See Mun Lee, Kong Mun Lo and Edward R.T. Tiekink*

Redetermination of the crystal structure of tetrakis(4-chlorobenzyl)tin(IV), $C_{28}H_{24}Cl_4Sn$

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Abstract

$[C_{28}H_{24}Cl_4Sn]$, orthorhombic, $Fdd2$ (no. 43), $a = 22.01600(10)$ Å, $b = 20.79690(10)$ Å, $c = 11.15230(10)$ Å, $V = 5106.24(6)$ Å³, $Z = 8$, $R_{gt}(F) = 0.0134$, $wR_{ref}(F^2) = 0.0370$, $T = 100(2)$ 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

Carbon disulfide (0.12 ml, 2 mmol) was slowly added to a stirred solution of diethanolamine (0.19 ml, 2 mmol) in

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	$0.12 \times 0.11 \times 0.08$ mm
Wavelength:	Cu $K\alpha$ radiation (1.54178 Å)
μ :	11.9 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
$\theta_{\max}$, completeness:	67.1° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	54924, 2283, 0.043
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2283
$N(\text{param})_{\text{refined}}$:	150
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

methanol at 273 K. The solution was stirred for 30 min. Next, potassium hydroxide (50° w/v, 0.23 ml) was added dropwise into the solution followed by stirring for another 30 min. Next, di(4-chlorobenzyl)tin dichloride (0.44 g, 1 mmol) in methanol was added into the mixture followed by stirring for 3 h. The solvent was gradually removed by evaporation until a white solid was obtained. The precipitate was recrystallized from methanol to yield a small number of colourless crystals which were characterized crystallographically and found to be the title compound. The crystal is a side-product from the anticipated reaction to form a dithiocarbamate complex. IR (Perkin Elmer Spectrum 400 F T Mid-IR/Far-IR spectrophotometer, ATR, cm^{-1}): 2925 (*m*), 1653 (*m*). ¹H-NMR (Bruker AVANCE-400 MHz, CDCl_3) δ [p.p.m.] 7.18 (s, 2H, 3-Ph-H), 6.66 (s, 2H, 2-Ph-H), 1.28 (s, 2H, CH_2). ¹³C-NMR (100 MHz, CDCl_3) δ [p.p.m.] 139.1 (s, 1-Ph-C), 128.8 (s, 4-Ph-C), 128.6 (s, 3-Ph-C), 124.2 (s, 2-Ph-C), 18.4 (s, CH_2).

Experimental details

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

Comment

The crystal structure of the title compound has been described previously based on room temperature data [5, 6]. The unsubstituted tetrabenzyls of titanium, hafnium, and tin have also been previously studied [7]. Herein, a low temperature (100 K) redetermination is described for a crystal obtained as a side-product of a reaction involving the (4-chlorophenyl)₂SnCl₂ precursor (see "Source of material"). The

*Corresponding author: Edward R.T. Tiekink, Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia, e-mail: edwardt@sunway.edu.my, Edward.Tiekink@gmail.com. <https://orcid.org/0000-0003-1401-1520>

See Mun Lee and Kong Mun Lo: Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Sn	0.750000	0.250000	0.39956(2)	0.01482(8)
Cl1	0.93396(3)	0.46406(3)	0.70842(7)	0.02979(15)
Cl2	0.44612(3)	0.33263(3)	0.48462(7)	0.02901(16)
C1	0.71437(11)	0.32293(12)	0.5212(2)	0.0181(5)
H1A	0.686949	0.352419	0.477310	0.022*
H1B	0.690993	0.302265	0.586500	0.022*
C2	0.76677(12)	0.35959(12)	0.5722(2)	0.0171(5)
C3	0.79066(12)	0.41251(12)	0.5109(2)	0.0186(5)
H3	0.771668	0.426570	0.439007	0.022*
C4	0.84159(12)	0.44501(12)	0.5528(2)	0.0196(5)
H4	0.857249	0.481000	0.510404	0.024*
C5	0.86905(11)	0.42408(12)	0.6570(2)	0.0209(5)
C6	0.84623(12)	0.37256(12)	0.7216(2)	0.0220(5)
H6	0.865147	0.359205	0.794033	0.026*
C7	0.79507(11)	0.34074(11)	0.6785(2)	0.0195(5)
H7	0.779080	0.305434	0.722419	0.023*
C8	0.67512(11)	0.21088(13)	0.2940(2)	0.0198(5)
H8A	0.681015	0.221560	0.208251	0.024*
H8B	0.674201	0.163474	0.301932	0.024*
C9	0.61624(12)	0.23875(12)	0.3374(3)	0.0184(5)
C10	0.58931(12)	0.29044(13)	0.2779(3)	0.0221(5)
H10	0.606860	0.305974	0.205683	0.027*
C11	0.53709(13)	0.31964(12)	0.3228(3)	0.0235(6)
H11	0.519395	0.355255	0.282494	0.028*
C12	0.51152(12)	0.29607(14)	0.4266(3)	0.0217(6)
C13	0.53589(14)	0.24365(12)	0.4865(3)	0.0203(6)
H13	0.516996	0.227244	0.556700	0.024*
C14	0.58845(11)	0.21563(12)	0.4418(2)	0.0189(5)
H14	0.605893	0.180107	0.482799	0.023*

molecular structure is shown in the figure (70% displacement ellipsoids with unlabelled atoms related by the symmetry operation i: $1/2 - x, 1/2 - y, z$). The tetrahedrally coordinated tin atom lies on a crystallographic 2-fold axis of symmetry. The independent Sn—C1 and Sn—C8 bond lengths are equal within experimental error at 2.181(2) and 2.183(2) Å, respectively. These values lie in the range 2.170(7)–2.184(6) Å for the 2-chloro analogue [8] (for which there is no crystallographically imposed symmetry) indicating no electronic influence upon the Sn—C bonds in these isomers. The range of tetrahedral angles is relatively narrow, ranging from 103.07(14)°, for C1—Sn—C1ⁱ, to 114.72(14), for the C8—Sn—C8ⁱ angle.

In the crystal of the title compound, phenyl-C—H···Cl interactions, involving only the Cl2 atom, are apparent [C3—H3···Cl2ⁱⁱ: H3···Cl2ⁱⁱ = 2.83 Å, C3···Cl2ⁱⁱ = 3.720(2) Å with angle at H3 = 157°; C6—H6···Cl2ⁱⁱⁱ: H6···Cl2ⁱⁱⁱ = 2.83 Å, C6···Cl2ⁱⁱⁱ = 3.759(3) Å with angle at H6 = 166° for symmetry operations ii: $1/4 + x, 3/4 - y, -1/4 + z$ and iii: $1/2 + x, y, 1/2 + z$]. As these interactions involve both independent benzyl substituents, a three-dimensional architecture ensues. This architecture is further consolidated by halogen bonding interactions whereby the Cl1 atoms self-associate by end-on interactions [Cl1···Cl1^{iv} = 3.2696(9) Å for symmetry operation iv: $2 - x, 1 - y, z$]. Further, $\pi \cdots \pi$ interactions between the independent rings [inter-centroid separation = 3.8915(15) Å and angle of inclination = 2.10(13)° for symmetry operation $5/4 - x, 1/4 + y, 1/4 + z$] are apparent.

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