Pergamon

PII : S0277–5387(97)00002–8

Polyhedron Vol. 16, No. 15, pp. 2547–2552, 1997

0277–5387/97 $17.00+0.00

Syntheses, X-ray crystal structures and catalytic activities of the manganese(II) butanedioic acid complexes $[Mn_2(O_2C(CH_2)_2CO_2)_2(phen)_2(H_2O)_4]\cdot 2H_2O$ and $\{[Mn(O_2C(CH_2)_2CO_2)(bipy)(H_2O)_2]\cdot H_2O\}_n$

Malachy McCann,[a]* Michael T. Casey,[a] Michael Devereux,[b]
Martin Curran[b] and George Ferguson[c]

[a] Chemistry Department, St Patrick's College, Maynooth, Co. Kildare, Ireland

[b] Dublin Insitute of Technology, Cathal Brugha Street, Dublin, Ireland

[c] Department of Chemistry and Biochemistry, University of Guelph, Ontario, Canada NIG 2W1

(Received 27 November 1996; accepted 12 December 1996)

Abstract—Manganese(II) acetate reacts with an ethanolic solution of butanedioic acid (*ca* 1 : 1 mol ratio) to produce the white complex $[Mn(O_2C(CH_2)_2CO_2)(H_2O)_2]$ (**1**) in high yield. Subsequent reaction of **1** with 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy) gives the yellow crystalline products $[Mn_2(O_2C(CH_2)_2CO_2)_2(phen)_2(H_2O)_4]\cdot 2H_2O$ (**2**) and $\{[Mn(O_2C(CH_2)_2CO_2)(bipy)(H_2O)_2]\cdot H_2O\}_n$ (**3**), respectively. Complexes **2** and **3** have been structurally characterized. Complex **2** is a centrosymmetric dimeric complex in which the unique manganese(II) atom has distorted octahedral coordination geometry and is ligated by a chelating phenanthroline and two *cisoid* water molecules. A pair of butanedioic dianionic ligands bridge the two metals with each diacid using only one carboxylate oxygen from each end. Complex **3** consists of infinite zigzag chains of composition $[Mn(O_2C(CH_2)_2CO_2)(bipy)(H_2O)_2]$, in which pairs of symmetry-related manganese(II) atoms are bridged by butanedioic dianionic ligands, the carboxylate functions of which coordinate to the metals in a unidentate fashion. Each manganese atom has a distorted octahedral coordination geometry and is ligated by a chelating bipyridyl ligand, two *cisoid* water molecules and two *cisoid* carboxylate oxygen atoms from separate bridging butanedioic ligands. IR, magnetic and conductivity data for the complexes are given. Complexes **2** and **3** are significantly better catalysts than **1** for the disproportionation of H_2O_2 in the presence of added imidazole. © 1997 Elsevier Science Ltd

Keywords: manganese(II); butanedioic acid; catalyst; hydrogen peroxide; X-ray.

The increasing interest in the coordination chemistry of carboxylic acids has been fueled by the knowledge that the RCO_2^- ion often participates as an important ligand in many metalloenzymes. Recently, our efforts have focused on the preparation, characterization and reactivity of metal complexes containing dicarboxylate ligands [1–3]. We are particularly interested in the synthesis of manganese(II) carboxylates and in their ability to mimic the action of manganocatalses. Manganese catalases are relatively rare enzymes and are found in a small number of thermophilic or lactate-requiring hemeless bacteria. The enzymes protect cells against oxidative stress through their role as catalysts for the disproportionation of hydrogen peroxide [eq. (1a)].

$$2H_2O_2 \rightarrow O_2 + 2H_2O \quad E_o = 1.1\ \text{V} \qquad (1a)$$

$$H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O \quad E_o = 1.35\ \text{V} \qquad (1b)$$

$$H_2O_2 \rightarrow O_2 + 2e^- + 2H^+ \quad E_o = -0.26\ \text{V} \qquad (1c)$$

---

* Author to whom correspondence should be addressed.

In this paper we present the synthesis and structural characterization of two new manganese(II) complexes of butanedioic acid [succinic acid $HO_2C(CH_2)_2CO_2H$]. The disproportionation of hydrogen peroxide by the complexes is also discussed.

RESULTS AND DISCUSSION

Manganese(II) acetate reacted with an ethanolic solution of butanedioic acid (*ca* 1 : 1 mol ratio) to produce the white complex $[Mn(O_2C(CH_2)_2CO_2)(H_2O)_2]$ (**1**) in high yield. Subsequent reaction of **1** with 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy) gave the yellow crystalline products $[Mn_2(O_2C(CH_2)_2CO_2)_2(phen)_2(H_2O)_4]\cdot 2H_2O$ (**2**) and $\{[Mn(O_2C(CH_{22}CO_2)(bipy)(H_2O)_2]\cdot H_2O\}_n$ (**3**), respectively.

The diaqua species **1** is undoubtedly related to the structurally characterized [4] polymeric tetraaqua complex $\{[Mn(O_2C(CH_2)_2CO_2)(H_2O)_4]\}_n$, in which the octahedral manganese(II) atom is coordinated by four water molecules and a single carboxylate oxygen atom from two different *cisoid* butanedioate ligands. The metal is on an inversion centre and the centre of the CH_2—CH_2 bond is on another inversion centre to give a polymeric structure.

The X-ray crystal structure of $[Mn_2(O_2C(CH_2)_2CO_2)_2(phen)_2(H_2O)_4]\cdot 2H_2O$ (**2**) is shown in Fig. 1 and selected bond distances and angles are listed in Table 1. The complex has a centrosymmetric dimeric structure in which the unique manganese(II) atom has distorted octahedral coordination geometry. The metal is ligated by two nitrogen atoms [N(11) and N(22)] from a chelating phenanthroline molecule and two oxygen atoms from two *cisoid* water molecules. In addition, a pair of butanedioic dianionic ligands bridge the two metals with each dicarboxylate ligand using one carboxylate oxygen from each end of the diacid [O(11), O(41)]. The central $(CH_2)_2$ chains of the butanedioic ligands are maximally extended [torsion angle C(1)—C(2)—C(3)—C(4) = 179.68 (10)°] and the Mn—Mn separation is 8.1345(7) Å. The plane of the phenanthroline ligand is inclined at 6.7(1)° to the coordination plane [O(11), O(3), N(11), N(22)] and the manganese atom is 0.185(1) Å from this plane away from O4. Individual dimeric molecules are linked by a three-dimensional network of hydrogen bonds involving all of the coordinated water molecules, the water molecules of crystallization and the carboxylate oxygen atoms (Fig. 2).

The X-ray crystal structure of the polymeric complex $\{[Mn(O_2C(CH_2)_2CO_2)(bipy)(H_2O)_2]\cdot H_2O\}_n$ (**3**) is shown in Fig. 3 and selected bond distances and angles are listed in Table 2. The complex consists of infinite zigzag chains of composition $[Mn(O_2C(CH_2)_2CO_2)(bipy)(H_2O)_2]$, in which pairs of symmetry related manganese(II) atoms are bridged by butanedioic dianionic ligands, the carboxylate functions of which coordinate the metals in a unidentate fashion. Each manganese atom has a distorted octahedral coordination geometry and is ligated by two nitrogen atoms [N(11) and N(21)] from a chelating bipyridine ligand, two oxygen atoms [O(1) and O(2)] from two *cisoid* water molecules and two *cisoid* carboxylate oxygen atoms [O(11) and O(41b)] from separate bridging butanedioic ligands. Unlike the situation in $[Mn_2(O_2C(CH_2)_2CO_2)_2(phen)_2(H_2O)_4]\cdot 2H_2O$ (**2**) the butanedioic ligands in **3** have the C(1)—C(2)—C(3)—C(4) torsion angle close to gauche [75.3(2)°], while the Mn—Mn separation [8.050(1) Å] is slightly shorter than in complex **2**. The plane of the bipyridine ligand is inclined at 5.6(1)° to the coordination plane [O(11), O(2), N(11) and N(21)], in which the manganese atom lies. The infinite chain conformation is stabilized by strong intra-chain hydrogen bonding involving the carboxylate oxygen atoms, the coordinated water molecules and the water molecules of crystallization. The coordinated water

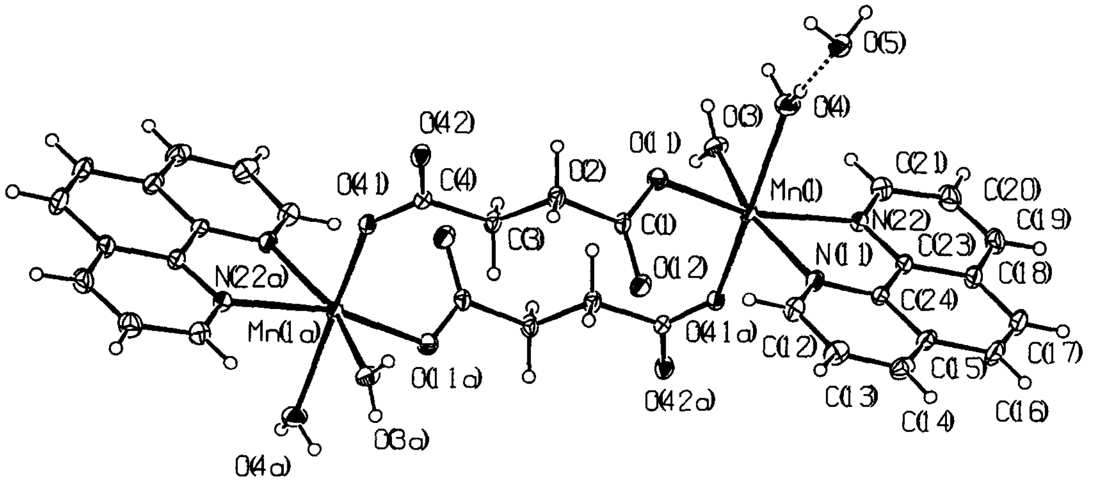

Fig. 1. A view of the centrosymmetric dimer of **2** with our numbering scheme. Thermal ellipsoids are at the 30% probability level. Atom labels ending in "a" are obtained from those of the coordinate list by the transformation $-x$, $-y$, $-z$.

Table 1. Selected bond lengths (Å) and bond angles (°) for [$Mn_2(bda)_2(phen)_2(H_2O)_4$[· $2H_2O$ (**1**)

Mn(1)—O(11)	2.1804(9)	Mn(1)—N(22)	2.3027(10)
Mn(1)—O(41)^{i}	2.1221(8)	C(1)—O(11)	1.286(2)
Mn(1)—O(3)	2.2436(9)	C(1)—O(12)	1.236(2)
Mn(1)—O(4)	2.2641(10)	C(4)—O(41)	1.265(2)
Mn(1)—N(11)	2.3106(10)	C(4)—O(42)	1.253(2)
O(41)^{i}—Mn(1)—O(11)	106.38(3)	O(4)—Mn(1)—N(22)	82.27(4)
O(41)—Mn(1)—O(3)	84.17(4)	O(41)^{i}—Mn(1)—N(11)	95.57(3)
O(11)—Mn(1)—O(3)	90.53(4)	O(11)—Mn(1)—N(11)	106.76(4)
O(41)^{i}—Mn(1)—O(4)	160.75(4)	O(3)—Mn(1)—N(11)	161.95(4)
O(11)—Mn(1)—O(4)	81.98(4)	O(4)—Mn(1)—N(11)	98.54(4)
O(3)—Mn(1)—O(4)	78.35(4)	N(22)—Mn(1)—N(11)	72.04(4)
O(41)^{i}—Mn(1)—N(22)	89.75(3)	O(12)—C(1)—O(11)	122.35(10)
O(11)—Mn(1)—N(22)	163.82(4)	O(42)—C(4)—O(41)	122.98(9)
O(3)—Mn(1)—N(22)	89.91(4)		

Symmetry transformations used to generate equivalent atoms: (i) $-x, -y, -z$.

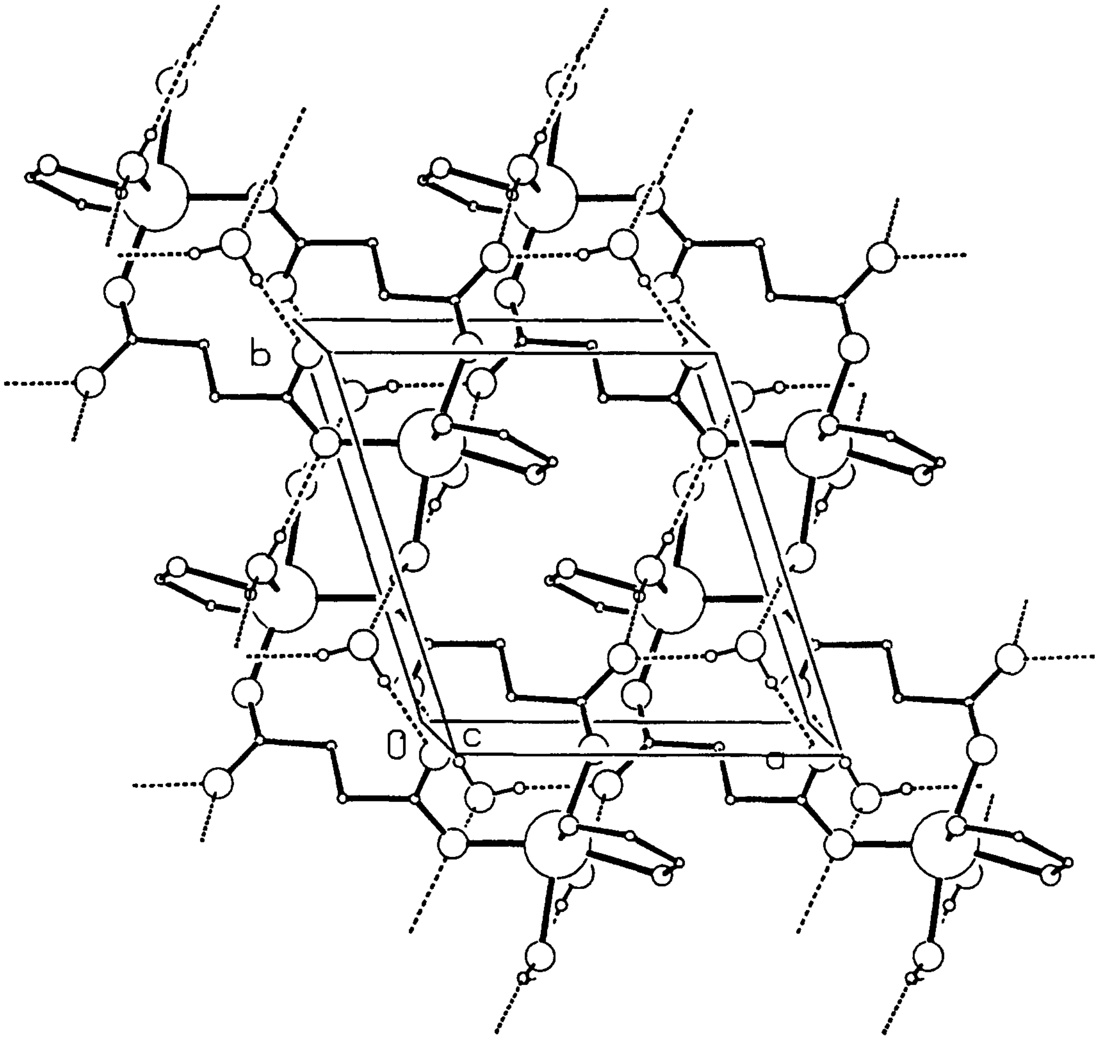

Fig. 2. A packing diagram for **2** showing the hydrogen bonding. For clarity, all the phenanthroline C atoms except two are omitted and the only H atoms shown are those of the water molecules.

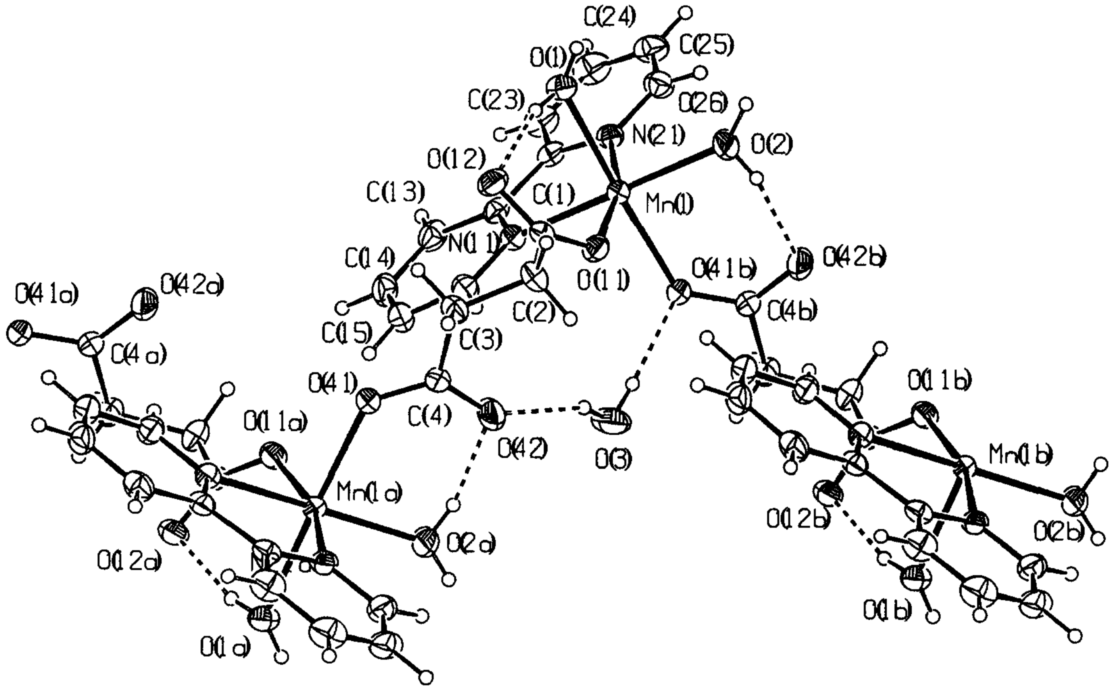

Fig. 3. A view of the part of the infinite chain system of **3** with our numbering scheme and showing the intra-chain of O—H···O hydrogen bonding. Thermal ellipsoids are at the 30% probability level. Atom labels ending in "a" and "b" are obtained from those of the coordinate list by the transformations: $-x, y+\frac{1}{2}, -z+\frac{1}{2}$ and $-x, y-\frac{1}{2}, -/+\frac{1}{2}$, respectively.

Table 2. Selected bond lengths (Å) and bond angles (°) for $\{[Mn(bda)(bipy)(H_2O)_2]\cdot H_2O\}_n$ (**2**)

Mn(1)—O(1)	2.2342(14)	C(1)—O(11)	1.256(2)
Mn(1)—O(2)	2.136(2)	C(1)—O(12)	1.253(2)
Mn(1)—O(11)	2.1452(13)	C(4)—O(42)	1.239(2)
Mn(1)—O(41)$^{\mathrm{i}}$	2.1696(13)	C(4)—O(41)	1.265(2)
Mn(1)—N(11)	2.280(2)	Mn(1)$^{\mathrm{ii}}$—O(41)	2.1696(13)
Mn(1)—N(21)	2.269(2)		
O(2)—Mn(1)—O(11)	99.47(8)	O(1)—Mn(1)—N(21)	85.32(6)
O(2)—Mn(1)—O(41)$^{\mathrm{i}}$	86.33(6)	O(2)—Mn(1)—N(11)	165.81(8)
O(11)—Mn(1)—O(41)$^{\mathrm{i}}$	91.61(5)	O(11)—Mn(1)—N(11)	94.14(5)
O(1)—Mn(1)—O(2)	91.04(6)	O(41)$^{\mathrm{i}}$—Mn(1)—N(11)	89.30(5)
O(1)—Mn(1)—O(11)	89.62(5)	O(1)—Mn(1)—N(11)	93.07(6)
O(1)—Mn(1)—O(41)$^{\mathrm{i}}$	177.25(5)	N(11)—Mn(1)—N(21)	72.06(6)
O(2)—Mn(1)—N(21)	94.77(8)	O(12)—C(1)—O(11)	123.5(2)
O(11)—Mn(1)—N(21)	164.97(6)	O(42)—C(4)—O(41)	124.8(2)
O(41)$^{\mathrm{i}}$—Mn(1)—N(21)	94.08(6)		

Symmetry transformations used to generate equivalent atoms: (i) $-x, -y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$.

molecules are also involved in inter-chain hydrogen bonding.

Complexes **1–3** had magnetic moments (*ca* $\mu_{\mathrm{eff}} = 5.9$ B.M. per Mn) in the region normally expected for isolated high spin manganese(II) d^5 complexes, i.e. those lacking any Mn—Mn interactions [5]. Aqueous solutions of **1**, **2** and **3** were highly conducting, implying that there was extensive de-coordination of the butanedioic dianionic ligands upon dissolution of the complexes in water.

$[Mn(O_2C(CH_2)_2CO_2)(H_2O)_2]$ (**1**), $[Mn_2(O_2C(CH_2)_2CO_2)_2(phen)_2(H_2O)_4]\cdot 2H_2O$ (**2**) and $\{[Mn(O_2C(CH_2)_2CO_2)(bipy)(H_2O)_2]\cdot H_2O\}_n$ (**3**) were each tested for their ability to catalyse the disproportionation of hydrogen peroxide in the presence of the added base imidazole. Under the specified experimental conditions the number of H_2O_2 molecules broken down by each manganese atom in the respective complexes during the first 1 min of the reaction was 604, 3344 and 2836, respectively. It should be noted that the concentration of H_2O_2 used in the present experiments (*ca* 11.6 M) greatly exceeds that normally expected to be found within living cells [6]. However, from the above results it is clear that the presence of bidentate chelating nitrogen donor ligands in the coordination sphere of the metal significantly enhances the ability of the manganese to disproportionate H_2O_2. A similar trend was recently observed amongst the manganese(II) hexanedioic and heptanedioic acid complexes $[Mn(O_2C(CH_2)_4CO_2)H_2O]$, $[Mn(O_2C(CH_2)_4CO_2)(phen)_2H_2O]\cdot7H_2O$, $[Mn(O_2C(CH_2)_5CO_2)]$ and $[Mn(phen)_2(H_2O)_2][Mn(O_2C$

Table 3. Summary of crystal data, data collection, structure solution and refinement details

	Complex **2**	Complex **3**
(a) Crystal data		
Formula	$C_{32}H_{32}Mn_2N_4O_{12}\cdot2(H_2O)$	$C_{14}H_{16}MnN_2O_6\cdot H_2O$
Molar mass	810.52	381.24
Colour, habit	Colourless, plate	Colourless, block
Crystal size, mm	0.42 × 0.42 × 0.21	0.42 × 0.40 × 0.39
Crystal system	Triclinic	Monoclinic
a (Å)	8.2564(6)	8.2952(6)
b (Å)	8.3943(6)	11.5596(9)
c (Å)	12.8793(11)	17.0774(15)
α ( )	95.365(9)	90
β ( )	104.560(6)	95.194(9)
γ ( )	106.718(6)	90
V (A³)	814.09(11)	1630.8(2)
Space group	$P\bar{1}$	$P2_1/c$
Z	1	4
Molecular symmetry	−1	None
F(000)	418	788
d_{calc} (g cm^{-3})	1.653	1.553
μ (mm^{-1})	0.855	0.848
(b) Data acquisition[a]		
Temperature (K)	294(1)	294(1)
Unit-cell reflections (θ-range °)	25 (19.3 29.0)	25 (10.0 17.3)
Maximum θ (°) for reflections	35	27
hkl range of reflections (%)	−13 12; 0 13; −20 20	−10 10; 0 14; 0.21
Variation in 3 standard reflections	1.0	1.5
Reflections measured	7139	3782
Unique reflections	7139	3549
R_{int}	0	0.018
Reflections with $I > 2\sigma(I)$,	5584	2850
Absorption correction type	Gaussian integration	ψ-scans
Minimum, maximum absorption correction	0.7108, 0.8481	0.6963, 0.7826
(c) Structure solution and refinement		
Refinement on	F^2	F^2
Solution method	Patterson heavy-atom	Patterson heavy atom
H-atom treatment	O—H refined, C—H riding	Riding
No. of variables in L.S. weights:	255	239
k in $w = 1/(\sigma^2F_o^2+k)$	$(0.0466P)^2+0.1225P$	$(0.0473P)^2+0.3937P$
$[P = (F_o^2+2F_c^2)/3]$		
R, R_w, gof	0.031, 0.086, 1.01	0.030, 0.085, 1.05
Density range in final Δ-map (e Å^{-3})	−0.309, 0.409	−0.265, 0.332
Final shift/error ratio	0.000	0.001
Secondary extinction type	SHELXL	SHELXL
Secondary extinction correction	0.023(2)	0.008(1)

[a] Data collection on an Enraf–Nonius CAD4 diffractometer with graphite monochromatized MO-K_α radiation (λ 0.71067 Å).

[b] All calculations were done on a Silicon Graphics 4D-35TG computer system with the NRCVAX system of programs (E.J. Gabe, Y. Le Page, J.-P. Charland, F. L. Lee and P. S. White, *J. Appl. Cryst.* 1989, **22,** 384) for refinement with observed data on *F*, or with SHELXL-93 (G.M. Sheldrick, 1993) for refinement with all data on F^2.

$(CH_2)_5CO_2)$ $(phen)_2H_2O]$ $(O_2C(CH_2)_5CO_2)\cdot 12.5H_3O$, respectively, where again the phenanthroline adducts proved to the better catalysts for hydrogen peroxide disproportionation [7].

EXPERIMENTAL

Chemicals were purchased from commercial sources and used without further purification. Instrumentation and microanalysis were as described previously [1, 2].

Crystallography

The crystals lost solvent when exposed to air and for the data collection suitable crystals were chosen and quickly coated with epoxy adhesive. The structures were solved *via* the heavy-atom method. Details of cell data, data collection, solution and refinement for **2** and **3** are summarized in Table 3. All water H atoms were clearly located in difference maps. The crystal of **2** diffracted unusually well and it was possible to measure intensity data to 2-theta of 70° with Mo radiation (well beyond the limits of the Cu sphere).

$[Mn(O_2C(CH_2)_2CO_2)(H_2O)_2]$ (**1**)

To a solution of butanedioic acid (1.05 g, 8.89 mmol) in ethanol (80 cm^3) was added $Mn(CH_3CO_2)_2\cdot 4H_2O$ (2.00 g, 8.16 mmol). The mixture was refluxed for 2 h and the product formed as a colourless solid. The suspension was allowed to cool to room temperature and then the product was filtered off. The solid was washed with two portions of ethanol and then air-dried at *ca* 25°C. Yield 1.45 g (86%). Found: C, 22.2; H, 3.2. Calc: C, 23.2; H, 3.9%. IR (KBr matrix): 3415, 2986, 1535, 1427, 1219, 837, 675, 601, 574 cm^{-1}. $\mu_{eff} = 5.96$ B.M. $\Lambda_M(H_2O) = 242$ S cm^2 mol^{-1}. The complex was soluble in water and insoluble in all other common solvents.

$[Mn_2(O_2C(CH_2)_2CO_2)_2(phen)(H_2O)_4]\cdot 2H_2O$ (**2**)

To a suspension of **1** (0.60 g, 2.90 mmol) in ethanol (80 cm^3) was added 1,10-phenanthroline (0.63 g, 3.50 mmol). The resulting mixture was refluxed for 2 h and on cooling to room temperature the bright yellow product precipitated. The solid was filtered off and then recrystallized from hot water to give light yellow crystals. The crystals were filtered off, washed with two small portions of cold water and then allowed to air dry. Yield: 0.49 g (42%). Found: C, 47.0; H, 4.6; N, 7.2. Calc: C, 47.4; H, 4.5; N, 6.9%. IR (KBr matrix): 3422, 3207, 3073, 2993, 1582, 1434, 1381, 850, 729, 675 cm^{-1}. $\mu_{eff} = 5.70$ B.M. per Mn. $\Lambda_M(H_2O) = 258$ S cm^2 mol^{-1}. The complex was soluble in warm water and insoluble in all other common solvents.

$\{[Mn(O_2C(CH_2)_2(bipy)(H_2O)_2]\cdot H_2O\}_n$ (**3**)

To a solution of **1** (0.50 g, 2.42 mmol) in water (70 cm^3) was added 2,2′-bipyridine (0.42 g, 2.69 mmol) and the mixture was then refluxed for 2 h to give a golden-brown solution. The solution was allowed to cool to room temperature and upon standing for several days yellow crystals of the product were deposited. The solid was filtered off, washed with two small portions of cold water and then allowed to dry in air. Yield: 0.58 g (63%). Found: C, 44.2; H, 4.7; N, 7.5. Calc: C, 44.1; H, 4.8; N, 7.4%. IR (KBr matrix): 3543, 3315, 3073, 2979, 2925, 1562, 1441, 1407, 1293, 1179, 1025, 776, 642 cm^{-1}. $\mu_{eff} = 6.00$ B.M. per Mn. $\Lambda_M(H_2O) = 154$ S cm^2 mol^{-1}. The complex was soluble in water and insoluble in all other common solvents.

Hydrogen peroxide disproportionation studies

Aqueous H_2O_2 (35% w/w. 10 cm^3, 114 mmol) was added to a solid mixture comprising the complex (*ca* 10 mg) and imidazole (50 mg) and the combination was stirred and thermostatted at 25°C. The evolved O_2 was measured volumetrically. It should be noted that in the absence of imidazole the complexes were practically inactive towards peroxide.

Acknowledgement—MC acknowledges the SRD funding scheme (DIT) for financial assistance.

REFERENCES

1. McCann, M., Casey, M. T., Devereux, M., Curran, M., Cardin, C. and Todd, A., *Polyhedron*, 1996, **15,** 2117.
2. McCann, M., Cronin, J. F., Devereux, M. and Ferguson, G., *Polyhedron*, 1995, **14,** 2379.
3. Casey, M. T., McCann, M., Devereux, M. Curran, M., Cardin, C., Convery, M., Quillet, V. and Harding, C., *J. Chem. Soc., Chem. Commun.*, 1994, 2463.
4. Gupta, M. P., Sahu, R. D., Ram, R. and Maulik, P. R., *Z. Kristallogr.*, 1983, **163,** 155.
5. Cotton, F. A. and Wilkinson, G., *Advanced Inorganic Chemistry*, 5th edn. Wiley, New York, 1988, p. 702.
6. Shank, M., Barynin, V. and Dismukes, G. C., *Biochemistry*, 1994, **33,** 15433, and refs therein.
7. McCann, M., Casey, M. T., Devereux, M., Curran, M. and McKee, V., *Polyhedron*, in press.