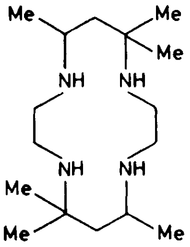
Radical Oxidation of Nickel(II) Complexes of Tetra-azamacrocyclic Ligands and the Reactions of the resulting Nickel(III) Complexes: A Pulse-radiolysis and Flash-photolysis Study

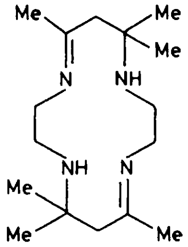
By **Kevin D. Whitburn** and **Gerald S. Laurence**,* Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia 5001

The nickel(II) complexes $[NiL]^{2+}$ [L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane (L^1), 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (L^2), or 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-1,4,8,11-tetraene (L^3)] are oxidised to the nickel(III) complexes in aqueous solutions by the radical ions $[Cl_2]^-$, $[Br_2]^-$, and $[(SCN)_2]^-$, generated by pulse radiolysis and flash photolysis. The outer-sphere electron-transfer reactions are diffusion controlled. Nickel(III) complexes of the ligands which contain NH groups (L^1 and L^2) are converted into nickel(II) complexes of radical forms of the ligands at pH >3. Hydroxyl radicals oxidise the nickel(II) complexes by initial H-atom abstraction from the ligand, and the nickel(III) complexes are then formed by proton-assisted intramolecular electron transfer. The nickel(II) ligand-radical complexes are more stable than the nickel(III) complexes and are intermediates in the decay of the nickel(III) complexes in water. The nickel(III) complexes are powerful oxidants and the rates of oxidation of Cl^-, Br^-, $[SCN]^-$, and $[N_3]^-$ are dependent on the reduction potentials of the complexes. Hydrogen peroxide is oxidised by the nickel(III) and nickel(II) ligand-radical complexes at similar rates. Oxidation of $[O_2]^-$ radical ion by the nickel(III) complexes is diffusion controlled; the rates of oxidation of HO_2 radicals are much smaller and are the same for all three complexes. Perhydroxyl radicals oxidise the nickel(II) complex of the saturated ligand, L^1, to the nickel(III) complex.

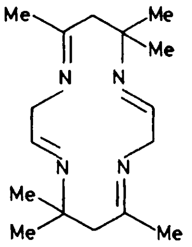
NICKEL(III) complexes of a number of macrocyclic ligands such as the 14-membered ring compounds L^1–L^3 are easily prepared by electrochemical [1] or chemical [2,3] oxidation of the nickel(II) complexes in non-aqueous solvents but are reduced in basic solvents such as water and pyridine. Complexes $[Ni^{III}LX_2]$ (X = Br, Cl, or NCO; L = dimethyl-substituted 14-membered tetra-azamacrocycle) have been prepared in aqueous solutions although they decompose after several hours.[3] From the changes in the oxidation of the ligand, co-ordinated ligand radicals have been inferred as intermediates in the reduction of nickel(III), copper(III),[4] and iron(III) [5] complexes of nitrogen-donor macrocyclic ligands by water, and a radical form of the ligand L^1 was detected as an intermediate in the reduction of the nickel(III) complex by water.[2] It has been suggested that co-ordinated radicals may be involved in the oxidation-reduction reactions by which the nickel(II) complex of L^2 is converted into the nickel(II) complexes of the ligands L^1 and L^3.[5,6] There is increasing evidence for the participation of co-ordinated ligand radicals in the oxidation-reduction reactions of other nitrogen-donor ligands such as porphyrins,[7] 2,2′-bipyridyl (bipy),[8] and phenanthroline,[9] but the factors controlling the formation and stability of these co-ordinated nitrogen-donor radicals are not well understood. We therefore chose the nickel complexes of the three related tetra-azamacrocyclic ligands L^1—L^3 to investigate the role of the imine function in the formation of ligand radicals. Both nickel(III) and nickel(II) ligand-radical species are formed in the free-radical oxidation of the nickel(II) complexes.



L^1



L^2



L^3

The kinetics of the formation and decay of the short-lived nickel(III) complexes of ammonia,[10] ethylenediamine,[11] glycine,[11] ethylenediaminetetra-acetate (edta),[12] and dimethylglyoxime [13] have been studied by pulse radiolysis, but in general the short lifetimes of nickel(III) complexes in aqueous solutions have prevented the study of the kinetics and mechanisms of the oxidation of substrates by nickel(III) complexes. Recently the kinetics of the oxidations of H_2O_2 [14] and Br^- ions [15] by the more stable $[Ni(bipy)_3]^{3+}$ ions have been shown to be similar to those for oxidations of the same substrates by other metal ions. We find that the macrocyclic nickel(III) complexes oxidise halide ions and aquametal ions by paths which are essentially independent of the degree of unsaturation of the macrocyclic ligand and which involve only the nickel(III) forms, since the conversion of the nickel(III) complexes into the nickel(II) ligand-radical complexes *via* intramolecular electron transfer is much slower than the intermolecular electron transfer to oxidisable substrates.

EXPERIMENTAL

Materials.—(5,7,7,12,14,14-*Hexamethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*nickel*(II) *perchlorate*, $[NiL^2][ClO_4]_2$. This complex was prepared by the method of Curtis [16] and Busch [17] and their co-workers and the i.r. and n.m.r. spectra confirmed the predominance of the N-*meso* form.[18]

(5,7,7,12,14,14-*Hexamethyl*-1,4,8,11-*tetra-azacyclotetradeca*-1,4,8,11-*tetraene*)*nickel*(II) *perchlorate*, $[NiL^3][ClO_4]_2$ (3). The complex was prepared by oxidising (2) with nitric acid [18] and was characterised by the i.r. and n.m.r. spectra.

(5,7,7,12,14,14-*Hexamethyl*-1,4,8,11-*tetra-azacyclotetradecane*)*nickel*(II) *perchlorate*, $[NiL^1][ClO_4]_2$ (1). The complex was prepared by the reduction of (2) with nickel–aluminium alloy in alkaline solution.[19]

5,7,7,12,14,14-*Hexamethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene bis(hydrogen perchlorate)*, $[H_2L^2][ClO_4]_2$. The free ligand was prepared by the direct reaction between ethylenediamine (en) and acetone referred to by Curtis.[20] The method avoids the necessity of preparing $[H_2en][ClO_4]_2$.[21] The preparation is sensitive to the presence of water, and carefully dried AnalaR reagents were used. Ethylenediamine (14 cm^3, 0.2 mol) was slowly added to a stirred refluxing solution of anhydrous magnesium perchlorate (90 g) in acetone (250 cm^3). The reaction is highly exothermic and care must be used when adding the ethylenediamine. The solution turned yellow and was heated under reflux for another 30 min after the addition of all the ethylenediamine. After cooling the solution, 1 mol dm^{-3} perchloric acid was added to bring the pH to *ca.* 5. The free ligand precipitated as white crystals which contained trace amounts of a yellow polymer. The product was filtered off and suspended in warm (40 °C) 1 mol dm^{-3} $HClO_4$ and the polymer separated by decantation. The ligand was recrystallised from aqueous ethanol and dried *in vacuo*. The i.r. spectrum agreed with that of Sadasavan and Endicott.[22]

All the other materials were AnalaR grade and solutions were made up in triple distilled water and deoxygenated when necessary by bubbling with oxygen-free nitrogen or argon before pulse radiolysis or flash photolysis.

Apparatus and Techniques.—The flash-photolysis and pulse-radiolysis techniques used in this laboratory have been described.[23,24] The photolysis flash has a half-width of 8 μs and a power of 500 J. The pulse-radiolysis experiments were carried out using the facility of the Australian Atomic Energy Research Establishment, Lucas Heights. The 1-MeV * electron pulses had a width of 3 μs. Thiocyanate dosimetry was used and yields were calculated using 7.6×10^3 dm^3 mol^{-1} cm^{-1} for the absorption coefficient of the $[(SCN)_2]^-$ radical anion at 475 nm.[25] Transient spectrophotometric data were obtained either as oscilloscope photographs or as digitised data stored in a PDP 11/10 computer (Digital Equipment Corp.).

Rate constants and absorbance measurements were reproducible to within $\pm 10\%$. Competition between first- and second-order reaction paths for transient decay was treated using a computer program to fit the data, with the separately measured second-order rate constant as input. In more complex cases a kinetic simulation program (KINSIM) was used to match the experimental data to a model for the reaction paths.[26]

Generation of Free Radicals.—Hydroxyl radicals were generated either by pulse radiolysis of solutions saturated with N_2O (pH $\geqslant 4$) or by flash photolysis of H_2O_2 solutions (1×10^{-3}—5×10^{-2} mol dm^{-3}). The low concentrations of the nickel(II) complexes did not interfere with the photolysis of H_2O_2. The reactions were independent of the source of OH radicals.

Dichlorine radical anions were generated by pulse radiolysis or flash photolysis using the methods previously described.[27] Hydroxyl radicals from the pulse radiolysis of water or the flash photolysis of H_2O_2 reacted with Cl^- ions (0.01—0.1 mol dm^{-3}) in acid solution to generate $[Cl_2]^-$ radical ions in 1 μs. Photolysis of $[FeCl]^{2+}$ ions in solutions containing Fe^{3+} (1×10^{-3} mol dm^{-3}) and Cl^- (0.1 mol dm^{-3}) and photolysis of $[Co(NH_3)_5Cl]^{2+}$ ions (1×10^{-4} mol dm^{-3}) in the presence of Cl^- ions also generated $[Cl_2]^-$. The photolysis of the cobalt(III) complex was useful at higher pH. In all photolyses of solutions containing Cl^- ions the flash light was filtered to remove wavelengths <250 nm and prevent the direct charge-transfer-to-solvent photolysis of the Cl^- ion.

Dibromine radical anions were generated by analogous methods, using Br^- and $[Co(NH_3)_5Br]^{2+}$ ions, or $[FeBr]^{2+}$ ions in solutions containing both Fe^{3+} and Br^-. In some cases the radical ions were produced by photolysis of $[Br_3]^-$ ions. Di-iodine radical anions were generated by flash photolysis of N_2O-saturated solutions of I^- (0.1 mol dm^{-3}).

Dithiocyanate radical anions were generated by pulse radiolysis of solutions of $[SCN]^-$ (1×10^{-3} mol dm^{-3}) or by photolysis of solutions of H_2O_2 (2×10^{-3} mol dm^{-3}) containing $[SCN]^-$ (1×10^{-3} mol dm^{-3}).

RESULTS AND DISCUSSION

Photolysis of Nickel(II) *Complexes*.—All the three nickel(II) complexes $[NiL][ClO_4]_2$ ($L = L^1$, L^2, or L^3) were photochemically inert. No transient changes in absorbance between 250 and 650 nm were observed when solutions of the complexes (5×10^{-5} mol dm^{-3}, pH 1—6) were flash-photolysed. Continued photolysis of the same solution had no further effect. Irradiation of the solutions with a 100-W Hg–Xe lamp, at wavelengths >260 nm, showed that the quantum yield for decomposition of the complexes was $<10^{-4}$. This low quantum yield allowed the free radicals to be generated by flash photolysis of solutions containing the nickel(II) complexes without interference.

The free diene ligand also has a low quantum yield for decomposition ($<10^{-4}$, pH 1—5) in the band at 220 nm attributed to the π–π^* transition in the C=N groups.[19,22]

Oxidation of Nickel(II) *Complexes*.—*By* $[Cl_2]^-$ *radical ions*. Dichlorine radical ions produced in solutions of the nickel(II) complexes (5×10^{-5} mol dm^{-3}) reacted within 5 μs to produce transient species with the absorption spectra shown in Figure 1. The spectra and initial yields were independent of pH (1—5) and the transients decayed relatively slowly ($t_{\frac{1}{2}} > 10$ ms). The absorption coefficients of the transients were obtained from pulse-radiolysis measurements and the spectra of Figure 1 are almost identical to spectra of the nickel(III) complexes of the same ligands produced by electrochemical oxidation in acetonitrile solution.[1] Rate constants for reaction (1) were determined by a competition method because the time resolution of the apparatus was not short enough for accurate measurements of the growth of the transient species. The reaction between $[Cl_2]^-$ and Fe^{2+}(aq) (k 3.3×10^6 dm^3 mol^{-1} s^{-1})[27] competed with (1) and the rate constants of Table 1 were obtained

$$[Cl_2]^- + [Ni^{III}L]^{2+} \longrightarrow [Ni^{III}L]^{3+} + 2Cl^- \quad (1)$$

from competition plots for 2×10^{-5} mol dm^{-3} $[NiL][ClO_4]_2$ and 1×10^{-3}—5×10^{-2} mol dm^{-3} Fe^{2+}(aq).

The free diene ligand reacted only slowly with $[Cl_2]^-$. No reaction could be detected at ligand concentrations $<1 \times 10^{-4}$ mol dm^{-3} but at concentrations near the limit of solubility of the ligand (*ca.* 1×10^{-3} mol dm^{-3})

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* Throughout this paper: 1 eV $\approx 1.60 \times 10^{-19}$ J.

the decay of the $[Cl_2]^-$ radicals was pseudo-first order, and the rate constant for the reaction is 3×10^7 dm^3 mol^{-1} s^{-1} at pH 3. This reaction is so much slower than the oxidation of the complexes ($\times 10^{-3}$) that it is improbable that reaction (1) takes place *via* initial attack of the $[Cl_2]^-$ radicals on the ligand. The diffusion-controlled rate constants for reaction (1) also indicate that ligand attack followed by metal oxidation by electron transfer to the ligand is an unlikely mechanism.

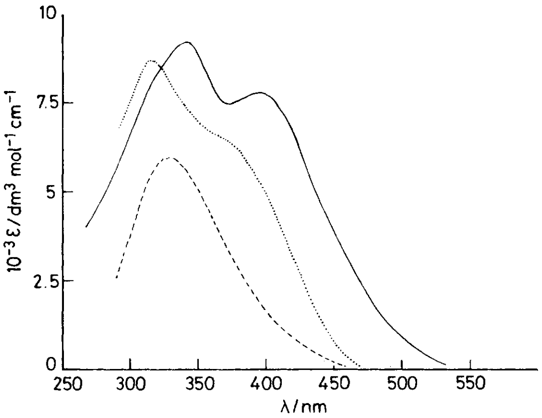

FIGURE 1 Spectra of the transient nickel(III) complexes produced by $[Cl_2]^-$ or $[Br_2]^-$ oxidation of $[NiL]^{2+}$ (L = L^1, L^2, or L^3) complexes in aqueous solution at pH 1. The spectra were taken 50 μs after the initiation of the reaction with the radicals, at halide-ion concentrations $\leqslant 1 \times 10^{-3}$ mol dm^{-3}. Spectra (····) and (——) correspond closely to those of the nickel(III) complexes in acetonitrile (ref. 1). (····) $[NiL^2]^{3+}$, (——) $[NiL^1]^{3+}$, and (— — —) $[NiL^3]^{3+}$

TABLE 1

Rate constants for radical oxidations of nickel(II) macrocyclic complexes and $Ni^{III}L$–$Ni^{II}L^{\bullet}$ conversion [a]

Radical	$[NiL^3]^{2+}$	$[NiL^2]^{2+}$	$[NiL^1]^{2+}$
OH	$(1.2 \pm 0.2) \times 10^{10}$	$(6.0 \pm 2) \times 10^9$	$(4.3 \pm 1.5) \times 10^9$
$[Cl_2]^-$	$(1.2 \pm 0.2) \times 10^{10}$	$(1.0 \pm 0.2) \times 10^{10}$	
$[Br_2]^-$	$(2.6 \pm 0.6) \times 10^9$	$(2.2 \pm 0.7) \times 10^9$	$(4.0 \pm 1.0) \times 10^9$
$[(SCN)_2]^-$	$\leqslant 5 \times 10^7$	$(6.0 \pm 1.0) \times 10^8$	$(1.0 \pm 0.5) \times 10^8$
HO_2 [b]			$(1.1 \pm 0.2) \times 10^7$

Reaction [c]		
$Ni^{II}L'\dot{C}H + H^+ \rightleftharpoons Ni^{III}L$	$k_7 = 6 \times 10^7$	$k_{-7} = 1 \times 10^3$
$Ni^{II}L'\dot{C}H \rightleftharpoons Ni^{II}L''\dot{N}$	$k_8 = 1 \times 10^6$ [d]	$k_{-8} = 1 \times 10^3$ [d]
$Ni^{II}L'' + H^+ \rightleftharpoons Ni^{II}L'\dot{N}H^+$	$K_9 = 1 \times 10^4$ [e]	

[a] Second-order rate constants in units of dm^3 mol^{-1} s^{-1} at 22 ± 2 °C and pH 1. [b] Only the complex $[NiL^1]^{2+}$ was oxidised by HO_2 radicals; pH 0.3. [c] For the complex $[NiL^2]^{2+}$. Values obtained by simulation of the experimental data of Figure 3, which have a precision of *ca.* 20%. [d] First-order rate constants in units of s^{-1} at 22 ± 2 °C. [e] Units of dm^3 mol^{-1} at 22 °C.

By $[Br_2]^-$ *radical ions.* In 5×10^{-5} mol dm^{-3} solutions of the nickel(II) complexes, $[Br_2]^-$ radical ions also reacted rapidly to produce transients with the same absorption spectra as Figure 1 if the Br^- concentration in the solution was low ($<1 \times 10^{-3}$ mol dm^{-3}). In solutions of complexes (1) and (2) at higher Br^- concentrations (up to 0.1 mol dm^{-3}) there were small (*ca.* 5 nm) shifts in the wavelength of the absorption maximum and small increases in the absorbance at longer wavelengths. The changes in the spectrum of complex (3) at high Br^- concentrations were larger, a broad shoulder appearing at *ca.* 400 nm. The spectra were nevertheless characteristic of nickel(III) species and the changes are probably due to the formation of $[NiL(Br)]^{2+}$ and $[NiL(Br)_2]^+$ species.

Rate constants for reaction (2) (L = L^2 or L^3) were measured by competition with the reaction between $[Br_2]^-$ and Fe^{2+}(aq) (*k* 4.0×10^6 dm^3 mol^{-1} s^{-1}).[27] The rate constant for reaction (2) (L = L^1) was estimated

$$[Br_2]^- + [Ni^{II}L]^{2+} \longrightarrow [Ni^{III}L]^{3+} + 2Br^- \quad (2)$$

from the relative yields of the nickel(III) complex and the $[Br_3]^-$ formed by disproportionation of the $[Br_2]^-$. The rate constants are given in Table 1.

No reaction could be detected between free ligand L^2 and $[Br_2]^-$ radical ions. The upper limit for the rate constant for this reaction is therefore *ca.* 10^5 dm^3 mol^{-1} s^{-1} and the reaction between $[Br_2]^-$ and ligand cannot interfere with reaction (2). Direct electron transfer between the nickel(II) centre and the $[Br_2]^-$ appears the only mechanism for reaction (2).

The absorption bands between 300 and 400 nm for complexes (1) and (2) (Figure 1) are the same in water as in acetonitrile[1] and are only slightly influenced by halide or pseudo-halide ligands in positions apical to the plane of the macrocyclic ring. A similar result was found for the octahedral low-spin nickel(III) complexes of a dimethyl-substituted tetra-azacyclotetradecane.[3] The nickel(I) complexes of L^1 and L^2 produced in aqueous solutions by reducing radicals[28] also have the same spectra in acetonitrile.[1] The assignment of the absorption bands in the 300—400 nm region for the nickel(III) complexes to a ligand-to-metal charge-transfer transition[4,29] is confirmed by our observation of the lack of solvent or apical-ligand effects. The spectrum of $[NiL^3]^{3+}$ (Figure 1) is similar to those of the other nickel(III) complexes, with a maximum at 325 nm.

By $[I_2]^-$ *radical ions.* At concentrations of the nickel(II) complexes up to 2×10^{-4}—3×10^{-4} mol dm^{-3} there was no detectable change in the rate of the $[I_2]^-$ disproportionation reaction. The rate constant for any reaction between $[I_2]^-$ and the nickel(II) complexes must therefore be $<10^7$ dm^3 mol^{-1} s^{-1}.

By $[(SCN)_2]^-$ *radical ions.* The decay of the $[(SCN)_2]^-$ radical ions was unaffected by complex (3) (2×10^{-4} mol dm^{-3}), and for reaction (3) (L = L^3) the rate constant is $\leqslant 5 \times 10^7$ dm^3 mol^{-1} s^{-1}. Complexes (1) and (2) reacted with $[(SCN)_2]^-$ radical ions to give transient nickel(III) complexes having spectra identical to those of Figure 1 at low (1×10^{-3} mol dm^{-1}) $[SCN]^-$ concentrations. The rate constants for reaction (3) ($L = L^1$ or L^2) were determined directly from the dependence of the growth of the absorbance at 366 nm due to the nickel(III) species, or the decay of the absorbance of

$$[(SCN)_2]^- + [Ni^{II}L]^{2+} \longrightarrow [Ni^{III}L]^{3+} + 2[SCN]^- \quad (3)$$

$[(SCN)_2]^-$ at 485 nm, on the nickel(II) concentration. The rate constants obtained at both wavelengths were identical and are given in Table 1.

The reactions of the nickel(II) complexes with $[Cl_2]^-$ and $[Br_2]^-$ are diffusion controlled and the rates are independent of the macrocyclic ligand or the halogen radical ion, despite the large differences between the standard reduction potentials of $[Cl_2]^-$ and $[Br_2]^-$ (2.29 and 1.77 V respectively).[30] The reduction potentials of the nickel(III) complexes lie between 1.85 and 1.65 V in acetonitrile.[31] The complex $[CuL^2]^{2+}$ is oxidised by $[Cl_2]^-$ at diffusion-controlled rates[32] although the reduction potential of the copper(III) complex is 0.3 V more positive than that of the nickel(III) complex.[4] The complex $[CoL^2]^{2+}$ reacts with the halogen radical ions at similar rates[33] and in this case the reduction potential of the cobalt(III) complex is at least 1 V lower than those of the nickel(III) complexes in water. These reactions between the $[X_2]^-$ radical ions and the macrocyclic complexes must be outer sphere and the factors which determine the mechanisms and rate constants of electron-transfer oxidations by the radical anions are somewhat obscure. The equivalent oxidations of the aqua-ions Fe^{2+},[27] Mn^{2+},[34] and Co^{2+} (ref. 30) take place by inner-sphere mechanisms at rates much lower than the outer-sphere reactions with the nickel(II) complexes, despite the much more favourable $\Delta G^{\ominus}$ value for the reactions between Fe^{2+} and $[Cl_2]^-$ or $[Br_2]^-$. The oxidations of the nickel(II) complexes by $[(SCN)_2]^-$ radical ions are somewhat slower than for the halogen radical ions which may reflect the smaller reduction potential of $[(SCN)_2]^-$ ions; $E^{\ominus}$ for $[(SCN)_2]^-$ radical ions is expected to lie between the value for $[Br_2]^-$ (1.77 V) and that for $[I_2]^-$ (1.0 V).[33]

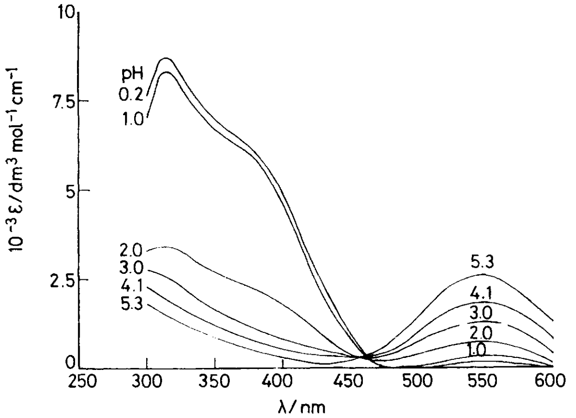

FIGURE 2 pH dependence of the transient spectrum produced by OH radical oxidation of $[NiL^2]^{2+}$, taken 50 μs after the initiation of the reaction with OH radicals. The absorption at 550 nm at higher pH corresponds to the nickel(II) ligand-radical species

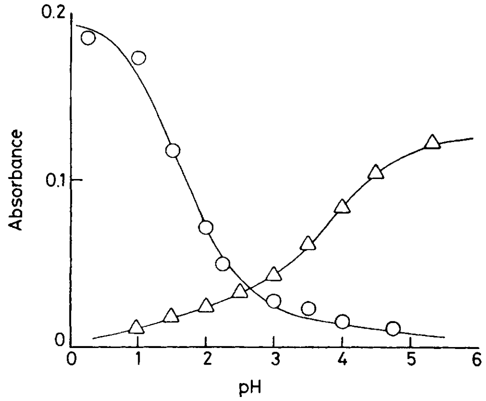

FIGURE 3 pH dependence of the yields of the $[NiL^2]^{3+}$ and $Ni^{II}L^2$-radical species from the OH radical oxidation of $[NiL^2]^{2+}$. The yields are expressed as the absorbances measured at 405 (○) and 546 nm (△) at constant total OH radical concentration. The full lines represent the absorbances calculated for the rate and equilibrium constants given in Table 1 for reactions (7)—(9)

By OH *radicals*. Hydroxyl radicals reacted rapidly with complex (3) to produce a nickel(III) complex with the same spectra as that from reaction (1). The rate constant for reaction (4) ($L = L^3$) was determined from the competition between reaction (4) and the reaction of OH with H_2O_2 (k 1.7×10^7 dm^3 mol^{-1} s^{-1}).[35]

$$OH + [Ni^{II}L]^{2+} \longrightarrow [Ni^{III}L]^{3+} + [OH]^- \quad (4)$$

Reaction between OH radicals and the nickel(II) complexes (1) and (2) containing NH groups produced more complex transient spectra (Figure 2). In addition to the characteristic absorbance due to Ni^{III} between 300 and 450 nm (Figure 1) a second absorbance with a maximum at 550 nm was formed. The spectra and initial yields of the species absorbing at 350 and 550 nm were pH dependent (Figure 3). The absorbance maximum at 550 nm has been identified as due to nickel(II) ligand-radical species, $Ni^{II}L^{\bullet}$ ($L = L^1$ or L^2). Barefield and Mocella[2] observed a $Ni^{II}L^1$ radical species with an absorption maximum at 540 nm in the water-promoted reduction of $[NiL^1]^{2+}$. The transient responsible for the absorption was identified from e.s.r. measurements, and was apparently formed by the reversible reaction (5) at high pH (*ca.* 5—7). The decay

$$Ni^{III}L + H_2O \rightleftharpoons Ni^{II}L^{\bullet} + [H_3O]^+ \quad (5)$$

of the $Ni^{II}L^1$ radical complex was similar to the decay which we observed for the absorbance at 550 nm.* At pH 5 the absorbance due to the nickel(III) complexes

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* Ferraudi and Patterson[36] observed a transient absorption with a maximum at 535 nm in the OH oxidation of $[NiL^2]^{2+}$. Their measurements were confined to pH > 4 and they therefore failed to observe the absorption due to the nickel(III) species at 320 nm. It is apparent from Figure 2 that the absorbance at 550 nm is the dominant one at pH > 4.

was converted into that of the $Ni^{II}L^{\bullet}$ species with a first-order rate constant of *ca.* 150 s^{-1}. This reaction was only observable in solutions which did not contain oxidisable substrates and was so slow that the initial yield of $Ni^{II}L^{\bullet}$ (measured within 10—100 μs of the production of the OH radicals) could not arise from reaction (5). The relative absorption coefficients of the nickel(III) and $Ni^{II}L^{\bullet}$ complexes ($L = L^1$ or L^2) were obtained from measurements of the relative absorbances during the slow conversion due to reaction (5), by assuming that this was the only reaction responsible for the loss of the nickel(III) absorbance.

The observation that the $Ni^{II}L^{\bullet}$ species were formed directly during a reaction between the nickel(II) complexes and OH radicals at a rate much greater than reaction (5) indicated that the nickel(III) and $Ni^{II}L^{\bullet}$ species were not in equilibrium at the time at which the measurements of the initial yields were made (<100 μs). The sum of the initial yields of the nickel(III) and $Ni^{II}L^{\bullet}$ complexes was not pH independent (Figure 3) and at least one other species must exist in this pH range. The rapid production of both these types of complex by the reaction with OH radicals was surprising. Oxidation of the complexes by $[Cl_2]^-$ and $[Br_2]^-$ radical ions does not produce any initial absorbance at 550 nm at pH 0.5—5.5, and oxidation of complex (3) by OH radicals only produces $[NiL^3]^{3+}$. The nickel(III) species produced by halogen-radical-anion oxidation are converted into the $Ni^{II}L^{\bullet}$ species only slowly even at pH 5. The results indicate that *both* Ni^{III} and $Ni^{II}L^{\bullet}$ must be produced by relatively rapid reactions during the oxidation of complexes (1) and (2) by OH radicals, and that the reactions responsible are pH dependent. We conclude that the initial attack by the OH radicals on the nickel(II) complexes is not of the same kind as that by $[Cl_2]^-$ or $[Br_2]^-$, although both reactions are diffusion controlled. The rate constants for the reaction of complexes (1) and (2) with OH radicals were pH independent despite the differences in the initial yields of the nickel(III) and $Ni^{II}L^{\bullet}$ species in the range pH 1—5 (Table 1), suggesting that both species are formed from an initial precursor which is the first product of the OH radical attack and whose yield is pH independent. It is probable that H-atom abstraction by OH radicals is the primary reaction rather than direct electron transfer from the nickel(II) centre. Hydrogen-atom abstraction is more efficient for OH radicals than for $[Cl_2]^-$ or $[Br_2]^-$ and therefore only the nickel(III) complexes are formed in the reactions with the radical anions.

A possible reaction scheme for the oxidation of complexes (1) and (2) by OH radicals is as in equations (6)—(9). The initial reaction, (6), involves H-atom abstraction at a carbon-atom site on the ligand at a pH-independent rate. We have observed that the reaction of OH radicals with the free diene ligand gives rise to a small transient absorbance in the range 300—400 nm with a pH-independent yield. The rate constant for this reaction was approximately the same as that for reaction between OH radicals and the nickel(II) complexes, 4×10^9 dm^3 mol^{-1} s^{-1}, and the transient did not absorb at 550 nm. This reaction is probably the equivalent of reaction (6) for the bound ligand. Reaction (7) is a proton-catalysed intramolecular electron transfer and produces the nickel(III) complex. The reaction may involve more than one step but we have been unable to determine this experimentally. The $Ni^{II}L^{\bullet}$ species which absorbs strongly at 550 nm is $Ni^{II}L''N^{\bullet}$ and may be formed both from the initial species $Ni^{II}L'\dot{C}H$ *via* reaction (8) or from Ni^{III} *via* reactions (7) and (8). The conversion of Ni^{III} into $Ni^{II}L''N^{\bullet}$ observed when nickel(III) complexes are produced by halogen radical anions takes place *via* reactions (7) and (8). Reactions (8) and (9) are analogous to those found in the rearrangements of alkylamino-radicals to α-aminoalkyl radicals.[37] These rearrangements are very rapid and pH dependent, and effectively the carbon-radical species, $Ni^{II}L'\dot{C}H$, is never present in concentrations which are more than a small fraction of the concentration of Ni^{III} or $Ni^{II}L''N^{\bullet}$.

$$OH + Ni^{II}L \longrightarrow Ni^{II}L'\dot{C}H + H_2O \qquad (6)$$

$$Ni^{II}L'\dot{C}H + H^+ \rightleftharpoons Ni^{III}L \qquad (7)$$

$$Ni^{II}L'\dot{C}H \rightleftharpoons Ni^{II}L''\dot{N} \qquad (8)$$

$$Ni^{II}L''\dot{N} + H^+ \rightleftharpoons Ni^{II}L''\dot{N}H^+ \qquad (9)$$

The initial yields of the transients from the reaction with OH radicals are kinetically determined by the relative rates of reactions (7)—(9) and the species do not reach equilibrium for the reactions until *ca.* 1 ms later. We have modelled the reaction scheme using the measured interconversion rate constant between Ni^{III} and $Ni^{II}L^{\bullet}$, the limiting yields of the Ni^{III} and $Ni^{II}L^{\bullet}$ species at low and high pH (Figure 3), and the absorption coefficients of the species. We have assumed that the differences in the spectra of the initial products from OH and $[Cl_2]^-$ oxidation are accounted for by the absorbance of the $Ni^{II}L''\dot{N}H^+$ present in the former case. The fit of the model using the rate constants for complex (2) given in Table 1 is shown in Figure 3. The model assumes that the rate constant measured for the reaction with OH radicals is that for the H-atom abstraction reaction, (6).

The oxidation of complex (1) gave results very similar to those for (2). Nickel(III) and nickel(II) L^1-radical species were both formed as initial products at pH 4, and the initial yields were pH dependent and not in equilibrium until after several milliseconds. A mechanism similar to that of reactions (6)—(9) is inferred. The data indicate that the rate constant for reaction (7) at pH 1 is approximately the same for the complexes (1) and (2).

Our results cannot be modelled by any reaction scheme in which the initial reaction with OH radicals produces only the nickel(III) complex. The initial OH radical attack must also establish a reaction path leading to the nickel(II) ligand-radical species. The most stable form of the nickel(II) L^1-radical complex is that for which the unpaired electron is located on the nitrogen atom.[3] Our observations that nickel(II) ligand-radical species having similar absorptions are formed from complexes (1) and (2) in which the NH groups on the ligands allow the stabilisation of the $>N^{\bullet}$ form of the ligand radical, but that the tetraene ligand L^3 is not oxidised by a Ni^{3+} centre in this way, agrees with the preferential formation of the $>N^{\bullet}$ radical species. Reaction (6) which involves H-atom abstraction from a CH_2 group on the ligand is similar to the reactions of OH radicals with aliphatic amines. Hydroxyl radicals react with the unprotonated forms of aliphatic amines with rate constants similar to those we have observed for reaction (6) (*ca.* 10^{10} dm^3 mol^{-1} s^{-1}) and the initial products are the radicals resulting from H-atom abstraction from the NH or CH_2 groups.[38] We suggest that reaction (6) results in the formation of the $>N-\dot{C}H$ group for all the macrocyclic ligands. The subsequent reactions are dependent on the ligand. The $Ni^{II}L^3$ $C^{\bullet}$-radical complex is converted into $[NiL^3]^{3+}$ reaction (7), at pH <5, but for the $C^{\bullet}$-radical species of complexes (1) and (2) the conversion to the $N^{\bullet}$-radical form competes with reaction (7). At pH > 4 the $Ni^{II}LN^{\bullet}$ radical is the more stable form for the ligands L^1 and L^2. The rates of conversion between the $Ni^{III}L$ and $Ni^{II}L^{\bullet}$ forms are of the same magnitude as other intramolecular electron-transfer reactions involving metal–ligand-radical species, such as the penta-aminecobalt(III) *p*-nitrobenzoate-radical complex.[39]

Conversion of Ni^{III} *into* $Ni^{II}L^{\bullet}$.—Conversion of the nickel(III) complexes into the $Ni^{II}L^{\bullet}$ forms ($L = L^1$ or L^2) was studied at pH >3. The decay of the oxidised species was much slower than the rate of interconversion. Using $[Br_2]^-$ and $[Cl_2]^-$ as oxidants only the nickel(III) species were produced initially and the characteristic nickel(III) absorbance (300—400 nm) decayed by a first-order reaction. The $Ni^{II}L^{\bullet}$ absorbance (550 nm) grew at the same rate. At pH $\geqslant 4.5$ the conversion into the $Ni^{II}L^{\bullet}$ species was complete. At pH <5 the conversion is described by reactions (7)—(9), but at higher pH the rate of conversion continued to increase. The dependence of the conversion rate at high pH is shown for the complex $[NiL^1]^{3+}$ in Figure 4. In the pH 6.5—7.5 region the results are uncertain because of difficulties in buffering the solutions. The existence of a reaction path formally described by reactions (10) and (11), with

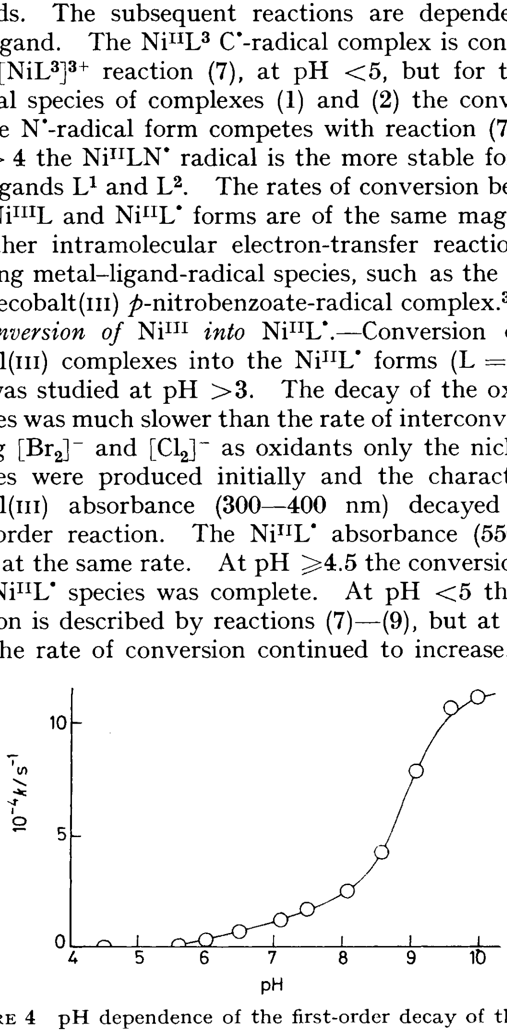

FIGURE 4 pH dependence of the first-order decay of the complex $[NiL^1]^{3+}$ at high pH. The data between pH 6.5 and 7.5 are subject to considerable error due to problems of buffering. The full line has been calculated from the values of the equilibrium and rate constants for reactions (10) and (11) given in the text

$$[Ni^{III}L]^{3+} \rightleftharpoons [Ni^{III}L]^{2+} + H^+ \quad (10)$$

$$[Ni^{III}L]^{2+} \longrightarrow [Ni^{II}L^{\bullet}]^{2+} \quad (11)$$

pK_a 8.8 [(10)] and $k = 1.1 \times 10^5$ s^{-1} [(11)] for the complex $[NiL^1]^{3+}$ is clearly shown in Figure 4. The data at lower pH suggest the existence of another base-dependent path, for which pK_a 6.0 and $k = 10^4$ s^{-1}, but this is much less well defined. The formal relation between the rate of conversion into the $Ni^{II}L^{\bullet}$ species and the pH does not establish the mechanism of this base catalysis. Deprotonation of the ligand may facilitate the electron transfer, or the rearrangement between carbon- and nitrogen-centred radicals, but hydrolysis of apical water molecules may be involved. Two-stage hydrolysis of the complex $[CoL^2]^{3+}$ has been observed.[29] A similar pH dependence was observed for the $[NiL^2]^{3+}$ system, with pK_a again 8.8.

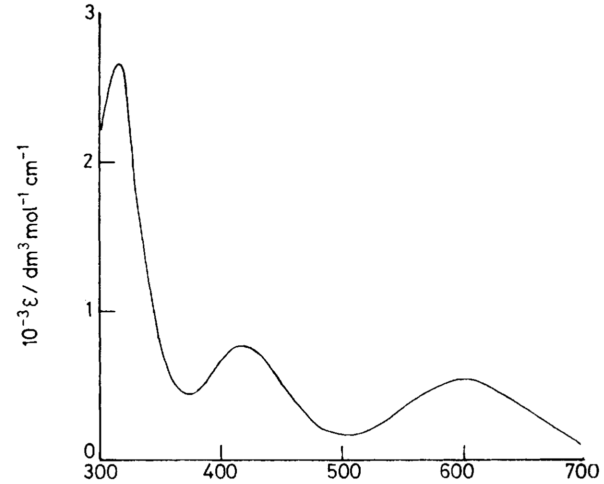

FIGURE 5 Spectrum of the transient observed during the decay of $[NiL^3]^{3+}$ at pH 7. The spectrum was measured 10 ms after the formation of $[NiL^3]^{3+}$ species using $[Br_2]^-$ radical ions as the oxidant, at low Br^- concentrations

The complex $[NiL^3]^{3+}$ was not converted into a nickel(II) ligand-radical form at pH <6, but decayed to the final products. At higher pH, $[NiL^3]^{3+}$ was converted into a species which absorbed at longer wavelengths (Figure 5). In this pH region the decay of the nickel(III) absorbance at 366 nm was first order, with the same rate constant as that for the growth of the new absorbance at 430 nm. The rate was pH dependent (pH 6—9) but we have not been able to establish the nature of the new intermediate formed. The spectrum of Figure 5 differs markedly from those of the radical species of complexes (1) and (2) with absorption maxima at 550 nm, and the formation of a nitrogen-centred free radical is less likely for tetraene L^3. A similar reaction apparently occurs in the decay of the complex $[Ni(edta)]^-$, and does not involve a ligand radical.[12] The rate constant for the conversion of $[NiL^3]^{3+}$ into the species absorbing at longer wavelengths was 200 s^{-1} at pH 8, and the intermediate decayed with a first-order rate constant of 8 s^{-1}, which was significantly faster than the decay of $[\mathrm{NiL^3}]^{3+}$ at pH 1. The hydrolysis of co-ordinated water molecules would cause an increase in the absorbance at longer wavelengths due to the $\mathrm{Ni^{III}}$–$[\mathrm{OH}]^-$ charge-transfer interaction, but this would not account for the absorbance at 600 nm. The intermediate may involve a carbon-centred free radical which is stabilised at high pH, or the initiation of base hydrolysis of the ligand.

The relatively long lifetimes for the radical species of complexes (1) and (2) in the absence of oxidising or reducing substrates make it probable that these ligand-N$^{\bullet}$ radical species are intermediates in the oxidation reactions used to prepare complex (2) from (1), and (3) from (2). The ligand oxidations take place when the nickel(II) complexes are treated with strong oxidising agents such as $\mathrm{HNO_3}$ or $[\mathrm{S_2O_8}]^{2-}$, and are the standard methods for preparing complex (3).[20] It is interesting to note that the complex (3) cannot be formed from $[\mathrm{CuL^2}]^{2+}$ in this way although we have been able to observe an equivalent radical form in the oxidations of $[\mathrm{CuL^2}]^{2+}$ by free radicals.[32] The initial step in the oxidations of the nickel(II) complexes must involve the formation of the nickel(II) ligand-N$^{\bullet}$ radical species which is further oxidised to produce the $\mathrm{-N{=}C}\!<$ function.

Decay of $\mathrm{Ni^{III}L}$.—The reactions of the nickel(III) complexes were dependent on the other chemical species in the solutions. Substrates such as halide ions and hydrogen peroxide were oxidised by the nickel(III) complexes. In the absence of competing reactions, the nickel(III) complexes and the nickel(II) ligand-radical complexes decayed by reactions which caused disruption of the ligand analogous to those observed by Barefield and Mocella.[2] Nickel(III) complexes were prepared by oxidation with $[\mathrm{Cl_2}]^-$ radical ions in the presence of low concentrations ($\leqslant 1 \times 10^{-3}$ mol dm^{-3}) of $\mathrm{Cl^-}$ ions and decayed by first-order reactions in the range pH 1—9. No intermediates other than the $\mathrm{Ni^{II}L^{\bullet}}$ species absorbing at 550 nm ($\mathrm{L = L^1}$ or $\mathrm{L^2}$) or at 430 and 600 nm ($\mathrm{L = L^3}$) were observed during the decay. The products of the reactions were apparently similar to those found previously.[2] At all pH values the relative rates of decay were $\mathrm{L^3 > L^2 > L^1}$. The spectra of the final solutions showed that some ligand had been lost, and at near neutral pH it was possible to observe the production of $\mathrm{H^+}$ ion from the decay. The very slow decay rates and the small concentrations of $\mathrm{Ni^{III}}$ produced by pulse radiolysis or flash photolysis ($< 5 \times 10^{-6}$ mol dm^{-3}) made investigation of the reactions difficult. If the decay involves oxidation of a nickel(II) ligand-radical complex by $\mathrm{Ni^{III}}$ as has been suggested,[2,5] then the first-order kinetics indicate that such a second-order process is not rate determining. The first-order decomposition of the $\mathrm{Ni^{II}L^1}$ radical complex [2] may occur by reaction of the ligand-radical complex with other decomposition fragments. Rate constants for the decay of the $\mathrm{Ni^{II}L^1}$ radical in water are not quoted in ref. 2 but from the $t_{\frac{1}{2}}$ value we estimate that the present rates are within $\pm 25\%$ of those found by Barefield and Mocella.[2]

In acid solution the rate of decay of the complex $[\mathrm{NiL^1}]^{3+}$ was so slow that it was possible to add substrates to the pale green solution of the nickel(III) complex after radical oxidation: $\mathrm{Br^-}$, $\mathrm{I^-}$, $[\mathrm{SCN}]^-$, and $\mathrm{H_2O_2}$ (0.01—0.1 mol dm^{-3}) caused rapid loss of the nickel(III) absorbance. The results agree with our measurements of the decay kinetics of the nickel(III) complexes in the presence of these substrates and with Barefield and Mocella.[2]

Reactions of $\mathrm{Ni^{III}}$ *with Reductants.—Halide and pseudo-halide ions.* The nickel(III) complexes react with halides such as $\mathrm{Br^-}$ and $\mathrm{I^-}$ to produce halogen. The kinetics of these reactions were studied at low pH because of the complications caused by competing reactions involving nickel(II) ligand-radical species at higher pH. The reactions were dependent on the relative $E^{\ominus}$ values for the nickel(III) complexes and the halide ions and the kinetics were similar to those found for the oxidation of halide ions by aquametal ions such as $\mathrm{Fe^{3+}(aq)}$.[40]

No reaction was observed between any of the nickel(III) complexes and low concentrations of $\mathrm{Cl^-}$. The complexes $[\mathrm{NiL}]^{3+}$ ($\mathrm{L = L^1}$ or $\mathrm{L^2}$) did not react with $\mathrm{Cl^-}$ at pH 1 even at $\mathrm{Cl^-}$ concentrations of 0.1—0.5 mol dm^{-3}.

However the complex $[\mathrm{NiL^3}]^{3+}$, which decayed by slow first-order kinetics in the presence of 1×10^{-3} mol dm^{-3} $\mathrm{Cl^-}$ at pH 1, decayed by a second-order process when the $\mathrm{Cl^-}$ concentration was 0.1 mol dm^{-3}, and the rate constant was dependent on the chloride concentration. The reaction was only slightly faster than the decay in the absence of $\mathrm{Cl^-}$, and after 75—80% completion of the reaction it was possible to detect the slow first-order process. The small range of concentrations over which the second-order reaction could be studied prevented a complete kinetic analysis but the reaction sequence is certainly the same as that found for the oxidation of $\mathrm{Br^-}$ ions by the nickel(III) complexes.

For reactions (12)—(14) the steady-state assumption, if reaction (12) is at equilibrium, leads to the rate expression (15). For $\mathrm{X = Cl^-}$ and $\mathrm{Ni^{III}} = [\mathrm{NiL^3}]^{3+}$,

$$[\mathrm{Ni^{III}L}]^{3+} + \mathrm{X^-} \rightleftharpoons [\mathrm{Ni^{III}L(X)}]^{2+} \qquad (12)$$

$$[\mathrm{Ni^{III}L(X)}]^{2+} + \mathrm{X^-} \rightleftharpoons [\mathrm{Ni^{II}L}]^{2+} + [\mathrm{X_2}]^- \qquad (13)$$

$$[\mathrm{Ni^{III}L}]^{3+} + [\mathrm{X_2}]^- \longrightarrow [\mathrm{Ni^{II}L}]^{2+} + \mathrm{X_2} \qquad (14)$$

$$-\frac{\mathrm{d}[\mathrm{Ni^{III}}]}{\mathrm{d}t} = \frac{2k_{13}k_{14}[\mathrm{Ni^{III}}]^2}{k_{-13}[\mathrm{Ni^{II}}] + k_{14}[\mathrm{Ni^{III}}]} \cdot \frac{K_{12}[\mathrm{X^-}]^2}{K_{12}[\mathrm{X^-}] + 1} \qquad (15)$$

the linear dependence of the second-order rate constant on the $\mathrm{Cl^-}$ concentration implies that a high proportion of $[\mathrm{NiL^3}]^{3+}$ is in a form which is already combined with at least one $\mathrm{Cl^-}$ ion at 0.1 mol dm^{-3} $\mathrm{Cl^-}$. The co-ordination of halide and pseudo-halide ions in low-spin d^7 octahedral complexes of $\mathrm{Ni^{III}}$ with planar macrocycle ligands has been observed by Gore and Busch.[3] The second-order dependence on the nickel(III) concentration implies that $k_{-13}[\mathrm{Ni^{II}}]$ is significantly greater than $k_{14}[\mathrm{Ni^{III}}]$ in the rate expression. Since we found k_{-13} to be 1.2×10^{10} dm^3 mol^{-1} s^{-1} (Table 1) and the concentration of Ni^{II} was at least 20 times greater than that of Ni^{III}, the second-order kinetics are accounted for. The product $k_{13}k_{14}$ for the reaction between Cl$^-$ and [NiL^3]$^{3+}$ was 2×10^{11} dm^6 mol^{-2} s^{-2} but the individual rate constants could not be evaluated. The complex [NiL^3]$^{3+}$ has the highest reduction potential of the three complexes and is the only one able to oxidise Cl$^-$.

All three nickel(III) complexes react with Br$^-$ ions at pH 1—5. Bromine was identified spectrophotometrically in the solutions after the reaction. For Br$^-$ concentrations between 0.005 and 0.1 mol dm^{-3} the nickel(III) complexes decayed by second-order reactions but the reactions were complicated at pH >3 probably because of the presence of the nickel(II) ligand-radical complexes. At low pH the observed second-order rate constants were dependent on the Br$^-$ concentration and inversely dependent on the nickel(II) concentration. The dependence on Br$^-$ was linear between 0.02 and 0.2 mol dm^{-3} (L^2 and L^3) but approached a second-order dependence at lower concentrations. The inverse dependence on the nickel(II) concentration is shown in Figure 6.

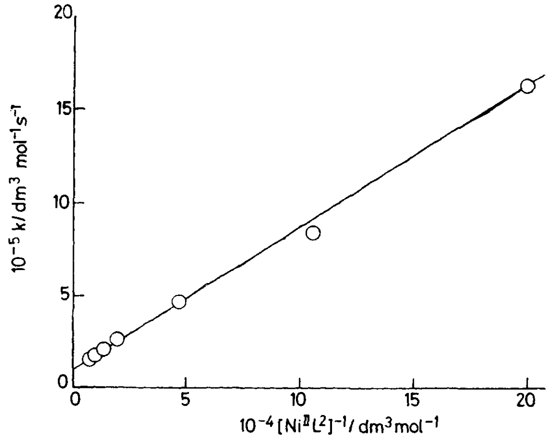

FIGURE 6 Dependence of the rate of disappearance of [NiL^2]$^{3+}$ on the concentration of [NiL^2]$^{2+}$ at pH 1 in 0.1 mol dm^{-3} bromide solution

The kinetics are as expected for reactions (12)—(14), X = Br$^-$, except for the intercept in the dependence of the observed rate on 1/[Ni^{II}], Figure 6. We have no explanation for this intercept, which may arise from a reaction between two nickel(III) species which is catalysed by Br$^-$ and which leads to eventual ligand oxidation. The slightly different spectra found for the nickel(III) complexes in bromide solutions suggests that the Br$^-$ co-ordinates to the Ni^{III}. At higher bromide-ion concentrations the dependence of the observed rate constant on [Br$^-$] is linear because K_{12}[Br$^-$] > 1. The second-order rate constants observed for the disappearance of the Ni^{III} arise because k_{-13}[Ni^{II}] > k_{14}[Ni^{III}]: the values of k_{-13} (Table 1) are *ca.* 2×10^9 dm^3 mol^{-1} s^{-1} and the concentrations of Ni^{II} were much higher than those of Ni^{III}. The rate constants k_{13} and k_{14} cannot be separately evaluated from the variations of the observed rate constant with [Br$^-$] and [Ni^{II}], but each dependence leads to an independent value of the product $k_{13}k_{14}$. For the complex [NiL^2]$^{3+}$ the agreement between the two sets of data was good: from the nickel(II) concentration dependence $k_{13}k_{14}$ was $(1.7 \pm 0.3) \times 10^{12}$ dm^6 mol^{-2} s^{-2}, and from the bromide-ion dependence $k_{13}k_{14}$ was $(2.1 \pm 0.3) \times 10^{12}$ dm^6 mol^{-2} s^{-2}.

Although iodide ion reacts with [NiL^1]$^{3+}$ to form I$_2$, the kinetics of oxidation of I$^-$ by the nickel(III) complexes were not investigated because I$^-$ was preferentially oxidised by the radicals used to generate the nickel(III) complexes.

When the pseudo-halide ions [SCN]$^-$ and [N$_3$]$^-$ were added to solutions of the nickel(II) complexes and Br$^-$ ions, the nickel(III) complexes generated by oxidation with [Br$_2$]$^-$ ions decayed more rapidly than in solutions containing Br$^-$ alone but still by a second-order process. The ions [SCN]$^-$ and [N$_3$]$^-$ were much more effective reducing agents than Br$^-$. Millimolar concentrations of [SCN]$^-$ or [N$_3$]$^-$ in the presence of 0.1 mol dm^{-3} Br$^-$ significantly increased the rate of loss of Ni^{III}. The rates of the reactions of the pseudo-halide ions with Ni^{III} were determined over a limited concentration range and the dependence on [Ni^{II}] was not investigated. Both ions are more readily oxidised than Br$^-$ and reactions (12)—(14), X = [SCN]$^-$ or [N$_3$]$^-$, are expected to describe the systems. The large increases in the observed rate constants for the loss of Ni^{III} for small (1×10^{-3} mol dm^{-3}) concentrations of the ions indicate that K_{12} is not a limiting factor in these cases, and the second-order kinetics imply that the observed rate constant, k_0, is given by (16). The values in Table 2 for

$$k_0 = k_{13}k_{14}[\mathrm{X}^-]/k_{-13}[\mathrm{Ni^{II}}] \qquad (16)$$

$k_{13}k_{14}/k_{-13}$ have been calculated on this assumption. In general, azide ion was oxidised more slowly than thiocyanate. The higher reduction potential for [N$_3$]$^-$ decreases the equilibrium constant k_{13}/k_{-13}, and the larger values of k_0 for the pseudo-halide ions compared with bromide are also due to the smaller reduction potentials.

The addition of the inert anion [SO$_4$]$^{2-}$ to solutions in which the nickel(III) complexes oxidised Br$^-$ reduced the rate of oxidation. Sulphate ions are not oxidised by Ni^{III}, but if [SO$_4$]$^{2-}$ ions are preferentially co-ordinated to the Ni^{III} the bromide ion oxidation will be retarded. The effect was much greater for complex [NiL^1]$^{3+}$ than for the complexes of L^2 or L^3.

Hydrogen peroxide and peroxy-radicals. Hydrogen peroxide increased the rate of decay of the nickel(III) and Ni^{II}L$^\bullet$ complexes. The systems were complex and relatively low (<100) ratios of [H$_2$O$_2$] to [Ni^{II}] were used to ensure that all the OH radicals used to generate the nickel(III) species were scavenged by the nickel(II) complexes [reaction (4)] and none reacted with the H$_2$O$_2$ to generate peroxy-radicals. The nickel(III) and nickel(II) ligand-radical complexes decayed by first-order reactions under these conditions with rate constants which were linear functions of the H$_2$O$_2$ concentration. The rate constants for $[NiL]^{3+}$ ($L = L^2$ or L^3) were pH independent (pH 1—4) but the rate constant for $[NiL^1]^{3+}$ increased with pH in this range. The rate constants for the reactions of the nickel(II) ligand radical species ($L = L^1$ or L^2) determined at pH 5 are included in Table 2.

TABLE 2

Rate constants for reductions of nickel(III) macrocyclic complexes [a]

Reaction		L^3	L^2	L^1
$Cl^- + [NiL]^{3+}$ [b]	$k_{13}k_{14}$	$(2.0 \pm 0.5) \times 10^{11}$		
$Br^- + [NiL]^{3+}$ [b]	$k_{13}k_{14}$	$(6.0 \pm 1.0) \times 10^{13}$	$(2.0 \pm 0.5) \times 10^{12}$	$(2.4 \pm 0.5) \times 10^{11}$
$[SCN]^- + [NiL]^{3+}$ [b]	$k_{13}k_{14}$	$(4.1 \pm 0.5) \times 10^{15}$	$(5.4 \pm 1.0) \times 10^{14}$	$(1.5 \pm 0.3) \times 10^{12}$
$[N_3]^- + [NiL]^{3+}$ [c]	$k_{13}k_{14}/k_{-13}$	$(1.0 \pm 0.3) \times 10^{8}$	$(9.0 \pm 1.5) \times 10^{6}$	$(2.0 \pm 0.3) \times 10^{6}$
$H_2O_2 + [NiL]^{3+}$ [d]	k_{11}	$(3.3 \pm 0.4) \times 10^{3}$	$(2.3 \pm 0.3) \times 10^{3}$	$(1.4 \pm 0.3) \times 10^{11}$ [e]
$H_2O_2 + Ni^{II}L^{\bullet}$ [f]	k_{15}		$(5 \pm 1) \times 10^{2}$	$(2 \pm 1) \times 10^{4}$
$HO_2 + [NiL]^{3+}$ [g]	k_{18}	$(8.5 \pm 1.0) \times 10^{5}$	$(1.6 \pm 0.3) \times 10^{5}$ [h]	$(1.0 \pm 0.2) \times 10^{5}$
$[O_2]^- + [NiL]^{3+}$ [i]	k_{18}	$(1.0 \pm 0.2) \times 10^{9}$	$(1.6 \pm 0.4) \times 10^{9}$ [h]	$(2.1 \pm 0.4) \times 10^{9}$

[a] Rate constants in units of $dm^3\ mol^{-1}\ s^{-1}$, products of rate constants in units of $dm^6\ mol^{-1}\ s^{-2}$ at 22 ± 2 °C; pH 1 except where otherwise noted. [b] Values of $k_{13}k_{14}$ computed using the values of k_{-13} in Table 1. Only $[NiL^3]^{3+}$ reacts with Cl^-. [c] Observed rate constants for overall reaction; values for k_{-13} not available for $[N_3]^-$. [d] No reverse reaction (k_{-17}) for $[NiL]^{3+}$ ($L = L^2$ or L^3). [e] Value for $k_{17}k_{18}$ computed using value for k_{-17} in Table 1; only $[NiL^1]^{2+}$ oxidised by HO_2. [f] At pH 5; no $Ni^{III}L^{\bullet}$ species formed from $[NiL^3]^{3+}$. [g] At pH 2.0. [h] The ratio $k(O_2^-) : k(HO_2)$ for reaction of the peroxy-radicals with $Ni^{II}(L{=}L^2)L^{\bullet}$ was 5 : 1. [i] At pH 6.2.

The reaction of $[NiL^1]^{3+}$ with H_2O_2 was complicated at pH <1 by the appearance of a second-order process which was retarded by $[NiL^1]^{2+}$, and the kinetic behaviour at this pH (0.3) resembled that for the reaction with halide ions. The oxidation of H_2O_2 by metal ions involves the intermediate formation of HO_2 or $[O_2]^-$ radicals and the retardation of the reaction between $[NiL^1]^{3+}$ and H_2O_2 suggested that the complex $[NiL^1]^{2+}$ was oxidised by HO_2 radicals in 0.5 mol dm^{-3} acid. For a general reaction scheme for the oxidation of H_2O_2 [reactions (17) and (18)] the steady-state rate expression is (19). The first order kinetics for $[NiL]^{3+}$ ($L = L^2$ or

$$[Ni^{III}L]^{3+} + H_2O_2 \rightleftharpoons [Ni^{II}L]^{2+} + H^+ + HO_2 \quad (17)$$

$$[Ni^{III}L]^{3+} + HO_2 \longrightarrow [Ni^{II}L]^{2+} + H^+ + O_2 \quad (18)$$

$$-\frac{d[Ni^{III}]}{dt} = \frac{2k_{17}k_{18}[Ni^{III}]^2[H_2O_2]}{k_{-17}[Ni^{II}L][H^+] + k_{18}[Ni^{III}L]} \quad (19)$$

L^3) imply that $k_{-17}[Ni^{II}] < k_{18}[Ni^{III}]$ for these complexes. We found that neither complex (2) nor (3) reacted with HO_2 radicals and the observed rate constants for the reaction with H_2O_2 therefore apply to reaction (17). The reverse of reaction (17) is acid dependent and accounts for the appearance of the retardation by Ni^{II} for the $[NiL^1]^{3+}$ complex only at high acid concentrations. Under these conditions the rate expression gives rise to second-order behaviour with a linear dependence on $[H_2O_2]$. At 0.5 mol dm^{-3} acid the value of $k_{17}k_{18}/k_{-17}$ was obtained from the gradient of the plot of the observed rate constant against $1/[Ni^{II}]$. There was no evidence for prior involvement of a coordinated $[HO_2]^-$ ion, which has been found for the oxidation of H_2O_2 by aquametal ions,[41] but not for the oxidation by $[Ni(bipy)_3]^{3+}$.[14]

The reactions between the nickel(II) complexes and peroxy-radicals could be studied in solutions containing H_2O_2 for which the ratio $[H_2O_2] : [Ni^{II}]$ was large enough for the H_2O_2 to scavenge all the OH radicals, converting them into HO_2 or $[O_2]^-$ radicals. In these conditions no reaction with complex (2) or (3) was observed. Complex (1) reacted with peroxy-radicals to give $[NiL^1]^{3+}$. The growth of the nickel(III) absorbance followed first-order kinetics and the rate constant was proportional to the concentration of the nickel(II) complex. The reaction was acid-catalysed and reliable kinetic measurements were possible only in 0.5 mol dm^{-3} acid. The rate constant for the reverse of reaction (17), k_{-17}, is $(1.1 \pm 0.2) \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$. The complex $[NiL^1]^{3+}$ has the lowest reduction potential of the three nickel(III) complexes and only $[NiL^1]^{2+}$ is oxidised by HO_2 radicals.

Reactions between nickel(III) complexes and peroxy-radicals were difficult to study because of the need to produce both transient species simultaneously. Photolysis of solutions containing H_2O_2 and the nickel(II) complexes for which the ratio $[H_2O_2] : [Ni^{II}L]$ was between the limits discussed above, generated both Ni^{III} and peroxy-radicals (HO_2 or $[O_2]^-$ depending on the pH), but the decay kinetics were complex and dependent on the ratio of the concentrations of Ni^{III} and HO_2 produced. For example, with $[NiL^1]^{2+}$ at 0.5 mol dm^{-3} acid it was possible to observe the reaction of $[NiL^1]^{3+}$ with HO_2 followed by the further oxidation of Ni^{II} by HO_2, if the concentration of HO_2 radicals was in excess of that of Ni^{III}. When Ni^{III} was in excess the reaction with H_2O_2 interfered. Competition between tetranitromethane and Ni^{III} for peroxy-radicals was used to estimate the rates of reaction of HO_2 and nickel(III) complexes. Tetranitromethane is reduced by peroxy-radicals to the intensely absorbing $[C(NO_2)_3]^-$ radical ion with a rate constant of $3.2 \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$ at pH 4.[42] The relative rates of reaction of the nickel(III) complexes with HO_2 and $[O_2]^-$ radicals were determined from the pH dependence, which was typical of reactions of peroxy-radicals. Although the different techniques were subject to large errors there was broad agreement between them, and the rate constants of Table 2 are believed to be correct within 50%. All the nickel(III) complexes react with HO_2 radicals at similar rates, and the independent measurement of the rate constant for the HO_2–$[NiL^1]^{3+}$ reaction, k_{18}, allowed k_{17} for $[NiL^1]^{3+}$ to be calculated from the previously measured value of

$k_{17}k_{18}/k_{-17}$, and compares well with that measured at higher pH where reaction (-17) does not occur.

Metal ions. The reactions of the nickel(III) complexes with aquated metal ions were studied in solutions in which halogen radical ions were used to generate the nickel(III) complexes. The relative concentrations of the nickel(II) complexes and the metal ions were normally such that $>90\%$ of the oxidising radicals reacted with the nickel(II) complexes. At the higher concentrations of $\mathrm{Fe^{2+}(aq)}$ ions some of the $[\mathrm{X_2}]^-$ ions oxidised the $\mathrm{Fe^{II}}$ as well as the $\mathrm{Ni^{II}}$ but the reaction was more rapid than that between the nickel(III) complexes and the $\mathrm{Fe^{2+}}$, and did not interfere. Second-order rate constants for reaction (20) were determined from the dependence of

$$[\mathrm{Ni^{III}L}]^{3+} + \mathrm{M}^{2+} \longrightarrow [\mathrm{Ni^{II}L}]^{2+} + \mathrm{M}^{3+} \qquad (20)$$

the first-order rate constants for the loss of the nickel(III) absorbance on the metal-ion concentration. All the nickel(III) complexes oxidised $\mathrm{Fe^{2+}}$ ions with similar rate constants, *ca.* 10^4 dm^3 mol^{-1} s^{-1} (Table 3). Only for $[\mathrm{NiL^3}]^{3+}$ was it possible to measure the rate of oxidation of $\mathrm{Mn^{2+}(aq)}$ ions. The rate of decay of the complexes $[\mathrm{NiL}]^{3+}$ ($\mathrm{L = L^1}$ or $\mathrm{L^2}$) was unchanged by the presence of 1×10^{-2} mol dm^{-3} $\mathrm{Mn^{2+}}$ and the upper limit for the rate constant for reaction (20) in these cases is 10 dm^3 mol^{-1} s^{-1}. None of the nickel(III) complexes reacted with $\mathrm{Co^{2+}(aq)}$ ions at a measurable rate, and the upper limit for the rate constants must also be 10 dm^3 mol^{-1} s^{-1}.

TABLE 3

Rate constants for $[\mathrm{NiL}]^{3+}$ oxidation of metal ions *

Metal ion	$\mathrm{L^3}$	$\mathrm{L^2}$	$\mathrm{L^1}$
$\mathrm{Fe^{2+}}$	$(3.6 \pm 0.4) \times 10^4$	$(2.1 \pm 0.4) \times 10^4$	$(4.2 \pm 0.5) \times 10^4$
$\mathrm{Mn^{2+}}$	$(1.5 \pm 0.2) \times 10^2$	$\leqslant 10$	$\leqslant 10$

* Second-order rate constants in units of dm^3 mol^{-1} s^{-1} at 22 ± 2 °C and pH 1. None of the nickel(III) complexes oxidised $\mathrm{Co^{2+}}$ ions.

The reactions of the nickel(III) complexes with $\mathrm{Fe^{2+}(aq)}$ ions are relatively slow and have almost the same rate constants. From the Marcus theory of outer-sphere electron-transfer reactions the range of *ca.* 0.2 V in the reduction potentials of the nickel(III) complexes would be expected to lead to a factor of *ca.* 100 between the rate constants for the $[\mathrm{NiL^3}]^{3+}$ and $[\mathrm{NiL^1}]^{3+}$ complexes, since large differences in the electron-exchange rates are not likely for the nickel complexes. For $[\mathrm{NiL^3}]^{3+}$ the rate constant for the oxidation of $\mathrm{Mn^{2+}(aq)}$ is only 200 times smaller than that for the oxidation of $\mathrm{Fe^{2+}(aq)}$ although $\Delta G^\ominus$ for the reaction is 70 kJ mol^{-1} more positive for $\mathrm{Mn^{2+}}$. The electron-transfer rates are smaller than the ligand-exchange rates for $\mathrm{Fe^{2+}(aq)}$ and $\mathrm{Mn^{2+}(aq)}$ and the reactions may be inner sphere. The rates of apical-ligand exchange for the nickel(III) macrocyclic complexes are of course unknown. The failure of $[\mathrm{NiL^1}]^{3+}$ to oxidise $\mathrm{Mn^{2+}}$ suggests that $E^\ominus$ for this complex is less than, or very close to, the value for $\mathrm{Mn^{2+}(aq)}$, 1.51 V, which confirms the ability of the $\mathrm{HO_2}$ radical to oxidise $[\mathrm{NiL^1}]^{2+}$.

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