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SYNTHESIS AND CATALASE ACTIVITY OF MANGANESE(II) COMPLEXES OF *CIS*-5-NORBORNENE-*ENDO*-2,3-DICARBOXYLIC ACID ($ndaH_2$): X-RAY CRYSTAL STRUCTURE OF $[Mn(\eta^1\eta^1\text{-nda})(phen)_2]\cdot EtOH\cdot H_2O$ (phen = 1,10-PHENANTHROLINE)

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Abstract—Manganese(II) chloride reacts with the sodium salt of *cis*-5-norbornene-*endo*-2,3-dicarboxylic acid ($ndaH_2$) in aqueous media to give the manganese(II) complex $[Mn(nda)H_2O]$ (**1**). Complex **1** reacts with 1,10-phenanthroline (phen) to give the mononuclear manganese(II) adduct $[Mn(\eta^1\eta^1\text{-nda})(phen)_2]\cdot EtOH\cdot H_2O$ (**2**). The X-ray crystal structure of **2** shows the manganese atom at the centre of a distorted N_4O_2 octahedron comprising four nitrogen atoms from two chelating phen ligands, and two oxygen atoms, one from each of the two carboxylate functions of the nda^{2-} ligand. Spectroscopic and magnetic data for **1** and **2** are reported, together with their catalytic activity towards the disproportionation of H_2O_2.

A number of manganese-containing non-haem catalases have recently been isolated and characterized.[1–3] These manganoenzymes are responsible for the catalytic disproportionation of hydrogen peroxide, which is important for cell detoxification.

$$2H_2O_2 \rightarrow 2H_2O+O_2$$

It is thought that these enzymes contain a binuclear $Mn^{III}(\mu^2\text{-}O^{2-})Mn^{III}$ core in which the metal centres are also ligated by O- and N-donor atoms from protein ligands. Evidence has accumulated that the manganese site of the pseudo-catalase from *Lactobacillus planatrum* comprises two manganese ions per protein subunit.[3] Currently there is a lot of interest in the preparation and characterization of multinuclear manganese complexes as models for the structural, spectral and functional properties of the biological enzymes.[4–11]

As part of our ongoing studies into the coordination chemistry of dicarboxylic acids[12–14] we

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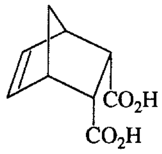
have been examining the reaction of *cis*-5-norbornene-*endo*-2,3-dicarboxylic acid ($ndaH_2$) with manganese(II) salts. The X-ray crystal structure of

$ndaH_2$



the free $ndaH_2$ molecule[15] shows it to have a rigidly defined geometry, with the orientation of the two *cisoid* carboxylate functions suitably orientated for metal coordination. In 1981, Delepierre *et al.*[16] studied the effects on the NMR spectrum of $ndaH_2$ as a consequence of binding it to a range of lanthanide metal ions in aqueous solution. Although the NMR spectra of the *in situ* generated complexes were discussed in detail the authors did not propose any structural formulae for them. Later, Geraldes *et al.*[17] investigated the use of $ndaH_2$ as a ligand for lanthanide paramagnetic shift and relaxation probes for NMR spectroscopy, but again no structural details were forthcoming. Midyanko *et al.* reported the synthesis of coordination compounds of 3*d* metals with the bis(hydroxylammonium) salt of $ndaH_2$[18] and the potassium salt of *cis*-5-norbornene-*endo*-2-oyl-hydroxylamine-3-carboxylate.[19] Mononuclear structures for these complexes were assigned on the basis of their physico-chemical properties but none of the samples were characterized using X-ray crystallography. More recently, Hartung and coworkers[20] have reacted *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride in aqueous media at 60°C with a number of transition metal nitrate salts in the presence of sodium hydroxide and an N,N-donor ligand {2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen)} to give mononuclear complexes with the general formula $[M(nda)(N,N\text{-donor})(H_2O)_3]\cdot 2.5H_2O$ $\{M = Mn^{(II)}, Co^{(II)}, Ni^{(II)}\}$. The manganese and cobalt bipy complexes $[M(\eta^1\text{-nda})(bipy)(H_2O)_3]\cdot 2.5H_2O$ were crystallographically characterized and found to be isostructural. Each metal atom was located at the centre of an N_2O_6 octahedron comprising one chelating bipy ligand, three water molecules and one nda^{2-} ligand coordinated by a single carboxylate oxygen atom.

Herein we report the synthesis and physical properties of the manganese(II) complexes $[Mn(nda)H_2O]$ (**1**) and $[Mn(\eta^1\eta^1\text{-nda})(phen)_2]\cdot EtOH\cdot H_2O$ (**2**) (phen = 1,10-phenanthroline). The X-ray crystal structure of the mononuclear complex **2** is also presented. Furthermore, details of the catalase-type activity of **1** and **2** are discussed.

RESULTS AND DISCUSSION

Synthetic routes to the mangenese(II) nda^{2-} complexes are summarized in Scheme 1. Manganese(II) chloride tetrahydrate reacts at room temperature with $ndaH_2$ in the presence of aqueous sodium hydroxide (1:1:2 molar ratio) to give $[Mn(nda)H_2O]$ (**1**) in 75% yield. The IR spectrum of the free acid $ndaH_2$ contains a broad $\nu(C{=}O)$ band centred at 1650 cm^{-1}, and upon coordination this band disappears and bands attributable to ν_{asymm} (OCO) and ν_{sym} (OCO) stretching modes appear at 1550 and 1465 cm^{-1}, respectively [$\Delta(OCO) = 85\ cm^{-1}$]. The magnetic moment of **1** (5.82 BM) is in the range expected for normal manganese(II) species, i.e. those lacking any Mn—Mn interactions.[21] The insolubility of **1** in water and in common organic solvents suggests that it may be polymeric with the magnetically isolated manganese(II) centres bridged by nda^{2-} ligands.[22]

When an ethanolic suspension of **1** is reacted with an excess of 1,10-phenanthroline, a yellow solution forms, from which pale yellow crystals of the manganese(II) complex $[Mn(\eta^1\eta^1\text{-nda})(phen)_2]\cdot EtOH\cdot H_2O$ (**2**) are recovered in good yield. The X-ray crystal structure of **2** is shown in Figs 1 and 2, and selected bond distances and bond angles are listed in Table 1. The manganese atom is ligated by four nitrogen atoms (N1a, N2a, N1b and N2b) from two chelating phen molecules and two oxygen atoms (O1 and O3), one from each of the two carboxylate moieties of the nda^{2-} ligand (Fig. 1). Thus, the two carboxylate functions of the nda^{2-} dianionic ligand are essentially monodentate with the two remaining carboxyl oxygens (O2 and O4) uncoordinated. As a result of the bite of the phen ligands (72.40 and 73.96°) the geometry of the complex is best described as irregular six-coordinate rather than octahedral. There is significant intermolecular association between two molecules of the complex caused by the presence of two bridging water molecules (O1w and O1wa in Fig. 2). These water molecules are hydrogen bonded to the uncoordinated carboxyl oxygens (O2 and O2a in Fig. 2) of the two nda^{2-} ligands. Furthermore, a molecule of ethanol is also hydrogen bonded to each of the bridging water oxygens (O1w and O1wa). The bond

$$MnCl_2\cdot 4H_2O + ndaH_2 \xrightarrow[-2NaCl]{2NaOH}$$

$$[Mn(nda)H_2O]\ (\mathbf{1})$$

$$\Big\downarrow \text{excess phen}$$

$$[Mn(\eta^1\eta^1\text{-nda})(phen)_2]\cdot EtOH\cdot H_2O\ (\mathbf{2})$$

Scheme 1.

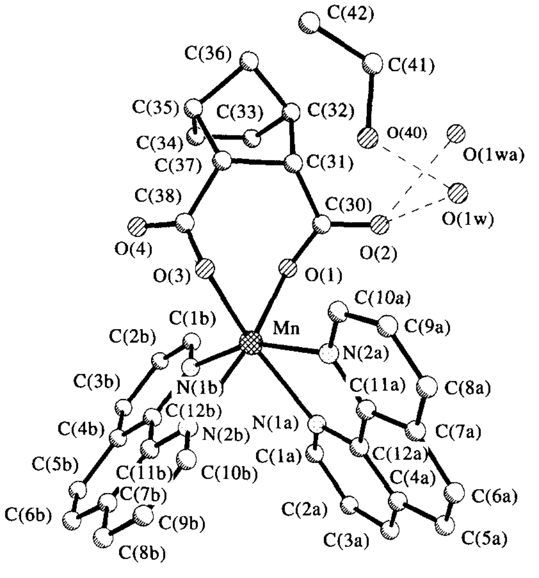


Fig. 1. X-Ray crystal structure of [Mn($\eta^1\eta^1$-nda)(phen)$_2$]·EtOH·H$_2$O (**2**).

angles and bond distances within the coordinated nda^{2-} ligand are essentially the same as those reported for the free acid ndaH$_2$.[15]

The structure of the N$_4$O$_2$ donor complex [Mn($\eta^1\eta^1$-nda)(phen)$_2$]·EtOH·H$_2$O, **2**, is significantly different to Hartung's manganese and cobalt N$_2$O$_4$ complexes [M(η^1-nda)(bipy)(H$_2$O)$_3$]·2.5H$_2$O.[20] In particular, the nda^{2-} ligand in the latter complexes is monodentate whilst in **2** it is bidentate. The two Mn—O(carboxylate) bonds in **2** (2.117 and 2.093 Å) are each slightly shorter than the single M—O(carboxylate) bond in Hartung's manganese complex (2.144 Å).

The IR spectrum of **2** shows bands attributable to $\nu_{\text{asymm.}}$ (OCO) and $\nu_{\text{symm.}}$ (OCO) stretching vibrations at 1545 and 1400 cm^{-1}, respectively. This Δ(OCO) value for **2** (145 cm^{-1}) is significantly different from that for **1** (85 cm^{-1}), suggesting that the coordination mode of the nda^{2-} ligand in the latter complex may be different from that in **2**. As with complex **1** the magnetic moment of **2** (5.71 BM) is within the range expected for normal mononuclear Mn$^{(II)}$ complexes.[21] Complexes **1** and **2** are air-stable in the solid state. Complex **2** dissolves readily in warm water and is a non-electrolyte in that solvent. Furthermore, **2** appears to be air-stable in aqueous media. The cyclic voltammogram of an ethanolic solution of **2** showed no redox behaviour between the switching potentials of −1.3 and +1.7 V (vs Ag/AgCl). It is thought that this apparent resistance of the complex towards oxidation may, at least to some extent, be a consequence of its irregular six-coordinate geometry.

We have recently described the synthesis and structure of the manganese(II) complex double salt [Mn$_2$($\eta^1\eta^1\mu$2-oda)(phen)$_4$H$_2$O)$_2$][Mn$_2$($\eta^1\eta^1\mu$2-oda)(phen)$_4$(η^1-oda)$_2$]·4H$_2$O (odaH$_2$ = octanedioc acid), and demonstrated the ability of the complex to catalyse the disproportionation of H$_2$O$_2$.[12] Furthermore, we have prepared and structurally characterized the dimeric and polymeric manganese(II) salicylate complexes [Mn$_2$(salH)$_4$(H$_2$O)$_4$] and {Mn$_2$(sal)$_2$(salH)(H$_2$O)(H$_3$O)(py)$_4$·2py}$_n$ (salH$_2$ = salicylic acid; py = pyridine), respectively, and investigated their reactivity towards H$_2$O$_2$.[23] Whereas [Mn$_2$(salH)$_4$(H$_2$O)$_4$] alone did not decompose H$_2$O$_2$ it was found that in the presence of added pyridine it vigorously disproportionated the

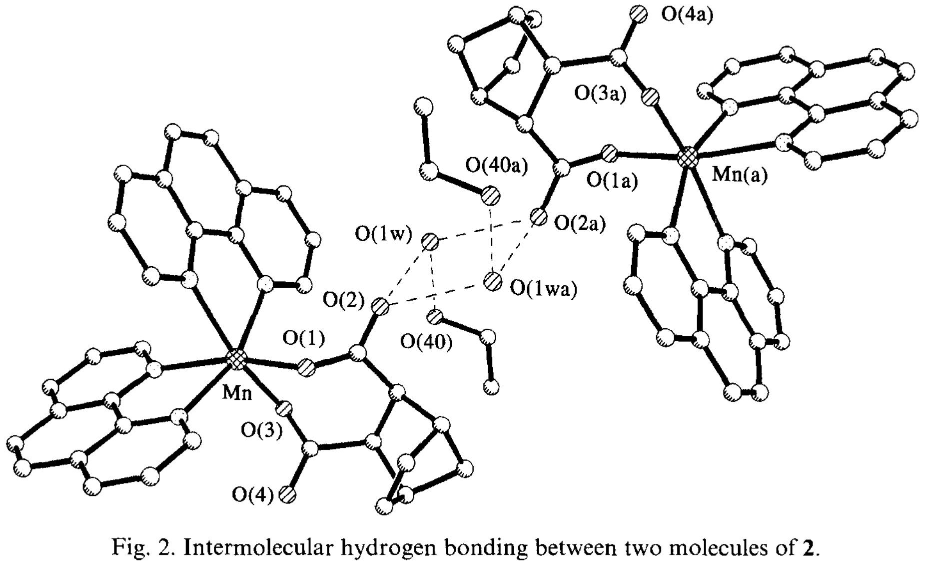


Fig. 2. Intermolecular hydrogen bonding between two molecules of **2**.

Table 1. Selected bond lengths (Å) and bond angles (°) for **2**

Mn—O(1)	2.117(3)	Mn—O(3)	2.093(3)
Mn—N(1a)	2.331(4)	Mn—N(2a)	2.261(3)
Mn—N(1b)	2.241(3)	Mn—N(2b)	2.285(3)
O(2)—O(1w)	2.797(4)	O(2)—O(1wa)[a]	2.821(4)
O(1)—Mn—O(3)	85.92(10)		
O(1)—Mn—N(1a)	100.33(11)		
O(1)—Mn—N(2a)	101.00(12)		
O(1)—Mn—N(1b)	90.28(11)		
O(1)—Mn—N(2b)	163.91(11)		
O(3)—Mn—N(1a)	161.85(85)		
O(3)—Mn—N(2a)	89.74(11)		
O(3)—Mn—N(1b)	108.32(11)		
O(3)—Mn—N(2b)	95.81(11)		
N(1a)—Mn—N(2a)	72.40(12)		
N(1b)—Mn—N(2b)	73.96(12)		
N(1a)—Mn—N(1b)	88.81(12)		
N(1a)—Mn—N(2b)	82.92(12)		
N(2a)—Mn—N(1b)	159.45(13)		
N(2a)—Mn—N(2b)	95.01(12)		
O(1)—C(30)—O(2)	123.1(4)		
O(3)—C(38)—O(4)	124.7(4)		

[a] O(1wa) = O(1w) under symmetry transformation $-x, 1-y, z$.

peroxide. Similarly, the somewhat sluggish reaction of $\{Mn_2(sal)_2(salH)(H_2O)(H_3O)(py)_4 \cdot 2py\}_n$ with H_2O_2 was greatly accelerated upon the addition of pyridine. The reactivity of the present complexes $[Mn(nda)H_2O]$ (**1**) and $[Mn(\eta^1\eta^1\text{-nda})(phen)_2] \cdot EtOH \cdot H_2O$(**2**) as catalysts for the disproportionation of H_2O_2 was investigated both in the absence and in the presence of imidazole. The results of these reactions are summarized in Fig. 3.

Complex **1** by itself did not react with H_2O_2. However, the inclusion of imidazole in the reaction mixture caused a copious evolution of O_2 (Fig. 3a), and during the first minute of the reaction each molecule of **1** disproportionated 1077 molecules of H_2O_2. In the absence of imidazole each molecule of complex **2** decomposed 861 molecules of H_2O_2 during the first minute of the reaction [Fig. 3b (i)]. Furthermore, in the presence of added imidazole a three-fold increase in O_2 evolution was observed during this first minute [Fig. 3b (ii)]. As expected, the base imidazole by itself (no added manganese complex) disproportionates H_2O_2 (Fig. 3c), but this reaction is much slower than the imidazole-containing manganese systems. Although the effects of added imidazole on the rate of H_2O_2 disproportionation in the manganese-containing systems are indeed quite marked the exact role of the heterocyclic base in these catalysis reactions is unclear.[8,24] Bruice and his coworkers[24] have suggested that the function of added imidazole in H_2O_2–Mn porphyrin systems was to accelerate the peroxide O—O bond homolysis and also to stabilize a $[Mn^{(IV)}{=}O]$ intermediate complex. These workers also concluded that in their reactions the imidazole did not act as a general-base catalyst.

EXPERIMENTAL

Cis-5-norbornene-*endo*-2,3-dicarboxylic acid and 1,10-phenanthroline were purchased from commercial sources and used without further purification. IR spectra (KBr discs) were recorded in the region of 4000–200 cm^{-1} on a Perkin–Elmer 783 grating spectrometer. Solid-state, room-temperature magnetic susceptibility measurements were made on a Johnson Matthey Magnetic Susceptibility Balance and conductivity measurements (26°C and 1.0 mM concentration) were obtained using an AGB model 10 conductivity meter. The cyclic voltammogram of a 4×10^{-3} mol dm^3 solution of **2** was recorded (*ca* 20°C and under N_2) using an EG&G Model 264A polarographic analyser, and the data was analysed using the EG&G Condecon software package. A glassy carbon disc and a platinum wire were used as the working and counter electrodes, respectively. Potentials were recorded

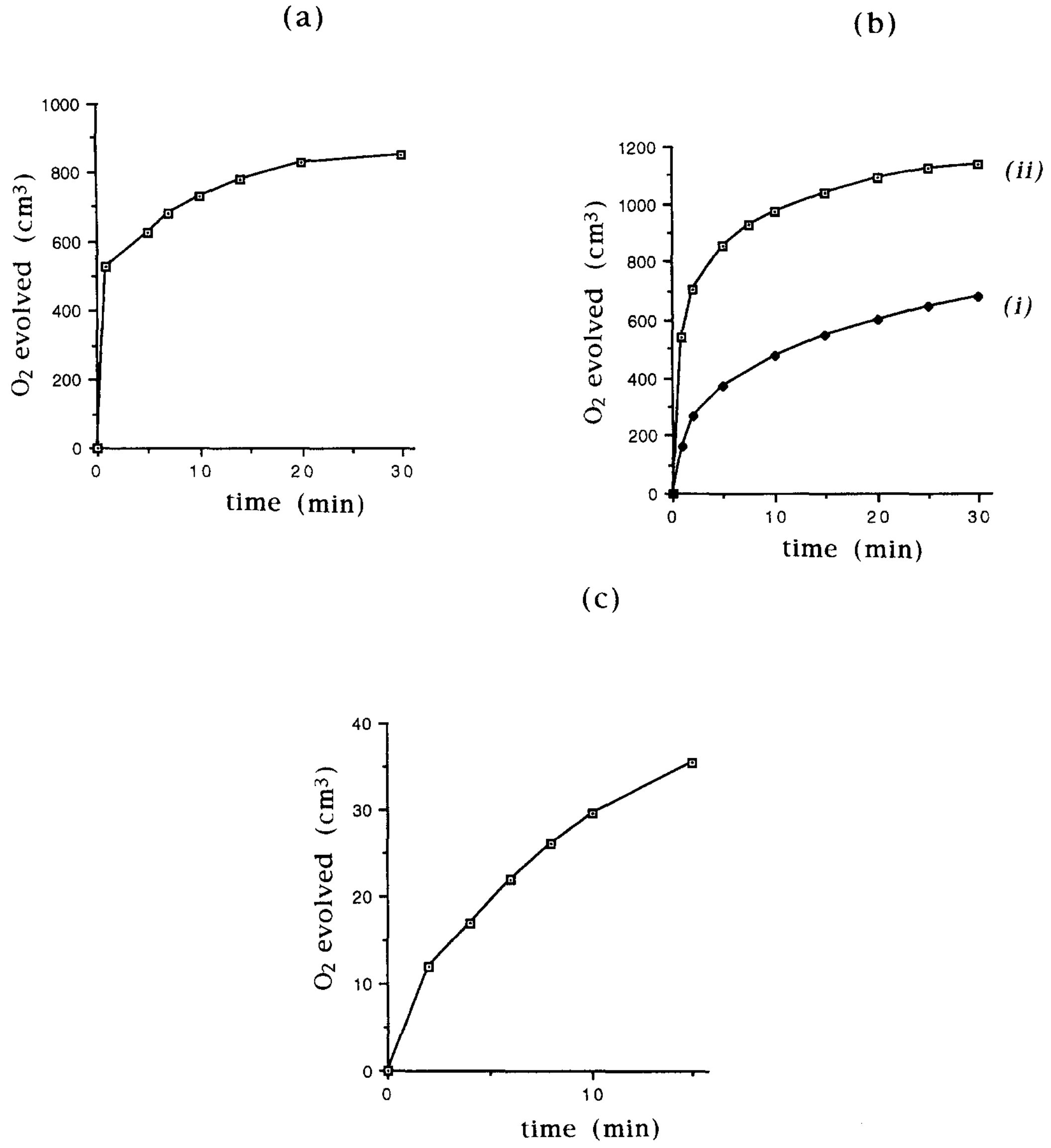


Fig. 3. Time course of O_2 evolution in H_2O_2 disproportionation by nda complexes. Conditions: H_2O_2 (35% w/w, 10 cm^3, 114 mmol), temperature = 25°C: (a) **1** (10.2 mg, 4.02×10^{-5} mol), with added imidazole (50 mg); (b) (*i*) **2** (10.1 mg, 1.53×10^{-5} mol), no imidazole present; (b) (*ii*) **2** (11.2 mg, 1.69×10^{-5} mol), with added imidazole (50 mg); (c) imidazole only (50 mg).

with respect to a silver–silver chloride reference electrode (3.5 M aqueous KCl), against which the ferrocene/ferrocenium(1+) couple had $E_{1/2} = +0.6$ V. Tetrabutylammonium perchlorate (0.1 M) dissolved in ethanol was used as the supporting-electrolyte/solvent system, and the scan rate was 10 mV s^{-1}. Elemental analyses were carried out by the Microanalytical Laboratory, University College Cork, Ireland.

Crystallography

Crystal data for **2**. $C_{35}H_{32}MnN_4O_6$, $M = 659.58$, yellow prism, $0.57 \times 0.35 \times 0.25$ mm, monoclinic, $a = 15.898(5)$, $b = 11.667(3)$, $c = 16.144(4)$ Å, $\beta = 94.88(1)^{\circ}$, $U = 2984(1)$ Å^3, $\mu = 0.498$ mm^{-1}, space group $P2_1/c$, $Z = 4$, $F(000) = 1372$.

Data collection and processing. Data were collected at 133 K on a Siemens P4 four-circle diffractometer using graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Unit cell parameters were determined by non-linear least-squares refinement of 32 accurately-centred reflections ($10 < 2\theta < 20^{\circ}$). Using the 1.8° ω-scans at 4° min^{-1}, 4060 reflections were collected in the range $4 < 2\theta < 45^{\circ}$; 3894 independent reflections ($R_{int} = 0.0269$) were used in the refinement. Crystal stability was monitored by recording three check reflections every 97 reflections and no significant variation was observed. The data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied based on ϕ-scan data ($T_{max} = 0.772$, $T_{min} = 0.696$).

Structure solution and refinement. The structure was solved by Patterson techniques,[25] which revealed the positions of the manganese atom and its coordination sphere. The remaining atoms were located from difference Fourier maps. All the non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Hydrogen atoms were inserted at calculated positions except for those involved in hydrogen bonding, these were located from difference maps. All the data were used for refinement on F^2 which converged with $wR2 = 0.1195$, GOOF = 1.105 for all data and the conventional $R1 = 0.0465$ ($I > 2\sigma(I)$) for 415 parameters. The final difference map showed no residual electron density above ± 0.29 e Å^{-3}. All programs used in the structure refinement are contained in the SHELXL-93 package.[26]

[Mn(nda)H_2O] (**1**)

To a solution of ndaH_2 (1.0 g, 5.49 mmol) and NaOH (0.48 g, 12.0 mmol) in distilled water (100 cm^3) was added $MnCl_2 \cdot 4H_2O$ (0.98 g, 4.96 mmol). The resulting colourless solution was stirred at room temperature for 3 h, and then concentrated by slow evaporation to yield light pink microcrystals of the product. The solid was filtered off, washed with a small volume of cold water and then air-dried at *ca* 25°C. Yield 0.94 g (75%). Found :C, 42.5; H, 3.9%. Calc.: C, 42.7; H, 4.0%; $\mu = 5.82$ BM; IR: 3410, 3000, 1650, 1550, 1480, 1430, 1350, 1315, 1250, 900, 655 cm^{-1}.

[Mn($\eta^1\eta^1$-nda)(phen)$_2$] · EtOH · H_2O (**2**)

To a suspension of **1** (0.37 g, 1.46 mmol) in an ethanol : water (4 : 1) mixture (100 cm^3) was added 1,10-phenanthroline (1.5 g, 8.32 mmol). The resulting mixture was refluxed for 0.75 h to give a pale yellow solution. Upon standing for several days yellow crystals of the product were deposited. The solid was filtered off, washed with a small portion of ice-cold ethanol and then air-dried at *ca* 25°C. Yield 0.25 g (65%). Found: C, 64.6; H, 4.7; N, 8.4%. Calc.: C, 63.7; H, 4.9; N, 8.5%; $\mu = 5.71$ BM; IR: 3800, 3000, 1610, 1590, 1545, 1520, 1430, 1400, 1375, 1350, 1305, 1290, 1100, 860, 750, 735, 640 cm^{-1}.

Hydrogen peroxide disproportionation studies

To a solid sample (*ca* 10 mg) of the manganese(II) complex was added aqueous H_2O_2 (35% w/w, 10 cm^3, 114 mmol). The mixture was stirred and thermostated at 25°C, and the evolved O_2 was measured volumetrically. In cases where imidazole (50 mg) was added this was introduced into the reaction vessel before the addition of H_2O_2.

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