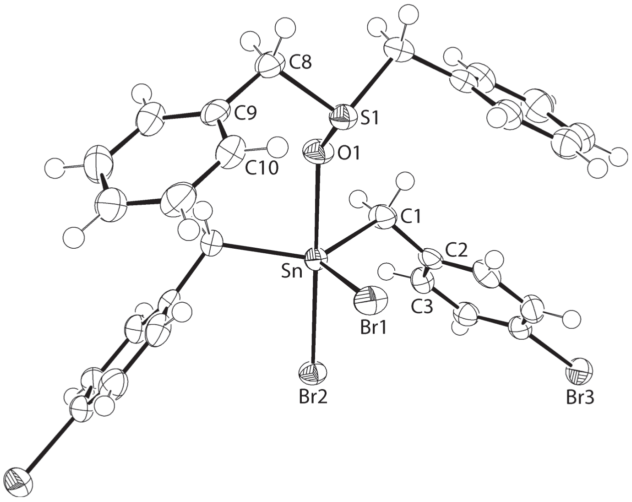
Z. Kristallogr. NCS 2020; 235(1): 139–141

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

Crystal structure of (dibenzyl sulphoxide-κ*O*) dibromido-bis(4-bromobenzyl-κ*C*)tin(IV), $C_{28}H_{26}Br_4OSSn$



https://doi.org/10.1515/ncrs-2019-0541
Received July 29, 2019; accepted August 25, 2019; available online September 9, 2019

Abstract

$C_{28}H_{26}Br_4OSSn$, monoclinic, *Cm* (no. 8), $a = 8.4055(1)$ Å, $b = 26.9988(3)$ Å, $c = 6.4207(1)$ Å, $\beta = 98.164(1)°$, $V = 1442.34(3)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0174$, $wR_{ref}(F^2) = 0.0454$, $T = 100(2)$ K.

CCDC no.: 1949173

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

The melting point of the compound was measured on a Electrothermal digital melting point apparatus and was uncorrected. The elemental analysis was performed on a Perkin-Elmer EA2400 CHN analyser. The IR spectrum was recorded using a Perkin-Elmer RX1 spectrophotometer as a Nujol mull between KBr plates from 4000 to 400 cm^{-1}. The ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded in $CDCl_3$ solution on a Bruker AVN FT-NMR 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane.

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	$0.13 \times 0.07 \times 0.03$ mm
Wavelength:	Cu *Kα* radiation (1.54184 Å)
μ:	14.4 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	67.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	17692, 2510, 0.040
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2498
$N(param)_{refined}$:	166
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Di(4-bromobenzyl)tin dibromide was synthesized by the direct reaction of 4-bromobenzyl bromide (Merck) and metallic tin powder (Merck) in toluene according to a literature procedure [5]. Di(4-bromobenzyl)tin dibromide (0.62 g, 1 mmol) and dibenzyl sulfoxide (Aldrich, 0.23 g, 1.0 mmol) were dissolved in chloroform (25 mL) and the mixture was refluxed for 2 h. After filtration, the filtrate was evaporated slowly until colourless crystals were formed. The crystals were filtered, washed with minimum amount of hexane and air-dried. Yield: 0.34 g (40.1%). **M.pt**: 418–420 K. **Anal. Calc.** for $C_{28}H_{26}Br_4OSSn$: C 39.62; H 3.09%. Found: C 39.10; H 2.81%. **IR** (cm^{-1}) 980 (m) ν(S—O), 501 (w) ν(Sn—O). **^{1}H NMR** ($CDCl_3$, ppm): δ 3.11 (m, 4H, CH_2), 3.92 (s, 4H, SCH_2), 6.83–7.18 (m, 8H, BrPh-H), 7.28–7.40 (m, 10H, Ph-H). **^{13}C{^{1}H} NMR** ($CDCl_3$, ppm): 35.4 (CH_2), 56.2 (SCH_2), 119.7, 128.4, 128.8, 121.2, 129.8, 130.2, 131.8, 135.1 (Ph-H).

Experimental details

The H atoms were geometrically placed (C—H = 0.95–0.99 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$. The absolute structure was determined based on differences in Friedel pairs.

***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. 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

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

Atom	*x*	*y*	*z*	$U_{\text{iso}}{*}/U_{\text{eq}}$
Sn	0.46363(3)	0.5000	0.38467(4)	0.01593(10)
Br1	0.41540(7)	0.5000	0.76184(9)	0.02340(15)
Br2	0.15628(7)	0.5000	0.24379(8)	0.01954(14)
Br3	0.02290(6)	0.25850(2)	0.21959(8)	0.02924(13)
S1	0.84061(18)	0.5000	0.7253(2)	0.0188(3)
O1	0.7397(5)	0.5000	0.5078(7)	0.0225(9)
C1	0.5227(5)	0.42751(15)	0.2760(7)	0.0214(9)
H1A	0.5540	0.4312	0.1339	0.026*
H1B	0.6183	0.4153	0.3699	0.026*
C2	0.3954(5)	0.38851(14)	0.2647(7)	0.0185(8)
C3	0.3060(6)	0.37553(15)	0.0714(7)	0.0207(8)
H3	0.3216	0.3932	−0.0521	0.025*
C4	0.1948(5)	0.33718(15)	0.0582(7)	0.0213(9)
H4	0.1351	0.3283	−0.0734	0.026*
C5	0.1723(5)	0.31206(15)	0.2396(7)	0.0218(9)
C6	0.2572(6)	0.32443(16)	0.4326(7)	0.0245(9)
H6	0.2401	0.3070	0.5559	0.029*
C7	0.3677(6)	0.36280(16)	0.4433(7)	0.0235(9)
H7	0.4258	0.3717	0.5758	0.028*
C8	0.9797(5)	0.55141(17)	0.7211(7)	0.0207(9)
H8A	1.0687	0.5483	0.8391	0.025*
H8B	1.0260	0.5512	0.5876	0.025*
C9	0.8897(5)	0.59888(15)	0.7409(7)	0.0202(8)
C10	0.8210(6)	0.60822(17)	0.9231(7)	0.0237(9)
H10	0.8320	0.5846	1.0339	0.028*
C11	0.7373(6)	0.65153(18)	0.9427(8)	0.0282(10)
H11	0.6894	0.6575	1.0658	0.034*
C12	0.7232(6)	0.68634(18)	0.7826(9)	0.0298(10)
H12	0.6664	0.7163	0.7969	0.036*
C13	0.7912(7)	0.67772(17)	0.6023(8)	0.0292(10)
H13	0.7811	0.7016	0.4925	0.035*
C14	0.8747(6)	0.63376(17)	0.5826(7)	0.0242(9)
H14	0.9218	0.6278	0.4589	0.029*

Comment

Recently, the X-ray crystal structure determination of (4-bromobenzyl)$_2$SnBr$_2$, the organotin precursor in the title compound, (4-bromobenzyl)$_2$SnBr$_2$[O= S(benzyl)$_2$], hereafter (I), became available [6]. In continuation of structural studies of diorgano sulphoxide adducts of organotin derivatives [7, 8], compound (I), was investigated by X-ray crystallography.

The molecular structure of (I) is shown in the figure (70% displacement ellipsoids; unlabelled residues are related by the symmetry operation (i) x, 1 − y, z) and has crystallographic mirror symmetry with the Sn, Br1, Br2, S1 and O1 atoms lying on the mirror plane. The molecule features a penta-coordinated tin centre within a C$_2$Br$_2$O donor set defined by two methylene-carbon, two bromide and sulphoxide-oxygen atoms. The coordination geometry approximates a trigonal-bipyramid with the axial positions occupied by the Br2 and O1 atoms [Br2—Sn—O1 = 179.47(10)°]. This description is quantified in the value of $\tau = 0.82$, compared to $\tau = 1.0$ for an ideal trigonal-bipyramid as opposed to $\tau = 0.0$ for an ideal square-pyramid [9, 10]. There are systematic differences in the magnitudes of the Sn—Br bond lengths relating to their positions in the coordination polyhedron. The axially-bound Br2 atom forms a longer bond [2.6131(7) Å] compared with the equatorially-bound Br1 atom [2.5115(6) Å]. Compared with the Sn—Br bond length [2.5143(2) Å] obtained for 2-fold symmetric (4-bromobenzyl)$_2$SnBr$_2$ [6], only the Sn—Br2 bond length has elongated despite the increase in the coordination number about the tin atom. The sulphoxide-benzyl rings are folded to be disposed over the bromobenzyl rings with the closest intramolecular contact between the residues being a bromobenzyl-methylene-C—H···C(benzyl-phenyl) contact [C1—-H1b···C14$^{\text{i}}$ = 2.74 Å].

There are four notable points of contact between residues in the molecular packing of (I). Thus, a benzyl-C—H···Br(tin-bound) contact [C8—H8a···Br2$^{\text{ii}}$: H8a···Br2$^{\text{ii}}$ = 2.91 Å, C8···Br2$^{\text{ii}}$ = 3.739(4) Å with angle at H8a = 142° for (ii) 1 + x, y, 1 + z] link molecules into a linear, supramolecular chain along [1 0 1]; from symmetry, each molecule participates in four such contacts. Weak bromobenzyl-phenyl-C—H···π(benzyl-phenyl) contacts [C4—H4···Cg(C9–C14)$^{\text{iii}}$: H4···Cg(C9–C14)$^{\text{iii}}$ = 2.92 Å, C4···Cg(C9–C14)$^{\text{iii}}$ = 3.579(5) Å with angle at H4 = 127° for (iii) −1 + x, 1 − y, −1 + z] contribute to the stability of the chain. The connections between the chains are of the type end-on, bromobenzyl-C—Br···π(benzyl) [C5—Br3···Cg(C2–C7)$^{\text{iv}}$: Br3···Cg(C2—C7)$^{\text{iv}}$ = 3.5846(18) Å, C5···Cg(C2—C7)$^{\text{iv}}$ = 5.477(4) Å with angle at Br3 = 171.00(14)° (iv) −1/2 + x, 1/2 − y, z] and, again, there are four such contacts per molecule, so a three-dimensional architecture ensues. The fourth point of contact between atoms is a secondary Sn···Br interaction [Sn···Br1$^{\text{v}}$ = 3.9618(6) Å compared with the sum of the van der Waals radii = 4.02° for (v) x, y, −1 + z] known to be important in crystals of main group elements [11, 12].

A further analysis of the molecular packing was conducted by calculating the Hirshfeld surfaces along with the two-dimensional fingerprint plots (overall and decomposed into individual contacts types) to determine the major types of contacts contributing to the surface. This was performed with Crystal Explorer 17 [13] in accord with established procedures [14]. There are four prominent contributions to the Hirshfeld surface that account for over 97% of all contacts. These are H···H [42.4%], Br···H/H···Br [32.5%], C···H/H···C [15.4%] and Br···C/C···Br [6.8%]. The aforementioned Sn···Br secondary bonding interaction contributes a mere 0.1% to the overall surface.

Acknowledgements: Sunway University Sdn Bhd is thanked for financial support of this work through Grant no. STR-RCTR-RCCM-001-2019.

References

1. Rigaku Oxford Diffraction: CrysAlis^{PRO}. Rigaku Corporation, Oxford, UK (2018).
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. Acta Crystallogr. **C71** (2015) 3–8.
4. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. J. Appl. Crystallogr. **45** (2012) 849–854.
5. Sisido, K.; Takeda, Y.; Kinugawa, Z.: Direct synthesis of organotin compounds I. di- and tribenzyltin chlorides. J. Am. Chem. Soc. **83** (1961) 538–541.
6. Lee, S. M.; Lo, K. M.; Tiekink, E. R. T.: Crystal structure of dibromidobis(4-bromobenzyl)tin(IV), $C_{14}H_{12}Br_4Sn$. Z. Kristallogr. NCS **234** (2019) 947–948.
7. Amin, N. A. B. M.; Hussen, R. S. D.; Lee, S. M.; Halcovitch, N. R.; Jotani, M. M.; Tiekink, E. R. T.: *trans*-Di-chlorido-bis(dimethyl sulfoxide-κ*O*)bis(4-fluorobenzyl-κC^1)-tin(IV): crystal structure and Hirshfeld surface analysis. Acta Crystallogr. **E73** (2017) 667–672.
8. Lee, S. M.; Lo, K. M.; Tiekink, E. R. T.: Crystal structure of (dibenzyl sulphoxide-κ*O*)bis(2-chlorobenzyl-κC^1)-dichloridotin(IV), $C_{28}H_{26}Cl_4OSSn$. Z. Kristallogr. NCS **234** (2019) 787–789.
9. 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.
10. Mejia-Rivera, F. J.; Alvarado-Rodríguez, J. G.; Andrade-López, N.; Cruz-Borbolla, J.; Jancik, V.: Intramolecular interactions Sn–*D* in organotin heterocyclic compounds $[\{D(C_6H_4CH_2)\}SnBr_2]$. Inorg. Chem. Commun. **97** (2018) 44–48.
11. Alcock, N. W.: Secondary bonding to nonmetallic elements. Adv. Inorg. Chem. Radiochem. **15** (1972) 1–58.
12. Tiekink, E. R. T.: Supramolecular assembly based on “emerging” intermolecular interactions of particular interest to coordination chemists. Coord. Chem. Rev. **345** (2017) 209–228.
13. Turner, M. J.; McKinnon, J. J.; Wolff, S. K.; Grimwood, D. J.; Spackman, P. R.; Jayatilaka, D.; Spackman, M. A.: Crystal Explorer v17. The University of Western Australia, Australia (2017).
14. Tan, S. L.; Jotani, M. M.; Tiekink, E. R. T.: Utilizing Hirshfeld surface calculations, non-covalent interaction (NCI) plots and the calculation of interaction energies in the analysis of molecular packing. Acta Crystallogr. **E75** (2019) 308–318.