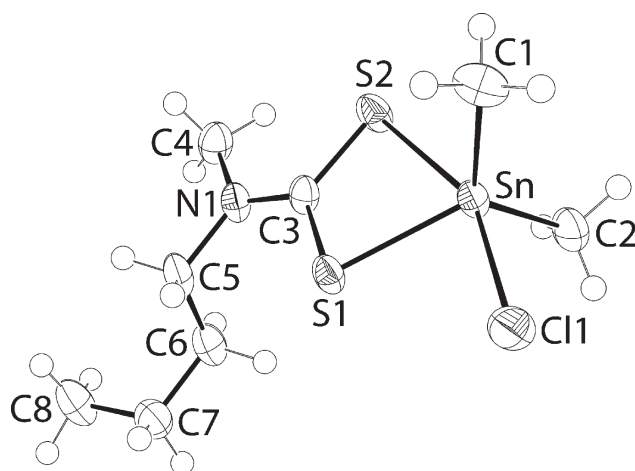


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Crystal structure of (*N*-*n*-butyl, *N*-methyl-dithiocarbamato- κ^2 *S,S'*)-chlorido-dimethyltin(IV), $C_8H_{18}ClNS_2Sn$



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Abstract

$C_8H_{18}ClNS_2Sn$, triclinic, $P\bar{1}$ (no. 2), $a = 6.4399(2)$ Å, $b = 9.6430(3)$ Å, $c = 11.6944(1)$ Å, $\alpha = 91.966(2)^\circ$, $\beta = 101.821(2)^\circ$, $\gamma = 105.391(3)^\circ$, $V = 682.30(3)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0227$, $wR_{ref}(F^2) = 0.0609$, $T = 100$ K.

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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

All chemicals and solvents were used as purchased without purification. The melting point was determined using a Mel-temp II digital melting point apparatus and was uncorrected.

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Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.08 × 0.06 × 0.03 mm
Wavelength:	Cu $K\alpha$ radiation (1.54178 Å)
μ :	19.3 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max} , completeness:	67.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	16394, 2444, 0.042
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 2399
$N(param)_{refined}$:	122
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

The solid-state IR spectrum was obtained on a Bruker Vertex 70v FTIR Spectrometer from 4000 to 400 cm⁻¹. The ¹H and ¹³C{¹H} NMR spectra were recorded at room temperature in CDCl₃ solution on a Bruker Ascend 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane.

The dithiocarbamate ligand was prepared in situ (acetone) from the reaction of CS₂ (Merck 0.25 mmol) with *n*-butylmethylamine (Merck, 0.25 mmol) and NaOH (0.02 mL; 50% w/v); CS₂ was added dropwise into the acetone solution (10 mL). The resulting mixture was kept at 273 K for 0.5 h. Dimethyltin dichloride (Merck, 0.25 mmol, 0.05 g) in acetone (10 mL) was added to the prepared sodium *n*-butyl(methyl)dithiocarbamate. The resulting mixture was stirred and refluxed for 2 h. The filtrate was evaporated slowly until a white precipitate was formed. The precipitate was recrystallized from acetone-methanol by slow evaporation to yield colourless crystals. Yield: 0.042 g (48.5%). **M.pt:** 369–370 K. IR (cm⁻¹) 1466 (m) ν (CN), 1071 (s) ν (CS), 749 (m) ν (CS), 553 (m) ν (SnS). ¹H NMR (CDCl₃, ppm): 0.97 (6H, ² $J(^{119}Sn^1H) = 74$ Hz, CH₃), 1.19 (3H, CH₃) 1.28–1.73 (m, 4H, CH₂CH₂), 3.35 (3H, N–CH₃), 3.70–3.74 (m, 2H, N–CH₂). ¹³C{¹H} NMR (CDCl₃, ppm): 9.9 (6H, ² $J(^{119}Sn^{13}C) = 548$ Hz, CH₃), 13.7 (Bu–CH₃), 19.9, 28.8 (Bu–CH₂), 42.8 (NCH₂), 58.0 (NCH₃), 197.8 (CS₂).

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.98–0.99 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$.

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	0.88424(2)	0.71732(2)	0.84888(2)	0.01924(9)
Cl1	0.84361(11)	0.93203(7)	0.74494(6)	0.03091(17)
S1	0.58280(10)	0.57512(6)	0.68894(5)	0.02078(15)
S2	0.79477(11)	0.43192(7)	0.87990(6)	0.02390(15)
N1	0.4509(4)	0.2927(2)	0.70830(19)	0.0216(5)
C1	1.2139(5)	0.7382(3)	0.8331(3)	0.0295(6)
H1A	1.3027	0.8385	0.8559	0.044*
H1B	1.2142	0.7112	0.7516	0.044*
H1C	1.2767	0.6744	0.8845	0.044*
C2	0.7909(5)	0.7750(3)	1.0032(3)	0.0307(6)
H2A	0.9226	0.8093	1.0670	0.046*
H2B	0.6889	0.6905	1.0251	0.046*
H2C	0.7179	0.8520	0.9889	0.046*
C3	0.5936(4)	0.4163(3)	0.7553(2)	0.0200(5)
C4	0.4537(5)	0.1557(3)	0.7590(3)	0.0272(6)
H4A	0.5328	0.1046	0.7172	0.041*
H4B	0.3017	0.0958	0.7514	0.041*
H4C	0.5284	0.1755	0.8421	0.041*
C5	0.2719(5)	0.2839(3)	0.6031(2)	0.0253(6)
H5A	0.2294	0.1865	0.5605	0.030*
H5B	0.3273	0.3553	0.5498	0.030*
C6	0.0692(5)	0.3131(3)	0.6362(3)	0.0268(6)
H6A	0.1126	0.4106	0.6787	0.032*
H6B	0.0155	0.2421	0.6901	0.032*
C7	-0.1193(5)	0.3043(3)	0.5298(3)	0.0294(6)
H7A	-0.2306	0.3449	0.5548	0.035*
H7B	-0.0600	0.3645	0.4706	0.035*
C8	-0.2318(5)	0.1516(3)	0.4733(3)	0.0344(7)
H8A	-0.1294	0.1163	0.4365	0.052*
H8B	-0.3632	0.1512	0.4135	0.052*
H8C	-0.2755	0.0886	0.5333	0.052*

Comment

The crystal structure determination was reported recently for the methyl ester of the dithiocarbamate ligand featured in the title compound, namely MeSC(=S)N(Me)*n*-Bu [5]. Herein, the isolation and crystallographic analysis of chlorido-dimethyl-tin(IV) ester of this dithiocarbamate ligand, Me₂Sn[S₂CN(Me)*n*-Bu]Cl, (I), is described in continuation of studies of related compounds [6]. Organotin compounds related to Me₂Sn[S₂CN(Me)*n*-Bu]Cl have been investigated for their biological potential pharmaceutical applications [7] as well as for their suitability as synthetic precursors for the generation of tin sulphide nanomaterials via chemical vapour deposition and related techniques [7, 8].

The molecular structure of (I) is shown in the figure (70% displacement ellipsoids). The tin atom exists within a C₂ClS₂ donor set defined by an asymmetrically coordinating dithiocarbamate ligand, the chloride atom and two methyl-carbon atoms. The Sn–S1 [2.4638(6) Å] and Sn–S2 [2.7111(7) Å] bond

lengths differ by approximately 0.25 Å, and consistent with this asymmetry is the systematic variation in the C3–S1, S2 bonds. Thus, the less tightly bound S2 atom forms a shorter C3–S2 bond [1.713(3) Å] than the more tightly bound S1 atom [1.751(3) Å], consistent with some double bond character in the former. The C3–S1, S2 bond lengths in (I) are intermediate between the formerly singly [1.7662(17) Å] and doubly [1.6590(18) Å] bonded distances in the MeSC(=S)N(Me)*n*-Bu ester [5]. The above variations in C–S bond lengths can also be compared with the experimental equivalence of the C–bonds, i.e. 1.7192(14) and C1–S2 = 1.7249(14) Å, in the recently determined salt of [−]S₂CN(CH₂CH₂)₂NPh [9]. A consistent feature in the organotin compound, (I), and in the cited ester [5] and salt [8] is the short C3–N bond, i.e. 1.317(4), 1.351(2) and 1.3419(18) Å, respectively, all indicative of significant double bond character in this bond and a major contribution of the ^{2−}S₂C=N⁺RR' canonical form to the overall electronic structure of the respective dithiocarbamate chromophore. The C₃S₂ donor set defines a highly distorted geometry. This is quantified in the value of τ of 0.51 which is almost exactly intermediate between the values for ideal trigonal-bipyramidal [1.0] and square-pyramidal [0.0] [10].

The molecular packing is largely devoid of directional interactions between molecules. A weak secondary Sn⋯S contact of 3.9510(7) Å is noted to occur between the Sn and S²ⁱ atoms (symmetry operation (i) 2 − x, 1 − y, 2 − z) which is marginally less than the sum of the van der Waals radii for these atoms of 3.97 Å [11]. Secondary bonding interactions are important in dithiocarbamate compounds, including organotin dithiocarbamate compounds [12–14]. In the present case, the Sn⋯S interactions lead to a supramolecular dimer. The dimers are linked into a linear supramolecular chain along the b-axis direction by methyl-C–H⋯Cl interactions [C4–H4a⋯Clⁱⁱ: H4a⋯Clⁱⁱ = 2.90 Å, C4–H4a⋯Clⁱⁱ = 3.742(4) Å with angle at H4a = 144° for (ii) x, −1 + y, z].

Finally, the calculated Hirshfeld surfaces as well as the two-dimensional fingerprint plots (full and delineated into individual contacts) were evaluated for the most significant percentage contributors to the surface. This was accomplished using literature protocols [15] and Crystal Explorer 17 [16]. Given the lack of directional interactions in the crystal, it is not surprising that the most significant contributions to the surface are from H⋯H contacts, at 64.3%. The next three contacts, i.e. Cl⋯H/H⋯Cl [15.7%], S⋯H/H⋯S [15.2%] and C⋯H/H⋯C [2.6%], account for the bulk of the remaining contacts on the calculated Hirshfeld surface.

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