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Electrostatic Effects in Coordination Kinetics. Reaction of Nickel(II) Ion with a Cationic Unidentate Ligand as a Function of Solvent Dielectric

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The kinetics of solvated Ni(II) ion reacting with a cationic ligand, N,N,N-trimethylethylenediammonium ion (tmen$^+$), have been studied as a function of solvent dielectric in methanol–water mixtures containing 0–90% methanol (by weight) at 25°, $\mu = 0.3\ M$ using the temperature-jump relaxation technique. By comparison of the experimental formation rate constants to the corresponding values for Ni(II) reacting with the neutral ammonia ligand, the value of the charge center-to-center distance between Ni(II) and tmen$^+$ in the "effective" ion pairs leading to complex formation is found to be 6.5 Å. In conjunction with a previously generated value for the reactive site center-to-center distance of 4 Å along with estimated steric factors, this value permits the calculation of a "reactive" ion-pair formation constant for charged bidentate ligands interacting with metal ions. The validity of the calculations in the current treatment is limited by the relatively high ionic strength necessitated in this study. The mechanistic implications for coordination reactions involving amino acids and monoprotonated diamines are considered.

Introduction

In recent reports emanating from this laboratory, we have attempted to quantify fundamental steric[1-3] and solvent[4-7] effects upon the kinetics of coordination reactions involving hexacoordinated transition metal ions in solution. For uncharged ligands, analysis of the data in terms of a dissociative mechanism has been reasonably straightforward. However, for charged multidentate ligands, such as the protonated polyamines,[2,3,6] the resolution of steric and solvent effects has been hampered by a lack of specific quantitative information on the magnitude of the accompanying electrostatic effects.

We now wish to report the results of a study in which we have attempted to establish the actual magnitude of such electrostatic interactions. For this purpose we have chosen to examine the kinetics of solvated Ni(II) ion reacting with a cationic unidentate ligand, N,N,N-trimethylethylenediammonium ion (tmen$^+$).

$$\begin{array}{c} CH_3 \\ | \\ H_2NCH_2CH_2NCH_3{}^+ \\ | \\ CH_3 \end{array}$$
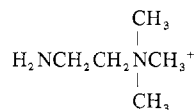
This ligand has been selected to serve as a model for singly charged bidentate ligands in which the charged site is located at the donor atom *not* involved in first-bond formation (*e.g.*, monoprotonated ethylenediamine, glycinate, etc.).

The kinetics of the Ni-tmen reaction have been studied as a

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(5) F. R. Shu and D. B. Rorabacher, *Inorg. Chem.*, **11**, 1496 (1972).

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function of solvent dielectric in methanol–water mixtures. By making the reasonable assumption that steric effects associated with tmen$^+$ will remain constant in all solvent compositions, a comparison of the resolved formation rate constants with corresponding values generated previously for the reaction between Ni(II) and NH$_3$ in the same solvent mixtures[4] allows us to isolate the electrostatic effects in the current system.

In analyzing the data, we have made a distinction between two distance parameters in the ion pairs leading to complex formation: (i) the center-to-center distance of closest approach between the solvated metal ion and the *reactive site* on the ligand, and (ii) the accompanying center-to-center distance between the solvated metal ion and the *charged site* on the ligand. Such a distinction, which appears to have been ignored by previous investigators, derives from the concept of a *reactive* outer-sphere complex in which the ligand must be properly oriented relative to the metal ion at the time of metal–solvent bond rupture in order to compete for the vacated coordination site. This concept is in accord with the hypothesis that a dissociative interchange (I_d) mechanism is operative in such ligand substitution reactions.

The use of a cationic rather than an anionic ligand in this work yields two definite advantages: (i) the possibility of extensive ion-pair formation in low dielectric media is eliminated, and (ii) the distinction between the two distance parameters is enhanced. The values generated for these two parameters are subsequently applied to an analysis of experimental rate constants which have been reported in the literature for reactions involving monoprotonated diamines and amino acids.

Experimental Section

Reagents. Ni(NO$_3$)$_2$·6H$_2$O (Baker "Analyzed Reagent") was used as the source of nickel ion in aqueous solution while Ni(ClO$_4$)$_2$ was used for all other solvent mixtures, the preparation, purification, and standardization procedures for the latter having been previously described.[4] The ligand salt, tmen·Br·HCl, was synthesized from 2-bromoethylphthalimide and trimethylamine as described in the literature[8,9] with the following modifications in purification. The final solution, resulting from heating the intermediate trimethyl-2-phthal-
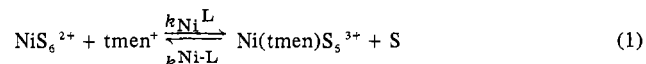
imidoethylammonium bromide with HCl (to cleave the phthalic acid moiety), was cooled overnight permitting most of the insoluble phthalic acid to precipitate out. Following filtration and evaporation to dryness, the remaining phthalic acid was removed by washing with acetone. Finally, the unreacted intermediate was removed by treating the product with aqueous $HClO_4$ to precipitate trimethyl-2-phthalimidoethylammonium perchlorate. Following subsequent filtration and evaporation, the purity of the final product was found to be much improved over that normally obtained, testing out at better than 98% pure as determined by titration of weighed samples of the final tmen·Br·$HClO_4$ with standard base.

All methanol-water mixtures were prepared on a weight per cent basis using absolute methanol (99.9%, J. T. Baker Chemical Co.) and distilled, deionized water. Acidity measurements were made using the nonaqueous pH* scales as previously described.[10] Ionic strength was maintained by the addition of $NaClO_4$ (G. F. Smith Chemical Co.).

Relaxation Measurements. The temperature-jump relaxation spectrometer used for the kinetic measurements has been previously described.[1,4] To minimize interference from internal convection caused by temperature reequilibration within the cell, which was accentuated by the low viscosity of the highly alcoholic media, the temperature increases effected were limited to 4.7° for 50%, 4.2° for 65%, 3.5° for 80%, and 3.3° for 90% methanol (by weight). The final temperature achieved was calibrated at 25.0 ± 0.2° in all solvents.

Results

As with our previous studies using ammonia and other unidentate amines as the substituting ligand,[1,4,5,7,11] the spectrophotometric changes accompanying the reaction of Ni(II) with tmen$^+$ were too small to be directly observable. Therefore, this reaction was coupled to an acid-base indicator as follows (where S represents a solvent molecule, either H_2O or CH_3OH).

$$NiS_6{}^{2+} + tmen^+ \underset{k^{\text{Ni-L}}}{\overset{k_{\text{Ni}}{}^{\text{L}}}{\rightleftharpoons}} Ni(tmen)S_5{}^{3+} + S \tag{1}$$

$$H^+ + tmen^+ \overset{K_H{}^C}{\rightleftharpoons} Htmen^{2+} \tag{2}$$

$$H^+ + In^- \overset{K_I{}^C}{\rightleftharpoons} HIn \tag{3}$$

Under the conditions used in this study, where only the 1:1 metal-ligand complex is present in significant concentration, the equation describing the relaxation behavior for a coupled system of this type has been shown to be[11]

$$1/\tau = k_{\text{Ni}}{}^{\text{L}}\{[\bar{\text{M}}]/(1+\alpha) + [\bar{\text{L}}]\} + k^{\text{Ni-L}} \tag{4}$$

where τ is the relaxation time of the system; $[\bar{\text{M}}]$ and $[\bar{\text{L}}]$ are the equilibrium molar concentrations of uncomplexed Ni(II) ion and unprotonated uncomplexed tmen$^+$, respectively, at the final temperature; and α is calculated as a function of the concentration equilibrium constants, $K_H{}^C$ and $K_I{}^C$, and the concentration terms, $[H^+]$, $[In^-]$, and $[L]$, as previously described.[1,4,11]

In conformance with the previous study on Ni(II) reacting with NH_3 in methanol-water mixtures,[4] the coupled indicators used in this study were Bromthymol Blue for water and 25% methanol and Bromcresol Green for 50-90% methanol, the $K_I{}^C$ values having been previously reported.[4] The protonation constants for tmen$^+$ in each solvent composition were determined from potentiometric titrations of tmen·Br·$HClO_4$ with standard NaOH solutions at 25°, $\mu = 0.007\,M$ using the nonaqueous pH* scales as previously described.[10] The pertinent equilibrium constants are listed in Table I.

(8) S. Gabriel, *Ber.*, **53**, 1985 (1920).
(9) G. A. Melson and R. G. Wilkins, *J. Chem. Soc.*, 4208 (1962).
(10) D. B. Rorabacher, W. J. MacKellar, F. R. Shu, and M. Bonavita, *Anal. Chem.*, **43**, 561 (1971).
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Table I. Equilibrium Constants Pertinent to the Nickel-tmen$^+$ Study (25°)

CH_3OH, wt %	CH_3OH, mol fraction	Log^a $K_H{}^C$	Log^b $K_I{}^C$	D^c
0	0	7.1	7.2^d	78.5
25	0.1578	6.9	7.7^d	67.0
50	0.3599	6.6	5.5^e	55.3
65	0.5108	6.2	5.8^e	48.5
80	0.6922	6.2	6.3^e	41.6
90	0.8350	6.8	6.9^e	37.0

^{a} $\mu = 0.007\,M$. ^{b} Reference 4: $\mu = 0.10\,M$. ^{c} Interpolated from the combined data of G. Akerlof, *J. Amer. Chem. Soc.*, **54**, 4125 (1932); P. S. Albright and L. G. Gosting, *ibid.*, **68**, 1061 (1946). ^{d} Bromthymol Blue indicator. ^{e} Bromcresol Green indicator.

It should be noted that upon correcting $K_H{}^C$ and $K_I{}^C$ to $0.3\,M$ ionic strength, the tabulated values of the former constant will increase while those of the latter constant will decrease slightly. For any reasonable corrections, however, it is found that the value of α is negligibly small in all solvent compositions studied under the conditions used, resulting in a simplification of eq 4 to the form[11]

$$1/\tau = k_{\text{Ni}}{}^{\text{L}}\{[\bar{\text{M}}] + [\bar{\text{L}}]\} + k^{\text{Ni-L}} \tag{5}$$

The stability constant values for the Ni(tmen)$^{3+}$ complex were not determined directly as the complex was too unstable to provide satisfactory data. Instead, an estimated value of $K_{\text{NiL}} = 10 = k_{\text{Ni}}{}^{\text{L}}/k^{\text{Ni-L}}$ was initially assumed in each solvent which, by iteration, led to a quick convergence of the formation and dissociation rate constants in the manner previously described.[1]

As a result of the weakness of the Ni(tmen)$^{3+}$ complex and the relatively large excess of metal ion to ligand in the solutions used for the relaxation experiments, the concentration sum in eq 5 closely approximated the total concentration of Ni(II) in solution. For this reason it was not deemed essential to determine the corrected values of $K_H{}^C$ at the ionic strength used in this work ($\mu = 0.3\,M$) since the potential corrections were less than the errors in the relaxation measurements themselves (*ca.* ±10%).

The experimentally obtained relaxation times, each representing the median value of four or more replicate relaxation curves, are tabulated in Table II where C_M and C_L represent the total concentrations of Ni(II) and tmen$^+$, respectively, in solution. The resolved formation and dissociation rate constants, generated by computer analysis according to eq 5, are listed in Table III where the values obtained in aqueous solution are seen to be in good agreement with previously determined values: $k_{\text{Ni}}{}^{\text{L}} = 4.2 \times 10^3\,M^{-1}\,\text{sec}^{-1}$[12] and $k^{\text{Ni-L}} = 40\text{-}45\,\text{sec}^{-1}$.[9,12]

Discussion

As shown in Table III, the reaction of Ni(II) with the positively charged ligand, tmen$^+$, exhibits considerably smaller formation rate constant values in all solvent compositions than were previously found for the corresponding reaction with the neutral ligand, NH_3.[4] Moreover, as visualized in Figure 1, the ratio between the formation rate constants for the NH_3 and tmen$^+$ systems exhibits a general increasing trend with increasing methanol. This trend is consistent with the expected relative influence of the dielectric upon reactions between species having charge products of 0 and +2, respectively. Thus, an initial examination of the data in Table III supports the premise that the relative rate constant

(12) J. C. Cassatt, Ph.D. Dissertation, State University of New York at Buffalo, 1969.

Table II. Relaxation Data for the Nickel-tmen$^+$ System in Methanol-Water Mixtures at 25°, C_L = 4.0 mM

pH*	C_M, mM	τ^{-1}, sec^{-1}	pH*	C_M, mM	τ^{-1}, sec^{-1}
0% CH$_3$OH (μ = 0.2 M)			0% CH$_3$OH (μ = 0.3 M)		
6.8	20.0^a	51.3	7.0	30.0	59.9
6.8	20.0	44.1	6.8	30.0^c	60.3
6.5	30.0	53.5	6.4	45.0^b	58.5
6.7	40.0^b	57.5	6.4	60.0	78.1
6.5	50.0	61.4	6.8	60.0^b	82.7
6.8	60.0	66.7	6.4	75.0^b	89.3
			6.7	90.0	87.7
0% CH$_3$OH (μ = 0.4 M)			25% CH$_3$OH (μ = 0.3 M)		
6.6	30.0	74.1	6.8	20.0	43.3
6.5	50.0	73.0	6.8	30.0	55.0
6.5	70.0	94.4	6.8	45.0	59.5
6.4	100.0	102	6.8	60.0	72.0
6.4	130.0	116	6.7	75.0	78.1
			6.7	90.0	83.4
50% CH$_3$OH (μ = 0.3 M)			65% CH$_3$OH (μ = 0.3 M)		
6.2	20.0	49.0	6.6	30.0	55.0
6.2	30.0	51.3	6.6	45.0	68.5
6.2	45.0	72.0	6.6	50.0	69.0
6.2	60.0	83.4	6.6	60.0	82.0
6.3	75.0	84.8	6.6	75.0	89.3
6.6	90.0	99.0	6.7	90.0	109
80% CH$_3$OH (μ = 0.3 M)			90% CH$_3$OH (μ = 0.3 M)		
6.5	20.0	52.1	6.4	20.0	44.5
6.5	30.0	55.6	6.4	30.0	47.2
6.5	50.0	80.6	6.4	45.0	51.8
6.5	60.0	90.9	6.4	60.0	63.7
6.5	75.0	90.9	6.4	75.0	80.0
6.5	90.0	102	6.4	90.0	80.6

^{a} C_L = 3.0 mM. ^{b} C_L = 6.0 mM. ^{c} C_L = 8.0 mM.
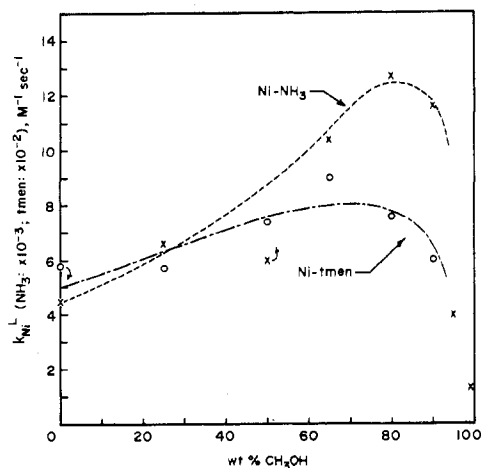
Figure 1. Comparative plots of the experimentally obtained formation rate constants as a function of methanol-water solvent composition for the Ni–NH$_3$ and Ni–tmen systems at 25°. (Note the difference in the ordinate scales for the two systems.) The broken curves represent the behavior predicted for each system by eq 25 where K_{os} is calculated from eq 13–15 and the effective value of k_1 (correlated to k^{M-S} in ref 4) is calculated from eq 22. The parameter values applied are: K_1' = 0.62, K_2' = 0.14, $k_{6:0}{}^{M-S}$ = 2.8 × 10^4 sec^{-1}, $k_{5:1}{}^{M-S}$ = 1.38 × 10^5 sec^{-1}, $k_{4:2}{}^{M-S}$ ≈ 1 × 10^3 sec^{-1}, a = 4 Å (all from ref 4); and (for Ni–tmen only) a' = 6.5 Å, p = 2.6, b ≈ 0.16, μ = 0.3 M. ×, Ni–NH$_3$ data (ref 4); o, Ni–tmen data (this work).

values for the two systems may be correlated to the magnitude of the electrostatic repulsions inherent in the Ni–tmen system.
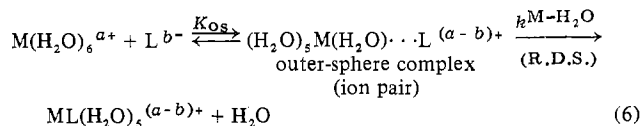
In examining the rate constant ratios tabulated in Table III, the cumulative effects of experimental errors are in evidence. In particular, it should be noted that the value of the formation rate constant reported previously for the Ni–NH$_3$ system

in 50% methanol was acknowledged to be anomalously low relative to the data obtained in all other solvent compositions.[4] Therefore, an interpolated value of $k_{Ni}{}^{NH_3}$ = 8.6 × 10^3 M^{-1} sec^{-1} has been utilized for 50% methanol instead of the experimental value ($k_{Ni}{}^{NH_3}$ = 6.0 × 10^3 M^{-1} sec^{-1}) in making our comparison to the Ni–tmen system.

It is also apparent from Table III and Figure 1 that the experimental value of $k_{Ni}{}^L$ obtained for the Ni–tmen system in aqueous solution at 0.3 M ionic strength is too large relative to values obtained either in other solvent compositions or at other ionic strengths. Therefore, a value of $k_{Ni}{}^L$ = 5.0 × 10^2 M^{-1} sec^{-1} has been utilized for comparison to the Ni–NH$_3$ system in 0% methanol in the remainder of this discussion. (Note that retention of the original rate constant value decreases the final value generated for a' by only 0.2 Å.)

Although no other adjustments have been made to the experimental data, it is evident from Table III that a slightly high value for the Ni–NH$_3$ formation rate constant in 25% methanol coupled with a similar error in the Ni–tmen constant in 65% methanol results in a fortuitous apparent constancy in the rate constant ratio, R, over the intermediate solvent compositions. Recognizing the foregoing experimental limitations, the significance of the observed trend in R values may be examined in the light of current mechanistic theory.

Dissociative Mechanism. The hypothesis that hexacoordinated metal ions undergo ligand substitution by a dissociative process[13-15] has been largely supported by kinetic studies over the past decade.[16-21] As generally formulated, the mechanism of substitution involves rapid equilibration of the reactant species in the bulk solution with an outer-sphere complex (contact ion pair) between the reacting partners followed by the rupture of an inner-sphere coordinate bond as the rate-determining step. This latter process is accompanied (or immediately followed) by the movement of the substituting ligand from the outer sphere into the vacated coordination site; *viz.*, for aquometal ions

$$M(H_2O)_6{}^{a+} + L^{b-} \underset{}{\overset{K_{os}}{\rightleftharpoons}} (H_2O)_5M(H_2O)\cdot\cdot\cdot L^{(a-b)+} \xrightarrow[\text{(R.D.S.)}]{k^{M-H_2O}}$$
$$\text{outer-sphere complex}$$
$$\text{(ion pair)}$$

$$ML(H_2O)_5{}^{(a-b)+} + H_2O \qquad (6)$$

Thus, the observed formation rate constants are presumed to represent the product of the two stepwise constants

$$k_{Ni}{}^L = K_{os}\cdot k^{M-H_2O} \qquad (7)$$

In accordance with the dissociative nature of this mechanism, the value of the rate constant for metal-solvent bond rupture, k^{M-H_2O}, appears to be independent of the nature of the substituting ligand, L^{b-}, and, thus, correlates closely with the rate constant for inner-sphere solvent exchange as deter-

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Table III. Resolved Rate Constants for the Nickel–tmen$^+$ and Nickel–Ammonia Systems at 25°, $\mu = 0.3\,M$

CH$_3$OH, wt %	$10^{-2}k_{Ni}{}^L$, M^{-1} sec^{-1}	k^{Ni-L}, sec^{-1}	$10^{-2}k_{Ni}{}^{NH_3}$,^{a} M^{-1} sec^{-1}	$k_{Ni}{}^{NH_3}/k_{Ni}{}^L$ $= R$	Remarks
0 ($\mu = 0.2$)	4.8 (±0.7)	38 (±3)			
0 ($\mu = 0.3$)	5.8 (±1.1)	41 (±7)	44.6	8.9^c	
0 ($\mu = 0.4$)	4.6 (±0.7)	57 (±6)			
25	5.7 (±0.5)	35 (±3)	66.9	11.7	High R
50	7.4 (±0.8)	34 (±5)	(86)^b	(11.6)	
65	9.0 (±0.6)	27 (±4)	104	11.6	Low R
80	7.6 (±1.0)	38 (±6)	127	16.8	
90	6.0 (±0.7)	30 (±4)	116	19.5	

^{a} $\mu = 0.1\,M$ (ref 4); based on a comparison of aqueous data at $\mu = 1.0\,M$ (ref 1), the same values are presumed valid for $\mu = 0.3\,M$. ^{b} Interpolated value; see text. ^{c} Calculated on the basis of $k_{Ni}{}^L = 5.0 \times 10^2\,M^{-1}$ sec^{-1} (see text).

mined by nmr measurements on the same metal ion species.[22,23] On the other hand, the value of the outer-sphere complex equilibrium constant, K_{os}, is dependent on both the size and charge of the substituting ligand in accordance with the expression[24-27]

$$K_{os} = \frac{4\pi N_A a^3}{3000} \cdot e^{-U^0(a')/kT} \cdot f_{\pm}{}^2 \tag{8}$$

where $U^0(a')$ represents the electrostatic free energy of the outer-sphere complex at infinite dilution

$$U^0(a') = Z_A Z_B e_0{}^2 / D a' \tag{9}$$

as contrasted to the thermal energy, kT,[28] and $f_{\pm}$ represents the Debye–Huckel mean ionic activity coefficient often expressed as[29]

$$\ln f_{\pm} = 2.303 \left(\frac{A Z_A Z_B (\mu)^{1/2}}{1 + Ba'(\mu)^{1/2}} + b\mu \right) \tag{10}$$

Definition of terms: N_A, Avogadro's number, a, center-to-center distance (in centimeters) of closest approach between the metal ion and the reactive site on the ligand in the outer-sphere complex, k, Boltzmann constant (in ergs), T, absolute temperature, Z_A and Z_B, formal charges on the metal ion and ligand, respectively, e_0, the unit electronic charge (in esu), D, dielectric constant of the reaction medium, a', center-to-center distance (in centimeters) between the charge sites on the metal and ligand in the reactive outer-sphere complex, μ, ionic strength (in M).]

The variables A and B in eq 10 may be defined as[29]

$$A = \sqrt{\frac{2\pi N_A}{1000}} \cdot \frac{e_0{}^3}{2.303(DkT)^{3/2}} \tag{11}$$

$$B = \sqrt{\frac{8\pi N_A}{1000}} \cdot \frac{e_0}{(DkT)^{1/2}} \tag{12}$$

while b is an empirical quantity dependent on both solvent and charge product and is treated as an adjustable parameter to suit experimental activity data at high ionic strength.[30]

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(30) C. W. Davies, *J. Chem. Soc.*, 2093 (1938).

Combining eq 8-12 and rearranging yields the following modified expression

$$K_{os} = \frac{4\pi N_A a^3}{3000} \cdot e^{-U(a')/kT} \tag{13}$$

where $U(a')$ is the electrostatic free energy term including activity coefficient corrections

$$U(a') = \frac{Z_A Z_B e_0{}^2}{D} \left(\frac{1}{a'} - \frac{\kappa}{1 + \kappa a'} \right) - 4.6b\mu kT \tag{14}$$

$$\kappa = \left(\frac{8\pi N_A e_0{}^2 \mu}{1000 DkT} \right)^{1/2} \tag{15}$$

Distance Parameters. Aside from the empirical constant b, which will be discussed later, all of the terms in eq 13-15 have well-defined values except for the two distance parameters a and a'. In searching through the literature we note that other investigators appear not to have treated these two distances as independent variables in kinetic studies but have assumed the two to be equal in value. This assumption is undoubtedly valid for spherically symmetrical ligands (such as Cl$^-$, SO$_4{}^{2-}$, or the recently studied CS$_3{}^{2-}$[31]) and, with proper treatment, may also be valid for ligands (such as CH$_3$COO$^-$) in which the charge center is located on the donor atom involved in initial coordinate bond formation as shown in later examples. However, it would appear to be totally inappropriate when applied to ligands such as the larger amino acids[32] where initial bond formation apparently involves a nitrogen donor atom remote from the charged carboxylate group.[12,33] A similar distinction between the two distance terms is seemingly required in the case of reactions involving protonated polyamine species where, again, the charged sites (*i.e.*, protonated nitrogen donor atoms) are removed from the site of initial bond formation.[2,6]

In examining the applicability of calculated values for the outer-sphere complex formation constant, K_{os}, to ligands such as α-aminobutyric acid, Kowalak, Kustin, Pasternack, and Petrucci[34] noted that the reduction in spherical symmetry inherent in such bulky ligands diminishes the fraction of outer-sphere pairs which represent *reactive* encounters. An attempt was made to correct for this by means of an empirical statistical factor. Considering only a single distance parameter, a (*i.e.*, presuming that our a and a' parameters are identical), these authors then observed that the value of K_{os}, as calculated by eq 13, was virtually insensitive

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(33) K. Kustin and R. F. Pasternack, *J. Phys. Chem.*, **73**, 1 (1969).
(34) A. Kowalak, K. Kustin, R. Pasternack, and S. Petrucci, *J. Amer. Chem. Soc.*, **89**, 3126 (1967).

to the assumed magnitude of this distance parameter over the range of feasible values: $3 \leqslant a \leqslant 8$ Å. Upon examination it is apparent that this lack of sensitivity results from a fortuitous compensation of the preexponential and exponential terms in eq 13 where an increase in the value of a (our a') *decreases* the magnitude of the exponential term by an amount which is almost exactly equivalent to the corresponding *increase* in the preexponential a^3 term under the experimental conditions used by Kowalak, *et al.* ($Z_A Z_B = -2$, $T = 20°$, $\mu = 0.1$ M).

Since the exponential term in eq 13 is dependent on the ionic charge product whereas the preexponential term is not, such a compensation should not occur for other values of $Z_A Z_B$. Thus, Cassatt and Wilkins[35] attempted to generate an experimental value of a single distance parameter, a (where a and a' were, again, not distinguished), by plotting rate constant values for Ni(II) reacting with 22 ligands of varying complexity having formal charges ranging from $+1$ to -3 (resulting in charge products from $+2$ to -6).

In attempting this analysis these authors (i) ignored the influence of steric effects and (ii) assumed that the value of a was invariant for ligands of differing size and structure. Moreover, these investigators failed to include the activity coefficient term in eq 8 in making their plot of log k_f vs. $Z_A Z_B$ according to the equation

$$\log k_f = \log \{k^{M-H_2O}(^4/_3 \pi a^3 N_A \cdot 10^{-3})\} - \frac{Z_A Z_B e_0^2}{2.3 DkTa} \tag{16}$$

The slope of the resulting plot was anomalously low yielding a value of $a = 8.5$ Å which, as noted by them, is "somewhat higher than that usually encountered with ion pairing."

In examining Cassatt and Wilkins' data, it is evident that, even if the variations in steric effects and the magnitude of a were randomly distributed over their entire plot, correction for the activity coefficient term for each point plotted would tend to increase the slope due to the variation in the magnitude of this term with varying charge product. In this manner a smaller value of their single distance parameter, a, would be generated.

In actual fact, inclusion of the activity coefficient term makes the graphical approach infeasible, except as an iterative technique, since calculation of the exponential term in eq 13 requires a foreknowledge of the distance parameter which we have designated as a' (eq 14). We suggest, however, that reasonable values for a and a' may be generated from experimental kinetic data providing that the proper type of comparison is made.

In our earliest study involving reactions with the neutral ligand NH_3,[11] where eq 8 and 13 simplify to

$$K_{os(Z_A Z_B = 0)} = 4\pi N_A a^3 / 3000 \tag{17}$$

(thereby eliminating a' as a contributing parameter), it was shown that a value of $a = 4$ Å gave excellent agreement between the $k_M^{NH_3}$ and k^{M-H_2O} values according to eq 7. This distance is consistent with the suggested model in which the outer-sphere ligands are located over the faces of the octahedrally solvated metal ion.[36] In a subsequent investigation on Ni(II) reactions with alkylamines[1] we observed that the rate constant values for ligand substitution decrease markedly with an increase in the size and/or number of alkyl groups substituted on the nitrogen donor atom. Even for methyl-

amine, a threefold decrease in rate constant was observed relative to that for ammonia.

This indicates that all metal–ligand encounters are not potentially reactive implying that ligand rotation cannot take place within the lifetime of a five-coordinate intermediate, in further support of a dissociative interchange (I_d) mechanism. Thus, the value of a cannot be regarded as proportional to the bulk ligand radius as has sometimes been implied.

In keeping with the concept of a dissociative interchange mechanism, we have chosen to regard ligands from the standpoint of "a donor atom with a tail," assuming a constant value of a (but not of a') for the *reactive* outer-sphere complex.[2,37] The decrease in formation rate constant accompanying increased substitution on the donor atom may then be attributed to the effect of steric hindrance phrased in terms of a "reduction in the solid angle corresponding to reactive encounters" as noted by Kowalak, *et al.*[34] This can be represented by an empirical entropic steric hindrance factor, p, in formulating the *reactive encounter* equilibrium constant, K_{re}, as

$$K_{re} = K_{os}/p \tag{18}$$

Having established the concept of a constant value for a (equal to 4 Å) for ligands related to ammonia, the value of a' for any charged ligand could, in principle, be evaluated from experimental rate data if a suitable estimate of the empirical steric factor, p, were available. Our previous studies[1,2] have led us to conclude that substitutions beyond the β carbon on alkylamines will not substantially alter the degree of steric hindrance exhibited in complex formation reactions with aquonickel(II) ion. Thus, for tmen$^+$, the ethylamine value of $p \approx 5$ (relative to NH_3) might be assumed to apply.[2] The validity of this assumption will be reexamined later.

Rather than seek to obtain a value of a' based on a single calculation, however, we have opted to examine the kinetic behavior of tmen$^+$ reacting with Ni(II) as a function of ionic strength and solvent dielectric which, in addition to temperature and ionic charge, are the accessible variables in the electrostatic (*i.e.*, exponential) term in eq 13. In this manner we have sought to establish whether a single value of a' can be generated which will adequately describe the variability in rate constant behavior as a function of these parameters.

Unfortunately, in testing the rate constant dependence upon ionic strength, the lack of an adequate relaxation amplitude at low reactant concentrations limited the minimum feasible ionic strength to about 0.2 M. This relatively high ionic strength not only decreases the sensitivity of the rate constant to the electrostatic contribution but has also made it apparent that the final term in eq 10 and 14 (*i.e.*, the $b\mu$ term) might not be negligible.

Since values of b have not appeared in the literature for all the solvent compositions utilized in this study, such values were generated by means of eq 10 from reported activity

(35) J. C. Cassatt and R. G. Wilkins, *J. Amer. Chem. Soc.*, **90**, 6045 (1968).

(36) As has been noted elsewhere [J. Neely and R. E. Connick, *J. Amer. Chem. Soc.*, **92**, 3476 (1970)], ligand–solvent exchange should occur at $^3/_4$ the rate of specific solvent–solvent exchange if the incoming species is conceived to be situated above a face of the octahedron at the time of exchange (leading to six coordination sites exchanging with eight species = $^3/_4$) assuming that the metal ion does not exhibit preferential discrimination among the outer-sphere species. However, this factor is generally obscured by steric effects and experimental errors and is thus ignored.

(37) D. B. Rorabacher, T. S. Turan, J. A. Defever, and W. G. Nickels, *Inorg. Chem.*, **8**, 1498 (1969); D. B. Rorabacher and D. B. Moss, *ibid.*, **9**, 1314 (1970).

coefficient data for HCl up to 0.5 M ionic strength in mixed methanol-water solvents.[38-42] The values obtained in this manner appear to contain large errors and cannot be presumed to extrapolate well beyond $\mu = 0.5\,M$.

Using Davies' suggestion[30] relative to charge product dependence, the b values calculated from the HCl data (where $Z_A Z_B = -1$) were then multiplied by -2 for application to the Ni-tmen system (where $Z_A Z_B = +2$). As indicated in Table IV, the magnitude of the applied correction factor, $e^{4.6b\mu}$, is relatively small for $\mu = 0.3\,M$ and remains fairly constant over the range of solvent compositions covered by this study. (The discontinuity in the value of b occurring at 40 and 60% methanol is apparently attributable to differences between activity coefficient data as obtained by different investigators and does not necessarily convey any physical significance.) Thus, a constant correction of $e^{4.6b\mu} \approx 0.8$ (corresponding to $b \approx -0.16$) has been utilized for the Ni-tmen system in all methanol-water mixtures.

Application of the foregoing correction term to eq 14 yields a predicted maximum for the value of K_{os} somewhere in the region of 0.4 M ionic strength in aqueous solution. As a result, K_{os} does not vary greatly in this region suggesting that relative trends in the rate constant behavior with changing ionic strength cannot be used as a sensitive indicator of the magnitude of a' within the experimentally accessible range. (The observed maximum in the experimental Ni-tmen complex formation rate constant at 0.3 M ionic strength, as listed in Table III, cannot be accounted for by eq 14 and appears to be primarily the result of experimental error.) Consequently, solvent dielectric appears to provide a much more promising variable for evaluating a'.

In analyzing the kinetic data for the Ni-tmen reaction as a function of solvent composition, it is evident from our previous study on the Ni-NH$_3$ system[4] that changes in the composition of the inner-solvation sphere of Ni(II) result in large changes in the value of k^{M-H_2O}. Such changes should be common to both reactions, however, and should cancel out in the rate constant ratio, R, defined for each specific solvent composition as (see Table III).

$$R = k_{Ni}^{NH_3}/k_{Ni}^{L} \tag{19}$$

Substituting eq 7 and 18 into eq 19 yields

$$R = K_{os(Z_A Z_B = 0)}/(K_{os(Z_A Z_B = 2)}/p) \tag{20}$$

which, upon substitution of eq 13-15 and 17 and rearrangement, leads to

$$p = R \exp\left\{ -\frac{Z_A Z_B e_0^2}{DkT}\left(\frac{1}{a'} - \frac{\kappa}{1 + \kappa a'}\right) + b\mu \right\} \approx \text{constant} \tag{21}$$

The value of the right-hand term in eq 21 was calculated for each solvent composition using the experimental R values listed in Table III by iterating a' values over the range $4 \leqslant a' \leqslant 9$ Å in increments of 0.5 Å. For each value of a' the standard deviation of the calculated p values was computed for all solvents. The results are given in Table V.

As plotted in Figure 2, the minimum in the relative per cent standard deviation in the p values calculated according

Table IV. Electrostatic Correction Terms and Calculated K_{os} Values for 0.3 M Ionic Strength at 25°

CH$_3$OH, wt %	b ($Z_A Z_B = -1$)	$e^{4.6b\mu}$ ($Z_A Z_B = +2$)	K_{os}, M^{-1} ($Z_A Z_B = +2$; $a = a' = 4$ Å)	K_{os}, M^{-1} ($Z_A Z_B = +2$; $a = 4$, $a' = 6.5$ Å)
0	0.089	0.78	0.0161	0.0466
10	0.069	0.83		
20	0.052	0.87		
25			0.0122	0.0412
40	0.140	0.68		
50			0.0084	0.0358
60	0.279 (?)			
65			0.0063	0.0307
80	0.062	0.84	0.0043	0.0261
90	0.09	0.78	0.0032	0.0229

Table V. Evaluation of "Best" Value of a' Based on Relative Rate Constants for Ni(II) Reacting with NH$_3$ and tmen$^+$ in Methanol-Water Mixtures at 25°

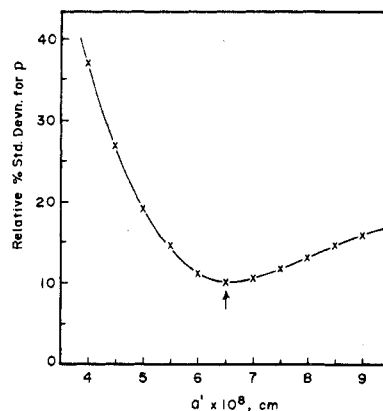| a', Å	Av calcd p	Rel % std dev for calcd p
4.0	0.59	37.0
4.5	0.96	26.9
5.0	1.34	19.1
5.5	1.76	14.8
6.0	2.20	11.1
6.5	2.65	10.0
7.0	3.09	10.5
7.5	3.51	11.7
8.0	3.92	13.1
8.5	4.31	14.6
9.0	4.67	15.8

Figure 2. Plot of the relative per cent standard deviation of the residual steric factor, p, for the Ni-tmen reaction calculated from the ratio of the experimental formation rate constants for the Ni-NH$_3$ and Ni-tmen systems in 0-90% methanol according to eq 21 for values of a' in the range 4-9 Å. The minimum occurring at $a' = 6.5$ Å is presumed to represent the effective value of the center-to-center distance between the charged sites on Ni(II) and tmen$^+$ in the *reactive* outer-sphere complex.

to eq 21 is seen to occur at $a' = 6.5$ Å. Considering the significance of the numerical values, the "best" value for this distance cannot be stipulated within any greater precision than about $a' = 6.5 \pm 0.5$ Å.

As noted in Figure 2, the relative per cent standard deviation becomes much less sensitive to changes in the absolute value of a' beyond the point of the minimum. It is perhaps pertinent to note, however, that the actual calculated p values (eq 21) show a distinct increasing trend with increasing methanolic content of the solvent (decreasing dielectric) for $a' > 7$ Å, whereas the trend is distinctly in the opposite direction for $a' < 5$ Å. In the region of the observed minimum, however, only random fluctuation of the calculated p values with changing solvent composition is observed in accordance

(38) J. M. Austin, A. Hunt, F. Johnson, and H. N. Parton in "Electrohemical Data," B. E. Conway, Ed., Elsevier, Amsterdam, 1952, p 94.

(39) G. Nonhebel and H. Hartley, *Phil. Mag.*, **50**, 298, 729 (1925).

(40) H. S. Harned and R. W. Ehlers, *J. Amer. Chem. Soc.*, **55**, 2179 (1933).

(41) H. S. Harned and H. C. Thomas, *J. Amer. Chem. Soc.*, **58**, 761 (1936).

(42) I. T. Oiwa, *J. Phys. Chem.*, **60**, 754 (1956).

with the presumed experimental errors in the R values as noted in Table III.

As a parallel test of the applicability of the resolved value of a' for the Ni-tmen system, we have attempted to resolve the rate constant values for nickel-solvent bond rupture in the various solvated Ni(II) species $[Ni(H_2O)_6{}^{2+}, Ni(H_2O)_5-(CH_3OH)^{2+},$ etc.] by treating the Ni-tmen data in a manner analogous to that utilized previously for the Ni-NH_3 data in methanol-water solvents.[4] This was accomplished by plotting the equation

$$\frac{k_{Ni}{}^L \Phi p}{K_{os}[H_2O]^2} = k_{6:0}{}^{M-S} + k_{5:1}{}^{M-S}K_1{}' \frac{[CH_3OH]}{[H_2O]} +$$

$$k_{4:2}{}^{M-S}K_1{}'K_2{}' \frac{[CH_3OH]^2}{[H_2O]^2} \qquad (22)$$

where $k_{6:0}{}^{M-S}$, $k_{5:1}{}^{M-S}$, and $k_{4:2}{}^{M-S}$ represent the rate constants for specific solvent-solvent exchange on $Ni(H_2O)_6{}^{2+}$, $Ni(H_2O)_5(CH_3OH)^{2+}$, and $Ni(H_2O)_4(CH_3OH)_2{}^{2+}$, respectively; $K_1{}'$ and $K_2{}'$ are the solvation equilibrium constants between these species as previously defined;[4] and Φ is defined as[4]

$$\Phi = [H_2O]^2 + K_1{}'[H_2O][CH_3OH] + K_1{}'K_2{}'[CH_3OH]^2 \qquad (23)$$

Assuming that only the first two terms in eq 22 are significant in the region 0-90% methanol,[4] a plot of this equation (using $K_1{}' = 0.62, K_2{}' = 0.14^4$) using the values calculated for K_{os} based on $a = 4$ Å and $a' = 6.5$ Å, as listed in Table IV, along with the corresponding value generated for p (equal to 2.6), as shown in Figure 3, yields $k_{6:0}{}^{M-S} = 2.8 \times 10^4$ sec^{-1} and $k_{5:1}{}^{M-S} = 1.3 \times 10^5$ sec^{-1}, values which are in excellent agreement with those evaluated for the Ni-NH_3 study. Such close agreement cannot be generated using other values for a'.

Significance of p Value. The average p values listed in Table V are, perhaps, deserving of comment. In earlier work we obtained a fivefold steric factor for Ni(II) reacting with ethylamine relative to ammonia.[1] In the present system a value of $p = 2.6$ (± 0.2) is generated for tmen$^+$ in the region of the "best" value for a'. We conclude that the actual steric factor for singly substituted donor atoms in ligands of this type lies within the interval of 2.4-5.

Part, but not all, of the discrepancy between the two experimental p values may be attributable to the $b\mu$ correction term applied to the tmen$^+$ system as shown in eq 14. It would appear reasonable that the value of b should depend on the charge separation distance, a', as well as on the charge product; and the influence of the species upon solvent structure may also be a factor. Thus, the absolute value of b calculated from the HCl data (where $a' \ll 6.5$ Å) may not apply for the Ni-tmen system. Since a common value of b was used for all solvent systems, however, the actual magnitude of this parameter utilized does *not* affect the position of the minimum obtained in Figure 2. Therefore, the value generated for a' in this work is independent of the value assumed for b.

Significance of a' Value. As previously discussed in the case of the protonated diamines,[2] bidentate ligands may exist in either a gauche or anti (previously called trans[2]) conformation as well as in intermediate conformational states. In addition, for each conformer, rotameric isomers may also exist in which the unshared electron pair on one donor atom is directed either toward or away from the opposing donor atom (designated, *e.g.*, as gauche-in and gauche-out, respectively). Some examples are depicted for tmen$^+$ in Figure 4.

The largest possible value of a' for a ligand such as tmen$^+$
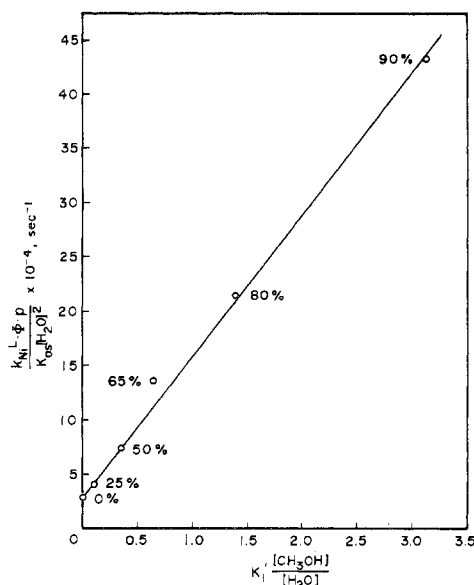
Figure 3. Resolution of the apparent solvent exchange rate constants for the $Ni(H_2O)_6{}^{2+}$ and $Ni(H_2O)_5(CH_3OH)^{2+}$ species calculated from the Ni-tmen data using eq 22. The K_{os} values applied are based on $a = 4$ Å and $a' = 6.5$ Å as tabulated in Table IV. Values for the other variables are $p = 2.6$, $K_1{}' = 0.62$, and $K_2{}' = 0.14$.
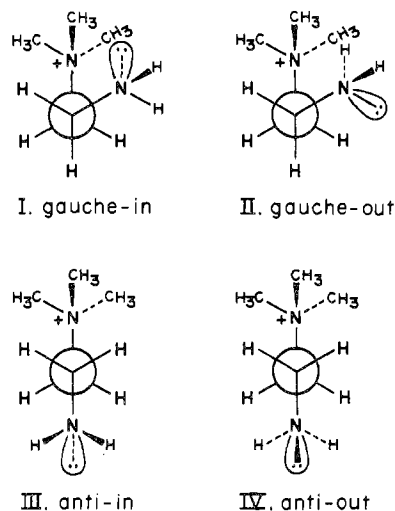
Figure 4. Representative conformational and rotational isomers for tmen$^+$ (Newman projections).

will be exhibited by the conformational rotamer "anti-out" (species IV in Figure 4). If the N-C-C bond angle in this conformer is presumed to be approximately 109.5° and the N-C and C-C bond distances are taken to be 1.47 and 1.54 Å, respectively, as has been reported for ethylenediamine,[43] a value of a' approximately equal to 7.8 Å would be consistent with the value of $a = 4$ Å which we have assumed for the reactive site center-to-center distance. For the "anti-in" rotamer (species III in Figure 4), the value of a' decreases to about 5.5 Å.

For the rotamers designated as "gauche-in" (species I in Figure 4) and "eclipsed-in" (not shown) the unshared electron pair is sterically inaccessible in tmen$^+$ due to the bulkiness of the quaternary ammonium group and appears to be hindered even in the case of ethylenediamine. In the case of the "gauche-out" and "eclipsed-out" rotamers, the value of a' should be approximately 6.5 Å with no evidence of steric

(43) E. J. Corey and J. C. Bailar, *J. Amer. Chem. Soc.*, **81**, 2620 (1959).

hindrance. Thus, the generated value of $a' = 6.5$ Å appears to represent a reasonable value for the averaged conformation of tmen$^+$ and related bidentate ligands as seen by an octahedrally solvated metal ion.

Related Systems. The Ni-tmen formation rate constants obtained in this work compare favorably with rate constant values previously reported for aquonickel(II) ion reacting with monoprotonated diamines at 25°. Thus, a value of $k_{Ni}^{HL} \approx 2 \times 10^2$ M^{-1} sec^{-1} has been found for the reaction involving monoprotonated ethylenediamine at 0.1 M ionic strength.[44] Similarly, the monoprotonated form of N,N-dimethylethylenediamine, which is structurally related to tmen$^+$ and appears to act as a unidentate ligand,[2] exhibits a formation rate constant with Ni(II) of 1.2×10^2 M^{-1} sec^{-1} at $\mu = 0.1$ M.[2] Considering the statistical correction required to compensate for the fact that the latter ligand will react only if the proton resides on the tertiary nitrogen donor atom, both of these protonated diamine systems exhibit reactivities which are within a factor of 2 to 3 of the tmen$^+$ system at comparable ionic strength. This difference may well be accounted for by intramolecular hydrogen bonding in the protonated diamines tending to favor the gauche-in conformer as previously suggested.[2]

For more hindered species, the effect of protonation upon complex formation rate constants is much more severe. As has already been suggested in the case of reactions involving monoprotonated bipyridyl and phenanthroline,[45] this undoubtedly reflects a closer proximity between the metal ion and the protonated site in the "effective" ion pair.

In the case of protonated amino acids, intramolecular hydrogen bonding should not be a significant factor due to the relative acidity of the carboxylate group, at least in aqueous solution.[10] Yet, the monoprotonated species of glycine and related ligands, which exist in the zwitterionic form

$$^+H_3NCH_2\overset{\overset{\displaystyle O}{\displaystyle \|}}{C}O^-$$

have been found to be kinetically unreactive[12,35] leading to the suggestion that attack at the carboxylic oxygen does not lead to a stable intermediate due to the lability of the metal-oxygen bond.

Since the two ends of the unprotonated glycinate ion have different electrostatic characteristics, the use of the reactive outer-sphere concept and the distance parameters generated in this work make it possible to test quantitatively the comparative mechanistic pathways available for these systems.

As illustrated in Figure 5 two reaction paths are available for metal-amino acid complex formation. Assuming rapid equilibration of the ion pair (outer-sphere complex), the rate constant for either pathway may be represented by the equation
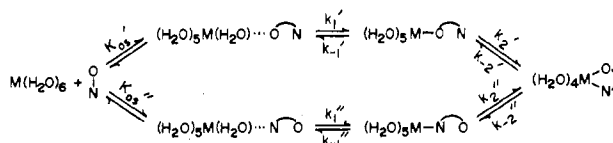
$$k_M^L = \frac{K_{os}}{p} \cdot \frac{k_1 k_2}{k_{-1} + k_2} \tag{24}$$

For either pathway, the maximum value of k_M^L will be generated when first-bond formation is the rate-determining step leading to the reduced equation

$$k_M^L = K_{os} \cdot k_1 / p \tag{25}$$

Figure 5. Schematic representation of the two alternate reaction mechanisms for a divalent aquometal ion reacting with a simple amino acid such as glycinate. The upper path (mechanism I) represents initial bonding to a carboxylate oxygen ($a' = 4$ Å) while the lower path (mechanism II) involves first-bond formation with an amine nitrogen ($a' = 6.5$ Å).

where, according to the dissociative mechanism, k_1 represents the rate constant for metal-water bond rupture.

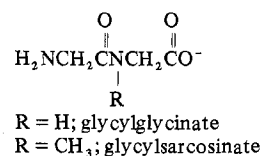For mechanism I, in which metal attack is at the carboxylate end, the value of K_{os} (based on $Z_A Z_B = -2$, $a = a' = 4$ Å) is calculated to be 2.0 M at 25°, $\mu = 0.3$ M. Using a value of $k_1 = 3 \times 10^4$ sec^{-1} for Ni(II),[22] and assuming that steric effects are minimal for substitution at a carboxylate group, eq 25 yields a maximum predicted rate constant of $k_{Ni}^L = 6 \times 10^4$ M^{-1} sec^{-1}.

For mechanism II, the value of K_{os} (calculated on the basis of $Z_A Z_B = -2$, $a = 4$ Å, $a' = 6.5$ Å) is 0.2 M^{-1} at 25°, $\mu = 0.3$ M, yielding a maximum predicted value of $k_{Ni}^L = 0.6 \times 10^4$ M^{-1} sec^{-1}. Considering the probability of some steric hindrance for attack at the primary nitrogen donor atom, this value should probably be reduced still further.

The rate constant measured by Cassatt and Wilkins for Ni(II) reacting with glycinate ion at 25°, $\mu = 0.3$ M, is $k_{Ni}^L = 2.2 \times 10^4$ M^{-1} sec^{-1}. Clearly, based on the above calculations, this value is too large to be accounted for by mechanism II and thus implies that mechanism I, involving initial bonding at the carboxylate group, is the dominant reaction path.

The relative lability of the nickel-carboxylic oxygen bond[46-48] (nearly equal to the lability of the nickel-water bond) and the slight rotational barrier required to bring the nitrogen donor atom into bonding position[2,37] suggest that ring closure should contribute to the rate-determining process (*i.e.*, $k_2 \lesssim k_{-1}$) for glycine reacting *via* mechanism I. This is presumed to account for the nearly threefold difference between the experimental rate constant value and our *maximum* calculated value cited above. The observed unreactivity of the zwitterion species,[12,33,35] $^+NH_3CH_2COO^-$, is then attributed to the combined effects of H$^+$ ionization and ring closure, as suggested by Cassatt and Wilkins,[35] in slowing down this pathway.

In compiling formation rate constant values for the 1:1 complexes of eight amino acids with Ni(II), Co(II), and Cu(II), Pasternack, Angwin, and Gibbs[32] noted that the anionic species of the simple amino acids (glycinate, α-alanate, leucinate, and serinate) react with $M(H_2O)_6^{2+}$ about ten times faster than do the corresponding species of glycylglycinate and glycylsarcosinate

$$H_2NCH_2\overset{\overset{\displaystyle O}{\displaystyle \|}}{C}N\underset{\underset{\displaystyle R}{\displaystyle |}}{CH_2}\overset{\overset{\displaystyle O}{\displaystyle \|}}{C}O^-$$

R = H; glycylglycinate
R = CH$_3$; glycylsarcosinate

They suggested that this difference indicates that, for the

(44) R. W. Taylor, H. K. Stepien, and D. B. Rorabacher, *Inorg. Chem.*, in press; a value of $k_{Ni}^{HL} = 6 \times 10^2$ M^{-1} sec^{-1} reported for this system in ref 35 ($\mu = 0.3$ M) appears to be in error due to the failure of the authors to account for the kinetic contribution of the unprotonated ligand species.

(45) R. G. Wilkins, *Pure Appl. Chem.*, **33**, 583 (1973).

(46) M. A. Pancholy and T. K. Saksena, *Acustica*, **18**, 299 (1967).

(47) H. Hoffmann, *Ber. Bunsenges. Phys. Chem.*, **73**, 432 (1969); U. Nickel, H. Hoffmann, and W. Jaenicke, *ibid.*, **72**, 526 (1968).

(48) G. Calvaruso, F. P. Cavasino, and E. DiDio, *J. Chem. Soc., Dalton Trans.*, 2632 (1972).

latter two species, a greater distance exists between the metal ion and the carboxylate group in the "effective" ion pair leading to stable complex formation. Identical behavior has now been reported for the related ligands, glycyl-L-leucinate and L-leucylglycinate.[49]

Although these authors did not attempt to analyze the underlying cause for the shift in kinetic behavior, the difference in reactivities in the two types of amino acids can be readily explained by the relative difficulty in closing the chelate ring *via* mechanism I. In line with our recent analysis of substituted diamine ligands,[2] much greater steric hindrance will be encountered in closing the chelate ring to the peptide nitrogen as compared to the primary amine nitrogen in glycine. In view of the noted lability of the metal–carboxylate bonds, the result is to slow down the ring closure process to the point where mechanism I becomes slower than mechanism II. The net result is that mechanism II then becomes the dominant reaction path as indicated by the close correlation between our predicted value of $k_{Ni}^{L} \leqslant 0.6 \times 10^4\ M^{-1}$ sec^{-1} and the experimentally obtained value of $0.3 \times 10^4\ M^{-1}$ sec^{-1} for Ni(II) reacting with glycylglycinate ion.[32] In fact, for these larger amino acids, the predicted rate constant for attack at the primary (terminal) nitrogen

(49) R. F. Pasternack, L. Gipp, and H. Sigel, *J. Amer. Chem. Soc.*, 94, 8031 (1972).

donor atom is very close to the experimental value since the value of a' greatly exceeds 6.5 Å (attack at the peptide nitrogen being sterically unfavorable[2]).

Conclusion

The concept of *reactive encounters* in the formation of an outer-sphere complex preceding ligand–solvent exchange at a metal ion center implies a distinction between two distance parameters in the calculation of the outer-sphere equilibrium constant for bulky ligands: (i) the reactive site center-to-center distance, a, and (ii) the charge center-to-center distance, a'. The former distance is presumed to be relatively independent of the bulk ligand dimensions, whereas the latter value is a function of ligand structure including conformational variations. Values generated for the two constants in this work appear to be consistent with experimental kinetic data and permit decisions to be made with respect to competitive mechanistic pathways. It is suggested that a more precise value of a' may be generated by selecting a reaction system which can be studied at lower ionic strength where electrostatic interactions will be magnified.

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Reactivity of Coordinated Carbonyl Groups. Formation of Nickel(II) Complexes with Macrocyclic and Noncyclic Ligands Derived from Benzil Monohydrazone
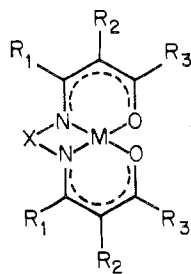
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Reactions between nickel(II) complexes containing a coordinated tetradentate "N$_2$O$_2$" ligand derived from benzil monohydrazone and various amines have been investigated. It has been shown that condensation reactions take place to produce both macrocyclic and noncyclic ligands. These new compounds have been characterized by a variety of physical techniques.

Introduction

The formation of Schiff base complexes by the condensation of amines with coordinated aldehydes or ketones is well known.[1] Recently, several authors have reported attempts to synthesize coordinated macrocyclic ligands by condensation reactions between diamines and the –CO group in complexes containing tetradentate ligands of type I. The re-

I, X = C$_2$H$_4$, C$_3$H$_6$, C$_6$H$_4$

activity of these systems toward diamines is dependent on the nature of the substituent in the R$_2$ (meso) position. When R$_2$ = –COR or –COOR, cyclization readily occurs with aliphatic diamines,[2] although no reaction is observed between ethylenediamine and complexes that do not have either of these substituents in the R$_2$ position.[3] Cyclization does occur however when compounds with X = C$_6$H$_4$ and R$_2$ = H or –COR are heated in molten *o*-phenylenediamine.[4] When R$_2$ and R$_3$ are part of a cyclohexane ring and X = C$_6$H$_4$, cyclization will not take place with either aliphatic or aromatic diamines.[5] If the cyclohexane ring contains a –C=O group, cyclization does not take place with *o*-phenylenediamine, but with ethylenediamine cyclization is observed, accompanied by amine exchange. The reactivity of the coordinated –CO group in complexes of type I is thus dependent on the nature of the ligand "backbone" and the amine used.

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