admixture of the D form. Racemic crystals were thus isolated, probably due to a lower solubility of the centrosymmetric substance.) Intensity data were collected by using a Hilger & Watts diffractometer (Mo Kα radiation, θ–2θ scan technique, $2\theta \leq 56°$, 3533 observed reflections with $I \geq 2\sigma(I)$). The structure was solved by Patterson and difference Fourier syntheses. The O(1), O(2), O(3), C(4A), and C(4B) atoms (see Figure 3) appeared disordered by two positions each, which were refined independently with a fixed occupancy factor of 0.5. The positional and anisotropic thermal parameters of all non-hydrogen atoms were refined (including H atoms as fixed contributions in calculated positions) to $R_f = 0.059$ and $R_{wF} = 0.065$.

Registry No. 1, 5874-58-8; **2**, 116279-38-0; **6** (R = $PhCH_2$), 116324-20-0; CP, 100-70-9; (*S*)-L^1, 116279-36-8; (*S*)-$L^1 \cdot 2HCl$, 116279-39-1; (*S*)-L^2, 113443-54-2; (*S*)-L^3, 116279-37-9; (*S*)-$L^3 \cdot 2HCl$, 116279-40-4; CuL^1, 116324-25-5; CuL^2, 116324-24-4; CuL^3, 116324-23-3; $[(CuL^2H_{-1})_2(NO_3)]^+NO_3^-$, 116324-22-2; picolinamide, 1452-77-3; picolinic acid, 98-98-6; 4-nitrophenyl picolinate, 74104-89-5; methyl glycinate, 616-34-2; methyl (*S*)-(*N*-benzoylprolyl)glycinate, 113443-55-3.

Supplementary Material Available: Tables of atomic coordinates, all bond distances and angles, and thermal parameters (5 pages). Ordering information is given on any current masthead page.

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Kinetics and Mechanism of the Ligand Substitution Reactions of Ethylenediaminetetraacetate Complexes of Ruthenium(III) in Aqueous Solution

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The kinetics of the substitution reactions of $Ru(edta)H_2O^-$ with SCN^-, N_3^-, thiourea, and substituted thiourea were studied as a function of pH (2–9), temperature (20–45 °C) and pressure (0.1–100 MPa). The activation parameters at pH 5 fall in the ranges $22 \leq \Delta H^{\ddagger} \leq 37$ kJ mol^{-1}, $-105 \leq \Delta S^{\ddagger} \leq -99$ J K^{-1} mol^{-1}, and $-12 \leq \Delta V^{\ddagger} \leq -7$ cm^3 mol^{-1} and support the operation of an associative ligand substitution mechanism. The results are discussed in terms of the extraordinary lability of the $Ru(edta)H_2O^-$ species, and arguments are presented in favor of an I_a mechanism.

Introduction

Our general interest in the substitution behavior of transition-metal edta (ethylenediaminetetraacetate) complexes was stimulated by reports on the catalytic activity of such complexes, especially those of Fe(II) and Fe(III), in the simultaneous removal of NO_x and SO_2 from flue gases of coal-fired power plants.[2–4] Furthermore, the edta ligand is generally used to remove traces of free metal ions that may, for instance, catalyze oxidation processes.[5] In such cases it is usually accepted that this ligand blocks off all of the coordination sites. However, many studies in recent years have shown that this is not necessarily the case, since edta can coordinate with between one and six donor atoms to the metal center, leaving the remaining coordination sites free for eventual catalytic activity.[6]

Preliminary studies on the substitution reactions of Fe^{III}(edta) in our laboratories revealed that many of these reactions are either too fast for conventional stopped-flow measurements or exhibit almost no UV–vis spectral changes.[7] In order to gain more insight into the fundamental nature of such substitution processes, we first studied the substitution behavior of the corresponding Ru(III) complex. This complex is significantly less reactive than the corresponding Fe(III) species, and the substitution reactions are accompanied by significant spectral changes. Furthermore, when Ru(III) is bound to edta, its lability is increased to such an extent (by at least 7 orders of magnitude) that it undergoes substitution more rapidly than Ru(II).[8] The edta complex of Ru(III) has been shown to be pentadentate in aqueous solution, for which the sixth coordination site of the metal center is occupied by a water molecule at low pH or by a hydroxide ion at high pH.[9] The complex exhibits two characteristic pK_a values, which are associated with the following equilibria:[10,11]

$$\mathrm{Ru(Hedta)H_2O} \overset{K_1}{\rightleftharpoons} \mathrm{Ru(edta)H_2O^-} + \mathrm{H^+} \qquad pK_1 = 2.4 \tag{1}$$

$$\mathrm{Ru(edta)H_2O^-} \overset{K_2}{\rightleftharpoons} \mathrm{Ru(edta)OH^{2-}} + \mathrm{H^+} \qquad pK_2 = 7.6 \tag{2}$$

Kinetics studies[9,12,13] on the substitution (anation) behavior of these complexes clearly indicate a maximum reactivity at $4 < \mathrm{pH} < 6$, where the observed rate constant is practically independent of pH. This was ascribed to the extreme lability of $Ru(edta)H_2O^-$ for which the specific ligand geometry enables an associative substitution mode.[9] However, the reason for this high lability is still unsettled in the literature.[6] In contrast, the corresponding reactions of the Ru(II) analogue are significantly slower and suggested to proceed according to a dissociative mechanism.[9,14,15]

In an effort to contribute toward the understanding of the high lability of Ru(III)–edta complexes, we have undertaken a systematic study of the substitution behavior of this complex with a series of nucleophiles. Some uncharged nucleophiles were selected in order to minimize electrostriction effects that may affect the interpretation of the activation parameters, especially the entropy and volume of activation.[16]

Experimental Section

Materials. $K[Ru(Hedta)Cl] \cdot 2H_2O$ was prepared from $K_2[RuCl_5(H_2O)]$ as described in the literature.[14,17] This complex was charac-

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Table I. Electronic Spectra of $Ru^{III}(edta)L$ Complexes[a]

complex	λ_{max}, nm	ϵ_{max}, $M^{-1}\ cm^{-1}$
$Ru^{III}(edta)H_2O^-$	350 sh	680 ± 30
	280	2800 ± 70
		3000 ± 200[b]
$Ru^{III}(edta)(thiourea)^-$	466	1960 ± 20
$Ru^{III}(edta)(DMTU)^-$	478	1920
$Ru^{III}(edta)(TMTU)^-$	474	2160
$Ru^{III}(edta)(SCN)^{2-}$	460	1010 ± 50
	358	974
	283	3000 ± 50
$Ru^{III}(edta)(N_3)^{2-}$	445	2010 ± 40
	448	2000[c]

[a] Measured in acetale buffer, pH 5.0, μ = 0.2 M (Na_2SO_4); DMTU = dimethylthiourea, and TMTU = tetramethylthiourea. [b] Reference 14. [c] Reference 22.

terized by using spectroscopic (IR and UV–vis) and analytical techniques.[18] In aqueous solution it hydrolyzes rapidly to $Ru(Hedta)H_2O$[14] for which the spectroscopic and kinetic data were in excellent agreement with those reported for an isolated sample of $Ru(Hedta)H_2O{\cdot}4H_2O$.[9] All other chemicals were of analytical reagent grade, and deionized water (Millipor) was used throughout this study. Acetate, citrate, phosphate, and borate buffers[19] were used to control the pH of the test solutions, and Na_2SO_4 was used to adjust the ionic strength (see Discussion).

Measurements. The substitution reactions were followed spectrophotometrically by using a Shimadzu UV 250 spectrophotometer and a Durrum D 110 stopped-flow instrument, at the absorption maximum of the substitution product. Kinetic measurements at elevated pressure (up to 100 MPa) were performed on a homemade high-pressure stopped-flow unit.[20] All the instruments used for kinetic measurements were thermostated to ±0.1 °C. The absorbance–time plots were analyzed with the aid of a data acquisition system,[21] and the corresponding first-order plots were linear for at least 2–3 half-lives of the reaction. pH measurements were carried out with a Radiometer PHM 64 instrument.

Results and Discussion

A series of preliminary experiments were performed in order to check the general procedures and conditions adopted in our investigations. Aquation of $Ru(Hedta)Cl^-$ occurs immediately on dissolving the potassium salt, and the kinetic behavior of the resulting aqua complex is in agreement with the earlier reported data.[9] The addition of other potential ligands, either as buffer components or to control the ionic strength of the medium, had no significant effect on the behavior of the system when these were added to the solution containing the entering nucleophile prior to mixing within the stopped-flow apparatus. The nucleophilicity of the selected ligands is so high that the interference of relatively high concentrations of the buffer and ionic strength components can be neglected.[12] The selected ligands are SCN^-, N_3^-, $SC(NH_2)_2$, $SC(NHMe)_2$, and $SC(NMe_2)_2$. On reaction with $Ru(Hedta)H_2O$, the produced products exhibit characteristic UV–vis spectra (see Table I). In some cases slow subsequent reactions are observed: the complex $Ru(edta)N_3^{2-}$ for instance undergoes an electron-transfer reaction to produce $Ru^{II}(edta)N_2$ and $(Ru^{II}(edta))_2N_2$;[14,22] during the reaction with SCN^- formation of 1:2 and 1:3 complexes takes place over a longer time scale when excess thiocyanate is used.

The observed pseudo-first-order rate constant depends on the concentration of the entering ligand and the pH of the solution. In general k_{obs}, the pseudo-first-order rate constant, increases linearly with increasing [L] as demonstrated for a few typical examples in Figure 1. The plots exhibit no meaningful intercepts, indicating that the reactions go to completion under the selected conditions. The pH dependence of the process (Figure 2) is associated with the substitution lability of the various edta complexes in equilibria 1 and 2, as indicated in reactions 3–5. According to this reaction scheme k_{obs} can be expressed as in (6).

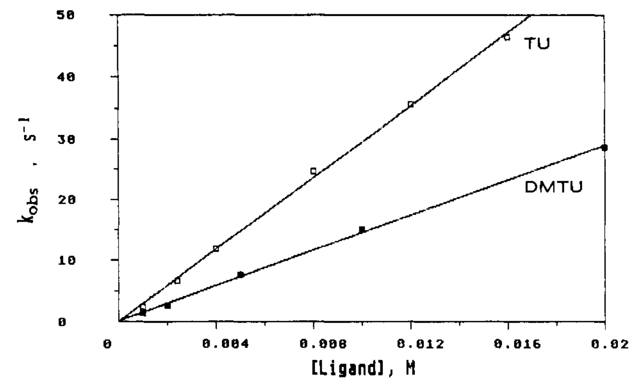

Figure 1. Dependence of k_{obs} on [L] for the reaction of $Ru(edta)H_2O^-$ with a series of ligands. [Ru(III)] = 1×10^{-4} M; pH 5.0 ([acetate buffer] = 0.1 M); ionic strength = 0.2 M (Na_2SO_4); temperature = 25 °C.

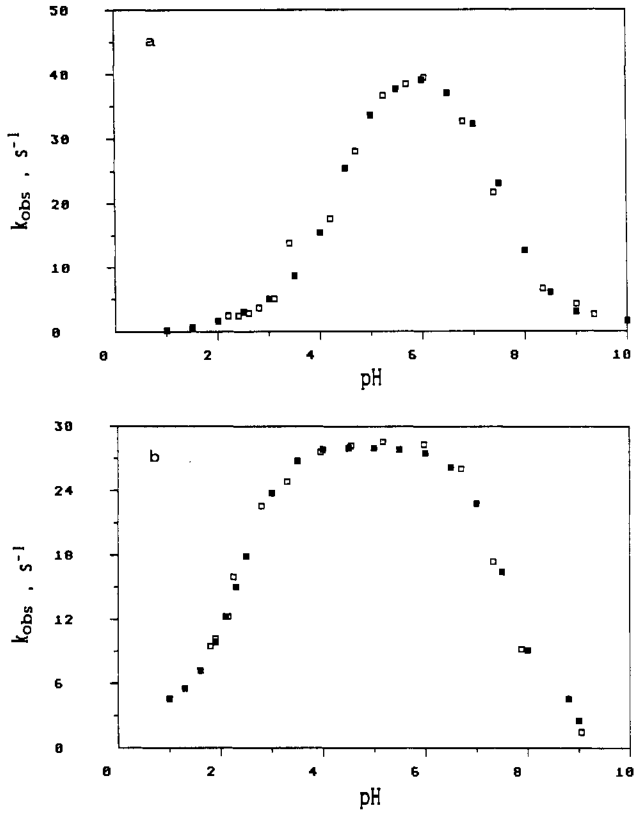

Figure 2. Variation of k_{obs} with pH for the reaction of $Ru(edta)H_2O^-$ with L: (a) L = N_3^-; (b) L = DMTU; (□) observed rate constant; (■) calculated by using resolved rate constants. [Ru(III)] = 1×10^{-4} M; [L] = 2×10^{-2} M; ionic strength = 0.2 M (Na_2SO_4); temperature = 25 °C.

$$Ru(Hedta)H_2O + L \xrightarrow{k_1} Ru(Hedta)L + H_2O \qquad (3)$$

$$Ru(edta)H_2O^- + L \xrightarrow{k_2} Ru(edta)L^- + H_2O \qquad (4)$$

$$Ru(edta)OH^{2-} + L \xrightarrow{k_3} Ru(edta)L^- + OH^- \qquad (5)$$

$$k_{obs} = \frac{(k_1[H^+]^2 + k_2K_1[H^+] + k_3K_1K_2)[L]}{[H^+]^2 + K_1[H^+] + K_1K_2} \qquad (6)$$

At high $[H^+]$, eq 6 reduces to $k_{obs} = k_1[L]$, whereas at low $[H^+]$ it reduces to $k_{obs} = k_3[L]$. This means that the pH dependence

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of k_{obs} should enable the estimation of k_1, k_2, and k_3. Indeed, Matsubara and Creutz[9] reported a bell-shaped pH dependence wtih a maximum value in the range $4 < pH < 6$ (i.e., where $k_{obs} = k_2[L]$) and minimum values at $pH \leq 1$ ($k_{obs} = k_1[L]$) and $pH \geq 9$ ($k_{obs} = k_3[L]$. The two inflections in the bell-shaped curve occur exactly at the pK_1 and pK_2 values. A similar result was found for the substitution reactions studied in this investigation. Two typical examples for the substitution by azide and dimethylthiourea are presented in Figure 2. It can be clearly seen that the bell-shaped curve exhibits inflections at pH = pK_1 and pK_2, with maximum values of k_{obs} in the range $4 < pH < 6$, i.e., where $k_{obs} = k_2[L]$ for the DMTU case. Furthermore, it follows that k_1 and k_3 are significantly smaller than k_2; for instance $k_1 = 130$ M^{-1} s^{-1} and $k_3 = 75$ M^{-1} s^{-1} compared to $k_2 = 1.42 \times 10^3$ M^{-1} s^{-1} for the substitution by dimethylthiourea. The latter values were obtained by plotting limiting forms of eq 6 as a function of $[H^+]$ at pH <5 and at pH >5, which resulted in k_2 values of 1.43 × 10^3 and 1.41 × 10^3 M^{-1} s^{-1}, respectively.

For the reaction of $Ru^{III}(edta)H_2O^-$ with N_3^-, the observed first-order rate constant remains constant over a smaller pH range, viz. form 5.5 to 6.5, due to the interference of the protonation of N_3^- at pH <5.5 since the pK_a of HN_3 is 4.34 (see Figure 2a). The decrease observed above a pH of 6.5 can once again be ascribed to the deprotonation of the coordinated water molecule to produce the less labile hydroxo species. A fit of the data over limited pH ranges resulted in rate constants of 1 ± 2 and 230 ± 15 M^{-1} s^{-1} for the reaction of HN_3 with $Ru(Hedta)H_2O$ and $Ru(edta)H_2O^-$, respectively, and in (2.1 ± 0.1) × 10^3 and 75 ± 10 M^{-1} s^{-1} for the reaction of N_3^- with $Ru(edta)H_2O^-$ and $Ru(edta)OH^{2-}$, respectively. These results clearly demonstrate the high lability of the $Ru(edta)H_2O^-$ species as well as the expected difference in nucleophilicity of HN_3 and N_3^-.

On the basis of the observed pH dependence of the process, temperature and pressure dependence studies were performed at pH 5–6, i.e., where a minor change in pH due to change in temperature and pressure will have no significant effect on k_{obs}. The observed rate data are summarized in Table II and the corresponding rate parameters in Table III. The slightly different rate and activation parameters reported for the reaction with azide at pH 5 are due to a minor contribution from the reaction with HN_3 under such conditions. The extraordinary substitution reactivity of $Ru(edta)H_2O^-$ is of primary importance in the interpretation of the reported activation parameters. The values of ΔS^* and ΔV^* clearly support the associative character of the substitution process. The extremely small values of ΔH^* and the very negative values of ΔS^* are in close agreement with those reported for the anation of $Ru(edta)H_2O^-$ by pyridine, pyrazine, isonicotinamide, acetonitrile, and 2-mercaptopyridine.[9,13] For this series of ligands ΔH^* varies between 24 and 35 kJ mol^{-1}, and ΔS^* varies between −79 and −100 J K^{-1} mol^{-1}. The significantly negative volumes of activation are the first to be reported for these systems and are characteristic for associatively activated processes. Furthermore, they are such that we can definitely rule out the operation of a dissociative reaction mode resulting from the eventual labilization of the Ru^{III}–H_2O bond due to possible hydrogen bonding between the pendant carboxylate group and the coordinated water molecule.[9] A comparison of ΔV^* for the neutral and anionic anating ligands reveals that there is no significant contribution arising from solvational changes during bond formation due to partial charge concentration in the case of the anionic ligands.[23] Furthermore, ΔV^* becomes more negative along the series thiourea (TU), Me_2TU, and Me_4TU, demonstrating the increased overlap of the van der Waals radii in the transition state with increasing partial molar volume of the entering group. Similar trends have been reported elsewhere for associative substitution processes.[16,24] The data in Table III furthermore demonstrate that the increase in steric hindrance on thiourea is accompanied by a significant decrease in k and an increase in ΔH^*,

Table II. Summary of k_{obsd} as a Function of Temperature and Pressure for the Reaction[a]

$$Ru^{III}(edta)H_2O + L \rightarrow Ru^{III}(edta)L + H_2O$$

ligand	[ligand], M	temp, °C	pressure, MPa	k_{obsd}, s^{-1}
thiourea	1.0 × 10^{-3}	25	0.1	2.45 ± 0.08
			5	2.76 ± 0.04
			25	2.94 ± 0.06
			50	3.07 ± 0.03
			75	3.28 ± 0.03
			100	3.64 ± 0.10
		20	0.1	1.97 ± 0.10
		25		2.45 ± 0.16
		30		2.84 ± 0.10
		35		3.37 ± 0.12
		40		3.70 ± 0.09
dimethylthiourea	1.0 × 10^{-3}	25	0.1	1.24 ± 0.01
			5	1.26 ± 0.03
			25	1.36 ± 0.01
			50	1.47 ± 0.03
			75	1.62 ± 0.02
			100	1.77 ± 0.06
		20	0.1	1.10 ± 0.01
		25		1.25 ± 0.01
		30		1.51 ± 0.02
		35		1.81 ± 0.06
		40		2.08 ± 0.04
tetramethylthiourea	2 × 10^{-3}	25	0.1	0.278 ± 0.005
			5	0.286 ± 0.006
			25	0.323 ± 0.008
			50	0.369 ± 0.004
			75	0.406 ± 0.016
			100	0.462 ± 0.020
	8 × 10^{-2}	20	0.1	8.0 ± 0.5
		25		11.1 ± 0.2
		30		14.4 ± 0.9
		35		17.6 ± 0.2
		40		19.7 ± 0.5
		45		22.6 ± 0.5
thiocyanate	5 × 10^{-3}	25	0.1	1.41 ± 0.01
			5	1.61 ± 0.01
			25	1.77 ± 0.03
			50	1.94 ± 0.02
			75	2.14 ± 0.03
			100	2.33 ± 0.03
azide[b]	2.3 × 10^{-3}	25	0.1	4.6 ± 0.1
			5	4.8 ± 0.1
			25	5.1 ± 0.1
			50	5.8 ± 0.1
			75	6.3 ± 0.1
			100	7.0 ± 0.2
		30	0.1	5.2 ± 0.1
		35.7		7.1 ± 0.4
		42		8.4 ± 0.4

[a] [Ru(III)] = 1 × 10^{-4} M; pH 5.0; [acetic acid/acetate buffer] = 0.1 M; ionic strength = 0.2 M (Na_2SO_4). [b] pH 6.0.

Table III. Summary of Rate Parameters for the Reaction[a]

$$Ru^{III}(edta)H_2O + L \rightarrow Ru^{III}(edta)L + H_2O$$

ligand	k, M^{-1} s^{-1}	ΔH^*, kJ mol^{-1}	ΔS^*, J K^{-1} mol^{-1}	ΔV^*, cm^3 mol^{-1}
thiourea	2970 ± 50	22.3 ± 1.4	−105 ± 5	−6.8 ± 0.6
dimethylthiourea	1450 ± 25	25.3 ± 1.3	−107 ± 4	−8.8 ± 0.2
tetramethylthiourea	154 ± 5	28.9 ± 3.3	−107 ± 11	−12.2 ± 0.5
azide	1885 ± 80	24.8 ± 1.4	−99 ± 5	−9.0 ± 0.6
	2070 ± 97[b]	26.4 ± 3.0[b]	−94 ± 10[b]	−9.9 ± 0.5[b]
thiocyanate	270 ± 27	37.2 ± 2.1	−75 ± 5.5	−9.6 ± 0.3

[a] Temp = 25 °C; [acetic acid/acetate buffer] = 0.1 M; ionic strength = 0.2 M; pH 5.0. [b] pH 6.0.

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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 $Ru(edta)H_2O^-$ 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^* is such that we cannot rule out the possibility of an I_a mechanism. In this respect it is interesting to note that ΔV^* for the anation of $Pd(Me_5dien)H_2O^{2+}$ and $Pd(Et_5dien)H_2O^{2+}$ by TU, Me_2TU, and Me_4TU has the values −9.3, −9.1, and −13.4 (Me_5dien), and −8.3, −10.2, and −12.7 (Et_5dien) $cm^3 mol^{-1}$, 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^* 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 $Ru(edta)H_2O^-$ complex, respectively. It follows that the reported values of ΔV^* 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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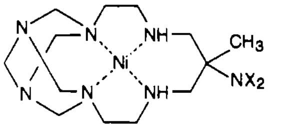
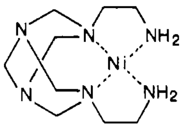
The square-planar nickel(II) complexes of the ligands 8-methyl-8-nitro-1,3,6,10,13,15-hexaazatricyclo[13.1.1.1^{13,15}]octadecane, 8-amino-8-methyl-1,3,6,10,13,15-hexaazatricyclo[13.1.1.1^{13,15}]octadecane, 3,7-bis(2-aminoethyl)-1,3,5,7-tetraazabicyclo[3.3.1]-nonane, and 9-methyl-9-nitro-1,4,7,11-tetraazacyclotridecane (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

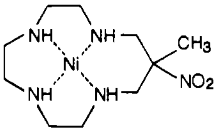
The study of the redox properties of nickel(II) macrocyclic complexes has received much attention in recent years.[3-6] When complexed in its low-spin electronic configuration, nickel(II) may be readily oxidized or reduced in one-electron steps to nickel(III) or nickel(I), respectively, in nonaqueous 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 electrochemical 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



I, X = O
II, X = H



III



IV

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