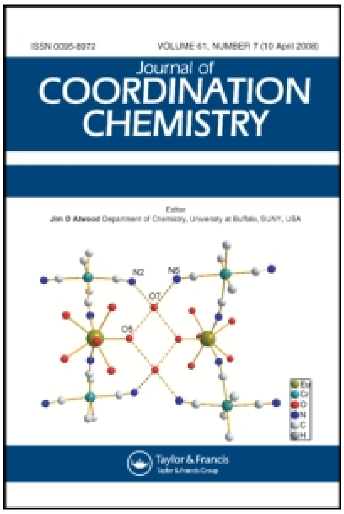

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KINETICS OF DISSOCIATION OF NICKEL COMPLEXES WITH PENTADENTATE LIGANDS

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KINETICS OF DISSOCIATION OF NICKEL COMPLEXES WITH PENTADENTATE LIGANDS

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The synthesis of the pentadentate ligands 1,4-bis(2-pyridylmethyl)-1,4,7-triazacyclononane (BPTAN) and 1,4,7-triazacyclononane-N,N'-diacetate (TCDA) are reported. The nickel(II) complexes of BPTAN and TCDA were synthesized and characterized by their elemental analyses, electrochemistry, and uv-vis spectra. The rate of nickel ion aquation from the BPTAN complex in aqueous solution in the presence of chloride ion was found to follow the rate law, Rate = $k_1[H^+]^2[Cl][NiL]/\{1 + k_2[Cl]\}$. At 60°C and $I = 2.0$ M, values for k_1 and k_2 were determined to be $(1.7 \pm 0.2) \times 10^{-6}$ M^{-3} s^{-1} and 0.15 ± 0.04 M^{-1} respectively. For NiTCDA(H_2O), the rate law was found to be independent of the chloride ion concentration. The rate law was found to follow the form, Rate = $k_1[H^+][NiL]/(1 + k_2[H^+])$. At 60°C and $I = 2.0$ M, k_1 and k_2 were found to be equal to 3 M^{-1} s^{-1} and 0.90 ± 0.07 M^{-1}, respectively. This work has shown NiBPTAN(H_2O)$^{2+}$ to be one of the most inert nickel complexes to ligand dissociation that has been reported.

KEYWORDS: kinetics, nickel, pentadentate, chelate

INTRODUCTION

Transition metal complexes of the macrocyclic ligand 1,4,7-triazacyclononane (TACN) and its derivatives have been extensively studied in the past decade.[1] When TACN is modified with compounds that contain donor groups at the three secondary amine positions hexadentate ligands can be formed. Transition metal complexes of these hexadentate ligands may be either charged or neutral and show large formation constants with most transition metal ions.[2–13] Such complexes may find useful applications in the field to Magnetic Resonance Imaging (MRI) and other therapeutic techniques.[8,10]

Our interest is with pentadentate ligands where only two of the secondary nitrogens of TACN are derivatised.[14–17] With the proper choice of pendant arm chelating group, this type of ligand may produce a transition metal complex which exhibits only one exchangeable coordinate site. Complexes of this type can then be used to investigate the reactivity at one metal coordination site with normally labile transition metal ions.[18] The ability to vary the nature of the pendant arm chelating groups may allow us to tune the chemistry at the metal's exchangable coordination site both electronically and structurally.

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While the magnitude of the formation constants for TACN and its substituted hexadentate derivatives with transition metals suggests the formation of stable complexes, the solution dynamics of these complexes is largely unexplored. In an attempt to develop this area, we present a comparison of the acid hydrolysis of a neutral and a cationic nickel complex formed with the bis-acetate and the bis-2-pyridylmethyl derivatives of TACN. The results show the more rigid pyridine derivative is more resistant to dissociation than the neutral acetate complex. The rate laws for the hydrolysis reactions are used to predict a mechanism for each reaction and to explore the solution behavior of the nickel complexes.

EXPERIMENTAL SECTION

Materials

Reagents were either ACS Certified grade or the best grade available. Acid solutions were standardized against sodium carbonate with methyl red indicator.

Physical Techniques

A Perkin-Elmer Lambda 3 spectrophotometer was used for UV-Visible absorption spectroscopy. The instrument was controlled and the data collected on an IBM-XT computer over a serial interface. Cyclic voltammetry was performed using a Bioanalytical Systems Inc. CV-27 with a Houston Instrument model 2000 X-Y recorder. A glassy carbon working electrode, a platinum auxiliary electrode and a saturated calomel reference electrode were used in all electrochemical experiments. Trifluoroacetic acid and potassium chloride were used as the supporting electrolytes. The $+2/+3$ redox couple for the pentaamminepyridineruthenium(II) ion (0.3 V *vs.* NHE) was used as an internal standard. NMR spectra were recorded on a Varian FT-80 NMR Spectrometer with tetramethylsilane as the internal standard. Elemental analysis was performed by Robertson Laboratories Inc.

Kinetic Data

The change in the concentration of the nickel complexes was monitored spectrophotometrically. The absorption at 563 nm was used for $NiBPTAN(H_2O)^{2+}$ and that at 530 nm was used for $NiTCDA(H_2O)$. Samples were maintained at constant temperature using water jacketed cell holders and a constant temperature circulating water bath. Pseudo-first-order rate constants for the hydrolysis of $NiTCDA(H_2O)$ were determined from a least-squares analysis of a plot of $In(A_t\text{-}A_f)$ *vs.* time. The plots were linear for more than three half-lives. The initial rate method was used to obtain pseudo-first-order rate constants for the hydrolysis of $NiBPTAN(H_2O)^{2+}$. Rate law expressions were determined by standard graphical methods of analysis using linear-least-squares fitting. The rate constants were checked using non-linear-least-squares fitting software. The uncertainty in the values of the rate constants were determined from the deviation between the two methods.

SYNTHESIS

1,4,7-Triazacyclononane trihydrobromide (TACN-3HBr) was synthesized by literature methods[19]

1,4,-Bis(2-pyridylmethyl)-1,4,7-triazacyclononane pentahydrobromide(BPTAN-5HBr) was prepared by mixing 1,4,7-triazacyclononane trihydrobromide (10.5 g, 0.028 mol) with 2-picolyl chloride hydrochloride (9.26 g, 0.056 mol) in a minimum amount of water. The pH of the solution was maintained between 7 and 8 by adding 4 M NaOH. After three days no further decrease in the pH was observed. The reaction mixture was concentrated and sufficient 48% hydrobromic acid was added to cause precipitation of NaBr. The salt was removed by filtration and the hydrobromide salt of the ligand precipitated by the addition of ethanol and ether to the filtrate. The ligand salt was recrystallized by dissolving in a minimum amount of water and adding an equal volume of 48% HBr. The solution was filtered and one volume of ethanol was added to the filtrate followed by ether until a turbid solution was obtained. The solution was cooled at 5°C for 24 hrs. During this time a cream colored precipitate formed. The solid was collected by filtration and washed with ethanol and then ether. The yield was 12.6 g (0.0176 mol, 63% yield). ^1H NMR ($DCCl_3$): ∂ 2.65 (s,4H), 2.74 (s,8H), 3.87 (s,4H), 7.1 (m,3). 7.5 (m,2), 7.63 (m,1), 8.48 (m,1), 8.57 (m,1).

Aquo[1,4-Bis(2-pyridylmethyl)-1,4,7-triazacyclononane]nickel(II) trifluoromethansulfonate

Nickel chloride hexahydrate (0.119 g, 0.5 mmol) and BPTAN·5HBr (0.356 g, 0.5 mmol) were dissolved in 5 ml of water and the pH of the solution raised to 5 with 1 M NaOH. The solution was warmed to approximately 70°C for one hour. The solution was cooled and filtered. The filtrate was diluted to 50 ml and absorbed on a SP Sephadex C-25 column (2.5 gm of dry resin, hydrated and acid washed). The column was washed with 0.1 M trifluoromethanesulfonic acid (HTFMS), followed by 0.2 M HTFMS to elute the complex. The blue eluent was collected and concentrated to a paste under reduced pressure. The paste was dissolved in a small amount of ethanol, and filtered. Ether was added to the filtrate until a turbid solution was obtained. The complex crystallized upon standing at 5°C for 24 hrs. Yield: 0.16 g (47%) Anal. Calcd. for $Ni(C_{18}H_{25}N_5)H_2O(F_3CSO_3)_2$: C, 34.98; H, 3.94; N, 10.2. Found: C, 35.26; H, 3.88; N, 10.04. {For the BF_4^- salt; Cald. for $Ni(C_{18}H_{25}N_5)H_2O(BF_4)_2$: C, 38.49; H, 4.84; N, 12.47. Found: C, 38.25; H, 4.80; N, 12.38} UV-Visible spectra in water: 865 nm (26), 810 nm (sh), 530 nm (15), 255 nm (27000), 216 nm (27000). Electrochemistry Ni(+ 2/ + 3) (0.1M TFA) 1.29 V *vs.* NHE.

1,4,7-triazacyclononane-N,N'-diacetate (TCDA)

The trihydrobromide salt of 1,4,7-triazacyclononane (3.72 g, 0.01 mol) and chloroacetic acid (1.89 g, 0.02 mol) were dissolved in approximately 30 ml of water. The solution was warmed to 45°C and the pH of the solution was maintained between 9 and 10 by the addition of solid lithium hydroxide monohydrate. After 24 hrs the pH of the solution became constant and the solution was cooled to room temperature. The pH of the solution was adjusted to 7, filtered and diluted to 50 ml with water. This solution contained a mixture of the mono, di, and tri-substituted macrocycle ligands. Attempts to obtain pure, 1,4,7-triazacyclononane-N,N'-diacetate were unsuccessful. The solution obtained directly from this reaction was used to prepare the nickel complex.

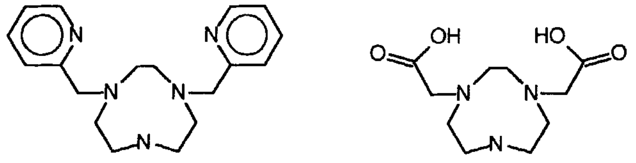
Aquo[1,4,7-triazacyclononane-N,N'-diacetate] nickel(II)

To 10 ml of the above ligand solution was added 0.5 g of nickel chloride hexahydrate. The solution was heated to 60°C for one hour. The reaction mixture was concentrated under reduced pressure. The complex was purified by column chromatography on Bio-gel P-2 gel filtration resin. Three bands were obtained. The desired product was the major band. This band was collected and a glassy solid obtained after removal of the solvent. The solid was crystallized from ethanol and ether. *Anal.* Calcd. for $Ni(C_{10}H_{17}N_3O_4)H_2O \cdot H_2O$:C, 35.54; H, 6.26; N, 12.43. Found: C, 35.38; H, 5.93; N, 12.61. UV-Visible spectra in water: 875 nm (19), 563 nm (9), 362 nm (12). Electrochemistry Ni(+2/+3) (0.1M KCl) 1.19 V *vs.* NHE

RESULTS

The synthesis of the macrocyclic portion of the ligand was performed using a published procedure. The pentadentate ligands were synthesized using procedures that were modified from those published for the synthesis of the analogous hexadentate ligands.[3,9] The BPTAN ligand was purified by fractional crystallization as the hydrobromide salt. The nickel complex was made by adding a slight excess of nickel(II) chloride to the hydrobromide salt of the ligand in water and adjusting the pH of the solution to 5 with 1 M sodium hydroxide solution. The purification of $NiBPTAN(H_2O)^{2+}$ utilized ion exchange chromatography followed by mixed solvent crystallization. Attempts to purify the TCDA ligand were not successful. The nickel TCDA complex was obtained by adding nickel(II) chloride to the reaction mixture from the ligand synthesis. Gel filtration chromatography was used to purify the neutral complex and the material was isolated by mixed solvent crystallization.

Ligand Structures



BPTAN TCDA

The nickel complexes were characterized by elemental analysis (see EXPERIMENTAL), uv-vis spectroscopy, and cyclic voltammetry. The $NiTCDA(H_2O)$

complex showed absorption bands at 875 nm (19), 563 nm (9), and 362 nm (12) when measured in either neutral or acidic aqueous solution. By cyclic voltammetry a redox couple was observed at 1.19 V *vs.* NHE when meaured in 0.1 M KCl. With a scan rate of 100 mV/s the peak to peak separation was 95 mV and the anodic and cathodic peak heights were approximately equal. The visible spectrum of the $NiBPTAN(H_2O)^{2+}$ complex in water consists of absorptions at 530 nm (15) and 865 nm (26) with a shoulder at 810 nm. The spectrum is unchanged when recorded in 2 M $HClO_4$, but shows a red shift of approximately 2 nm when recorded in 2 M HCl. Ligand centered absorptions dominate the UV region of the spectrum with peaks at 255 nm and 216 nm. A redox couple was observed at 1.29 V *vs.* NHE in 0.1 M trifluoroacetic acid. At a scan rate of 100 mV/s the peak to peak separation of the cathodic and anodic waves was 70 mV and the ratio of the cathodic and anodic peak heights was approximately one.

Experiments were performed to determine the effect of the hydrogen ion concentration and the chloride ion concentration on the rate of hydrolysis of the $NiTCDA(H_2O)$ complex. Pseudo-first-order rate constants for the conditions studied are given in Table 1. The observed rate law was found to fit the expression; Rate = $k_1[H^+][NiL]/(1 + k_2[H^+])$. In one molar ionic strength and at 60°C values for k_1 and k_2 were found to be $(1.2 \pm 0.1) \times 10^{-3}$ M^{-1} s^{-1} and 0.23 ± 0.15 M^{-1}, respectively in hydrochloric acid solutions and $(9.5 \pm 0.3) \times 10^{-4} M^{-1} s^{-1}$ and 0.2 ± 0.1 M^{-1} in perchloric acid solutions. In two molar ionic strength and at 60°C values for k_1 and k_2 were $(2.5 \pm 0.1) \times 10^{-3}$ M^{-1} s^{-1} and 0.90 ± 0.07 M^{-1}, respectively when measured in hydrochloric acid solution. An analysis of the effect of temperature on the rate constant yielded an activation energy of 76 ± 3 kJ/mol for the hydrolysis reaction when measured in 2 M hydrochloric acid over the temperature range of 30 to 60°C.

The hydrolysis of $NiBPTAN(H_2O)^{2+}$ did not go to completion under the conditions studied. Figure 1 shows the percentage of the complex remaining in

Table 1 Rates of acid hydrolysis of $NiTCDA(H_2O)$.

Conditions	Temperature (°C)	Pseudo-first-order rate (sec^{-1})
2.0 M HCl	30	$(1.13 \pm 0.01) \times 10^{-4}$
2.0 M HCl	40	$(3.12 \pm 0.01) \times 10^{-4}$
2.0 M HCl	50	$(8.32 \pm 0.01) \times 10^{-4}$
2.0 M HCl	60	$(1.7 \pm 0.01) \times 10^{-3}$
1.5 M HCl/0.5 M KCl	60	$(1.66 \pm 0.01) \times 10^{-3}$
1.0 M HCl/1 M KCl	60	$(1.28 \pm 0.01) \times 10^{-3}$
0.5 M HCl/1.5 M KCl	60	$(8.50 \pm 0.01) \times 10^{-4}$
1.0 M HCl	60	$(9.50 \pm 0.01) \times 10^{-4}$
0.75 M HCl/0.25 M KCl	60	$(8.35 \pm 0.01) \times 10^{-4}$
0.5 M HCl/0.5 M KCl	60	$(5.67 \pm 0.01) \times 10^{-4}$
0.25 M HCl/0.75 M KCl	60	$(2.75 \pm 0.01) \times 10^{-4}$
2.0 M $HClO_4$	60	$(1.2 \pm 0.1) \times 10^{-3}$
1.0 M $HClO_4$	60	$(7.2 \pm 0.1) \times 10^{-4}$
0.75 M $HClO_4$/0.25 M $NaClO_4$	60	$(5.9 \pm 0.1) \times 10^{-4}$
0.7 M $HClO_4$/0.3 M $NaClO_4$	60	$(5.7 \pm 0.1) \times 10^{-4}$
0.6 M $HClO_4$/0.4 M $NaClO_4$	60	$(5.2 \pm 0.1) \times 10^{-4}$
0.5 M $HClO_4$/0.5 M $NaClO_4$	60	$(4.5 \pm 0.1) \times 10^{-4}$
0.4 M $HClO_4$/0.6 M $NaClO_4$	60	$(3.7 \pm 0.1) \times 10^{-4}$
0.3 M $HClO_4$/0.7 M $NaClO_4$	60	$(2.7 \pm 0.1) \times 10^{-4}$
0.25 M $HClO_4$/0.75 M $NaClO_4$	60	$(2.2 \pm 0.1) \times 10^{-4}$

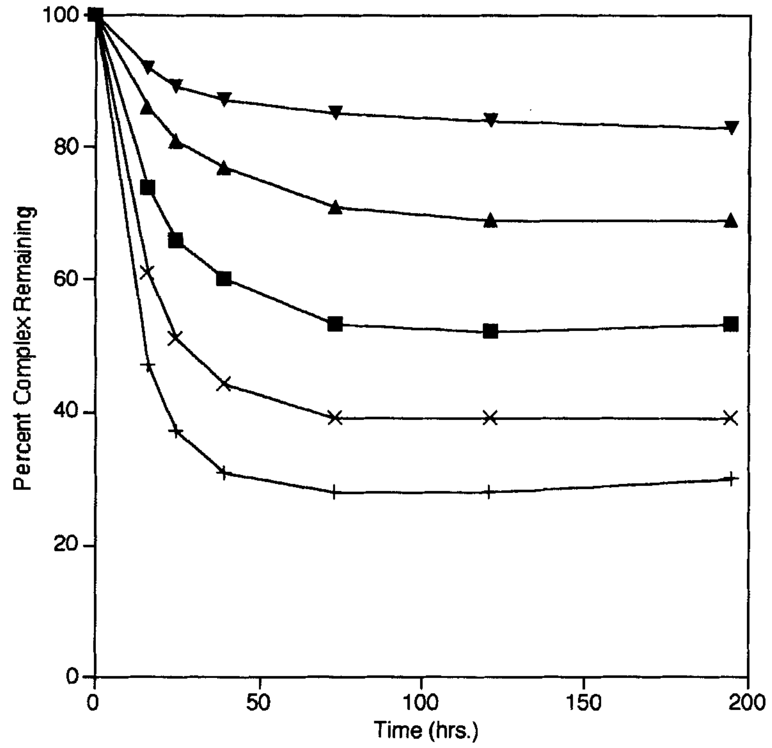


Figure 1 Percentage of NiBPTAN$(H_2O)^{2+}$ remaining *vs.* time at different hydrogen ion concentrations. T = 60°C, I = 2 M, chloride media, $[H^+]$ 2 M(+), 1.6 M (×), 1.2 M (■), 0.8 M (▲), 0.4 M (▼).

solution as a function of time for five different initial hydrogen ion concentrations. The initial rate method was used to obtain pseudo-first-order rate constants for the conditions studied. Values for the observed rate constants for the hydrolysis of NIBPTAN$(H_2O)^{2+}$ are listed in Table 2. The pseudo-first-order rate constant for the hydrolysis of NiBPTAN$(H_2O)^{2+}$ at 60°C were determined to be $(4.7 \pm 0.3) \times 10^{-7}$ s^{-1} and $(1.08 \pm 0.04) \times 10^{-5}$ s^{-1} when measured in two molar perchloric acid and

Table 2 Rates of acid hydrolysis of $[NiBPTAN(H_2O)]^{+2}$

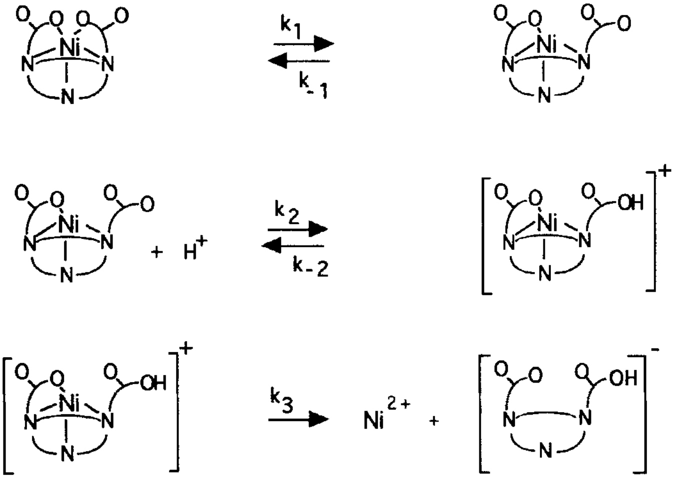
Conditions	Temperature (°C)	Pseudo-first-order rate (sec^{-1})
2.0 M $HClO_4$	60	$(4.7 \pm 0.3) \times 10^{-7}$
0.5 M HCl/1.5 M $HClO_4$	60	$(3.2 \pm 0.1) \times 10^{-6}$
1.0 M HCl/1.0 M $HClO_4$	60	$(6.5 \pm 0.1) \times 10^{-6}$
1.5 M HCl/0.5 M $HClO_4$	60	$(8.7 \pm 0.1) \times 10^{-6}$
1.0 M HCl/1.0 M KCl	60	$(2.6 \pm 0.1) \times 10^{-6}$
1.5 M HCl/0.5 M KCl	60	$(5.5 \pm 0.3) \times 10^{-6}$
2.0 M HCl	60	$(1.08 \pm 0.04) \times 10^{-5}$
2.0 M HCl	50	$(3.3 \pm 0.1) \times 10^{-6}$
2.0 M HCl	40	$(1.0 \pm 0.1) \times 10^{-6}$
1.0 M HCl	60	$(8.7 \pm 0.1) \times 10^{-7}$
1.0 M HCl	50	$(3.6 \pm 0.1) \times 10^{-7}$

two molar hydrochloric acid, respectively. Experiments were performed to determined both the effect of the hydrogen ion and the chloride ion concentrations on the rate of the hydrolysis reaction. The observed rate law was found to fit the expression; Rate = $k_1[H^+]^2[Cl^-][NiL]/(1 + k_2[Cl^-])$. Values for k_1 and k_2 were found to be $(1.7 \pm 0.2) \times 10^{-6}$ M^{-3} s^{-1} and 0.15 ± 0.04 M^{-1}, respectively at 60°C and two molar ionic strength over the chloride ion concentration range of 0.5 M to 2 M and the hydrogen ion concentration range of 1 M to 2 M. The activation energy for the hydrolysis reaction was determined to be 103 ± 2 kJ/mol when measured in 2 M hydrochloric acid over the temperature range of 40 to 60°C.

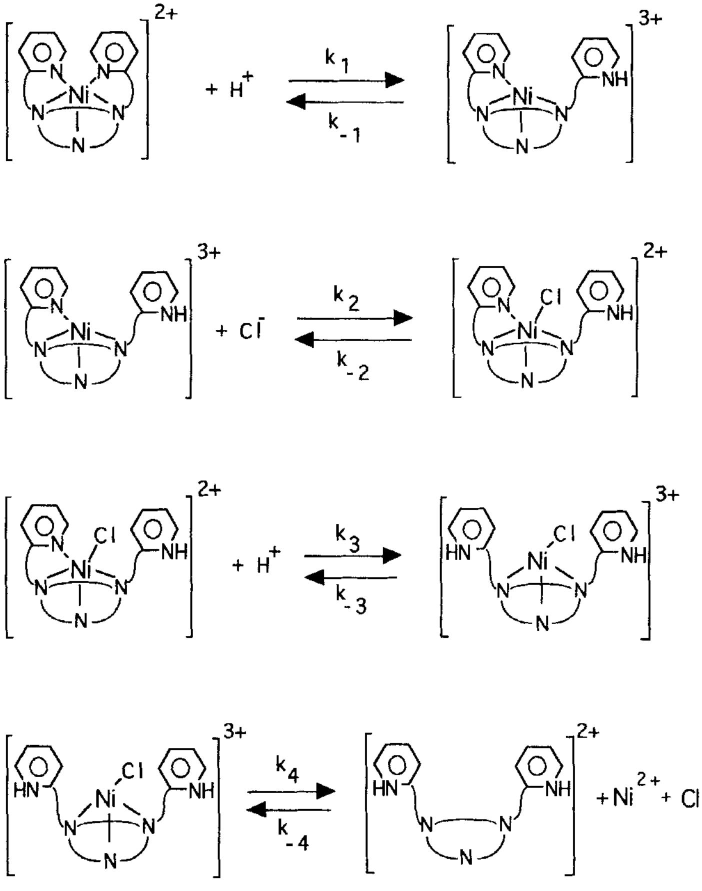
DISCUSSION

The synthesis of these pentadentate ligands was performed to produce transition metal complexes with characteristically labile metal ions that are stable under acidic aqueous conditions. In addition, it was desired that the complexes contain at least one available coordination site on the metal ion to act as a binding site for a substrate molecule. The stability of these complexes was first addressed. This study was conducted to investigate the rate and mechanism of the acid hydrolysis of these complexes.

The experimentally determined rate laws for the hydrolysis of the $NiBPTAN(H_2O)^{2+}$ and $NiTCDA(H_2O)$ complexes can be fit to multi-step mechanisms. These mechanisms call for the stepwise dissociation of the ligand from the metal ion and are based upon the mechanisms proposed by Margerum[20] for the hydrolysis of nickel and copper complexes of polydentate ligands. Shown in Schemes 1 and 2 are pictorial representations of the general steps required in each mechanism. Each of the steps proposed in these mechanisms can be broken down into of a series of fundamental reaction processes. No information about the details



Scheme 1 Mechanism for the Hydrolysis of $NiTCDA(H_2O)$.



Scheme 2 Hydrolysis mechanism for $\mathrm{NiBPTAN(H_2O)^{2+}}$.

of these fundamental steps could be obtained from the experimental data so they have not been included in the hydrolysis schemes.

The mechanism proposed for the hydrolysis of $\mathrm{NiTCDA(H_2O)}$ utilizes an initial rapid formation of an activated complex followed by the reversible protonation of the activated complex. The rate determining step is the loss of the metal from this protonated form of the complex. This mechanism yields a rate law of the form: $\mathrm{Rate} = k_1k_2k_3[\mathrm{NiL}][\mathrm{H^+}]/((k_{-2}+k_3)(k_{-1}+k_2[\mathrm{H^+}]))$. We have proposed that one of the carboxylate groups leaves the coordination sphere of the metal in the activated form of the complex and becomes protonated in the second step of the mechanism. This is in agreement with the hydrolysis mechanisms proposed for nickel complexes with other aminocarboxylate ligands[20]. The insensitivity of the visible spectra of the complex to the pH of the solution and the paramagnetism of the complex makes analysis of the protonated form of the complex difficult. The visible spectral results suggest that either the protonated intermediate has a spectrum which is similar to the unprotonated form of the complex or that the concentration of the intermediate under the conditions studied is small.

The rate law for the hydrolysis of $NiBPTAN(H_2O)^{2+}$ suggests a more complex mechanism. Multiple pathways for hydrolysis seem to be present. The complex shows an acid dependent rate law in the absence of chloride ion. The details of this rate law have not been studied due to the very small reaction rates observed in chloride free media. In the presence of chloride ion, the proposed mechanism, shown in Scheme 2, consists of (1) the reversible protonation of the complex, (2) the reversible coordination of chloride ion to the nickel, (3) the addition of a second proton to the complex and (4) the loss of the nickel ion from the ligand. Due to the lack of basic sites on the surface of the complex, the formation of an activated form of the complex prior to the addition of each of the hydrogen ions should be necessary. In the activated form of the complex one of the nitrogen atoms leaves the coordination sphere of the nickel ion creating a site for protonation of the ligand. We propose that the pyridyl nitrogens are the sites that accept protons. This is in agreement with the chemistry of the nickel complex of the hexadentate ligand 1,4,7-tris(3-aminopropyl)-1,4,7-triazacyclononane which shows reversible protonation at the primary amine sites.[7] Alternatively, the rearrangement of the ligand to allow the remaining secondary nitrogen of the macrocycle to become protonated may be involved in one of the protonation steps. The TACN macrocycle coordinated in such a bidentate fashion has been reported.[21,22] The replacement of a nitrogen donor atom in the coordination environment of the nickel ion with an oxygen atom from water is expected to produce a change in the visible spectrum of the complex. The insensitivity of the visible spectra of the complex to the pH of the solution suggests that the concentrations of the intermediate species of the hydrolysis reaction are small. The role of the chloride ion may be to reduce the overall charge on the complex, thereby decreasing the electrostatic repulsion that the second protonation step would otherwise experience. Chloride ion is known to accelerate the hydrolysis of nickel complexes with some tetraamine macrocycles,[23] but the details of the effect on the rate law have not been reported to our knowledge. The proposed rate determining step is the loss of the nickel ion from the complex that contains both the chloride and hydrogen ions. Based upon the observation that the reaction does not go to completion, this step must be reversible under the conditions that we have studied. This mechanism would yield an initial rate law for the reaction in the presence of chloride ion in the form; $\text{Rate} = k_1k_2k_3k_4[NiL][H^+]^2[Cl^-]/\{(k_{-1} + k_2[Cl^-])(k_{-2} + k_3[H^+])(k_{-3} + k_4)\}$. If the term $k_3[H^+]$ is small compared to k_{-2} the rate law can be simplified to the form found experimentally.

The addition of these pendent arm chelating groups to the TACN ligand has significantly decreased the rate of acid hydrolysis for the ligand's nickel complexes. In 1 M HCl at 25°C the half-life for the acid hydrolysis of $NiTCDA(H_2O)$ can be estimated at five hours and the rate for $NiBPTAN(H_2O)^{2+}$ at 277 days. Under similar conditions, the rate of acid hydrolysis of $NiTACN(H_2O)_3{}^{2+}$ is only 70 minutes.[24] This makes the $NiBPTAN(H_2O)^{2+}$ complex one of the most resistant nickel complexes towards acid hydrolysis that has been reported. The root of the stability of these complexes may be due to the ability of the TCDA and the BPTAN ligands to form complexes with nickel(II) that have a minimum amount of strain energy. Additional contributions to the stability of the BPTAN complex may arise from the decreased flexibility of the chelating arms in going from acetate to

2-methylpyridyl. The activation energies for the hydrolysis of the two compounds support these ideas.

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References

1. P. Chaudhuri and K. Wieghardt, *Prog. Inorg. Chem.* **35** 329 (1987).
2. P.V. Bernhardt and G.A. Lawrance, *Coord. Chem. Rev.*, **104,** 297 (1990).
3. (a) L. Christiansen, D.N. Hendrickson, H. Toftlund, S.R. Wilson, and C.-L. Xie, *Inorg. Chem.* **25** 2813 (1986). (b) K. Wieghardt, E. Schöffman, B. Nuber, and J. Weiss, *Inorg. Chem.* **25** 4877 (1986).
4. K. Wieghardt, U. Bossek, P. Chaudhuri, W. Herrmann, B.C. Menke and J. Weiss, *Inorg. Chem.* **21,** 4308 (1982).
5. D.A. Moore, P.E. Fanwick, and M.J. Welch, *Inorg. Chem.* **28,** 1504 (1989).
6. D.A. Moore, P.E. Fanwick, and M.J. Welch, *Inorg. Chem.* **29,** 672 (1990).
7. G.W. Bushnell, D.G. Fortier, and A. McAuley, *Inorg. Chem.* **27,** 2626 (1988).
8. W.P. Cacheris, S.K. Nickle, and A.D. Sherry, *Inorg. Chem.* **26,** 958 (1987).
9. A. Bevilacqua, R.I. Gelb, W.B. Hebard, and L.J. Zompa, *Inorg. Chem.* **26,** 2699 (1987).
10. E. Brucher, and A.D. Sherry, *Inorg. Chem.* **29,** 1555 (1990).
11. M.J. Van der Merwe, J.C.A. Boeyens, and R.D. Hancock, *Inorg. Chem.* **24,** 1208 (1985).
12. C.F.G.C. Geraldes, A.D. Sherry, and W.P. Cacheris, *Inorg. Chem.* **28,** 3336 (1989).
13. M. Di Vaira, B. Cosimelli, F. Mani, and P. Stoppioni, *J. Chem. Soc., Dalton Trans.* 331 (1991).
14. A. Neves, W. Walz, K. Wieghardt, B. Nuber, and J. Weiss, *Inorg. Chem,* **27,** 2484 (1988).
15. C. Flassbeck, K. Wieghardt, E. Bill, C. Butzlaff, A.X. Trautwein, B. Nuber, and J. Weiss, *Inorg. Chem.* **31,** 21 (1992).
16. L.R. Gahan, G.A. Lawrance, and A.M. Sargeson, *Aust. J. Chem.* **35,** 1119 (1982).
17. W.S. Szulbinski, P.R. Warburton, D.H. Busch and N.W. Alcock, *Inorg. Chem.* **32,** 297 (1993).
18. W.S. Szulbinski, P.R. Warburton, and D.J. Busch, *Inorg. Chem.* **32,** 5368 (1993).
19. J.E. Richman, and T.J. Atkins, *J. Am. Chem. Soc.* **96,** 2268 (1974).
20. D.W. Margerum, G.R. Cayley, D.C. Weatherburn, and G.K. Pagenkopf, *ACS Monogr.* No. 174, 1–220 (1978).
21. G. Hunter, A. McAuley, and T.W. Whitcombe, *Inorg. Chem.* **27,** 2634 (1988).
22. K. Wieghardt, M. Koppen, W. Swiridoff, and J. Weiss, *J. Chem. Soc., Dalton Trans.* 1869, (1983).
23. F. Wagner, and E.K. Barefield, *Inorg. Chem.* **15,** 408 (1976).
24. L.J. Murphy, Jr. and L.J. Zompa, *Inorg. Chem.* **18,** 3278 (1979).