Oxidation of a Nickel(II) Complex with an Unsaturated Macrocyclic Ligand in Aqueous Solutions. A Pulse Radiolytic Study

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The kinetics of oxidation of Ni^{II}L by Br$_2^-$ and OH radicals in aqueous solutions were studied. The kinetics of the aquation reaction Ni^{III}LBr^{2+} → Ni^{III}L + Br$^-$ was found to be base catalyzed. The pK of the reaction Ni^{III}L^{3+} ⇌ Ni^{III}L(OH)$^{2+}$ was determined, pK = 3.45, and the redox potential of the couple Ni^{III}L^{3+}/Ni^{II}L^{2+} is 1.34 V. The mechanism of decomposition of Ni^{III}L is discussed. The spectra of the different intermediates are reported.

Introduction

An increased interest in the chemistry of transition-metal complexes with uncommon oxidation states has developed in recent years.[1] Complexes with unstable oxidation states were suggested as intermediates in catalytic, electrocatalytic, and biological redox processes. A special group of such complexes are those with macrocyclic ligands which were shown to stabilize uncommon oxidation states mainly in aprotic media.[2]

Trivalent nickel complexes are an example of complexes with uncommon oxidation states. A series of stable Ni(III) complexes with macrocyclic ligands in aprotic solvents was reported.[2-5] Furthermore, Ni(III) complexes were suggested as unstable intermediates in catalytic[6,7] and electrocatalytic[8] oxidation processes in aqueous media. Recently, stable Ni(III) complexes, in aqueous media, with EDTA[9,10] or tetrapeptides[11] as ligands were reported.

We have decided to study the oxidation of Ni^{II}L (where L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) by Br$_2^-$ with the hope of obtaining the following information.

(a) We believed that the oxidation process will follow the inner-sphere mechanism of eq 1. Thus ligand-exchange

$$\text{Ni}^{II}\text{L}^{2+} + \text{Br}_2 \xrightarrow{k_1} \text{Ni}^{III}\text{Br}^{2+} + \text{Br}^- \qquad (1)$$

reaction 2 could be studied. This would be the first ligand-

$$\text{Ni}^{III}\text{LBr}^{2+} \rightarrow \text{Ni}^{III}\text{L}^{3+} + \text{Br}^- \qquad (2)$$
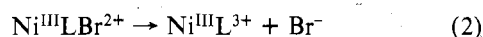
exchange reaction studied for a Ni(III) complex with a low-spin d^7 electron configuration.

(b) We hoped to obtain information concerning the chemical properties of Ni^{III}L, e.g., the mechanism of decomposition, the redox potential, the acid dissociation constants of coordinated water, and the absorption spectra of Ni^{III}LBr^{2+}, Ni^{III}L-(H$_2$O)$_2$$^{3+}$, and Ni^{III}L(OH)(H$_2$O)$^{2+}$.

Experimental Section

Materials. The ligand as its perchloric salt LH$_2$(ClO$_4$)$_2$ was prepared by adding slowly 27 g of HClO$_4$ to a cold solution of 400 mL of acetone and 17.6 g of ethylenediamine. The ligand was obtained as a white precipitate which was washed with cold acetone and dried. The complex NiL(ClO$_4$)$_2$ was prepared by refluxing nickel acetate with the ligand in a 1:1 mixture of ethanol and water. The yellow precipitate was recrystallized from water. Anal. Calcd: C, 35.70; H, 6.30; N, 10.55. Found: C, 35.69; H, 5.95; N, 10.41. All other materials were of AR grade and were used without further treatment. All water used was triply distilled.

Procedure. Most of the optical studies were carried out at the electron linear accelerator at the Hebrew University of Jerusalem. Pulses of 5-MeV electrons, 200 mA, 0.1–1.5 μs were used. The dose per pulse was 100–3000 rd, 1 rd = 6.24 × 10^{13} eV g^{-1}. The procedures for preparation of samples, irradiation, observation of the optical changes, and evaluation of the results were described earlier in detail.[12]

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Table I. Rates of Reactions Following the Formation of Ni^{III}LBr^{2+} in Acidic Solutions[a]

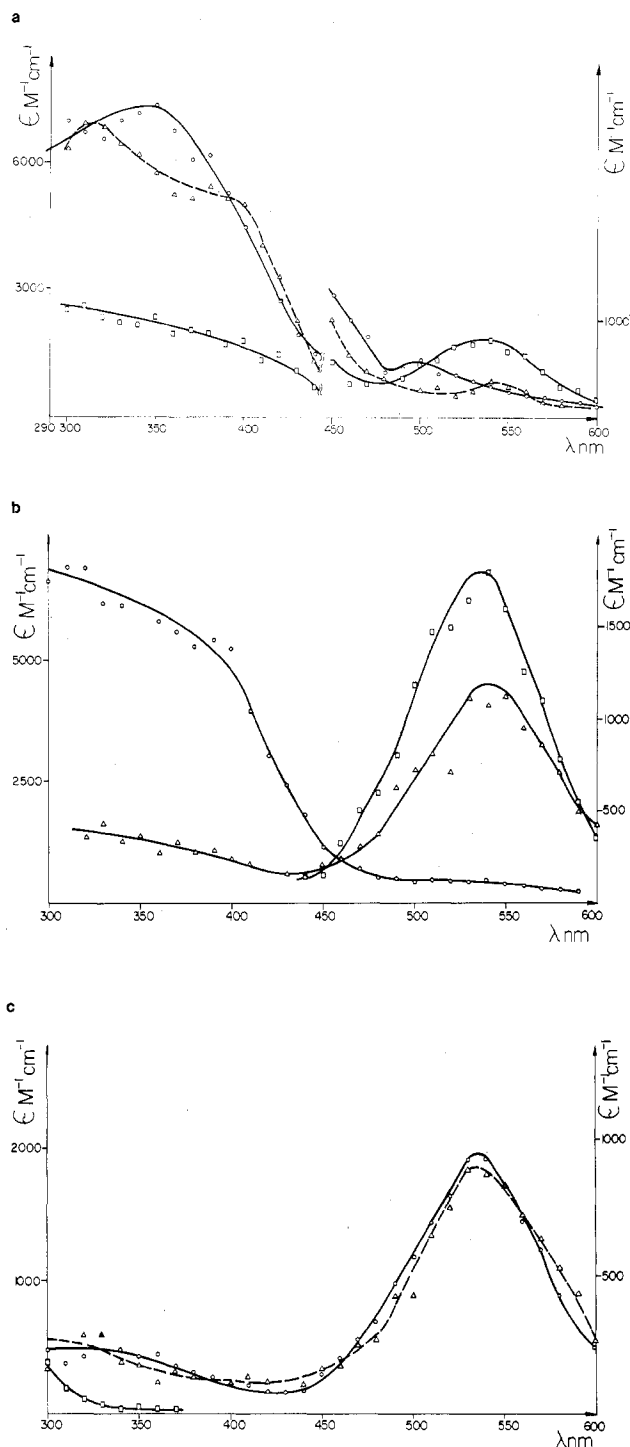| pH	$10^5 \times$ [Ni^{II}L^{2+}], M	$10^2 \times$ [Br$^-$], M	$10^{-4} \times k_{10}$,[b] s^{-1}	k_9,[c] s^{-1}	$10^{-4}k$,[d] M^{-1} s^{-1}
3.0	2.0	1.0	2.8	133	53
	4.0	1.0	3.2	119	35
	7.0	1.0	3.4	115	31
	10.0	1.0	3.5	118	25
	4.0	2.0		148	53
	4.0	4.0		158	116
	4.0	7.0		153	260
	4.0	10.0	4.4	e	360
3.5	4.0	1.0	3.2	83	15
	4.0				0.1
3.9	4.0	1.0		63	7.2
4.4	4.0	1.0	3.6	67	3.5

[a] All solutions were N$_2$O saturated. [b] First reaction observed; for identification as k_{10}, see Discussion. [c] Second reaction observed; for identification as k_9, see Discussion. [d] Third reaction observed corresponding to reactions 14 and 15; see Discussion. [e] Could not be measured due to increase in rate of last reaction.

The conductivity studies and some of the optical measurements were carried out at the Van de Graaff generator at the Hahn-Meitner-Institute in Berlin. Pulses of 1.6-MeV electrons, 25 mA, 0.5–5 μs were used. The dose per pulse was 150–1500 rd. The procedure and the equipment used were described earlier in detail.[13]

Results

When N$_2$O-saturated solutions containing (1–10) × 10^{-2} M NaBr and (1–10) × 10^{-5} M Ni^{II}L(ClO$_4$)$_2$ in the pH range 3.0–10.5 are irradiated, the formation of unstable intermediates, with absorption bands in the visible and near-UV, is observed. The absorption spectra of these intermediates at different times after the pulse at pH 3.0, 4.9, and 9.5 are plotted in Figure 1.

In solutions with pH <4.5, four consecutive reactions are observed. The first reaction obeys a first-order rate law, the rate observed being proportional to [Ni^{II}L]. The specific rate of this reaction is (9 ± 1.5) × 10^9 M^{-1} s^{-1} and is pH independent in the range 3.0 ≤ pH ≤ 10.0. In acidic solutions, 3.0 ≤ pH ≤ 4.0, this reaction causes a decrease in conductivity of 400 cm^2 Ω^{-1} mol^{-1}. The effect of pH and the concentrations of Br$^-$ and Ni^{II}L^{2+} on the rates of the following three reactions, the first two of which obey a first-order rate law and the third a second-order rate law, are summed up in Table I. The second reaction causes an increase in the conductivity of ΔΛ ≈ 80 cm^2 Ω^{-1} mol^{-1} in the pH range 3–4. The third reaction is also accompanied by an increase in conductivity which is pH dependent; at pH >4.0 the conductivity increase at this step is about 320 cm^2 Ω^{-1} mol^{-1}, i.e., the total conductivity change from the pulse to this stage is zero, at pH 3.8 conductivity increase in this step is about 175 cm^2 Ω^{-1} mol^{-1}, and at pH 3.0 the conductivity increase in this step is small.

Figure 1. Absorption spectra of the intermediates obtained in N_2O-saturated solutions containing 4×10^{-5} M $Ni^{II}L$ and 0.01 M NaBr (the dose per pulse intensity was $\sim 6 \times 10^{19}$ eV L^{-1}). (a) pH 3.0: (O) 6 μs after the pulse, ($\triangle$) 200 μs after the pulse, ($\square$) 50 ms after the pulse (the left scale is for the 300–450-nm region and right scale is for the 450–600-nm region). (b) pH 4.9: (O) 50 μs after the pulse, left scale, ($\square$) 100 ms after the pulse, right scale, ($\triangle$) 50 μs after the pulse on a solution containing no bromide, right scale. (c) pH 9.5: (O) 15 μs after the pulse, left scale, ($\square$) 0.85 s after the pulse, left scale, ($\triangle$) 50 μsec after the pulse on a solution containing no bromide, right scale.

In neutral solutions, $5.0 < pH < 7.5$, the first reaction observed is followed by two consecutive reactions only. The rates of these reactions were found to obey first-order rate laws and were independent of the concentration of $Ni^{II}L$ or Br^-. The observed rates are summed up in Table II. The de-

Table II. Rates of Reactions Following the Formation of $Ni^{III}LBr$ in Neutral Solutions[a]

pH	$10^2 \times$ [Br$^-$], M	$10^3 \times$ [KH$_2$PO$_4$], M	k_9,[b] s^{-1}	k,[c] s^{-1}
4.8	1.0		80	0.068
4.9				0.01[d]
4.9	1.0		140	0.052
5.2	1.0	1.0	4.7×10^3	
5.3	1.0		6.1×10^4	
5.4	1.0		6.6×10^4	0.062
5.5	1.0		380[e]	
5.5	2.0			0.040
5.5	4.0			0.038
5.5	10.0			0.037
6.15	1.0	1.0	1.5×10^4	
6.2	1.0		6.4×10^4	0.17
6.6	1.0	1.0	2.1×10^4	
7.2	1.0	1.0	7.0×10^4	

[a] All solutions were N_2O saturated. $Ni^{II}L$ concentrations in the range $(2–10) \times 10^{-5}$ M had no effect; most experiments were carried out at 4×10^{-5} M. The dose per pulse was $\sim 6 \times 10^{19}$ eV L^{-1}. [b] First reaction observed after formation of intermediate; for identification as k_9, see Discussion. [c] Rate of decomposition of $Ni^{III}LOH^{2+}$; see Discussion. [d] Better described as second-order reaction; see Results. [e] The dose per pulse was $\sim 6 \times 10^{18}$ eV L^{-1}.

Table III. Rate of Decomposition of $Ni^{III}L$ in Alkaline Solutions[a]

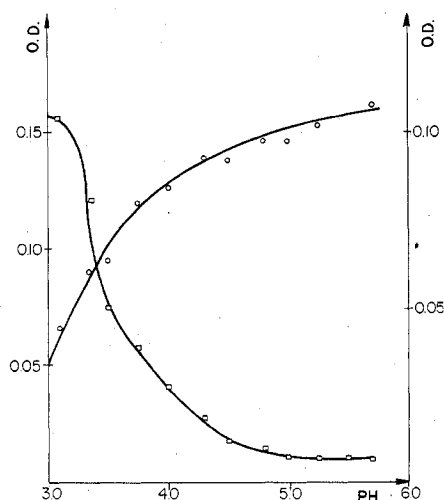| pH	$10^5 \times$ [Ni^{II}L], M	$10^2 \times$ [Br$^-$], M	k, s^{-1}
8.2	4.0	1.0	0.76
8.4	4.0	1.0	0.90
8.6	4.0	10.0	1.16
9.2	4.0	1.0	4.0
9.5	1.0	1.0	7.8
9.5	2.0	1.0	7.7
9.5	4.0	1.0	7.8
9.5	4.0	2.0	8.0
9.5	4.0	7.0	4.6
9.5	4.0	10.0	3.8
9.6	2.0		10
9.6	7.0		11
10.0	4.0	1.0	19
10.5	4.0	1.0	52

[a] N_2O-saturated solutions.

termination of the rate of the last reaction in this pH range is rather inaccurate as it is somewhat too slow to be measured using the experimental setup.

In alkaline solutions, pH >8.0, only one reaction following the formation of the intermediate was observed. This reaction obeyed a first-order rate law independent of the concentration of $Ni^{II}L$ or Br^-. The dependence of the rate of this reaction on pH is summed up in Table III. The reactions at pH 8.2 are not accompanied by any change in conductivity.

The pH effect on the optical density due to the last intermediate, ~ 90 ms after the pulse, was measured. The results are summed up in Figure 2.

N_2O-saturated solutions containing $(1–10) \times 10^{-5}$ M $Ni^{II}L(ClO_4)_2$ and no bromide, in the pH range $3.5 \leq pH \leq 9.6$, were irradiated. In the whole pH range only two reactions, the formation of an intermediate and its decomposition, were observed. The formation of the intermediate obeyed a first-order rate law, the rate observed being proportional to $[Ni^{II}L]$ with $k = 2.5 \times 10^9$ M^{-1} s^{-1} at pH 5.7. The decomposition reaction in the absence of bromide was pH dependent; at pH 3.5 the reaction seemed to obey a second-order rate law with $2k/\epsilon l = 2.3 \times 10^{-1}$ s^{-1}, though a first-order rate of $k \approx 2 \times 10^{-2}$ s^{-1} could also describe the results. Again, due
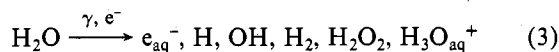
Figure 2. Optical densities of transient as function of pH after identical pulses: (□) 320 nm, left scale; (○) 540 nm, right scale. N$_2$O-saturated solutions were used containing 0.01 M NaBr + 5 × 10^{-5} M Ni^{II}L, and optical densities were measured 90 ms after the pulse.

to the slow rate of this reaction, only the first 2 half-lives of it could be followed. At pH 4.9 the reaction seemed also to obey a second-order rate law with $2k/\epsilon l \approx 2 \times 10^{-1}$ s^{-1}, though a first-order rate of $\sim 1 \times 10^{-2}$ s^{-1} would also describe the results. The preference of the second-order rate law is due to the effect of dose on the rate. (The measurements were carried out at 550 nm.) At pH 9.6 this reaction obeyed a first-order rate law with $k = 10 \pm 1$ s^{-1}.
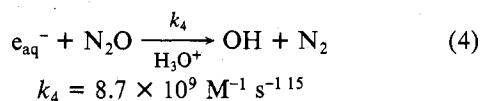
The spectra of the intermediate formed in N$_2$O-saturated solutions containing Ni^{II}L and no bromide at pH 4.9 and 9.5 are plotted in Figure 1.
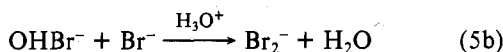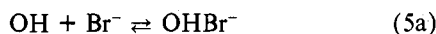
Discussion

The radiolysis of water can be summed up by eq 3, where

$$H_2O \xrightarrow{\gamma, e^-} e_{aq}^-, H, OH, H_2, H_2O_2, H_3O_{aq}^+ \qquad (3)$$

$G_{e_{aq}^-} = 2.65$, $G_{OH} = 2.65$, $G_H = 0.60$, $G_{H_2} = 0.45$, and $G_{H_2O_2} = 0.75$. (G is defined as the number of product molecules formed by the absorption of 100 eV by the solution.[14]) In N$_2$O-saturated solutions, [N$_2$O] $\approx 2 \times 10^{-2}$ M and reaction

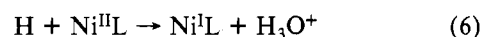$$e_{aq}^- + N_2O \xrightarrow[H_3O^+]{k_4} OH + N_2 \qquad (4)$$

$$k_4 = 8.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \text{ }^{15}$$

4 occurs. As $k_{e_{aq}^- + Ni^{II}L} = 7.8 \times 10^{10}$ M^{-1} s^{-1} ^{16} and [Ni^{II}L] $\leq$ 1 × 10^{-4} M, all hydrated electrons are transformed into OH radicals under the experimental conditions.[17] In solutions containing bromide, reaction 5 occurs.[18] As $k_{OH + Ni^{II}L} = 2.5$

$$OH + Br^- \rightleftarrows OHBr^- \qquad (5a)$$
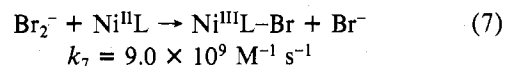
$$OHBr^- + Br^- \xrightarrow{H_3O^+} Br_2^- + H_2O \qquad (5b)$$

$$k_5 > 10^9 \text{ M}^{-1} \text{ s}^{-1} \text{ at pH} \leq 9.5$$

× 10^9 M^{-1} s^{-1} (see above) and [Br$^-$]/[Ni^{II}L] > 100, it is clear that all hydroxyl radicals are transformed under the experimental conditions into Br$_2^-$ radical anions. Thus, the only radicals which might participate in the reactions studied under the experimental conditions are Br$_2^-$ and H atoms with a relative yield of 9:1.

The rate of formation of the first transient in this study, 9 × 10^9 M^{-1} s^{-1}, is considerably higher than $k_6 = 9 \times 10^8$ M^{-1} s^{-1}.[16] Furthermore, the absorption spectra observed for this intermediate, at the different pH's (Figure 1), differ considerably from that of Ni^{I}L formed in reaction 6.[16] The latter

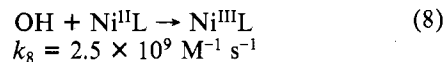$$H + Ni^{II}L \rightarrow Ni^I L + H_3O^+ \qquad (6)$$

reaction is also expected to cause an increase, and not a decrease, in conductivity. We conclude that the first reaction observed in our study at pH $\leq$7.5 is eq 7. The conductivity
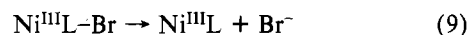
$$Br_2^- + Ni^{II}L \rightarrow Ni^{III}L-Br + Br^- \qquad (7)$$

$$k_7 = 9.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

change as a result of reaction 5 followed by reaction 7 is $\Delta\Lambda = -\Lambda^0_{H_3O^+} - \Lambda^0_{Br^-} - \Lambda^0_{Ni^{II}L} + \Lambda^0_{Ni^{III}LBr} \approx 400$ cm^2 Ω^{-1} mol^{-1}, in agreement with observation.

The identification of the first product as Ni^{III}L–Br is supported by the following argument. The spectrum and kinetic properties of the product formed in reaction 8 (in

$$OH + Ni^{II}L \rightarrow Ni^{III}L \qquad (8)$$

$$k_8 = 2.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

solutions containing no bromide) are nearly identical with those of the last intermediate formed in the solutions containing bromide (Figure 1 and Table II). It is thus suggested that the second reaction observed in neutral solutions, $5 \leq$ pH $\leq$ 7.5, is (9).

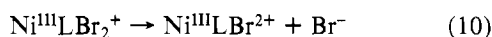$$Ni^{III}L-Br \rightarrow Ni^{III}L + Br^- \qquad (9)$$

The observation that the molar absorption coefficients observed for the product of reaction 9 are somewhat larger than those of the product of reaction 8 might be due to some competition of the reaction OH + OH $\rightarrow$ H$_2$O$_2$, $k = 1.1 \times 10^{10}$ M^{-1} s^{-1}, and more probably to a side reaction in which OH radicals add to the double bond of the ligand. It was suggested[19] that OH radicals react with Co^{II}L by addition to the double bond on the ligand with $k = 3.2 \times 10^9$ M^{-1} s^{-1}. It seems that in this respect the M^{II}L complexes resemble the M^{II}NTA complexes, NTA $\equiv$ nitrilotriacetic acid, where the reactions Ni^{II}NTA + OH $\rightarrow$ Ni^{III}NTA and Co^{II}NTA + OH $\rightarrow$ Co^{II}N(ĊHCO$_2^-$)(CH$_2$CO$_2^-$)$_2$ were shown to occur.[20] The plausible reasons for this unexpected observation (as Co^{III}L and Co^{III}NTA are stable and Ni^{III}L and Ni^{III}NTA are unstable) were discussed earlier in detail.[20]

The results, Table II, indicate that reaction 9 is pH dependent. The results seem to indicate a major increase in k_9 when the pH changes from 4.9 to 5.3. This observation is explained by the pH change caused by the pulse due to reactions 5 and 7. These reactions consume ca. 6 × 10^{-6} M H$_3$O$^+$ and thus cause a large increase in pH to solutions with $5 <$ pH < 9. Thus it is found, Table II, that k_9 depends on the pulse intensity. We therefore checked the effect of the addition of a buffer on k_9. The results, Table II, clearly indicate that reaction 9 is base catalyzed. It is thus suggested that the third reaction in acid solutions, Table I, with $k \approx 120$ s^{-1} corresponds also to reaction 9. At pH 8.2, $k_9 \approx 2.5 \times 10^5$ s^{-1} and above this pH, reaction 7 becomes rate determining and thus at pH 9.5 the formation of Ni^{III}L as the product of reaction 7 is observed (Figure 1).
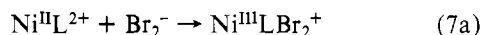
The observation that k_9 is base catalyzed is in agreement with the known mechanism for ligand exchange of trivalent metal complexes, e.g., Co(III). It is of interest to note that the observed rate of k_9 is several orders of magnitude slower than that observed for similar complexes of Co^{II}L–X, though both have a low-spin d^7 configuration.[21] This result demonstrates the charge effect on the ligand substitution rate in complexes of this type.

The second reaction observed in acid solutions obeyed a first order rate law, with $k = (3.5 \pm 0.5) \times 10^4$ s^{-1}. The rate is independent of pulse intensity and nearly independent of pH and Ni^{II}L and Br$^-$ concentrations (Table I). The reaction causes changes in the shape of the absorption bands mainly at 500 and 300–350 nm (Figure 1); however, it has nearly no effect on the molar absorption coefficients. The specific

conductivity change due to this reaction is $+80$ cm^2 Ω^{-1} mol^{-1}. The changes in the absorption spectra, Figure 1a, clearly indicate that this reaction is not due to a decrease in $[Ni^{III}LBr^{2+}]$ as it is accompanied by an increase in absorption at some wavelengths. The observations are best explained by attributing this process to reaction 10 which is expected to

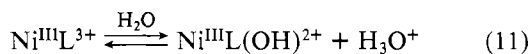$$Ni^{III}LBr_2^+ \rightarrow Ni^{III}LBr^{2+} + Br^- \qquad (10)$$

cause an increase in the conductivity similar to that observed. If this suggestion is correct, then reaction 7 has to be rewritten as 7a. However, as in no other system involving oxidation
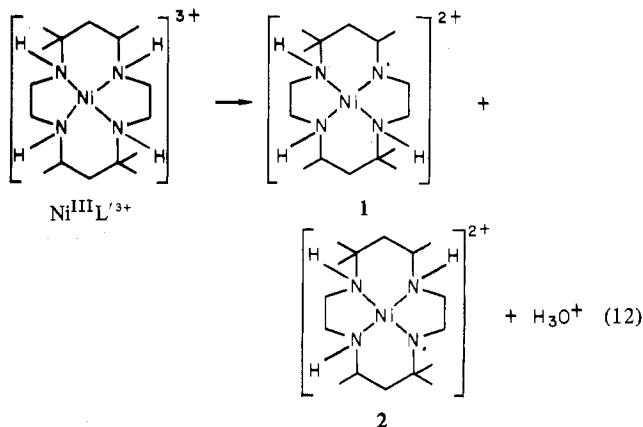
$$Ni^{II}L^{2+} + Br_2^- \rightarrow Ni^{III}LBr_2^+ \qquad (7a)$$

by Br_2^-, an intermediate concerning a bound Br_2^{2-} group with a considerable lifetime was observed, we feel that this suggested mechanism is speculative. It will be of interest if other studies will corroborate this mechanism. Alternatively, reaction 10 must be considered a side reaction of unknown nature.

The absorption spectrum of the product of reaction 9, $Ni^{III}L$, depends strongly on pH, Figures 1 and 2. The results indicate a pK of 3.45 ± 0.1. This result is in agreement also with the conductivity measurements. It is suggested that this pK is due to equilibrium 11. This equilibrium has to be accompanied

$$Ni^{III}L^{3+} \underset{}{\overset{H_2O}{\rightleftarrows}} Ni^{III}L(OH)^{2+} + H_3O^+ \qquad (11)$$

by a major stereochemical rearrangement of the complex in order to explain the major changes in the absorption spectrum. The strong absorption band of $Ni^{III}L(OH)^{2+}$ at 540 nm is attributed to a d–d transition in a highly unsymmetrical $Ni^{III}L(OH)^{2+}$ complex.[22] In an earlier study it was suggested[5] that when $Ni^{III}L'$ is dissolved in water a free radical centered on a nitrogen atom, with an absorption band at 540 nm, is formed according to eq 12. As the only difference between

the ligands L and L' is that the latter is fully saturated, the nature of the absorbing species at 540 nm in both systems is expected to be similar. The observation that intermediates with similar spectra are formed in nonaqueous solutions in the presence of pyridine and triethylamine[5] suggests that under those conditions the $Ni^{III}L'$ complex has a similar configuration. The identification of the red intermediate, with the absorption band at 540 nm, as a mixture of **1** and **2**, was based mainly on the EPR spectrum of the intermediate which could be roughly simulated assuming a 1.1:1 mixture of these radicals.[5] However, it is plausible that the EPR signal observed in this study does not belong to the red intermediate but to one of its decomposition products; i.e., compounds **1** and **2** might be decomposition products of the red intermediate. The authors themselves point out that under their experimental conditions they observed also an EPR signal due to $Ni^{III}L'$.[5] Furthermore, it is unclear at what pH these studies were carried out as the authors point out[5] that 1 mol of H_3O^+ is

released immediately upon dissolution of 1 mol of $Ni^{III}L'$ in water; on the other hand, they state that acidifying the solutions to pH ~ 4.5 by the addition of strong acids inhibited the formation of the red intermediate; as it is highly unlikely that solutions containing less than 2×10^{-5} M $Ni^{III}L'$ were used, the starting pH of the solutions must have been higher than 7. Finally the authors point out that upon cooling the red solutions "the partially frozen samples consisted of a green solid phase and a red liquid phase" indicating that the conversion of the green form to the red one is "a truly phase-change phenomenon". Such a "phase change" fits better a stereochemical rearrangement which might be affected by the lattice of the solid than a chemical equilibrium reaction like reaction 12.

Furthermore, it was shown that the intermediate with the absorption band at 540 nm reacts with oxygen with $k \approx 20$ M^{-1} s^{-1}.[5] The latter rate is considerably lower than that expected for aliphatic free radicals and similar to $k_{Ni^{III}EDTA+O_2}$ $= 6.5 \times 10^2$ m^{-1} s^{-1}.[9] (The rate of reaction of secondary amine radicals of the type $R_1R_2N\cdot$ with oxygen is unknown; however, $k_{\cdot NH_2+O_2} = 3 \times 10^8$ M^{-1} s^{-1} in aqueous solutions.[23]) All of the other chemical evidence given in support of **1** and **2** as the intermediate[5] would also fit $Ni^{III}L'(OH)^{2+}$.

Our preference for $Ni^{III}L(OH)^{2+}$ as the intermediate is based on the following observations:

(a) The pK value of 3.45 seems much too low for an amine bound to a trivalent metal center. All other data concerning nickel(III)–amine complexes indicate that such a pK is above 11,[12] e.g., as observed for Co(III), Ru(III), and other trivalent metal complexes.

(b) Our data indicate (see below) that the $Ni^{III}L$ complex has a further pK above 11.0, and we attribute this pK to the dissociation of the nitrogen–hydrogen bond.

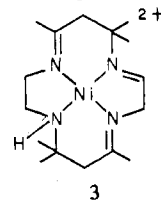(c) In the absence of bromide the rate of decomposition of $Ni^{III}L^{3+}$ is very similar to that of $Ni^{III}L(OH)^{2+}$. However, the rate of decomposition of $Ni^{III}L'^{3+}$ is expected to be considerably lower than that of intermediates **1** and **2**. We observed, indeed, a base-catalyzed decomposition of $Ni^{III}L$ in alkaline solutions which is attributed to a mechanism involving intermediates parallel to **1** and **2**.

(d) The rate of reaction of the red absorbing intermediate with O_2 is low.

(e) The observed pK of 3.45 is in full agreement with expectation for a trivalent metal inner-sphere water molecule dissociation. Thus for $Co^{III}L(H_2O)_2^{3+} \rightarrow Co^{III}L(OH)(H_2O)^{2+}$ $+ H_3O^+$, a pK of 4.2 was reported.[24]
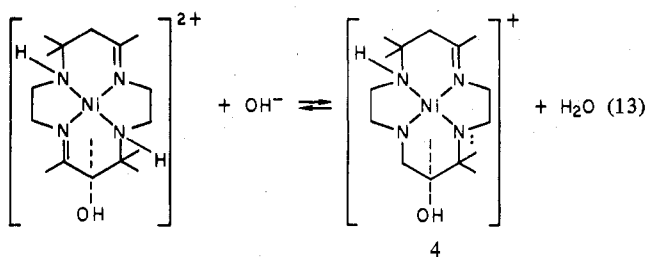
We thus conclude that reactions 7, 10, 9, and 11 best describe the mechanism of formation of $Ni^{III}L(H_2O)_2^{3+}$ and $Ni^{III}L(OH)^{2+}$ in the system studied.

The products of decomposition of $Ni^{III}L$ were not characterized.[25] The mixed first- and second-order rate law observed in neutral solutions is in agreement with that observed for $Ni^{III}L'$.[5] In parallel to the latter study, we expect that the products are a complicated mixture of ligand fragments and complex **3**. The latter is expected to be formed by dispro-
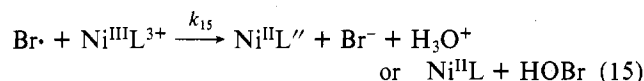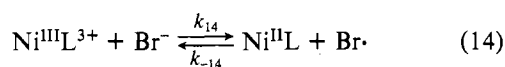

portionation of $Ni^{III}L(OH)^{2+}$, a reaction which should be second order in $Ni^{III}L$. On the other hand, hydrogen-abstraction reactions between $Ni^{III}L$ and ligand fragments are expected to contribute to an observed first-order law. A "mixed" rate law observed is thus expected in agreement with the experimental observations.

In alkaline solutions, pH ≥ 8.5, the rate of decomposition of Ni^{III}L(OH)$^{2+}$ (or Ni^{III}L(OH)$_2^+$ which might exist in this pH region) is pH dependent, the rate being pseudo first order in [OH$^-$], within experimental accuracy: d[Ni^{III}L]/dt = (2.0 ± 0.5) × 10^5 [OH$^-$]. This observation can be explained by reaction 13, with the assumption that intermediate **4** is

considerably more reactive than Ni^{III}L(OH)$^{2+}$. Similar observations were reported earlier for Ni^{III}-(NH$_2$CH$_2$CH$_2$NH$_2$)$_3^{3+}$ [12] and amine complexes of other high-valent transition metals.[26-29]
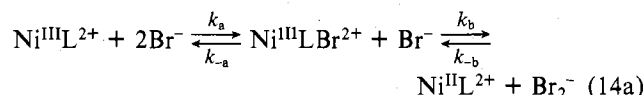
The decomposition of Ni^{III}L^{3+} in acid solutions containing bromide obeys a second-order rate law. The rate of this reaction is proportional to bromide concentration; it increases with decreasing pH and decreases slightly with increasing Ni^{II}L concentration (Table I). All of these observations are in agreement with the mechanism of eq 14 and 15 (where

$$Ni^{III}L^{3+} + Br^- \underset{k_{-14}}{\overset{k_{14}}{\rightleftharpoons}} Ni^{II}L + Br\cdot \qquad (14)$$

$$Br\cdot + Ni^{III}L^{3+} \xrightarrow{k_{15}} Ni^{II}L'' + Br^- + H_3O^+$$
$$\text{or} \quad Ni^{II}L + HOBr \qquad (15)$$

Ni^{II}L″ stands for an oxidized form of the ligand or a mixture of Ni$_{aq}^{2+}$ and ligand fragments). The rate law obtained from this mechanism with the assumption of the steady-state approximation for Br· is

$$-\frac{d[Ni^{III}L]}{dt} = \frac{2k_{14}k_{15}[Ni^{III}L]^2[Br^-]}{k_{-14}[Ni^{II}L] + k_{15}[Ni^{III}L]}$$

Remembering that reaction 14 is an abbreviated form of (14a)

$$Ni^{III}L^{2+} + 2Br^- \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} Ni^{III}LBr^{2+} + Br^- \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}}$$
$$Ni^{II}L^{2+} + Br_2^- \qquad (14a)$$

and assuming that $k_{-a} > k_b$, we obtain $k_{14} = k_a k_b/k_{-a}$, and $k_{-14} = k_{-b} = k_7 = 9 \times 10^9$ M^{-1} s^{-1}. The results clearly indicate the second-order dependence on [Ni^{III}L] and the first-order dependence on [Br$^-$]. The slight dependence of the rate on [Ni^{II}L] indicates that under the experimental conditions k_{-14}[Ni^{II}L] ≈ k_{15}[Ni^{III}L] and as [Ni^{III}L] ≈ 0.2[Ni^{II}L], k_{15} ≈ $5k_{-14}$. We could not increase [Ni^{II}L] as at higher concentration Ni^{I}L is formed by the competition between the reactions e$_{aq}^-$ + Ni^{II}L and e$_{aq}^-$ + N$_2$O and by the reaction H + Ni^{II}L (see above).[16,17] The kinetic data obtained at pH 3.0 fit k_{14} = 420 M^{-1} s^{-1} and k_{15} = 4.5 × 10^{10} M^{-1} s^{-1}. The latter value is reasonable if reaction 15 is rewritten as Br$_2^-$ + Ni^{III}L^{3+} with the assumption of a diffusion-controlled rate. Remembering that $k_{-a} = k_9 = 120$ s^{-1} at pH 3.0, we obtain $k_a k_b$ = 5 × 10^4; from the slight dependence of k_9 on [Br$^-$], Table I, k_a ≈ 1300 ± 300 M^{-1} s^{-1} can be calculated and therefore k_b ≈ 40 M^{-1} s^{-1}.

Finally, from k_{14} = 420 M^{-1} s^{-1}, k_{-14} = 9 × 10^9 M^{-1} s^{-1}, and the redox potential of the Br$_2^-$/2Br$^-$ couple, E° = 1.77 V,[30]

the redox potential of Ni^{III}L^{3+}/Ni^{II}L^{2+} can be calculated as E° = 1.34 ± 0.05 V. This value is similar to that reported for this complex in acetonitrile solutions.[2] The pH dependence of the rate of decomposition of Ni^{III}L in the presence of bromide indicates that Ni^{III}L(OH)$^{2+}$ is a considerably weaker oxidizing agent in agreement with expectation.[31]

Registry No. Br$_2^-$, 12595-70-9; Ni^{II}L^{2+}, 18444-38-7; Ni^{III}LBr^{2+}, 68540-00-1; Ni^{III}L(H$_2$O)$_2^{3+}$, 67375-44-4; Ni^{III}LBr$_2^+$, 68540-01-2; NiL(ClO$_4$)$_2$, 36539-75-0.

References and Notes

(1) D. Meyerstein, *Acc. Chem. Res.*, **11**, 43 (1978), and references therein.
(2) F. V. Lovecchio, E. S. Gore, and D. H. Busch, *J. Am. Chem. Soc.*, **96**, 3109 (1974).
(3) D. C. Olson and J. Vaselevskis, *Inorg. Chem.*, **8**, 1611 (1969).
(4) N. Takvorgan, K. Farmey, V. Katovic, F. Lovecchio, E. S. Gore, L. B. Anderson, and D. H. Busch, *J. Am. Chem. Soc.*, **96**, 731 (1974).
(5) K. Barefield and M. T. Mocella, *J. Am. Chem. Soc.*, **97**, 4238 (1975).
(6) M. Anbar, *Adv. Chem. Ser.*, No. 49, 126 (1965).
(7) K. Bouchal and F. Hrabak, *Collect. Czech. Chem. Commun.*, **31**, 4651 (1965).
(8) I. Fried and D. Meyerstein, *Isr. J. Chem.*, **8**, 865 (1976).
(9) J. Lati and D. Meyerstein, *Int. J. Radiat. Phys. Chem.*, **7**, 611 (1975).
(10) J. Lati, J. Koresh, and D. Meyerstein, *Chem. Phys. Lett.*, **33**, 286 (1975).
(11) F. P. Bossu and D. W. Margerum, *Inorg. Chem.*, **16**, 1210 (1977).
(12) J. Lati and D. Meyerstein, *Inorg. Chem.*, **11**, 2393, 2397 (1972).
(13) M. Kelm, J. Lilie, A. Henglein, and E. Janata, *J. Phys. Chem.*, **78**, 882 (1974).
(14) M. S. Matheson and L. M. Dorfman, "Pulse Radiolysis", M.I.T. Press, Cambridge, Mass., 1969.
(15) M. Anbar, M. Bambenek and A. B. Ross, *Natl. Stand. Ref. Data Ser. Nat. Bur. Stand.*, No. 43 (1972).
(16) A. M. Tait, M. Z. Hoffman, and E. Hayon, *Inorg. Chem.*, **15**, 934 (1976).
(17) Due to the competition between reaction 4 and the reaction e$_{aq}^-$ + H$_3$O$^+$ → H, we were unable to extend this study to pH's lower than 3.0.
(18) D. Behar, *J. Phys. Chem.*, **76**, 1815 (1972); D. Zehavi and J. Rabani, *ibid.*, **76**, 312 (1972).
(19) A. M. Tait, M. Z. Hoffman, and E. Hayon, *Int. J. Radiat. Phys. Chem.*, **8**, 691 (1976).
(20) J. Lati and D. Meyerstein, *J. Chem. Soc., Dalton Trans.*, 1104 (1978).
(21) J. F. Endicott, J. Lilie, J. M. Kuszaj, B. S. Ramaswamz, W. G. Schmonsees, M. G. Simic, M. D. Glick, and D. P. Rillema, *J. Am. Chem. Soc.*, **99**, 429 (1977).
(22) One of the reviewers suggested that the absorption coefficient observed, ε 1700 M^{-1} cm^{-1}, is too high for a d–d transition. We point out that for Ni(II) complexes with unsaturated macrocyclic ligands d–d transitions with ε 922 M^{-1} cm^{-1} were reported by D. H. Busch, D. G. Pilsbury, F. V. Lovecchio, A. M. Tait, Y. Hung, S. Jackels, M. C. Rakowski, W. P. Schammel, and L. Y. Martin, *ACS Symp. Ser.*, No. 38, 32 (1977).
(23) P. B. Pagsberg, Riso Report No. 256, Riso National Laboratory, Roskilde, Denmark, 1972.
(24) D. P. Rillema, J. F. Endicott, and J. R. Barber, *J. Am. Chem. Soc.*, **95**, 6987 (1973).
(25) Due to the high reactivity of Br$_2^-$ and Ni^{III}L they are expected to react with the products of radiolysis. Indeed it was observed that the kinetics of decomposition are changed after a few pulses are delivered to the solution. Thus our conversion rates had to be kept to a few percent only, and therefore the products could not be characterized.
(26) V. L. Goedken and D. H. Busch, *J. Am. Chem. Soc.*, **94**, 7355 (1972).
(27) H. L. Chum, V. R. Koch, L. L. Miller, and R. A. Osteryoung, *J. Am. Chem. Soc.*, **97**, 3264 (1975).
(28) L. F. Lindoi, *Chem. Soc. Rev.*, **4**, 421 (1975).
(29) S. E. Diamond, G. M. Tom, and H. Taube, *J. Am. Chem. Soc.*, **97**, 2661 (1975).
(30) A. T. Thoronton and G. Lawrence, *J. Chem. Soc., Dalton Trans.*, 1632 (1972).
(31) After this work was submitted for publication the works of G. Ferraudi and L. Patterson, *J. Chem. Soc., Chem. Commun.*, 755 (1977), and P. Maruthamuthu, L. K. Patterson, and G. Ferraudi, *Inorg. Chem.*, **17**, 3157 (1978), were brought to our attention. These authors described a similar study on the same compound and reached similar conclusions. Their data are in very good agreement with ours with one exception: they do not find the pK at pH 3.45. We have discussed the results with them and do not know what causes this discrepancy, and this point will be further studied. We thank the authors for sending us their data prior to publication.