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A carboxylato-supported alkoxo-bridged dimanganese(III) complex: bis(μ-benzoato-*O*:*O*′)bis[3-(3-methoxysalicylideneamino)propanolato-*O*,*N*,*O*′:*O*′]dimanganese(III)

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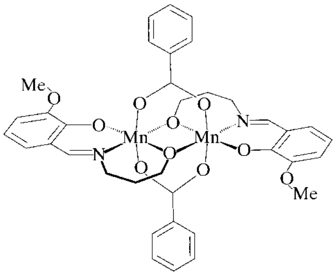
The title compound, $[Mn_2(C_{11}H_{13}NO_3)_2(C_7H_5O_2)_2]$, is a centrosymmetric dinuclear manganese(III) complex in which the two Mn atoms are bridged by two alkoxo groups and supported by two carboxylate groups, with an Mn···Mn distance of 2.8720 (15) Å.

Comment

Dinuclear manganese(III) complexes are of current interest because they can mimic the active sites of manganese-containing enzymes (Limburg *et al.*, 1999). Recently, it has been postulated that photosystem-II has two oxo-bridged dimanganese dimers connected by two carboxylate groups (Tommos & Babcock, 1998; Hoganson & Babcock, 1997). In manganese catalase (Halm & Bender, 1988) and manganese peroxidase (Wariishi *et al.*, 1988), the dimanganese sites are also found to be bridged by oxo groups. Because of the lack of suitable crystals, detailed structural information of some enzymes is still limited. Therefore, it is important to synthesize di- or polymeric manganese complexes. In this paper, we report a dimanganese(III) complex with an Mn···Mn distance of 2.8720 (15) Å.

The title complex, (I), is a discrete dinuclear manganese compound (Fig. 1). The two Mn atoms are related by a crystallographic inversion centre. The coordination geometry around each Mn atom is an elongated octahedron. The imino N, phenolic O and two bridging alkoxo O atoms form the equatorial plane around the Mn atom. The in-plane distances for Mn—N1 [2.000 (3) Å], Mn—O3 [1.896 (2) Å], Mn—O4 [1.859 (2) Å] and Mn—O3^i [1.939 (2) Å; symmetry code: (i) $1 - x, -y, 1 - z$] are comparable to those in other Mn^{III} complexes, *e.g.* [Mn(salpn)(EtOH)$_2$] [H$_2$salpn = *N*,*N*′-bis-(salicylidene)-1,3-diaminopropane] [Mn—N 2.017 (2) and 2.028 (2) Å; Mn—O 1.874 (2) and 1.891 (2) Å] (Gohdes & Armstrong, 1992) and [Mn(salpa)(MeOH)Cl]$_2$ (H$_2$salpa = 3-salicylidene-amino-1-propanol) [Mn—N 1.995 (4) Å; Mn—O 1.853 (3) and 1.926 (3) Å] (Larson *et al.*, 1992). Two carboxylate O atoms coordinate to the Mn atom *via* the elongated axial direction, with Mn—O1 and Mn—O2 bond distances of 2.262 (3) and 2.216 (3) Å. These bonds are considerably longer than those found in the equatorial plane, which could be due in part both to the Jahn–Teller distortion and to the different type of ligands and their mode of coordination. The Mn$_2$O$_2$ core is exactly planar by symmetry. The Mn···Mn distance of 2.8720 (15) Å is similar to the distances found in [Mn(salpa)(acetato)]$_2$ [2.869 (1) Å] (Mikuriya *et al.*, 1981) and [Mn(salpa)(benzoato)]$_2$ [2.855 (2) Å] (Zhang, Zhou *et al.*, 1999), but somewhat shorter than found in [Mn(salpa)-(MeOH)Cl]$_2$ [3.011 (1) Å] (Larson *et al.*, 1992) and [Mn(salpa)-(H$_2$O)Cl]$_2$ [3.001 (1) Å] (Zhang, Sun *et al.*, 1999). This indicates that the effect of two bridging carboxylate groups instead of four individual axial monodentate ligands, such as chloride, water or methanol, on the Mn$_2$O$_2$ core is to lead to a marked decrease in the manganese–manganese separation. Consequently, the angle O3—Mn—O3^i is expanded to



(I)

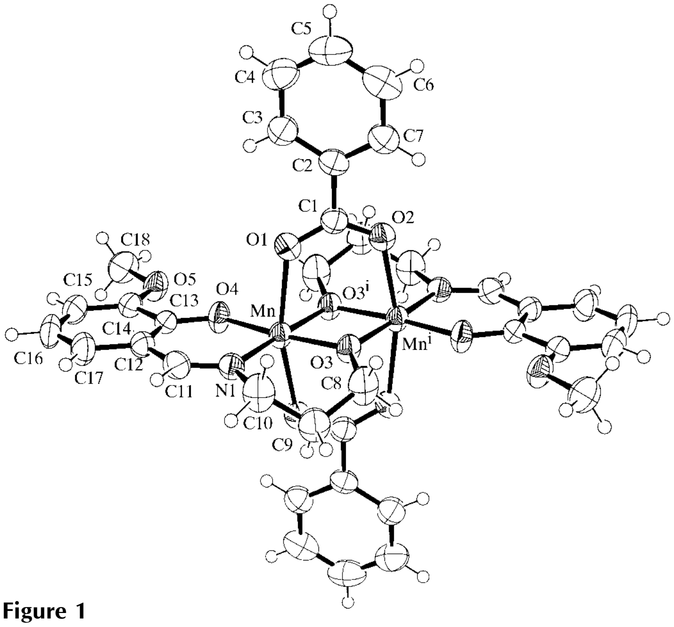


Figure 1
ORTEP-3 (Farrugia, 1997) view of compound (I) showing the labelling of the non-H atoms [symmetry code: (i) $1 - x, -y, 1 - z$]. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

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83.1 (1)°. This angle is similar to that found in [Mn(salpa)(acetato)]$_2$ [83.66 (7)°] but larger than that in [Mn(salpa)(MeOH)Cl]$_2$ [78.2 (1)°]. Concerning the intermolecular packing between the dimers, there are no π-stacking interactions as might have been expected (Janiak, 2000). Some tilted C—H$\cdots\pi$ interactions exist between the benzoate ring and the aromatic moiety of the salicylidene ligand (Janiak *et al.*, 2000). The shortest intermolecular ring-centroid$\cdots$ring-centroid (*Cg*) contacts (with interplanar angle) are $Cg1\cdots Cg2^{ii}$ = 4.71 Å (54.7°) and $Cg2\cdots Cg1^{iii}$ = 4.59 Å (54.7°), where *Cg*1 is the centroid of the C2–C7 phenyl ring and *Cg*2 is the centroid of the C12–C17 salicyl ring [symmetry codes: (ii) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (iii) $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$]. The shortest intermolecular aromatic C—H$\cdots$*Cg* contacts are C6—H6$A\cdots Cg2^{iv}$ = 2.90 and C16—H16$A\cdots Cg1^{v}$ = 3.27 Å [symmetry codes: (iv) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (v) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; calculated with the program *PLATON* (Spek, 1998)].

Experimental

Compound (I) was synthesized by the reaction of the ligand with manganese benzoate in a 1:1 molar ratio in ethanol. To an ethanolic solution (20 ml) of 3-methoxysalicylaldehyde (1.52 g, 10 mmol) was added 3-amino-1-propanol (0.75 g, 10 mmol) with stirring over a period of 30 min at 323 K; the solution turned yellow. To this solution was added manganese benzoate dihydrate (3.0 g, 10 mmol); the colour turned green rapidly. The resulting solution was then put aside for several days. Crystals were obtained by slow evaporation of the solvent at room temperature (yield 3.1 g, 82%). Crystal analysis, IR (KBr pellet, cm^{-1}): 3050 (*w*), 3000 (*w*), 2900 (*m*), 2850 (*w*), 1615 (*s*), 1588 (*s*), 1545 (*s*), 1460 (*s*), 1440 (*s*), 1375 (*s*), 1375 (*s*), 1315 (*s*), 1250 (*s*), 1220 (*s*), 1165 (*w*), 1080 (*s*), 1060 (*s*), 950 (*m*), 870 (*m*), 735 (*s*), 670 (*m*), 630 (*s*), 610 (*s*), 485 (*w*).

Crystal data

$[Mn_2(C_{11}H_{13}NO_3)_2(C_7H_5O_2)_2]$
M_r = 766.55
Monoclinic, $P2_1/n$
a = 13.009 (3) Å
b = 9.333 (5) Å
c = 15.162 (5) Å
β = 113.24 (2)°
V = 1691.5 (11) Å^3
Z = 2
D_x = 1.505 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 2959 reflections
θ = 1.8–25.0°
μ = 0.81 mm^{-1}
T = 293 (2) K
Plate, brown
0.50 × 0.20 × 0.18 mm

Data collection

Siemens *SMART* CCD diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Blessing, 1995)
T_{min} = 0.737, T_{max} = 1.000
6242 measured reflections
2959 independent reflections
2088 reflections with $I > 2\sigma(I)$
R_{int} = 0.039
θ_{max} = 25.0°
$h = -9 \rightarrow 15$
$k = -11 \rightarrow 6$
$l = -18 \rightarrow 14$

Refinement

Refinement on F^2
$R(F)$ = 0.047
$wR(F^2)$ = 0.116
S = 1.06
2954 reflections
226 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0404P)^2 + 0.9800P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.002$
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}

H atoms were treated using appropriate riding models (C—H = 0.93 and 0.97 Å). $U_{iso}(H) = 1.2U_{eq}(C)$, except for the H atoms of the methyl group (C18) for which $U_{iso}(H) = 1.5U_{eq}(C)$.

Table 1
Selected geometric parameters (Å, °).

Mn—O4	1.859 (2)	Mn—N1	2.000 (3)
Mn—O3	1.896 (2)	Mn—O2^i	2.216 (3)
Mn—O3^i	1.939 (2)	Mn—O1	2.262 (3)

O4—Mn—O3	174.46 (10)	O3—Mn—O1	83.72 (10)
O4—Mn—O3^i	91.80 (10)	O3^i—Mn—O1	83.85 (10)
O3—Mn—O3^i	83.00 (10)	N1—Mn—O1	94.83 (11)
O4—Mn—N1	92.44 (11)	O2^i—Mn—O1	164.26 (9)
O3—Mn—N1	92.72 (11)	C1—O1—Mn	123.7 (2)
O3^i—Mn—N1	175.63 (11)	C1—O2—Mn^i	124.6 (2)
O4—Mn—O2^i	95.42 (11)	C8—O3—Mn	132.3 (2)
O3—Mn—O2^i	85.91 (10)	C8—O3—Mn^i	127.7 (2)
O3^i—Mn—O2^i	83.16 (10)	C13—O4—Mn	130.8 (2)
N1—Mn—O2^i	97.47 (11)	C11—N1—Mn	123.0 (3)
O4—Mn—O1	93.84 (11)	C10—N1—Mn	120.0 (2)

Symmetry code: (i) $1 - x, -y, 1 - z$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXTL-Plus*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1457). Services for accessing these data are described at the back of the journal.

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