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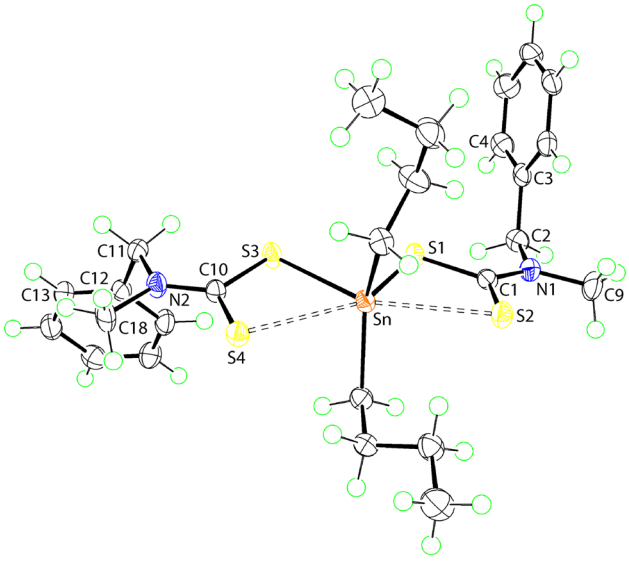
Crystal structure of bis[benzyl(methyl) carbamodithioato-κ^2S,S']-di-*n*-butyltin(IV), $C_{26}H_{38}N_2S_4Sn$



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Abstract

$C_{26}H_{38}N_2S_4Sn$, triclinic, $P\bar{1}$ (no. 2), a = 9.6272(1) Å, b = 12.1043(2) Å, c = 13.3584(2) Å, α = 82.296(1)°, β = 86.611(1)°, γ = 66.912(1)°, V = 1419.02(4) Å^3, Z = 2, $R_{gt}(F)$ = 0.0235, $wR_{ref}(F^2)$ = 0.0612, T = 100 K.

CCDC no.: 2213005

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size	0.27 × 0.20 × 0.11 mm
Wavelength:	Cu *K*α radiation (1.54184 Å)
μ:	10.0 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	75.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	37,119, 5854, 0.033
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 5841
$N(param)_{refined}$:	302
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

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

N–Methylbenzylamine and di-n-butyltin(IV) chloride were purchased from Sigma–Aldrich, carbon disulphide and ammonium solution (25%) were supplied by Merck, and chloroform and ethanol (95%) by System Chemicals.

The title compound was prepared *via* an *in situ* method: *N*-methylbenzylamine (30 mM) was added to ethanol (50 mL) followed by stirring for 1 h under cold temperature (*ca* 277 K) conditions. The ammonia solution (about 2 mL) was added to the mixture followed by another 30 min stirring. Then, a chilled solution comprising carbon disulphide (30 mM) and ethanol (50 mL) was added drop wise with stirring for 90 min. After that, di-*n*-butyltin(IV) chloride (15 mM) which had been dissolved in ethanol (50 mL) was added drop wise to the yellow solution with further stirring for 2 h. The white

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Sn	0.68916 (2)	0.59595 (2)	0.77648 (2)	0.01437 (5)
S1	0.59304 (5)	0.48920 (4)	0.66375 (3)	0.01677 (9)
S2	0.44073 (5)	0.52679 (4)	0.86335 (3)	0.01913 (10)
S3	0.86956 (5)	0.58409 (4)	0.62689 (3)	0.01739 (9)
S4	0.89463 (5)	0.72904 (4)	0.78246 (3)	0.01732 (9)
N1	0.35489 (17)	0.43578 (14)	0.71937 (12)	0.0176 (3)
N2	1.04222 (17)	0.71252 (14)	0.60711 (12)	0.0174 (3)
C1	0.4512 (2)	0.48021 (16)	0.74830 (14)	0.0155 (3)
C2	0.3658 (2)	0.39303 (17)	0.62068 (15)	0.0178 (4)
H2A	0.401166	0.444241	0.570281	0.021*
H2B	0.263747	0.403351	0.600404	0.021*
C3	0.4714 (2)	0.26160 (16)	0.61822 (14)	0.0163 (3)
C4	0.5095 (2)	0.21761 (18)	0.52511 (15)	0.0204 (4)
H4	0.471697	0.270418	0.464893	0.024*
C5	0.6024 (2)	0.09730 (19)	0.51937 (16)	0.0237 (4)
H5	0.627313	0.068069	0.455432	0.028*
C6	0.6589 (2)	0.01945 (17)	0.60713 (17)	0.0222 (4)
H6	0.722506	−0.062925	0.603351	0.027*
C7	0.6220 (2)	0.06279 (17)	0.69997 (16)	0.0202 (4)
H7	0.660592	0.009995	0.760073	0.024*
C8	0.5286 (2)	0.18340 (17)	0.70565 (15)	0.0188 (4)
H8	0.503768	0.212478	0.769650	0.023*
C9	0.2402 (2)	0.4204 (2)	0.79051 (17)	0.0240 (4)
H9A	0.168833	0.499838	0.806301	0.036*
H9B	0.289176	0.371256	0.852715	0.036*
H9C	0.185873	0.379783	0.760100	0.036*
C10	0.9454 (2)	0.68047 (16)	0.66750 (14)	0.0153 (3)
C11	1.0894 (2)	0.67291 (17)	0.50641 (14)	0.0173 (4)
H11A	1.064418	0.602086	0.500620	0.021*
H11B	1.200276	0.646952	0.499647	0.021*
C12	1.0145 (2)	0.77102 (16)	0.42105 (14)	0.0163 (3)
C13	1.0988 (2)	0.82209 (17)	0.35781 (15)	0.0187 (4)
H13	1.203747	0.796966	0.369377	0.022*
C14	1.0309 (2)	0.90965 (18)	0.27774 (16)	0.0221 (4)
H14	1.089805	0.943868	0.234916	0.027*
C15	0.8780 (2)	0.94739 (18)	0.25992 (16)	0.0218 (4)
H15	0.831835	1.006994	0.204929	0.026*
C16	0.7923 (2)	0.89701 (19)	0.32351 (16)	0.0228 (4)
H16	0.687208	0.922744	0.312085	0.027*
C17	0.8602 (2)	0.80941 (18)	0.40342 (16)	0.0207 (4)
H17	0.801235	0.775361	0.446387	0.025*
C18	1.1072 (2)	0.7939 (2)	0.63789 (17)	0.0255 (4)
H18A	1.170961	0.811056	0.583192	0.038*
H18B	1.168311	0.755276	0.698550	0.038*
H18C	1.025694	0.869657	0.652497	0.038*
C19	0.8258 (2)	0.46745 (17)	0.89439 (14)	0.0185 (4)
H19A	0.924400	0.475071	0.895146	0.022*
H19B	0.775556	0.486449	0.960360	0.022*
C20	0.8524 (2)	0.33720 (18)	0.88100 (17)	0.0257 (4)
H20A	0.906075	0.317351	0.816164	0.031*
H20B	0.753651	0.330509	0.877484	0.031*
C21	0.9450 (2)	0.24495 (19)	0.96707 (18)	0.0280 (4)
H21A	0.897812	0.270530	1.032446	0.034*
H21B	0.941626	0.165350	0.961319	0.034*
C22	1.1088 (2)	0.2310 (2)	0.96693 (17)	0.0279 (4)
H22A	1.155895	0.207226	0.901930	0.042*
H22B	1.162781	0.168659	1.021480	0.042*
H22C	1.113416	0.308125	0.977275	0.042*
C23	0.5244 (2)	0.77921 (16)	0.75972 (14)	0.0165 (3)
H23A	0.555598	0.825554	0.702423	0.020*
H23B	0.426504	0.778322	0.742007	0.020*
C24	0.5010 (2)	0.84549 (16)	0.85242 (14)	0.0175 (4)
H24A	0.437428	0.931959	0.833227	0.021*
H24B	0.600282	0.840651	0.873559	0.021*
C25	0.4274 (2)	0.79717 (18)	0.94263 (15)	0.0217 (4)
H25A	0.335313	0.790351	0.919913	0.026*
H25B	0.497931	0.715202	0.969577	0.026*
C26	0.3854 (3)	0.8784 (2)	1.02614 (17)	0.0307 (5)
H26A	0.312985	0.958989	1.000376	0.046*
H26B	0.476366	0.884997	1.049182	0.046*
H26C	0.339849	0.843823	1.082769	0.046*

precipitate that formed was filtered, then washed 3 times with cold ethanol to remove unwanted residues. The precipitate was dried in a vacuum desiccator. Yield 75%. Colourless crystals were obtained from the slow evaporation (3–4 days) of its chloroform/ethanol solution (1:2 *v*/*v*). Melting point (MPA120 EZ–Melt Automated Melting Point Apparatus): 365.6–368.8 K. A crystal harvested from the mother liquor was transferred directly to the liquid–N_2 cold-stream for analysis by X-ray crystallography.

Experimental details

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

Comment

Organotin dithiocarbamates are well-known to possess several useful properties such as being efficient molecular precursors for the deposition of tin sulphide thin films to biological activity [5], i.e. demonstrating potential as anti-cancer [6] and anti-bacterial agents [7]. It was in the context of biological investigations [8], that the title compound, $(n\text{–}Bu)_2Sn[S_2CN(Me)CH_2Ph]_2$, hereafter (I), was investigated crystallographically.

The molecular structure of (I) is shown in the figure (70% displacement ellipsoids). The tin atom in (I) is coordinated by two, asymmetrically bound dithiocarbamate ligands [Sn–S1 = 2.5334(4) and Sn–S3 = 2.5497(4)]. This

asymmetry is reflected in the large values of Δ(Sn–S) = [Sn–S_{long} – Sn–S_{short}] = 0.43 and 0.46 Å for the S1- and S3-dithiocarbamate ligands, respectively. The asymmetric mode of coordination exhibited by the dithiocarbamate ligands is seen experimentally in the systematic differences in the associated C–S bond lengths which are rather disparate [C1–S1, S2 = 1.7477(19) & 1.6910(19) Å and 1.7528(19) & 1.6944(19) Å]. The remaining positions in the immediate environment of the tin atom are occupied by the α-carbon atoms of the *n*-butyl substituents. If a C_2S_2 donor set is assumed, the range of angles subtended at the tin atom is broad, *i.e.* 80.289(14)°, for S1–Sn–S3, to 137.83(7)°, for C19–Sn–C23. The distortion from an ideal tetrahedral geometry is also reflected in the value of the geometric parameter τ_4 [9]. This is computed from the equation $\tau_4 = [360 - (\alpha + \beta)/141]$, where α and β are the two widest angles subtended at the tin centre [9]. For an ideal tetrahedral geometry, $\tau_4 = 1.00$ and for an ideal square-planar geometry, τ_4 = 0.00. In (I), τ_4 = 0.80, which is close to τ_4 = 0.85, calculated for a trigonal-pyramidal arrangement. A common description [5] for the molecular geometry observed for (I) is a skewed trapezoidal-bipyramidal geometry with the short trapezoidal edge defined by the more tightly bound S1 and S3 atoms, and the longer edge by the S2 and S4 atoms.

There are three closely related crystal structures to (I) in the literature, namely $Ph_2Sn[S_2CN(Me)CH_2C_6H_4F\text{-}4]_2$, and $Me_2Sn[S_2CN(Me)CH_2C_6H_4Y\text{-}4]_2$, for Y = F & Br [10]. All three molecular structures resemble that observed in (I). Further, it was noted in a recent overview of $(n\text{–}Bu)_2Sn[S_2CN(R')R'']_2$ molecules [11], that all molecular structures resemble, at least to a first approximation, that noted above for (I).

The most notable aggregate in the crystal is a centrosymmetric dimer within which S3 contacts are apparent [C11–H11a···$S3^i$: H11a···$S3^i$ = 2.86 Å, C11···$S3^i$ = 3.666(2) Å with angle at H11a = 139° for symmetry operation (i): 2 – *x*, 1 – *y*, 1 – *z*]. The dimeric aggregates form columns along the *a*-axis. Within columns are reinforcing benzyl–C–H···π(benzyl) contacts [C13–H13···Cg(C12–C16)^i: H13···Cg(C12–C16)^i = 2.65 Å with angle at H13 = 148° and C16–H16···Cg(C12–C16)^{ii}: H16···Cg(C12–C16)^{ii} = 2.91 Å with angle at H16 = 139° for (ii): 1 – *x*, 1 – *y*, 1 – *z*] implying the C12–C16 benzyl ring forms two such interactions, one to either side of the ring. There are no apparent directional interactions between columns, at least based on standard distance criteria [12].

An analysis of the calculated Hirshfeld surface was conducted [13, 14] in order to probe further the nature of the supramolecular association operating in the crystal of (I). Practically, all surface contacts involve H with by far the greatest contribution due to H···H contacts, *i.e.* 68.9%, but at separations greater than van der Waals distances. The next most prominent contributions to the Hirshfeld surface come from C···H/H···C [16.9%] and S···H/H···S [13.2%] contacts. The next contribution is 0.6% for N···H/H···N with the balance coming from N···N and S···S, each contributing 0.2%.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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