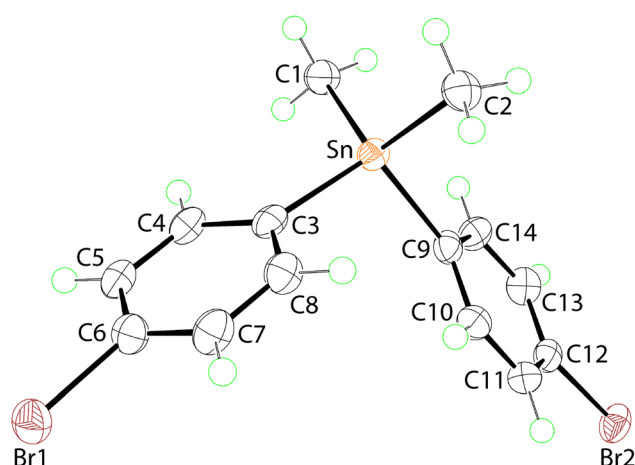


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Crystal structure of dimethyl-bis(4-bromophenyl- κC^1)tin(IV), $C_{14}H_{14}Br_2Sn$



<https://doi.org/10.1515/ncrs-2021-0287>

Received July 15, 2021; accepted July 29, 2021;

published online August 13, 2021

Abstract

$C_{14}H_{14}Br_2Sn$, monoclinic, $P2_1/c$ (no. 14), $a = 12.9848(2)$ Å, $b = 18.9911(2)$ Å, $c = 6.0550(1)$ Å, $\beta = 99.136(1)^\circ$, $V = 1474.19(4)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0193$, $wR_{ref}(F^2) = 0.0490$, $T = 100$ K.

CCDC no.: 2100051

The molecular structure 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

A solution of 1,4-dibromobenzene (Sigma, 23.6 g, 0.1 mol) in dry ether (50 mL) was added dropwise to magnesium turnings (Merck, 2.4 g, 0.1 mol) suspended in dry ether (150 mL)

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Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.08 × 0.07 × 0.04 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	19.9 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max} , completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	18,097, 2634, 0.036
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 2553
$N(param)_{refined}$:	156
Programs:	CRYSA LIS ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

in a three necked flask equipped with a reflux condenser, a nitrogen supply source and a dropping funnel filled with the 1,4-dibromobenzene solution. After the addition was complete, the reaction mixture was refluxed with stirring for 2 h. This was followed by the addition of dimethyltin dichloride (Merck, 11 g, 0.05 mol). The reaction mixture was subsequently refluxed for 2 h. This was followed by hydrolysis with 20% aqueous ammonium chloride solution (200 mL). The organic layer was separated, washed with distilled water and dried over molecular sieves. The solution was then filtered and concentrated to obtain a white crystalline solid. The precipitate was recrystallised from chloroform and colourless crystals were obtained from the slow evaporation of the solvent. Yield: 8.05 g (34.9%). **M.pt** (Stuart SMP30 digital melting point apparatus; uncorrected): 524–526 K (dec). **IR** (Bruker Vertex 70v FTIR Spectrometer; cm⁻¹): 2930 (s) $\nu(C-H)$, 1495 (m) $\nu(C=C)$. **¹H NMR** (Bruker Ascend 400 MHz NMR spectrometer; CDCl₃; ppm relative to Me₄Si): δ 0.98 (s, 6H, CH₃), 7.13–7.59 (m, 8H, Ph–H). **¹³C{¹H} NMR** (as for ¹H NMR): 11.4 (CH₃), 115.3, 123.7, 129.7, 137.5 (Ph–C).

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–0.98 Å) and refined as riding with $U_{iso}(H) = 1.2–1.5U_{eq}(C)$.

Comment

The title compound, Me₂Sn(C₆H₄Br-4)₂, hereafter (I), is only the third crystal structure containing the

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

Atom	x	y	z	U_{iso}^*/U_{eq}
C1	0.2838 (2)	0.68751 (14)	1.1539 (4)	0.0220 (5)
H1A	0.266085	0.731926	1.074459	0.033*
H1B	0.350087	0.692791	1.255230	0.033*
H1C	0.228649	0.675204	1.240375	0.033*
C2	0.3176 (2)	0.50108 (14)	1.0459 (4)	0.0224 (6)
H2A	0.389460	0.494796	1.121796	0.034*
H2B	0.302950	0.467407	0.922266	0.034*
H2C	0.269316	0.492960	1.152390	0.034*
C3	0.1665 (2)	0.60827 (13)	0.6553 (4)	0.0184 (5)
C4	0.1014 (2)	0.66750 (14)	0.6205 (4)	0.0198 (5)
H4	0.111032	0.704779	0.726430	0.024*
C5	0.0234 (2)	0.67328 (14)	0.4358 (4)	0.0202 (5)
H5	-0.019947	0.713827	0.415086	0.024*
C6	0.0100 (2)	0.61841 (15)	0.2822 (5)	0.0212 (5)
C7	0.0699 (2)	0.55801 (15)	0.3137 (5)	0.0238 (6)
H7	0.058335	0.520313	0.209580	0.029*
C8	0.1474 (2)	0.55325 (14)	0.5004 (4)	0.0218 (5)
H8	0.188339	0.511650	0.523196	0.026*
C9	0.4346 (2)	0.62597 (13)	0.7692 (4)	0.0181 (5)
C10	0.4484 (2)	0.59212 (15)	0.5693 (4)	0.0209 (5)
H10	0.394178	0.562922	0.495495	0.025*
C11	0.5388 (2)	0.60013 (14)	0.4767 (4)	0.0212 (6)
H11	0.546345	0.577355	0.340460	0.025*
C12	0.6178 (2)	0.64204 (14)	0.5872 (4)	0.0193 (5)
C13	0.6081 (2)	0.67698 (14)	0.7842 (5)	0.0225 (6)
H13	0.662918	0.705789	0.857312	0.027*
C14	0.5159 (2)	0.66877 (14)	0.8719 (4)	0.0208 (5)
H14	0.508060	0.692980	1.005534	0.025*
Br1	-0.09056 (2)	0.62811 (2)	0.01873 (5)	0.02498 (8)
Br2	0.74478 (2)	0.64959 (2)	0.46927 (5)	0.02530 (9)
Sn	0.29792 (2)	0.60609 (2)	0.91768 (3)	0.01673 (7)

Sn(C₆H₄Br-4) fragment, the others being Sn(C₆H₄Br-4)₄ [5] and the anion in the salt [4-Me₂NC₅H₄NH][Me₂SnBr₂(C₆H₄Br-4)] [6]. The structure determination of (I) was undertaken as part of recent and on-going investigations of related 4-halophenyltin species [7, 8].

The molecular structure of (I) is shown in the Figure (70% displacement ellipsoids). The molecule lacks symmetry with the tin atom within a C₄ donor set defined by two methyl-C and two phenyl-C atoms. The range of angles subtended at the tin atom is a low 104.88(10)°, for C2–Sn–C9, to a wide 116.74(10)°, for C1–Sn–C2, consistent with a distorted tetrahedral geometry for the tin atom. The Sn–C bond lengths are indistinguishable, ranging from 2.134(3) Å, for Sn–C1, to 2.147(3) Å, for Sn–C9. The dihedral angle between the phenyl rings is 68.47(12)°.

In the crystal, molecules assemble largely devoid of directional interactions according to an analysis based

on PLATON [9]. Thus, methyl-C–H···π(C₆H₄Br) contacts [C1–H1c···Cg(C3–C8)]ⁱ: H1c···Cg(C3–C8)ⁱ = 2.74 Å with angle at H1c = 168° and C2–H2a···Cg(C9–C14)]ⁱⁱ: H2a···Cg(C9–C14)]ⁱⁱ = 2.87 Å with angle at H2a = 125° for symmetry operations (i): x, y, 1 + z and (ii): 1 – x, 1 – y, 2 – z] are apparent and occur between molecules arranged in a zig-zag chain aligned along the c-axis. The most prominent contacts between chains are type II [10] Br···Br halogen bonding interactions [Br1···Br2]ⁱⁱⁱ = 3.6807(4) Å cf. the sum of the van der Waals radii = 3.70 Å [9]; C6–Br1···Br2]ⁱⁱⁱ = 172.36(9)° and C12]ⁱⁱⁱ–Br2]ⁱⁱⁱ···Br1 = 93.79(7)° for (iii) –1 + x, y, –1 + z]. Additional Br···Br contacts are noted, at separations just greater than the sum of the van der Waals radii [Br1···Br2]^{iv} = 3.7459(4) Å for (iv): –1 + x, y, z].

Additional information on the molecular packing was obtained through an analysis of all surface contacts in the crystal of (I). This was accomplished by the calculation of the Hirshfeld surfaces and two-dimensional fingerprint plots (full and decomposed into individual contacts) using Crystal Explorer 17 [11] and literature protocols [12]. The Hirshfeld surface analysis indicated the dominance of hydrogen in the surface contacts, namely H···H [39.9%], Br···H/H···Br [26.8%] and C···H/H···C [26.2%]. The next most significant contacts are due to Br···Br [3.5%] and Br···C/C···Br [3.1%] contacts with a minor contribution from C···C [0.4%] contacts.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: Crystallographic research at Sunway University is supported by Sunway University Sdn Bhd (Grant No. GRTIN-IRG-08-2021).

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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