Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Chloro{2,2′-[(1*S*,2*S*)-1,2-diphenyl-1,2-ethanediylbis(nitrilomethylidyne)]-diphenolato-κ^4O,N,N',O'}(ethanol-κO)manganese(III)

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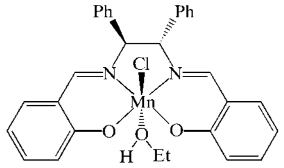
Received 18 November 2003
Accepted 5 January 2004
Online 31 January 2004

The crystal structure of the title compound, [MnCl($C_{28}H_{22}N_2O_2$)(C_2H_6O)], has been determined at 173 (2) K in the non-centrosymmetric space group $P2_12_12_1$. The asymmetric unit contains two molecular units. An intermolecular O—H···Cl hydrogen bond is formed between the OH group of an ethanol molecule coordinated to the Mn atom and the coordinated Cl^- anion, and so polymeric chains of Mn-containing fragments are formed [O—H···Cl = 3.1281 (16) and 3.1282 (15) Å]. The Mn atoms have a pseudo-octahedral coordination sphere, with the four donor atoms of the Schiff base forming an equatorial plane [Mn—O distances are 1.8740 (13), 1.8717 (13), 1.8749 (13) and 1.8823 (13) Å, and Mn—N distances are 1.9868 (15), 1.9910 (14), 1.9828 (15) and 1.9979 (14) Å]. The axial positions are occupied by an ethanol molecule [Mn—O distances of 2.3069 (15) and 2.3130 (15) Å] and a Cl^- ligand [Mn—Cl distances of 2.5732 (6) and 2.5509 (6) Å].

Comment

Manganese–Schiff base complexes are actively used as catalysts due to their ability to epoxidize unfunctionalized alkenes highly stereoselectively (Lane & Burgess, 2003). The Katsuki–Jacobsen reaction is, to date, one of the most convenient methods of enantiomeric epoxidation of alkenes (Jacobsen, 1993, 1995; Katsuki, 1995). Interest in the structural characterization of various species in the reaction stems from the need to improve enantioselectivity and from an ongoing controversy over the reaction mechanism (Linker, 1997).

It has been shown that subtle changes in the nature of the axial ligands in Mn–Schiff base compounds and the solvent used for crystallization have a significant impact on the crystal structure of the complex (Horwits *et al.*, 1995; Martínez *et al.*, 2002). Moreover, axial coordination of various ligands to the oxomanganese(V) catalytically active species in the epoxidation reaction has been shown to have a significant impact on rate enhancement and enantioselectivity (El-Bahraoui *et al.*, 2001). We report here the crystal structure of the title Mn^{III} complex with *N*,*N*′-bis(salicylidene)stilbenediamine (stien), [Mn^{III}Cl(stien)(EtOH)], (I), which has a Cl^- anion and an ethanol molecule coordinated in the axial positions. The closely related compound [Mn(stien)(Me_2CO)$_2$](PF_6) has previously only been characterized in cationic form (Zhang *et al.*, 1990). We discuss here the differences caused by the change of coordination number and counter-ion.



(I)

Compound (I) crystallizes in the non-centrosymmetric space group $P2_12_12_1$. Two molecules having very similar geometry constitute the asymmetric unit. One of the molecules is shown in Fig. 1 and a superposition of the two molecules is presented in Fig. 2. The Mn atoms have pseudo-octahedral coordination spheres, with four donor atoms of the Schiff base forming the equatorial plane. The axial positions are occupied by an ethanol molecule and a Cl^- ligand.

Equatorial bond lengths and angles in the Mn coordination sphere of (I) are typical for salen complexes [salen is *N*,*N*′-ethylenebis(salicylideneamine)]. The axial sites in Mn–salen complexes are readily available for coordination, and only six-coordinate species are formed in the presence of coordinating solvents. As may be expected for a pseudo-octahedral complex, the displacements of the Mn atoms of (I) from the least-squares planes determined by the donor atoms of the Schiff base ligand are relatively small [0.0449 (7) Å for Mn1 and 0.0746 (7) Å for Mn2] compared with the values for related five-coordinate complexes [0.387 (1) and 0.451 (1) Å; Hirotsu *et al.*, 1995].

Jahn–Teller distortion, expected for a d^4 ion, leads to a significant elongation of the axial Mn—O bond [2.3069 (15) and 2.3130 (15) Å] compared with the in-plane Mn—O distances. The disorder observed in the coordinated ethanol molecule is similar to that observed by Oki & Hodgson (1990) in related Mn–Schiff base complexes.

The Mn—Cl bond distances observed in (I) [2.5732 (6) and 2.5509 (6) Å] are somewhat longer than the value of 2.4680 (16) Å observed for a simple octahedral Mn–salen complex (Martínez *et al.*, 2002) and the value of 2.391 (3) Å observed in [Mn{7-Phsal-(*S*,*S*)-stien}Cl] [7-Phsal-(*S*,*S*)-stein is 7,7′-diphenyl-*N*,*N*′-bis(salicylidene)-(*S*,*S*)-stilbenediamine; Hirotsu *et al.*, 1995], and are comparable with the Mn—Cl distance of 2.572 (1) Å in [MnCl(5,5′-Cl-salen)(H_2O)] (Horwitz *et al.*, 1995). Based on analysis of structural data for various five-coordinate manganese(III) and iron(III) Schiff base complexes, Pecoraro & Butler (1986) showed that the distance from the Cl atom to the centre of the basal plane of

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DOI: 10.1107/S0108270104000204

the coordinating atoms is constant regardless of the metal ion and equals 2.7 Å. The displacements of the Cl atoms from an N_2O_2 least-squares plane in (I) are slightly smaller, at 2.6055 (9) and 2.6162 (9) Å.

Comparison of the geometry of stien in the free ligand (Korendovych & Rybak-Akimova, 2003) and in its Mn^{III} complex, (I), shows that coordination of Mn causes slight elongation of the C═N bond [mean bond length of 1.288 (2) Å in (I) *versus* 1.270 Å in the free ligand] and shortening of the phenol C—O bond [mean bond length of 1.317 (2) Å in (I) *versus* 1.348 Å in the free ligand]. These values are close to those observed for the cationic Mn^{III}(stien) complex (phenol C—O = 1.319 Å and C═N = 1.275 Å; Zhang *et al.*, 1990).

The central chelate rings of (I) adopt δ *gauche* conformations, with the phenyl rings occupying equatorial positions. The corresponding N—C—C—N torsion angles are 43.86 (17) and 43.80 (16)°. Comparison of these values with that observed for an unsubstituted octahedral Mn–salen complex (46.70°; Martínez *et al.*, 2002) suggests that the phenyl substituents do not introduce substantial steric strain to the five-membered chelate ring. Interestingly, the corresponding dihedral angle in the cationic form of the complex, $[Mn(stien)(Me_2CO)_2](PF_6)$, is smaller, at 37.22°.

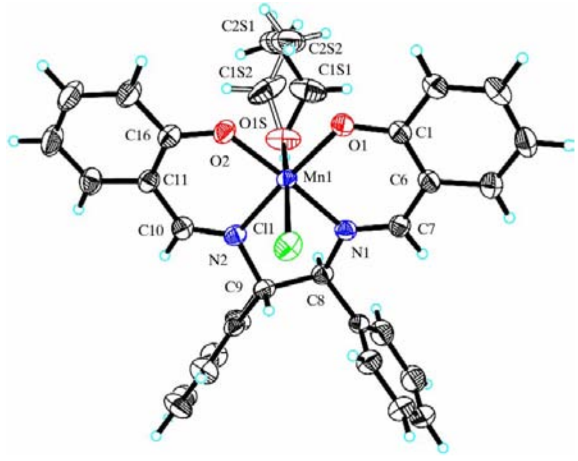

Figure 1
A view of a molecule of (I), showing the atom-labelling scheme for selected atoms. For clarity, only one of the two crystallographically independent molecules is shown. Displacement ellipsoids are drawn at the 50% probability level.

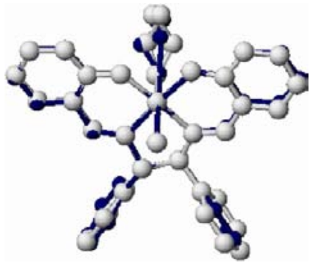

Figure 2
A superposition of the two crystallographically independent molecules of (I) (fit based on the N_2O_2 equatorial plane). The fragment containing Mn1 is shown in light grey and that containing Mn2 is shown in dark grey.

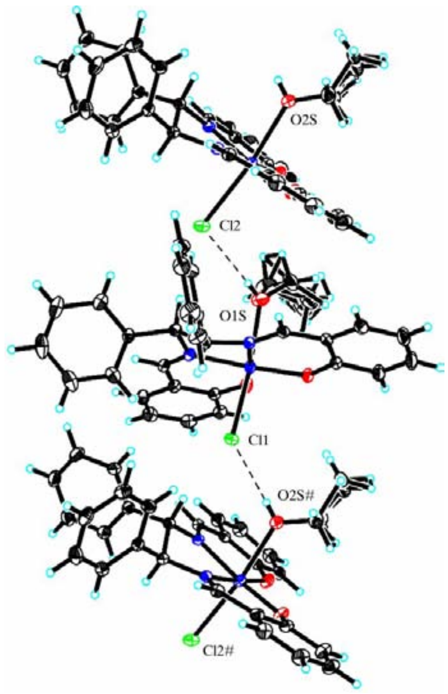

Figure 3
A view of (I) showing the polymeric hydrogen-bonded array, with displacement ellipsoids drawn at the 30% probability level. Atoms labelled with a hash (#) are at the symmetry position ($x + 1$, y, z).

An interesting feature of (I) is the formation of polymeric chains of Mn-containing fragments *via* hydrogen bonds formed between the OH group of the coordinated ethanol molecule and the coordinated Cl^- ligand (Fig. 3 and Table 2). The polymeric chains are formed along the crystallographic *c* axis. Both of the Mn–Schiff base complexes that constitute the asymmetric unit participate in this chain formation. The angle between the planes, determined by the N_2O_2 donor set of the ligand in the chain, is 40.09 (4)°. The formation of polymeric chains in (I), in contrast with the 'intricate arrays' observed for an Mn^{III}–salen complex with a water molecule in the axial position, where each coordinated water molecule forms two hydrogen bonds with the phenol O atoms of a neighbouring complex (Martínez *et al.*, 2002), is probably caused by the presence of bulky phenyl substituents and by only one H atom of the coordinated solvent being available for bonding.

Experimental

The title compound was prepared according to the general procedure of Jacobsen (Zhang & Jacobsen, 1991). (1*S*,2*S*)-(−)-1,2-Diphenyl-1,2-ethanediamine (99% purity, 99% e.e.), salicylaldehyde, LiCl and $Mn(CH_3CO_2)_2·4H_2O$ were purchased from Acros. All reagents were used as received without further purification. Salicylaldehyde (576 mg, 2.76 mmol) was added to a solution of (1*S*,2*S*)-(−)-1,2-diphenyl-1,2-ethanediamine (500 mg, 2.36 mmol) in absolute ethanol (12 ml) and the reaction mixture was refluxed for 1 h. The resulting Schiff base [H_2(1*S*,2*S*)-stien] was crystallized by cooling followed by the addition of few drops of water. Solid $Mn(OAc)_2·4H_2O$ (1.15 g, 4.72 mmol) was added to the ligand redissolved in hot absolute ethanol (25 ml) and the reaction mixture was refluxed for 1 h. Solid LiCl (250 mg) was then added to the reaction mixture, which was heated to reflux for an additional 30 min. The crude product, obtained by removal of the solvent *in vacuo*, was redissolved in dichloromethane and filtered to remove excess reagents. Concentration of the solution to *ca* 20 ml followed by cooling to 273 K produced dark-brown needles of the Mn^{III}(stien) complex in 83% yield. Slow evaporation of a solution in ethanol yielded crystals of (I).

Crystal data

$[MnCl(C_{28}H_{22}N_2O_2)(C_2H_6O)]$
M_r = 554.93
Orthorhombic, $P2_12_12_1$
a = 13.3857 (19) Å
b = 19.467 (3) Å
c = 20.823 (3) Å
V = 5425.9 (14) Å^3
Z = 8
D_x = 1.359 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 7828 reflections
θ = 2.2–28.2°
μ = 0.62 mm^{-1}
T = 173 (2) K
Block, brown
0.25 × 0.15 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.861, T_{max} = 0.941
41 965 measured reflections

13 026 independent reflections
11 709 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 28.3°
$h = -17 \rightarrow 17$
$k = -25 \rightarrow 23$
$l = -26 \rightarrow 27$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.076
S = 1.04
13 026 reflections
709 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0383P)^2 + 0.5484P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Absolute structure: Flack (1983), 5759 Friedel pairs
Flack parameter = 0.017 (9)

Table 1
Selected geometric parameters (Å, °).

Mn1—O2	1.8717 (13)	O1—C1	1.319 (2)
Mn1—O1	1.8740 (13)	Mn2—O3	1.8749 (13)
Mn1—N1	1.9868 (15)	Mn2—O4	1.8823 (13)
Mn1—N2	1.9910 (14)	Mn2—N4	1.9828 (15)
Mn1—O1S	2.3069 (15)	Mn2—N3	1.9979 (14)
Mn1—Cl1	2.5732 (6)	Mn2—O2S	2.3130 (15)
N1—C7	1.286 (2)	Mn2—Cl2	2.5509 (6)
O2—Mn1—O1	92.03 (6)	O3—Mn2—O4	92.35 (6)
O2—Mn1—N1	175.03 (6)	O3—Mn2—N4	175.29 (6)
O1—Mn1—N1	92.52 (6)	O4—Mn2—N4	92.03 (6)
O2—Mn1—N2	92.73 (6)	O3—Mn2—N3	92.87 (6)
O1—Mn1—N2	174.07 (6)	O4—Mn2—N3	170.89 (6)
N1—Mn1—N2	82.61 (6)	N4—Mn2—N3	82.56 (6)
O2—Mn1—O1S	90.10 (6)	O3—Mn2—O2S	90.81 (6)
O1—Mn1—O1S	92.63 (6)	O4—Mn2—O2S	87.73 (6)
N1—Mn1—O1S	87.68 (6)	N4—Mn2—O2S	87.64 (6)
N2—Mn1—O1S	83.82 (6)	N3—Mn2—O2S	84.73 (6)
O2—Mn1—Cl1	95.08 (4)	O3—Mn2—Cl2	94.33 (4)
O1—Mn1—Cl1	95.53 (5)	O4—Mn2—Cl2	96.93 (5)
N1—Mn1—Cl1	86.48 (4)	N4—Mn2—Cl2	86.85 (4)
N2—Mn1—Cl1	87.59 (4)	N3—Mn2—Cl2	90.11 (4)
O1S—Mn1—Cl1	170.16 (4)	O2S—Mn2—Cl2	172.90 (4)
N1—C8—C9—N2	43.86 (17)	N3—C36—C37—N4	43.80 (16)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1S—H1*S*···Cl2	0.73 (3)	2.41 (3)	3.1281 (16)	166 (3)
O2S—H2*S*···Cl1^{i}	0.74 (3)	2.39 (3)	3.1282 (15)	176 (3)

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

Carbon-bound H atoms were placed in idealized positions, with C—H distances in the range 0.95–1.00 Å, and refined using a riding model, with U_{iso}(H) = 1.2 or 1.5U_{eq}(C). The H atoms bound to the coordinated ethanol O atoms were found in a difference Fourier map and refined isotropically. Both coordinated ethanol molecules exhibit orientational disorder, which was modelled with a set of two positions for each molecule. The disordered C atoms were presumed to have the same anisotropic displacement parameters. Furthermore, C—O and C—C distances within the same molecule were restrained to be the same for both orientations. The occupancies of sites 1 and 2 converged at 0.507 (12) and 0.493 (12), respectively, for the molecule containing Mn1, and at 0.695 (10) and 0.305 (10), respectively, for the molecule containing Mn2.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*/*PC* (Bruker, 2000).

The authors are grateful to Dr Richard J. Staples for helpful discussions. The CCD-based X-ray diffractometer at Tufts University was purchased through Air Force DURIP grant No. F49620-01-1-0242.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1142). Services for accessing these data are described at the back of the journal.

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