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Diaquabis(vanillinato-κ^2O,O')manganese(II)

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Key indicators

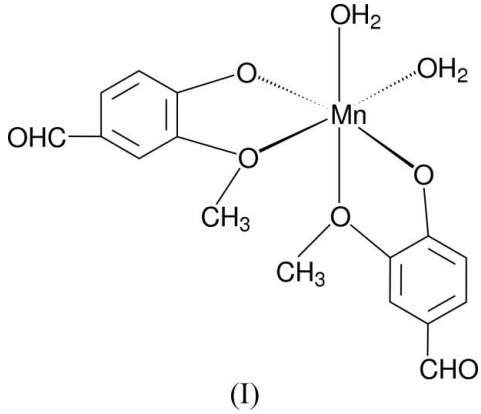
Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.003 Å
R factor = 0.028
wR factor = 0.100
Data-to-parameter ratio = 18.0

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

In the title complex, $[Mn(C_8H_7O_3)_2(H_2O)_2]$, the Mn^{II} atom is located on a twofold axis and is coordinated by two vanillinate anions and two water molecules in a distorted octahedral geometry. The vanillinate ligand chelates to the Mn^{II} atom through its methoxy and hydroxy O atoms, with greatly differing Mn—O bond distances [2.3506 (14) and 2.0901 (12) Å].

Comment

Water oxidation in the photosynthetic process of green plants (Bruckner *et al.*, 1993) is generally believed to occur at the manganese cluster located in the reaction centre of photosystem II (Vincent & Christou, 1989). In order to mimic this manganese cluster, a series of manganese complexes have been synthesized, among which some crystal structures revealed the existence of significant electrostatic interaction between the Mn atom and the ligand (Nie *et al.*, 2001; Hu *et al.*, 2001; Liu & Xu, 2003). The structure of the title complex, (I), provides a new example of this electrostatic interaction in an Mn^{II} complex.



(I)

The molecular structure of (I) is illustrated in Fig. 1. The Mn^{II} atom is located on a twofold axis. Two vanillinate anions and two water molecules coordinate to the Mn^{II} atom in a *cis* fashion in a distorted octahedral geometry. The vanillinate ligand chelates to the Mn^{II} atom with greatly differing Mn—O bond distances: the Mn—O1 bond is longer than the Mn—O2 bond by 0.2605 (18) Å (Table 1), implying a weaker coordination interaction between atoms Mn and O1. However, the O1—Mn—O4 angle of 168.45 (5)° is close to the expected value of 180° and much larger than the O2—Mn—O2^{iii} angle of 156.79 (5)° [symmetry code: (iii) $-x$, y, $\frac{1}{2}-z$], implying significant overlap between the atomic orbitals of atoms Mn and O1. This fact clearly suggests a significant contribution from the electrostatic interaction in the Mn—O bonding.

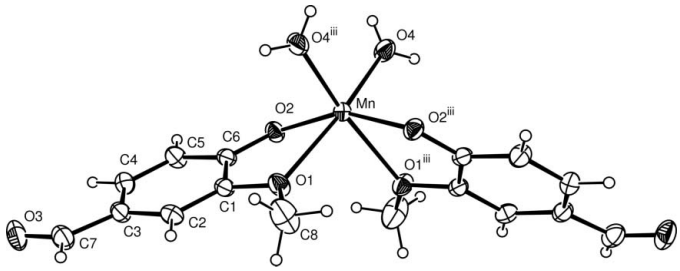


Figure 1
The structure of (I), showing 30% probability displacement ellipsoids [symmetry code: (iii) $-x, y, \frac{1}{2} - z$].

The coordinated water molecules are hydrogen bonded to the aldehyde and hydroxyl O atoms of neighbouring complex molecules (Fig. 2 and Table 2).

Experimental

An ethanol solution (20 ml) containing vanillin (0.152 g, 1 mmol), $Mn(OAc)_2{\cdot}4H_2O$ (0.245 g, 1 mmol) and NaOH (0.08 g, 2 mmol) was refluxed for 2 h. The yellow solution was cooled to room temperature and filtered. Yellow crystals of (I) were obtained from the filtrate after one week.

Crystal data

$[Mn(C_8H_7O_3)_2(H_2O)_2]$	D_x = 1.460 Mg m^{-3}
M_r = 393.24	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 6329 reflections
a = 22.4629 (5) Å	θ = 3.4–27.5°
b = 10.5743 (2) Å	μ = 0.78 mm^{-1}
c = 7.8600 (2) Å	T = 296 (1) K
β = 106.5648 (9)°	Block, yellow
V = 1789.50 (7) Å^3	0.30 × 0.24 × 0.22 mm
Z = 4	

Data collection

Rigaku R-AXIS RAPID diffractometer	2050 independent reflections
ω scans	1795 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	R_{int} = 0.011
T_{min} = 0.757, T_{max} = 0.843	θ_{max} = 27.5°
8384 measured reflections	$h = -29 \rightarrow 29$
	$k = -13 \rightarrow 13$
	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.028	$w = 1/[\sigma^2(F_o^2) + (0.0624P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.100	$(\Delta/\sigma)_{max} < 0.001$
S = 1.19	$\Delta\rho_{max}$ = 0.30 e Å^{-3}
2050 reflections	$\Delta\rho_{min}$ = −0.36 e Å^{-3}
114 parameters	

Table 1
Selected bond lengths (Å).

Mn—O1	2.3506 (14)	O1—C8	1.420 (3)
Mn—O2	2.0901 (12)	O2—C6	1.312 (2)
Mn—O4	2.1118 (14)	O3—C7	1.223 (3)
O1—C1	1.380 (2)		

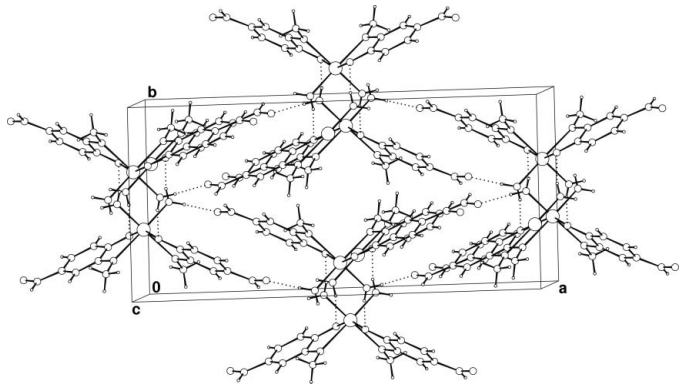


Figure 2
A molecular packing diagram for (I), with dashed lines indicating the hydrogen bonding.

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4A···O3^{i}	0.85	1.88	2.726 (2)	176
O4—H4B···O2^{ii}	0.79	1.93	2.6977 (18)	166

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

Water H atoms were located in a difference Fourier map and their positional parameters and displacement parameters were fixed [U_{iso}(H) = 0.05 Å^2]. The H atoms of the vanillinate anions were placed in calculated positions, with C—H = 0.93 Å (phenyl and aldehyde group) or 0.96 Å (methyl), and included in the final cycles of refinement in a riding model, with U_{iso}(H) = 1.2U_{eq}(carrier atom).

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al*., 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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