Redox Reactions of Free Radicals with Ni(II) Complexes. A Pulse Radiolytic Study

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Oxidation of $Ni[Me_6[14]-4,11-dieneN_4]^{2+}$, $Ni[Me_6[14]aneN_4]^{2+}$, and $Ni[Me_6[14]-1,4,8,11-tetraeneN_4]^{2+}$ by radiolytically generated ·OH, Cl_2^-, Br_2^-, and $(NCS)_2^-$ has been studied by spectral and chemical methods. In each case, oxidation produces intermediates characterized as Ni(III) complexes. Transient spectra of the intermediates formed by anion radical reaction strongly resemble spectra of Ni(III) analogues produced in nonpolar solvents with absorption bands in the region 300–400 nm. The decay rates of such intermediates depend on the anion radical used and may vary by 3 orders of magnitude ($k \simeq 1$–(3×10^3) s^{-1}), indicating involvement of the associated anion in the intermediate oxidation product. Hydroxyl radical reactions with $Ni[Me_6[14]-4,11-dieneN_4]^{2+}$ and $Ni[Me_6[14]aneN_4]^{2+}$ generate intermediates with absorption peaks in the region 535–550 ($\epsilon \sim 10^3$ M^{-1} cm^{-1}). Decay of intermediates generated by anion radicals yields stable transients with spectra comparable to those produced directly via ·OH. These processes precede formation of final products. Mechanisms for product formation from Ni(III) intermediates suggest the involvement of base-assisted hydrolysis.

Introduction

Electrochemical oxidations of Ni(II) macrocyclic complexes to produce Ni(III) species have been carried out for a considerable number of compounds[2-5] in nonaqueous solvents. The stability of the Ni(III) complexes in such media has permitted good characterization by EPR and optical spectroscopy. By contrast, they have been found in aqueous solution to be generally unstable and difficult to study by conventional means. Mechanistically, such oxidized metal centers have been evoked to explain processes by which some chemical agents (e.g., NO_3H, Br_2) act to introduce double bonds into macrocyclic ligand rings via oxidative dehydrogenation.[6-8] Participation of such oxidation states in these reactions suggests that reaction channels passing through Ni(III) intermediates would provide, wherever operative, pathways with activation barriers smaller than those encountered in direct oxidation of the ligands. The associated kinetics may be dependent on structural characteristics of the substrates which have little influence on the redox potentials. However, limited information about the kinetic aspects of these reactions has been obtained, especially with respect to the nature and transformation of short-lived intermediates.[9] And without such information which correlates variations in the ligand and central ion to kinetic behavior, the formulation of a satisfactory mechanism for metal-mediated macrocyclic ligand oxidation cannot readily be achieved.

Pulse-radiolysis techniques are particularly suited to time-resolved study of unstable oxidation states for metal complexes in aqueous media. Both a powerful reducing species, e_{aq}^- ($E^\circ = -2.7$ V),[10a] and an oxidizing agent, the hydroxyl radical, ·OH ($E^\circ = 1.9$ V),[10] are generated when high-energy electrons are deposited in water. Further, secondary radicals of various oxidizing powers (Br_2^-, Cl_2^-, $(NCS)_2^-$) may be produced from ·OH. Though considerable work has been carried out using e_{aq}^- to obtain kinetic parameters associated with central metal ions in lower oxidation states,[11-13] less attention has also been given to reactions of ·OH radicals with mono- and bidentate complexes.[14-17] Very little has been done to exploit the possibilities presented by the other oxidizing species available.

In the present study we have applied optical pulse radiolysis techniques to investigations of Ni(II) macrocycle oxidation by ·OH, Cl_2^-, Br_2^-, and $(NCS)_2^-$. These studies have been complemented by synthetic work in which $Ni[Me_6[14]-4,11-dieneN_4]^{3+}$ was prepared by persulfate oxidation of the Ni(II) dienes in acidic aqueous solution. The properties of the material so generated provide several points of comparison with the species produced by oxidizing radicals. Principal attention has been given to the complex $[Ni[Me_6[14]-4,11-dieneN_4]](ClO_4)_2^1$ (I). For purposes of comparison, some

I   II   III
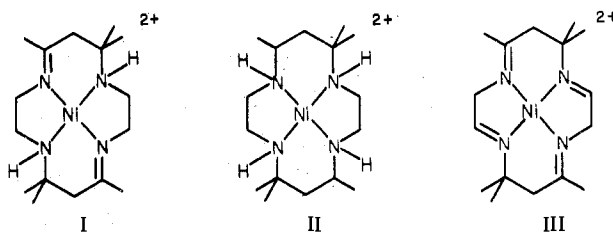
measurements have been carried out with $[Ni[Me_6[14]-aneN_4]](ClO_4)_2^1$ (II) and $[Ni[Me_6[14]-1,4,8,11-tetraeneN_4]](ClO_4)_2^1$ (III), especially with regard to transient kinetics and spectra. It is the goal of these studies to elucidate the reaction pathways initiated by the different radical oxidants and to determine the mechanisms by which the Ni(III) metal center participates in ligand degradation via oxidative processes.

Experimental Section

Radiolytic Procedures. Optical pulse radiolysis measurements were made with a computerized system similar to that described earlier.[18] However, some modifications in data treatment have been made to utilize a Hewlett-Packard 9830A calculator off line.[19] The apparatus now makes use of the Notre Dame 10-MeV linear accelerator which has the capability of providing, at the limit, 5-ns pulses at currents of up to 7 A. A 500-mm Bausch and Lomb monochromator was used in these studies. With cutoff filters, it was found that less than 1% of the light emerging from the exit slits at wavelengths down to 260 nm could be associated with scatter above 300 nm. Thiocyanate dosimetry was carried out at each experimental session to calibrate the output signal of a secondary emission monitor (Dose) against radical concentrations produced in the radiolysis cell by the Linac electron pulse. Absorbance data is presented here in dimensions of extinction coefficient by the parameter ϵ generated from the function

$$\epsilon = Abs \cdot K / Dose \cdot [G \text{ value}]$$

where Abs is absorbance for a particular pulse and K is chosen such that ϵ for $(NCS)_2^-$ is 7600 M^{-1} cm^{-1} in N_2O-saturated systems.[20] This means that ϵ represents absorbance data normalized against the dose delivered to the system for each pulse. A flow system was used to ensure that fresh solution was brought to the radiolysis cell between electron pulses. Where processes in the time range above 200 ms were investigated, solution did not flow during the time of measurement but was replenished after each irradiation. Solutions of the complexes containing appropriate concentrations of $HClO_4$ or buffer were deaerated and saturated with N_2O.

In ESR experiments, involving irradiated solutions, a sample tube containing solution to be irradiated was placed before the Linac over a Dewar flask on a scaffold arrangement which could be triggered remotely. With this device the ESR tube was dropped into liquid nitrogen within 1 s after irradiation. It is estimated that complete freezing of such a sample requires 5–7 s. The ESR spectrum was obtained in a Varian spectrometer provided with a cavity thermostated at −160 °C. The ESR measurements involving powder samples were

Table I. Kinetics of Ni(II) Macrocyclic Complex Oxidation by Various Radical Agents

| | rate constant | | | | | | | |
| | oxidn of complexes ($10^{-9}k$,[a] M^{-1} s^{-1}) | | | | transformn of transient oxidn products (s^{-1}) | | | |
complex cation	·OH	Br_2^-	Cl_2^-	$(NCS)_2^-$	H_2O	Br^- [c]	Cl^- [b,c]	NCS^- [c]
Ni[Me$_6$[14]aneN$_4$]$^{2+}$	1.9	3.4	2.0	1.0 ± 0.4		2 × 10^3	10	10
Ni[Me$_6$[14]-4,11-dieneN$_4$]$^{2+}$	3.0	9.8	9.6		5 × 10^4	1 × 10^2	1	
Ni[Me$_6$[14]-1,4,8,11-tetraeneN$_4$]$^{2+}$	4.1	9.5	8.7			3 × 10^3	13	

[a] The rate of ·OH reaction is the same for production of intermediates in aneN$_4$ and dieneN$_4$ systems. [b] These values are subject to about a 25% uncertainty due to the difficulty of adapting the pulse radiolysis monitoring system to measurement of weakly absorbing transients at times >10 ms. [c] Anion concentrations: [Br$^-$] = 5 × 10^{-3} M (pH 5), [Cl$^-$] = 10^{-2} M (pH 2), [NCS$^-$] = 2 × 10^{-2} M (pH 5).

carried out at room temperature by simply introducing into the ESR cavity a sample tube containing the powder.

Ni(II) in irradiated solutions was analyzed with dimethylglyoxime or rubeanhidric acid by procedures already described in the literature.[21]

Materials and Synthesis. Literature procedures were used for the synthesis of [Ni[Me$_6$[14]-4,11-dieneN$_4$]](ClO$_4$)$_2$,[22] [Ni[Me$_6$[14]-1,4,8,11-tetraeneN$_4$]](ClO$_4$)$_2$[7] and [Ni[Me$_6$[14]aneN$_2$]](ClO$_4$)$_2$.[22] Complexes were recrystallized several times by addition of 5.0 M NaClO$_4$. Two further recrystallizations were carried out from distilled water. The infrared and the visible–ultraviolet spectra agreed well with literature reports.[22,7]

The synthesis of [Ni[Me$_6$[14]-4,11-dieneN$_4$](OH$_2$)$_2$](ClO$_4$)$_3$ was carried out by oxidation of Ni[Me$_6$[14]-4,11-dieneN$_4$]$^{2+}$ with a stoichiometric amount of sodium persulfate.[23] This oxidation was carried out at 40 °C by a dropwise addition of the sodium persulfate solution to a solution of the parent nickel(II) complex (~3 g) in 3 M HClO$_4$ (~20 cm^3). A green powder was precipitated with solid sodium perchlorate. A fraction of this powder was recrystallized from acetonitrile by the procedure of Olson and Vasilevskis.[2] The ultraviolet–visible absorption spectrum of the product in acetonitrile agrees with that reported for [Ni[Me$_6$[14]-4,11-dieneN$_4$]-(CH$_3$CN)$_2$](ClO$_4$)$_3$.[2]

Other materials were of reagent grade and were used without further purifications. Water for the radiolysis experiment was obtained from a Milli-R015 Millipore filtering system. Neither hydrated electron nor ·OH lifetime measurements gave evidence of impurities which could interfere with the studies carried out here.

Results

Formation of Intermediates Produced by Reactions with ·OH. Optical pulse radiolysis measurements were carried out in N$_2$O-saturated solutions of the three Ni(II) macrocyclic complexes. In the presence of nitrous oxide, hydrated electrons are converted to ·OH via the reaction

$$e_{aq}^- + N_2O + H_2O \rightarrow N_2 + \cdot OH + OH^- \qquad (1)$$
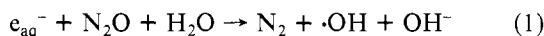
The associated rate constant, $k_{e_{aq}^-+N_2O}$ has a value of 5.6 × 10^9 M^{-1} s^{-1}.[24] All three complexes were found to react efficiently with ·OH giving rate constants of (3.0 ± 1.0) × 10^9 M^{-1} s^{-1} (see Table I). The rates of reaction were determined by following the growth of transient absorption associated with ·OH attack as a function of macrocycle concentration. Concentrations of the complexes were adjusted so that the disappearance of ·OH by processes other than the reaction with substrate could not interfere. Because of the high reactivity of e_{aq}^- toward these macrocyclic complexes ($k_{e_{aq}^-+Cx}$ = (5–8) × 10^{10} M^{-1} s^{-1}), a few percent of e_{aq}^- produced will react directly with the complex. However, the extent of reaction is small at the complex concentrations used, and no spectral contribution characteristic of the Ni(I) species[12] was observed. It may well be that small quantities of Ni(I) react efficiently with N$_2$O. Magnitudes of rate constants are in good agreement with those reported for a variety of metal complexes and may be specifically compared to the ·OH reaction rate constants reported for Ni(II) mono- and bidentate complexes.[14–17] While differences in ·OH rate constants with complexes of ethylenediamine have been observed as a function of pH,[15] the values found here were essentially unaffected by acid concentration over the range of our measurements, pH 4–9.
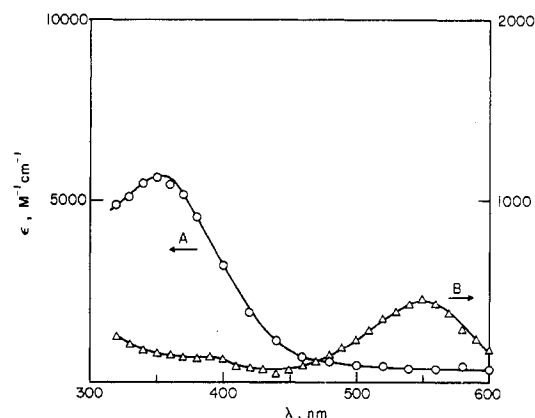

Figure 1. Transient spectra produced by ·OH oxidation of (A) Ni[Me$_6$[14]-1,4,8,11-tetraeneN$_4$]$^{2+}$ and (B) Ni[Me$_6$[14]aneN$_4$]$^{2+}$. Studies were carried out in N$_2$O-saturated solutions at pH 5. Concentrations of 2 × 10^{-4} M complex were used. Curves represent transient absorption at the end of ·OH reaction.

In the initial spectra resulting from ·OH attack (pH 5), as well as in subsequent spectral transformations, the Ni-[Me$_6$[14]aneN$_4$]$^{2+}$ and Ni[Me$_6$[14]-4,11-dieneN$_4$]$^{2+}$ complexes exhibit comparable behavior while the Ni[Me$_6$[14]-1,4,8,11-tetraeneN$_4$]$^{2+}$ complex differs markedly from the first two. Indeed, quite simple behavior was observed in the case of Ni[Me$_6$[14]-1,4,8,11-tetraeneN$_4$]$^{2+}$. The absorption spectrum (Figure 1), with its peak at 345 nm and a small shoulder in the region above 500 nm, shows some general characteristics associated with those observed for Ni(III) macrocyclic complexes prepared in acetonitrile.[2] No transformation of the initial spectrum other than by the uniform decay process described below was observed ($\tau \approx 0.5$ s, pH 5). Reaction of ·OH with Ni[Me$_6$[14]aneN$_4$]$^{2+}$ at the same pH failed to produce large transient absorption in the UV region but was characterized by appearance of an intermediate in the region 500–600 nm whose half-life is the same order of magnitude as that produced in the diene. The spectrum is also included in Figure 1. By contrast, Ni[Me$_6$[14]-4,11-dieneN$_4$]$^{2+}$ in the same pH region exhibited more complicated spectral and kinetic properties. A long-wavelength absorption band (ca. 500–600 nm) having a peak extinction coefficient of about 10^3 M^{-1} cm^{-1} is observed in addition to the UV band around 300–400 nm (Figure 2[25]). In this case there are some decay of the UV absorbance and a corresponding growth in the 500–600-nm region. Such a process was observed over the period of 50 μs after the pulse, and the spectral changes associated with this process are shown in Figure 2. An isosbestic point may be seen at ~490 nm indicating interconversion between two separate intermediates over the time region indicated. However, irradiating a concentrated solution of Ni[Me$_6$[14]-4,11-dieneN$_4$]$^{2+}$ under conditions of nanosecond resolution indicates that these two intermediates are produced simultaneously from initial ·OH attack. In the case of the Ni[Me$_6$[14]aneN$_4$]$^{2+}$ complex this interconversion process is much less pronounced involving only
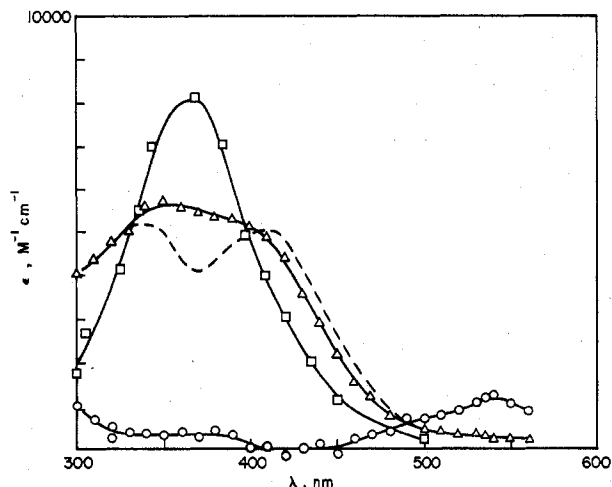
Figure 3. Transient spectra for the oxidation of $Ni[Me_6[14]aneN_4]^{2+}$ by Br_2^-. The solution contained 5×10^{-3} M KBr and 4×10^{-4} M complex; it was N_2O saturated and the pH was adjusted to 5. The curves represent spectra measured at various intervals after the pulse: (□) 2 μs, (△) 30 μs, (○) 7 ms. They may be assigned to (□) Br_2^-, (△) the transient oxidation product, and (○) the stable intermediate. The dotted line represents the normalized spectrum of planar Ni-$[Me_6[14]aneN_4]^{3+}$ in acetonitrile.[2]

about a 2% further growth in the red band.

Decay of the intermediates formed in ·OH attack is very dependent on pH, though at pH 5 disappearance of the Ni-$[Me_6[14]-1,4,8,11-tetraeneN_4]^{2+}$ intermediate is 2 orders of magnitude faster than for those produced from the other two complexes. The pH-dependent behavior of the $Ni[Me_6-[14]-4,11-dieneN_4]^{2+}$ intermediate is described in detail below. In our experiments we did not see formation of Ni(I) from ·H atom reaction with Ni(II) indicating that such reaction must be quite slow compared to ·OH reaction.

Oxidation of Ni(II) Macrocycles with Anion Radicals Cl_2^-, Br_2^-, and $(NCS)_2^-$. Reactions producing the anion radicals Cl_2^-, Br_2^-, and $(NCS)_2^-$ from ·OH are multistep processes but proceed overall via reaction 2. With excess halide the overall

$$\cdot OH + X^- \xrightarrow{X^-} OH^- + X_2^- \qquad (2)$$
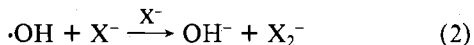
rate constants[17] for (2) are 10^{10} M^{-1} s^{-1} for chloride (pH 2) and 10^{10} M^{-1} s^{-1} for bromide (pH 5). Thiocyanate reacts with an overall rate constant of 1×10^{10} M^{-1} s^{-1} (pH 5). In these studies halide concentrations of $5 \times 10^{-3}-2 \times 10^{-2}$ M were used with complex concentrations of 10^{-4} M. For each macrocycle system, reaction kinetics were monitored through the following sequential steps: (a) formation of X_2^- from ·OH; (b) disappearance of X_2^- by reaction with complex to form a *transient oxidation product*; (c) transformation of this transient product into a relatively *long-lived intermediate*. The spectra associated with Br_2^- oxidation of $Ni^{II}[Me_6[14]-aneN_4]^{2+}$ are given in Figure 3 showing all three observed reaction steps. In Figure 4 data from Br_2^- oxidation of the $Ni[Me_6[14]-1,4,8,11-tetraeneN_4]^{2+}$ and $Ni[Me_6[14]-4,11-dieneN_4]^{2+}$ are given. This figure includes only transient oxidation products and long-lived intermediates, as the Br_2^- spectrum is constant in all cases. In both Figures 3 and 4 literature spectra for analogous Ni(III) complexes, electrolytically produced in acetonitrile, are normalized and superimposed on the spectra of the transient oxidation products. In each case, the apparent extinction coefficient, ϵ, for transient oxidation product was found to be half the extinction coefficient reported by Olson and Vasilevskis[2] in acetonitrile. For the $Ni[Me_6[14]-1,4,8,11-tetraeneN_4]^{2+}$, the spectrum produced by ·OH attack has been added for purposes of comparison. Although the kinetics for growth and decay differ markedly,
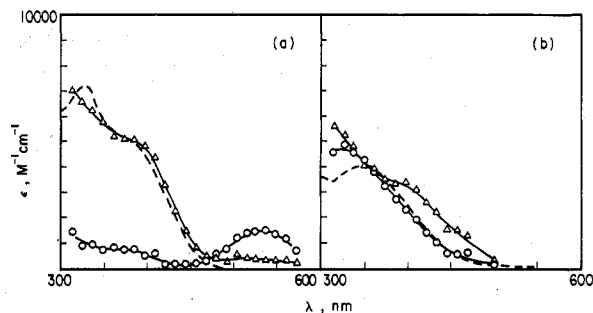
Figure 4. Transient spectra produced by Br_2^- oxidation of (a) Ni-$[Me_6[14]-4,11-dieneN_4]^{2+}$ and (b) $Ni[Me_6[14]-1,4,8,11-tetraeneN_4]^{2+}$. Each solution contained 1×10^{-4} M complex and 5×10^{-3} M KBr. Pulse radiolysis was done in N_2O-saturated solutions adjusted to pH 5. The curves represent spectra at intervals after the radiolytic pulse as follows: (a) (△) 0.2 ms, (○) 3 ms; (b) (△) 0.2 ms, (○) 14 ms. The dotted line in portion (a) of the figure represents the normalized spectrum for analogous Ni(III) macrocyclics produced electrolytically in acetonitrile[2] while the portion (b) the dotted line is the transient spectrum produced by ·OH attack on the nickel(II)–tetraene compounds.

spectra of the transient oxidation products obtained by Cl_2^- oxidation are essentially the same as with Br_2^-.

At the concentrations of halide used here, formation of X_2^- occurs in less than 1 μs. Process b was monitored by following changes in optical absorption at wavelengths where spectra of X_2^- and the transient differ significantly. Pseudo-first-order rate constants were obtained from concentration-dependent behavior of appropriate optical growth or decay. They are included in Table I. In general, halide oxidation of the macrocycles occurs with rate constants comparable to those observed for ·OH attack. Oxidation by $(NCS)_2^-$ proceeds with rate constants an order of magnitude lower.

Transformation c is, in each case, a first-order process; associated rate constants involving Cl_2^- and Br_2^- were also obtained optically and are given in Table I. It may be seen that disappearance of the intermediate oxidation product is much slower in the presence of Cl^- or $(NCS)^-$ than with Br^-. However, when $Ni[Me_6[14]-4,11-dieneN_4]^{2+}$ and $Ni[Me_6-[14]aneN_4]^{2+}$ were oxidized by ·OH in the presence of 0.02 M Cl^- at pH 7 where Cl_2^- is not formed, no significant production or stabilization of the UV absorption was seen.

Redox Reactions of the Long-Lived Intermediate Produced by ·OH Reaction with $Ni[Me_6[14]-4,11-dieneN_4]^{2+}$. The presence of either ferrous ions or iodide ions, in concentrations well below the limit for a direct reaction with ·OH, enhanced the decay of the long-lived transient of the $Ni[Me_6[14]-4,11-dieneN_4]^{2+}$ ($k_{Fe^{2+}} = 2 \times 10^5$ M^{-1} s^{-1}; $k_{I^-} = 3 \times 10^4$ M^{-1} s^{-1}).

It is additionally expected that reactions between charged species will vary with solution ionic strength. Therefore variations in redox kinetics of the intermediate with ionic strength should yield some insight into the nature of its charge if a clean electron-transfer reaction is used. In N_2-purged solutions, e_{aq}^- and ·OH are produced in almost equal quantities. Hydrated electrons are known to reduce Ni(II) to Ni(I)[12] which would be expected to transfer an electron rapidly to any Ni(III) species. At pH 5, the reaction between $Ni^I[Me_6-[14]-4,11-dieneN_4]^+$ and the long-lived intermediate was found to obey good second-order kinetics for 2×10^{-4} M Ni-$[Me_6[14]-4,11-dieneN_4]^{2+}$. This rate constant varied only a few percent when the dose was changed by a factor of 5. When monitored at 450 nm, in the absorption band for Ni-$[Me_6[14]-4,11-dieneN_4]^+$, or 535 nm, the band of the intermediate, the transient absorption decayed to negligible values showing a quantitative annihilation of the transient species by the Ni(I) complex. With increases in ionic strength

using NaClO$_4$, the decay rate was seen to increase. Rate data were plotted as a function of the ionic strength according to the classical relationship (3), where k is the second-order rate

$$\log k - \log k_0 = 1.02 Z_a Z_b \sqrt{\nu_\mu} \Big/ (1 + \sqrt{\nu_\mu}) \qquad (3)$$

constant and $Z_a Z_b$ is the product of the charges of the reacting species.[26]

As may be seen in Figure 5,[25] a straight-line plot was obtained whose slope, determined by least squares, is 2.93 ± 0.05. This gives a value for $+Z_a + Z_b$ of essentially 3 indicating a charge of 3 for the long-lived nickel complex. The value of the rate constant when extrapolated to zero ionic strength is 8 × 10^7 M^{-1} s^{-1}. This value is in good agreement with rate constant reported for oxidation of Ni(I) by various metal complexes.[12]

**Decay of the Intermediate Produced by ·OH Reactions with Ni[Me$_6$[14]-4,11-dieneN$_4$]$^{2+}$.** In acidic media the intermediate produced from Ni[Me$_6$[14]-4,11-dieneN$_4$]$^{2+}$ is very long-lived—up to 40-s half-life at pH 4—and the kinetics of the decay appear to follow reasonably a first-order rate law. As the pH is increased, the measured half-life falls in proportion to changes in H$^+$ concentration. In the pH 4–11 interval the half-life of the diene transient decreases by 4 orders of magnitude (see Figure 6[25]). Following ·OH attack, the absorption obtained at 535 nm is constant (±10%) over the range of pH values used (4–11). Indeed, the yield of the long-lived species at 535 nm, after correcting for losses of e$_{aq}^-$ to H$^+$, remains essentially constant for pH as low as 2.5. However, absorption in the UV region is enhanced to an extent similar to that reported by Myerstein in Br$_2^-$ oxidation of the diene (see Acknowledgment).

Reaction Products. The reaction of ·OH with 5 × 10^{-4}–1 × 10^{-4} M Ni[Me$_6$[14]-4,11-dieneN$_4$]$^{2+}$ in 10^{-4} M HClO$_4$ was studied when enough radiation had been given to convert 30–40% of the starting material into products. Analyses for Ni^{2+}(aq) using the analytical procedures described above (see Experimental Section) gave negative results under such conditions. Spectral changes observed in the region below 300 nm suggested some possible transformation of the parent complex into a triene product.

Isomers of Ni[Me$_6$[14]-4,11-dieneN$_4$](OH$_2$)$_2$$^{3+}$. The green [Ni[Me$_6$[14]-4,11-dieneN$_4$](OH$_2$)$_2$](ClO$_4$)$_3$ complex produced by persulfate oxidation exhibits pronounced stability as a solid at room temperature. However, dissolution in aqueous media with pH ≥1 produced a metastable reddish pink species. The pink color turns green when solutions are rapidly frozen at −180 °C or transforms to a yellow color upon standing at room temperature. Similar behavior was reported by Barefield and Mocella[9] for a reddish pink species which was obtained with dissolution of Ni[Me$_6$[14]aneN$_4$]$^{3+}$ in aqueous solution.

In addition, samples of [Ni[Me$_6$[14]-4,11-dieneN$_4$]-(OH$_2$)$_2$](ClO$_4$)$_3$ were warmed to 50 °C under vacuum for 2 h. Such treatment produces a brown solid which is stable at room temperature. Dissolution of this compound in acetonitrile produces a green solution of the Ni[Me$_6$[14]-4,11-dieneN$_4$](CH$_3$CN)$_2$$^{3+}$ species. However, the transient pink color is observed when water is added to the solid compound or its acetonitrile solutions. In addition the green color was not restored by cooling at −180 °C in the powder.

Electron Spin Resonance Spectrum. Limitations in the sensitivity of the ESR method require that a significant concentration of the oxidized Ni[[14]-4,11-dieneN$_4$]$^{2+}$ intermediate be obtained. However, in irradiated solution, the very fast reaction of the solvated electron with Ni[Me$_6$-[14]-4,11-dieneN$_4$]$^{2+}$ (k = 7 × 10^{10} M^{-1} s^{-1}, see ref 12) limited the concentration of complex that could be used without interference with the conversion of e$_{aq}^-$ to ·OH. The solubility of N$_2$O in H$_2$O is 0.025 M. Because of this, concentrations
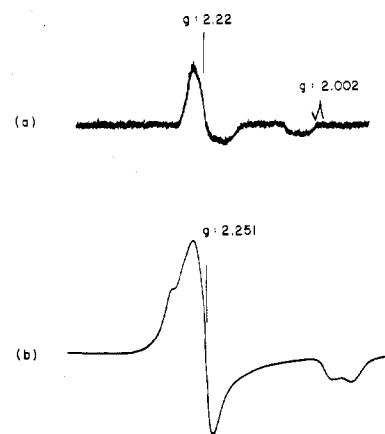
Figure 7. ESR spectra for (a) the ·OH-oxidized Ni[Me$_6$[14]-4,11-dieneN$_4$]$^{2+}$ intermediate in frozen N$_2$O-saturated solution and (b) the brown isomer of the [Ni[Me$_6$[14]-4,11-dieneN$_4$](OH$_2$)$_2$]-(ClO$_4$)$_3$. The Ni(II) complex concentration was 3 × 10^{-4} M.

of complex greater than 3 × 10^{-4} M were not desirable. Samples at pH 3.8 were irradiated to produce about a 5 × 10^{-5} M concentration of intermediate. The ESR spectrum of the intermediate obtained by the procedure described (see Experimental Section) presented most of the features of those reported for Ni(III) complexes of macrocyclic ligands.[3] A doublet was observed with $g \simeq 2.22$ where lines corresponding to $g_\parallel$ were reported for Ni[Me$_6$[14]dieneN$_4$]$^{3+}$ in acetonitrile. Also lines corresponding to $g_\perp \simeq 2.02$ were observed with a smaller intensity but were still well differentiated from the background noise and the signals of the charge centers generated by irradiation of the quartz (see Figure 7). The spectrum has been communicated previously and is included here for purposes of discussion.[27]

The EPR spectrum of the solid brown compound, Figure 7, has the same features comparable with those reported for various low-spin Ni(III) complexes. This suggests strongly that such a compound is some isomeric form of the green complex where Ni(III) is in a tetragonal coordination sphere.

Discussion

One report has been made of an ESR spectrum associated with irradiation of Ni^{II}EDTA and was assigned to the presence of a Ni(III) species.[28] However, interpretations of ·OH attack on Ni(II) complexes (e.g., various amines) have relied heavily on transient spectra exhibiting features which are similar in several different complexes, but which are not characteristic for radicals of the associated ligands.[14,15] Such spectra did not always exhibit the features of comparable Ni(III) complexes in nonaqueous solvents.[14,15]

In the present study it has been observed that the spectral and kinetic properties of transient products associated with ·OH attack on Ni(II) macrocyclics vary markedly as functions of ligand structure. Hydroxyl radical attack on Ni[Me$_6$-[14]-1,4,8,11-tetraeneN$_4$]$^{2+}$ gives rise to a transient spectrum very similar to that expected for the Ni(III) analogue in nonaqueous solvents; ·OH reactions with Ni[Me$_6$[14]aneN$_4$]$^{2+}$ and Ni[Me$_6$[14]-4,11-dieneN$_4$]$^{2+}$ yield absorption bands which are wholly unlike those found for the Ni(III) complexes in acetonitrile.[2] These results alone leave unresolved several questions concerning the site of ·OH attack—metal center or ligand—and the effects of macrocyclic ligand structure on this process.

Oxidation by Anion Radicals. The use of the anion radicals Cl$_2^-$, Br$_2^-$, and (NCS)$_2^-$ as oxidants yields data which appear to provide a link between the behavior of the Ni(III) macrocyclics generated in acetonitrile and the pathway for ·OH oxidation in aqueous systems. From Figures 3 and 4 it may be seen that the transient oxidation products generated with

Br_2^- exhibit absorption spectra very similar in band structure to those reported for the analogous Ni(III) complexes in acetonitrile,[2] though apparent extinction coefficients, ϵ, for the Ni(III) species produced by anion radicals are smaller. This difference in ϵ cannot be explained by loss of X_2^- through competition. The oxidation with $(NCS)_2^-$, a radical that has no tendencies to abstract hydrogen, produces extinctions with almost the same values of those obtained with Cl_2^- and Br_2^-. Besides, these reactions were carried out under conditions such that loss of X_2^- radicals by radical–radical processes were not significant (see Results).

The rates of Ni(II) complex oxidation by the various agents ·OH, Br_2^-, Cl_2^-, and $(NCS)_2^-$ were shown to vary between 10^9 and 10^{10} M^{-1} s^{-1} (see Table I). It may be seen that reactions involving $Ni[Me_6[14]aneN_4]^{2+}$ are uniformly smaller than those for the other two complexes and that oxidation by ·OH is marginally slower than oxidation by anion radicals. However, the differences presented by the data are too small to be definitively assigned to specific molecular parameters.

Though the transient oxidation product spectra generated by the various anion radicals are the same for a given macrocycle, the kinetics of subsequent transformations into more stable intermediates vary drastically among the oxidants (see Table I). Such behavior suggests the involvement of the anions themselves in the transient oxidation product. The water molecules coordinated at the positions axial to the planar ligand are not drawn in the structures given in (4) but are assumed.

$$\text{(structure)} + X_2^- \longrightarrow \text{(structure)} + X^- \quad (4)$$
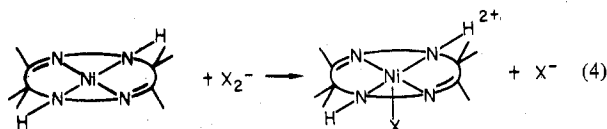
If oxidation does take place by an inner-sphere mechanism, an anion, X^-, from the radical, X_2^-, could remain coordinated for some time after the electron transfer (eq 4).

This indicates that Ni(II) macrocyclic complexes should be more axially labile than their Ni(III) derivatives. In fact, since the presence of Cl^- cannot significantly extend the lifetime of the short-lived $Ni[Me_6[14]-4,11-dieneN_4]^{3+}$ intermediate species when this complex is formed by direct oxidation with ·OH, one must assume that the axial H_2O is not as easily removed as in the corresponding Ni(II) complex. Moreover, comparable behavior can be expected for complexes of the isoelectronic ions Co(II) and Ni(III) with regard to axial substitution. Studies carried out on $Co^{II}LXY$ (L is a macrocyclic ligand) show that the aquation step of the "second ligand", as indicated in eq 5 and 6, has a rate constant $>10^3$ s^{-1}.[29]

$$CoLXY + H_2O \rightarrow CoL(OH_2)X^+ + Y^- \quad (5)$$

$$CoL(OH_2)X + H_2O \rightarrow CoL(OH_2)_2^{2+} + X^- \quad (6)$$
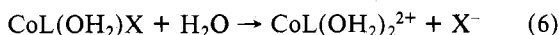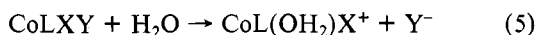
The long lifetimes obtained with Ni(III) complexes might be a consequence of the differences in the nature of the axial bond, e.g., a reduction of the repulsive Coulombic interaction, going from Co(II) to Ni(III) metal ions.[29,30]

Variation in the transformation rates of the short-lived transient oxidation product into the long-lived intermediate shows a large dependence on the ligand X^- already present (see eq 4 and Table I). Such an effect might be used as an indication that the dissociation or aquation of the metal–ligand X^- bond makes a significant contribution to the rate of conversion from the short-lived to the long-lived species. The influence of the macrocyclic ligand on the axial substitution rate is clear from the values obtained for $Ni[Me_6[14]aneN_4]^{2+}$ and $Ni[Me_6[14]-4,11-dieneN_4]^{2+}$ (Table I). Changes in steric hindrance at the reactive positions as a function of ligand could contribute to this effect.

Transients Generated by ·OH. The data presented above strongly argue that oxidation via the anion radicals produces short-lived Ni(III) intermediates in aqueous solution. Information pivotal to our understanding of ·OH reactions is provided by the observation that these Ni(III) species transform into long-lived intermediates whose spectral structures are identical with those generated by ·OH oxidation of the Ni(II) complexes. For both $Ni[Me_6[14]-1,4,8,11-tetraeneN_4]^{2+}$ and $Ni[Me_6[14]-4,11-dieneN_4]^{2+}$, oxidation by Br_2^- and ·OH yield the same levels of absorption for the long-lived intermediate. Comparing Br_2^- data for the oxidation of $Ni[Me_6[14]aneN_4]^{2+}$ with that from ·OH reaction indicates some loss of ·OH attack by processes other than electron transfer from the Ni(II) metal center, processes which do not give transient absorption in the range 300–600 nm. While in all three cases, oxidation by ·OH seems to produce short-lived Ni(III) species, the nature of the long-lived intermediates merits further attention. Certainly the EPR of frozen, irradiated $Ni[Me_6[14]-4,11-dieneN_4]^{2+}$ revealed the presence of a tripositive metal center produced by ·OH oxidation.

Barefield and Mocella have suggested that $Ni[Me_6[14]aneN_4]^{3+}$ produced in acetonitrile will, upon mixing with water, undergo deprotonation and electron transfer from an amine group to the metal center, according to the equilibrium indicated in eq 7.[9] They observed a peak red absorption with

$$\text{(structure)}^{3+} \rightleftharpoons \text{(structure)}^{2+} + H^+ \quad (7)$$
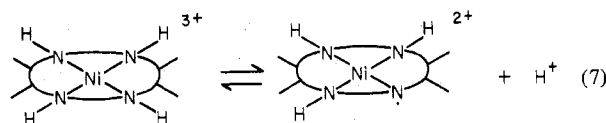
a maximum at 540 nm which they assigned to the radical, basing this assignment in part on ESR evidence obtained from flow-system studies in which acetonitrile containing the Ni(III) species was mixed with H_2O. The parent solid Ni(III) compound was reported to be green, and at pH 1–2 or in frozen solution a green, not red, intermediate was formed. Their absorption band at 540 nm is very similar in position to that obtained in this work via ·OH attack although the extinction coefficients differ considerably between these two species. An extinction coefficient of ca. 10^4 M^{-1} cm^{-1} was reported by these authors while we found ϵ for the $Ni[Me_6[14]aneN_4]^{2+}$ intermediate to be 1200 M^{-1} cm^{-1} obtained by Br_2^-. Moreover, the shift of the equilibrium (7) toward the Ni(III) species with increasing acid concentrations ($1 \leq pH \leq 11$) was not observed in our studies. The green product, obtained in the present studies by persulfate oxidation of aqueous $Ni[Me_6[14]-4,11-dieneN_4]^{2+}$, was characterized as the dieno complex with the same tetragonal structure as the bis(acetonitrile) derivative obtained by Olson et al. However, it should be noted that its preparation from aqueous solution may bring about binding of water molecules at the axial positions of the complex. We feel that the cumulative evidence strongly indicates that the species exhibiting the 540-nm absorption—whether powder or solution or whether generated by oxidizing radicals or other synthetic methods—is a Ni(III) complex. It might be suggested that in the flow system of Barefield and Mocella the rather long-lived red Ni(III) species undergoes degradation to produce a short-lived radical (see below) whose steady-state concentration in the flow cavity is sufficiently high to be observed by EPR.

The tripositive charge found here by ionic strength measurements for the long-lived oxidation products of the Ni-$[Me_6[14]-4,11-dieneN_4]^{2+}$ is not consistent with the structure of the free radical indicated in eq 7. The protonation of the radical would provide the required charge; nevertheless, protonation of a coordinated amine radical requires formation of a single-electron N–H bond and hence is not expected to take place in the range of acid concentrations used here. An
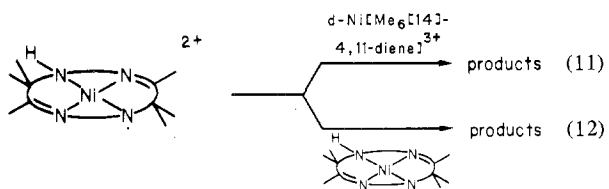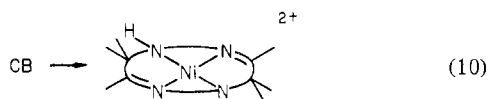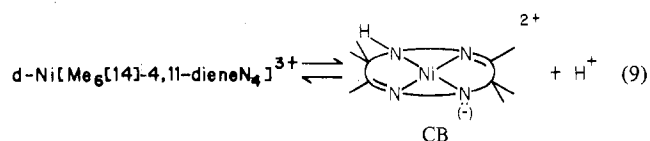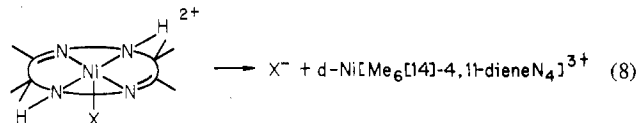
alternative explanation for generation of the 535-nm band in Ni[Me$_6$[14]-4,11-dieneN$_4$]$^{2+}$ via oxidation or addition of ·OH in imine groups can be safely rejected since intermediates with similar features were not produced in reactions with Ni-[Me$_6$[14]-1,4,8,11-tetraeneN$_4$]$^{2+}$. Additionally, the 540-nm band was observed for ·OH reaction with Ni[Me$_6$[14]aneN$_4$]$^{2+}$ where no imine groups are present.

In preliminary study of the diene and tetraene systems, it was noted that occurrence of the enhanced absorption at 535–540 nm for these complexes appeared to correlate with the flexibility of the ligand systems.[27] It was suggested that occurrence of the 530–540-nm band may reflect perturbation of the ligand structure but without loss of the 3+ charge of the central metal ion [eq 4 and 8]. The four double bonds of the tetraene ligand prevent any distortion, and in the Ni(III) form the ligand system would remain planar. The ane species has no double bonds to provide rigidity and hence would provide no stability for the planar precursor. Strong absorption below 400 nm is not observed here. The diene complex constitutes an intermediate case. With two double bonds it exhibits some rigidity and hence a source of some stability for the planar precursor which was observed in the low-wavelength band and which could transform only slowly to a perturbed structure (eq 8) where the d prefix indicates a distorted ligand. The transformation of Ni[Me$_6$[14]-4,11-dieneN$_4$]$^{3+}$ from green to red during warming appears to reflect a distortion in which the red species is trapped in the distorted configuration but in which relaxation occurs when placed in acetonitrile. If the disappearance of the blue band could be assigned to radical deprotonation (eq 7), there is little reason that the kinetics of the ane and diene intermediates should differ.

The assignment of the 535–540-nm band to a Ni(III) complex suggests that the associated distortion contributes to removal of the inversion center. This mechanism, namely, reduction of the microsymmetry of the metal-center environment, could increase the intensity of the symmetry-forbidden d–d transitions.[31–33] An example of such behavior has been demonstrated by the distinct spectra of Co(II) complexes with ligands in either planar or tetrahedral configuration.[33] Indeed, the brown isomer of the tetragonal (green) [Ni-[Me$_6$[14]-4,11-dieneN$_4$](OH$_2$)$_2$](ClO$_4$)$_3$ can be assigned as a species where the coordination sphere of Ni(III) has a reduced microsymmetry. It is feasible that the easy elimination of axially coordinated solvent, due to the strong Jahn–Teller effect in a d^7 configuration,[29] and the size of the metal center, smaller than Co(II), contribute to a distorted configuration. The structural distortion is also noticeable in the splitting of $g_\perp$ and its shift to $g_\perp > 2.20$.[34,32] Nevertheless, restrictions imposed by the rigidity of the framework of the macrocyclic ligand probably introduce limitations to the degree of the distortion. In retrospect, one may now suggest that the binding of X$^-$ to the Ni(III) complexes following X$_2^-$ oxidation serves to stabilize the planar configuration of the ligand system as opposed to assuming the perturbed arrangement.

Decay Processes of the Long-Lived Ni(III) Intermediates. The observed chemical transformation of the Ni[Me$_6$[14]-4,11-dieneN$_4$]$^{3+}$ intermediate to a more highly unsaturated product is in good agreement with reports of oxidative *ligand dehydrogenation* mechanisms which propose that metal centers in upper oxidation states are responsible for this kind of process. The long-lived stable intermediates found in these reactions suggest that the decay processes may have characteristics similar to those observed with oxidized metalloporphyrins[35] and Ni(III) and Ag(III) macrocycles[36] in which species with metal centers in upper oxidation states convert into cation radicals. The largely base-assisted decay observed with Ni[Me$_6$[14]-4,11-dieneN$_4$]$^{3+}$ indicates that the acid character of the dieno ligand might be enhanced by the highly

charged metal center. This observation has a parallel with the increase of the acidity in ammonia and amino groups when coordinated to tripositive or quadripositive metal ions.[37] In such a case, it is reasonable to suggest a base-assisted mechanism by which the oxidative dehydrogeneration of the [Me$_6$[14]-4,11-dieneN$_4$] ligand can proceed. The value of the equilibrium constant K for any such acid–base dissociation, step 9, would be very small. From the pH effect on the stability of the diene intermediate a limit of $K_{eq} < 10^{-9}$ M, may be set which is reasonable for the weak acidity of coordinated amino groups and $K \cdot k_{10} \simeq 10^{-5}$ s^{-1} M. This suggests that step 10 might be rather fast, namely $k_{10} > 10^4$ s^{-1}. Besides, the termination steps (11) and/or (12) should be even faster than (10) for a first-order decay of the long-lived intermediate in the mechanism indicated by reactions 8–12.

$$\longrightarrow \; X^- + \text{d-Ni[Me}_6\text{[14]-4,11-dieneN}_4]^{3+} \quad (8)$$

$$\text{d-Ni[Me}_6\text{[14]-4,11-dieneN}_4]^{3+} \rightleftharpoons \quad + \; H^+ \quad (9)$$

CB

$$CB \longrightarrow \quad (10)$$

$$\longrightarrow \text{products} \quad (11)$$
$$\longrightarrow \text{products} \quad (12)$$

The rapid decay of Ni[Me$_6$[14]-1,4,8,11-tetraeneN$_4$]$^{3+}$, compared to d-Ni[Me$_6$[14]-4,11-dieneN$_4$]$^{3+}$, is to be expected from differences in the ligand structure. In fact, the [Me$_6$-[14]-1,4,8,11-tetraenoN$_4$] ligand provides more easily dissociable hydrogens due to the simultaneous influence of two imine functions on the same methylene group (see eq 13).

$$\rightleftharpoons \quad + \; H^+ \quad (13)$$

CB

$$CB \longrightarrow \quad (14)$$
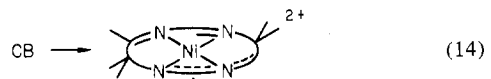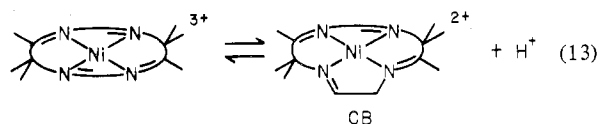
Besides, the conversion toward the Ni(II) cation ligand radical (eq 14) might be faster than with the [Me$_6$[14]dieneN$_4$] ligand (eq 10), because of the extended π system of the conjugated base. It should be noted that the mechanism proposed here for the oxidation of the Ni[[14]-4,11-dienN$_4$]$^{3+}$ (reactions 8–12) and Ni[[14]-1,4,8,11-tetraeneN$_4$]$^{3+}$ (reactions 13 and 14) predicts that oxidation of the ligand of Ni[Me$_6$[14]-aneN$_4$]$^{3+}$ should be slower than or as slow as the process with Ni[[14]dieneN$_4$]$^{3+}$.

Conclusions

Data presented here have shown that the central metal ion in Ni(II) macrocyclics may be readily oxidized through a variety of radiolytically generated agents: Cl$_2^-$, Br$_2^-$, (NCS)$_2^-$, and ·OH. Spectra of the oxidized complexes strongly indicate that Ni(III) macrocylics in water may exist either in the

well-established planar ligand form or in some distorted configuration. From ESR and ionic strength measurements it may be concluded that the proposed distorted form of the complex would retain its Ni(III) character though exhibiting an absorption band in the red region, at 535–540 nm. This band may well be due to removal of forbiddenness in d–d transitions which accompanies alteration in ligand system geometry. The planar ligands of these Ni(III) complexes may be stabilized against transformation to the distorted form either by (a) introduction of double bonds into the ligand system which reduces ligand flexibility or by (b) binding of the planar form—presumably at one of the axial positions—to an anion generated by reduction of the anion radical when Ni(III) is produced.

The strong dependence of Ni(III) macrocyclic lifetime on pH indicates that oxidation of the ligand to give a higher degree of unsaturation in the ligand system proceeds principally from a deprotonated form of the Ni(III) macrocyclic. Formation of cation radicals from direct ligand oxidation by ·OH, while not totally excluded from possibility, seems to be kinetically unfavorable. It is feasible that higher activation barriers make the ligand oxidation too slow to compete with the pathway that leads to the same kind of products through an oxidized metal center.

Note Added in Proof. We wish to thank Dr. Dan Meyerstein for kindly making available to us—prior to revision of this paper—the manuscript of which he is coauthor: "Oxidation of a Ni(II) Complex with an Unsaturated Macrocyclic Ligand in Aqueous Solutions. A Pulse Radiolysis Study". Where there is overlap in the two works, quite good agreement is found concerning experimental detail and most interpretations. Those areas in which interpretations do diverge should, we feel, provide the basis for further fruitful study.

Registry No. Ni[Me$_6$[14]aneN$_4$]$^{2+}$, 18444-42-3; Ni[Me$_6$[14]-4,11-dieneN$_4$]$^{2+}$, 18444-38-7; Ni[Me$_6$[14]-1,4,8,11-tetraeneN$_4$]$^{2+}$, 18444-46-7; [Ni[Me$_6$[14]-4,11-dieneN$_4$](OH$_2$)$_2$](ClO$_4$)$_3$, 67375-45-5; ·OH, 3352-57-6; Br$_2^-$, 12595-70-9; Cl$_2^-$, 12595-89-0; (NCS)$_2^-$, 66555-10-0.

Supplementary Material Available: Figure 2, decay of the transient absorption spectrum generated by reactions of ·OH with Ni[Me$_6$-[14]-4,11-dieneN$_4$]$^{2+}$; Figure 5, ionic strength effects; Figure 6, pH effects (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Ligand abbreviations: [Me$_6$[14]-4,11-dieneN$_4$], 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; [Me$_6$[14]-1,4,8,11-N$_2$], 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,4,8,11-tetraene; [Me$_6$[14]ane], 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecaane.
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