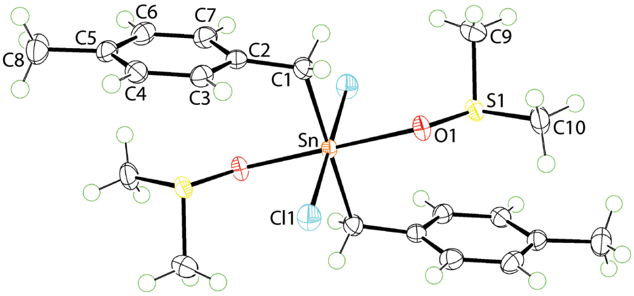
DE GRUYTER Z. Kristallogr. NCS 2020; 235(5): 1235–1237

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

Crystal structure of dichlorido-bis(dimethyl sulphoxide-κ*O*)-bis(4-methylbenzyl-κC^1)tin(IV), $C_{20}H_{30}Cl_2O_2S_2Sn$



https://doi.org/10.1515/ncrs-2020-0282
Received June 10, 2020; accepted June 25, 2020; available online July 11, 2020

Abstract

$C_{20}H_{30}Cl_2O_2S_2Sn$, monoclinic, $P2_1/n$ (no. 14), $a = 8.2430(1)$ Å, $b = 13.7471(1)$ Å, $c = 11.1619(2)$ Å, $\beta = 110.864(2)°$, $V = 1181.90(3)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0164$, $wR_{ref}(F^2) = 0.0445$, $T = 100(2)$ K.

CCDC no.: 2012228

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

Di(4-methylbenzyl)tin dichloride was synthesized by the direct reaction of 4-methylbenzyl chloride (Merck) and metallic tin powder (Merck) in toluene according to a literature procedure [5]. Di(4-methylbenzyl)tin dichloride (0.40 g, 1.0 mmol) and dimethyl sulphoxide (Merck, 0.14 mL,

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.12 × 0.11 × 0.05 mm
Wavelength:	Cu *Kα* radiation (1.54184 Å)
μ:	12.4 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	14266, 2105, 0.020
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2051
$N(param)_{refined}$:	127
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

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

Atom	*x*	*y*	*z*	$U_{iso}*/U_{eq}$
Sn	0.5	0.5	0.5	0.01157(7)
Cl1	0.32862(6)	0.49166(2)	0.25754(4)	0.01891(10)
S1	0.61206(5)	0.73651(3)	0.57748(3)	0.01483(10)
O1	0.56601(14)	0.65583(7)	0.47547(10)	0.0163(2)
C1	0.7390(2)	0.47050(12)	0.46739(15)	0.0164(3)
H1A	0.739541	0.508839	0.392459	0.020*
H1B	0.837803	0.492977	0.542868	0.020*
C2	0.76585(19)	0.36606(11)	0.44419(15)	0.0143(3)
C3	0.72325(19)	0.32899(11)	0.31983(15)	0.0150(3)
H3	0.685381	0.372134	0.248733	0.018*
C4	0.7355(2)	0.23017(11)	0.29892(15)	0.0158(3)
H4	0.706428	0.206786	0.213732	0.019*
C5	0.78993(19)	0.16469(11)	0.40094(16)	0.0166(3)
C6	0.8378(2)	0.20182(11)	0.52483(16)	0.0183(3)
H6	0.878969	0.158843	0.595950	0.022*
C7	0.8263(2)	0.30068(12)	0.54596(15)	0.0174(3)
H7	0.860264	0.324221	0.631407	0.021*
C8	0.7966(2)	0.05704(12)	0.37749(18)	0.0245(4)
H8A	0.889091	0.043589	0.343838	0.037*
H8B	0.684984	0.035752	0.315152	0.037*
H8C	0.820100	0.021786	0.458239	0.037*
C9	0.8428(2)	0.73326(12)	0.64729(17)	0.0237(4)
H9A	0.879513	0.671690	0.693232	0.035*
H9B	0.883640	0.787595	0.707382	0.035*
H9C	0.892229	0.738697	0.579663	0.035*
C10	0.5912(2)	0.84531(11)	0.48602(16)	0.0215(3)
H10A	0.657895	0.838938	0.429217	0.032*
H10B	0.635611	0.900485	0.544079	0.032*
H10C	0.468594	0.856248	0.434541	0.032*

***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. https://orcid.org/0000-0003-1401-1520
Kong Mun Lo and See Mun Lee: Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia

2.0 mmol) were heated in 95% ethanol (20 mL) and stirred for 2 h. After filtration, the filtrate was evaporated slowly until colourless crystals formed. Yield: 0.30 g (54%). **M.pt** (Meltemp II digital melting point apparatus): >573 K (dec.). **IR** (Bruker Vertex 70v FTIR Spectrophotometer; cm^{-1}): 903 (m) ν(S—O), 298 (s) ν(Sn—Cl). **NMR** (Bruker Ascend 400 MHz NMR spectrometer, chemical shifts relative to Me_4Si, DMSO-*d*6 solution, p.p.m. at 50°): δ 2.25 (s, 3H, CH_3), 2.28 (s, 2H, CH_2), 2.37 (s, 3H, SCH_3), 2.50 (s, 3H, SCH_3), 7.00–7.24 (m, 4H, Ph-H). **$^{13}C\{^1H\}$ NMR** (as for ^1H NMR): δ 21.2 (CH_3), 40.8, 42.6 (SCH_3), 63.2 (CH_2), 127.0, 128.5, 130.0, 134.0 (Ph—C).

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95–0.99 Å) and refined as riding with $U_{\mathrm{iso}}(H) = 1.2–1.5U_{\mathrm{eq}}(C)$. Owing to poor agreement, one reflection, i.e. (−3 2 8), was removed from the final cycles of refinement.

Comment

The crystal and molecular structures of the title compound, $(4\text{-}MeC_6H_4CH_2)_2SnCl_2(DMSO)_2$ (I), were determined in connection with on-going studies into the structural chemistry of diorganotin dihalide adducts of diorgano sulphoxides, which can adopt five- and six-coordinate geometries depending on the number of coordinated diorgano sulphoxide molecules [6–8]. The molecular structure of (I) is shown in the figure (70% displacement ellipsoids; unlabelled atoms are related by the symmetry operation $1 - x, 1 - y, 1 - z$) and has the Sn atom located on a centre of inversion.

The Sn atom is hexa-coordinated within an all-trans $C_2Cl_2O_2$ donor set defined by the methylene-C1 [2.1652(15) Å], DMSO-O1 [2.2508(10) Å] and chlorido-Cl1 [2.5709(4) Å] atoms. The phenyl ring of the benzyl residue is folded to be disposed over the DMSO molecule. The arrangement enables the formation of an intramolecular S(lone-pair)···π(phenyl) contact with the S1···Cg(C2–C7) separation = 3.23 Å; see [9] for a recent discussion on S(lone-pair)···π(arene) interactions. It is noted that the resonances ascribed to DMSO-methyl substituents are distinct in both the ^1H and $^{13}C\{^1H\}$ NMR spectra suggesting the S(lone-pair)···π(phenyl) contact persists in DMSO-*d*6 solution.

There are three structures in the literature of general formula $R_2SnCl_2(DMSO)_2$. While the $4\text{-}FC_6H_4CH_2$ derivative [6] has an all-trans conformation as found in (I), the R = Me [10] and R = Ph [11] species have the chloride atoms cis and the Sn-bound organo-substituents, trans. The structural diversity broadens when the nature of the R groups in the sulphoxide molecule are changed, e.g. five-coordinate geometries are found in each of $(2\text{-}ClC_6H_4CH_2)_2SnCl_2[(PhCH_2)_2S{=}O]$ [7] and $(4\text{-}BrC_6H_4CH_2)_2SnBr_2[(PhCH_2)_2S{=}O]$ [8].

In the crystal of (I), directional methyl-C—H···Cl [C10—H10b···Cl1^{i}: H10b···Cl1^{i} = 2.78 Å, C10···Cl1^{i} = 3.7166(17) Å with angle at H10b = 161° for symmetry operation (i) $1/2 + x, 3/2 - y, 1/2 + z$] and C—H···π(phenyl) interactions [C9—H9c···Cg(C2–C7)^{ii}: H9c···Cg(C2–C7)^{ii} = 2.71 Å with angle at H9c = 134° for (ii) $2 - x, 1 - y, 1 - z$] assemble molecules into a three-dimensional architecture.

The molecular packing was further analysed by calculating the Hirshfeld surface and the full- and delineated two-dimensional fingerprint plots, employing Crystal Explorer 17 [12] and standard protocols [13]. The analysis shows all surface contacts involve H with by far the greatest contribution of 67.8% being from H···H contacts. The next most important contributions are from Cl···H/H···Cl and C···H/H···C contacts, making percentage contributions of 14.9 and 11.5%, respectively. Smaller contributions are made by O···H/H···O [3.8%] and S···H/H···S [2.1%] contacts.

Acknowledgements: Sunway University Sdn Bhd is thanked for financial support of this work through Grant No. STR-RCTR-RCCM-001-2019.

References

1. Rigaku Oxford Diffraction: CrysAlis^{PRO}. Rigaku Corporation, Oxford, UK (2018).
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. Sisido, K.; Takeda, Y.; Kinugawa, Z.: Direct synthesis of organotin compounds I. di- and tribenzyltin chlorides. J. Am. Chem. Soc. **83** (1961) 538–541.
6. Amin, N. A. B. M.; Hussen, R. S. D.; Lee, S. M.; Halcovitch, N. R.; Jotani, M. M.; Tiekink, E. R. T.: *trans*-Di-chlorido-bis(dimethyl sulfoxide-κ*O*)bis(4-fluorobenzyl-κC^1)-tin(IV): crystal structure and Hirshfeld surface analysis. Acta Crystallogr. **E73** (2017) 667–672.
7. Lee, S. M.; Lo, K. M.; Tiekink, E. R. T.: Crystal structure of (dibenzyl sulphoxide-κ*O*)bis(2-chlorobenzyl-κC^1)-dichloridotin(IV), $C_{28}H_{26}Cl_4OSSn$. Z. Kristallogr. NCS **234** (2019) 787–789.
8. Lee, S. M.; Lo, K. M.; Tiekink, E. R. T.: Crystal structure of (dibenzyl sulphoxide-κ*O*)dibromido-bis(4-bromobenzyl-κ*C*) tin(IV), $C_{28}H_{26}Br_4OSSn$. Z. Kristallogr. NCS **235** (2020) 139–141.
9. Silva, R. F. N.; Sacco, A. C. S.; Caracelli, I.; Zukerman-Schpector, J.; Tiekink, E. R. T.: Sulfur(lone-pair)···π interactions with FAD in flavoenzymes. Z. Kristallogr. NCS **233** (2018) 531–537.
10. Isaacs, N. W.; Kennard, C. H. L.: Crystal structure of *cis*-dichloro-*cis*-bis(dimethylsulphoxide)-*trans*-di-methyltin(IV). J. Chem. Soc. A (1970) 1257–1261.
11. Sadiq-ur-Rehman; Saeed, S.; Ali, S.; Shahzadi, S.; Helliwell, M.: Dichloridobis(dimethyl sulfoxide-κ*O*)diphenyltin(IV). Acta Crystallogr. **E63** (2007) m1788.

12. Turner, M. J.; Mckinnon, J. J.; Wolff, S. K.; Grimwood, D. J.; Spackman, P. R.; Jayatilaka, D.; Spackman, M. A.: Crystal Explorer v17. The University of Western Australia, Australia (2017).
13. Tan, S. L.; Jotani, M. M.; Tiekink, E. R. T.: Utilizing Hirshfeld surface calculations, non-covalent interaction (NCI) plots and the calculation of interaction energies in the analysis of molecular packing. Acta Crystallogr. **E75** (2019) 308–318.