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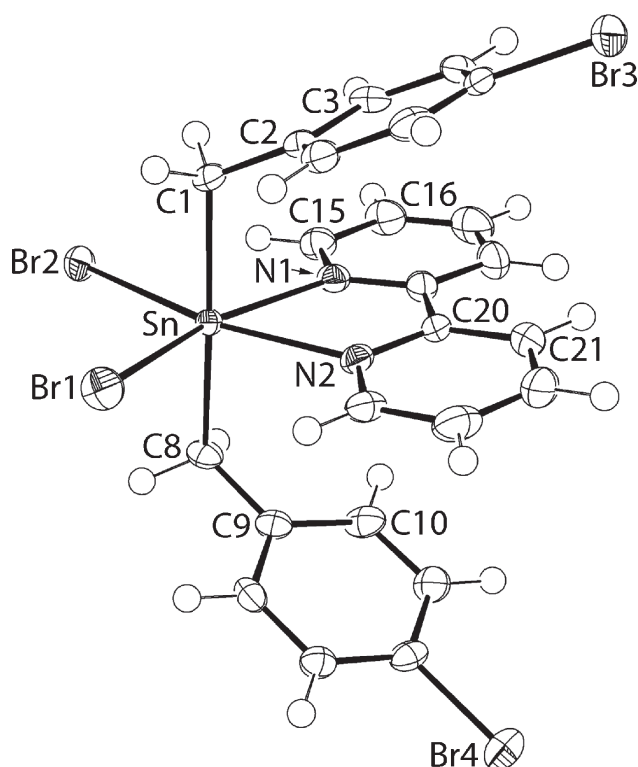# Crystal structure of (2,2′-bipyridyl)bis(4-bromobenzyl)dibromidotin(IV), $C_{24}H_{20}Br_4N_2Sn$

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, $\beta = 100.748(1)°$, $V = 2508.29(4)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0254$, $wR_{ref}(F^2) = 0.0688$, $T = 100(2)$ 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

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Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	$0.22 \times 0.12 \times 0.07$ mm
Wavelength:	Cu $K\alpha$ radiation (1.54178 Å)
μ:	15.7 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	30929, 4485, 0.044
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4381
$N(param)_{refined}$:	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 ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded in CDCl$_3$ 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) ν(CN), 1482, 1097 (s) ν(CN), 467 (m) ν(SnN). **^{1}H NMR** (DMSO-d$_6$, ppm): δ 3.10 (s, 2H, Ph—CH$_2$), 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). **^{13}C{^{1}H} NMR** (DMSO-d$_6$, ppm): δ 71.1 (CH$_2$), 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

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

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, $(4\text{-}BrC_6H_4CH_2)_2SnBr_2$, featured in the title compound, $(4\text{-}BrC_6H_4)_2SnBr_2(2,2'\text{-bipyridyl})$, was described [6]. By contrast to the approximately 50 analogous structures of bipyridyl-type (NN) ligands with R_2SnCl_2, there are only three species of the general formula $R_2SnBr_2(NN)$ reported, namely R = Me, NN = 4,4′-bis(but-3-en-1-yl)-2,2′-bipyridine [7], R = CF_2CF_3, NN = 1,10-phenanthroline [8] and R = $3\text{-}BrC_6H_4CH_2$, NN = 4,7-diphenyl-1,10-phenanthroline [9]. Given this paucity of data for $R_2SnBr_2(NN)$, 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 $Br_2C_2N_2$ 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 strucure of $(4\text{-}BrC_6H_4CH_2)_2SnBr_2$ 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, $(4\text{-}BrC_6H_4CH_2)_2SnBr_2(O=S(CH_2Ph)_2$ [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)° for symmetry operation (i) 2 − x, 1 − y, 1 − z] and end-on C—Br$\cdots\pi$(N2-pyridyl) interactions [C5—Br3$\cdots$Cg(N2,C20—C24)^{ii}: Br3$\cdots$Cg(N2,C20—C24)^{ii} = 3.9096(13) Å, C5$\cdots$Cg(N2,C20—C24)^{ii} = 5.563(3) Å with angle at Br3 = 143.56(9)° 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 Å, C16$\cdots$Br1^{iii} = 3.746(4) Å with angle at H16 = 142° for (iii) 1/2 + x, 3/2 − y, −1/2 + z] and phenyl-Br$\cdots$Br(phenyl) [Br3$\cdots$Br4^{iv} = 3.5737(4) Å 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$_6$H$_4$)$_2$SnCl$_2$(2,2′-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.

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. Haberecht, M. C.; Bats, J. W.: Private communication to the Cambridge Structural Database. Refode: SODYER (2014).
8. Klösener, J.; Wiesemann, M.; Niemann, M.; Neumann, B.; Stammler, H.-G.; Hoge, B.: Synthesis of mono-, bis- and tris(pentafluoroethyl)tin derivatives, $(C_2F_5)_{4-n}SnX_n$ (X=Ph, Me, Cl, Br, Cp; n = 1-3). Chem. Eur. J. **23** (2017) 8295–8303.
9. Bhaskar, C.; Chandrasekar, S.; Mohandas, T.; Butcher, R. J.: Di-bromido-bis-(3-bromo-benzyl-κC)(4,7-diphenyl-1,10-phenanthroline-κ^{2}N,N′)tin(IV). IUCrData **4** (2019) x190336.
10. Buntine, M. A.; Hall, V. J.; Kosovel, F. J.; Tiekink, E. R. T.: Influence of crystal packing on molecular geometry: a crystallographic and theoretical investigation of selected diorganotin systems. J. Phys. Chem. A **102** (1998) 2472–2482.
11. Buntine, M. A.; Hall, V. J.; Tiekink, E. R. T.: The crystal and molecular structures of R_2SnCl_2(1,10-phenanthroline), R = iPr, Cy, CH$_2$Ph and R$_2$ = Me, Ph: a comparison between solid state and theoretical structures. Z. Kristallogr. **213** (1998) 669–678.
12. Malenov, D. P.; Janjić, G. V.; Medaković, V. B.; Hall, M. B.; Zarić, S. D.: Noncovalent bonding: stacking interactions of chelate rings of transition metal complexes. Coord. Chem. Rev. **345** (2017) 318–341.
13. Tiekink, E. R. T.: Supramolecular assembly based on "emerging" intermolecular interactions of particular interest to coordination chemists. Coord. Chem. Rev. **345** (2017) 209–228.
14. Lee, S. M.; Lo, K. M.; Tiekink, E. R. T.: Crystal structure of (dibenzyl sulphoxide-κO)dibromido-bis(4-bromobenzyl-κC)tin(IV), $C_{28}H_{26}Br_4OSSn$. Z. Kristallogr. NCS **234** (2019). doi: 10.1515/ncrs-2019-0541.
15. Cavallo, G.; Metrangolo, P.; Milani, R.; Pilati, T.; Priimagi, A.; Resnati, G.; Terraneo, G.: The halogen bond. Chem. Rev. **116** (2016) 2478–2601.
16. Lee, S. M.; Lo, K. M.; Tiekink, E. R. T.: Crystal structure of (2,2′-bipyridyl)bis(4-chlorobenzyl)dichloridotin(IV), $C_{24}H_{20}Cl_4N_2Sn$. Z. Kristallogr. NCS **234** (2019). doi: 10.1515/ncrs-2019-0508.
17. 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).
18. 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.