Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1074). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Chloro[*N*,*N'*-ethylenebis(3-imino-1-phenyl-1-butanonato-*N*,*O*)]manganese(III), $[MnCl(C_{22}H_{22}N_2O_2)]$

Y.-L. Feng and S.-X. Liu*

Department of Chemistry, Fuzhou University, Fuzhou, Fujian 350002, People's Republic of China

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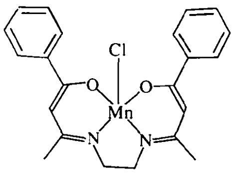
Abstract

The structure determination of chloro[1,1'-diphenyl-3,3'-(1,2-ethanediyldiimino)di-1-butanonato-*N*,*N'*,*O*,*O'*]-manganese(III), reveals a distorted square-pyramidal coordination at the Mn atom, with an N_2O_2 basal plane composed of atoms from the Schiff base ligand and a chlorine ligand in the axial position.

Comment

Mn^{III}-Schiff base complexes are among the simplest models for the active sites of manganoenzymes. Manganese complexes of the Schiff base ligand *N*,*N'*-ethylenebis(3-imino-1-phenyl-1-butanonato) (abbreviated to bzacen^{2-}) have been studied and shown to have three main structure types. Examples of these are mononuclear [Mn(bzacen)(pyrimidine)(NCS)] (Feng & Liu, 1996), bridged dinuclear $[Mn_2(bzacen)_2(MeOH)_2(\mu\text{-}4,4'\text{-bipy})](ClO_4)_2$ (where bipy is bipyridine; Liu & Feng, 1996) and the chain compound $[Mn(bzacen)(CH_3COO)]$ (Haider, Hashem, Khan, Malik & Hursthouse, 1985). The present work is part of a study of manganese complexes of the Schiff base ligand bzacen^{2-} and reports the structure of [MnCl(bzacen)], (I).



(I)

The five-coordinate Mn atom is chelated through covalent bonds to the N(1), N(2), O(1) and O(2) atoms of the Schiff base ligand lying in the basal plane, the Cl atom being in the axial position (Fig. 1). The deviations of the four N or O atoms from the basal plane are less than 0.081 Å. The Mn—O and Mn—N bond distances agree with the average values found in similar complexes reported by us (Feng & Liu, 1996; Liu & Feng, 1996). The Mn^{III} ion is therefore in a distorted square-pyramidal configuration. The Mn(1)—Cl(1) bond length of 2.415 (2) Å is longer than the corresponding value of 2.381 (1) Å found in [MnCl(acen)] (Boucher & Day, 1977), but shorter than that of 2.461 (1) Å found in [MnCl(salen)] (Pecoraro & Butler, 1986) and that of 2.574 (9) Å found in $[Mn(C_{34}H_{38}ClN_2O_6)]$ (Nagata, Imagawa, Yamada & Mukaiyama, 1994). The Mn—Cl bonds in these complexes are significantly longer than the normal value of 2.32 Å, being approximately 2.34 Å (Pecoraro & Butler, 1986). The distance of the Mn atom from the basal plane is 0.304 (2) Å for the title complex, the corresponding distances being 0.344 Å for [MnCl(acen)] and 0.19 Å for [MnCl(salen)]. Because of the displacement of 0.304 Å, the Mn—Cl bond length in the title complex must be longer than 2.4 Å so that the Cl atom is just in contact with the imine N atom. In other words, the distance between N(2) and Cl(1) of 3.270 (3) Å agrees with the sum of the van der Waals radii for N—Cl of 3.20 Å (Pauling, 1960). This means that the distances of the Cl atom from the atoms of the basal plane are all about 2.7 Å due to van der Waals contacts within these complexes (Pecoraro & Butler, 1986). Delocalization of double bonds within the O(1)—C(1)—C(2)—C(3)—N(1) and O(2)—C(10)—C(9)—C(7)—N(2) chelate rings is observed in the title complex, as was also found in [Mn(acen)Cl] (Boucher & Day, 1977). The two six-membered Mn—O—C—C—C—N rings are respectively planar, the dihedral angle between them being 25.9 (3)°.

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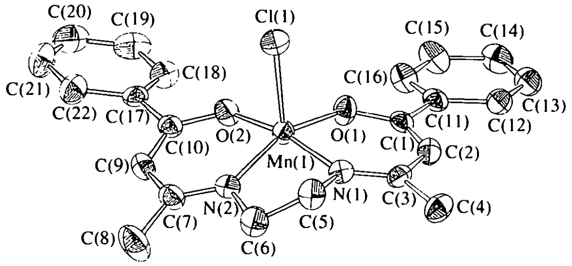

Fig. 1. The molecular structure of [MnCl(bzacen)] showing the atom-numbering scheme and 30% probability displacement ellipsoids.

Experimental

H_2bzacen (0.020 mol) and $[Mn(CH_3COO)_3].2H_2O$ (0.024 mol) were mixed in chloroform (30 ml) and the solution refluxed. Solid NaCl (0.024 mol) was added under stirring. The precipitate which formed was isolated by filtration and recrystallized to give crystals of the title compound.

Crystal data

$[MnCl(C_{22}H_{22}N_2O_2)]$
$M_r = 436.82$
Triclinic
$P\bar{1}$
$a = 10.914\,(2)$ Å
$b = 13.287\,(2)$ Å
$c = 7.317\,(2)$ Å
$\alpha = 93.43\,(2)°$
$\beta = 94.44\,(2)°$
$\gamma = 110.890\,(9)°$
$V = 984.0\,(3)$ Å^3
$Z = 2$
$D_x = 1.47$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10–15°$
$\mu = 0.800$ mm^{-1}
$T = 298$ K
Flake
0.40 × 0.30 × 0.25 mm
Red–brown

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.606$, $T_{\max} = 0.946$
4107 measured reflections
3892 independent reflections
2227 observed reflections $[I > 3\sigma(I)]$
$R_{\rm int} = 0.036$
$\theta_{\max} = 26.05°$
$h = 0 \rightarrow 13$
$k = -16 \rightarrow 16$
$l = -9 \rightarrow 9$
3 standard reflections monitored every 150 reflections
intensity decay: 1.7%

Refinement

Refinement on *F*
$R = 0.0446$
$wR = 0.0535$
$S = 1.172$
2227 reflections
254 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$B_{\rm eq} = (4/3)\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Mn(1)	0.31615 (7)	0.22608 (6)	−0.0444 (1)	2.27 (3)
Cl(1)	0.2030 (1)	0.1233 (1)	0.1934 (2)	3.44 (5)
O(1)	0.4874 (3)	0.2247 (3)	0.0128 (5)	3.1 (1)
O(2)	0.3690 (3)	0.3638 (3)	0.0877 (4)	2.8 (1)
N(1)	0.2751 (4)	0.1041 (3)	−0.2296 (5)	2.3 (1)
N(2)	0.1737 (4)	0.2522 (3)	−0.1901 (5)	2.4 (1)
C(1)	0.5435 (5)	0.1628 (4)	−0.0592 (6)	2.3 (2)
C(2)	0.4814 (5)	0.0802 (4)	−0.1924 (7)	2.6 (2)
C(3)	0.3511 (5)	0.0517 (4)	−0.2756 (6)	2.4 (2)
C(4)	0.3033 (5)	−0.0418 (4)	−0.4212 (7)	3.3 (2)
C(5)	0.1371 (5)	0.0690 (4)	−0.3090 (7)	3.2 (2)
C(6)	0.1047 (5)	0.1665 (4)	−0.3401 (7)	3.5 (2)
C(7)	0.1432 (5)	0.3386 (4)	−0.1748 (7)	2.9 (2)
C(8)	0.0372 (7)	0.3508 (5)	−0.3054 (9)	5.3 (3)
C(9)	0.2074 (5)	0.4262 (4)	−0.0393 (7)	3.1 (2)
C(10)	0.3119 (4)	0.4341 (4)	0.0846 (6)	2.3 (2)
C(11)	0.6835 (5)	0.1925 (4)	0.0159 (6)	2.5 (2)
C(12)	0.7568 (5)	0.1281 (4)	−0.0288 (7)	3.0 (2)
C(13)	0.8867 (5)	0.1588 (5)	0.0425 (8)	3.7 (2)
C(14)	0.9468 (5)	0.2505 (5)	0.1592 (8)	3.7 (2)
C(15)	0.8752 (5)	0.3144 (4)	0.2017 (8)	3.6 (2)
C(16)	0.7467 (5)	0.2863 (4)	0.1307 (7)	3.2 (2)
C(17)	0.3695 (5)	0.5281 (4)	0.2251 (6)	2.5 (2)
C(18)	0.4985 (5)	0.5580 (4)	0.3006 (7)	3.0 (2)
C(19)	0.5520 (6)	0.6448 (4)	0.4327 (7)	3.8 (2)
C(20)	0.4780 (7)	0.7027 (4)	0.4923 (8)	4.4 (2)
C(21)	0.3508 (7)	0.6738 (5)	0.4179 (8)	4.9 (3)
C(22)	0.2962 (6)	0.5875 (4)	0.2846 (7)	3.8 (2)

Table 2. *Selected geometric parameters (Å, °)*

Mn(1)—O(1)	1.890 (3)	N(1)—C(3)	1.309 (5)
Mn(1)—O(2)	1.888 (3)	N(1)—C(5)	1.468 (6)
Mn(1)—N(1)	1.947 (4)	N(2)—C(7)	1.306 (6)
Mn(1)—N(2)	1.961 (4)	N(2)—C(6)	1.476 (6)
Mn(1)—Cl(1)	2.415 (2)	C(1)—C(11)	1.485 (6)
O(1)—C(1)	1.299 (5)	C(5)—C(6)	1.486 (7)
O(2)—C(10)	1.295 (5)	C(10)—C(17)	1.484 (6)
O(1)—Mn(1)—N(1)	90.7 (1)	C(6)—N(2)—Mn(1)	113.7 (3)
O(1)—Mn(1)—N(2)	156.7 (2)	O(1)—C(1)—C(2)	123.5 (4)
O(1)—Mn(1)—Cl(1)	100.5 (1)	O(1)—C(1)—C(11)	113.2 (4)
O(2)—Mn(1)—O(1)	89.5 (1)	C(2)—C(1)—C(11)	123.2 (4)
O(2)—Mn(1)—N(1)	166.4 (2)	C(1)—C(2)—C(3)	125.8 (4)
O(2)—Mn(1)—N(2)	91.4 (1)	N(1)—C(3)—C(2)	122.2 (4)
O(2)—Mn(1)—Cl(1)	96.8 (1)	N(1)—C(3)—C(4)	121.1 (4)
N(1)—Mn(1)—N(2)	83.1 (2)	C(2)—C(3)—C(4)	116.6 (4)
N(1)—Mn(1)—Cl(1)	96.5 (1)	N(1)—C(5)—C(6)	108.6 (4)
N(2)—Mn(1)—Cl(1)	102.6 (1)	N(2)—C(6)—C(5)	109.4 (4)
C(1)—O(1)—Mn(1)	129.7 (3)	N(2)—C(7)—C(9)	123.1 (4)
C(10)—O(2)—Mn(1)	129.0 (3)	N(2)—C(7)—C(8)	120.9 (5)
C(3)—N(1)—C(5)	121.4 (4)	C(9)—C(7)—C(8)	116.1 (4)
C(3)—N(1)—Mn(1)	128.0 (3)	C(10)—C(9)—C(7)	125.1 (4)
C(5)—N(1)—Mn(1)	110.5 (3)	O(2)—C(10)—C(9)	124.1 (4)
C(7)—N(2)—C(6)	119.3 (4)	O(2)—C(10)—C(17)	115.1 (4)
C(7)—N(2)—Mn(1)	126.7 (3)	C(9)—C(10)—C(17)	120.7 (4)

The data were corrected for Lp effects. The structure was solved by direct (*MITHRIL*; Gilmore, 1983) and Fourier methods, and refined by full-matrix least squares (Peterse & Palmy, 1966). All H atoms were located from difference Fourier maps and geometrical calculations. All calculations were performed on a MicroVAX II computer using *TEXSAN* software (Molecular Structure Corporation, 1985).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1098). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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