SYNTHESIS AND CATALASE ACTIVITY OF MANGANESE(II) COMPLEXES OF CIS-5-NORBORNENE-ENDO-2,3-DICARBOXYLIC ACID (ndaH2): X-RAY CRYSTAL STRUCTURE OF [Mn(η⁴-nda)(phen)2] • EtOH • H2O (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 (ndaH2) in aqueous media to give the manganese(II) complex [Mn(nda)H2O] (1). Complex 1 reacts with 1,10-phenanthroline (phen) to give the mononuclear manganese(II) adduct [Mn(~/lql-nda)(phen)2] • EtOH • H2O (2). The X-ray crystal structure of 2 shows the manganese atom at the centre of a distorted N4O2 octahedron comprising four nitrogen atoms from two chelating phen ligands, and two oxygen atoms, one from each of the two carboxylate functions of the nda²⁻ ligand. Spectroscopic and magnetic data for 1 and 2 are reported, together with their catalytic activity towards the disproportionation of H2O2.

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.

2H2O2 → 2H2O + O2

It is thought that these enzymes contain a binuclear Mn(II)(μ²-O2²⁻)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 plantarum 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 acids12-14 we
have been examining the reaction of cis-5-norbornene-endo-2,3-dicarboxylic acid (ndaH₂) with manganese(II) salts. The X-ray crystal structure of the free ndaH₂ molecule 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. studied the effects on the NMR spectrum of ndaH₂ 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. investigated the use of ndaH₂ 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 3d metals with the bis(hydroxylammonium) salt of ndaH₂ and the potassium salt of cis-5-norbornene-endo-2-oxyl-hydroxylamine-3-carboxylate. 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 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 \[ [Mn(nda)(N,N-donor)\cdot EtOH\cdot H₂O] \]. 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. The manganese and cobalt bipy complexes [Mn(η⁶-nda)(bipy)(H₂O)₂]·2.5H₂O were crystallographically characterized and found to be isostructural. Each metal atom was located at the centre of an N₂O₆ octahedron comprising one chelating bipy ligand, three water molecules and one nda⁻² ligand coordinated by a single carboxylate oxygen atom.

RESULTS AND DISCUSSION

Synthetic routes to the manganese(II) nda⁻² complexes are summarized in Scheme 1. The reaction of manganese(II) chloride tetrahydrate with ndaH₂ in the presence of aqueous sodium hydroxide (1:1:2 molar ratio) to give \([Mn(nda)H₂O]\) in 75% yield. The IR spectrum of the free acid ndaH₂ contains a broad ν(C=O) band centred at 1650 cm⁻¹, and upon coordination this band disappears and bands attributable to νₚₛₚₚ (OCO) and νₚₚ (OCO) stretching modes appear at 1550 and 1465 cm⁻¹, respectively. The magnetic moment of Mn is in the range expected for normal manganese(II) species, i.e. those lacking any Mn—Mn interactions. 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. 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 \([Mn(η⁶-nda)(phen)\cdot EtOH\cdot H₂O] (2)\) 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. 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 intramolecular 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

\[
\text{MnCl}_2 \cdot 4\text{H}_2\text{O} + \text{ndaH}_2 \overset{2\text{NaOH}}{\rightarrow} \text{ndaH}_2\cdot 2\text{NaCl} + \text{Mn(nda)H}_2\text{O} \]

Scheme 1.
angles and bond distances within the coordinated nda$^{2-}$ ligand are essentially the same as those reported for the free acid nda$^{2-}$.\textsuperscript{15}

The structure of the N$_{2}$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(nda)$_2$(bipy)$_2$(H$_2$O)$_2$] · 2H$_2$O.\textsuperscript{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 $\nu_{\text{asym}}$ (OCO) and $\nu_{\text{symm}}$ (OCO) stretching vibrations at 1545 and 1400 cm$^{-1}$, respectively. This $\Delta$(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.\textsuperscript{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$_2$(nda)$_2$(phen)$_2$](H$_2$O)$_2$ · [Mn$_2$(nda)$_2$(phen)$_2$](nda)$_2$ · 4H$_2$O (ndaH$_2$ = octanedioc acid), and demonstrated the ability of the complex to catalyse the disproportionation of H$_2$O$_2$.\textsuperscript{12} Furthermore, we have prepared and structurally characterized the dimeric and polymeric manganese(II) salicylate complexes [Mn$_2$(sal)$_4$(H$_2$O)$_4$] and {Mn$_2$(sal)$_2$(sal)$_2$(H$_2$O)$_2$(H$_2$O)(py)$_2$}$_n$ (salH$_2$ = salicylic acid; py = pyridine), respectively, and investigated their reactivity towards H$_2$O$_2$.\textsuperscript{23} Whereas [Mn$_2$(sal)$_4$(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. 1. X-Ray crystal structure of [Mn($\eta^1\eta^1$-nda)(phen)$_2$] · EtOH · H$_2$O (2).

Fig. 2. Intermolecular hydrogen bonding between two molecules of 2.
peroxide. Similarly, the somewhat sluggish reaction of \(\{\text{Mn}_2(\text{sal})_2(\text{salH})(\text{H}_2\text{O})(\text{py})_4\text{H}_2\text{O}\}\text{py})_4\) with \(\text{H}_2\text{O}_2\) was greatly accelerated upon the addition of pyridine. The reactivity of the present complexes \([\text{Mn}(\text{nda})\text{H}_2\text{O}]\) (1) and \([\text{Mn}(\eta^1\eta^1\text{nda})(\text{phen})_2] \cdot \text{EtOH} \cdot \text{H}_2\text{O}(2)\) as catalysts for the disproportionation of \(\text{H}_2\text{O}_2\) 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 \(\text{H}_2\text{O}_2\). However, the inclusion of imidazole in the reaction each molecule of 1 disproportionated 1077 molecules of \(\text{H}_2\text{O}_2\). In the absence of imidazole each molecule of complex 2 decomposed 861 molecules of \(\text{H}_2\text{O}_2\) during the first minute of the reaction [Fig. 3b (ii)]. Furthermore, in the presence of added imidazole a three-fold increase in \(\text{O}_2\) evolution was observed during this first minute [Fig. 3b (ii)]. As expected, the base imidazole by itself (no added manganese complex) disproportionates \(\text{H}_2\text{O}_2\) (Fig. 3c), but this reaction is much slower than the imidazole-containing manganese systems. Although the effects of added imidazole on the rate of \(\text{H}_2\text{O}_2\) 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 \(\text{H}_2\text{O}_2\)-Mn porphyrin systems was to accelerate the peroxide \(\text{O}--\text{O}\) bond homolysis and also to stabilize a \([\text{Mn}^{IV}=\text{O}]\) 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 \(\times 10^{-3}\) 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

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

<table>
<thead>
<tr>
<th>Bond Length/Angle</th>
<th>Value 1</th>
<th>Error 1</th>
<th>Value 2</th>
<th>Error 2</th>
</tr>
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<tr>
<td>Mn—O(1)</td>
<td>2.117(3)</td>
<td></td>
<td>Mn—O(3)</td>
<td>2.093(3)</td>
</tr>
<tr>
<td>Mn—N(1a)</td>
<td>2.331(4)</td>
<td></td>
<td>Mn—N(2a)</td>
<td>2.261(3)</td>
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<tr>
<td>Mn—N(1b)</td>
<td>2.241(3)</td>
<td></td>
<td>Mn—N(2b)</td>
<td>2.285(3)</td>
</tr>
<tr>
<td>O(2)—O(1w)</td>
<td>2.797(4)</td>
<td></td>
<td>O(2)—O(1wa)</td>
<td>2.821(4)</td>
</tr>
</tbody>
</table>

*O(1wa) = O(1w) under symmetry transformation — x, 1 — y, z.*
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$_4$O$_6$, M = 659.58, yellow prism, 0.57 x 0.35 x 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-$K\alpha$ 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$^\circ$ o-scans at 4$^\circ$ 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 ($T_{\text{max}} = 0.772$, $T_{\text{min}} = 0.696$).

**Structure solution and refinement.** The structure was solved by Patterson techniques, 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 programs used in the structure refinement are contained in the SHELXL-93 package.

$[\text{Mn(nda)}\text{H}_2\text{O}] \cdot \text{EtOH} \cdot \text{H}_2\text{O}$ (2)

To a suspension of 1 (0.37 g, 1.46 mmol) in an ethanol: water (4:1) mixture (100 cm$^3$) was added a solution of 50 mg 50% ethanol (0.14 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, 8.5%; μ = 5.82 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$_2$O$_2$ (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$_2$O$_2$.

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**REFERENCES**


22. Recently we have synthesized and structurally characterized the copper(II) species \([\text{Cu(oda)(py)}_2(H_2O)]_2\) (odaH$_2$ = octanedioic acid) in which the copper centres are bridged by oda$^{2-}$ ligands to give a polymeric complex. This result is as yet unpublished.


