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[Benzoylacetone (4-methoxybenzoyl)hydrazonato-κ^3O,N^2,O']dichloroiron(III)

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Key indicators

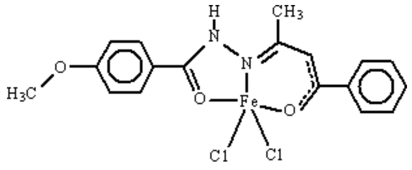
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.042
wR factor = 0.100
Data-to-parameter ratio = 17.9

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

In the title complex, [Fe($C_{18}H_{17}N_2O_3$)Cl_2], the Fe^{III} species has a distorted trigonal–bipyramidal geometry, defined by two O atoms and one N atom from the tridentate hydrazone ligand and two Cl^- anions. A hydrogen-bonded dimer is formed *via* two N—H···Cl intermolecular hydrogen bonds across a center of inversion.

Comment

The biological activities and chemical versatilities of metal–hydrazone complexes continue to attract considerable attention. A number of metal complexes with hydrazone ligands have been structurally characterized to date, in which the hydrazone ligands are formed by condensing hydrazine with acetylacetones, salicylaldehydes and their derivatives (Liu & Gao, 1998; Gao *et al.*, 1998; Chen *et al.*, 1999). As yet, there is little information about the structures of Fe^{III}–hydrazone complexes (Aruffo *et al.*, 1982, 1984). Recently, we reported the complex [Fe(HL')Cl_2(CH_3OH)]·CH_3OH [H_2L' = 3-methoxysalicylaldehyde (4-methoxybenzoyl)hydrazone], in which the Fe^{III} species adopts six-coordinate octahedral geometry (Huo *et al.*, 2004). In the present paper, we report the crystal structure of [benzoylacetone (4-methoxybenzoyl)-hydrazonato-κ^3O,N,O']dichloroiron(III), [Fe(HL)Cl_2], (I), prepared by the reaction of H_2L [benzoylacetone (4-methoxybenzoyl)hydrazone] and $FeCl_3\cdot 6H_2O$ in methanol.



(I)

As shown in Fig. 1, the uncoordinated hydrazide atom N2 remains protonated, so that the organic hydrazone ligand (H_2L) bears a formal charge of −1. The Fe^{III} atom has a distorted trigonal–bipyramid geometry, with a Cl_2NO_2 donor set defined by two O atoms and one N atom from the

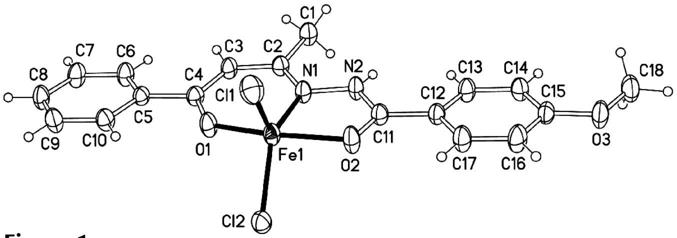


Figure 1
View of (I), with 30% probability displacement ellipsoids (small spheres for the H atoms).

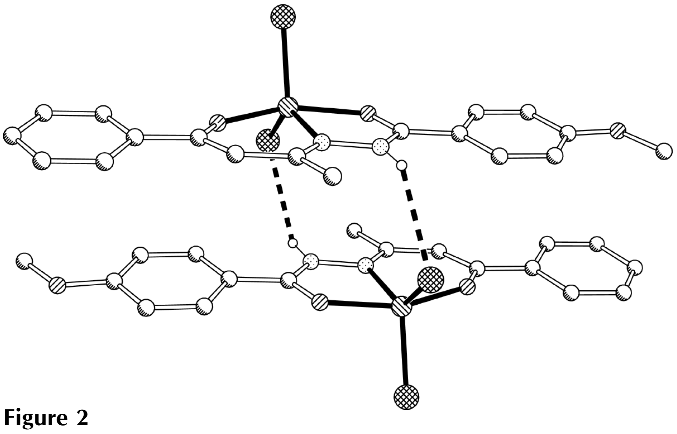


Figure 2

The hydrogen-bonded (dashed lines) dimeric structure of (I), with C—H H atoms omitted for clarity.

tridentate hydrazone HL^- ligand and two Cl^- anions (Table 1). The equatorial plane is defined by atoms N1, Cl1 and Cl2, with the Fe atom displaced by 0.1012 (8) Å from this plane. The axial sites are occupied by two atoms O1 and O2, with the O1—Fe1—O2 angle being 158.22 (8)°. The Fe—O1 bond distance is shorter than that of Fe—O2 (Table 1). It should be noted that the O1—C4, O2—C11, C2—N1 and C3—C4 distances are relatively short, consistent with partial double-bond character. The five-membered O2/C9/N1/N2/Fe1 chelate ring (r.m.s. deviation = 0.0220 Å) and the six-membered O1/C1/C6/C7/N1/Fe1 chelate ring (r.m.s. deviation = 0.0583 Å) are both approximately planar, the dihedral angle between them being 4.66 (5)°. The two benzene rings are coplanar with a dihedral angle of 0.63 (5)°, and the tridentate hydrazone ligand is nearly planar with an overall r.m.s. deviation of 0.0878 Å. The protonated atom N1 of the hydrazone ligand forms an intermolecular N—H···Cl hydrogen bond with a Cl atom of an adjacent molecule, giving rise to the formation of a hydrogen-bonded dimer across a center of inversion (Table 2 and Fig. 2).

Experimental

The hydrazone ligand H_2L [benzoylacetone (4-methoxybenzoyl)-hydrazone] was synthesized by condensing benzoylacetone with an equimolar amount of 4-methoxybenzoylhydrazine in ethanol (Gao *et al.*, 1998). A methanol solution (15 ml) of $FeCl_3\cdot6H_2O$ (2 mmol) was added dropwise to a methanol solution (15 ml) containing H_2L (2 mmol). The resulting mixture was refluxed with stirring for 30 min, cooled slowly to room temperature and then filtered. Black crystals of (I) were obtained from the filtrate over a period of several days. Analysis calculated for $C_{18}H_{17}Cl_2FN_2O_3e$: C 49.58, H 3.93, N 6.42%; found: C 49.72, H 4.03, N 6.36%.

Crystal data

$[Fe(C_{18}H_{17}N_2O_3)Cl_2]$
$M_r = 436.09$
Monoclinic, $P2_1/c$
$a = 7.5958$ (3) Å
$b = 13.4330$ (3) Å
$c = 18.5880$ (4) Å
$\beta = 94.973$ (3)°
$V = 1889.48$ (10) Å^3
$Z = 4$
$D_x = 1.533$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 17064 reflections
$\theta = 3.1$–27.5°
$\mu = 1.10$ mm^{-1}
$T = 293$ (2) K
Prism, black
0.39 × 0.26 × 0.18 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.673$, $T_{max} = 0.827$
17967 measured reflections
4303 independent reflections
3411 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 27.4°$
$h = -8 \rightarrow 9$
$k = -17 \rightarrow 17$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.100$
$S = 1.05$
4303 reflections
240 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0455P)^2 + 0.877P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Fe1—Cl1	2.2192 (8)	N1—C2	1.326 (3)
Fe1—Cl2	2.2382 (7)	O1—C4	1.289 (3)
Fe1—N1	2.070 (2)	O2—C11	1.259 (3)
Fe1—O1	1.916 (2)	C3—C4	1.379 (3)
Fe1—O2	2.039 (2)		
Cl1—Fe1—Cl2	110.07 (3)	O1—Fe1—N1	84.70 (7)
N1—Fe1—Cl1	116.79 (6)	O1—Fe1—O2	158.22 (8)
N1—Fe1—Cl2	132.47 (6)	O2—Fe1—Cl1	97.16 (6)
O1—Fe1—Cl1	99.64 (7)	O2—Fe1—Cl2	91.86 (6)
O1—Fe1—Cl2	95.28 (6)	O2—Fe1—N1	75.37 (7)

Table 2

Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H19···Cl2^i	0.89 (2)	2.75 (2)	3.438 (2)	135 (2)

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

H atoms on C atoms were placed in calculated positions, with C—H = 0.93 (aromatic) or 0.96 Å (methyl) and $U_{iso}(H) = 1.2U_{eq}(C)$ or $U_{iso}(H) = 1.5U_{eq}(C_{methyl})$ in the riding-model approximation. The H atom on the N atom was located in a difference map and refined with an N—H distance restraint of 0.90 (1) Å and the constraint $U_{iso}(H) = 1.5U_{eq}(N)$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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