Oxidation of First-row Bivalent Transition-metal Complexes containing Ethylenediaminetetra-acetate and Nitrilotriacetate Ligands by Free Radicals: A Pulse-radiolysis Study

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The kinetics of reaction of OH radicals with the ligands (L) ethylenediaminetetra-acetate (edta) and nitrilotriacetate (nta), and their complexes [ML] (M = Zn^{II}, Cu^{II}, Ni^{II}, Co^{II}, Fe^{II}, and Mn^{II}), have been studied. All these reactions have similar rate constants, although a hydrogen-abstraction reaction from the ligand is observed for the free ligands and their complexes with Zn^{II}, Mn^{II}, and Co^{II}. For $[Co(edta)]^{2-}$ a partial oxidation to $[Co(edta)]^-$ is observed. On the other hand, when M = Ni^{II}, Cu^{II}, or Fe^{II} the metal is oxidized by the OH radicals. The reasons for these observations are discussed in detail. The spectra, and kinetics of decomposition, of the unstable intermediates formed by the reactions of the OH radicals are reported and discussed. The reactions of nickel(III) complexes with I^-, Br^-, and O_2 are reported. The kinetics of oxidation of the complexes (M = Fe^{II}, Mn^{II}, or Co^{II}) by $[O_2]^{-\cdot}$, $^{\cdot}O_2CH_2CMe_2OH$, $[Br_2]^{-\cdot}$, $[(NCS)_2]^{-\cdot}$, and $[I_2]^{-\cdot}$, the latter only with M = Fe^{II}, have also been studied. The kinetics indicate an inner-sphere mechanism for these reactions. The kinetics of hydrolysis of $[Mn^{III}L(X)]$ and $[Co^{III}L(X)]$ thus formed are reported.

TRANSITION-METAL complexes containing ethylenediaminetetra-acetate (edta) and nitrilotriacetate (nta) as ligands are used in many systems which involve redox processes, *e.g.* analytical chemistry, Fenton's reagent in neutral or alkaline media, *etc.* They are also generally accepted as simple models for some transition-metal complexes in biological systems. Though some of these systems involve oxidizing free radicals, little is known on the mechanism of oxidation of these complexes by free radicals. It is generally accepted that hydroxyl radicals react with the iron complexes according to equations (1) and (2).[1] Thus it is suggested that

$$[Fe(edta)]^{2-} + OH \longrightarrow [Fe(edta)]^- + [OH]^-; \quad k_1 = 5.0 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}\ \text{(this work)} \qquad (1)\ *$$

$$[Fe(edta)]^- + OH \longrightarrow [Fe(\text{partially oxidized ligand})] + \text{oxidation products}; \quad k_2 = 5.2 \times 10^8\ dm^3\ mol^{-1}\ s^{-1}\ \text{(ref. 2)} \qquad (2)$$

hydroxyl radicals oxidize a low-valent central metal cation without affecting the ligand, but attack the ligand with a very high rate when the central cation is in a high oxidation state. Recently the products of oxidation of the $[Cu(edta)]^{2-}$, $[Ni(edta)]^{2-}$, $[Co(edta)]^-$, and $[Fe(edta)]^-$ by hydroxyl radicals were reported.[2-7] The results were interpreted by assuming an attack on the ligand since it was believed that all the central cations have high oxidation states. However, we have shown [8,9] that for nickel the reaction occurring is as in (3).

$$[Ni(edta)]^{2-} + OH \longrightarrow [Ni(edta)]^- + [OH]^-; \quad k_3 = 2.5 \times 10^9\ dm^3\ mol^{-1}\ s^{-1} \qquad (3)$$

It seemed of interest to study the factors affecting the site of attack by the oxidizing radical. In the present work we have studied the effect of three variables on the mechanisms of these oxidation reactions; (*a*) the nature of the central cation, reactions with complexes of Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} being studied; (*b*) the nature of the ligand, edta and nta being chosen as they are very similar but differ in the number of ligation sites; and (*c*) the nature of the oxidizing radical, reactions of OH, $[Br_2]^-$, $[I_2]^-$, $[(NCS)_2]^-$, $[O_2]^-$, and $\cdot O_2CH_2CMe_2OH$ being studied.

EXPERIMENTAL

Materials.—All the compounds were of AnalaR grade and were used without further treatment. The salt $Na_2[H_2edta]$ and nitrilotriacetic acid were supplied by E. Merck. The salts Na[Co(edta)] and Na[Mn(edta)] were prepared according to procedures described in the literature. All the solutions were prepared using triply distilled water. The pH was adjusted by adding $HClO_4$ or Na[OH] as required. The solutions were saturated with N_2O or argon (Matheson) which were purified from trace amounts of oxygen by bubbling through three wash bottles containing acidic (H_2SO_4) solutions of $V[SO_4]$ followed by a wash bottle containing triply distilled water. Solutions saturated with a mixture of N_2O and O_2 were prepared by mixing by the syringe technique the required volumes of solutions saturated with one of these gases. Solutions of $[Fe(edta)]^{2-}$ and $[Fe(nta)]^-$ were prepared by adding solid $Fe[SO_4]$ to deaerated solutions of the ligand at the required pH; the latter was then remeasured in the absence of oxygen.

Procedure.—Samples for the pulse-radiolysis experiments

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* In this paper the formulae $[M(edta)]^{2-}$ and $[M(nta)]^-$ represent the edta and nta complexes of divalent cations and $[M(edta)]^-$ and $[M(nta)]$ represent complexes of trivalent cations. The use of this notation does not imply that those are the actual structures of these complexes in aqueous solutions. In fact, H_2O and OH^- clearly act as ligands in these systems and thus the nature of these complexes depends on pH.

[1] C. Walling, *Accounts Chem. Res.*, 1975, **8**, 125.

[2] K. P. Kundu and N. Matsuura, *Internat. J. Radiation Phys. Chem.*, 1975, **7**, 565.

[3] S. N. Bhattacharyya and K. P. Kundu, *Internat. J. Radiation Phys. Chem.*, 1971, **3**, 1.

[4] S. N. Bhattacharyya and K. P. Kundu, *Internat. J. Radiation Phys. Chem.*, 1973, **5**, 183.

[5] S. N. Bhattacharyya and K. P. Kundu, *Radiation Res.*, 1972, **51**, 45.

[6] S. N. Bhattacharyya and K. P. Kundu, *Radiation Effects*, 1976, **29**, 231.

[7] N. Matsuura, N. Shinohara, M. Nishikawa, and M. Takizawa, *Bull. Chem. Soc. Japan*, 1968, **41**, 1284.

[8] J. Lati and D. Meyerstein, *Internat. J. Radiation Phys. Chem.*, 1975, **7**, 611.

[9] J. Lati, J. Koresh, and D. Meyerstein, *Chem. Phys. Letters*, 1975, **33**, 286.

were prepared as described earlier.[10] The pulse-radiolysis experiments were carried out using 0.05—1.0-μs, 5-MeV,* 200-mA pulses from the linear electron accelerator at the Hebrew University of Jerusalem. The dose per pulse was 100—3 000 rad. The experimental set-up in Jerusalem and the method used for evaluating the results have been described elsewhere.[10] All the experiments were at 22 ± 2 °C. Irradiations at low dose rates were carried out in a Noratom ^{60}Co γ source with a dose rate of *ca.* 1.8×10^4 rad min^{-1}.

Spectrophotometric measurements were carried out on a Cary 17 spectrophotometer. Molar absorption coefficients for the unstable intermediates were determined by assuming that the yield of the oxidizing radicals formed in N_2O-saturated solutions is equal to the yield of $[Fe(CN)_6]^{3-}$ in neutral N_2O-saturated solutions containing 1×10^{-3} mol dm^{-3} $K_4[Fe(CN)_6]$. The yield of $[Fe(CN)_6]^{3-}$ was determined at 420 nm where $\varepsilon[Fe(CN)_6{}^{3-}] = 1\,000$ dm^3 mol^{-1} cm^{-1} and $G[Fe(CN)_6{}^{3-}] = 6.1$.[11b] The absorption coefficients were calculated assuming that all the oxidizing radicals react with the substrate.

All the rate constants quoted were obtained from plots of ln*D* or 1/*D* against time which were linear for at least three half-lives (*D* = optical density).

RESULTS AND DISCUSSION

The radiolysis of water may be described by equation (4),[11] the yields of the products in neutral solutions being

$$H_2O \xrightarrow{\gamma, e^-} e^-(aq), H, OH, H_2, H_2O_2, [H_3O]^+ \qquad (4)$$

$G[e^-(aq)] = 2.65$, $G(OH) = 2.65$, $G(H) = 0.60$, $G(H_2) = 0.45$, and $G(H_2O_2) = 0.75$ (where G is defined as the number of molecules of product formed on absorption of

$$e^-(aq) + N_2O \longrightarrow N_2 + O^-; \quad k_{5a} = 5.6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ (ref. 12)} \qquad (5a)$$

$$O^- + H_2O \rightleftharpoons OH + [OH]^-; \quad pK_{5b}\ 11.9 \pm 0.2 \text{ (ref. 13)} \qquad (5b)$$

100 eV by the sample). Reaction (5) is used to transform the hydrated electrons into the oxidizing hydroxyl radicals, and (6)—(10) to transform the primary free radicals into the secondary $[X_2]^{\cdot-}$, $[O_2]^{\cdot-}$, $^{\bullet}CH_2CMe_2OH$, and $^{\bullet}O_2CH_2CMe_2OH$ free radicals.

In the following sections the results obtained for the different systems studied will be described and discussed

$$OH + X^- \longrightarrow OH^- + X; \quad X + X^- \rightleftharpoons [X_2]^{\cdot-} \qquad (6)$$

($X = I$,[14,15] Br,[14,16] or SCN [17])

$$e^-(aq) + O_2 \longrightarrow [O_2]^{\cdot-} \qquad (7)$$

$$[O_2]^{\cdot-} + [H_3O]^+ \rightleftharpoons [HO_2]^-; \ pK\ 4.85$$

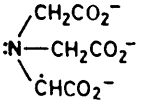
$$H + O_2 \longrightarrow HO_2^{\bullet} \qquad (8)$$

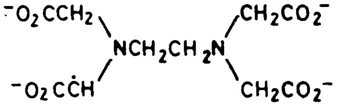
$$OH + Bu^tOH \longrightarrow {}^{\bullet}CH_2CMe_2OH \qquad (9)$$

$$^{\bullet}CH_2CMe_2OH + O_2 \longrightarrow {}^{\bullet}O_2CH_2CMe_2OH \qquad (10)$$

separately. Some comparisons between the systems and observed trends are then made.

The Oxidation of the Free Ligands and Their Zinc(II) *Complexes*.—Hydroxyl radicals are expected to react with edta and nta complexes of transition-metal cations *via* two alternative routes: (*a*) by hydrogen abstraction from the ligand; (*b*) electron transfer with the central cation. It seemed reasonable to start this study by following the reactions of hydroxyl radicals with the free ligands and their zinc(II) complexes. Evidently, OH radicals are expected to abstract hydrogen atoms from the free ligands, producing the intermediates (1)—(3). Intermediates (1) [18] and (2) [19] were identified as the products of reaction by e.s.r. spectroscopy. Intermediate (3) was not observed in these studies and seems to be at most a side product,† although it has been suggested as the major product by one worker.[1] Intermediates (1) and (2) will be present in solution in one or more of their different acid-base forms depending on the pH.[20] It is reasonable to expect that the OH radical will also abstract a hydrogen atom from $[Zn(nta)]^-$ and $[Zn(edta)]^{2-}$ since the oxidation of Zn^{II} to Zn^{III} is thermodynamically highly unfavourable.


(1)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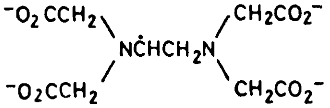
(3)

When N_2O-saturated solutions containing 1×10^{-4}—10^{-3} mol dm^{-3} of nta, edta, $[Zn(nta)]^-$, and $[Zn(edta)]^{2-}$ in the range pH 4—9 were irradiated the formation of intermediates with absorption bands with

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* Throughout this paper: 1 eV ≈ 1.60×10^{-19} J; 1 rad = 10^{-2} J kg^{-1}; 1 cal = 4.184 J.

† One of the referees has pointed out that the fact that intermediate (3) was not observed in the e.s.r. experiments might be due to its reaction with H_2O_2, $[Ti(edta)]^-$, or $[Ti(edta)]$. However, this seems to be only a remote possibility since more reactive radicals, *e.g.* $Me\dot{C}HOH$ and $^{\bullet}CH_2CH_2OH$ are known to react only slowly with H_2O_2, $Ti^{III}(aq)$, and $Ti^{IV}(aq)$ (G. Czapski, A. Samuni, and D. Meisel, *J. Phys. Chem.*, 1971, **75**, 3271; D. Behar, A. Samuni, and R. Fessenden, *ibid.*, 1973, **77**, 2055). The reactions of free radicals with $[Ti(edta)]^-$ and $[Ti(edta)]$ are expected to be even slower since the mechanism of these reactions involves the formation of titanium–carbon bonds.

[10] H. Cohen and D. Meyerstein, *Inorg. Chem.*, 1974, **13**, 2434; Y. Harel and D. Meyerstein, *J. Amer. Chem. Soc.*, 1974, **96**, 2720 and refs. therein.

[11] (*a*) M. S. Matheson and L. M. Dorfman, 'Pulse Radiolysis,' M.I.T. Press, Cambridge, Massachusetts, 1969; (*b*) G. E. Adams, J. W. Boag, and B. D. Michael, *Trans. Faraday Soc.*, 1965, **61**, 492.

[12] J. P. Keene, *Radiation Res.*, 1964, **22**, 1.

[13] J. Rabani and M. S. Matheson, *J. Phys. Chem.*, 1966, **70**, 761.

[14] A. T. Thornton and G. Laurence, *J.C.S. Dalton*, 1972, 1632.

[15] J. K. Thomas, *Trans. Faraday Soc.*, 1965, **61**, 702.

[16] D. Behar, *J. Phys. Chem.*, 1972, **76**, 1815; D. Zehavi and J. Rabani, *ibid.*, p. 312.

[17] D. Behar, P. L. T. Bevan, and G. Scholes, *J. Phys. Chem.*, 1972, **76**, 1537.

[18] P. Neta and R. W. Fessenden, *J. Phys. Chem.*, 1971, **75**, 738.

[19] R. Poupko, B. L. Silver, and A. Lowenstein, *Chem. Comm.*, 1968, 453.

[20] P. Neta, M. Simic, and E. Hayon, *J. Phys. Chem.*, 1970, **74**, 1214.

maxima at 290 nm was observed. The spectra for edta and $[Zn(edta)]^{2-}$ at pH 9 are shown in Figure 1. The other spectral data are summarized in Table 1. Since the free ligands and their zinc complexes react very slowly with $e^-(aq)$,[21] the intermediates observed are attributed to the reactions of OH radicals. This identification is verified by the observation that no intermediates are observed, down to 290 nm, in identical solutions containing also 0.1 mol dm^{-3} Bu^tOH.

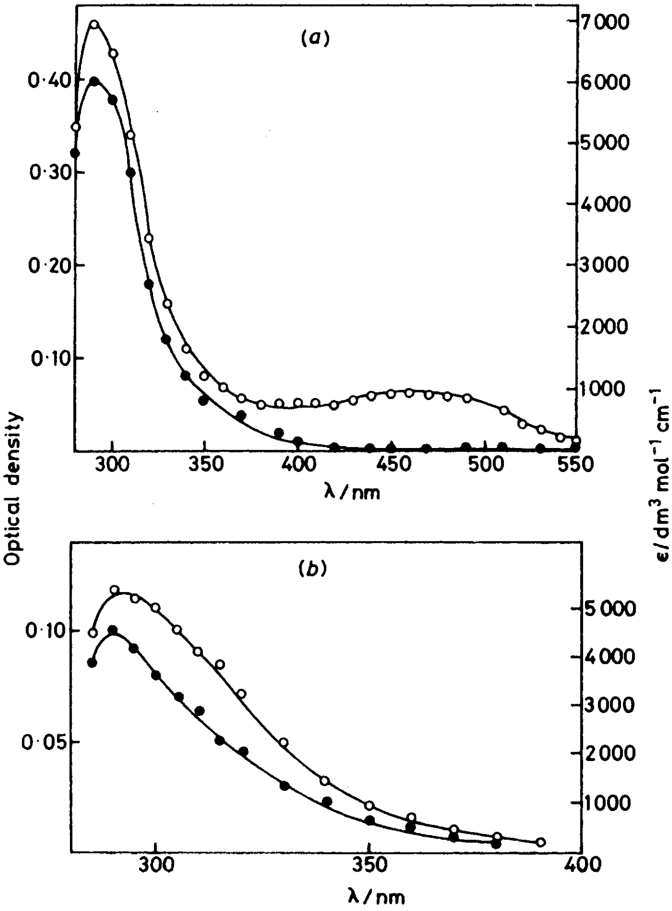

FIGURE 1 Absorption spectra of intermediates observed 10 (○) and 500 μs after the pulse (●). Solution (saturated with N_2O) composition; (*a*) 1×10^{-3} mol dm^{-3} edta, pH 9.0; (*b*) 4×10^{-4} mol dm^{-3} $[Zn(edta)]^{2-}$, pH 9.3

The rates of reaction of OH radicals with nta, edta, $[Zn(nta)]^-$, and $[Zn(edta)]^{2-}$ were determined directly by following the formation of the intermediates, and by competition with $[NCS]^-$;[11,17,22] both techniques gave identical results (Table 1). Attempts to oxidize any of these solutes by $[Br_2]^-$ in N_2O-saturated solutions containing 0.1 mol dm^{-3} NaBr failed, the disappearance of $[Br_2]^{\cdot-}$ being unaffected by these solutes. The upper limit for the rate constants for reaction with $[Br_2]^{\cdot-}$ is 1×10^7 dm^3 mol^{-1} s^{-1}.

The kinetics of decomposition of the intermediates were followed. For all the four intermediates, a first-order reaction followed by a second-order reaction was observed. The rate constants for these reactions are summarized in Table 1. The first reaction, which is not reported in the literature,[20] could be due to: (*a*) a small impurity, probably a transition-metal cation, in the ligands (however, ligands from different sources gave similar results); or (*b*) a contribution from a second site of attack by OH radicals, *e.g.* electron transfer from one of the carboxyl groups, or from a non-bonding electron on the nitrogen atom or intermediate (3). The observation that the spectra after the first reaction differ considerably from those before it, mainly at >400 nm (see Figure 1), supports the suggestion that the two reactions observed are due to two different radicals. (The changes in the spectra are smaller for the nta system and the zinc complexes.) The second reaction observed is most probably a disproportionation which is followed by hydrolysis reactions giving the final products, *e.g.* glyoxalic acid, CO_2, formaldehyde, and the amino-carboxylate ligand with one less acetate residue.[23-25]

The intermediates formed react rapidly with oxygen added to the solution, the rate constants for these reactions being summarized in Table 1. No absorption above 300 nm remains after this reaction. The addition of small quantities of I^- and Br^- did not affect the kinetics of disappearance of the intermediates, thus $k < 1 \times 10^6$ dm^3 mol^{-1} s^{-1} for intermediate + I^- or Br^-. The yield of hydrogen peroxide in a N_2O-saturated solution containing 4×10^{-4} mol dm^{-3} edta at pH 4.1 was $G(H_2O_2) = 0.63 \pm 0.06$, *e.g.* somewhat smaller than the molecular yield.[11]

The results clearly demonstrate that similar reactions occur for the free ligands nta and edta and their zinc(II) complexes. The largest difference is in the rates of the second-order disappearance of the intermediates formed in nta and $[Zn(nta)]^-$ solutions. This difference stems from the different electrical charges of the intermediates, *e.g.* −2 or −3 depending on pH for the intermediate in the nta solution and −1 for the intermediate in the $[Zn(nta)]^-$ solution. The corresponding charges for the edta solutions are −3 or −4 for the free ligand and −2 for the solutions of the zinc(II) complex. Of special interest is the observation that all the four intermediates exhibit a very fast reaction with oxygen, which is typical of aliphatic free radicals. Thus the results support our expectations that OH radicals do abstract hydrogen atoms from the ligands and also in their zinc(II) complexes. Furthermore, the data supply information on the chemical properties of the free radicals formed.

The Oxidation of $[Cu(nta)]^-$ *and* $[Cu(edta)]^{2-}$. When N_2O-saturated solutions containing 4×10^{-4} mol dm^{-3} $[Cu^{II}L]$ in the range pH 4—10 were irradiated the formation of unstable intermediates was observed. The

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[21] M. Anbar and D. Meyerstein, *Trans. Faraday Soc.*, 1969, **65**, 1812, 1818.

[22] J. H. Baxendale and D. A. Scott, *Chem. Comm.*, 1967, 1699.

[23] S. N. Bhattacharyya and K. P. Kundu, *Internat. J. Radiation Phys. Chem.*, 1972, **4**, 31.

[24] S. N. Bhattacharyya and E. V. Srisankar, *Internat. J. Radiation Phys. Chem.*, 1976, **8**, 667.

[25] S. N. Bhattacharrya and N. C. Saha, *Radiation Res.*, 1976, **68**, 234.

spectra observed in $[Cu(edta)]^{2-}$ solutions of pH 9.0 are shown in Figure 2. Similar results were obtained at pH 4.0. In solutions containing $[Cu(nta)]^-$ at pH 9.0 an intermediate having $\lambda_{max.}$ 320 nm and $\varepsilon_{max.}$ 1 700 dm^3 mol^{-1} cm^{-1} was observed. These results are similar to those reported for other copper(II) complexes with amino-acid ligands.[26] The rate constants for reaction of OH radicals with $[Cu(nta)]^-$ and $[Cu(edta)]^{2-}$ were $(2.6 \pm 0.4) \times 10^9$ and $(3.0 \pm 0.4) \times 10^9$ dm^3 mol^{-1} s^{-1} respectively in the range pH 4—9 (measured both by observing the kinetics of formation of the intermediates and by competition with $[NCS]^-$). Both $[I_2]^{\cdot-}$ and $[Br_2]^{\cdot-}$ were unreactive towards the $[Cu^{II}L]$ complexes, the upper limit for the rate constants of these reactions being 5×10^6 dm^3 mol^{-1} s^{-1}.

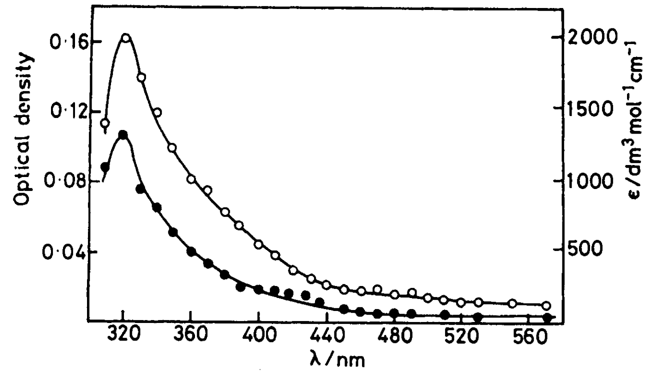

FIGURE 2 Absorption spectra of $[Cu(edta)]^{2-}$ 20 μs (○) and 1 ms (●) after the pulse. Solution composition: 2×10^{-4} mol dm^{-3} $[Cu(edta)]^{2-}$, pH 9.0, saturated with N_2O

TABLE 1

Data for the reaction of OH radicals with the free ligands and their zinc(II) complexes

Solute (L)	pH	$\lambda_{max.}$[a] nm	$\varepsilon_{max.}$[a] dm^3 mol^{-1} cm^{-1}	$10^{-8}k(OH + L)$[b] dm^3 mol^{-1} s^{-1}	$10^{-2}k_D{}^1$[c] s^{-1}	$2k_D{}^2$[d] dm^3 mol^{-1} s^{-1}	$10^{-8}k(R^{\cdot} + O_2)$[e] dm^3 mol^{-1} s^{-1}
edta	4.0			4.0	30	2.3×10^7	2.0
	4.5	290	5 600				
	5.0				30	9.0×10^6	
	6.5				8.0	8.0×10^6	
	8.0				9.0	3.6×10^6	
	9.0	290	7 000	20	2.6	1.0×10^6	4.5
nta	4.0	280	5 600	7.5	30	5.0×10^7	1.7
	4.5	290	2 600				
	5.0				27	3.6×10^6	
	6.5				40	5.5×10^5	
	8.0					1.7×10^5	
	9.0	290	5 700	25		1.0×10^5	3.0
	11.3	280	9 700			5×10^6	
$[Zn(edta)]^{2-}$	4.0			35	5.0	1.0×10^7	2.3
	4.5	290	2 650				
	5.0				5.0	2.4×10^6	
	7.0				5.0	3.1×10^6	
	9.0	290	5 200	35	5.0	2.0×10^6	4.0
$[Zn(nta)]^-$	4.0			20	40	3.7×10^8	1.5
	5.0	280	2 400			2.6×10^7	
	7.0				7	1.6×10^7	
	9.0	290	5 200	20	8.0		3.4

[a] Measured *ca.* 50 μs after the pulse. [b] Rate constant of reaction of OH radical with solute. [c] Rate constant of first decomposition reaction. [d] Rate constant of second decomposition reaction. [e] Rate constant of reaction of intermediate with O_2. [f] From ref. 20.

The kinetics of decomposition of the intermediates were examined. The intermediate formed in $[Cu(edta)]^{2-}$ solution decomposes by two consecutive first-order reactions, the rates of these reactions being independent of the complex concentration or the pulse intensity; their dependence on pH is shown in Figure 3. The intermediate formed in $[Cu(nta)]^-$ solution decomposes in one first-order reaction, the dependence of the rate of this reaction on pH being shown in Figure 4. At pH $\leqslant$ 6 the rate of the latter reaction depends also on the complex concentration, as also shown in Figure 4. The reason for this dependence on concentration seems to be that at these pH values some of the $[Cu(nta)]^-$ dissociates into $Cu^{2+}(aq)$ and nta^{3-}; thus some of the OH radicals react with $Cu^{2+}(aq)$ forming $Cu^{III}(aq)$. The effect of nta on the decomposition of $Cu^{III}(aq)$ was studied by adding low nta concentrations to a N_2O-saturated solution containing 1×10^{-3} mol dm^{-3} $Cu^{2+}(aq)$. The results are summarized in Table 2. In all cases, after the decomposition reaction was over a brown precipitate slowly formed. This precipitate is most probably Cu_2O observed as the major final product by Bhattacharyya and Kundu,[4] and may also contain Cu^0. The kinetics of decomposition of the intermediates were not affected by the addition of 2×10^{-4} mol dm^{-3} I^-, Br^-, or O_2 to the solutions, *i.e.* the rate constants for reaction of the intermediates with these additives are

TABLE 2

Effect of nta on the rate of decomposition of $Cu^{III}(aq)$[a]

10^5[nta] mol dm^{-3}	$10^{-3}k_{obs.}$[b] s^{-1}	$10^{-8}k\{Cu^{III}(aq) + [Cu(nta)]^-\}$[c] dm^3 mol^{-1} s^{-1}
0	*d*	
2	3.0	1.5
4	5.2	1.3
8	8.0	1.0
		Mean = $(1.3 \pm 0.3) \times 10^8$

[a] All the solutions contained 1.0×10^{-3} mol dm^{-3} $Cu[SO_4]$ at pH 3.9 and were saturated with N_2O. [b] Observed rate constant. [c] See text. [d] Second-order decomposition $k = 5 \times 10^8$ dm^3 mol^{-1} s^{-1}.

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[26] D. Meyerstein, *Inorg. Chem.*, 1971, **10**, 2244.

$<10^5$ dm^3 mol^{-1} s^{-1} in the $[Cu(edta)]^{2-}$ solution and $<10^7$ dm^3 mol^{-1} s^{-1} in the $[Cu(nta)]^-$ solution. However, the addition of O_2 suppressed the formation of the precipitate, and supports its identification as Cu_2O or Cu^0.

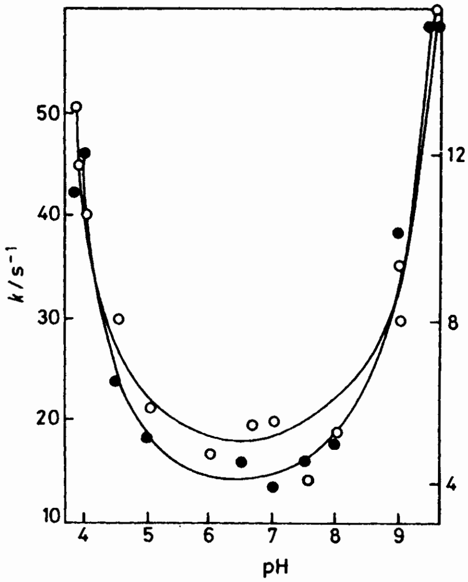

FIGURE 3 Dependence of the rates of decomposition of $[Cu(edta)]^-$ on pH: (○) first reaction, right-hand scale; (●) second reaction, left-hand scale. Solution composition: 4×10^{-4} mol dm^{-3} $[Cu(edta)]^{2-}$, saturated with N_2O

The intermediates formed in the reaction are identified

$$OH + [Cu^{II}L] \longrightarrow [Cu^{III}L] + [OH]^- \quad (11)$$

as $[Cu^{III}L]$ complexes [equation (11)] for the following reasons. (*a*) They do not react with oxygen. If the intermediates were formed by hydrogen-atom abstraction from the ligands they would be aliphatic free radicals and would react quickly with oxygen, as was observed in the $[Zn^{II}L]$ systems. (*b*) The spectroscopic and kinetic properties of the intermediates resemble those of copper(III) amino-acid complexes.[26] The absorption band observed for these $[Cu^{III}L]$ complexes is attributed to a charge transfer from the ligand to metal. Thus the band maximum shifts to the red the smaller is the expected optical electronegativity of the ligand.[26] (For further support of this identification see *general discussion*.)

The kinetics of decomposition of $[Cu(edta)]^-$ are clearly intramolecular. The first fast reaction, which has only a minor effect on the absorption spectrum, is believed to be a rearrangement; clearly the ligand coordination sphere of the copper(III) complex is expected to differ from that of the copper(II) complex. Similar rearrangement reactions were observed in the $[Ni(edta)]^-$ system.[8] The second reaction is attributed to an intramolecular electron transfer, *i.e.* either as in (12) or by the two-electron reaction (13). These reactions are expected to be followed by disproportionation of the copper(I) complexes yielding Cu^0 or by precipitation of Cu_2O. The final products observed in this system are

$$[Cu^{III}(edta)]^- \longrightarrow [Cu^{II}\{(^-O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2^-)(CH_2CO_2^{\bullet})\}] \xrightarrow{-CO_2} [Cu^{II}\{(^-O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2^-)(CH_2^{\bullet})\}] \xrightarrow{H_2O} [Cu^{I}\{(^-O_2CCH_2)_2NCH_2CH_2NH(CH_2CO_2^-)\}] + CH_2O + [H_3O]^+ \quad (12)$$

$$[Cu^{III}(edta)]^- \xrightarrow{H_2O} [Cu^{I}\{(^-O_2CCH_2)_2NCH_2CH_2NH(CH_2CO_2^-)\}] + CH_2O + CO_2 + [H_3O]^+ \quad (13)$$

mainly Cu_2O, CH_2O, and CO_2,[4] in accordance with the suggested mechanism. However, we believe that the experimental evidence confirms that the hydroxyl radicals oxidize the central copper ion and do not abstract a hydrogen atom from the ligand. The question whether the decomposition reaction is a one- or two-electron transfer cannot be solved on the basis of the available experimental data. The mechanism of decomposition of $[Cu(nta)]$ seems to be similar. The pH effect on the rates of decomposition [Figure 4] is explained by the different forms of $[Cu^{III}L]$ complexes formed. In the nta case at higher pH the complex is expected to be $[Cu(nta)(OH)]^-$ and $[Cu(nta)(OH)_2]^{2-}$ and the redox potential is expected to decrease with pH thus decreasing the rate of the intramolecular reaction. For $[Cu(edta)]^{2-}$ it is known that at pH > 7 some of the complex is in the form $[Cu(edta)(OH)]^{3-}$;[27] thus the $[Cu(edta)]^-$ complex formed at different pH values will have different compositions. Probably, at pH *ca.* 7 most of the complex will be octahedral $[Cu(edta)]^-$, whereas at lower and higher pH some water

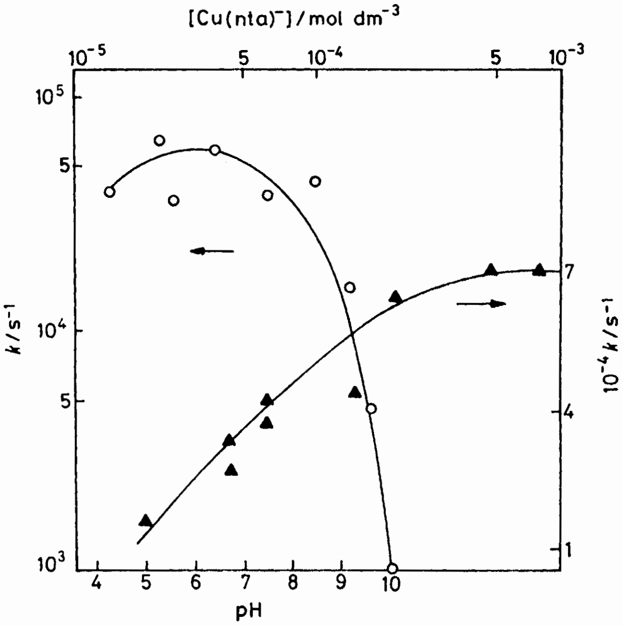

FIGURE 4 Dependences of the rate of decomposition of $[Cu(nta)]$ on pH (○), solution composition 4×10^{-4} mol dm^{-3} $[Cu(nta)]^-$, and on the concentration of $[Cu(nta)]^-$ (▲), at pH 5.0, in N_2O-saturated solutions

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[27] 'Stability Constants of Metal-Ion Complexes,' eds. L. G. Sillén and A. E. Martell, The Chemical Society, London, 1964, no. 17.

molecules will be bound to the copper thus increasing the oxidation potential and the rate of decomposition. The

$$\mathrm{Cu^{III}(aq)} + [\mathrm{Cu^{II}(nta)}]^- \xrightarrow{k_{14}} \mathrm{Cu^{2+}(aq)} + [\mathrm{Cu^{III}(nta)}] \quad (14)$$

$$[\mathrm{Cu^{III}(nta)}] \longrightarrow [\mathrm{Cu^{I}(ida)}] + \mathrm{CH_2O} + \mathrm{CO_2} \quad (15)$$

effect of nta on the decomposition of $\mathrm{Cu^{III}(aq)}$ is explained by the sequence (14) followed by (15) (ida = iminodiacetate) where $k_{14} = (1.2 \pm 0.3) \times 10^8$ dm^3 mol^{-1} s^{-1}. Similar results were reported for the $\mathrm{Cu^{III}}$ + [Cu(GlyO)] reaction (GlyO = glycinate).[26]

TABLE 3

Effect of acid on the decomposition of $[\mathrm{Ni(edta)}]^-$ *

$10^4[\mathrm{Ni(edta)}^-]$ mol dm^{-3}	$[\mathrm{HClO_4}]$ mol dm^{-3}	$10^3k_{\mathrm{obs.}}$ s^{-1}	$10^3k\{[\mathrm{H_3O}]^+ + [\mathrm{Ni(edta)}]^-\}$ dm^3 mol^{-1} s^{-1}
2	0.12	4.6	37
2	0.25	7.0	28
2	0.50	14	28
2	1.00	28	28
1	0.50	12	24
4	0.50	14	28

* All the solutions contained excess of $[\mathrm{Ni(edta)}]^{2-}$, and were prepared by irradiation at pH 4.0. These solutions were then mixed with solutions containing perchloric acid in the absence of air using the syringe technique. The disappearance of $[\mathrm{Ni(edta)}]^-$ was followed at 300 nm using the Cary 17. Accuracy, ±10%.

The Oxidation of $\mathrm{Ni^{II}}$, nta, *and* $[\mathrm{Ni(edta)}]^{2-}$.—The observation that $[\mathrm{Ni(edta)}]^-$ is the product of reaction of OH radicals with $[\mathrm{Ni(edta)}]^{2-}$ [8] and the e.s.r.[9] and u.v. spectra and the chemical[9] and electrochemical properties[28] of $[\mathrm{Ni(edta)}]^-$ have been reported earlier. We have now measured the effect of acid on the rate of decomposition of $[\mathrm{Ni(edta)}]^-$ (Table 3). The absorption spectrum of $[\mathrm{Ni(edta)}]^-$ did not change during its decomposition; thus it seems that the rate-determining step is the acid-catalysed dissociation of the ligand and not the oxidation of water or free ligand by the $\mathrm{Ni^{3+}(aq)}$ formed.

TABLE 4

Spectral data for products of reaction of free radicals with cobalt(II) complexes, $\mathrm{R^\bullet} + [\mathrm{Co^{II}L}]$

		L = nta				L = edta			
		After reaction[a]		Final products[b,g]		After reaction[a]		Final products[b,f]	
$\mathrm{R^\bullet}$	pH	$\lambda_{\mathrm{max.}}$/nm	$\varepsilon_{\mathrm{max.}}$/dm^3 mol^{-1} cm^{-1}	$\lambda_{\mathrm{max.}}$/nm	$\varepsilon_{\mathrm{max.}}$/dm^3 mol^{-1} cm^{-1}	$\lambda_{\mathrm{max.}}$/nm	$\varepsilon_{\mathrm{max.}}$/dm^3 mol^{-1} cm^{-1}	$\lambda_{\mathrm{max.}}$/nm	$\varepsilon_{\mathrm{max.}}$/dm^3 mol^{-1} cm^{-1}
OH	4.0	290	3 000	<290		290, 540	1 850, 160	380 540	130, 160
$\mathrm{HO_2}$	4.0	350^{c}	2 100^{c}	350,^{c} 570	270, *ca.* 100	350^{c}	2 300^{c}	550^{d}	300^{d}
$\mathrm{{}^\bullet O_2CH_2CMe_2OH}$	4.5	330^{c}	4 200^{c}	400, 570	130, 280	320^{c}	3 900^{c}	570^{d}	300^{d}
$[\mathrm{Br_2}]^{\bullet-}$	4.8	340^{c}	1 000^{c}	390, 580	80, 130	*e*	*e*	560^{d}	300^{d}
$[\mathrm{(NCS)_2}]^{\bullet-}$	4.8	350,^{c} 580	2 850,^{c} 280	350,^{c} 580	2 100,^{c} 280	*e*	*e*	550^{d}	380^{d}

[a] Measured at the end of the first reaction which corresponds to $\mathrm{R^\bullet} + [\mathrm{Co^{II}L}]$. In some cases ε is only a lower limit as some of the radicals reacted *via* $2\mathrm{R^\bullet} \longrightarrow$ products. [b] As obtained several seconds after the pulse, or from irradiation in the γ source. [c] A strong absorption band exists in the u.v. We could not detect the maximum of this band and the absorption coefficient on the red branch of the band is given. [d] Solutions irradiated in the $^{60}\mathrm{Co}$ γ source only. [e] No reaction between free radical and $[\mathrm{Co(edta)}]^{2-}$ observed in the pulse-radiolysis experiments. [f] For $[\mathrm{Co(edta)}]^-$: $\lambda_{\mathrm{max.}}$ 380 and 540 nm and $\varepsilon_{\mathrm{max.}}$ 225 and 324 dm^3 mol^{-1} cm^{-1} respectively (I. A. Shini and W. C. E. Higginson, *J. Chem. Soc.*, 1958, 260). [g] For [Co(nta)]: $\lambda_{\mathrm{max.}}$ 400 and 560 nm and $\varepsilon_{\mathrm{max.}}$ 290 and 300 dm^3 mol^{-1} cm^{-1} respectively (K. L. Chens, *Analyt. Chem.*, 1958, **30**, 1036).

When $\mathrm{N_2O}$-saturated solutions containing 4×10^{-4} mol dm^{-3} [Ni(nta)] were irradiated the formation of an unstable intermediate was observed. The absorption spectrum of this intermediate has a maximum at 290 ± 5 nm with ε 2 050 ± 300 and 1 600 ± 250 dm^3 mol^{-1} cm^{-1} at pH 4 and 9 respectively. The rate constant for reaction of OH radicals with $[\mathrm{Ni(nta)}]^-$ is 1.4×10^9 dm^3 mol^{-1} s^{-1} in the range pH 4—9; $[\mathrm{Br_2}]^{\bullet-}$ does not react with $[\mathrm{Ni(nta)}]^-$.

The disappearance of the absorption due to the intermediate occurs in two successive first-order reactions. The first has a rate constant of 3×10^3 s^{-1} and causes only slight changes in the absorption spectrum of the intermediate. This reaction is very similar to that observed in the $[\mathrm{Ni(edta)}]^-$ system[8] and is therefore attributed also to a rearrangement of the complex. The rate constant for the second reaction depends slightly on pH, being 2.5×10^{-2}, 3.0×10^{-2}, 4.0×10^{-2}, and 5.2×10^{-2} s^{-1} at pH 4.5, 6.5, 7.5, and 9.0 respectively. After this reaction no residual absorbance at >300 nm remains.

The intermediate reacts also with $\mathrm{O_2}$, $\mathrm{Br^-}$, and $\mathrm{I^-}$ with rate constants of 4.0×10^3, 2×10^3, and 4×10^2 dm^3 mol^{-1} s^{-1} respectively. The fact that the intermediate decomposes by a first-order reaction, that it reacts relatively slowly with oxygen, and that it oxidizes $\mathrm{Br^-}$ and $\mathrm{I^-}$ clearly suggests its identification as [Ni(nta)]. The properties of [Ni(nta)] seem to be similar to those of

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[28] E. Fuchs, G. Ginsburg, J. Lati, and D. Meyerstein, *Electroanalyt. Chem. Interfac. Electrochem.*, 1976, **73**, 83.

$[\mathrm{Ni(edta)}]^{1-}$;[8] however, the results indicate that the oxidation potential of [Ni(nta)] is higher, and thus this complex is unstable, oxidizing its ligand in an intramolecular first-order reaction. {The products are most probably $[\mathrm{Ni(ida)}]^+$, CH_2O, and CO_2 in parallel to the [Ni(edta)] system.[5,8]} Furthermore, [Ni(nta)] oxidizes Br^- while $[\mathrm{Ni(edta)}]^-$ does not.

The exact mechanism of reaction of $[\mathrm{Ni(edta)}]^-$ (ref. 8) and [Ni(nta)] with O_2 is unclear. It is believed that the oxygen penetrates the inner co-ordination sphere and then either oxidizes the nickel to $\mathrm{Ni^{IV}}$ which then oxidizes the ligand by a two-electron transfer process, see above, or that the oxygen and the $\mathrm{Ni^{III}}$ concertedly oxidize the ligand.

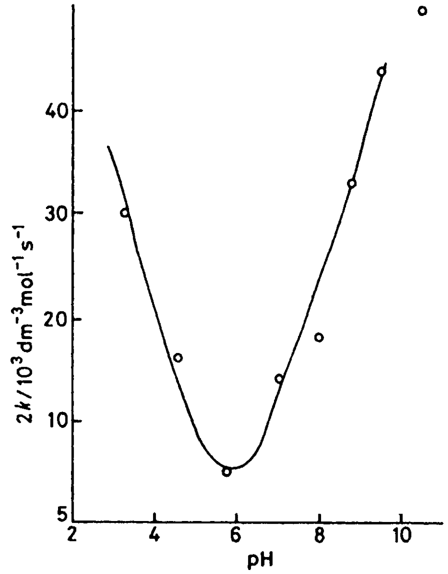

FIGURE 5 Dependence of the rate of the second decomposition reaction observed in the $[\mathrm{Co(edta)}]^{2-}$ system on pH. Solution composition: 4×10^{-4} mol dm^{-3} $[\mathrm{Co(edta)}]^{2-}$, saturated with N_2O

The Oxidation of $[\mathrm{Co(nta)}]^-$ *and* $[\mathrm{Co(edta)}]^{2-}$.—(*a*) *Reaction with* OH *radicals*. When N_2O-saturated solutions containing 4×10^{-4} mol dm^{-3} $[\mathrm{Co(edta)}]^{2-}$ or $[\mathrm{Co(nta)}]^-$ were irradiated the formation of unstable intermediates was observed. The data concerning the absorption spectra of these intermediates are summarized in Table 4. The spectrum of the stable products in $[\mathrm{Co(edta)}]^{2-}$ solution is identical to the reported spectrum of $[\mathrm{Co(edta)}]^-$, which is a stable complex, but the observed absorption coefficients, calculated assuming that all the radicals are transformed into this product, are considerably lower than those of $[\mathrm{Co(edta)}]^-$ (Table 4). In the $[\mathrm{Co(nta)}]^-$ system the intermediate has no absorption peaks at *ca.* 550 and 380 nm, only at 290 nm. After two relatively fast decomposition reactions, no products with absorption bands at >300 nm were observed in this system. The results thus indicate that OH radicals do not oxidize $[\mathrm{Co(nta)}]^-$ to [Co(nta)], although the latter is a stable complex, and only a relatively low percentage of the OH radicals oxidize $[\mathrm{Co(edta)}]^{2-}$ to stable $[\mathrm{Co(edta)}]^-$. The rate constants for reaction of OH radicals with $[\mathrm{Co(nta)}]^-$ and $[\mathrm{Co(edta)}]^{2-}$ are $(5.0 \pm 1.0) \times 10^9$ and $(3.5 \pm 0.7) \times 10^9$ dm^3 mol^{-1} s^{-1} respectively, independent of pH in the range $4 < pH < 9$. The first reaction by which the intermediate is removed is first order with rate constants of $(9 \pm 2) \times 10^3$ and $(5 \pm 1) \times 10^3$ s^{-1} for the edta and nta systems respectively. The second decomposition reaction is second order with rates which depend on pH (see Figure 5 for the edta system). In the nta system the observed rate constants ($2k$) were 5×10^7, 2.0×10^6, 7.5×10^5, and 4.0×10^6 dm^3 mol^{-1} s^{-1} at pH 3,7, 5.0, 6.5, and 10.0 respectively.

The addition of 2×10^{-5} mol dm^{-3} O_2 to the N_2O-saturated solutions caused drastic changes which are

$$\begin{array}{lll} & \nearrow [\mathrm{Co(edta)}]^- + [\mathrm{OH}]^- & (16) \\ \mathrm{OH} + [\mathrm{Co(edta)}]^{2-} & & \\ & \searrow [\mathrm{Co(edta - H)}]^{2-} + \mathrm{H_2O} & (17) \end{array}$$

discussed in detail in the following section. Here we only point out that the intermediates observed react rapidly with oxygen.

The results clearly indicate that OH radicals react with $[\mathrm{Co(edta)}]^{2-}$ by two parallel reactions (16) and (17), the relative yield of the two products depending on pH (edta — H represents the free radical obtained by hydrogen abstraction from one of the acetate groups of edta). On the other hand, the reaction of OH radicals with $[\mathrm{Co(nta)}]^-$ seems to proceed *via* hydrogen-atom abstraction from the ligand only. The spectra, and kinetics of decomposition, of the intermediates and their pH dependence resemble those observed for the corresponding zinc(II) complexes.

(*b*) *Reactions with* $[\mathrm{Br_2}]^{-\cdot}$, $[\mathrm{(NCS)_2}]^{-\cdot}$, $[\mathrm{O_2}]^{-\cdot}$, *and* $\cdot\mathrm{O_2CH_2CMe_2OH}$. The reactions with $[\mathrm{Br_2}]^{-\cdot}$ and $[\mathrm{(NCS)_2}]^{-\cdot}$ were studied in N_2O-saturated solutions containing 0.1 mol dm^{-3} Br^- and 0.1 mol dm^{-3} $[\mathrm{NCS}]^-$ respectively. Reactions with $[\mathrm{O_2}]^{-\cdot}$ were studied in O_2-saturated solutions; under these conditions reaction (9) occurs. However, since identical kinetics, although with somewhat smaller optical changes, were observed in solutions containing 1.2×10^{-2} mol dm^{-3} N_2O and 2.6×10^{-4} mol dm^{-3} O_2 it was concluded that reaction (18)

$$[\mathrm{Co^{II}(edta - H)}] + \mathrm{O_2} \xrightarrow{\mathrm{H_2O}} [\mathrm{Co^{II}(edta\ oxidized)}] + [\mathrm{O_2}]^{-\cdot} \quad (18)$$

occurs and thus most of the radicals are transformed into $[\mathrm{O_2}]^{-\cdot}$ radicals. A similar mechanism was suggested, on the basis of product analysis, to occur in the radiolysis of aerated solutions of $[\mathrm{Co(edta)}]^-$.[6] Reactions with $\cdot\mathrm{O_2CH_2CMe_2OH}$ were studied in solutions containing 0.1 mol dm^{-3} $\mathrm{Bu^tOH}$, 1.2×10^{-2} mol dm^{-3} N_2O, and 2.6×10^{-4} mol dm^{-3} O_2; under these conditions reactions (5a), (9), and (10) transform all the OH radicals and $e^-(aq)$ into $\cdot\mathrm{O_2CH_2CMe_2OH}$ radicals.

The rate constants for reaction of these radicals with the cobalt(II) complexes are summarized in Table 5.

The spectroscopic properties of the products of reaction, as observed immediately after the reaction ended and several minutes later, are summarized in Table 4. The spectra of the intermediates and final products in the $[Co(nta)]^- + [Br_2]^{-\cdot}$ system are plotted in Figure 6. The products of reaction of $[O_2]^{-\cdot}$ and RO_2 with $[Co(edta)]^{2-}$ were stable for several minutes. The rates of reaction of $[Br_2]^{-\cdot}$ and $[(NCS)_2]^{-\cdot}$ with $[Co(edta)]^{2-}$ (Table 5) are too slow to be studied by pulse radiolysis; thus the kinetics of decomposition of the oxidation products, which could be obtained only by long irradiations at low dose rates, were not studied. The kinetics of transformation of the primary products observed in the nta systems into stable products are summarized in Table 5.

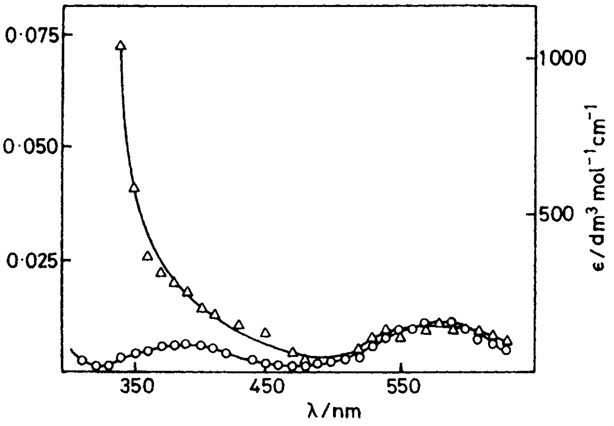

FIGURE 6 Spectra observed for N_2O-saturated solutions containing 4×10^{-4} mol dm^{-3} $[Co(nta)]^-$ and 1×10^{-2} mol dm^{-3} NaBr at pH 6.0, 100 μs (△) and 10 ms (○) after the pulse

The strong u.v. absorption bands of the products of reaction of the free radicals with $[Co^{II}L]$ (Table 4) indicate that these products are $[Co(edta)(O_2H)]^{2-}$, $[Co(edta)(O_2R)]^{2-}$, $[Co(nta)Br]^-$, $[Co(nta)(NCS)]^-$, $[Co(nta)(O_2H)]^-$, and $[Co(nta)(O_2R)]^-$, whereas the spectra of the final products indicate that $[Co(edta)]^-$ and $[Co(nta)]$ are formed in all these systems (Table 4 and Figure 6). The results indicate that the reaction $[Co(nta)(NCS)]^- \longrightarrow [Co(nta)] + [NCS]^-$ is an equilibrium under the experimental conditions, and that the final products are a mixture of $[Co(nta)]$ and $[Co(nta)(NCS)]^-$. Thus the oxidation of $[Co(nta)]^-$ and $[Co(edta)]^{2-}$ by $[Br_2]^{-\cdot}$, $[(NCS)_2]^{-\cdot}$, $[O_2]^{-\cdot}$, and RO_2 occur *via* the inner-sphere mechanism. The results are insufficient for distinguishing between mechanisms involving six- or seven-co-ordinate intermediates. The observation that the edta complex is oxidized slower than that of nta, although the former is a stronger reducing agent, suggests that the free radicals penetrate more readily the inner co-ordination sphere of $[Co(nta)]^-$. The latter observation and the low probability for the existence of outer-sphere complexes of the type $[Co(edta)]^{2-}$, $X_2^{-\cdot}$ or $[Co(nta)]^-$, $X_2^{-\cdot}$ lead us to speculate that the oxidation reactions involve seven-co-ordinate intermediates.

TABLE 5

Kinetic data for the reactions of free radicals ($R^\cdot$) with $[Co^{II}L]$ complexes

$R^\cdot$	pH	$10^{-6}k\{R^\cdot + [Co(edta)]^{2-}\}$[a] dm³ mol⁻¹ s⁻¹	$10^{-7}k\{R^\cdot + [Co(nta)]^-\}$[a] dm³ mol⁻¹ s⁻¹	$k\{[Co(nta)X]^- \longrightarrow [Co(nta)] + X^-\}$[b] s⁻¹
$[O_2]^{-\cdot}$	5.0	2.0	15	
$^\cdot O_2CH_2CMe_2OH$	5.0	2.5	9.5	
	7.0	2.0	73	0.8
	9.0	1.8	70	0.4
$[Br_2]^{-\cdot}$	7.0	$5 \times 10^4 < k < 7 \times 10^6$[c]	7.5	870
$[(NCS)_2]^{-\cdot}$	5.0	$6 \times 10^4 k < 1 \times 10^7$[c]	4.6	23
	6.2			100
	7.5		5.5	150

[a] Accuracy, ±15%. [b] Accuracy, ±10%. [c] Upper limit from pulse-radiolysis experiments. Lower limit estimated from the yield of $[Co(edta)]^-$ in the ^{60}Co γ source and its dose rate.

The kinetics of the ligand-exchange reactions observed for the $[Co(nta)X]^-$ complexes (Table 5) indicate that the relative rates of ligand loss are $[RO_2]^- < [NCS]^- < Br^-$ and that the loss of $[NCS]^-$ is base catalysed. Both these observations are in accord with the usual trends for cobalt(III) complexes.

Finally, it should be pointed out that the fact that $[O_2]^{-\cdot}$ radicals oxidize $[Co(edta)]^{2-}$, and, as can be deduced from the redox potential,[29] reduce $[Co(edta)]^-$, must affect the yields of the final products in the radiolysis of aerated $[Co(edta)]^-$ solutions. Thus it seems that the mechanism suggested in the literature [6] for the latter system has to be reconsidered.

The Oxidation of $[Fe(edta)]^{2-}$ *and* $[Fe(nta)]^-$.—The rates of reactions of these complexes with OH, $[Br_2]^{-\cdot}$, $[(NCS)_2]^{-\cdot}$, and $[I_2]^{-\cdot}$ were determined (Table 6). In all these systems only the oxidation reaction was observed

TABLE 6

Rate constants for reaction of free radicals ($R^\cdot$) with $[Fe^{II}L]$ complexes *

$R^\cdot$	pH	$10^{-8}k$ $\{R^\cdot + [Fe(nta)]^-\}$ dm⁻³ mol⁻¹ s⁻¹	$k\{R^\cdot + [Fe(edta)]^{2-}\}$ dm³ mol⁻¹ cm⁻¹
OH	4.5		5.0×10^9
	6.2	25	7.5×10^9
	6.0	50	
	11.0	11	
$[(NCS)_2]^{-\cdot}$	4.8	1.1	1.0×10^8
$[Br_2]^{-\cdot}$	4.8	2.0	2.0×10^8
$[I_2]^{-\cdot}$	4.8	1.1	$<5 \times 10^7$

* Accuracy, ±15%.

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[29] Y. A. Ilan, D. Meisel, and G. Czapski, *Israel J. Chem.*, 1974, **12**, 891.

and the products seemed to be independent of the oxidizing radical (as judged from the spectral change at a given wavelength) and stable. However, the products were sensitive to the analysing light and therefore their stability was studied only during the first 10 ms. These results indicate that the products of reaction are [Fe(edta)]$^-$ and [Fe(nta)], and that no intermediates can be observed. The results obtained are not very helpful in determining the detailed mechanism of oxidation of the iron(II) complexes by the [X_2]$^{\cdot-}$ radicals. Two basic alternatives exist. (*a*) An inner-sphere mechanism, in which case the product should be [Fe^{III}L(X)]. However, since the products are identified as [Fe^{III}L] it has to be assumed that $k > 1 \times 10^5$ s^{-1} for [Fe^{III}L(X)] $\longrightarrow$ [Fe^{III}L] + X$^-$ if this mechanism is correct. The latter assumption seems to be compatible with the known properties of iron(III) complexes. (*b*) An outer-sphere mechanism, which was not observed for the oxidation of the complexes of Mn^{II} and Co^{II} by the same radicals. However, the lower redox potential of the [Fe^{III}L]–[Fe^{II}L] couple might enable this mechanism.

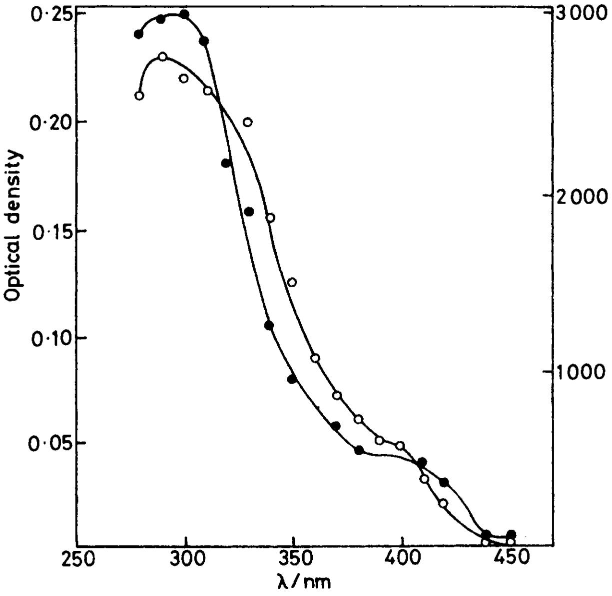

FIGURE 7 Spectra observed in N_2O-saturated solutions containing 4×10^{-4} mol dm^{-3} [Mn(nta)]$^-$ at pH 5.0, 10 μs (●) and 1 ms (○) after the pulse

The observation that the rates of oxidation by [Br_2]$^{\cdot-}$ and [$(NCS)_2$]$^{\cdot-}$ of [Fe(edta)]$^{2-}$ and [Fe(nta)]$^-$ are equal and that [I_2]$^{\cdot-}$ reacts considerably faster with the latter complex than with the former, although [Fe(edta)]$^{2-}$ is the better reducing agent, supports the inner-sphere mechanism. However, the observed rates are higher by a factor of 20 than those of the reaction Br_2 + [Fe(edta)]$^{2-}$ which was suggested to follow a substitution-controlled inner-sphere mechanism.[30] (For a general discussion of the mechanism of oxidation by [X_2]$^{\cdot-}$ radicals see below.)

The Oxidation of [Mn(edta)]$^{2-}$ *and* [Mn(nta)]$^-$.—(*a*) *Reactions with* OH *radicals.* When N_2O-saturated solutions containing 4×10^{-4} mol dm^{-3} complex were irradiated the formation of unstable intermediates was observed. The absorption spectra observed at different times after the pulse in the [Mn(nta)]$^-$ systems are shown in Figure 7. In [Mn(edta)]$^{2-}$ solutions at pH 5 the absorption spectrum has maxima at 290 and 430 nm with $\varepsilon_{\max.}$ 2 800 and 820 dm^3 mol^{-1} cm^{-1}. In both systems no absorption at >300 nm remained after the decomposition of the unstable intermediates, although [Mn(edta)]$^-$ and [Mn(nta)] have absorption bands at *ca.* 480 nm and are stable in aqueous solutions.

The rate constant for reaction of OH with [Mn(edta)]$^{2-}$ was 1.5×10^9 and 3.0×10^9 dm^3 mol^{-1} s^{-1} at pH 4.5 and 9.0 respectively, and with [Mn(nta)]$^-$ was 1.5×10^9 and 2.5×10^9 dm^3 mol^{-1} s^{-1} at the same pH values. The kinetics of decomposition of the unstable intermediates consisted of two consecutive processes in both systems (Figure 7). The first process obeyed a first-order rate law with $k = 2.5 \times 10^3$ and 3.0×10^3 s^{-1} in the edta and nta systems respectively, in the range pH 4—9. The second process obeyed a second-order rate law with $2k = 5.8 \times 10^7$ dm^3 mol^{-1} s^{-1} for the nta system at pH 4.5—5.5 and with a rate dependent on pH in the edta system (Figure 8).

These results clearly indicate that OH radicals do not oxidize the [Mn^{II}L] complexes to [Mn^{III}L], since the latter are known to be stable. Furthermore, the spectra and the decomposition kinetics of the unstable intermediates resemble those observed in the [Zn^{II}L] and free-ligand systems. The pH dependence of the second decomposition reaction is different from that observed in the [Zn^{II}L] systems but resembles that observed in the [Co^{II}L] systems. It is therefore concluded that the reaction of OH radicals with the manganese(II) complexes leads to a hydrogen abstraction from the ligands.

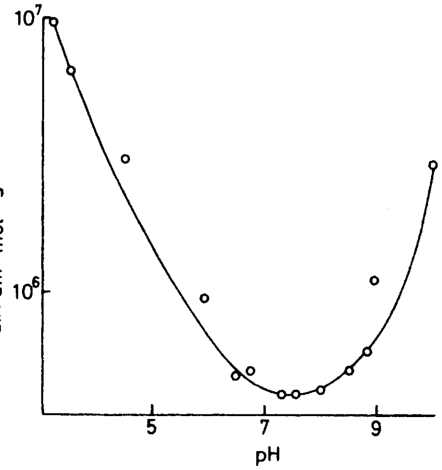

FIGURE 8 Dependence of the second decomposition reaction observed in N_2O-saturated solutions containing 5×10^{-4} mol dm^{-3} [Mn(edta)]$^{2-}$ on pH

(*b*) *Reactions with* [Br_2]$^{\cdot-}$, [$(NCS)_2$]$^{\cdot-}$, [O_2]$^{\cdot-}$, *and* $^{\cdot}O_2CH_2CMe_2OH$. The rates of reaction of these radicals with [Mn^{II}L] under similar conditions to those described for [Co^{II}L] were studied (Table 7). The spectra of the

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[30] W. H. Woodruff and D. W. Margerum, *Inorg. Chem.*, 1974, **13**, 2578.

unstable intermediates formed in the reactions of $[(NCS)_2]^{\cdot -}$, $[O_2]^{\cdot -}$, and $^{\cdot}O_2CH_2CMe_2OH$ consisted of a band at *ca.* 480 nm and a second much stronger band with a maximum at $\lambda < 300$ nm and $\varepsilon > 1\,000$ dm^3 mol^{-1} cm^{-1}. A typical spectrum is shown in Figure 9. The spectra of the stable products, 1—10 min after the irradiation, consisted of one band at *ca.* 480 nm; these results are summarized in Table 8. In the reaction of $[Br_2]^{\cdot -}$ with $[Mn(nta)]^-$ the direct formation of the stable products without any detectable intermediates was observed. The kinetics of decomposition of the intermediates in all these systems obeyed a first-order rate law. The rate constants obtained are summarized in Table 7.

TABLE 7

Kinetic data for the reactions of free radicals ($R\cdot$) with $[Mn^{II}L]$ complexes

$R^{\cdot}$	pH	$10^{-6}k\{R^{\cdot} + [Mn(edta)]^{2-}\}$ [a] dm^3 mol^{-1} s^{-1}	$k\{[Mn(edta)X]^{2-} \longrightarrow [Mn(edta)]^- + X^-\}$ [b] s^{-1}	$k\{R^{\cdot} + [Mn(nta)]^-\}$ [a] dm^3 mol^{-1} s^{-1}	$k\{[Mn(nta)X]^- \longrightarrow [Mn(nta)] + X^-\}$ [b] s^{-1}
$[O_2]^{\cdot -}$	4.5	30	1.8×10^3	4.0×10^8	3.0×10^3
	5.5	7.5	9.0×10^1	1.2×10^8	
$^{\cdot}O_2CH_2CMe_2OH$	4.5			1.5×10^8	
	5.5	6.5	1.0×10^3	1.5×10^8	
	7.0	6.0	3.0×10^1	2.2×10^8	8.0×10^1
	9.0	17	2.0×10^1	1.1×10^8	2.0×10^1
$[Br_2]^{\cdot -}$	3.6			7.0×10^6	$< 5 \times 10^3$ [c]
	4.5			2.0×10^7	
	5.5	$5 \times 10^4 < k < 9 \times 10^5$ [d]		2.0×10^7	
$[(NCS)_2]^{\cdot -}$	4.5			1.3×10^7	2.0×10^2
	5.0	$5 \times 10^4 < k < 7 \times 10^6$ [d]		4.0×10^7	

[a] Accuracy, ±15%. [b] Accuracy, ±10%. [c] The formation of [Mn(nta)] was observed without any intermediate; thus the rate of Br^- loss has to be higher than 5×10^3 s^{-1}. [d] Upper limit from pulse-radiolysis experiments; lower limit estimated from yield in ^{60}Co γ source (see Table 5).

TABLE 8

Spectral data for products of reaction of free radicals with $[Mn^{II}L]$ complexes, $R^{\cdot} + [M^{II}L]$

		$L = nta^{3-}$				$L = edta^{4-}$ [c]			
		After reaction [a]		Final products [b]		After reaction [a]		Final products	
$R^{\cdot}$	pH	$\lambda_{max.}$/nm	$\varepsilon_{max.}$/dm^3 mol^{-1} cm^{-1}	$\lambda_{max.}$/nm	$\varepsilon_{max.}$/dm^3 mol^{-1} cm^{-1}	$\lambda_{max.}$/nm	$\varepsilon_{max.}$/dm^3 mol^{-1} cm^{-1}	$\lambda_{max.}$/nm	$\varepsilon_{max.}$/dm^3 mol^{-1} cm^{-1}
$[O_2]^{\cdot -}$	4.5	350,[d]	2 600,[d]	350,[d]	310,[d]	350,[d]	800,[d]	350,[d]	130,[d]
		470	*ca.* 500	460	350	475	>150 [e]	475	>110 [e]
$^{\cdot}O_2CH_2CMe_2OH$	4.5	350,[d]	1 500,[d]	350,[d]	320,[d]	350,[d]	660,[d]	350,[d]	380,[d]
		480	*ca.* 500	480	350	490	*ca.* 700	490,	480
	5.5			460 [e]	350 [e]			460 [e]	350 [e]
$[Br_2]^{\cdot -}$	4.0					[f]	[f]	500 [e]	400 [e]
	5.5	460	>150 [g]	460	150 [g]				
$[(NCS)_2]^{\cdot -}$	4.5					[f]	[f]	490 [e]	340 [e]
	5.5	350,[d]	800,[d]	350,[d]	100,[d]				
		460	>350 [g]	460	>250 [g]				

[a] Measured at the end of the reaction $R^{\cdot} + [Mn^{II}L]$. [b] Stable products as obtained several seconds after the pulse or from irradiations in the γ source. [c] For $[Mn(edta)]^-$ which was dissolved in water: $\lambda_{max.}$ 490 and 470 nm and $\varepsilon_{max.}$ 460 and 420 dm^3 mol^{-1} cm^{-1} at pH 4.5 and 5.5 respectively. [d] A strong absorption band exists in the u.v. We could not detect the maximum of this band and the absorption coefficient on the red branch of the band is given. [e] Solutions irradiated in the ^{60}Co γ source only. [f] No reaction between the free radical and the $[Mn(edta)]^{2-}$ was observed in the pulse-radiolysis experiments. [g] Lower limit for absorption coefficient since competition between the reactions $R^{\cdot} + [Mn^{II}L]$ and $R + R^{\cdot}$ was observed.

The results clearly indicate that the radicals $[Br_2]^{\cdot -}$, $[(NCS)_2]^{\cdot -}$, $[O_2]^{\cdot -}$, and $O_2CH_2CMe_2OH$ oxidize $[Mn(nta)]^-$ and $[Mn(edta)]^{2-}$ (in the latter case some of the reactions are too slow to be measured) *via* the inner-sphere mechanism. The decomposition reaction of the intermediates clearly represents the loss of a ligand from the inner ligation sphere of $[Mn(nta)X]^-$ and $[Mn(edta)X]^{2-}$. For $X = Br^-$ the latter reaction is fast and thus only the direct formation of [Mn(nta)] is observed. The similarity of the manganese(II) and cobalt(II) oxidations is clearly demonstrated. The reaction of $[O_2]^{\cdot -}$ with the $[Mn^{II}L]$ complexes is a good model for the manganese-containing hyperoxide dismutase enzyme.[31,32]

General Discussion and Comparison between the Different Systems Studied.—(*a*) *Oxidations by* OH *radicals*. In Table 9 are rate constants for reaction of OH radicals with different complexes of edta and nta. All the rate constants range between 2×10^9 and 5×10^9 dm^3 mol^{-1} s^{-1}, the only exceptions being the complexes with $M = H^+$, Co^{3+}, and Fe^{3+}. In the latter systems the reaction observed is hydrogen abstraction from the $R^1R^2NCH_2CO_2^-$ group. It is known that the inductive effect of H^+ in $R^1R^2\overset{+}{N}HCH_2CO_2^-$ decreases the rate of the hydrogen-abstraction reaction in many similar sys-

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[31] M. Pick, J. Rabani, F. Yost, and I. Fridovich, *J. Amer. Chem. Soc.*, 1974, **96**, 7329.

[32] M. E. McAdam, R. A. Fox, F. Lavelle, and E. M. Fielden, *Biochem. J.*, 1977, **165**, 71, 80.

tems.[33,34] It is also known that Co^{3+} has a similar, although smaller, inductive effect [35,36] and the same is expected for Fe^{3+}. It is expected that the inductive effect of the M^{2+} cations will be considerably smaller, in agreement with the observations. The inductive effect should also be affected by the electronic configuration of the central cation, in the order $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$. It is of interest that there seems to be no correlation between the redox potential of the $[M^{III}L]$–$[M^{II}L]$ couple and the nature of the reaction occurring. Thus $[Fe^{II}L]$ is the strongest reducing agent in the series and is indeed oxidized to $[Fe^{III}L]$ by OH radicals, but $[Cu^{II}L]$ and $[Ni^{II}L]$ are also oxidized to the metal(III) *trivalent* complexes although the latter are unstable. On the other hand, the $[Mn^{III}L]$ and $[Co^{III}L]$ complexes are stable but the OH radicals do not oxidize their metal(II) complexes to the metal(III) species. {The reaction of $[Co(edta)]^{2-}$ with OH radicals proceeds *via* two parallel mechanism, oxidation and hydrogen abstraction.} The observation that the rates of reaction of OH with the complexes of the metal(II) cations are very similar is difficult to explain. The question arising is why in some systems (M = Mn, Zn, or Co) is a hydrogen-abstraction mechanism observed whereas in the others (M = Fe, Cu, or Ni) an oxidation of the central cation and *no* hydrogen abstraction is observed. Some plausible explanations of these observations are as follows.

(*i*) It could be argued that in all the complexes

$$\mathrm{OH} + [\mathrm{M^{II}L}] \longrightarrow \mathrm{H_2O} + [\overline{\mathrm{M^{II}\{NR^1R^2(\dot{C}HCOO}}{}^-)\}] \quad (19)$$

studied the first reaction occurring is a hydrogen abstraction from the ligand [equation (19)]. According to this hypothesis this reaction is followed in some of the complexes by a fast intramolecular electron transfer [equation (20)]. This reaction has to be very fast since the addition of oxygen in the nickel and copper systems has no effect on the observed kinetics. This mechanism

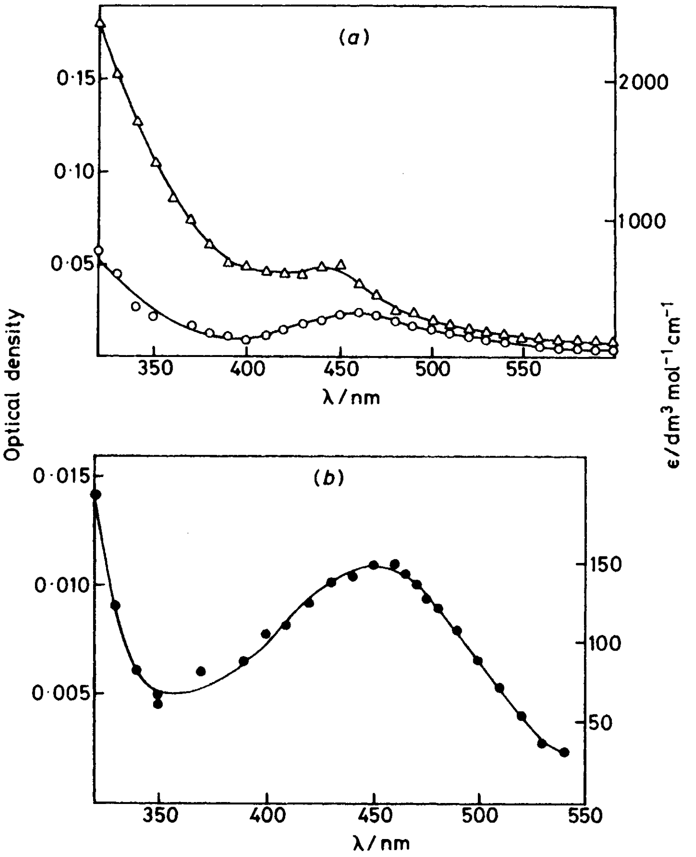

FIGURE 9 (*a*) Spectra observed 100 μs (△) and 20 ms after the pulse (○) in O_2-saturated solutions containing 4×10^{-4} mol dm^{-3} $[Mn(nta)]^-$ and 1.0 mol dm^{-3} Bu^tOH at pH 5.5. (*b*) Spectrum observed 500 μs after the pulse in N_2O-saturated solutions containing 4×10^{-4} mol dm^{-3} $[Mn(nta)]^-$ and 1×10^{-2} mol dm^{-3} NaBr at pH 5.0

seems unreasonable since reaction (20) would be expected to be more efficient in the cobalt and manganese systems,

$$[\overline{\mathrm{M^{II}\{NR^1R^2(\dot{C}HCOO}}{}^-)\}] \xrightarrow{\mathrm{H_2O}} [\overline{\mathrm{M^{III}\{NR^1R^2(CH_2COO}}{}^-)\}] \quad (20)$$

where the $[M^{III}L]$ complexes are stable, than those of Cu and Ni; however, the observations indicate the reverse order.*

(*ii*) It can be argued that the inductive effect of Ni^{II} and Cu^{II} is considerably larger than that of Co^{II}, Mn^{II}, and Zn^{II} (see above). If the inductive effect causes a decrease in the rate of hydrogen abstraction to

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* One of the referees suggested that the free radicals $[\overline{\mathrm{M^{II}\{NR^1R^2(\dot{C}HCOO}}{}^-)\}]$ might reduce the central cation to $[\mathrm{M^I(^-O_2CCH{=}\overset{+}{N}R^1R^2)}]$ and that the latter are the observed intermediates and not the metal(III) complexes. This suggestion seems to disagree with the following observations. (*a*) The intermediate obtained in the [Ni(edta)] system oxidizes I^- to $[I_3]^-$ quantitatively.[8] It is hard to visualize a mechanism by which Ni^I would oxidize I^-. (*b*) The rates of reaction of the intermediates obtained in the copper and nickel systems with O_2 are considerably lower than expected for their metal(I) complexes.[37] (*c*) It is hard to believe that the free radicals involved are strong enough reductants to reduce Ni^{II} to Ni^I. Thus for the $Ni^{2+}(aq)$–$Ni^+(aq)$ couple a redox potential of -2.7 V was estimated (J. H. Baxendale and R. S. Dixon, *Z. Phys. Chem.*, 1964, **43**, 161; M. Breitenkamp, A. Henglein, and J. Lilie, *Ber. Bunsengesellschaft Phys. Chem.*, 1976, **80**, 974). Even if this estimate is too high, radicals of the type $NR^1R^2(CHCO_2^-)$ are not expected to reduce $Ni^{2+}(aq)$. Indeed only $e^-(aq)$ is known to reduce $Ni^{2+}(aq)$ and $Fe^{2+}(aq)$ whereas H, CO_2^-, $\cdot CH_2OH$, and other radicals do not. The reduction of the edta and nta complexes is energetically even less favourable and indeed these ligands reduce the rate of reaction of $e^-(aq)$ with these cations.[21] Alternatively, the referee suggested that the intermediates observed are metal(III) intermediates formed by the reaction of the metal(I) complexes with N_2O. However, as stated above, it seems difficult to believe that metal(I) complexes can be formed by the reaction of these radicals with the metal(II) complexes. Furthermore, this would require that the rates of reaction of the metal(I) complexes with N_2O are $>3.5 \times 10^7$ dm^3 mol^{-1} s^{-1}, whereas their rates of reaction with O_2 are considerably lower. The latter requirement is not in accord with observations for other metal(I) complexes (see ref. 37 and refs. therein).

[33] M. Anbar, D. Meyerstein, and P. Neta, *J. Chem. Soc.* (*B*), 1966, 742.

[34] W. M. Garrison, *Current Topics Radiation Res.*, 1968, **4**, 43.

[35] H. Cohen and D. Meyerstein, *J.C.S. Dalton*, 1976, 1976.

[36] N. Shinohara, personal communication.

[37] D. Meyerstein, *Accounts Chem. Res.*, 1978, **11**, 43.

$k < 6 \times 10^8$ dm^3 mol^{-1} s^{-1} the results could be explained since we would not be able to detect a hydrogen-abstraction reaction if it amounts to less than 20%. However, it is difficult to believe that the inductive effect in the complexes of Cu^{II} and Ni^{II} is as large as in those of Fe^{III} and Co^{III} (Table 9).

TABLE 9

Rate constants ($\times 10^9$ dm^3 mol^{-1} s^{-1}) for reactions of OH radicals with different complexes of edta and nta [a]

	M									
L	—	H$^+$	Zn^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Co^{3+}	Fe^{2+}	Fe^{3+}	Mn^{2+}
edta	2.0	0.4 [b]	3.5	3.0	2.5	5.0	0.5 [c]	5.0 [b]	0.5 [d]	3.0
nta	2.5	0.75 [b]	2.0	2.6	1.4	3.5		5.0 [b]		2.5

[a] All solutions at pH 9.0; accuracy, ±20%. [b] pH 5.0. [c] From ref. 6. [d] From ref. 2.

(*iii*) The fact that OH radicals oxidize the [Ni^{II}L] and [Cu^{II}L] complexes although the redox potentials of the couples [M^{III}L]–[M^{II}L] for these systems are more positive than those for the corresponding [Mn^{II}L] and [Co^{II}L] which are not oxidized seems to stem from the different reorganization energies required in the reactions (21). The free-energy gain in these reactions is

$$[\mathrm{M^{II}L}] + \mathrm{OH} \longrightarrow [\mathrm{M^{III}L}] + [\mathrm{OH}]^-(\mathrm{aq}) \qquad (21)$$

very large since the redox potential of the OH–[OH]$^-$(aq) couple is [38] *ca.* 2.4 V at pH 7 and those for the [M^{III}L]–[M^{II}L] couples lie in the range $0.1 < E^\ominus < 1.2$ V for the different complexes studied. However, a simple outer-sphere oxidation reaction should be written as in (21a)

$$[\mathrm{M^{II}L}] + \mathrm{OH} \longrightarrow [\mathrm{M^{III}L}] + [\mathrm{OH}]^- \qquad (21a)$$

where the product [OH]$^-$ is formed with the hydration sphere of the OH radicals. Since the hydration energy of OH radicals is very small,[38] and that of [OH]$^-$ is 110 kcal mol^{-1},[38] it is clear that reaction (21a) is endothermic, and therefore (21) should have a large activation energy due to the large reorganization energy required.* The same argument could be rephrased in a more 'orthodox' fashion by reasoning that, due to the large difference in the hydration energy of OH$^\bullet$ and [OH]$^-$, the self-exchange rate of these reactants *via* the outer-sphere mechanism is very slow. It is therefore suggested that the OH radicals interact strongly with the complex prior to the electron-transfer process, by some kind of overlap with the carbonyl groups of the carboxylates. It is also plausible that the hydrogen-abstraction reaction proceeds *via* the same very short-lived intermediate, which would explain the observation that hydrogen abstraction takes place only from NCH$_2$CO$_2^-$ and not from the NCH$_2$CH$_2$N group. Such a mechanism could account for the following experimental observations.

(1) The difference in the course of reaction for the different metal cations. The larger expected reorganization energy required in the oxidation of $t_{2g}^5e_g^2$ Co^{II} to t_{2g}^6 Co^{III} and of d^5 Mn^{II} to Jahn–Teller-distorted d^4 Mn^{III} should slow down the rate of the electron-transfer process, which involves only a small net free-energy gain. The reorganization energy required in the oxidation of Fe^{II} and Ni^{II} (these metals form octahedral complexes both in the bi- and tri-valent oxidation states) and of the distorted copper(II) octahedral complex to d^8 Cu^{III} (which is expected to be similarly distorted) is expected to be considerably smaller. (2) If a common 'intermediate' exists for both the hydrogen-abstraction and the electron-transfer processes it is probable that, although the rates are similar in the different systems studied, only one product is observed in each system. {The only exception to this rule is the reaction OH + [Co(edta)]$^{2-}$.} More experimental data on similar systems are required in order to verify this hypothesis and to obtain a better understanding of the nature of the suggested intermediate.

(*b*) *Oxidations by* [Br$_2$]$^{\bar{\cdot}}$ [(NCS)$_2$]$^{\bar{\cdot}}$, [I$_2$]$^{\bar{\cdot}}$, [O$_2$]$^{\bar{\cdot}}$, *and* $^\bullet$O$_2$CH$_2$CMe$_2$OH. The observations concerning the reactions of these radicals with the different complexes studied can be summarized as follows. (*i*) These radicals do not abstract a hydrogen from the ligand in any of the complexes studied. (*ii*) The radicals [Br$_2$]$^{\bar{\cdot}}$, [(NCS)$_2$]$^{\bar{\cdot}}$, and [I$_2$]$^{\bar{\cdot}}$ do not oxidize the [Cu^{II}L] and [Ni^{II}L] complexes, although the oxidation potential of [Br$_2$]$^{\bar{\cdot}}$ at least is sufficient. (*iii*) All these radicals, with the exception of [I$_2$]$^{\bar{\cdot}}$, oxidize the [Co^{II}L] and [Mn^{II}L] *via* the inner-sphere mechanism. The rates observed are higher for the nta than for the edta complexes, although the latter are better reducing agents,[27] and are very high for inner-sphere reactions in some of the systems. (*iv*) All these radicals oxidize the [Fe^{II}L] complexes. In this system there seems to be no difference between the nta and edta complexes, but the rate constant for [Fe(nta)]$^-$ + [I$_2$]$^{\bar{\cdot}}$ is greater than for [Fe(edta)]$^{2-}$ + [I$_2$]$^{\bar{\cdot}}$. The exact mechanism, inner or outer sphere, is not clear for the [Fe^{II}L] system.

$$\mathrm{R^1R^2CH_2} + [\mathrm{X_2}]^{\bar{\cdot}} \text{ (or RO}_2) \longrightarrow \mathrm{R^1R^2CH^\bullet} + \mathrm{HX} + \mathrm{X^-} \text{ (or RO}_2\mathrm{H}) \qquad (22)$$

These results are in accord with the following argu-

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* Similar arguments are correct also for the oxidation of [Fe(CN)$_6$]$^{4-}$ by OH radicals. It seems therefore that also this reaction is not a simple outer-sphere process. An inner-sphere mechanism, *e.g.* involving a seven-co-ordinate intermediate, seems unreasonable for this system as the only product is [Fe(CN)$_6$]$^{3-}$. It is suggested, therefore, that there is a strong interaction between the OH radical and [Fe(CN)$_6$]$^{4-}$, perhaps similar to that observed in the reactions of OH with the halides.[16,17] Such an 'intermediate' was indirectly invoked in order to explain the pH effect on the rate of the reaction OH + [Fe(CN)$_6$]$^{4-}$,[39] an effect which is also incompatible with an inner-sphere mechanism.

[38] W. M. Latimer, 'Oxidation Potentials,' 2nd edn., Prentice-Hall, New Jersey, 1961.

[39] D. Zehavi and J. Rabani, *J. Phys. Chem.*, 1972, **76**, 3703.

ments. (1) Reaction (22) is endothermic and thus no hydrogen abstraction by these radicals is observed. (2) The outer-sphere oxidations of the edta and nta complexes by the free radicals studied are not expected to be fast. The total free-energy gain in these reactions is <1.2 V,[14,27] with the exception of the iron(II) complexes. Furthermore, the reactions require rather large reorganization energies both on the metal (see above) and the radical centre. Thus the redox potentials of $\mathrm{Br_2]^{\dot{-}}}$–$2\mathrm{Br^-}$ and $[\mathrm{O_2}]^{\dot{-}}$–$\mathrm{H_2O_2}$ are 1.77 (ref. 14) and 1.69 V (ref. 29) respectively but the products in an outer-sphere oxidation would be $[\mathrm{Br_2}]^{2-}$ and $[\mathrm{O_2}]^{2-}$. Thus it is not surprising that the oxidation reactions observed occur *via* the inner-sphere mechanism. (3) The rates of reaction are rather high for inner-sphere reactions. However, it is known that some of the metal-(II) and -(III) complexes with these ligands have seven sites in their inner co-ordination sphere. Furthermore, the rate of exchange of the water molecule in the inner co-ordination sphere is accelerated by these ligands, thus $k = 3.2 \times 10^4$, 6.3×10^5, 6.3×10^6, 4.4×10^8, and 1.5×10^9 s^{-1} were reported for the water exchange of $[\mathrm{Ni(OH_2)_6}]^{2+}$, $[\mathrm{Ni(edta)(OH_2)}]^{2-}$, $[\mathrm{Mn(OH_2)_6}]^{2+}$, $[\mathrm{Mn(edta)(OH_2)}]^{2-}$ and $[\mathrm{Mn(nta)(OH_2)_2}]^-$ respectively.[40] For $[\mathrm{Co(OH_2)_6}]^{2+}$ and $[\mathrm{Fe(OH_2)_6}]^{2+}$ the rate constants are 2.5×10^6 and 2.0×10^6 s^{-1} respectively[40] and thus rate constants of the order of 5×10^8 s^{-1} are reasonable for their edta and nta complexes. The rate constants for reaction of the free radicals with the $\mathrm{Fe^{II}}$, $\mathrm{Co^{II}}$, and $\mathrm{Mn^{II}}$ are within this range.

The observation that the nta complexes are more reactive than the edta complexes, although the latter are better reducing agents, might be due to steric factors affecting the penetration of the oxidizing radical into the inner co-ordination sphere. This would be particularly relevant if a seven-co-ordinate intermediate has to be considered for the edta complexes.

The fact that no oxidation of the $[\mathrm{Ni^{II}L}]$ complexes was observed can be easily explained by the low rate of ligand exchange of $[\mathrm{Ni(edta)(OH_2)}]^{2-}$ (k 6.3×10^5 s^{-1}).[40] The lack of reactivity of the $[\mathrm{Cu^{II}L}]$ complexes must be due to other reasons, since the ligand-exchange rates of copper(II) complexes are very high. The oxidation potential of the $[\mathrm{Cu^{III}L}]$–$[\mathrm{Cu^{II}L}]$ couple is higher than for all the other complexes studied (see below); thus the free-energy gain in the reactions $[\mathrm{Cu^{II}L}] + [\mathrm{Br_2}]^{\dot{-}} \longrightarrow [\mathrm{Cu^{III}L(Br)}] + \mathrm{Br^-}$ is <16 kcal mol^{-1}. If the $\mathrm{Br^-}$ is released without its full hydration sphere the free-energy gain will be even smaller and thus explains the experimental observations.

(*c*) *Spectra of the intermediates.* The results indicate that the central metal cations have little influence if any on the spectra of the radicals $[\overline{\mathrm{M}\{\mathrm{NR^1R^2}(\dot{\mathrm{C}}\mathrm{HCOO}}{}^{-})\}]$ obtained by hydrogen abstraction from the ligand. The absorption bands in the near u.v. of the $[\mathrm{M^{III}L}]$ complexes are attributed to L ⟶ M charge-transfer transitions. This has been confirmed for the iron(III) and $[\mathrm{Co(edta)}]^-$ complexes by their photochemistry.[41,42] The fact that the absorption maxima of $[\mathrm{Ni^{III}L}]$ and $[\mathrm{Cu^{III}L}]$ are shifted considerably to the red relatively to those of $[\mathrm{Fe^{III}L}]$ and $[\mathrm{Co^{III}L}]$ is in accord with the relative oxidation potentials. Furthermore, the results suggest that the $[\mathrm{Cu^{III}L}]$ complexes are stronger oxidizing agents than $[\mathrm{Ni^{III}L}]$. This conclusion is in agreement with the relative stability of the $[\mathrm{M^{III}L}]$ complexes.[26,37,43]

(*d*) *Mechanisms of decomposition of the metal*(III) *complexes.* The decomposition of [Ni(nta)], [Cu(nta)], and $[\mathrm{Cu(edta)}]^-$, the three unstable metal(III) complexes obtained in this study, follow first-order rate laws. The rate of decomposition decreases along the series [Cu(nta)], $[\mathrm{Cu(edta)}]^-$, [Ni(nta)], and $[\mathrm{Ni(edta)}]^-$ in agreement with the expected redox potentials. The most reasonable mechanism of decomposition is an intramolecular electron transfer from the carboxylate group to the metal followed by release of $\mathrm{CO_2}$ and the formation of the radical $\mathrm{M^{II}(NCH_2^{\bullet})}$. In the copper complex a further electron transfer, or a direct two-electron transfer, is expected yielding $\mathrm{Cu^{I}(N{=}CH_2)}$ which is then hydrolyzed. The exact fate of $\mathrm{Ni^{II}(NCH_2^{\bullet})}$ is difficult to determine since the rate-determining step is the electron-transfer reaction producing this radical. Plausible decomposition paths of similar radicals were discussed for the corresponding iron(II) and cobalt(II) radicals.[42,43] Similar mechanisms for the thermal oxidative degradation of edta by $\mathrm{Ce^{IV}}$,[44] or photochemical degradation of $[\mathrm{Fe(edta)}]^-$ and $[\mathrm{Co(edta)}]^-$,[42,43] have been proposed.

Another plausible mechanism for the oxidation of the ligand by the central cation is the reverse of reaction (20). This mechanism was ruled out for the decomposition of copper(III) complexes containing amino-ligands, since $[\mathrm{Cu(en)_2}]^{3+}$ (en = ethylenediamine) decomposes slowly *via* a second-order process.[26] Furthermore, the results indicated that complexes containing α-, β-, and γ-amino-acids and α-aminoisobutyric acid as ligands decomposed at similar rates, suggesting that the rate-determining step is the electron transfer from the carboxylate group.[26] We therefore believe that the mechanism of decomposition is better described by the electron-transfer mechanism.*

(*e*) *Mechanisms of decomposition of the free radicals obtained by hydrogen abstraction from the ligands.* This

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* It should be pointed out that experiments designed to obtain a full analysis of all the final products in these and similar systems failed. This is due to two reasons: (*a*) it seems that many products with similar functional groups are formed and the analytical procedures are complicated; (*b*) in order to obtain sufficient product for analysis the radiation dose delivered to the sample has to be large, causing decomposition of 20—50% of the original ligand. Under these conditions the products participate in the radiolytic processes and thus secondary products are also observed and the yield of the primary products is decreased.

[40] C. H. Langford and V. S. Sastri, ' Reaction Mechanisms in Inorganic Chemistry,' ser. 1, vol. 9, *M.T.P. Internat. Rev. Sci.*, Butterworths, Oxford, 1972, p. 203.

[41] P. Natarajan and J. F. Endicott, *J. Phys. Chem.*, 1973, **77**, 1823, 2049.

[42] P. Natarajan and J. F. Endicott, *J. Amer. Chem. Soc.*, 1973, **95**, 2740.

[43] J. Lati and D. Meyerstein, *Inorg. Chem.*, 1972, **11**, 2393.

[44] S. B. Hanna, W. R. Caroll, S. A. Attiya, and W. H. Webb, *Z. Naturforsch.*, 1975, **B30**, 409 and refs. therein.

subject was not the aim of this study but several points should be noted. (*i*) All these intermediates react with O_2 in a fast reaction indicating that they are free radicals. (*ii*) In all the systems studied, $[\overline{\mathrm{M^{II}\{NR^1R^2(\dot{C}HCOO}}^-)\}]$ (M = Zn, Mn, or Co), the decomposition reaction involves two steps, a fast first-order process followed by a slower second-order process. (*iii*) The second-order process involves most probably a disproportionation reaction (23) as would be expected for similar aliphatic radicals. Such a mechanism is also in agreement with the final

$$2\,[\overline{\mathrm{M^{II}\{NR^1R^2(\dot{C}HCOO}}^-)\}] \xrightarrow{\mathrm{H_2O}} [\overline{\mathrm{M^{II}\{NR^1R^2(CH_2COO}}^-)\}] + [\overline{\mathrm{M^{II}\{NR^1R^2[CH(OH)COO}}^-]\}] \quad (23)$$

products observed.[23-25] Reaction (23) is most probably followed by (24). It is of interest to note that the nature of the central cation affects the rate of reaction (23) (compare M = Co to Mn or Zn). (*iv*) We have no explanation at the moment for the first-order process observed

$$[\overline{\mathrm{M^{II}\{NR^1R^2[CH(OH)COO}}^-]\}] \xrightarrow{\mathrm{H_2O}} [\mathrm{M^{II}(NR^1R^2H)}] + \mathrm{CHOCO_2}^- \text{ (or } \mathrm{CH_2O + CO_2}) \quad (24)$$

in these systems. The most probable path would be some hydrolysis of the $[\overline{\mathrm{M^{II}\{NR^1R^2(CHCOO}}^-)\}]$ radicals. However, the kinetic data or the product analysis available give no indication as to the exact nature of this process.

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