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Manganese(II) complexes of hexanedioic and heptanedioic acids: X-ray crystal structures of [Mn(O₂C(CH₂)₄CO₂)(phen)₂H₂O] · 7H₂O and [Mn(phen)₂(H₂O)₂][Mn(O₂C(CH₂)₅CO₂)(phen)₂H₂O](O₂C(CH₂)₅CO₂) · 12.5H₂O

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Abstract—$Mn(CH_3CO_2)_2 \cdot 4H_2O$ reacts with ethanolic solutions of hexanedioic and heptanedioic acids (*ca* 1 : 1 mol ratio) to produce the respective manganese(II) complexes $[Mn(O_2C(CH_2)_4CO_2)H_2O]$ (1) and $[Mn(O_2C-(CH_2)_5CO_2)]$ (2). Subsequent reaction of 1 and 2 with 1,10-phenanthroline (phen) (*ca* 1 : 2 mol ratio) in aqueous ethanol gives $[Mn(O_2C(CH_2)_4CO_2)(phen)_2H_2O] \cdot 7H_2O$ (3) and $[Mn(phen)_2(H_2O)_2][Mn(O_2C(CH_2)_5CO_2 (phen)_2H_2O](O_2C(CH_2)_5CO_2) \cdot 12.5H_2O$ (4), respectively. Complexes 3 and 4 have been structurally characterised. The asymmetric unit in 3 has a manganese(II) atom coordinated to four nitrogen atoms from two chelating phenanthroline ligands, one oxygen atom from a unidentate $(O_2C(CH_2)_4CO_2)^{-2}$ ligand and one oxygen atom from a water molecule which is in a *cisoid* position with respect to the diacid ligand. The asymmetric unit in 4 contains two mononuclear manganese(II) species, the dication $[Mn(phen)_2(H_2O)_2]^{2+}$ and the neutral manganese heptanedioate complex $[Mn(O_2(CH_2)_5CO_2)(phen)(H_2O)]$, along with a non-coordinated $(O_2C(CH_2)_5CO_2)^{2-}$ counter dianion. In the dication $[Mn(phen)_2(H_2O)_2]^{2+}$ the manganese atom is coordinated to four nitrogen atoms from two chelating phenanthroline ligands and two oxygen atoms from two *cisoid* water molecules. In the neutral fragment $[Mn(O_2C(CH_2)_5CO_2)(phen)_2(H_2O)]$ the metal atom is coordinated to four nitrogen atoms from two chelating phenanthroline ligands, one oxygen atom from a unidentate $(O_2C(CH_2)_5CO_2)^{2-}$ ligand and one oxygen atom from a water molecule which is *cis* with respect to the coordinated carboxylate oxygen of the heptanedioate ligand. IR, magnetic and conductivity data for the complexes are given. All four complexes are catalysts for the disproportionation of H_2O_2 in the presence of added imidazole. © 1997 Elsevier Science Ltd

As part of our ongoing efforts to synthesise and structurally characterise molybdenum(II) [1], copper(II) [2,3] and manganese(II) [4] complexes of α,ω-dicarboxylic acids we report here the preparation and properties of manganese(II) complexes of hexanedioic acid $(HO_2C(CH_2)_4CO_2H)$ and heptanedioic acid

$(HO_2C(CH_2)_5CO_2H)$. X-ray crystallographic details for two complexes are given along with results for the catalytic disproportionation of hydrogen peroxide by all of the new complexes.

RESULTS AND DISCUSSION

$Mn(CH_3CO_2)_2 \cdot 4H_2O$ reacted with ethanolic solutions of hexanedioic and heptanedioic acids (*ca* 1 : 1

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mol ratio) to produce the white manganese(II) complexes $[Mn(O_2C(CH_2)_4CO_2)H_2O]$ (**1**) and $[Mn(O_2C-(CH_2)_5CO_2]$ (**2**), respectively, in almost quantitative yield. Subsequent reaction of **1** and **2** with 1,10-phenanthroline (phen) (*ca*, 1 : 2 mol ratio) in aqueous ethanol gave good yields of the respective yellow, crystalline complexes $[Mn(O_2C(CH_2)_4CO_2)(phen)_2 H_2O] \cdot 7H_2O$ (**3**) and $[Mn(phen)_2(H_2O)_2][Mn(O_2C (CH_2)_5CO_2)(phen)_2H_2O](O_2C(CH_2)_5CO_2) \cdot 12.5H_2O$ (**4**).

The X-ray crystal structure of $[Mn(O_2C-(CH_2)_4CO_2)(phen)_2(H_2O)] \cdot 7H_2O$ (**3**) is shown in Fig. 1, and selected bond lengths and angles are listed in Table 1. The asymmetric unit has a manganese atom coordinated to four nitrogen atoms [N(1a), N(2a), N(1b) and N(2b)] from two chelating phenanthroline ligands, one oxygen atom from a unidentate $O_2C(CH_2)_4CO_2]^{2-}$ ligand [Mn—O(21) = 2.1395(13) Å] and one oxygen atom from a water molecule [Mn—O(1) = 2.154(2) Å] which is in a *cisoid* position with respect to the $O_2C(CH_2)_4CO_2]^{2-}$ ligand. The pendant carboxylate oxygen atoms of the $(O_2C(CH_2)_4CO_2)^{2-}$ ligand [O(23) and O(24)] are uncoordinated. The manganese atom is six-coordinate but quite far removed from regular octahedral geometry due to the small bite angles of the phenanthroline ligands [N(1a)—Mn—N(2a) = 72.94(6)°,

N(2b)—Mn—N(1b) = 72.86(6)°]. The mean planes of the phenanthroline ligands are inclined to each other at an angle of 80.74(3)°. There is a single intramolecular hydrogen bond between the uncoordinated carboxylate oxygen atom O(22) and the coordinated water molecule [O(22)---O(1) = 2.619(2) Å]. In addition, there is an extensive hydrogen bonding network through the crystal, involving all of the water molecules as well as the $(O_2C(CH_2)_4CO_2)^{2-}$ ligand. There are also significant intermolecular π-π interactions between the phenanthroline ligands as can be seen in the packing plot projected down the z axis (Fig. 2).

The X-ray crystal structure of $[Mn(phen)_2(H_2O)_2]$ $[Mn(O_2C(CH_2)_5CO_2)(phen)_2H_2O](O_2CH_2)_5CO_2) \cdot 12.5H_2O$ (**4**) is shown in Fig. 3, and selected bond lengths and angles are listed in Table 2. The asymmetric unit contains two mononuclear manganese(II) species, the dication $[Mn(phen)_2(H_2O)_2]^{2+}$ and the neutral manganese heptanedioate complex $[Mn(O_2C-(CH_2)_5CO_2)(phen)_2(H_2O)]$, along with a non-coordinated heptanedioate counter dianion and 13 solvate water molecules (one of which [O(13w)] was refined with 50% occupancy). In the dication $[Mn(phen)_2 (H_2O)_2]^{2+}$ (Fig. 4) the manganese atom [Mn(1)] is coordinated to four nitrogen atoms [N(1a), N(2a), N(1b) and N(2b)] from two chelating phenanthroline
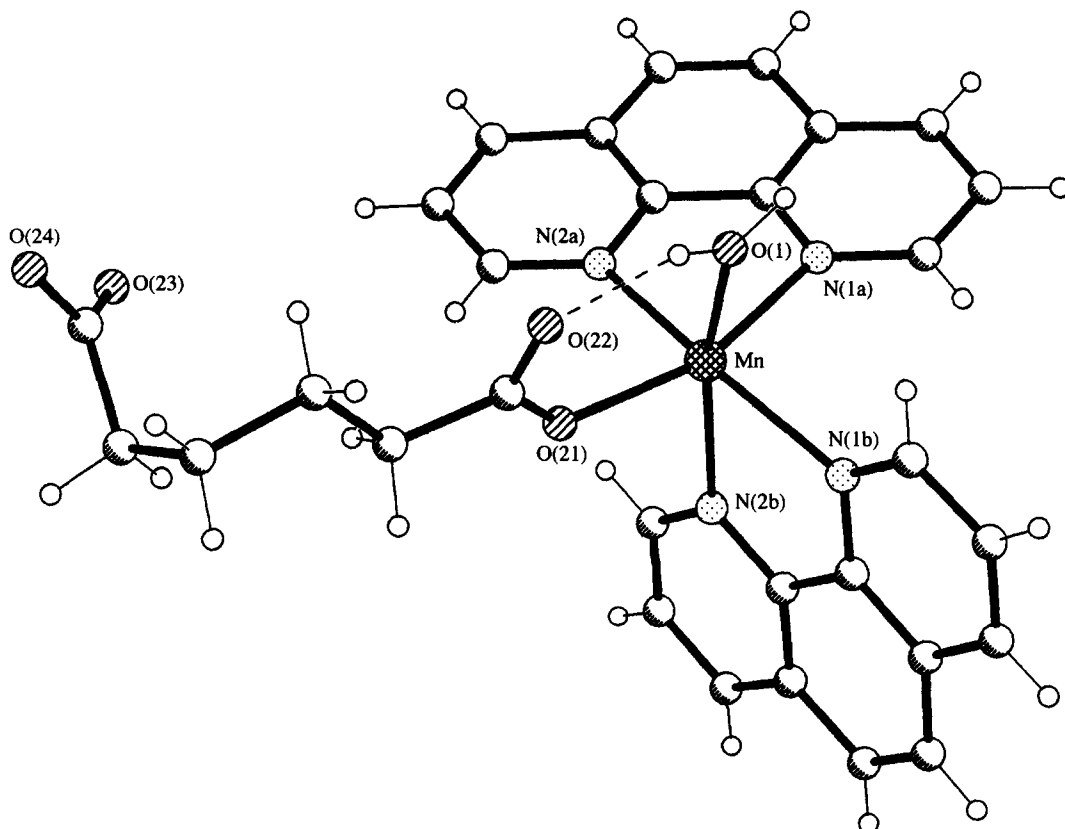

Fig. 1. X-ray crystal structure of $[Mn(O_2C(CH_2)_4CO_2(phen)_2(H_2O)] \cdot 7H_2O$ (**3**) (water molecules of crystallization not shown).

Table 1. Selected bond lengths (Å) and bond angles (°) for [Mn(O$_2$C(CH$_2$)$_4$CO$_2$)(phen)$_2$ (H$_2$O)]·7H$_2$O (3)

Mn—O(21)	2.1395(13)	Mn—O(1)	2.154(2)
Mn—N(2b)	2.271(2)	Mn—N(1a)	2.276(2)
Mn—N(2a)	2.282(2)	Mn—N(1b)	2.292(2)
O(21)—Mn—O(1)	88.19(6)	O(21)—Mn—N(2b)	91.02(5)
O(1)—Mn—N(2b)	161.80(6)	O(21)—Mn—N(1a)	161.68(6)
O(1)—Mn—N(1a)	91.11(6)	N(2b)—Mn—N(1a)	95.24(6)
O(21)—Mn—N(2a)	89.45(6)	O(1)—Mn—N(2a)	103.81(6)
N(2b)—Mn—N(2a)	94.37(6)	N(1a)—Mn—N(2a)	72.94(6)
O(21)—Mn—N(1b)	102.36(6)	O(1)—Mn—N(1b)	89.55(6)
N(2b)—Mn—N(1b)	72.86(6)	N(1a)—Mn—N(1b)	95.94(6)
N(2a)—Mn—N(1b)	162.54(6)		
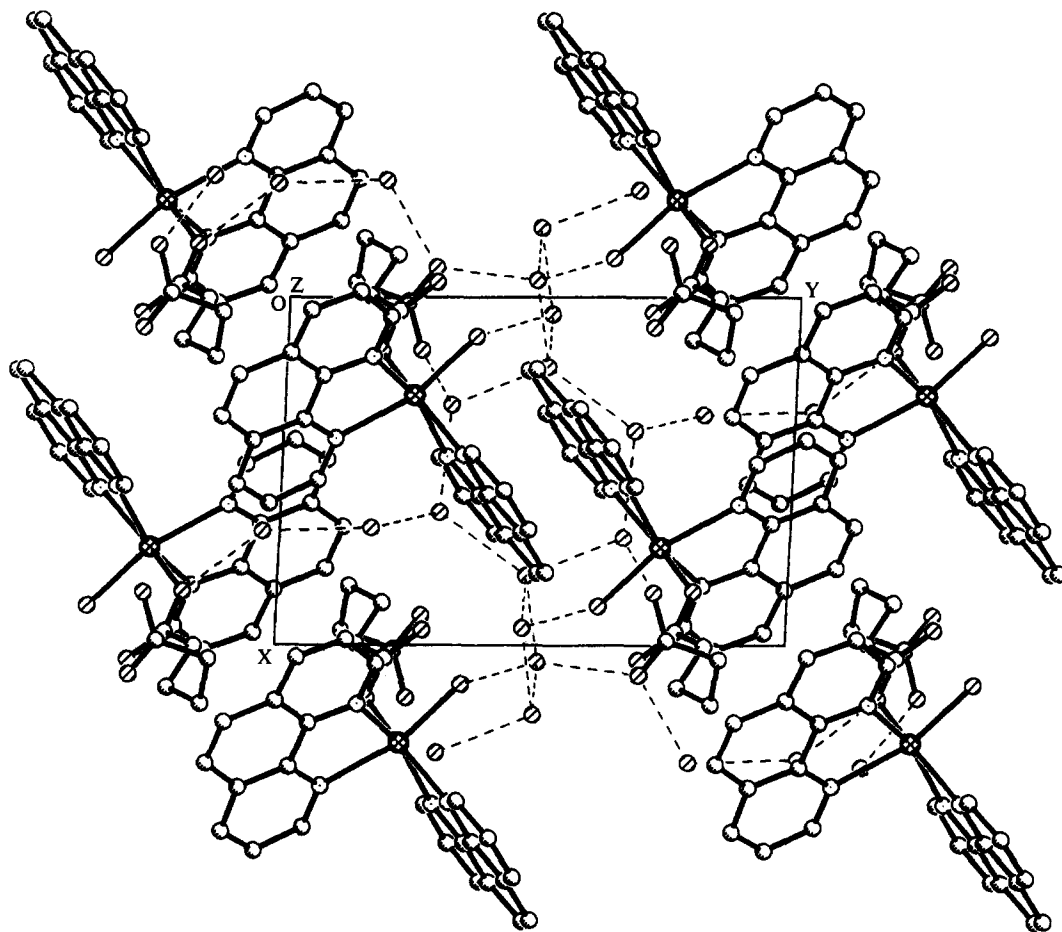
Fig. 2. Packing diagram for (3) viewed down the z axis.

ligands and two oxygen atoms [O(1a) and O(1b)] from two *cisoid* water molecules. Mn(1) is six-coordinate but quite far removed from regular octahedral geometry due to the small bite angles of the phenanthroline ligands [N(1a)—Mn(1)—N(2a) = 66.4 (2)°, N(1b)—Mn(1)—N(2b) = 70.8(2)°] which chelate Mn(1) in a highly asymmetric fashion [Mn(1)—N(1a) = 2.149(4) Å, Mn(1)—N(2a) = 2.402(5) Å; Mn(1)—N(1b) = 2.087(4) Å, Mn(1)—N(2b) =

2.319(4) Å]. The mean planes of the phenanthroline ligands are inclined to each other at an angle of 78.2(1)° about Mn(1).

In the neutral fragment [Mn(O$_2$C(CH$_2$)$_5$CO$_2$) (phen)$_2$(H$_2$O)] (Fig. 5) the manganese atom [Mn(2)] is coordinated to four nitrogen atoms [N(1c), N(2c), N(1d) and N(2d)] from two chelating phenanthroline ligands, one oxygen atom from a unidentate (O$_2$C(CH$_2$)$_5$CO$_2$)$^{2-}$ ligand [Mn(2)—O(10) =

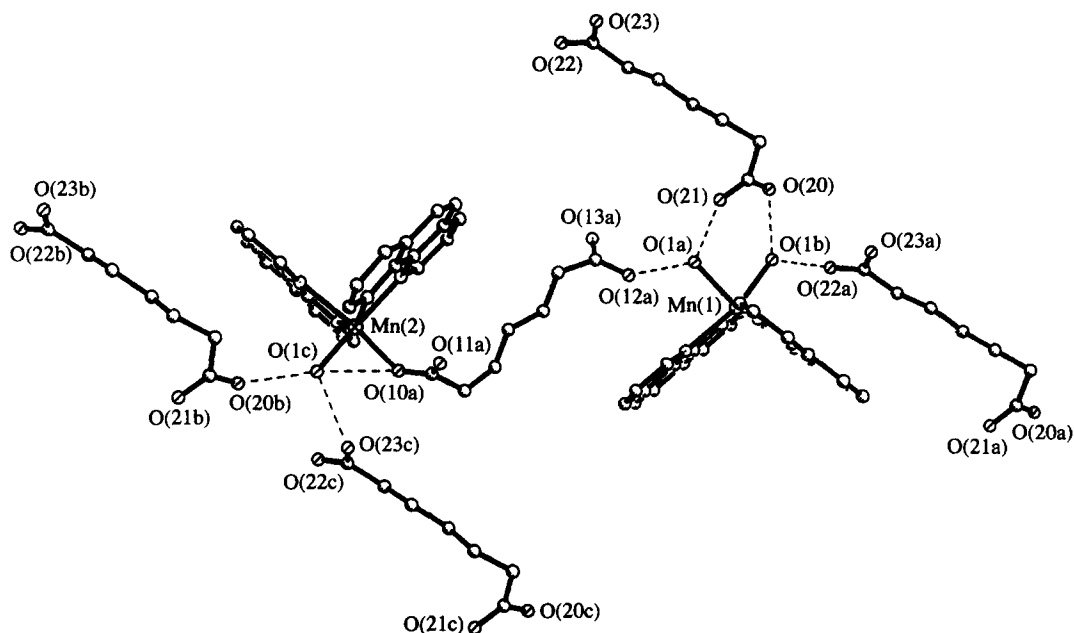Fig. 3. X-ray crystal structure of [Mn(phen)$_2$(H$_2$O)$_2$][Mn(O$_2$C(CH$_2$)$_5$CO$_2$)(phen)$_2$(H$_2$O)](O$_2$C(CH$_2$)$_5$CO$_2$)·12.5H$_2$O (4). Water molecules of crystallization are not shown.

Table 2. Selected bond lengths (Å) and bond angles (°) for [Mn(phen)$_2$(H$_2$O)$_2$][Mn(O$_2$C (CH$_2$)$_5$CO$_2$)(phen)$_2$H$_2$O)](O$_2$C(CH$_2$)$_5$CO$_2$)·12.5H$_2$O (4)

Mn(1)—N(1b)	2.087(4)	Mn(1)—O(1b)	2.113(4)
Mn(1)—N(1a)	2.149(4)	Mn(1)—O(1a)	2.151(4)
Mn(1)—N(2b)	2.319(4)	Mn(1)—N(2a)	2.402(5)
Mn(2)—O(10)	2.093(4)	Mn(2)—O(1c)	2.104(4)
Mn(2)—N(2d)	2.131(4)	Mn(2)—N(1c)	2.194(5)
Mn(2)—N(1d)	2.289(5)	Mn(2)—N(2c)	2.406(4)
N(1b)—Mn(1)—O(1b)	97.1(2)	N(1b)—Mn(1)—N(1a)	152.6(2)
O(1b)—Mn(1)—N(1a)	101.5(2)	N(1b)—Mn(1)—O(1a)	101.6(2)
O(1b)—Mn(1)—O(1a)	83.11(14)	N(1a)—Mn(1)—O(1a)	100.5(2)
N(1b)—Mn(1)—N(2b)	70.8(2)	O(1b)—Mn(1)—N(2b)	162.2(2)
N(1a)—Mn(1)—N(2b)	94.6(2)	O(1a)—Mn(1)—N(2b)	86.6(2)
N(1b)—Mn(1)—N(2a)	93.8(2)	O(1b)—Mn(1)—N(2a)	90.1(2)
N(1a)—Mn(1)—N(2a)	66.4(2)	O(1a)—Mn(1)—N(2a)	163.8(2)
N(2b)—Mn(1)—N(2a)	103.3(2)	O(10)—Mn(2)—O(1c)	89.8(2)
O(10)—Mn(2)—N(2)	111.0(2)	O(1c)—Mn(2)—N(2d)	96.0(2)
O(10)—Mn(2)—N(1c)	93.8(2)	O(1c)—Mn(2)—N(1c)	103.7(2)
N(2d)—Mn(2)—N(1c)	148.4.(2)	O(10)—Mn(2)—N(1d)	91.9(2)
O(1c)—Mn(2)—N(1d)	165.1(2)	N(2d)—Mn(2)—N(1d)	69.6(2)
N(1c)—Mn(2)—N(1d)	91.0(2)	O(10)—Mn(2)—N(2c)	158.9(2)
O(1c)—Mn(2)—N(2c)	91.39(14)	N(2d)—Mn(2)—N(2c)	89.8(2)
N(1c)—Mn(2)—N(2c)	65.4(2)	N(1d)—Mn(2)—N(2c)	92.3(2)

2.093(4) Å] and one oxygen atom from a water molecule [Mn(2)—O(1c) = 2.104(4) Å[which is in a *cisoid* position with respect to the coordinated carboxylate oxygen of the (O$_2$C(CH$_2$)$_5$CO$_2$)$^{2-}$ ligand. The oxygen atoms of the pendant carboxylate group [O(12) and O(13)] and the carboxylate oxygen O(11) are uncoordinated. Like Mn(1), Mn(2) is quite far removed from regular octahedral geometry due to the small bite angles of the phenanthroline ligands

[N(1c)—Mn(2)—N(2c) = 65.4(2)°, N(2d)—Mn(2) —N(1d) = 69.6(2)°] which chelate Mn(2) in a highly asymmetric fashion [Mn(2)—N(1c) = 2.194(5) Å, Mn(2)—N(2c) = 2.406(4) Å; Mn(2)—N(1d) = 2.289(5) Å, Mn(2)—N(2d) = 2.131(4)Å]. The mean planes of the phenanthroline ligands are inclined to each other at an angle of 88.2(1)° about Mn(2).

Within [Mn(O$_2$C(CH$_2$)$_5$CO$_2$)(phen)$_2$(H$_2$O)] there is a hydrogen bond between the coordinated carboxylate
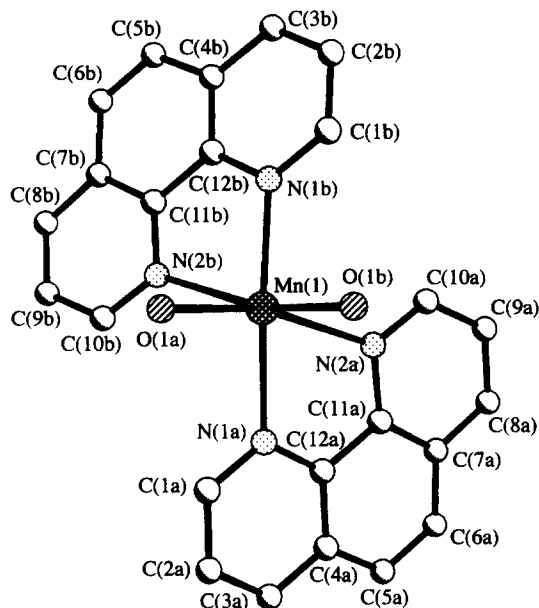
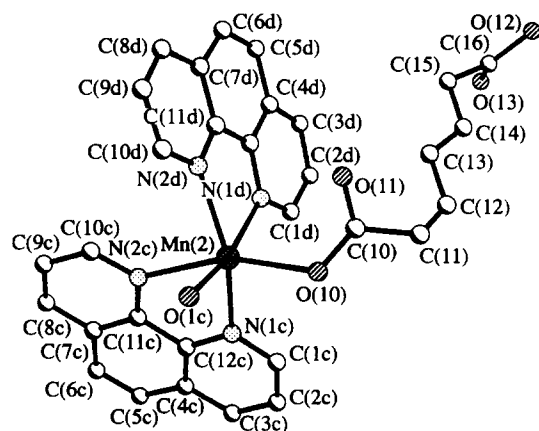Fig. 4. Structure of the [Mn(phen)$_2$(H$_2$O)$_2$]$^{2+}$ dication in (4).

Fig. 5. Structure of the neutral component [Mn(O$_2$C-(CH$_2$)$_5$CO$_2$)(phen)$_2$(H$_2$O)] in (4).

oxygen atom [O(10)] and the coordinated water molecule [O(1c)] (Fig. 3). There is an extensive hydrogen bonding network through the crystal, involving all of the water molecules (both coordinated and non-coordinated) as well as the coordinated (O$_2$C (CH$_2$)$_5$CO$_2$)$^{2-}$ ligand and the (O$_2$C(CH$_2$)$_5$CO$_2$)$^{2-}$ counter anion. In addition, there are significant inter-molecular π–π interactions between the phen-anthroline ligands which can be seen in the packing plot projected down the x-axis (Fig. 6).

Although the X-ray crystal structure of [Mn (phen)$_2$ (H$_2$O)$_2$] [Mn(O$_2$C(CH$_2$)$_5$CO$_2$) (phen)$_2$ (H$_2$O)] (O$_2$C(CH$_2$)$_5$CO$_2$) · 12.5H$_2$O (4) is unique, the [Mn(O$_2$C(CH$_2$)$_5$CO$_2$)(phen)$_2$(H$_2$O)] moiety of the complex is isostructural with [Mn(O$_2$C(CH$_2$)$_4$ CO$_2$)(phen)$_2$(H$_2$O)] (3) (Fig. 1). However, in the [Mn(O$_2$C(CH$_2$)$_5$CO$_2$)(phen)$_2$(H$_2$O)] fragment of 4

the chelating phenanthroline ligands are unsym-metrical and the Mn—O(carboxylate) [Mn(2)—O(10) = 2.093(4) Å] and Mn—O(water) [Mn(2)—O(1c) = 2.104(4) Å] bond distances are shorter than in complex 3 [Mn—O(carboxylate) = 2.1395(13) Å, Mn—O(water) = 2.154(2) Å].

The only other known structurally characterised mononuclear complexes containing medium length saturated aliphatic dicarboxylic acids are the cop-per(II) species [Cu(O$_2$C(CH$_2$)$_5$CO$_2$)(phen)$_2$] · 11.73 H$_2$O and [Cu(O$_2$C(CH$_2$)$_6$CO$_2$)(phen)$_2$] · 12H$_2$O [2]. However, in contrast to the unidentate coordination mode of the diacids in the present manganese com-plexes the dicarboxylate ligands in these copper com-plexes are chelating through one of the carboxylate moieties, the other carboxylate group remaining unco-ordinated. The structures of 3 and the [Mn(O$_2$C-(CH$_2$)$_5$CO$_2$)(phen)$_2$H$_2$O] component of 4 are also quite different from that of the polymeric nickel(II) hexanedioate complex {[Ni(O$_2$C(CH$_2$)$_4$CO$_2$) (H$_2$O)$_4$]}$_n$ [5]. In the latter species the metal is coor-dinated by a single carboxylate oxygen from two transoid diacid ligands. A single carboxylate oxygen from the opposite ends of the diacid ligands is joined to a neighbouring metal centre, thus generating a poly-meric chain.

Aqueous solutions of 1–4 were highly conducting, implying that there was extensive de-coordination of the dianionic diacid ligands upon dissolution of the complexes in water. As expected, complex 4, which already has ionic components in the solid state {[Mn(phen)$_2$(H$_2$O)$_2$]$^{2+}$ and (O$_2$C(CH$_2$)$_5$CO$_2$)$^{2-}$}, was the best conductor (Λ$_M$(H$_2$O) = 219 S cm^2 mol^{-1}).

[Mn(O$_2$C(CH$_2$)$_4$CO$_2$)H$_2$O] (1), [Mn(O$_2$C(CH$_2$)$_5$ CO$_2$)] (2), [Mn(O$_2$C(CH$_2$)$_4$CO$_2$)(phen)$_2$H$_2$O] · 7H$_2$O (3) and [Mn(phen)$_2$(H$_2$O)$_2$][Mn(O$_2$C(CH$_2$)$_5$CO$_2$) (phen)$_2$H$_2$O](O$_2$C(CH$_2$)$_5$CO$_2$) · 12.5H$_2$O (4) were each tested for their ability to catalyse the dis-proportionation of hydrogen peroxide in the presence of the added base imidazole. The number of H$_2$O$_2$ molecules broken down by each manganese atom in the respective complexes during the first 1 min of the reaction was 1196, 1738, 5470 and 5794, respectively. These figures clearly demonstrate that the presence of the bidentate chelating nitrogen donor ligand phen-anthroline in the coordination sphere of the metal significantly enhances the ability of the manganese to disproportionate H$_2$O$_2$. A similar trend has been observed amongst the manganese(II) butanedioic acid complexes [Mn(O$_2$C(CH$_2$)$_2$CO$_2$)(H$_2$O)$_2$], [Mn$_2$(O$_2$C-(CH$_2$)$_2$CO$_2$)$_2$(phen)$_2$(H$_2$O)$_4$] · 2H$_2$O and {[Mn(O$_2$C-(CH$_2$)$_2$CO$_2$)(bipy)(H$_2$O)$_2$] · H$_2$O}$_n$, where again the phenanthroline and 2,2'bipyridine (bipy) species were found to be the more aggressive peroxide dis-proportionation catalysts [6].

EXPERIMENTAL

Chemicals were purchased from commercial sour-ces and used without further purification. Instru-
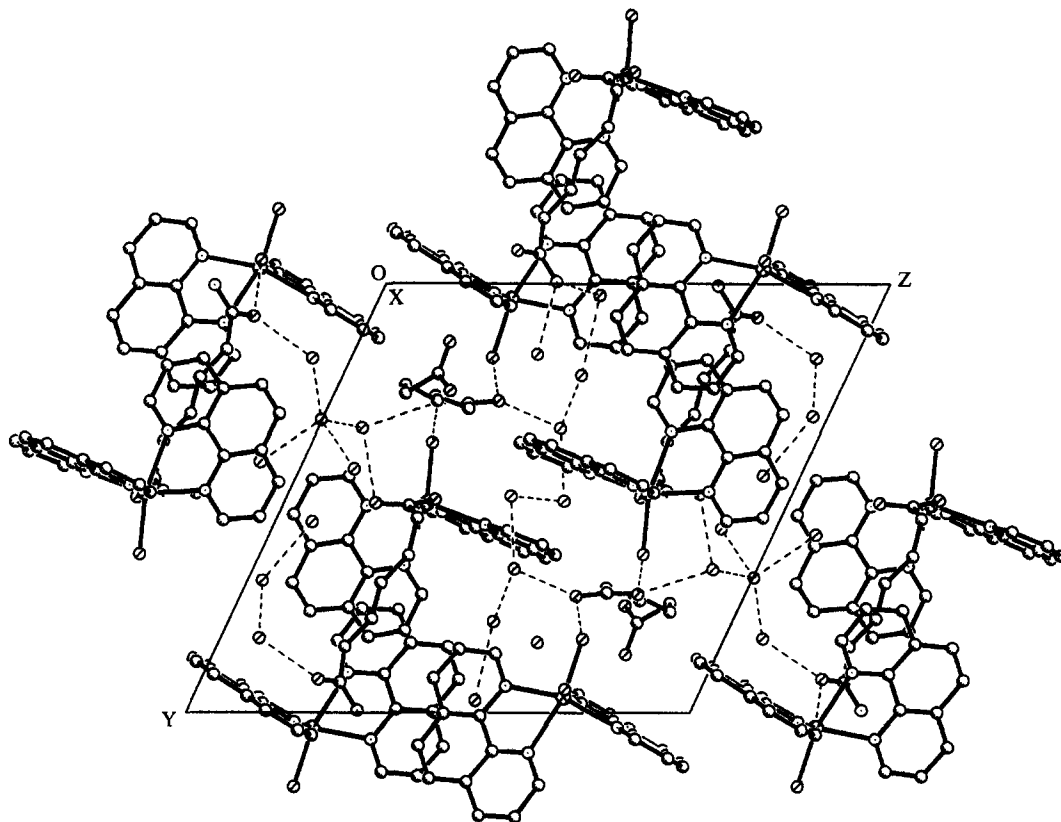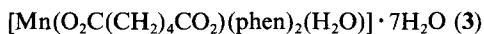
Fig. 6. Packing diagram for (**4**) projected down the x axis.

mentation and microanalysis were as described previously [2].

[Mn(O₂C(CH₂)₄CO₂)(phen)₂(H₂O)] · 7H₂O (3)

$[Mn(O_2C(CH_2)_4CO_2)(phen)_2(H_2O)] \cdot 7H_2O$ (**3**)

Crystal data

$C_{31}H_{40}MnN_4O_{12}$, $M_r = 703.60$, yellow block, $0.80 \times 0.52 \times 0.43$ mm, triclinic, space group $P\bar{1}$, $a = 9.045(1)$, $b = 13.667(1)$, $c = 14.931(2)$ Å, $\alpha = 69.967(8)$, $\beta = 74.40(1)$, $\gamma = 87.19(1)°$, $U = 1668.4(5)$ Å³, $\mu = 0.464$ mm⁻¹, $Z = 2$, $F(000) = 738$, $\lambda = 0.71073$ Å.

Data collection and processing

Data were collected at room temperature on a Siemens P4 four-circle diffractometer using graphite monochromated Mo-K_α radiation. Unit cell parameters were determined by non-linear least-squares refinement of 29 accurately-centred reflections ($9 < \theta < 25°$). Using 1.8° ω-scans at 5° min⁻¹, 6095 reflections were collected in the range $4 < 2\theta < 50°$, 5700 unique reflections ($R_{int} = 0.0620$) were used in

the refinement. Crystal stability was monitored by recording three check reflections every 97 reflections and no decomposition was observed. The data were corrected for Lorentz and polarization effects and a semi-empirical absorption correction was applied based on ψ scan data ($T_{max} = 0.825$, $T_{min} = 0.734$).

Structure analysis and refinement

The structure was solved by direct methods [7], which revealed most of the non-hydrogen atoms and the remaining atoms were located from difference Fourier maps. Hydrogen atoms bonded to carbon were inserted at calculated positions with isotropic temperature factors riding on those of their carrier atoms. The hydrogen atoms associated with water molecules were located from difference maps and not refined, they were assigned a common, fixed atomic displacement parameter. All the data were used for refinement on F^2 which converged with $wR2 = 0.0993$, GOOF = 1.013 and the conventional $R = 0.0350$ ($I > 2\sigma(I)$) for 424 parameters. The final difference map showed no significant residual electron density. All programs used in the structure refinement are contained in the SHELXL-93 package [7].

[Mn(phen)$_2$(H$_2$O)$_2$][Mn(O$_2$C(CH$_2$)$_5$CO$_2$)(phen)$_2$(H$_2$O)] (O$_2$C(CH$_2$)$_5$CO$_2$) $\cdot$ 12.5H$_2$O (**4**)

Crystal data

C$_{62}$H$_{67}$Mn$_2$N$_8$O$_{23.5}$, M_r = 1410.12, yellow block, 0.89 × 0.52 × 0.36 mm, triclinic, space group $P\bar{1}$, a = 12.379(2), b = 16.480(2), c = 18.544(2) Å, α = 110.134(9), β = 109.990(1), γ = 98.12(1)°, U = 3190.9(7) Å, μ = 0.484 mm^{-1}, Z = 2, $F(000)$ = 1466, λ = 0.71073 Å.

Data collection and processing

Data were collected at 153(2) K on a Siemens P4 four-circle diffractometer using graphite mono-chromated Mo-K_α radiation. Unit cell parameters were determined by non-linear least-squares refinement of 32 accurately-centred reflections (10 < 2θ < 25°). Using 1.6° ω scans at 6° min^{-1}, 9027 reflections were collected in the range 4 < 2θ < 50°, 8545 unique reflections (R_{int} = 0.0279) were used in the refinement. Crystal stability was monitored by recording three check reflections every 97 reflections and no decomposition was observed. The data were corrected for Lorentz and polarisation effects and a semi-empirical absorption correction was applied based on ψ-scan data (T_{max} = 0.927, T_{min} = 0.865).

Structure analysis and refinement

The structure was solved by direct methods [7], which revealed most of the non-hydrogen atoms and the remaining atoms were located from difference Fourier maps. Hydrogen atoms bonded to carbon were inserted at calculated positions with isotropic temperature factors riding on those of their carrier atoms. The hydrogen atoms associated with water molecules were not included. All the data were used for refinement on F^2 which converged with $wR2$ = 0.1911, GOOF = 1.055 and the conventional R = 0.0708 (I > 2$\sigma(I)$) for 865 parameters. The final difference map showed no significant residual electron density. All programs used in the structure refinement are contained in the SHELXL-93 package [7].

[Mn(O$_2$C(CH$_2$)$_4$CO$_2$)H$_2$O] (**1**)

To a solution of hexanedioic acid (0.66 g, 4.52 mmol) in ethanol (80 cm^3) was added Mn(CH$_3$CO$_2$)$_2$$\cdot$4H$_2$O (1.00 g, 4.08 mmol). The mixture was refluxed for 2 h and the product precipitated as a white solid. After cooling to room temperature the solid was filtered off, washed with two portions of ethanol and then dried in air. Yield: 0.80 g (90%). Found: C, 33.6; H, 4.8. Calc.: C, 33.2; H, 4.6%. IR (KBr matrix): 3523, 2952, 1555, 1421, 1327, 1213, 716, 521 cm^{-1}. μ_{eff} = 5.77 B.M. Λ_M(H$_2$O) = 169 S cm^2 mol^{-1}.

The complex was soluble in water and insoluble in all other common solvents.

[Mn(O$_2$C(CH$_2$)$_5$CO$_2$)] (**2**)

This white solid was prepared in the same manner as (**1**) using heptanedioic acid (1.40 g, 8.74 mmol) and Mn(CH$_3$CO$_2$)$_2$$\cdot$4H$_2$O (1.95 g, 7.96 mmol). Yield: 1.65 g (97%). Found: C, 39.0; H, 5.1. Calc.: C, 39.5; H, 4.7%. IR (KBr matrix): 2939, 1575, 1441, 1407, 1307, 1099, 803, 662, 434 cm^{-1}. μ_{eff} = 5.44 B.M. Λ_M(H$_2$O) = 136 S cm^2 mol^{-1}. The complex was soluble only in water.

[Mn(O$_2$C(CH$_2$)$_4$CO$_2$)(phen)$_2$H$_2$O] $\cdot$ 7H$_2$O (**3**)

To a suspension of [Mn(O$_2$C(CH$_2$)$_4$CO$_2$)H$_2$O] (**1**) (1.15 g, 5.30 mmol) in an ethanol : water mixture (4 : 1, 120 cm^3) was added 1,10-phenanthroline (2.10 g, 11.65 mmol). The mixture was refluxed for 2 h and the resulting yellow solution was allowed to cool to room temperature. On standing for several days the product formed as yellow crystals. The crystals were filtered off, washed with ice-cold ethanol and then dried in air. Yield: 2.05 g (55%). Found: C, 51.0; H, 5.2; N, 7.9. Calc.: C, 51.2; H, 5.7; N, 7.9%. IR (KBr matrix): 3389, 3194, 2925, 1569, 1522, 1407, 857, 736 cm^{-1}. μ_{eff} = 5.88 B.M. Λ_M(H$_2$O) = 136 S cm^2 mol^{-1}. The complex was soluble in methanol, ethanol, benzyl alcohol and warm water, and was insoluble in all other common solvents.

[Mn(phen)$_2$(H$_2$O)$_2$][Mn(O$_2$C(CH$_2$)$_5$CO$_2$)(phen)$_2$H$_2$O] (O$_2$C(CH$_2$)$_5$CO$_2$) $\cdot$ 12.5H$_2$O (**4**)

This yellow crystalline solid was prepared in the same manner as (**3**) using [Mn(O$_2$C(CH$_2$)$_5$CO$_2$)] (**2**) (0.40 g, 1.88 mmol) in an ethanol : water mixture (4 : 1, 75 cm^3) and 1,10-phenanthroline (0.85 g, 4.72 mmol). Yield: 0.98 g (74%). Found: C, 53.0; H, 4.8; N, 8.1. Calc.: C, 52.8; H, 4.8; N, 5.9%. IR (KBr matrix): 3409, 3060, 2946, 1582, 1428, 1401, 1307, 1152, 1112, 857, 729 cm^{-1}. μ_{eff} = 5.98 B.M. per Mn. Λ_M(H$_2$O) = 219 S cm^2 mol^{-1}. The complex was soluble in water, methanol, warm benzyl alcohol and warm ethanol.

Hydrogen peroxide disproportionation studies

Aqueous H$_2$O$_2$ (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.

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