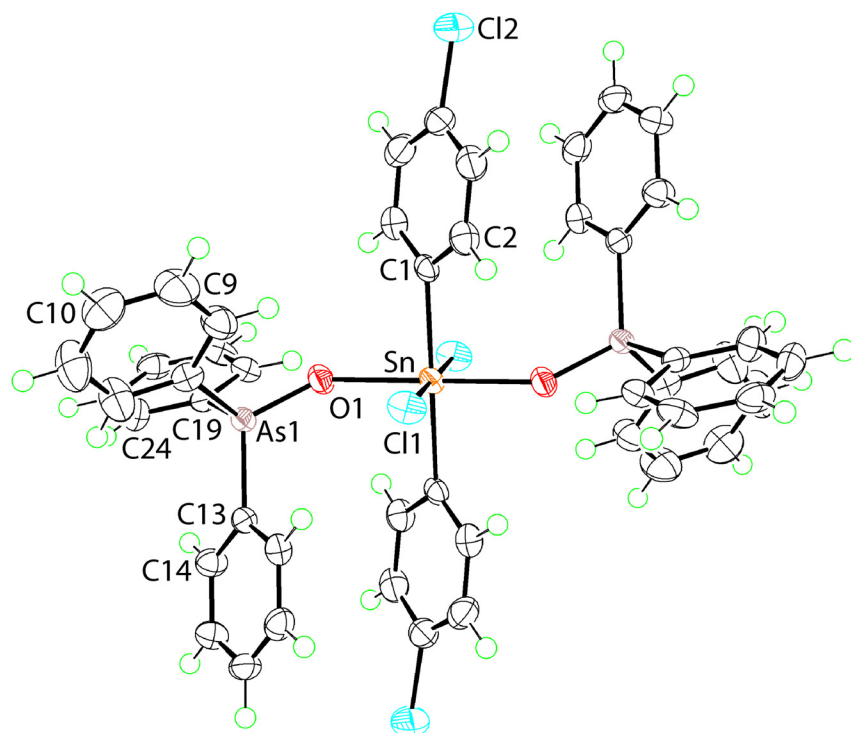


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# Crystal structure of dichlorido-bis(4-chlorophenyl- $\kappa$ C)-bis(triphenylarsine oxide- $\kappa$ O)tin(IV), $C_{48}H_{38}As_2Cl_4O_2Sn$



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## Abstract

$C_{48}H_{38}As_2Cl_4O_2Sn$ , monoclinic,  $P2_1/n$  (no. 14),  $a = 10.8019(1)$  Å,  $b = 14.6976(1)$  Å,  $c = 13.6266(1)$  Å,  $\beta = 90.983(1)^\circ$ ,  $V = 2163.07(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $R_{gt}(F) = 0.0199$ ,  $wR_{ref}(F^2) = 0.0514$ ,  $T = 100$  K.

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The molecular structure is shown in Figure. 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	0.17 × 0.08 × 0.05 mm
Wavelength:	Cu K $\alpha$ radiation (1.54184 Å)
$\mu$ :	8.98 mm <sup>-1</sup>
Diffractometer, scan mode:	XtaLAB Synergy, $\omega$
$\theta_{max}$ , completeness:	67.1°, >99%
$N(hkl)_{measured}$ , $N(hkl)_{unique}$ , $R_{int}$ :	27,906, 3862, 0.033
Criterion for $I_{obs}$ , $N(hkl)_{gt}$ :	$I_{obs} > 2\sigma(I_{obs})$ , 3740
$N(param)_{refined}$ :	259
Programs:	CrysAlis <sup>PRO</sup> [1], SHELX [2, 3], WinGX/ORTEP [4]

## Source of material

4-Chlorophenylmagnesium bromide was prepared from the Grignard reaction of magnesium (Merck) and 4-bromochlorobenzene (Fluka) conducted in tetrahydrofuran. Tetra(4-chlorophenyl)tin was synthesised from the reaction of stannic chloride (Fluka) with

**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>).

Atom	x	y	z	<i>U</i> <sub>iso</sub> */ <i>U</i> <sub>eq</sub>
Sn	0.500000	0.500000	0.500000	0.01548 (6)
As	0.33355 (2)	0.55829 (2)	0.72391 (2)	0.01507 (7)
Cl1	0.67305 (4)	0.46365 (3)	0.62143 (3)	0.02407 (11)
Cl2	0.37653 (6)	0.06412 (4)	0.41341 (5)	0.04122 (15)
O1	0.36794 (13)	0.51268 (9)	0.61576 (10)	0.0210 (3)
C1	0.45751 (18)	0.35727 (12)	0.48995 (13)	0.0171 (4)
C2	0.55420 (19)	0.29428 (14)	0.47827 (14)	0.0226 (4)
H2	0.637669	0.313991	0.485059	0.027*
C3	0.5292 (2)	0.20371 (14)	0.45695 (15)	0.0259 (4)
H3	0.594780	0.161476	0.448592	0.031*
C4	0.4074 (2)	0.17611 (13)	0.44812 (15)	0.0269 (5)
C5	0.3103 (2)	0.23531 (15)	0.46423 (15)	0.0268 (4)
H5	0.227027	0.214600	0.460999	0.032*
C6	0.33725 (18)	0.32578 (14)	0.48524 (14)	0.0214 (4)
H6	0.271223	0.366939	0.496644	0.026*
C7	0.36874 (17)	0.46888 (13)	0.82239 (14)	0.0197 (4)
C8	0.4180 (2)	0.38646 (14)	0.79338 (16)	0.0293 (5)
H8	0.434378	0.374948	0.726240	0.035*
C9	0.4431 (2)	0.32091 (16)	0.86433 (19)	0.0376 (5)
H9	0.476946	0.263998	0.845540	0.045*
C10	0.4193 (2)	0.33752 (16)	0.96161 (18)	0.0358 (5)
H10	0.436081	0.291896	1.009401	0.043*
C11	0.3709 (3)	0.42069 (18)	0.99009 (18)	0.0401 (6)
H11	0.354660	0.432126	1.057260	0.048*
C12	0.3465 (2)	0.48692 (16)	0.92023 (17)	0.0334 (5)
H12	0.314754	0.544417	0.939288	0.040*
C13	0.42003 (17)	0.66765 (13)	0.76029 (13)	0.0174 (4)
C14	0.35395 (19)	0.74511 (13)	0.78554 (15)	0.0225 (4)
H14	0.265991	0.744577	0.784315	0.027*
C15	0.4185 (2)	0.82360 (14)	0.81269 (15)	0.0257 (4)
H15	0.374187	0.876804	0.830402	0.031*
C16	0.5458 (2)	0.82444 (14)	0.81398 (15)	0.0255 (4)
H16	0.589183	0.878195	0.832411	0.031*
C17	0.61130 (19)	0.74669 (14)	0.78833 (14)	0.0241 (4)
H17	0.699243	0.747830	0.788734	0.029*
C18	0.54907 (18)	0.66756 (13)	0.76218 (14)	0.0200 (4)
H18	0.593701	0.614130	0.745811	0.024*
C19	0.15911 (17)	0.58243 (12)	0.71498 (14)	0.0168 (4)
C20	0.10286 (18)	0.57105 (13)	0.62314 (15)	0.0205 (4)
H20	0.150685	0.555464	0.567744	0.025*
C21	-0.02398 (19)	0.58282 (14)	0.61387 (16)	0.0254 (4)
H21	-0.063742	0.574145	0.551850	0.031*
C22	-0.09342 (19)	0.60717 (14)	0.69434 (16)	0.0255 (4)
H22	-0.180425	0.614961	0.687312	0.031*
C23	-0.03613 (19)	0.62016 (15)	0.78506 (15)	0.0258 (4)
H23	-0.083693	0.638102	0.839770	0.031*
C24	0.09033 (19)	0.60703 (14)	0.79611 (15)	0.0231 (4)
H24	0.129638	0.614766	0.858448	0.028*

4-chlorophenylmagnesium bromide in a 1:4 molar ratio. Subsequently, di(4-chlorophenyl)tin dichloride was synthesised from the comproportionation reaction of tetra(4-chlorophenyl)tin with stannic chloride (Fluka) in

a 1:1 molar ratio to obtain a white precipitate. Di(4-chlorophenyl)tin dichloride (0.42 g, 1 mmol) and triphenylarsine oxide (Sigma, 0.65 g, 2 mmol) were dissolved separately in ethanol (50 mL) and mixed to give a white precipitate. The white precipitate was recrystallised from methanol and colourless crystals were obtained from the slow evaporation of the solvent. Yield: 0.71 g (67.2%). **M.p** (Stuart SMP30 digital melting point apparatus; uncorrected): 496–499 K. **IR** (Bruker Vertex 70v FTIR Spectrometer; cm<sup>-1</sup>): 1085 (m) ν(C–C), 995 (m) ν(As–O), 472 (w) ν(Sn–O). **<sup>1</sup>H NMR** (Bruker Ascend 400 MHz NMR spectrometer; CDCl<sub>3</sub>; ppm relative to Me<sub>4</sub>Si): 7.13–7.61 (m, 34H, Ph–H), 8.02 (d, 4H, Ph–H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (as for <sup>1</sup>H NMR): 127.4, 127.9, 129.4, 130.9, 131.7, 132.5, 135.3, 137.4 (Ph–C).

## Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95 Å) and refined as riding with *U*<sub>iso</sub>(H) = 1.2–1.5*U*<sub>eq</sub>(C).

## Comment

The majority of mononuclear triorganoarsine adducts of organotin halides have been shown by X-ray crystallography to fall into two distinct structural motifs, namely five-coordinate, trigonal-bipyramidal for triorganotin mono-halide species (4-MeC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>3</sub>SnCl(O=AsPh<sub>3</sub>) [5], (4-ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>3</sub>SnCl(O=AsPh<sub>3</sub>) [6], Ph<sub>3</sub>SnCl(O=AsPh<sub>3</sub>) [7], (4-ClC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>SnCl(O=AsPh<sub>3</sub>) [7] and Ph<sub>3</sub>SnBr(O=AsPh<sub>3</sub>) [8], and a rarer, recently described six-coordinate, distorted octahedral species (4-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SnCl<sub>2</sub>(O=AsPh<sub>3</sub>)<sub>2</sub> [9] for a diorganotin dihalide. In continuation of studies in this area, a new six-coordinate species, the title compound (4-ClC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SnCl<sub>2</sub>(O=AsPh<sub>3</sub>)<sub>2</sub>, hereafter (I), was determined with details described herein.

The molecular structure of (I) is shown in the Figure (70% displacement ellipsoids); the tin(IV) centre is located on an inversion centre. The tin atom is coordinated by two chlorido atoms, two oxido atoms of the Ph<sub>3</sub>As=O molecules and two ipso-carbon atoms derived from the 4-chlorophenyl groups. The, *all-trans*-C<sub>2</sub>Cl<sub>2</sub>O<sub>2</sub> donor set defines an approximate octahedral geometry. The Sn–O1–As1 angle, at 147.48(8)°, is bent in accord with expectation. The Sn–Cl1, Sn–O1 and Sn–C1 bond lengths are 2.5321(4), 2.1530(13) and 2.1513(18) Å, respectively. The comparable bond lengths in the isostructural methyl derivative, i.e. (4-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SnCl<sub>2</sub>(O=AsPh<sub>3</sub>)<sub>2</sub> [9], are 2.5500(4), 2.1667(14) and 2.139(2) Å, respectively,

indicating the Sn–Cl and Sn–O bond lengths are systematically longer, an observation related to the electron-donating nature of the 4-tolyl substituents, compared with the electron-withdrawing nature of the 4-chlorophenyl groups of (I).

The most prominent intermolecular interactions in the crystal of (I) are  $\pi(\text{chlorophenyl})\cdots\pi(\text{As-phenyl})$  [ $Cg(C1-C6)\cdots Cg(C13-C18)^i = 3.6455(11)$  Å, angle =  $5.10(9)^\circ$  and slippage =  $1.3$  Å for symmetry operation (i)  $1-x, 1-y, 1-z$ ] and  $\text{As-phenyl-C-H}\cdots\pi(\text{As-phenyl})$  [ $C9-H9\cdots Cg(C19-C24)^{ii} = 2.58$  Å with angle at H9 =  $155^\circ$ , and  $C10-H10\cdots Cg(C13-C18)^{iii} = 2.94$  Å with angle at H10 =  $146^\circ$  for (ii):  $1/2-x, -1/2+y, 3/2-z$  and (iii):  $1-x, 1-y, 2-z$ ]. These interactions extend in three-dimensions in the crystal. In isostructural  $(4\text{-MeC}_6\text{H}_4)_2\text{SnCl}_2(\text{O}=\text{AsPh}_3)_2$  [9], comparable  $\pi(4\text{-methylphenyl})\cdots\pi(\text{As-phenyl})$  and  $\text{As-phenyl-C-H}\cdots\pi(\text{As-phenyl})$  contacts are evident in the crystal.

To conduct a further comparison between the isostructural compounds (I) and the 4-tolyl analogue [9], the Hirshfeld surface contacts were calculated along with the two-dimensional fingerprint plots (full and delineated into individual contacts) employing Crystal Explorer 17 [10] following literature protocols [11]. The calculations on (I) showed a predominance of  $\text{H}\cdots\text{H}$  contacts, contributing 48.2% to the overall surface contacts, followed by  $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$  [32.4%] and  $\text{Cl}\cdots\text{H}/\text{H}\cdots\text{Cl}$  [15.6%] contacts. These values compare with 58.7, 33.1 and 7.0%, respectively, calculated for the 4-tolyl analogue [9], showing reduced and enhanced contributions from  $\text{H}\cdots\text{H}$  and  $\text{Cl}\cdots\text{H}/\text{H}\cdots\text{Cl}$  contacts, respectively. Further reflecting the additional chloride substituents in the crystal of (I),  $\text{Cl}\cdots\text{C}/\text{C}\cdots\text{Cl}$  [1.8%] and  $\text{Cl}\cdots\text{Cl}$  [1.1%] contacts are also noted.

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