

## Synthesis and Structure of the Mn<sup>II</sup> Complex Salt [Mn<sub>2</sub>(η<sup>1</sup>η<sup>1</sup>μ<sub>2</sub>-oda)(phen)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>][Mn<sub>2</sub>(η<sup>1</sup>η<sup>1</sup>μ<sub>2</sub>-oda)(phen)<sub>4</sub>(η<sup>1</sup>-oda)<sub>2</sub>]-4H<sub>2</sub>O (odaH<sub>2</sub> = Octanedioic acid): a Catalyst for H<sub>2</sub>O<sub>2</sub> Disproportionation

Michael T. Casey,<sup>\*a</sup> Malachy McCann,<sup>\*a</sup> Michael Devereux,<sup>\*b</sup> Martin Curran,<sup>b</sup> Christine Cardin,<sup>\*c</sup> Moira Convery,<sup>d</sup> Valerie Quillet<sup>e</sup> and Charlie Harding<sup>f</sup>

<sup>a</sup> Chemistry Department, St. Patrick's College, Maynooth, Co. Kildare, Ireland

<sup>b</sup> Dublin Institute of Technology, Cathal Brugha Street, Dublin, Ireland

<sup>c</sup> Department of Chemistry, The University, Whiteknights, Reading, UK RG6 2AD

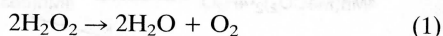
<sup>d</sup> Department of Biochemistry and Molecular Biology, University of Leeds, Leeds, UK LS2 9JT

<sup>e</sup> Chemistry Department, Trinity College, Dublin, Ireland

<sup>f</sup> Open University, Milton Keynes, UK MK7 6AA

The synthesis and X-ray crystal structure of the Mn<sup>II</sup> complex double salt [Mn<sub>2</sub>(η<sup>1</sup>η<sup>1</sup>μ<sub>2</sub>-oda)(phen)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>][Mn<sub>2</sub>(η<sup>1</sup>η<sup>1</sup>μ<sub>2</sub>-oda)(phen)<sub>4</sub>(η<sup>1</sup>-oda)<sub>2</sub>]-4H<sub>2</sub>O is reported, together with its catalytic activity towards the disproportionation of H<sub>2</sub>O<sub>2</sub>.

For the past decade considerable attention has been focused on the bioinorganic chemistry of manganese and, in particular, on multinuclear Mn metalloenzymes.<sup>1</sup> In addition to the tetra-Mn photosynthetic water-oxidizing complex a small number of Mn containing non-haem catalases have recently been isolated and characterised.<sup>2-4</sup> These manganoenzymes are responsible for the catalytic disproportionation of hydrogen peroxide, eqn (1), important for cell detoxification.



As part of our continuing studies into the coordination chemistry of dicarboxylic acids<sup>5</sup> we investigated the reactions of Mn<sup>II</sup> with the saturated aliphatic dicarboxylic acid octanedioic acid HO<sub>2</sub>C(CH<sub>2</sub>)<sub>6</sub>CO<sub>2</sub>H (odaH<sub>2</sub>). Manganese(II) acetate reacts with odaH<sub>2</sub> (ca. 1:1 mol ratio) to give a white Mn<sup>II</sup> complex of stoichiometry Mn(oda)H<sub>2</sub>O **1** (Scheme 1). An ethanolic suspension of **1** reacts with an excess of phen to produce yellow crystals of the dimanganese(II,II) complex double salt [Mn<sub>2</sub>(η<sup>1</sup>η<sup>1</sup>μ<sub>2</sub>-oda)(phen)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>][Mn<sub>2</sub>(η<sup>1</sup>η<sup>1</sup>μ<sub>2</sub>-oda)(phen)<sub>4</sub>(η<sup>1</sup>-oda)<sub>2</sub>]-4H<sub>2</sub>O **2**. The X-ray crystal structures of the 'concertina shaped' dianion and dication components of **2** are shown in Fig. 1(a) and 1(b), respectively.† The asymmetric unit consists of two half molecules of **2** and four water molecules. In the dianion [Mn<sub>2</sub>(η<sup>1</sup>η<sup>1</sup>μ<sub>2</sub>-oda)(phen)<sub>4</sub>(η<sup>1</sup>-oda)<sub>2</sub>]<sup>2-</sup> each of the two symmetry related Mn<sup>II</sup> atoms are ligated by the nitrogen atoms [N(1)–N(4)] of two chelating phen groups. An oda<sup>2-</sup> ligand bridges the two metals by using one carboxylate oxygen [O(3)] from each end of the diacid [Mn(1)–O(3) = 2.147 Å]. The other carboxylate oxygen [O(4)] at either end of the bridging oda<sup>2-</sup> ligand is on the limits of coordination distances<sup>6</sup> to the metal [Mn(1)–O(4) = 3.06 Å]. A monodentate oda<sup>2-</sup> ligand is strongly bonded to each metal *via* a single carboxylate oxygen [O(1)] [Mn(1)–O(1) = 2.178 Å], and the second oxygen of this carboxylate function [O(2)] is again found to be on the limits of coordination [Mn(1)–O(2) = 2.97 Å]. The pendant carboxylate oxygen atoms of this oda<sup>2-</sup> [O(5) and O(6)] are uncoordinated, and there is also some disorder in the ligand. Each Mn atom in Fig. 1(a) is depicted as being at the centre of a distorted N<sub>4</sub>O<sub>2</sub> octahedron. However, although the long Mn–O distances of 2.97 and 3.06 Å are on the limits of coordination, the distortion of the N(1)–Mn(1)–N(3) angle from ca. 180° to 147.31° suggests that the whole chromophore may possibly be described as being pseudo eight coordinate (MnN<sub>4</sub>O<sub>2</sub>).

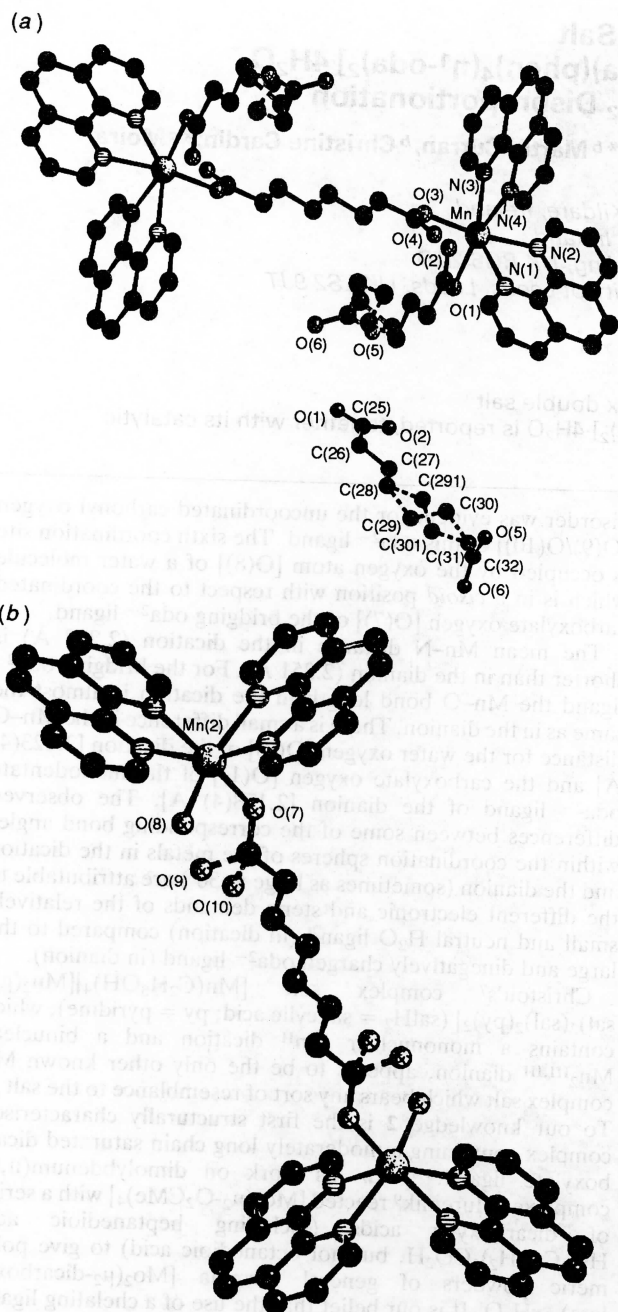
The structure of the dication [Mn<sub>2</sub>(η<sup>1</sup>η<sup>1</sup>μ<sub>2</sub>-oda)(phen)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> is basically similar to that of the dianion in that each of the two symmetry related Mn<sup>II</sup> atoms has a distorted octahedral N<sub>4</sub>O<sub>2</sub> coordination geometry. Each metal is surrounded by two chelating phen groups and one carboxylate oxygen atom [O(7)] from the bridging oda<sup>2-</sup> ligand. Some

disorder was evident for the uncoordinated carbonyl oxygen [O(9)/O(10)] of this oda<sup>2-</sup> ligand. The sixth coordination site is occupied by the oxygen atom [O(8)] of a water molecule which is in a *cisoid* position with respect to the coordinated carboxylate oxygen [O(7)] of the bridging oda<sup>2-</sup> ligand.

The mean Mn–N distance in the dication (2.287 Å) is shorter than in the dianion (2.351 Å). For the bridging oda<sup>2-</sup> ligand the Mn–O bond length in the dication is almost the same as in the dianion. There is a small difference in the Mn–C distance for the water oxygen [O(8)] of the dication [2.123(4) Å] and the carboxylate oxygen [O(1)] of the monodentate oda<sup>2-</sup> ligand of the dianion [2.178(4) Å]. The observed differences between some of the corresponding bond angles within the coordination spheres of the metals in the dication and the dianion (sometimes as large as 30°) are attributable to the different electronic and steric demands of the relatively small and neutral H<sub>2</sub>O ligand (in dication) compared to the large and dinegatively charged oda<sup>2-</sup> ligand (in dianion).

Christou's<sup>7</sup> complex salt [Mn(C<sub>2</sub>H<sub>5</sub>OH)<sub>4</sub>][Mn<sub>2</sub>(μ<sub>2</sub>-sal)<sub>2</sub>(sal)<sub>2</sub>(py)<sub>2</sub>] (salH<sub>2</sub> = salicylic acid; py = pyridine), which contains a mononuclear Mn<sup>II</sup> dication and a binuclear Mn<sub>2</sub><sup>III,III</sup> dianion, appears to be the only other known Mn complex salt which bears any sort of resemblance to the salt **2**. To our knowledge **2** is the first structurally characterised complex containing a moderately long chain saturated dicarboxylate ligand.<sup>8-10</sup> In his work on dimolybdenum(II,II) complexes Murenik<sup>9</sup> reacted [Mo<sub>2</sub>(μ<sub>2</sub>-O<sub>2</sub>CMe)<sub>4</sub>] with a series of dicarboxylic acids (including heptanedioic acid HO<sub>2</sub>C(CH<sub>2</sub>)<sub>5</sub>CO<sub>2</sub>H, but not octanedioic acid) to give polymeric powders of general formula [Mo<sub>2</sub>(μ<sub>2</sub>-dicarboxylate)<sub>2</sub>·xH<sub>2</sub>O]. It is our belief that the use of a chelating ligand like phen promotes the breakdown of polymeric dicarboxylate complexes into simpler binuclear structures (like **2** and [Cu<sub>2</sub>(η<sup>1</sup>η<sup>1</sup>μ<sub>2</sub>-bdoa)(phen)<sub>4</sub>]bdoa·13H<sub>2</sub>O, where bdoaH<sub>2</sub> = benzene-1,2-dioxyacetic acid<sup>5a</sup>). In these binuclear complexes the chelating phen ligand 'caps' each end of structure and inhibits polymerization of the complexes *via* the bifunctional dicarboxylate ligand. In this context we have found that PPh<sub>3</sub> also functions as a capping ligand in the formation of the Cu<sup>I</sup> complex [Cu(η<sup>1</sup>-bdoaH)(PPh<sub>3</sub>)<sub>3</sub>].<sup>5b</sup>

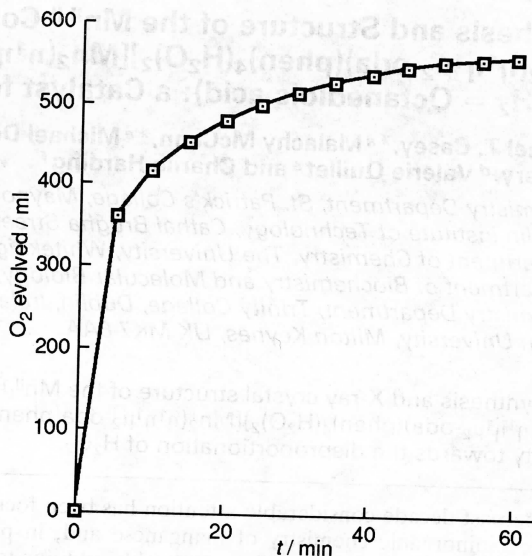
Complex **1** was insoluble in all common solvents and is thought to be polymeric through the bifunctional dicarboxylate oda<sup>2-</sup> ligand. It is interesting that the *v*<sub>asymm.</sub> (OCO) and *v*<sub>symm.</sub> (OCO) carboxylate bands in the IR spectra of **1** and **2** appeared at very similar frequencies,‡ suggesting that the oda<sup>2-</sup> ligand in **1** also has η<sup>1</sup>η<sup>1</sup>-coordination. The room temperature magnetic moments for **1** and **2** (μ = 5.74 and 5.80 BM, respectively) were within the range expected for isolated Mn<sup>II</sup> centres. In addition, the magnetic moment of **2** was almost independent of temperature. The double salt **2** dissolves in warm water and in warm ethanol, and the molar conductivity of an aqueous solution of **2** (Λ<sub>M</sub> = 318 S cm<sup>2</sup> mol<sup>-1</sup>) implies that it ionizes extensively in that solvent.



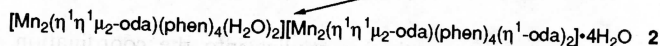
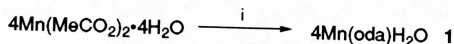
**Fig. 1** Crystal structure of (a) dianion and, (b) dication components of **2**. Selected corresponding bond lengths (Å) and bond angles (°) for dianion and dication { $\}$ : Mn(1)–N(1) 2.326(4) {Mn(2)–N(5) 2.282(4)}, Mn(1)–N(2) 2.382(4) {Mn(2)–N(6) 2.296(4)}, Mn(1)–N(3) 2.345(4) {Mn(2)–N(7) 2.285(4)}, Mn(1)–N(4) 2.350(4) {Mn(2)–N(8) 2.285(4)}, Mn(1)–O(3) (bridging oda<sup>2-</sup>) 2.147(4), Mn(1)–O(4) 3.06 {Mn(2)–O(7) (bridging oda<sup>2-</sup>) 2.140(4)}, Mn(1)–O(1) (monodentate oda<sup>2-</sup>) 2.178(4), Mn(1)–O(2) 2.97 {Mn(2)–O(8) (H<sub>2</sub>O) 2.123(4)}; O(3)–Mn(1)–O(1) 90.7(2) {O(7)–Mn(2)–O(8) 91.3(2)}, O(3)–Mn(1)–N(3) 85.5(2) {O(7)–Mn(2)–N(6) 98.3(2)}, O(3)–Mn(1)–N(1) 118.9(2) {O(7)–Mn(2)–N(8) 98.5(2)}, O(3)–Mn(1)–N(4) 95.8(2) {O(7)–Mn(2)–N(5) 85.9(2)}, O(1)–Mn(1)–N(1) 81.9(2) {O(8)–Mn(2)–N(8) 99.5(2)}, O(1)–Mn(1)–N(2) 93.6(2) {O(8)–Mn(2)–N(7) 91.4(2)}, O(1)–Mn(1)–N(3) 121.7(2) {O(8)–Mn(2)–N(6) 91.2(2)}, N(1)–Mn(1)–N(2) 70.30(14) {N(7)–Mn(2)–N(8) 72.46(14)}, N(3)–Mn(1)–N(4) 70.9(2) {N(5)–Mn(2)–N(6) 72.6(2)}, N(2)–Mn(1)–N(3) 84.81(14) {N(7)–Mn(2)–N(6) 90.26(14)}, N(1)–Mn(1)–N(3) 147.31(14).

Furthermore, an aqueous solution of **2** was electroinactive between the switching potentials +1.3 and –1.1 V.‡

Whereas the solid **1** was unreactive towards hydrogen peroxide complex **2** catalytically disproportionates the com-



**Fig. 2** Time course of O<sub>2</sub> evolution in H<sub>2</sub>O<sub>2</sub> disproportionation by **2** at 25 °C. Conditions: H<sub>2</sub>O<sub>2</sub> (35% w/w, 5 ml 57.1 mmol) added to solid **2** (12.6 mg, 5.13 μmol) to give a yellow solution, no colour changes were observed during the reaction. Evolved O<sub>2</sub> measured volumetrically.



**Scheme 1** Reagents and conditions: i, Mn(MeCO<sub>2</sub>)<sub>2</sub>·4H<sub>2</sub>O (4.08 mmol), octanedioic acid (4.74 mmol), refluxing ethanol (100 ml), 2 h, 76%; ii, **1** (2.04 mmol), phen (6.27 mmol), refluxing ethanol (50 ml), 0.75 h, 51%.

pound at 25 °C (Fig. 2). During the first 5 min of the reaction each molecule of **2** decomposed ca. 6 × 10<sup>3</sup> molecules of H<sub>2</sub>O<sub>2</sub>. The performance of **2** as a catalyst for this disproportionation reaction appears to be superior to that of most of the binuclear manganese catalase mimetic complexes reported thus far.<sup>11</sup>

M. D. thanks Noel O'Reilly (DIT) for technical assistance, and M. C. thanks the SRD funding scheme (DIT) for financial assistance.

Received, 19th August 1994; Com. 4/05104A

### Footnotes

† Crystal data for C<sub>128</sub>H<sub>124</sub>Mn<sub>4</sub>N<sub>16</sub>O<sub>22</sub>: *M* = 2458.17, monoclinic, *P*2<sub>1</sub>/*c* (No. 14), *a* = 15.383(2), *b* = 21.167(2), *c* = 18.288(2) Å, β = 100.853(6)°, *U* = 5854(1) Å<sup>3</sup>, *D<sub>c</sub>* = 1.35 g cm<sup>-3</sup>, *Z* = 2, *F*(000) = 2484, λ = 0.71069 Å, μ(Mo-Kα) = 0.5 mm<sup>-1</sup>. A flat yellow rectangular crystal (0.3 × 0.3 × 0.2 mm<sup>3</sup>) was mounted (Enraf-Nonius CAD4) and 9798 reflections in the θ range 1° to 25° were measured. The data was merged (*R* = 0.0490) to give 9172 unique reflections of which 6784 had |*F*<sub>obs</sub>| > 4σ|*F*<sub>obs</sub>|. The structure was refined by full-matrix least square analysis to a final *R* value of 0.0697 using SHELXS. Some disorder was present in the oda<sup>2-</sup> ligands: in the dication two possible carbonyl oxygen positions were located, whilst in the dianion the hydrocarbon chain was found to be disordered. In both cases the positions were separated and refined with half occupancy. The hydrogens were located using the AFIX routines and given common temperature factors for similar environments. A value of 1.20 was obtained for the goodness of fit after refining the weighting scheme, and the highest peak in the final difference map was 0.47 eÅ<sup>-3</sup>. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ IR (CsI matrix)  $\text{cm}^{-1}$ : **1**: 3550, 2940, 1560, 1420, 1355, 1190, 1000, 810, 710, 425; **2**: 3400, 2940, 1570, 1520, 1425, 870, 850, 730; UV-VIS **2** ( $\text{H}_2\text{O}$ ):  $\lambda = 345 \text{ nm}$  (sh).

§ A glassy carbon disk and a Pt wire were used as the working and counter electrodes, respectively. Aqueous KCl was used as supporting electrolyte, and potentials are quoted with respect to a Ag/AgCl reference electrode.

## References

- 1 E. J. Larson and V. L. Pecoraro, in *Manganese Redox Enzymes*, ed. V. L. Pecoraro, VCH, New York, 1992, ch. 1.
- 2 V. V. Barynin and A. I. Grebenko, *Dokl. Akad. Nauk. SSSR*, 1986, **286**, 461.
- 3 G. S. Algood and J. J. Perry, *J. Bacteriol.*, 1986, **168**, 563.
- 4 Y. Kono and I. Fridovich, *J. Biol. Chem.*, 1983, **258**, 6015.
- 5 (a) M. McCann, M. Devereux, C. Cardin and M. Convery, *Polyhedron*, 1994, **13**, 221; (b) M. Devereux, M. McCann, J. F. Cronin, C. Cardin, M. Convery and V. Quillet, *Polyhedron*, 1994, **13**, 2539.
- 6 R. Rardin, W. B. Tolman and S. J. Lippard, *New. J. Chem.*, 1991, **15**, 417.
- 7 J. B. Vincent, K. Folting, J. C. Huffman and G. Christou, *Inorg. Chem.*, 1986, **25**, 996.
- 8 M. Bianchi, G. Menchi, P. Frediani, F. Piacenti, A. Scrivanti and U. Matteoli, *J. Mol. Cat.*, 1989, **50**, 277.
- 9 R. J. Mureinik, *J. Inorg. Nucl. Chem. Lett.*, 1976, **38**, 1275.
- 10 B. N. Figgis and D. J. Martin, *Inorg. Chem.*, 1966, **5**, 100.
- 11 P. Mathur, M. Crowder and G. C. Dismukes, *J. Am. Chem. Soc.*, 1987, **109**, 5227; H. Sakiyama, H. Ōkawa and M. Suzuki, *J. Chem. Soc., Dalton Trans.*, 1993, 3823; H. Sakiyama, H. Ōkawa and M. Suzuki, *J. Chem. Soc., Chem. Commun.*, 1993, 882; C. Higuchi, H. Sakiyama, H. Ōkawa, R. Isobe and D. E. Fenton, *J. Chem. Soc., Dalton Trans.*, 1994, 1097; T. Nagata, Y. Ikawa and K. Maruyama, *J. Chem. Soc., Chem. Commun.*, 1994, 471; Y. Naruta and K. Maruyama, *J. Am. Chem. Soc.*, 1991, **113**, 3595; U. Bossek, M. Saher, T. Weyhermüller and K. Wieghardt, *J. Chem. Soc., Chem. Commun.*, 1992, 1780; E. J. Larson and V. L. Pecoraro, *J. Am. Chem. Soc.*, 1991, **113**, 7809; E. J. Larson and V. L. Pecoraro, *J. Am. Chem. Soc.*, 1991, **113**, 3810.