

which means that the associative process is sterically hindered in such cases.

These results can be accommodated for in terms of a net distortion of the metal-ligand bonds within the $\text{Ru}(\text{edta})\text{H}_2\text{O}^-$ complex due to hydrogen bonding between the free carboxylate oxygen and the coordinated water molecule.⁹ This results in the creation of an open area and accessible site for associative substitution. As mentioned before, this hydrogen-bonding effect may result in the partial labilization of the coordinated water molecule, such that the operation of an interchange (I_a) mechanism seems feasible. Furthermore, the absolute magnitude of ΔV^\ddagger is such that we cannot rule out the possibility of an I_a mechanism. In this respect it is interesting to note that ΔV^\ddagger for the anation of $\text{Pd}(\text{Me}_3\text{dien})\text{H}_2\text{O}^{2+}$ and $\text{Pd}(\text{Et}_3\text{dien})\text{H}_2\text{O}^{2+}$ by TU, Me_2TU , and Me_4TU has the values -9.3 , -9.1 , and -13.4 (Me_3dien), and -8.3 , -10.2 , and -12.7 (Et_3dien) $\text{cm}^3 \text{mol}^{-1}$, respectively.²⁵ The anation reactions of these sterically hindered diethylenetriamine (dien) complexes proceed via a limiting A mechanism that presumably involves a trigonal-bipyramidal transition state. These values are

in close agreement with those found in the present study. In both cases the observed ΔV^\ddagger consists of a volume decrease due to bond formation (increasing with the partial molar volume of the entering group) that is partially offset by an increase in volume due to bond lengthening. The latter is associated with the square-pyramidal to trigonal-bipyramidal transition during associative substitution of a square-planar complex and the labilization of the coordinated water molecule during the interchange (I_a) substitution process of the octahedral $\text{Ru}(\text{edta})\text{H}_2\text{O}^-$ complex, respectively. It follows that the reported values of ΔV^\ddagger can equally well support the operation of an I_a or A mechanism. However, in terms of the extraordinary pH dependence of the process, especially the suppression of the substitution reaction on protonation of the edta ligand, we prefer the operation of an interchange process where both distortion of the metal-ligand bonds and labilization of the coordinated water molecule contribute toward the observed lability.

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Nickel(I) and Nickel(III) Complexes of Substituted Tetraaza Macrocycles Formed by Pulse Radiolysis and Electrochemistry of Nickel(II) Precursors

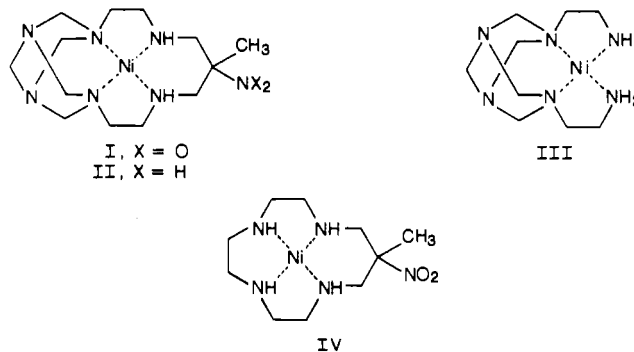
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The square-planar nickel(II) complexes of the ligands 8-methyl-8-nitro-1,3,6,10,13,15-hexaazatricyclo[13.1.1.1^{13,15}]octadecane, 8-amino-8-methyl-1,3,6,10,13,15-hexaazatricyclo[13.1.1.1^{13,15}]octadecane, 3,7-bis(2-aminoethyl)-1,3,5,7-tetraazabicyclo[3.3.1]nonane, and 9-methyl-9-nitro-1,4,7,11-tetraazacyclotridecane (I-IV) react rapidly with hydroxyl radicals and aquated electrons (e_{aq}). The initial transient products of these reactions decay via first-order kinetics within a few milliseconds in neutral aqueous solution at 22 °C in all cases. Electronic spectra and decay rate constants, as well as formation rate constants, are reported for all transients. Reaction of the nitro-substituted complexes with e_{aq} led to electron addition to the nitro group rather than to the metal center; otherwise, a Ni^{I} transient is observed. Following reaction with OH, the product of the initial decay remains a Ni^{III} species. This is more long-lived, and stabilization of Ni^{III} by axial coordination of the pendant amine in II is indicated. No notable stabilization of Ni^{I} or Ni^{III} from the presence of the bicyclic azamethylene "football" in I-III occurs. Cyclic voltammetry in acetonitrile identified both one-electron oxidation and one-electron reduction processes for the nickel(II) complexes, as well as nitro group reduction, where this group was pendant to the macrocycle.

Introduction

The study of the redox properties of nickel(II) macrocyclic complexes has received much attention in recent years.³⁻⁶ When complexed in its low-spin electronic configuration, nickel(II) may be readily oxidized or reduced in one-electron steps to nickel(III) or nickel(I), respectively, in nonaqueous solvents, although the products of these reactions are commonly unstable. Recently, we have developed the synthesis of a square-planar macrotricyclic nickel(II) complex (I).⁷ This ligand in the complex binds via two secondary nitrogen and two tertiary nitrogen donor atoms and contains a pendant nitro group as well as a "football"-shaped tricyclic structure comprising tertiary nitrogens connected by methylene linkages. An interesting feature from an electro-



chemical viewpoint is that this complex contains two competing sites for redox activity. It is well-known that nickel(I) can be formed from reactions of the nickel(II) species in aqueous solution with a reasonably strong reductant.^{8,9} The pendant nitro group

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is also electroactive, with several studies, generally including coupled ESR measurements, having been reported on the radical anions of nitro compounds.¹⁰⁻¹² Similarly, nickel(III) transients have been generated in situ via pulse and γ radiolysis.^{5,13-15} The nitro group has also been suggested to be capable of oxidation to its radical cation, on the basis of γ -radiolysis and ESR experiments.¹⁶

To allow a discrimination between nickel and nitro group reduction or oxidation, this study was extended to include II, in which the nitro group has been replaced by a primary amino group. This ensured that the only electroactive site on the molecule was the metal center and that any changes due to redox processes involved either nickel(I) or nickel(III) products. This must be qualified by saying that reactions involving powerful oxidants such as OH may also result in hydrogen abstraction competing with direct metal ion oxidation, and this result is inherently possible in the saturated ligands employed. The macrocyclic effect is also studied by comparisons of the two macrotricyclic complexes with their bicyclic precursor (III).¹⁷ To complete the study, a macro monocyclic analogue (IV) has been investigated to determine any effect of the bulky tricyclic structure in I on the redox chemistry of the complex. To complement the pulse-radiolysis experiments, complexes were investigated by voltammetry in acetonitrile solvent.

Experimental Section

Physical Methods. Cyclic voltammetry was performed with a Bio-analytical Systems Inc. CV-27 controller coupled with a Houston Instruments Omnigraphic 100 X-Y recorder. A glassy-carbon working electrode was employed with a silver-silver chloride or gold wire reference and a platinum counter electrode. All solutions contained dried sodium perchlorate in acetonitrile and were purged with argon or nitrogen. Ferrocene was employed as an internal reference, and potentials are cited versus SHE.

Pulse radiolysis experiments were performed with a Van de Graaff electron accelerator that delivered electron pulses (3 μ s) at ca. 1 MeV (1 eV = 1.60×10^{-19} J) through the thin wall of a 1 cm optical path cell, as previously described.¹⁸ Dosimetry was performed with an aerated aqueous solution of potassium thiocyanate, employing values of $\epsilon = 7600$ M⁻¹ cm⁻¹ (480 nm) and $G(\text{OH}) = G[(\text{NCS})_2^{\cdot-}] = 2.8$; a dose of approximately 40 Gy was observed. For experiments involving the aquated electron (e_{aq}), solutions of complexes (10^{-3} M) dissolved in triply distilled water contained *tert*-butyl alcohol (0.1 M) to act as a scavenger of OH radicals. Experiments with OH radicals were conducted in solutions saturated with nitrous oxide to scavenge e_{aq} .

Formation rate constants for reactions of e_{aq} with all complexes were determined by monitoring the decay kinetics of e_{aq} at 580 nm for at least four different concentrations of each complex, yielding the second-order rate constant from a plot of observed rate constant versus complex concentration. For reactions with OH radicals, the formation rate constants were determined via competition with thiocyanate for OH at various concentrations of both complex and thiocyanate. The optical density change due to formation of $(\text{SCN})_2^{\cdot-}$ at 450 nm was measured. The product of OH oxidation of each complex did not absorb significantly at the chosen wavelength. It can be shown that the complex formation rate constant (k_f) is related to the observed optical density change (ΔOD), the concentrations of complex ($[\text{C}]$) and thiocyanate ($[\text{SCN}^-]$), and the formation rate constant for the reaction of OH with thiocyanate ($k_f' = 6.6 \times 10^9$ M⁻¹ s⁻¹) via

$$\frac{1}{\Delta\text{OD}} = \frac{1}{\Delta\text{OD}'} + \frac{k_f}{k_f'(\Delta\text{OD}')} \frac{[\text{C}]}{[\text{SCN}^-]} \quad (1)$$

where $\Delta\text{OD}'$ is the optical density change in the absence of complex.

Table I. Electronic Spectral Maxima for Initial Transients Produced by Reaction of Nickel(II) Complexes with OH and e_{aq} in Water

precursor ^a	λ_{max} , nm (ϵ_{max} , M ⁻¹ cm ⁻¹)		ref
	e_{aq}	OH	
I	290 (640)	545 (410), 370 sh (~600), 310 (~1100)	<i>b</i>
II	360 (720)	545 (2900), 390 sh (~1200), 340 (~1800)	<i>b</i>
III	360 (540)	530 (620), 300 sh (~400)	<i>b</i>
IV	290 (3800)	520 (3400), 360 (~800), 310 (~2400)	<i>b</i>
Ni(teta) ²⁺		550 (1000), 380 sh (~600)	13
Ni(tetb) ²⁺	380 (5150)	550 (1200), ~380 (~1100), ~330 (~1300)	9, 20
Ni([14]dieneN ₄) ²⁺		535 (1000), 270 (~6000)	21
Ni(CRH) ²⁺		550 (700), 400 (~800), 320 (~1300)	22
Ni(cyclam) ²⁺	375 (4500)	545 (1000), 300 (2500)	8, 34
Ni(<i>N</i> -Me ₄ cyclam) ²⁺	355 (3150)		8
Ni(Me ₁₀ cyclam) ²⁺	335 (3600)		8

^a *teta* = *meso*-5,7,7,12,14,14-hexamethylcyclam; *tetb* = *rac*-5,7,7,12,14,14-hexamethylcyclam; Me₁₀cyclam = *C-meso*-1,4,5,7,7,8,11,12,14,14-decamethylcyclam; cyclam = 1,4,8,11-tetraazacyclotetradecane; *N*-Me₄cyclam = 1,4,8,11-tetramethylcyclam; CRH = *rac*-2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadecane-1,13,15-triene; [14]dieneN₄ = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. ^b This work; measured in water at 22 °C.

Table II. Formation and Decay Rate Constants for Initial Transients Produced by Reaction of Nickel(II) Complexes with e_{aq} and OH

pre-cursor	e_{aq}		OH	
	$10^{-10}k_f$, M ⁻¹ s ⁻¹	$10^{-3}k_d^a$, s ⁻¹	$10^{-9}k_f$, M ⁻¹ s ⁻¹	$10^{-3}k_d^b$, s ⁻¹
I	2.5	1.8	9.9	8.1
II	1.9	3.5	9.7	1.5
III	1.1	22	9.7	3.5
IV	5.0	3.5	9.9	3.6

^a Products of decay display no bands above 260 nm. ^b Products of decay Ni(III) species.

Absorbance spectra of transients were constructed from averaged sets of optical density changes measured immediately after the electron pulse at 5–20-nm intervals between 250 and 620 nm. Dosimetry permitted conversion of optical density changes into molar absorptivities, and addition of known spectra of precursor nickel(II) species permitted construction of absorption spectra of the transient species formed. First-order decay rate constants of these transients were determined at the most sensitive wavelengths from an average of several independent traces. The data were subjected to a standard least-squares program that calculated the first-order decay rate constants (k_d).

Compounds. The macrotricyclic complex I and its analogue II were prepared via nitroethane/formaldehyde condensations about the precursor III as previously described.⁷ Complex III was prepared from a literature synthesis.¹⁷ The macro monocyclic complex IV was prepared via a route similar to that described for I.¹⁹ All complexes were characterized by using nuclear magnetic resonance (¹H and ¹³C), infrared, and ultraviolet-visible spectroscopy. Satisfactory elemental analyses were obtained in all cases.

Results

Pulse Radiolysis. The transients produced via reaction of the Ni^{II} complexes with hydroxyl radicals and aquated electrons were characterized by electronic spectroscopy. The formation and decay rate constants of these transients were determined as described in the Experimental Section. Absorbance maxima of each transient, measured approximately 10 μ s after the pulse, are shown in Table I. Formation and decay rate constants of each transient, second and first order, respectively, were determined to an accuracy of approximately 10%. The data are given in Table II. It was apparent that all formation rates were effectively diffusion controlled.

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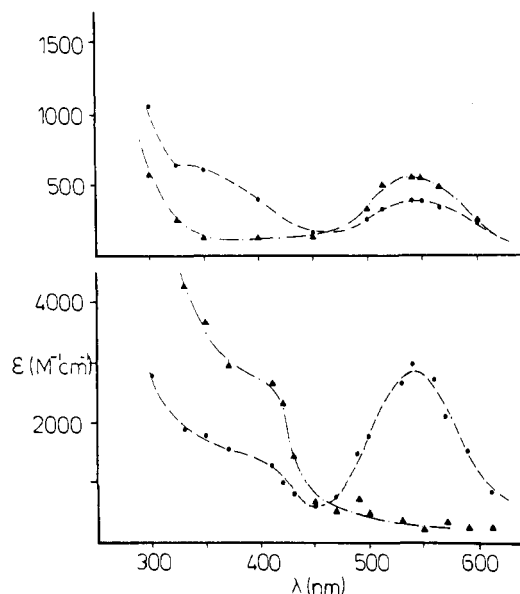


Figure 1. Electronic spectra of Ni^{III} complexes formed by the oxidation of Ni^{II} precursors with OH . Solutions of the perchlorate salts of complex (1×10^{-4} M) in triply distilled water were saturated with N_2O . Curves are shown (\bullet) $10 \mu\text{s}$ after the pulse and (\blacktriangle) 10ms after the pulse for I (top) and II (bottom).

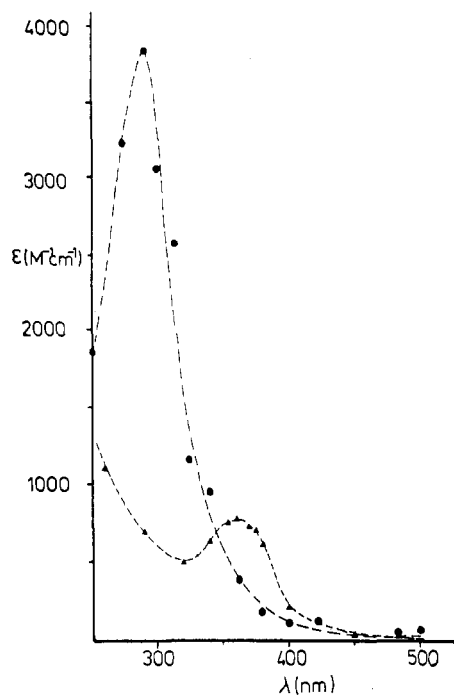


Figure 2. Electronic spectra of Ni^{I} compounds formed by the reduction of Ni^{II} precursors with e_{aq} . Solutions of the perchlorate salts (1×10^{-4} M) in triply distilled water contained 0.1M *tert*-butyl alcohol. Curves observed $10 \mu\text{s}$ after the pulse are shown for IV and II, complexes with and without a nitro substituent, respectively.

Initial decay processes occurred with half-lives of $<1 \text{ms}$. Further decay processes were indicated with the Ni^{III} complexes formed following OH oxidation, but accurate measurements were not accessible with our facility. Nevertheless, these processes were apparently complete within seconds, or less than 1min in all cases. This behavior largely parallels that observed earlier with oxidation of the Ni^{II} complex of *tetb* (*rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) and was not pursued.²⁰ The behavior of compound II with the OH radical differs notably from the others. Whereas the nitro-substituted macrocycles produce

Table III. Cyclic Voltammetry of Nickel(II) Complexes in Acetonitrile^a

compd	$E_{1/2}, \text{V}^b$	$\Delta E, \text{mV}$	i_a/i_c	assgnt ($n^e = 1$)
I	+1.74	irrev		$\text{Ni}^{\text{II}} \rightarrow \text{Ni}^{\text{III}}$
	-0.86	irrev		$-\text{NO}_2$ redn
	-1.09	irrev		$-\text{NO}_2$ redn
	-1.29	80	1.0	$\text{Ni}^{\text{III}} \rightarrow \text{Ni}^{\text{I}}$
II	+1.37	irrev		$\text{Ni}^{\text{II}} \rightarrow \text{Ni}^{\text{III}}$
	-1.30	120	1.0	$\text{Ni}^{\text{III}} \rightarrow \text{Ni}^{\text{I}}$
III	+1.49	90	1.1	$\text{Ni}^{\text{II}} \rightarrow \text{Ni}^{\text{III}}$
	-1.11	110	1.0	$\text{Ni}^{\text{III}} \rightarrow \text{Ni}^{\text{I}}$
IV	+1.11	~ 300	~ 2	$\text{Ni}^{\text{II}} \rightarrow \text{Ni}^{\text{III}}$
	-1.02	irrev		$-\text{NO}_2$ redn ^d
	-1.24	irrev		$-\text{NO}_2$ redn ^d
	-1.38	irrev		$\text{Ni}^{\text{III}} \rightarrow \text{Ni}^{\text{I}}$

^a Measured at ambient temperature; 0.1M NaClO_4 electrolyte; ferrocene used as an internal reference. ^b Cited versus SHE; for irreversible processes, the wave maximum is given. ^c Number of electrons in the process estimated by wave height comparisons with known compounds and by internal comparisons. ^d An approximately two-electron oxidation process assigned to reoxidation of nitro reduction products was observed near 0V on reversal of cathodic scans.

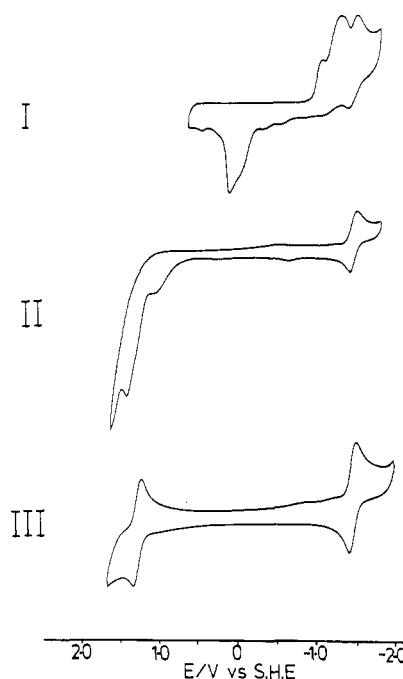


Figure 3. Cyclic voltammograms for Ni^{II} complexes I–III in acetonitrile containing 0.1M NaClO_4 , determined at ambient temperature. The complications due to the nitro group in I compared with the case of II are obvious, as is the definition of both $\text{Ni}^{\text{II/III}}$ and $\text{Ni}^{\text{III/I}}$ processes.

transients that show rapid and considerable first-order decrease of the absorbance in the range $300\text{--}450 \text{nm}$ while retaining the major absorbance at 550nm , the amine-substituted macrocycle complex exhibits an initially similar spectrum that shows an increase in absorption in the $300\text{--}450\text{-nm}$ region while effectively losing the band near 550nm (Figure 1). This variation is apparently associated with the availability of a coordinating pendant amine in II alone, as discussed later. Reactions with e_{aq} lead to distinctly different behavior when a nitro group is pendant to the ring, as in I and IV, compared to the behavior when no such substituent is present (Figure 2). The role of the nitro substituent in the chemistry is also discussed below.

Electrochemistry. All four Ni^{II} complexes exhibited one-electron metal-centered oxidation and reduction reactions in acetonitrile. These couples were not observed in water, being generally beyond the solvent limit. The complexes with nitro substituents showed extra waves due to reduction and eventual reoxidation of the nitro group and the nitro radical anion, respectively. The reoxidation of these radicals or their decay products complicates the simple metal-centered oxidation processes observed in II and III, and

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several anodic waves are observed in cyclic voltammograms of the nitro-substituted complexes I and IV. Data from cyclic voltammetry are collected in Table III. The complications to the redox behavior are clearly seen in the comparative voltammograms for I-III, shown in Figure 3.

Discussion

Nickel(III) from OH Oxidation. Initial products of hydroxyl radical oxidation displayed qualitatively similar absorption spectra (Table I). The spectra are similar to several previously characterized nickel(III) macrocycle spectra generated radiolytically, and hence the transients observed here can be assigned as nickel(III) complexes.^{13,20-22} Comparisons with literature spectra appear in Table I, where all spectra were determined in the absence of coordinating anions in solution. It has been demonstrated that sulfate ions may coordinate in the axial positions of Ni(cyclam)²⁺ (cyclam = 1,4,8,11-tetraazacyclotetradecane) and Ni(tetb)²⁺ to produce species that do not absorb strongly in the visible region of the spectrum, although these are not the initial products.^{20,23} The sulfato complex of (tetb)Ni^{III} is relatively stable and has been assigned as octahedral, whereas the ion formed in the absence of sulfate is believed to be square pyramidal, with a water molecule occupying the fifth coordination site depending on the pH of the solution.²⁰

For I and IV, the initial transient, arising from oxidation of the Ni^{II} center to Ni^{III} prior to spectroscopic characterization, decays by a first-order process (rate constant $\sim 2 \times 10^3 \text{ s}^{-1}$) with a decrease in absorbance in the region 300–450 nm (Figure 1). This behavior parallels that previously observed with Ni(tetb)³⁺, where this change (rate constant $2.6 \times 10^3 \text{ s}^{-1}$) has been assigned to a rearrangement or isomerization reaction that preserves the integrity of the Ni^{III} ion.²⁰ A slower process follows, in which oxidation of the ligand by the Ni^{III} center is the most likely chemistry. The assignment of the first process in the macrocycle complexes is supported by the behavior of nonmacrocylic III, which displays different behavior with the shoulder at 400 nm increasing rather than decreasing. This may not be surprising since the ligand of III is not macrocyclic and may adapt to conformational or configurational changes in ways different from those of the more structurally rigid macrocyclic relatives.

The behavior of compound II, where a primary amine is pendant to the macrocycle, differs substantially. The initial transient itself is essentially the same, indicating that the same oxidation of Ni^{II} to Ni^{III} occurs. This is followed, however, by a marked decrease of the major absorbance band at 550 nm and an increase in the 300–450-nm region. This "reverse" behavior is qualitatively similar to that observed by unsubstituted or simply alkyl-substituted macrocycles bound to nickel(III) in the presence of sulfate ion, where a relatively stable octahedral Ni(macrocycle)(SO₄)₂⁻ complex is formed during the first-order decay of the initial transient.^{20,23} In the case of II, no added coordinating anions are present. However, the primary amine pendant to the ring is capable of coordination to Ni^{II} as an axial ligand in analogous complexes.²⁴ It is possible that the transient formed following the initial decay is in this case an octahedral ion with the primary amine occupying one axial site and a water molecule in the sixth site. There is evidence that axial coordination by pendant arms can stabilize Ni^{III},²⁵ supporting the assignment. The lifetime of the second species is not exceptionally long, however (decay in <1 min estimated, but not measured), supported by the fact that we have not yet been able to isolate a Ni^{III} complex from chemical oxidation.

Voltammetry indicated a Ni^{II/III} oxidation occurs in acetonitrile for all four complexes studied. All processes were detected at

potentials more positive than +1 V (versus SHE) and with the exception of III gave completely irreversible waves; i.e., no cathodic process was observed near the anodic wave upon switching the scan direction. A quasi-reversible couple observed with the acyclic molecule III may reflect greater flexibility and adaptability to change in coordination geometry. A similar effect has been noticed in the redox behavior of acyclic copper(II) complexes compared with that of macrocyclic analogues, with the former exhibiting quasi-reversible and the latter irreversible voltammetric behavior, assigned in that case to the inability of the macrocycles to adapt to a change in coordination geometry.²⁶ The irreversible oxidations observed in the voltammetry of the complexes studied here are consistent with a rapid reaction following oxidation, and this supports the pulse-radiolysis results.

Nickel(I) and Nitro Radicals. There is an obvious difference in the reaction of e_{aq} when a nitro group is pendant to the macrocycle ring. With such a pendant, an absorption maximum at 290 nm is observed (in I and IV), whereas otherwise a maximum at 360 nm is observed (in II and III). Several Ni^I aza macrocyclic complexes have been observed before and display a maximum in the range 335–380 nm (Table I).^{8,9} The spectra of the d⁹ Ni^I complexes are qualitatively similar to those of pseudo-square-planar copper(II) macrocycles, with the main transition being presumably ²T₂ ← ²E, split under the influence of a tetragonal distortion. One presumes only a small change in coordination geometry upon reduction, since both low-spin d⁸ and low-spin d⁹ complexes prefer a planar arrangement of ligands around the metal ion. However, the bond lengths would be expected to be significantly longer in the paramagnetic product than in the diamagnetic precursor.^{7,26} Thus, accommodating the metal ion in the ligand cavity would be difficult, and this results in relatively short-lived species, since the larger ion would tend to dissociate from the ligand.

It has been found that Ni^I macrocycles are stabilized by alkaline solution and also by methylation of the ligand, but this was not pursued here. Certainly, the azamethylene "football" in II and III does not alter the lifetime of the Ni^I ion markedly alone.

The spectra of I and IV transients from reaction with e_{aq} are unquestionably characteristic of a nitro radical (–NO₂[•]). Although there have been several reports of radiolytic studies of nitro radical anions, most have been concerned with purely organic systems.¹⁰⁻¹² These studies generally employed ESR spectroscopy to characterize the nitro radical anion, usually attached to an aromatic ring. A report of reactions of (*o*-, *m*-, and *p*-nitrobenzoato)pentamminecobalt(III) complexes with e_{aq} detected nitro radical anions as intermediates in the reduction of the cobalt(III) center to cobalt(II).²⁷ The intermediate displayed an ultraviolet maximum at 330 nm, and the intermediate decayed by a first-order process in an intramolecular electron transfer followed by metal–ligand dissociation. In this study, the absorbance due to –NO₂[•] occurs at 290 nm. This shift in wavelength is to be expected, as the macrocyclic ligand is saturated whereas the conjugated nitrobenzoate ion has the stabilizing aromatic system adjacent to the nitro group. A blue shift is expected and observed. Similar maxima have been observed in reactions of e_{aq} with Cu^{II} and Co^{III} complexes of nitro-substituted macrocycles.²⁹ The observed decay we see may involve intramolecular reduction of the metal center by the radical anion, since this type of chemistry is known, although no Ni^I species with sufficient lifetime to be detected spectrophotometrically forms. An unusual observation was made in that the extinction coefficient of the absorption for the nitro radical anion in the transient from I with one-fifth the value of its analogue from IV. Therefore, it appears that there is a competition for e_{aq} between the Ni^{II} center and the nitro group, resulting in a lower yield of radical anion. Although no Ni^I band was observed around 360 nm, the more intense radical

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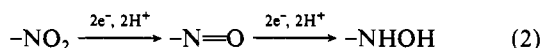
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absorbance may easily mask this band because of its close proximity.

Voltammetry identified Ni^{II/I} couples in all four complexes, with quasi-reversible behavior seen except for the case of IV, where the smaller cavity may be less appropriate for Ni^I, promoting irreversible behavior. It appears that the nickel(I) species are significantly more stable in aprotic solution than the nickel(III) species, from voltammetric behavior. However, the reverse appears to be the case in aqueous solution with no evidence of nickel(I) remaining ~100 μs after the pulse.

The nitro group electrochemistry of I and IV was also studied. While there have been several reports³⁰⁻³² of nitro group electrochemistry, electrochemical studies of nitro groups on coordinated ligands have appeared only recently.^{26,33,34} In aqueous solution nitro groups are electrochemically reduced in two steps to hydroxylamine



This appears as a single, four-electron wave usually and is clearly irreversible. This typical behavior was observed for I and IV in water, reduction occurring at -0.91 V versus Ag/AgCl in both cases. The redox behavior of the nitro group in acetonitrile was

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quite different. In the voltammograms of I and IV, two one-electron steps are observed near -1.1 V versus Ag/AgCl, and the process is irreversible. The aprotic conditions clearly make a mechanism such as eq 2 unreasonable, since a ready source of protons is not available. Only upon the addition of an anhydrous acid is a multielectron wave at a more positive potential observed. The two steps seen in acetonitrile presumably relate to reduction to a radical anion and then to a dianion. This has been observed in the nonaqueous electrochemistry of nitro aromatic compounds where delocalization of the negative charge is possible.³⁰ However, such a reaction on a saturated system would seem less likely at face value. It is possible that there is some metal-nitro anion interaction that acts to stabilize the radical via an axial metal orbital overlap with the pendant nitro group orbitals.

Conclusions

It is apparent that a pendant nitro group on a saturated ligand coordinated to Ni^{II} is an effective trap for e_{aq}⁻, forming an intermediate with a nitro radical anion. In the absence of the nitro group, the Ni^{II} center is readily reduced by e_{aq}⁻ to its monovalent state. Rapid first-order decay processes operate in either case. With OH, the first observable species is a Ni^{III} compound in all cases studied, and this rapidly reacted by a first-order process. Both Ni^{III/I} and Ni^{III/III} processes were observed voltammetrically, but only in aprotic solution. The unusual tricyclic "football" structures in I-III did not appear to offer any added stabilization to either Ni^I or Ni^{III} complexes, when compared with other known compounds. However, there is clear evidence that the amine pendant on II can act to stabilize a Ni^{III} species, presumably by acting as an axial ligand for an octahedral ion.

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Transition-Metal Pteridine Complexes. Preparation and Characterization of Cobalt(II) Pteridines

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The formation, isolation, and structural characterization of cobalt(II) pteridine complexes are described. The ligands are 4-oxopteridines with substituents at the 2-, 6-, and 7-positions of the pteridine core. Electronic and infrared spectral data on the series of complexes indicate that the pteridine ligands are coordinated to divalent cobalt via the oxygen atom in the 4-position and the pyrazine ring nitrogen in the 5-position. Two cobalt complexes of the chelate 2-(ethylthio)-4-oxopteridine (ethp) have been structurally characterized by single-crystal X-ray diffraction. Co(ethp)₂(H₂O)₂·2DMF (DMF = *N,N*-dimethylformamide) crystallizes in the triclinic space group *P* $\bar{1}$ with cell dimensions *a* = 7.468 (3) Å, *b* = 8.358 (3) Å, *c* = 12.309 (4) Å, α = 101.46 (2)°, β = 94.44 (2)°, and γ = 101.93 (2)° defining a volume of 731.1 (5) Å³ for *Z* = 1. The cobalt atom sits on the crystallographic inversion center, placing the two pteridine chelates in a trans configuration and the aquo ligands in the remaining axial sites of a distorted octahedron. Co(ethp)₂(imid)₂ (imid = imidazole) crystallizes in the monoclinic space group *C*2/*c* with cell parameters *a* = 22.329 (4) Å, *b* = 16.096 (3) Å, *c* = 13.205 (2) Å, and β = 129.84° defining a volume of 3644 (1) Å³ for *Z* = 4. The cobalt in this complex also has distorted-octahedral geometry, but the chelating pteridine ligands occupy cis positions, leaving two cis coordination sites for the imidazole ligands. The Co-N bond lengths to the pteridine ligands increased by 0.08 Å from the aquo to the imidazole complex, apparently resulting from imidazole coordination trans to this bond.

Pteridines are fused-ring nitrogen heterocyclic compounds that are ubiquitous in nature. They are found as the core structures of folic acid and flavin adenine dinucleotide (FAD) and function as cofactors for enzymes involved in hydroxylation¹ and methyl transfer,² as redox mediators,³ and as pigments for eyes and wings in certain insects.⁴ Variation of the substituents on the pteridine core of folates has provided a synthetic anticancer drug, metho-

trexate.⁵ The majority of the naturally occurring pteridine compounds have the 2-amino-4-oxo substitution pattern on the

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