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Aqua[*N*,*N*'-ethylenebis(5-nitrosalicylideneiminato)]-methanolmanganese(III) perchlorate

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The title compound, $[Mn(C_{16}H_{12}N_4O_6)(CH_4O)(H_2O)]ClO_4$, arose as an unexpected oxidation product, and contains an Mn^{III} cation coordinated by an equatorial salen-type ligand and Jahn–Teller-distorted axially coordinated water and methanol molecules. A network of O—H···O and O—H···N hydrogen bonds helps to establish the crystal packing.

Comment

The chemistry of higher-valent manganese complexes, especially salen-type complexes of Mn^{III} and Mn^{IV}, is of much current interest. This is due to their relevance in such diverse areas as biological redox systems involving manganese (Pecoraro, 1992), reactivity with water (Asada *et al.*, 2000), facilitation of transport of amphiphilic molecules across liquid membranes (Pike *et al.*, 2001; Rosa *et al.*, 1998), formation of high-spin metal–cyanide clusters (Choi *et al.*, 2004; Miyasaka *et al.*, 1996, 1998) and photopromoted oxidative cyclization of substrates (Fukuda *et al.*, 1998).

(I)
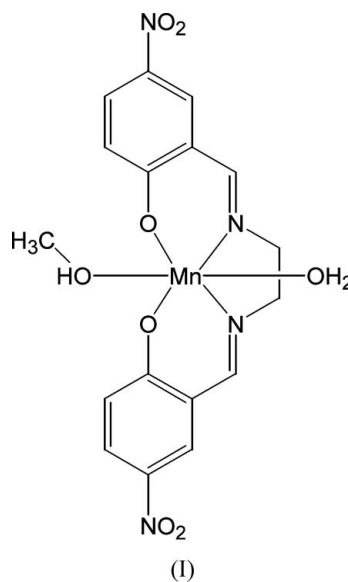
As part of a program involving the study of molecular recognition through intermolecular hydrogen-bonding interactions, the title compound, (I) (Fig. 1), was synthesized from 5-nitrosalicylaldehyde, manganese(II) perchlorate, and 2-(2-aminoethylamino)ethanol in the presence of base. Compound (I) must have resulted from the oxidation and hydrolysis of the preformed manganese(II) Schiff base complex. In the title compound, the metal atom is coordinated by an equatorial tetradentate salen ligand and axial methanol and water molecules, resulting in a *cis*-MnN_2O_4 grouping. A search of
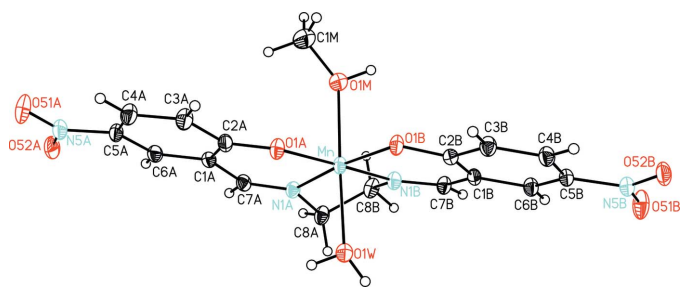
Figure 1
View of (I), showing 20% probability displacement ellipsoids (H atoms are represented by spheres of arbitrary radii).

version 5.26 of the Cambridge Structural Database (Allen, 2002) revealed eight examples of Mn–salen-type complexes, which also contain both a coordinated alcohol group and a coordinated water molecule (Asada *et al.*, 2000; Pike *et al.*, 2001; Rosa *et al.*, 1998; Choi *et al.*, 2004; Miyasaka *et al.*, 1996, 1998; Fukuda *et al.*, 1998; Nishikari *et al.*, 2000; Oki & Hodgson 1990). The bond lengths in (I) (Table 1) show the usual pattern of inequivalent Mn—O and Mn—N distances observed in other Mn^{III}–salen complexes. In all cases (Allen, 2002), the longer Mn—O distance and shorter Mn—N distance are from the same salicyladimine group. Compound (I) also shows the usual Jahn–Teller tetragonal distortion observed for Mn^{III} complexes, the Mn—O$_{water}$ and Mn—O$_{methanol}$ distances being substantially lengthened at 2.263 (3) and 2.233 (3) Å, respectively.

Both the methanol and the water molecules participate in intermolecular hydrogen bonding (Table 2).

Experimental

Mn(ClO$_4$)$_2$·6H$_2$O (3.62 g, 10 mmol), 5-nitrosalicylaldehyde (1.67 g, 10 mmol) and 2-(2-aminoethylamino)ethanol (0.52 g, 5 mmol) were refluxed in methanol in the presence of trimethylamine (5ml). The resulting solution was filtered and allowed to evaporate slowly. After several days, 5.34 g of dark-brown crystals of (I) were obtained.

Crystal data

[Mn(C$_{16}$H$_{12}$N$_4$O$_6$)(CH$_4$O)(H$_2$O)]ClO$_4$
$M_r = 560.74$
Triclinic, $P\bar{1}$
$a = 8.3102$ (15) Å
$b = 10.3320$ (16) Å
$c = 13.995$ (2) Å
$\alpha = 84.549$ (13)°
$\beta = 79.701$ (15)°
$\gamma = 72.128$ (12)°
$V = 1124.2$ (3) Å^3

$Z = 2$
$D_x = 1.657$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 36 reflections
$\theta = 2.5–11.4°$
$\mu = 0.78$ mm^{-1}
$T = 293$ (2) K
Plate, dark-brown
$0.49 \times 0.32 \times 0.07$ mm

Data collection

Siemens P4S diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.837$, $T_{max} = 0.947$
5181 measured reflections
5169 independent reflections
3452 reflections with $I > 2\sigma(I)$

$R_{int} = 0.015$
$\theta_{max} = 27.5°$
$h = -10 \rightarrow 0$
$k = -13 \rightarrow 12$
$l = -18 \rightarrow 17$
3 standard reflections every 97 reflections intensity decay: none
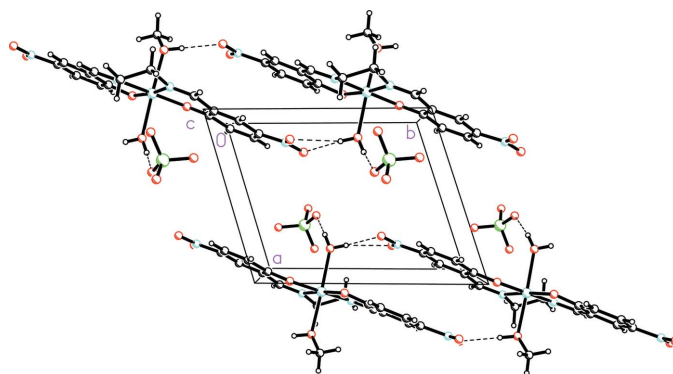

Figure 2
The molecular packing of (I) viewed down the c axis. Dashed lines indicate the hydrogen-bonding interactions.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.146$
$S = 1.03$
5169 reflections
324 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0653P)^2 + 0.3336P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.023$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn—O1A	1.893 (2)	Mn—N1A	1.994 (3)
Mn—O1B	1.914 (2)	Mn—O1M	2.233 (3)
Mn—N1B	1.982 (3)	Mn—O1W	2.263 (3)
N1A—C8A—C8B—N1B	45.6 (4)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1M—H1M$\cdots$O52A^i	0.82	2.06	2.877 (4)	179
O1W—H1W1$\cdots$O52B^{ii}	0.82 (1)	2.11 (1)	2.905 (4)	166 (5)
O1W—H1W2$\cdots$O12A	0.82 (1)	2.12 (3)	2.842 (5)	148 (5)

Symmetry codes: (i) $x, y - 1, z$; (ii) $x, y + 1, z$.

The water H atoms were located in a difference map and then refined with an O—H distance restraint of 0.82 (2) Å and the constraint $U_{iso}(H) = 1.2U_{eq}(O)$. All other H atoms were initially located in a difference map, and then repositioned in idealized locations (O—H = 0.82, C—H = 0.93–0.97 Å) and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C,O)$ or $U_{iso}(H) = 1.5U_{eq}(methyl C)$. The methyl groups were rotated to fit the electron density.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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