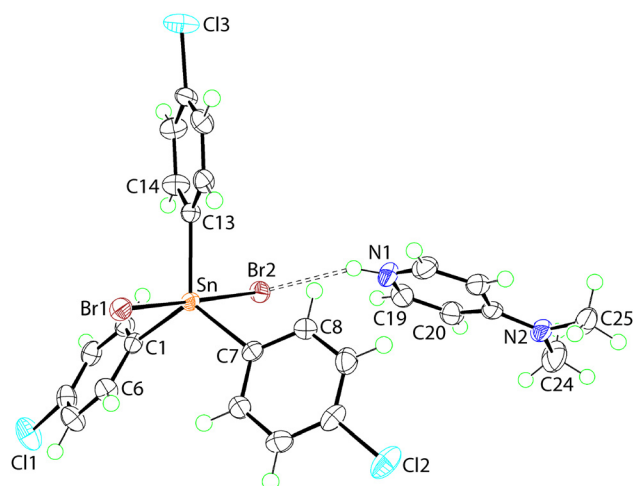See Mun Lee, Kong Mun Lo and Edward R.T. Tiekink*

Crystal structure of 4-(dimethylamino)pyridinium dibromido-tris(4-chlorophenyl-κ*C*)stannate(IV), C$_{25}$H$_{23}$Br$_2$Cl$_3$N$_2$Sn

Abstract

C$_{25}$H$_{23}$Br$_2$Cl$_3$N$_2$Sn, monoclinic, $P2_1/c$ (no. 14), a = 10.9372(1) Å, b = 23.1045(1) Å, c = 11.1856(1) Å, β = 106.942(1)°, V = 2703.91(4) Å^3, Z = 4, $R_{gt}(F)$ = 0.0167, $wR_{ref}(F^2)$ = 0.0393, T = 100 K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The 4-chlorophenylmagnesium bromide was prepared from the Grignard reaction of magnesium (Merck) and

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.11 × 0.06 × 0.05 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	13.8 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	33,913, 4828, 0.030
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 4720
$N(param)_{refined}$:	303
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

4-bromochlorobenzene (Fluka) [in tetrahydrofuran]. Tetra(4-chlorophenyl)tin was synthesised from the reaction of stannic chloride (Fluka) with 4-chlorophenylmagnesium bromide in a 1:4 M ratio. Then, tetra(4-chlorophenyl)tin (0.56 g, 1 mmol) and 4-dimethylaminopyridine hydrobromide perbromide (Sigma, 0.37 g, 1 mmol) were dissolved separately in ethanol (50 mL) and refluxed for 3 h. The solution was filtered and colourless crystals were isolated upon cooling to room temperature. Yield: 0.39 g (53.0%). **M.pt** (Stuart SMP30 digital melting point apparatus; uncorrected): 443–446 K. **IR** (Bruker Vertex 70v FTIR Spectrometer; cm^{-1}): 1647(s) ν(C=N), 1564 (m) ν(C=C), 1213 (m) ν(C–N). **^{1}H NMR** (Bruker Ascend 400 MHz NMR spectrometer; CDCl$_3$; ppm relative to Me$_4$Si): δ 3.26 (s, 6H, CH$_3$), 6.74 (d, 2H, J = 7.6 Hz, Pyr–H), 7.41–7.58 (m, 12H, Ph–H), 8.11 (d, 2H, J = 7.6 Hz, Pyr–H); N–H not obs. **^{13}C{^{1}H} NMR** (as for ^{1}H NMR): 40.3 (CH$_3$), 106.5, 129.1, 129.8, 134.6, 136.9, 138.1, 157.4 (Ph–C).

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–0.98 Å) and refined as riding with U_{iso}(H) = 1.2–1.5U_{eq}(C).

Comment

The most closely related literature precedent to the title salt [HNC$_5$H$_4$NMe$_2$-4][(4-ClC$_6$H$_4$)$_3$SnBr$_2$], hereafter (I), is that of

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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	0.63974 (2)	0.64027 (2)	0.49327 (2)	0.01374 (4)
Br1	0.68992 (2)	0.53357 (2)	0.41966 (2)	0.01794 (5)
Br2	0.58593 (2)	0.75285 (2)	0.55734 (2)	0.01852 (5)
Cl1	0.68523 (6)	0.55697 (2)	1.07652 (5)	0.03297 (12)
Cl2	0.06916 (4)	0.61027 (3)	0.07387 (5)	0.03105 (12)
Cl3	1.14326 (5)	0.74996 (2)	0.35204 (5)	0.02950 (12)
C1	0.66374 (16)	0.61341 (8)	0.68234 (17)	0.0162 (4)
C2	0.72681 (17)	0.64767 (9)	0.78515 (19)	0.0184 (4)
H2	0.763042	0.683599	0.771842	0.022*
C3	0.73708 (18)	0.62983 (9)	0.90633 (19)	0.0210 (4)
H3	0.781964	0.652725	0.975805	0.025*
C4	0.68081 (19)	0.57811 (9)	0.92412 (19)	0.0234 (4)
C5	0.6169 (2)	0.54339 (9)	0.82474 (19)	0.0242 (4)
H5	0.578417	0.508123	0.838421	0.029*
C6	0.61049 (18)	0.56127 (9)	0.70474 (18)	0.0203 (4)
H6	0.568628	0.537310	0.635973	0.024*
C7	0.45310 (17)	0.63465 (8)	0.36284 (18)	0.0152 (4)
C8	0.41610 (18)	0.67073 (9)	0.25912 (18)	0.0195 (4)
H8	0.472108	0.700546	0.249073	0.023*
C9	0.29813 (19)	0.66381 (10)	0.16971 (19)	0.0230 (4)
H9	0.273523	0.688494	0.098801	0.028*
C10	0.21726 (17)	0.62032 (9)	0.18592 (18)	0.0207 (4)
C11	0.25093 (18)	0.58432 (9)	0.28888 (19)	0.0219 (4)
H11	0.193936	0.555058	0.299454	0.026*
C12	0.36930 (18)	0.59150 (9)	0.37671 (19)	0.0200 (4)
H12	0.393515	0.566619	0.447324	0.024*
C13	0.79704 (16)	0.67764 (8)	0.44376 (18)	0.0158 (4)
C14	0.88807 (19)	0.70998 (9)	0.53146 (19)	0.0210 (4)
H14	0.877311	0.716632	0.611598	0.025*
C15	0.99407 (18)	0.73263 (9)	0.50377 (19)	0.0215 (4)
H15	1.056132	0.754322	0.564299	0.026*
C16	1.00760 (18)	0.72299 (9)	0.38615 (18)	0.0182 (4)
C17	0.91855 (18)	0.69153 (9)	0.29641 (18)	0.0199 (4)
H17	0.928852	0.685733	0.215815	0.024*
C18	0.81359 (17)	0.66852 (9)	0.32645 (17)	0.0177 (4)
H18	0.752484	0.646320	0.266115	0.021*
N1	0.42164 (16)	0.83364 (8)	0.32415 (18)	0.0268 (4)
H1N	0.4830 (18)	0.8100 (9)	0.363 (2)	0.032*
N2	0.09412 (15)	0.92419 (8)	0.15652 (17)	0.0230 (4)
C19	0.3708 (2)	0.86802 (10)	0.3943 (2)	0.0272 (5)
H19	0.410121	0.870051	0.481959	0.033*
C20	0.26427 (19)	0.89986 (10)	0.3420 (2)	0.0254 (4)
H20	0.230130	0.924170	0.392828	0.031*
C21	0.20385 (18)	0.89686 (9)	0.2112 (2)	0.0207 (4)
C22	0.26543 (19)	0.86245 (9)	0.1404 (2)	0.0230 (4)
H22	0.232416	0.861132	0.051948	0.028*
C23	0.37158 (19)	0.83144 (10)	0.1994 (2)	0.0255 (4)
H23	0.410949	0.807862	0.151571	0.031*
C24	0.0276 (2)	0.95824 (12)	0.2287 (2)	0.0369 (6)
H24A	0.026822	0.936805	0.304086	0.055*
H24B	−0.060435	0.965505	0.177766	0.055*
H24C	0.071913	0.995211	0.252620	0.055*
C25	0.04387 (19)	0.92537 (9)	0.0206 (2)	0.0261 (5)
H25A	0.101960	0.947459	−0.014240	0.039*
H25B	−0.040560	0.943745	−0.003469	0.039*
H25C	0.036431	0.885714	−0.011786	0.039*

the triphenyl analogue [5]. The motivation behind recent structural studies [6, 7] which involve the inclusion of halide substituents in the substituents of organotin compounds is to evaluate the propensity of halogen-bond formation in their crystals. In continuation of these studies, full crystallographic details of (I) are described herein.

The asymmetric unit of the title structure of (I) is shown in the figure (70% displacement ellipsoids). The tin atom in the anion is penta-coordinated by two bromido atoms and three ipso-carbon atoms derived from the 4-chlorophenyl groups. The, $trans\text{-}C_3Br_2$ donor set defines an approximate trigonal-bipyramidal geometry with the Sn atom lying 0.0520(11) Å out of the C_3-plane in the direction of the Br1 atom. The axial angle, Br1–Sn–Br2, is 177.134(8)°. A discrepancy is noted in the Sn–Br bond lengths with Sn–Br1 [2.7055(2) Å] being shorter than Sn–Br2 [2.8056(2) Å] by about 0.1 Å.

Similar structural features are noted in the literature precedent [$HNC_5H_4NMe_2$-4][Ph_3SnBr_2], but as the anion has crystallographically imposed two-fold symmetry, the two Sn–Br bond lengths are equivalent [2.7801(3) Å]; the Br–Sn–Br angle is 178.64(2)°.

The most prominent connection between the constituents of the salt in the crystal is a charge-assisted pyridinium-N–H···Br hydrogen bond [see the Figure; N1–H1n···Br2: H1n···Br2 = 2.51(2) Å, N1···Br2 = 3.2841(19) Å with angle at H1n = 147.4(18)°]. This feature of the molecular packing readily accounts for the elongation of the Sn–Br2 bond length with respect to the Sn–Br1 bond (see above). Layers of molecules, two molecules thick, assemble in the ac-plane and feature pyridinium-phenyl-C–H···Br [C23–H23···Br2^i: H23···Br2^i = 2.81 Å, C23···Br2^i = 3.740(2) Å with angle at H23 = 165° for symmetry operation (i) x, $3/2−y$, $−1/2+z$] and methyl-C–H···Br [C25–H25b···Br1^{ii}: H25b···Br1^{ii} = 2.87 Å, C25···Br1^{ii} = 3.823(2) Å with angle at H25b = 165° for (ii) $−1+x$, $3/2−y$, $−1/2+z$] interactions. Additional stability to the layers is afforded by close methyl-C–H···π(chlorophenyl) and phenyl-Cl···π(chlorophenyl) contacts. The layers stack along the b-axis without directional interactions between them [8].

To gain more insight into the molecular packing, following literature precedents [9], the Hirshfeld surfaces and two-dimensional fingerprint plots were calculated on the two-molecular aggregate with the use of Crystal Explorer 17 [10]. The overwhelming majority of surface contacts involve H, i.e. H···H [27.1%], Cl···H/H···Cl [25.6%], C···H/H···C [24.2%] and, to a lesser extent, Br···H/H···Br [12.8%]. The next most significant contacts, reflecting, in part, the intra-layer phenyl-Cl···π(chlorophenyl) contacts are Cl···C/C···Cl, at 4.9%. Putative halogen-bonding contacts between Cl and Br are negligible and occur at separations greater than the respective

sums of the van der Waals radii [8], i.e. Br···Cl/Cl···Br [0.7%] and Cl···Cl [0.3%].

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