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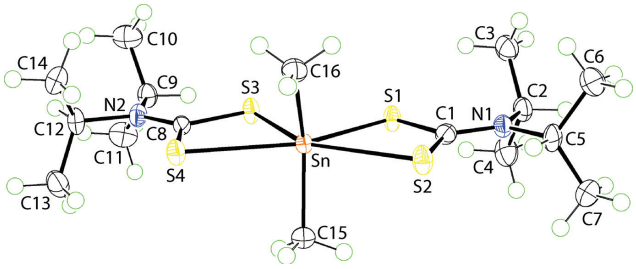
Crystal structure of dimethylbis (diisopropyldithiocarbamato-κ²*S*,*S*′)tin(IV), $C_{16}H_{34}N_2S_4Sn$



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Abstract

$C_{16}H_{34}N_2S_4Sn$, monoclinic, $P2_1/n$ (no. 14), $a = 10.6234(1)$ Å, $b = 16.0898(1)$ Å, $c = 13.2405(1)$ Å, $\beta = 92.853(1)°$, $V = 2260.37(3)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0197$, $wR_{ref}(F^2) = 0.0513$, $T = 100(2)$ K.

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The molecular structure of the title complex 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

Diisopropylamine (Sigma-Aldrich; 1.41 mL, 10 mmol) dissolved in ethanol (30 mL) was stirred under ice-bath conditions at 277 K for 20 mins. 25% Ammonia solution (1 to 2 mL) was added to provide basic conditions. Then, a cold ethanolic solution of carbon disulfide (0.60 mL, 10 mmol) was added dropwise into the solution followed by stirring for about 2 h.

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Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.08 × 0.06 × 0.05 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	12.4 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, omega scans
θ_{max}, completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	27623, 4029, 0.032
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3894
$N(param)_{refined}$:	218
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Sn	0.50287(2)	0.62722(2)	0.84311(2)	0.01258(6)
S1	0.51424(6)	0.74660(3)	0.72015(4)	0.01577(12)
S2	0.50813(6)	0.79508(4)	0.93499(4)	0.01930(13)
S3	0.49526(6)	0.53913(3)	0.68433(4)	0.01630(12)
S4	0.49068(6)	0.45101(3)	0.87891(4)	0.01690(12)
N1	0.51494(19)	0.90498(12)	0.78342(14)	0.0154(4)
N2	0.48543(19)	0.37369(12)	0.69808(15)	0.0162(4)
C1	0.5128(2)	0.82518(15)	0.81205(18)	0.0160(5)
C2	0.5285(2)	0.93465(15)	0.67749(18)	0.0191(5)
H2	0.533234	0.996607	0.682296	0.023*
C3	0.4124(3)	0.91647(17)	0.60777(19)	0.0234(5)
H3A	0.405870	0.856470	0.595912	0.035*
H3B	0.420499	0.945198	0.543150	0.035*
H3C	0.336582	0.936108	0.639622	0.035*
C4	0.6514(3)	0.90782(17)	0.6329(2)	0.0252(6)
H4A	0.721797	0.919507	0.681479	0.038*
H4B	0.663121	0.938572	0.570227	0.038*
H4C	0.648295	0.848108	0.618448	0.038*
C5	0.5101(2)	0.97241(15)	0.86025(18)	0.0180(5)
H5	0.496181	0.945145	0.926646	0.022*
C6	0.3992(3)	1.03040(17)	0.8380(2)	0.0253(6)
H6A	0.412952	1.061924	0.776192	0.038*
H6B	0.391548	1.068952	0.894676	0.038*
H6C	0.321651	0.997711	0.828822	0.038*
C7	0.6358(3)	1.01753(17)	0.8713(2)	0.0269(6)
H7A	0.702545	0.977675	0.890393	0.040*
H7B	0.631656	1.060250	0.923791	0.040*

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H7C	0.654105	1.043735	0.806864	0.040*
C8	0.4898(2)	0.44446(14)	0.75033(18)	0.0148(5)
C9	0.4896(2)	0.37275(15)	0.58505(17)	0.0177(5)
H9	0.504156	0.431311	0.563170	0.021*
C10	0.3639(3)	0.34570(19)	0.53632(19)	0.0265(6)
H10A	0.348915	0.287134	0.552164	0.040*
H10B	0.365175	0.352691	0.462855	0.040*
H10C	0.296341	0.379797	0.562483	0.040*
C11	0.6002(3)	0.32151(18)	0.55112(19)	0.0260(6)
H11A	0.677215	0.338464	0.589458	0.039*
H11B	0.610504	0.330587	0.478816	0.039*
H11C	0.584061	0.262461	0.563235	0.039*
C12	0.4702(2)	0.28983(15)	0.74482(18)	0.0180(5)
H12	0.462363	0.249980	0.686887	0.022*
C13	0.5866(3)	0.26226(16)	0.8078(2)	0.0238(6)
H13A	0.661127	0.267494	0.767612	0.036*
H13B	0.576611	0.204189	0.828298	0.036*
H13C	0.596839	0.297359	0.868183	0.036*
C14	0.3481(2)	0.28128(16)	0.79964(19)	0.0224(5)
H14A	0.354796	0.312831	0.862990	0.034*
H14B	0.333096	0.222536	0.814516	0.034*
H14C	0.277781	0.302956	0.756686	0.034*
C15	0.6918(2)	0.61925(16)	0.90212(19)	0.0198(5)
H15A	0.731758	0.674013	0.898833	0.030*
H15B	0.738243	0.579404	0.862161	0.030*
H15C	0.692668	0.600646	0.972629	0.030*
C16	0.3151(2)	0.62850(16)	0.89108(19)	0.0199(5)
H16A	0.316147	0.624579	0.964976	0.030*
H16B	0.268623	0.581157	0.861225	0.030*
H16C	0.273732	0.680358	0.869161	0.030*

After that, dimethyltin(IV) chloride (Merck; 2.20 g, 10 mmol) dissolved in ethanol (20–30 mL) was added dropwise into the aforementioned solution which was further stirred for about 2 h. Next, the white precipitate that formed was filtered, washed with cold ethanol a few times to remove the impurities. Finally, the precipitate was dried in a dessicator. The recrystallisation process was carried out by dissolving the compound in a chloroform and ethanol mixture (1:1 *v*/*v*). This solution was allowed to slowly evaporate at room temperature yielding colourless crystals of the title compound. Yield: 62%. **M.pt** (Electrothermal digital melting point apparatus): 354.5–368.0 K. **Elem. Anal.** (Perkin-Elmer 2400 CHN Analyser): Calc. for $C_{16}H_{34}N_2S_4Sn$: C 38.35; H 6.78; N 5.59; S 25.59%. Found: C 37.74; H 6.00; N 4.08; S 23.675. **IR** (Thermo Nicolet 6700 IR Spectrophotometer; ATr cm^{-1}): 2972 ν(C—H), 1474 ν(C—N), 1193 ν(N—C), 1037 ν(C—S), 582 ν(Sn—C). **^{1}H NMR** (Bruker Ascend NMR 400 MHz Spectrophotometer; $CDCl_3$; ppm relative to Me_4Si): δ 1.33 (6H, Sn—CH_3); 1.46 (24H, NC(H)—CH_3); 5.46 (4H, N—CH). **^{13}C{^{1}H} NMR** (as for ^{1}H NMR): δ 198.11 (NCS_2); 15.60 (Sn—CH_3); 58.04 (NCH); 19.94 (—CH_3). **^{119}Sn{^{1}H} NMR** (as for ^{1}H NMR with ppm relative to Me_4Sn): −327.09.

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.98–1.00 Å) and refined as riding with $U_{iso}(H) = 1.2$–$1.5U_{eq}(C)$. Owing to poor agreement, two reflections, i.e. (−2 4 13) and (0 4 13), were omitted from the final cycles of refinement.

Comment

Recently [5], it was reported that approximately 10% of diorganotin bis(dithiocarbamate) compounds, i.e. molecules with the general formula $R_2Sn(S_2CNR'R'')_2$, feature Sn···S secondary bonding interactions [6, 7] in their crystals, a well-documented phenomenon in the structural chemistry of organotin dithiocarbamates [8]. As part of continuing structural studies in this area [5, 9–11], the title compound, $Me_2Sn[S_2CN(iPr)_2]_2$, was characterised spectroscopically, crystallographically as well as by an analysis of the calculated Hirshfeld surfaces.

The molecular structure of the title compound is shown in the figure (70% displacement ellipsoids). The tin atom is coordinated in an asymmetric mode by two dithiocarbamate ligands [Sn—S1, S2 = 2.5247(6) and 2.9616(7) Å; Sn—S3, S4 = 2.5334(6), 2.8786(6) Å]. The asymmetric coordination mode is reflected in the values of Δ(Sn—S) = (Sn—S_{long}) – (Sn—S_{short}) = 0.44 and 0.35 Å for the S1- and S3-dithiocarbamate ligands, respectively, and results is significant disparity in the associated C—S bond lengths [C1—S1, S2 = 1.755(2) and 1.701(2) Å; C8—S3, S4 = 1.758(2) and 1.705(2) Å] with the longer C—S bonds being associated with the shorter Sn—S bonds. The two tin-bound methyl substituents are orientated to lie over the weaker Sn—S bonds; the C15—Sn—C16 angle is 140.9(1)°. Overall, the coordination geometry is based on a skew-trapezoidal bipyramidal geometry, as is usually, but not always, found for $R_2Sn(S_2CNR'R'')_2$ molecules [8].

The crystal of the title compound is largely devoid of directional interactions [12]. Centrosymmetrically related molecules are connected by a weak Sn···S secondary bond with Sn···$S4^i$ = 3.8873(6) Å, a distance which is marginally less than the sum of the respective van der Waals radii of 3.97 Å [12]; symmetry operation (i): $1 - x$, $1 - y$, $2 - z$. This brings into close proximity two S4 atoms, being separated by 3.5698(7) Å, compared with the sum of the van der Waals radii of 3.60 Å.

In order to evaluate the molecular packing in more detail, the Hirshfeld surfaces were calculated along with the full and delineated two-dimensional fingerprint plots [13, 14].

Contacts involving hydrogen atoms contribute 99.6% of all surface contacts, with H···H contacts being by far the most dominant at 80.1%. The only other significant contacts to the surface are provided by S···H/H···S contacts at 17.2%; C···H/H···C contacts amount to 2.3%. While S···S contacts contribute 0.4% to the calculated Hirshfeld surface, no surface contacts are ascribed to Sn···S/S···Sn interactions although the appearance of red colouration about the tin and sulphur atoms, indicative of contacts less than the sum of the van der Waals radii, were the only features evident on the Hirshfeld surface mapped over d_{norm}.

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