

catena-Poly[[diaquamanganese(II)]-bis[μ -(2,4-dichlorophenoxy)acetato- κ^2 O:O']]

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Key indicators

Single-crystal X-ray study
 T = 273 K
 Mean σ (C–C) = 0.003 Å
 R factor = 0.031
 wR factor = 0.090
 Data-to-parameter ratio = 17.1

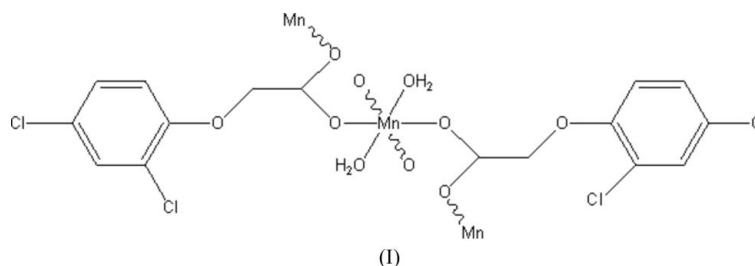
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title complex, $[\text{Mn}(\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3)_2(\text{H}_2\text{O})_2]_n$, is a coordination polymer containing the flexible 2,4-dichlorophenoxyacetate ligand. The Mn^{II} atom, which lies on a centre of inversion, is coordinated by four O atoms from two 2,4-dichlorophenoxyacetate ligands and two water molecules and displays an octahedral geometry. An ideal three-dimensional framework is formed by the flexible phenoxyacetate ligands *via* intramolecular hydrogen-bond interactions.

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Comment

New organic–inorganic hybrid materials based on polyoxometallates have attracted much attention due to the diversity of their structures and the vast range of potential applications in many fields, such as catalysis, electrical conductivity, magneto-chemistry and photochemistry (Hill & Prosser-McCarthy, 1995; Rhule *et al.*, 1998; Yamase *et al.*, 1999). However, the organic molecules introduced into these polyoxometallate-based materials are mostly restricted to organonitrogen ligands (Kang *et al.*, 1989; Luan *et al.*, 2000; Reinoso *et al.*, 2003). Extended polyoxomolybdates containing carboxyl ligands are rare (Liu *et al.*, 1987; Quintal *et al.*, 2001), which may be due to the fact that the negative charge on carboxyl ligands prevents charge balance with the polyoxomolybdate anions. In the course of our development of the chemistry of organic–inorganic hybrid materials based on polyoxomolybdates, only carboxyl ligands are introduced into the polyoxomolybdate system. 2,4-Dichlorophenoxyacetic acid (2,4-DPOAH), which shows biological activity and is widely used in agriculture, has a versatile binding ability. Structures of complexes of 2,4-DPOAH have not been reported to date, but the reaction of 2,4-DPOAH with MnSO_4 yielded a novel Mn^{II} polymer, $[\text{Mn}(\text{C}_8\text{H}_5\text{O}_3\text{Cl}_2)_2(\text{H}_2\text{O})_2]_n$ (I), which features a three-dimensional architecture.



The structure of (I) can be described as follows. The Mn^{II} centre, which lies on a center of inversion, has an octahedral geometry, which is defined by six O atoms from four 2,4-dichlorophenoxyacetate ligands and two water molecules

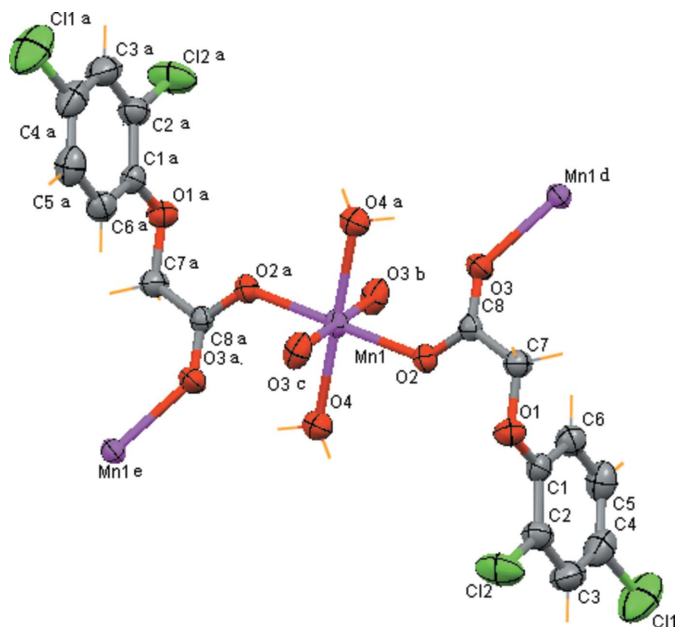


Figure 1

The structure of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted. [Symmetry codes: (a) $-x, 1 - y, 2 - z$; (b) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (c) $-x, \frac{1}{2} + y, \frac{3}{2} - z$; (d) $-x, -\frac{1}{2} + y, \frac{3}{2} - z$; (e) $-x, \frac{1}{2} + y, \frac{5}{2} - z$.]

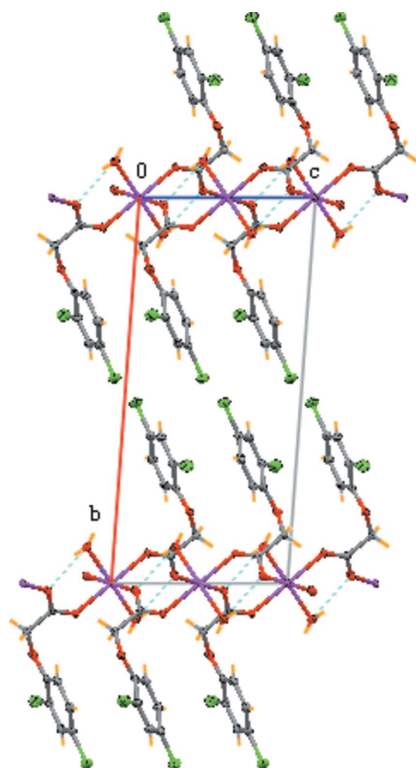


Figure 2

A packing diagram of the title complex, viewed along the b axis. H atoms have been omitted.

(Fig. 1). The coordination bond lengths and angles at the Mn^{II} atom are given in Table 1, and the C8–C7–O1–C1 torsion angle is $-83.07(3)^\circ$. The overall structure is that of a three-dimensional coordination polymer (Fig. 2), in which the shortest Mn \cdots Mn distance is $5.428(3) \text{ \AA}$.

Experimental

The title complex was prepared by the addition of stoichiometric amounts of MnSO₄ (20 mmol) and NaOH (30 mmol) to a hot aqueous solution (25 ml) of 2,4-dichlorophenoxyacetic acid (20 mmol). The resulting solution was filtered, and yellow single crystals of (I) were obtained at room temperature over several days (yield 58%).

Crystal data

[Mn(C₈H₅Cl₂O₃)₂(H₂O)₂]
 $M_r = 531.01$
 Monoclinic, $P2_1/c$
 $a = 17.6086(9) \text{ \AA}$
 $b = 7.3070(4) \text{ \AA}$
 $c = 8.0274(4) \text{ \AA}$
 $\beta = 94.156(3)^\circ$
 $V = 1030.14(9) \text{ \AA}^3$

$Z = 2$
 $D_x = 1.712 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 1.20 \text{ mm}^{-1}$
 $T = 273(2) \text{ K}$
 Block, yellow
 $0.40 \times 0.35 \times 0.20 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.645, T_{\max} = 0.795$

10969 measured reflections
 2412 independent reflections
 2139 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.020$
 $\theta_{\text{max}} = 27.7^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.090$
 $S = 1.09$
 2412 reflections
 141 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0452P)^2 + 0.4394P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.46 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.47 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

Mn1–O3 ⁱ	2.1644 (12)	Mn1–O2	2.1695 (11)
Mn1–O2 ⁱⁱⁱ	2.1695 (11)	Mn1–O4	2.2289 (15)
O3 ⁱ –Mn1–O2	80.16 (5)	O3 ⁱⁱⁱ –Mn1–O4	90.65 (6)
O3 ⁱⁱⁱ –Mn1–O2	99.84 (5)	O2 ⁱⁱ –Mn1–O4	91.37 (5)
O3 ⁱ –Mn1–O4	89.35 (6)	O2–Mn1–O4	88.63 (5)

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

Water H atoms were located in a difference Fourier map and were refined isotropically. Other H atoms were placed in calculated positions, with C–H = $0.93\text{--}0.97 \text{ \AA}$, and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1998); software used to prepare material for publication: SHELXTL.

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