metal-organic compounds

Aquachloro[N,N′-ethylenebis(salicylideneiminato)]manganese(III)

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The title compound, aquachloro{2,2′-[1,2-ethanediylbis(nitrilomethylidyne)]diphenolato-$\kappa^4O,N,N′,O′$}manganese(III), [MnCl($C_{16}H_{14}N_2O_2$)(H_2O)], is a neutral manganese(III) complex with a pseudo-octahedral metal centre. The equatorial plane comprises the four donor atoms of the tetradentate Schiff base ligand [Mn—O 1.886 (4) and 1.893 (4) Å, and Mn—N 1.978 (5) and 1.982 (5) Å], with a water molecule [Mn—O 2.383 (4) Å] and a Cl⁻ ligand [Mn—Cl 2.4680 (16) Å] completing the coordination sphere. The distorted geometry is highlighted by the marked displacement of the Mn[III] ion out of the least-squares plane of the four Schiff base donor atoms by 0.165 (2) Å. These monomeric Mn[III] centres are then linked into a polymeric array *via* hydrogen bonds between the coordinated water molecule and the phenolic O-atom donors of an adjacent Mn[III] centre [O—H···O 2.789 (5) and 2.881 (5) Å].

Comment

Manganese–Schiff base complexes continue to be of interest, due principally to the uncertainty that still surrounds the mechanism of the Jacobsen–Katsuki epoxidation. This is a reaction that represents one of the most efficient means for the formation of C—O bonds in asymmetric synthesis (Jacobsen & Cavallo, 2001). However, the recent discovery of new enzymatic systems that contain a single Mn ion at their


(I)
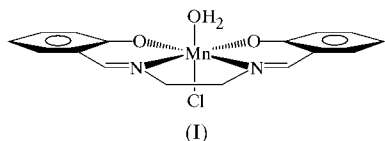
active centres, *viz.* manganese lipoxygenease (Su & Oliw, 1998) and germin (Woo *et al.*, 2000), has also served to maintain this interest. We are currently engaged in a systematic investigation of the binding modes of carboxylate donors in manganese–Schiff base complexes, following earlier investigations (Watkinson *et al.*, 1999), during which the title compound, (I), was unexpectedly isolated.

In (I), the metal centre adopts a pseudo-octahedral geometry. The equatorial plane comprises the tetradentate Schiff base ligand, with the coordination sphere being completed by an axial water molecule and a Cl⁻ ion (Fig. 1). This geometry is comparable with the analogous complex of the related bis(5-chlorosalicylidene)ethylenediamine (5-Cl-salen) ligand (Horwitz *et al.*, 1995). However, there are subtle and significant differences between the two structures. In the present case, the δ isomer is only observed in the unit cell and there are also marked differences in the axial bond lengths. This is principally reflected by the Mn—Cl distance, which is 2.4680 (16) Å in (I), compared with 2.572 (1) Å in the 5-Cl-salen complex (Horwitz *et al.*, 1995). The Mn—Cl distance in (I) is more comparable with the value of 2.493 (1) Å observed in [Mn(salpn)Cl(MeOH)] (Law *et al.*, 1995) and reflects the effect that substituents on the aryl ring have on this distance. Electron-withdrawing substituents have previously been shown to shorten this bond length significantly, *e.g.* Mn—Cl = 2.306 (4) Å when a nitro group is positioned *para* to the phenolic donor (Bermejo *et al.*, 1996), whilst electron-donating substituents lengthen it (Horwitz *et al.*, 1995).

The Mn—Cl distance in (I) also compares favourably with the values observed in the related square-pyramidal Mn[III]–Schiff base complexes [Mn(salen)Cl] (Pecoraro & Butler, 1986) and [Mn(salpn)Cl] (Watkinson *et al.*, 1999) of 2.461 (1) and 2.4521 (18) Å, respectively. This similarity is further emphasized by the marked displacement of 0.165 (2) Å for the Mn[III] ion from the O1/N1/N2/O2 least-squares plane, which is far greater than that observed in the related octahedral complex [0.084 (3) Å; Horwitz *et al.*, 1995] and is more comparable with square–pyramidal geometry [*e.g.* 0.19 Å; Pecoraro & Butler, 1986], emphasizing the distorted nature of the octahedral geometry.

This shortening of the Mn—Cl bond and displacement of the Mn[III] ion from the least-squares plane of the Schiff base donor ligand is reflected in a commensurate lengthening of the Mn—O3 distance to 2.383 (4) Å [*cf.* 2.319 (3) Å; Horwitz *et al.*, 1995]. The angle between the least-squares planes of the aromatic rings of the ligand is 9.2 (3)°, which is intermediate between the analagous angles of 20.86 (Pecoraro & Butler, 1986) and 3.95° (Horwitz *et al.*, 1995) in related systems.
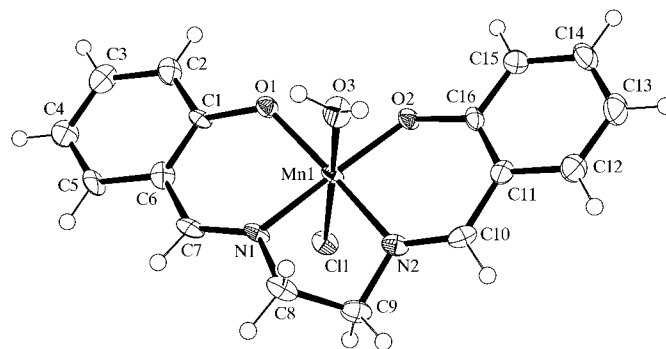
Figure 1
A view of the molecular structure of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

In the presence of hydrogen-bond donors on the ligands, such species have been shown to form intimate dimers in the solid state (Bermejo *et al.*, 1996). In their absence, very weakly associated dimers have also been shown to exist (Watkinson *et al.*, 1999). In the present case, however, rather than the formation of dimers, an intricate array of hydrogen bonds
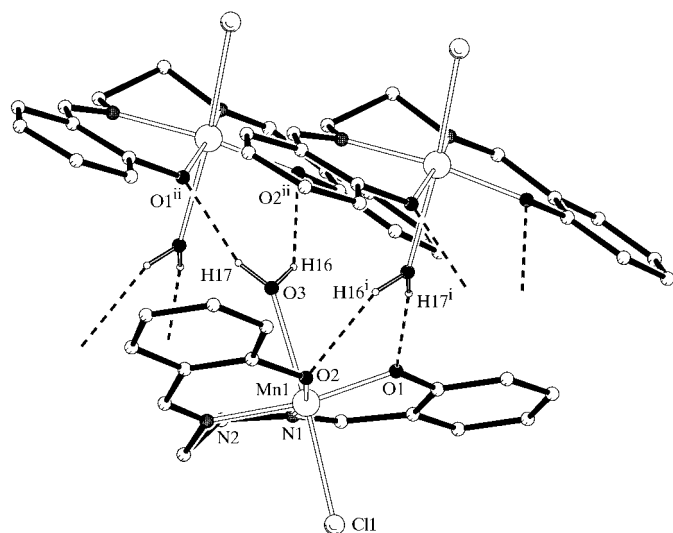

Figure 2
The molecular structure of (I), showing the polymeric hydrogen-bonded array. H atoms not involved in the hydrogen bonding have been omitted for clarity. [Symmetry codes: (i) $1 - x$, $y - \frac{1}{2}$, $-z$; (ii) $1 - x$, $\frac{1}{2} + y$, $-z$.]

between the coordinated water molecule of one Mn centre and the two phenolic O-atom donors of an adjacent Mn centre results in the formation of a polymeric array (Fig. 2 and Table 2). As all other bond lengths and angles about the metal centres are essentially identical in these octahedral Mn^{III} complexes (Table 1), the subtle changes in the axial bonding observed in this and other compounds further serves to emphasize the important effects that ligand substitution can have.

Experimental

Compound (I) was prepared whilst attempting to synthesize [Mn(salen)(O$_2$CCH$_3$)] by a modified procedure. Manganese(II) chloride (0.47 g, 0.004 mol) and H$_2$salen (1.00 g, 0.004 mol) were added to a round-bottomed flask containing ethanol (120 ml). Triethylamine (5 drops) was added and the resulting mixture refluxed in air for 2 h before being allowed to cool to 313 K. Sodium acetate (0.31 g, 0.004 mol) in absolute ethanol (5 ml) and silver tetrafluoroborate (0.72 g, 0.004 mol) were added, and the mixture was heated at reflux for a further 2 h. The resulting mixture was allowed to cool to room temperature and the insoluble material that had formed was removed by filtration. The filtrate was reduced in volume to *ca* 25 ml and layered with diethyl ether (250 ml), and the dark-brown crystalline product, (I), which resulted was collected by filtration.

Crystal data

[MnCl(C$_{16}$H$_{14}$N$_2$O$_2$)(H$_2$O)]	D_x = 1.6 Mg m^{-3}
M_r = 374.7	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 25
a = 10.418 (4) Å	reflections
b = 6.627 (3) Å	θ = 8.1–13.9°
c = 11.733 (5) Å	μ = 1.04 mm^{-1}
β = 106.29 (2)°	T = 160 (2) K
V = 777.5 (6) Å^3	Prism, brown
Z = 2	0.3 × 0.2 × 0.1 mm

Data collection

Enraf–Nonius CAD-4 diffractometer	R_{int} = 0.030
Non-profiled $\omega/2\theta$ scans	θ_{max} = 25°
Absorption correction: ψ scan (North *et al.*, 1968)	$h = -12 \rightarrow 11$
T_{min} = 0.675, T_{max} = 0.902	$k = 0 \rightarrow 7$
1562 measured reflections	$l = 0 \rightarrow 13$
1488 independent reflections	2 standard reflections
1324 reflections with $I > 2\sigma(I)$	frequency: 60 min
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0720P)^2$
$R(F)$ = 0.037	$+ 0.0385P]$
$wR(F^2)$ = 0.099	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.04	$(\Delta/\sigma)_{max} < 0.001$
1488 reflections	$\Delta\rho_{max}$ = 0.44 e Å^{-3}
184 parameters	$\Delta\rho_{min}$ = −0.60 e Å^{-3}
H atoms: see below	Absolute structure: Flack (1983)
	Flack parameter = 0.01 (4)

Table 1
Selected geometric parameters (Å, °).

Mn1—Cl1	2.4680 (16)	Mn1—O3	2.383 (4)
Mn1—O1	1.893 (4)	Mn1—N1	1.978 (5)
Mn1—O2	1.886 (4)	Mn1—N2	1.982 (5)
O1—Mn1—O2	93.78 (16)	O3—Mn1—N2	83.89 (16)
O1—Mn1—O3	85.92 (15)	N1—Mn1—N2	82.2 (2)
O2—Mn1—O3	85.29 (16)	O1—Mn1—Cl1	97.08 (12)
O1—Mn1—N1	90.74 (17)	O2—Mn1—Cl1	99.30 (12)
O1—Mn1—N2	168.06 (18)	O3—Mn1—Cl1	174.31 (12)
O2—Mn1—N1	169.17 (17)	N1—Mn1—Cl1	89.89 (12)
O2—Mn1—N2	91.58 (17)	N2—Mn1—Cl1	92.57 (13)
O3—Mn1—N1	85.22 (16)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H17$\cdots$O1^i	0.82	2.01	2.789 (5)	160
O3—H16$\cdots$O2^i	0.81	2.18	2.881 (5)	145

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

H atoms attached to C atoms were treated as riding, with C—H distances in the range 0.95–0.99 Å, using *SHELXL*97 defaults (Sheldrick, 1997). The water H atoms were located in difference maps and included as such in the calculations. The aromatic rings were treated as rigid hexagons during the least-squares refinement.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1994); cell refinement: *CAD-4-PC Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to refine structure: *SHELXL*97

metal-organic compounds

(Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *PLUTON* in *PLATON* (Spek, 1998); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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