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Crystal structure of (dibenzyl sulphoxide- κO)bis(2-chlorobenzyl- κC^1)dichloridotin(IV), $C_{28}H_{26}Cl_4OSSn$

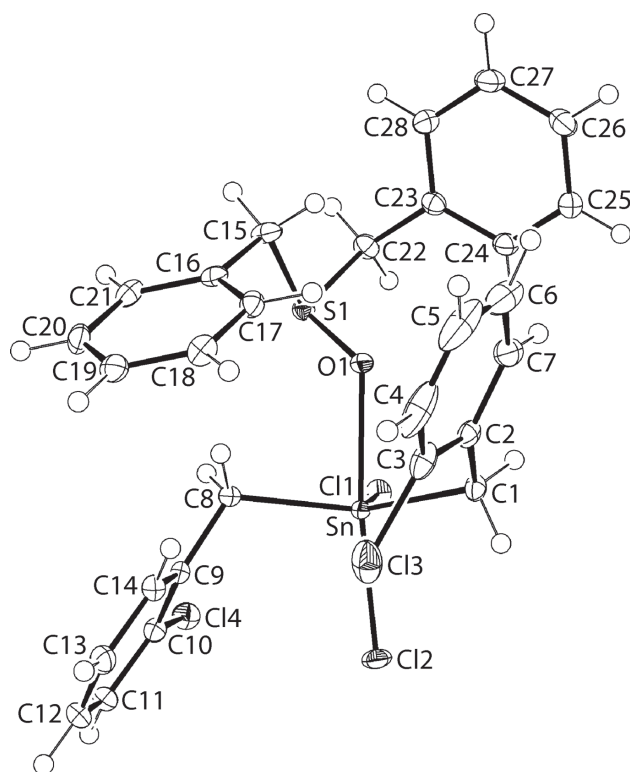


Table 1: Data collection and handling.

Crystal:	Slab, colorless
Size:	0.50 × 0.40 × 0.30 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.42 mm ⁻¹
Diffractometer, scan mode:	Bruker SMART, φ and ω -scans
θ_{\max} , completeness:	28.4°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	27156, 6871, 0.015
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 6626
$N(\text{param})_{\text{refined}}$:	316
Programs:	Bruker programs [1], SHELX [2–4], WinGX and ORTEP [5]

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

The elemental analysis was performed on a Perkin-Elmer EA2400 CHN analyser. The IR spectrum was recorded using a Perkin-Elmer RX1 spectrophotometer in a Nujol mull between KBr plates. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded in CDCl_3 solution on a Bruker AVN FT-NMR spectrometer with chemical shifts relative to Me_4Si for ^1H and CDCl_3 for $^{13}\text{C}\{^1\text{H}\}$.

Di(2-chlorobenzyl)tin dichloride was prepared from the direct synthesis of tin powder (Sigma-Aldrich) and 2-chlorobenzyl chloride (Sigma-Aldrich) in toluene [6]. The ligand, dibenzyl sulphoxide (Sigma-Aldrich; 0.46 g, 2.0 mmol) and di(2-chlorobenzyl)tin dichloride (0.44 g, 1 mmol) were heated in 95% ethanol (50 mL) for 0.5 h followed by filtration. The filtrate was evaporated until colourless crystals formed. Yield: 0.43 g (64%). *M.pt.*: 404–406 K. Anal. Calcd. for $C_{28}H_{26}Cl_4OSSn$: C, 50.11; H, 3.91. Found: C, 50.00; H, 3.52. **IR** (cm^{-1}) 988 (s) $\nu(\text{S}=\text{O})$, 500 (*m*) $\nu(\text{Sn}-\text{O})$. **^1H NMR** (CDCl_3 , p.p.m.): δ 3.22 (s, 4H, 2-ClPh-CH₂), 3.79 (s, 4H, SCH₂), 7.06–7.18 (m, 8H, 2-ClPh-H), 7.21–7.38 (m, 10H, SCH₂Ph-H). **^{13}C NMR** (CDCl_3 , p.p.m.): δ 55.7 (s, -SCH₂), 36.2 (s, 2-ClPh-CH₂), 135.1, 133.3, 130.8, 130.3, 129.2, 129.0, 128.9, 128.7, 127.5, 127.1 (phenyl-C).

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Abstract

$C_{28}H_{26}Cl_4OSSn$, monoclinic, $P2_1/c$ (no. 14), $a = 10.6342(2)$ Å, $b = 12.9298(3)$ Å, $c = 20.3576(4)$ Å, $\beta = 101.820(1)^\circ$, $V = 2739.78(10)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0197$, $wR_{\text{ref}}(F^2) = 0.0520$, $T = 100(2)$ K.

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

Atom	x	y	z	U_{iso}^*/U_{eq}
Sn	0.47540(2)	0.68796(2)	0.06810(2)	0.01038(3)
Cl1	0.35208(4)	0.71266(3)	−0.04186(2)	0.01775(7)
Cl2	0.31041(4)	0.58423(3)	0.10261(2)	0.02123(8)
Cl3	0.63697(5)	0.60439(4)	0.22130(2)	0.03233(11)
Cl4	0.16760(4)	0.84419(3)	0.08007(2)	0.02096(8)
S1	0.62684(3)	0.88295(3)	−0.00742(2)	0.01378(7)
O1	0.63445(10)	0.77471(8)	0.02206(6)	0.0151(2)
C1	0.61099(15)	0.56421(12)	0.07189(8)	0.0157(3)
H1A	0.576774	0.502481	0.091063	0.019*
H1B	0.618122	0.546895	0.025421	0.019*
C2	0.74205(15)	0.58606(12)	0.11172(8)	0.0171(3)
C3	0.76659(18)	0.60201(13)	0.18066(9)	0.0232(3)
C4	0.8896(2)	0.61801(15)	0.21808(12)	0.0412(6)
H4	0.903747	0.626010	0.265418	0.049*
C5	0.9912(2)	0.62212(16)	0.18534(16)	0.0508(8)
H5	1.075916	0.633423	0.210269	0.061*
C6	0.97047(19)	0.60995(16)	0.11697(16)	0.0451(7)
H6	1.040441	0.614745	0.094644	0.054*
C7	0.84734(17)	0.59062(14)	0.08027(11)	0.0273(4)
H7	0.834477	0.580346	0.033158	0.033*
C8	0.46438(15)	0.83067(12)	0.12083(8)	0.0161(3)
H8A	0.553138	0.852423	0.141034	0.019*
H8B	0.427819	0.883861	0.087356	0.019*
C9	0.38835(16)	0.83147(12)	0.17481(8)	0.0155(3)
C10	0.25477(16)	0.84022(12)	0.16276(8)	0.0167(3)
C11	0.18681(16)	0.84616(13)	0.21410(9)	0.0203(3)
H11	0.096062	0.854024	0.204116	0.024*
C12	0.25319(18)	0.84046(14)	0.27999(9)	0.0222(3)
H12	0.207865	0.843545	0.315604	0.027*
C13	0.38572(18)	0.83026(13)	0.29407(8)	0.0209(3)
H13	0.431217	0.826063	0.339304	0.025*
C14	0.45197(16)	0.82619(12)	0.24203(8)	0.0180(3)
H14	0.542867	0.819643	0.252353	0.022*
C15	0.77335(16)	0.94458(13)	0.03643(8)	0.0194(3)
H15A	0.848796	0.902662	0.031534	0.023*
H15B	0.781812	1.013957	0.017222	0.023*
C16	0.76747(15)	0.95397(12)	0.10923(8)	0.0157(3)
C17	0.81963(15)	0.87638(12)	0.15417(8)	0.0170(3)
H17	0.861789	0.819031	0.139020	0.020*
C18	0.81003(16)	0.88282(13)	0.22113(8)	0.0196(3)
H18	0.846544	0.830252	0.251765	0.024*
C19	0.74728(16)	0.96579(13)	0.24333(8)	0.0203(3)
H19	0.740147	0.969603	0.289028	0.024*
C20	0.69492(16)	1.04321(13)	0.19888(9)	0.0212(3)
H20	0.651986	1.100055	0.214088	0.025*
C21	0.70543(16)	1.03742(12)	0.13203(8)	0.0193(3)
H21	0.670068	1.090716	0.101697	0.023*
C22	0.66228(15)	0.87030(13)	−0.09132(8)	0.0176(3)
H22A	0.588301	0.836714	−0.121129	0.021*
H22B	0.671921	0.940294	−0.109375	0.021*
C23	0.78116(16)	0.80908(12)	−0.09318(8)	0.0159(3)
C24	0.77685(16)	0.70171(13)	−0.09309(8)	0.0183(3)

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H24	0.697573	0.667330	−0.093964	0.022*
C25	0.88781(16)	0.64430(13)	−0.09172(9)	0.0207(3)
H25	0.884074	0.570894	−0.091599	0.025*
C26	1.00392(17)	0.69369(14)	−0.09054(9)	0.0216(3)
H26	1.079907	0.654302	−0.088939	0.026*
C27	1.00871(17)	0.80089(14)	−0.09172(9)	0.0231(3)
H27	1.087867	0.834975	−0.091683	0.028*
C28	0.89789(17)	0.85851(13)	−0.09294(9)	0.0214(3)
H28	0.901653	0.931901	−0.093623	0.026*

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–0.99 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$. Owing to poor agreement, four reflections, i.e. (0 2 0), (−11 10 2), (−13 0 2) and (−11 9 2), were removed from the final cycles of refinement.

Discussion

In general, the reaction of a diorganotin dichloride precursor with monodentately coordinating acyclic dialkylsulphoxide ligands, e.g. dimethylsulphoxide, leads to the formation of 1:2 adducts in which the tin atom is in a six-coordinate, octahedral environment. Two examples relevant to the present study are *trans*-Ph₂SnCl₂·2OSBz₂ [7] and *trans*-(4-FBz)₂SnCl₂·2OSMe₂ [8]; Bz is benzyl. There are only three examples where mononuclear 1:1 diorganotin dichlorido-sulphoxide adducts have been structurally described in the literature, i.e. Me₂SnCl₂·OSBz₂ [9], Ph₂SnCl₂·OS(Ph)Bz [10] and Ph₂SnCl₂·OS(CH₂)₄ [11]. In the present work, as continuation of studies in this area [8], another example of a 1:1 adduct, (2-ClBz)₂SnCl₂·OSBz₂, is described.

The molecular structure (Figure, 50% displacement ellipsoids) features a five-coordinate tin centre defined by two chlorido ligands, the oxygen atom of the OSBz₂ ligand and two substituted benzyl-C atoms. The resultant C₂Cl₂O donor set is highly distorted. A measurement of the distortion in five-coordinate geometries is τ [12] which has a value of 0.0 for an ideal square-pyramidal geometry and 1.0 for a trigonal bipyramid. In the present case, τ computes to 0.60. One contribution to the distortion is found in the presence of an intramolecular Sn···Cl3 interaction of 3.4134(6) Å. There is a clear disparity in the Sn–Cl bond lengths with the Sn–Cl1 bond [2.3728(4) Å], with the Cl1 atom approximately opposite to the weakly associated Cl3 atom, being significantly shorter than the Sn–Cl2 bond [2.4239(4) Å], which is opposite the sulphoxide-O1 atom [2.3764(11) Å]. The structure of

$(2\text{-ClBz})_2\text{SnCl}_2$ is available for comparison in which the tin atom lies on the 2-fold axis of symmetry [13]. It is interesting to note that the key Cl1-Sn-Cl2 [$93.146(14)^\circ$ cf. $98.95(2)^\circ$] and Cl-Sn-C8 [$136.67(6)^\circ$ cf. $135.87(11)^\circ$] angles in the present and literature structures are, to a first approximation, the same so that the main influence of the coordination of OSBz_2 is to elongate the Sn-Cl2 bond; both Sn-Cl bonds are equivalent [$2.3740(7)$ Å] in $(2\text{-ClBz})_2\text{SnCl}_2$ [13].

An analysis of the molecular packing points to the importance of phenyl- $\text{C-H}\cdots\text{Cl}$ interactions in stabilizing the crystal [$\text{Cl3-H13}\cdots\text{Cl1}^i$: $\text{H13}\cdots\text{Cl1}^i = 2.77$ Å, $\text{Cl3}\cdots\text{Cl1}^i = 3.4759(17)$ Å with angle at $\text{H13} = 132^\circ$; $\text{C19-H19}\cdots\text{Cl2}^{ii}$: $\text{H19}\cdots\text{Cl2}^{ii} = 2.80$ Å, $\text{C19}\cdots\text{Cl2}^{ii} = 3.6532(17)$ Å with angle at $\text{H19} = 150^\circ$; $\text{C21-H21}\cdots\text{Cl1}^{iii}$: $\text{H21}\cdots\text{Cl1}^{iii} = 2.81$ Å, $\text{C21}\cdots\text{Cl1}^{iii} = 3.7048(16)$ Å with angle at $\text{H21} = 158^\circ$; symmetry operations: i: $x, 3/2 - y, 1/2 + z$; ii: $1 - x, 1/2 + y, 1/2 - z$; iii: $1 - x, 2 - y, -z$]. The result of these contacts is the formation of a supramolecular layer in the bc -plane. The only other contacts of note are parallel ring- $\text{C-Cl}\cdots\pi(\text{phenyl})$ interactions and these serve to further consolidate the aforementioned layers [$\text{C3-Cl3}\cdots\text{Cg}(\text{C9-C14})^{iv} = 3.6254(8)$ Å with angle at $\text{Cl3} = 93.02(6)^\circ$ for iv: $1 - x, -1/2 + y, 1/2 - z$]. The layers stack along the a axis with no directional interactions between them.

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References

1. Bruker.: APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, WI, USA (2012).
2. Sheldrick, G. M.: SADABS. University of Göttingen, Germany (1996).
3. Sheldrick, G. M.: SHELXT – Integrated space-group and crystal-structure determination. *Acta Crystallogr.* **A71** (2015) 3–8.
4. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
5. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. *J. Appl. Cryst.* **45** (2012) 849–854.
6. Sisido, K.; Takeda, Y.; Kinugawa, Z.: Direct synthesis of organotin compounds I. di- and tribenzyltin chlorides. *J. Am. Chem. Soc.* **83** (1961) 538–541.
7. de Sousa, G. F.; Sabino, J. R.; Vencato, I.; Filgueiras, C. A. L.; Ardisson, J. D.: Synthesis, structural and spectral studies of five- and six-coordinate adducts of organotin(IV) halides containing dibenzylsulfoxide (dbso) as ligand. The crystal structures of $\text{fac-[MeSnCl}_3(\text{dbso})]$ and $\text{trans-[Ph}_2\text{SnCl}_2(\text{dbso})_2]$. *J. Braz. Chem. Soc.* **20** (2009) 1425–1423.
8. Amin, N. A. B. M.; Hussien, R. S. D.; Lee, S. M.; Halcovitch, N. R.; Jotani, M. M.; Tiekink, E. R. T.: $\text{trans-Dichloridobis(dimethyl sulfoxide-}\kappa\text{O)bis(4-fluorobenzyl-}\kappa\text{C}^1\text{)tin(IV)}$: crystal structure and Hirshfeld surface analysis. *Acta Crystallogr.* **E73** (2017) 667–672.
9. Ng, S. W.; Rheingold, A. L.: Crystal structure of dimethyltin dichloride-dibenzylsulfoxide. *J. Organomet. Chem.* **378** (1989) 339–345.
10. Tan, G.-X.; Zhang, C. F.; Liu, X.-C.: Benzyl phenyl sulfoxide- κO dichloridodiphenyltin(IV). *Acta Crystallogr.* **E67** (2011) m632.
11. Howie, R. A.; Harrison, W. T. A.; de Lima, G. M.; Wardell, J. L.; Wardell, S. M. S. V.: Tetrahydrothiophene-1-oxide, TMSO, complexes of tin(IV) halides: crystal structures of $\text{SnCl}_4(\text{TMSO})_2$ [two polymorphs], $\text{SnBr}_4(\text{TMSO})_2$ and $\text{Ph}_2\text{SnCl}_2(\text{TMSO})_n$ ($n = 1$ and 2). *Z. Kristallogr. CM* **225** (2010) 448–455.
12. Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C.: Synthesis, structure, and spectroscopic properties of copper(II) compounds containing nitrogen-sulphur donor ligands; the crystal and molecular structure of aqua[1,7-bis(*N*-methylbenzimidazol-2'-yl)-2,6-dithiaheptane]-copper(II) perchlorate. *J. Chem. Soc. Dalton Trans.* (1984) 1349–1356.
13. Lo, K. M.; Ng, S. W.: Dichloridobis(2-chlorobenzyl)tin(IV). *Acta Crystallogr.* **E66** (2010) m966.