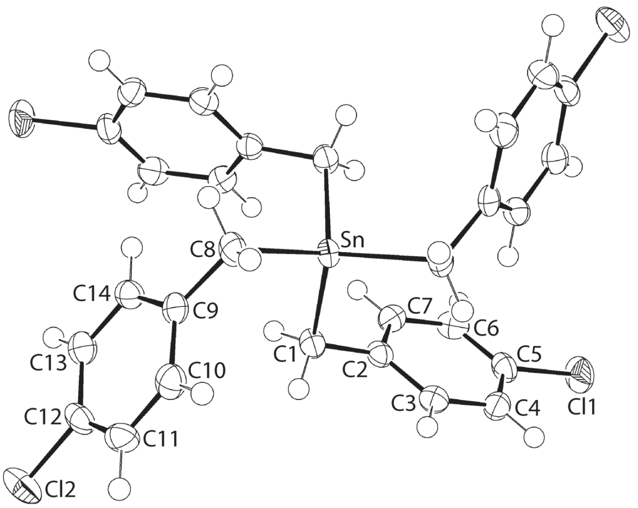
DE GRUYTER Z. Kristallogr. NCS 2019; 234(4): 777–778

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

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



https://doi.org/10.1515/ncrs-2019-0100
Received February 1, 2019; accepted March 16, 2019; available online April 4, 2019

Abstract

[$C_{28}H_{24}Cl_4Sn$], orthorhombic, *Fdd*2 (no. 43), $a = 22.01600(10)$ Å, $b = 20.79690(10)$ Å, $c = 11.15230(10)$ Å, $V = 5106.24(6)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0134$, $wR_{ref}(F^2) = 0.0370$, $T = 100(2)$ K.

CCDC no.: 1903633

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 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 ElmerSpectrum 400 F T Mid-IR/Far-IR spectrophotometer, ATR, cm^{-1}): 2925 (*m*), 1653 (*m*). ^{1}H-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). ^{13}C-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).

Table 1: Data collection and handling.

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

Experimental details

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

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)$_2$SnCl$_2$ 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 (Å^2).

Atom	*x*	*y*	*z*	$U_{\text{iso}}*/U_{\text{eq}}$
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—C1$^{\text{i}}$, to 114.72(14), for the C8—Sn—C8$^{\text{i}}$ angle.

In the crystal of the title compound, phenyl-C—H$\cdots$Cl interactions, involving only the Cl2 atom, are apparent [C3—H3$\cdots$Cl2$^{\text{ii}}$: H3$\cdots$Cl2$^{\text{ii}}$ = 2.83 Å, C3$\cdots$Cl2$^{\text{ii}}$ = 3.720(2) Å with angle at H3 = 157°; C6—H6$\cdots$Cl2$^{\text{iii}}$: H6$\cdots$Cl2$^{\text{iii}}$ = 2.83 Å, C6$\cdots$Cl2$^{\text{iii}}$ = 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$\cdots$Cl1$^{\text{iv}}$ = 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.

Acknowledgements: Sunway University is thanked for support of studies in organotin chemistry.

References

1. Agilent Technologies: CrysAlis$^{\text{PRO}}$. Agilent Technologies, Santa Clara, CA, USA (2017).
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. Acta Crystallogr. **C71** (2015) 3–8.
4. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. J. Appl. Crystallogr. **45** (2012) 849–854.
5. Zhang, F.-X.; Kuang, D.-X.; Xu, Z.-F.; Wang, J.-Q.: Study on synthesis, crystal structure and quantum chemistry of the tetra(*p*-chlorobenzyl)tin. Wuji Huaxue Xuebao Chin. J. Inorg. Chem. **18** (2002) 854–858.
6. Yin, H.-D.; He, G.-F.; Zhou, Z.-X.: Synthesis and crystal structures of tetra(*p*-chlorobenzyl)tin (p-$ClPhCH_2)_4Sn$. Huaxue Shiji Chemical Reagents **25** (2003) 323–328.
7. Davies, G. R.; Jarvis, J. A. J.; Kilbourn, B. T.: The crystal and molecular structures (at −40 °C) of the tetrabenzyls of titanium, hafnium, and tin. J. Chem. Soc. D (1971) 1511–1512.
8. Zhang, F.-X.; Tao, J.; Tang, D.-D.; Luo, J.; Tang, P.; Kuang, D.-Z.; Feng, Y.-L.; Zhu, X.-M.: Syntheses, crystal structures and quantum chemistry of tri(3,5-difluorobenzyl) tin chloride and tetra(*o*-chlorobenzyl)tin chloride and tetra(*o*-chlorobenzyl)tin. Wuji Huaxue Xuebao Chin. J. Inorg. Chem. **33** (2017) 644–650.