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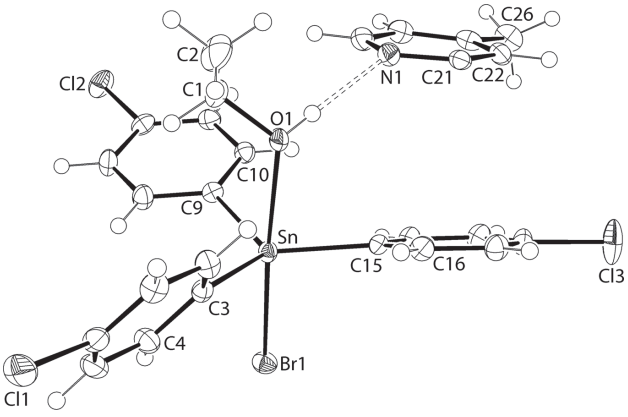
Crystal structure of bromido-tri(4-chlorophenyl-κ¹*C*)-(ethanol-κ¹*O*)tin(IV) — 4,4′-dimethyl-2,2′-bipyridine (2/1), $C_{52}H_{48}Br_2Cl_6N_2O_2Sn_2$



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Abstract

$C_{52}H_{48}Br_2Cl_6N_2O_2Sn_2$, triclinic, $P\bar{1}$ (no. 2), $a = 8.8297(1)$ Å, $b = 12.2632(2)$ Å, $c = 12.6884(2)$ Å, $\alpha = 84.191(1)°$, $\beta = 83.940(1)°$, $\gamma = 76.086(1)°$, $V = 1322.04(3)$ Å^3, $Z = 1$, $R_{gt}(F) = 0.0222$, $wR_{ref}(F^2) = 0.0621$, $T = 100(2)$ K.

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The components of the asymmetric unit are 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

General: All chemicals and solvents were used as purchased without purification. The melting point was determined using a Mel-temp II digital melting point apparatus and was uncorrected. The solid-state IR spectrum was obtained on a Bruker Vertex 70v FTIR Spectrometer from 4000 to 400 cm^{-1}. The ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at room temperature in $CDCl_3$ solution on a Bruker Ascend 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane.

Synthesis: Tetra(4-chlorophenyl)tin was synthesized from the reaction of stannic chloride (Fluka) with 4-chlorophenylmagnesium bromide (Fluka) in a 1:4 molar ratio. Tetra(4-chlorophenyl)tin (0.57 g, 1 mmol) and 4-(dimethylamino)pyridine hydrobromide perbromide (Sigma-Aldrich, 0.36 g, 1 mmol) were dissolved in ethanol (50 mL). The resulting mixture was stirred at room temperature until a colourless solution was obtained. 4,4′-Dimethyl-2,2′-dipyridyl (Sigma-Aldrich, 0.18 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: 0.34 g (50.6%). *M*.pt: 395–397 K. **IR** (cm^{-1}) 1644 (*s*) ν(C—N), 1561 (*s*) ν(C—N), 509 (w) ν(Sn—O). **^{1}H NMR** ($CDCl_3$, p.p.m.): δ 1.30 (s, 3H, ethanol-CH_3) 2.43 (s, 3H, CH_3), 3.23 (s, 2H, OCH_2), 7.11 (d, 6H, $J = 7.70$, Ph—H), 7.59 (d, 1H, $J = 6.50$ Hz, py—H), 8.11 (d, 1H, $J = 6.82$, py—H), 8.22 (s, 1H, py—H), 8.53 (d, 6H, $J = 7.68$, Ph—H); the hydroxy-O—H was not observed. **^{13}C{^{1}H} NMR** ($CDCl_3$, p.p.m.): δ 21.2 (CH_3), 23.0 (CH_3), 40.2 (OCH_2), 116.7, 129.4, 135.4, 137.3 (Ph—H), 122.1, 124.6, 139.0, 149.0, 156.2 (py—H).

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.10 × 0.08 × 0.05 mm
Wavelength:	Cu *Kα* radiation (1.54184 Å)
μ:	12.4 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	67.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	31356, 4730, 0.038
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4577
$N(param)_{refined}$:	303
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Sn	0.73807(2)	0.34325(2)	0.32425(2)	0.01554(6)
Br1	0.82458(3)	0.50549(2)	0.40150(2)	0.02187(8)
Cl1	1.32005(6)	0.22787(6)	−0.05566(5)	0.03271(14)
Cl2	0.12395(6)	0.67606(5)	0.10294(5)	0.03057(14)
Cl3	0.65562(9)	0.07952(6)	0.80098(5)	0.04340(17)
O1	0.65514(18)	0.18457(13)	0.26191(12)	0.0192(3)
H1O	0.589(3)	0.160(2)	0.302(2)	0.029*
N1	0.4237(2)	0.11121(15)	0.40045(16)	0.0201(4)
C1	0.6116(3)	0.1884(2)	0.15543(19)	0.0262(5)
H1A	0.659181	0.243684	0.109560	0.031*
H1B	0.496455	0.214307	0.155373	0.031*
C2	0.6636(4)	0.0754(2)	0.1101(2)	0.0410(7)
H2A	0.777979	0.050722	0.107402	0.062*
H2B	0.629927	0.081345	0.038175	0.062*
H2C	0.616754	0.020336	0.155270	0.062*
C3	0.9358(2)	0.30000(18)	0.21079(17)	0.0178(4)
C4	1.0063(3)	0.3850(2)	0.16265(19)	0.0232(5)
H4	0.971705	0.458935	0.185578	0.028*
C5	1.1256(3)	0.3635(2)	0.0822(2)	0.0265(5)
H5	1.172840	0.422038	0.050181	0.032*
C6	1.1751(2)	0.2558(2)	0.04900(19)	0.0228(5)
C7	1.1093(3)	0.1693(2)	0.0961(2)	0.0239(5)
H7	1.145237	0.095355	0.073241	0.029*
C8	0.9903(3)	0.19163(19)	0.17717(19)	0.0219(5)
H8	0.945409	0.132342	0.210118	0.026*
C9	0.5369(2)	0.44804(17)	0.25672(18)	0.0169(4)
C10	0.3869(2)	0.46200(18)	0.30821(18)	0.0186(4)
H10	0.371967	0.422596	0.375468	0.022*
C11	0.2586(3)	0.53288(19)	0.26251(19)	0.0206(4)
H11	0.156574	0.542364	0.298043	0.025*
C12	0.2825(3)	0.58921(19)	0.16438(19)	0.0214(5)
C13	0.4308(3)	0.5779(2)	0.11177(19)	0.0240(5)
H13	0.445601	0.617902	0.044816	0.029*
C14	0.5570(3)	0.5070(2)	0.15883(19)	0.0226(5)
H14	0.659006	0.498686	0.123521	0.027*
C15	0.7096(2)	0.25247(18)	0.47340(17)	0.0167(4)
C16	0.7999(2)	0.14475(19)	0.49814(18)	0.0202(4)
H16	0.873449	0.107795	0.445433	0.024*
C17	0.7837(3)	0.09094(19)	0.59844(19)	0.0222(5)
H17	0.846220	0.017788	0.615195	0.027*
C18	0.6748(3)	0.1455(2)	0.67406(18)	0.0228(5)
C19	0.5814(3)	0.2521(2)	0.65189(19)	0.0232(5)
H19	0.506017	0.287884	0.704282	0.028*
C20	0.6009(3)	0.30488(18)	0.55139(18)	0.0201(4)
H20	0.538864	0.378333	0.535167	0.024*
C21	0.4339(2)	0.05090(18)	0.49552(18)	0.0178(4)
C22	0.3257(3)	0.08082(18)	0.58212(19)	0.0204(4)
H22	0.338496	0.037974	0.648620	0.025*
C23	0.1995(3)	0.17291(19)	0.5717(2)	0.0218(5)
C24	0.1851(3)	0.23137(19)	0.4723(2)	0.0239(5)
H24	0.098688	0.293174	0.460424	0.029*
C25	0.2991(3)	0.19791(19)	0.3907(2)	0.0233(5)
H25	0.288231	0.239204	0.323311	0.028*
C26	0.0870(3)	0.2089(2)	0.6659(2)	0.0290(5)
H26A	0.129000	0.257287	0.706258	0.043*
H26B	0.072418	0.142143	0.711514	0.043*
H26C	−0.013938	0.250655	0.641314	0.043*

U_{iso}(H) = 1.2–1.5U_{eq}(C). The O-bound H-atom was located in a difference Fourier map but, was refined with a distance restraint of O—H = 0.84 ± 0.01 Å, and with U_{iso}(H) set to 1.5U_{eq}(O).

Comment

The title compound became available during recent studies of the binding of bis(substituted-benzyl)tin dihalides by molecules with potentially neutral, bridging ligands, such as 4,4′-bipyridyl-*N*-oxide [5]. The title compound is formulated as {(4-ClC_6H_5)$_3$Sn[*O*(*H*)CH_2CH_3]Br}$_2$(4,4′-dimethyl-2,2′-dipyridyl) (I), and was characterized by X-ray crystallography.

The molecular structures comprising the asymmetric unit of (I) are shown in the figure (50% displacement ellipsoids; the full 4,4′-dimethyl-2,2′-dipyridyl molecule is generated by the application of the symmetry operation (i) $1-x$, $-y$, $1-z$). The tin atom in (I) is penta-coordinated by a bromide atom [2.6050(3) Å], three *ipso*-carbon atoms of the three 4-chlorophenyl groups [Sn—C3, C9, C15 = 2.141(2), 2.131(2) and 2.119(2) Å] and the oxygen atom [2.4634(15) Å] of the ethanol molecule. The 4-chlorophenyl substituents occupy equatorial positions in a distorted trigonal-bipyramidal geometry. The Br1—Sn—O1 axial angle is 176.63(4)°, and the tin atom lies 0.2174(12) Å out of the plane through the C3, C9 and C15 atoms in the direction of the Br1 atom. There are discrepancies in the angles subtended at the tin atom by the phenyl substituents with the angles subtended by the phenyl-C15 atom [C3—Sn—C15 = 124.36(8)° and C9—Sn—C15 = 119.12(8)°] being systematically wider than the C3—Sn—C9 angle [113.42(8)°]. While the C9—Sn—C15 is close to the ideal, the deviation from 120° of the narrowest angle is correlated with the wide dihedral angle formed between the C3- and C9-rings, *i.e.* 60.40(7)°, suggesting minimal steric repulsion between them and hence, the narrow angle.

As indicated in the figure, there is an ethanol-O—H···N(pyridyl) hydrogen bond [O1—H1o···N1: H1o···N1 = 1.98(3) Å, O1···N1 = 2.807(2) Å with angle at H1o = 176(2)°] between the title complex and the organic component of this co-crystal. Bonding parameters are in the expected ranges [6]. As the 4,4′-dimethyl-2,2′-dipyridyl is disposed about a crystallographic centre of inversion, a three-molecule aggregate ensues. Further stability to these aggregates is provided by π···π interactions between the chlorophenyl and pyridyl rings [inter-centroid *Cg*(C15–C20)···*Cg*(N1,C21–C25) distance = 3.8951(14) Å with angle of inclination = 13.28(11)°]. The aggregates assemble in the crystal *via* a combination of weak non-covalent interactions. A supramolecular layer parallel to (0 1 1) is formed through the agency of chlorophenyl-C—H···π(chlorophenyl) interactions [C19—H19···*Cg*(C9—C14)^{ii}: H19···*Cg*(C9—C14)^{ii} = 2.98 Å, C19···*Cg*(C9–C14)^{ii} = 3.471(3) Å with angle

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at H19 = 114° for symmetry operation (ii) $1-x$, $1-y$, $1-z$]. The connections between layers to consolidate the three-dimensional architecture are of the type end-on chlorophenyl-C—Cl···π(chlorophenyl) [C12—Cl2···*Cg*(C3—C8)^{iii}: Cl2···*Cg*(C3—C8)^{iii} = 3.4361(12) Å with angle at Cl2 = 142.34(8)° for (iii) $1-x$, $1-y$, $-z$] interactions.

Further insight into the molecular packing was achieved through an analysis of the calculated Hirshfeld surface employing Crystal Explorer 17 [7] and established procedures [8], including the calculation of the full and decomposed two-dimensional fingerprint plots. The four major contributing contacts to the overall Hirshfeld surface (*i.e.* for both components of the asymmetric unit) are, in descending order H···H [33.2%], Cl···H/H···Cl [25.3%], C···H/H···C [18.9%] and Br···H/H···Br [10.7%]. There are several other contacts to the surface but, at distances at or greater than the sum of the respective van der Waals radii, such as Cl···C/C···Cl [3.4%], Cl···Cl [1.9%] and N···H/H···N [1.6%]. Subsequently, calculations were performed on the tin compound itself as well as upon the entire 4,4′-dimethyl-2,2′-dipyridyl molecule. For the former, the percentage contributions for the four most important contacts are, to a first approximation, the same, H···H [34.6%], Cl···H/H···Cl [26.9%], C···H/H···C, Br···H/H···Br [9.2%]. As anticipated from the chemical composition, greater variations are not for the bipyridyl molecule, with significant increases to the surface of the molecule from H···H [41.9%] and C···H/H···C [25.9%] contacts complemented by notable decreases from Cl···H/H···Cl [8.3%] and Br···H/H···Br [7.5%] contacts. Also, the relative importance of N···H/H···N [6.3%] contacts increases.

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