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Dichlorobis[*N*-(2-oxymethylphenyl)salicylideneiminato]diiron(III)

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Key indicators

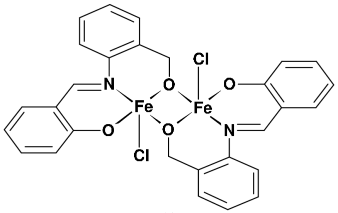
Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.006 Å
R factor = 0.040
wR factor = 0.123
Data-to-parameter ratio = 16.8

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

The title compound, $[FeCl(C_{14}H_{11}NO_2)]_2$, represents the first structurally characterized complex of the *N*-(2-oxymethylphenyl)salicylideneiminate tridentate ligand. The molecule of the binuclear iron complex occupies a special position on a crystallographic inversion centre. The Fe atoms are bridged by two O atoms originating from the alcohol, rather than the phenolic hydroxyl groups, with an Fe$\cdots$Fe separation of 3.1282 (7) Å. The coordination polyhedron of the Fe atoms can be described as square pyramidal, with an O_3N basal plane and an apical Cl atom or, alternatively, as trigonal bipyramidal, with the N atom and one of the bridging O atoms in the axial positions.

Comment

The construction of metal-assembled complexes containing a unique polynuclear core has received extensive attention recently (see, for instance, Hoshino *et al.*, 2003). We are interested in the syntheses of such metal complexes with ONO-tridentate ligands containing hydroxyl groups at both peripheral positions of the ligand framework (Koikawa *et al.*, 2003). These tridentate ligands form various kinds of polynuclear complexes due to the ability of the hydroxyl groups to act as good bridging atoms. The *N*-(2-hydroxymethylphenyl)salicylideneimine ligand, H_2L, derived from salicylaldehyde and 2-aminobenzylalcohol, was first reported by Syamal & Kale (1980). They described the syntheses and magnetic properties of Cu^{II} and Fe^{III} complexes of H_2L, and concluded that the compounds were dinuclear complexes. However, we recently found that the Cu^{II} complex with a monochlorosubstituted analog, L'^{2-} [H_2L' = *N*-(2-hydroxymethyl-4-chlorophenyl)salicylideneimine, $HOCH_2C_6H_3(Cl)N=CHC_6H_4OH$], has a tetranuclear structure $[CuL']_4$, which was obtained by oxidation of $[CuL'']_4$ [H_2L'' = 2-(2-hydroxymethyl-4-chlorophenyl)aminomethylphenol, $HOCH_2C_6H_3(Cl)NHCH_2C_6H_4OH$] (Yamashita *et al.*, 2000). While attempting to prepare other tetranuclear complexes with L^{2-} or its analogs, we obtained single crystals of the title complex, $[FeCl(L)]_2$, (I). Its structure, reported here, is the first of a metal complex with the tridentate L^{2-} ligand.



(I)

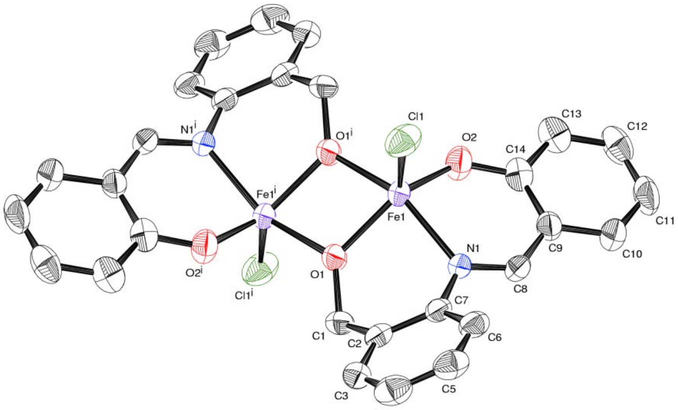


Figure 1
View of the title complex, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level; H atoms are omitted for clarity. [Symmetry code: (i) $1 - x, -y, 1 - z$.]

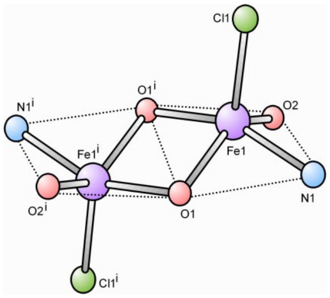


Figure 2
The diiron core structure of the dimeric molecule of (I). [Symmetry code: (i) $1 - x, -y, 1 - z$.]

The crystal structure of the title compound (I) is built of dimeric molecules occupying special positions on crystallographic inversion centers (Fig. 1). Two modes of dimerization are conceivable for (I), either through bridging alcohol or bridging phenolic O atoms. The X-ray results clearly show that the alcohol O atom functions as a bridge between the two iron atoms with an Fe1$\cdots$Fe1^i [symmetry code: (i) $1 - x, -y, 1 - z$] separation of 3.1282 (7) Å (Table 1). Each Fe atom is coordinated by the bridging alcohol O atoms O1 and O1^i, the non-bridging phenolic oxygen O2, the imine N atom N1, and the terminal chloride Cl1. The coordination polyhedron of atom Fe1 is intermediate between trigonal bipyramidal (TBP) and square pyramidal (SP) (Fig. 2). The degree of distortion (τ) from TBP to SP can be estimated by the method of Addison & Rao (1984). Analysis of the geometry of the Fe1 environment gives a value of $\tau = 0.40$, indicating an exceedingly distorted square pyramid as the coordination polyhedron. Atom Fe1 deviates by 0.547 (1) Å from the basal plane formed by O1, O1^i, O2 and N1; the apical position of the coordination SP is occupied by Cl1, with an Fe1–Cl1 distance of 2.220 (1) Å. Alternatively, the almost planar O1, O2, Cl1, Fe1 arrangement and wide N1–Fe1–O1^i angle of 157.00 (8)° characterize the TBP polyhedron of Fe1 coordination. The distorted coordination geometry of the Fe atom is very similar to that in $[FeCl(SALPA)]_2$ [SALPA = *N*-(3-hydroxypropyl)-salicylideneiminate] (Bertrand *et al.*, 1973).

Experimental

The title complex was prepared according to Jezowska-Trzebiatowska *et al.* (1988). Dark-brown crystals were obtained by recrystallization from dichloromethane.

Crystal data

$[Fe_2Cl_2(C_{28}H_{22}N_2O_4)]$
$M_r = 633.09$
Monoclinic, $P2_1/n$
$a = 10.182$ (2) Å
$b = 12.131$ (2) Å
$c = 11.300$ (2) Å
$\beta = 106.11$ (1)°
$V = 1340.9$ (4) Å^3
$Z = 2$
$D_x = 1.568$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.1$–12.4°
$\mu = 1.32$ mm^{-1}
$T = 296.1$ K
Prism, dark brown
0.30 × 0.20 × 0.20 mm

Data collection

Rigaku AFC-5*S* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.724$, $T_{max} = 0.768$
3405 measured reflections
3081 independent reflections
1809 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 15$
$l = -14 \rightarrow 14$
3 standard reflections every 150 reflections intensity decay: 1.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.123$
$S = 1.00$
3079 reflections
183 parameters
H-atom parameters constrained
$w = (1/[\sigma(F_o^2) + 0.0006F_o^2])/(4F_o^2)$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.02$ e Å^{-3}
$\Delta\rho_{min} = -1.65$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Fe1—Cl1	2.220 (1)	C3—C4	1.373 (6)
Fe1—O1	1.962 (3)	C4—C5	1.372 (7)
Fe1—O1^i	1.981 (2)	C5—C6	1.387 (6)
Fe1—O2	1.862 (3)	C6—C7	1.386 (5)
Fe1—N1	2.090 (2)	C8—C9	1.418 (6)
O1—C1	1.428 (4)	C9—C10	1.406 (6)
O2—C14	1.324 (5)	C9—C14	1.419 (5)
N1—C7	1.431 (5)	C10—C11	1.354 (8)
N1—C8	1.303 (5)	C11—C12	1.381 (7)
C1—C2	1.506 (5)	C12—C13	1.374 (6)
C2—C3	1.388 (6)	C13—C14	1.402 (7)
C2—C7	1.401 (5)	Fe1—Fe1^i	3.1282 (7)
Cl1—Fe1—O1	116.90 (9)	C7—C2—C1	121.5 (4)
Cl1—Fe1—O2	110.3 (1)	C4—C3—C2	121.6 (4)
Cl1—Fe1—N1	98.46 (9)	C5—C4—C3	120.1 (4)
Cl1—Fe1—O1^i	101.64 (3)	C6—C5—C4	120.0 (4)
O1—Fe1—O2	132.8 (1)	C7—C6—C5	120.0 (4)
O1—Fe1—N1	86.0 (1)	N1—C7—C2	118.4 (3)
O1—Fe1—O1^i	74.99 (7)	N1—C7—C6	121.1 (3)
O2—Fe1—N1	89.5 (1)	C2—C7—C6	120.4 (4)
O2—Fe1—O1^i	93.90 (8)	C9—C8—N1	126.9 (3)
N1—Fe1—O1^i	157.00 (8)	C10—C9—C14	118.0 (4)
C1—O1—Fe1	128.5 (2)	C10—C9—C8	118.4 (4)
C1—O1—Fe1^i	125.5 (2)	C14—C9—C8	123.6 (3)
Fe1—O1—Fe1^i	105.0 (1)	C11—C10—C9	122.1 (4)
C14—O2—Fe1	132.8 (3)	C12—C11—C10	119.5 (4)
C7—N1—C8	118.6 (3)	C13—C12—C11	121.2 (5)
C7—N1—Fe1	117.3 (2)	C14—C13—C12	120.3 (4)
C8—N1—Fe1	123.4 (3)	O2—C14—C9	122.0 (4)
C2—C1—O1	110.9 (3)	O2—C14—C13	119.0 (3)
C3—C2—C7	118.0 (3)	C9—C14—C13	118.9 (4)
C3—C2—C1	120.4 (3)		

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

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Two reflections giving bad agreements with F_c were excluded from the refinement. H atoms were placed in geometrically calculated positions (C—H = 0.95 Å) and included in the refinement in the riding-model approximation, with $U_{\rm iso} = 1.2U_{\rm eq}$ of the carrier atom. The residual highest peak and deepest hole are 1.89 Å from N1 and 0.88 Å from O2, respectively.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *CrystalStructure* (Rigaku/MSC and Rigaku Corporation, 2003); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 1996); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

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