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Kinetics of Dissociation and Isomerization of *cis*-$Ni([14]aneN_4)(H_2O)_2{}^{2+}$ in Aqueous Perchloric Acid Solutions

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The kinetics of isomerization of the folded macrocyclic complex *cis*-$Ni([14]aneN_4)(H_2O)_2{}^{2+}$ to planar $Ni([14)aneN_4)^{2+}$ have been studied in aqueous 0.1-3 M perchloric acid at 25 °C. At these acidities dissociation competes with isomerization. The rate law for dissociation of the folded isomer is $k = 3 \times 10^6[H^+]$ s^{-1}. The folded isomer is a likely intermediate in the extremely slow acid dissociation of the planar complex. A mechanism for this dissociation is proposed, and from rate constants for isomerization and dissociation, the half-life for the dissociation of the planar complex is estimated to be approximately 30 years. From perchloric acid solutions of greater than 3 M, a new isomer of planar $Ni([14]aneN_4)^{2+}$ was isolated; this isomer is a configurational isomer, in which the nitrogen configurations are the same as in the folded form.

A facile method for the preparation of nickel(II) complexes containing the macrocyclic ligand $[14]aneN_4$ in the folded geometry has recently been described.[1] The complex ion *cis*-$Ni([14]aneN_4)(H_2O)_2{}^{2+}$ slowly isomerizes in aqueous solution to the planar complex (a mixture[2] of planar $Ni([14]aneN_4)^{2+}$ and *trans*-$Ni([14]aneN_4)(H_2O)_2{}^{2+}$). The isomerization, studied over the pH range 1-10, is acid and base catalyzed, and the rate reaches a minimum at pH 3, where the half-life is 250 days at 25 °C. The previous paper pointed out that the folded isomer is a likely intermediate in the formation and dissociation reactions of $Ni([14]aneN_4)^{2+}$. The dissociation of planar $Ni([14]aneN_4)^{2+}$ in acidic solution is extremely slow,[3] and it is unlikely that folded or partially unwrapped intermediates could be detected. In the present study we report the dissociation of the folded complex in 0.1-3 M $HClO_4$, the results of which provide information about the "unwrapping" of a macrocyclic tetraaza ligand from nickel(II). In addition, in even higher concentrations of perchloric acid (4-12 M), an isomeric form of planar $Ni([14]aneN_4)^{2+}$, differing in the conformation of coordinated nitrogens, is observed and can be isolated.

Experimental Section

The complex *cis*-$Ni([14]aneN_4)X_2$ (X = Cl, Br) was prepared as previously described.[1] A typical preparation of the unstable planar isomer, α-$Ni([14]aneN_4)(ClO_4)_2$, was as follows: 0.67 g of *cis*-$Ni([14]aneN_4)Br_2$ was dissolved in 2.0 mL of water. To this violet solution was added 6.0 mL of 70% $HClO_4$. The resulting orange solution, from which orange needles began to crystallize, was cooled in the refrigerator. The orange crystals were filtered, washed with absolute ethanol and ether, and air-dried (*caution! explosive*); yield 0.56 g. Anal. Calcd: C, 26.23; H, 5.28; N, 12.24. Found: C, 26.26; H, 5.35; N, 12.01.

Isomerization rates were determined as previously described.[1] Effective molar absorptivities of $Ni([14]aneN_4)^{2+}$ at 450 nm used were as follows [$[ClO_4^-]$ (M), ϵ (M^{-1} cm^{-1})]: 0.10, 50; 0.50, 54; 1.0, 56; 2.0, 57; 3.0, 58.

Results and Discussion

The isomerization of *cis*-$Ni([14]aneN_4)(H_2O)_2{}^{2+}$ to *trans*-$Ni([14]aneN_4)(H_2O)_2{}^{2+}$ over the pH range 1-10 was studied earlier.[1] The trans isomer is in rapid equilibrium with planar $Ni([14)aneN_4)^{2+}$, and the appearance of the latter was monitored at 450 nm ($\epsilon = 50$ at $[ClO_4^-] = 0.10$). The reaction is acid catalyzed in the pH range 1-3; the rate constant was found to be 5.8×10^{-6} M^{-1} s^{-1}.

Table I. Isomerization and Dissociation Reactions of *cis*-$Ni([14]aneN_4)(H_2O)_2{}^{2+}$ at 25 °C

$[HClO_4]$, M	10^5k_{obsd}, s^{-1}	A_{obsd}/A_{calcd}	10^5k_{isom}, s^{-1}	10^5k_{diss}, s^{-1}
0.1	0.058			
0.5	0.33	0.73	0.24	0.09
1.0	0.49	0.61	0.30	0.19
2.0	1.06	0.51 ± 0.05 ($N = 3$)	0.54	0.52
3.0	1.4	0.38 ± 0.02 ($N = 4$)	0.5	0.9

In the more acidic solutions studied in the present work (up to 3 M $HClO_4$), dissociation of the folded isomer competes with isomerization (eq 1). When reactions were followed to

$$\text{trans complex} \xleftarrow{k_{isom}} \text{cis complex} \xrightarrow{k_{diss}} Ni^{2+} + \text{protonated ligand} \quad (1)$$

completion, the absorbance at t_∞, A_{obsd}, was less than the calculated value, A_{calcd}, as shown in Figure 1. The observed rates of formation, k_{obsd}, of the planar product were obtained by using the usual first-order kinetic treatment, by plotting $\ln (A_\infty - A_t)$ vs. t. For two concurrent, competing first-order reactions, the ratio of rate constants can be obtained from the product ratio.[4] The product ratio (Ni^{2+}/trans complex) can be readily calculated from the ratio of absorbances $R = A_{obsd}/A_{calcd}$. The relationship between R, k_{diss}, and k_{isom} is shown in eq 2.

$$k_{diss} = (1 - R)k_{isom}/R \quad (2)$$

As well, for two concurrent competing reactions, the observed rate of loss of reactant or rate of formation of either product is given by eq 3.[4]

$$k_{obsd} = k_{isom} + k_{diss} \quad (3)$$

By use of eq 2 and 3, the rates of isomerization and dissociation can be obtained from the observed rates and corresponding product ratios as shown in Table I. The data of Table I show that the rate of dissociation appears to be first order in $[H^+]$ up to 3 M $HClO_4$, although the range of $HClO_4$ concentrations over which rates could be measured is small. The rate law for dissociation is $k_{diss} = 3 \times 10^{-6}[H^+]$ s^{-1}. Similar results were observed by Murphy and Zompa[5] who studied the acid dissociation of nickel(II) complexes of cyclic triamines in acid concentrations up to 5 M. In contrast, the isomerization appears to level off at the highest acid concen-

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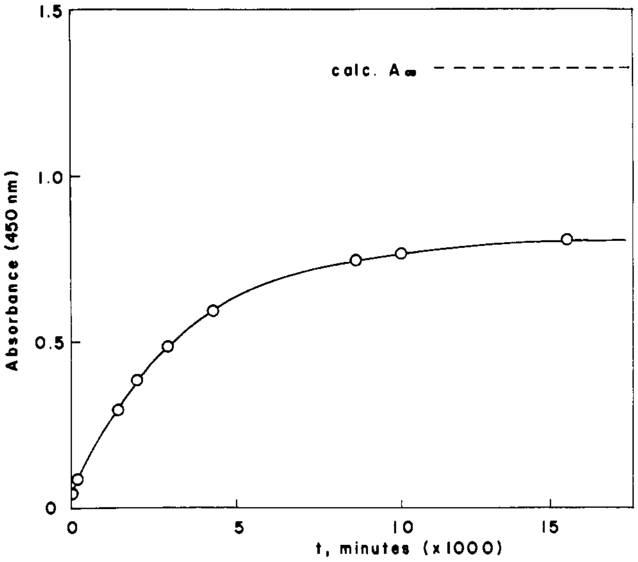

Figure 1. Isomerization/dissociation of *cis*-Ni([14]aneN$_4$)(H$_2$O)$_2^{2+}$ in 1.0 M HClO$_4$ at 25 °C ([complex]$_0$ = 2.36 mM, path length 5 cm, A_∞(calcd) = 1.32, A_∞(obsd) = 0.806).

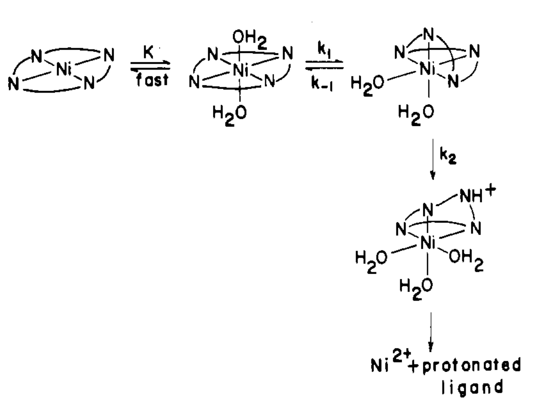

Figure 2. Proposed mechanism for the isomerization and dissociation of Ni^{2+}–[14]aneN$_4$ complexes.

trations; until further studies are performed, it is fruitless to speculate whether this is a change in order with respect to [H$^+$] or an ionic strength effect.

The mechanism proposed for the isomerization and dissociation of *cis*-Ni([14]aneN$_4$)(H$_2$O)$_2^{2+}$ is shown in Figure 2. Isomerization is shown horizontally, dissociation vertically. A similar general mechanism for complexes of macrocyclic ligands has been suggested by Busch.[6] In the present study all of the rate or equilibrium constants shown in Figure 2 have been evaluated ($k_{\text{diss}} = k_2[\text{H}^+]$, $k_{\text{isom}} = k_{-1}[\text{H}^+]$). The equilibrium constant K_1 (k_1/k_{-1}) for trans–cis isomerization has been estimated, with equilibrium constant data, to be 2×10^{-3}.[1] The trans → cis rate constant k_1 can thus be estimated. Since the k_{-1} path is acid catalyzed, the k_1 path must be also. The planar-trans equilibrium constant K is dependent on perchlorate ion concentration and can be evaluated spectrophotometrically[2] by using the effective molar absorptivity data given in the Experimental Section and a molar absorptivity of 64 for the planar complex.[2]

After this work was completed, a study of the dissociation of the unstable blue form of (*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)copper(2+) was published by Liang and Chung.[7] Their findings were similar, although they found recoordination of the partially dissociated protonated amine to be faster than the subsequent dissociation step. This is a result of the structure of the macrocyclic ligand, maintaining the uncoordinated amine in proximity to the metal ion, and is in contrast to the behavior observed with many linear polyamines.[8]

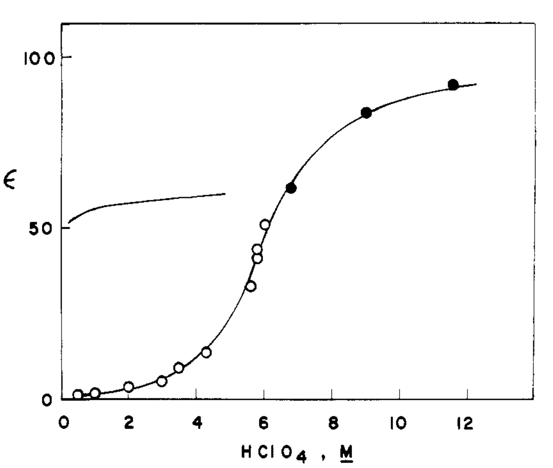

Figure 3. Effective molar absorptivity, A/bC_T, at 450 nm for the isomeric complex α-Ni([14]aneN$_4$)$^{2+}$, as a function of perchloric acid concentration: open circles, solutions prepared from *cis*-Ni([14]aneN$_4$)$^{2+}$; solid circles, solutions prepared from α-Ni([14]aneN$_4$)(ClO$_4$)$_2$. The curve shown without data points is for the stable or β form of Ni([14]aneN$_4$)$^{2+}$.

Evaluation of all the rate or equilibrium constants shown in Figure 2 permits the estimation of the rate of dissociation of planar Ni([14]aneN$_4$)$^{2+}$ in acidic solution. This complex is extremely kinetically inert. Measurement of the rate of dissociation has been attempted previously; Busch reported no detectable dissociation in 0.3 M HClO$_4$ over a period of many months.[3]

From the mechanism of Figure 2, the rate constant for dissociation of Ni([14]aneN$_4$)$^{2+}$ in acid is

$$k_d = KK_1k_2[\text{H}^+] \tag{4}$$

From data for 1.0 M HClO$_4$ ($K = 0.14$, $K_1 = 0.002$, $k_2 = 3 \times 10^{-6}$ M^{-1} s^{-1}), k_d is estimated to be 8×10^{-10} s^{-1}, corresponding to a half-life of approximately 30 years. In order to obtain an estimate of the rate of dissociation of Ni([14]aneN$_4$)$^{2+}$, a solution of several times recrystallized Ni([14]aneN$_4$)(ClO$_4$)$_2$ was prepared in 1.0 M HClO$_4$ and maintained at 25 °C. After 164 days, the absorbance had decreased by 2.1%; after 589 days, by 5.4%. The rate constant calculated from these measurements is $k_d = 1 \times 10^{-9}$ s^{-1}. Agreement between this measured value and the k_d estimated above from eq 4 is surprisingly good. The greatest source of error in the calculated value probably arises in the estimation of K_1 (k_1/k_{-1}) from equilibrium constant measurements.[1] As described previously, this estimate of K_1 should be a lower limit; a larger value of K_1 would improve the agreement between calculated and experimental values.

The Configurational Isomer α-Ni([14]aneN$_4$)$^{2+}$

Although the isomerization of violet *cis*-Ni([14]aneN$_4$)(H$_2$O)$_2^{2+}$ to yellow Ni([14]aneN$_4$)$^{2+}$ occurred over several days even in 3 M HClO$_4$, it was observed that solutions of the cis complex became yellow immediately in perchloric acid solutions more concentrated than 3 M. A band at 450 nm is observed, but the reaction is reversible; upon dilution, the spectrum of the cis complex is regenerated. The intensity of the band at 450 nm, indicative of a square-planar NiN$_4^{2+}$ complex, is favored by increasing [ClO$_4^-$] in the same way as is observed for other octahedral to planar conversions. Figure

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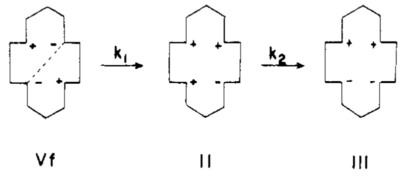

Figure 4. Proposed configurational isomers involved in the isomerization of *cis*-Ni([14]aneN_4)$(H_2O)_2^{2+}$.

3 shows the variation of effective molar absorptivity as a function of perchloric acid concentration. The molar absorptivity of the complex is 100 M^{-1} cm^{-1}, in contrast to that of "normal" Ni([14]aneN_4)$^{2+}$, which has a molar absorptivity of 64. From relatively concentrated solutions of perchloric acid, crystals of α-Ni([14]aneN_4)$(ClO_4)_2$ can be isolated. The perchlorate concentrations necessary to stabilize the α planar form are quite high and are similar to those necessary to produce the low-spin form of Ni(trien)$^{2+}$.[9,10]

The isomeric complex, α-Ni([14]aneN_4)$^{2+}$, must be a configurational isomer, in which the nitrogens have a different configuration than that of the stable β isomer. (The unstable isomer is designated the α isomer in conformity with the designations applied to similar configurational isomers of (*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(2+) by Curtis[11].) The stable planar Ni([14]aneN_4)$(ClO_4)_2$ has structure III,[12] in which the five-membered rings are gauche and the six-membered rings adopt the chair form. This geometry, the lowest energy of the five possible planar forms,[13] has two amine hydrogens on adjacent nitrogens above the plane of the complex, while the other two are below the plane.

The α planar complex presumably has the same nitrogen configuration as the folded isomer Vf.[13] Two amine hydrogens on opposite nitrogens are above the plane (structure II). No kinetic evidence was found to suggest otherwise: dissolution of orange α-Ni([14]aneN_4)$(ClO_4)_2$ in water gave violet solutions of *cis*-Ni([14]aneN_4)$(H_2O)_2^{2+}$, and these solutions isomerized to the stable planar form at the same rate as solutions prepared from the original samples of the folded isomer.

A reasonable kinetic scheme for isomerization would require the successive inversion of two amine protons (Vf → II → III). The isomerization reaction was found to be acid and base catalyzed, first order in either [H^+] or [OH^-].[1] Since two protons are being inverted, yet the reaction is only first order in acid or base, it is necessary to postulate that the second inversion is more rapid than the first. Base catalysis likely arises from the familiar conjugate-base mechanism. Ionization of an amine proton on the nitrogen to be inverted could provide a simple pathway for inversion. Acid catalysis may occur via the mechanism recently suggested by Margerum.[8,14] At relatively high proton concentrations, a metal–nitrogen bond may be broken and the nitrogen protonated before the metal ion is solvated. This may require a relatively modest lengthening of the metal–nitrogen bond distance before the metal–nitrogen bond is effectively "broken". This mechanism, which gives rise to a [H^+] dependence of dissociation rates, is particularly applicable to dissociation reactions of macrocycles, where the donor atoms are constrained by the ligand structure to remain close to the metal ion.

In summary, generation of the folded isomer of Ni([14]aneN_4)$^{2+}$ permits the examination of isomerization and dissociation pathways in acid solution and has provided an estimate of the extremely slow rate of acid dissociation of Ni([14]aneN_4)$^{2+}$. Because of the extreme kinetic inertness of the [14]aneN_4 complex, a systematic study of the acid dissociation rate law is difficult. The [13]aneN_4 complex, a more labile system, will permit a fuller elucidation of the mechanism of dissociation of a nickel(II)–N_4 macrocyclic complex.[15]

Registry No. *cis*-Ni([14]aneN_4)$(H_2O)_2^{2+}$, 78684-35-2; Ni([14]aneN_4)$^{2+}$, 46365-93-9.

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1,2-Bis(*F*-alkyl)cyclo-1,2-diaza-3-sulfanes, 1,2-Bis(*F*-alkyl)cyclo-1,2-diaza-3,4,5-trisulfanes, and 1,2-Bis(*F*-alkyl)cyclo-1,2-diaza-3,4,5,6-tetrasulfanes, $R_f\overline{N-S_x-N}R_f$ (x = 1, 3, 4)

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A new class of sulfur–nitrogen heterocyclic compounds with the general formula $R_f\overline{N-S_x-N}R_f$ (where R_f = CF_2Cl or C_2F_5 and x = 1, 3, or 4) results from the photolysis of $R_fN{=}NR_f$ and S_2Cl_2. These heterocyclic compounds are pale yellow, high-boiling liquids that decompose on standing at 25 °C. The new compound $CF_2ClN{=}NCF_2Cl$ was synthesized by photolysis of CF_2ClNCl_2 at 0 °C.

Introduction

In the chemistry of inorganic heterocycles, sulfur–nitrogen compounds are important both historically and currently. Tetrasulfur tetranitride, first prepared in 1835, is one of the oldest and most studied of all inorganic heterocycles, yet its chemistry still challenges the imagination. There are a very large number of cyclic sulfur–nitrogen compounds in which the nitrogen atoms are in the 1,3- or 1,4-positions, e.g., N_2S_2, $N_2S_3^+$, N_2S_4, $N_3S_4^+$, and N_4S_4, but there are few examples of cyclic sulfur–nitrogen heterocyclic compounds in which the nitrogen atoms are vicinal.[2,3] While the synthesis of these

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(1) Present address: Department of Chemistry, Baldwin-Wallace College, Berea, OH 44017.

(2) Roesky, H. W. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 240 and references therein.