Marcus–Hush correlations and the implication is that both systems are essentially adiabatic. The probability that the electron-tunneling and nuclear-tunneling factors cancel to the same degree in each system seems too remote to contemplate. The argument regarding adiabatic behavior would not be secure, however, if the partner ions in the activated complex could be considered to reach the transition-state energy essentially by independent activation.[38]

Registry No. $[Co(sep)]^{3+}$, 72496-77-6; $[Co(sar)]^{3+}$, 85664-13-7; $[Co(en)_3]^{3+}$, 14878-41-2; $[Co(diamsarH_2)]^{5+}$, 85663-73-6; $[Co(azamesar)]^{3+}$, 85664-08-0; $[Co(ammesarH)]^{4+}$, 85663-85-0; $[Co(diamsar)]^{3+}$, 85663-96-3; $[Co(NH_3)_6]^{3+}$, 14695-95-5; $[Co(bpy)_3]^{3+}$, 19052-39-2; $[Co(phen)_3]^{3+}$, 18581-79-8; Cr^{2+}, 22541-79-3; Eu^{2+}, 16910-54-6; V^{2+}, 15121-26-3; U^{3+}, 22578-81-0.

Supplementary Material Available: Tables containing the experimental kinetic data and data for calculation of k_{12}^{calcd} including work terms (12 pages). Ordering information is given on any current masthead page.

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Acid Cleavage of Nickel(II) Complexes Containing *cis,cis*-1,3,5-Cyclohexanetriamine (tach), Crystal Structure of $[Ni(tach)(H_2O)_3](NO_3)_2$, and a Correlation between Structure and Reactivity of Nickel–Polyamine Complexes

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The cleavage of $Ni(tach)_2^{2+}$ (tach = *cis,cis*-1,3,5-cyclohexanetriamine) to give $Ni(tach)(H_2O)_3^{2+}$ is strictly first order in complex, and no intermediate species has been detected. The observed rate constant is strongly acid dependent, and for HCl and HBF_4 the rate law is $k_{\text{obsd}} = k_1/\{1 + (b + c[H^+])^{-1} + (e + f[H^+])^{-1}\}$ with a limiting rate constant $k_1 = 0.78 \pm 0.02$ s^{-1}, $\Delta H^* = 72 \pm 2$ kJ mol^{-1}, and $\Delta S^* = -6 \pm 6$ J K^{-1} mol^{-1} (25 °C, $\mu = 1.0$ M). The limiting rate is ascribed to the first Ni–N bond rupture, apparently not involving the chair–boat (skew boat) conformational change of the ligand in the rate-determining step; the acid dependence is traced to a competition between protonation and rechelation of partly dissociated amine ligand. Cleavage in acetate/acetic acid buffers shows that the reaction is catalyzed by acetate and/or acetic acid and that the acid dependence has to be more complex than that indicated above. Cleavage of the Ni–N bonds in acid for $Ni(tach)(H_2O)_3^{2+}$ is markedly slower than for $Ni(tach)_2^{2+}$ at the same acid concentrations and has a rate law of the form $k_{\text{obsd}} = k_0 + k_{HX}[HX]$ (25 °C, $\mu = 3.0$ M, $k_0 \approx 6 \times 10^{-5}$ s^{-1}, HX = $HClO_4$, HCOOH, $Cl_2CHCOOH$, CH_3COOH, and $H_2PO_4^-$). The behavior is accommodated by a mechanism similar to that proposed for the bis complex. An X-ray crystallographic analysis of $[Ni(tach)(H_2O)_3](NO_3)_2$ (space group *Pnma*, $Z = 4$, $a = 14.142$ (2) Å, $b = 12.637$ (2) Å, and $c = 8.000$ (1) Å) showed the amine coordinated tridentate to the Ni^{2+} ion with Ni–N distances (2.07 Å) ~0.06 Å shorter than those in $[Ni(tach)_2](NO_3)_2$; conversely Ni–O distances (2.10 Å) are ~0.05 Å longer than in $Ni(H_2O)_6^{2+}$. An analogous trend is observed for the Ni–N and Ni–O distances of $Ni(en)_n^{2+}$ (n = 1–3); Ni–N and Ni–O bond distances decrease with increasing number of water oxygen atoms in the first coordination sphere. Within each family of complexes the rates of Ni–N or Ni–O bond rupture correlate with bond lengths: short bonds are cleaved more slowly than long bonds.

Introduction

The complex ion $Ni(tach)(H_2O)_3^{2+}$ (tach = *cis,cis*-1,3,5-triaminocyclohexane) is strikingly inert to substitution of the ligand by water. It is cleaved by strong acids with a reaction half-life $t_{1/2} \approx 3600$ s (0.7 M $HClO_4$, 25 °C).[7] By comparison, $Ni(dien)(H_2O)_3^{2+}$ (dien = 3-azapentane-1,5-diamine) decomposes much more rapidly in acid;[8] it has a reaction half-life $t_{1/2} \approx 0.05$ s. $Ni(tach)_2^{2+}$ with six nitrogens as ligand atoms is somewhat less labile ($t_{1/2} \approx 1$ s). Acid catalysis of the decomposition of $Ni(tach)_2^{2+}$ to $Ni(tach)(H_2O)_3^{2+}$ and of the latter to $Ni(H_2O)_6^{2+}$ and H_3tach^{3+} requires proton concentrations at which the rate constants for cleavage of related nickel amine complexes appear to be pH independent.[9] It is therefore difficult to compare observed rate constants for hydrolysis of different nickel amine complexes directly.

The constitution and conformational flexibility of the coordinating amine ligand might be one of the factors determining the rate constant of the cleavage reaction. Specifically, the activation energy for chair–boat interconversion of the cyclohexane ring in tach or of a six-membered chelate ring might be coupled with the activation energy for Ni–N rupture.

Such observations and ideas prompted us to investigate in some detail the kinetics of the cleavage of tach from $Ni(tach)_2^{2+}$ and $Ni(tach)(H_2O)_3^{2+}$ in acid solution. X-ray crystallographic investigations of both ions have been carried out[10,11] in order to define the denticity of the ligand and the precise geometry of the complex cations. Structural data have been compared to kinetic data to see whether correlations exist between the two classes of experimental results.

Experimental Section

Syntheses. The complexes $[Ni(tach)_2]Cl_2$ and $[Ni(tach)(H_2O)_3]Cl_2$ were synthesized as previously described.[12] $Ni(tach)(en)(H_2O)^{2+}$

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Figure 1. Stereoscopic drawing of $Ni(tach)(H_2O)_3^{2+}$ showing atomic numbering.[43]

was synthesized by mixing equimolar amounts of the $Ni(tach)(H_2O)_3^{2+}$ complex and en (en = 1,2-ethanediamine) in aqueous solution. It was also isolated as a crystalline perchlorate salt.

Kinetics. The kinetics were followed with either a Cary 118C or a Cary 16K spectrophotometer by monitoring absorbance changes at 600 nm ($Ni(tach)_2^{2+}$) or 590 nm ($Ni(tach)^{2+}$) for complex concentrations in the range 2–10 mM. Linear plots of log $(A - A_\infty)$ vs. time were obtained over at least 4 half-lives to yield the pseudo-first-order rate constants, which have been used in the kinetic analysis. The reactions were usually initiated by mixing solutions of complex and acid or buffer at 25 °C at an ionic strength of 1.0 or 3.0 M in a hand-operated stopped-flow reactor. This allowed the absorbance change to be monitored accurately within 0.5 s of mixing. In attempts to observe intermediate species, some experiments were carried out on a shorter time scale ($\geq$10 ms) using a Durrum stopped-flow reactor.

In the study of $Ni(tach)_2^{2+}$, ionic strength was usually maintained at 1.0 M with sodium chloride, in the presence of varying concentrations of acetate anion (OAc^-). Perchlorate solutions could not be used because of the low solubility of $[Ni(tach)_2](ClO_4)_2$. One set of experiments was performed with sodium tetrafluoroborate as the electrolyte background. For pH values below 1.2, concentrated acid solutions (0.1–1.0 M) were employed. Higher pH values were obtained, in the absence of acetate ion, with use of an aniline-2-sulfonate buffer ([buffer] = 0.06 M). For solutions containing acetate ion, the pH was adjusted by varying [HOAc]. The pH was measured with a Radiometer G202B glass electrode and a saturated calomel electrode in association with a Radiometer PHM26 meter, standardized against tetraoxalate (pH 1.68) and phthalate (pH 4.01) buffers. The pH of solutions immediately after reaction was also measured, and ΔpH was always <0.05.

Dissociation of $Ni(tach)(H_2O)_3^{2+}$ was measured in a range of solutions: in acids, $HClO_4$ (0.05–3.0 M, μ = 3.0 M ($NaClO_4$)), HNO_3 (3 M), HCl (3 M); in the buffer solutions, HCOOH/HCOONa (0.17–1.0 M in acid), CH_3COOH/CH_3COONa (1.0–3.0 M in acid), $Cl_2CHCOOH/Cl_2CHCOONa$ (0.3–2.9 M in acid); in NaH_2PO_4 (0.1–3.0 M); in saturated *p*-chloroaniline in $HClO_4$ (0.5–1.25 M).

Kinetic Calculations. The parameters in the rate expressions (7) and (11) were determined by minimization of $\sum(k_{obsd} - k_{calcd})^2/\sigma^2(k_{obsd})$ by (nonlinear) regression analysis; all rate constants were assumed to have the same relative error.

X-ray Structure Determination. Crystal data and details of the intensity measurements and structure analysis are given as supplementary material.

Results

Structural Aspects. Atomic coordinates, thermal parameters, and bond lengths and angles for the $[Ni(tach)(H_2O)_3](NO_3)_2$ complex are given as supplementary material. A drawing of the molecule with the numbering system used is shown in Figure 1. Selected bond distances and angles for $Ni(tach)(H_2O)_3^{2+}$ (average of two determinations) and $Ni(tach)_2^{2+}$ are collected in Table I.

The difference between the geometries of the tach ligands in the mono and bis complexes are not substantial (Table I). Contrary to Huffmann et al.[11] we find that differences in the Ni–N distances and the N–Ni–N angles *are* significant. They may be rationalized in terms of the height of the NiN_3 pyramid. This height decreases on going from $Ni(tach)_2^{2+}$ to $Ni(tach)(OH_2)_3^{2+}$, and since the base of the pyramid is unchanged, this implies a shortening of the Ni–N bonds (average 0.064 Å). The Ni–O distances in $Ni(tach)(H_2O)_3^{2+}$ are longer (by an average of 0.05 Å) than in $Ni(H_2O)_6^{2+}$.

Kinetics. $[Ni(tach)_2]^{2+}$. The pH–rate constant profile is sigmoid, as shown in Figure 2, and reaches a limiting rate constant of 0.78 (±0.02) s^{-1} (25 °C, μ = 1.0 M) in the high-acidity region. This limiting value is independent of the acid anion; high concentrations of HCl, HBF_4, and CF_3COOH yield the same value within experimental error. Indeed, the rate constant–pH profile from pH 0 to pH 3 was essentially the same for HCl and HBF_4 (Figure 2 and Table II).

In acetate/acetic acid buffers the anion and the total acid become involved in the rate law. Dissociation rate constants at a particular pH increase with increasing concentrations of added acetate ion in a nonlinear manner (Table II and Figure 2). For a particular concentration of added acetate, the rate constant–pH profile appears to almost parallel that of the

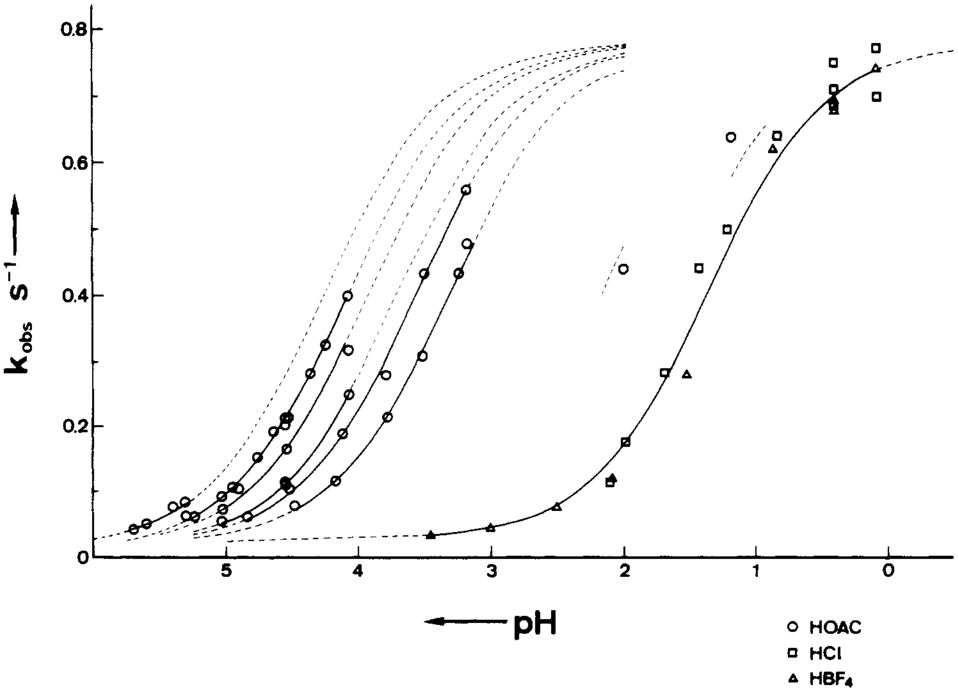

Figure 2. Cleavage of $Ni(tach)_2^{2+}$ ion in acid and buffer solutions at 25 °C, μ = 1.0 M. The curves are a calculated least-squares fit of the data to Scheme I and eq 7.

Table I. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for $Ni(tach)(H_2O)_3^{2+}$, $Ni(tach)_2^{2+}$, and $Cu(tach)_2^{2+}$

	Ni(tach)-$(H_2O)_3^{2+}$ [a]	Ni-$(tach)_2^{2+}$ [b]	Cu-$(tach)_2^{2+}$ [c]
Ni-N1[d]	2.065 (6)	2.131 (3)	2.353
Ni-N2	2.072 (4)	2.134 (2)	2.070
Ni-O1	2.085 (6)		
Ni-O2	2.109 (5)		
N1-C1	1.479 (10)	1.491 (5)	1.485
N2-C3	1.487 (7)	1.488 (2)	1.485
C1-C2	1.533 (8)	1.520 (3)	1.527
C2-C3	1.515 (8)	1.532 (3)	1.527
C3-C4	1.518 (7)	1.522 (3)	1.527
N1···N2	2.900 (7)	2.922 (3)	3.005
N2···N2′	3.016 (6)	3.016 (3)	2.936
O1···O2	2.864 (7)		
O2···O2′	3.008 (6)		
N1-Ni-N2	89.1 (2)	86.5 (1)	85.4
N2-Ni-N2′	93.4 (2)	89.9 (1)	90.3
O1-Ni-O2	86.2 (2)		
O2-Ni-O2′	91.0 (2)		
N1-C1-C2	109.8 (4)	110.8 (1)	111.0
N2-C3-C2	109.8 (4)	109.8 (1)	111.0
N2-C3-C4	110.2 (5)	110.6 (2)	110.8
C2′-C1-C2	110.7 (6)	110.0 (2)	110.6
C1-C2-C3	114.4 (5)	113.5 (2)	114.4
C2-C3-C4	110.9 (5)	111.5 (2)	111.2
C3-C4-C3′	116.4 (6)	114.7 (2)	113.0
C2′-C1-C2-C3	52.0	52.5	50.8
C1-C2-C3-C4	−49.8	−50.8	−52.2
C2-C3-C4-C3′	49.9	48.9	52.6

[a] Average of two determinations (this work and ref 11). [b] From ref 10. [c] From ref 10, $Cu(tach)_2(ClO_4)_2$, averaged with respect to the approximate mirror plane. [d] Atomic labels are given for $Ni(tach)(H_2O)_3$; for $Ni(tach)_2^{2+}$ and $Cu(tach)_2^{2+}$ they should be changed accordingly.

strong acids, except that it is displaced to a higher pH region (Figure 2). At low acetate ion concentrations and high acetic acid concentrations (5–6 M) a limiting rate constant is reached (~0.7 s^{-1}), which is somewhat less than that observed for HBF_4 and HCl, but under these conditions the solvent can also be considered to be altered significantly.

The temperature dependence of the limiting rate constant was determined (0.5 M HCl, μ = 1.0 M): at 6.3 °C, 0.100 ± 0.004 s^{-1}; at 15.6 °C, 0.290 ± 0.015 s^{-1}; at 25 °C, 0.72 ± 0.02 s^{-1}. These yield activation parameters $\Delta H^{\ddagger} = 72 \pm 2$ kJ mol^{-1} and $\Delta S^{\ddagger} = -6 \pm 6$ J K^{-1} mol^{-1}.

A rate-limiting condition at high pH is also reached in the vicinity of pH ~6, provided acetate or anilinium sulfonate buffer supply the protons to capture the dissociated tach (Figure 2).

$[Ni(tach)(H_2O)_3]^{2+}$. Dissociation of tach from the mono complex is much slower than from the bis complex under acid conditions, and the dissociation in HNO_3 (0.5–0.8 M) has been reported to follow a rate law of the form[7]

$$k_{obsd} = k_0 + k_{H^+}[HNO_3] \qquad (1)$$

where $10^4k_0 = 1.3$ s^{-1} and $10^4k_{H^+} = 1.4$ M^{-1} s^{-1} (25 °C). The present data confirm this rate law also for perchloric acid and show that it holds up to 3 M $HClO_4$, with $10^4k_0 = 0.6$ s^{-1} and $10^4k_{H^+} = 1.7$ M^{-1} s^{-1}. Other acids such as CH_3COOH, HCOOH, and $Cl_2CHCOOH$ exhibit similar behavior, with k_{obsd} a linear function of the acid concentration (Table III). In all these instances the acid-independent term k_0 is practically the same (~0.6 × 10^{-4} s^{-1}; Figure 3). The acid-dependent term, however, varies considerably; 10^4k_{HX} is 0.6, 2.3, and 4.7 M^{-1} s^{-1} for CH_3COOH, HCOOH, and $Cl_2CHCOOH$, respectively. These rate constants increase with decreasing pK_a of the acid (4.9, 3.9, and 1.6, respectively). No dependence on the *p*-chloroanilinium ion concentration is observed, and the rate constant for this acid (0.6 × 10^{-4} s^{-1}) is consistent with the acid-independent term in the other instances. The rate constants for HCl (3 M) and HNO_3 (3 M) differ from that of $HClO_4$ (3 M) (Table III), which implicates these two anions in the hydrolysis reaction.

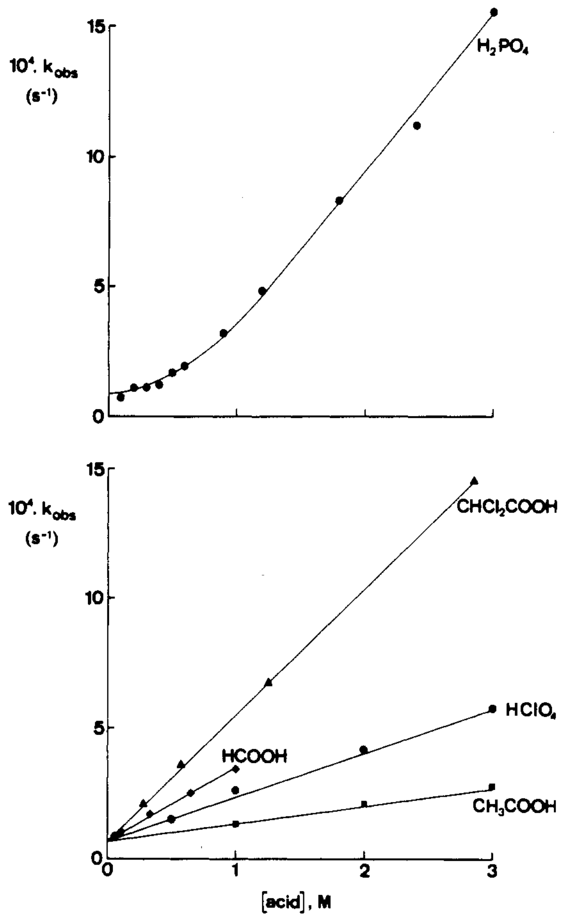

Figure 3. Cleavage of $Ni(tach)(H_2O)_3^{2+}$ in acid solutions at 25 °C. The solid lines are calculated from eq 2 or eq 9.

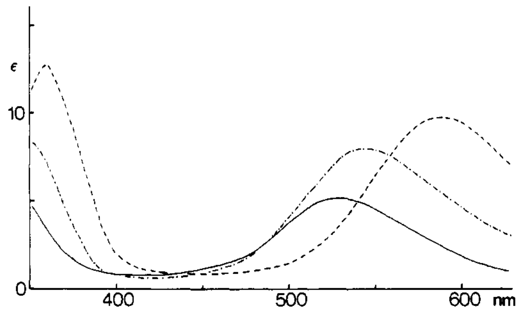

Figure 4. Visible absorption spectra of $Ni(tach)_2^{2+}$ (—), $Ni(tach)(H_2O)_3^{2+}$ (---), and $Ni(tach)(en)(H_2O)^{2+}$ (-·-·).

The dependence of the rate on $[H_2PO_4^-]$ is more complicated than for other acids (Figure 3). The data at 25 °C fit a rate law of the form

$$k_{obsd} = \frac{0.6 \times 10^{-4}}{1 + [H_2PO_4^-]} + \frac{6.9 \times 10^{-4}[H_2PO_4^-]^2}{1 + [H_2PO_4^-]} \ s^{-1} \qquad (2)$$

At low $[H_2PO_4^-]$ this rate law also yields the same acid-independent term as for the other media.

Spectra. The visible spectra of $Ni(tach)_2^{2+}$, $Ni(tach)(H_2O)_3^{2+}$, and $Ni(tach)(en)(H_2O)^{2+}$ in solution are depicted in Figure 4. The spectrum of crystalline $[Ni(tach)(en)(H_2O)](ClO_4)_2$ is essentially the same as the cor-

Table II. Rates of Dissociation of [Ni(tach)$_2$]Cl$_2$ in Aqueous Acid Solutions[a]

No Acetate Added[b]

	k_{obsd}, s^{-1}			k_{obsd}, s^{-1}	
pH	Cl$^-$[c]	BF$_4^-$[c]	pH	Cl$^-$[c]	BF$_4^-$[c]
0.09[e]	0.70	0.74	1.52		0.28
0.09[e]	0.77		1.69	0.282	
0.41[f]	0.687	0.69	1.98	0.177	
0.41[f]	0.71[g]	0.68	2.09		0.14
0.41[f]	0.75		2.10[j]	0.135	
0.87[h]		0.62	2.50		0.095
0.84[h]	0.64		3.01		0.042
1.22[i]	0.50		3.46		0.033
1.43	0.44				

Acetate Added

[HOAc], M	pH	k_{obsd}, s^{-1}	[HOAc], M	pH	k_{obsd}, s^{-1}
		[OAc$^-$] = 0.05 M[d]			
6.0	2.22	0.69	0.5	3.51	0.31
2.0	2.82	0.66	0.25	3.77	0.215
1.5	3.18	0.48	0.1	4.17	0.115
1.0	3.23	0.433	0.05	4.48	0.079
		[OAc$^-$] = 0.1 M[d]			
3.0	3.00	0.645	0.25	4.11	0.19
2.0	3.18	0.56	0.1	4.52	0.105
1.0	3.50	0.435	0.1	4.55	0.11
0.5	3.79	0.28	0.05	4.85	0.064
		[OAc$^-$] = 0.15 M[d]			
0.45	4.07	0.25	0.05	5.03	0.0537
0.15	4.55	0.111			
		[OAc$^-$] = 0.3 M[d]			
0.9	4.07	0.32	0.1	5.03	0.073
0.3	4.55	0.166			
		[OAc$^-$] = 0.5 M[d]			
1.5	4.07	0.40	0.3	4.77	0.155
1.0	4.24	0.326	0.2	4.90	0.104
0.75	4.36	0.283	0.2	4.95	0.106
0.5	4.52	0.213	0.167	5.03	0.093
0.5	4.53	0.213	0.1	5.23	0.061
0.5	4.55	0.202	0.1	5.30	0.062
0.4	4.64	0.194			
		[OAc$^-$] = 1.0 M[d]			
0.2	5.30	0.084	0.1	5.60	0.050
0.2	5.40	0.078	0.1	5.70	0.042
		[OAc$^-$] = 4.364 × 10^{-4} M[d]			
1.0	1.19	0.64			
		[OAc$^-$] = 2.755 × 10^{-3} M[d]			
1.0	1.99	0.44			

[a] Conditions: 25 °C, μ = 1.0 M (NaCl). Rate Constants are the average of at least two independent runs with an average error of ±5%. [b] pH maintained with aniline-2-sulfonate buffer (0.06 M) unless otherwise specified. [c] No acetate present; NaCl/HCl or NaBF$_4$/HBF$_4$ mixtures. [d] pH adjusted by varying [HOAc]. [e] [H$^+$] = 1.0 M; pH calculated from the expression $-\log([\mathrm{H}^+]\gamma^\pm) =$ pH, with $\gamma^\pm = 0.813$. [f] [H$^+$] = 0.5 M; pH calculated. [g] Rates also determined at 6.3 °C (0.100 ± 0.004 s^{-1}) and 15.6 °C (0.290 ± 0.015 s^{-1}), yielding $\Delta H^\ddagger = 72$ (2) kJ mol^{-1} and $\Delta S^\ddagger = -6$ (6) J K^{-1} mol^{-1}. [h] [H$^+$] = 0.2 M. [i] [H$^+$] = 0.1 M. [j] [H$^+$] = 0.01 M.

responding solution spectrum.

Discussion

The overall reactions and their equilibrium constants are[13]

$$\mathrm{Ni(tach)_2^{2+} + 3H^+ \rightleftarrows Ni(tach)(H_2O)_3^{2+} + H_3tach^{3+}} \tag{3}$$

$$\log K_2 = 19.7 \tag{3a}$$

$$\mathrm{Ni(tach)(H_2O)_3^{2+} + 3H^+ \rightleftarrows Ni(H_2O)_6^{2+} + H_3tach^{3+}} \tag{4}$$

$$\log K_1 = 15.7 \tag{4a}$$

Table III. Rates of Dissociation of [Ni(tach)(H$_2$O)$_3$]Cl$_2$ in Aqueous Solution[a]

[HClO$_4$],[b] M	10^4 × k_{obsd}, s^{-1}	10^4 × k_{calcd}, s^{-1}	[ClC$_6$H$_4$NH$_3^+$], M	10^4 × k_{obsd},[f] s^{-1}
0.05	0.8	0.7	0.5	0.54
0.5	1.5	1.5	0.75	0.56
1.0	2.6	2.3	1.0	0.58
2.0	4.2	4.0	1.25	0.58
3.0	5.8[c]	5.7		

[HCOOH], M	[HCOO$^-$], M	10^4 × k_{obsd}, s^{-1}	10^4 × k_{calcd},[d] s^{-1}
0.10	0.013	1.1	1.1
0.33	0.042	1.7	1.6
0.66	0.083	2.5$_5$	2.5
1.00	0.125	3.4$_5$	3.5

[Cl$_2$CHCOOH], M	[Cl$_2$CHCOO$^-$], M	10^4 × k_{obsd}, s^{-1}	10^4 × k_{calcd},[d] s^{-1}
0.28	0.51	2.1	2.0
0.57	0.53	3.6	3.5
1.25	0.55	6.8	6.8
2.88	0.62	14.5	14.5

[CH$_3$COOH], M	[CH$_3$COO$^-$], M	10^4 × k_{obsd}, s^{-1}	10^4 × k_{calcd},[d] s^{-1}
1.0	0.1	1.3	1.3
2.0	0.1	2.1	2.0
3.0	0.1	2.8	2.7

[H$_2$PO$_4^-$],[g] M	10$^4k_{obsd}$, s^{-1}	10$^4k_{calcd}$,[e] s^{-1}
0.1	0.7	0.9
0.2	1.1	1.0
0.3	1.1	1.1
0.4	1.2	1.2
0.5	1.7	1.7
0.6	1.9	1.9
0.9	3.2	3.1
1.2	4.8	4.6
1.8	8.3	8.2
2.4	11.2	11.8
3.0	15.5	15.5

[a] At 25 °C; rate constant average error ±5%. [b] μ = 3.0 M (NaClO$_4$). [c] In 3 M HCl, 10$^4k_{obsd}$ = 13.1 s^{-1}; in 3 M HNO$_3$, 10$^4k_{obsd}$ = 9.2 s^{-1}. [d] Calculated from eq 11 with the common intercept $k_0 = 6 \times 10^{-5}$ s^{-1} and with $k_{\mathrm{HClO_4}} = 1.7 \times 10^{-4}$ M^{-1} s^{-1}, $k_{\mathrm{CH_3COOH}} = 0.6 \times 10^{-4}$ M^{-1} s^{-1}, $k_{\mathrm{HCOOH}} = 2.3 \times 10^{-4}$ M^{-1} s^{-1}, and $k_{\mathrm{CHCl_2COOH}} = 4.7$ M^{-1} s^{-1}. [e] Calculated from eq 2. [f] pH 3.0 ± 0.1; buffers prepared from *o*-chloroaniline/HClO$_4$. [g] [NaH$_2$PO$_4$] + [NaClO$_4$] = 3.0 M.

Previous studies have shown that in acid the Ni(tach)$_2^{2+}$ ion dissociates ~1000-fold faster than the Ni(tach)(H$_2$O)$_3^{2+}$ ion.[7,12] Each reaction can therefore be followed separately without interference. Also the complete cleavage of one tach residue (>99%) from Ni(tach)$_2^{2+}$ occurs at pH <6.5; the same process for Ni(tach)(H$_2$O)$_3^{2+}$ occurs at pH <5.5.[12]

The cleavage reactions are first order in the complex ion but show a complex dependence on both the type of acid used and its concentration, as displayed in the Results section. While acid hydrolyses of simple Ni(II) amine complexes usually display pH-independent rates in the pH range 1–4,[9,14–18] complexes of multidentate macrocycles such as

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[13] The pK_a's of tach are (20 °C, 0.1 M NaClO$_4$) 10.23 (3), 8.72 (2), and 7.15 (2); the stability constants are log K_1(Ni(tach)$^{2+}$) = 10.4 (1) and log K_2(Ni(tach)$_2^{2+}$) 6.41 (5).[12]

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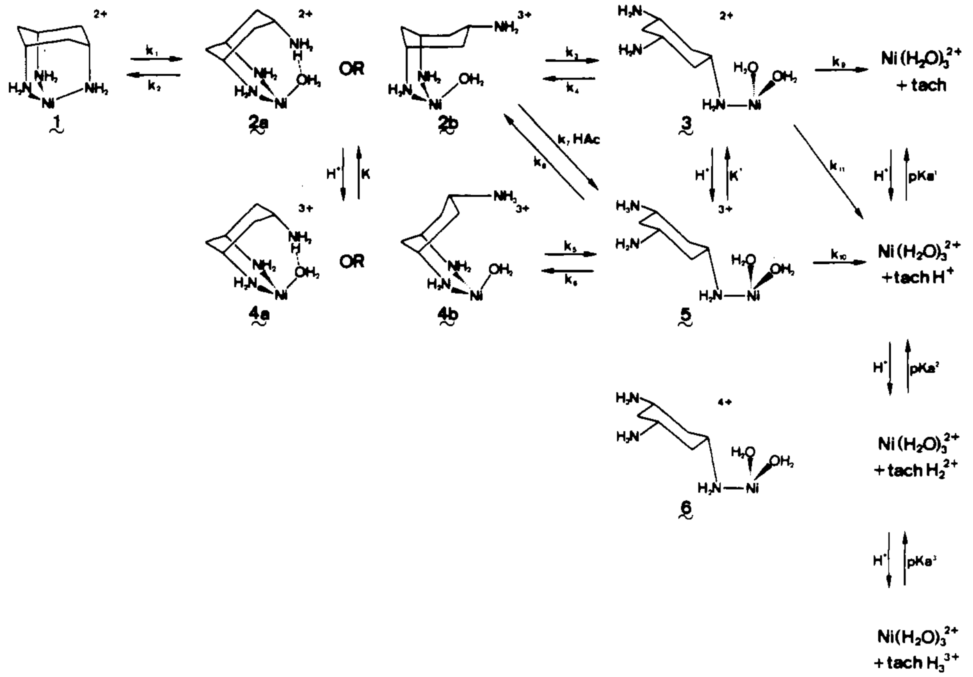
[15] Shamsuddin Ahmed, A. K.; Wilkins, R. G. *J. Chem. Soc.* **1959**, 3700–3708.

[16] Shamsuddin Ahmed, A. K.; Wilkins, R. G. *J. Chem. Soc.* **1960**, 2895–2900.

[17] Shamsuddin Ahmed, A. K.; Wilkins, R. G. *J. Chem. Soc.* **1960**, 2901–2906.

Scheme I



1,4,7-triazacyclononane and 1,5,9-triazacyclododecane exhibit acid-catalyzed cleavage reactions as well.[19] The acid dependence of the reaction needs to be accommodated: the addition of H^+ to a coordinated NH_2 group does not seem reasonable since the only basic site is consumed by coordination to the metal ion. However, protons can be consumed by a partially cleaved chelate or another bound ligand with a lone pair of electrons suitable for accepting a proton, e.g., H_2O or OH^-. There is a remote possibility that H^+ could add to the filled nonbonding d orbitals of the metal ion, thereby activating release of the ligand. Such paths have been justified for substitution reactions of amine complexes of Ru(II) and Os(II),[20] but the d orbitals for these complexes extend much further than for the first-row elements, where there does not seem to be much evidence, if any, for proton addition at metal centers. We therefore consider it as improbable here and have sought an explanation for the role of the acid as scavenging a released amino group. No intermediates with a partly bonded tach ligand could be detected spectrophotometrically under the conditions of our experiments; i.e., rapid consecutive rupture and reformation of all three Ni–N bonds has to be taken into account to explain the pattern of observed rate constants. The hydrolyses of the two complexes have been analyzed with this background in mind.

Hydrolysis of the $\mathbf{Ni(tach)_2^{2+}}$ Ion. The dependence on H^+ on the release of the multidentate ligand bound to Ni(II) cannot be accommodated by the reaction scheme of eq 5,

$$\mathrm{Ni(tach)_2^{2+} + 3H^+ \overset{K}{\rightleftharpoons} Ni(tach)(Htach)(H_2O)^{3+} + 2H^+ \xrightarrow{k} Ni(tach)(H_2O)_3^{2+} + H_3tach^{3+}} \qquad (5)$$

where an amino group is released rapidly and is scavenged by H^+ to give a protonated partly bound ligand, which then dissociates by a rate-determining step. Such a path has been invoked for dissociation of Ni(II) multidentate amine complexes,[19] and it requires a rate law of the form

$$k_{\mathrm{obsd}} = \frac{a[\mathrm{H^+}]}{1 + b[\mathrm{H^+}]} \qquad (6)$$

Such a rate law does not account for data in the high-pH region. Moreover, the intermediate complex ion would have to show a $pK_a \approx 1.5$ for deprotonation of the partially dissociated tach ligand and would have to be stable enough to be detected ($t_{1/2} \approx 1$ s). Such a pK_a is far lower than that expected for a dangling amine group attached to Ni(II).[21] Also, rapid acidification of the complex to below pH 1 (the rate-limiting region) should convert it to the protonated form, which would then dissociate with a reaction half-life of ~1 s. No evidence for such an intermediate was detected even when the mixing and observations were carried out on a millisecond time scale. The presumed intermediate $\mathrm{Ni(tach)(Htach)(H_2O)^{3+}}$ should also be spectroscopically very similar to $\mathrm{Ni(tach)(en)(H_2O)^{2+}}$, and the latter complex is clearly distinguishable from $\mathrm{Ni(tach)_2^{2+}}$ and $\mathrm{Ni(tach)(H_2O)_3^{2+}}$ (Figure 4). Stopped-flow experiments at 10 different wavelengths between 500 and 600 nm demonstrated that no rapid change in absorbance occurred when solutions of the bis complex and a strong acid were mixed. A slow change from the absorbance expected for the bis complex directly to that expected for the mono complex was observed as a first-order process with a rate constant of $\sim 0.6\ \mathrm{s^{-1}}$ at pH 1 ($\mu = 0.1$ M). All these results are inconsistent with the preequilibrium proposed.

The same conclusion arises from the fact that the dissociation rate is not a simple function of pH but depends on the type of buffer and on the buffer concentration. In a series of acetate buffers of constant pH, the rate increases with the buffer concentration, but not in a linear manner. The fact that the rate does not increase linearly with [HOAc] in a series of solutions of constant pH, with increasing $[\mathrm{H^+}]$ in solutions of a strong acid, nor with increasing concentration of *p*-chloroanilinium ion makes it doubtful that general acid catalysis is involved. Such a mechanism would require rate-determining proton transfer from H_3O^+ and HOAc to $\mathrm{Ni(tach)_2^{2+}}$, and there does not appear to be a reasonable site for proton acceptance on the bis complex.

All the phenomena observed can be understood, however, within the framework of Scheme I. Spontaneous rupture of one of the six Ni–N bonds is the first of a series of rate-determining steps. The rupture process produces an intermediate

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Table IV. Results of Least-Squares Analysis of Rate Constants[a]

	a, s^{-1}	b	c, M^{-1}	d,[b] M^{-1}	e	f, M^{-1}	g,[b] M^{-1}	$\Sigma[100(\Delta/k_{obsd})]^2/F$
Ia	0.78 ± 0.02	0.038 ± 0.003	23.8 ± 1.6	1.33 ± 0.12	0.046 ± 0.017	(2.0 ± 0.5) × 10^4	0.3 ± 0.2	51.15
Ib	0.77 ± 0.02	0.040 ± 0.003	23.8 ± 1.7	1.29 ± 0.12		(2.0 ± 0.6) × 10^4	0.71 ± 0.18	57.95
Ic	0.78 ± 0.02	0.038 ± 0.003	23.8 ± 1.6	1.27 ± 0.09	0.064 ± 0.013	(2.5 ± 0.3) × 10^4		52.09
IIa	0.78 ± 0.02	0.046 ± 0.017	(2.0 ± 0.5) × 10^4	0.3 ± 0.2	0.038 ± 0.003	23.8 ± 1.6	1.33 ± 0.12	51.15
IIb	0.77 ± 0.02		(2.0 ± 0.6) × 10^4	0.71 ± 0.18	0.040 ± 0.003	23.8 ± 1.7	1.29 ± 0.12	57.95
IIc	0.78 ± 0.02	0.064 ± 0.013	(2.5 ± 0.3) × 10^4		0.038 ± 0.003	23.8 ± 1.6	1.27 ± 0.09	52.09

[a] Symbols are as in eq 7; $\Delta = k_{obsd} - k_{calcd}$, F = degrees of freedom. There are 51 degrees of freedom for Ia and IIa and 52 degrees of freedom for all other cases. [b] $[H^+]$ and $[Ac^-]$ have been used in the calculations to obtain d/K_a, etc. For solution Ia $d/K_a = (4.7 \pm 0.4) \times 10^4$ and $g/K_a = (1.1 \pm 0.9) \times 10^4$; $K_a = 10^{-4.55} = [H^+][Ac^-]/[HAc]$.

2 with one tridentate and one bidentate triamine. Subsequently, dissociation and reformation rates are sufficiently fast that they all contribute to the observed rate almost over the entire range of experimental conditions and only a small amount of the intermediate is present at any time. Coordination of the acid or the acid anion is also implied in some instances.

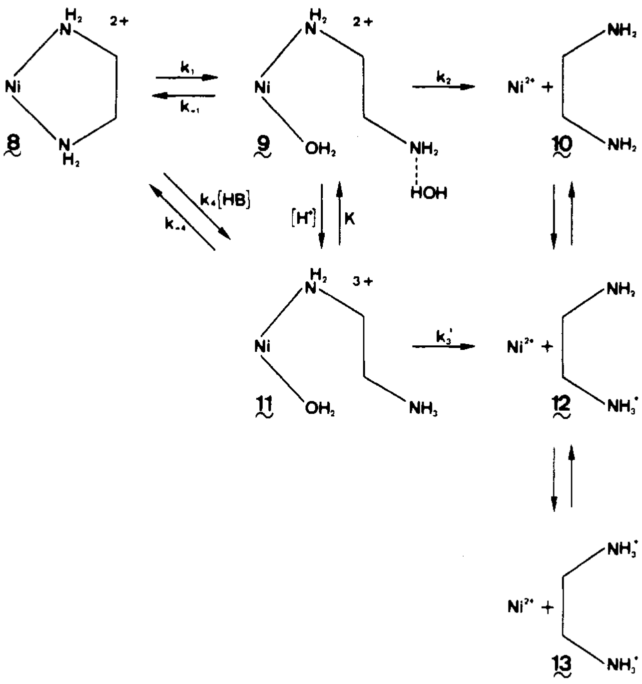
A rate expression consistent with all observed data is given in eq 7. The rate expression is derived by a steady-state treatment[22] and has the form

$$k_{calcd} = a/\{1 + [b + cH + d(HA)]^{-1} + [e + fH + g(HA)]^{-1}\} \quad (7)$$

where $H = [H^+]$ and $HA = [CH_3COOH]$ and $a = k_1$, $b = k_3/k_2$, $c = k_5K/k_2$, $d = k_7/k_2$, $e = k_9k_5K/(k_6k_2K')$, $f = k_{10}k_5K/(k_6k_2)$, $k = k_{11}k_5K/(k_6k_2K')$, $K = [4]/([H^+][2])$, and $K' = [5]/(]H^+][3])$. It accounts for all reactions in Scheme I that are marked by arrows (k_1–k_{11}). Since eq 7 is symmetric with respect to exchange of b, c, d and e, f, g, all least-squares fits to the data occur in numerically equivalent pairs (Table IV). The simplest scheme to fit all data is Ic or IIc; adding the additional terms g or d leads to statistically insignificant improvement in the least-squares fit (Ia, IIa). Introducing g or d instead of e or b, which are the least well determined, does not change the number of adjustable parameters, but the fit depreciates (Ib, IIb).

On the basis of our kinetic data we cannot distinguish between the sets of solutions I and II. This distinction can only be made from general chemical reasoning. Before we develop arguments to distinguish between solutions I and II, a few remarks concerning the intermediates in Scheme I are in order: For intermediates **2** and **4** the tach molecule acts as a bidentate ligand. This restricts the conformations of the ligand to the triaxial chair or to a boat conformation. The energies of the two intermediates **2a** and **2b** cannot be very different since **2a** shows two unfavorable $NH_2 \cdots NH_2$ diaxial interactions (17–33 kJ mol^{-1}),[23] which are probably compensated in part by a good intramolecular hydrogen bond between an activated water molecule as proton donor and an amine group as acceptor (estimated at ~−20 kJ mol^{-1}); intermediate **2b** for its part shows an unfavorable boat conformation (~16 kJ mol^{-1}).[24-26] Similar arguments apply to **4a** and **4b** except that the intramolecular hydrogen bond between the ammonium group as donor and the coordinated water molecule as acceptor is less favorable energetically than hydrogen bonds to surrounding solvent water molecules, thus favoring **4b**. Intermediates **3**, **5**, and **6** contain tach or its protonated variants as monodentae ligands. Coordination imposes no restrictions on the conformation of the ligand, which is very likely to be in the triequatorial conformation, 25–50 kJ mol^{-1} more stable than the triaxial conformation.[23] Intramolecular hydrogen bonds as in **2a** or **4a** are improbable for geometric reasons.

Scheme II



With this background in mind we compare the solutions I and II (Table IV). The salient difference is in constants c and f, whereas a, b, d, e, and g are of the same order or magnitude in both sets. Instead of analyzing c and f directly, we have chosen to compare the competition ratios $c/b = k_5K/k_3$ or $f/e = k_{10}K'/k_9$ between the protonated and the unprotonated species **2** and **4** or **3** and **5**, respectively. They are 6 (2) × 10^2 and 4 (4) × 10^5 M for solution I and vice versa for solution II. Numerical values of analogous ratios are available also for some other ions:[27,28] $Cr(chxn)^{3+}$, $Ni(chxn)^{2+}$, $Ni(en)^{2+}$, and $Ni(en)_3^{2+}$ (chxn = *trans*-cyclohexane-1,2-diamine) with competition ratios $k'_3K/k_2 \approx 1$, 10^6, 4×10^6, and 2×10^8 M^{-1}, respectively (Scheme II). A small value of k_5K/k_3 ($k_{10}K'/k_9$, k'_3K/k_2) implies $k_5K < k_3$ ($k_{10}K' < k_9$, $k'_3K < k_2$); i.e., the unprotonated intermediate **2** (**3**, **9**) competes very effectively with the protonated one, **4** (**5**, **11**). If the protonation constants K or K' in **2**, **3**, and **9** are assumed to be $<10^8$ M^{-1},[21] a competition ratio $\ll 10^8$ M^{-1} implies that the more highly charged, protonated intermediates **4**, **5**, and **11** react more slowly than **2**, **3**, and **9**. This seems intuitively unreasonable and requires an explanation: the very low value for $Cr(chxn)^{3+}$ has been attributed to intermediate **7**.[27] It probably shows a good hydrogen bond that is due to increased acidity of coordinated water (proton donor) and proximity of a NH_2–group from the conformationally rigid chxn (proton acceptor). As a result

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(22) Equation 7 is obtained by applying steady-state conditions to the sum of concentrations of **2** and **4** as well as **3** and **5** (Scheme I).
(23) Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. "Conformational Analysis"; Interscience: New York, 1965.
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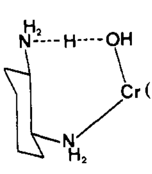

7

of the intramolecular hydrogen bond, the bound water becomes more like a coordinated OH^-, which in turn weakens the remaining Cr–N bonds and accelerates subsequent Cr–N bond rupture. Intramolecular acceleration is much less for Ni(chxn)$^{2+}$ with the same rigid ligand but with a metal ion of lower charge. For $Ni(en)_3{}^{2+}$ the acceleration is hardly significant. The competition ratios for $Ni(tach)_2{}^{2+}$ are 6 (2) × 10^2 and 4 (4) × 10^5 M^{-1} for solution I and vice versa for solution II (Table IV). The first number indicates significant acceleration, whereas the second one does not. If we opt for the set of solutions I, the intermediate **2a** provides the intramolecular hydrogen bond necessary to explain the observed acceleration. Intermediates **3** and **5** show dangling amine groups, and the competition ratio is very similar to that of Ni(chxn)$^{2+}$, as expected. If we choose the set of solutions II a rationalization of the competition ratios is not found so easily.

The least-squares analysis of the kinetic data for $Ni(tach)_2{}^{2+}$ may be summarized as follows: there are two numerically equivalent sets of interpretations (Table IV); comparison of ratios of reaction rates for protonated and unprotonated intermediates **4** and **2** with the likely structures of these intermediates and with analogous values of related compounds suggests that one set of interpretations (I) is chemically more reasonable than the other.[29]

The data available do not allow a resolution of all the rate and equilibrium constants for Scheme I. Two limiting conditions were identified, however, one at low pH, the other at high pH (Figure 3). The limiting rate constant at pH ~0 is $k_{calcd} = k_1 = 0.78 \pm 0.02\ s^{-1}$; it is independent of anion (Cl^-, BF_4^-, or CH_3COO^-), anion basicity, or ability of the anion to coordinate to the Ni(II) ion. All these factors are consistent with the assignment of the rate constant to the first Ni–N bond rupture, which should be independent of $[H^+]$ and anion concentration for an octahedral, coordinatively saturated bis-tridentate complex where there are no sites for coordination or proton addition.

The limiting rate constant at pH ≥4 takes the form

$$k_{calcd} = k_1/\{1 + k_2/k_3 + k_6k_2K'/(k_5k_9K)\} \qquad (8)$$

and implies that the rate constant ratios k_2/k_3 and possibly $k_6k_2K'/(k_5k_9K)$ contribute to the observed rate constant. k_2 exceeds k_3 by a factor of ~25; i.e., rechelation is faster than spontaneous dissociation of the second amine group and is therefore responsible for the slowing down of the reaction at higher pH (Figure 2).

A reasonable path for the acetic acid catalysis would seem to be substitution of water by acetic acid, followed by substitution of the second NH_2 group by H_2O and by protonation of the doubly dissociated tach ligand intramolecularly. An equivalent path would be substitution of the second NH_2 group on Ni by acetic acid followed by intramolecular protonation and possibly exchange of acetic acid for water. Alternative paths involve acetate ions instead of acetic acid and intermolecular protonation instead of an intramolecular process. The exchange reactions H_2O/CH_3COOH, H_2O/CH_3COO^-, etc. postulated in the above mechanisms should occur with rate constants on the order of $10^4\ s^{-1}$ and are expected to be kinetically irrelevant. The various paths proposed above are kinetically indistinguishable, but when $[CH_3COO^-]$ is low and $[CH_3COOH]$ is high, a substantial contribution from one of them is required.

Hydrolysis of the $[Ni(tach)(H_2O)_3]^{2+}$ Ion. The rate law for the hydrolysis of $Ni(tach)(H_2O)_3{}^{2+}$ appears to be quite different from and simpler than that of $Ni(tach)_2{}^{2+}$ at least superficially:

$$k_{obsd} = k_0 + k_{HX}[HX] \qquad (9)$$

If, on the other hand, we plot k_{obsd} vs. estimates of $-\log [H^+]$, the data look very similar to those in Figure 3, except for a shift of the pH–k_{obsd} profile toward lower pH values by about 2 units and a decrease in k_{obsd} by about 3 orders of magnitude.

From a chemical point of view it is likely that the dissociation process for the second tach is qualitatively the same as that of the first one with only quantitative differences. The data for $Ni(tach)(H_2O)_3{}^{2+}$ will be analyzed on the basis of this assumption. In order to understand the quantitative differences in the two sets of data, eq 7 may be rewritten in slightly different form:

$$k_{calcd} = [a'(b' + c'H + d'(HA))]/\{1 + [b' + c'H + d'(HA)] + [b' + c'H + d'(HA)][(e' + f'H + g'(HA))]^{-1}\} \qquad (7a)$$

From the qualitative differences in the rate vs. pH profile it follows that the primed rate constants for the hydrolysis reaction of Ni(tach)$^{2+}$ are smaller than those for the reaction of $Ni(tach)_2{}^{2+}$, i.e., $a' < a$, $b' < b$, etc. Three regimes may be distinguished for eq 7a:

(1) $[H^+] \approx [HA] \approx 0$ implies $k = a'b'/\{1 + b' + b'/e'\}$, but since $b' < b \ll 1$

$$k_{calcd} = a'b'/\{1 + b'/e'\} < a'b' \qquad (10)$$

(2) The proton concentration starts to influence the rates but is not yet dominant, i.e. $b' < c'H < 1$ and $e' < f'H$, and then $k_{calcd} \approx (a'b' + a'c'H)/\{1 + c'/f'\}$. By analogy with c/f (~10^{-3}) we may expect that $c'/f' \ll 1$ and therefore with $[HA] = 0$

$$k_{calcd} \approx a'b' + a'c'H \qquad (11)$$

Note that this is a linear rate law of the form observed experimentally for $HClO_4$. From regression calculations $a'b' = 0.75\ (8) \times 10^{-4}\ s^{-1}$ and $a'c' = 1.70\ (5) \times 10^{-4}\ M^{-1}\ s^{-1}$. Assuming that the maximal proton concentration is $[H^+] \approx [HClO_4] = 3$ M, it follows that $c' \lesssim 0.03\ M^{-1}$ and $a' > 0.006\ s^{-1}$.

(3) Finally, if $1 < c'H$

$$k_{calcd} \approx a' \qquad (12)$$

This third regime is certainly not realized in any of the experiments with $Ni(tach)(H_2O)_3{}^{2+}$ since there is no indication that the rate constant becomes independent of acid concentration.

Note that the acid-independent term $a'b'$ is extrapolated to be 0.75 (8) × $10^{-4}\ s^{-1}$ for $HClO_4$ but is measured to be only 0.56 (2) × $10^{-4}\ s^{-1}$ in *p*-chloroanilinium buffer where $[H^+] \approx 10^{-3}$ M. The difference is not significant, but the trend is clear. It indicates that at proton concentrations $[H^+] < 10^{-3}$ M the limiting regime described above as (1) is being reached.

The analysis of the kinetic data for proton-catalyzed hydrolysis of Ni(tach)$^{2+}$ may be summarized as $a' \geq 0.006\ s^{-1}$ ($a = 0.78\ s^{-1}$), $b' \leq 0.004$ ($< 0.038 = b$), and $c' \leq 0.03\ M^{-1}$

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(27) Mønsted, L. *Acta Chem. Scand., Ser. A* **1976**, *A30*, 599–608. $k_1 = 6.98 \times 10^{-6}\ s^{-1}$, $k_{-1}/K = 106 \times 10^{-6}\ M^{-1}\ s^{-1}$, $k'_3 = 18.5 \times 10^{-6}\ s^{-1}$, $k_2/K = 22.9 \times 10^{-6}\ M^{-1}\ s^{-1}$, $K \approx 0.5\ (0.5) \times 10^2$ M (70 °C, $\mu = 1.0$ M).

(28) The data from ref 15–17 have been reanalyzed in accord with ref 27 and Scheme II: $Ni(en)_3{}^{2+}$, $k_1 = 87\ s^{-1}$, $k_{-1}/k_2 = 1.8$, $k'_3K/k_2 = 2 \times 10^8\ M^{-1}$; $Ni(en)(H_2O)_4{}^{2+}$, $k_1 = 0.011\ s^{-1}$, $k_1/k_2 \approx 17$, $k'_3K/k_2 = 4 \times 10^6\ M^{-1}$; $Ni(chxn)(H_2O)_4{}^{2+}$ (less accurate values, 0.3 °C), $k_1 = 0.0016\ s^{-1}$, $k_{-1}/k_2 \approx 11$, $k'_3K/k_2 \approx 10^6\ M^{-1}$.

(29) Correlation matrix elements larger than 0.5 are found for solution Ia between *a* and *c* (−0.73), *a* and *d* (−0.57), *d* and *f* (−0.71), *d* and *g* (0.54), *e* and *g* (−0.75), and *f* and *g* (−0.83).

($<23.8\ \text{M}^{-1} = c$), implying that the inequalities $a' < a$, etc. invoked above to understand the quantitative differences of the rate data for Ni(tach)_2^{2+} and Ni(tach)^{2+} pass the numercial test. There is thus no evidence that could preclude interpretation of the Ni(tach)^{2+} data in terms of the same Scheme I and eq 7 used also for the interpretation of the Ni(tach)_2^{2+} data. The important point is that $a \geq 0.006\ \text{s}^{-1}$. This shows that breaking of the first Ni–N bond in $\text{Ni(tach)(H}_2\text{O)}_3^{2+}$ is comparable in rate to the analogous step in $\text{Ni(chxn)(H}_2\text{O)}_4^{2+}$ ($0.04\ \text{s}^{-1}$) for example. The very low observed reactivity of $\text{Ni(tach)(H}_2\text{O)}_3^{2+}$ at $[\text{H}^+] \lesssim 10^{-3}$ M is a consequence of $b' = k_3/k_2 < 0.004$; i.e., rechelation (k_2) of the singly dissociated tach ligand is 2–3 orders of magnitude faster than the breaking of the second Ni–N bond (k_3). This is analogous to the situation for Ni(tach)_2^{2+}, where rechelation is 1–2 orders of magnitude faster than breaking of the second Ni–N bond.

The competition ratio $c'/b' = k_5K/k_3$ equals $3.5\ \text{M}^{-1}$, 2 orders of magnitude less than for Ni(tach)_2^{2+} ($6 \times 10^2\ \text{M}^{-1}$). A similar decrease is observed on going from Ni(en)_3^{2+} ($10^8\ \text{M}^{-1}$) to Ni(en)^{2+} ($4 \times 10^6\ \text{M}^{-1}$).

The experiments with CH_3COOH and HCOOH cover a rather narrow range of proton concentrations: $4 \times 10^{-4} < [\text{H}^+] < 10^{-4}$ M and $[\text{H}^+] \approx 10^{-3}$ M, respectively. The contribution of $a'c'H$ to k_{obsd} is therefore very small. Provided that $d'(\text{HA}) < 1$, the rate law is linear, as observed:

$$k_{\text{calcd}} \cong [a'b' + a'd'(\text{HA})]/(1 + d'/g') \qquad (13)$$

Regression analysis yields for CH_3COOH $a'b'/(1 + d'/g') \cong 0.57\ (6) \times 10^{-4}\ \text{s}^{-1}$ and $a'd'/(1 + d'/g') = 0.75\ (3) \times 10^{-4}\ \text{M}^{-1}\ \text{s}^{-1}$ and for HCOOH $a'b'/(1 + d'/g') \cong 0.68\ (7) \times 10^{-4}\ \text{s}^{-1}$ and $a'd'/(1 + d'/g') = 2.77\ (10) \times 10^{-4}\ \text{M}^{-1}\ \text{s}^{-1}$. For the experiments with CHCl_2COOH the proton concentration is $10^{-2} \lesssim [\text{H}^+] \lesssim 10^{-1}$ M. Again, with $d'(\text{HA}) < 1$ the rate law is linear as observed:

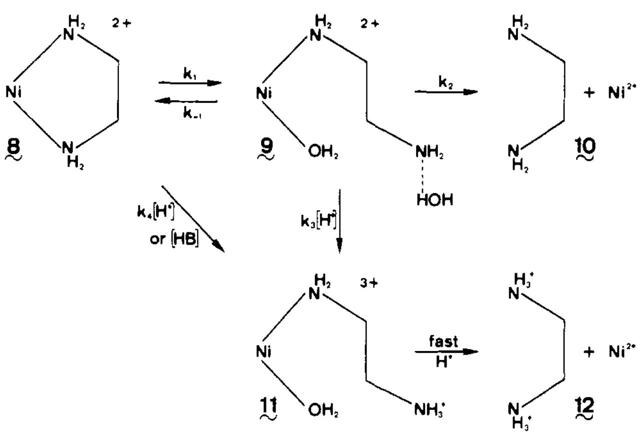
$$k_{\text{calcd}} \cong [a'b' + a'c'10^{-1} + a'd'(\text{HA})]/(1 + d'/g') \qquad (14)$$

Regression analysis gives $(a'b' + a'c'10^{-1})/(1 + d'/g') = 0.80\ (15) \times 10^{-4}\ \text{s}^{-1}$ and $a'd'/(1 + d'/g') = 4.71\ (9) \times 10^{-4}\ \text{M}^{-1}\ \text{s}^{-1}$. It is therefore difficult to deduce further inequalities from these data.

The role of CH_3COOH, HCOOH, and CHCl_2COOH in catalyzing hydrolysis of $\text{Ni(tach)(H}_2\text{O)}_3^{2+}$ is probably similar to that for Ni(tach)_2^{2+}, but here we cannot exclude catalysis of the first step, **1** → **4** (Scheme I) via a species like $\text{Ni(tach)(CH}_3\text{COOH)(H}_2\text{O)}_2^{2+}$ or a similar complex. If such catalysis of **1** → **4** occurs, the limiting rate for high acetic acid concentration relates to $\text{Ni(tach)(CH}_3\text{COOH)(H}_2\text{O)}_2^{2+}$ and is not necessarily the same as for high proton concentration. The main consequence of this would be that the lower limit of a' cannot be derived from CH_3COOH, HCOOH, and CHCl_2COOH data but only from the HClO_4 data, where it was found that $a' \geq 0.006\ \text{s}^{-1}$. This is only a factor of 3 lower, however, than the limit one would obtain from the CHCl_2COOH data assuming $d'/g' \ll 1$.

Hydrolysis of Ni(en)_n^{2+} and Related Ions. A comparison of the results described above for Ni(tach)^{2+} and Ni(tach)_2^{2+} with those obtained for Ni(en)_n^{2+} (n = 1, 3)[15-18] shows a number of similarities and differences: the observed rate constant for hydrolysis of Ni(en)_3^{2+} with NiN_6 coordination is constant for pH values less than 6 or 7; the observed rate constant for hydrolysis of $\text{Ni(en)(H}_2\text{O)}_4^{2+}$ with NiN_2O_4 coordination increases with increasing proton concentration until it becomes constant only at pH <4. This behavior is analogous to that of Ni(tach)_2^{2+} and $\text{Ni(tach)(H}_2\text{O)}_3^{2+}$, where again the NiN_6 system reaches a limiting rate at lower proton concentrations ($[\text{H}^+] \approx 1$ M) than the NiN_3O_3 system ($[\text{H}^+] > 3$ M). For both Ni(en)_3^{2+} and Ni(tach)_2^{2+} there is no indication that addition of a general acid, like CH_3COOH, affects the limiting rate, i.e. the breaking of the first Ni–N bond, in a significant way.[30] Ni(en)^{2+} and Ni(tach)^{2+}, on the other hand, have water molecules in their coordination sphere that may be replaced by general acids. These in turn may assist the breaking even of the first Ni–N bond. For Ni(en)^{2+} such an effect has been demonstrated.[18] The assistance (i.e. the acid-catalyzed rate constant) increases with increasing pK of the acid. Assistance is also observed for Ni(tach)^{2+}, but at proton concentrations where the first Ni–N bond rupture is far from rate limiting. It is therefore not possible to decide unambiguously which of the three Ni–N bond ruptures is catalyzed by the general acid. Also, the catalytic efficiency decreases with increasing pK_a of the general acid.

Scheme III



The detailed mechanism offered previously[18] for the dissociation kinetics of Ni(en)_n^{2+} (n = 1, 3) is shown in Scheme III. The ethylenediamine dissociation pathway is represented by the sequence **8** → **9** → **10** ($k_\text{d} = k_1k_2/k_{-1}$). The H^+ dependence between pH 4 and 7.3 is accounted for by pathway **8** → **9** → **11** → **12** ($k_\text{H} = k_1k_3/k_{-1}$). Ring opening with solvent replacement (**8** → **9**) is rate determining around pH 4 ($k_{1\text{d}} = k_1$). For Ni(en)^{2+}, a further increase in rate is observed at very low pH, **8** → **11** (k_4).[30]

While we agree with the general mechanism, we interpret the observed rate data somewhat differently (Scheme II). Instead of assigning $k_\text{H} = k_1k_3/k_{-1}$ to Ni–N bond rupture followed by rate-determining protonation of intermediate **9**, we prefer diffusion-controlled protonation with equilibrium constant K followed by the second Ni–N bond rupture with rate constant k'_3; i.e., $k_\text{H} = k_1Kk'_3/k_{-1}$. The constant k_4 is the same as in Scheme II; the only additional constant in Scheme II, k_{-4}, is fixed by the condition that the equilibrium constant for the cycle **8** → **9** → **11** → **8** has to equal 1. On the basis of such an interpretation, the general type of scheme outlined above for the Ni(tach)_2^{2+} and $\text{Ni(tach)(H}_2\text{O)}_3^{2+}$ ions (Scheme I) would apply equally well, for Ni(en)_n^{2+} (Scheme II) and for other multidentate amine complexes of Ni^{2+}.[28]

Structure and Reactivity. It has been argued that the first Ni–N bond rupture in both Ni(tach)_2^{2+} and Ni(tach)^{2+} could lead to an unfavorable boat conformation of either the remaining six-membered chelate ring as in **2a** or of the six-membered carbocycle as in **2b**. Such changes could be re-

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(30) For Ni(en)_3^{2+} a term involving $k_4[\text{H}^+]$ has been postulated to explain a change in rate constant from 75 ($\pm$12) s^{-1} at 0.52 M HClO_4 to 109 ($\pm$9) s^{-1} at 2.09 M HClO_4, where NaClO_4 is used to maintain the ionic strength constant (μ = 4 M, Scheme III[18]). It can be argued, however, that the observed changes in rate constant arise from the substitution of Na^+ by H^+ and that the rates would change little if the hydrolyses were conducted in $\text{LiClO}_4/\text{HClO}_4$ media. For $[\text{CH}_3\text{COOH}]$ varying between ~0.1 and 1.4 M the rate constants are actually constant within experimental error.

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Table V. Rate Constants and Activation Parameters for the First Aquation Step of Selected Nickel(II) Amine Complexes

complex[a]	k,[b] s^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	ref
$Ni(NH_3)^{2+}$	5.8	55	−47	14
$Ni(Me_3en)^{3+}$	40	62	−7	14
$Ni(en)^{2+}$	0.15	81	12	15
$Ni(en)_2{}^{2+}$	5	78	31	17
$Ni(en)_3{}^{2+}$	87	70	29	17
$Ni(bn)^{2+}$	0.02	72–76	−36 to −25	16
$Ni(bn)_2{}^{2+}$	0.26	62	−47	17
$Ni(bn)_3{}^{2+}$	8.3	56	−40	17
$Ni(chxn)^{2+}$	0.04	77	−15	16
$Ni(dien)^{2+}$	14	70	12	8
$Ni(ptn)^{2+}$	63	70	23	8
$Ni(trien)^{2+}$	15	57	−30	8
$Ni(tren)^{2+}$	66	54	−28	8
Ni(*N*-pren)$^{2+}$	0.32	69	−23	8
$Ni(tach)_2{}^{2+}$	0.8	72	−6	*c*

[a] Aqua ligands have been deleted for clarity. Ligand abbreviations are as follows: $Me_3en^+ = NH_2CH_2CH_2NMe_3{}^+$; bn = *rac*-2,3-butanediamine; chxn = 1,2-diaminocyclohexane; dien = 1,5-diamino-3-azapentane; ptn = 1,2,3-triaminopropane; trien = 1,8-diamino-3,6-diazaoctane; tren = tris(2-aminoethyl)amine; *N*-pren = *N*-propylethylenediamine. [b] $T = 25$ °C. [c] This work.

flected in the activation enthalpy associated with k_1 in Scheme I. A comparison as in Table V shows that the activation enthalpy of $Ni(tach)_2{}^{2+}$ falls around the middle of a fairly narrow range of values pertaining to a wide variety of amine ligands, i.e. the conformational changes accompanying the first Ni–N bond rupture cannot be too unfavorable.

The process **1** → **2a** lengthens one Ni–N bond through a pivoting motion of the ligand around an axis containing the two remaining nitrogen atoms. The early stages of such a motion are modeled in the corresponding Jahn–Teller-distorted Cu(II) complex with one long and two short Cu–N bonds (see Table I, $Ni(tach)^{2+}$ and $Cu(tach)_2{}^{2+}$); apart from the distances the main structural differences between $Ni(tach)^{2+}$ and $Cu(tach)_2{}^{2+}$ are found in the relatively soft N–M–N bond angles. This simple observation suggests that the chair–boat interconversion of the chelate ring cannot contribute significantly to the activation enthalpy of the first Ni–N bond rupture. In the process **1** → **2b** the lengthening of one Ni–N bond is accompanied by a chair–boat interconversion of the six-membered carbocycles. Such an interconversion is known to have an activation enthalpy of ~40 kJ mol^{-1}, but since the transition state for the chair–boat interconversion no longer shows two unfavorable $NH_2\cdots NH_2$ diaxial interactions, it is stabilized relative to the triaxial ground state by 17–33 kJ mol^{-1}, i.e. by almost as much as the chair–boat interconversion barrier itself; the simple calculation again shows that even if a conformational interconversion of the ligand is involved, it cannot contribute significantly to the activation enthalpy of the first Ni–N bond rupture. Thus, from both models it appears unlikely that the energy of the first transition state is affected by the special structure of the tach ligand.

The above combination of structural and energetic arguments provides additional evidence for the hypothesis that during rupture of the first Ni–N bond tach retains its triaxial conformation and that the low observed reactivity of $Ni(tach)_2{}^{2+}$ and expecially $Ni(tach)^{2+}$ is due mainly to the fact that rechelation (Scheme I, k_2) is faster than the second Ni–N bond rupture (k_3).

A comparison of the coordination geometries of $Ni(tach)_2{}^{2+}$, $Ni(tach)(H_2O)_3{}^{2+}$, and $Ni(H_2O)_6{}^{2+}$ shows several trends (Tables I and VI). Substitution of one tach by three H_2O molecules shortens the average Ni–N distance by 0.063 Å. Substitution of three H_2O molecules on $Ni(H_2O)_6{}^{2+}$ by one tach molecule lengthens the average Ni–O distance by 0.05 Å, and the average interligand N–Ni–N angle (92.4°) in $[Ni(tach)_2]^{2+}$ is slightly larger than the average N–Ni–O angle in $[Ni(tach)(H_2O)_3]^{2+}$ (90.8°). Given that the kinetic analysis is largely correct, the rate of loss of the first NH_2 group from $Ni(tach)_2{}^{2+}$ is 10–10^2 times greater than that from $Ni(tach)(H_2O)_3{}^{2+}$, and it is tempting to ascribe the difference to the shortened Ni–N bond lengths in $Ni(tach)(H_2O)_3{}^{2+}$ (0.063 Å). The argument is the following: The structural changes undergone by an octahedral Ni(II) complex on the way to the transition state of a dissociative ligand substitution reaction include, among other things, the lengthening of the bond between nickel and the leaving group. If we assume that the transition-state energy is higher for the rupture of short and energetically more stable bonds than for the rupture of longer, less stable bonds between the same type of atoms, the observed trend in the rates is understandable in terms of the bond length differences observed in the ground states. The effect may also be significant for replacement of H_2O since the more strongly bonded H_2O molecules in $Ni(H_2O)_6{}^{2+}$ are replaced by NH_3 about 100 times more slowly than the less strongly bonded ones in $Ni(tach)(H_2O)_3{}^{2+}$ (Table VI).[32] Assuming reasonable force constants, we estimate that differences in bond angles (Table I) are about 1 order of magnitude less important energetically than differences in bond lengths; as a consequence they are probably unimportant in determining the rate of substitution reactions of $Ni(tach)_2{}^{2+}$. They may be relevant, however, to the differences in rate for water substitution in complexes with a constant number of N donor atoms in the coordination sphere but different constitutions of the corresponding polyamine ligands.[32]

Table VI. Some Geometric and Kinetic Data for Ni–Amine Complexes[a]

NiL_n	d(Ni–N), Å	k_1(Ni–N), s^{-1}	d(Ni–O), Å	k(Ni–O), s^{-1}
$Ni(tach)_2{}^{2+}$	2.13[10]	0.8		
$Ni(tach)^{2+}$	2.07[d]	≳0.006	2.10[d]	38 × 10^6 [b] [32]
Ni^{2+}			2.05[e]	28 × 10^4 [b] [32]
$Ni(en)_3{}^{2+}$	2.13[c]	87[17]		
$Ni(prop)_3{}^{2+}$	2.14[30]			
$Ni(en)_2{}^{2+}$		5[17]		5.4 × 10^6 [f] [31]
$Ni(prop)_2{}^{2+}$	2.11[36]		2.15[36]	
$Ni(chxn)_2{}^{2+}$	2.10[37]		2.13[37]	
$Ni(en)^{2+}$	2.07[38]	0.15[17]	2.09[38]	4.4 × 10^5 [f] [31]
Ni^{2+}			2.05[e]	4.4 × 10^4 [f] [31]

[a] Structures are included only if $R \leqslant 0.07$. [b] Rate of substitution of H_2O by NH_3. [c] Average of three determinations.[33-35] [d] Average of two determinations (ref 11 and this work). [e] Average of four determinations.[39-41] [f] Rate of water exchange.

Similar conclusions follow from a consideration of $Ni(en)_n{}^{2+}$ (n = 1–3) and related complexes (Table VI). The Ni–N as well as the Ni–O bond lengths decrease with increasing number of H_2O molecules in the first coordination sphere. The rate constants k_1 for the first Ni–N bond rupture and the rate

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constants *k* or H_2O exchange decrease with decreasing bond lengths. The same trend is observed for the corresponding activation enthalpies (Table V). This trend is analogous to that observed for the hydrolysis of organic ketals[42] and indicates that bond length is one of the rate-determining factors in a dissociation reaction.

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Registry No. $[Ni(tach)_2]^{2+}$, 31724-12-6; $[Ni(tach)(H_2O)_3](NO_3)_2$, 78654-70-3; $[Ni(tach)(H_2O)_3]^{2+}$, 25625-39-2; $[Ni(tach)(en)(H_2O)](ClO_4)_2$, 87655-59-2.

Supplementary Material Available: A description of crystal data, details of intensity measurements and of structure analysis, listings of atomic coordinates and vibrational parameters and selected bond lengths, bond angles, and torsion angles for $[Ni(tach)(H_2O)_3{}^{2+}](NO_3)_2$, a half normal probability plot comparing positional parameters determined in ref 11 and in this work, and a table of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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Base-Catalyzed Hydration of Cobalt(III)-Coordinated Dimethylcyanamide and Linkage Isomerization of the Derived N-Bound Dimethylurea Complex

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The dimethylcyanamide complex ion $[(NH_3)_5CoNCN(CH_3)_2]^{3+}$ has been synthesized and the rate law for its base hydrolysis established: $-d[\text{complex}]/dt = k_{OH}[\text{complex}]$; $k_{OH} = 3.06 \pm 0.03\ M^{-1}\ s^{-1}$ (25 °C, $\mu = 1.0$ M (KCl)). The many-fold rate enhancement for the hydrolysis of the substituted nitrile on coordination to Co(III) is discussed in relation to data for other nitriles. The hydrolysis product, the deprotonated dimethylurea complex $[(NH_3)_5CoNHCON(CH_3)_2]^{2+}$, has been isolated. It is stable in basic solution but rapidly isomerizes to its O-bonded linkage isomer $[(NH_3)_5CoOC(NH_2)N(CH_3)_2]^{3+}$ in acid solution; only a little (~3%) competitive hydrolysis (to yield $[(NH_3)_5CoOH_2]^{3+}$ and $NH_2CON(CH_3)_2$) is observed. Kinetic data for the pH region 0–5 establish the rate law $-d[\text{complex}]/dt = k[H^+]/(K_a' + [H^+])$, where $k = (1.60 \pm 0.02) \times 10^{-2}\ s^{-1}$, $pK_a' = 2.92 \pm 0.03$ ($\mu = 1.0$ M (KCl), 25 °C), $\Delta H^* = 80.9$ kJ/mol, and $\Delta S^* = -7.7$ J/(deg mol). The pK_a' value for the reactive entity in this urea-*N* to urea-*O* linkage isomerization reaction, the $[(NH_3)_5CoNH_2CON(CH_3)_2]^{3+}$ ion, agrees well with that determined independently, 2.89 ± 0.04. The site of protonation, at the bound N or exo-O atom, and the mechanism of the rearrangement process are discussed in relation to corresponding data for analogous amide and other systems. The oxygen-bonded dimethylurea complex hydrolyzes slowly to give the corresponding aqua or hydroxo product and free ligand. There is no detectable (<1%) hydrolysis of the ligand (C–N cleavage) to produce oxygen-bonded carbamate and free amine. The rate law $-d[\text{complex}]/dt = [k_x + k_{OH}K_w/([H^+] + K_a')][\text{complex}]$ is established; at 25 °C ($\mu = 1.0$ M ($NaClO_4$)), $k_s = 3.8 \times 10^{-5}\ s^{-1}$, $k_{OH} = 10.3\ M^{-1}\ s^{-1}$, and $pK_a' = 13.48$. The acid-base process corresponds to net deprotonation of the ligand in strong OH^- to give $[(NH_3)_5CoOC(NH)N(CH_3)_2]^{2+}$, and this ion is argued to be relatively unreactive. Comparisons are made with the previously studied urea-*O* and sulfamate-*O* systems. Proton and carbon-13 NMR data are presented that establish the ground-state structures of the dimethylurea-*O* and -*N* complexes and related derivatives. Restricted rotation about the $C\overset{...}{-}N(CH_3)_2$ bond, induced by coordination to Co(III), is observed in the low-temperature ^1H NMR spectra of the oxygen-bonded and protonated-nitrogen-bonded dimethylurea complexes.

Introduction

In attempts to mimic aspects of the chemistry of the nickel metalloenzyme jack bean urease,[2,3] we are currently examining the H^+- and OH^--promoted reactions of a number of Co(III) and Rh(III) complexes of N- and O-coordinated ureas.[4] The enzyme is a very efficient catalyst of the hydrolysis of urea to produce ammonia and carbonic acid.[5] It contains 2 mol of Ni(II)/mol of active sites,[2,3] and at least one of these metal ions is involved in its mechanism of action.[6,7] An hypothesis for its detailed mechanism has recently been presented.[7] It involves nucleophilic attack by OH^-, coordinated to one Ni(II) ion, on urea which is coordinated to the other nickel ion through its carbonyl oxygen. In our previous examination of the base-catalyzed hydrolysis of the [(urea)pentaamminecobalt(III)]$^{3+}$ ion, we found that O coordination of urea to cobalt(III) did not provide sufficient activation of the carbonyl group to enable the anticipated urea hydrolysis (to produce the $[(NH_3)_5CoO_2CNH_2]^{2+}$ ion) to compete with the facile base-catalyzed (S_N1CB) hydrolysis of the cobalt–oxygen bond.[4a] We sought to prepare the corresponding N-bonded urea complex to comment on the alternative possibility that urea might N coordinate with Ni(II) at the active site of urease

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