

Structural studies on manganese(III) and manganese(IV) complexes of tetrachlorocatechol and the catalytic reduction of dioxygen to hydrogen peroxide

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Abstract

The mononuclear complexes $(\text{Bu}_4\text{N})[\text{Mn}(\text{Cl}_4\text{Cat})_2(\text{H}_2\text{O})(\text{EtOH})]$ and $(\text{Bu}_4\text{N})_2[\text{Mn}(\text{Cl}_4\text{Cat})_3]$ ($\text{H}_2\text{Cat} = 1,2\text{-dihydroxybenzene}$) have been synthesised and characterised by X-ray diffraction. This work provides a direct, independent, synthesis of these complexes and an interesting example of how solvent effects can promote the formation of either a manganese(III) or manganese(IV) complex of the same ligand. The characterisation of $(\text{Bu}_4\text{N})[\text{Mn}(\text{Cl}_4\text{Cat})_2(\text{H}_2\text{O})(\text{EtOH})]$ supports previous work that manganese(III) is extremely reluctant to form tris (catecholato) complexes due to the short ‘bite distance’ of catecholate oxygen atoms (2.79 Å) which are unable to span the elongated coordination axes of the Jahn-Teller distorted Mn(III) ion and explains the 2:1 and 3:1 tetrachlorocatechol:manganese ratios in the Mn(III) and Mn(IV) complexes, respectively. Hydrogen peroxide production using dioxygen and hydroxylamine as substrates in acetonitrile/water mixtures, under ambient conditions, can be demonstrated with both complexes, suggesting that neither labile coordination sites nor the oxidation state of the manganese are important to the catalytic system. Turn over frequencies (TOF, moles of H_2O_2 per moles of manganese per hour) of $\sim 10\,000\text{ h}^{-1}$ are obtained and this compares very favourably with the commercial production of hydrogen peroxide by the autoxidation of 2-ethylanthrahydroquinone (AO process). © 2003 Elsevier B.V. All rights reserved.

Keywords: Manganese; Tetrachlorocatechol; Catecholate complexes; Hydrogen peroxide; Hydroxylamine; Dioxygen activation catalyst

1. Introduction

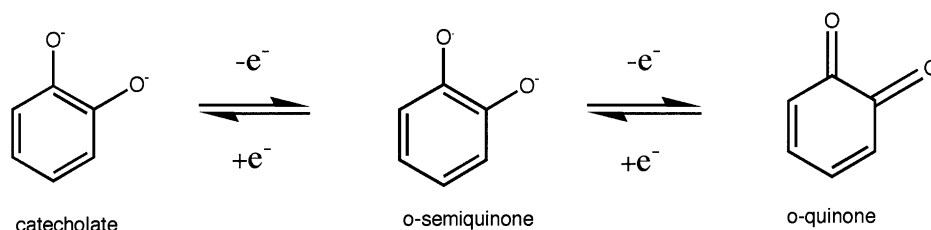
Transition metal complexes containing catechol and semiquinone ligands show a unique facility for electron transfer between the metal and chelated ligand [1] and these redox characteristics have been recognised as being important in reactions catalysed by certain enzymes that include galactose oxidase [2–4], ribonucleotide reductase [5] and PSII [6]. The non-innocent, redox-active, nature of catecholate complexes, in which catechols can be oxidised to the semiquinone and *o*-quinone forms, pro-

vide an interesting challenge for both synthetic and theoretical chemists [7] (Scheme 1).

Thus, in the case of manganese, valence tautomerism has been observed between Mn^{IV} -catecholate and Mn^{II} -semiquinone forms and the interconversion of these forms can occur with small changes of temperature [8]. Current interest in manganese catecholate chemistry has also been stimulated by their involvement in catechol oxidation and dioxygen activity [1,7]. The interaction of manganese complexes with dioxygen can either be in a reversible manner forming complexes of the type $\text{M}-\text{O}_2$ (in which the ‘ O_2 ’ moiety is preserved) [9,10] but whose identity is somewhat controversial [11,12] or through non-reversible reactions to produce manganese-*o*-semiquinone complexes [13,14], free benzoquinone [15,16],

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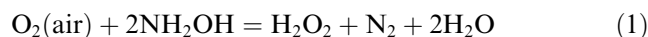


Scheme 1.

or even oxidative carbon-carbon bond cleavage products of catechol [14,17]. The discovery of manganese dioxygenase enzymes, a new class of extradiol dioxygenases with Mn(II) at the active site [18–21] and the ‘catalase-like’ properties [22] of manganese-based systems has added to the biological significance of higher-valent manganese chemistry and show that these systems are implicated in both the oxidative and reductive cycles of oxygen in natural systems. There is also an interest in the use of these systems as synthetic magnets [23,24].

Most work in this field has involved the preparation of model manganese complexes of 3,5-di-*tert*-butylcatechol (*dtbCatH*₂) [25], with little work in the area of the activation of dioxygen by manganese complexes of other catechols.

We have, for a number of years, been interested in manganese-catecholate systems that can efficiently reduce dioxygen to hydrogen peroxide. Aqueous, oxygenated, mixtures of manganese(II) chloride and Tiron (1,2-dihydroxybenzene-3,5-disulfonate, disodium salt monohydrate) efficiently catalyse the reduction of dioxygen to hydrogen peroxide with hydroxylamine at pH 8.0 and ambient temperatures (Eq. (1)) [26]:



This system has been described by the Institute of Applied Catalysis (iAc) as the ‘most successful’ method for the local and in situ generation of hydrogen peroxide by ‘enzyme-like’ processes [27].

A single crystal structural study has recently been completed on $[\text{Na}]_5[\text{Mn}(3,5\text{-(SO}_3)_2\text{Cat})_2] \cdot 10\text{H}_2\text{O}$, and this has been shown to be based on a bis-catecholate complex exhibiting the Jahn-Teller distortion to give a pseudo-octahedral complex with the oxygen atoms of sulfonate groups in neighbouring molecules occupying the axial positions [28].

Manganese(III), uniquely amongst other first row transition metals that forms trivalent ions – Ti, V, Cr and Fe, is extremely reluctant to form tris (catecholato) complexes which arise from the short bite distance of catechol which limits the ability of this ligand to span the elongated coordination axes of the Jahn-Teller distorted Mn(III) ion [29].

The potassium salt of the bis Mn (III) complex of tetrachlorocatechol (Cl_4CatH_2 , tccH_2) has been re-

ported by Pierpont et al. [25] who carried out a structural study on the complex $\text{K}[\text{Mn(III)}(\text{Cl}_4\text{Cat})_2(\text{OPPh}_3)] \cdot \text{H}_2\text{O} \cdot (\text{CH}_3)_2\text{CO}$ with tetrachlorocatechol being generated in situ from the reduction of tetrachlorobenzoquinone using triphenylphosphine. We describe herein the formation of a new tetrabutylammonium salt of the bis Mn(III) complex from the oxidation of mixtures of the $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{tccH}_2 \cdot \text{H}_2\text{O}$ and tetrabutylammonium hydroxide with air (dioxygen). By a judicious change of solvent, the tris Mn(IV) complex can be isolated and single crystal X-ray structural determinations of both are reported. Recently, Gatteschi and coworkers [30] have reported a structural study on the ditetraphenylphosphonium salt of Mn(IV)-tris-tcc from the oxidation of the potassium salt of Mn(III)-bis-tcc using tetraphenylphosphonium chloride as an alkali-metal chelator in acetonitrile. Gatteschi’s alternative synthetic method for Mn(IV)-tris-tcc was based on the reaction of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ with in situ generated tcc^{2-} (from the reaction of tetrachloro-1,2-benzoquinone and triphenylphosphine neutralised with a methanolic solution of $(\text{Bu})_4\text{N}^+\text{OH}^-$), initially under argon, with a rather long and complicated work up procedure. Indeed a similar procedure was first used by Pierpont [25] who obtained the potassium salt of Mn(III)-bis-tcc with the use of KOH instead of $(\text{Bu})_4\text{N}^+\text{OH}^-$. The direct synthetic method reported here using tetrachlorocatechol (rather than the quinone) is very quick and easier to carry out leading to the formation of both complexes independently.

2. Experimental

2.1. Preparation of complexes

These syntheses were performed in open reaction vessels without any special conditions.

2.1.1. $(\text{Bu}_4\text{N})[\text{Mn}(\text{Cl}_4\text{Cat})_2(\text{H}_2\text{O})(\text{EtOH})]$

$\text{Mn}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ (0.38 g, 1.1 mmol) was added to a solution of tetrachlorocatechol monohydrate (0.66 g, 2.5 mmol) in 20% aqueous EtOH (50 ml). $(\text{Bu})_4\text{N}^+\text{OH}^-$ (~40% aqueous, 1.0 ml, 1.5 mmol) was added and the solution darkened immediately. This dark green solution was refluxed for 1 h and then left to cool slowly to

room temperature. Long dark yellow–green needles were isolated. Yield: 0.38 g (40%).

2.1.2. $(\text{Bu}_4\text{N})_2[\text{Mn}(\text{Cl}_4\text{Cat})_3]$

$\text{Mn}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ (0.38 g, 1.1 mmol) was added to solution of tetrachlorocatechol monohydrate (0.88 g, 3.5 mmol) in acetone (50 ml). $(\text{Bu}_4\text{N})^+\text{OH}^-$ (~40% aqueous, 1.5 ml, 2.3 mmol) was added and the solution darkened immediately. This dark blue solution was refluxed for 1 h and then left for several days to concentrate where upon small dark green crystals were isolated. Yield: 0.67 g (48%).

2.2. Physical measurements

Infrared spectra were recorded on Perkin–Elmer Paragon FT-IR 1000 spectrophotometer as KBr discs. Magnetic measurements were carried out using a Sherwood Scientific magnetic susceptibility balance. A Philips PU 8720 spectrophotometer was used for UV–Vis spectra on aqueous solutions of the complex and for the determination of hydrogen peroxide colorimetrically. C, H, N and Cl analysis was carried out by MEDAC Ltd. (Brunel University) and manganese was determined

spectrophotometrically using a Perkin–Elmer Plasma 40 spectrophotometer. Hydrogen peroxide production runs were performed in a dreschel bottle immersed in a water-bath at 20 ± 1 °C. Dioxygen was provided from a cylinder via a sintered-glass inlet into a well-stirred solution. Plastic spatulae and de-ionised water were used to avoid contamination by metal ions that might decompose H_2O_2 and to avoid addition of adventitious sources of manganese(II).

2.3. Crystallographic data and refinement of structure

The crystal data of $(\text{Bu}_4\text{N})_2[\text{Mn}(\text{Cl}_4\text{Cat})_2(\text{H}_2\text{O})]$ (EtOH) and $(\text{Bu}_4\text{N})_2[\text{Mn}(\text{Cl}_4\text{Cat})_3]$ and the parameters of data collection are summarised in Table 1. Data were collected on a Bruker–Nonius KappaCCD situated at the window of an FR591 rotating anode generator [$\lambda(\text{Mo K}\alpha) = 0.71073$ Å]. The structures were solved by direct methods using the crystallographic package SHELXS97 [31] and refined using full-matrix least-squares [32] on F^2 . Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from the difference map and isotropically refined except for those attached to carbon, which were placed in calculated

Table 1

Crystal data and structure refinement for $(\text{Bu}_4\text{N})[\text{Mn}(\text{Cl}_4\text{Cat})_2(\text{H}_2\text{O})(\text{EtOH})]$ and $(\text{Bu}_4\text{N})_2[\text{Mn}(\text{Cl}_4\text{Cat})_3]$

Identification code	$(\text{Bu}_4\text{N})[\text{Mn}(\text{Cl}_4\text{Cat})_2(\text{H}_2\text{O})(\text{EtOH})]$	$(\text{Bu}_4\text{N})_2[\text{Mn}(\text{Cl}_4\text{Cat})_3]$
Empirical formula	$\text{C}_{30}\text{H}_{44}\text{Cl}_8\text{MnNO}_6$	$\text{C}_{50}\text{H}_{72}\text{Cl}_{12}\text{MnN}_2\text{O}_6$
Formula weight (g mole ⁻¹)	853.20	1277.44
Temperature (K)	150(2)	120(2)
Wavelength Mo K α (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1$
<i>a</i> (Å)	10.1751(3)	9.6128(3)
<i>b</i> (Å)	24.2470(7)	18.9994(6)
<i>c</i> (Å)	15.2289(6)	16.2805(5)
β (°)	104.9560(10)	97.836(2)
<i>V</i> (Å ³)	3629.9(2)	2945.66(16)
<i>Z</i>	4	2
<i>d_x</i> (Mg m ⁻³)	1.561	1.440
μ (mm ⁻¹)	0.995	0.815
<i>F</i> (000)	1760	1326
Crystal	needle; dark yellow	block; dark green
Crystal size (mm)	0.46 × 0.08 × 0.06	0.10 × 0.10 × 0.10
θ range (°)	3.24–25.40	3.03–25.02
Index ranges	$-12 \leq h \leq 12$; $-21k \leq 29$; $-18 \leq l \leq 18$	$-9 \leq h \leq 11$; $-22 \leq k \leq 20$; $-19 \leq l \leq 19$
<i>N_{collect}</i>	21133	19318
<i>N_{indt}</i>	6538 [<i>R_{int}</i> = 0.0913]	9344 [<i>R_{int}</i> = 0.0619]
Data completeness	0.978	0.987
Absorption correction	semi-empirical from equivalents	
Maximum and minimum transmission	0.9427 and 0.6575	0.9229 and 0.9229
Refinement method	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	6538/36/451	9344/1/640
Goodness-of-fit on <i>F</i> ²	1.003	0.948
<i>R</i> ₁	0.0689 [<i>F</i> ² > 2σ <i>F</i> ²]	0.0457 [<i>F</i> ² > 2σ <i>F</i> ²]
<i>wR</i> ₂	0.1558	0.0766
ρ_{max} (e Å ⁻³)	0.888	0.504
ρ_{min} (e Å ⁻³)	-0.557	-0.345

positions. Some disorder is observed in the terminal groups of the butyl chains in the TBA molecule, which was modelled over two fractionally occupied sites.

2.4. Hydrogen peroxide production

Samples of the complexes (1.25, 2.50, 5.00 or 10.0 μmol) were separately added to a dreschel bottle containing ACS grade NH_2OH (3.30 g, 50%, w/w, aqueous, 0.0500 M) in a 1:1 mixture of acetonitrile and de-ionised water (total volume 100.0 cm^3). Dioxygen gas at a rate of 1.5 $\text{dm}^3 \text{min}^{-1}$ was bubbled through the rapidly stirred solution which was equilibrated 20 ± 1 $^\circ\text{C}$. A blank was also run with no complex added. Aliquots of the solution were removed at defined periods and analysed for hydrogen peroxide concentration using the colorimetric method based on titanium(IV) sulphate [33,34].

3. Results and discussion

3.1. Preparation of complexes

The preparative methodology employed is interesting in that the use of the bulky $(\text{Bu})_4\text{N}^+\text{OH}^-$ base would appear to be important in keeping anionic forms of tetrachlorocatechol apart thus mitigating against polymerisation reactions [28,35] and possibly stabilising reduced, anionic, forms of tetrachlorocatechol for subsequent coordination to the manganese(II) ion. Thereafter, rapid oxidation to either Mn(III)-bis-tcc or Mn(IV)-tris-tcc occurs, with the use of the more polar aqueous-ethanol solvent mixture stabilising the formation of Mn(III)-bis-tcc by occupying coordination sites around the Mn(III) ion while the use of the relatively non-polar, poorly coordinating, acetone as solvent leads to the formation of Mn(IV)-tris-tcc. The use of alkali metal containing bases are reported to lead to the formation of particularly stable alkali metal-catecholate complexes which would prevent the formation of the tris Mn(IV)-tcc complex [30]; this was avoided in this synthetic method. The formation of these complexes indicate that the catecholate oxygens still possess strong electron-donating properties, despite the electronegative effect of the four chlorine atoms on the benzene ring, to stabilise tetravalent manganese [8,13,29,36–39].

3.2. Descriptions of the structures

3.2.1. $(\text{Bu}_4\text{N})[\text{Mn}(\text{Cl}_4\text{Cat})_2(\text{H}_2\text{O})(\text{EtOH})]$

This structure consists of manganese (III) ions occupying a crystallographic centre of symmetry within a distorted octahedral environment being coordinated by six oxygen atoms. Four of these oxygen atoms arise from two centrosymmetrically related coplanar catechol

rings with the remaining two oxygen atoms from either two water or two ethanol molecules (Fig. 1). The two Mn–O(catechol) bond lengths on either side of the molecule are almost identical at 1.896(4) and 1.916(3) \AA (Table 2). The bond distance between the manganese and the water or ethanol oxygen atoms are much longer (Mn–OH₂ = 2.294(4) \AA and Mn–OHCH₂CH₃ = 2.280 \AA) due to the effects of Jahn-Teller distortion. Each $[\text{Mn}(\text{Cl}_4\text{Cat})_2(\text{H}_2\text{O})(\text{EtOH})]^-$ complex ion is associated with a tetrabutylammonium cation (the asymmetric unit consists of two half molecules of $[\text{Mn}(\text{Cl}_4\text{Cat})_2(\text{H}_2\text{O})(\text{EtOH})]^-$ whose charges are balanced by a single TBA and hence Fig. 1 shows the connectivity and numbering scheme but does not exhibit the correct stoichiometry). The disorder in the terminal parts of the butyl arms of the TBA molecule is not shown in Fig. 1 for clarity purposes.

The isolation of this complex provides further evidence that manganese(III) is extremely reluctant to form tris (catecholato) complexes due to the short ‘bite distance’ of catecholate oxygen atoms, calculated to be 2.79 \AA , which are unable to span the elongated coordination axes of the Jahn-Teller distorted Mn(III) ion.

3.2.2. $(\text{Bu}_4\text{N})_2[\text{Mn}(\text{Cl}_4\text{Cat})_3]$

This structure consists of discrete mononuclear propeller-like anions with a 2-fold symmetry and two tetrabutylammonium cations (Fig. 2). The manganese atom is coordinated to six oxygen atoms from the bidentate catecholate ligands in a trigonally distorted octahedral geometry.

3.2.3. General comments

The average Mn–O (catecholate) bond lengths in both $(\text{Bu}_4\text{N})[\text{Mn}(\text{Cl}_4\text{Cat})_2(\text{H}_2\text{O})(\text{EtOH})]$ (range 1.896–1.916 \AA) and $(\text{Bu}_4\text{N})_2[\text{Mn}(\text{Cl}_4\text{Cat})_3]$ (range 1.889–1.911 \AA) are about 1.90 \AA and are comparable to that found for other structurally characterised manganese catecholate complexes [28,29,37] (note that the Mn–O bond lengths in $(\text{Bu}_4\text{N})_2[\text{Mn}(\text{Cl}_4\text{Cat})_3]$ (range 1.877–1.892 \AA , average 1.88 \AA) isolated by Gatteschi [30] are somewhat lower and may reflect the lower temperature of 20 K at which the structural study was carried out compared to 120 K in our study). This similarity in the Mn–O bond lengths despite the difference in charge on the metal ion has been commented on before [25] and indeed quite similar bond lengths have been found in previously structurally determined $[\text{Mn}^{\text{III}}(3,5\text{-}(\text{SO}_3)_2\text{Cat})_2]^{5-}$ (range 1.906–1.907 \AA , average 1.91 \AA) [28] and $[\text{Mn}^{\text{IV}}(\text{dtbCat})_2]$ (range 1.874–1.922 \AA , average 1.90 \AA) [29,37], showing that the Mn–O bond length is also quite independent of the nature of the substituent on the catecholate ring. The average O–Mn–O bite angle is about 94° in $(\text{Bu}_4\text{N})[\text{Mn}(\text{Cl}_4\text{Cat})_2(\text{H}_2\text{O})(\text{EtOH})]$ and 86° in $(\text{Bu}_4\text{N})_2[\text{Mn}(\text{Cl}_4\text{Cat})_3]$. In the latter, this deviation from an ideal octahedron is due to the constraints by three

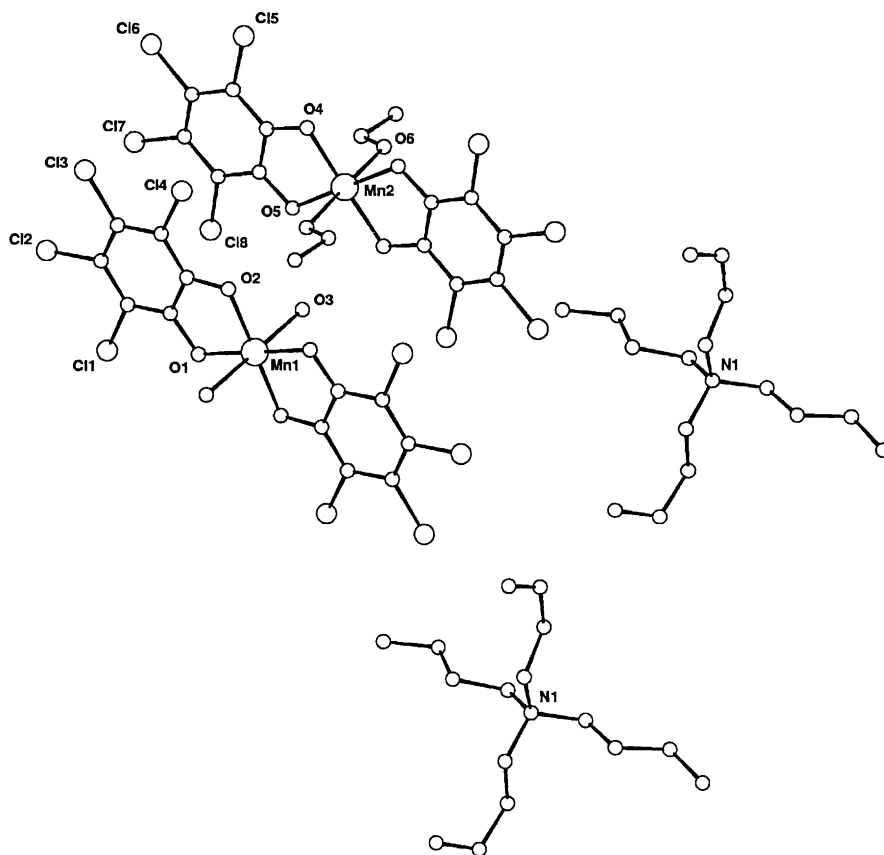


Fig. 1. Diagram of $(\text{Bu}_4\text{N})[\text{Mn}(\text{Cl}_4\text{Cat})_2(\text{H}_2\text{O})(\text{EtOH})]$ showing the atomic numbering scheme.

5-membered chelate rings, resulting in the observed trigonal distortion of the manganese coordination sphere (average twist angle of about 54°). These values are again typical for catechol complexes. Metal-catecholates generally have C–O bond lengths of 1.34–1.36 Å, e.g. $[\text{Cr}(\text{Cat})_3]^{3-}$ 1.349 (5) Å; $[\text{Fe}(\text{Cat})_3]^{3-}$ 1.349 (3) Å [40]. The C–O bond lengths in $(\text{Bu}_4\text{N})[\text{Mn}(\text{Cl}_4\text{Cat})_2(\text{H}_2\text{O})(\text{EtOH})]$ and $(\text{Bu}_4\text{N})_2[\text{Mn}(\text{Cl}_4\text{Cat})_3]$ are in the range 1.33–1.35 Å and longer than that expected for metal-semiquinone complexes (1.28 Å); the Cl–C2 distances in the two complexes are in the range 1.37–1.40 Å which is also consistent with coordinated catechols (~ 1.40 Å) rather than coordinated semiquinones (1.44 Å).

3.3. Analysis and magnetic study of complexes

3.3.1. $(\text{Bu}_4\text{N})[\text{Mn}(\text{Cl}_4\text{Cat})_2(\text{H}_2\text{O})(\text{EtOH})]$

Found: C, 42.78; H, 5.35; N, 1.81; Cl, 33.23; Mn, 6.03. $\text{C}_{30}\text{H}_{44}\text{Cl}_8\text{MnNO}_6$ requires C, 42.23; H, 5.20; N, 1.64; Cl, 33.24; Mn, 6.44. A magnetic susceptibility measurement produced a value for μ of 4.87 BM. This fits for Mn^{3+} (d^4) high spin ($\mu = 4.90$ BM).

3.3.2. $(\text{Bu}_4\text{N})_2[\text{Mn}(\text{Cl}_4\text{Cat})_3]$

Found: C, 46.03; H, 5.97; N, 2.08; Cl, 33.44; Mn, 4.50. $\text{C}_{50}\text{H}_{72}\text{Cl}_{12}\text{MnN}_2\text{O}_6$ requires C, 47.01; H, 5.68; N, 2.19; Cl, 33.30; Mn, 4.30. A magnetic susceptibility

measurement produced a value for μ of 3.97 BM. This fits for Mn^{4+} (d^3) high spin ($\mu = 3.87$ BM).

3.4. UV–Vis and IR spectroscopy

3.4.1. $(\text{Bu}_4\text{N})[\text{Mn}(\text{Cl}_4\text{Cat})_2(\text{H}_2\text{O})(\text{EtOH})]$

$\lambda_{\text{max}}/\text{nm}$ (CH_3CN) ~ 700 (sh, $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 270) and 613.3 (323.5) can be assigned to d–d transitions to produce a pale green solution; $\lambda_{\text{max}}/\text{nm}$ 436.0 (1320) probably a LMCT (ligand-to-metal charge transfer) on the basis of its high molar absorptivity which is responsible for the dark yellow colour of the complex in the solid state and in more dilute solution; $\lambda_{\text{max}}/\text{nm}$ 297 (sh, 10 784), 287 (sh, 11 275) and 214.4 (279 804) due to tetrachlorocatechol. The LMCT at 436.0 nm can be assigned to a LMCT transition of catecholato $\rightarrow \text{Mn}^{\text{III}}$, this being at exactly the same wavelength as that previously found for $[\text{Na}]_5[\text{Mn}(\text{3,5-(SO}_3)_2\text{Cat})_2] \cdot 10\text{H}_2\text{O}$ [26]. The d–d transitions at ~ 700 and 613.3 nm are equivalent to energy gaps of ~ 171 and $195.2 \text{ kJ mol}^{-1}$, respectively, which are again quite similar to that found for $[\text{Na}]_5[\text{Mn}(\text{3,5-(SO}_3)_2\text{Cat})_2] \cdot 10\text{H}_2\text{O}$. Gatteschi [30] reported only a single d–d transition at 635 nm ($150 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) for $\text{K}[\text{Mn}(\text{Cl}_4\text{cat})_2(\text{OPPh}_3)] \cdot \text{H}_2\text{O} \cdot \text{Me}_2\text{CO}$. However, by using a 4 cm path length (cell) we were able to obtain much greater spectral detail and a much more accurate value for the higher energy transition.

Table 2

(a) Selected bond lengths (Å) and angles (°) for (Bu ₄ N)[Mn(Cl ₄ Cat) ₂ (H ₂ O)(EtOH)]	
<i>Bond lengths</i>	
Mn(1)–O(1)	1.913(3)
Mn(1)–O(2)	1.896(4)
Mn(1)–O(3)	2.294(4)
Mn(2)–O(4)	1.899(4)
Mn(2)–O(5)	1.903(4)
Mn(2)–O(6)	2.280(5)
O(1)–C(1)	1.334(7)
C(1)–C(2)	1.369(8)
C(2)–Cl(1)	1.723(6)
C(8)–Cl(5)	1.707(7)
<i>Bond angles</i>	
O(1)–Mn(1)–O(2)	94.23(16)
O(1)–Mn(1)–O(2) ⁱ	85.77(16)
O(1)–C(1)–C(2)	124.4(5)
C(1)–O(1)–Mn(1)	110.8(3)
O(4)–Mn(2)–O(5)	93.82(18)
O(4)–Mn(2)–O(5) ⁱⁱ	86.18(18)
O(4)–C(7)–C(8)	122.3(6)
C(7)–O(4)–Mn(2)	110.5(4)
(b) Selected bond lengths (Å) and angles (°) for (Bu ₄ N) ₂ [Mn(Cl ₄ Cat) ₃]	
<i>Bond lengths</i>	
Mn(1)–O(1)	1.902(3)
Mn(1)–O(2)	1.911(3)
O(1)–C(1)	1.333(5)
C(1)–C(2)	1.384(6)
C(2)–Cl(1)	1.737(5)
<i>Bond angles</i>	
O(1)–Mn(1)–O(2)	84.95(14)
O(1)–Mn(1)–O(6)	94.41(13)
O(1)–C(1)–C(2)	124.4(5)
C(1)–O(1)–Mn(1)	111.9(3)

IR data $1/\lambda/\text{cm}^{-1}$: 3418 (broad, O–H stretch, water and ethanol); 1433 (C–O stretch, catecholate); 810 (C–Cl) stretch.

3.4.2. (Bu₄N)₂[Mn(Cl₄Cat)₃]

$\lambda_{\text{max}}/\text{nm}$ (CH₃CN) ~ 700 (sh, ~ 6000), 615.2 ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ 6290) and ~ 425 (sh, ~ 1300) can be assigned to LMCTs on the basis of their high molar absorptivity which are responsible for the dark green colour of the complex in the solid state and in solution; $\lambda_{\text{max}}/\text{nm}$ 312.6 (27 161), ~ 250 (sh, 36 500) and 222.0 (91 035) due to tetra-chlorocatechol. The absorption band at 615.2 nm with two distinct shoulders at ~ 700 and ~ 425 nm is typical of high-valent Mn^{IV} catecholate species [8,13,29,30,36–39]. The 615.2 nm band can be assigned to a LMCT transition of catecholato \rightarrow Mn^{IV} on the basis of comparison to previously reported tris (catecholate) Mn^{IV} complexes [29,30,36,37] while the remaining two bands may, on the basis of the spectrum for (Bu₄N)[Mn(Cl₄Cat)₂(H₂O)(EtOH)] (above), be assigned to LMCT transitions of catecholato \rightarrow Mn^{III}.

IR data $1/\lambda/\text{cm}^{-1}$: 1422 (C–O stretch, catecholate); 793 (C–Cl stretch).

3.5. Hydrogen peroxide production

The curves for the production of H₂O₂ using hydroxylamine (NH₂OH, 0.500 M) and dioxygen (1.5 dm³ min⁻¹) as substrates in 1:1 aqueous acetonitrile with different weights of (Bu₄N)[Mn(Cl₄Cat)₂(H₂O)(EtOH)] and (Bu₄N)₂[Mn(Cl₄Cat)₃] are shown in Figs. 3 and 4, respectively. With no complex added there is virtually

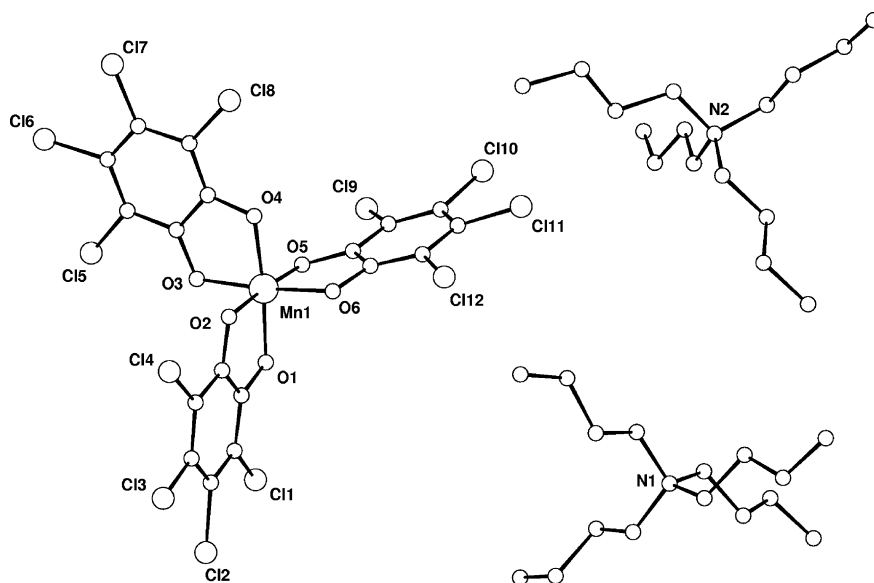


Fig. 2. Diagram of (Bu₄N)₂[Mn(Cl₄Cat)₃] showing the atomic numbering scheme.

no H_2O_2 production. The rates of H_2O_2 production then increase steadily with increasing amounts of complex between 1.25 and 5.00 μmol . With 10.0 μmol of each complex (not shown), the rate of H_2O_2 production is faster than that using 5.00 μmol , but there is then quite rapid decomposition of the H_2O_2 , suggesting a slower manganese catalysed decomposition of H_2O_2 . The slower rate of H_2O_2 production with $(\text{Bu}_4\text{N})_2[\text{Mn}(\text{Cl}_4\text{Cat})_3]$ compared to $(\text{Bu}_4\text{N})[\text{Mn}(\text{Cl}_4\text{Cat})_2(\text{H}_2\text{O})(\text{EtOH})]$ at 1.25 μmol may be due to the difficulty in weighing out very small amounts of solid and the sensitivity of the catalytic process to these small variations in the amount of complex. Nevertheless, the strong similarity in the rates of production of H_2O_2 production with the two complexes suggest that neither the oxidation state of the manganese nor labile coordination sites around the metal are important in catalysis. Fig. 5 shows a log plot of weight of manganese complex against initial rate of reaction (taken by the gradient through $t = 0, 2, 5$ and 10 min). The slopes for both

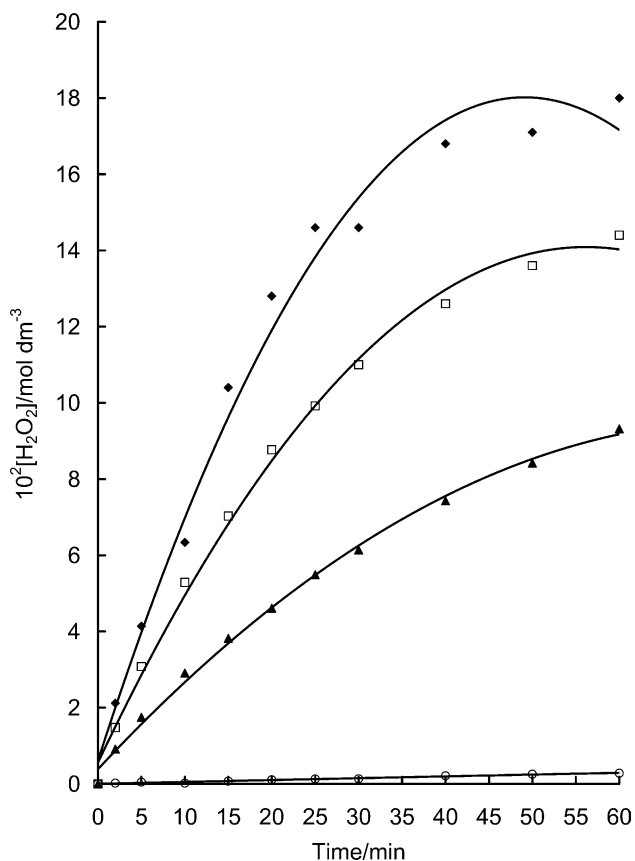


Fig. 3. The catalytic production of H_2O_2 with O_2 using NH_2OH as substrate at $20 \pm 1^\circ\text{C}$ with different weights of $(\text{Bu}_4\text{N})[\text{Mn}(\text{Cl}_4\text{Cat})_2(\text{H}_2\text{O})(\text{EtOH})]$. In all runs the initial $[\text{NH}_2\text{OH}]$ was 0.500 M (3.30 g, 50% aqueous). O_2 ($1.5 \text{ dm}^3 \text{ min}^{-1}$) was introduced into a rapidly stirred 1:1 aqueous-acetonitrile solution (total volume 100 cm^3). Weights of complex: (O) none; (▲) 1.1 mg (1.25 μmol); (□) 2.2 mg (2.50 μmol); (◆) 4.4 mg (5.00 μmol).

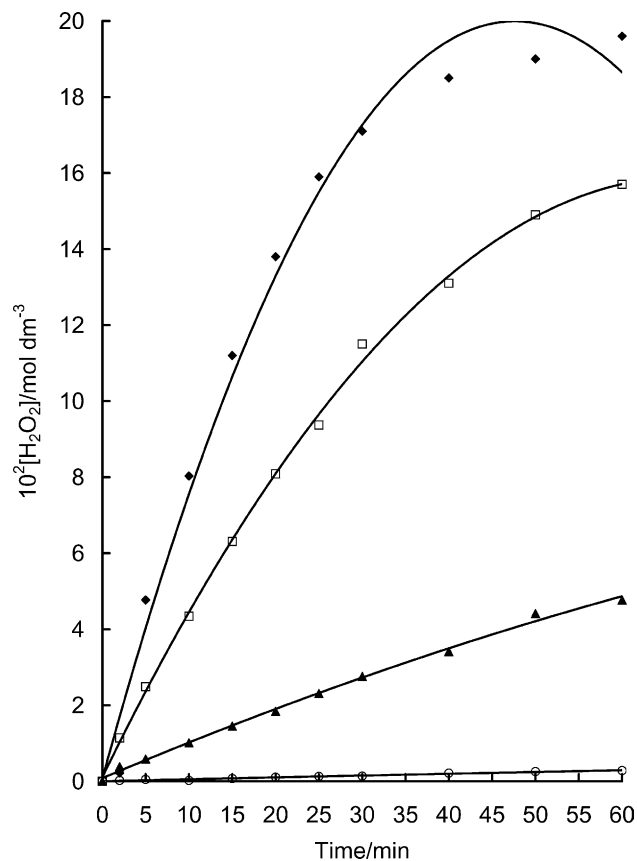


Fig. 4. The catalytic production of H_2O_2 with O_2 using NH_2OH as substrate at $20 \pm 1^\circ\text{C}$ with different weights of $(\text{Bu}_4\text{N})_2[\text{Mn}(\text{Cl}_4\text{Cat})_3]$. In all runs the initial $[\text{NH}_2\text{OH}]$ was 0.500 M (3.30 g, 50% aqueous). O_2 ($1.5 \text{ dm}^3 \text{ min}^{-1}$) was introduced into a rapidly stirred 1:1 aqueous-acetonitrile solution (total volume 100 cm^3). Weights of complex: (O) none; (▲) 1.6 mg (1.25 μmol); (□) 3.2 mg (2.50 μmol); (◆) 6.4 mg (5.00 μmol).

complexes are quite similar and average to about 0.74; this fractional order in manganese complex may suggest the involvement of radical species in the mechanism for H_2O_2 production. Both these complexes formed a dark blue solution in acetonitrile but this colour was rapidly discharged on the addition of aqueous hydroxylamine suggesting the formation of manganese(II) species. The use of 1:1 aqueous-acetonitrile mixtures is interesting in that there appears to be no dependence of the catalytic system on the concentration of tetrachlorocatechol, unlike that observed previously with $[\text{Na}]_5[\text{Mn}(\text{3,5-}(\text{SO}_3)_2\text{Cat})_2] \cdot 10\text{H}_2\text{O}$ in aqueous solution [28] where an ~ 30 -fold excess of Tiron over Mn^{II} was required to ensure a good rate of H_2O_2 production. Unpublished work suggests a dependence of the rate of H_2O_2 production on the ratio of water and acetonitrile in the reaction mixture, with lower and higher amounts of acetonitrile than that used here producing lower rates. These results suggest that a 1:1 aqueous acetonitrile mixture may provide the ideal conditions for stabilising radical species formed during this catalytic process.

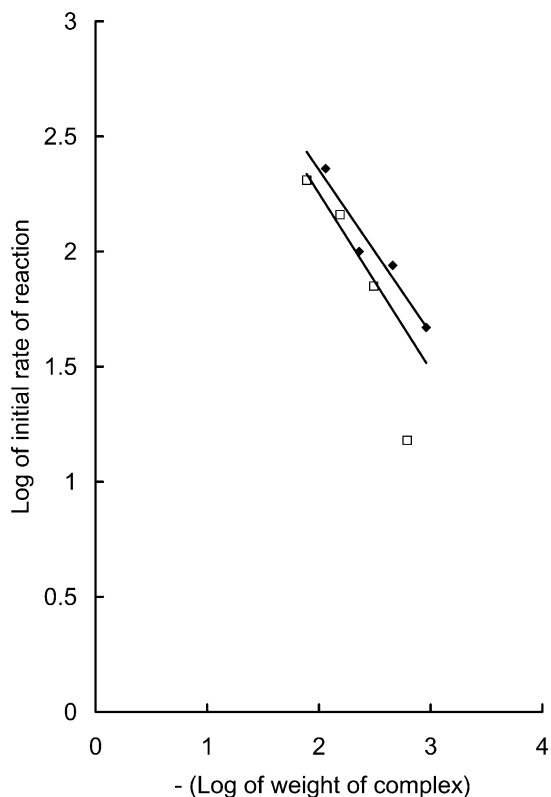


Fig. 5. Log weight of complex against log of initial rate of reaction. (◆) $(\text{Bu}_4\text{N})[\text{Mn}(\text{Cl}_4\text{Cat})_2(\text{H}_2\text{O})(\text{EtOH})]$; (□) $(\text{Bu}_4\text{N})_2[\text{Mn}(\text{Cl}_4\text{Cat})_3]$.

4. Conclusions and perspectives

The similarity of the hydrogen peroxide curves for $(\text{Bu}_4\text{N})[\text{Mn}(\text{Cl}_4\text{Cat})_2(\text{H}_2\text{O})(\text{EtOH})]$ and $(\text{Bu}_4\text{N})_2[\text{Mn}(\text{Cl}_4\text{Cat})_3]$ suggests that the mechanism of hydrogen peroxide production is the same in both cases. It is worthy of note that although $(\text{Bu}_4\text{N})[\text{Mn}(\text{Cl}_4\text{Cat})_2(\text{H}_2\text{O})(\text{EtOH})]$ contains the Mn^{III} ion and $(\text{Bu}_4\text{N})_2[\text{Mn}(\text{Cl}_4\text{Cat})_3]$ the Mn^{IV} ion, it is probable that these pre-catalysts are reduced to Mn^{II} in the presence of NH_2OH and that it is the in situ generated $[\text{Mn}(\text{Cl}_4\text{Cat})_2(\text{H}_2\text{O})(\text{EtOH})]^{2-}$ and $[\text{Mn}(\text{Cl}_4\text{Cat})_3]^{4-}$ that are the active form of the catalyst [28]. Pecoraro [22] has shown that on model manganese catalase enzymes, hydroxylamine can be used as a good reducing agent to prepare the fully reduced (Mn^{II}) active form from $\text{Mn}^{\text{III/IV}}$ forms. This may explain why the different starting oxidation states of the manganese atom in the two complexes are unimportant to the catalytic reduction of dioxygen to hydrogen peroxide. The fact that the presence of labile coordination sites around the metal are also unimportant would suggest that the reduction of dioxygen occurs via an outer-sphere mechanism without the coordination dioxygen and hydroxylamine to the manganese atom. Pierpont and Lange [1] have proposed a mechanism for hydrogen peroxide production in this system based on the reduction of bound O_2 by coordinated

catechol in which hydroxylamine acts as a sacrificial reductant to regenerate the catalyst from the oxidised quinone form of the catechol. While the results here would lend support to such a mechanism, this does not explain why the substrate requirements in this system are so specific to hydroxylamine (or hydrazine) with a requirement for at least one hydrogen atom at each end of the substrate molecule (e.g. no H_2O_2 production with 1,1-dimethylhydrazine) [16]. It could be that the reaction proceeds via a hydrogen-bonded stabilised intermediate that is crucial to the catalytic reduction of dioxygen by inorganic amine.

The coordination chemistry of manganese higher valent complexes with O and N donor ligands is an area of tremendous variety in which patterns are developing based on both the electronic and structural motif characteristics provided by the ligand environment. The isolation and characterisation of $\text{Na}_5[\text{Mn}(3,5\text{-(SO}_3)_2\text{Cat})_2] \cdot 10\text{H}_2\text{O}$ [28] and $(\text{Bu}_4\text{N})[\text{Mn}(\text{Cl}_4\text{Cat})_2(\text{H}_2\text{O})(\text{EtOH})]$ provides further clear evidence of the inability of manganese(III) to form tris (catecholato) complexes. It was thought this provided a firm basis for postulating a mechanism by which this system can activate small inorganic molecules by the utilisation of vacant sites on the manganese atom. However the almost exactly similar catalytic characteristics exhibited by using $(\text{Bu}_4\text{N})_2[\text{Mn}(\text{Cl}_4\text{Cat})_3]$ indicate that neither vacant sites (nor the oxidation state of the manganese atom) are important in the catalytic mechanism. This result would lend support to an outer sphere mechanism for hydrogen peroxide production involving the reduction of bound O_2 by coordinated catechol in which hydroxylamine acts as a sacrificial reductant to regenerate the catalyst from the oxidised quinone form of the catechol, as proposed by Pierpont and Lange [1]. The electronic, non-innocent, characteristics provided by catecholate ligands, in particular their ability to undergo two electron, single step, oxidation to semi-quinone and quinone species together with the electronic fine-tuning provided by the substituents on the catecholate ring and the complimentary nature of the manganese atom forming stable oxidation states of +II, +III and +IV, provide the enzyme-like characteristics of this system's unique ability to activate O_2 for reduction to hydrogen peroxide using small inorganic amines. A similar electronic-structural motif involving the *o,o'*-dihydroxy azo structural unit has been found to be important for the efficient Mn^{II} oxidation of organic dyes in alkaline media [41]. With the system described here, clean technology processes can be envisaged which can, not only generate hydrogen peroxide in situ in aqueous solution, but also selectively catalyse important organic oxidation transformations under ambient conditions.

A remarkable feature of this enzyme-like system are the high TOF of 10000 h^{-1} which are due to the rapid production of hydrogen peroxide and the tiny (μM)

quantities of manganese complex which are used. These results are obtained under near ambient conditions (room temperature, pH 8.0, only slight positive pressures of O₂) and compare very favourably with the commercial production of hydrogen peroxide by the auto-oxidation of 2-ethylanthrahydroquinone in an organic solvent. The characteristics of this system are even more remarkable when one considers the ability of these relatively high concentrations of H₂O₂ and NH₂OH to coexist. This is probably due to the absence of 'free' metal ions to catalyse their mutual redox decomposition. In Pecoraro's manganese-catalase systems [22], the addition of hydrogen peroxide to the enzyme in the presence of hydroxylamine results in a rapid conversion to a catalytically inactive, superoxidised form that contains a dioxo-bridged Mn^{III/IV} dinuclear metal centre. Clearly the nature of the ligand environment around a manganese atom can radically change the behaviour and properties of the resulting complex.

Work is continuing to search for alternative substrates to hydroxylamine to make this process more economically viable as well as using this and similar systems to activate other small molecules under ambient conditions and in the modelling of natural systems.

5. Supplementary material

Complete crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre with CCDC No. 218044 for (Bu₄N)[Mn(Cl₄Cat)₂(H₂O)(EtOH)] and CCDC No. 218045 for (Bu₄N)₂[Mn(Cl₄Cat)₃]. Copies of the data can be obtained free of charge on application to: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033, email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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