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Formation and reaction of O=Mn^{V} species in the oxidation of phenolic substrates with H_2O_2 catalysed by the dinuclear manganese(IV) 1,4,7-trimethyl-1,4,7-triazacyclononane complex $[Mn^{IV}_2(\mu\text{-}O)_3(TMTACN)_2](PF_6)_2$

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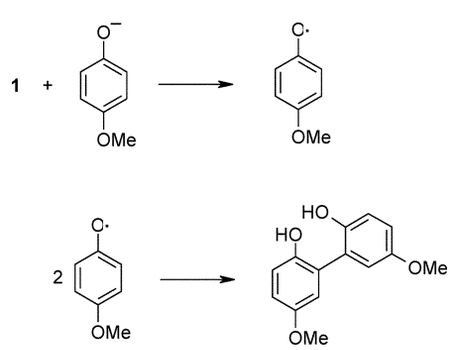
The oxidation of phenolic substrates with H_2O_2 catalysed by $[Mn^{IV}_2(\mu\text{-}O)_3(TMTACN)_2](PF_6)_2$ **1**, (TMTACN, 1,4,7-trimethyl-1,4,7-triazacyclononane) has been investigated by use of ESI mass spectrometry. The role of the phenols as one-electron reductants and as co-ligands in the stabilisation and reaction of an intermediate O=Mn^{V} species has been analysed and the presence of a variety of manganese species in solution has been explained. Our results lead to a proposed mechanism for the catalytic oxidation of phenols in this system.

Introduction

Manganese complexes derived from TMTACN ligands (*e.g.* **1**) have been found to be highly active catalysts both for low-temperature bleaching[1] and, also for the epoxidation of alkenes[2–5] by H_2O_2, a reaction which has been improved by the inclusion of a co-ligand, such as oxalate[6] or ascorbic acid.[7]

We have previously described[8] a mechanistic investigation of the oxidation of a number of azonaphthol dyes with H_2O_2 and **1**, as well as related mononuclear analogues, and have reported preliminary findings relating to the oxidation of phenols.[9,10] For example, we have identified polyphenols and diphenoquinones as oxidation products in the reaction of 4-methoxyphenol and 2,6-dimethoxyphenol by **1** and H_2O_2;[9] these evidently arise from typical coupling reactions of phenoxyl radicals and provide support for the occurrence of one-electron transfer reactions. From EPR experiments it is also clear that the dinuclear complex **1** is capable of reduction by phenols, *via* a Mn^{III}/Mn^{IV} species, ultimately to mononuclear Mn^{II}, and that addition of H_2O_2 regenerates the active oxidant.[9] We have also utilised ESI-mass spectrometry to identify an O=Mn^{V}-containing species in the oxidation of 4-methoxyphenol with H_2O_2 catalysed by **1**. We proposed that oxidation of the phenol to the appropriate bi- and poly-phenols, as described in Scheme 1, leads to the formation of a mixed complex, Mn^{III}(TMTACN)(biphenol) that is oxidised by H_2O_2 to the analogous O=Mn^{V} complex **2**,[10] the potential active species.



Scheme 1

A possibly related oxidation of phenols by **1** and either periodic acid or Oxone® in pyridine has been reported by Barton and co-workers.[11] For example, 2,4-di-*t*-butylphenol reacts with periodic acid to give the corresponding biphenol in 90% yield (the same methodology was used to convert α-terpinene to *p*-cymene in >95% yield). Mechanistic studies point to an active species of the type O=Mn^{V}–Mn^{IV} which is formed from the oxidation of a Mn^{III}–Mn^{IV} species by periodic acid or Oxone®.[11]

Our interest in O=Mn^{V} species as potential oxidants also reflects the suggestion that they are the active species in systems involving Mn–salen[12,13] and Mn–porphyrins,[14] as well as in enzymatic cycles such as that of PSII.[15] The aim of the experiments described here was to establish the formation and role of O=Mn^{V} species in reactions of a range of phenols and H_2O_2 catalysed by **1** and to study the influence of the nature of the phenolic substrate on their stability and reactivity. ESI-MS has thus been used to study oxidation of the phenolic substrates **3**–**9** shown below, chosen to provide examples with different potential for binding to Mn (as monomers and/or dimers) and for differing ease of oxidation. Electrospray ionisation (ESI) is now recognised as being capable of producing intact ions, with multiple charges, from remarkably large, complex and fragile parent species[16] (*cf.* the Feichtinger and Plattner[17,18] study of the detailed mechanism of oxygen transfer from iodosylbenzene to a Mn(III)–salen complex, which identified the oxomanganese species formed upon oxidation).

Results and discussion

1 Species formed during the reaction of phenols with $[Mn_2(\mu\text{-}O)_3(TMTACN)_2](PF_6)_2$ and H_2O_2

a Initial ESI-MS studies; reactions of 4-methoxyphenol 3. In a typical experiment, **3** was reacted with catalyst **1** in the presence and absence of H_2O_2, and the species detected by ESI-MS analysed as a function of time. Experiments were carried out in aqueous solution at pH *ca.* 10.5 (borate buffer) and *ca.* 60 °C, with, in some cases, added acetonitrile or methanol. Typical concentrations employed were [**1**] 10^{-4} mol dm^{-3}, [substrate (phenol)] 10^{-2} mol dm^{-3} and [H_2O_2] 10^{-1} mol dm^{-3}, and reactions were followed over a period of *ca.* 45 min.

In the absence of H_2O_2, an aqueous solution of **1** gave a mass spectrum with two major peaks, *m*/*z* 250 and 645, which are assigned to **10** and its complex with PF_6^-, respectively (see Fig. 1). When an excess of **3** was present in the ratio of 1 : 100 (**1** : **3**), a new peak at *m*/*z* 500 was immediately detected, suggesting the occurrence of a one-electron transfer reaction from the

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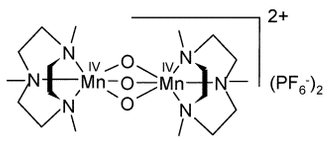

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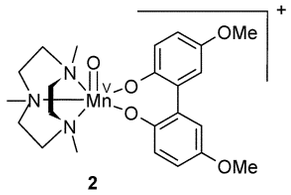

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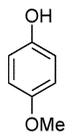

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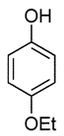

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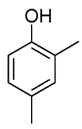

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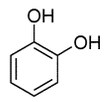

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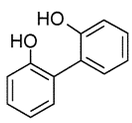

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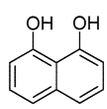

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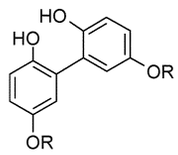

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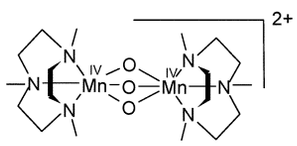

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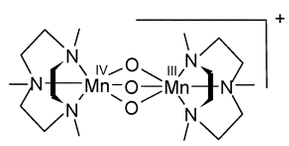

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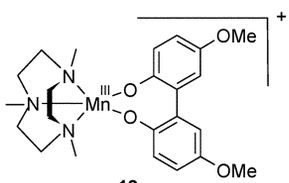

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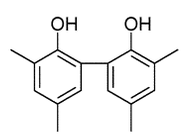

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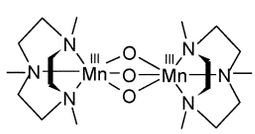

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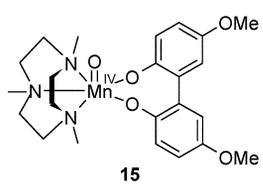

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phenol to **1** to give the Mn^{III}–Mn^{IV} species **11** (see Fig. 2), which has been identified both by EPR spectroscopy at 77 K and ESI-MS (see *e.g.* refs 9 and 10). When the mixture of **1** and **3**, at pH 10.5, was left to stand at 60 °C for 5 min, a new peak at *m*/*z* 470 (assigned to **12**) was also observed. When H_2O_2 was added to a mixture of **1** and **3** (**1** : **3** : H_2O_2, 1 : 100 : 500) this became a major peak after a short induction period (*ca.* 5 min) and a new peak at *m*/*z* 486 assigned to **2** also appeared (see Fig. 3a). Further support for this assignment derives from corresponding observations of reactions of the ethoxy counterpart **4** (see below) and from experiments with $H_2{}^{18}O$ and $H_2{}^{18}O_2$ described previously.[10]

In experiments with **3**, the ratio between the relative intensities of **12** and **2** was found to be dependent on the concentration of H_2O_2 used with the latter favoured by higher [H_2O_2], suggesting that **2** is formed by oxidation of **12**. Furthermore, in an experiment with increased hydrogen peroxide concentration (ratio of 1000 to 1 for H_2O_2 to **1**), the build-up of **12** after 5 min at 60 °C was clearly followed by that of **2** after 10–15 min. For the following 30 min the species **2** with *m*/*z* 486 was effectively the only species detected (Fig. 3b). After approximately 45 min, new peaks at *m*/*z* 170, 172, 188, associated with the ligand (*m*/*z* 172) and its decomposition products (*m*/*z* 170, 188) were detected (Fig. 3c; see also ref. 8). The proposed cleavage of the dinuclear complex into **12** and **2** is discussed later in the text.

b Reaction of other phenols. Using the substrates **4**–**9** we explored the possibility of forming Mn^{III} and Mn^{V} species, equivalent to **12** and **2**, with potential chelate ring-sizes of 5, 6 and 7. In addition, the substituents on the phenoxy ligands should provide information on the importance of electronic effects on the stabilisation and reactivity of any Mn^{V} species generated. Co-ligands which do not have two hydroxy groups will, of course, require oxidation and phenolic coupling to generate the appropriate chelating species. The standard conditions described above were used in comparative experiments to identify the species formed when the potential co-ligands were mixed with **1**, and to determine which co-ligands are able to stabilise O=Mn^{V} species after addition of H_2O_2. In general, as different conditions were explored, we noted that the formation of Mn^{V} over Mn^{III} (for those substrates that give both) was favoured at higher values of pH, temperature and H_2O_2 concentration. We also noted that only for the ligands **4** and **5**, was an induction period observed as described for **3** (above). Results are summarised in Table 1.

Table 1 Mn^{III} and $O{=}Mn^{V}$ species detected by ESI-MS during reaction of H_2O_2, **1**, and phenols **3**–**9**[a]

Substrate	Mn(III) species *cf.* **12**	*m/z* (+)ESI-MS	Mn(V) species *cf.* **2**	*m/z* (+)ESI-MS	Other species	*m/z* (−)ESI-MS
3	√	470	√	486	×	—
4	√	498	√	514	×	—
5	√	466	√	482	×	—
6	√	334	×	–	√	271
7	√	410	(√)	426	×	—
8	√	384	×	—	×	
9	√	470	√	486	×	—

[a] For conditions, see text.

Fig. 1 Species detected by (+) ESI-MS from **1** in aqueous solution (see text).

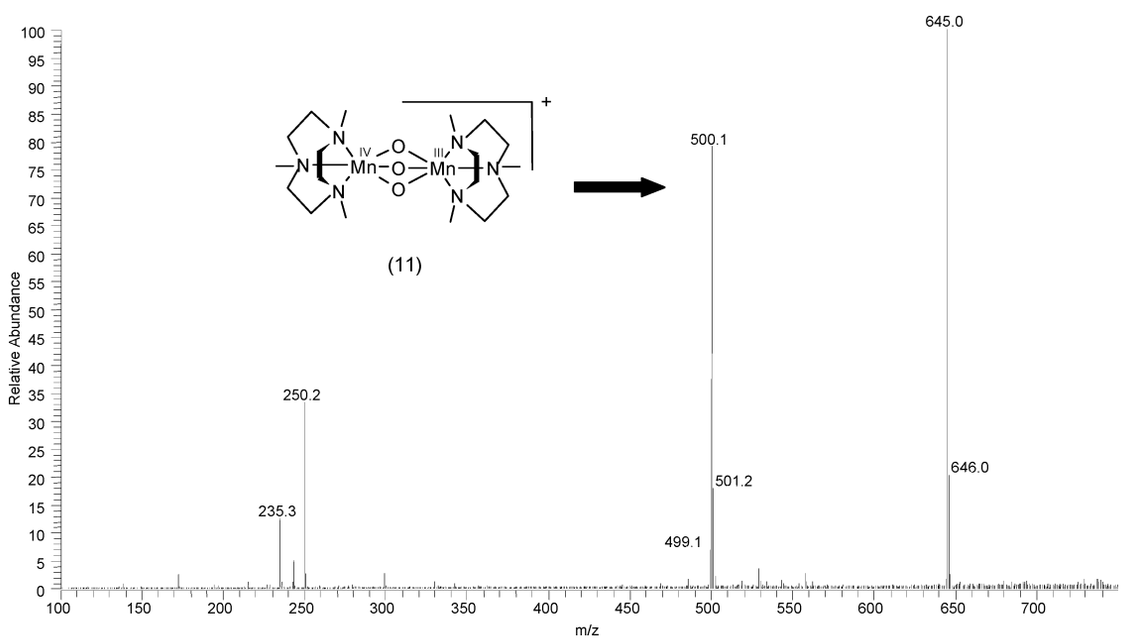


Fig. 2 Species detected by (+)ESI-MS after addition of 4-methoxyphenol to an aqueous solution of **1** (see text).

i 4-Ethoxyphenol, ***4****.* This behaved in a manner closely similar to **3**. With concentration ratio **1** : **4** : H_2O_2 of 1 : 10 : 1000, ESI-MS showed a peak at *m/z* 498 after 5 min, and then another at *m/z* 514 started to grow after *ca.* 10 min. These peaks are assigned to Mn^{III}(TMTACN)(**9**, R = Et) and $O{=}Mn^{V}$(TMTACN)(**9**, R = Et), equivalent to **12** and **2** respectively (see Table 1). The relative proportion of the $O{=}Mn^{V}$ and the Mn^{III} species and its variation with time was identical to that observed from **3**. In the absence of H_2O_2, ESI-MS showed immediate formation of **11** (*cf.* also similar behaviour of **5**).

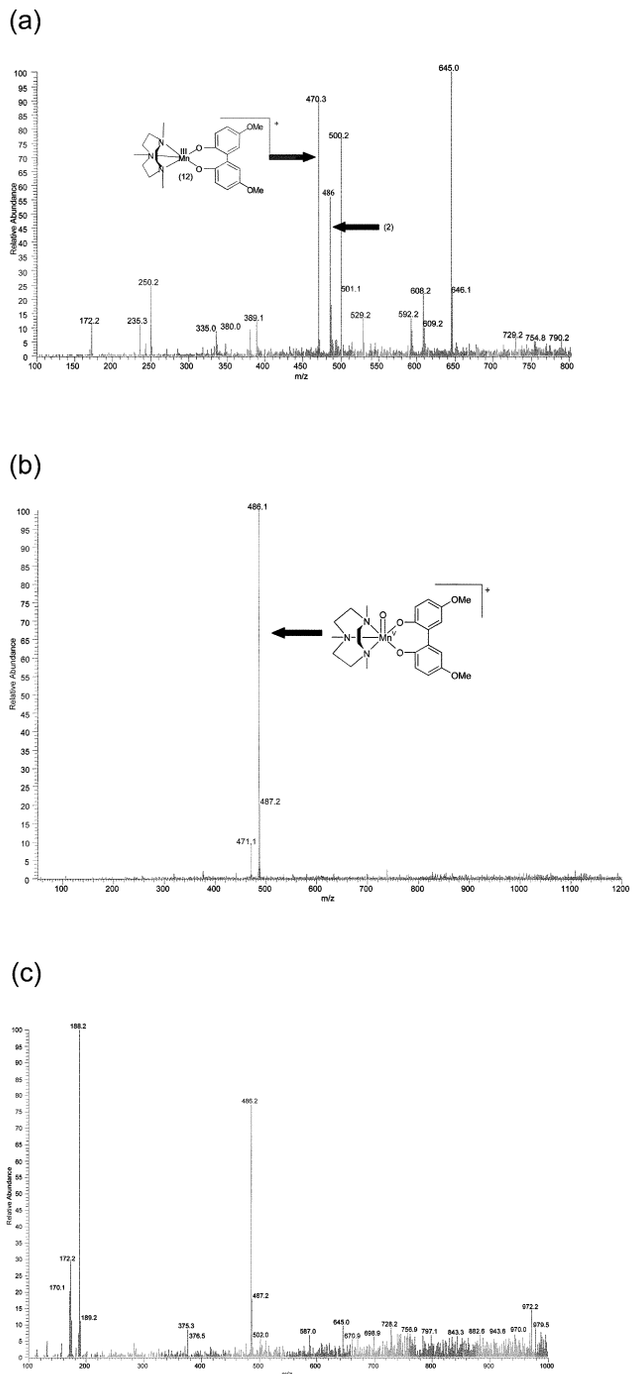


Fig. 3 **a** Species detected by (+)ESI-MS from an aqueous solution of **1**, 4-methoxyphenol and hydrogen peroxide (1 : 100 : 500) after 5 min at 60 °C **b** as Fig. 3a, after 15 minutes **c** as Fig. 3a, after 45 minutes.

*ii 2,4-Dimethylphenol, **5**.* As with **3** and **4** there was an induction period of *ca.* 5 minutes before the peak at *m*/*z* 466 [assigned to the manganese(III) complex of the appropriate dimer, Mn^{III}(TMTACN)(**13**)] was observed. In due course a peak at *m*/*z* 482 [assigned to O=Mn^{V} (TMTACN)(**13**)] was also observed, but its size was relatively small compared to the corresponding O=Mn^{V} species for **3** and **4**.

*iii Catechol, **6**.* The good binding and reducing properties of catechol for Mn are reflected in the immediate observation of **11** (*m*/*z* 500) and the rapid formation of a species with *m*/*z* 334, assigned to Mn^{III}(TMTACN)(**6**), and also a small proportion of $Mn^{III}(\mathbf{6})_2$ (*m*/*z* 271, negative ion ESI-MS), when **1** and catechol were mixed under the standard conditions but with no hydrogen peroxide. No oxidation by H_2O_2 of the Mn^{III}(TMTACN)(**6**) complex to the corresponding O=Mn^{V} species was observed. We believe that catechol is very easily oxidised and the complex formed with Mn^{III} is readily destroyed upon addition of oxidant.

*iv 2,2′-Biphenol, **7**.* A mixture of **7** and the complex **1** led to immediate detection of **11** (*m*/*z* 500) and the complex Mn^{III}-(TMTACN)(**7**) (*m*/*z* 410). No induction period was observed under the standard conditions with hydrogen peroxide, the ESI-mass spectrum of the complex Mn^{III}(TMTACN)(**7**) also being detected. By using higher concentrations of H_2O_2 it was possible to detect a small peak from the appropriate O=Mn^{V} species (with *m*/*z* 426). The results suggest that, under standard conditions with H_2O_2, **7** is capable of stabilising the Mn^{III} but not the O=Mn^{V} species, and that electron-donating groups, as in **9**, are necessary to stabilise the higher oxidation state sufficiently for it to be readily detectable by ESI-MS.

*v 1,8-Dihydroxynaphthalene, **8**.* The formation of the species Mn^{III}(TMTACN)(**8**) (*m*/*z* 384) was observed immediately after mixing **8** with **1** in the absence of H_2O_2. However, after 2–3 min a brown solid (possibly MnO_2) precipitated out of solution; the substrate was also degraded more rapidly in the presence of H_2O_2.

*vi 5,5′-Dimethoxy-2,2′-biphenol, **9**, R = Me.* The reaction of **9**, R = Me with **1** and H_2O_2 was very similar to that of **3** with the exception that it showed no induction period, with immediate observation of ions with *m*/*z* 470 and 486, assigned to **12** and **2**. This suggests that the induction period observed with the phenolic substrates **3**–**5** is due to the necessity of prior formation of the appropriate biphenol, and that once this is formed, it reacts rapidly with **1** to form the complex Mn^{III}(TMTACN)(biphenol) **12**. In the absence of hydrogen peroxide, strong peaks from **11** and **12** were detected instantaneously.

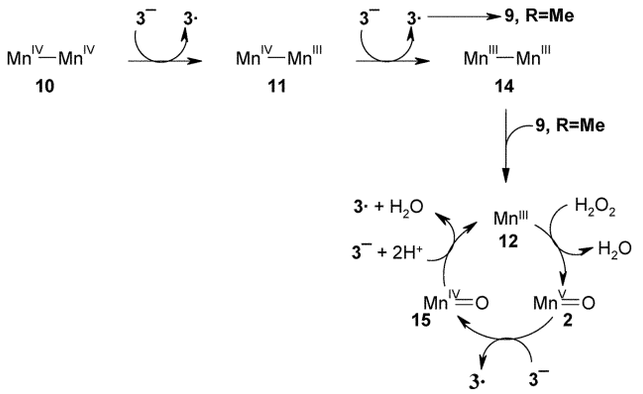
The trends in the results of these substrates can be broadly described as follows. First, we note the apparent strong ability for dihydroxy compounds to bind to manganese, and this increases in the cases where its binding leads to the formation of a ring size of 5 or 6. We suggest that, in the case of **6** and **8**, this makes the formation of a $Mn^{III}(\text{co-ligand})_2$ complex more favourable at the expense of the appropriate mixed Mn^{III}-(TMTACN)(co-ligand) complex, (and its O=Mn^{V} counterpart).

Secondly, the use of biphenols **6**–**9** removes the induction period, suggesting that the induction period for the formation of O=Mn^{V} species observed with monophenols may be due to the formation of sufficient biphenol to bind to manganese, rather than to the breaking up of **1**, which appears to be rapid once the biphenol is formed. The rapidity of initial electron transfer is also confirmed by the ESI-MS experiments with **6**–**9**.

Thirdly, there appears to be an influence of the electronic effect of substituents on the ligand on the stabilisation of the higher oxidation state of the manganese, in the order OMe ≈ OEt > Me > H). As would be anticipated, electron-donating groups stabilise the O=Mn^{V} complex.

2 Proposed catalytic cycle for the oxidation of phenols by $[Mn_2(\mu\text{-}O)_3(TMTACN)_2](PF_6)_2$

The outline mechanism in Scheme 2 is proposed to account both for the species observed by ESI-MS and for the catalytic oxidation of phenols, for which evidence has previously been obtained. This involves two initial one-electron oxidation steps in which, for example, the anion of **3** is oxidised to the appropriate phenoxyl radical and **1** is reduced to **11** (detected by ESR and ESI-MS) and **14**, respectively. It is known[19] that the Mn^{IV}–Mn^{IV} species **1** is capable of oxidising phenols, and pre-mixing **1** with **3** prior to the addition of H_2O_2 shortens the lag phase from *ca.* 2–3 min to around 30 s, indicating that the initial oxidation sequence is responsible for the lag phase. We suggest that $Mn_2^{III}(\mu\text{-}O)_3(TMTACN)_2$, **14**, is very unstable and splits into mononuclear species, which together with the biphenol form the monomeric complex **12** (detected by ESI-MS). It is proposed that the latter is then oxidised by hydrogen



Scheme 2

peroxide to the active oxidant, the O=Mn^{V} species, **2**, which is stabilised by the biphenol: this is then reduced by $\mathbf{3}^{-}$ *via* one-electron transfer to give an (undetected) species **15**. A further one-electron reduction gives **12** to close the catalytic cycle.

Experimental

Chemical reagents

Commercially available chemicals were purchased from Aldrich, Sigma, and Lancaster and were used without further purification. Deionised water was used in all experiments. All other solvents used were analytical grade. Hydrogen peroxide solution (31% by weight) was purchased from Fisons and the peroxide content was regularly checked during the course of this research. $[Mn_2(\mu\text{-}O)_3(TMTACN)_2](PF_6)_2$ was provided by Unilever. 1,8-Naphthalenediol (**8**) was provided by Dr. J. Ragot. Compound **9** was synthesised by the procedure in ref. 20.

Electrospray mass spectrometry

Electrospray mass spectra were recorded on a Finnigan LCQ MAT Standard Edition Spectrometer. The intermediates were detected using the settings obtained after optimisation of the system for the detection of species **2** (*m*/*z* 486). The following settings were employed: sheath gas flow rate (arb) = 40, octapole 1 offset = −2.25 V, auxiliary gas flow rate (arb) = 0, lens voltage = −30 V, spray voltage = 4.2 kV, octapole 2 offset = −5 V, capillary temp = 250 °C, octapole RF amplitude = 400 V p-p, capillary voltage =15 V, flow rate = 5–50 μl min^{-1}, tube lens offset = 0 V.

The sample injection was carried out over a period of 45 min, and the build up and decay of the intermediates was followed with time. Positive ESI-MS allowed the detection of the intermediates in the catalytic cycle, whereas negative ESI-MS allowed the detection of the phenolic ligands and their oxidation products.

Acknowledgements

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