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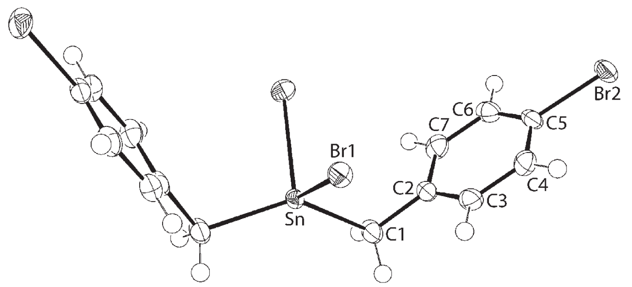
Crystal structure of dibromidobis(4-bromobenzyl)tin(IV), $C_{14}H_{12}Br_4Sn$



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Abstract

$C_{14}H_{12}Br_4Sn$, monoclinic, $I2/a$ (no. 15), $a = 12.6379(2)$ Å, $b = 4.9674(1)$ Å, $c = 26.1845(4)$ Å, $\beta = 94.507(1)°$, $V = 1638.71(5)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0142$, $wR_{ref}(F^2) = 0.0358$, $T = 100$ 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.

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	$0.07 \times 0.03 \times 0.02$ mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	23.7 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	67.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	10027, 1450, 0.031
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1418
$N(param)_{refined}$:	87
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

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

Atom	x	y	z	$U_{iso}*/U_{eq}$
Sn	0.250000	−0.00473(4)	0.500000	0.01254(7)
Br1	0.39552(2)	0.32357(5)	0.52646(2)	0.01689(7)
Br2	0.41779(2)	0.70829(5)	0.27602(2)	0.02498(8)
C1	0.29003(19)	−0.1656(5)	0.42709(7)	0.0202(5)
H1A	0.350663	−0.291059	0.432852	0.024*
H1B	0.228858	−0.268688	0.411326	0.024*
C2	0.31845(18)	0.0518(5)	0.39113(8)	0.0163(4)
C3	0.42172(17)	0.1525(5)	0.39318(7)	0.0188(5)
H3	0.473217	0.086032	0.418448	0.023*
C4	0.45068(18)	0.3473(5)	0.35910(8)	0.0193(5)
H4	0.521338	0.413915	0.360804	0.023*
C5	0.37503(19)	0.4434(5)	0.32252(8)	0.0179(4)
C6	0.27165(18)	0.3493(5)	0.31938(8)	0.0195(5)
H6	0.220605	0.416788	0.294006	0.023*
C7	0.24382(18)	0.1548(5)	0.35391(7)	0.0189(5)
H7	0.172856	0.090381	0.352247	0.023*

Source of material

The melting point (uncorrected) was measured on an Mel-Temp II melting point apparatus. ^{1}H and $^{13}\{^1$H$\}$C NMR spectra were recorded in DMSO-d$_6$ solution on a Bruker Ascend 400 MHz NMR (Billerica, MA, USA) spectrometer.

Di(4-bromobenzyl)tin dibromide was prepared from the direct reaction of 4-bromobenzyl bromide (Merck, 0.50 g, 2.0 mmol) and metallic tin powder (Sigma-Aldrich, 0.12 g, 1.0 mmol) in toluene according to a literature procedure [5]. After refluxing for 5 h, fine white powders were observed in the mixture and the contents of the reaction vessel became grey. The obtained slurry was filtered after cooling and the residue was extracted with acetone/toluene. Colourless crystals suitable for crystallographic studies were obtained from the slow evaporation of the filtrate. Yield: 0.32 g (52%). M. pt: 453–455 K. ^{1}H NMR (DMSO-d$_6$, p.p.m.): δ 7.19–7.21 (d, 4H, PhH, ^{3}J = 8.32 Hz), 7.38–7.40 (d, 4H, PhH, ^{3}J = 8.32 Hz), 3.10 (s, 4H, Ph—CH$_2$). ^{13}C$\{^1$H$\}$ NMR (DMSO-d$_6$, p.p.m.): δ 50.8 (–CH$_2$), 118.1, 139.9, 132.1, 139.4 (Ph—C).

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Experimental details

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

Comment

Interest in diorganotin dihalido molecules similar to the title compound [6, 7] relate to the ability of the diorganotin centre to increase its coordination number *via* intra- and intermolecular Sn···X secondary [8] interactions. Besides structural consequences, the formation of intramolecular Sn···X interactions has implications for the stability and function of organotin species investigated as potential anti-tumour agents [9].

The molecule is illustrated in the figure (70% displacement ellipsoids; unlabelled atoms are related by the symmetry operation (i) 1/2 − x, y, 1 − z). The title complex has crystallographic two-fold symmetry with the tin atom lying on the two-fold axis. The tin atom is tetrahedrally coordinated by two bromido atoms [Sn—Br1 = 2.5143(2) Å] and two methylene-carbon ligands [2.166(2) Å] derived from the 4-bromobenzyl substituents. The resulting Br_2C_2 donor set exhibits significant deviations from the regular tetrahedral geometry with the angles correlating with steric effects. Thus, the narrowest angle of 99.125(12)° is subtended by the bromido atoms and the widest angle of 136.70(12)° by the methylene-carbon atoms. From symmetry, the phenyl rings are orientated towards the same side of the molecule but, are splayed as seen in the dihedral angle between them of 88.7(5)°.

In the molecular packing, a three-dimensional architecture is sustained by a combination of side-on C—Br···π, secondary Sn···Br interactions and Br···Br halogen bonding. Globally, molecules assemble into columns parallel to the *b*-axis, with connections between them being of the type C—Br···π [C5—Br2···Cg(C2—C7)$^{\mathrm{ii}}$: Br2···Cg(C2—C7)$^{\mathrm{ii}}$ = 3.5754(10) Å with angle at Br2 = 92.65(7)° for symmetry operation (ii) x, 1 + y, z] and Sn···Br [Sn···Br$^{\mathrm{ii}}$ = 3.8464(3) Å]. Interactions between columns to form layers in the *ab*-plane involve the coordinated bromido ligands [Br1···Br1$^{\mathrm{iii}}$ = 3.5414(4) Å for (iii): 1 − x, 1 − y, 1 − z]. The layers are connected along the *c*-axis by bromo···bromo interactions [Br2···Br2$^{\mathrm{iv}}$ = 3.5761(4) Å for (iv): 1 − x, −1/2 + y, 1/2 − z].

The crystal structure of the isostructural all-chloro derivative of the title compound is known [10]. The Cl—Sn—Cl and C—Sn—C angles in the literature known compound are 98.68(3) and 136.15(12)°, respectively, both marginally smaller than in the present structure.

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