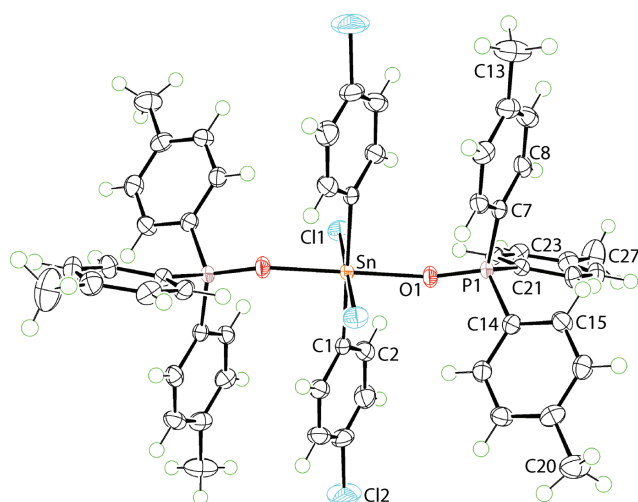


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# Crystal structure of dichlorido-bis(tri-4-tolylphosphane oxide- $\kappa O$ )-di(4-chlorophenyl- $\kappa C$ ) tin(IV), $C_{54}H_{50}Cl_4O_2P_2Sn$



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

Crystal:	Colourless prism
Size:	0.16 × 0.09 × 0.07 mm
Wavelength:	Cu K $\alpha$ radiation (1.54184 Å)
$\mu$ :	6.94 mm <sup>-1</sup>
Diffractometer, scan mode:	XtaLAB Synergy, $\omega$
$\theta_{\max}$ , completeness:	67.1°, >99%
$N(hkl)_{\text{measured}}$ , $N(hkl)_{\text{unique}}$ , $R_{\text{int}}$ :	29831, 4456, 0.031
Criterion for $I_{\text{obs}}$ , $N(hkl)_{\text{gt}}$ :	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$ , 4442
$N(\text{param})_{\text{refined}}$ :	289
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	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Sn	0.5	0.5	0.5	0.01135(6)
Cl1	0.48213(4)	0.28146(4)	0.39601(3)	0.02058(9)
Cl2	−0.10294(5)	0.14634(6)	0.60456(5)	0.04445(14)
P1	0.72827(4)	0.49620(4)	0.77255(3)	0.01281(9)
O1	0.60867(12)	0.45710(11)	0.65899(9)	0.0167(2)
C1	0.30138(16)	0.38557(17)	0.52719(13)	0.0152(3)
C2	0.27049(18)	0.25421(18)	0.54681(15)	0.0208(3)
H2	0.335669	0.214778	0.544315	0.025*
C3	0.1460(2)	0.1796(2)	0.57000(16)	0.0260(4)
H3	0.126456	0.090463	0.584241	0.031*
C4	0.05127(19)	0.2377(2)	0.57192(15)	0.0257(4)
C5	0.07686(19)	0.36607(19)	0.55054(15)	0.0238(4)
H5	0.009405	0.403466	0.550625	0.029*
C6	0.20254(18)	0.44062(18)	0.52878(14)	0.0189(3)
H6	0.221385	0.529821	0.514866	0.023*
C7	0.90243(17)	0.60417(16)	0.76815(13)	0.0147(3)
C8	1.00713(17)	0.55561(17)	0.76938(14)	0.0177(3)
H8	0.991071	0.465798	0.780436	0.021*
C9	1.13457(18)	0.63917(18)	0.75439(15)	0.0215(4)
H9	1.205633	0.605861	0.756214	0.026*
C10	1.16047(18)	0.77025(18)	0.73682(15)	0.0215(4)
C11	1.05491(18)	0.81763(17)	0.73533(14)	0.0199(3)
H11	1.070937	0.907234	0.723679	0.024*
C12	0.92714(17)	0.73581(17)	0.75062(14)	0.0171(3)
H12	0.856420	0.769460	0.749156	0.020*
C13	1.2985(2)	0.8581(2)	0.7189(2)	0.0342(5)
H13A	1.375140	0.907273	0.792849	0.051*

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## Abstract

$C_{54}H_{50}Cl_4O_2P_2Sn$ , triclinic,  $P\bar{1}$  (no. 2),  $a = 10.6360(2)$  Å,  $b = 10.8406(2)$  Å,  $c = 12.5727(2)$  Å,  $\alpha = 94.152(1)^\circ$ ,  $\beta = 107.195(2)^\circ$ ,  $\gamma = 112.549(2)^\circ$ ,  $V = 1250.31(4)$  Å<sup>3</sup>,  $Z = 1$ ,  $R_{\text{gt}}(F) = 0.0194$ ,  $wR_{\text{ref}}(F^2) = 0.0529$ ,  $T = 100(2)$  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 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub> <sup>*</sup> / <i>U</i> <sub>eq</sub>
H13B	1.281534	0.924005	0.673803	0.051*
H13C	1.328611	0.800314	0.678271	0.051*
C14	0.69504(17)	0.58366(16)	0.88010(14)	0.0151(3)
C15	0.80447(17)	0.65539(17)	0.98559(14)	0.0186(3)
H15	0.899399	0.660442	1.000256	0.022*
C16	0.77508(18)	0.71882(17)	1.06839(15)	0.0200(3)
H16	0.849930	0.766306	1.139898	0.024*
C17	0.63699(19)	0.71408(16)	1.04843(15)	0.0195(3)
C18	0.52886(18)	0.64266(17)	0.94330(15)	0.0196(3)
H18	0.434222	0.638382	0.928598	0.024*
C19	0.55643(17)	0.57766(16)	0.85961(14)	0.0173(3)
H19	0.481088	0.529183	0.788529	0.021*
C20	0.6072(2)	0.7870(2)	1.13763(17)	0.0288(4)
H20A	0.516807	0.796357	1.102680	0.043*
H20B	0.687805	0.877764	1.171161	0.043*
H20C	0.597698	0.734312	1.197247	0.043*
C21	0.73420(16)	0.34161(16)	0.81115(13)	0.0147(3)
C22	0.67015(17)	0.22399(17)	0.72528(14)	0.0174(3)
H22	0.624531	0.226779	0.648705	0.021*
C23	0.67350(18)	0.10320(17)	0.75236(15)	0.0205(3)
H23	0.629173	0.023360	0.693830	0.025*
C24	0.74065(18)	0.09702(17)	0.86372(15)	0.0214(4)
C25	0.80076(18)	0.21415(18)	0.94902(15)	0.0208(3)
H25	0.844146	0.210667	1.025852	0.025*
C26	0.79813(17)	0.33527(17)	0.92337(14)	0.0183(3)
H26	0.839986	0.414269	0.982389	0.022*
C27	0.7512(3)	−0.0317(2)	0.89280(19)	0.0399(5)
H27A	0.675880	−0.110302	0.833045	0.060*
H27B	0.737259	−0.042571	0.965779	0.060*
H27C	0.847232	−0.025965	0.898517	0.060*

### Source of material

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 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. Tri (4-tolyl)phosphine oxide was prepared by the oxidation of tri(4-tolyl)phosphine (Merck) with 30% hydrogen peroxide (Merck) in ethanol. Di(4-chlorophenyl)tin dichloride (0.41 g, 1.0 mmol) and tri(4-tolyl)phosphine oxide (0.64 g, 2.0 mmol) were heated in 95% ethanol (50 mL) for 1 h. After filtration, the filtrate was evaporated slowly until a white crystalline compound was formed. Yield: 0.49 g (46.5%). **M. pt** (Stuart SMP30 digital melting point apparatus; uncorrected): 468–470 K. **IR** (Bruker Vertex 70v FTIR Spectrometer; cm<sup>−1</sup>): 1599 (m) ν(C=C), 1475 (m) ν(C=C), 1149 (s) ν(P=O), 1089 (s)

ν(P–Ar), 810 (s) ν(C–Cl). **<sup>1</sup>H NMR** (Bruker Ascend 400 MHz NMR spectrometer; CDCl<sub>3</sub>; ppm relative to Me<sub>4</sub>Si): δ 2.39 (s, 18H, CH<sub>3</sub>), 7.20–7.26 (m, 16H, Ph-H), 7.36–7.42 (m, 12H, Ph-H), 7.82 (d, *J* = 8.53 Hz, 4H, Ph-H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (as for <sup>1</sup>H NMR): 21.6 (CH<sub>3</sub>), 126.9, 128.5, 129.3, 131.9, 132.2, 135.9, 136.7, 143.0 (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*<sub>iso</sub>(H) = 1.2–1.5*U*<sub>eq</sub>(C).

### Comment

While recent attention has been devoted to evaluating the molecular structures of bis(sulphoxide) [5] and bis(triorganoarsane) [6] adducts of R<sub>2</sub>SnCl<sub>2</sub> molecules, reflecting a long-term interest [7], investigations now turn to bis(triorganophosphane) adducts of R<sub>2</sub>SnCl<sub>2</sub>. Despite their rather simple preparation and structures, there are only relatively few mononuclear structures available for these compounds, namely Me<sub>2</sub>SnCl<sub>2</sub>[O=P(4-tolyl)<sub>3</sub>]<sub>2</sub> [8], Et<sub>2</sub>SnCl<sub>2</sub>[O=PPh<sub>3</sub>]<sub>2</sub> [9], Ph<sub>2</sub>SnCl<sub>2</sub>[O=PPh<sub>3</sub>]<sub>2</sub> [10], Ph<sub>2</sub>SnCl<sub>2</sub>[O=P(tBu)<sub>2</sub>Me]<sub>2</sub> [11] and Ph<sub>2</sub>SnCl<sub>2</sub>[O=P(Cy)<sub>2</sub>C(=S)N(H)Ph]<sub>2</sub> [7]. The common feature of the crystallographically determined structures is an all-*trans* C<sub>2</sub>Cl<sub>2</sub>O<sub>2</sub> coordination geometry for Sn. Herein, the crystal and molecular structures of (4-ClC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SnCl<sub>2</sub>[O=P(4-tolyl)<sub>3</sub>]<sub>2</sub>, (I), are described, as an extension of these studies.

The molecular structure of (I) is shown in the figure (70% displacement ellipsoids; unlabelled atoms are related by the symmetry operation (i) 1 − *x*, 1 − *y*, 1 − *z*). The Sn atom is located on a centre of inversion and, as anticipated, is octahedrally coordinated by ipso-C [2.1441(15) Å], Cl [2.5333(4) Å] and oxide-O [2.1746(11) Å] atoms. The Sn–O1–P1 angle is 152.99(7)° indicating a significant deviation from linearity. By virtue of the Sn atom being located on a centre of inversion, when the molecule is viewed down the O1–Sn–O1<sup>i</sup> axis, the phenyl rings have a staggered arrangement. Finally, a pair of Sn- and P-bound rings face each other in the molecule, being indicative of an intramolecular π⋯π stacking interaction; the inter-centroid separation is 3.7847(10) Å with an angle of inclination = 3.73(8)°.

The most closely related structure in the literature is of the analogue where the 4-chlorophenyl substituents of (I) are replaced by methyl groups [8]. In this case, the Sn–C [2.1168(15) Å], Sn–Cl [2.5735(4) Å] and Sn–O [2.2387(11) Å] bond lengths have contracted, elongated and elongated, respectively, consistent with the relatively electropositive nature of the methyl substituents compared to the electronegative 4-chlorophenyl groups in (I).

Non-covalent interactions dominate the packing with the only apparent directional interactions being of the type methyl-C—H $\cdots\pi$ (phenyl-P) [C20—H20a $\cdots$ Cg(C21—C26)<sup>ii</sup>: H20a $\cdots$ Cg(C21—C26)<sup>ii</sup> = 2.95 Å with angle at H20a = 138° for (ii) 1 − x, 1 − y, 2 − z] and P-phenyl-C—H $\cdots\pi$ (chlorophenyl) [C25—H25 $\cdots$ Cg(C7—C12)<sup>iii</sup>: H25 $\cdots$ Cg(C7—C12)<sup>iii</sup> = 2.65 Å with angle at H25 = 154° for (iii) 2 − x, 1 − y, 2 − z]. These contacts lead to a supramolecular layer in the ac-plane. The layers stack along the b-axis without directional interactions between them. To probe the supramolecular association further, the Hirshfeld surface as well as the full and delineated two-dimensional fingerprint plots were calculated using Crystal Explorer 17 [12] and standard protocols [13].

The analysis reveals the H $\cdots$ H contacts, at 59.6%, to be the most prominent with a sizeable contribution from H $\cdots$ C/C $\cdots$ H, i.e. 22.4%, reflecting to a certain extent, the C—H $\cdots\pi$  contacts mentioned above. The H $\cdots$ Cl/Cl $\cdots$ H contacts amount to 15.6% but, at separations greater than the sum of their van der Waals radii; the only other contacts making more than a 1% contribution to the calculated Hirshfeld surface are Cl $\cdots$ C/C $\cdots$ Cl contacts, at 1.4%.

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