Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Chloro(1-isopropylidene-4-methyl-3-thiosemicarbazidato-κ^2N^3,S)dimethyltin(IV)

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Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.005 Å
R factor = 0.023
wR factor = 0.062
Data-to-parameter ratio = 22.5

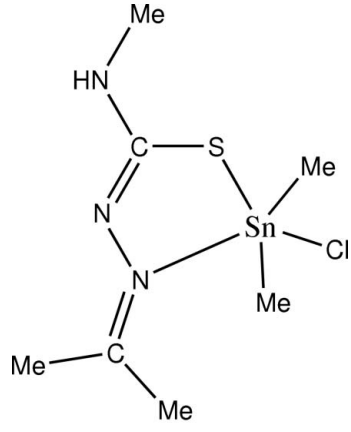
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 18 October 2005
Accepted 21 October 2005
Online 31 October 2005

In the title compound, $[Sn(CH_3)_2(C_5H_{10}N_3S)Cl]$, the 1-isopropylidene-4-methyl-3-thiosemicarbazidate ligand has a Z configuration and is chelated to the Sn atom through the S and hydrazinic N atoms in a distorted trigonal–bipyramidal pentacoordination environment. The molecular structure is stabilized by intramolecular C—H···N and intermolecular N—H···S hydrogen bonds. The latter link the molecules into dimers.

Comment

The two possible E and Z configurations of thiosemicarbazide (TSCZ) can be depicted by the formation of, respectively, monodentate and bidentate modes of coordination in a metal complex. Some silver(I)–thiosemicarbazide complexes, such as $[Ag_2(TSCZ)_6]Cl_2$], (II), and $[Ag_2(TSCZ)_4I_2]$, (III) (Bonamartini *et al.*, 1987), display a monodentate coordination through the S atom. On the other hand, both zinc and nickel complexes, $[Zn(TSCZ)_2](NO_3)_2$, (IV) (Tong *et al.*, 2000), and $[Ni(TSCZ)_2](C_4H_4O_4)\cdot C_4H_6O_4$, (V) (Li *et al.*, 2003), formed with the TSCZ ligand having a Z configuration, are chelated in a bidentate manner through the S and hydrazinic N atoms without undergoing deprotonation. Monodentate chelation without deprotonation was also observed in bis(acetonethiosemicarbazone-*S*)dichlorodiphenyltin(IV), (VI) (Teoh *et al.*, 1997).



(I)

However, in the title compound, (I), the ligand has a Z configuration, and therefore it is chelated to atom Sn1 in a bidentate manner through atoms S1 and N3 (Fig. 1), analogous to what was observed in bis[acetone-*N*(4)-phenylthiosemicarbazone]chlorodimethyltin(IV), (VII) (de Sousa *et al.*, 2004). The geometry of atom Sn1 is distorted trigonal–bipyramidal, with atoms Sn1, N3, S1 and Cl1 occupying the

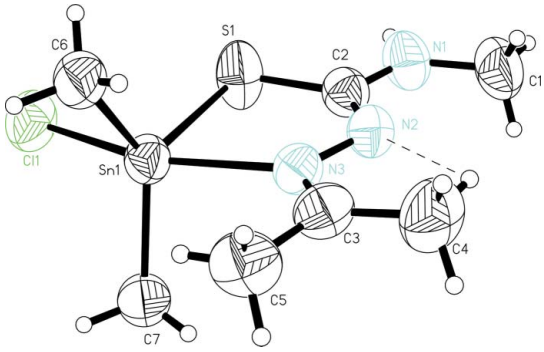


Figure 1
The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The dashed line indicates the intramolecular C—H···N hydrogen bond.

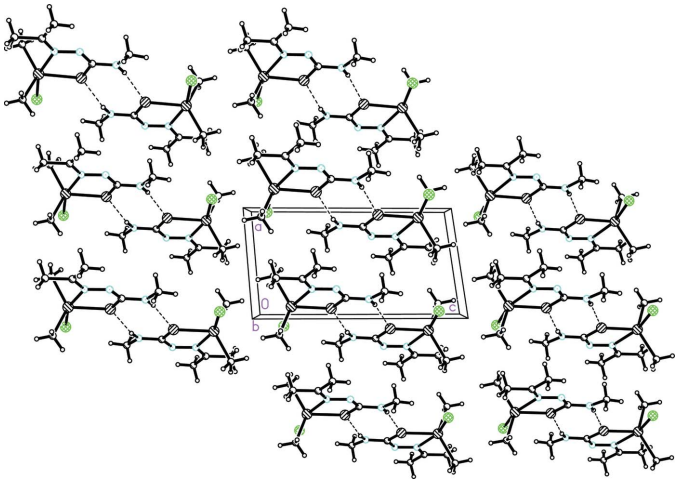


Figure 2
A packing diagram for (I). N—H···S hydrogen bonds are shown by dashed lines.

equatorial plane. The chelating ligand is essentially planar, with a maxiumum deviation of 0.03 (3) Å for atom C2 in the Sn1/N1/N2/N3/C2/C3/C4/C5 fragment. Atoms S1 and C1 deviate by only 0.191 (1) and 0.157 (5) Å, respectively, from the mean plane.

Significant lengthening of the C2═S1 double bond [1.760 (3) Å] and shortening of the C2—N2 bond [1.280 (4) Å] compared with those in the *E* configuration of free acetone-4-methylthiosemicarbazone, (VIII) [1.689 (2) and 1.361 (3) Å, respectively; Parsons *et al.*, 2000] indicate that deprotonation of the hydrazinic atom N2 has occurred during the complexation. Other bond lengths and angles are within normal ranges (Allen *et al.*, 1987) and are comparable with the corresponding values in (VII).

The molecular structure of (I) is stabilized by intramolecular C—H···N and intermolecular N—H···S hydrogen bonds (Table 2). In the crystal structure, the N—H···S intermolecular hydrogen bonds link the molecules into dimers, which are stacked along the *b* axis (Fig. 2). In constrast, the presence of a phenyl group in (VII) allows the formation of intermolecular hydrogen bonds between the amino H and Cl atoms to form a one-dimensional polymeric chain.

Experimental

A mixture of 4-methylthiosemicarbazide (0.105 g, 2 mmol) and dimethyltin(IV) dichloride (0.219 g, 1 mmol) in a mixed solvent of acetone-absolute ethanol (30 ml; 1:3 *v*/*v*) was refluxed for 2h. After cooling to room temperature, the solution was filtered. Colourless single crystals of (I) were obtained after a few days by slow evaporation of the solution at room temperature (yield 80%, m.p. 454.3–455.5K).

Crystal data

$[Sn(CH_3)_2(C_5H_{10}N_3S)Cl]$
M_r = 328.43
Triclinic, $P\overline{1}$
a = 7.5419 (16) Å
b = 7.7652 (16) Å
c = 12.703 (3) Å
α = 95.485 (3)°
β = 93.302 (3)°
γ = 118.389 (3)°
V = 647.0 (2) Å^3
Z = 2
D_x = 1.686 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5170 reflections
θ = 1.6–26.5°
μ = 2.31 mm^{-1}
T = 273 (2) K
Block, colourless
0.48 × 0.34 × 0.19 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.403, T_{max} = 0.668
6879 measured reflections
2656 independent reflections
2498 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 26.5°
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.062
S = 1.11
2656 reflections
118 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0311P)^2 + 0.1504P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Sn1—C6	2.117 (3)	N1—C2	1.346 (4)
Sn1—C7	2.118 (3)	N1—C1	1.440 (4)
Sn1—N3	2.361 (2)	N2—C2	1.280 (4)
Sn1—S1	2.4158 (10)	N2—N3	1.394 (3)
Sn1—Cl1	2.5273 (10)	N3—C3	1.287 (4)
S1—C2	1.760 (3)		
C6—Sn1—C7	128.61 (13)	C6—Sn1—Cl1	94.03 (9)
C6—Sn1—N3	94.70 (10)	C7—Sn1—Cl1	95.49 (9)
C7—Sn1—N3	92.54 (10)	N3—Sn1—Cl1	160.59 (6)
C6—Sn1—S1	115.16 (9)	S1—Sn1—Cl1	83.92 (3)
C7—Sn1—S1	116.02 (10)	C2—S1—Sn1	100.20 (9)
N3—Sn1—S1	76.68 (6)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4A···N2	0.96	2.21	2.668 (4)	108
N1—H1D···S1^{i}	0.86	2.65	3.501 (3)	169

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

H atoms were located in a difference map and repositioned geometrically, with N—H = 0.86 and C—H = 0.96 Å. They were

constrained to ride on their parent atoms, with U_{iso}(H) = 1.2 (1.5 for methyl) times U_{eq}(C,N).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT*; data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 2003).

The authors thank Universiti Kebangsaan Malaysia for financial support and facilities.

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