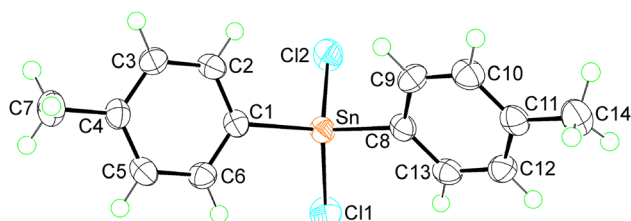


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Crystal structure of dichlorido-bis(4-methylphenyl- κC^1)tin(IV), $C_{14}H_{14}Cl_2Sn$



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Abstract

$C_{14}H_{14}Cl_2Sn$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 8.2912(1)$ Å, $b = 9.6221(1)$ Å, $c = 18.5616(2)$ Å, $V = 1480.82(3)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0142$, $wR_{ref}(F^2) = 0.0347$, $T = 100$ 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.

Source of material

The title compound was prepared following a multi-step synthesis. Initially, 4-methylphenylmagnesium bromide was prepared from the Grignard reaction, conducted in tetrahydrofuran, of magnesium (Merck) and 4-bromotoluene (Fluka). Subsequently, tetra(4-methylphenyl)tin was synthesised from the reaction of stannic chloride (Fluka) with 4-methylphenylmagnesium bromide in a 1:4 M ratio. Tetra(4-methylphenyl)tin (10.0 g, 20.7 mmol) and anhydrous stannic chloride (Fluka, 5.39 g, 20.7 mmol) were mixed in a round-bottomed flask fitted

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Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.09 × 0.07 × 0.05 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	16.8 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max} , completeness:	67.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	38312, 2639, 0.040
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 2618
$N(param)_{refined}$:	157
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

with a reflux condenser. The reaction mixture was then heated with stirring in an oil bath at 473–493 K for 3 h. The resulting brown viscous liquid was dissolved in chloroform (150 mL) and boiled with activated charcoal for 10 min. After filtration, the chloroform solution was concentrated to a small volume. Slow evaporation of the concentrated solution gave the product as a white crystalline solid. Yield: 5.35 g (69.5%). M.pt (Stuart SMP30 digital melting point apparatus; uncorrected): 321–322 K (Lit. [5]: 322–323 K). IR (Bruker Vertex 70v FTIR Spectrometer; cm⁻¹): 1560 (*m*) $\nu(C=C)$, 794 (*w*) $\nu(C-H)$, 277 (*w*) $\nu(Sn-Cl)$. ¹H NMR (Bruker Ascend 400 MHz NMR spectrometer; CDCl₃; ppm relative to Me₄Si): δ 2.41 (*s*, 6H, CH₃), 7.29–7.47 (*m*, 4H, Ph-H), 7.54–7.67 (*m*, 4H, Ph-H). ¹³C{¹H} NMR (as for ¹H NMR): δ 21.7 (CH₃), 130.5, 133.5, 134.9, 142.3 (Ph-C).

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–0.98 Å) and refined as riding with $U_{iso}(H) = 1.2–1.5U_{eq}(C)$. The crystal was refined as an inversion twin with the minor component = 0.074(7).

Comment

In crystal engineering endeavours, to systematically replace substituents while retaining space group symmetry offers opportunities to tailor chemical and physical

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Sn	0.55837 (3)	0.53509 (2)	0.34302 (2)	0.02290 (7)
Cl1	0.56232 (15)	0.33157 (8)	0.41163 (5)	0.03720 (19)
Cl2	0.31081 (10)	0.52845 (10)	0.28244 (4)	0.03371 (18)
C1	0.5463 (5)	0.7073 (3)	0.41350 (16)	0.0220 (6)
C2	0.4743 (4)	0.8302 (3)	0.39066 (17)	0.0240 (7)
H2	0.427956	0.835529	0.343940	0.029*
C3	0.4701 (4)	0.9443 (3)	0.43564 (17)	0.0250 (7)
H3	0.421188	1.028018	0.419476	0.030*
C4	0.5369 (4)	0.9382 (3)	0.50481 (16)	0.0243 (7)
C5	0.6073 (4)	0.8141 (4)	0.52696 (18)	0.0265 (7)
H5	0.652294	0.807884	0.573918	0.032*
C6	0.6131 (4)	0.6999 (3)	0.48201 (18)	0.0239 (7)
H6	0.662612	0.616295	0.497929	0.029*
C7	0.5358 (5)	1.0640 (3)	0.55302 (19)	0.0347 (8)
H7A	0.540008	1.034330	0.603490	0.052*
H7B	0.436823	1.117408	0.544716	0.052*
H7C	0.629677	1.122278	0.542248	0.052*
C8	0.7400 (4)	0.5162 (3)	0.26390 (17)	0.0236 (7)
C9	0.7637 (4)	0.6277 (3)	0.21719 (19)	0.0281 (8)
H9	0.698230	0.708345	0.221031	0.034*
C10	0.8830 (4)	0.6206 (3)	0.1652 (2)	0.0296 (7)
H10	0.897950	0.696945	0.133443	0.036*
C11	0.9816 (4)	0.5042 (3)	0.15818 (18)	0.0265 (7)
C12	0.9548 (5)	0.3925 (3)	0.20462 (17)	0.0275 (7)
H12	1.019064	0.311249	0.200175	0.033*
C13	0.8357 (4)	0.3980 (3)	0.25727 (17)	0.0253 (7)
H13	0.819593	0.321236	0.288646	0.030*
C14	1.1155 (4)	0.5018 (4)	0.10386 (19)	0.0347 (9)
H14A	1.080827	0.550186	0.060062	0.052*
H14B	1.142538	0.405248	0.092130	0.052*
H14C	1.210588	0.548329	0.123880	0.052*

properties. This concept is no better illustrated than by the chloro/methyl exchange [6]. As electronegative-chloride and electropositive-methyl groups occupy approximately the same volume, substitution of one by the other in the same crystal symmetry potentially enables control of, for example, electronic properties in the crystalline manifold. In continuation of on-going studies of opportunities offered by the chloro/methyl exchange [7, 8], herein, the crystal and molecular structures of (4-MeC₆H₄)₂SnCl₂, hereafter (I) and a known compound [5], was studied and compared with the recently reported crystal structure of the chloro analogue (4-ClC₆H₄)₂SnCl₂ [9].

The molecular structure of (I), which lacks crystallographic symmetry, is shown in the figure (70% displacement ellipsoids). The donor set defining an approximate tetrahedral geometry for the tin atom is C₂Cl₂, with the range of angles subtended at the tin atom being 104.55(4)°, for Cl1–Sn–Cl2, to 122.12(13)° for C1–Sn–C8, in accord with expectation as the rings have a greater steric pro-

file. The Sn–Cl bond lengths are experimentally distinct [Sn–Cl1 = 2.3362(8) Å and Sn–Cl2 = 2.3413(8) Å], whereas the Sn–C distances are equivalent [Sn–C1 = 2.112(3) Å and Sn–C7 = 2.114(3) Å]. The observed molecular geometry for (I) and patterns in bond lengths match very closely that noted for (4-ClC₆H₄)₂SnCl₂ [9].

In accord with the distance criteria in PLATON [10], the only directional intermolecular contact in the crystal of (I) is a weak methyl–C–H⋯π(4-tolyl) contact [C14–H14b⋯Cg(C1–C6)ⁱ: H14b⋯Cg(C1–C6)ⁱ = 2.90 Å, C14⋯Cg(C1–C6)ⁱ = 3.527(4) Å with the angle at H14b = 123° for symmetry operation (i) 2 – x, –1/2 + y, 1/2 – z] occurring within helical chains along the *b*-axis. This description of the molecular packing differs significantly from the observed molecular packing in (4-ClC₆H₄)₂SnCl₂, which is not isostructural with (I). Prominent in the crystal of (4-ClC₆H₄)₂SnCl₂ were Sn⋯Cl secondary-bonding as well as C–Cl⋯π(phenyl) contacts [9].

To gain a further appreciation of the molecular packing, a detailed analysis of all surface contacts in the crystal of (I) was conducted by the calculation, using Crystal Explorer 17 [11], of the Hirshfeld surfaces and two-dimensional fingerprint plots (full and delineated into individual contacts), following established protocols [12]. The analysis revealed the dominance of three types of surface contacts, namely H⋯H [38.4%], Cl⋯H/H⋯Cl [3.7%] and C⋯H/H⋯C [28.2%] with the next most significant contacts being Cl⋯C/C⋯Cl at 1.6%.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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