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Syntheses, characterizations and crystal structures of monomeric or macrocyclic compounds of di- or triorganotin (IV) moieties with 4,4′-thiodibenzenethiol

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Abstract

Six organotin compounds with 4,4′-thiodibenzenethiol (LH_2) of the type $R_nSnL_{4-n}SnR_n$ ($n = 3$: R = Me **1**, Ph **2**, $PhCH_2$ **3**, $n = 2$: R = Me **4**, Ph **5**, $PhCH_2$ **6**) have been synthesized. All compounds were characterized by elemental analysis, IR and NMR (^1H, ^{13}C, and ^{119}Sn) spectra. The structures of compounds **1**, **2**, **4**, **5** and **6** were also determined by X-ray diffraction analysis, which revealed that compounds **1** and **2** were monomeric structures, compounds **4**, **5** and **6** were centrosymmetric dinuclear macrocyclic structures, and all the tin(IV) atoms are four-coordinated. Furthermore, supramolecular structures were also found in compounds **1**, **2**, **4**, **5** and **6**, which exhibit one-dimensional chains, two-dimensional networks or three-dimensional structures through intermolecular C–H···S weak hydrogen bonds (WHBs), non-bonded Sn···S interactions or C–H···π interactions.

Keywords: S ligand; Macrocyclic compounds; Crystal structure; Tin

1. Introduction

Recently, developments in coordination chemistry have produced numerous macrocyclic compounds through the appropriate coordination geometry of organometallic compounds and certain organic ligands [1]. Furthermore, non-covalent weak molecular forces (such as hydrogen bonds, van der Waals forces, non-bonded contacts and C–H···π interactions), capable of connecting these metallic subunits into looser and more intriguing supramolecular infrastructures, have been widely investigated in structural biology, structural chemistry and the pharmaceutical sciences [2]. Among them organotin compounds are attracting more and more attention mainly due to their intriguing, and often complicated, architectures and topologies [3], and also for their potential industrial applications and biological activities [4]. More recently, flexible multidentate ligands have been employed in order to gain access to topologies not available from logical combinations of rigid building blocks. de Sousa, for example, has reported a series of diorganotin compounds based on the flexible 2,6-diacetylpyridine ligand [5], Silva et al. have reported some five- and six-membered chelate organotin mercaptide compounds [6], and in particular Baul and co-workers have reported a cyclic dinuclear organotin compound [7]. In our previous work, we have reported several novel organotin mercaptide compounds which were obtained from flexible multidentate ligands, such as pentacoordinated compounds with 2,5-dithiobiurea [8], tetranuclear or dinuclear monomers or three-dimensional polymers with *meso*-2,3-dimercaptosuccinic acid [9]. To continue our research on organotin(IV) complexes in this field, we choose another interesting ligand: 4,4′-thiodibenzenethiol.

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This ligand was chosen for the following reasons: first, it has two thiol groups so it should form strong covalent bonds with an organotin moiety; second, the conformational flexibility of this ligand will allow for the formation of various and interesting molecular and supramolecular structures; third, 4,4′-thiodibenzenethiol can bond to more than one organotin moiety in one discrete molecule, which will increase the opportunities for supramolecular assembly from these compounds through intermolecular weak interactions. Here, we report the syntheses and characterizations of six organotin compounds constructed from 4,4′-thiodibenzenethiol (LH_2). With a 1:2:2 molar ratio of LH_2:R_3SnCl:EtONa three dinuclear monomeric compounds (**1**–**3**) of the type $R_3SnLSnR_3$ [R = Me **1**, Ph **2**, $PhCH_2$ **3**] were obtained, and with a 1:1:2 molar ratio of LH_2:R_2SnCl_2:EtONa three dinuclear macrocyclic compounds (**4**–**6**) of the type $(R_2SnL)_2$ [R = Me **4**, Ph **5**, $PhCH_2$ **6**] were obtained.

2. Experimental

2.1. Materials and measurements

Trimethyltin chloride, triphenyltin chloride, dimethyltin dichloride, diphenyltin dichloride and 4,4′-thiodibenzenethiol are commercially available, and they were used without further purification. Dibenzyltin dichloride and tribenzyltin chloride were prepared by a standard method reported in the literature [10]. The melting points were obtained with a Kofler micro-melting point apparatus and were uncorrected. Infrared-spectra were recorded on a Nicolet-6700 spectrophotometer using KBr discs and sodium chloride optics. ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Varian Mercury Plus 400 spectrometer operating at 400, 100.6 and 149.2 MHz, respectively. The spectra were acquired at 298 K; ^{13}C spectra are broadband proton decoupled. The chemical shifts are reported in ppm with respect to the references and are stated relative to external tetramethylsilane (TMS) for ^{1}H and ^{13}C NMR, and neat tetramethyltin for ^{119}Sn NMR. Elemental analyses were performed with a PE-2400II apparatus.

2.2. X-ray crystallography

Crystals were mounted in Lindemann capillaries under nitrogen. All X-ray crystallographic data were collected on a Bruker SMART CCD 1000 diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 298(2) K. A semi-empirical absorption correction was applied to the data. The structures were solved by direct methods using SHELXS-97 and refined against F^2 by full-matrix least squares using SHELXL-97. Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in Table 1.

2.3. Syntheses of the complexes **1–6**

2.3.1. $[(CH_3)_3\,SnSC_6H_4]_2S$ (**1**)

The reaction was carried out under a nitrogen atmosphere. 4,4′-Thiodibenzenethiol (0.250 g, 1 mmol) and sodium ethoxide (0.136 g, 2 mmol) were added to benzene (20 ml) in a Schlenk flask and stirred for 5 min. Trimethyltin chloride (0.399 g, 2 mmol) was added to the reaction mixture, which was then stirred for 12 h at 40 °C. After filtration the solvent was gradually removed by evaporation under vacuum until a solid product was obtained. The solid was recrystallized from ether-petroleum and colorless crystals were formed. Yield: 86%. M.p. 97–99 °C. *Anal.* Calc.

Table 1
Crystal, data collection and structure refinement parameters for compounds **1**, **2**, **4**, **5** and **6**

Compound	1	2	4	5	6
Empirical formula	$C_{18}H_{26}S_3Sn_2$	$C_{48}H_{38}S_3Sn_2$	$C_{28}H_{28}S_6Sn_2$	$C_{48}H_{36}S_6Sn_2$	$C_{52}H_{44}S_6Sn_2$
M	575.95	948.34	794.24	1042.51	1098.61
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2(1)/c$	$P1$	$P2(1)/n$	$P\bar{1}$	$P2(1)/n$
a (Å)	22.923(7)	9.829(4)	6.378(2)	9.051(3)	14.762(4)
b (Å)	7.341(2)	9.853(4)	14.684(5)	10.305(4)	11.832(3)
c (Å)	14.155(4)	12.685(5)	16.205(6)	13.480(5)	15.370(4)
α (°)	90	87.932(5)	90	68.961(4)	90
β (°)	97.828(5)	76.041(5)	92.584(6)	71.938(4)	117.664(3)
γ (°)	90	63.765(4)	90	82.460(5)	90
V (Å^3)	2359.7(13)	1065.9(8)	1516.0(9)	1115.4(7)	2377.6(11)
Z	4	1	2	1	2
μ (mm^{-1})	2.380	1.350	2.078	1.433	1.349
Reflections collected	11 522	5450	7224	5756	12 080
Independent reflections	4075	4426	2667	3836	4198
R_{int}	0.0881	0.0213	0.0562	0.0361	0.0544
$R_1[I > 2\sigma(I)]/R_1$	0.0672	0.0584	0.0423	0.0552	0.0443
(all data)	0.1679	0.0701	0.0679	0.0933	0.0915
$wR_1[I > 2\sigma(I)]/wR_1$	0.1554	0.1459	0.0945	0.0812	0.0900
(all data)	0.2117	0.1556	0.1090	0.0906	0.1144

for $[(CH_3)_3SnSC_6H_4]_2S$: C, 37.53; H, 4.55. Found: C, 37.26; H, 4.30%. IR (KBr, cm^{-1}): ν(Sn–C), 557; ν(Sn–S), 312. ^1H NMR ($CDCl_3$, ppm): δ 0.34 (s, 9H, $^2J_{SnH} = 27.2$ Hz), 7.06 (d, 2H), 7.23 (d, 2H). ^{13}C NMR ($CDCl_3$, ppm): δ 29.6 ($^1J(^{119}Sn–^{13}C) = 390.4$ Hz), 131, 131.6, 133.3, 134, 135, 135.2. ^{119}Sn NMR ($CDCl_3$, ppm): 100.4.

2.3.2. *[Ph$_3$ SnSC$_6$H$_4$]$_2$S (**2**)*

Compound **2** was prepared in the same way as that for compound **1**. Yield: 92%. M.p. 153–155 °C. *Anal.* Calc. for $[Ph_3SnSC_6H_4]_2S$: C, 60.79; H, 4.04. Found: C, 60.50; H, 3.90%. IR (KBr, cm^{-1}): ν(Sn–C), 546; ν(Sn–S), 309. ^1H NMR ($CDCl_3$, ppm): δ 6.8 (d, 2H), 7.2 (d, 2H), 7.2–7.7 (m, 15H). ^{13}C NMR ($CDCl_3$, ppm): δ 124.9 ($^1J(^{119}Sn–^{13}C) = 402.8$ Hz), 128.7–129.2, 129.9–130.9, 131.67, 133.7, 135.4–135.7, 136.2–137.0, 137.3, 137.4. ^{119}Sn NMR ($CDCl_3$, ppm): −60.5.

2.3.3. *[(PhCH$_2$)$_3$ SnSC$_6$H$_4$]$_2$S (**3**)*

Compound **3** was prepared in the same way as that for compound **1**. Yield: 80%. M.p. 100–102 °C. *Anal.* Calc. for $[(PhCH_2)_3SnSC_6H_4]_2S$: C, 62.81; H, 4.88. Found: C, 62.96; H, 4.74%. IR (KBr, cm^{-1}): ν(Sn–C), 551; ν(Sn–S), 322. ^1H NMR ($CDCl_3$, ppm): δ 2.4 (s, 6H), 6.7–7.4 (m, 19H). ^{13}C NMR ($CDCl_3$, ppm): δ 22.7 ($^1J(^{119}Sn–^{13}C) = 440.3$ Hz), 124.7, 124.8, 127.9–128.1, 128.7–129.1, 130.9–131.5, 132.4, 134, 135.8–135.9, 139.4. ^{119}Sn NMR ($CDCl_3$, ppm): 37.7.

2.3.4. *[(CH$_3$)$_2$Sn(SC$_6$H$_4$)$_2$S]$_2$ (**4**)*

The reaction was carried out under a nitrogen atmosphere. 4,4′-Thiodibenzenethiol (0.250 g, 1 mmol) and sodium ethoxide (0.136 g, 2 mmol) were added to benzene (20 ml) in a Schlenk flask and stirred for 5 min. Dimethyltin dichloride (0.219 g, 1 mmol) was added to the reaction mixture, which was then stirred for 12 h at 40 °C. After filtration, the solvent was gradually removed by evaporation under vacuum until a solid product was obtained. The solid was recrystallized from ether–petroleum and colorless crystals were formed. Yield: 89%. M.p. 199–201 °C. *Anal.* Calc. for $[(CH_3)_2Sn(SC_6H_4)_2S]_2$: C, 42.34; H, 3.55. Found: C, 42.10; H, 3.32%. IR (KBr, cm^{-1}): ν(Sn–C), 575; ν(Sn–S), 319. ^1H NMR ($CDCl_3$, ppm): δ 0.6 (s, 6H), 7.1 (d, 2H), 7.3 (d, 4H), 7.4 (d, 2H). ^{13}C NMR ($CDCl_3$, ppm): δ 30.0 ($^1J(^{119}Sn–^{13}C) = 502.2$ Hz), 128.2, 128.6, 130.5, 132.4, 132.5. ^{119}Sn NMR ($CDCl_3$, ppm): 86.4.

2.3.5. *[(Ph)$_2$Sn(SC$_6$H$_4$)$_2$S]$_2$ (**5**)*

Compound **5** was prepared in the same way as that for compound **4**. Yield: 81%. M.p. 160–162 °C. *Anal.* Calc. for $[(Ph)_2Sn(SC_6H_4)_2S]_2$: C, 55.30; H, 3.48. Found: C, 55.05; H, 3.20%. IR (KBr, cm^{-1}): ν(Sn–C), 558; ν(Sn–S), 305. ^1H NMR ($CDCl_3$, ppm): δ 6.8–7.5 (m, 18H). ^{13}C NMR ($CDCl_3$, ppm): δ 128.8 ($^1J(^{119}Sn–^{13}C) = 503.3$ Hz), 129.1, 129.4, 130.2, 131.1, 131.8, 133.8, 135.8, 136.0, 136.7, 136.9, 137.5. ^{119}Sn NMR ($CDCl_3$, ppm): −61.2.

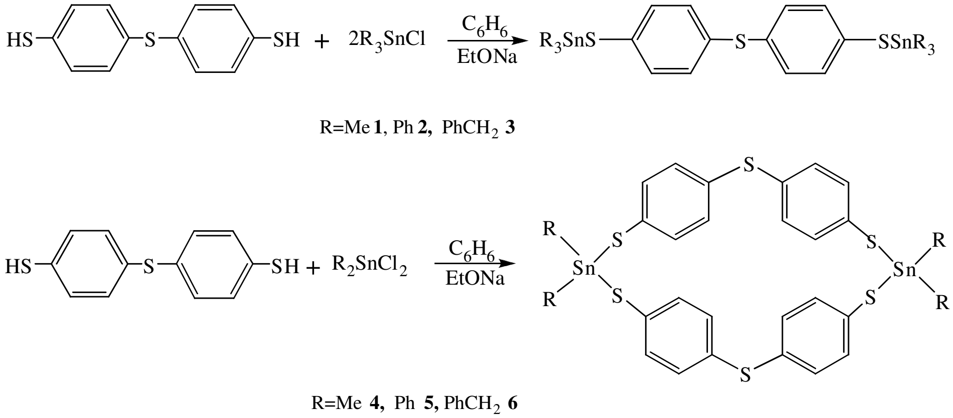
2.3.6. *[(PhCH$_2$)$_2$Sn(SC$_6$H$_4$)$_2$S]$_2$ (**6**)*

Compound **6** was prepared in the same way as that for compound **4**. Yield: 79%. M.p. 143–145 °C. *Anal.* Calc. for $[(PhCH_2)_2Sn(SC_6H_4)_2S]_2$: C, 56.84; H, 4.04. Found: C, 56.62; H, 3.81%. IR (KBr, cm^{-1}): ν(Sn–C), 530; ν(Sn–S), 320. ^1H NMR ($CDCl_3$, ppm): δ 2.5 (s, 4H), 6.7–7.4 (m, 18H). ^{13}C NMR ($CDCl_3$, ppm): δ 26.0 ($^1J(^{119}Sn–^{13}C) = 443.8$ Hz), 27.9, 125.4, 128.0–128.4, 128.8–128.9, 130.7–131.4, 134.9, 135.8, 136.4, 136.5, 137.2. ^{119}Sn NMR ($CDCl_3$, ppm): 23.0.

3. Results and discussion

3.1. *Syntheses*

The reactions of triorganotin(IV) chloride with 4,4′-thiodibenzenethiol in a 2:1 stoichiometry and diorganotin(IV) dichloride with 4,4′-thiodibenzenethiol in a 1:1 stoichiometry, depending on the nature of the starting acceptor and reaction conditions, afforded air-stable compounds. The syntheses procedures are shown in Scheme 1.



Scheme 1.

3.2. IR spectra

The IR spectra show that the strong absorption at 2560 cm^{-1} in the free ligand due to the –SH group is absent in the spectra of all the compounds **1–6**, and at the same time a new absorption appears in the region 305–322 cm^{-1}. All these values are located within the range for Sn–S vibrations observed in common organotin thiolate derivatives (300–400 cm^{-1}) [11], consequently, they can be assigned to ν(Sn–S).

3.3. NMR spectra

The ^{1}H NMR data show that the signal of the –SH proton in the spectrum of the ligand is absent in all of the compounds, indicating the removal of the –SH proton and the formation of Sn–S bonds. The $^{2}J_{\text{SnH}}$ values of compounds **1** and **4** are 27.2 Hz and 83.2 Hz, which are similar to those previously reported for four-coordinated tetrahedral tin(IV) adducts [12]. The ^{13}C NMR spectra of all the compounds show a significant downfield shift of all carbon resonances, compared with the free ligand.

The ^{119}Sn NMR data show that compounds **1–6** have only one signal (100.4, −60.5, 37.7, 86.4, −61.2 and 23 ppm, respectively), they are all well in accordance with values that have been reported in the literature which lie in the range from +200 to −60 ppm [13].

3.4. X-ray crystallographic studies

3.4.1. Crystal structures of 1 and 2

The molecular structures of compounds **1** and **2** are illustrated in Figs. 1 and 3, respectively. Selected bond lengths (Å) and angles (°) are listed in Table 2.

X-ray crystal structure analysis reveals that compounds **1** and **2** are monomeric with one ligand bonding to two tin atoms through Sn–S bonds. Each of the tin atoms is four-coordinated. Distortion from strict tetrahedral coordination is partly because of the bonding variance. The four primary bonds to Sn are three methyl groups and one sulfur atom for **1** and three phenyl groups and one sulfur atom for **2**. The Sn–C bond lengths are consistent with those reported in other triorganotin derivatives [14]. The

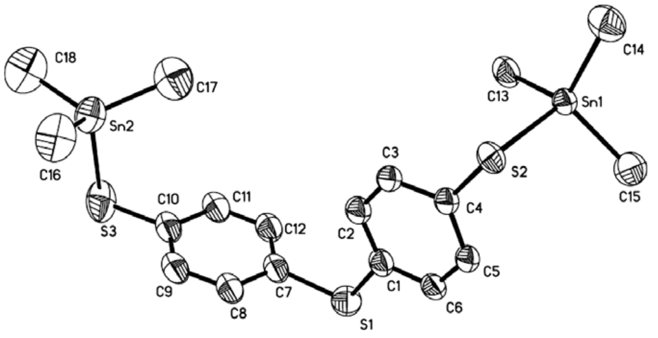


Fig. 1. Molecular structure of compound **1**; ellipsoids at 30% probability; hydrogen atoms have been removed for clarity.

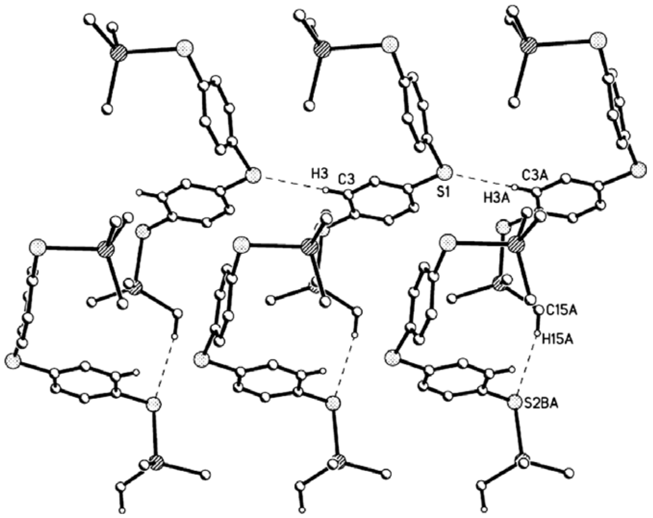


Fig. 2. Two-dimensional network of compound **1** connected through C–H···S WHBs, unattached hydrogen atoms have been removed for clarity.

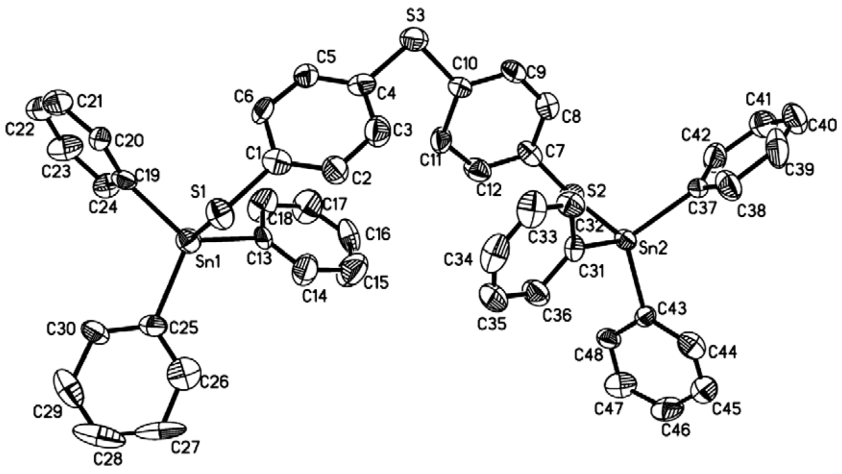


Fig. 3. Molecular structure of compound **2**; hydrogen atoms have been removed for clarity.

Table 2
Selected bond lengths (Å) and bond angles (°) for compounds **1** and **2**

*[(CH$_3$)$_3$SnSC$_6$H$_4$]$_2$S (**1**)*			
Sn(1)–C(14)	2.10(15)	Sn(2)–C(16)	2.07(19)
Sn(1)–C(15)	2.11(15)	Sn(2)–C(17)	2.08(2)
Sn(1)–C(13)	2.12(13)	Sn(2)–C(18)	2.11(2)
Sn(1)–S(2)	2.44(4)	Sn(2)–S(3)	2.43(6)
C(14)–Sn(1)–C(15)	114.7(6)	C(16)–Sn(2)–C(17)	109.8(8)
C(14)–Sn(1)–C(13)	113.1(6)	C(16)–Sn(2)–C(18)	108.4(8)
C(15)–Sn(1)–C(13)	112.3(6)	C(17)–Sn(2)–C(18)	119.2(9)
C(14)–Sn(1)–S(2)	103.5(4)	C(16)–Sn(2)–S(3)	107.5(6)
C(15)–Sn(1)–S(2)	106.3(4)	C(17)–Sn(2)–S(3)	107.4(6)
C(13)–Sn(1)–S(2)	105.8(4)	C(18)–Sn(2)–S(3)	103.8(6)
*[Ph$_3$SnSC$_6$H$_4$]$_2$S (**2**)*			
Sn(1)–C(25)	2.12(15)	Sn(2)–C(31)	2.10(17)
Sn(1)–C(13)	2.15(16)	Sn(2)–C(43)	2.13(12)
Sn(1)–C(19)	2.17(14)	Sn(2)–C(37)	2.15(13)
Sn(1)–S(1)	2.43(4)	Sn(2)–S(2)	2.42(3)
C(25)–Sn(1)–C(13)	111.4(6)	C(31)–Sn(2)–C(43)	112.6(6)
C(25)–Sn(1)–C(19)	110.4(6)	C(31)–Sn(2)–C(37)	112.8(6)
C(13)–Sn(1)–C(19)	112.9(6)	C(43)–Sn(2)–C(37)	112.5(5)
C(25)–Sn(1)–S(1)	107.6(4)	C(31)–Sn(2)–S(2)	106.8(4)
C(13)–Sn(1)–S(1)	105.7(5)	C(43)–Sn(2)–S(2)	104.5(3)
C(19)–Sn(1)–S(1)	108.5(4)	C(37)–Sn(2)–S(2)	107.0(4)

Sn–S bonds lengths [the Sn–S bond lengths are between 2.43(6) and 2.44(4) Å] are slightly less than the sum of the covalent radii of Sn and S (2.44 Å) [15].

Compounds **1** and **2** exhibit interesting intermolecular interactions as shown in Figs. 2, 4 and 5: the molecules of **1** are connected through C(15)–H(15)···S(2) (C···S, 3.85 Å; H···S, 2.94 Å; C–H···S, 158.5°) and C(3)–H(3)···S(1) WHBs (C···S, 3.91 Å; H···S, 2.99 Å; C–H···S, 175.9°) into a two-dimensional network in the *bc* plane. In compound **2**, there are two loose two-dimensional networks through different WHBs in different directions: one that consists of discrete molecules connected through C(24)–H(24)···S(3) (C···S, 3.70 Å; H···S, 2.98 Å; C–H···S, 135.1°) and C(28)–H(28)···S(2) (C···S, 3.80 Å; H···S, 2.99Å; C–H···S, 146.3°) WHBs (Fig. 4) in the *bc* plane, and another that is connected through C(30)–H(30)···π (37–42) [H···π (centroid), 3.51 Å; C–H···π (centroid), 122.0°] and C(46)–H(46)···π (37–42) [H···π (centroid), 3.38 Å; C–H···π (centroid), 138.1°] interactions (Fig. 5) along the $[11\bar{1}]$ and $[\bar{1}10]$ directions.

The values for the C–H···S WHB are longer than an intramolecular C–H···S WHB in (r-2, c-4)-3-benzyl-2,4,5,5-tetraphenyl-1,3-thiazolidine (C···S, 3.04 Å; H···S, 2.55 Å and C–H···S, 110°) [16], but they are closely in agreement with values that have been reported in the literature [15,17], whilst the parameters for the C–H···π interactions in the compound are in agreement with those that have been reported in the literature [17,18].

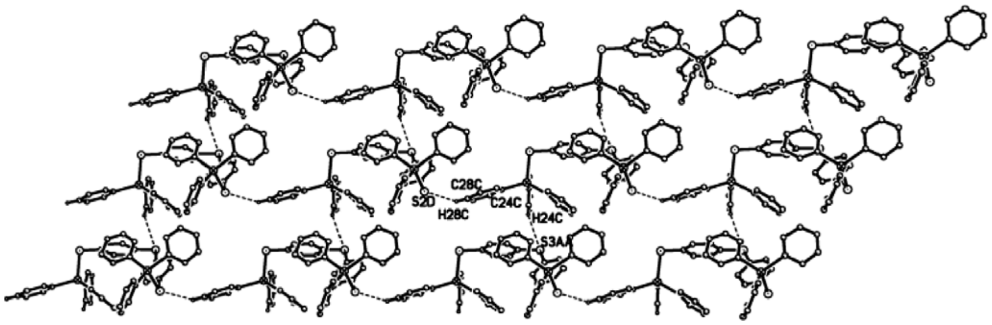


Fig. 4. Two-dimensional network of compound **2** by C–H···S WHBs along the *bc* plane, unattached hydrogen atoms have been removed for clarity.

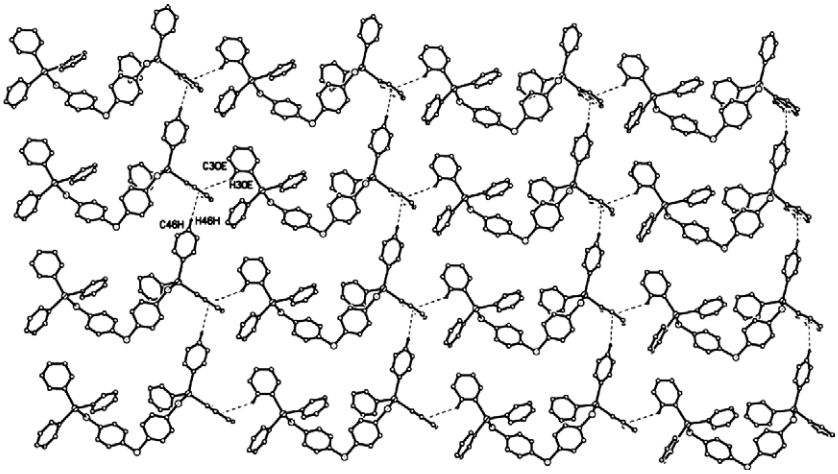


Fig. 5. Two-dimensional network of compound **2** connected through C–H···π interactions along the $[11\bar{1}]$ and $[\bar{1}10]$ directions, unattached hydrogen atoms have been removed for clarity.

3.4.2. Crystal structure of **4**, **5** and **6**

Perspective view of the molecular structures of compounds **4**, **5** and **6** are illustrated in Figs. 6, 8 and 10, respectively. Selected bond lengths (Å) and angles (°) are listed in Table 3.

Compounds **4**, **5** and **6** all proved to be centrosymmetric dinuclear macrocyclic compounds with 4,4′-thiodibenzenethiol bridging the adjacent tin atoms with a twenty-four member $Sn_2S_6C_{16}$ ring, and the ring can be valued by the transcyclic distances (Sn(1)–Sn(1)# = 12.51 Å and C(2)–

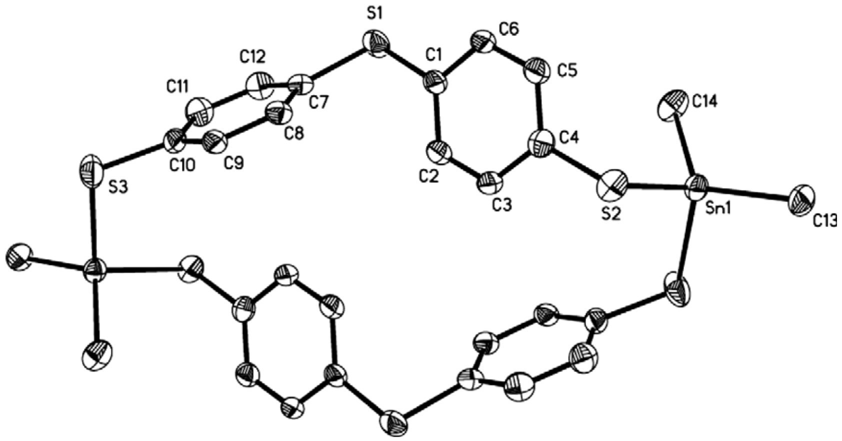


Fig. 6. Molecular structure of compound **4**; ellipsoids at 30% probability; hydrogen atoms have been removed for clarity.

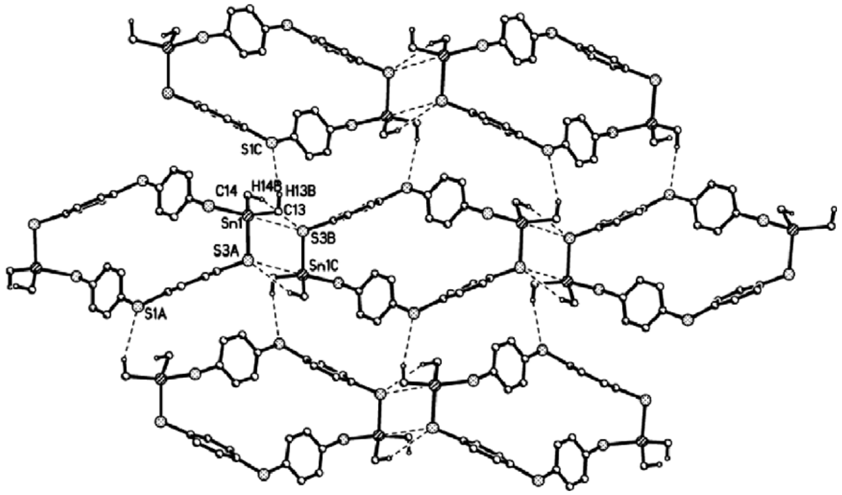


Fig. 7. Two-dimensional network of compound **4** connected through C–H· · ·S WHBs and non-bonded Sn· · ·S contacts, unattached hydrogen atoms have been removed for clarity.

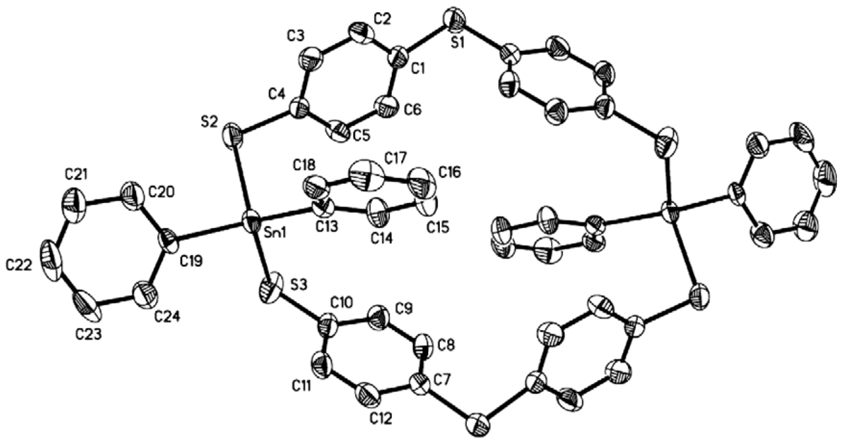


Fig. 8. Molecular structure of compound **5**; ellipsoids at 30% probability; hydrogen atoms have been removed for clarity.

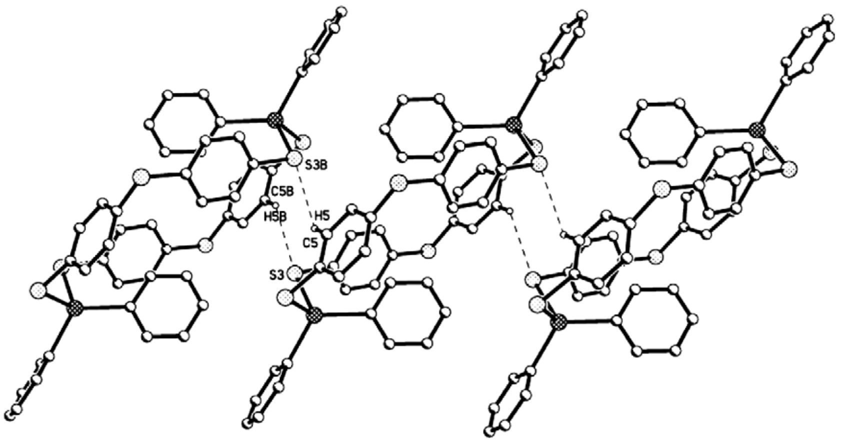


Fig. 9. One-dimensional chain of compound **5**, unattached hydrogen atoms have been removed for clarity.

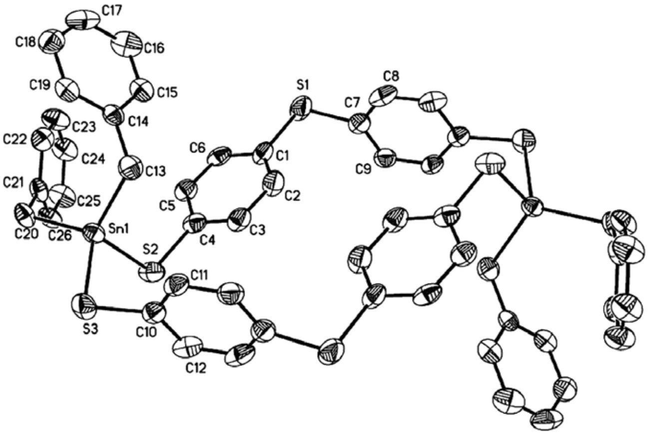


Fig. 10. Molecular structure of compound **6**; ellipsoids at 30% probability; hydrogen atoms have been removed for clarity.

Table 3
Selected bond lengths (Å) and bond angles (°) for compounds **4**, **5** and **6**

*[$(CH_3)_2Sn(SC_6H_4)_2S]_2$ (**4**)*			
Sn(1)–C(14)	2.12 (7)	Sn(1)–S(2)	2.42 (17)
Sn(1)–C(13)	2.12 (6)	Sn(1)–S(3)#1	2.45(2)
C(14)–Sn(1)–C(13)	120.8(3)	C(14)–Sn(1)–S(3)#1	107.6(2)
C(14)–Sn(1)–S(2)	107.8(18)	C(13)–Sn(1)–S(3)#1	104.0(19)
C(13)–Sn(1)–S(2)	107.5(19)	S(2)–Sn(1)–S(3)#1	108.7(6)
*[$(Ph)_2Sn(SC_6H_4)_2S]_2$ (**5**)*			
Sn(1)–C(13)	2.12(6)	Sn(1)–S(3)	2.42(19)
Sn(1)–C(19)	2.13(5)	Sn(1)–S(2)	2.42(18)
C(13)–Sn(1)–C(19)	120.9(2)	C(13)–Sn(1)–S(2)	107.8 (15)
C(13)–Sn(1)–S(3)	112.2(17)	C(19)–Sn(1)–S(2)	101.1(16)
C(19)–Sn(1)–S(3)	107.5(19)	S(3)–Sn(1)–S(2)	105.7(7)
*[$(PhCH_2)_2Sn(SC_6H_4)_2S]_2$ (**6**)*			
Sn(1)–C(20)	2.15(6)	Sn(1)–S(2)	2.41(18)
Sn(1)–C(13)	2.15(6)	Sn(1)–S(3)	2.43(19)
C(20)–Sn(1)–C(13)	115.7(2)	C(20)–Sn(1)–S(3)	114.4(16)
C(20)–Sn(1)–S(2)	108.0(17)	C(13)–Sn(1)–S(3)	106.7(19)
C(13)–Sn(1)–S(2)	111.5(19)	S(2)–Sn(1)–S(3)	99.4(7)

C(2)# = 3.89 Å for **4**; Sn(1)–Sn(1)# = 10.42 Å and C(8)–C(8)# = 6.75 Å for **5**; Sn(1)–Sn(1)# = 11.42 Å and C(2)–C(2)# = 4.44 Å for **6**). The units are [$(CH_3)_2SnL$], [$(Ph)_2SnL$] and [$(PhCH_2)_2SnL$], respectively, in which the primary bonds of the ligand to tin occur through the two sulfur atoms. To the best of our knowledge, dinuclear macrocyclic compounds in common organotin derivatives of thionate have so far only rarely been reported [19].

Each of the tin atoms in compounds **4**, **5** and **6** has a distorted tetrahedral coordination. The four primary bonds to Sn are two Sn–C and two Sn–S bonds. The Sn–C bond lengths are consistent with those found in compounds **1** and **2**. The Sn–S bond lengths are 2.42(17) Å [Sn(1)–S(2)], 2.45(2) Å [Sn(1)–S(3)#1] (#1 = $-x+2, -y+1, -z+1$) for **4**; 2.42(19) Å [Sn(1)–S(3)], 2.42(18) Å [Sn(1)–S(2)] for **5** and 2.41(18) Å [Sn(1)–S(2)], 2.43(19) Å [Sn(1)–S(3)] for **6**, similar to those found in compounds **1** and **2**. Distortion from a strict tetrahedral coordination is partly because of the bonding variance. The deviation from an ideal tetrahedron is manifested by the bond angles (see Table 3), all of which deviate from the idea value of 109.5°.

Analyses of the supramolecular infrastructure of the compounds **4**, **5** and **6** reveal that weak intermolecular non-bonded Sn···S contacts, C–H...S and C–H···π WHBs play important roles in the supramolecular arrangements. The C–H···π interactions can also be viewed as an edge-to face π–π interaction [18d].

The supramolecular structure of compound **4** is a two-dimensional network in the *bc* plane, as shown in Fig. 7, in which the discrete molecules are connected through intermolecular C–H···S (C···S, 3.62–3.75 Å; H···S, 2.87–2.96 Å; C–H···S, 135.0–140.6°) WHBs. This loose structure is further stabilized by non-bonded Sn(1)···S(3) interactions. The Sn(1)···S(3) distance (3.700 Å) is shorter than that in compounds $(PhCH_2)_2Sn(SC_5H_5N_2)_2$ and $(PhCH_2)_2SnCl(SC_5H_5N_2)$ [20], and also shorter than the sum of the Van der waals radii of Sn and S (4.0 Å) [21].

In compound **5**, an intermolecular C(5)–H(5)···S(3) (C···S, 3.65Å; H···S, 2.97 Å; C–H···S, 130.3°) WHB connects the discrete molecules into a linear chain, as shown in Fig. 9.

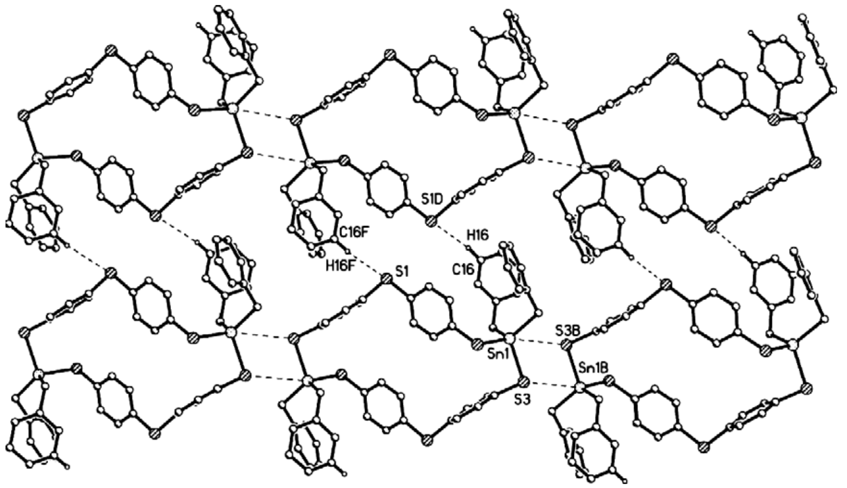


Fig. 11. Two-dimensional network of compound **6** connected through C–H···S WHBs and non-bonded Sn···S contacts, unattached hydrogen atoms have been removed for clarity.

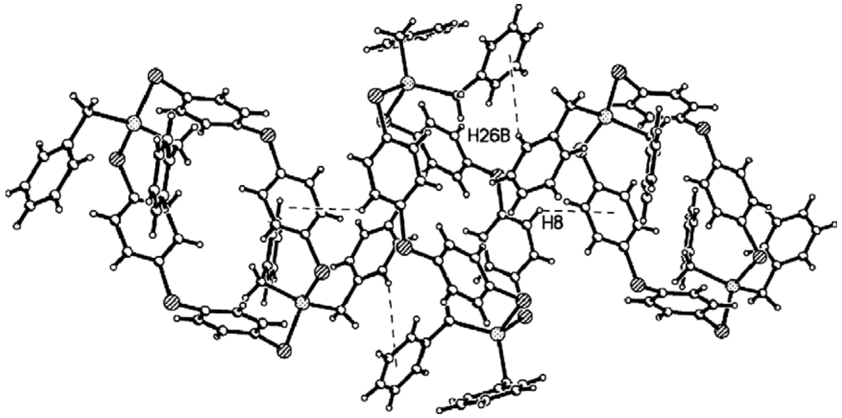


Fig. 12. One dimensional chain of compound **6** connected through C–H···π interactions along the [1 1 1] direction.

In compound **6**, the two-dimensional network in the *ac* plane (as shown in Fig. 11) is connected by C–H···S WHBs (C···S, 3.81Å; H···S, 2.95 Å; C–H···S, 153.6°) and non-bonded Sn···S interactions, and the linear chain along the [1 1 1] direction is connected by C–H···π [H···π (centroid), 3.36–3.51 Å; C–H···π (centroid), 131.5–136.3°] interactions at the same time (as shown in Fig. 12), forming a three-dimensional structure.

4. Conclusion

4,4′-Thiobisbenzenethiol has been shown to be able to form monomeric compounds with triorganotin moieties, and also to form dinuclear macrocyclic compounds with diorganotin moieties due to the flexibility of the ligand and the nature of the starting acceptor. The supramolecular structures described in this paper demonstrate that weak intermolecular interactions have enormous potential for assembling discrete molecular systems into one-dimensional chains, two-dimensional networks or three-dimensional structures, in which the subunits are organometallic compounds.

The current study also provides aids in the fundamental understanding of molecular recognition, and insight into the interpretation of supramolecular aggregation in crystal engineering.

5. Supplementary material

CCDC 636269, 636268, 636266, 636267, 636265 contains the supplementary crystallographic data for **1**, **2**, **4**, **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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