

Crystal and molecular structure of $\text{H}_2\text{C}(\text{SnPh}_2\text{OMe})_2 \cdot \text{MeOH}$

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Abstract

The single-crystal X-ray structure analysis is reported of $\text{CH}_2(\text{SnPh}_2\text{OMe})_2 \cdot \text{MeOH}$. The molecule contains two pentacoordinated tin atoms, which are linked by one carbon and one oxygen atom to give a four-membered ring. In the crystal structure, the molecules are connected via hydrogen bridges giving rise to a one-dimensional polymer. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Tin; Pentacoordination; Hydrogen bonding; X-ray structure

1. Introduction

Metal alkoxides have attracted considerable attention as they represent versatile precursors that meet the requirements for sol–gel conversion to metal oxide materials [1]. In this context the structures of tin(IV) alkoxides $\text{Sn}(\text{OR})_4$ ($\text{R} = \text{alkyl, aryl}$) were extensively investigated and were the subject of a recent review [2]. As an important conclusion it was pointed out that the degree of association within these compounds decreases with an increasing steric demand of the alkoxy ligands, e.g. $\text{Sn}(\text{O}t\text{-Bu})_4$ [3a,b] is a monomer whereas $\text{Sn}(\text{O}i\text{-Pr})_4 \cdot i\text{-PrOH}$ [3a,c] is a dimer.

In contrast, structural information on organotin(IV) alkoxides $\text{R}_n\text{Sn}(\text{OR}')_{4-n}$ ($\text{R, R}' = \text{alkyl, aryl}; n = 1-3$) are rather limited. We are aware of only three examples for which X-ray diffraction data are available, namely for Me_3SnOMe (**A**) [4a], $\text{Ph}_3\text{SnO}i\text{-Bu} \cdot i\text{-BuOH}$ (**B**) [4b], and $i\text{-PrSn}(\text{O}i\text{-Pr})_3$ (**C**) [4c], respectively (Chart 1).

In the structure of Me_3SnOMe (**A**) almost planar trimethyltin groups are linked by two methoxy ligands forming infinite one-dimensional zigzag chains with nearly ideally trigonal bipyramidal coordinated tin atoms [4a]. In $\text{Ph}_3\text{SnO}i\text{-Bu} \cdot i\text{-BuOH}$ (**B**) the tin atom exhibits a distorted trigonal bipyramidal configuration with the isobutoxy ligand being more strongly bonded to tin than isobutanol, i.e. the coordination of the tin atom in **B** can be best regarded to be [4 + 1] [4b]. In the crystal lattice the individual molecules of **B** are connected via hydrogen bridges. Isopropyltin triisopropylate, $i\text{-PrSn}(\text{O}i\text{-Pr})_3$ (**C**), contains a dimer with both tin atoms possessing an almost ideal trigonal bipyramidal configuration [4c]. Considering the structural diversity in compounds **A–C**, further investigations on the structures of organotin alkoxides are welcome.

In a previous paper we reported the synthesis of $\text{H}_2\text{C}(\text{SnPh}_2\text{OMe})_2$ [5], and herein we present the X-ray structure of its methanol adduct.

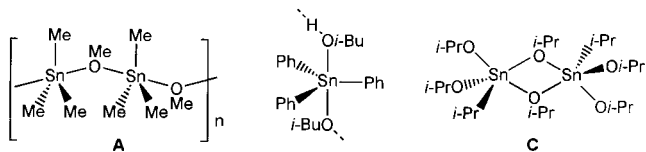


Chart 1.

2. Experimental

The title compound was prepared according to the procedure already published [5]. A single crystal of the dimensions $0.30 \times 0.15 \times 0.10$ mm suitable for X-ray diffraction analysis was obtained after recrystallization from methanol–benzene [5].

Crystal data and structure solution of $\text{H}_2\text{C}(\text{SnPh}_2\text{OMe})_2 \cdot \text{MeOH}$: $\text{C}_{28}\text{H}_{32}\text{O}_3\text{Sn}_2$, $M_r = 653.92$,

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monoclinic, $P2_1/c$, $a = 9.436(1)$, $b = 25.738(1)$, $c = 11.705(1)$ Å, $\beta = 104.586(1)^\circ$, $V = 2751.1(4)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.579$ g cm⁻³, $\lambda(\text{Mo-K}\alpha) = 0.71069$ Å, $F(000) = 1296$, $\mu = 1.841$ mm⁻¹, $T = 291(1)$ K. The data collection covered almost the whole sphere of reciprocal space with 360 frames via ω -rotation ($\Delta/\omega = 1^\circ$) at 2×20 s per frame on a Nonius KappaCCD diffractometer with a completeness of 97.8% in the θ range of 3.44–27.49°. The structure was solved by direct methods SHELXS-97 [6a] and refined by full-matrix least-squares calculations using all measured F^2 data and SHELXL-97 [6b]. All non-H atoms were refined anisotropically. The H atom of the hydroxy group, O(1)H, was located in the difference Fourier map and refined isotropically. The other H atoms were placed in geometrically calculated positions using a riding model (including free rotation about C–C) and refined with common isotropic temperature factors for different

Table 1
Selected bond lengths (Å), bond angles, and torsion angles (°) for $\text{H}_2\text{C}(\text{SnPh}_2\text{OMe})_2 \cdot \text{MeOH}^a$

Bond lengths			
Sn(1)–O(1)	2.347(2)	Sn(1)–O(3)	2.144(2)
Sn(1)–C(4)	2.120(3)	Sn(1)–C(11)	2.118(3)
Sn(1)–C(21)	2.128(3)	Sn(2)–O(2)	2.133(2)
Sn(2)–O(3)	2.271(2)	Sn(2)–C(4)	2.138(3)
Sn(2)–C(31)	2.130(3)	Sn(2)–C(41)	2.132(3)
O(1)–O(2a)	2.491(3)	O(1)–C(1)	1.394(5)
O(1)–H(1)	0.67(4)	O(2)–C(2)	1.387(4)
O(2)–H(1b)	1.86(4)	O(3)–C(3)	1.410(3)
Bond angles			
O(1)–Sn(1)–O(3)	171.00(8)	O(1)–Sn(1)–C(4)	91.2(1)
O(1)–Sn(1)–C(11)	90.1(1)	O(1)–Sn(1)–O(21)	86.3(1)
O(3)–Sn(1)–C(4)	79.80(9)	O(3)–Sn(1)–C(11)	95.7(1)
O(3)–Sn(1)–C(21)	97.61(9)	C(4)–Sn(1)–C(11)	126.2(1)
C(4)–Sn(1)–C(21)	120.3(1)	C(11)–Sn(1)–C(21)	113.5(1)
O(2)–Sn(2)–O(3)	166.61(7)	O(2)–Sn(2)–C(4)	90.01(9)
O(2)–Sn(2)–C(31)	93.2(1)	O(2)–Sn(2)–C(41)	96.0(1)
O(3)–Sn(2)–C(4)	76.62(9)	O(3)–Sn(2)–C(31)	93.2(1)
O(3)–Sn(2)–C(41)	92.0(1)	C(4)–Sn(2)–C(31)	120.8(1)
C(4)–Sn(2)–C(41)	123.7(2)	C(31)–Sn(2)–C(41)	114.8(2)
Sn(1)–O(1)–O(2a)	126.6(1)	Sn(1)–O(1)–C(1)	122.6(2)
Sn(1)–O(1)–H(1)	111(4)	O(2a)–O(1)–C(1)	101.1(2)
O(2a)–O(1)–H(1)	17(4)	C(1)–O(1)–H(1)	117(4)
Sn(2)–O(2)–C(2)	121.5(2)	Sn(2)–O(2)–H(1b)	126(1)
C(2)–O(2)–H(1b)	108(1)	Sn(1)–O(3)–C(3)	128.2(2)
Sn(2)–O(3)–C(3)	132.6(2)	Sn(1)–O(3)–Sn(2)	99.16(7)
Sn(1)–C(4)–Sn(2)	104.3(1)		
Torsion angles			
O(1)–Sn(1)–O(3)–Sn(2)	1.3(6)	O(1)–Sn(1)–C(4)–Sn(2)	–176.1(1)
O(2)–Sn(2)–O(3)–Sn(1)	5.5(4)	O(2)–Sn(2)–C(4)–Sn(1)	177.5(1)
O(3)–Sn(1)–C(4)–Sn(2)	3.2(1)	O(3)–Sn(2)–C(4)–Sn(1)	–3.1(1)
C(4)–Sn(1)–O(3)–Sn(2)	–3.0(1)	C(4)–Sn(2)–O(3)–Sn(1)	3.0(1)

^a Symmetry transformations used to generate equivalent atoms: $a = x, -y + 0.5, z - 0.5$; $b = x, -y + 0.5, z + 0.5$.

C–H types (C–H_{prim.} 0.96 Å, U_{iso} 0.152(6) Å²; H_{aryl} C–H 0.93 Å, U_{iso} 0.106(3) Å²). Disordered atoms were found for a phenyl group with occupancies of 0.5 (C(42), C(43), C(44), C(42'), C(43'), and C(44')).

$R_1 = 0.0284$ for 4011 [$I > 2\sigma(I)$] and $wR_2 = 0.0666$ for 6171 independent reflections with 331 refined parameters. The max./min. residual electron densities were 0.431 and -0.756 e Å⁻³. Selected bond lengths, bond angles, and torsion angles are listed in Table 1.

3. Discussion

The molecular structure of $\text{H}_2\text{C}(\text{SnPh}_2\text{OMe})_2 \cdot \text{MeOH}$ comprises two crystallographically independent tin atoms, Sn(1) and Sn(2), which are linked by the C(4)–carbon atom of the methylene group, and the O(3)–oxygen atom of the bridging methoxy group, giving rise to the formation of a four-membered OSn₂C ring (Fig. 1) with a mean deviation from planarity of 0.028 Å. Both tin atoms Sn(1) and Sn(2) exhibit distorted trigonal bipyramidal configurations with the equatorial positions being occupied by C(4), C(11), C(21) and C(4), C(31), C(41), respectively. In accordance with Bent's rule [7], the axial positions are occupied by O(1) and O(3), and O(2) and O(3), respectively. The only moderate distortion from the ideal trigonal bipyramidal configuration is manifested by (i) the O(1)–Sn(1)–O(3) and O(2)–Sn(2)–O(3) angles of 171.00(8) and 166.61(7)°, respectively, being different from the ideal angle of 180°, and (ii) the geometrical goodness parameter [8] being 86.9° for Sn(1) and 80.1° for Sn(2). For the ideal trigonal bipyramid, the latter value amounts to 90°. The Sn–O distances vary between 2.347(2) and 2.133(2) Å and differ for Sn(1) and

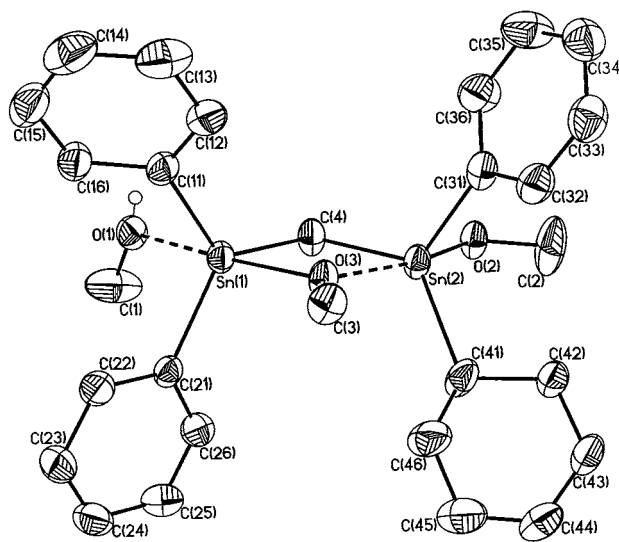


Fig. 1. General view (SHELXTL-PLUS) of $\text{H}_2\text{C}(\text{SnPh}_2\text{OMe})_2 \cdot \text{MeOH}$ showing 30% probability displacement ellipsoids and the atom numbering.

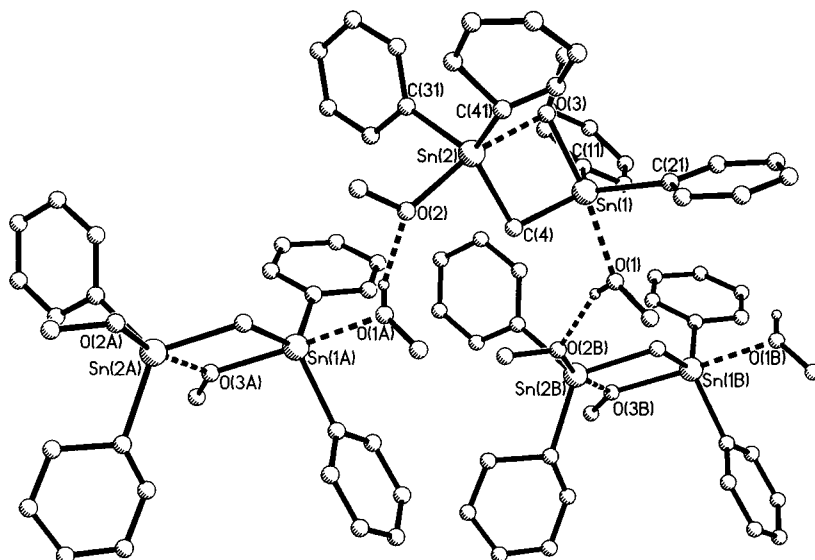


Fig. 2. Perspective view (SHELXTL-PLUS) of three $\text{H}_2\text{C}(\text{SnPh}_2\text{OMe})_2 \cdot \text{MeOH}$ connected through hydrogen bonding in the crystal lattice.

$\text{Sn}(2)$ by 0.203(2) and 0.138(2) Å, respectively. For $\text{Ph}_3\text{SnO}i\text{-Bu}\cdot i\text{-BuOH}$, (**B**), this difference amounts to 0.485 Å [4b]. Utilizing the bond order concept [9] to quantify the degree of distortion, the axial bond orders at $\text{Sn}(1)$ and $\text{Sn}(2)$ amount to 0.63/0.33 and 0.65/0.41, respectively. The sum of the apical bond orders lies slightly below for $\text{Sn}(1)$ (0.96) and slightly above for $\text{Sn}(2)$ (1.06), the theoretical sum, 1.00, but the average of these two values (1.01) nearly exactly matches the theoretical value [9a]. The $\text{Sn}-\text{C}$ distances are in the range of 2.118(3) and 2.138(3) Å and show no particularities.

The $\text{Sn}(1)-\text{C}(4)-\text{Sn}(2)$ angle amounts to $104.3(1)^\circ$ which is smaller than the corresponding angles in related phenyl-substituted methylene-bridged ditin compounds ($\text{Ph}_2\text{BrSn})\text{CH}_2 \cdot \text{HMPA}$ ($106.8/106.3^\circ$) [10], $\text{H}_2\text{C}(\text{SnPh}_2\text{Cl})_2$ ($113.4(10)^\circ$) [11], ($\text{Ph}_2\text{ClSn})\text{CH}_2 \cdot \text{HMPA}$ (114.0°) [10], $\text{H}_2\text{C}(\text{SnPhBr}_2)_2$ ($115.1(5)^\circ$) [12], $[\text{MeN}(\text{CH}_2\text{CH}_2\text{S})_2(\text{Ph})\text{Sn}]_2\text{CH}_2$ (120.93°) [13], and $\text{H}_2\text{C}(\text{SnPh}_3)_2$ ($122.8(1)/122.4(1)^\circ$) [14].

The individual molecules of $\text{H}_2\text{C}(\text{SnPh}_2\text{OMe})_2 \cdot \text{MeOH}$ are linked by a hydrogen bond between two oxygen atoms, O(1) and O(2a), giving rise to the formation of a one-dimensional polymer in the solid state (Fig. 2). The intermolecular O(1)...O(2a) distance amounts to 2.491(3) Å which is rather short when compared with that reported for $\text{Ph}_3\text{SnO}i\text{-Bu}\cdot i\text{-BuOH}$ (**B**), (2.687 Å) [4b]. Intermolecular hydrogen bridges of 2.464/2.497 and 2.703(8) Å have been reported for the tin alkoxide derivatives $\text{Sn}_3\text{O}(O\text{-}i\text{-Bu})_{10} \cdot 2i\text{-BuOH}$ [3b] and $\text{Sn}(O\text{-}i\text{-Pr})_4 \cdot i\text{-PrOH}$ [3c], respectively. A similar polymeric arrangement as for the title compound was observed for $\text{H}_2\text{C}(\text{SnPh}_2\text{Cl})_2$ in which the molecules are linked by weak intermolecular $\text{Sn}\dots\text{Cl}$ bonds [11].

4. Supplementary material

Crystallographic data for the analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 149 682 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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References

- [1] (a) L.L. Hench, J.K. West, *Chem. Rev.* 90 (1990) 33. (b) K.G. Caulton, L.G. Hubert-Pfalzgraf, *Chem. Rev.* 90 (1990) 969. (c) L.G. Hubert-Pfalzgraf, *Polyhedron* 13 (1994) 1181.
- [2] M.J. Hampden-Smith, T.A. Wark, C.J. Brinker, *Coord. Chem. Rev.* 112 (1992) 81.
- [3] (a) M.J. Hampden-Smith, T.A. Wark, A. Rheingold, J.C. Huffman, *Can. J. Chem.* 69 (1991) 121. (b) H. Reuter, M. Kremsler, *Z. Anorg. allg. Chem.* 615 (1992) 137. (c) H. Reuter, M. Kremsler, *Z. Anorg. allg. Chem.* 598–599 (1991) 259.
- [4] (a) A.M. Domingos, G.M. Sheldrick, *Acta Crystallogr. Sect. B* 30 (1974) 519. (b) H. Reuter, D. Schröder, *Acta Crystallogr. Sect. C* 49 (1993) 954. (c) H. Reuter, D. Schröder, *J. Organomet. Chem.* 455 (1993) 83.
- [5] M. Gielen, K. Jurkschat, *J. Organomet. Chem.* 273 (1984) 303.
- [6] (a) G.M. Sheldrick, *Acta Crystallogr. Sect. A* 46 (1990) 467. (b) G.M. Sheldrick, University of Göttingen, 1997.

- [7] H.A. Bent, *Chem. Rev.* 61 (1961) 275.
- [8] (a) M. Dräger, *J. Organomet. Chem.* 251 (1983) 209. (b) U. Kolb, M. Beuter, M. Dräger, *Inorg. Chem.* 33 (1994) 4522.
- [9] (a) D. Britton, J.D. Dunitz, *J. Am. Chem. Soc.* 103 (1981) 2971. (b) M. Dräger, *Z. Anorg. allg. Chem.* 423 (1976) 53. (c) M. Beuter, U. Kolb, A. Zickgraf, E. Bräu, M. Bletz, M. Dräger, *Polyhedron* 16 (1997) 4005.
- [10] M. Gielen, K. Jurkschat, J. Meunier-Piret, M. van Meerssche, *Bull. Soc. Chem. Belg.* 93 (1984) 379.
- [11] J. Meunier-Piret, M. Van Meerssche, K. Jurkschat, M. Gielen, *J. Organomet. Chem.* 288 (1985) 139.
- [12] S. Hadjikakou, K. Jurkschat, M. Schürmann, unpublished result.
- [13] R. Willem, K. Jurkschat, J. Meunier-Piret, M. van Meerssche, K. Jurkschat, A. Tzschach, *J. Organomet. Chem.* 277 (1984) 335.
- [14] D. Dakternieks, R. Altmann, K. Jurkschat, E.R.T. Tiekink, *Z. Kristallogr.* 213 (1998) 525.