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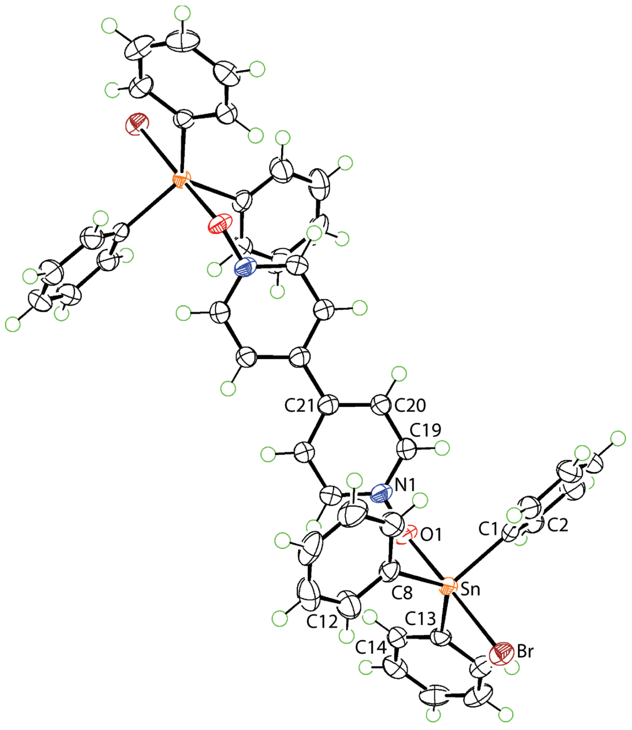
Kong Mun Lo, See Mun Lee and Edward R.T. Tiekink*

Crystal structure of bis{bromido-triphenyltin(IV)} (μ_2-[4,4′-bipyridine]1,1′-dioxide-$\kappa^2O:O'$), $C_{46}H_{38}Br_2N_2O_2Sn_2$



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Abstract

$C_{46}H_{38}Br_2N_2O_2Sn_2$, monoclinic, $P2_1/n$ (no. 14), $a = 9.8452(1)$ Å, $b = 12.2087(1)$ Å, $c = 17.4284(1)$ Å, $\beta = 102.224(1)°$, $V = 2047.35(3)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0160$, $wR_{ref}(F^2) = 0.0427$, $T = 100(2)$ 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 the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	$0.13 \times 0.08 \times 0.05$ mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	12.3 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	47512, 3660, 0.034
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3602
$N(param)_{refined}$:	244
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

Tetraphenyltin (0.85 g, 2 mmol) and 4-(dimethylamino) pyridine hydrobromide perbromide (Sigma-Aldrich; 0.72 g, 2 mmol) were dissolved in ethanol (50 mL). The resulting mixture was stirred at room temperature until a colourless solution was obtained. Next, 4,4′-bipyridine-1,1′-dioxide (Sigma-Aldrich, 0.19 g, 1 mmol) in ethanol (5 mL) was added to the mixture which was then refluxed for 2 h. After filtration, the filtrate was evaporated slowly until colourless crystals formed. The crystals were filtered, washed with a minimum amount of hexane and air-dried. Yield: 0.54 g (51.5%). **M.pt** (Mel-temp II digital melting point apparatus): 481–483 K. **IR** (Bruker Vertex 70v FTIR Spectrophotometer; cm^{-1}): 1175 (m) ν(C—N), 550 (m) ν(Sn—O). **^{1}H NMR** (Bruker Ascend 400 MHz NMR spectrometer; 323 K; $CDCl_3$; p.p.m. relative to Me_4Si): δ 7.41–7.47 (m, 30H, Ph—H), 7.64–7.69 (m, 4H, bipyridine-H), 8.20–8.26 (m, 4H, bipyridine-H). **^{13}C{^{1}H} NMR** (as for ^{1}H NMR): δ 122.9, 129.1, 130.2, 132.7, 136.2, 137.3, 139.9 (aromatic-C). **^{119}Sn{^{1}H} NMR** (as for ^{1}H NMR; p.p.m. relative to Me_4Si): δ −65.6.

Experimental details

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

***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. https://orcid.org/0000-0003-1401-1520
Kong Mun Lo and See Mun Lee: 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_{iso}*/U_{eq}
Sn	0.47825(2)	0.36702(2)	0.75948(2)	0.01735(5)
Br	0.47321(2)	0.58076(2)	0.78787(2)	0.02327(6)
O1	0.48130(14)	0.17967(11)	0.74469(8)	0.0237(3)
N1	0.48667(17)	0.13557(12)	0.67572(10)	0.0214(3)
C1	0.69951(19)	0.36523(14)	0.76843(11)	0.0203(4)
C2	0.7814(2)	0.30574(16)	0.82648(12)	0.0256(4)
H2	0.740232	0.264731	0.861927	0.031*
C3	0.9250(2)	0.30472(17)	0.83414(13)	0.0292(4)
H3	0.981807	0.264240	0.875332	0.035*
C4	0.9848(2)	0.36268(17)	0.78173(14)	0.0296(5)
H4	1.082686	0.361028	0.786430	0.035*
C5	0.9027(2)	0.42302(17)	0.72253(13)	0.0275(4)
H5	0.943725	0.462273	0.686198	0.033*
C6	0.7594(2)	0.42603(16)	0.71634(12)	0.0242(4)
H6	0.702547	0.469276	0.676839	0.029*
C7	0.3577(2)	0.37985(15)	0.64197(11)	0.0211(4)
C8	0.4230(2)	0.37928(18)	0.57836(12)	0.0293(4)
H8	0.521160	0.372412	0.587221	0.035*
C9	0.3456(3)	0.3887(2)	0.50212(13)	0.0364(5)
H9	0.391203	0.388531	0.459210	0.044*
C10	0.2027(2)	0.39817(19)	0.48850(13)	0.0352(5)
H10	0.149740	0.404195	0.436354	0.042*
C11	0.1378(2)	0.3988(2)	0.55083(14)	0.0363(5)
H11	0.039499	0.405282	0.541786	0.044*
C12	0.2154(2)	0.39013(19)	0.62733(13)	0.0317(4)
H12	0.169323	0.391315	0.670030	0.038*
C13	0.40259(18)	0.31803(15)	0.86057(11)	0.0191(4)
C14	0.31267(18)	0.22954(16)	0.85837(11)	0.0230(4)
H14	0.279682	0.192224	0.810196	0.028*
C15	0.2704(2)	0.19495(17)	0.92579(13)	0.0276(4)
H15	0.207180	0.135570	0.923155	0.033*
C16	0.3204(2)	0.24705(17)	0.99654(12)	0.0303(4)
H16	0.292193	0.223242	1.042676	0.036*
C17	0.4116(2)	0.33397(18)	0.99999(12)	0.0309(4)
H17	0.447046	0.369178	1.048722	0.037*
C18	0.4516(2)	0.36999(15)	0.93242(12)	0.0242(4)
H18	0.513025	0.430585	0.935174	0.029*
C19	0.6107(2)	0.11883(15)	0.65641(11)	0.0209(4)
H19	0.693621	0.143452	0.690405	0.025*
C20	0.61721(19)	0.06640(15)	0.58787(11)	0.0204(4)
H20	0.705129	0.054771	0.574958	0.024*
C21	0.49704(19)	0.02961(15)	0.53646(11)	0.0213(4)
C22	0.3714(2)	0.05092(19)	0.55852(13)	0.0307(5)
H22	0.286800	0.028730	0.524976	0.037*
C23	0.3676(2)	0.10320(18)	0.62758(13)	0.0293(4)
H23	0.280927	0.116661	0.641576	0.035*

Comment

Recently, the crystal structure determination of a one-dimensional coordination polymer, [benzyl$_2$SnCl$_2$(L)]$_n$, where L is the μ$_2$-bridging 4,4′-bipyridine *N*,*N*′-dioxide (systematic name: [4,4′-bipyridine]1,1′-dioxide) molecule, was investigated by X-ray crystallographic methods [5]. Until then, the only other related structures available of neutral organotin compounds were those of the *cis*- and *trans*-isomers of (4-fluorobenzyl)$_2$SnCl$_2$(L) [6], also one-dimensional coordination polymers with topologies depending on the disposition of the *N*-donor atoms of the L ligands. The common feature of the three structures are six-coordinate, octahedral geometries for the tin centres. Herein, the crystal and molecular structures of a new species, namely binuclear [Ph$_3$SnBr]$_2$L, (I), are described along with an analysis of the calculated Hirshfeld surfaces.

The molecular structure of (I), located about crystallographic centre of inversion, is shown in the figure (70% displacement ellipsoids; unlabelled atoms are related by the symmetry operation $1 - x, -y, 1 - z$). The penta-coordinated tin atom exists in a trigonal-bipyramidal geometry defined by three *ipso*-carbon atoms, occupying positions in the trigonal plane, the L-bound oxygen atom [2.3027(13) Å] and a bromide atom [2.6583(2) Å]. The angles in the trigonal plane vary from a narrow 114.65(7)°, for C1—Sn—C7, to a wide 126.05(7)°, for C7—Sn—C13. The Br—Sn—O1 axial angle is 175.62(3)°. The ligand L is folded over to be disposed over the C1- and C7-phenyl rings, i.e. the rings involved in the narrow C—Sn—C bond angle.

In the crystal of (I), two contacts less than the sum of the respective van der Waals radii are noted [7], namely phenyl-C—H⋯Br [C17—H17⋯Br^i: H17⋯Br^i = 2.86 Å, C17⋯Br^i = 3.777(2) Å with angle at H17 = 164° for symmetry operation (i) $1 - x, 1 - y, 2 - z$] and π—π stacking between pyridyl and tin-bound phenyl rings [inter-centriod Cg(N1,C19—C23)⋯Cg(C1—C6)^{ii} = 3.5580(11) Å with inter-planar angle = 9.24(10)° for (ii) $3/2 - x, -1/2 + y, 3/2 - z$]. With (I) being a centrosymmetric molecule, these interactions extend in three-dimensions to stabilise the molecular packing.

In order to evaluate the molecular packing in more detail, a further analysis of the molecular packing of (I) was conducted with the Crystal Explorer 17 program [8] following standard protocols [9]. Thus, the Hirshfeld surfaces were calculated for the full centrosymmetric molecule as were the full and delineated two-dimensional fingerprint plots. This analysis shows that over 90% of all surface contacts involve hydrogen: H⋯H [53.5%], C⋯H/H⋯C [24.5%] and Br⋯H/H⋯Br [12.8%]. The remaining contacts all make small contributions, i.e. C⋯C [4.1%], O⋯H/H⋯O [2.4%], Br⋯C/C⋯Br [1.6%], N⋯C/C⋯N [0.7%] and N⋯H/H⋯N [0.4%], generally at distances greater than the respective sums of the van der Waals radii [7].

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