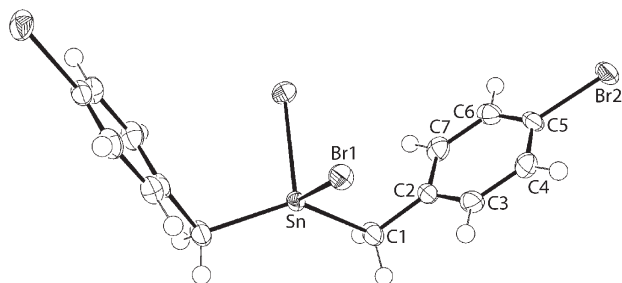


See Mun Lee, Kong Mun Lo and Edward R.T. Tiekink*

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, $\beta = 94.507(1)^\circ$, $V = 1638.71(5)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0142$, $wR_{ref}(F^2) = 0.0358$, $T = 100$ 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.

Source of material

The melting point (uncorrected) was measured on an Mel-Temp II melting point apparatus. ¹H and ¹³C NMR spectra were recorded in DMSO-d₆ 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

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.07 × 0.03 × 0.02 mm
Wavelength:	Cu Kα 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 (Å²).

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*

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. ¹H NMR (DMSO-d₆, p.p.m.): δ 7.19–7.21 (d, 4H, PhH, ³J = 8.32 Hz), 7.38–7.40 (d, 4H, PhH, ³J = 8.32 Hz), 3.10 (s, 4H, Ph–CH₂). ¹³C{¹H} NMR (DMSO-d₆, p.p.m.): δ 50.8 (–CH₂), 118.1, 139.9, 132.1, 139.4 (Ph–C).

*Corresponding author: Edward R.T. Tiekink, Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia, e-mail: edwardt@sunway.edu.my, Edward.Tiekink@gmail.com. <https://orcid.org/0000-0003-1401-1520>

See Mun Lee and Kong Mun Lo: Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia

Experimental details

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

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 Br₂C₂ 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)ⁱⁱ: Br2···Cg(C2–C7)ⁱⁱ = 3.5754(10) Å with angle at Br2 = 92.65(7)° for symmetry operation (ii) $x, 1 + y, z$] and Sn···Br [Sn···Brⁱⁱ = 3.8464(3) Å]. Interactions between columns to form layers in the *ab*-plane involve the coordinated bromido ligands [Br1···Br1ⁱⁱⁱ = 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^{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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