{-}B_{10}CH_{11})$ (III). The third band (R_f 23) yielded 0.004 g (0.015 mmol, 2%) of orange crystals identified as unchanged II. Total recovery was 84%. Other runs are given in Table V.

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Registry No. I, 51329-55-6; II, 51329-56-7; III, 51329-57-8; IV, 51329-58-9; $[(\eta\text{-}C_5H_5)_2Ni]^+B_9CH_{10}^-$, 51518-87-7; $CsB_{10}CH_{13}$, 51391-30-1; $B_{10}H_{12}CN(CH_3)_3$, 31117-16-5; $NiBr_2\cdot 2C_2H_4(OCH_3)_2$, 18346-62-8; $Na_3B_{10}CH_{11}$, 51391-29-8; $[(\eta\text{-}C_5H_5)_3Ni_2]^+BF_4^-$, 37298-59-2.

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Steric Constraints in Coordination Reactions. Kinetic Study of the Reaction of Aquonickel(II) with *N*-Methyl-Substituted Ethylenediamines

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The formation and dissociation rates of the 1:1 complexation reactions of aquonickel(II) ion with *N,N*-dimethylethylenediamine, *N,N'*-dimethylethylenediamine, and *N,N,N'*-trimethylethylenediamine have been investigated at 25.0° and 0.1 *M* ionic strength over a pH range of 5.7–7.6 using stopped-flow kinetic techniques. Protonation constants of the ligands and the 1:1 stability constants of the Ni(II) complexes were also determined. Formation reactions in all cases were first order in Ni(II) and in ligand. Steric effects superimposed upon internal conjugate base rate enhancements are seen for the reactions with unprotonated ligands. Evidence for the presence of steric constraints in dissociation rate steps is also presented. Tentative estimates of the magnitude of internal conjugate base effects are made and presented in graphical form.

Introduction

The general features of the octahedral complexation reactions of aquometal ions with a wide variety of ligands have been thoroughly studied[1-3] and are well known. In particular, hexaaquonickel(II) has been the subject of intensive study in recent years.[4,5] It has become apparent and is generally accepted that a dissociative mechanism, as proposed by Eigen,[6] involving a rapid diffusion-controlled association of reactants to form an "outer-sphere" complex followed by the rate-determining step of metal–water bond rupture, is the mechanistic pathway for reactions of nickel(II) with most ligands. However, recent studies of the reactions of Ni(II) ion with alkylamines[7] and *N*-alkyl-substituted ethylenediamines[8] have shown that steric constraints exert a pronounced rate-depression effect on the formation rate constants.

Other ligands such as *N,N,N',N'*-tetrakis(2-hydroxyethyl)ethylenediamine (TKED) and *N,N,N',N'*-tetrakis(2-hydroxypropyl)ethylenediamine (THPED)[9,10] and β-alanine[11] react anomalously slowly with Ni(II) and Co(II). These results have been rationalized by assuming that the rate-determining step in the reaction mechanism is shifted to the loss of a second water molecule. In these reactions, "sterically controlled substitution" may occur when steric constraints block "normal substitution"[4] or when chelate ring closure is sufficiently slow so as to become the rate-determining step. In studies with highly basic N-substituted diamines,[8,9] an internal conjugate base (ICB) mechanism has been postulated[12] to explain anomalously rapid reaction rates which are ap-

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parently superimposed on steric factors. ICB rate enhancements have also been observed in the formation reactions of Ni(II) ion with a variety of multidentate ligands including 2-(2-aminoethylpyridine),[13] 2-aminomethylpyridine,[14] *N,N'*-bis(2-picoly)ethylenediamine (BPEDA), and *N,N'*-dibenzylethylenediamine (DBEDA)[15] and the protonated polyamine Htrien$^+$.[16]

From these studies it is evident that ICB rate enhancements and sterically caused rate depressions occur simultaneously in appropriate ligands and that the mechanistic details of such substitution reactions are still unclear. The present study was undertaken in an attempt to unravel further the intimate mechanistic details of combined ICB and steric effects. The previous studies, cited above, have involved ligands which were quite sterically hindered thus obscuring the absolute magnitudes of the ICB rate enhancements. In reactions with aquonickel(II) ion, the ligands chosen for this work, *N,N*-dimethylethylenediamine (*N,N*-DiMeen), *N,N'*-dimethylethylenediamine (*N,N'*-DiMeen), and *N,N,N'*-trimethylethylenediamine (TriMeen) are expected to have more modest steric constraints associated with their formation reactions, thus allowing ICB factors to be more rigorously evaluated.

This study was also undertaken to learn more about the conformational effects postulated to arise from proton sharing in monoprotonated ethylenediamines[8] and the relationship of these effects to steric constraints and the reaction mechanism. Furthermore, questions regarding the existence of steric influence in dissociation rate constants, arising from the previous study of *N*-alkyl-substituted ethylenediamines,[8] are explored. Therefore, the formation and dissociation rates of aquonickel(II) reacting with the title ligands were investigated by stopped-flow kinetic techniques and are reported and compared to those of other ligands.

Experimental Section

Reagents. TriMeen, *N,N*-DiMeen, and *N,N'*-DiMeen were obtained from the Aldrich Chemical Co. The ligands were obtained as impure yellow liquids and purified by vacuum fractional distillation over BaO. A Beckman GC-2A gas chromatograph fitted with a 6 ft × 1/4 in. diameter column packed with 30% Silicone 200 on 30–60 mesh Chromasorb W was used to check the purity of the ligands. The distillations were found to be successful in eliminating all but trace amounts of impurities. Aqueous solutions of the ligands were standardized by acid–base potentiometric titration.

Solutions of sodium perchlorate (G. F. Smith Chemical Co.) used for ionic strength control were filtered before use but not further purified. Nickel perchlorate (G. F. Smith Chemical Co.) was purified by dissolution in water and filtration and then was twice recrystallized from aqueous solution. The crystals were washed with reagent grade ether and dried in an oven at 80°. Solutions of nickel perchlorate were standardized by titration with EDTA at pH 10 using Murexide indicator.[17] All other chemicals were reagent grade and used without further purification. All solutions were prepared with doubly distilled water.

Kinetic, Spectrophotometric, and pH Measurements. The Ni(II) complex formation reactions were followed spectrophotometrically at 240 nm using the stopped-flow technique. An Aminco-Morrow stopped-flow mixing chamber was mounted in place of the cell compartment on a Beckman DU-2 spectrophotometer. The output from an R-136 photomultiplier mounted on the stopped-flow apparatus was interfaced with an Aminco kinetic photometer and then fed into a Tektronix Type 564B storage oscilloscope. Kinetic runs were recorded photographically with a Polaroid camera. All reactions were studied at 25.0 ± 0.1° and 0.1 *M* ionic strength and a borate–mannitol buffer was used to maintain constant pH.

Equilibrium spectrophotometric measurements were made at 240 nm with a Beckman DU spectrophotometer equipped with a 10-cm thermostated cell compartment maintained at 25.0 ± 0.1°. Molar absorptivity values of the 1:1 complexes determined at 240 nm are 217, 69.2, and 263 for Ni(*N,N*-DiMeen), Ni(*N,N'*-DiMeen), and NiTriMeen, respectively.

All pH measurements were made using a Corning Model 12 pH meter. During potentiometric measurements, the titration vessel, a tall-form beaker, was maintained at 25.0 ± 0.1° by surrounding it with an outer jacket of coiled 1/4-in. diameter copper tubing through which was circulated the thermostating liquid. The titration vessel was also continuously swept with moist nitrogen gas to minimize carbon dioxide uptake.

Calculations of kinetic runs, stability constants, and protonation constants were made using a Xerox Sigma 6 digital computer.

Results

Protonation Constants. The protonation constants of these ligands were determined in triplicate by potentiometric titration of the acidified ligand solutions using standard sodium hydroxide solution. The constants determined were mixed-mode constants defined by the relationships

$$K_{\mathrm{H1}} = [\mathrm{HL}^+]/a_{\mathrm{H}}[\mathrm{L}] \qquad (1)$$

$$K_{\mathrm{H2}} = [\mathrm{H_2L}^{2+}]/a_{\mathrm{H}}[\mathrm{HL}^+] \qquad (2)$$

The constants were calculated using an iterative computer program based on a modification of the Bjerrum $\bar{n}_{\mathrm{H}}$ method[18] as applied by Jonassen.[19] These protonation constants are shown in Table I along with available literature values[20–27] for comparative purposes.

Stability Constants. The stability constants of the 1:1 nickel(II)–diamine complexes were determined by both spectrophotometric and titrimetric techniques. In the spectrophotometric method, the absorbances of the nickel complexes were measured at 240 nm as a function of pH and the stability constants and molar absorptivities were simultaneously determined utilizing an iterative technique. In all cases at least a tenfold excess of nickel was used to ensure 1:1 complex formation.

The potentiometric technique used was a modified method of Bjerrum[18] in which an excess of nickel was used. The stability constants determined by these two methods are in excellent agreement both with each other and with the kinetically determined constants. All three constants are presented in Table I.

Kinetic Measurements. Over the pH range 5.7–7.6, the kinetics of the 1:1 nickel–diamine complex formation reactions were found to be first order with respect to both metal and ligand. The overall reversible second-order forma-

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Table I. Mixed-Mode Protonation Constants and Nickel Stability Constants of *N*-Methyl-Substituted Ethylenediamines at 25.0°

Ligand	Medium	log K_{H1}	log K_{H2}	log K_{NiL}	Ref
N,N-DiMeen	0.1 *M* $NaClO_4$	9.70	6.55	5.76 (kinetic) 5.87 (spectro) 5.77 (titrim)	This work
	0.1 *M* KCl	9.53	6.63		20
	0.16 *M* $NaClO_4$	9.60	6.32		21
	0.1 *M* $NaClO_4$	9.59[a]	6.46[a]		22
N,N'-DiMeen	0.1 *M* $NaClO_4$	10.15	7.16	6.87 (kinetic) 6.90 (spectro) 6.82 (titrim)	This work
	0.1 *M* KCl	10.16	7.40	6.65	20
	0.1 *M* KNO_3	9.88	7.01		23
	0.1 *M* KNO_3		7.4		24
	0.5 *M* KNO_3	10.29	7.47	7.11	25, 26
	0.1 *M* $NaClO_4$	10.08[a]	7.07[a]	6.84	27
TriMeen	0.1 *M* $NaClO_4$	9.77	6.40	5.45 (kinetic) 5.38 (spectro) 5.44 (titrim)	This work

[a] Calculated constants from data given in references.

tion and first-order dissociation rate law which the system obeyed may be represented by

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

where k_f and k_d represent the observed formation and dissociation rate constants, respectively, and $[\Sigma L]$ is the concentration of the uncomplexed ligand

$$[\Sigma L] = [L] + [HL^+] + [H_2L^{2+}] \qquad (4)$$

The integrated form of eq 3 used to resolve the observed formation rate constant may be expressed as[9]

$$\ln\left(\frac{2X-R-Q}{2X-R+Q}\right) = \ln\left(\frac{R+Q}{R-Q}\right) + k_fQt \qquad (5)$$

where $R = (ab/X_e) + X_e$, $Q = (R^2 - 4ab)^{1/2}$, a, $b = [Ni^{2+}]$, $[\Sigma L]$ at time zero, $X = [NiL^{2+}]$ at any time t, and $X_e = [NiL^{2+}]$ at infinite time. The observed dissociation rate constant may then be calculated from the equilibrium data obtained after the reaction was completed.

All kinetic runs yielded excellent second-order graphical plots. The observed rate constants obtained as a function of pH are presented in Tables II-IV. In most cases, these rate constants represent the average of four replicate stopped-flow determinations. As anticipated, the formation rate constants increase, while the dissociation rate constants decrease with increasing pH. This pH dependency of the reaction rate was utilized to resolve the observed rate constants into those representing the reaction of aquonickel ion with unprotonated and monoprotonated ligand species. The equations used for this resolution were

$$k_f[\Sigma L]/[L] = k_{Ni}{}^{L} + k_{Ni}{}^{HL}K_{H1}a_H \qquad (6)$$

$$k_d = k^{NiL} + k_H{}^{NiL}[H^+] \qquad (7)$$

where $k_{Ni}{}^{L}$ and $k_{Ni}{}^{HL}$ represent the formation rate constants while k^{NiL} and $k_H{}^{NiL}$ represent the dissociation rate constants for the reaction of aquonickel ion with unprotonated and monoprotonated ligand, respectively. The graphical resolution of these four rate constants using eq 6 and 7 and least-squares analysis yielded good straight-line plots for all three ligand systems. The plots of eq 6 and 7 are presented in Figures 1 and 2, respectively. In general, the rate data below pH 6 could not be used in resolving the individual rate constants since the low degree of complexation at these pH values resulted in rate constants insufficiently reliable for graphical analysis. The resolved rate constants obtained in this study are presented in Table V.

Table II. Experimental Rate Constants for the Reaction of Nickel Ion with *N,N*-DiMeen (25.0°, $\mu = 0.1\ M$, $[Ni^{2+}] = 7.55 \times 10^{-3}\ M$)

pH	$10^3[N,N$-DiMeen$]$, *M*	$10^{-1}k_f$, M^{-1} sec^{-1}	$10k_d$, sec^{-1}
5.81	3.12	0.784	6.89
5.96	3.64	1.48	6.38
6.09	3.12	2.05	5.41
6.30	1.56	2.87	4.14
6.33	2.60	2.85	4.36
6.33	3.64	2.80	4.94
6.56	2.08	5.43	2.25
6.75[a]	2.60	7.22	2.17
6.97[b]	2.08	9.23	1.06
7.24[a]	1.56	11.9	0.624
7.59[b]	2.08	21.8	0.330

[a] $[Ni^{2+}] = 5.03 \times 10^{-3}\ M$. [b] $[Ni^{2+}] = 2.52 \times 10^{-3}\ M$.

Table III. Experimental Rate Constants for the Reaction of Nickel Ion with *N,N'*-DiMeen (25.0°, $\mu = 0.1\ M$, $[Ni^{2+}] = 7.55 \times 10^{-3}\ M$)

pH	$10^3[N,N'$-DiMeen$]$, *M*	k_f, M^{-1} sec^{-1}	10^2k_d, sec^{-1}
5.76	2.61	0.428	4.12
5.95	3.91	1.83	4.00
6.08	2.61	2.12	3.74
6.29	1.30	4.12	3.68
6.29	2.61	3.52	3.55
6.30	3.91	3.72	3.81
6.52[a]	1.26	6.75	2.27
6.59[a]	2.61	8.74	2.85
6.76[a]	2.61	13.8	2.40
6.98[b]	2.61	23.4	1.57
7.23[a]	2.61	36.0	1.10
7.41[b]	1.30	93.0	1.17
7.58[b]	1.30	65.4	0.497

[a] $[Ni^{2+}] = 5.03 \times 10^{-3}\ M$. [b] $[Ni^{2+}] = 2.52 \times 10^{-3}\ M$.

Discussion

Thermodynamic Constants. It is well known that steric effects play a very important role in determining the magnitude of nickel(II) complex stability constants for several series of related diamines.[20,26,28,29] Although thermodynamic constants do not provide details as to the exact role of steric hindrance in reaction mechanisms, they do provide qualitatively useful clues to the existence and order of magnitude of steric constraints. Probably the most useful application of thermodynamic constants is the calculation of the

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Table IV. Experimental Rate Constants for the Reaction of Nickel Ion with TriMeen (25.0°, $\mu = 0.1\ M$, $[Ni^{2+}] = 5.03 \times 10^{-3}\ M$)

pH	10^3[TriMeen], M	k_f, M^{-1} sec^{-1}	$10^2 k_d$, sec^{-1}
5.69[a]	2.42	1.42	23.2
5.80	1.21	3.02	15.6
5.83[a]	1.21	2.99	16.7
5.95	1.21	4.07	15.0
6.06	1.21	3.99	12.7
6.31	1.21	4.81	9.46
6.31	2.42	5.20	11.3
6.33	1.21	3.95	11.0
6.54	1.21	6.46	7.33
6.54[b]	1.21	8.47	6.71
6.55	1.21	7.00	7.09
6.76[b]	1.21	8.10	5.48
6.79[b]	1.21	9.22	5.13
6.98	1.21	11.8	3.47
7.00[b]	1.21	11.6	4.43
7.19	1.21	14.4	2.54
7.40[b]	1.21	20.5	1.93
7.59[b]	1.21	23.4	1.57

[a] $[Ni^{2+}] = 7.55 \times 10^{-3}\ M$. [b] $[Ni^{2+}] = 2.52 \times 10^{-3}\ M$.

Table V. Resolved Rate Constants for Nickel(II) Ion Reactions with *N*-Methyl-Substituted Ethylenediamines (25.0°, $\mu = 0.1\ M$)

Ligand	$k_{Ni}{}^{L}, M^{-1}$ sec^{-1}	$k_{Ni}{}^{HL}, M^{-1}$ sec^{-1}	k^{NiL}, sec^{-1}	$k_H{}^{NiL}, M^{-1}$ sec^{-1}
en[a]	3.5×10^5	180	8×10^{-3}	
N,N-DiMeen	3.2×10^4	69	5×10^{-2}	7.1×10^5
N,N'-DiMeen	4.3×10^4	29	1×10^{-2}	4.2×10^4
TriMeen	2.9×10^3	9.6	2×10^{-2}	1.9×10^5
TeMeen[b]	3.6×10^2	0.2	1×10^{-1}	

[a] R. W. Taylor, H. K. Stepien, and D. B. Rorabacher, submitted for publication. [b] Reference 8.

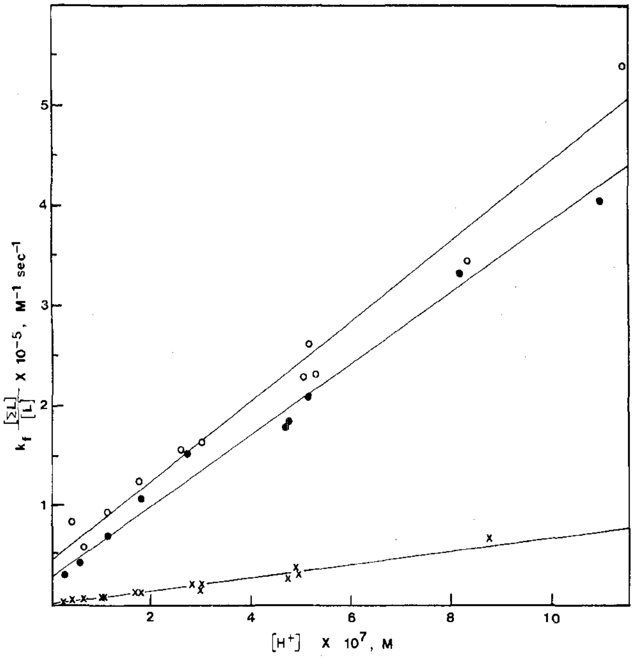

Figure 1. Resolution of formation rate constants showing pH dependency of the reaction of aquonickel(II) with (●) *N,N*-DiMeen, (○) *N,N'*-DiMeen, and (×) TriMeen (plot of eq 6).

"Bjerrum steric function,"[30] which is the ratio of the logarithm of the average complex stability constant to the logarithm of the protonation constant of the ligand, log K_{NiL}(av)/log K_{H1}. It has been successfully used to correlate nickel and copper complex stability constants to the steric bulk of alkyl substituents in a series of related diamine complexes.[26,29] The relationship has been modified by Rorabacher[7,8] to compare only the ratio of the 1:1 stability constants to the ligand protonation constants (log K_{NiL}/log K_{H1}), which gives a more reasonable representation of steric constraints by presumably eliminating the role of ligand–ligand interactions which may occur in higher order complexes.

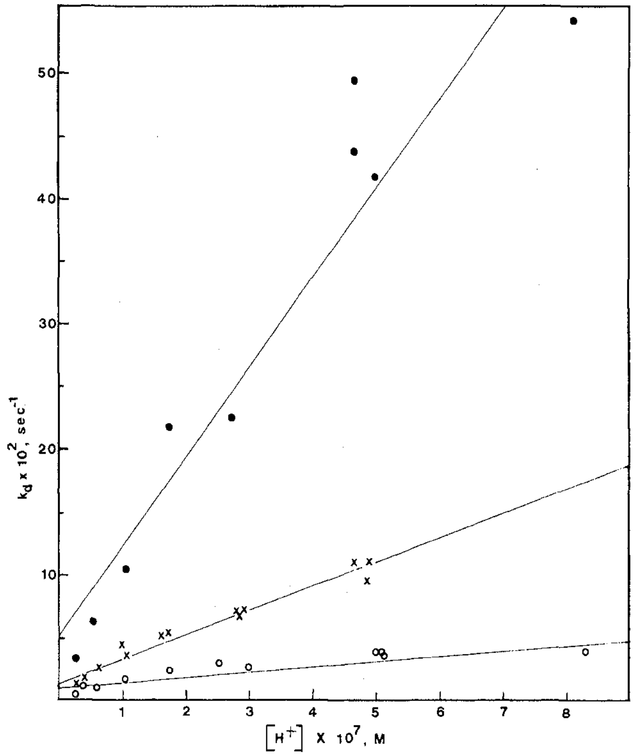

Figure 2. Resolution of the dissociation rate constants showing pH dependency of the dissociation of (●) Ni(*N,N*-DiMeen), (○) Ni(*N,N'*-DiMeen), and (×) NiTriMeen (plot of eq 7).

In this study, the Bjerrum steric function relationship has been used to predict roughly the magnitude of steric influence by methyl substituents on the nitrogen donor atoms of ethylenediamine. Table VI compares the relationship calculated in this work with that previously reported.

As in the previous study with *N*-ethyl-substituted ethylenediamines,[8] a systematic decrease in the magnitude of the steric function clearly indicates the presence of increasing steric influence with increasing substitution. Although the magnitude of the steric function in this study is not as large as previously determined, the trends with methyl substitution parallel those found with ethyl substitution, and the existence of a modest steric effect, reflected in the kinetic rate constants, is predicted. The resolved formation rate constants presented in Table V show that the Bjerrum steric function has correctly predicted the order of decreasing formation rate constants ($k_{Ni}{}^{L}$) for *N*-methyl-substituted ethylenediamines.

Dissociation Kinetics. It has been proposed in a previous study[8] that steric constraints in coordination reactions of aquonickel(II) with bidentate amines are reflected principally in the formation rate constants. In Table V, the dissociation rate constants, k^{NiL}, show a 14-fold rate difference between unsubstituted ethylenediamine and the fully *N*-methyl-substituted ethylenediamine (TeMeen), while the formation rate constants, $k_{Ni}{}^{L}$, have a difference over this

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Table VI. Bjerrum Steric Function of *N*-Alkyl-Substituted Ethylenediamines (25.0°, $\mu = 0.1\ M$)[a]

Ligand	$\log K_{\mathrm{NiL}}/\log K_{\mathrm{H1}}$	Ligand	$\log K_{\mathrm{NiL}}/\log K_{\mathrm{H1}}$
en	0.73		
N,N'-DiEten	0.56	*N,N'*-DiMeen[b]	0.68
N,N-DiEten	0.46	*N,N*-DiMeen[b]	0.60
TriEten	<0.3	TriMeen[b]	0.55
TeEten	<0.1	TeMeen	0.39

[a] Reference 8. [b] This work.

range of about 1000.[31] The dissociation rate effects, although considerably smaller, provide interesting comparisons with previous studies and are considered below.

Using the notation of Wilkins,[4] the reaction sequence for a dissociative mechanism of Ni(II) ion with an unprotonated ligand may be represented as shown in Figure 3, where K_{os} represents the outer-sphere association complex equilibrium constant, k_2 and k_3 represent the formation rate constants for the singly bonded complex and the doubly bonded complex, respectively, and k_{-3} and k_{-2} represent the dissociation rate constants for the first and second nickel-nitrogen bond rupture from the dissociation of the doubly bonded complex. The dissociation rate constant for these diamine complexes may be represented by

$$k^{\mathrm{NiL}} = k_{-2}k_{-3}/(k_{-2} + k_3) \tag{8}$$

Under the conditions of moderate pH as used in this study, it can be assumed that $k_3 >> k_{-2}$ and the dissociation rate constant simplifies to

$$k^{\mathrm{NiL}} = k_{-2}k_{-3}/k_3 \tag{9}$$

The three individual rate constants incorporated in k^{NiL} provide useful insights into the reaction mechanism.

There is no *a priori* reason to believe that the dissociation rate constants k_{-2} and k_{-3} cannot reflect steric effects. In fact, molecular models seem to indicate that such steric effects are possible and that tertiary amines should facilitate nickel-nitrogen bond breaking to a greater extent than either secondary or primary amines. Furthermore, the monoamine study of Rorabacher and Melendez-Cepeda[7] can be interpreted as showing a modest increase in dissociation rate ranging from ammonia (7.1 $\mathrm{sec^{-1}}$) to methylamine (7.7 $\mathrm{sec^{-1}}$) to dimethylamine (11.3 $\mathrm{sec^{-1}}$). However, no rate constants for tertiary amines were determined, apparently due to the low stability of the 1:1 complexes. If kinetic studies of trimethylamine or other tertiary amines were successful, it is quite possible that the dissociation rate constants would be several times larger than those of primary amines. The assumption that k_{-2} is constant[8] is thus questionable and open to further investigation. A comparison of the dissociation rate constants, k^{NiL}, for the ligands *N,N'*-DiMeen, TriMeen, and *N,N'*-DiEten indicate a marked similarity between them. If the steric effects of these ligands were manifested in k_3 only, one would expect rather dissimilar rate constants. In fact, the constancy of k^{NiL} (~0.015 $\mathrm{sec^{-1}}$) implies that either some other step in the reaction sequence offsets the steric effect in k_3 or k_3 is void of steric hindrance. It appears that for these three ligands, any steric effects that do exist are very similar.

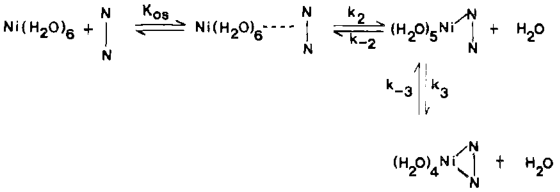

Figure 3. Schematic representation of the dissociative mechanism of Ni(II) reacting with ethylenediamines. Protonated ligands should react similarly and are not shown. Charges are also omitted for clarity.

Studies by Wilkins[32,33] of the dissociation rates of the nickel complexes of en and TeMeen under highly acidic conditions indicate that the dissociation rates of these two ligands are nearly the same at 0.15 $\mathrm{sec^{-1}}$. Under the conditions he used, the dissociation rate constant was equal to k_{-3} implying that the breaking of the first nickel-nitrogen bond in the complex is void of steric constraint. Under the moderate pH conditions of this study, the value determined by Wilkins can be taken to be the extreme upper limit for the rate constant, k^{NiL}, that can be manifested by steric effects in bidentate amines (*i.e.*, when $k_{-2} >> k_3$, $k^{\mathrm{NiL}} = 0.15\ \mathrm{sec^{-1}}$).

The very rapid dissociations of both TeMeen and *N,N*-DiMeen give evidence for steric influence in the dissociation mechanism. Surprisingly, *N,N*-DiMeen appears to dissociate more rapidly than TriMeen, even though its nitrogen donor atoms are less substituted. Its value of 0.05 $\mathrm{sec^{-1}}$ appears anomalously large compared to the other two ligands studied in this work. This means that either k_3 is approximately equal to k_{-2} or k_{-3} is unusually large for this ligand. If $k_3 \approx k_{-2}$, k^{NiL} as calculated from eq 8 would be similar to the experimental value for *N,N*-DiMeen. However, the differences in k^{NiL} between *N,N*-DiMeen and TriMeen could not be rationalized. It is noteworthy that the ethyl analog of this ligand, *N,N*-DiEten, previously studied also dissociates very rapidly and is assumed to function in a unidentate manner.[8] However, since the dissociation rate constants of the three *N*-methyl-substituted diamines are about two orders of magnitude smaller than unidentate amines ($k_{\mathrm{Ni}}{}^{\mathrm{L}} \approx 5\ \mathrm{sec^{-1}}$), they cannot be unidentate. The large k^{NiL} rate constant for *N,N*-DiMeen relative to that of TriMeen is puzzling and seems to indicate that the k_3 formation step is not sterically controlling the rate of dissociation as previously postulated.

A possible explanation for this large rate constant lies in the magnitude of the first nickel-nitrogen bond-breaking step. Immediately following Ni-N bond rupture, the amine must rotate out of bonding position and extend itself in order to enable a water molecule to coordinate with the nickel and occupy a site vacated by the nitrogen donor atom. It is evident from molecular models that a methyl group substituted on a nitrogen donor atom still bonded in the singly bonded complex can sterically hinder rotation away from the metal thus slowing down the rate of dissociation. *N,N*-DiMeen, having no such methyl substitution to hinder rotation, is free to extend itself smoothly away from the metal and the reaction proceeds more rapidly. TeMeen dissociates even more rapidly probably because the large steric bulk associated with the tetramethyl substitution either causes a large increase in k_{-3} due to a bond rotation effect or is due to a combined increase in k_{-2} and decrease in k_3. From the present data, it is impossible to tell which ef-

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(31) This difference in formation rate between TeMeen and en is somewhat misleading since ICB effects may be superimposed on steric rate depressions. In fact, the large difference in the basicity of these two ligands (en, $\log K_{\mathrm{H1}} = 9.99$; TeMeen, $\log K_{\mathrm{H1}} = 9.14$) leads to the prediction that the difference in formation rates is more likely about a factor of 200. For the protonation constants of en and TeMeen see D. B. Rorabacher, W. J. MacKeller, F. R. Shu, and M. Bonavita, *Anal. Chem.*, 43, 561 (1971), and ref 8.

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

(33) R. G. Wilkins, *J. Chem. Soc.*, 4475 (1962).

fect predominates at this time. However, it is likely that k_3 does not unilaterally control dissociation rates and it is conceivable that all three rate steps are sterically influenced by *N*-alkyl substitution.

Formation Rate Constants. According to the dissociative mechanism as generally formulated, the rate-determining step in the formation reactions of nickel(II) complexes is at the point of first nickel(II)-water bond rupture. This rate step is labeled as k_2 in Figure 3. Since the equilibrium step involved in the formation and dissociation of an outer-sphere complex is very rapid, the observed formation rate constant may be expressed as $k_{\mathrm{Ni}}{}^{\mathrm{L}} = K_{\mathrm{os}}k_2$ for reactions with unprotonated ligands.[34] This rate constant may be theoretically calculated, assuming that subsequent steps with multidentate ligands are rapid and introducing a statistical factor of 2 for the unprotonated diamines, to yield values of 8.7×10^3 and 1.7×10^3 M^{-1} sec^{-1} for reactions of Ni(II) with unprotonated and monoprotonated ethylenediamines, respectively.[35]

When the results in Table V are compared to the theoretical calculations for unprotonated ligands, both dimethylethylenediamines show overall about a fivefold rate enhancement, TriMeen shows a slight rate depression, and TeMeen, studied previously, reacts substantially slower than predicted. In all of these ligands, the basicity of the nitrogen donor atoms is sufficiently high to promote internal conjugate base rate enhancements[12] and these accelerative effects in fact are clearly seen for the two dimethyl ligands.

Protonated N-substituted ethylenediamines cannot undergo ICB rate enhancement but, as evidenced from increased steric effects relative to unprotonated ligands, even for ethylenediamine itself,[8] may contain both bulk or "primary" steric factors (equally present in both unprotonated and monoprotonated ligands) and "secondary" steric effects, existing only in protonated ligands. The existence of secondary steric factors is based on the assumption that back-side steric crowding of alkyl substituents can increase the degree of intramolecular proton sharing, thus shifting the conformation equilibrium between trans and gauche conformers to the latter conformation.[8,36] It can be seen from molecular models that this proton sharing is most favored when ethyl or larger alkyl groups are substituted on the same nitrogen donor atom. However, for the two dimethyl ligands used in this study and to a less extent for TriMeen, only minor effects can be attributed to back-side crowding. With *N,N'*-DiMeen, in particular, back-side steric crowding by alkyl substitutents should be nonexistent. Assuming the tendencies to proton share in en, *N,N*-DiMeen, and *N,N'*-DiMeen are very similar, a comparison of the formation rate constants of the protonated ligands species should yield the bulk steric factors present in the latter two ligands. A convenient way to make this comparison is through the use of the organic substituent function[8,9]

$$E_{\mathrm{s}} = \log\,(k/k_0) \qquad (10)$$

where k and k_0 are rate constants representing the substituted and reference ligands, respectively. Values of log E_{s} for the methyl-substituted diamines studied in this work as well as some related ligands have been calculated and are listed in Table VII.

. Comparison of the E_{s} values in Table VII for the protonated dimethyl ligands with Hen$^+$ results in estimates of bulk steric rate depression of threefold for *N,N*-DiMeen and sixfold for *N,N'*-DiMeen. Next, evaluation of the E_{s} values of the unprotonated forms of these ligands with a simultaneous correction for the bulk steric factors calculated yields rate enhancements attributable to ICB effects of 100 and 250 for *N,N*-DiMeen and *N,N'*-DiMeen, respectively. Similar comparisons using the data from protonated and unprotonated TriMeen may be made, giving an estimated ICB rate enhancement of about 60. This calculation, however, is somewhat uncertain since back-side crowding is expected to be more significant for the protonated ligand.

A very interesting comparison of the effect of steric influence on formation rate constants may be made by considering methyl *vs.* ethyl substitution.[8] In *N,N'*-DiMeen and *N,N'*-DiEten, the ICB effects are expected to be very similar since the protonation constants of the two ligands are nearly exactly the same. Any difference in the rate constants of the unprotonated ligands would thus reflect the bulk steric difference between methyl and ethyl substitution in secondary amines. The magnitude of this difference is fourfold. It is notable that this fourfold difference is also the same as that obtained in comparing the formation reactions of the protonated ligands. These results imply that only bulk steric interactions are important and add credence to the arguement that back-side crowding does not influence the degree of proton sharing in H(*N,N'*-DiMeen)$^+$ or H(*N,N'*-DiEten)$^+$. This lack of added steric influence in protonated secondary amines such as *N,N'*-DiEten presumably means that only tertiary diamines exhibit back-side crowding. Furthermore, the ICB effect may be calculated for this ligand from the data obtained previously[37] to give a rate enhancement of 250. Unfortunately, similar comparisons cannot be made between the tri- and tetrasubstituted ligands, since the ethyl derivatives do not react to a sufficient extent for study by stopped flow.

The estimates of ICB rate enhancements for the formation rates of Ni(II) complexes may be conveniently represented by plotting the magnitude of this effect *vs.* protonation constants of the ligands. If the primary driving force in the ICB mechanism is ligand basicity, a direct relationship is predicted to exist between the magnitude of the effect and ligand basicity. Figure 4, showing a plot of log ICB rate enhancement *vs.* log K_{H1} for several basic (log $K_{\mathrm{H1}} > 8$) multidentate ligands, yields a fairly good linear relationship and can be used as a starting point in correlating ICB effects to rate constants for other ligands.

A test of this postulation may be made using the recent kinetic study by Steinhaus and Amjad[15] of the formation reactions of Ni(II) with the aromatic ligands BPEDA and

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[34] Formation reactions with protonated ligands may be similarly expressed as $k_{\mathrm{Ni}}{}^{\mathrm{HL}} = K_{\mathrm{os}}'k_2'$. See ref 8.

[35] The values for the formation rate constants are based on the calculation of K_{os} from the equation

$$K_{\mathrm{os}} = \frac{4}{3}\pi a^3 N_{\mathrm{A}} \times 10^{-3} \exp\left[-\left(\frac{Z_1 Z_2 e_0{}^2}{a'DkT} - \frac{Z_1 Z_2 e_0{}^2 \kappa}{DkT(1 + \kappa a')}\right)\right]$$

where $\kappa = (8\pi N_{\mathrm{A}} e_0 \mu/1000DkT)^{1/2}$, $a = 4$ Å is the distance of closest approach for ethylenediamine, $a' = 8$ Å is the distance of the protonated nitrogen on ethylenediamine from the Ni(II) ion when the ligand is fully extended, and the other terms have been previously defined.[4] Using these assumptions, K_{os} is calculated to be 0.16 and 0.062 for the unprotonated and monoprotonated ligands, respectively: M. Eigen, *Z. Phys. Chem.* (*Frankfurt am Main*), 1, 176 (1954); R. M. Fuoss, *J. Amer. Chem. Soc.*, 80, 5059 (1958); ref 8. The value of k_2 is taken to be 2.7×10^4 sec^{-1} from the nmr exchange experiments of T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 37, 307 (1962).

[36] E. Grunwald and E. K. Ralph, *Accounts Chem. Res.*, 4, 107 (1971).

[37] The E_{s} value for H(*N,N'*-DiEten)$^+$ is -2.3 while that for *N,N'*-DiEten is 0.1.[8]

Table VII. Organic Substituent Function for *N*-Methyl-Substituted Ethylenediamines (25.0°, $\mu = 0.1\ M$)

Ligand	log $k_{\mathrm{Ni}}{}^{\mathrm{L}}$, M^{-1} sec^{-1} Theoret	Exptl	E_s
en[a]	3.9	5.5	1.6
N,N-DiMeen	3.9	4.5	0.6
N,N'-DiMeen	3.9	4.6	0.7
TriMeen	3.9	3.5	−0.4
TeMeen[a]	3.9	2.6	−1.3
Hen$^+$ [a]	3.2	2.3	−0.9
H(*N,N*-DiMeen)$^+$	3.2	1.8	−1.4
H(*N,N'*-DiMeen)$^+$	3.2	1.5	−1.7
HTriMeen$^+$	3.2	1.0	−2.2
HTeMeen$^+$ [a]	3.2	−0.7	−3.9

[a] Reference 8.

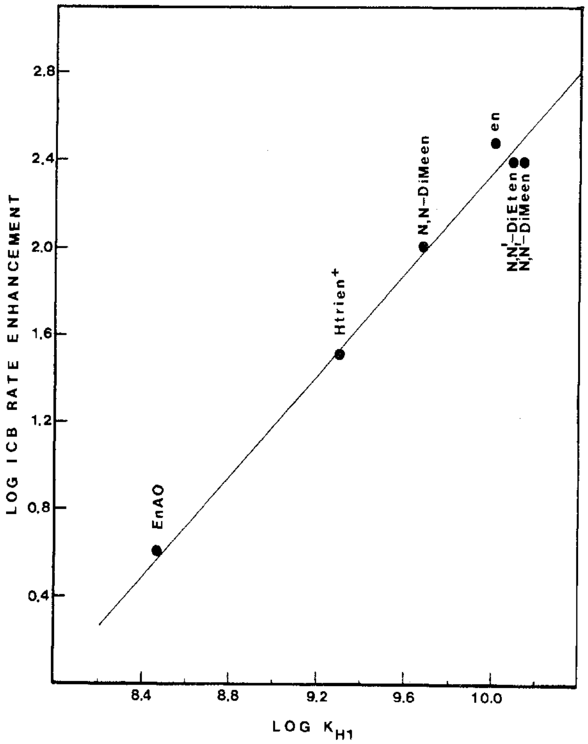

Figure 4. Internal conjugate base rate enhancements as a function of ligand basicity: plot of log ICB *vs.* log K_{H1}. ICB rate enhancement for 2,2′-ethylenediaminobis(2-methyl-3-butanone)dioxime (EnAO) (log $K_{\mathrm{H1}} = 8.45$) is estimated to be approximately 4: R. K. Murmann, *J. Amer. Chem. Soc.*, 84, 1349 (1962). For Htrien$^+$ (log $K_{\mathrm{H1}} = 9.3$) the ICB effect is about 30-fold: ref 16. For en (log $K_{\mathrm{H1}} = 9.99$) the ICB effect is about 300: ref 8.

DBEDA. BPEDA (log $K_{\mathrm{H1}} = 8.26$) is estimated to give an ICB rate enhancement of threefold, in good agreement with the graphical extrapolation from Figure 4. However, DBEDA (log $K_{\mathrm{H1}} = 8.85$), estimated by Steinhaus also to have a threefold ICB effect, does not agree with the graphical estimate of about tenfold. This apparent discrepancy may be readily explained by looking at the experimental rate constants of DBEDA and HDBEDA$^+$. Clearly, the formation rate constant of the monoprotonated ligand is too large, particularly in view of the fact that it is about 3 times larger than the corresponding rate constant of the structurally similar secondary ethylenediamine, H(*N,N'*-DiEten)$^+$. Apparently, the aromatic rings on HDBEDA$^+$ tend to prohibit sterically proton sharing and thus limit the degree of steric hinderance present in the monoprotonated ligand species. Estimating that the magnitude of this effect is three- or fourfold, based on the rate constant of H(*N,N'*-DiEten)$^+$, excellent agreement with the graphical interpolation results. It can also be seen that the estimates of the ICB rate enhancements reported for the two polyamino alcohols TKED and THPED[9] are in good agreement with values taken from Figure 4.

Conclusions

The results of this study begin to show the nature of the respective roles of steric and ICB effects in Ni(II) complexation reaction mechanisms. From this work, several generalizations regarding octahedral complexation reactions may be drawn.

(1) The modest steric effects due to *N*-methyl substitution in ethylenediamines may be used to advantage in isolating ICB from steric factors. It appears that in higher order substitution, large steric constraints may obscure subtle features of reaction mechanisms. (2) Seemingly, steric effects arising from intramolecular proton sharing in multidentate amines are much more pronounced in secondary nitrogen donor atoms than in primary ones. It is logical to expect that tertiary nitrogen donor atoms would be even more affected. This tendency may be a general phenomenon and future kinetic studies with basic multidentate ligands must consider this possibility. (3) The ICB effect appears to be a direct function of multidentate ligand basicity. The graphical proof of this correlation (Figure 4) is useful in predicting ICB effects in other ligands. Experiments are now under way in this laboratory to test the correlation with ligands of higher basicity. 1,3-Propanediamine (log $K_{\mathrm{H1}} \approx 10.6$), for example, is a ligand which should react at an even faster rate than ethylenediamine unless ring closure becomes the rate-determining step in the reaction. (4) In ligands having moderate steric influence upon reaction rate, the dissociation rate constants, as well as the formation rate constants, seem to reflect steric constraints. The exact role that is played by dissociation rate steps is complex and merits further study.

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Registry No. *N,N*-DiMeen, 108-00-9; *N,N'*-DiMeen, 110-70-3; TriMeen, 105-04-4; [Ni(*N,N*-DiMeen)$(H_2O)_4]^{2+}$, 31355-69-8; [Ni(*N,N'*DiMeen)$(H_2O)_4]^{2+}$, 31274-28-9; [Ni(TriMeen)$(H_2O)_4]^{2+}$, 31274-30-3; $Ni(H_2O)_6{}^{2+}$, 15365-79-4.