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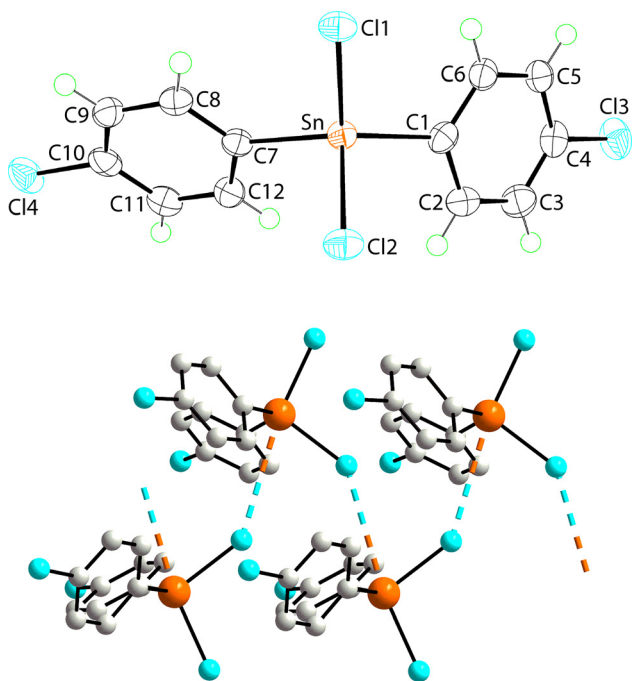
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Crystal structure of dichlorido-bis(4-chlorophenyl-κC^1)tin(IV), $C_{12}H_8Cl_4Sn$

Abstract

$C_{12}H_8Cl_4Sn$, monoclinic, $P2_1/c$ (no. 14), $a = 13.4238(1)$ Å, $b = 18.2079(2)$ Å, $c = 5.7617(1)$ Å, $\beta = 95.506(1)°$, $V = 1401.77(3)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0272$, $wR_{ref}(F^2) = 0.0798$, $T = 100$ 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.

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Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	$0.26 \times 0.06 \times 0.04$ mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	21.3 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	17318, 2491, 0.042
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2456
$N(param)_{refined}$:	154
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

The title compound was prepared from a multi-step synthesis. Initially, 4-chlorophenylmagnesium bromide was prepared from the Grignard reaction of magnesium (Merck) and 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. Tetra(4-chlorophenyl)tin (5 g, 10.3 mmol) and anhydrous stannic chloride (Fluka, 2.7 g, 10.3 mmol) were mixed together in a round-bottomed flask fitted with a reflux condenser. The reaction mixture was then heated with stirring by 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 and the filtrate was evaporated slowly until a colourless crystalline compound was formed. Yield: 3.02 g (67.0%). M.pt (Stuart SMP30 digital melting point apparatus; uncorrected): 354–356 K (lit.: 361 K [5]). **IR** (Bruker Vertex 70v FTIR Spectrometer; cm^{-1}): 1562 (m) v(C=C), 723 (w) v(C–H), 723 (w) v(C–Cl), 270 (w) v(Sn–Cl). **^{1}H NMR** (Bruker Ascend 400 MHz NMR spectrometer; CDCl$_3$; ppm relative to Me$_4$Si): δ 7.50–7.55 (m, 4H, Ph–H), 7.60–7.66 (m, 4H, Ph–H). **^{13}C\{^{1}H\} NMR** (as for ^{1}H NMR): δ 130.0, 134.7, 136.2, 138.9 (Ph–C).

Experimental details

The atoms were geometrically placed (C–H = 0.95 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$. Owing to poor

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

Atom	x	y	z	$U_{iso}*/U_{eq}$
Sn	0.69707 (2)	0.38500 (2)	0.14457 (3)	0.01743 (11)
Cl1	0.71380 (5)	0.30683 (3)	−0.17040 (10)	0.02162 (16)
Cl2	0.68098 (5)	0.50129 (3)	−0.02919 (11)	0.02462 (17)
Cl3	1.08960 (6)	0.37999 (4)	0.92412 (15)	0.0347 (2)
Cl4	0.23910 (5)	0.34664 (4)	0.45676 (14)	0.03184 (19)
C1	0.8316 (3)	0.38803 (14)	0.3654 (5)	0.0209 (6)
C2	0.8474 (2)	0.44579 (16)	0.5220 (5)	0.0253 (6)
H2	0.802879	0.486491	0.512635	0.030*
C3	0.9282 (2)	0.44429 (17)	0.6928 (5)	0.0288 (6)
H3	0.939041	0.483496	0.801085	0.035*
C4	0.9923 (2)	0.38482 (15)	0.7019 (6)	0.0234 (7)
C5	0.9801 (2)	0.32818 (16)	0.5405 (5)	0.0232 (6)
H5	1.026672	0.288785	0.544848	0.028*
C6	0.8990 (2)	0.33008 (15)	0.3729 (5)	0.0211 (5)
H6	0.889385	0.291425	0.262309	0.025*
C7	0.5536 (2)	0.36617 (15)	0.2538 (5)	0.0190 (5)
C8	0.4833 (2)	0.32459 (15)	0.1188 (5)	0.0210 (6)
H8	0.501629	0.300018	−0.016197	0.025*
C9	0.3858 (2)	0.31884 (15)	0.1809 (5)	0.0232 (6)
H9	0.337130	0.291553	0.086473	0.028*
C10	0.3607 (2)	0.35287 (15)	0.3795 (5)	0.0238 (6)
C11	0.4306 (3)	0.39390 (16)	0.5203 (6)	0.0235 (6)
H11	0.412298	0.416897	0.658026	0.028*
C12	0.5269 (2)	0.40051 (17)	0.4558 (5)	0.0217 (6)
H12	0.575122	0.428522	0.549389	0.026*

agreement, three reflections, i.e. (1 0 0), (2 0 0) and (1 1 0), were omitted from the final cycles of refinement.

Comment

The crystal structure determination of the title compound $(4\text{-}ClC_6H_4)_2SnCl_2$, hereafter (I), a known compound [5], was studied in continuation of long-term interests in the structural chemistry of diorganotin dihalides, i.e. R_2SnX_2, and their adducts with chelating bipyridine-type molecules, i.e. $R_2SnX_2(NN)$ [6–8]. Recently, the structures of $(4\text{-}ClC_6H_4)_2SnCl_2(NN)$ for NN = 1,10-phenanthroline [9] and $(4\text{-}ClC_6H_4CH_2)_2SnCl_2(NN)$ for NN = 2,2'-bipyridine [10] became available. The present report of the structure determination of (I) now enables a comparison of the geometric parameters about the tin atoms in these systems and the influence of the chloro-substituted rings upon molecular packing.

The molecular structure of (I) is shown in the upper view of the figure (70% displacement ellipsoids); the molecule lacks crystallographic symmetry. The tin atom in (I) exists within a distorted tetrahedral geometry defined by a C_2Cl_2 donor set. The minimum and maximum angles subtended at the tin atom, i.e. 102.99(8)° for Cl2–Sn–C7, and 125.29(11)° for C1–Sn–C7, are consistent with the increased steric pressure induced by the 4-chlorophenyl substituents. While the Sn–Cl bond lengths are experimentally distinct [Sn–Cl1 = 2.3341(6) Å and Sn–Cl2 = 2.3432(6) Å], the Sn–C distances are equivalent [Sn–C1 = 2.108(4) Å and Sn–C7 = 2.111(3) Å].

As mentioned in the Introduction, there are closely related structures available for comparison [8–10]. The most closely related structure is that of $(4\text{-}ClC_6H_4)_2$ $SnCl_2(1,10\text{-phenanthroline})$, hereafter (II) [9]. Here, the tin atom is found within a $C_2Cl_2N_2$ donor set with a cis disposition of the chlorido atoms which form experimentally equivalent Sn–Cl bond lengths [Sn–Cl = 2.4934(4) and 2.4960(4) Å] which are significantly longer than those found in (I), reflecting the increased coordination number in (II).

As shown in the lower view of the figure (H atoms are removed for clarity), the most notable feature in the crystal of (I) are zig-zag supramolecular chains along the c-axis (glide-symmetry) where molecules are connected by Sn···Cl···Sn secondary-bonding interactions [Sn···Cl1^i = 3.6525(7) Å for symmetry operation (i): x, 1/2−y, 1/2+z; shown as dashed lines in the image]. Such secondary-bonding interactions are well-documented in the structural chemistry of diorganotin dihalides [11]; DFT calculations proved these Sn···X interactions exerted a significant influence upon the molecular geometry about the tin atoms [11]. The only other directional bonding interactions apparent in the molecular packing are end-on Sn–Cl···π(phenyl) contacts [Sn–Cl2···Cg(C7–C12)^{ii}: Cl2···Cg(C7–C12)^{ii} = 3.4685(13) Å, with angle at Cl2 = 152.70(3)° for symmetry operation (ii) 1−x, 1−y, −z]. The latter contacts link the aforementioned chains into double chains. The connections between the double chains within a three-dimensional architecture are of the type Cl···Cl halogen bonding but at separations greater than the sum of their van der Waals radii, i.e. 3.50 Å [12]. The closest halogen bonding contact is noted for Cl1···Cl1^{iii} [3.5471(8) Å for (iii) x, 1/2−y, −1/2+z].

A further analysis of the molecular packing was achieved by the calculation of Hirshfeld surfaces and two-dimensional fingerprint plots (full and delineated into individual contacts). This was accomplished employing the Crystal Explorer 17 program [13] following established protocols [14]. The identified Sn···Cl [1.0%] and Cl···π [13.0%] contacts in the molecular packing make relatively minor contributions to the overall Hirshfeld surface. Significant contributions are made by Cl···H/H···Cl [41.1%], C···H/H···C [18.9%], H···H [16.0%] and Cl···Cl [8.9%] contacts but at separations greater than the sum of the respective van der Waals radii.

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