

C7	0.5254 (7)	0.1436 (3)	0.6474 (4)	0.0292 (2)
C8	0.4388 (6)	0.1947 (3)	0.7252 (4)	0.0279 (2)
C9	0.5509 (7)	0.2523 (3)	0.7966 (5)	0.0355 (1)
C10	0.4787 (8)	0.2984 (3)	0.8750 (5)	0.0406 (1)
C11	0.2975 (8)	0.2849 (3)	0.8848 (5)	0.0406 (1)
C12	0.1842 (7)	0.2273 (3)	0.8150 (5)	0.0355 (1)
C13	0.2529 (7)	0.1824 (3)	0.7333 (4)	0.0304 (1)

Table 2. Selected geometric parameters (Å, °)

Co—O1	2.132 (3)	O4—C12	1.347 (7)
Co—O2	2.099 (3)	O5—C6	1.224 (6)
Co—N1	2.139 (4)	N1—C1	1.339 (7)
O2—C7	1.263 (5)	N1—C5	1.339 (6)
O3—C7	1.258 (6)	N2—C6	1.327 (7)
O1—Co—O2	93.4 (1)	O4—C12—C11	115.2 (5)
O1—Co—N1	87.6 (1)	O4—C12—C13	124.4 (4)
O2—Co—N1	91.3 (1)	N1—C5—C4	123.0 (5)
Co—O2—C7	126.3 (3)	O5—C6—N2	121.8 (5)
Co—N1—C1	120.6 (3)	N2—C6—C2	117.9 (4)
Co—N1—C5	122.0 (4)	O2—C7—O3	123.3 (5)
O1—Co—O2—C7	-10.3 (4)	O1—Co—N1—C5	-132.6 (4)
N1—Co—O2—C7	-98.0 (4)	O2—Co—N1—C1	139.6 (4)
O1—Co—N1—C1	46.3 (4)	O2—Co—N1—C5	-39.3 (4)

Some of the H-atom positions were determined from difference synthesis and were refined isotropically. The remaining H atoms were positioned geometrically at a distance of 0.95 Å from their parent C atoms and a riding model was used during the refinement process.

Data collection: *MolEN* (Fair, 1990). Cell refinement: *MolEN*. Data reduction: *MolEN*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1329). Services for accessing these data are described at the back of the journal.

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[Fe(HL)Cl₂].EtOH, where HL is the monoanion of benzoylacetone *S-n*-propylisothiosemicarbazone

GYULA ARGAY,^a ALAJOS KÁLMÁN^a AND VUKADIN M. LEOVAC^b

^a*Institute of Chemistry, Chemical Research Center, Hungarian Academy of Sciences, PO Box 17, H-1525 Budapest, Hungary, and* ^b*University of Novi Sad, Faculty of Sciences, Institute of Chemistry, Trg D. Obradovica 3, 21000 Novi Sad, Yugoslavia. E-mail: akalman@cric.chemres.hu*

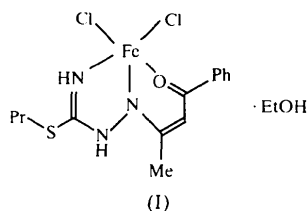
(Received 26 March 1999; accepted 3 June 1999)

Abstract

In the title compound, (benzoylacetone *S-n*-propylisothiosemicarbazone-*O,N*^{1,N}⁴)dichloroiron(III) ethanol solvate, [Fe(C₁₄H₁₈N₃OS)Cl₂].C₂H₅OH, the Fe^{III} ion has a distorted square-pyramidal environment. In the equatorial plane, iron(III) is coordinated by one O and two N atoms from the chelate ligand and by one Cl atom, while the apical position is occupied by the second Cl ligand. The molecule is connected to neighbouring symmetry-equivalent molecules through hydrogen bonds of different types.

Comment

The synthesis of an iron(III) complex with benzoylacetone *S*-methylthiosemicarbazone (H₂L¹) resulting in the formula [Fe(HL¹)Cl₂] has been published previously (Leovac *et al.*, 1994). On the basis of IR spectroscopic and conductometric data, it has been supposed that this complex has a pentacoordinate structure, established by coordinating a monoanion of the tridentate *O,N,N*-ligand H₂L¹. However, the question as to whether either square-pyramidal (SP) or trigonal-bipyramidal (TBP) coordination occurs remained unanswered. By solving the crystal and molecular structures of a newly synthesized analogous iron(III) complex, (I), having a similar tridentate benzoylacetone *S-n*-propylisothiosemicarbazone ligand, the SP configuration of the iron(III) nucleus has been established.



The distorted square pyramid formed around iron(III) is depicted in Fig. 1. The deviations of the N1, N3, O1 and Cl1 atoms from the basal least-squares plane are -0.178 (3), 0.194 (3), -0.152 (2) and 0.017 (1) Å, respectively, and -0.544 (1) Å for the Fe1 atom. The apical Fe1—Cl2 distance is slightly shorter than the equatorial Fe1—Cl1 bond length (Table 1). A similarly distorted SP geometry was found in *S*-methyl-*N*¹-[1-(2'-oxyphenyl)ethylidene isothiosemicarbazidato-*O,N,N,N*]-dichloroiron(III) (Yampolskaya *et al.*, 1985). The average differences in the bond lengths and angles (0.033 Å and 1.5° , respectively) agree well with the corresponding values listed in Table 1 for the title compound. It is the only known *O,N,N,Cl,Cl*-pentacoordinated iron(III) complex published so far (Yampolskaya *et al.*, 1985).

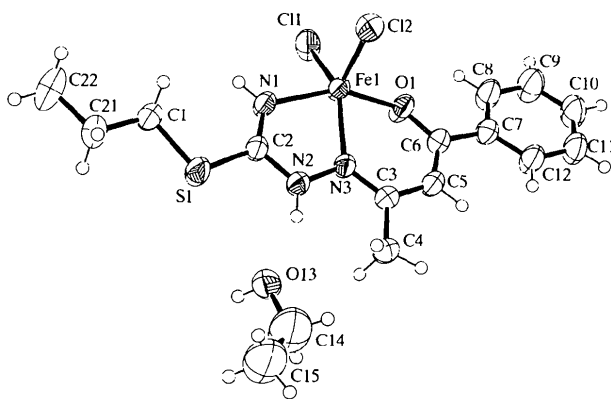


Fig. 1. An ORTEP drawing (Burnett & Johnson, 1996), with ellipsoids at the 50% probability level.

To estimate the probability of the observed SP *versus* the alternative TBP coordination around pentacoordinated iron(III) nuclei, complexes with the general formula $\text{Fe}(\text{O}, \text{N}, \text{N}, \text{X}, \text{X})$, where $\text{X} = \text{O}, \text{N}$ or Cl , were retrieved from the Cambridge Structural Database (CSD, October 1998 release; Allen & Kennard, 1993). This data search revealed *ca* 90 structures with such coordination polyhedra, of which only eight structures were found to possess the TBP configuration. The majority (*ca* 50%) of the remaining 82 structures is dominated by the $\text{Fe}(\text{N}, \text{N}, \text{N}, \text{N}, \text{O})$ SP coordination, with oxygen in an apical position. There are 14 structures in which the coordination polyhedra possess one Cl atom exclusively

in an apical position. The Fe—Cl distances vary in the range 2.212–2.256 Å, with a mean value of 2.234 (11) Å.

The search of the CSD was followed by analysis of the τ descriptor ($\tau = 0$ for SP and $\tau = 1$ for TBP), obtained using PLATON (Spek, 1990), with respect to the denticity and flexibility of the ligands. The predominant SP coordination can be attributed mainly to the rigidity of the multidentate (>2) ligands. In particular, the planar tetradentate porphyrin ring (*e.g.* CETWON, DIXRAD, MPORFE10 *etc.*) excludes the formation of TBP geometry. Similarly, rigid tridentate ligands, such as the thiosemicarbazone moiety in the title compound ($\tau = 0.15$) and in the analogous DISNOI compound ($\tau = 0.20$; Yampolskaya *et al.*, 1985), hinder the formation of any approximately collinear ($\sim 175 \pm 5^\circ$) X—Me—Y apical bond which characterizes TBP geometry. The five-membered ring of the thiosemicarbazone moiety imposes a bite angle of 75.1 (1) $^\circ$ on the iron(III) centre, resulting in the 'largest' bridging angle (ba) of $\text{O1—Fe—N1} = 153.8$ (1) $^\circ$. In contrast, the sporadic TBP polyhedra are most likely formed by two flexible bidentate and one monodentate ligand, like in WESRIV ($\tau = 0.76$ and $\text{ba} = 167.3^\circ$; Whalen *et al.*, 1994) and ZACNEW ($\tau = 0.83$ and $\text{ba} = 176.0^\circ$; Goldberg *et al.*, 1995), and in the binuclear complex OCPSLI ($\tau = 0.75$ and $\text{ba} = 169.7^\circ$ for Fe1, and $\tau = 0.63$ and $\text{ba} = 167.5^\circ$ for Fe2; Davies & Gatehouse, 1973). Interestingly, nearly perfect TBP coordination could also be found in the binuclear complex KEZVOA10 ($\tau = 0.93$ and $\text{ba} = 176.7^\circ$ for Fe1, and $\tau = 0.92$ and $\text{ba} = 177.7^\circ$ for Fe2; Dong *et al.*, 1993), with a tetradentate ligand being flexible enough *via* its three Csp^3 atoms bound

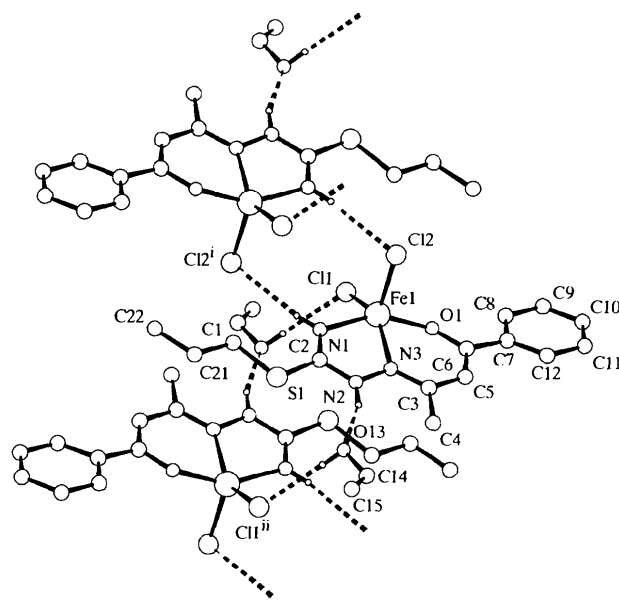


Fig. 2. Hydrogen bonds to neighbouring molecules in (I). H atoms not involved in hydrogen bonds have been omitted. [Symmetry codes: (i) $-x, -y, -z + 1$; (ii) $-x + 1, -y, -z + 1$.]

to the ligating tetrahedral N2 atom. With sufficient flexibility in VOVDIT, even a pentadentate ligand builds up TBP geometry ($\tau = 0.79$ and $ba = 168.7^\circ$; Liu *et al.*, 1991). However, owing to steric hindrances among bulky monodentate ligands, instead of the expected TBP, only a distorted SP is developed in NONXOD (Hikichi *et al.*, 1997), with low τ (0.33) and ba (168.0°) values. These rules are also valid for the binuclear iron(III) complex SERPUA (Solari *et al.*, 1990), in which there is one SP ($\tau = 0.13$ and $ba = 139.8^\circ$) Fe1(N,N,O,O,Cl) and one distorted TBP ($\tau = 0.53$ and $ba = 175.8^\circ$) Fe2(O,O,O,O,Cl) polyhedron sharing a pair of phenolic O atoms.

Hydrogen-bonding geometry is given in Table 2. The hydrogen-bond system shown in Fig. 2 can be described by $R_3^2(8)$ and $R_4^4(14)$ symbols [for Cl2—Fe1—N1—H1...Cl2ⁱ—Fe1ⁱ—N1ⁱ—H1ⁱ... and Cl1—Fe1—N3—N2—H2...O13—H13...Cl1ⁱⁱ—Fe1ⁱⁱ—N3ⁱⁱ—N2ⁱⁱ—H2ⁱⁱ...O13ⁱⁱ—H13ⁱⁱ... rings, respectively; symmetry codes: (i) $-x, -y, 1-z$; (ii) $1-x, -y, 1-z$] according to the hydrogen-bond classification of Bernstein *et al.* (1995).

Experimental

Black monocrystals of the title compound were obtained by the reaction of a warm ethanolic solution of the ligand, prepared in an analogous way to the *S*-methyl derivative (Leovac *et al.*, 1994), and FeCl₃·6H₂O in a 1:1 molar ratio. In the temperature range 100–350 K, the compound has $\mu_{\text{eff}} = 6.5$ (1) μ_{B} , which is characteristic of monomeric high-spin iron(III) complexes.

Crystal data

[Fe(C ₁₄ H ₁₈ N ₃ OS)Cl ₂]- C ₂ H ₆ O	Mo K α radiation
$M_r = 449.19$	$\lambda = 0.71073 \text{ \AA}$
Triclinic	Cell parameters from 25 reflections
$P\bar{1}$	$\theta = 14.94\text{--}15.87^\circ$
$a = 8.739$ (1) \AA	$\mu = 1.104 \text{ mm}^{-1}$
$b = 11.680$ (2) \AA	$T = 293$ (2) K
$c = 11.858$ (2) \AA	Prism
$\alpha = 69.46$ (1) $^\circ$	$0.25 \times 0.15 \times 0.10 \text{ mm}$
$\beta = 71.69$ (1) $^\circ$	Black
$\gamma = 68.87$ (1) $^\circ$	
$V = 1032.5$ (3) \AA^3	
$Z = 2$	
$D_x = 1.445 \text{ Mg m}^{-3}$	
D_m not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer	3173 reflections with $I > 2\sigma(I)$
ω - 2θ scans	$R_{\text{int}} = 0.012$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$\theta_{\text{max}} = 29.42^\circ$
$T_{\text{min}} = 0.859$, $T_{\text{max}} = 0.895$	$h = -11 \rightarrow 12$
6088 measured reflections	$k = 0 \rightarrow 16$
5678 independent reflections	$l = -15 \rightarrow 16$
	3 standard reflections frequency: 60 min intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.039$	$\Delta\rho_{\text{max}} = 0.453 \text{ e \AA}^{-3}$
$wR(F^2) = 0.097$	$\Delta\rho_{\text{min}} = -0.382 \text{ e \AA}^{-3}$
$S = 0.875$	Extinction correction: none
5678 reflections	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)
232 parameters	
H atoms constrained	
$w = 1/[\sigma^2(F_o^2) + (0.0420P)^2$ $+ 0.4248P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Selected geometric parameters (\AA , $^\circ$)

Fe1—N1	2.045 (2)	Fe1—Cl1	2.258 (1)
Fe1—N3	2.102 (2)	Fe1—Cl2	2.244 (1)
Fe1—O1	1.926 (2)		
N1—Fe1—Cl1	93.59 (6)	O1—Fe1—N1	153.76 (9)
N1—Fe1—N3	75.12 (8)	Cl2—Fe1—Cl1	106.11 (3)
O1—Fe1—N3	83.91 (7)	N1—Fe1—Cl2	101.01 (7)
O1—Fe1—Cl1	94.56 (6)	N3—Fe1—Cl2	108.91 (6)
N3—Fe1—Cl1	144.63 (7)	O1—Fe1—Cl2	100.58 (7)

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

$D\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
N1—H1...Cl2 ⁱ	0.85	2.82	3.649 (2)	165
N2—H2...O13	0.86	2.02	2.838 (3)	159
O13—H13...Cl1 ⁱⁱ	0.81	2.46	3.264 (2)	172

Symmetry codes: (i) $-x, -y, 1-z$; (ii) $1-x, -y, 1-z$.

Data collection: CAD-4 EXPRESS (Enraf–Nonius, 1994). Cell refinement: CAD-4 EXPRESS. Data reduction: XCAD4 (Harms, 1996). Program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997b). Molecular graphics: ORTEPIII (Burnett & Johnson, 1996) and PX (Párkányi, 1998). Software used to prepare material for publication: SHELXL97.

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N,N,N',N'-Tetramethylguanidinium tetrachloroantimonate(III) at 295 and 92 K

MACIEJ BUJAK, PRZEMYSŁAW OSADCZUK AND JACEK ZALESKI

Institute of Chemistry, University of Opole, Oleska 48, 45-052 Opole, Poland. E-mail: zaleski@uni.opole.pl

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Abstract

The crystal structure of *N,N,N',N'*-tetramethylguanidinium tetrachloroantimonate(III), (C₅H₁₄N₃)[SbCl₄], has been determined at 295 and 92 K. Each Sb atom is surrounded by six Cl atoms forming an irregular [SbCl₆]³⁻ octahedron. The octahedra are connected with each other in infinite zigzag chains. There is one crystallographically independent *N,N,N',N'*-tetramethylguanidinium cation in the crystal structure. It is linked to the [SbCl₆]³⁻ octahedra through N—H...Cl hydrogen bonds. The deformation of the octahedral coordination of the Sb^{III} atom is related to the presence of N—H...Cl hydrogen bonds.

Comment

Many halogenoantimonates(III), organic–inorganic salts defined by the general formula *R_aSb_bX_c* (*R* is an organic cation; *X* = chlorine, bromine or iodine; *a*, *b* and *c* are stoichiometric coefficients, where *c* = 3*b* + *a*), show a number of phase transitions, some of

them to ferroelectric, ferrielectric and ferroelastic phases (Jakubas & Sobczyk, 1990). These phase transitions are related mostly to the molecular dynamics of the cations embedded in the anionic sublattices. One of the subgroups of halogenoantimonates(III) constitutes salts of *RSbX₄* stoichiometry. In this group, several different anionic sublattices were found composed either of polyanions or of isolated units. The polyanionic chains may be built in three different ways: (i) as [SbX₆]³⁻ octahedra connected by edges, possessing four bridging and two terminal halogen atoms (Porter & Jacobson, 1970), (ii) as [SbX₆]³⁻ octahedra linked in such a way that two out of three independent Sb atoms have three bridging and three terminal Sb—X bonds, while the third independent Sb atom has five bridging and one terminal Sb—X bond (Lipka, 1980), and (iii) as [SbX₅]²⁻ square pyramids connected by corners (Ensinger *et al.*, 1983).

Larger cations break the polyanionic chains, leading to the formation of three different isolated units composed of (i) four octahedra forming [Sb₄X₁₆]⁴⁻ units (Ensinger *et al.*, 1982; Kozawa & Uchida, 1990), (ii) three octahedra connected by faces, forming [Sb₃X₁₂]³⁻ anions (Borgsen *et al.*, 1991), and (iii) two square pyramids linked by an edge (Belz *et al.*, 1992).

Until now, guanidinium chloroantimonates(III) have been analysed by IR, NMR, differential scanning calorimetry (DSC), X-ray, dielectric, pyroelectric and dilatometric methods (Pająk & Zaleski, 1994; Zaleski *et al.*, 1994, 1995). The compounds were characterized by a number of solid–solid phase transitions attributed to changes in the dynamics of the cationic sublattices.

We have synthesized *N,N,N',N'*-tetramethylguanidinium chloroantimonates(III) to study the structure and properties of the resulting salts. Our interest was directed towards the effect of the presence of phase transitions and the deformation of the octahedral coordination of the Sb^{III} atom on the N—H...Cl hydrogen-bonding scheme.

In our earlier work, we noticed that significant changes in Sb—Cl bond lengths take place at phase transitions and are caused by changes in the hydrogen-bonding scheme (Zaleski & Pietraszko, 1996). It should be noted however that changes in Sb—Cl bond lengths also take place with decreasing temperature (Bujak & Zaleski, 1998, 1999). They are much smaller, but are also correlated with changes in strength of the N—H...Cl hydrogen bonds.

The title compound, (I), has the most common anionic sublattice structure for salts of *RSbX₄* stoichiometry, namely polymeric one-dimensional chains.

