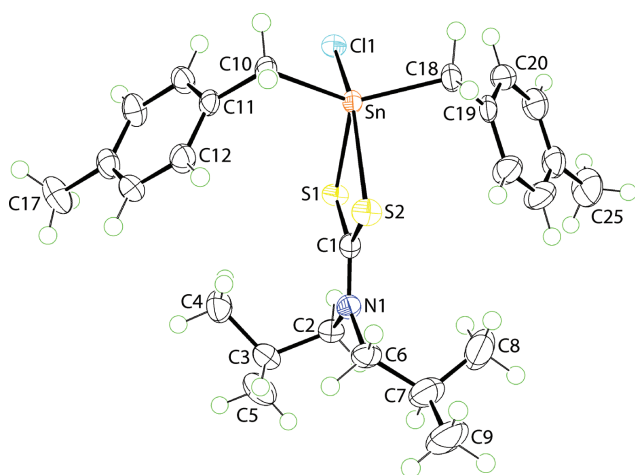


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# Crystal structure of chlorido-[(*N,N*-di-isobutyl)dithiocarbamato- $\kappa^2 S, S'$ ]-di(4-methylbenzyl- $\kappa C$ )tin(IV), $C_{25}H_{36}ClNS_2Sn$



**Table 1:** Data collection and handling.

Crystal:	Colourless prism
Size:	0.20 × 0.10 × 0.05 mm
Wavelength:	Cu K $\alpha$ radiation (1.54184 Å)
$\mu$ :	10.1 mm <sup>-1</sup>
Diffractometer, scan mode:	XtaLAB Synergy, $\omega$
$\theta_{\max}$ , completeness:	67.1°, >99%
$N(hkl)_{\text{measured}}$ , $N(hkl)_{\text{unique}}$ , $R_{\text{int}}$ :	32576, 4742, 0.027
Criterion for $I_{\text{obs}}$ , $N(hkl)_{\text{gt}}$ :	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$ , 4689
$N(\text{param})_{\text{refined}}$ :	277
Programs:	CrysAlis <sup>PRO</sup> [1], SHELX [2, 3], WinGX/ORTEP [4]

**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub> */ <i>U</i> <sub>eq</sub>
Sn	0.32072(2)	0.62021(2)	0.26717(2)	0.01420(5)
Cl1	0.14992(3)	0.50107(3)	0.22970(2)	0.01823(8)
S1	0.39366(3)	0.38789(3)	0.28874(2)	0.01771(8)
S2	0.53179(3)	0.63007(4)	0.31355(2)	0.02076(9)
N1	0.59931(11)	0.36894(13)	0.33100(6)	0.0180(3)
C1	0.51945(12)	0.45457(16)	0.31359(7)	0.0168(3)
C2	0.58566(12)	0.21860(16)	0.33484(7)	0.0200(3)
H2A	0.642944	0.172478	0.316173	0.024*
H2B	0.517544	0.192383	0.309951	0.024*
C3	0.58728(13)	0.16795(18)	0.40224(8)	0.0238(3)
H3	0.651566	0.206044	0.428352	0.029*
C4	0.49016(14)	0.21583(19)	0.42979(8)	0.0304(4)
H4A	0.426448	0.177988	0.405108	0.046*
H4B	0.486809	0.316460	0.428835	0.046*
H4C	0.494622	0.183893	0.473179	0.046*
C5	0.59518(17)	0.01082(19)	0.40287(9)	0.0365(4)
H5A	0.596382	−0.022752	0.445811	0.055*
H5B	0.660253	−0.017278	0.387040	0.055*
H5C	0.533975	−0.028017	0.376163	0.055*
C6	0.70847(12)	0.41990(18)	0.34769(8)	0.0226(3)
H6A	0.736068	0.388002	0.390439	0.027*
H6B	0.707329	0.521637	0.348323	0.027*
C7	0.78356(15)	0.37217(19)	0.30254(10)	0.0347(4)
H7	0.796942	0.271648	0.309317	0.042*
C8	0.73919(18)	0.3940(3)	0.23494(10)	0.0457(5)
H8A	0.673653	0.341155	0.225007	0.069*
H8B	0.790711	0.363086	0.208221	0.069*

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## Abstract

$C_{25}H_{36}ClNS_2Sn$ , monoclinic,  $P2_1/n$  (no. 14),  $a = 12.7694(1)$  Å,  $b = 9.7283(1)$  Å,  $c = 21.5640(2)$  Å,  $\beta = 97.978(1)^\circ$ ,  $V = 2652.85(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $R_{\text{gt}}(F) = 0.0167$ ,  $wR_{\text{ref}}(F^2) = 0.0444$ ,  $T = 100(2)$  K.

CCDC no.: 2017015

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

## Source of material

Di(4-methylbenzyl)tin dichloride was synthesised by the direct reaction of 4-methylbenzyl chloride (Merck) and

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Table 2 (continued)

Atom	x	y	z	$U_{iso}^*/U_{eq}$
H8C	0.724282	0.491876	0.227544	0.069*
C9	0.88855(15)	0.4488(3)	0.32016(12)	0.0473(5)
H9A	0.939201	0.418970	0.292671	0.071*
H9B	0.916938	0.428499	0.363771	0.071*
H9C	0.876548	0.547983	0.315274	0.071*
C10	0.27071(12)	0.71387(16)	0.34898(7)	0.0187(3)
H10A	0.321931	0.786106	0.365173	0.022*
H10B	0.200938	0.758058	0.337236	0.022*
C11	0.26303(13)	0.61003(15)	0.39907(7)	0.0172(3)
C12	0.34667(13)	0.58788(18)	0.44667(8)	0.0229(3)
H12	0.409402	0.640835	0.447723	0.027*
C13	0.33993(13)	0.48944(18)	0.49275(8)	0.0249(3)
H13	0.397839	0.477354	0.525041	0.030*
C14	0.25032(14)	0.40850(17)	0.49252(7)	0.0230(3)
C15	0.16671(14)	0.43159(18)	0.44506(7)	0.0244(3)
H15	0.104059	0.378436	0.443910	0.029*
C16	0.17279(13)	0.53050(17)	0.39939(7)	0.0214(3)
H16	0.114133	0.544115	0.367739	0.026*
C17	0.24328(17)	0.29975(18)	0.54150(8)	0.0332(4)
H17A	0.312297	0.289477	0.567309	0.050*
H17B	0.222515	0.212101	0.520981	0.050*
H17C	0.190441	0.326905	0.568058	0.050*
C18	0.34809(13)	0.69845(16)	0.17719(7)	0.0196(3)
H18A	0.284236	0.748296	0.157801	0.023*
H18B	0.407310	0.764948	0.183354	0.023*
C19	0.37367(13)	0.58752(16)	0.13351(7)	0.0184(3)
C20	0.29712(13)	0.53714(17)	0.08733(8)	0.0242(3)
H20	0.227297	0.572871	0.083718	0.029*
C21	0.32042(15)	0.43543(19)	0.04619(8)	0.0280(4)
H21	0.266235	0.403195	0.014905	0.034*
C22	0.42062(16)	0.38016(17)	0.04978(9)	0.0290(4)
C23	0.49736(15)	0.4293(2)	0.09643(9)	0.0358(4)
H23	0.566793	0.392209	0.100351	0.043*
C24	0.47469(14)	0.5314(2)	0.13747(8)	0.0290(4)
H24	0.528924	0.563612	0.168733	0.035*
C25	0.4450(2)	0.2712(2)	0.00409(10)	0.0444(5)
H25A	0.378769	0.235172	-0.018475	0.067*
H25B	0.484611	0.196259	0.026924	0.067*
H25C	0.487442	0.311317	-0.025857	0.067*

metallic tin powder (Merck) in toluene according to a literature procedure [5]. The dithiocarbamate ligand was prepared *in situ* from the reaction of CS<sub>2</sub> (Merck 0.25 mmol) with diisobutylamine (Merck, 0.25 mmol) and KOH (0.03 mL; 50% w/v) in methanol solution (15 mL); CS<sub>2</sub> was added dropwise. The resulting mixture was kept at 273 K for 0.5 h. Di(4-methylbenzyl)tin dichloride (0.25 mmol, 0.10 g) in methanol (10 mL) was added to the prepared potassium diisobutyl dithiocarbamate. The resulting mixture was stirred and refluxed for 2.5 h. The filtrate was evaporated slowly until a beige precipitate was formed. The precipitate was recrystallised from acetone-methanol by slow evaporation to yield colourless crystals. Yield: 0.070 g (49.2%). **M.pt** (Stuart SMP30 digital melting point apparatus; uncorrected): 379–381 K. **IR** (Bruker Vertex 70v FTIR Spectrometer; cm<sup>-1</sup>): 1465

(s) v(C–N), 1250 (m) v(C–N), 1088 (m) v(C–S), 599 (m) v(Sn–S). **<sup>1</sup>H NMR** (Bruker Ascend 400 MHz NMR spectrometer; CDCl<sub>3</sub>; ppm relative to Me<sub>4</sub>Si): δ 0.89–1.02 (m, 18H, CH<sub>3</sub>), 2.15–2.23 (m, 4H, -CH<sub>2</sub>), 2.30–2.43 (m, 2H, CH), 3.17–3.25 (4H, NCH<sub>2</sub>), 7.00–7.22 (8H, Ph–H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (as for <sup>1</sup>H NMR): 20.2 (CH<sub>3</sub>), 21.0 (CH<sub>3</sub>), 27.1 (CH), 35.7 (CH<sub>2</sub>), 63.8 (NCH<sub>2</sub>), 127.9, 128.8, 130.3, 136.1 (Ph–C), 197.4 (CS).

### Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–1.00 Å) and refined as riding with  $U_{iso}(H) = 1.2–1.5U_{eq}(C)$ .

### Comment

Molecules/complexes of the general formula R<sub>2</sub>Sn(S<sub>2</sub>CNR'R'')Cl have been well-studied, by both crystallographic methods [6] and by computational chemistry [7, 8]. By contrast to many other organotin systems, these are robust molecules in that only one structural motif is consistently observed [6], namely one based on a distorted trigonal-bipyramid geometry owing to an asymmetric mode of coordination of the dithiocarbamate ligand. Very recent structural studies [9, 10] confirm this and it was in the context of these investigations, that the title compound, (4-MeC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>2</sub>Sn[S<sub>2</sub>CN(i-Bu)<sub>2</sub>]Cl, (I), was isolated and characterised crystallographically: the results of this study are reported herein.

The molecular structure of (I) is shown in the figure (70% displacement ellipsoids) and features a distorted trigonal bipyramidal geometry whereby the Sn atom is within a C<sub>2</sub>ClS<sub>2</sub> donor set. The Sn atom is asymmetrically coordinated by the dithiocarbamate ligand [Sn–S1 = 2.4641(4) Å and Sn–S2 = 2.7434(4) Å], the chloride [Sn–Cl1 = 2.5027(4) Å] and two methylene-C atoms [Sn–C10 = 2.1594(14) Å and Sn–C18 = 2.1574(15) Å]. The coordination geometry is highly distorted with the value of  $\tau = 0.35$ , compared with values of 0.0 and 1.0 for ideal square-pyramidal and trigonal-bipyramidal coordination geometries, respectively [11], indicative of a geometry tending towards square-pyramidal. The widest angles subtended at the Sn atom are Cl1–Sn–S2 = 154.415(11)° and C10–Sn–C18 = 133.56(6)°, and the narrowest, S1–Sn–S2 = 68.697(11)°, corresponds to the chelate angle. The parameters within the dithiocarbamate ligand follow the expected trends in that the longer C–S bond length [C1–S1 = 1.7462(15) Å] is associated with the shortest Sn–S1 bond, and the shorter C–S bond [C1–S2 = 1.7145(15) Å] is associated with the longer Sn–S2 bond. The relatively short C–N bond [C1–N1 = 1.330(2) Å] is consistent with a relatively significant contribution of the dithiolate canonical form, i.e. [2<sup>-</sup>S<sub>2</sub>C=N<sup>+</sup>(i-Bu)<sub>2</sub>], to the overall electronic structure of the dithiocarbamate ligand. Globally, the benzyl

residues are folded to lie over the  $SnS_2C$  chelate ring. In all respects, the structure of (I) conforms to the structural motif adopted universally by  $R_2Sn(S_2CNR'R'')Cl$  molecules [6].

The molecular packing of (I) is largely devoid of specific points of contacts between atoms and residues. The presence of methyl- $C-H \cdots \pi$ (phenyl) contacts  $[C25-H25c \cdots Cg(C19-C24)]^i = 2.96 \text{ \AA}$  with angle at  $H25c = 161^\circ$  for symmetry operation (i)  $1 - x, 1 - y, -z$  link molecules into centrosymmetric dimers. The only other close contacts less than the sum of the van der Waals radii are methyl- $H \cdots H$ (phenyl)  $[H4a \cdots H20^{ii}] = 2.26 \text{ \AA}$  for (ii)  $1/2 - x, -1/2 + y, 1/2 - z$ . The result of the above interactions is the assembly of molecules in a plane parallel to (1 0 1). These layers pack without directional interactions between them.

The analysis of the Hirshfeld surfaces and two-dimensional fingerprint plots (overall and decomposed) calculated for (I), using Crystal Explorer 17 [12] following standard protocols [13], confirm the lack of directional interactions in the crystal of (I). The  $H \cdots H$  contacts contribute 70.9% of all contacts and the two-dimensional fingerprint plot shows a characteristic feature at  $d_i + d_e \sim 2.2 \text{ \AA}$  corresponding to the  $H4a \cdots H20$  interaction, mentioned above. Other significant contacts to the surface also involve H atoms:  $C \cdots H/H \cdots C$  [13.1%],  $Cl \cdots H/H \cdots Cl$  [8.3%] and  $S \cdots H/H \cdots S$  [7.0%].

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