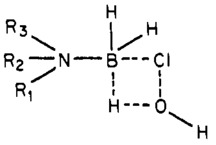
Titration data, the apparent absence of H_2 evolution, and the demonstration of a 3:1 *redox* stoichiometry (*N*-chloromorpholine serves as a two-electron oxidant of I^-) have been interpreted as evidence for essentially quantitative oxidation of all hydridic hydrogen by hypochlorite. Stoichiometric and kinetic studies of the reaction of NaOCl with $Me_iNH\cdot BH_3$ (Table IV) suggest such a pattern of reactivity to be generally characteristic of secondary amine–boranes. The question is raised, then, as to whether tertiary amine–boranes react by a distinctly different pathway from secondary amine–boranes or whether chloroboranes are formed via a single mechanism in both systems, in which case observed stoichiometric and kinetic differences reflect differences in (subsequent) reactivity of tertiary and secondary amine–chloroboranes.

Implication of HOCl as the reagent involved in rate-limiting attack seems to be a common feature in the reactions of both tertiary and secondary amine–boranes. If different mechanisms are involved, then, necessarily, the mode of attack by HOCl on the borane adducts must be different. A speculative model of a (four-center) activated complex leading to the formation of chloroborane–amine is depicted in I and involves an orientation of OH and Cl with respect to a B–H bond *opposite* to what has been suggested for HOCl attack on Mbn.[1] Defense of such a model requires one to accept the notion that when R_1, R_2, or R_3 = H, the favored pathway involves attack by oxygen of the HOCl molecule (rather than chlorine) at boron. This might be considered a reflection of differences in the capacity of N-bonded substituents (alkyl vs. hydrogen) to transmit electron density inductively to the boron center. Alternatively, the presence of an N–H group might permit a hydrogen-bonded interaction with HOCl that would stabilize an activated complex favoring O-atom attack on boron. Subsequent attack on amine–monochloroboranes and amine–dichloroboranes would be expected to occur at progressively slower rates due to the electron-withdrawing influence of boron-bonded chlorine.



I

R_1, R_2, R_3 = alkyl

The alternate view, that chloroboranes are formed in either case, requires acceptance of the premise that, unlike the case with tertiary amine–boranes, successive chlorination of secondary amine–boranes proceeds progressively *faster* as more chlorine is introduced into the coordination sphere of boron. It also requires stepwise chlorination from $R_2NH\cdot BH_3$ through $R_2NH\cdot BCl_3$ to occur quantiatively without hydrolytic loss of hydridic hydrogen, followed by rapid hydrolysis of the amine–trichloroborane to produce free secondary amine, which will be subject to rapid chlorination. Though not disproven, this scheme seems unlikely in view of the reported instability of secondary amine–haloboranes in aqueous media.[14]

Of the two alternatives, we tend to favor that involving separate transition-state configurations. Admittedly, there are disadvantagous features to a scheme that suggests an apparently subtle change from N–H to N–alkyl to cause an alteration in reaction pathway as opposed to a change in the rate of a comparable transformation proceeding by a common pathway. On the other hand, the B–H bond is not inherently highly polarized and it may not be unreasonable to imagine N-alkyl substitution to alter the directional polarization of a transition-state configuration, particularly in view of the well-known changes effected by B-substitution on reaction mechanism in the hydrolysis of amine–boranes[9,10,13,15-18] as well as the effect of N-substitution in establishing the relative importance of acid-independent and acid-dependent pathways for hydrolysis of alkylamine–, arylamine–, and selected heterocyclic amine–boranes.[9,10,18]

Acknowledgment. This research was supported by the Robert A. Welch Foundation (Grant P-162). We also acknowledge assistance of the TCU Research Fund.

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Equilibria and Kinetics of Complexation of Bidentate Ligands with the Macrocyclic Complex $Ni([14]aneN_4)^{2+}$

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The kinetics of reaction of several bidentate ligands X (ethylenediamine, glycinate, oxalate) with planar $Ni([14]aneN_4)^{2+}$ to produce cis octahedral $Ni([14]aneN_4)(X)$ has been examined. Both forward and reverse rate constants have been determined. The forward reaction is first order in nickel complex, independent of [X] over the range 2–40 mM, and first order in $[OH^-]$; the rate law is $k_f = 13[OH^-]\ s^{-1}$. The reverse reaction is first order in nickel complex, first order in $[OH^-]$, and inverse first order in [X]; the rate law is $2.6 \times 10^{-2}[OH^-]/[X]\ s^{-1}$. A mechanism is proposed for the reaction. In the forward direction, the folding of the macrocycle (base-catalyzed trans → cis isomerization) is rate determining, followed by rapid coordination of the bidentate ligand. In the reverse direction, rapid preequilibrium dissociation of the bidentate ligand is followed by rate-determining cis → trans isomerization. This mechanism is in sharp contrast to a recent study of the reaction of bidentate ligand with the related complex $Ni(trien)^{2+}$. Stability constants for the reaction of X with $Ni([14]aneN_4)^{2+}$ are reported.

Introduction

The kinetic stability of nickel(II) macrocycle complexes is strongly influenced by the macrocycle ring size, with the saturated tetraaza macrocycle $[14]aneN_4$ (1,4,8,11-tetraazacyclotetradecane) providing a complex of remarkable kinetic inertness toward dissociation.[1] Tetradentate macrocyclic ligands exhibit an overriding tendency to coordinate to metal ions in a planar geometry. This is especially true in the case

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of nickel(II) complexes, where the in-plane ligand field exerted by the macrocycle stabilizes low-spin, square-planar nickel(II). The formation and dissociation reactions of macrocyclic complexes, however, must involve intermediates in which the ligand is coordinated in a folded, cis geometry. Such intemediates have been postulated,[2] but little kinetic evidence has been provided.

Recently, a paper from our laboratory described a facile preparative path to the folded complex *cis*-$Ni([14]aneN_4)(H_2O)_2^{2+}$ and reported a kinetic study of the folded-to-planar isomerization.[3] In the present study, the kinetics of reaction of bidentate ligands (X = en, Gly^-, ox^{2-}) with the planar $Ni([14]aneN_4)^{2+}$ complex (eq 1) is examined.

$$Ni([14]aneN_4)^{2+} + X \rightleftharpoons Ni([14]aneN_4)(X) \quad k_f,\ k_r,\ K \qquad (1)$$

The study was undertaken in order to obtain kinetic and equilibrium information about the reverse isomerization process, from the planar to the folded geometry. Before the experiments were performed, it was assumed that the reaction would be first order in the attacking bidentate ligand as has been found for a large number of other systems.[4] Somewhat surprisingly, it was found that the rate is independent of the concentration of the bidentate ligand. The rate step of the reaction is determined by the macrocycle. This is in sharp contrast to a recent study by Steinhaus and Lee,[5] on the reaction of bidentate ligands with the related complex $Ni(trien)^{2+}$ (trien = $H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$).

Experimental Section

Reagents. $Ni([14]aneN_4)(ClO_4)_2$ was synthesized by the method of Barefield[6] and recrystallized several times from water. Glycine and sodium oxalate were reagent grade and were used as received. Ethylenediamine was redistilled; a stock solution was prepared by weight and standardized by pH titration.

Kinetic Measurements. The rate of formation of the mixed-ligand complex was measured by observing the disappearance of planar $Ni([14]aneN_4)^{2+}$ at 450 nm, by using a Cary 14 spectrophotometer and thermostated 10-cm cells (initial concentrations: $Ni([14]aneN_4)^{2+}$, 1.0–2.2 mM; X, 2.0–40.5 mM). Rate constants were obtained from plots of $\ln (A - A_\infty)$ vs. time. All rates were measured at 25 °C; ionic strength was adjusted to 0.10 by addition of sodium perchlorate. Reaction pH was adjusted by using borate buffer or by using the bidentate ligands (en or Gly) as buffers. No difference was detectable in reactions with and without borate buffer. Hydronium and hydroxide ion concentrations were obtained from $-\log [H^+] = pH - 0.11$ and $\log K_W = -13.78$ for 25 °C, $I = 0.10$.

Results

The stability constants of the mixed-ligand complexes are relatively low, owing to the planar tendency of the macrocycle. As a result, with ligand concentrations of 2–40 mM, particularly at the lower pH values, the reaction did not proceed to completion but rather to a position of equilibrium. From each kinetic run, therefore, the stability constant of the mixed-ligand complex could be calculated in addition to the rate constant, by using the equilibrium absorbance A_∞.

Stability Constants. The equilibrium constant for reaction 1 was calculated by using eq 2–4 (L = $[14]aneN_4$; X = en, Gly^-, ox^{2-}). Charges are omitted for clarity.

$$[NiL] = A_\infty/b\epsilon \qquad (2)$$

Table I. Stability Constants for Binding of Bidentate Ligands to Nickel(II) Centers

reaction	log K^a
$Ni(H_2O)_6^{2+}$ + en	7.6
$Ni(H_2O)_6^{2+}$ + Gly^-	5.9
$Ni(H_2O)_6^{2+}$ + ox^{2-}	5.3
$Ni(en)_2(H_2O)_2^{2+}$ + en	4.3
$Ni(trien)(H_2O)_2^{2+}$ + en	5.3^b
$Ni(trien)(H_2O)_2^{2+}$ + Gly^-	$4.0,^{c,d}$ 4.34 ± 0.02^e
$Ni([14]aneN_4)(H_2O)_2^{2+}$ + en	$2.56 \pm 0.05^{f,g}$
$Ni([14]aneN_4)(H_2O)_2^{2+}$ + Gly^-	$2.75 \pm 0.10^{f,g}$
$Ni([14]aneN_4)(H_2O)_2^{2+}$ + ox^{2-}	$2.6 \pm 0.2^{f,g}$
cis-$Ni([14]aneN_4)(H_2O)_2^{2+}$ + en	$4.2^{d,f}$
cis-$Ni([14]aneN_4)(H_2O)_2^{2+}$ + Gly^-	$4.4^{d,f}$
cis-$Ni([14]aneN_4)(H_2O)_2^{2+}$ + ox^{2-}	$4.2^{d,f}$

[a] From ref 8, unless otherwise noted. [b] Reference 4. [c] Reference 5. [d] From kinetic measurements. [e] Israeli, Y. J.; Volpe, R. *Bull. Soc. Chim. Fr.* **1971**, 3119. [f] This work. [g] NiL is a mixture of planar (70%) and octahedral (30%).

The molar absorptivity of planar $Ni([14]aneN_4)^{2+}$ depends on the concentration of perchlorate ion.[7] The following values of ϵ, determined in this study, were used in the calculations ($[ClO_4^-]$/M, ϵ/M^{-1} cm^{-1}): 0.002, 38; 0.01, 40; 0.03, 42; 0.05, 45; 0.10, 50. Resolution of the spectra of the mixed-ligand complexes into Gaussian bands showed that there was no significant contribution of the mixed-ligand species to the absorbance at 450 nm.

$$K = \frac{[NiL]_T - A_\infty/b\epsilon}{(A_\infty/b\epsilon)([X]_T - [NiL]_T + A_\infty/b\epsilon)\alpha} \qquad (3)$$

$$\alpha = (1 + K_1^H[H^+] + K_1^H K_2^H[H^+]^2)^{-1} \qquad (4)$$

In eq 3 and 4 $[NiL]_T$ and $[X]_T$ are the analytical concentrations and K_1^H and K_2^H are the protonation constants of the ligands. Equation 4 calculates the fraction of ligand in the complexing form. For en, $\log K_1^H = 10.0$ and $\log K_2^H = 7.0$; for Gly^-, $\log K_1^H = 9.6$.[8] All experiments with oxalate were performed at pH 9.62 ± 0.03, buffered with 0.05 M borate. The protonation constants of oxalate are small, and no corrections for protonated ligand are necessary at the pH values used in this study.

The stability constants obtained are listed in Table I with, for comparison, the corresponding stability constants of the ligands with aquonickel(II). The value for the en complex is in excellent agreement with the earlier value ($\log K = 2.6 \pm 0.1$) determined under conditions of no added $NaClO_4$.[4]

The similarity between the results for the three ligands is surprising. The stability constants are essentially identical, within experimental error, while the values for reaction with aquonickel(II) illustrate the much stronger binding constant of a nitrogen donor compared to a carboxylate. There is no doubt, however, that the mixed-ligand complexes are as formulated in eq 1. The spectra of the product solution in each case is in agreement with the expected nickel(II) chromophore, and in the case of the en complex, C,H,N, analysis[4] of the readily isolated violet precipitate is in agreement with the formula $Ni(C_{10}H_{24}N_4)(C_2H_8N_2)(ClO_4)_2$.

Kinetics of Formation of NiLX. Under the experimental conditions used (small K, excess [X]), reaction 1 is reversible and first order or pseudo first order in each direction. Plots of $\ln (A - A_\infty)$ vs. t under conditions of reversibility[9] yield k_{obsd} values given by eq 5. Since $k_f/k_r = K$, the forward and reverse

$$k_{obsd} = k_f + k_r \qquad (5)$$

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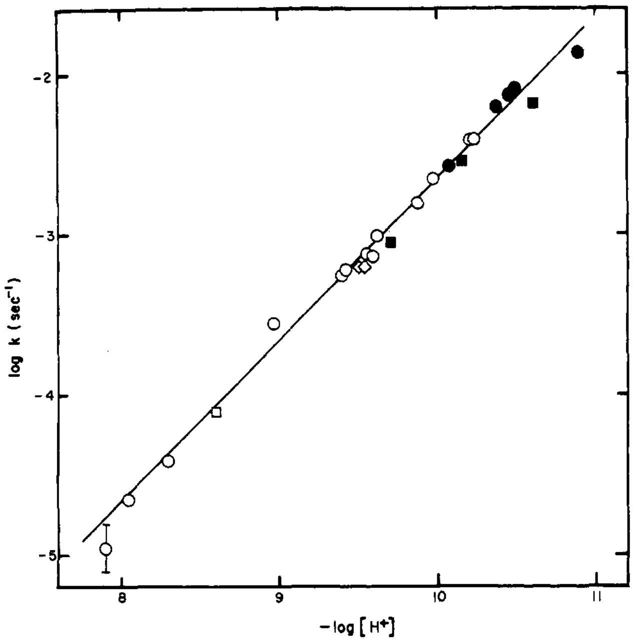

Figure 1. Variation of log k_f as a function of $-\log [H^+]$ ([X] = 2, 4, 10, 20, 40, mM; 25 °C; $I = 0.10$ M ($NaClO_4$)): circles, glycinate; squares, ethylenediamine; diamonds, oxalate. Open symbols indicate reactions run in 0.050 M borate buffer; solid symbols indicate those run without borate buffer. The line is calculated by using eq 6.

components of k_{obsd} can be determined. The extent of reaction $R = [NiLX]/[NiL]_T$ can be readily calculated from the expression $R = (A_0 - A_\infty)/A_0$, from which the individual rate constants can be obtained: $k_f = Rk_{obsd}$, $k_r = (1 - R)k_{obsd}$.

Plots of ln $(A - A_\infty)$ vs t were linear over several half-lives, even when $[X]_T \sim [NiL]_T$, indicating a reaction zero order in X. After correction for reversibility, k_f was found to be independent of [X] and base catalyzed (Figure 1). Within experimental error, runs using 2, 4, 10, 20, and 40 mM ligand concentrations fall on the same line when log k_f is plotted vs. $-\log [H^+]$. As well, results from all three ligands are identical. The line has a least-squares slope of 1.04 ± 0.02 and correlation coefficient of 0.997. The rate law is given by eq 6.

$$k_f = 13[OH^-] \tag{6}$$

In view of the observed ligand independence and base catalysis of the formation reaction, a mechanism is proposed in which the rate-determining step is isomerization of the macrocycle from planar to folded, followed by rapid coordination of the bidentate ligand (eq 7). An alternative mechanism

$$\text{planar} \xrightleftharpoons{\text{slow}} \text{folded} \xrightarrow{X} \text{NiLX} \tag{7}$$

would be the one suggested by Steinhaus[5] for the analogous reaction of $Ni(trien)^{2+}$ + X (X = 1,10-phenanthroline, glycine). In this mechanism (eq 8), a monodentate intermediate,

$$\text{NiL} + \text{X} \xrightleftharpoons{\text{rapid}} \text{NiL-X*} \xrightarrow{\text{slow}} \text{NiLX} \tag{8}$$

Ni(trien)-X* in rapid equilibrium with reactants is formed, followed by rate-determining ring closure. This mechanism predicts first-order dependence on X at low concentrations, shifting to zero-order dependence on X at high [X] when the intermediate is fully formed. For the $Ni([14]aneN_4)^{2+}$ system, this mechanism is discarded on the basis of the following arguments: (i) No deviation from zero order is detected, even at the lowest ligand concentrations. (ii) Zero-order dependence on [X] requires complete formation of the monodentate intermediate, yet estimates of the equilibrium constant for monodentate coordination of a nitrogen donor of either ethylenediamine or glycine[10] to a Ni(II) tetraaza complex suggest that, even at the highest concentration of X used, less than 50% of the intermediate complex would be formed. (iii) The proposed intermediate would be octahedral or at least more than four-coordinate, yet when absorbance data from kinetic runs was extrapolated to $t = 0$, there was no detectable decrease in A_0, from that calculated for the square-planar complex NiL^{2+}, by using the molar absorptivities given above. Formation of a few percent of an octahedral intermediate would have been detected.

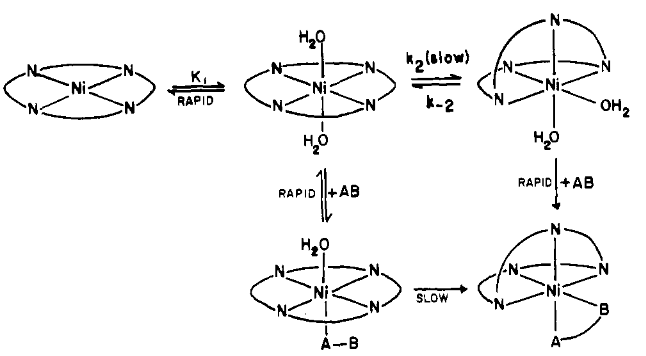

Figure 2. Two possible mechanisms for the reaction of a bidentate ligand (here shown as AB) with planar $Ni([14]aneN_4)^{2+}$.

The two possible paths for reaction are shown in Figure 2. An additional factor to be considered in the $Ni([14]aneN_4)^{2+}$ system is the extremely rapid low-spin–high-spin equilibrium K_1[11] (at 25 °C, 0.10 M $NaClO_4$, $K_1 = 0.4$ (70% low-spin NiL^{2+}, 30% high-spin *trans*-$NiL(H_2O)_2^{2+}$).

Consider first the mechanism proposed by Steinhaus[5] for the reaction of $Ni(trien)^{2+}$ with glycine. This mechanism, rapid formation of the intermediate followed by rate-determining ring closure, when applied to the $Ni([14]aneN_4)^{2+}$ case, would be the lower path shown in Figure 2. The slow ring closure, perhaps 100 times slower than "normal" ring closure rates, was attributed by Steinhaus for the $Ni(trien)^{3+}$ case to steric hindrance by the trien ligand. Spectral evidence[12] indicates that the trien complex is already in the cis geometry, *cis*-$Ni(trien)(H_2O)_2^{2+}$, and so the actual path for the trien reaction is simply the rapid coordination of the ligand to the folded complex, shown as the single vertical step on the right in Figure 2. If this mechanism were to be applied in the present case, the NiL complex would be planar (*trans*-$NiL(H_2O)_2^{2+}$) and the slow ring closure would be the result of steric and kinetic effects of the concomitant folding of the macrocycle.

Second, consider the alternate path, initial isomerization of the planar to the folded form followed by rapid coordination of X. Cassatt and Wilkins[13] measured the rate of reaction of a number of ligands with aquonickel(II); for glycinate, the rate constant is approximately 2×10^4 M^{-1} s^{-1}. This will be used here as an estimate of the rate of reaction of Gly^- with *cis*-$Ni([14]aneN_4)(H_2O)_2^{2+}$. In an earlier study[4] in our laboratory, the (reverse) isomerization rate of *cis*-$Ni([14]aneN_4)(H_2O)_2^{2+}$ to the trans form was measured; it is also base catalyzed and has the rate law (9). It was estimated that k_2

$$k_{-2} = 560[OH^-] \tag{9}$$

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(10) Estimated by using the equation of Jackobs and Margerum (Jackobs, N. E.; Margerum, D. W. *Inorg. Chem.* **1967**, *6*, 2038) from which log $K = 1.9$ or by using log K_5 for Ni^{2+}–NH_3 (log $K_5 = 0.9$) and including a statistical factor of 5, from which log $K = 1.6$. Coupled with $K_1 = 0.4$, the overall K would be ca. 20. This estimate does not include the steric interactions expected from the macrocycle.

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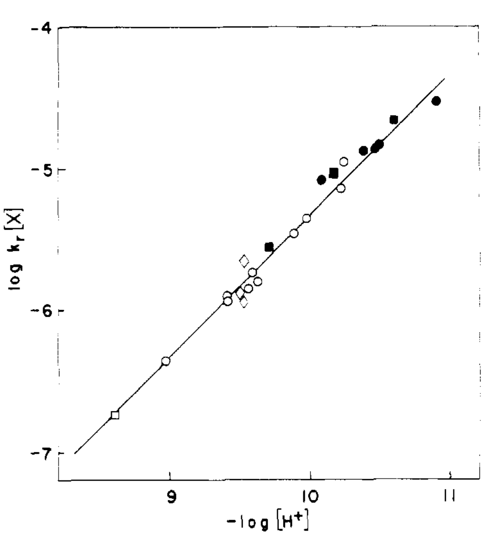

Figure 3. Variation of k_r[X] as a function of -log [H$^+$]. For the meaning of symbols, see Figure 1. The line is calculated by using eq 12.

is at least 100 times slower. Thus, even at the lowest Gly$^-$ concentration used, the subsequent coordination of X is much faster than base-catalyzed isomerization. These estimates confirm that macrocycle folding can indeed be the rate-determining step.

The rate and equilibrium constants involved in the proposed mechanism are defined in (10). The ligand-independent,

$$\mathrm{Ni([14]aneN_4)^{2+}} \overset{K_1}{\rightleftharpoons} \textit{trans}\text{-}\mathrm{Ni([14]aneN_4)(H_2O)_2}^{2+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \textit{cis}\text{-}\mathrm{Ni([14]aneN_4)(H_2O)_2}^{2+} \underset{k_{-3}}{\overset{k_3[\mathrm{X}]}{\rightleftharpoons}} \mathrm{Ni([14]aneN_4)(X)} \qquad (10)$$

base-catalyzed formation rate k_f is give by eq 11. Since K_1

$$k_f = K_1 k_2[\mathrm{OH^-}] \qquad (11)$$

= 0.4, k_2 is calculated to be 30 M^{-1} s^{-1}. This cis–trans equilibrium constant can thus be calculated from the kinetic data: $K_2 = k_2/k_{-2} = 30/560 = 0.055$. From K_1 (determined spectrophotometrically) and K_2, the percentages of planar, trans, and cis in aqueous solution at equilibrium (25 °C, I = 0.1) are calculated to be 69%, 29%, and 2%, respectively.

From the measured equilibrium constant for the formation of NiLX and the rate and equilibrium constants calculated from kinetic data, the equilibrium constant K_3 for the reaction of bidentate ligand with *cis*-Ni([14]aneN$_4$)(H$_2$O$_2$$^{2+}$ can be calculated. Thus, K(measd) = $K_1K_2K_3$, and hence $K_3 = k_{-2}K/K_1k_2$. From data for ethylenediamine (log K = 2.56 ± 0.05, K = 360 M^{-1}), a value of $K_3 = 1.6 \times 10^4$ (log K_3 = 4.2) is obtained. Similarly, from the stability constant values of glycine and oxalate, log K_3 values of 4.4 and 4.2, respectively, are obtained. These values can be compared with some literature values in Table I.

Kinetics of the Reverse Reaction. Since the rate law for the forward reaction does not contain [X], the reverse rate law is expected to be inverse first order in [X]. A plot of log k_r[X] vs. -log [H$^+$] was linear (Figure 3) with slope 0.92 ± 0.04 (correlation coefficient 0.98) while a plot of log k_r vs. -log [H$^+$] was scattered (correlation coefficient 0.64). The unit slope shows that the reverse reaction is also base catalyzed. (The deviation of the least-squares line from 1.00, the larger error in the slope, and the smaller correlation coefficient for the reverse reaction, compared to the forward reaction, reflect the fact that, for many of the rates measured, k_r was a minor contribution to k_{obsd}.) The rate expression is given by eq 12,

$$k_r = k_{-2}k_{-3}[\mathrm{OH^-}]/k_3[\mathrm{X}] \qquad (12)$$

the data of Figure 3 yielding a value of 2.6×10^{-2} s^{-1} for $k_{-2}k_{-3}/k_3$. As was observed for the forward reaction, the reverse reaction is independent of the identity of the ligand, at least within experimental error. Although this seems paradoxical at first glance (that the reverse rate is inverse first order in ligand concentration but independent of the identity of the ligand), it is simply another manifestation of the steric effect of the coordinated macrocycle on the binding of the bidentate ligand. This steric hindrance, particularly between NH$_2$ groups on the bidentate ligands en and Gly and ring methylenes of the macrocycle, gave rise to similar stability constants for three different ligands. The reverse rate constant k_r is a composite of k_{-2} (cis–trans isomerization of the macrocyclic complex) and K_3 (the stability constant for binding of X, which has essentially the same value for all three of the ligands). As well, the first-order dependence on [OH$^-$] tends to conceal small differences in the reverse rate, if indeed there are differences.

From eq 12 and the previously measured rate constant k_{-2} for the folded to planar isomerization,[4] the stability constant K_3 can be calculated. Since the reverse rate constant was the same for the three ligands studied, only a single value of K_3 can be calculated. A value of $K_3 = 2.2 \times 10^4$ M^{-1} (log K_3 = 4.3) is obtained, in excellent agreement with the values found in the forward rate study.

Conclusions

The results presented above are consistent with a mechanism in which rearrangement of the macrocycle geometry is the rate-determining step. Rearrangement from planar to folded requires inversion of two of the coordinated nitrogens.[14] Base catalysis of the rearrangement is assumed to occur via the conjugate base mechanism proposed for cobalt(III) complexes.[15] Hydroxide catalysis of the inversion of nitrogen atoms in the related, copper(II) complex of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane has been reported.[16] The rearrangement occurs by means of coordinated hydroxide. A similar mechanism cannot be ruled out at this time.

It is interesting to compare the rate laws and mechanisms for the substitution of bidentate ligands at three different nickel(II) centers: Ni(H$_2$O)$_6$$^{2+}$, Ni(trien)$^{2+}$, Ni([14]aneN$_4$)$^{2+}$. In the case of hexaaquonickel(II), the rate law is k[Ni^{2+}][X] and the mechanism is the familiar Eigen–Wilkins water loss mechanism. The rate of substitution is limited by the rate of loss of coordinated water from Ni(H$_2$O)$_6$$^{2+}$. Substitution of glycine on Ni(trien)$^{2+}$ should be faster than on Ni(H$_2$O)$_6$$^{2+}$, since Margerum has shown that coordinated nitrogens increase the lability of remaining coordinated water molecules. Substitution is found to be slower, however, and the results of Steinhaus and Lee demonstrate that in the case of a highly substituted nickel(II) center, chelate-ring closure can be rate determining, leading to a rate law in which the order in the entering ligand decreases from first order toward zero order. In contrast to this second study, however, the present work provides an example in which rearrangement of the tetraaza ligand, prior to coordination of the bidentate ligand, is rate determining. The high-spin–low-spin equilibrium and (presumably) steric crowding of the remaining coordination sites by the macrocycle combine to lower the stability constant for

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monodentate binding of the ligand X, so that the alternate path (proposed by Steinhaus for the Ni(trien)$^{2+}$ + Gly reaction) is not favorable. It is likely that other nickel(II) tetraaza ligand complexes that have either planar or *trans*-diaquo geometries and therefore must undergo rearrangement of the tetraaza ligand in order to react with polydentate ligands will react by a mechanism similar to the one proposed in this study.

Registry No. en, 107-15-3; Ni([14]aneN$_4$)$^{2+}$, 46365-93-9; glycine, 56-40-6; oxalic acid, 144-62-7.

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Equilibrium and Kinetic Studies of Substitution Reactions of Fe(TIM)XY^{2+} in Aqueous Solution

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Equilibrium and rate constants for substitution reactions of some bisligated complexes of Fe(TIM) (TIM is 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) in aqueous acetonitrile solutions are reported at 23 °C and an ionic strength of 0.5 M. The equilibrium constant for the replacement of CH_3CN by H_2O (K_1) in Fe(TIM)$(CH_3CN)_2^{2+}$ is 0.023 ± 0.002 whereas the same replacement in Fe(TIM)(CO)CH_3CN^{2+} (K_3) is 1.1 ± 0.1. The mechanism and the rates of establishment of these equilibria are dramatically affected by the π-accepting nature of the trans ligand, namely CH_3CN or CO. Substitution trans to CH_3CN is very rapid, with equilibration occurring on the time scale of milliseconds. On the other hand, the rate of approach to equilibrium in the replacement of CH_3CN for H_2O in Fe(TIM)(CO)CH_3CN^{2+} is complicated by two paths, one in which the ligand trans to the CO is directly replaced and the other in which the CO leaves, equilibration of the coordination sphere of the Fe(II) center occurs, and CO then recoordinates. This rate of approach to equilibrium occurs with a rate constant dependent upon the [CH_3CN], being about 3×10^{-3} s^{-1} at a [CH_3CN] of 1.0 M. In delineation of the complexities of the rate of approach to the equilibrium described by K_3, the rate constant for CO loss from Fe(TIM)(CO)H_2O^{2+} was determined to be 3.6×10^{-3} s^{-1}, and rate constants for all other steps involved were determined.

Introduction

Since the synthesis of 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene (hereafter abbreviated TIM) by Rose and co-workers in 1969,[2] a number of interesting chemical and physical properties of Fe(TIM)XY^{n+} molecules have been reported.[3-6] These properties led us to consider the possibility that this iron complex could act as a sensitizer for a number of photolytic reactions in aqueous solution. This possibility is given some credence by the report of Rose and co-workers, who have established that the bis(methanol) adduct, Fe(TIM)$(CH_3OH)_2^{2+}$, is oxidized by dioxygen in air and that the resultant Fe(III) complex is then susceptible to photolysis that leads to oxidation of methanol to formaldehyde accompanied by regeneration of the original Fe(II) complex.[4] Moreover, our attention was drawn even more strongly to this molecule by the report of Incorvia and Zink,[5] who found that photolyses of Fe(TIM)(CO)CH_3CN^{2+} are different depending on the solvent in which the photolysis takes place, a result that they interpreted as a highly unusual solvent mediation of a primary photophysical event. We decided, therefore, that further study of this molecule was appropriate to learn more about both its thermal and photolytic properties.

A variety of questions are raised by these considerations, excluding how the processes take place. Among them are the following: What, if any, are the substitutions that take place in Fe(TIM)XY^{2+} in aqueous solutions? What is the time scale in which substitution reactions of the axial ligands take place? What is the affinity of the Fe(TIM)$^{n+}$ center for axial ligands with back-bonding characteristics? What can be said of the inherent oxidation–reduction reactivity of Fe(TIM)XY^{2+}? In this and following reports on this molecule we will address these questions.

Our initial experiments on Fe(TIM)XY^{2+} quickly established that substitution reactions occurred on two separate time scales, one on the order of less than a second and the other on the order of minutes to hours. In this paper we report equilibria occurring when Fe(TIM)$(CH_3CN)_2^{2+}$ and Fe(TIM)(CO)CH_3CN^{2+} are in aqueous acidic acetonitrile solution and the kinetics of the slower processes of substitutions. In future papers, we will discuss the rapid substitution reactions of Fe(TIM)$(CH_3CN)_2^{2+}$, Fe(TIM)$(CH_3CN)H_2O^{2+}$, and Fe(TIM)$(H_2O)_2^{2+}$[7] and results of oxidation–reduction kinetics of Fe(TIM)XY^{2+}.[8]

Experimental Section

Materials. [Fe(TIM)$(CH_3CN)_2$]$(PF_6)_2$ was synthesized according to the procedure of Reichgott and Rose,[4] modified as indicated. Argon was used as an inert gas, and the reaction was stirred for 48 h at 35 °C under a stream of this gas rather than being sealed for 24 h under nitrogen. The crude yield contained a substantial amount of a tan-brown impurity, which was removed by recrystallization; about 0.5 g of the crude material was added to approximately 7 mL of CH_3CN, and the mixture was filtered quickly. Cold ethanol (about 50 mL) was added, and the mixture was filtered as soon as possible. The burgundy-colored solid thus obtained was washed with cold ethanol and cold ether quickly, so as to avoid any oxidation. [Fe(TIM)(CO)CH_3CN]$(PF_6)_2$ was prepared by the published procedure.[3] Solutions of Fe(TIM)XY^{2+} were prepared from the solid material by weight or analyzed for iron content by utilization of the 550-nm peak of Fe(TIM)$(CH_3CN)_2^{2+}$, where the extinction coefficient in

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