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Inorganica Chimica Acta 348 (2003) 115–122

Inorganica Chimica Acta

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Manganese catalysed reduction of dioxygen to hydrogen peroxide: structural studies on a manganese(III)–catecholate complex

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Received 20 August 2002; accepted 15 November 2002

Abstract

The complex $[Na]_5[Mn(3,5\text{-}(SO_3)_2Cat)_2]\cdot 10H_2O$ ($H_2Cat = 1,2$-dihydroxybenzene) has been synthesised and characterised by X-ray diffraction (triclinic system, space group $P\bar{1}$). The characterisation of this complex supports previous work that manganese(III) is extremely reluctant to form tris (catecholato) complexes due to the short 'bite distance' of catecholate oxygen atoms (2.60 Å) which are unable to span the elongated coordination axes of the Jahn–Teller distorted Mn(III) ion. Hydrogen peroxide production is demonstrated with $[Na]_5[Mn(3,5\text{-}(SO_3)_2Cat)_2]\cdot 10H_2O$ using dioxygen and hydroxylamine as substrates at pH 8.0 in aqueous solution under ambient conditions. In the presence of added Tiron (1,2-dihydroxybenzene-3,5-disulfonate, disodium salt monohydrate) turn over frequency (TOF) in H_2O_2 (the number of moles of H_2O_2 per moles of manganese per hour) of $\sim 10\,000$ h^{-1} are obtained. The redox and structural motif characteristics imposed on this system by catecholate ligands together with the precise electronic requirements determined by the substituents on the catechol ring provide the enzyme-like characteristics of this system's unique ability to activate O_2 for reduction to hydrogen peroxide.

Keywords: Manganese; Tiron; Catecholate complexes; Hydrogen peroxide; Hydroxylamine; Dioxygen activation

1. Introduction

The chemistry of higher valent manganese has been the subject of intense research in recent years because it is known to play a central role in photosynthetic dioxygen evolution [1]. Model complexes invariably contain oxygen donor ligands complexed to manganese in dimeric or higher polymeric forms with the manganese in the III and/or IV oxidation states [1,2]. More recently there are has been interest in the 'catalase-like' properties of these types of complexes and demonstrate that higher valent manganese is implicated both in the oxidative and reductive cycles of oxygen in natural systems [3]. As many of these complexes are paramagnetic there is also interest in the use of such materials as synthetic magnets [4].

Transition metal complexes containing catechol and semiquinone ligands show a unique facility for electron transfer between the metal and chelated ligand [5] and these redox characteristics have been recognised as being important in reactions catalysed by certain enzymes that include galactose oxidase [6], ribonucleotide reductase [7] and PSII [8]. The non-innocent, i.e., redox-active, nature of catecholate complexes provide an interesting challenge for both synthetic and theoretical chemists [9]. This arises from the ease which catechols can be oxidised to the semiquinone and *o*-quinone forms.

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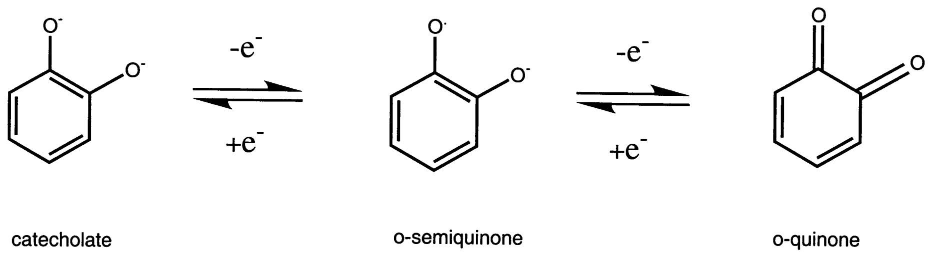
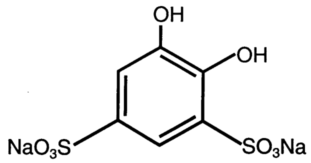
doi:10.1016/S0020-1693(02)01511-6



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 [10].

The synthesis of catecholate complexes is difficult unless the pH is kept low and/or inert atmospheres are used because catechols are prone to oxidation and polymerisation, complicating the synthesis of metal complexes. For these reasons there are few examples of isolated higher valent manganese–catecholate complexes reported in the literature [11] and none of Tiron (1,2-dihydroxybenzene-3,5-disufonate, disodium salt monohydrate, $Na_2H_2L\cdot H_2O$):



Na_2H_2L

$[M^{III}L_2]^{5-}$

$[M^{III}L_3]^{9-}$

Complexes of this ligand would be especially difficult to isolate from aqueous solution due to the water-solubilising sulfonate groups and the high complex charges of −9 and −5 for tris and bis M(III) complexes, respectively.

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 [11a]. The results reported here support this view 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. Thus while complexes of the type $[Na]_3[Mn(Cat)_3]\cdot 0.5NaOH\cdot 6H_2O$ and $[K]_3[Mn(Cat)_3]\cdot 3H_2O$ have been reported on the basis of elemental analysis [12], these were only obtained as pasty solids, using high concentrations of ligand and base and could not be purified. Under catalytic conditions it would be expected that there would be lower catechol–Mn ratios thus providing vacant sites for the coordination of substrate molecules.

There has been a growing interest in catalytic systems for the in situ, aqueous generation of H_2O_2 due to the transport, storage and handling problems associated with bulk supplies of H_2O_2. The use of hydrogen peroxide as an oxidising agent and disinfectant is highly desirable because of its favourable environmental characteristics and such systems have potential applications in the formulation of liquid laundry detergents, the bleaching of pulp in paper manufacture, the disinfection of process waters and the oxidation of organic substrates. It is envisaged that the use of hydrogen peroxide will increase markedly in the coming decade as the problems of activating this molecule are overcome [13].

We have, for a number of years, been interested in a manganese–catecholate system that can efficiently reduce dioxygen to hydrogen peroxide. Aqueous, oxygenated, mixtures of manganese(II) chloride and Tiron efficiently catalyse the reduction of dioxygen to hydrogen peroxide with hydroxylamine at pH 8.0 and room temperature (Eq. (1)):

$$O_2(\text{air}) + 2NH_2OH = H_2O_2 + N_2 + 2H_2O \qquad (1)$$

The production of H_2O_2 in this catalytic system has been found to be very sensitive to the nature of the substituents on the catechol ring in particular the electronic effect of these substituents; this study also showed that none of a range of other first row transition-metals tried showed any appreciable activity to produce H_2O_2 in this system [14]. Turn over frequency (TOF, the number of moles of H_2O_2 per mole of manganese per hour) of 10 000 h^{-1} were obtained using either aqueous solutions of manganese(II) [14] or manganese(II) bound on a clay (montmorillonite) support [15]. This system has recently 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 [16]. We are now able to report on the successful isolation of the pre-catalyst to this system which may provide an insight into the mechanism of H_2O_2 generation in this system.

2. Experimental

2.1. Complex preparation

The synthesis of $[Na]_5[Mn(3,5\text{-}(SO_3)_2Cat)_2]\cdot 10H_2O$ was performed in an open vessel without special conditions. The only precaution taken was to ensure that the pH of the solutions was kept below 7.0 to avoid rapid oxidation and/or polymerisation of Tiron.

2.1.1. $[Na]_5Mn(3,5\text{-}(SO_3)_2Cat)_2]\cdot 10H_2O$

A solution of Tiron (1.05 g, 3.15 mmol) in 20% aqueous EtOH (~ 50 ml) was added to $Mn(ClO_4)_2\cdot 6H_2O$ (0.38 g, 1.05 mmol) in 20% aqueous EtOH (~ 10 ml). The pH of the resulting colourless solution was taken up carefully to ~ 6.3 using a few drops of ~ 40% aqueous $(Bu)_4N^+OH^-$. An immediate milky white precipitate formed and the solution turned olive green. The mixture was heated and a few drops of water were added to redissolve the precipitate. The hot solution was carefully decanted from any remaining insoluble material into a hot receiver flask and the dark olive green solution left at room temperature for several days. The small dark green needle-shaped crystals deposited were carefully removed from the solution and dried from excess solvent using filter-paper. Yield 0.24 g (31%).

2.2. Physical measurements

Infrared spectra were recorded on a Perkin–Elmer Paragon FT-IR 1000 spectrophotometer as KBr discs. A Philips PU 8720 spectrophotometer was used to obtain UV–Vis spectra of aqueous solutions of the complex and for the determination of hydrogen peroxide colorimetrically. C, H analysis was carried out by MEDAC Ltd (Brunel University) and manganese was determined spectrophotometrically as MnO_4^- by oxidation with potassium periodate [17]; good results were obtained by using at least 100 mg of sample. Hydrogen peroxide production runs were performed in a catalytic bomb (Parr mini-reactor), equilibrated in a water-bath at 25.0 °C. Dioxygen was provided from a cylinder. 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). All kinetic runs were performed in duplicate.

2.3. Crystallographic data collection and refinement of structure

The crystal data of $[Na]_5[Mn(3,5\text{-}(SO_3)_2Cat)_2]\cdot 10H_2O$ and the parameters of data collection are summarised in Table 1. All data were collected at 150 K with Mo Kα radiation of $\lambda = 0.71069$ Å on a Nonius Kappa CCD area detector diffractometer. The structures were solved by direct methods using the crystallographic package SHELXS97 [18] and refined using full-matrix least-squares [19] 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 positions.

Table 1
Crystal data and structure refinement for $[Na]_5[Mn(3,5\text{-}(SO_3)_2Cat)_2]\cdot 10H_2O$

Identification code	$[Na]_5[Mn(3,5\text{-}(SO_3)_2Cat)_2]\cdot 10H_2O$
Formula weight	882.44
Temperature (K)	150(2)
Wavelength Mo Kα (Å)	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	7.8214(5)
b (Å)	9.4574(8)
c (Å)	11.510(1)
α (°)	67.879(4)
β (°)	84.909(5)
γ (°)	69.866(5)
V (Å^3)	740.7(1)
Z	1
d_x (Mg m^{-3})	1.981
μ (mm^{-1})	0.909
$F(000)$	448
Crystal size (mm)	0.15 × 0.03 × 0.03
θ Range (°)	1.91–27.42
Index ranges	$-9 \le h \le 10$; $-12 \le k \le 11$; $-14 \le l \le 14$
$N_{collect}$	9521
N_{indt}	3311[$R_{int} = 0.0672$]
N_{obs}	2185 [$I > 2\sigma(I)$]
Data completeness	0.981
Absorption correction	semi-empirical from equivalents
Maximum and minimum transmission	0.9732 and 0.8757
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	3311/0/256
Goodness-of-fit on F^2	1.023
R_1	0.0474 [$I > 2\sigma(I)$]
wR_2	0.1017
ρ_{max} (e Å^{-3})	0.758
ρ_{min} (e Å^{-3})	−0.695

2.4. Hydrogen peroxide production

2.4.1. With $[Na]_5[Mn(3,5\text{-}(SO_3)_2Cat)_2]\cdot 10H_2O$

The powdered complex (4.4 mg, 0.0050 mmol) was added to the pyrex reactor vessel containing ACS grade $NH_2OH\cdot HCl$ (3.48 g, 0.50 M) buffered using 4-(2-hydroxyethyl)-1-piperazinepropanesulfonic acid (EPPS, 2.5 g. 0.1 mol dm^{-3}) at pH 8.0 using semiconductor grade, carbonate-free, NaOH(aq) in de-ionised water (total volume 100.0 cm^3). Dioxygen gas at a pressure of three bars was bubbled through the rapidly stirred solution which was equilibrated 25.0 °C. Aliquots of the solution were removed at defined periods and analysed for hydrogen peroxide concentration using the colorimetric method based on titanium(IV) sulphate [20,21]. The experiment was repeated with added Tiron in the reaction solution (0.0498 g, 1.50 mM).

2.4.2. *With aqueous Mn(II)*

The above procedure was followed with added Tiron (0.0498 g, 1.50 mM) but an aqueous solution of $MnCl_2 \cdot 4H_2O$ (10.0 ml, 0.50 mM) added, in place of the complex, prior to making the reaction solution up to 100.0 cm^3 and adjusting to pH 8.0 (NaOH(aq)).

3. Results and discussion

3.1. *Preparation of $Na_5[Mn(3,5\text{-}(SO_3)_2Cat)_2]\cdot 10H_2O$*

The preparation of this complex is interesting in that the use of the bulky $(Bu)_4N^+OH^-$ base would appear to be important in keeping anionic forms of Tiron apart thus mitigating against polymerisation reactions [22] and possibly stabilising reduced, anionic, forms of catechol for subsequent coordination to a metal centre. When a ~5% (w/v) fresh aqueous solution of NaOH was used in place of $(Bu)_4N^+OH^-$ only microcrystalline material was produced with no significant improvement in yield. It is noteworthy also that the excess 'large' $(Bu)_4N^+$ cation is rejected within the complex in favour of the limiting (ignoring the presence of adventitious Na^+) 'small' Na^+ ions associated with each Tiron molecule (each of which can only provide four of the five Na^+ ions in the final complex). Presumably the 'hard' Na^+ ions are favoured in coordinating to sulfonate, catecholate and water oxygens.

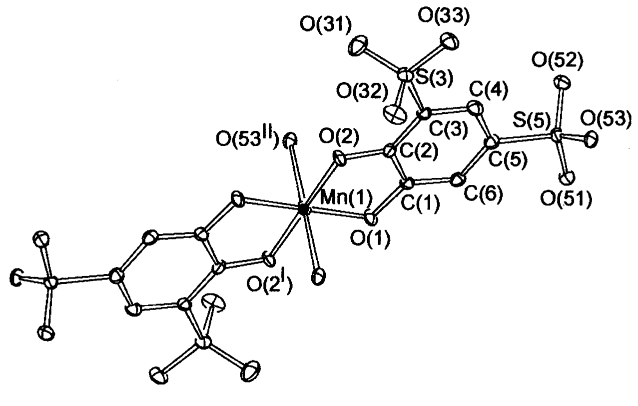


Fig. 1. ORTEP [19] diagram of the Mn centre in $[Na]_5[Mn(3,5\text{-}(SO_3)_2Cat)_2]\cdot 10H_2O$. The Mn(1) atom lies on a centre of symmetry. Symmetry codes: I = (−*x*, −*y*, −*z*); II = (*x*−1, *y*, *z*). Ellipsoid plots at 50% probability.

Table 2
Selected bond lengths (Å) and angles (°) for $[Na]_5[Mn(3,5\text{-}(SO_3)_2Cat)_2\cdot 10H_2O$

Bond lengths	
Mn–O(1)	1.906(2)
Mn–O(2)	1.907(2)
Mn–O(53)#2	2.311(3)
O(1)–C(1)	1.363(4)
C(1)–C(2)	1.411(5)
S(5)–O(51)	1.459(2)
S(5)–O(52)	1.453(3)
S(5)–O(53)	1.473(3)
Bond angles	
O(1)–Mn–O(2)	86.0(1)
O(1)–Mn–O(2)#1	94.0(1)
O(1)–C(1)–C(2)	115.8(3)
C(1)–O(1)–Mn	110.8(2)

3.2. *Description of the structure*

The structure of $Na_5[Mn(3,5\text{-}(SO_3)_2Cat)_2]\cdot 10H_2O$ consists of chains of $[(3,5\text{-}(SO_3)_2Cat)Mn(3,5\text{-}(SO_3)_2Cat)]^{5-}$ running parallel to the **a** axis with five Na^+ ions acting as counter cations. Each Mn(III) ion occupies a crystallographic centre of symmetry within a distorted octahedral environment being coordinated by four oxygen atoms from two centrosymmetrically related coplanar catechol rings and two oxygen atoms from two sulfonate groups of neighbouring molecules (Fig. 1). The resulting *trans* arrangement of the ligands minimises steric interaction between the substituent sulfonate groups of the coordinated catechol rings and so the two Mn–O(catechol) bond lengths on either side of the molecule are almost identical at 1.906(2) and 1.907(2) Å (Table 2). The bond distance between the

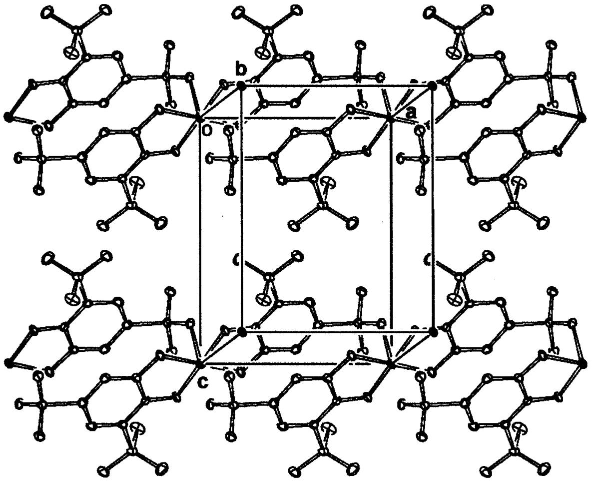


Fig. 2. Molecular structure showing polymeric $[Na]_5[Mn(3,5\text{-}(SO_3)_2Cat)_2]\cdot 10H_2O$. Linking of the $[(3,5\text{-}(SO_3)_2Cat)Mn(3,5\text{-}(SO_3)_2)Cat)]^{5-}$ anions into chains parallel to the **a** direction. Molecular orientation as in Fig. 1. The manganese atoms lie on the corners of the unit cell. The water molecules and sodium ions have been omitted for clarity. Ellipsoid plots at 50% probability.

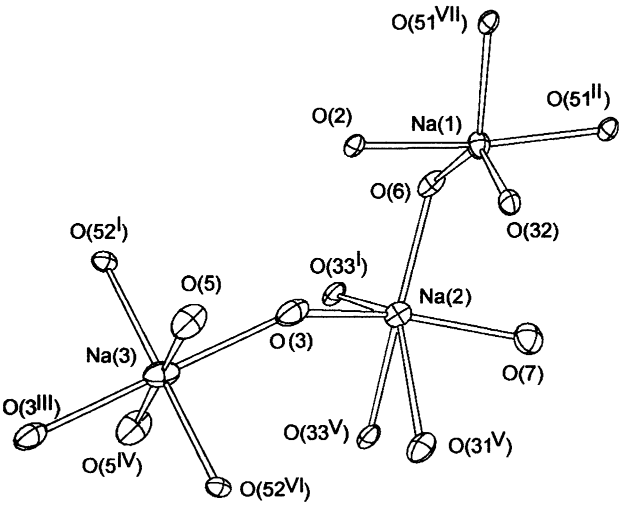


Fig. 3. Molecular structure of the three sodium centres in $[Na]_5[Mn(3,5\text{-}(SO_3)_2Cat)_2]\cdot 10H_2O$. The Na(3) atom lies on an inversion centre at (0, 0, −0.5). Symmetry codes: I = (x−1, y, z); II = (x−1, y+1, z); III = (−x, −y, −z−1); IV = (−x, 1−y, −z−1); V = (1−x, −y, −z−1); VI = (1−x, −y, −z). Ellipsoid plots at 50% probability.

manganese and the sulfonate oxygen atoms of neighbouring $[(3,5\text{-}(SO_3)_2Cat)Mn(3,5\text{-}(SO_3)_2)Cat)]^{5-}$ anions which lie above and below the plane of the catechol rings is much longer (Mn–OSO$_2$ = 2.311(3) Å) owing to the effects of Jahn–Teller distortion. These long bonds also serve to join one anion to its neighbours to form chains running parallel to the direction of the ***a*** axis (Fig. 2).

The five sodium ions occur in two centrosymmetrically related pairs (Na(1) and Na(2)) while the third sodium Na(3) occupies a centre of symmetry at (0.0, −0.5). Examination of the coordination environment about the sodium ions reveals the origin of the stability of the $Na_5[Mn(3,5\text{-}(SO_3)_2Cat)_2]\cdot 10H_2O$ lattice and explains the high aqueous solubility of the salt. Each $[(3,5\text{-}(SO_3)_2Cat)Mn(3,5\text{-}(SO_3)_2)Cat)]^{5-}$ anion is connected to the surrounding network of hydrated sodium ions by no less than 14 O–Na contacts and 12 hydrogen bonds. As shown in Fig. 3, sodium Na(1) and its centrosymmetric pair are five coordinate to three oxygen atoms of separate sulfonate groups, O(51)X2 and O(32), and a catecholate oxygen O(2), and a water molecule O(6). Sodium Na(2) and its centrosymmetric pair are octahedrally coordinated with two oxygens O(31) and O(33) of the same sulfonate in a bidentate fashion and an oxygen O(33) from another sulfonate together with three water molecules O(3), O(6) and O(7). The small bite angle of 55.1(1)° subtended by the bidentate sulfonate group results in a noticeably less regular geometry for this sodium Na(2) compared with sodium Na(3) which is also essentially octahedrally coordinated. Sodium Na(3) occupies a centre of symmetry and is coordinated with an oxygen of a sulfonate group (Na(3)–O(52) = 2.426(3) Å) and two water molecules (Na(3)–O(3) = 2.637(4) Å, Na(3)–O(5) = 2.415(4) Å) together with their centrosymmetrically related counterparts. The coordination polyhedra of the three sodium ions are linked together by shared water molecules–oxygen O(6) is shared between sodium Na(1) and Na(2) while oxygen O(3) is common to Na(2) and Na(3). All of the water hydrogen atoms participate in hydrogen bonding (see Tables in the Supplementary Material for more detailed information). This results in an intricate three dimensional network of hydrated sodium ions linked to interpenetrating chains of $[(3,5\text{-}(SO_3)_2Cat)Mn(3,5\text{-}(SO_3))Cat)]^{5-}$ anions by shared sulfonate and catecholate oxygen atoms and by hydrogen bonds. Water molecule O(4) is the only one whose oxygen atom is not directly coordinated to sodium. The coordination of a catechol oxygen atom to a sodium ion indicates that they retain some Lewis basicity despite being coordinated to the strongly Lewis acidic Mn(III) ion.

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 2.60 Å, which are unable to span the elongated coordination axes of the Jahn–Teller distorted Mn(III) ion.

Metal–catecholates generally have C–O bond lengths of 1.34–1.36 Å e.g. $[Cr(Cat)_3]^{3-}$ 1.349 (5) Å; $[Fe(Cat)_3]^{3-}$ 1.349 (3) Å [23] and the average C–O bond length in $[Mn(3,5\text{-}(SO_3)_2Cat)_2]^{5-}$ of 1.357 (6) Å is within this range and longer than that expected for

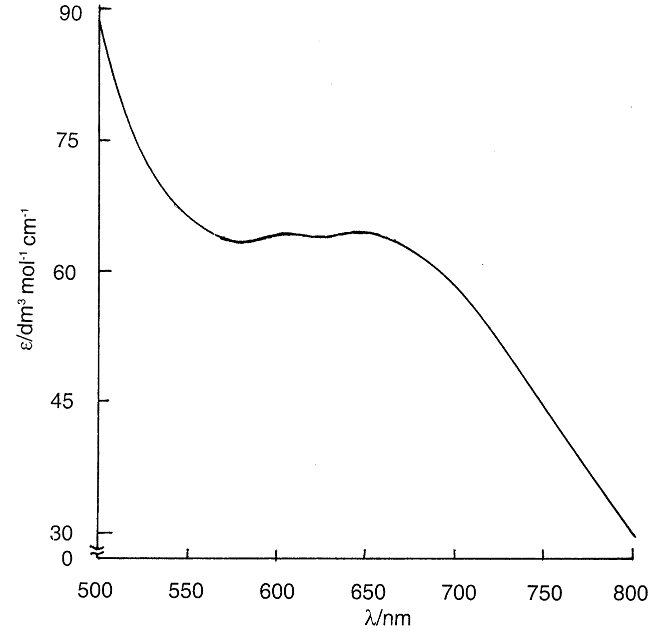


Fig. 4. Visible spectrum of $[Na]_5[Mn(3,5\text{-}(SO_3)_2Cat)_2]\cdot 10H_2O$ in water.

metal–semiquinone complexes (1.28 Å). The C1–C2 distance (1.419 Å) is also consistent with coordinated catechols (1.40 Å) rather than coordinated semiquinones (1.44 Å). The O–Mn–O bite angle is 86.0°, again a typical value for a catechol complex.

3.3. Analysis and magnetic study of $[Na]_5[Mn(3,5\text{-}(SO_3)_2Cat)_2]\cdot 10H_2O$

Found: C, 16.35; H, 2.53; Mn, 6.23. $C_{12}H_{24}O_{26}S_4Na_5Mn$ requires C, 6.33; H, 2.75; Mn, 6.23%. A magnetic susceptibility measurement using a Guoy apparatus produced a value for μ of 4.89 BM. This fits for Mn^{3+} (d^4) high spin ($\mu = 4.90$ BM).

3.4. UV–Vis and IR spectroscopy

A solution of $[Na]_5[Mn(3,5\text{-}(SO_3)_2Cat)_2]\cdot 10H_2O$ exhibits six bands: λ_{max} (nm) (H_2O) 648.8 (ε ($dm^3\ mol^{-1}\ cm^{-1}$) 64.4) and 605.6 (64.2) can be assigned to d–d transitions Fig. 4 (this doublet was achieved using a 4 cm glass cell); λ_{max} (nm) 436.0 (1 145) probably a LMCT on the basis of its high molar absorptivity which is responsible for the intense olive green colour of the complex in the solid state and in solution; λ_{max} (nm) 311.2 (6235), 238.7 (19 964) and 211.7 (46 043) due to Tiron. The d–d transitions are equivalent to energy gaps of 184.5 and 197.7 kJ mol^{-1}, respectively.

IR data ν (cm^{-1}): 3444 b, 1651 m, 1578 w, 1451 s 1414 s, 1261 s, 1202 s, 1162 s, 1095 s, 1055 s, 1036 s, 958 s, 882 w, 868 m, 780 m, 755 m, 709 m, 636 s, 560 s, 538 s, 470 m. The infrared spectrum of $[Na]_5[Mn(3,5(SO_3)_2\text{-}Cat)_2]\cdot 10H_2O$ is typical of metal–catecholate complexes. Thus the absorption at 470 cm^{-1} can be assigned to the Mn–O vibration, the C–O stretch is at 1055 cm^{-1} and/or 1095 cm^{-1} while the broad absorption at 3444 cm^{-1} is due to lattice water.

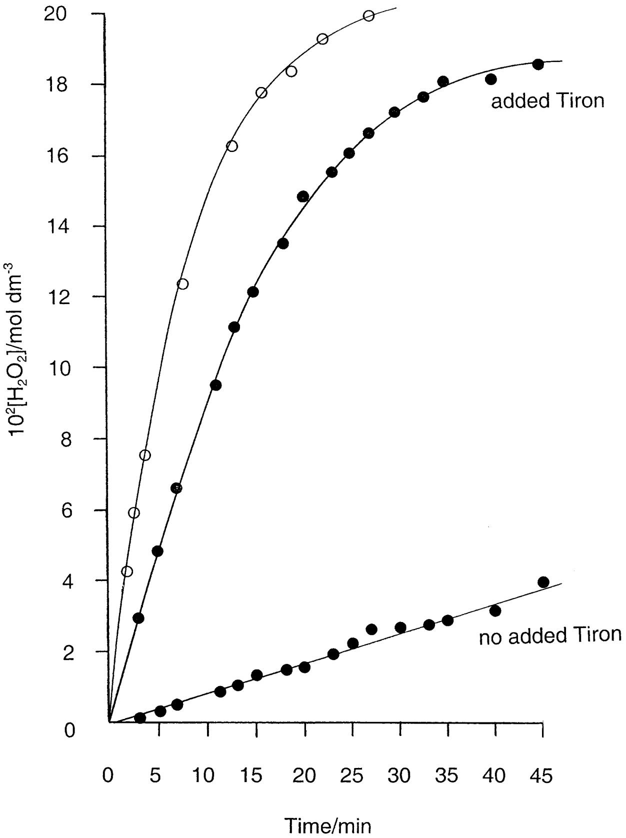


Fig. 5. The catalytic production of H_2O_2 with O_2 using NH_2OH as substrate at 25 ± 0.5 °C. In all runs the initial [$NH_2OH\cdot HCl$] was 0.50 M (3.48 g), O_2 3 bar was introduced into a rapidly stirred solution (total volume 100 cm^3) and pH 8.0 (4-(2-hydroxyethyl)-1-piperazine-propanesulfonate (EPPS) buffer, 2.50 g, 0.10 M). (O) Aqueous solution of $MnCl_2\cdot 4H_2O$ (10.0 ml, 0.50 mM) and [Tiron] 1.50 mM (0.0498 g) (●) $[Na]_5[Mn(3,5\text{-}(SO_3)_2Cat)_2]\cdot 10H_2O$ complex (4.4 mg, 0.0050 mmol) with [Tiron] 1.50 mM (0.0498 g) and no added Tiron.

3.5. Hydrogen peroxide production

The curves for the production of H_2O_2 using hydroxylamine (NH_2OH, 0.50 M) and dioxygen (3 bar) as substrates with either $Na_5[Mn(3,5\text{-}(SO_3)_2Cat)_2]\cdot 10H_2O$ (4.4 mg, 0.050 mM) or aqueous Mn(II) (0.050 mM) buffered at pH 8.0 are shown in Fig. 5. The approximately eightfold slower rate of H_2O_2 production with $Na_5[Mn(3,5\text{-}(SO_3)_2Cat)_2]\cdot 10H_2O$ can be improved to be almost identical to that in the aqueous Mn(II) experiment with added Tiron (0.0498 g, 1.50 mM), at the same concentration as with Mn(II) aqueous. This result shows the high dependence of the catalytic system on coordinated Tiron and that an ~ 30-fold excess over Mn(II) is required.

The similarity of the hydrogen peroxide curve for $Na_5[Mn(3,5\text{-}(SO_3)_2Cat)_2]\cdot 10H_2O$ (with added Tiron) with the aqueous Mn(II) curve suggests that the mechanism of hydrogen peroxide production is the same in both cases. It is worthy of note that although $Na_5[Mn(3,5\text{-}(SO_3)_2Cat)_2]\cdot 10H_2O$ contains the Mn(III) ion, it is probable that this pre-catalyst is reduced to Mn(II) in the presence of NH_2OH and that it is the in situ generated $[Mn(II)(3,5\text{-}(SO_3)_2Cat)_2]^{6-}$ that is the active form of the catalyst. A solution magnetic measurement of the reaction solution (split tube method) has shown the presence of five unpaired electrons due to the high-spin Mn(II) ion [14]. Evidence for this also comes from work by Pecoraro [3] on model manganese catalase enzymes in which hydroxylamine can be used as a good reducing agent to prepare the fully reduced (Mn_2(II)) active form from Mn(III/IV) forms.

Mechanisms for the generation of hydrogen peroxide can be put forward which involve a manganese(II) bis catecholate complex with dioxygen and hydroxylamine occupying vacant coordination sites to produce a transient octahedral manganese(II) complex through which electrons can be transferred from hydroxylamine to dioxygen [14]. Pierpont and Lange have proposed a different mechanism for hydrogen peroxide production based on the reduction of bound O_2 by coordinated Tiron in which hydroxylamine acts as a sacrificial reductant to regenerate the catalyst from the oxidised quinone form of Tiron [5]. However, this suggestion 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) [14]. Work is continuing to enable us to define a plausible mechanism for the generation of H_2O_2 in this system.

4. Conclusions and perspectives

The co-ordination 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 the redox, electronic and structural motif characteristics provided by the ligand environment. The isolation and characterisation of $Na_5[Mn(3,5\text{-}(SO_3)_2Cat)_2]\cdot 10H_2O$ provides further clear evidence of the inability of manganese(III) to form tris catecholato complexes. This provides a basis for postulating a mechanism by which this system can activate small inorganic molecules by the utilisation of vacant sites on the manganese atom. Analysis of the structure of $[Mn(III)(3,5\text{-}(SO_3)_2Cat)_2]^{5-}$ reveals the chemical significance of the short bite distance of the Tironate ligand, and that of catechols in general. The redox characteristics of catecholate ligands together with the precise electronic requirements at manganese(II), as determined by substituents on the catecholate ring, 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 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 [24]. With the system described here, clean technology processes can be envisaged which can generate hydrogen peroxide and use this in situ generated hydrogen peroxide to selectively catalyse important organic oxidation transformations under ambient conditions.

A remarkable feature of this enzyme-like system are the high TOF of 10 000 h^{-1} which are due to the rapid production of hydrogen peroxide and the tiny (μM) quantities of manganese which are used. These results are obtained under near ambient conditions (room temperature, pH 8.0, only slight positive pressures of O_2) and compare very favourably with the commercial production of hydrogen peroxide by the autooxidation 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 H_2O_2 and NH_2OH 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 [3], 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 for the use of 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 structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 175757. 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).

Acknowledgements

We wish to thank Timothy Brown for performing the kinetic runs using $[Na]_5[Mn(3,5\text{-}(SO_3)_2Cat)_2]\cdot 10H_2O$. We wish to acknowledge support from The Nuffield Foundation UG Bursary Scheme (1995 and 1998). We are grateful to Dr Mark E. Light and Dr Ann L. Bingham at the EPSRC X-ray crystallography service in the Department of Chemistry at the University of Southampton, United Kingdom for coordinating the data collection on our sample.

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