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Crystal structure of (*N*-benzyl-*N*-methyl-dithiocarbamato- $\kappa^2 S, S'$)di(4-chlorobenzyl)chloridotin(IV), $C_{23}H_{22}Cl_3NS_2Sn$

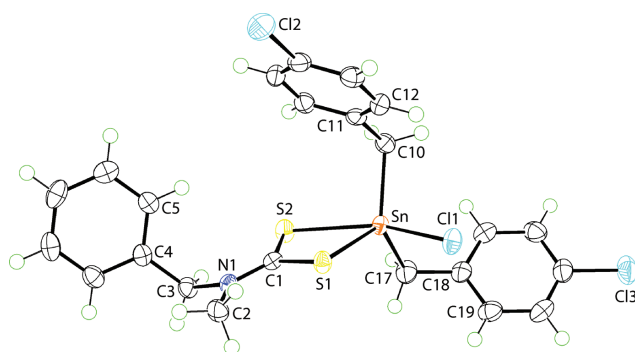


Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.17 × 0.10 × 0.10 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	13.1 mm ⁻¹
Diffractometer, scan mode:	Bruker APEXII, φ and ω
θ_{\max} , completeness:	67.1°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	28919, 4335, 0.039
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4229
$N(\text{param})_{\text{refined}}$:	272
Programs:	Bruker [1], SHELX [2, 3], WinGX and ORTEP [4]

<https://doi.org/10.1515/ncrs-2019-0881>

Received December 3, 2019; accepted January 16, 2020; available online February 7, 2020

Abstract

$C_{23}H_{22}Cl_3NS_2Sn$, triclinic, $P\bar{1}$ (no. 2), $a = 9.3954(1)$ Å, $b = 10.2747(1)$ Å, $c = 12.8743(2)$ Å, $\alpha = 99.427(1)^\circ$, $\beta = 94.247(1)^\circ$, $\gamma = 95.817(1)^\circ$, $V = 1214.51(3)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0167$, $wR_{\text{ref}}(F^2) = 0.0446$, $T = 100(2)$ K.

CCDC no.: 1978269

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-chlorobenzyl)tin dichloride was synthesised by the direct reaction of 4-chlorobenzyl chloride (Aldrich) and metallic tin powder (Merck) in toluene according to a literature procedure [5]. The dithiocarbamate ligand was prepared *in situ* from the reaction of CS_2 (Merck 0.25 mmol) with *N*-methylbenzylamine (Acros, 0.25 mmol) and KOH (0.03 mL;

50% w/v) in methanol solution (15 mL); CS_2 was added dropwise. The resulting mixture was kept at 273 K for 0.5 h. Di(4-chlorobenzyl)tin dichloride (0.25 mmol, 0.111 g) in methanol (10 mL) was added to the prepared potassium *N*-methylbenzyl dithiocarbamate. The resulting mixture was stirred and refluxed for 2 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: 0.072 g (47.9%). **M.pt** (Mel-temp II digital melting point apparatus; uncorrected): 391–392 K. **IR** (Bruker Vertex 70v FTIR Spectrometer; cm^{-1}): 560 (m) $\nu(Sn-S)$, 1499 (s) $\nu(C-N)$, 1211 (m) $\nu(C-S)$, 1010 (s) $\nu(C-N)$. **¹H NMR** (Bruker Ascend 400 MHz NMR spectrometer; $CDCl_3$; ppm relative to Me_4Si): δ 3.00–3.08 (4H, $-CH_2-$), 3.17–3.25 (2H, $N-CH_2$), 4.86 (3H, $N-CH_3$), 7.10–7.37 (13H, Ph-H). **¹³C{¹H} NMR** (as for ¹H NMR): 35.7 (CH_2), 42.3 (CH_2), 61.4 (CH_3), 127.8, 128.3, 128.6, 129.3, 129.7, 133.5, 136.2, 139.4 (Ph-C), 197.8 (CS).

Experimental details

The C-bound H atoms were geometrically placed ($C-H = 0.95-0.99$ Å) and refined as riding with $U_{\text{iso}}(H) = 1.2-1.5 U_{\text{eq}}(C)$.

Comment

Recent structural studies on organotin dithiocarbamate molecules of the general formula $R_2Sn(S_2CNR'R'')Cl$ confirm the adoption of very similar structural motifs and the presence of highly distorted five-coordinate geometries [6, 7]. This structural homogeneity matches literature precedents

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Sn	0.24001(2)	0.67949(2)	0.82179(2)	0.01528(5)
Cl1	0.42842(5)	0.69311(4)	0.96736(3)	0.02267(9)
Cl2	0.36285(6)	0.01355(4)	0.62114(4)	0.03407(12)
Cl3	0.20085(7)	1.01771(5)	1.34520(4)	0.03782(13)
S1	0.43335(4)	0.65898(4)	0.70412(3)	0.01776(9)
S2	0.13574(4)	0.67298(4)	0.61763(3)	0.01996(9)
N1	0.36586(15)	0.68606(14)	0.50664(11)	0.0160(3)
C1	0.31362(18)	0.67438(16)	0.59734(13)	0.0159(3)
C2	0.51936(19)	0.68462(19)	0.49239(14)	0.0215(4)
H2A	0.569578	0.774152	0.516010	0.032 [*]
H2B	0.531261	0.655538	0.417477	0.032 [*]
H2C	0.559676	0.623222	0.534183	0.032 [*]
C3	0.27602(19)	0.70873(17)	0.41364(14)	0.0186(3)
H3A	0.321485	0.786129	0.386580	0.022 [*]
H3B	0.180586	0.729327	0.434973	0.022 [*]
C4	0.25738(18)	0.58852(17)	0.32702(13)	0.0173(3)
C5	0.20382(18)	0.46468(17)	0.34761(14)	0.0179(3)
H5	0.176170	0.456276	0.415922	0.022 [*]
C6	0.19080(19)	0.35366(18)	0.26856(15)	0.0217(4)
H6	0.153498	0.269527	0.282662	0.026 [*]
C7	0.2323(2)	0.36537(19)	0.16871(15)	0.0243(4)
H7	0.225058	0.289033	0.115001	0.029 [*]
C8	0.2840(2)	0.4883(2)	0.14776(14)	0.0243(4)
H8	0.311027	0.496480	0.079270	0.029 [*]
C9	0.29650(19)	0.59963(19)	0.22639(14)	0.0215(4)
H9	0.331945	0.683878	0.211488	0.026 [*]
C10	0.12043(19)	0.49561(17)	0.84102(14)	0.0185(3)
H10A	0.121080	0.491312	0.917315	0.022 [*]
H10B	0.019339	0.493652	0.812396	0.022 [*]
C11	0.18183(18)	0.37702(17)	0.78584(14)	0.0171(3)
C12	0.28872(19)	0.31930(17)	0.83693(14)	0.0200(4)
H12	0.324379	0.357114	0.907542	0.024 [*]
C13	0.3443(2)	0.20765(17)	0.78689(15)	0.0215(4)
H13	0.417665	0.169818	0.822546	0.026 [*]
C14	0.2912(2)	0.15261(17)	0.68443(15)	0.0219(4)
C15	0.1855(2)	0.20781(18)	0.63070(14)	0.0227(4)
H15	0.149900	0.169068	0.560262	0.027 [*]
C16	0.13256(19)	0.32016(18)	0.68117(14)	0.0198(4)
H16	0.061669	0.359349	0.644204	0.024 [*]
C17	0.1694(2)	0.87214(18)	0.87071(15)	0.0237(4)
H17A	0.229918	0.939862	0.841977	0.028 [*]
H17B	0.068989	0.871132	0.840847	0.028 [*]
C18	0.1775(2)	0.90998(17)	0.98866(14)	0.0197(4)
C19	0.2908(2)	0.99686(18)	1.04470(16)	0.0248(4)
H19	0.363634	1.034308	1.007462	0.030 [*]
C20	0.2992(2)	1.02984(18)	1.15419(16)	0.0267(4)
H20	0.377247	1.089089	1.191803	0.032 [*]
C21	0.1929(2)	0.97533(18)	1.20727(15)	0.0246(4)
C22	0.0783(2)	0.88876(18)	1.15467(16)	0.0259(4)
H22	0.005375	0.852369	1.192418	0.031 [*]
C23	0.0724(2)	0.85626(18)	1.04539(15)	0.0236(4)
H23	−0.005175	0.795938	1.008360	0.028 [*]

established for R₂Sn(S₂CNR'R'')Cl over the years by X-ray crystallography and confirmed by geometry-optimisation calculations for this class of compound [8–10]. It turns out that the appearance of one structural motif is unusual for organotin dithiocarbamates [10] with a greater variety of coordination geometries known for other organotin dithiocarbamate compounds, R_{4-n}Sn(S₂CNR'R'')_n, for example, in monoorganotin, RSn(S₂CNR'R'')₂Cl [11], and diorganotin, R₂Sn(S₂CNR'R'')₂ [12], systems. Herein, a new R₂Sn(S₂CNR'R'')Cl derivative is characterised crystallographically, namely the species with R = (4-ClC₆H₄)CH₂, R' = Me and R'' = PhCH₂, hereafter (I). We note that the structure of a Sn derivative with the identical dithiocarbamate ligand has been reported in the literature [13].

The molecular structure of (I) is shown in the figure (70% displacement ellipsoids). The tin atom is coordinated in an asymmetric mode by the dithiocarbamate ligand [Sn–S1 = 2.4535(4) Å and Sn–S2 = 2.7240(4) Å]. The remaining positions in the five-coordinate geometry are occupied by the chloride and two methylene-carbon atoms. The disparity in the Sn–S bond lengths of 0.27 Å is reflected in systematic differences in the associated C–S bond lengths [C1–S1 = 1.7488(17) Å and C1–S2 = 1.7095(17) Å] with the short Sn–S bond being associated with the long C–S, and vice versa. The chloride forms a Sn–Cl1 bond length [2.4572(4) Å] which is intermediate between the Sn–S bonds and lies in a position approximately *trans* to the S2 atom [Cl1–Sn–S2 = 155.323(14)°], and may account for some of the lengthening of the Sn–S2 bond. This is in fact the widest angle in the C₂ClS₂ donor set with the narrowest angle being the chelate angle, that is, S1–Sn–S2 = 69.467(13)°. The coordination geometry is highly distorted and this is quantified by the geometric parameter τ [14]. In (I), τ computes to 0.53, a value intermediate between the ideal trigonal-pyramidal and square-pyramidal geometries for which the τ values are 1.0 and 0.0, respectively [14].

In the crystal, there are methylene-C–H... π (benzyl-dithiocarbamate) and tin-bound-benzyl-phenyl-C–H... π (tin-bound-benzyl) interactions [C10–H10...Cg(C4–C9)ⁱ: H10...Cg(C4–C9)ⁱ = 2.60 Å, C10...Cg(C4–C9)ⁱ = 3.5835(19) Å with angle at H10b = 172° and C22–H22...Cg(C11–C16)ⁱⁱ: H22...Cg(C11–C16)ⁱⁱ = 2.77 Å, C22...Cg(C11–C16)ⁱⁱ = 3.704(2) Å with angle at H22 = 169° for symmetry operations (i) $-x, 1-y, 1-z$ and (ii) $-x, 1-y, 2-z$]. These combine with benzyl-C–Cl... π (chelate ring) interactions [C14–Cl2...Cg(Sn, S1, S2, C1)ⁱⁱⁱ: Cl2...Cg(Sn, S1, S2, C1)ⁱⁱⁱ = 3.7583(6) Å, C14...Cg(Sn, S1, S2, C1)ⁱⁱⁱ = 4.9363(18) Å with angle at Cl2 = 123.18(6)° for (iii) $x, -1+y, z$]. It is noted that chelate rings often participate in supramolecular interactions as has been reviewed recently [15, 16]. In the present case, it is apparent that the

Cl2 atom is directed to the centroid of the chelate ring rather than any specific atom with the closest approach being to the C1 atom, at 3.43 Å, a separation greater than the sum of the van der Waals radii of 3.25 Å [17]. The S_2CN chromophore is well known to be electron-rich, owing to the significant contribution of the di-thiolate canonical form for dithiocarbamate, that is $^{2-}S_2C=N^+R'R''$, and it is this characteristic that distinguishes the structural chemistry of dithiocarbamate compounds from other 1,1-dithiolate ligands such as xanthate ($^-S_2COR'$) and dithiophosphate [$^-S_2P(OR')(OR'')$], resulting in a significantly greater propensity to form $C-H \cdots \pi$ (chelate) interactions compared with other dithiolate ligands [18, 19]. The connections between the double-layer along the a -axis direction are of the type tin-bound-benzyl- $C-H \cdots Cl$ (tin-bound) [C12–H12 \cdots Cl1^{iv}: H12 \cdots Cl1^{iv} = 2.87 Å, C12 \cdots Cl1^{iv} = 3.5510(18) Å with angle at H12 = 130° for (iv) 1 – x , 1 – y , 2 – z].

The most prominent surface contacts impacting upon the calculated Hirshfeld surface were obtained from an analysis of the two-dimensional (full and delineated) fingerprint plots performed with Crystal Explorer 17 [20] employing literature protocols [21]. Clearly, the most prevalent surface contacts in the crystal are $H \cdots H$ contacts, contributing 38.2% of all surface contacts. These are followed by significant surface contacts of the type $Cl \cdots H/H \cdots Cl$ [26.8%], consistent with the relatively high number of chloride atoms in the molecule, $C \cdots H/H \cdots C$ [21.8%], $S \cdots H/H \cdots S$ [6.7%] and $S \cdots C/C \cdots S$ [2.3%] and $C \cdots C$ [3.0%] contacts.

Acknowledgements: Sunway University Sdn Bhd is thanked for financial support of this work through Grant no. STR-RCR-RCM-001-2019.

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