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Kinetics of oxidation of hydrogen peroxide by dioxo-bridged manganese(III,IV) complexes

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The dioxo-bridged manganese(III,IV) complexes $[L_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}L_2]^{3+}$ [L = 2,2′-bipyridine (bipy) **1** or 1,10-phenanthroline (phen) **2**] quantitatively oxidised H_2O_2 to O_2, and were themselves reduced to Mn^{II}. The bipy complex follows biphasic kinetics but the phen complex follows a single exponential profile. For **1**, the mononuclear complex $[Mn(bipy)_2(H_2O)(OH)]^{2+}$ is the intermediate, which is a solvolysis product of $\mathbf{1}^{+}$, generated by two-electron reduction of $\mathbf{1}^{3+}$ by hydrogen peroxide. The reaction rate increased with increasing $[H^+]$ and decreasing [L]. The aqua derivatives of **1** and **2** have greater kinetic activities than their respective parents. The reactions follow an inner-sphere mechanism though all other redox reactions studied so far for **1** and **2** proceed *via* an outer-sphere model.

The 2,2′-bipyridine (bipy) complex, $[(bipy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bipy)_2]^{3+}$ **1** and its 1,10-phenanthroline (phen) analogue $[(phen)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(phen)_2]^{3+}$ **2** are considered to be 'first-generation' models[1] of photosystem II. Both complexes are well characterised in the solid state[2] but they decompose in aqueous solutions[2c,3] unless stabilised in HL^+–L (L = bipy or phen) buffer in the range pH 4.0–6.0. Thus stabilised, the compounds are reasonably resistant against redox decomposition, but aquate partly[4] to $[Mn_2(\mu\text{-}O)_2L_3(H_2O)_2]^{3+}$ (L = bipy **1a** or phen **2a**). Such solutions oxidise simple inorganic and organic reducing agents *via* an outer-sphere path; inner-sphere reactions are unknown. Oxidation reactions of hydrogen peroxide are generally inner sphere. Only very strong oxidising agents like $[Ni(bipy)_3]^{3+}$ react *via* an outer-sphere mechanism. The binuclear manganese complexes **1** and **2** are mild oxidising agents[2c,5] and their reactions with H_2O_2 are likely to follow inner-sphere paths. In this paper we explore this mechanistic possibility and thus contribute to the general understanding of the mechanism of redox reactions involving oxo-bridged complexes of high-valent manganese.

Experimental

Materials

The solutions of hydrogen peroxide were prepared by dilution of 30% (w/v) stabiliser-free hydrogen peroxide (G.R., E. Merck) and standardised by iodometry using starch indicator.[6] All other materials were described earlier.[4,7]

Physical measurements and kinetics

Rapid kinetics of complex **1** was measured at 25.0 ± 0.1 °C with a stopped-flow spectrophotometer (HITECH-500) interfaced with a personal computer for rapid data acquisition and analysis of absorbance *vs.* time data for rate constants. The slower kinetics of the phenanthroline complex was measured *in situ* in the thermostatted (25.0 ± 0.1 °C) cell housing (CPS 240A) of a Shimadzu (UV-1601PC) spectrophotometer. The monitoring wavelength was 410 nm, where the reaction products and the buffers absorb negligibly. The reactions for the phenanthroline complex obeyed excellent first-order kinetics at least up to 90% reaction. The first-order rate constants, k_0, were evaluated as usual from least-squares analysis of *A vs. t* data. These data (512 data points were collected by the stopped-flow apparatus for each experiment) for the bipyridine complex gave an excellent fit using equation (1) for an irreversible biphasic consecutive reaction. The program used for this purpose was based on a least-squares method and was provided with the stopped-flow apparatus. It led to a_f, a_s, A_∞, k_f and k_s (where k_f, k_s are rate constants for the fast and slow reactions respectively and a_f, a_s are corresponding amplitudes in units of absorbance).

$$A = a_f\,[\exp(-k_f t)] + a_s\,[\exp(-k_s t)] + A_\infty \qquad (1)$$

The ionic strength was maintained at 1.0 mol dm^{-3} with $NaNO_3$. The pH values of solutions were measured using an Orion (710A) pH-meter with a calibrated electrode. The reaction mixtures were buffered in the range pH 4–6, with c_{bipy} (= [bipy] + [Hbipy$^+$]) 2–10 mmol dm^{-3} and c_{phen} (= [phen] + [Hphen$^+$]) 3–12 mmol dm^{-3}. All kinetic experiments were carried out under pseudo-first-order conditions with the reductant in large excess (10^2–10^3 times over **1** and 10–60 times over **2**).

All data, except for the stopped-flow *A vs. t* outputs, were analysed using the built-in least-squares program of a Casio (model fx 3600P) calculator, the reported errors are standard deviations.

Stoichiometry

The reaction stoichiometries were measured under the kinetic conditions. An excess of hydrogen peroxide was mixed in a single portion with the manganese(III,IV) complexes. The unreacted hydrogen peroxide was estimated iodometrically.[6] Oxygen evolved in the reaction of 0.10 mmol complex with 0.50 mmol H_2O_2 in a total volume of 100 cm^3 was collected by downward displacement of water in a microburette (5 cm^3). A parallel blank was run without the complex. Measured volumes were corrected to normal temperature and pressure as usual.

Results and Discussion

Six independent measurements yielded a consumption ratio, $\Delta[\text{complex}]:\Delta[H_2O_2] = 0.66 \pm 0.04$ and 0.67 ± 0.05 for complexes **1** and **2** respectively. The corresponding $[O_2]:[\text{complex}]$ ratio was 1.5 ± 0.1 and 1.45 ± 0.05. The results indicate quantitative oxidation of H_2O_2 to O_2 according to equation (2). The reactions involve a net three-electron change and must occur in steps. The observed biphasic kinetics also indicates a multistep reaction. In an attempt to detect any intermediate, 0.2 mmol dm^{-3} of **1** in c_{bipy} = 10 mmol dm^{-3} at pH 4.5 was mixed with 0.2

$$2[Mn_2(\mu\text{-}O)_2L_4]^{3+} + 2\,H^+ + 3\,H_2O_2 \longrightarrow 4\,Mn^{II} + 8\,L + 3\,O_2 + 4\,H_2O \qquad (2)$$

Table 1 Representative kinetic data[a] for oxidation of hydrogen peroxide by $[(phen)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(phen)_2]^{3+}$ with H_2O_2

pH	10^3c_L/mol dm^{-3}	$10^3[H_2O_2]$/mol dm^{-3}	10^3k_0/s^{-1}
4.20	4.0	1.0	7.49 (7.42)
	5.0		6.66 (6.74)
	6.0		6.19 (6.23)
	7.0		5.86 (5.82)
	9.0		5.14 (5.21)
	9.0		5.12[b]
	10.0[c]		4.96 (4.98)
	11.0		4.82 (4.78)
4.60	6.0[c]	0.50	2.25 (2.28)
		0.75	3.45 (3.42)
		1.00	4.49 (4.57)
		1.50	6.79 (6.86)
		1.75	8.09 (8.00)
		2.00	9.15 (9.14)
		2.50	11.36 (11.42)
4.0	10.0	1.00	6.01 (5.94)
4.11			5.29 (5.38)
4.20			4.96 (4.98)
4.31			4.55 (4.53)
4.40			4.30 (4.27)
4.52			3.87 (3.94)
4.61			3.76 (3.74)
4.73[c]			3.61 (3.52)
4.82			3.50 (3.40)
4.91			3.20 (3.30)
5.0			3.26 (3.20)

[a] Average of at least three experiments; standard deviation, 2–5%. Reactions were carried out at 25.0 °C; [complex] = 0.05 mmol dm^{-3}; I = 1.0 mol dm^{-3} ($NaNO_3$). [b] [Complex] varied in the range 0.05–0.2 mmol dm^{-3}; k_0 varied within 3–5%. [c] Reaction medium purged with purified dinitrogen.

Table 2 Representative kinetic data[a] for the oxidation of hydrogen peroxide by $[(bipy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bipy)_2]^{3+}$ at 25.0 °C

pH	10^3c_{bipy}/ mol dm^{-3}	$10^3[H_2O_2]$/ mol dm^{-3}	k_f/s^{-1}	$10k_s$/s^{-1}
4.82	13.0	10.0	0.38 (0.34)	0.75 (0.74)
		20.0	0.66 (0.68)	1.45 (1.48)
		30.0	1.01 (1.02)	2.10 (2.22)
		40.0	1.33 (1.36)	3.00 (2.96)
		50.0	1.73 (1.73)	3.80 (3.70)
	100.0[b]		3.40 (3.40)	7.40 (7.41)
4.25	2.0[b]	50.0	12.6 (12.5)	31.2 (31.3)
	3.0		8.60 (8.57)	21.0 (21.2)
	4.0		6.80 (6.60)	16.1 (16.2)
	5.0		5.40 (5.41)	12.9 (13.2)
	6.0		4.30 (4.62)	11.1 (11.15)
4.88	2.0		6.85 (7.10)	18.3 (17.5)
4.71	3.0		5.50 (5.49)	14.2 (13.4)
4.88	4.0[b]		4.16 (3.89)	9.30 (9.29)
5.19	5.0		2.87 (2.90)	6.60 (6.78)
5.37	6.0		2.55 (2.45)	5.55 (5.60)

[a] Average of at least three experiments; standard deviation, 3–5%. Reactions were carried out at 25.0 °C; [complex] = 0.1 mmol dm^{-3} and I = 1.0 mol dm^{-3} ($NaNO_3$). [b] Reaction medium purged with purified dinitrogen.

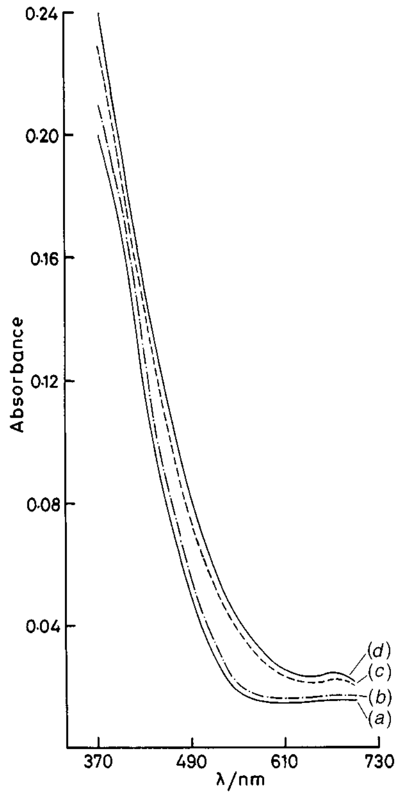

Fig. 1 (*a*) Known spectrum of $[Mn(bipy)_2(H_2O)(OH)]^{2+}$. (*b*) The final spectrum of complex **1** mixed with H_2O_2 in 1:1 molar proportion: [complex], 0.2 mmol dm^{-3}; c_{bipy}, 10.0 mmol dm^{-3}; $[H_2O_2]$, 0.2 mmol dm^{-3}; pH, 4.50, 25.0 °C. (*c*) Spectrum of **1** (0.667 × 10^{-4} mol dm^{-3}) at pH, 4.50. (*d*) Spectrum (*c*) in the presence of 2.66 × 10^{-4} mol dm^{-3} $Mn(NO_3)_2$, *i.e.* that expected for reaction without an intermediate

mmol dm^{-3} H_2O_2. The resulting spectrum is distinctly different from that expected for equation (2) proceeding without any intermediate. The difference is specially noticeable at high wavelengths, where the manganese(III,IV) dimers exhibit a characteristic absorption band. Instead, the spectrum showed striking similarities to that[8] for $[Mn(bipy)_2(H_2O)(OH)]^{2+}$ **3** [Fig. 1(*a*)].

Tables 1 and 2 show some representative first-order rate constants. One can use the known k_f, k_s and ε value for complex **1** along with the parameters a_f, a_s and A_∞ to evaluate the ε for the intermediate (suggestion made by a referee). The value at 410 nm is close (110%) to the value known[8] for **3**. These observations indicate that **1** is reduced by H_2O_2 *via* the intermediate **3**. The first-order rate constants k_0, k_f and k_s increase with increase in $[H_2O_2]$ according to equation (3) (x is o, f or s, as the case

$$k_x = p_x[H_2O_2] \qquad (3)$$

may be); there is no indication for rate saturation up to the highest $[H_2O_2]$ used. Increase in k_x is apparent also with increase in $[H^+]$ but k_x decreased with increase in c_L and remained unchanged with change in [complex].

The variations of k_f and k_s with [bipy], the molar concentration of free bipyridine base, are nicely fit by equations (4a) and (4b) respectively (Fig. 2). The dependence of k_o on [phen] is

$$k_f = \{a + (b/[bipy])\}[H_2O_2] \qquad (4a)$$

$$k_s = \{a' + (b'/[bipy])\}[H_2O_2] \qquad (4b)$$

more complex, but is fit by the linear relation (5). Here K_2

$$k_o(K_2 + [phen]) = (c[phen] + d)[H_2O_2] \qquad (5)$$

(3.92 × 10^{-4} mol dm^{-3}) is the ligand dissociation constant[7] for complex **2**; *c* and *d* are constants.

Equation (8) and the literature value[9] for K_{Hbipy} (10$^{-4.42}$ mol

$$Hbipy^+ \xrightleftharpoons{K_{Hbipy}} H^+ + bipy \qquad (6)$$

$$Hphen^+ \xrightleftharpoons{K_{Hphen}} H^+ + phen \qquad (7)$$

$$[L] = K_{HL}c_L/(K_{HL} + [H^+]) \qquad (8)$$

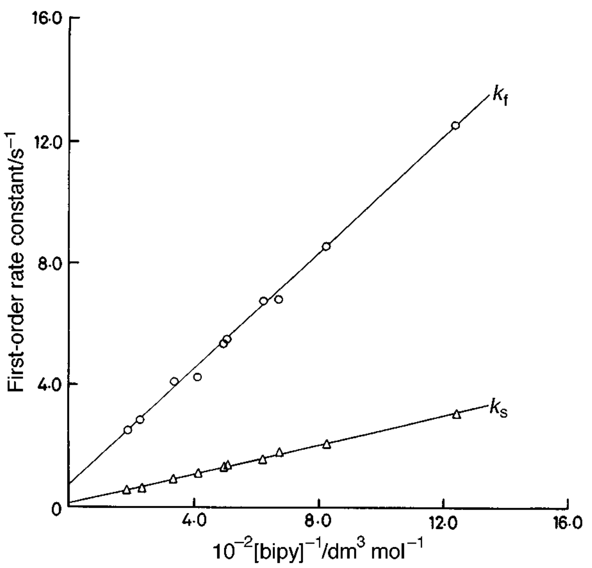

Fig. 2 Plots of k_f and k_s against $[\text{bipy}]^{-1}$. [Complex], 0.1 mmol dm^{-3}; $[H_2O_2]$, 50 mmol dm^{-3}; c_{bipy}, 2–6 mmol dm^{-3}; $I = 1.0$ mol dm^{-3}; pH, 4.25–5.37; 25.0 °C

$$\underset{\mathbf{1}^{3+}}{[\text{Mn}_2(\mu\text{-O})_2(\text{bipy})_4]^{3+}} + 2\,H_2O \xrightleftharpoons{K_1} \underset{\mathbf{1a}^{3+}}{[\text{Mn}_2(\mu\text{-O})_2(\text{bipy})_3(H_2O)_2]^{3+}} + \text{bipy} \quad (9)$$

$$\mathbf{1}^{3+} + H_2O_2 \xrightarrow{k_1} \mathbf{1}^{+} + 2\,H^{+} + O_2 \quad (10)$$

$$\mathbf{1a}^{3+} + H_2O_2 \xrightarrow{k_{1a}} \mathbf{1a}^{+} + 2\,H^{+} + O_2 \quad (11)$$

$$\mathbf{1}^{+} + 3\,H^{+} \xrightarrow{\text{fast}} \underset{\mathbf{3}}{[\text{Mn}(\text{bipy})_2(H_2O)(OH)]^{2+}} + 2\,\text{bipy} + \text{Mn}^{\text{II}} \quad (12)$$

$$\mathbf{1a}^{+} + 3\,H^{+} \xrightarrow{\text{fast}} \underset{\mathbf{3a}}{[\text{Mn}(\text{bipy})(H_2O)_3(OH)]^{2+}} + 2\,\text{bipy} + \text{Mn}^{\text{II}} \quad (13)$$

$$\mathbf{3} + 2\,H_2O \xrightleftharpoons{K_1'} \mathbf{3a} + \text{bipy} \quad (14)$$

$$\mathbf{3} + H_2O_2 \xrightarrow{k_1'} \text{Mn}^{\text{II}} + 2\,\text{bipy} + H_2O + HO_2^{\bullet} \quad (15)$$

$$\mathbf{3a} + H_2O_2 \longrightarrow \text{Mn}^{\text{II}} + \text{bipy} + H_2O + HO_2^{\bullet} \quad (16)$$

$$HO_2^{\bullet} + \text{Mn}^{\text{III}} \xrightarrow{\text{fast}} H^{+} + O_2 + \text{Mn}^{\text{II}} \quad (17)$$

Scheme 1

$$\underset{\mathbf{2}^{3+}}{[\text{Mn}_2(\mu\text{-O})_2(\text{phen})_4]^{3+}} + 2\,H_2O \xrightleftharpoons{K_2} \underset{\mathbf{2a}^{3+}}{[\text{Mn}_2(\mu\text{-O})_2(\text{phen})_3(H_2O)_2]^{3+}} + \text{phen} \quad (18)$$

$$\mathbf{2}^{3+} + H_2O_2 \xrightarrow{k_2} \text{Products } (\text{Mn}^{\text{II}}, O_2, H^{+}) \quad (19)$$

$$\mathbf{2a}^{3+} + H_2O_2 \xrightarrow{k_{2a}} \text{Products } (\text{Mn}^{\text{II}}, O_2, H^{+}) \quad (20)$$

Scheme 2

dm^{-3}) and K_{Hphen} ($10^{-4.95}$ mol dm^{-3}) yielded [L] corresponding to a given c_L.

The observed kinetics indicates no proton loss by H_2O_2, which is a very weak acid. Nevertheless, the observed increase in rate with decreases in [L] clearly shows the involvement of a ligand-dissociation equilibrium (9). Earlier studies[2c,3,4] showed that these equilibria are an integral part of the solution chemistry of complexes **1** and **2**. Schemes 1 and 2 therefore appear to be logical explanations for the stoichiometric, kinetic and spectral observations.

Table 3 Kinetic parameters at 25.0 °C, $I = 1.0$ mol dm^{-3}

k_1 13.5 ± 0.8	k_1' 2.18 ± 0.05	k_2 2.74 ± 0.03 dm^3 mol^{-1} s^{-1}
$10^2K_1k_{1a}$ 19.1 ± 0.9	$10^2K_1'k_{1a}'$ 4.87 ± 0.3	$10^3K_2k_{2a}$ 4.8 ± 0.1 s^{-1}

* $k_{2a} = 12.2 \pm 0.9$ dm^3 mol^{-1} s^{-1} using $K_2 = 3.92 \times 10^{-4}$ mol dm^{-3}.

In aqueous solution the two-electron reduced dimers $\mathbf{1}^{+}$ and $\mathbf{1a}^{+}$, proposed in Scheme 1, are fragile[10] and dissociate irreversibly and rapidly to manganese-(II) and -(III) monomers. Our kinetic results along with the synthetic and kinetic studies (see later) of Heyward and Wells[8] suggest that the intermediate manganese(III) monomer be present as **3** in equilibrium with **3a**. In contrast, manganese(III)–phenanthroline monomers are rare; the complexes $[\text{Mn}(\text{phen})_2(H_2O)(OH)]^{2+}$ and $[\text{Mn}(\text{phen})(H_2O)_3(OH)]^{2+}$ are unknown and both of the known monomers, $[\text{Mn}(\text{phen})Cl_3(H_2O)]$[11] and $[\text{Mn}(\text{phen})_2Cl_2]^{+}$,[12] are highly unstable in aqueous media. In Scheme 2 therefore we have not attributed kinetic significance to any intermediate manganese–phenanthroline monomer. This explains why monophasic kinetics is observed for $\mathbf{2}^{+}$: the reactions occur in steps, but only the first step is rate determining; all subsequent steps are rapid. Schemes 1 and 2 lead to equations (21)–(23). These are same as

$$k_f = (k_1[\text{bipy}] + K_1k_{1a})[H_2O_2]/(K_1 + [\text{bipy}]) \quad (21)$$

$$k_s = (k_1'[\text{bipy}] + K_1'k_{1a}')[H_2O_2]/(K_1' + [\text{bipy}]) \quad (22)$$

$$k_o = (k_2[\text{phen}] + K_2k_{2a})[H_2O_2]/(K_2 + [\text{phen}]) \quad (23)$$

the empirical equations (4) and (5) for $a = k_1$, $b = K_1k_{1a}$, $a' = k_1'$, $b' = K_1'k_{1a}'$, $c = k_2$, $d = K_2k_{2a}$ and provided both K_1 and K_1' are $\ll$[bipy]. The constants k_2 and K_2k_{2a} were evaluated from the least-squares intercept and slope of a plot of $k_o(K_2 + [\text{phen}])$ *versus* [phen] at constant $[H_2O_2]$. Similarly, the least-squares intercept and slope of k_f plotted against $[\text{bipy}]^{-1}$ gave k_1 and K_1k_{1a}, while a plot of k_s *versus* $[\text{bipy}]^{-1}$ gave k_1' and $K_1'k_{1a}'$. These constants (Table 3) reproduce k_x within 7% (see parenthetical values in Tables 1 and 2). The minimum value for [bipy] used in experiments was 8.07×10^{-4} mol dm^{-3}. We, therefore, set the upper limit for K_1 and K_1' at 8×10^{-5} mol dm^{-3}. This upper limit is 5 times smaller compared to the known K_2. This is indeed expected since the lower basicity of bipyridine suggests lower stability for its complex.

The aqua complexes **1a** and **2a** exhibit greater kinetic activity than their respective parents while reacting with H_2O_2 (Table 3), NO_2^{-}[4,7] and $S_2O_3^{2-}$.[13] Aqua complexes exhibit greater activity also in several redox reactions of mononuclear chelates of high-valent manganese.[14] There may be four possible reasons for the higher reactivity: (*i*) replacement of a chelating ligand by a weaker donor like H_2O makes the metal centre more open and more electron deficient; (*ii*) hydrogen bonding with H_2O in the aqua complexes may stabilise the oxidant-reductant precursor; this is not possible for the parents; (*iii*) the metal–ligand bonds are more flexible in an aqua complex, which therefore faces a lower Frank–Condon barrier when reduced, and (*iv*) the reductant can approach an aqua species closer than the parent species.

The phenanthroline complexes are more rigid than the bipyridine complexes. One can expect that the Frank–Condon barrier for the bipy complex to be lower than that for its phen analogue. Accordingly, rate constants for the bipy complexes are higher.

Heyward and Wells[15] measured the stopped-flow kinetics for the oxidation of H_2O_2 by $[\text{Mn}(\text{bipy})_2(H_2O)(OH)]^{2+}$ **3** in acid perchlorate media ($[H^{+}]$, 0.2–1.0 mol dm^{-3}). The rate constants reported by them are ≈15% higher than those measured by us in the range pH 4.25–5.37 but otherwise comparable conditions. Under the acidic conditions adopted by them the aqua complex

$[Mn(bipy)(H_2O)_3(OH)]^{2+}$ **3a** should be preponderant. Now, **3a** should be kinetically more active than **3**. Hence, the higher rate observed by Heyward and Wells is expected.

Mechanism for electron transfer

All the earlier kinetics studied for complexes **1** and **2** fit well into an outer-sphere, one-electron transfer model. However the couple $H_2O_2–HO_2^{\bullet}$ ($E = 1.7$ V)[16] has a high thermodynamic barrier. These complexes and their aqua derivatives are weakly oxidising. Consequently, an outer-sphere mechanism is not possible with H_2O_2 even if the self-exchange reaction for the couple $H_2O_2–HO_2^{\bullet}$ is diffusion controlled ($k \approx 10^{10}$ s^{-1}).

Inner-sphere complex formation occurs in many oxidation reactions of H_2O_2 by metal complexes like $[Mn^{III}(cdta)(H_2O)]^-$ (H_4cdta = cyclohexane-1,2-diyldinitrilotetraacetic acid),[17] $[Mn(bipy)_2(H_2O)(OH)]^{2+}$[15] and Mn^{3+}(aq).[18,19] Similar inner-sphere adduct formation followed by electron transfer appears logical in the present cases. Though there is no replaceable water molecule present in the $[Mn_2(\mu\text{-}O)_2L_4]^{3+}$ complexes, adduct formation with hydrogen peroxide can still occur through hydrogen bonding with the oxo-bridge. The distinction between inner- and outer-sphere reactions is not appropriate in this case because there is no substitution in the metal co-ordination sphere, but the concept of strong overlap is still appropriate.

Acknowledgements

We gratefully acknowledge financial assistance from the Department of Science and Technology (New Delhi), and the award of a junior research fellowship (to B. M.) by the University Grants Commission (New Delhi). Professor S. Mitra (Tata Institute of Fundamental Research, Mumbai) kindly allowed R. B. to use the stopped-flow instrument at his laboratory.

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Received 9*th April* 1997; *Paper* 7/02437A