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Nickel(III)-Promoted Deprotonation of an Amine Group of Cyclam. Characterization of the Violet Transient through Stopped-Flow Spectrophotometric Techniques and Determination of the pK_A Value

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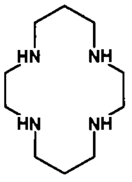
The violet transient that forms when a solution of $[Ni^{III}(cyclam)]^{3+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane, **1**) is added to a solution buffered at a pH = 7 ± 1 has been characterized by fast data acquisition spectrophotometry. The violet color originates from a fast decaying absorption band centered at 539 nm ($\epsilon = (1.33 \pm 0.10) \times 10^3$ M^{-1} cm^{-1}), pertinent to a species which forms through the deprotonation of an amine group of the macrocycle in the $[Ni^{III}(cyclam)]^{3+}$ complex and whose pK_A is 7.1 ± 0.1, as determined by spectral studies at varying pH. A pK_A value of 7.1 ± 0.2 has also been obtained by the pH dependance of $E_{1/2}(Ni^{III}/Ni^{II})$, determined through differential pulse voltammetry investigations. The transient decays according to a second order pattern ($k = (5.0 \pm 0.2) \times 10^3$ M^{-1} s^{-1}), ascribed to a "disproportionation" process, in which an electron is transferred from the negatively charged nitrogen atom of the violet species to the Ni^{III} center of another violet species.

Introduction

Cyclam (1,4,8,11-tetraazacyclotetradecane), **1**, is a very special ligand for obtaining stable nickel(III) complexes.[1,2] Low-spin Ni^{III} species can be prepared through chemical (using peroxy disulfate or nitrosonium salts) or anodic oxidation of the corresponding Ni^{II} complexes, in aqueous or non-aqueous media. Ni^{III} complex salts can be easily isolated as solids, and for some of them the crystal structure has been determined.[3] In any case, the metal complex displays an axially elongated stereochemistry, with the macrocycle spanning the four equatorial sites and the two apical positions being occupied by anions or solvent molecules.



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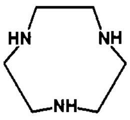

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The $[Ni^{III}(cyclam)]^{3+}$ species is fairly stable in solution.[4] In the case of aqueous media, persistence is strongly affected by the solution acidity. The higher the acidity, the longer the persistence of the trivalent complex. In particular, the bright green $[Ni^{III}(cyclam)]^{3+}$ lasts indefinitely in aqueous 1 M H_2SO_4, at room temperature. The green color results from the tail in the visible region of a strong charge-transfer band (ligand-to-metal) centered at ca. 310 nm. The solution stability drastically decreases with increasing pH. In particular, if the solution is made definitively alkaline (e.g. 1 M in NaOH) the strong green color instantaneously disappears and a much less intense yellow-orange color forms, pertinent to a low-spin Ni^{II} species. However, if the solution is made only slightly basic, a *violet transient color* forms, which lasts for the twinkling of an eye, to leave room again to the yellow color of the divalent complex.

The appearance of the violet transient color was first observed by Barefield,[5] when he dissolved the solid $[Ni^{III}(cyclam)(CH_3CN)_2](ClO_4)_3$ and $[Ni^{III}(ms\text{-}CTH)(CH_3CN)_2](ClO_4)_3$ complexes (CTH: 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) in water, pyridine, or triethylamine. On the basis of flow experiments with the $[Ni^{III}(ms\text{-}CTH)(CH_3CN)_2](ClO_4)_3$ complex, performed in the cavity of an ESR spectrometer, he ascribed the red-violet transient species to a Ni^{II} –ligand radical complex, which forms in the course of the reaction of the Ni^{III} macrocyclic complex with base. Such a view was criticized by Ferraudi,[6] who carried out oxidation of the $[Ni^{II}(CT)]^{2+}$ (CT = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) by radiolytically generated species and measured the transient spectra of the intermediate that formed. In particular, it was suggested that the transient species absorbing at 535–550 nm ($\epsilon \approx 10^3$ M^{-1} cm^{-1}) was an authentic Ni^{III} complex and that the ESR spectrum reported by Barefield could refer to a short-lived radical produced through fast degradation in the flow cavity of the spectrometer. Subsequently, Meyerstein[7] carried out pulse radiolysis investigations on solutions of varying pH of the same complex, $[Ni^{II}(CT)]^{2+}$, characterized a clean and reversible acid dissociation process with a pK_A value of 3.45, and assumed that the hydrogen ion was released by one of the two axially bound water molecules of the Ni^{III} tetraazamacrocyclic complex. A fast decaying transient, absorbing at 545 nm, was generated through pulse radiolysis experiments on $[Ni^{II}(cyclam)]^{2+}$ solutions at varying pH, and again the formation of the transient chromophore was ascribed to the deprotonation of one of the two water molecules apically coordinated in the Ni^{III} tetraazamacrocyclic complex.[8]

We have now investigated the solution properties of the violet transient, which forms during the reaction of aqueous $[Ni^{III}(cyclam)]^{3+}$ with solutions of varying pH, by means of a diode array fast data acquisition spectrophotometer. The apparatus used is equipped with a rapid mixing device and is able to record full 200-620-nm spectra at time intervals as small as 3.5 ms. Continuous-flow and stopped-flow spectra have indicated that the violet color of the transient originates from a rather strong

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[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1993.

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band (ϵ = (1.33 ± 0.10) × 10^3 M^{-1} cm^{-1}) centered at 539 nm. Such a band corresponds to a fast decaying Ni^{III} complex of monodeprotonated cyclam. The pK_A value for the Ni^{III}-promoted deprotonation of one of the four equivalent secondary amine groups of cyclam, which has been obtained from spectral measurements, is 7.1 ± 0.1. The same value is also obtained from independent differential pulse voltammetry experiments, carried out on solutions of the $[Ni^{II}(cyclam)]^{2+}$ complex at varying pH.

The metal-promoted deprotonation of the secondary amine groups of a fully saturated macrocycle had previously been observed and unambiguously characterized by Wieghardt[9] in the case of the $[Fe^{III}([9]\text{-}aneN_3)_2]^{3+}$ complex ([9]-aneN_3: 1,4,7-triazacyclononane, **2**). The deep blue Fe^{III} complex (λ = 542 nm, ϵ = 1800 M^{-1} cm^{-1}) forms at a much higher pH (pK_A = 11.4) and is much more kinetically stable than the Ni^{III} tetraazamacrocyclic transient, lasting in solution for 2–3 h.

Experimental Section

Materials. $[Ni^{II}(cyclam)](ClO_4)_2$ was prepared as described.[10] Buffer solutions used in spectrophotometric and electrochemical investigations were prepared by mixing appropriate amounts of 2,6-lutidine and standard perchloric acid solutions.

Caution! Although no difficulties were encountered, perchlorate salts are potentially explosive and must be handled with extreme care.

Fast Acquisition Spectrophotometric Studies. Spectra of the violet transient were taken by using a high speed diode array spectrophotometer coupled to a stopped-flow system. The spectrophotometer was a TIDAS (transputer integrated diode array system) apparatus, manufactured by J&M GmbH, Aalen, Germany. The 512-diode array can acquire a 512 point spectrum (range 200–620 nm) in a time as short as 1.3 ms, with a wavelength resolution of 0.8 nm. Up to 1000 spectra can be acquired and stored in the memory of the transputer board. The stopped-flow module associated to the spectrophotometer (SFM-3, Bio-Logic, Claix, France) consisted of a three-syringe system with two mixers. The three syringes are driven by independent stepping motors, operating at 6400 steps per motor turn. The observation chamber was a quartz cuvette with an optical path of 5 mm (SFM-3 TC-50/10). The movement of the syringes, the flow rate, and the flow stop as well as fast spectral data acquisition were controlled by a Model 486/33 personal computer through dedicated software. The SFM-3 module was thermostated at 25.0 °C through circulating water. In a typical experiment, syringe 1 contained a degassed $[Ni^{III}(cyclam)]^{3+}$ solution ($\approx 10^{-3}$ M), freshly prepared through controlled potential electrolysis, and syringe 3 contained a degassed solution adjusted to the desired pH with a 2,6-lutidine buffer (0.1 M). The flow rate of each syringe was 2.00 mL s^{-1}, thus, the total flow rate after mixing was 4 mL s^{-1}. At this flow rate, the time the solution takes to travel from the mixer to the observation chamber is 6 ms (dead time). In a first part of the experiment (continuous-flow mode) the mixed solution was allowed to flow through the cuvette, and the spectrophotometer recorded steady-state spectra. Then, the flow was stopped, and spectra of the immobilized solution were taken.

Figure 1 reports a typical reaction profile. In particular, the diagram in Figure 1 reports the intensity of the maximum of the absorption band centered at 539 nm (pertinent to the violet transient) vs time. In the continuous-flow mode interval, (a) 600 ms, spectra were taken every 20 ms. In the stopped-flow mode, (b) 3.5 s, spectra were taken every 50 ms.

Electrochemistry. Voltammetry experiments were performed in a conventional three-electrode cell, thermostated at 25.0 °C, under a dinitrogen atmosphere, by using an EG&G Princeton Applied Research Model 273 potentiostat/galvanostat, driven by a personal computer. The working electrode was a platinum microsphere, the counter-electrode was a platinum coil, and the reference electrode was a calomel electrode, saturated with sodium chloride to avoid precipitation of $KClO_4$ in the separating ceramic frit. In the controlled-potential electrolysis (CPE) experiments, the working electrode was a platinum gauze and the working half-cell was separated from the counter-electrode half-cell by a salt bridge containing aqueous $NaClO_4$. CPE experiments were carried out to oxidize quantitatively solutions of $[Ni^{II}(cyclam)](ClO_4)_2$, which were 0.1 M in $NaClO_4$ and had been adjusted to pH = 2 with standard perchloric acid. The green solution of $[Ni^{III}(cyclam)]^{3+}$ which formed on exhaustive electrolysis was used in stopped-flow spectrophotometric experiments. Such solutions were fairly stable over the time required for a complete spectrophotometric run: the intensity of the band of the $[Ni^{III}(cyclam)]^{3+}$ species decreased less than 3% 20 min after the completion of the electrolysis.

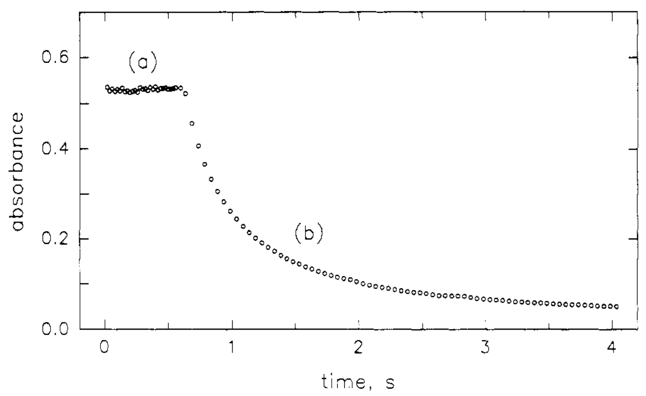

Figure 1. Variation of the intensity of the absorption band of the violet transient, centered at 539 nm under continuous-flow conditions, portion a, and under stopped-flow conditions, portion b. During portion (a) spectra were taken every 20 ms, during portion (b) spectra were taken every 50 ms.

Results

1. Determination of the pK_A Value by Fast Data Acquisition Spectrophotometry. Preliminary experiments performed with test tubes, by mixing a slightly acidic solution of $[Ni^{III}(cyclam)]^{3+}$ and an aqueous buffer solution, showed that the visual detection of the transient violet color is possible with buffer solutions ranging over the pH 6-8 interval. Mixing with more acidic buffers did not make the green color of the $[Ni^{III}(cyclam)]^{3+}$ complex change (apart from the decrease in intensity due to the dilution). On the other hand, mixing with more basic solutions caused the Ni^{III} green color to disappear, and the solution took a pale yellow color.

The same experiments were performed in the mixing device of a stopped flow module. In particular, one of the syringes contained a solution which was 2 × 10^{-3} M in $[Ni^{III}(cyclam)]^{3+}$ (freshly prepared through controlled potential electrolysis), 0.1 M in $NaClO_4$, and 0.01 M in $HClO_4$. The other syringe contained a buffer solution adjusted at the desired pH. The flow was maintained for some hundreds of milliseconds, and spectra were taken every 20 ms. In general, after 200 ms or less, reproducible steady-state spectra were obtained. Compared to those of the Ni^{III} chromophore before mixing, such spectra showed a new band centered at 539 nm. When the flow was stopped, the absorption band rapidly decayed, to disappear completely within 2 s or less. A family of spectra taken under stopped-flow conditions (pH of the final solution: 7.5) is shown in Figure 2. For sake of clarity, sampled spectra at 100-ms intervals have been reported in Figure 2. Several experiments were carried out, in which the pH of the buffer solution was varied over the pH 5-9 range. In these experiments, the intensity of the absorption band at 539 nm of the steady-state spectrum was found to vary with the pH of the buffer solution. Such a pH dependence is displayed in Figure 3. In particular, the intensity of the band was observed to develop and increase from pH 6 to pH 7.5 (hollow symbols in Figure 3). At higher pH values, the intensity of the band rapidly decreased (filled symbols). Appearance of a band and increase of its intensity with increasing pH would suggest that a new species (having a different color) forms due to the release of a proton by the $[Ni^{III}(cyclam)]^{3+}$ complex. We suggest that such a process is correctly described by the equilibrium

$$[Ni^{III}(HL)]^{3+} = [Ni^{III}(L^-)]^{2+} + H^+ \qquad (1)$$

in which HL is the tetramine macrocycle *cyclam* and L^- is its

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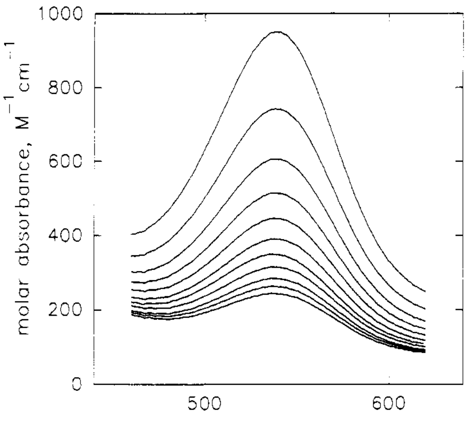

Figure 2. Absorption spectra under stopped-flow conditions of the violet transient species formed through the reaction of $[Ni^{III}(cyclam)]^{3+}$ with a buffer solution of pH 7.5. At this pH, 74% of the Ni^{III} complex is deprotonated. Spectra reported in the figure have been taken every 100 ms.

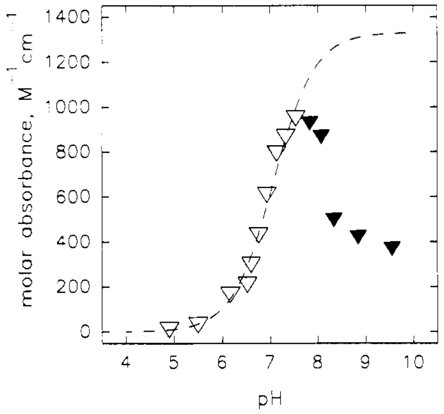

Figure 3. pH dependance of the intensity of the band of the violet transient (λ = 539 nm) taken at t = 0. Nonlinear curve fitting on eq 2, using data up to pH = 7.5 (hollow symbols) gave pK_A = 7.1 ± 0.1 (see dotted line). Data at higher pH values (filled symbols) do not fit, probably due to the very fast decay of the violet transient.

deprotonated form. If K_A is the acidic dissociation constant related to eq 1, the absorbance of the band centered at 539 nm and pertinent to the $[Ni^{III}(L^-)]^{2+}$ chromophore should depend upon the hydrogen ion concentration, according to the following law:

$$A = A_L \frac{K_A}{K_A + [H^+]} \qquad (2)$$

In eq 2, A indicates the molar absorbance of the $[Ni^{III}(L^-)]^{2+}$ chromophore at the investigated pH, whereas A_L represents the limiting value of the absorbance (100% of the $[Ni^{III}(L^-)]^{2+}$ complex present in solution). Nonlinear fitting of eq 2 (dependent variable, A; independent variable, $[H^+]$) gave the following values for the A_L and K_A parameters: $A_L = 1330 \pm 100$ M^{-1} cm^{-1}; $K_A = 8.5 \times 10^{-8} \pm 1.5 \times 10^{-8}$ ($pK_A = 7.1 \pm 0.1$). The dotted line in Figure 2, which has been calculated by using the above defined A_L and K_A values, fits well the data used in the minimization process.

It has to be recalled that, in the experimental conditions, the solution reaches the observation chamber 6 ms after the mixing. Thus, to carry out correct calculations, one should take into account the decay of the violet chromophore and of the intensity of the pertinent absorption band occuring during this period. Stopped-flow experiments showed that the decay of the violet transient obeys to a second order pattern (*vide infra*). Then, absorbance at $t = 0$ was calculated through the $\{1/A = 1/A_L + 2k_{obs}t\}$ linear plot. However, corrected values do not differ significantly from the experimental ones: even at the higher investigated pH, the calculated value is less than 2% higher than the measured value.

Filled symbols in Figure 3 were considered "bad points" and were not taken into account in the curve-fitting treatment for eq 2. Stopped-flow experiments indicated that the decay of the violet chromophore in more basic solutions (i.e. those corresponding to the filled symbols in Figure 3) does not follow the "regular" second-order kinetic pattern, but takes place according to a more complicated mechanism and, in particular, at a much higher rate. It is possible that, in such conditions, the decay of the violet species that occurs during the "aging" of the solution, before the spectrum is taken, is significant.

It should be noted that deprotonation of an amine group of a saturated macrocycle had already been observed in the case of the iron(III) 1:2 complex with 1,4,7-triazacyclononane (HT): $[Fe^{III}(HT)_2]^{3+}$.[9] In that case, a deep blue trivalent species formed in a distinctly alkaline solution (λ = 542 nm, ϵ = 1800 M^{-1} cm^{-1}; pK_A = 11.4). Such a species is rather stable from a kinetic point of view and persists in solution over a period of hours, allowing a full characterization of its solution properties. In particular, the ESR spectrum of the blue frozen solution was that expected for the $[Fe^{III}(T^-)(HT)]^{2+}$ species, an amidoiron(III) complex, in which one of the three equivalent amine groups of one of the two triaza rings coordinated to the iron(III) center was deprotonated. Such an evidence ruled out the formation of an iron(II) complex with a radical ligand: $[Fe^{II}(^{\cdot}T^-)(HT)]^{2+}$, aminyliron(II).

Noticeably, the energy of the rather strong absorption band responsible for the violet color of the $[Ni^{III}(L^-)]^{2+}$ complex is very close to that observed for the $[Fe^{III}(T^-)(HT)]^{2+}$ chromophore (539 and 542 nm, respectively). The extremely short lifetime of the amidonickel(III) complex prevents from a further characterization. In particular, it should be noted that in the most favorable situation (pH = 7.5) only 74% of the $[Ni^{III}(L^-)]^{2+}$ species was present in the observation cuvette, under continuous-flow conditions. At higher pH values, the rate of decomposition increases to such an extent to prevent the achievement of 100% of the violet species.

2. Determination of the pK_A Value by Differential Pulse Voltammetry Experiments. Cyclic voltammetry experiments on solutions of $[Ni^{II}(cyclam)]^{2+}$, made 0.1 M in $NaClO_4$, using a platinum microsphere as a working electrode, disclosed a reversible profile over the pH range 2-6, with an $E_{1/2}$ value of 744 mV vs SCE (separation of the anodic and cathodic peaks, ΔE_p = 60 mV; ratio of the peak currents, i_a/i_p = 1). The electrochemically reversible process corresponds to the following redox change:

$$[Ni^{II}(cyclam)]^{2+} = [Ni^{III}cyclam)]^{3+} + e^- \qquad (3)$$

Notice that in the half-reaction 3, the solvent molecules coordinated to the divalent and trivalent metal centers have been omitted for sake of clarity. In particular, in the octahedral low-spin Ni^{III} species, two water molecules should occupy the axial sites, whereas the Ni^{II} complex exists as an equilibrium mixture of the low-spin square form (yellow, 72%) and of the high-spin diaquo octahedral form (pale blue, 28%).[12] However, for solutions of pH > 6, the CV profile loses its features of reversibility and flattens ($\Delta E_p \approx 100$ mV), even at the highest investigated potential scan rates, preventing the determination of reliable $E_{1/2}$ values. Reversible or quasi-reversible signals have been obtained on carrying out differential pulse voltammetry experiments (pulse height, 25 mV; pulse width, 50 ms; scan rate, 10 mV s^{-1}), even at pH > 6. Thus, determination of reliable $E_{1/2}$ values was possible in an extended pH region (up to pH 8). In particular, it was observed that the $E_{1/2}$ value associated with the Ni^{III}/Ni^{II} redox change remains constant over the pH 2-6 range (744 mV) and

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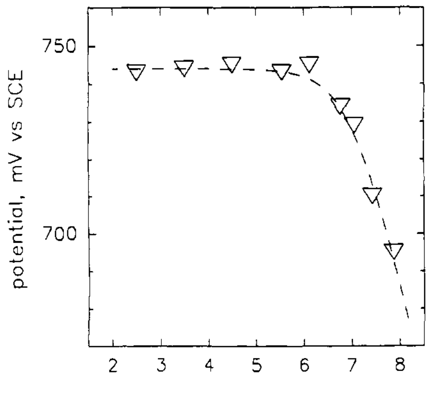
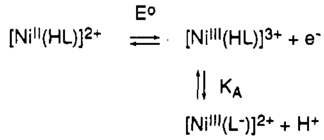


Figure 4. pH dependance of the $E_{1/2}(\mathrm{Ni^{III}/Ni^{II}})$ value measured by differential pulse voltammetry, using a platinum working electrode. Nonlinear fitting on eq 4 (dotted line in the figure) gave a pK_A of 7.1 ± 0.2 for the deprotonation of the trivalent complex.

Scheme 1



becomes distinctly and progressively less positive at higher pH values. Corresponding data are displayed in Figure 4. The pH dependence of the $E_{1/2}(\mathrm{Ni^{III}/Ni^{II}})$ value can be accounted for on the basis of Scheme 1.

According this scheme, the measured potential E (mV) should be expressed by the equation:

$$E\,(\mathrm{mV}) = E^\circ + 59.16 \log \frac{K_A}{K_A + [H^+]} \tag{4}$$

Equation 4 has been rearranged

$$E\,(\mathrm{mV}) = 744 + a \log \frac{b}{b + [H^+]} \tag{5}$$

and minimized through a nonlinear fitting procedure on the E and $[H^+]$ variables. On minimization, the following values were obtained for the a and b parameters: $a = -58 \pm 8$ mV, which is in agreement with the reversible release of one hydrogen ion by the oxidized form of the redox couple (i.e. $[\mathrm{Ni^{III}cyclam}]^{3+}$); $b = 8.7 \times 10^{-8} \pm 3.0 \times 10^{-8}$, i.e. p$K_A$ = 7.1 ± 0.2, which is in excellent agreement with the pK_A value obtained by spectrophotometric techniques under continuous-flow conditions (pK_A = 7.1 ± 0.1, *vide supra*). The dotted line in Figure 4, which has been calculated from eq 5, using the a and b values obtained through the nonlinear minimization procedure, fits quite well the experimental points.

3. Kinetics of the Decomposition of the Amidonickel(III) Complex. When, in the experiments with the rapid data acquisition spectrophotometer, the solution flow through the observation cuvette is stopped, the band at 539 nm decays quickly, to disappear in a couple of seconds (see Figures 1 and 2). Quite interestingly, the decay of the concentration of the $[\mathrm{Ni^{III}(L^-)}]^{2+}$ species (calculated from the absorbance), in experiments with solutions 0.1 M in $\mathrm{NaClO_4}$, does not follow a first-order kinetics. On the contrary, the reciprocal of the concentration of the violet chromophore increases linearly with the time, indicating a reaction kinetically of second order. The slope of the least-squares straight line gave the $2k_{obs}$ value at any investigated pH.[13] In particular, $2k_{obs}$ values were found to increase with the pH, as shown in Figure 5.

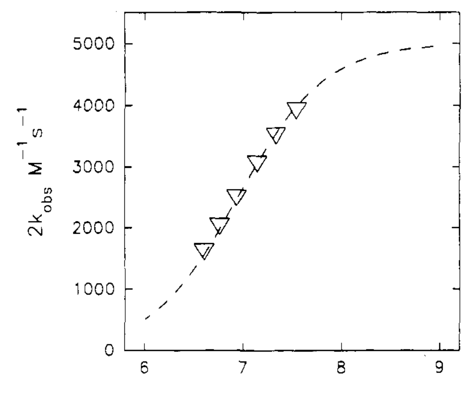


Figure 5. pH dependance of $2k_{obs}$ for the second order decay of the violet transient. Non-linear fitting on eq 7 (dotted line in the figure) gave the following values: $k = 5000 \pm 200$ $\mathrm{M^{-1}\,s^{-1}}$; pK_A = 6.9 ± 0.1.

It should be noticed that a rate law with a second-order dependence on the concentration of the violet species was observed until pH = 7.5. At higher pH values, the decay followed neither first- nor second-order kinetics and, in any case, the decrease of the band intensity was considerably faster, indicating a different, more complicated mechanism. Thus, in the investigated pH range, decomposition of the violet transient takes place through the reaction of two $[\mathrm{Ni^{III}(L^-)}]^{2+}$ ions:

$$[\mathrm{Ni^{III}(L^-)}]^{2+} + [\mathrm{Ni^{III}(L^-)}]^{2+} \xrightarrow{k} \text{products} \tag{6}$$

It should be noted that when the investigated reactant is involved in an acid-base equilibrium, $2k_{obs}$ and $2k$ are related through the following equation:[14]

$$2k_{obs} = 2k \frac{K_A}{K_A + [H^+]} \tag{7}$$

Nonlinear fitting on the variables $2k_{obs}$ and $[H^+]$ gave the following values for $2k$ and K_A parameters: $2k = (5.0 \pm 0.2) \times 10^3$ $\mathrm{M^{-1}\,s^{-1}}$; pK_A = 6.9 ± 0.1. Again, the pK_A value determined by a third independent method satisfactorily agrees with the values determined spectrophotometrically and electrochemically. The dotted line in Figure 4 has been calculated through eq 7, by using the $2k$ and K_A values obtained from the minimization procedure.

At this stage of the investigation, the nature of the products of reaction 6 can only be matter of hypothesis. It should be noted that a second-order kinetics was observed also by Wieghardt for the slow decomposition of the blue $[\mathrm{Fe^{III}(T^-)(HT)}]^{2+}$ complex.[9] He proposed that one $[\mathrm{Fe^{III}(T^-)(HT)}]^{2+}$ ion releases an electron from one of the deprotonated rings, to give the unstable $[\mathrm{Fe^{III}(T^\cdot)(HT)}]^{2+}$ complex. Then, a hydrogen ion is released and a C=N double bond forms on the macrocycle. On the other hand, the second $[\mathrm{Fe^{III}(T^-)(HT)}]^{2+}$ ion takes the electron on the metal center, to give the $[\mathrm{Fe^{II}(T^-)(HT)}]^{2+}$ complex; then, uptake of a proton should restore the stable $[\mathrm{Fe^{II}(HT)_2}]^{2+}$ complex. When a similar mechanistic approach is applied to the nickel–cyclam system, the Scheme 2 is obtained. According to Scheme 2, the final solution should contain 50% of the $[\mathrm{Ni^{II}(cyclam)}]^{2+}$ complex and 50% of its monoimine derivative **3a** or **3b**. The formation of a $\mathrm{Ni^{II}}$ unsaturated macrocyclic species has been hypothesized also by Barefield for the *ms*-CTH system. Moreover, oxidative ligand dehydrogenation promoted by metal centers (e.g. $\mathrm{Fe^{II}}$,[15] $\mathrm{Ni^{III}}$,[16] $\mathrm{Ag^{III}}$[17]) is a common behavior for tetraazamacrocyclic complexes.

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[13] The second order rate constant for a reaction of the type 2A → products is designated by convention $2k$ (ref 14, p 10). In particular, the slope of the $1/[A]$ vs t straight line is $2k_{obs}$.

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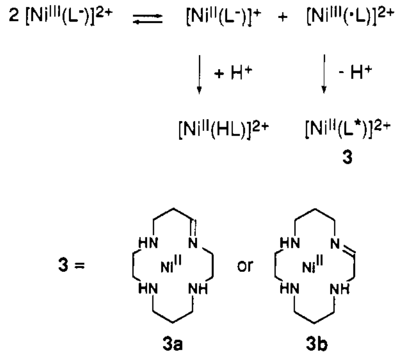
[17] Mocella, M. T.; Barefield, E. K. *Inorg. Chem.* **1973**, *12*, 2829.

Scheme 2



In the spectrum of the final solution a band centered at 460 nm ($\epsilon = 60$ M^{-1} cm^{-1}) is present, which is typical of the [Ni^{II}(cyclam)]$^{2+}$ complex and of any square low-spin Ni^{II} chromophore. In particular, [Ni^{II}(cyclam)]$^{2+}$ and **3** are expected to display quite similar d–d spectra. Moreover, a new band at 200 nm is present ($\epsilon = 2 \times 10^4$ M^{-1} cm^{-1}), which can be assigned to an MLCT transition of a Ni^{II} complex with a coordinated imino group complex (**3a** or **3b**).

Discussion

The present investigation has clearly defined and characterized the acid–base features of the violet transient that forms when the [Ni^{III}(cyclam)]$^{3+}$ complex, very stable in acidic media, is put into a neutral solution. In particular, the same pK_A value has been obtained through three independent methods (spectrophotometric, electrochemical, kinetic). Our hypothesis on the nature of the violet transient (it should be the amidonickel(III) species [Ni^{III}(L$^-$)]$^{2+}$, rather than the aminyl species [Ni^{II}(·L)]$^{2+}$) does not rest on any direct experimental evidence, but it is rather based on the analogy with the Fe^{III}–1,3,7-triazacyclononane system, for which the much higher kinetic stability allowed a sound and unambiguous characterization of the deprotonated complex (which was an authentic Fe^{III} species).[9] Noticeably, the two complexes [Ni^{III}(L$^-$)]$^{2+}$ and [Fe^{III}(T$^-$)(HT)]$^{2+}$ present a rather strong absorption band of almost the same energy (539 and 542 nm, respectively). Barefield, in his pioneering work of 1975,[5] proposed, on the basis of continuous-flow experiments in the cavity of an ESR spectrometer, that the violet transient formed from the reaction with bases of Ni^{III} complexes of cyclam-like macrocycles was a Ni^{II} ligand radical complex. It is possible that the red-violet intermediate underwent degradation to produce a radical species before the ESR spectrum under continuous-flow conditions was taken. It should also be noted that Barefield carried out most of the investigations on the *ms*-CTH complex, and not on the cyclam analogue, whose violet transient species was decaying too fast. On our hand, we could not perform continuous-flow and stopped-flow spectrophotometric investigations on the the [Ni^{III}(*ms*-CTH)]$^{2+}$ complex, as it is not stable enough in moderately acidic solutions and, in particular, cannot be prepared through controlled-potential electrolysis in 0.01 M HClO$_4$ and in 0.1 M NaClO$_4$, due to decomposition.

In any case, the very first step of the deprotonation of the [Ni^{III}(cyclam)]$^{3+}$ complex must involve one of the four equivalent amine groups: the acidic dissociation constant measured in this work exactly refers to this event. Then, in a period well below the time scale of the stopped-flow experiment, an electron may be more or less definitively transferred to a d orbital of the metal center (a complete transfer would generate the aminylnickel(II) species).

A completely different hypothesis had been put forward by Meyerstein on the nature of the transient ($\lambda = 540$ nm, $\epsilon = 1700$ M^{-1} cm^{-1}) that formed through deprotonation of the [Ni^{III}(CT)]$^{2+}$ complex produced by oxidation of the divalent complex by radiolytically generated Br$_2^-$ and OH radicals.[7] In particular, it was suggested that the hydrogen ion is released by one of the water molecules axially bound to the Ni^{III} center, according to the following equilibrium (HL = CT):

$$[\mathrm{Ni^{III}(HL)(H_2O)_2}]^{3+} = [\mathrm{Ni^{III}(HL)(H_2O)(OH)}]^{2+} + \mathrm{H^+} \tag{8}$$

We observe that the release of a proton from an apically bound water molecule in the elongated octahedron cannot substantially alter the N$_4$O$_2$ donor set. Deprotonation of an apically coordinated water molecule may only produce a moderate shift of the ligand field bands of a transition metal complex. In the present case, a very strong absorption band ($\epsilon > 10^3$ M^{-1} cm^{-1}) develops, which indicates a large alteration of the donor set. Noticeably, very similar spectral features ($\lambda = 542$ nm, $\epsilon = 1\,800$ M^{-1} cm^{-1}) have been observed for the Fe^{III}–1,3,7-triazacyclononane system, whose amidonickel(III) nature has been unequivocally defined through the ESR experiment.[9] Moreover, it should be noted that Meyerstein's assignment could be ruled out also on the basis of Barefield's observation that the violet deprotonated complex of macrocycle **2** formed also *in the absence of water*, e.g. in anhydrous pyridine and triethylamine.[5]

Finally, the acid dissociation processes involving [Ni^{III}(cyclam)]$^{3+}$ and [Fe^{III}([9]aneN$_3$)$_2$]$^{3+}$ should be compared. It may seem rather paradoxical that the deprotonated species that forms more easily (the Ni^{III} complex, at pH = 7) lasts in solution less than 2 s, whereas the species whose deprotonation requires distinctly basic conditions (the Fe^{III} complex, pH > 11) persists for more than 2 h. In this connection, it should be noted that the free energy change associated to the acidic dissociation process results from the balance of the following terms: (i) the endothermic contribution due to the deprotonation of the NH group; (ii) the exothermic effect associated to the strengthening of the M^{III}–N bond, when an amine group is replaced by an amido group. As term i should not vary for triaza and tetraaza rings, the difference $\Delta\Delta G° = -RT\{\mathrm{p}K_A(\mathrm{Fe^{III}}) - \mathrm{p}K_A(\mathrm{Ni^{III}})\} = 6$ kcal mol^{-1} should give a rough measure of term ii; i.e., it should express the relative advantage experienced on deprotonation by the Ni^{III} tetraazamacrocyclic complex compared to the Fe^{III} triazamacrocyclic complex. Such an effect can be accounted for by considering that the in-plane interactions in the cyclam complexes are stronger than those exerted by the six-coordinating bis(triaza) system. In particular, the steric constraints in the tetraaza ring may generate especially strong metal–ligand coplanar interaction. Such constraints are not present in complexes with out-of-plane coordinating ligands like [9]aneN$_3$. It is interesting to note that in the case of the diene macrocycle CT, whose smaller hole and increased rigidity induce stronger metal–ligand in-plane interactions, more pronounced acidic tendencies have been observed (pK_A = 3.4).[7]

The above evidence indicates that the acidity of a metal-bound amine group is strongly dependent upon the coordinative environment and the structural features of the ligand. Thus, it happens that in presence of steric constrictive effects deprotonation of the amine group of cyclam or CT *precedes* that of the loosely bound apical water. As discussed above, the free energy change associated with the deprotonation of the [Ni^{III}(cyclam)(H$_2$O)$_2$]$^{3+}$ complex results from the balance of the very endothermic deprotonation of the secondary amine group and the strongly exothermic contribution associated with the formation of the metal–amide bond. Such an interaction is especially exothermic as (i) it takes place in the equatorial plane and (ii) the rigid macrocyclic framework forces the donor atom into a particularly close and favorable position. Deprotonation of a water molecule is less endothermic than that of a secondary amine group. However, the term associated with the formation of an M^{III}–OH bond should be much less endothermic as (i) the apical position is less favorable for establishing strong coordinative interactions and (ii) the hydroxide ligand atom does not profit from any constrictive effect. In conclusion, the formation of the violet transient is a further evidence of the *macrocyclic effect*, i.e. it is something related to the very favorable preorientation of the donor atoms in a cyclic 14-membered tetraaza ligand. It is not fortuitous that the violet transient forms only with Ni^{III} complexes of cyclam and strictly related macrocycles and does not form with tetraaza macrocycles of different atomicity or with open-chain tetramines.

As far as the kinetic behavior is concerned, the electron transfer process from an amidometal(III) species to another one (which is a *disproportionation* reaction) is much faster for the nickel complex than for the iron complex: $2k$ values are 5000 and 6.7 $M^{-1}\ s^{-1}$, respectively. In the case of the coordinatively saturated Fe^{III} system the electron transfer process takes place surely through an *outer-sphere* mechanism. On the other hand, the nickel macrocyclic complex has two labile coordination sites (the apical ones), available for the coordination of a bridging anion (a ClO_4^-, in the present case), and is therefore open to an *inner-sphere* mechanism, which could make the electron transfer much faster. Moreover, in the case that both iron and nickel systems undergo an outer-sphere electron transfer, the rate constant of the disproportionation process should depend upon the associated $\Delta E°$ value, according to the Marcus equation:[18] the higher the $\Delta E°$, the faster the electron transfer process. In particular, the envisaged disproportionation process can be considered as the sum of the two half-reactions (9) and (10). Thus, $\Delta E° = E_1 - E_2$.

$$+\ [M^{III}(L^-)]^{2+} + e^- = [M^{II}(L^-)]^+ \quad E_1 \qquad (9)$$

$$-\ [M^{III}(^{\bullet}L)]^{3+} + e^- = [M^{III}(L^-)]^{2+} \quad E_2 \qquad (10)$$

The E_2 value refers to a process which is totally localized on the ligand and should not be too different for the two considered polyazamacrocyclic complexes. On the other hand, E_1 refers to a metal-centered redox change and is obviously very sensitive to the nature of the metal. In particular, E_1 is expected to be considerably more positive for nickel than for iron. This occurs in the gas phase, prior to coordination of any ligand (third ionization potential, $I_3(Ni) = 35.17$ V, $I_3(Fe)$ 30.65 V) and, more significantly, for aqueous metal complexes of the (undeprotonated) macrocycles: $E°\{[Ni^{III,II}(cyclam)]^{3+/2+}\} = 0.97$ V vs NHE, $E°\{[Fe^{III,II}([9]aneN_3)_2]^{3+/2+}\} = 0.10$ V vs NHE. It is reasonable to assume that such a trend is maintained for redox couples involving trivalent complexes of deprotonated macrocycles. Thus, it is the high oxidizing power of Ni^{III} complexes that contributes substantially to the fast decomposition of the violet transient species.

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(18) Haim, A. *Progr. Inorg. Chem.* **1983**, *30*, 273.