

Intramolecularly coordinated organotin(IV) sulphides and their reactivity to iodine

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Abstract

Organotin(IV) sulphides (LSnPhS)₂ (**3**) and (LSnPh₂)₂S (**4**) containing O,C,O chelating ligand (L = 2,6-(*t*-BuOCH₂)₂C₆H₃[−]) were prepared by the reaction of parent organotin chlorides LSnPhCl₂ (**1**) and LSnPh₂Cl (**2**) with Na₂S · 9H₂O in toluene/water. Both sulphides were characterized by the help of elemental analysis, ESI-mass spectrometry, ¹H, ¹³C ¹¹⁹Sn NMR spectroscopy and the molecular structure of **3** was determined by X-ray diffraction techniques. Compounds **3** and **4** react with I₂ to organotin iodides LSnPhI₂ (**5**) and LSnPh₂I (**6**), instead of intended iodolysis of phenyl groups. Triorganotin iodide **6** reacts with the additional molecule of I₂ forming an ionic organotin compound [LSnPh₂]⁺ I₃[−] (**7**), which is unstable in solution and decomposes to Ph₂SnI₂ and 2,6-(*t*-BuOCH₂)₂C₆H₃I (**8**).

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1. Introduction

Organotin(IV) sulphides have been extensively studied over the last two decades and a variety of interesting structures depending on the organic groups bonded to the central tin atom both in the solid state and in solution have been observed. The diorganotin compounds were shown to form cyclic trimers (Me₂SnS)₃ and (Ph₂SnS)₃ [1] or a polymer (*i*-Pr₂SnS)_{*n*} [2]. Dimeric structures with central Sn₂S₂ core can be stabilized by bulky ligands (*t*Bu₂SnS)₂ [3] or [(2,4,6-*i*Pr₃C₆H₂)₂SnS]₂ [4]. Tokitoh et al. reported on utilization of sterically crowded aryls 2,4,6-triisopropylphenyl (Tip) and 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tb) for formation of unusual (Tb)(Tip)SnE₄ rings (E =

S, Se) [5]. Adamantane-like structures have been detected in diorganotin sulphides in which two tin atoms are bridged by a single methylene carbon atom [6] or propylene bridge [7]. Recently, Dakternieks et al. also reported on anionic diorganotin sulphides of the type [S(SnR₂Cl)₂Cl][−] [8]. Monoorganotin sulphides can be usually encountered as (RSn)₄E₆ compounds with adamantane-like structure [9]. On the other hand, triorganotin derivatives form simple sulphur bridged structures R₃SnSSnR₃ with various Sn–S–Sn bond angles depending on groups R [10].

One of the possibilities of stable central Sn₂S₂ ring formation is using of chelating ligands [11]. The O,C,O-coordinating pincer-type ligand (2,6-[(EtO)₂(O)P]₂-4-*t*BuC₆H₂[−]) was used for stabilization of a rare example of organotin sulfide containing terminal Sn–Cl bond 2,6-[(EtO)₂(O)P]₂-4-*t*BuC₂H₆Sn(S)Cl [12]. Organotin sulphides were also used as ligands in transition metals coordination sphere [13].

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Here, we report on the reaction of intramolecularly coordinated organotin chlorides LSnPhCl_2 (**1**) and LSnPh_2Cl (**2**) containing another type of O,C,O – coordinating pincer-type ligand **L** ($\text{L} = 2,6\text{-}(t\text{BuOCH}_2)_2\text{C}_6\text{H}_3^-$) with $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ yielding organotin sulphides $(\text{LSnPhS})_2$ (**3**) and $(\text{LSnPh}_2)_2\text{S}$ (**4**). Investigation on the reactions of the resulting sulphides **3** and **4** with molecular iodine is also included. All derivatives were characterized by elemental analysis, ESI-MS, ^1H , ^{13}C and ^{119}Sn NMR spectroscopy.

2. Experimental

2.1. General remarks

^1H , ^{13}C ^{119}Sn NMR spectra were recorded on Bruker AMX360 and Bruker500 Avance spectrometers respectively, using 5 mm tuneable broad-band probes. Appropriate chemical shifts in ^1H , ^{13}C and ^{119}Sn NMR spectra were calibrated on the residual signals of the solvent (CDCl_3 : $\delta(^1\text{H}) = 7.27$ ppm and $\delta(^{13}\text{C}) = 77.23$ ppm) or external Me_4Sn ($\delta(^{119}\text{Sn}) = 0.0$ ppm). Positive-ion electrospray ionization (ESI) mass spectra were measured on an ion trap analyzer Esquire 3000 (Bruker Daltonics, Bremen, Germany) in the range m/z 50–1500. The samples were dissolved in acetonitrile and analyzed by direct infusion at the flow rate 5 $\mu\text{l}/\text{min}$. The selected precursor ions were further analyzed by MS/MS analyses under the following conditions: the isolation width $m/z = 8$, the collision amplitude in the range 0.8–1.0 V depending on the precursor ion stability, the ion source temperature 300 °C, the tuning parameter compound stability 100%, the flow rate and the pressure of nitrogen 4 l/min and 10 psi, respectively.

2.2. X-ray structure determination

The X-ray data for single crystals of **3**, **5** and **6** were obtained at 150 K using Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo K_α radiation ($\lambda = 0.71073$ Å), a graphite monochromator, and the ϕ and ω scan mode. The absorption corrections were made [14] by integration or multi-scan [15] methods. Data reductions were performed with DENZO-SMN [16]. Structures were solved by direct methods (Sir92) [17] and refined by full matrix least-square based on F^2 (SHELXL97) [18]. All hydrogen atoms were positioned geometrically and refined on their parent carbon atoms, with $\text{C-H} = 0.93$ Å and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ H atoms, and $\text{C-H} = 0.96$ Å and $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$ for methyl hydrogen atoms.

2.3. Synthesis of $[2,6\text{-}(t\text{BuOCH}_2)_2\text{C}_6\text{H}_3\text{SnPhS}]_2$ (**3**)

$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (0.4 g, 1.7 mmol) in 30 ml of water was added to a solution of $2,6\text{-}(t\text{BuOCH}_2)_2\text{C}_6\text{H}_3\text{SnPhCl}_2$ (0.85 g, 1.64 mmol) in toluene (30 ml) and the reaction mixture was stirred overnight. Then the toluene fraction was separated and water layer was washed twice with toluene

10 ml. Combined toluene fractions were dried over Na_2SO_4 and evaporated *in vacuo* to dryness. The crude product was washed with hexane to yield **3**: 0.5 g (63%). Mp: 224–226 °C. Anal. Calcd for $\text{C}_{44}\text{H}_{60}\text{Sn}_2\text{O}_4\text{S}_2$ (MW 954.47): C, 55.37; H, 6.34; Found: C, 55.56; H, 6.54%. Positive-ion MS: m/z 995 $[\text{M}+\text{K}]^+$; m/z 979 $[\text{M}+\text{Na}]^+$, 100%; m/z 479 $[\text{LSnPhSH}]^+$. ^1H NMR (CDCl_3): 1.03 and 1.05 (18H, s, $(\text{CH}_3)_3\text{CO}$), 4.75 and 4.85 (4H, s, OCH_2), 7.23–7.37 (6H, m, Ar-H3,4,5L and Ar-H3,4,5-Ph), 7.67 and 8.00 (2H, d, Ar-H2,6-Ph). ^{13}C NMR (CDCl_3): 27.5 (s, $(\text{CH}_3)_3\text{CO}$), 65.3 and 65.5 (s, OCH_2), 75.6 and 75.7 (s, $(\text{CH}_3)_3\text{CO}$), 126.4 and 126.6 (s, Ar-C3,5-L), 128.0 and 128.2 (s, Ar-C3,5-Ph), 128.9 and 129.1 (s, Ar-C4-L), 129.2 overlap of two signals (s(br), Ar-C4-Ph), 135.9 and 136.1 (s, Ar-C2,6-Ph), 137.6 and 137.6 (s, Ar-C1-L), 147.4 and 147.5 (s, Ar-C2,6-L), 148.4 and 148.5 (s, Ar-C1-Ph). ^{119}Sn NMR (CDCl_3): -74.6 ($^2J(^{119}\text{Sn}, ^{117}\text{Sn}) = 226$ Hz), -79.5 ($^2J(^{119}\text{Sn}, ^{117}\text{Sn}) = 226$ Hz).

2.4. Synthesis of $[2,6\text{-}(t\text{BuOCH}_2)_2\text{C}_6\text{H}_3\text{SnPh}_2]_2\text{S}$ (**4**)

$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (0.45 g, 1.9 mmol) in 30 ml of water was added to a solution of $2,6\text{-}(t\text{BuOCH}_2)_2\text{C}_6\text{H}_3\text{SnPh}_2\text{Cl}$ (2.08 g, 3.73 mmol) in toluene (30 ml) and the reaction mixture was stirred overnight. Then the toluene fraction was separated and water layer was washed twice with toluene 10 ml. Combined toluene fractions were dried over Na_2SO_4 and evaporated *in vacuo* to dryness. The white material was extracted with hexane (2×50 ml) and evaporating of the solvent yielded **4**: 1.1 g (54%). Mp: 128–131 °C. Anal. Calcd for $\text{C}_{56}\text{H}_{70}\text{Sn}_2\text{O}_4\text{S}$ (MW 1076.62): C, 62.48; H, 6.55. Found: C, 62.71; H, 6.62%. Positive-ion MS: m/z 1117 $[\text{M}+\text{K}]^+$; m/z 1101 $[\text{M}+\text{Na}]^+$; m/z 523 $[\text{LSnPh}_2]^+$; m/z 467 $[\text{LSnPh}_2\text{-butene}]^+$; m/z 411 $[\text{LSnPh}_2\text{-2*butene}]^+$, 100%; m/z 351 $[\text{LSnPh}_2\text{-2*butene-2*HCOH}]^+$. ^1H NMR (CDCl_3): 0.88 (18H, s, $(\text{CH}_3)_3\text{CO}$), 4.36 (4H, s, OCH_2), 7.18–7.49 (13H, m, Ar-H). ^{13}C NMR (CDCl_3): 27.8 (s, $(\text{CH}_3)_3\text{CO}$), 66.6 (s, OCH_2), 73.8 (s, $(\text{CH}_3)_3\text{CO}$), 126.6 (s, Ar-C3,5-L), 128.5 (s, Ar-C3,5-Ph), 128.9 (s, Ar-C4-Ph), 129.8 (s, Ar-C4-L), 136.5 (s, Ar-C2,6-Ph), 143.4 (s, Ar-C1-Ph), 147.7 (s, Ar-C2,6-L), (Ar-C1-L) not detected. ^{119}Sn NMR (CDCl_3): -84.4 .

2.5. Synthesis of $2,6\text{-}(t\text{BuOCH}_2)_2\text{C}_6\text{H}_3\text{SnPhI}_2$ (**5**)

I_2 (115 mg, 0.46 mmol) was added to a solution of **3** (216 mg, 0.23 mmol) in CH_2Cl_2 (30 ml). The resulting mixture was stirred for 12 h and then evaporated *in vacuo*. The residue was extracted with hexane (2×50 ml) and evaporation of the solvent gave **5** as pale yellow powder. Yield: 210 mg (66%). Mp: 122–125 °C. Anal. Calcd for $\text{C}_{22}\text{H}_{30}\text{SnO}_2\text{I}_2$ (MW 698.98): C, 37.80; H, 4.33. Found: C, 38.12; H, 4.56%. Positive-ion MS: m/z 573 $[\text{M}-\text{I}]^+$; m/z 517 $[\text{M}-\text{I}-\text{butene}]^+$; m/z 461 $[\text{M}-\text{I}-2^*\text{butene}]^+$, 100%. Negative-ion MS: m/z 127 $[\text{I}]^-$, 100%. ^1H NMR (CDCl_3): 1.07 (18H, s, $(\text{CH}_3)_3\text{CO}$), 4.73 (4H, s, OCH_2), 7.33 (2H, d, Ar-H3,5-L), 7.41 (4H, m, Ar-H4-L and H3,4,5-Ph), 7.75

(2H, d, Ar-H2,6-Ph). ^{13}C NMR (CDCl_3): 27.8 (s, $(\text{CH}_3)_3\text{CO}$), 64.9 (s, OCH_2), 76.9 (s, $(\text{CH}_3)_3\text{CO}$), 127.2 (s, Ar-C3,5-L), 128.6 (s, Ar-C3,5-Ph), 130.6 (s, Ar-C4-Ph), 130.8 (s, Ar-C4-L), 134.5 (s, Ar-C2, 6-Ph), 141.7 (s, Ar-C1-Ph), 147.2 (s, Ar-C2,6-L), (Ar-C1-L) not detected. ^{119}Sn NMR (CDCl_3): -391.8.

2.6. Synthesis of 2,6-(*t*BuOCH₂)₂C₆H₃SnPh₂I (6)

I₂ (31 mg, 0.12 mmol) was added to a solution of **4** (132 mg, 0.12 mmol) in CH_2Cl_2 (30 ml). The resulting mixture was stirred for 12 h and then evaporated *in vacuo*. The residue was extracted with hexane (2 × 50 ml) and evaporation of the solvent gave **6** as pale yellow powder. Yield: 100 mg (63%). Mp: 130–133 °C. Anal. Calcd for C₂₈H₃₅SnO₂I (MW 649.18): C, 51.81; H, 5.43 Found: C, 52.09; H, 5.65%. Positive-ion MS: *m/z* 523 [M - I]⁺, 100%; *m/z* 467 [M - I - butene]⁺; *m/z* 411 [M - I - 2*butene]⁺. Negative-ion MS: *m/z* 127 [I]⁻, 100%. ^1H NMR (CDCl_3): 0.94 (18H, s, $(\text{CH}_3)_3\text{CO}$), 4.58 (4H, s, OCH_2), 7.36–7.42 (9H, m, Ar-H3,4,5-L and Ar-H3,4,5-Ph), 7.77 (4H, d, Ar-H2,6-Ph). ^{13}C NMR (CDCl_3): 27.9 (s, $(\text{CH}_3)_3\text{CO}$), 66.7 (s, OCH_2), 75.4 (s, $(\text{CH}_3)_3\text{CO}$), 126.9 (s, Ar-C3,5-L), 128.7 (s, Ar-C3,5-Ph), 129.6 (s, Ar-C4-Ph), 130.3 (s, Ar-C4-L), 136.0 (s, Ar-C2,6-Ph), 142.6 (s, Ar-C1-Ph), 147.9 (s, Ar-C2,6-L), (Ar-C1-L) not detected. ^{119}Sn NMR (CDCl_3): -182.9.

2.7. NMR tube experiment – reaction of 6 with I₂ in 1:1 molar ratio

I₂ (40 mg, 0.16 mmol) was put into a NMR tube under argon atmosphere and then CDCl_3 solution of **6** 103 mg (0.16 mmol) was added. The resulting solution was immediately studied by ^1H , ^{13}C and ^{119}Sn NMR spectroscopy and ESI mass spectrometry (see Section 3).

2.7.1. NMR data for [2,6-(*t*BuOCH₂)₂C₆H₃SnPh₂]⁺I₃⁻ (7)

^1H NMR (CDCl_3): 1.25 (18H, s, $(\text{CH}_3)_3\text{CO}$), 5.07 (4H, s, OCH_2), 7.40–7.69 (9H, m, Ar-H3,4,5-L and Ar-H3,4,5-Ph), 7.82 (4H, d, Ar-H2,6-Ph). ^{13}C NMR (CDCl_3): 28.5 (s, $(\text{CH}_3)_3\text{CO}$), 65.5 (s, OCH_2), 85.0 (s, $(\text{CH}_3)_3\text{CO}$), 124.9

(s, Ar-C3,5-L), 130.7 (s, Ar-C3,5-Ph), 132.6 (s, Ar-C4-Ph), 134.8 (s, Ar-C4-L), 136.6 (s, Ar-C2,6-Ph), 140.2 (s, Ar-C1-Ph), 143.9 (s, Ar-C2,6-L), (Ar-C1-L) not detected. ^{119}Sn NMR (CDCl_3): -20.7. Positive-ion MS: *m/z* 523 [LSnPh₂]⁺, 100%; *m/z* 467 [LSnPh₂-butene]⁺; *m/z* 411 [LSnPh₂-2*butene]⁺. Negative-ion MS: *m/z* 381 [I₃]⁻; *m/z* 127 [I]⁻, 100%.

2.7.2. NMR data of the mixture of 2,6-(*t*BuOCH₂)₂C₆H₃I (8) and Ph₂SnI₂ after complete decomposition of 7

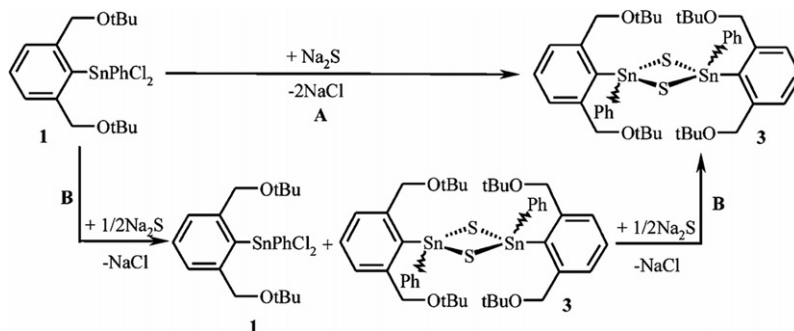
^1H NMR (CDCl_3): 1.33 (18H, s, $(\text{CH}_3)_3\text{CO}$ - **8**), 4.47 (4H, s, OCH_2 - **8**), 7.44 (1H, t, Ar-H4 - **8**), 7.47–7.52 (8H, m, Ar-H3,5 - **8** and Ar-H3,4,5-Ph₂SnI₂), 7.67 (4H, d, Ar-H2,6-Ph₂SnI₂). ^{13}C NMR (CDCl_3): 27.9 (s, $(\text{CH}_3)_3\text{CO}$ - **8**), 69.2 (s, OCH_2 - **8**), 74.0 (s, $(\text{CH}_3)_3\text{CO}$ - **8**), 100.9 (s, Ar-C1 - **8**), 127.5 (s, Ar-C3,5 - **8**), 130.7 (s, Ar-C3,5-Ph₂SnI₂), 132.6 (s, Ar-C4-Ph₂SnI₂), 134.8 (s, Ar-C4 - **8**), 136.6 (s, Ar-C2,6-Ph₂SnI₂), 140.2 (s, Ar-C1-Ph₂SnI₂), 143.9 (s, Ar-C2,6 - **8**). ^{119}Sn NMR (CDCl_3): -242.2, Ph₂SnI₂. Positive-ion MS: *m/z* 415 [**8** + K]⁺; *m/z* 399 [**8** + Na]⁺, 100%. Negative-ion MS: *m/z* 127 [I]⁻, 100%.

3. Results and discussion

3.1. Organotin sulphides

The reaction of LSnPhCl₂ (**1**) (L = 2,6-(*t*BuOCH₂)₂-C₆H₃) [19] with 1 equiv of Na₂S · 9H₂O in toluene/water gives the expected diorganotin sulphide (LSnPhS)₂ (**3**) in good yield (Scheme 1A). The attempt to prepare (LSnPhCl)₂S by the reaction of **1** with Na₂S · 9H₂O in 1:0.5 ratio yielded only a mixture of **3** and starting **1** as shown by ^1H and ^{119}Sn NMR spectroscopy (Scheme 1B). The addition of the next 0.5 equiv of Na₂S · 9H₂O to this mixture led to a smooth formation of **3**.

The dimeric nature (LSnPhS)₂ of **3** was proven by ESI mass spectra, where the molecular adduct with sodium ion [M+Na]⁺ at *m/z* 979 as the base peak accompanied by molecular adduct with potassium ion [M+K]⁺ at *m/z* 995 were detected. The ^{119}Sn NMR spectra of **3** revealed two signals of very similar chemical shifts at -74.6 and -79.5 ppm and both are accompanied by satellites coming from coupling with adjacent ^{117}Sn tin nucleus $^2J(^{119}\text{Sn}$,



Scheme 1. Preparation of compound **3**.

^{117}Sn) = 226 Hz. Analogously ^1H and ^{13}C NMR spectra contained two sets of signals approximately in 1:1 integral ratio in CDCl_3 at room temperature. The presence of two sets of signals in ^1H , ^{13}C and ^{119}Sn NMR spectra of diorganotin sulphides containing phenyl and chelating ligand was attributed to the formation of two possible isomers – *cis/trans* in respect to the central Sn_2S_2 ring [11b] and analogous isomers were also obtained also with simple aryl ligands on the central tin atom [5a]. These findings prove the presence of both *cis* and *trans* isomers in CDCl_3 solution of **3** (Fig. 1).

The structure of one of these isomers *trans*-**3** (single crystals were obtained from solution containing both *cis/trans* isomers) in the solid state was established by X-ray diffraction study (Fig. 2, Table 1). The molecular structure of *trans*-**3** is formed as a centrosymmetric dimer with planar Sn_2S_2 core. The bond distances between the tin atoms and sulphur atoms within this ring are nearly identical Sn1-S2 2.429(3) and Sn1-S2a 2.424(2) Å as well as bonding angles Sn1-S2-Sn1a 88.91(9)° and S2-Sn1-S2a 91.09(8)°. On the other hand, Sn-S bond distances within central Sn_2S_2 ring in organotin sulphide containing another O,C,O chelating

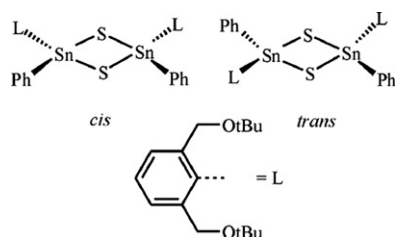


Fig. 1. Possible isomers *cis/trans* of compound **3**.

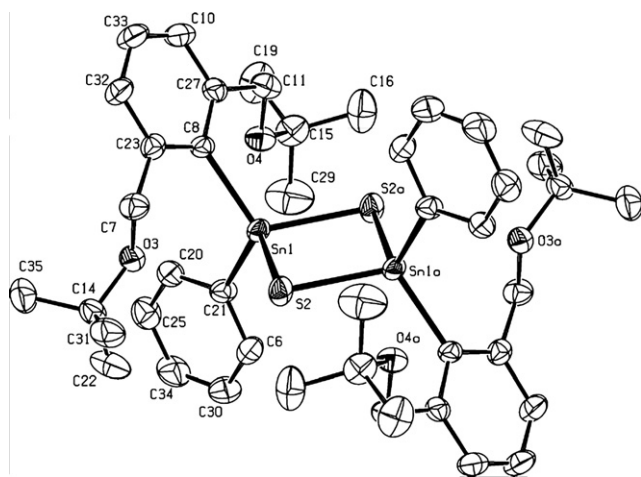


Fig. 2. ORTEP drawing (50% probability atomic displacement ellipsoids) of *trans*-**3**. Hydrogen atoms have been omitted for clarity (symmetry code a: $-x, -y, -z$). Selected bond distance (Å): S2-Sn1 2.429(3), S2a-Sn1 2.424(2), O3-Sn1 2.927(7), O4-Sn1 2.993(5), Sn1-C8 2.138(7), Sn1-C21 2.122(6). Selected bonding angles (°): S2-Sn1-S2a 91.09(8), Sn1-S2-Sn1a 88.91(9), O3-Sn1-O4 115.83(16), C8-Sn1-C21 114.8(3), C8-Sn1-S2a 113.2(2), C8-Sn1-S2 113.8(2), C21-Sn1-S2a 111.4(3), C21-Sn1-S2 110.3(2).

ligand [2,6-[(EtO) $_2$ (O)P] $_2$ -4-*t*Bu $_2$ C $_6$ H $_4$ Sn(S)Cl] $_2$ are a bit different (2.533 vs. 2.357 Å) maybe as a consequence of stronger Sn-O intramolecular interactions in this compound [12]. Similar non-symmetric Sn_2S_2 rings were also obtained with other chelating ligands [11,20]. Both O,C,O chelating ligands are placed mutually *trans* in respect to the central Sn_2S_2 core in **3**. The polyhedron of the central tin atom can be described as a distorted bi-capped tetrahedron, since both oxygen donor atoms are, although very weakly, coordinated to the tin atom (O3-Sn1 2.927(7), O4-Sn1 2.993(5) Å) in *cis* position (O3-Sn1-O4 115.83(16)°). Both intramolecular Sn-O interactions in **3** are comparable to those found in parent dichloride **1** (O-Sn 2.775(1) and 2.882(1) Å) [19] but considerably weaker than values in organotin cations stabilized by the same O,C,O-coordinating pincer-type ligand (range of Sn-O distances 2.270(2)–2.394(3) Å), where both oxygen donor atoms are coordinated in *trans* fashion (range of O-Sn-O angles 148.90(6)–150.67(5)°) [21]. Similarly, stronger intramolecular Sn-O interactions were found in organotin compounds containing another O,C,O-coordinating pincer-type ligand (2,6-[(EtO) $_2$ (O)P] $_2$ -4-*t*Bu $_2$ C $_6$ H $_4$) [12,22].

The reaction of LSnPh_2Cl (**2**) [19] with 0.5 equiv of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ in toluene/water gives desired triorganotin sulphide (LSnPh_2) $_2\text{S}$ (**4**) in moderate yield (Scheme 2). In the positive-ion ESI mass spectra $[\text{M}+\text{Na}]^+$ (m/z 1101) and $[\text{M}+\text{K}]^+$ (m/z 1117) adducts of molecule proved the composition of **4** (see Section 2). The ^{119}Sn NMR spectrum of **4** revealed signal at -84.4 ppm suggesting (pseudo)tetrahedral environment at the tin atom and is comparable to that found for $\text{Ph}_3\text{SnSSnPh}_3$ (-54 ppm) [10b]. The ^1H , ^{13}C NMR spectra of **4** also contain only one set of signals that is in accordance with non-existence of any other isomer in solution of **4**.

3.2. Reaction of organotin sulphides with I_2

The attempt to form organotin iodide (LSnI) $_2$ by a phenyl abstraction by the reaction of compound **3** and two equivalents of I_2 failed. Interestingly, elimination of sulphur was observed and the product was characterized as diorganotin compound LSnPhI_2 (**5**) (Scheme 3). Similar reaction was discovered by Wuest and co-workers, when the reaction of hexaphenyldistannathiane with iodine afforded Ph_3SnI [23]. The value $\delta(^{119}\text{Sn}) = -391.8$ ppm of **5** is shifted upfield when compared to Ph_2SnI_2 -242.2 ppm indicating the presence of an intramolecular Sn-O interaction. However, the ^1H and ^{13}C NMR spectra of **5** contain only one set of signals in the whole studied temperature range (300–215 K) indicating fast dynamic dissociation-association process of both ligands' arms [24].

Single crystals of **5** were obtained by crystallization from saturated CHCl_3 /hexane solution (Table 1) and the molecular structure of compound **5** is depicted in Fig. 3. Both donor oxygen atoms in **5** are coordinated to the central tin atom only very weakly with bond distances O1-Sn1 2.843(3) and O2-Sn1 2.789(3) Å, similarly to compound

Table 1
Crystal data and structure refinement of **3**, **5** and **6**

	3	5	6
Empirical formula	C ₄₄ H ₆₀ O ₄ S ₂ Sn ₂	C ₂₂ H ₃₀ O ₂ SnI ₂ · CHCl ₃	C ₂₈ H ₃₅ IO ₂ Sn
Color	Colourless	White	Yellowish
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>cn</i>
<i>a</i> (Å)	14.7660(8)	16.749(3)	12.0610(13)
<i>b</i> (Å)	9.9300(10)	9.6214(19)	11.4860(6)
<i>c</i> (Å)	19.5960(14)	19.163(4)	19.783(3)
β (°)	129.801(7)	110.73(3)	98.638(10)
<i>Z</i>	2	4	4
μ (mm ⁻¹)	1.265	3.317	2.095
<i>D</i> _x (Mg m ⁻³)	1.436	1.882	1.585
Crystal size (mm)	0.3 × 0.2 × 0.15	0.2 × 0.07 × 0.05	0.43 × 0.31 × 0.25
Crystal shape	Plate	Needle	Plate
θ range (deg)	1–27.5	1–27.5	1–27.5
<i>T</i> _{min} , <i>T</i> _{max}	0.714, 0.815 ^a	0.654, 1.000 ^b	0.418, 0.623 ^b
No. of reflections measured	19892	18198	18061
No. of unique reflections; <i>R</i> _{int}	4978, 0.045	6028, 0.052	5891, 0.036
No. of observed ref. [<i>I</i> > 2 σ (<i>I</i>)]	2899	4880	3440
No. of parameters	236	286	289
<i>S</i> ^c all data	1.173	1.065	1.293
Final <i>R</i> ^c indices [<i>I</i> > 2 σ (<i>I</i>)]	0.056	0.038	0.058
<i>wR</i> 2 ^c indices (all data)	0.141	0.098	0.165
$\Delta\rho$, maximum, minimum, [e Å ⁻³]	1.064, -1.597	1.414, -1.242	1.213, -2.149

^a Correction by integration.

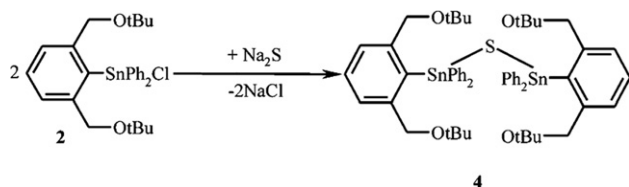
^b SORTAV program.

^c Definitions: $R(F) = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $wR_2 = [\Sigma (w(F_o^2 - F_c^2)^2) / \Sigma (w(F_o^2)^2)]^{1/2}$, $S = [\Sigma (w(F_o^2 - F_c^2)^2) / (N_{\text{reflns}} - N_{\text{params}})]^{1/2}$.

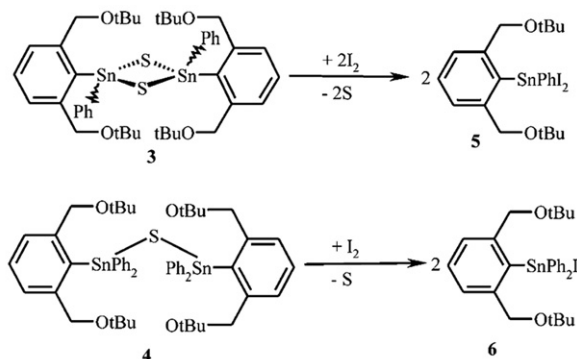
3. The coordination polyhedron of the tin atom in **5** can be described as a bi-capped tetrahedron formed by C1, C17, I1 and I2 atoms, that is *cis* attacked by two oxygen donor atoms O1 and O2 (angle O1–Sn1–O2 120.17(9)°). The main deviations from the ideal tetrahedral environment can be seen in angles I1–Sn1–I2 88.81(3)° and C1–Sn1–C17

121.23(19)° as a consequence of present weak intramolecular Sn–O interactions.

Similarly, the treatment of triorganotin sulphide **4** with 1 equiv of I₂ yielded organotin iodide LSnPh₂I (**6**) instead of phenyl abstraction (Scheme 3). Nevertheless, this reaction provides an alternative path to compound **6**, which



Scheme 2. Preparation of compound **4**.



Scheme 3. Reactions of organotininsulphides **3** and **4** with I₂.

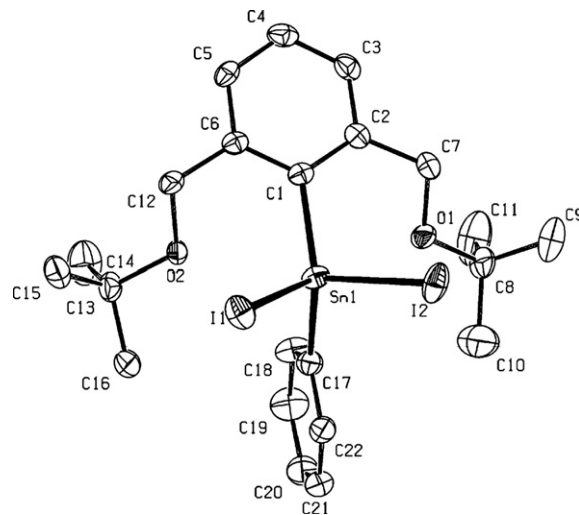


Fig. 3. ORTEP drawing (50% probability atomic displacement ellipsoids) of **5**. Hydrogen atoms have been omitted for clarity. Selected bond distance (Å): O1–Sn1 2.843(3), O2–Sn1 2.789(3), Sn1–C1 2.137(4), Sn1–C17 2.117(5), Sn1–I1 2.7664(7), Sn1–I2 2.7693(7). Selected bonding angles (°): O1–Sn1–O2 120.17(9), C1–Sn1–C17 121.23(19), C1–Sn1–I1 115.01(11), C1–Sn1–I2 108.85(13), C17–Sn1–I1 107.36(15), C17–Sn1–I2 110.87(14), I1–Sn1–I2 88.81(3).

was shown to be inaccessible by the iodolysis of LSnPh_3 previously [21a]. Derivative **6** was characterized by ESI-MS spectra, ^1H and ^{13}C NMR spectra. The value $\delta(^{119}\text{Sn}) = -182.9$ ppm of **6** is well comparable to the value -204.7 ppm of the less sterically demanding analogue 2,6-(MeOCH_2) $_2\text{C}_6\text{H}_3\text{SnPh}_2\text{I}$ [21a].

The molecular structure of **6** was determined by the help of X-ray diffraction measurements (Fig. 4, Table 1). Only one of the oxygen donor atoms O4 is coordinated to the central tin atom through medium strong intramolecular interaction O4–Sn1 2.696(6) Å (this value indicates stronger intramolecular interaction, than that found in diorganotin iodide **5**). The second oxygen atom O3 interacts with the tin atom only insignificantly O3–Sn1 3.200(6) Å. The resulting coordination polyhedron of Sn1 can be described as a distorted trigonal bipyramid with ligand and phenyls *ipso* carbon atoms C5, C6 and C24 in the equatorial plane (Σ of angles in SnC_3 girdle 349°). The axial positions are occupied by donor oxygen atom O4 and iodine I1 (O3–Sn1–I1 $169.13(13)^\circ$). Similar coordination polyhedron has been recently found in triorganotin carboxylate 2,6-(MeOCH_2) $_2\text{C}_6\text{H}_3\text{SnPh}_2(\text{O}_2\text{CCF}_3)$ [21a].

A crucial step of the preparation of **6** is to rigorously follow 1:1 stoichiometric ratio of **4** and I_2 , otherwise product **6** is accompanied by an impurity detected by the ^1H and ^{119}Sn NMR spectroscopy (the signal at -242.2 ppm in the ^{119}Sn NMR and with $\delta(^1\text{H}, \text{CH}_2\text{O}) = 4.47$ ppm). The explanation is that compound **6** is able to react with addi-

tional equiv of I_2 . So the treatment of **6** with I_2 in a NMR tube (CDCl_3) led to a smooth (within 30 min) and clean formation of ionic organotin derivative $[\text{LSnPh}_2]^+\text{I}_3^-$ (**7**). The presence of organotin cation was clearly established by ^1H NMR spectrum, where the signal of the CH_2O group is significantly shifted to lower field (5.07 ppm) and also ^{119}Sn NMR spectrum revealed only one signal at -20.7 ppm, which is a value typical for triorganotin cations containing O,C,O – coordinating pincer-type ligand [21]. Compound **7** is then unstable in CDCl_3 solution and is slowly transformed to new products ($\delta(^1\text{H}, \text{CH}_2\text{O}) = 4.47$ ppm and $\delta(^{119}\text{Sn}) = -242.2$ ppm) (Fig. 5). The plausible explanation is formation of organotin compound Ph_2SnI_2 along with 2,6-(*t*BuOCH $_2$) $_2\text{C}_6\text{H}_3\text{I}$ (**8**) (Scheme 4).

There are several pieces of evidence for this statement: (i) $\delta(^{119}\text{Sn}) = -242.2$ ppm really corresponds to Ph_2SnI_2 [25] (ii) there are no visible $^nJ(^{119}\text{Sn}, ^{13}\text{C})$ couplings to aromatic carbons of the ligand L in ^{13}C NMR spectra, although $^nJ(^{119}\text{Sn}, ^{13}\text{C})$ are obtained for phenyls of Ph_2SnI_2 ($^2J(^{119}\text{Sn}, ^{13}\text{C}(2,6)) = 61.7$, $^3J(^{119}\text{Sn}, ^{13}\text{C}(3,5)) = 76.3$, $^4J(^{119}\text{Sn}, ^{13}\text{C}(4)) = 16.6$ Hz) (iii) the signal which is appropriate to *C-*ipso** of the ligand in compound **8** is significantly shifted to higher field $\delta(^{13}\text{C}) = 100.9$ ppm as a consequence of the presence of the C–I bond, also other aromatic iodides displayed $\delta(^{13}\text{C})$ of C–I carbon close to this value (for example, PhI 94.3 ppm, 2-(CH_3) $\text{C}_6\text{H}_4\text{I}$ 101.8 ppm, 2-(CH_2Cl) $\text{C}_6\text{H}_4\text{I}$ 99.4 ppm, etc. [26]) (iv) the presence of **8** was unambiguously confirmed by ESI mass spectra of this mixture, where signals at m/z 399 (m/z 415) correspond to $[\mathbf{8}+\text{Na}]^+$ ($[\mathbf{8}+\text{K}]^+$) (v) finally ^1H , ^{119}Sn HMBC NMR spectra revealed no cross-peaks between the tin signal at -242 ppm and the region of OCH_2 groups of ligand L in ^1H NMR spectrum, but this cross peak was obtained in parent iodide **6**. This means that organotin cation incorporated in compound **7** undergoes an unusual attack of I_3^- , which leads to a disruption of a commonly very strong pincer ligand–metal

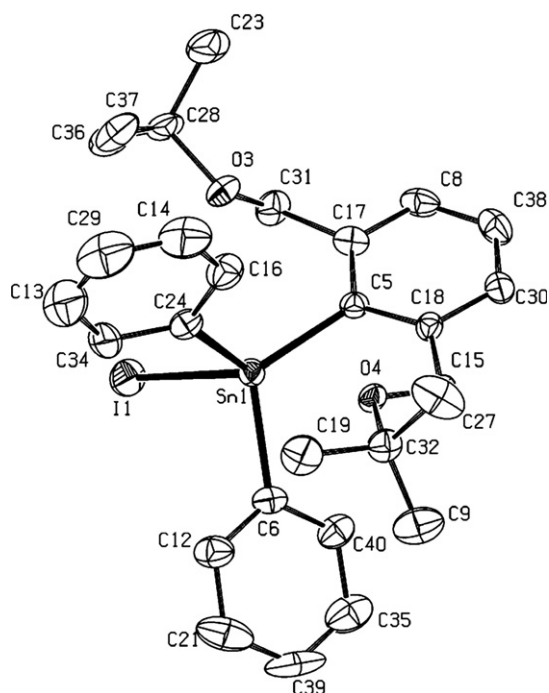


Fig. 4. ORTEP drawing (50% probability atomic displacement ellipsoids) of **6**. Hydrogen atoms have been omitted for clarity. Selected bond distance (Å): O3–Sn1 3.200(6), O4–Sn1 2.696(6), Sn1–C5 2.143(4), Sn1–C6 2.152(8), Sn1–C24 2.119(8), Sn1–I1 2.7857(8). Selected bonding angles ($^\circ$): I1–Sn1–O4 $169.13(13)$, C5–Sn1–C6 $112.8(3)$, C6–Sn1–C24 $119.4(3)$, C5–Sn1–C24 $116.3(3)$.

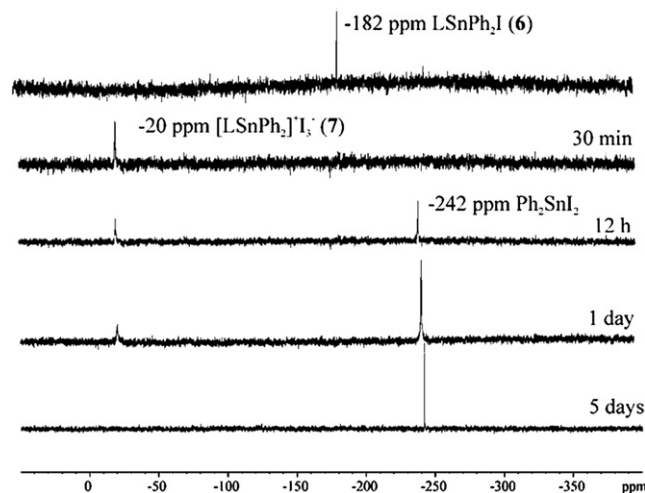
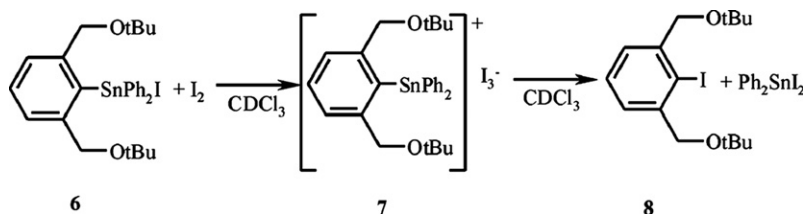


Fig. 5. ^{119}Sn NMR spectra (CDCl_3 , 300 K) showing formation of **7** and its decomposition to Ph_2SnI_2 .



Scheme 4. Formation and decomposition of ionic compound 7.

bond [27] and formation of Ph_2SnI_2 . This reaction path represents novel chemical behaviour of the O,C,O – coordinating pincer-type ligand in organotin(IV) chemistry.

4. Conclusions

To summarize, two novel organotin sulphides **3** and **4** were prepared and structurally characterized. Their reaction with iodine proceeded to corresponding organotin iodides **5** and **6** instead of the intended phenyl abstraction. Moreover triorganotin compound **6** is able to react with additional eq. I_2 to give ionic triorganotin compound $[\text{LSnPh}_2]^+ \text{I}_3^-$ **7** that is unstable in solution and decomposes to Ph_2SnI_2 and the organic compound 2,6- $(t\text{BuOCH}_2)_2\text{C}_6\text{H}_3\text{I}$ **8**.

5. Supplementary material

CCDC 635831, 635687 and 635832 contain the supplementary crystallographic data for **3**, **5** and **6**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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