Pulse and γ-Radiolysis of Nickel(II) Nitrilotriacetate in Aqueous Solutions

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The radiolysis of the title complex $[Ni(nta)]^-$ has been studied by pulse radiolysis and by product analysis after γ-radiolysis. Hydroxide radicals abstract a hydrogen from the ligand of the complex, $k = (1.2 \pm 0.1) \times 10^9$ dm³ mol⁻¹ s⁻¹, to give complex radicals which react with various metal ions such as Cu^{2+}, Ir^{IV}, and Ni^{2+} and in their absence with $[Ni(nta)]^-$ by electron transfer. Reaction of O_2 with the radicals is comparatively slow, $k = (3.9 \pm 0.4) \times 10^3$ dm^3 mol^{-1} s^{-1}. Ligand-oxidation products and their yields are consistent with the mechanisms of the reactions suggested. Hydrated electrons reduce the complex to $[Ni(nta)]^{2-}$, $k = (1.5 \pm 0.1) \times 10^9$ dm^3 mol^{-1} s^{-1}, which rapidly disappears through a bimolecular reaction, $2k = (1.5 \pm 0.1) \times 10^9$ dm^3 mol^{-1} s^{-1}, which is independent of pH in the range 5—9.

THE radiolysis of transition-metal complexes possessing aminocarboxylate ligands has been extensively studied by γ-radiolytic methods involving [1-3] product analysis and by pulse radiolysis.[4-6] For most metal complexes studied the results from either method are complementary. However, in the case of $[Ni(edta)]^{2-}$ (edta = ethylenediaminetetra-acetate), while γ-radiolysis results indicated the formation of a radical [1b] *via* hydrogen abstraction from the ligand by OH, pulse-radiolysis data [6] supported the formation of a fairly long-lived $[Ni(edta)]^-$ by oxidation of the metal ion by OH. Recently, it was also claimed that OH oxidizes the metal ion [6b] in $[Ni(nta)]^-$ (nta = nitrilotriacetate).

In the course of our studies [2,5] on the radiolysis of nta complexes of the first-row transition-metal ions we have investigated the radiolysis of $[Ni(nta)]^-$ by both γ- and pulse-radiolysis.

EXPERIMENTAL

All chemicals used in the experiments were of analytical reagent grade and were used without further purification. t-Butyl alcohol used as OH scavenger was purified by repeated crystallization. Solutions were made in triply distilled water for γ-radiolysis and with water from a Milli-R015 filtering system for pulse radiolysis. High-purity gases were used to saturate or deaerate solutions, respectively. A gas-mixing apparatus having two Matheson Co. R-2-15-AA tubes fitted with regulatory valves was used for obtaining solutions with mixtures of N_2O and O_2. Concentrations of the respective gases were calculated from their partial pressures assuming the validity of Henry's law.

Nickel(II) nitrilotriacetate, referred to as $[Ni(nta)]^-$ or $Ni(R_2NCH_2COO^-)$, was prepared and purified as described for the other nta complexes.[2c,5]

Analytical.—Iminodiacetic acid, H_2ida, or any other compound having a primary or secondary nitrogen atom, was estimated by use of the ninhydrin [7] reagent. Glyoxylic acid was determined with 2,4-dinitrophenylhydrazine,[8] extracting the hydrazone into aqueous $Na_2[CO_3]$, while formaldehyde was estimated by use of both chromotropic acid (4,5-dihydroxynaphthalene-2,7-disulphonic acid) [9] and 2,4-dinitrophenylhydrazine.[10] Hydrogen peroxide was determined by use of tri-iodide [11] and titanium(III) sulphate.[12] No interference from the other species present in solution was observed in any of the determinations.

Spectrophotometric measurements were made in a Hilger Uvispeck spectrophotometer while spectra were recorded in a Cary 14 spectrophotometer.

Irradiations.—Solutions were γ-irradiated by a 2.8 kCi ^{60}Co γ-source and the absorbed dose was determined by the iron(II) sulphate dosimeter, taking $G(Fe^{3+}) = 15.6$.

Pulse Radiolysis.—The pulse radiolysis set-up and the off-line calculator for analysing data have been described [13,14] elsewhere. The LINAC delivers 10 MeV † electron pulses of width 5—50 ns with currents up to 7 A. The dose delivered, varying from 300 to 3 000 rad per pulse, was monitored by secondary emission monitors whose outputs were in turn calibrated against the thiocyanate dosimeter. A 450-W xenon lamp was used for absorption measurements. Interference filters were employed to eliminate scattered light at wavelengths below 280 nm.

Solutions were buffered with 10^{-3} mol dm^{-3} phosphate at pH = 7. Dissociation of the complex into free aqueous metal ions was calculated to be $<1\%$ for $[Ni(nta)^-] \geqslant 5 \times 10^{-4}$ mol dm^{-3} at pH = 7, using the known [15] stability-constant data.

The flow rate of the solution was adjusted to be slow enough to avoid loss of signal due to removal of the solution during the scan, while adequate to prevent repeated pulsing of the same solution. All kinetic and spectral data were averaged over at least 10 pulses up to a maximum of 50 pulses for each decay or wavelength respectively. Rate constants for pseudo-first-order reactions of OH and e⁻(aq) with the complex were calculated from the plot of $T_{1/2}$ against $[Ni(nta)^-]^{-1}$ for various doses.

Irradiation of water and aqueous solutions produces the radical and molecular products in equation (1) with yields (G values) shown in parentheses. The G values may vary [16]

$$H_2O \rightsquigarrow e^-(aq)\ (2.7),\ OH\ (2.7),\ H\ (0.6),\ H^+\ (2.7),\ H_2O_2\ (0.75),\ H_2\ (0.45) \quad (1)$$

somewhat in concentrated solutions of highly reactive scavengers.

RESULTS AND DISCUSSION

Formaldehyde was the principal product of radiolysis of $[Ni(nta)]^-$ in deaerated and N_2O-saturated solutions together with small amounts of H_2ida and glyoxylic acid. Yields of all three compounds increased linearly with dose. The spectra of irradiated and non-irradiated solutions also indicated the presence of a product absorb-

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† Throughout this paper: 1 eV ≈ 1.60×10^{-19} J; 1 rad = 10^{-2} J kg^{-1}.

TABLE 1

Observed G values in the radiolysis of $[Ni(nta)]^-$ (1×10^{-2} mol dm^{-3}) in neutral aqueous solution

Scavenger (S)	[S]/ mol dm^{-3}	$G(H_2ida)$	G(CHOCOOH)	$G(CH_2O)$	$G(H_2O_2)$
None		0.3	0.3	1.7 ± 0.1 [a] *ca.* 0.2 [b]	
N_2O	1.6×10^{-2} [c]	0.8 ± 0.1	0.9 ± 0.1	2.1 ± 0.1 [a] *ca.* 0.2	0.7 ± 0.1
O_2	2.6×10^{-4} [d]	2.6 ± 0.2	2.8 ± 0.2		2.7 ± 0.2

[a] Determined by use of chromotropic acid. [b] Determined by use of 2,4-dinitrophenylhydrazine. [c] For N_2O-saturated solution. [d] For aerated solution.

ing in the u.v. region as shown in Figure 1. In the presence of Bu^{t}OH this spectrum was absent as also were the other ligand-oxidation products given above. In aerated solutions, however, no formaldehyde was observed; H_2ida and glyoxylic acid were the only products and were formed in equal amounts. Table 1 lists the observed G values for the products under various conditions of γ-radiolysis.

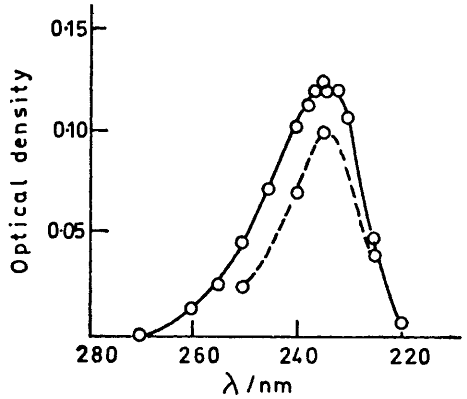

FIGURE 1 Difference spectrum of the product upon γ-radiolysis of 1×10^{-2} mol dm^{-3} $[Ni(nta)]^-$ at a dose of 2.84×10^{18} eV g^{-1}; (——), N_2O-saturated solution; (– – –), deaerated solution

Table 2 summarizes the rate constants and spectral characteristics of the different species observed in pulse radiolysis. Pulse radiolysis of N_2O-saturated solutions of $[Ni(nta)]^-$ yielded a fairly long-lived transient (Figure 2) with $\lambda_{max.} = 290$ nm ($\varepsilon_{max.} = 2\,050 \pm 180$ dm^3 mol^{-1} cm^{-1}) independent of the concentration of $[Ni(nta)]^-$ in the range 4×10^{-4}—5×10^{-3} mol dm^{-3}. The spectral properties of this species as well as the rate constants for its formation and reaction with O_2, Table 2, show that it is the same transient observed by Lati and Meyerstein.[6b]

Similarity of the spectrum with that of the nta radical [6b, 17] would indicate that the reaction is essentially due to hydrogen abstraction from the ligand by OH [equation (2)]. However, the above authors [6b] suggested that the

$$Ni(R_2NCH_2COO^-) + OH \longrightarrow Ni(R_2N\dot{C}HCOO^-) + H_2O \quad (2)$$

transient is produced by the oxidation of the metal ion by OH [equation (3)]. This conclusion was based on

$$[Ni(nta)]^- + OH \longrightarrow [Ni(nta)] + OH^- \quad (3)$$

their observation of: (*a*) a relatively fast first-order decay which produces only slight changes in the spectrum; (*b*) a slow first-order decay of the transient, attributed to intramolecular electron transfer from the ligand to the Ni^{III}, and (*c*) reactions of the transient with Br$^-$ and I$^-$.

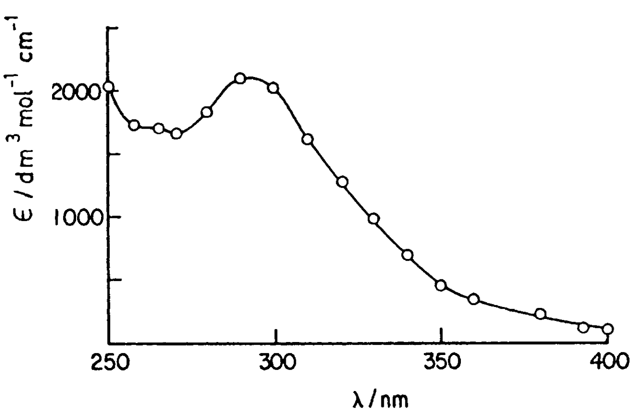

FIGURE 2 Absorption spectrum of the intermediate 8 μs after the pulse in N_2O-saturated 6×10^{-4} mol dm^{-3} $[Ni(nta)]^-$ solutions at pH = 7

TABLE 2

Kinetic and spectral characteristics of the reactions and transients observed in the pulse radiolysis of $[Ni(nta)]^-$.

Reactants	Products	Rate constant/ [a] dm^3 mol^{-1} s^{-1}	$\lambda_{max.}$ [b]/nm
$[Ni(nta)]^- + OH$	$Ni(R_2N\dot{C}HCOO^-) + H_2O$	$k_2 = 1.2 \times 10^9$	290 (2 050 ± 180)
$Ni(R_2N\dot{C}HCOO^-) + M^{n+}$	$Ni(R_2\overset{+}{N}CHCOO^-) + M^{(n-1)+}$	k_7 $M^{n+} = Ir^{4+}, 3.6 \times 10^7$ $Ni^{2+}, 3.6$ [c] $\times 10^3$ $[Ni(nta)]^-$, *ca.* 58	
$Ni(R_2N\dot{C}HCOO^-) + Cu^{2+}$	$Ni\{R_2NCH(Cu)COO^-\}$	$k_8 = 7.8 \times 10^7$	290 (1 460 ± 150)
$Ni(R_2N\dot{C}HCOO^-) + O_2$	$Ni(R_2NCH\dot{O}_2COO^-)$	$k_{11} = 3.9 \times 10^3$	
$e^-(eq) + [Ni(nta)]^-$	$[Ni(nta)]^{2-}$	$k_{14} = 1.5 \times 10^9$	300 (1 980 ± 180) [d]
$2[Ni(nta)]^{2-}$	$[\{Ni(nta)\}_2]^{4-}$	$2k_{15} = 1.5 \times 10^9$	
$CO_2^{\cdot -} + [Ni(nta)]^{2-}$	$Ni + CO_2 + nta^{2-}$	$k_{16} \geqslant 1.5 \times 10^9$	

[a] Errors are ±10% unless otherwise indicated. [b] Values of ε/dm^3 mol^{-1} cm^{-1} are given in parentheses. [c] ±20%. [d] pH = 7.

Our experiments with various initial concentrations of [Ni(nta)]$^-$ revealed no sign of decay of the transient signal up to at least 10 ms after the pulse, as shown in Figure 3(*a*), at any wavelength in the range 270—340 nm where the transient has observable absorption. Also, the decay of the transient was found to be pseudo-first order and the half-life decreased from $\geqslant$20 s at [Ni(nta)$^-$] *ca.* 6 × 10^{-4} mol dm^{-3} to *ca.* 4 s at 3 × 10^{-3} mol dm^{-3} as shown in Figure 3(*b*). The signal decay remained unaffected in the presence of Br$^-$ and hence it is presumed that there is no reaction between Br$^-$ and the transient. Figure 3(*d*) shows the decay of the absorption signal in 10^{-3} mol dm^{-3} [Ni(nta)]$^-$ solution containing 10^{-4} mol dm^{-3} Br$^-$. Taking $k = 2 \times 10^3$ dm^3 mol^{-1} s^{-1},[6b] the half-life should have been 3.5 s if there was a reaction between Br$^-$ and the transient.

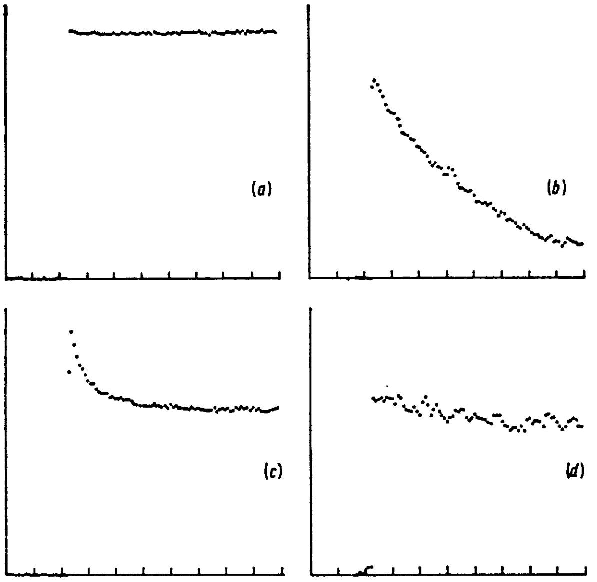

FIGURE 3 Transient signals, λ = 290 nm, obtained in the pulse radiolysis of: (*a*) 6 × 10^{-4} mol dm^{-3} [Ni(nta)]$^-$ in N$_2$O-saturated solution at pH 7, 100 μs between each point; (*b*) 3 × 10^{-3} mol dm^{-3} [Ni(nta)]$^-$ in N$_2$O-saturated solution at pH 7, 100 ms between each point; (*c*) 6 × 10^{-4} mol dm^{-3} [Ni(nta)]$^-$ in deaerated solution at pH 7, 100 μs between each point; and (*d*) 8 × 10^{-4} mol dm^{-3} [Ni(nta)]$^-$ + 1 × 10^{-4} mol dm^{-3} NaBr in N$_2$O-saturated solution at pH 7, 100 ms between each point

However, when [Ni(nta)]$^-$ prepared by mixing equal amounts of Ni[SO$_4$] and Na$_3$[nta] solutions was irradiated a fast first-order decay was seen which resulted in a small decrease of the signal at 290 nm, with a half-life of 185 μs. This decay was absent when solutions of solid Na[Ni(nta)] from different batches were pulse radiolysed.

In order to see whether traces of free metal ions could be responsible for the differences between samples prepared by mixing the ions in solution and solutions of the pure complex we followed the decay of the signal in presence of Cu^{2+}(aq), Ni^{2+}(aq), and IrCl$_6{}^{2-}$. The decay of the signal was rapid in the presence of 10^{-4} mol dm^{-3} Cu^{2+}(aq) or IrCl$_6{}^{2-}$. In the latter case the decrease of absorbance at 490 nm ($\lambda_{\text{max.}}$ of IrCl$_6{}^{2-}$) due to the depletion of Ir$^{\text{IV}}$ by reaction with the transient was also followed. With Ni^{2+}(aq) the reaction was slow, as evident from the rate constants in Table 2.

It is unlikely that [Ni(nta)], if formed, would react with metal ions in their higher oxidation states. Since both Cu^{2+}(aq) and Ir$^{\text{IV}}$ react at comparable rates although their oxidation potentials [18] are vastly different, outer-sphere oxidation of Ni$^{\text{III}}$ to Ni$^{\text{IV}}$ can be ruled out. Moreover, such a reaction is clearly impossible with Ni^{2+}(aq).

In deaerated solutions of 10^{-3} mol dm^{-3} [Ni(nta)]$^-$ without any added scavengers the decay of the signal due to [Ni(nta)]$^{2-}$ [equation (14)] was independent of the decay of the OH reaction product [Figure 3(*c*)]. If the product is Ni$^{\text{III}}$ it is not clear why the decay of Ni$^{\text{I}}$ is unaffected by the presence of Ni$^{\text{III}}$. However, if the transient is a radical all the observed results can be readily explained.

Figure 4 shows the spectrum of the product formed after the reaction between Cu^{2+}(aq) and the transient is complete. It shows no resemblance to either Cu^{3+}(aq) (refs. 6*b* and 19) or Cu$^+$(aq),[20,21] which could form through reactions (4) or (5). The third possibility that

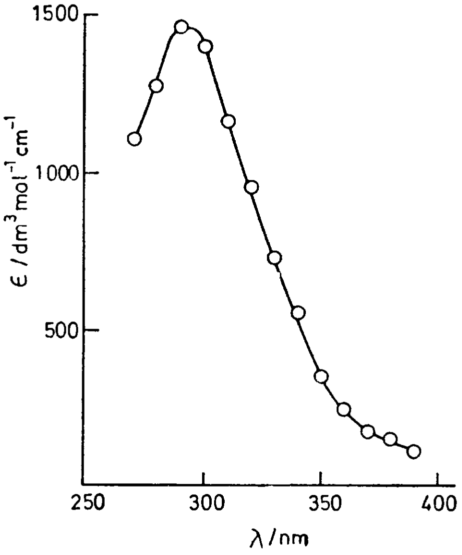

FIGURE 4 Absorption spectrum of the product formed on pulse radiolysis of 6 × 10^{-4} mol dm^{-3} [Ni(nta)]$^-$ + 1 × 10^{-4} mol dm^{-3} Cu[SO$_4$] in N$_2$O-saturated solution at pH 7, between 0.9 and 1.3 ms after the pulse

$$[\text{Ni(nta)}] + \text{Cu}^{2+}(\text{aq}) \longrightarrow [\text{Ni(nta)}]^- + \text{Cu}^{3+}(\text{aq}) \qquad (4)$$

$$\text{Ni(R}_2\text{N}\dot{\text{C}}\text{HCOO}^-) + \text{Cu}^{2+}(\text{aq}) \longrightarrow \text{Ni(R}_2\text{N}\overset{+}{\text{C}}\text{HCOO}^-) + \text{Cu}^+(\text{aq}) \qquad (5)$$

the product is [Cu(nta)]$^{2-}$ formed through ligand exchange either before or after reduction of Cu^{2+}(aq) could also be discarded since [Cu(nta)]$^{2-}$ showed no absorption between 300 and 500 nm when [Cu(nta)]$^-$ was irradiated in presence of Bu^{t}OH, where [Cu(nta)]$^{2-}$ forms by reaction with e$^-$(aq). Accordingly it is presumed that the reaction proceeds through the formation of a Cu–C bond [2c] [equation (6)].

With $Ni^{2+}(aq)$, $[Ni(nta)]^-$, and Ir^{IV} the reaction is probably outer-sphere electron transfer as can be seen from the large differences between the rate constants and for the rates of water exchange from their inner spheres. Iridium(IV), being substitution inert, cannot follow the inner-sphere mechanism. The $[Ni(nta)]^{2-}$ and

$$Cu^{2+}(aq) + Ni(R_2N\dot{C}HCOO^-) \longrightarrow Ni\{R_2NCH(Cu)COO^-\} \quad (6)$$

$$Ni(R_2N\dot{C}HCOO^-) + M^{n+} \longrightarrow Ni(R_2N\overset{+}{C}HCOO^-) + M^{(n-1)+} \quad (7)$$

$$Ni(R_2N\dot{C}HCOO^-) + [Ni(nta)]^- \longrightarrow Ni(R_2N\overset{+}{C}HCOO^-) + [Ni(nta)]^{2-} \quad (8)$$

$$Ni(R_2N\overset{+}{C}HCOO^-) \xrightarrow{H_2O} Ni(R_2NCH_2OH) + CO_2 \quad (9a)$$

$$\xrightarrow{H_2O} Ni\{R_2NCH(OH)COO^-\} + H^+ \quad (9b)$$

Ni^+ formed in reactions (7) and (8) decay very fast (discussed later) and hence the rate-determining step would be their formation through reactions (7) and (8).

The low yields of H_2ida obtained in γ-radiolysis in comparison with the other nta complexes [2,5] can be explained by the above scheme of reactions. Both the product complexes in reactions (9a) and (9b) have tertiary nitrogen atoms which would not respond to the ninhydrin reagent. The small amounts of H_2ida and glyoxylic acid can be attributed to the disproportionation [2,5] of the radical [equation (10].

$$2Ni(R_2N\dot{C}HCOO^-) \xrightarrow{H_2O} Ni(R_2NH) + Ni(R_2NCH_2COO^-) + CHOCOO^- \quad (10)$$

The product in reaction (9a) could lead to the formation of CH_2O under the drastic conditions required in the chromotropic acid [9] method for determination of formaldehyde (heating for *ca.* 30 min in concentrated H_2SO_4). However, under the milder conditions employed in the determination by use of 2,4-dinitrophenylhydrazine,[10] formaldehyde could not be detected. The difference spectrum shown in Figure 1 is probably due to this hydroxy-compound since the increase in optical density at $\lambda_{max.}$ from deaerated to N_2O-saturated solutions is exactly paralleled by the corresponding increase in $G(CH_2O)$.

Thus the product yields in the radiolysis in deaerated and N_2O-saturated solutions will be given by $G_{OH} = G(CH_2O) + G(R_2NCHOHCOO^-) + 2G(H_2ida)$, which compares favourably with the observed yields.

Reaction with Oxygen.—Pulse radiolysis of $[Ni(nta)]^-$ solutions saturated with a 1 : 1 mixture of N_2O and O_2 ($[O_2] = 7 \times 10^{-4}$ mol dm^{-3}, assuming Henry's law) showed a relatively slow reaction between the radical and oxygen after which no significant absorption remained. The reaction can be attributed to the formation of peroxy-radicals similar to the radiolyses [2a,5] of nta and $[Co(nta)]^-$ [equation (11)]. Co-ordination of the ligand with Ni apparently slows down the reaction of O_2 with the radical which would indicate that the electron density on the α-carbon atom is reduced in the complex.

$$Ni(R_2N\dot{C}HCOO^-) + O_2 \longrightarrow Ni(R_2NCH\dot{O}_2COO^-) \quad (11)$$

The peroxy-radicals would hydrolyse to yield H_2ida and glyoxylic acid [equation (12)], the HO_2 formed

$$Ni(R_2NCH\dot{O}_2COO^-) \xrightarrow{H_2O} Ni(R_2NH) + CHOCOO^- + HO_2 \quad (12)$$

$$HO_2 + HO_2(O_2^-) \longrightarrow H_2O_2 + O_2 \quad (13a)$$

ultimately leading to H_2O_2 [equation (13a)]. Accordingly, the product yields in aerated solutions would correspond to $G_{OH} = G(H_2ida) = G(CHOCOO^-)$.

The H atoms are likely to be scavenged by oxygen to form HO_2 [reaction (19)] which leads to the production of more H_2O_2 through reaction (13a). The yield of H_2O_2 in the system [equation (13b) †] would then be determined by reactions (12), (13a), and (19) and the fraction of $e^-(aq)$ scavenged by O_2 to yield O_2^-. Taking $k\{e^-(aq) + O_2\} = 2.0 \times 10^{10}$ dm^3 mol^{-1} s^{-1}, $[O_2] = 2.6 \times 10^{-4}$ mol dm^{-3}, $k\{e^-(aq) + [Ni(nta)]^-\} = k_{14} = 1.5 \times 10^9$ dm^3 mol^{-1} s^{-1}, and $[Ni(nta)^-] = 1 \times 10^{-2}$ mol dm^{-3} (Table 1), $G(H_2O_2) = 2.7$. The yields of H_2ida, glyoxylic acid, and H_2O_2 shown in Table 1 are in support of this mechanism.

$$G(H_2O_2) = G_{H_2O_2} + \tfrac{1}{2}(G_{OH} + G_H) + \tfrac{1}{2}G\{e^-(aq)\} \frac{k\{e^-(aq) + O_2\}[O_2]}{k\{e^-(aq) + O_2\}[O_2] + k\{e^-(aq) + [Ni(nta)]^-\}[Ni(nta)^-]} \quad (13b)$$

Reaction with $e^-(aq)$.—The spectrum of $[Ni(nta)]^{2-}$ formed by the fast reaction between $e^-(aq)$ and $[Ni(nta)]^-$ is shown in Figure 5. The rate constant for reaction (14) was determined by observing the decay of the $e^-(aq)$

$$e^-(aq) + [Ni(nta)]^- \longrightarrow [Ni(nta)]^{2-} \quad (14)$$

signal at 560 nm for various concentrations of the complex, in the presence of Bu^tOH to scavenge the OH radicals at pH = 7. The t-butyl alcohol radicals (as well as methanol and ethanol radicals) showed no reactivity toward either $[Ni(nta)]^-$ or $[Ni(nta)]^{2-}$.

Decay of the $[Ni(nta)]^{2-}$ was second order and independent of pH in the range 5—9. Variations of the initial concentration of $[Ni(nta)]^-$ did not affect the decay and hence in analogy with the $[Co(nta)]^-$ system [5] it can be concluded that the nickel(I) species also disappears by association [equation (15)]. No metallic or

$$2[Ni(nta)]^{2-} \longrightarrow [\{Ni(nta)\}_2]^{4-} \quad (15)$$

colloidal Ni could be obtained in the presence of Bu^tOH and the solutions remained clear even after repeated pulses (5—6 pulses of 3 krad each), which rules out disproportionation of $[Ni(nta)]^{2-}$. However, in the presence of formate ions as OH scavenger the spectrum in Figure 6

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† $G(H_2O_2)$ is the experimentally measured amount of hydrogen peroxide in the system while $G_{H_2O_2}$ is the yield of molecular hydrogen peroxide as given by equation (1).

was obtained upon γ-radiolysis of 10^{-2} mol dm^{-3} [Ni(nta)]$^-$ in deaerated solutions. Pulse radiolysis of N_2O-saturated solutions of *ca.* 10^{-3} mol dm^{-3} [Ni(nta)]$^-$ in the presence of 5×10^{-2} mol dm^{-3} formate showed no interaction between the $CO_2^{\bullet -}$ radicals and [Ni(nta)]$^-$.

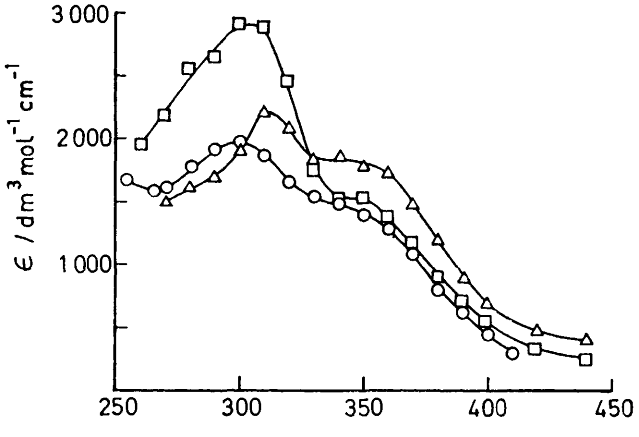

FIGURE 5 Transient absorption spectrum of [Ni(nta)]$^{2-}$ on pulse radiolysis of 6×10^{-4} mol dm^{-3} [Ni(nta)]$^-$ + 0.1 mol dm^{-3} Bu^{t}OH. pH = 5.5 (□), 7(○), or 8.9 (△)

However, in deaerated solutions containing formate ions where e$^-$(aq) reacts through reaction (14), the initial signal decayed rapidly to yield a residual absorption at $\lambda \leqslant 310$ nm similar to that in Figure 6. This is probably due to the reduction of [Ni(nta)]$^{2-}$ by $CO_2^{\bullet -}$[equation (16)] to form colloidal Ni.

$$[\mathrm{Ni(nta)}]^{2-} + CO_2^{\bullet -} \longrightarrow \mathrm{Ni} + CO_2 + \mathrm{nta}^{2-} \quad (16)$$

In the absence of scavengers for either OH or e$^-$(aq) the spectrum obtained was a composite of Figures 2 and 5. The decay of [Ni(nta)]$^{2-}$ was unaffected by the presence of the radical [Figure 3(*c*)] and after this decay the absorption that remained was identical with that in Figure 2.

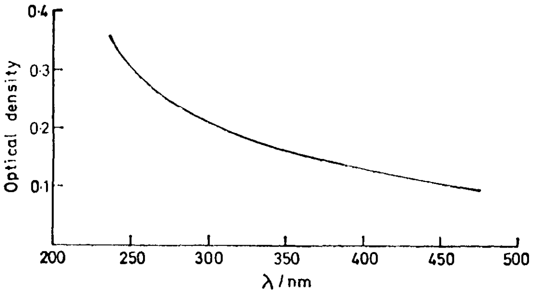

FIGURE 6 Difference spectrum of the product formed upon γ-radiolysis of deaerated 1.5×10^{-3} mol dm^{-3} [Ni(nta)]$^-$ + 2.0×10^{-2} mol dm^{-3} Na[O_2CH] at a dose of 4.3×10^{18} eV g^{-1}

The spectrum of [Ni(nta)]$^{2-}$ ($\lambda_{max.} = 300$ nm, $\varepsilon = 1.98 \times 10^3$ dm^3 mol^{-1} cm^{-1} at pH 7) shows some interesting features. At all three pH values studied the spectrum is characterized by a broad absorption band between 270 and 370 nm with two absorption maxima. In comparison to the spectrum[21,22] of free Ni$^+$(aq), [Ni(nta)]$^{2-}$ has a fairly intense band at 350 nm which is very weak in the former spectrum. In the case of [Ni(nta)]$^{2-}$ the charge-transfer band is likely to be from the metal to ligand as against transfer from metal to solvent in Ni$^+$(aq). This band (300 nm) increases considerably in intensity between pH 7 and 5.5. The increase would be expected in acid solutions due to the favouring of charge transfer as a result of protonation of the nitrogen atom. It is likely that the band at 350 nm arises from some *d*-level transitions in Ni$^{\mathrm{I}}$. The relatively high intensity of this peak in comparison with usual *d*-level transitions is probably due to the overlapping charge-transfer band.

Reaction of H *Atoms.*—Nothing conclusive could be discerned about the fate of the H atoms by either pulse radiolysis or by product estimation. The transient signal in N_2O-saturated solutions showed no increase due to the formation of the radical through reaction (17) over longer periods of time. It is possible that the H atoms

$$\mathrm{Ni(R_2NCH_2COO^-)} + \mathrm{H} \longrightarrow \mathrm{Ni(R_2N\dot{C}HCOO^-)} + \mathrm{H_2} \quad (17)$$

interact directly with the metal ion to reduce it to [Ni(nta)]$^{2-}$, reaction (18). In aerated solutions the H

$$[\mathrm{Ni(nta)}]^- + \mathrm{H} \longrightarrow [\mathrm{Ni(nta)}]^{2-} + \mathrm{H}^+ \quad (18)$$

atoms would be scavenged by O_2 to form HO_2 [equation (19)] which ultimately leads to the production of H_2O_2.

$$\mathrm{H} + O_2 \longrightarrow HO_2 \quad (19)$$

Conclusions.—The lack of reactivity of the metal centre in [Ni(nta)]$^-$ towards the oxidizing radicals can be attributed to the large redox potential for the couple [Ni(nta)]–[Ni(nta)]$^-$ and the consequent necessity for reaction through inner-sphere processes. Oxidation of [Ni(nta)]$^-$ by OH to [Ni(nta)] would not be expected for two reasons. (1) The redox potential for the couple [M(nta)]–[M(nta)]$^-$ would be more positive for Ni than Co and accordingly the outer-sphere oxidation would be less favoured in [Ni(nta)]$^-$. Earlier studies[5,6b] indicate that [Co(nta)]$^-$ is not oxidized by OH. (2) The rate of water exchange from Ni^{2+} is low, *ca.* 10^4 s^{-1}, and even if this rate is increased by an order of magnitude due to the presence of the nta ligand the rate of inner-sphere oxidation would still be unable to compete with hydrogen abstraction[6b] from the ligand. Even in the case of [Co(nta)]$^-$, which is likely[6b] to have a *ca.* 10^2-fold higher water-exchange rate, the inner-sphere oxidation is unable[5] to compete with hydrogen abstraction from the ligand. Only in the case of [Cu(nta)]$^-$ would inner-sphere oxidation have a comparable rate with hydrogen abstraction from the ligand, in accordance with the observed results[2c,6b] that [Cu(nta)]$^-$ is oxidized at least partially to [Cu(nta)].

The lack of reaction of Br_2^- with [Ni(nta)]$^-$ can again be traced to the low water-exchange rates for [Ni(nta)]$^-$ and the very fast reaction of Br_2^- with itself.[23]

The decay of the $[Ni(nta)]^-$ radical seems to occur predominantly by electron-transfer processes in contrast to the disproportionation of the $[Co(nta)]^-$ radical. It is plausible that disproportionation can proceed only between two free ligand radicals or between a co-ordinated and a free ligand radical, in which case, Co^{II} being more labile, disproportionation as in equations (20)—(22) would be more favourable for $[Co(nta)]^-$ than for $[Ni(nta)]^-$.

$$M^{II}(R_2N\dot{C}HCOO^-) \rightleftharpoons M^{2+} + R_2N\dot{C}HCOO^- \quad (20)$$

$$2R_2N\dot{C}HCOO^- \longrightarrow R_2N\overset{+}{\dot{C}}HCOO^- + R_2N\ddot{C}HCOO^- \quad (21)$$

$$R_2N\dot{C}HCOO^- + M^{II}(R_2N\dot{C}HCOO^-) \longrightarrow R_2N\overset{+}{\dot{C}}HCOO^- + M^{II}(R_2N\ddot{C}HCOO^-) \quad (22)$$

The lower reduction potential[21] of Ni for the couple M^{II}–M^{I} would also partially account for the electron-transfer process [reaction (8)]. The importance of redox potentials is clearly brought out by the effect of the various metal ions studied. Thus Ir^{IV} reacts *ca.* 10^4 times faster than $Ni^{2+}(aq)$ and the latter *ca.* 10^2 times faster than $[Ni(nta)]^-$. That these reactions do not take place through inner-sphere processes is clear from the opposite trends in rate constants for reduction and water exchange. Iridium(IV) is substitution inert; $Ni^{2+}(aq)$ is labile but is expected to have a lower water-exchange rate than $[Ni(nta)]^-$. However, the rate constant for the reaction increases in the order $[Ni(nta)]^- < Ni^{2+}(aq) < Ir^{IV}$. The ion $Cu^{2+}(aq)$ was found to react *via* the inner-sphere mechanism which is not surprising in view of its very high water-exchange rates.

Lack of reactivity of $CO_2^{\cdot -}$ and alcohol radicals (methanol, ethanol, and Bu^tOH) towards $[Ni(nta)]^-$ can be traced to their high bimolecular decay rates and the low water-exchange rate for Ni^{II}. It is known[21,22] that $Ni^{2+}(aq)$ reacts with $CO_2^{\cdot -}$ with $k < 10^5$ dm^3 mol^{-1} s^{-1} and that this reaction can only be observed under sufficiently high concentrations of $Ni^{2+}(aq)$ where it can compete with the bimolecular decay of $CO_2^{\cdot -}$. Earlier results[5] indicate that these radicals react with $[Co(nta)]^-$ through the intermediate formation of Co–C bonds.

Both the reactions of $[Ni(nta)]^{2-}$ with itself [reaction (15)] as well as with $CO_2^{\cdot -}$ [reaction (16)] are fast which implies that the exchange rate for Ni^I is quite high. Being a d^9 ion, Ni^I would be expected to be very labile.

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