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catena-Poly[[(1,10-phenanthroline-κ^2N,N')manganese(II)]-di-μ-salicylato-$\kappa^4O:O'$]

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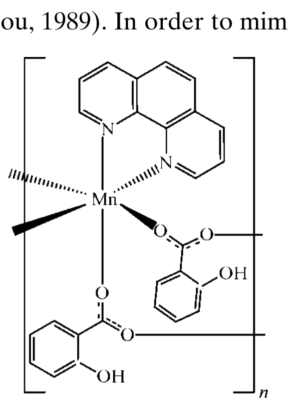
In the title polymeric complex, $[Mn(C_7H_5O_3)_2(C_{12}H_8N_2)]_n$, the Mn^{II} atom is located on a twofold axis and displays a distorted octahedral coordination geometry, formed by four salicylate anions and one 1,10-phenanthroline (phen) molecule. The salicylate anions doubly bridge the Mn^{II} atoms to form one-dimensional polymeric chains. A comparison of Mn—O bond distances with the corresponding Mn—O—C angles suggests a significant electrostatic content in the Mn—O bonds. A face-to-face distance of 3.352 (7) Å between neighbouring parallel phen planes indicates π–π stacking interactions between polymeric chains.

Comment

The structure and properties of multinuclear Mn complexes have attracted much scientific attention due to their potentially useful electronic or magnetic properties and their presence in various biosystems (Yachandra *et al.*, 1996), especially in the oxygen-evolving complex of photosystem II (PSII). The process of water splitting is generally believed to occur at an Mn cluster located in the reaction centre of PSII (Vincent & Christou, 1989). In order to mimic the Mn cluster, a series of Mn complexes have been synthesized and their crystal structures determined in our laboratory (Xu *et al.*, 1997; Li *et al.*, 2002; Su *et al.*, 2004). Among these, the X-ray structures of several Mn^{II} complexes showed evidence of significant electrostatic content in the coordination bond between the Mn^{II} atom and the ligand (Nie *et al.*, 2001; Liu *et al.*, 2003), which may play an important role for oxygen release during photosynthesis. As part of our ongoing investigation, the title polymeric Mn^{II} complex, (I), has been prepared and its structure determined.



(I)

A segment of the polymeric structure of (I) is illustrated in Fig. 1. The Mn^{II} atom is located on a twofold axis and is coordinated by four salicylate anions and one phenanthroline (phen) molecule, displaying distorted octahedral coordination geometry. The phen ligand lies on a twofold axis and chelates to the Mn^{II} atom with normal bond distances and angles. Crystallographically independent salicylate anions coordinate to the Mn^{II} atom with appreciably different Mn—O bond distances and Mn—O—C angles (Table 1). It is noteworthy that the shorter Mn—O1 bond corresponds to the larger Mn—O1—C1 angle, whereas the longer Mn—O2^{i} bond corresponds to the smaller (normal) Mn—O2^{i}—C1^{i} angle [symmetry code: (i) $1-x, 1-y, 1-z$].

A similar situation is observed in some reported Mn^{II} complexes incorporating non-chelating carboxylates. The Mn—O(carboxyl) bond distances and corresponding Mn—O—C angles found in these Mn^{II} complexes are summarized in Table 3. In these structures, the Mn—O—C angles range from 121.1 (2) to 170.10 (6)° and the Mn—O bond distances range from 2.050 (4) to 2.278 (2) Å. A comparison of the bond distances with the bond angles shows that the Mn—O bond

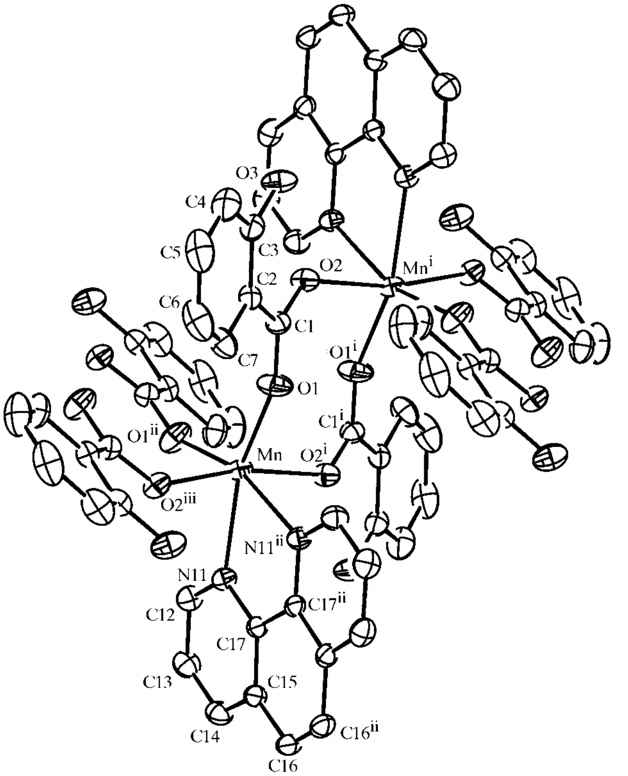


Figure 1
A segment of the polymeric structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity. [Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $1-x, y, \frac{1}{2}-z$; (iii) $x, 1-y, z-\frac{1}{2}$.]

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distances are independent of the corresponding Mn—O—C angles. In some structures, even though the larger Mn—O—C angles imply poor overlap between the atomic orbitals of the Mn atom and the molecular orbitals of the ligand, the shorter Mn—O bond distances indicate a stronger interaction between them. This finding strongly suggests the existence of a significant electrostatic content in the Mn—O(carboxyl) bonds.

The salicylate anions act as bridging ligands in (I). Neighbouring Mn^{II} atoms are bridged by two salicylate anions to form zigzag polymeric chains along the *c* axis, as shown in Fig. 2. The polymeric chain has a repeat unit formed by two salicylate anions and two Mn^{II} atoms related by an inversion centre. The repeat unit of the eight-membered ring assumes a chair configuration, with the Mn atoms deviating from the basal plane formed by two carboxyl groups by 0.856 (3) Å. The Mn···Mn separation in the eight-membered ring is 4.8252 (5) Å.

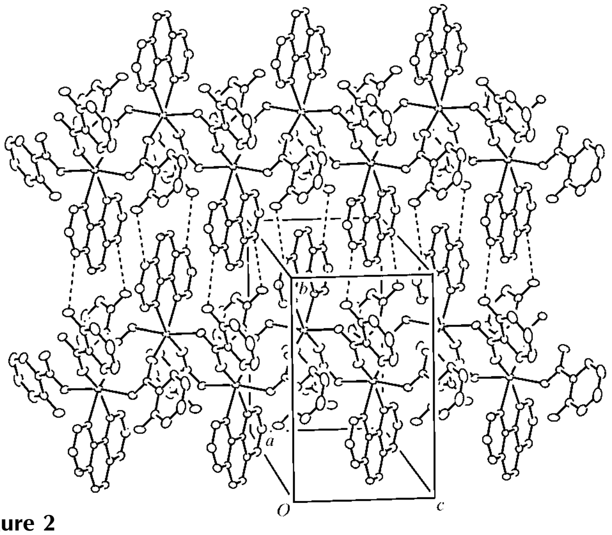

Figure 2
A unit-cell packing diagram for (I), showing the parallel arrangement of the phen rings and the interchain C—H···O hydrogen bonds (dashed lines).

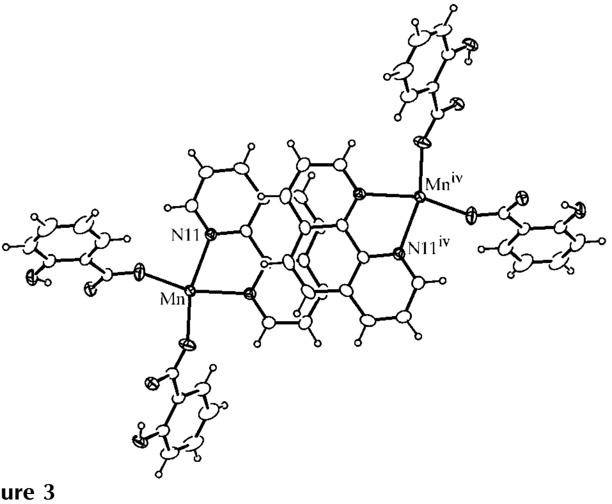

Figure 3
The π–π stacking between the phen rings of (I). [Symmetry code: (iv) $1 - x, 2 - y, 1 - z$.]

A parallel arrangement of the phen ligands of neighbouring polymeric chains is illustrated in Fig. 2. The face-to-face distance of 3.352 (7) Å between parallel N11-phen and N11^{iv}-phen planes [symmetry code: (iv) $1 - x, 2 - y, 1 - z$], and a partially overlapped arrangement (Fig. 3) suggest a π–π interaction. The shortest distance between the centroids of the aromatic rings of neighbouring phen ligands is 3.8384 (12) Å.

The hydroxyl group of the salicylate is free from coordination in (I), which differs from the situation found in *catena*-poly[[bis(1*H*-benzimidazole)salicylatocopper(II)]-μ-salicylato] (Li *et al.*, 2005). However, the hydroxyl group is involved in an intramolecular hydrogen bond with the carboxyl O atom (Table 2), which also forms weak C—H···O hydrogen bonds, both with the phen ligands (Fig. 2) and with the salicylate anions of adjacent polymeric chains.

Experimental

Each reagent was commercially available and of analytical grade. $Mn(CH_3COO)_2·4H_2O$ (0.25 g, 1 mmol), salicylic acid (0.14 g, 1 mmol), 1,10-phenanthroline (0.20 g, 1 mmol) and Na_2CO_3 (0.05 g, 1 mmol) were dissolved in a water–ethanol solution (20 ml, 1:1 *v*/*v*). The resulting solution was refluxed for 5 h, then cooled to room temperature and filtered. Pale-yellow single crystals of (I) were obtained from the filtrate after 3 d.

Crystal data

$[Mn(C_7H_5O_3)_2(C_{12}H_8N_2)]$
$M_r = 509.36$
Orthorhombic, *Pbcn*
$a = 23.5785$ (5) Å
$b = 12.1715$ (3) Å
$c = 7.6545$ (2) Å
$V = 2196.73$ (9) Å^3
$Z = 4$
$D_x = 1.540$ Mg m^{-3}

Mo *K*α radiation
Cell parameters from 10 105 reflections
$\theta = 2.7–24.4°$
$\mu = 0.65$ mm^{-1}
$T = 295$ (2) K
Platelet, pale yellow
0.20 × 0.18 × 0.03 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.875$, $T_{max} = 0.976$
13 706 measured reflections

1965 independent reflections
1544 reflections with $I > 2\sigma(I)$
$R_{int} = 0.043$
$\theta_{max} = 25.2°$
$h = -28 \rightarrow 28$
$k = -14 \rightarrow 14$
$l = -9 \rightarrow 8$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.081$
$S = 1.04$
1965 reflections
159 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0411P)^2 + 0.6755P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn—O1	2.0774 (15)	Mn—N11	2.2946 (17)
Mn—O2^{i}	2.2375 (15)		
O1—Mn—O1^{ii}	108.08 (9)	O2^{iii}—Mn—N11	88.71 (6)
O1—Mn—O2^{iii}	91.44 (6)	O2^{i}—Mn—N11	82.33 (6)
O1—Mn—O2^{i}	95.07 (6)	N11—Mn—N11^{ii}	72.49 (8)
O2^{iii}—Mn—O2^{i}	168.90 (7)	Mn—O1—C1	154.50 (16)
O1—Mn—N11	162.07 (7)	C1—O2—Mn^{i}	132.62 (13)
O1—Mn—N11^{ii}	89.76 (6)		

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 - x, y, \frac{1}{2} - z$; (iii) $x, 1 - y, z - \frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O2	0.90	1.71	2.525 (2)	148
C5—H5···O3$^{\rm iv}$	0.93	2.52	3.417 (3)	161
C14—H14···O3$^{\rm v}$	0.93	2.45	3.323 (3)	157

Symmetry codes: (iv) $\frac{3}{2} - x, \frac{1}{2} - y, z - \frac{1}{2}$; (v) $1 - x, y + 1, \frac{1}{2} - z$.

Table 3
A comparison of the Mn—O(carboxyl) bond distances (Å) and corresponding Mn—O—C angles (°) for selected $\mathrm{Mn^{II}}$ complexes incorporating non-chelating carboxylate ligands.

Carboxylate ligand	Mn—O	Mn—O—C
Benzoate[a]	2.050 (4)	165.8 (4)
Salicylate[b]	2.0774 (15)	154.50 (16)
Salicylate[c]	2.087 (2)	152.94 (16)
Isophthalate[d]	2.104 (2)	161.8 (2)
Succinate[e]	2.117 (3)	136.8 (3)
DL-Malate[f]	2.1174 (17)	146.76 (14)
Salicylate[g]	2.1227 (18)	170.10 (6)
Isophthalate[h]	2.141 (2)	148.3 (2)
Aspartate[j]	2.1593 (19)	147.09 (19)
Hydrogen phthalate[k]	2.171 (4)	156.8 (4)
Salicylate[l]	2.200 (12)	124.4 (6)
Benzoate[m]	2.201 (4)	125.9 (4)
Salicylate[n]	2.219 (3)	121.1 (2)
Benzoate[p]	2.224 (14)	121.9 (12)
Dihydro-orotate[q]	2.2352 (16)	125.37 (16)
Salicylate[b]	2.2375 (15)	132.62 (13)
Glutarate[r]	2.278 (2)	128.47 (18)

References: (*a*) Milios *et al.* (2004); (*b*) this work; (*c*) Devereux *et al.* (1996); (*d*) Nie *et al.* (2001); (*e*) Liu *et al.* (2003); (*f*) Fleck *et al.* (2001); (*g*) Rissanen *et al.* (1987); (*h*) Hu *et al.* (2001); (*j*) Ciunik (1987); (*k*) Bermejo *et al.* (1999); (*l*) Tan *et al.* (1997); (*m*) Wang *et al.* (1994); (*n*) Tan *et al.* (1996); (*p*) Vincent *et al.* (1987); (*q*) Castan *et al.* (1998); (*r*) Kim *et al.* (2004).

The hydroxyl H atom was located in a difference Fourier map and refined riding in its as-found position, with a fixed isotropic displacement parameter of 0.05 Å^2. Aromatic H atoms were placed in calculated positions (C—H = 0.93 Å) and were included in the final cycles of refinement in riding mode, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1227). Services for accessing these data are described at the back of the journal.

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