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Dichloro(methanol-*κO*)[3-methoxysalicylaldehyde (4-methoxybenzoyl)hydrazonato-κ^3*O*,*O′*,*N*]iron(III) methanol solvate

Li-Hua Huo, Shan Gao,* Ji-Wei Liu, Jing Li, Hui Zhao and Jing-Gui Zhao

College of Chemistry and Chemical Technology,
Heilongjiang University, Harbin 150080,
People's Republic of China

Correspondence e-mail:
shangao67@yahoo.com

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The Fe^{III} atom in the title complex, $[Fe(HL)Cl_2(CH_3OH)]\cdot CH_3OH$, [$H_2L$ = 3-methoxysalicylaldehyde (4-methoxybenzoyl)hydrazone, $C_{16}H_{15}N_2O_4$], is coordinated by two O atoms and one N atom of the tridentate hydrazone ligand, two chloride anions and one methanol molecule, thus defining a distorted octahedral geometry. A chain structure is constructed by hydrogen-bond interactions.

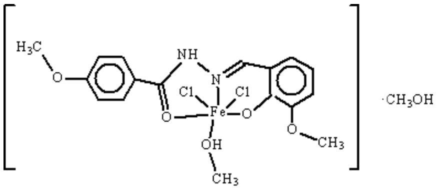
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
R factor = 0.065
wR factor = 0.187
Data-to-parameter ratio = 17.5

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

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 (Iskander *et al.*, 2000*a*,*b*; Dutta *et al.*, 1995; Liu & Gao, 1998; Gao *et al.*, 1998). As yet, there is little information about the structures of iron–hydrazone complexes (Aruffo *et al.*, 1982, 1984). The 3-methoxysalicylaldehyde (4-methoxybenzoyl)hydrazone molecule is a potentially tridentate chelating agent formed by condensing 3-methoxysalicylaldehyde with 4-methoxybenzoylhydrazine. Recently, we have obtained the title iron(III) complex, $[Fe(HL)Cl_2(CH_3OH)]\cdot CH_3OH$, (I), by the reaction of iron trichloride hexahydrate and H_2L hydrazone ligand in methanol solution; the crystal structure is reported here.



(I)

As shown in Fig. 1, the asymmetric unit of (I) consists of the $[Fe(HL)Cl_2(CH_3OH)]$ complex and one free methanol molecule. A bifurcated intramolecular hydrogen bond (O—H···Cl/Cl) is formed between methanol and atoms Cl1 and Cl2, with O···Cl bond distances of 3.201 (4) and 3.352 (5) Å, and O—H···Cl bond angles of 151 (7) and 126 (6)°, respectively (Table 2). The uncoordinated hydrazidic atom N2 remains protonated, so that the organic hydrazone ligand bears a formal charge of −1. The Fe atom is bound by three O atoms, two chloride anions and one N atom that define a distorted octahedral configuration, with atoms O5 and Cl2 occupying the axial positions [O—Fe—Cl = 174.4 (1)°]. The equatorial plane is defined by atoms O1, O2 and N1 of the tridentate hydrazone ligand and atom Cl1, the Fe atom being displaced by 0.152 (5) Å from the least-squares equatorial plane. The Fe—Cl2 distance of 2.280 (2) Å is longer than the

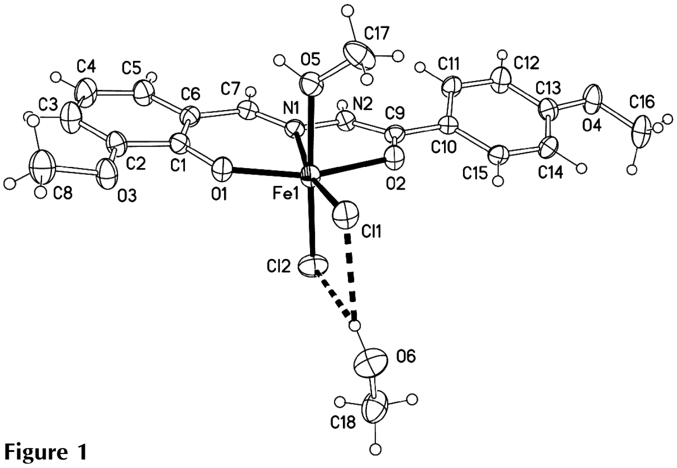


Figure 1
*ORTEP*II (Johnson, 1976) plot of (I), with 30% probability ellipsoids (arbitrary spheres for the H atoms). O—H···Cl hydrogen bonds are indicated by dashed lines.

Fe—Cl1 distance of 2.247 (2)°, and the Fe1—O1 distance of 1.897 (3) Å is the shortest among all the coordination bond lengths. The five-membered O2/C9/N1/N2/Fe1 chelate ring (r.m.s. deviation = 0.04 Å) and the six-membered O1/C1/C6/C7/N1/Fe1 chelate ring (r.m.s. deviation = 0.01 Å) are both approximately planar, the dihedral angle between them being 5.95 (5)°. The dihedral angle between the two benzene rings in the hydrazone ligand is 15.4 (5)°. A chain structure is formed by intermolecular hydrogen bonds between adjacent molecules (Table 2 and Fig. 2).

Experimental

The ligand 3-methoxysalicylaldehyde (4-methoxybenzoyl)hydrazone was synthesized by condensing 3-methoxysalicylaldehyde with equimolar 4-methoxybenzoylhydrazine in ethanol. Iron trichloride hexahydrate (1 mmol) was added to a 30 ml methanol solution containing 3-methoxysalicylaldehyde (4-methoxybenzoyl)hydrazone (1 mmol). The resulting mixture was refluxed with stirring for 1.5 h, and then cooled slowly to room temperature and filtered. Black prism-shaped crystals were obtained from the solution after several days. CHN analysis calculated for $C_{18}H_{23}Cl_2FeN_2O_6$: C 44.11, H 4.73, N 5.72%; found: C 43.97, H 4.83, N 5.69%.

Crystal data

$[Fe(C_{16}H_{15}N_2O_4)Cl_2(CH_4O)]\cdot CH_4O$
$M_r = 490.13$
Monoclinic, $P2_1/c$
$a = 17.226 (3)$ Å
$b = 10.622 (2)$ Å
$c = 12.096 (2)$ Å
$\beta = 105.42 (3)°$
$V = 2133.6 (7)$ Å^3
$Z = 4$
$D_x = 1.526$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12723 reflections
$\theta = 3.0–27.4°$
$\mu = 0.99$ mm^{-1}
$T = 293 (2)$ K
Prism, black
0.37 × 0.23 × 0.16 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.710$, $T_{max} = 0.857$
12872 measured reflections
4757 independent reflections
2849 reflections with $I > 2\sigma(I)$
$R_{int} = 0.081$
$\theta_{max} = 27.5°$
$h = -22 \rightarrow 22$
$k = -13 \rightarrow 13$
$l = -15 \rightarrow 15$

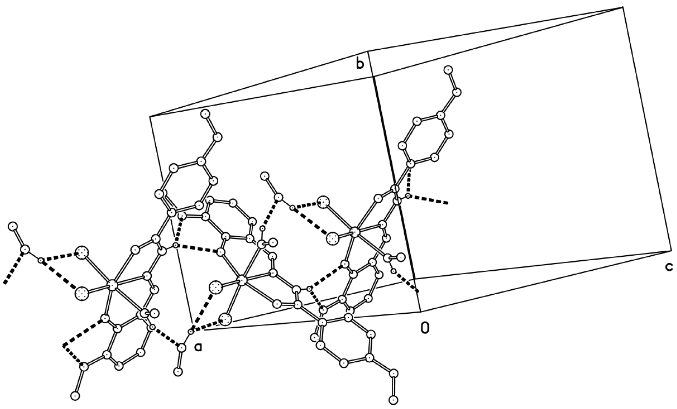


Figure 2
Part of the hydrogen-bond chain structure in (I).

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.065$
$wR(F^2) = 0.187$
$S = 1.02$
4757 reflections
272 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0998P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.64$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Fe1—Cl1	2.247 (2)	N1—N2	1.371 (5)
Fe1—Cl2	2.280 (2)	N1—C7	1.259 (6)
Fe1—N1	2.135 (4)	N2—C9	1.309 (6)
Fe1—O1	1.897 (3)	O1—C1	1.294 (5)
Fe1—O2	2.033 (3)	O2—C9	1.253 (5)
Fe1—O5	2.104 (4)		
Cl1—Fe1—Cl2	96.34 (6)	O2—Fe1—Cl1	96.35 (9)
N1—Fe1—Cl1	167.6 (1)	O2—Fe1—Cl2	88.3 (1)
N1—Fe1—Cl2	91.6 (1)	O2—Fe1—N1	74.3 (1)
O1—Fe1—Cl1	103.3 (1)	O2—Fe1—O5	87.6 (1)
O1—Fe1—Cl2	98.8 (1)	O5—Fe1—Cl1	87.9 (1)
O1—Fe1—N1	84.8 (1)	O5—Fe1—Cl2	174.4 (1)
O1—Fe1—O2	158.2 (1)	O5—Fe1—N1	83.6 (1)
O1—Fe1—O5	83.7 (1)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H19···O1^{i}	0.903 (17)	2.33 (3)	3.123 (4)	148 (4)
N2—H19···O3^{i}	0.903 (17)	2.11 (3)	2.872 (5)	142 (4)
O5—H20···O6^{i}	0.84 (4)	1.84 (2)	2.646 (5)	158 (6)
O6—H21···Cl1	0.85 (6)	2.43 (4)	3.201 (4)	151 (7)
O6—H21···Cl2	0.85 (6)	2.79 (6)	3.352 (5)	126 (6)

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

The H atoms of the hydroxy groups and on N2 were located in a difference Fourier map and refined isotropically. Other H atoms were placed in calculated positions and were allowed to ride on their parent C atoms [C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}$ for the aromatic H atoms; C—H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}$ for the methyl H atoms].

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC,

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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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