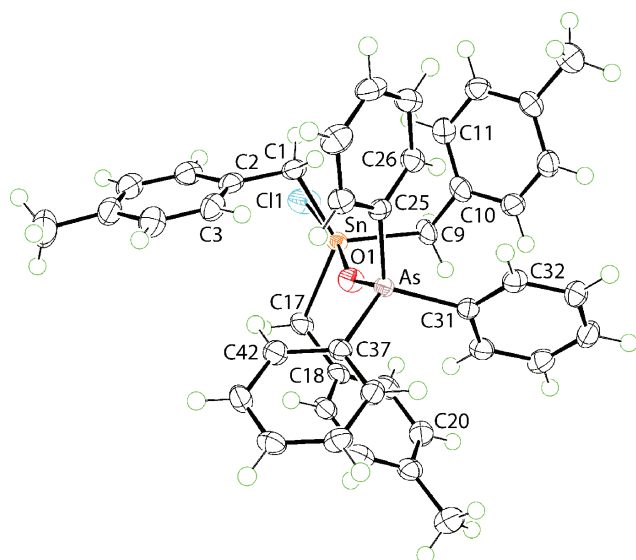


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# Crystal structure of chlorido-tris(4-methylbenzyl- $\kappa C$ )-(triphenylarsine oxide- $\kappa O$ )tin(IV), $C_{42}H_{42}AsClOSn$



**Table 1:** Data collection and handling.

Crystal:	Colourless prism
Size:	0.15 × 0.09 × 0.06 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
$\mu$ :	7.58 mm <sup>-1</sup>
Diffractometer, scan mode:	XtaLAB Synergy, $\omega$
$\theta_{\max}$ , completeness:	67.1°, >99%
$N(hkl)_{\text{measured}}$ , $N(hkl)_{\text{unique}}$ , $R_{\text{int}}$ :	43809, 6436, 0.032
Criterion for $I_{\text{obs}}$ , $N(hkl)_{\text{gt}}$ :	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$ , 6274
$N(\text{param})_{\text{refined}}$ :	418
Programs:	CrysAlis <sup>PRO</sup> [1], SHELX [2, 3], WinGX/ORTEP [4]

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Sn	0.52984(2)	0.17358(2)	0.85374(2)	0.01452(4)
As	0.45399(2)	0.40968(2)	0.71793(2)	0.01291(5)
Cl1	0.59826(3)	0.01332(4)	0.93590(3)	0.02912(10)
O1	0.46934(7)	0.28693(11)	0.76795(6)	0.0192(2)
C1	0.61765(10)	0.15021(16)	0.78014(10)	0.0195(4)
H1A	0.625008	0.227028	0.754728	0.023*
H1B	0.666676	0.129331	0.808214	0.023*
C2	0.59725(10)	0.05389(16)	0.72564(10)	0.0200(4)
C3	0.55775(11)	0.08061(17)	0.65882(10)	0.0226(4)
H3	0.544896	0.161813	0.647309	0.027*
C4	0.53686(11)	-0.00906(18)	0.60882(11)	0.0272(4)
H4	0.509277	0.011889	0.564083	0.033*
C5	0.55549(11)	-0.12918(18)	0.62284(11)	0.0272(4)
C6	0.59635(11)	-0.15533(17)	0.68870(12)	0.0271(4)
H6	0.611222	-0.236097	0.699172	0.033*
C7	0.61603(10)	-0.06655(17)	0.73964(11)	0.0239(4)
H7	0.642690	-0.087994	0.784724	0.029*
C8	0.53099(14)	-0.2265(2)	0.56898(13)	0.0393(5)
H8A	0.572566	-0.284982	0.567108	0.059*
H8B	0.519099	-0.190584	0.521033	0.059*
H8C	0.485396	-0.267103	0.583804	0.059*
C9	0.54611(11)	0.31694(16)	0.93253(9)	0.0205(4)
H9A	0.495309	0.352064	0.938951	0.025*
H9B	0.565781	0.280922	0.979396	0.025*
C10	0.59830(10)	0.41647(17)	0.91632(9)	0.0200(4)
C11	0.67408(10)	0.39611(17)	0.90110(9)	0.0209(4)
H11	0.692607	0.315901	0.899872	0.025*

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## Abstract

$C_{42}H_{42}AsClOSn$ , monoclinic,  $P2_1/n$  (no. 14),  $a = 17.5342(1)$  Å,  $b = 11.1174(1)$  Å,  $c = 18.5675(1)$  Å,  $\beta = 95.405(1)^\circ$ ,  $V = 3603.36(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $R_{\text{gt}}(F) = 0.0184$ ,  $wR_{\text{ref}}(F^2) = 0.0465$ ,  $T = 100(2)$  K.

**CCDC no.:** 1981098

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.

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Table 2 (continued)

Atom	x	y	z	$U_{iso}^*/U_{eq}$
C12	0.72262(10)	0.49056(17)	0.88781(10)	0.0211(4)
H12	0.774017	0.473965	0.878804	0.025*
C13	0.69715(10)	0.60937(17)	0.88745(10)	0.0215(4)
C14	0.62192(10)	0.63036(17)	0.90212(10)	0.0222(4)
H14	0.603171	0.710530	0.902194	0.027*
C15	0.57371(10)	0.53574(17)	0.91669(9)	0.0214(4)
H15	0.522827	0.552817	0.927143	0.026*
C16	0.74866(12)	0.71236(19)	0.87188(12)	0.0318(4)
H16A	0.750143	0.720424	0.819467	0.048*
H16B	0.800472	0.696937	0.894599	0.048*
H16C	0.728961	0.786856	0.891406	0.048*
C17	0.42186(10)	0.07919(15)	0.85301(10)	0.0205(4)
H17A	0.414345	0.029213	0.808776	0.025*
H17B	0.423953	0.024578	0.895263	0.025*
C18	0.35457(10)	0.16240(15)	0.85531(10)	0.0175(3)
C19	0.33787(10)	0.21684(16)	0.91982(10)	0.0208(4)
H19	0.369938	0.201437	0.962975	0.025*
C20	0.27536(11)	0.29299(17)	0.92215(10)	0.0225(4)
H20	0.265075	0.327747	0.966963	0.027*
C21	0.22742(10)	0.31940(16)	0.85995(11)	0.0220(4)
C22	0.24428(10)	0.26578(17)	0.79544(10)	0.0219(4)
H22	0.212767	0.282430	0.752133	0.026*
C23	0.30614(10)	0.18863(16)	0.79328(10)	0.0193(4)
H23	0.315788	0.152814	0.748576	0.023*
C24	0.16105(12)	0.40462(19)	0.86216(13)	0.0330(5)
H24A	0.148089	0.412805	0.912129	0.050*
H24B	0.116705	0.373109	0.831921	0.050*
H24C	0.175122	0.483474	0.843877	0.050*
C25	0.54415(9)	0.45079(15)	0.67217(9)	0.0153(3)
C26	0.60873(10)	0.48629(15)	0.71676(9)	0.0182(3)
H26	0.606385	0.494102	0.767453	0.022*
C27	0.67642(10)	0.51007(16)	0.68625(10)	0.0215(4)
H27	0.720734	0.534117	0.716172	0.026*
C28	0.67954(10)	0.49883(17)	0.61223(11)	0.0237(4)
H28	0.725920	0.515765	0.591590	0.028*
C29	0.61521(11)	0.46293(18)	0.56807(10)	0.0252(4)
H29	0.617824	0.454844	0.517428	0.030*
C30	0.54690(10)	0.43878(16)	0.59792(9)	0.0201(4)
H30	0.502718	0.414396	0.567921	0.024*
C31	0.42834(9)	0.54320(15)	0.77577(9)	0.0159(3)
C32	0.45952(10)	0.65618(16)	0.76556(10)	0.0179(3)
H32	0.490348	0.669758	0.726934	0.022*
C33	0.44507(10)	0.74905(16)	0.81250(10)	0.0215(4)
H33	0.467075	0.826135	0.806717	0.026*
C34	0.39867(10)	0.72939(17)	0.86766(10)	0.0234(4)
H34	0.388679	0.793228	0.899457	0.028*
C35	0.36658(10)	0.61662(18)	0.87676(10)	0.0228(4)
H35	0.334297	0.603987	0.914379	0.027*
C36	0.38159(10)	0.52248(16)	0.83107(9)	0.0193(4)
H36	0.360283	0.445071	0.837430	0.023*
C37	0.37291(9)	0.37674(16)	0.64442(9)	0.0155(3)
C38	0.31917(10)	0.46473(16)	0.62303(9)	0.0185(3)
H38	0.321975	0.541872	0.645134	0.022*
C39	0.26135(10)	0.43858(17)	0.56900(9)	0.0207(4)
H39	0.224091	0.497843	0.554215	0.025*
C40	0.25790(10)	0.32629(17)	0.53662(10)	0.0206(4)

Table 2 (continued)

Atom	x	y	z	$U_{iso}^*/U_{eq}$
H40	0.218544	0.309246	0.499289	0.025*
C41	0.31137(10)	0.23852(17)	0.55821(10)	0.0219(4)
H41	0.308582	0.161624	0.535804	0.026*
C42	0.36907(10)	0.26332(16)	0.61273(10)	0.0194(4)
H42	0.405559	0.203312	0.628212	0.023*

### Source of material

Tri(4-methylbenzyl)tin chloride was prepared from the direct reaction of 4-methylbenzyl chloride (Merck) and metallic tin powder (Merck) in water according to a literature procedure [5]. Tri(4-methylbenzyl)tin chloride (0.47 g, 1.0 mmol) and triphenylarsine oxide (Sigma-Aldrich, 0.32 g, 1.0 mmol) were heated in 95% ethanol (30 ml) for 1 h. After filtration, the filtrate was evaporated slowly until colourless crystals were formed. Yield: 0.45 g (56.8%). **M.pt** (Mel-temp II digital melting point apparatus): 345–347 K. **<sup>1</sup>H NMR** (Bruker Ascend 400 MHz NMR spectrometer; CDCl<sub>3</sub>; ppm relative to Me<sub>4</sub>Si): δ 2.27 (s, 9H, CH<sub>3</sub>), 2.62 (s, 6H, CH<sub>2</sub>), 6.74 (d, 6H, *J* = 745 Hz, Benzyl-H), 6.89 (d, 6H, *J* = 748 Hz, Benzyl-H), 7.44–7.62 (m, 15H, Ph-H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (as for <sup>1</sup>H NMR): 20.9 (CH<sub>3</sub>), 28.5 (CH<sub>2</sub>), 128.1, 128.7, 129.0, 129.3, 131.1, 131.7, 133.6, 136.4 (Ph-C). **<sup>119</sup>Sn{<sup>1</sup>H} NMR** (as for <sup>1</sup>H with ppm relative to Me<sub>4</sub>Sn): –227.8.

### Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–0.99 Å) and refined as riding with  $U_{iso}(H) = 1.2–1.5U_{eq}(C)$ .

### Comment

Recently, the X-ray crystal structure determination of an tri-organosarsine oxide adduct of an organotin halide species was described, namely six-coordinate (4-MePh)<sub>2</sub>SnCl<sub>2</sub>(O=AsPh<sub>3</sub>)<sub>2</sub> [6]. This study complemented a relatively small number of known literature precedents. Hexa-coordinate tin centres are also noted in the one-dimensional coordination polymer  $\{[(n\text{-Bu})_2\text{SnCl}_2]\text{O}=\text{As}(\text{Ph}_2)\text{CH}_2\text{CH}_2\text{As}(\text{Ph}_2)=\text{O}[(n\text{-Bu})_2\text{SnCl}_2]\}_n$ , [7]. The remaining structures exhibit five-coordinate tin centres, i.e. mononuclear (4-ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>3</sub>SnCl(O=AsPh<sub>3</sub>) [8], Ph<sub>3</sub>SnCl<sub>2</sub>(O=AsPh<sub>3</sub>) [9] and (4-ClC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>SnCl(O=AsPh<sub>3</sub>) [9], and binuclear (Ph<sub>3</sub>SnCl)O=As(Ph<sub>2</sub>)CH<sub>2</sub>CH<sub>2</sub>As(Ph<sub>2</sub>)=O(Ph<sub>3</sub>SnCl) [10]. Herein, in continuation of structural studies in this area [6, 9], the crystal and molecular structures of the triphenylarsine oxide adduct of tri(4-methylbenzyl)tin chloride, (4-MeC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>3</sub>SnCl(O=AsPh<sub>3</sub>), (I), are described.

The molecular structure of (I) is shown in the figure (70% displacement ellipsoids) and features a penta-coordinated tin

centre, within a distorted trigonal bipyramidal geometry. The three positions in the trigonal plane are occupied by the three tin-bound 4-methylbenzyl substituents with the range of C–Sn–C angles being a narrow 117.26(7)°, for C1–Sn–C9, to a wide 127.65(7)°, for C1–Sn–C17. The axial positions are occupied by chloride [2.5683(4) Å] and oxido-O1 [2.2209(11) Å] atoms, which subtend an angle of 169.90(3)° at the tin centre. The arsenic atom is tetrahedrally coordinated with the range of tetrahedral angles being narrow, i.e. 108.13(7)°, for C25–As–C31, to 111.03(7)°, for O1–As–C31. The angle subtended at the oxido-O1 atom is bent, i.e. Sn–O1–As = 155.50(7)°. When viewed down the approximate spine of the molecule, the conformation of the aryl substituents is relatively close to eclipsed, as opposed to staggered.

There are three closely related literature precedents to (I), namely (4-ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>3</sub>SnCl(O=AsPh<sub>3</sub>) [8], Ph<sub>3</sub>SnCl<sub>2</sub>(O=AsPh<sub>3</sub>) [9] and (4-ClC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>SnCl(O=AsPh<sub>3</sub>) [9]. Not unexpectedly, these feature very similar coordination geometries. Indeed, (I) and (4-ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>3</sub>SnCl(O=AsPh<sub>3</sub>) [8] are isostructural.

The molecular packing in the crystal of (I) features non-covalent interactions of the type C–H···π but, no other directional contacts [11]. The C–H···π interactions involve 4-tolyl and 4-tolyl [C12–H12···Cg(C2–C7)<sup>i</sup>: H12···Cg(C2–C7)<sup>i</sup> = 2.89 Å C12···Cg(C2–C7)<sup>i</sup> = 3.8174(19) Å with angle at H12 = 167° for symmetry operation (i) 3/2 – x, 1/2 + y, 3/2 – z], 4-tolyl and arsenic-bound phenyl [C22–H22···Cg(C31–C36)<sup>ii</sup>: H22···Cg(C31–C36)<sup>ii</sup> = 2.97 Å, C22···Cg(C31–C36)<sup>ii</sup> = 3.647(2) Å with angle at H22 = 129° for (ii) 1/2 – x, –1/2 + y, 3/2 – z] and arsenic-bound phenyl and 4-tolyl [C38–H38···Cg(C18–C23)<sup>iii</sup>: H38···Cg(C18–C23)<sup>iii</sup> = 2.97 Å; C38···Cg(C18–C23)<sup>iii</sup> = 3.6634(19) Å with angle at H38 = 131° for (iii) 1/2 – x, 1/2 + y, 3/2 – z] as donors and acceptors. The C–H···π interactions connect molecules into a supramolecular layer in the *ab*-plane; these stack along the *c*-axis without directional interactions between them.

A further analysis of the molecular packing of (I) was conducted with aid of the program Crystal Explorer 17 [11] using standard procedures [12]. Thus, the Hirshfeld surfaces were calculated along with the full and decomposed two-dimensional fingerprint plots. This analysis indicated the dominance of three types of surface contacts operating in the crystal of (I), namely H···H [68.6%], C···H/H···C [25.3%] and Cl···H/H···Cl [6.1%]. A similar study was performed on isostructural (4-ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>3</sub>SnCl(O=AsPh<sub>3</sub>) (II) [8]. This showed, again, the dominance of H···H [43.3%], C···H/H···C [21.9%] and Cl···H/H···Cl [28.3%] contacts to the surface plus smaller contributions by Cl···C/C···Cl

[5.5%] and Cl···Cl [1.0%] contacts. In the crystal of (II), the decrease in H···H and C···H/H···C contacts is accompanied by an increase in Cl···H/H···Cl contacts, compared with (I). However, the latter occur at longer separations than the sum of the van der Waals radii, i.e. 2.95 Å [13], indicating their minimal participation in directional interactions, consistent with the isostructural relationship between (I) and (II).

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