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

Crystal structure of (2,2'-bipyridyl)bis(4-bromobenzyl)dibromidotin(IV), $C_{24}H_{20}Br_4N_2Sn$

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.22 × 0.12 × 0.07 mm
Wavelength:	Cu K α radiation (1.54178 Å)
μ :	15.7 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω
$\theta_{\max}$, completeness:	67.1°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	30929, 4485, 0.044
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4381
$N(\text{param})_{\text{refined}}$:	280
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

the atoms including atomic coordinates and displacement parameters.

Source of material

The melting point of the compound was measured on a Melt-Temp II digital melting point apparatus and was uncorrected. The IR spectrum was measured on a Bruker Vertex 70v FTIR spectrophotometer from 4000 to 400 cm⁻¹. The ¹H and ¹³C{¹H} NMR spectra were recorded in CDCl₃ solution on a Bruker Ascend 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane.

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, 1.0 mmol) and 2,2'-bipyridine (Aldrich, 0.16 g, 1.0 mmol) were heated in 95% ethanol (30 mL) and stirred for 2 h. After filtration, the filtrate was evaporated slowly until colourless crystals were formed. Yield: 0.42 g (54.2%). **M.pt:** 465–467 K. IR (cm⁻¹) 1586 (m) $\nu(\text{CN})$, 1482, 1097 (s) $\nu(\text{CN})$, 467 (m) $\nu(\text{SnN})$. **¹H NMR** (DMSO-d₆, ppm): δ 3.10 (s, 2H, Ph-CH₂), 7.18–7.32 (m, 2H, Ph-H), 7.49–7.60 (m, 2H, Ph-H), 7.77–7.87 (m, 1H, bipy-H), 8.09–8.13 (m, 1H, bipy-H), 8.45–8.48 (d, 1H, bipy-H), 8.76–8.80 (m, 1H, bipy-H). **¹³C{¹H} NMR** (DMSO-d₆, ppm): δ 71.1 (CH₂), 118.1, 125.5, 130.8, 132.1 (Ph-C), 121.8, 126.0, 139.3, 149.0, 153.7 (bipy-C).

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–0.99 Å) and refined as riding with

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Abstract

$C_{24}H_{20}Br_4N_2Sn$, monoclinic, $P2_1/n$ (no. 14), $a = 9.3186(1)$ Å, $b = 16.2615(1)$ Å, $c = 16.8482(1)$ Å, $\beta = 100.748(1)^\circ$, $V = 2508.29(4)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0254$, $wR_{\text{ref}}(F^2) = 0.0688$, $T = 100(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of

*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 (Å²).

Atom	x	y	z	U_{iso}^*/U_{eq}
Sn	0.90693(2)	0.80694(2)	0.46094(2)	0.01015(8)
Br1	0.80742(3)	0.85195(2)	0.59351(2)	0.02153(10)
Br2	1.18629(3)	0.86061(2)	0.49199(2)	0.01685(9)
Br3	0.61849(3)	0.38481(2)	0.40064(2)	0.02523(10)
Br4	0.19446(3)	0.94430(2)	0.24467(2)	0.02203(10)
N1	0.9227(3)	0.74801(15)	0.33496(13)	0.0146(5)
N2	0.6826(2)	0.74562(16)	0.40155(14)	0.0140(5)
C1	0.9890(3)	0.69134(17)	0.51694(17)	0.0149(6)
H1A	1.0881	0.6821	0.5054	0.018*
H1B	0.9988	0.6973	0.5762	0.018*
C2	0.8997(3)	0.61702(18)	0.49149(17)	0.0150(6)
C3	0.9281(3)	0.56959(19)	0.42624(17)	0.0159(6)
H3	1.0061	0.5846	0.4001	0.019*
C4	0.8437(3)	0.50124(19)	0.39961(17)	0.0180(6)
H4	0.8628	0.4698	0.3552	0.022*
C5	0.7319(3)	0.47960(19)	0.43854(17)	0.0168(6)
C6	0.7023(3)	0.5238(2)	0.50419(18)	0.0183(6)
H6	0.6266	0.5070	0.5314	0.022*
C7	0.7855(3)	0.59280(19)	0.52899(17)	0.0165(6)
H7	0.7641	0.6245	0.5727	0.020*
C8	0.8480(3)	0.92369(18)	0.40082(17)	0.0150(6)
H8A	0.8728	0.9687	0.4406	0.018*
H8B	0.9072	0.9315	0.3584	0.018*
C9	0.6906(3)	0.93006(18)	0.36335(16)	0.0145(6)
C10	0.6383(3)	0.8981(2)	0.28615(16)	0.0184(6)
H10	0.7053	0.8741	0.2568	0.022*
C11	0.4920(3)	0.9006(2)	0.25182(17)	0.0189(6)
H11	0.4580	0.8774	0.2000	0.023*
C12	0.3950(3)	0.93752(18)	0.29436(17)	0.0157(6)
C13	0.4414(3)	0.96956(19)	0.37062(17)	0.0154(6)
H13	0.3738	0.9940	0.3993	0.019*
C14	0.5893(3)	0.96530(18)	0.40475(16)	0.0157(6)
H14	0.6221	0.9869	0.4574	0.019*
C15	1.0446(3)	0.7537(2)	0.30375(17)	0.0176(6)
H15	1.1252	0.7836	0.3328	0.021*
C16	1.0580(4)	0.7177(2)	0.23069(18)	0.0218(7)
H16	1.1453	0.7231	0.2097	0.026*
C17	0.9406(4)	0.6738(2)	0.18967(18)	0.0256(7)
H17	0.9468	0.6479	0.1399	0.031*
C18	0.8142(4)	0.6674(2)	0.22070(18)	0.0221(7)
H18	0.7324	0.6381	0.1922	0.026*
C19	0.8080(3)	0.70469(19)	0.29462(17)	0.0165(6)
C20	0.6776(3)	0.70164(18)	0.33275(17)	0.0156(6)
C21	0.5517(3)	0.6578(2)	0.2992(2)	0.0237(7)
H21	0.5494	0.6259	0.2518	0.028*
C22	0.4306(4)	0.6614(2)	0.3357(2)	0.0282(8)
H22	0.3447	0.6316	0.3138	0.034*
C23	0.4354(3)	0.7086(2)	0.4040(2)	0.0251(7)
H23	0.3523	0.7130	0.4289	0.030*
C24	0.5634(3)	0.74942(19)	0.43552(17)	0.0174(6)
H24	0.5672	0.7814	0.4831	0.021*

$U_{iso}(H) = 1.2U_{eq}(C)$. The maximum and minimum residual electron density peaks of 0.90 and 1.11 eÅ⁻³, respectively, were located 1.07 and 0.98 Å from the Sn atom, respectively.

Comment

Very recently, the crystal and molecular structures of the organotin precursor, (4-BrC₆H₄CH₂)₂SnBr₂, featured in the title compound, (4-BrC₆H₄)₂SnBr₂(2,2'-bipyridyl), was described [6]. By contrast to the approximately 50 analogous structures of bipyridyl-type (NN) ligands with R₂SnCl₂, there are only three species of the general formula R₂SnBr₂(NN) reported, namely R = Me, NN = 4,4'-bis(but-3-en-1-yl)-2,2'-bipyridine [7], R = CF₂CF₃, NN = 1,10-phenanthroline [8] and R = 3-BrC₆H₄CH₂, NN = 4,7-diphenyl-1,10-phenanthroline [9]. Given this paucity of data for R₂SnBr₂(NN), the title compound was synthesised and characterised crystallographically.

The molecule is illustrated in the figure (70% displacement ellipsoids) and features a distorted octahedral geometry for the tin atom based on two carbon atoms of the substituted benzyl groups, two bromide atoms and two nitrogen atoms of the 2,2'-bipyridyl molecule. In the Br₂C₂N₂ donor set, the benzyl-carbon atoms are mutually trans, and each of the bromide atoms is trans to a pyridyl-nitrogen atom. While there is a definite disparity in the Sn—Br bond lengths [Sn—Br1 = 2.6752(3) Å and Sn—Br2 = 2.7027(3) Å], the Sn—N bond lengths [Sn—N1 = 2.358(2) Å and Sn—N2 = 2.363(2) Å] are equal within experimental error. Non-systematic variations in geometric parameters in related organotin compounds of bipyridyl-type ligands were shown by DFT calculations to be the result of molecular packing considerations rather than having any chemical significance [10, 11]. The major distortions from the ideal octahedral geometry in the cis angles is seen in the N1—Sn—N2 chelate angle of 69.27(8)°, and in terms of trans angles, in the N1—Sn—Br1 angle of 162.19(6)°. Globally, the phenyl rings of the benzyl substituents are folded over the molecule to be orientated towards the 2,2'-bipyridyl molecule. This is reflected in close inter-centroid ring separations of 3.5663(17) Å between the chelate and C2-phenyl rings, and 3.6720(17) Å between the N2-pyridyl and C9-phenyl rings. The importance of stabilising interactions between chelate and organic rings is now well documented [12, 13], at least in the context of intermolecular interactions.

As mentioned above, the structure of (4-BrC₆H₄CH₂)₂SnBr₂ became available recently [6]. The molecule has crystallographic two-fold symmetry with the tetrahedrally coordinated tin atom lying on the axis. The Sn—Br bond distances are each 2.5143(2) Å, that is, considerably shorter than those in the title compound, reflecting the influence of the increased coordination number at the tin atom in the title structure. Such a trend was not as pronounced in the recently described structure of the sulphoxide adduct, (4-BrC₆H₄CH₂)₂SnBr₂(O=S(CH₂Ph)₂) [14], where only one of the Sn—Br bond lengths elongated significantly, i.e.

the axially-bound bromide atom in a trigonal-bipyramidal geometry.

The three-dimensional molecular packing is sustained by weak non-covalent interactions. Thus, supramolecular layers parallel to $(1\ 0\ -1)$ are constructed by $\pi \cdots \pi$ interactions between centrosymmetrically-related C2-phenyl rings $[Cg(C2-C7) \cdots Cg(C2-C7)^i = 3.7569(17)^\circ$ for symmetry operation (i) $2-x, 1-y, 1-z]$ and end-on $C-Br \cdots \pi(N2\text{-pyridyl})$ interactions $[C5-Br3 \cdots Cg(N2, C20-C24)^{ii}; Br3 \cdots Cg(N2, C20-C24)^{ii} = 3.9096(13)\text{ \AA}, C5 \cdots Cg(N2, C20-C24)^{ii} = 5.563(3)\text{ \AA}$ with angle at $Br3 = 143.56(9)^\circ$ for (ii) $3/2-x, -1/2+y, 1/2-z]$. The connections between layers are of the type $C-H \cdots Br$ $[C16-H16 \cdots Br1^{iii}; = H16 \cdots Br1^{iii} = 2.95\text{ \AA}, C16 \cdots Br1^{iii} = 3.746(4)\text{ \AA}$ with angle at $H16 = 142^\circ$ for (iii) $1/2+x, 3/2-y, -1/2+z]$ and phenyl- $Br \cdots Br$ (phenyl) $[Br3 \cdots Br4^{iv} = 3.5737(4)\text{ \AA}$ for (iv) $1/2-x, -1/2+y, 1/2-z]$. The importance of halogen bonding in crystals has been reviewed recently [15].

To evaluate the molecular packing further and to compare this to the structure of the all-chloro analogue $(4-ClC_6H_4)_2SnCl_2(2,2'\text{-bipyridyl})$ [16], Crystal Explorer 17 [17] was employed following established protocols [18] to calculate the Hirshfeld surfaces as well as the two-dimensional fingerprint plots (full and delineated into individual contacts). Nearly equal contributions to the calculated Hirshfeld surface are provided by $H \cdots H$ [40.2%] and $H \cdots Br/Br \cdots H$ [40.8%] contacts. The next most significant contributions are due to $H \cdots C/C \cdots H$ [11.1%] and then fall away to $Br \cdots C/C \cdots Br$ [3.1%], $Br \cdots Br$ [2.3%] and $C \cdots C$ [1.9%]. When compared to the all-chloro derivative [16], the $H \cdots H$ [42.3%] and $H \cdots Cl/Cl \cdots H$ [38.7%] contacts, respectively, increase and decrease by approximately the same extent. The contribution of contacts between halogen(Cl) and C atoms is reduced [2.0%], but the percentage contribution of the other identified contacts remain about the same.

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