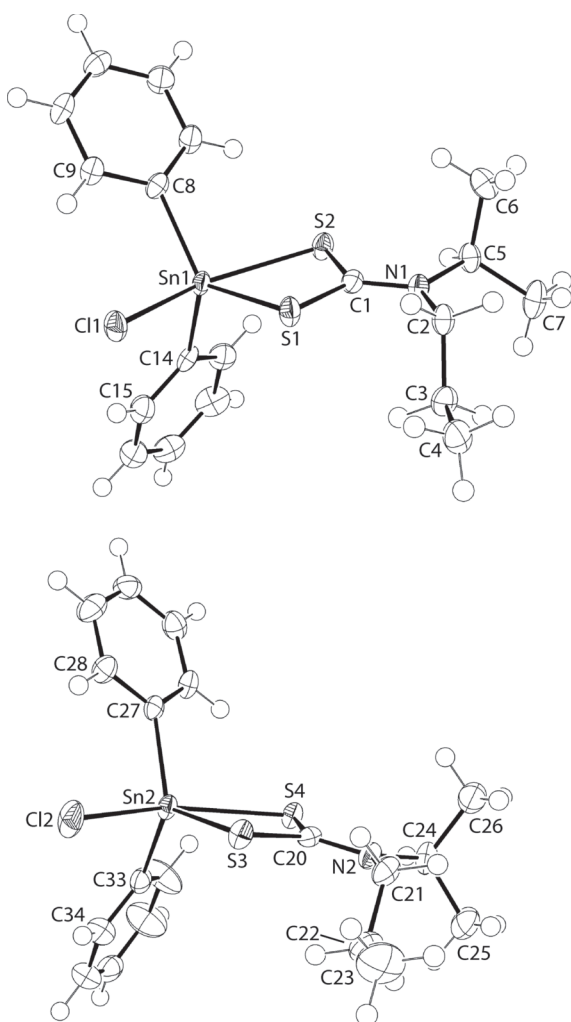


See Mun Lee, Kong Mun Lo and Edward R.T. Tiekink*

Crystal structure of chlorido-diphenyl-(isopropyl (propyl)carbamodithioato- $\kappa^2 S, S'$)tin(IV), $C_{19}H_{24}ClNS_2Sn$



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Abstract

$C_{19}H_{24}ClNS_2Sn$, triclinic, $P\bar{1}$ (no. 2), $a = 10.1894(1)$ Å, $b = 14.0236(2)$ Å, $c = 14.5114(2)$ Å, $\alpha = 91.070(1)^\circ$, $\beta = 96.997(1)^\circ$, $\gamma = 98.222(1)^\circ$, $V = 2035.59(5)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0211$, $wR_{ref}(F^2) = 0.0556$, $T = 100(2)$ K.

CCDC no.: 1957378

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

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.16 × 0.09 × 0.06 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	13.1 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max} , completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	48998, 7265, 0.034
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 7034
$N(param)_{refined}$:	439
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

All chemicals and solvents were used as purchased without purification. The melting point was determined on a Mel-temp II digital melting point apparatus and was uncorrected. The IR spectrum was obtained on a Bruker Vertex 70v FTIR Spectrometer from 4000 to 400 cm⁻¹.

The dithiocarbamate ligand was prepared *in situ* (methanol) from the reaction of CS₂ (Merck 0.25 mmol) with isopropyl(*n*-propyl)amine (Alfa Aesar, 0.25 mmol) and KOH (0.03 mL; 50% w/v); CS₂ was added drop-wise into the methanolic solution (15 mL). The resulting mixture was kept at 273 K for 0.5 h. Diphenyltin dichloride (0.25 mmol, 0.09 g) in methanol (10 mL) was added to the prepared potassium isopropyl-*n*-propyl dithiocarbamate. The resulting mixture was stirred and refluxed for 2 h. The filtrate was evaporated

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Sn1	0.29681(2)	0.50913(2)	0.20104(2)	0.01305(5)
Cl1	0.20862(5)	0.58071(4)	0.05728(3)	0.01851(11)
S1	0.51360(5)	0.54532(4)	0.14276(4)	0.01681(11)
S2	0.48866(5)	0.44108(4)	0.31606(4)	0.01597(11)
N1	0.72222(16)	0.49820(12)	0.25025(12)	0.0135(3)
C1	0.59125(19)	0.49484(14)	0.24007(15)	0.0137(4)
C2	0.80146(19)	0.54385(15)	0.17977(15)	0.0158(4)
H2A	0.751369	0.528051	0.117246	0.019*
H2B	0.886377	0.516830	0.182353	0.019*
C3	0.8326(2)	0.65321(16)	0.19414(16)	0.0186(4)
H3A	0.749904	0.679685	0.203196	0.022*
H3B	0.897730	0.669757	0.250525	0.022*
C4	0.8902(2)	0.69760(17)	0.11006(17)	0.0232(5)
H4A	0.967137	0.666869	0.097754	0.035*
H4B	0.918710	0.766856	0.122525	0.035*
H4C	0.821735	0.687643	0.055785	0.035*
C5	0.7909(2)	0.44837(15)	0.32799(15)	0.0164(4)
H5	0.735014	0.445690	0.380232	0.020*
C6	0.7961(2)	0.34522(17)	0.29588(17)	0.0227(5)
H6A	0.704979	0.312152	0.277237	0.034*
H6B	0.839271	0.311320	0.346844	0.034*
H6C	0.847242	0.345735	0.242888	0.034*
C7	0.9288(2)	0.50159(19)	0.36431(17)	0.0257(5)
H7A	0.988322	0.499751	0.316327	0.039*
H7B	0.964951	0.470538	0.419793	0.039*
H7C	0.921900	0.568770	0.380212	0.039*
C8	0.16850(19)	0.37313(15)	0.18152(15)	0.0146(4)
C9	0.0589(2)	0.36164(16)	0.11294(15)	0.0173(4)
H9	0.043024	0.413287	0.073630	0.021*
C10	−0.0277(2)	0.27468(17)	0.10167(16)	0.0209(5)
H10	−0.101443	0.266933	0.053980	0.025*
C11	−0.0069(2)	0.19963(16)	0.15952(16)	0.0203(5)
H11	−0.066588	0.140654	0.152002	0.024*
C12	0.1018(2)	0.21081(16)	0.22874(17)	0.0212(5)
H12	0.116048	0.159600	0.268970	0.025*
C13	0.1896(2)	0.29704(16)	0.23909(16)	0.0191(4)
H13	0.264544	0.304041	0.285818	0.023*
C14	0.25981(19)	0.61706(15)	0.29714(15)	0.0157(4)
C15	0.1999(2)	0.69557(16)	0.26487(17)	0.0213(5)
H15	0.178060	0.702168	0.199991	0.026*
C16	0.1719(2)	0.76427(17)	0.32719(18)	0.0252(5)
H16	0.129483	0.816824	0.304647	0.030*
C17	0.2054(2)	0.75657(17)	0.42163(18)	0.0249(5)
H17	0.186454	0.803622	0.464100	0.030*
C18	0.2669(2)	0.67945(18)	0.45377(17)	0.0265(5)
H18	0.291197	0.674272	0.518589	0.032*
C19	0.2932(2)	0.60985(16)	0.39238(16)	0.0211(5)
H19	0.334301	0.556901	0.415427	0.025*
Sn2	0.29554(2)	0.07307(2)	0.68663(2)	0.01405(5)
Cl2	0.09550(5)	−0.04057(4)	0.62779(4)	0.02780(13)
S3	0.21280(5)	0.05799(4)	0.83896(4)	0.01713(11)
S4	0.47280(5)	0.17403(4)	0.81987(3)	0.01521(10)
N2	0.37993(17)	0.13865(13)	0.98338(12)	0.0157(4)
C20	0.36089(19)	0.12676(14)	0.89191(15)	0.0142(4)
C21	0.2754(2)	0.10127(16)	1.04139(15)	0.0188(4)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H21A	0.187042	0.110172	1.008808	0.023*
H21B	0.289763	0.139921	1.100485	0.023*
C22	0.2729(2)	−0.00537(18)	1.06352(17)	0.0261(5)
H22A	0.262791	−0.044303	1.004799	0.031*
H22B	0.358837	−0.014245	1.099730	0.031*
C23	0.1592(3)	−0.0408(2)	1.1184(2)	0.0409(7)
H23A	0.169768	−0.003012	1.177081	0.061*
H23B	0.160405	−0.108958	1.131519	0.061*
H23C	0.073857	−0.033189	1.082226	0.061*
C24	0.5044(2)	0.19648(17)	1.03192(16)	0.0204(5)
H24	0.571350	0.205541	0.986660	0.025*
C25	0.5638(2)	0.14378(19)	1.11376(18)	0.0295(5)
H25A	0.503758	0.139210	1.161893	0.044*
H25B	0.650969	0.179305	1.139168	0.044*
H25C	0.574844	0.078838	1.093002	0.044*
C26	0.4775(2)	0.29593(17)	1.06142(17)	0.0255(5)
H26A	0.432365	0.325542	1.008195	0.038*
H26B	0.562325	0.336504	1.083751	0.038*
H26C	0.420390	0.289737	1.111310	0.038*
C27	0.2554(2)	0.19319(15)	0.60531(14)	0.0146(4)
C28	0.1354(2)	0.18840(16)	0.54688(16)	0.0193(4)
H28	0.067778	0.134397	0.548131	0.023*
C29	0.1140(2)	0.26208(18)	0.48688(17)	0.0248(5)
H29	0.031710	0.258643	0.447554	0.030*
C30	0.2125(2)	0.34059(16)	0.48420(16)	0.0223(5)
H30	0.197925	0.390870	0.442903	0.027*
C31	0.3323(2)	0.34577(16)	0.54178(17)	0.0223(5)
H31	0.399977	0.399531	0.539671	0.027*
C32	0.3538(2)	0.27265(16)	0.60262(15)	0.0179(4)
H32	0.435819	0.276851	0.642449	0.021*
C33	0.4408(2)	−0.01222(16)	0.65181(15)	0.0178(4)
C34	0.4109(3)	−0.11193(17)	0.64007(18)	0.0269(5)
H34	0.323774	−0.143426	0.646799	0.032*
C35	0.5085(3)	−0.16546(18)	0.61846(19)	0.0325(6)
H35	0.488397	−0.233714	0.612151	0.039*
C36	0.6336(3)	−0.12066(19)	0.60616(17)	0.0283(5)
H36	0.699650	−0.157813	0.591201	0.034*
C37	0.6635(3)	−0.0215(2)	0.6156(2)	0.0407(7)
H37	0.749332	0.009961	0.605666	0.049*
C38	0.5668(3)	0.03219(19)	0.6397(2)	0.0360(7)
H38	0.588175	0.100249	0.647869	0.043*

slowly until a colourless precipitate was formed. The precipitate was recrystallised from its acetone-methanol solution. The title compound was a side-product/incomplete reaction product obtained from the slow evaporation of the solvent. Yield: 0.02 g (17%). **M.pt:** 381–383 K. **IR** (cm^{−1}) 550 (w) ν(Sn–S), 1477 (s) ν(C–N), 1187 (m) ν(C–S), 1048 (s) ν(C–N).

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) = 1.2–1.5*U*_{eq}(C).

Comment

Molecules/complexes of the general formula $R_2Sn(S_2CNR'R'')Cl$ have been the subject of structure determinations by both X-ray crystallography and computational chemistry for nearly 20 years [5, 6]. These studies showed that tin-ligand parameters were sometimes influenced significantly by the crystalline/solid state environment, often leading to non-systematic variations that were not evident in their calculated gas-phase structures. Interest in this area continues [7, 8] and indeed, there are now over 70 mononuclear species of this type in the crystallographic literature [9]. Herein, a new derivative, $Ph_2Sn[S_2CN(i-Pr)n-Pr]Cl$, (I), is described, which was synthesised in the context of evaluating the biological potential of organotin dithiocarbamates [10].

The molecular structures of the two independent molecules comprising the asymmetric unit of (I) are shown in the figure (70% displacement ellipsoids). The tin atom in each molecule is penta-coordinated by two ipso-carbon atoms of the phenyl groups, a chloride and two sulphur atoms derived from an asymmetrically chelating dithiocarbamate ligand. The asymmetry in the Sn–S bonds [Sn1–S1, S2 = 2.4501(5), 2.7049(5) Å and Sn2–S3, S4 = 2.4622(5), 2.7058(5) Å] is reflected in the magnitude of $\Delta(Sn-S) = (Sn-S_{long} - Sn-S_{short}) = 0.25$ and 0.26 Å, respectively. There is a small disparity in the Sn1–Cl1 [2.4591(5) Å] and Sn2–Cl2 [2.4534(5) Å] bond lengths. The asymmetric mode of coordination of the dithiocarbamate ligand influences the C–S bond lengths with the C–S bonds associated with the more tightly bound sulphur atoms [C1–S1 = 1.745(2) Å and C20–S3 = 1.752(2) Å] being longer than the C–S bonds involving the less tightly bound sulphur atoms [C1–S2 = 1.722(2) Å and C20–S4 = 1.712(2) Å]. Typically for dithiocarbamate ligands [11], the relatively short C1–N1 [1.319(3)] and C20–N2 [1.322(3) Å] bond lengths are indicative of significant contributions of the dithiolate, $^{-}S_2C=N^{+}(i-Pr)n-Pr$, canonical form to the electronic structure of the ligand.

The resulting C_2ClS_2 donor set is highly distorted and this is seen in a quantitative measure of a five-coordinate geometry, i.e. τ [12]. For an ideal square-pyramidal geometry, $\tau = 0.0$ whereas for an ideal trigonal-bipyramidal geometry, $\tau = 1.0$. In the present study, the values of τ compute to 0.49 and 0.58 for the Sn1 and Sn2 atoms, respectively. The distortions arise partly to the acute chelate angles: S1–Sn1–S2 [69.663(16)°] and S3–Sn2–S4 [69.447(16)°] as reflected, for example, in the trans Cl1–Sn1–S2 [154.209(16)°] and Cl2–Sn2–S4 [154.996(18)°] angles. The molecular structures described herein conform to the motif always seen for mononuclear molecules/complexes of the general formula $R_2Sn(S_2CNR'R'')Cl$ [10].

The molecular packing is largely devoid of directional points of contact between atoms/residues [13], with the exception of methyl- and phenyl-C–H... π (phenyl) interactions [C6–H6c...Cg(C8–C13)ⁱ: H6c...Cg(C8–C13)ⁱ = 2.93 Å, C6...Cg(C8–C13)ⁱ = 3.784(2) Å with angle at H6c = 146° and C36–H36...Cg(C27–C32)ⁱⁱ: H36...Cg(C27–C32)ⁱⁱ = 2.68 Å, C36...Cg(C27–C32)ⁱⁱ = 3.489(3) Å with angle at H36 = 143° for symmetry operations (i) 1 + x, y, z and (ii) 1 – x, –y, 1 – z]. Each of these interactions occurs between like-molecules. In the case of the Sn1-molecule, the result of these contacts is the formation of a linear supramolecular chain along the a-axis direction. For the Sn2-molecule, the specified interaction leads to a centrosymmetric dimer. The dimers stack in columns parallel to the chains. Globally, the crystal comprises alternating layers of chains and dimers stacked along the b-axis.

A further analysis of the intermolecular connectivity was performed by evaluating the calculated Hirshfeld surfaces using Crystal Explorer 17 [14] following literature procedures [15]; the full and decomposed two-dimensional fingerprint plots were also calculated. There are four dominant contacts to the Hirshfeld surface for the entire asymmetric unit in (I), namely H...H [55.5%], H...C/C...H [23.9%], Cl...H/H...Cl [9.2%] and S...H/H...S [8.7%] but, generally beyond the sum of the respective van der Waals radii. A recent study [16] emphasised how different molecules/complexes comprising the asymmetric unit could present different percentage profiles depending on the intermolecular interactions they form. Accordingly, each of the Sn1- and Sn2-molecules/complexes in (I) were analysed separately. Not surprisingly, the same major contributions are evident but, in different percentages, i.e. H...H [59.1% for the Sn1-molecule and 52.8% for the Sn2-molecule/complex], H...C/C...H [23.5 and 24.6%], Cl...H/H...Cl [9.0 and 8.3%] and S...H/H...S [7.1 and 10.6%]. Thus, small differences between the independent molecules are seen in the percentage contributions for the H...H and S...H/H...S contacts. Further, for the Sn2-molecule, C...C contacts amounts to 2.3% of the Hirshfeld surface contacts compared with 0.2% for the Sn1-molecule complex.

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