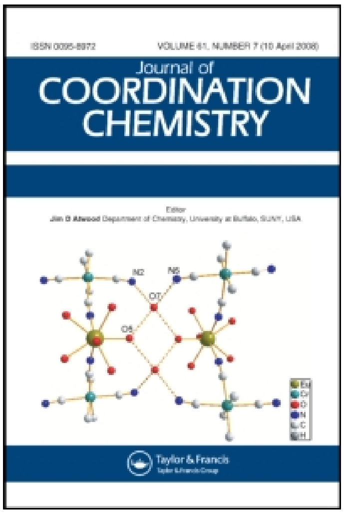

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Syntheses, characterizations and crystal structures of triorganotin(IV) complexes with amine derivatives of 6-amino-1,3,5-triazine-2,4-dithiol

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Syntheses, characterizations and crystal structures of triorganotin(IV) complexes with amine derivatives of 6-amino-1,3,5-triazine-2,4-dithiol

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Four new triorganotin(IV) complexes: $Me_3SnL^1SnMe_3$ (**1**), $Ph_3SnL^1SnPh_3$ (**2**), $[Me_3SnL^2]_n$ (**3**), $Ph_3SnL^2SnPh_3$ (**4**) have been synthesized from 6-anilino-1,3,5-triazine-2,4-dithiol (L^1H_2) and 6-(dibutylamino)-1,3,5-triazine-2,4-dithiol (L^2H_2). All were characterized by elemental analyses, IR and NMR spectra and X-ray diffraction analyses. Crystal structures show that **1**, **2** and **4** are monomers with one ligand coordinated to two triorganotin moieties; complex **3** is a helical chain. Significant C–H $\cdots \pi$, N–H $\cdots \pi$ interactions and intermolecular hydrogen bonds stabilize these structures.

Keywords: Triorganotin; 6-Anilino(or dibutylamino)-1,3,5-triazine-2,4-dithiol; Crystal structure

1. Introduction

We have an on-going interest in organotin-sulfur chemistry, partly from their potential biological activities and industrial applications [1–3], and also because of their supramolecular organometallic chemistry [4]. Recent investigation on organotin(IV) complexes has focused on structures to examine their versatile bonding modes [5], especially for organotin(IV) derivatives from heterocyclic thionates which show unusual geometries and moderate biological activities against various bacteria and fungi [3b].

Our contributions have included five- and six-membered thiol/thione heterocycles; for example, organotin-substituted tetrazole thiolates adopt monomer [6, 7], trimer [8], polymer [9] and sheet [10] structures, all containing σ-Sn-ligand bonds.

To continue our studies on coordination of organotin(IV) moieties with thiol sulfur and heterocyclic nitrogen [11–14], we chose 6-anilino-1,3,5-triazine-2,4-dithiol and 6-(dibutylamino)-1,3,5-triazine-2,4-dithiol with potential multidentate possibilities from deprotonated thiol and more than one coordinated active heterocyclic nitrogen.

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In this article, we report the syntheses and characterizations of four new organotin(IV) complexes. The X-ray crystallography of all four complexes show that the complexes contain the thiolate form of the ligand, i.e. the ligand is linked to the tin primarily through sulfur.

2. Experimental

2.1. *Materials and measurements*

Trimethyltin chloride, triphenyltin chloride, 6-anilino-1,3,5-triazine-2,4-dithiol and 6-(dibutylamino)-1,3,5-triazine-2,4-dithiol are commercially available and were used without further purification. The melting points were obtained with X-4 digital micro-melting point apparatus and are 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 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*

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 and the structure was 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 1–4*

2.3.1. Synthesis of $Me_3SnL^1SnMe_3$ (1). The reaction is carried out under nitrogen. 6-Anilino-1,3,5-triazine-2,4-dithiol (0.236 g, 1 mmol) and sodium ethoxide (0.136 g, 2 mmol) were added to ethanol (20 mL) in a Schlenk flask and stirred for 10 min. Then the trimethyltin chloride (0.399 g, 2 mmol) was added, the reaction mixture was stirred for 12 h at 40°C, filtered and the solvent gradually removed by evaporation under vacuum until solid is obtained. The solid is then recrystallized from ethanol giving colorless crystals. Yield: 78%, m.p.: 144–146°C. Anal. Found: C, 31.80; H, 4.07; N, 9.78%. Calcd for $C_{15}H_{24}N_4S_2Sn_2$: C, 32.06; H, 4.30; N, 9.97%. IR (KBr, cm^{-1}): ν(C=N), 1629, ν(Sn–C), 556; ν(Sn–N), 457, ν(Sn–S), 312. ^{1}H NMR ($CDCl_3$, ppm): δ 0.36–0.56(t, 18H, $^{2}J_{Sn,H} = 56$Hz, Sn–CH_3), 6.89(s, 1H, Ph–NH), 7.19(s, 1H, Ph), 7.34–7.36(d, 2H, Ph), 7.39–7.41(d, 2H, Ph). ^{13}C NMR ($CDCl_3$, ppm): δ 26.60 ($^{1}J(^{119}Sn–^{13}C)$, 390 Hz); 123.59, 125.26, 129.05, 137.04(Ph–NH); 162.12, 181.34. ^{119}Sn NMR ($CDCl_3$, ppm): δ 73.67.

Table 1. Crystal, data collection and structure refinement parameters for **1**, **2**, **3** and **4**.

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_{15}H_{24}N_4S_2Sn_2$	$C_{45}H_{36}N_4S_2Sn_2$	$C_{14}H_{27}N_4S_2Sn$	$C_{47}H_{48}N_4S_2Sn_2$
M	561.88	934.28	434.21	970.39
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Triclinic
Space group	$P2(1)/n$	Pbca	Pbca	$P\bar{1}$
Unit cell dimensions (Å, °)				
a	6.5223(19)	9.4295(16)	14.7909(19)	12.614(5)
b	22.028(3)	26.316(5)	15.393(2)	12.991(5)
c	16.089(3)	32.855(6)	35.764(3)	14.521(5)
α	90	90	90	99.703(4)
β	96.245(2)	90	90	103.300(4)
γ	90	90	90	90.821(5)
V(Å^3)	2297.8(8)	8153(2)	8142.5(16)	2279.2(14)
Z	4	8	16	2
μ (mm^{-1})	2.359	1.364	1.460	1.223
Reflections collected	11800	39042	38695	11644
Independent reflections	4046	7032	6936	7782
R_{int}	0.0576	0.0870	0.1859	0.0323
$R_1[I>2\sigma(I)]/R_1$	$R_1=0.0482$	$R_1=0.0663$	$R_1=0.0920$	$R_1=0.0540$
(all data)	$R_1=0.0933$	$R_1=0.1275$	$R_1=0.2010$	$R_1=0.1019$
$wR_1[I>2\sigma(I)]/wR_1$	$wR_2=0.0997$	$wR_2=0.1004$	$wR_2=0.1834$	$wR_2=0.1278$
(all data)	$wR_2=0.1235$	$wR_2=0.1224$	$wR_2=0.2263$	$wR_2=0.1720$

2.3.2. Synthesis of $Ph_3SnL^1SnPh_3$ (2).

Compound **2** is prepared in the same way as **1** by adding triphenyltin chloride (0.771 g, 2 mmol) to 6-anilino-1,3,5-triazine-2,4-dithiol (0.236 g, 1 mmol) and sodium ethoxide (0.136 g, 2 mmol). The solid is then recrystallized from ethanol giving colorless crystals. Yield: 81%, m.p.: 158–160°C. Anal. Found: C, 57.64; H, 3.67; N, 5.89%. Calcd for $C_{45}H_{36}N_4S_2Sn_2$: C, 57.85; H, 3.78; N, 6.00%. IR (KBr, cm^{-1}): ν(C=N), 1640, ν(Sn–C), 470, ν(Sn–S), 308. ^{1}H NMR ($CDCl_3$, ppm): δ 6.09(s, 1H, NH–Ph), 7.06–7.08(m, 5H, Ph–NH), 7.40–7.68(m, 30H, Ph–Sn). ^{13}C NMR ($CDCl_3$, ppm): δ 121.20 ($^1J(^{119}Sn–^{13}C)$, 379Hz), 124.42, 128.73, 129.03, 129.33, 129.82, 136.60, 136.82, 137.04, 139.57, 160.50. ^{119}Sn NMR ($CDCl_3$, ppm): δ −100.25.

2.3.3. Synthesis of $[Me_3SnL^2]_n$ (3).

Compound **3** is prepared in the same way as **1** by adding trimethyltin chloride (0.199 g, 1 mmol) to 6-(dibutylamino)-1,3,5-triazine-2,4-dithiol (0.272 g, 1 mmol) and sodium ethoxide (0.136 g, 2 mmol). The solid is then recrystallized from ethanol and colorless crystals formed. Yield: 70%, m.p.: 160–162°C. Anal. Found: C, 38.60; H, 6.11; N, 12.80%. Calcd for $C_{14}H_{27}N_4S_2Sn$: C, 38.72; H, 6.27; N, 12.90%. IR (KBr, cm^{-1}): ν(C=N), 1643, ν(Sn–C), 536 ν(Sn–S), 320. ^{1}H NMR ($CDCl_3$, ppm): δ 0.60(t, 18H, $^2J_{Sn,H}=56.8$Hz, Sn–CH_3), 0.95(t, 6H, CH_3), 1.30(m, 4H, –CH_2–Me), 1.58(m, 4H, CH_2–Et), 3.54(t, 4H, CH_2–N). ^{13}C NMR ($CDCl_3$, ppm): δ−3.0($^1J(^{119}Sn–^{13}C)$, 479Hz), 14.10, 20.36, 30.05, 47.51, 160.24, 179.22. ^{119}Sn NMR ($CDCl_3$, ppm): δ 106.53.

2.3.4. Synthesis of $Ph_3SnL^2SnPh_3$ (4).

Compound **4** is prepared in the same way as **1** by adding triphenyltin chloride (0.399 g, 2 mmol) to 6-(dibutylamino)-1,3,5-triazine-2,4-dithiol (0.272 g, 1 mmol) and sodium ethoxide (0.136 g, 2 mmol). The solid is then recrystallized from ethanol giving colorless crystals. Yield: 84%, m.p.: 169–171°C. Anal. Found: C, 57.98; H, 4.72; N, 5.67%. Calcd for $C_{47}H_{48}N_4S_2Sn_2$: C, 58.17; H, 4.99;

N, 5.77%. IR (KBr, cm^{-1}): ν(C=N), 1639, ν(Sn–C), 480; ν(Sn–S), 301. ^1H NMR ($CDCl_3$, ppm): δ 0.67(t, 6H, CH_3), 0.93(m, 4H, $-CH_2$–Me), 1.55(s, 4H, $-CH_2$–Et), 2.86(t, 4H, $-CH_2$–N), 7.66–7.69(t, 30H, Ph–Sn). ^{13}C NMR ($CDCl_3$, ppm): δ 14.03, 19.82, 29.42, 45.28, 128.55($^1J(^{119}Sn\text{-}^{13}C)$, 390.4Hz), 128.85, 129.14, 129.58, 129.64, 129.71, 136.69, 136.91, 137.13, 139.71, 161.52, 179.09. ^{119}Sn NMR ($CDCl_3$, ppm): δ− 102.09.

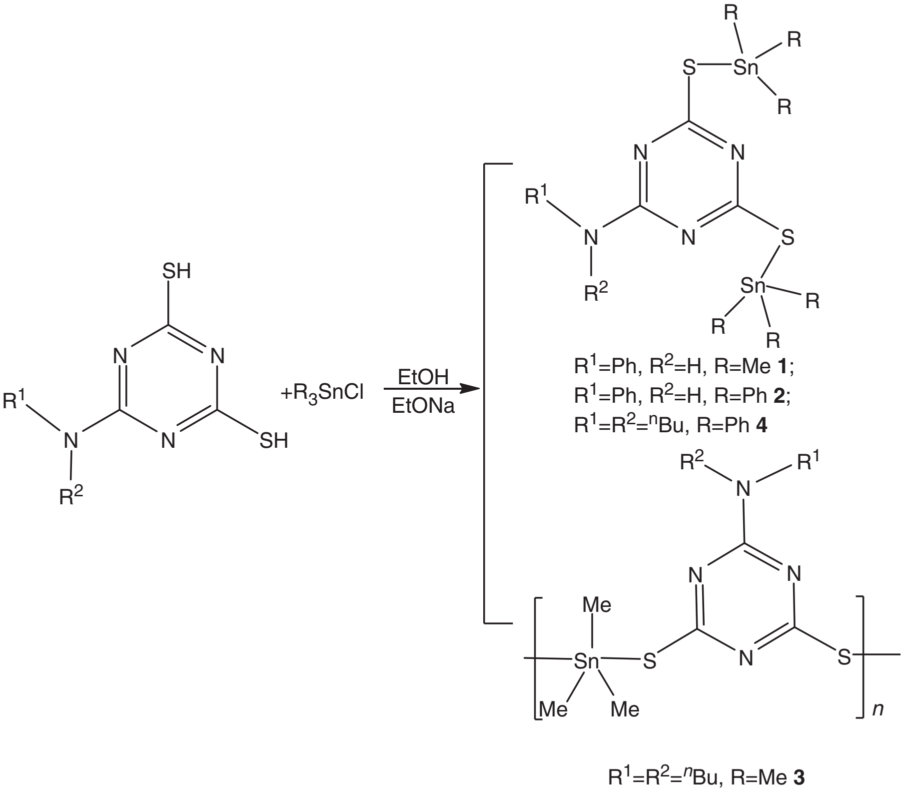
3. Results and discussion

3.1. *Syntheses*

The synthesis of **1**–**4** are shown in scheme 1.

3.2. *IR spectra*

Comparing the IR spectra of the free ligand with **1**–**4**, the bands at 2560–2410 cm^{-1}, which appear in the spectra of the free ligand as the m(S–H) vibration, are absent in **1**–**4**, indicating metal-ligand bond formation through these sites. The absorption



Scheme 1. Preparation of complexes **1**–**4**.

about 310 cm^{-1} region for all complexes, absent in the spectrum of the ligand, is assigned to the Sn–S stretching mode consistent with the range for Sn–S vibrations observed for organotin derivatives of thiolate (300–400 cm^{-1}) [15]. The band at 1629 cm^{-1} in the spectra of **1** assignable to ν(C=N) [14] is considerably shifted to lower frequency with respect to the free ligand 1640–1650 cm^{-1}, confirming coordination of the heterocyclic N to tin. The stretching frequency is lowered owing to displacement of electron density from N to Sn, resulting in weakening of the C=N bond as reported in the literature [16]. The weak- or medium-intensity band in the region 467 cm^{-1} can be assigned to Sn–N stretching vibrations, consistent with a number of organotin(IV) derivatives [17].

3.3. *NMR spectra*

^{1}H NMR data show the –SH proton to be absent in all of the complexes, indicating removal of the –SH proton and the formation of Sn–S bonds. The $^{2}J_{\mathrm{Sn,H}}$ values of trimethyltin derivatives **1** and **3** (56 and 56.8 Hz, respectively) are similar to those previously reported for four-coordinated tetrahedral tin(IV) adducts [18]. The structural changes occurring in ligand upon deprotonation and coordination to Sn should be reflected by the changes in the ^{13}C NMR spectra. The ^{13}C NMR spectra of all complexes show significant downfield shifts of all carbons, compared with the free ligand, a consequence of electron transfer from the ligand to the acceptor, as reported in the literature [19].

The ^{119}Sn NMR data of **1**–**4** show only one signal (73.67, −100.25, 106.53 and −102.09 ppm, respectively). Complexes **1** and **3** (73.67 and 106.53 ppm) are in the range of 200 to −60 ppm, reported in the literature [20], typical of four-coordinate triphenyltin complexes. Complexes **2** and **4** (−100.25 and −102.09 ppm) are in the range −40 to −120 ppm, typical of four-coordinate trimethyltin complexes [21].

Intermolecular interactions in solid **3** are lost in solution showing that the complex is tetrahedral monomer in solution as indicated by their higher frequency ^{119}Sn chemical shift values (106.53 ppm). Comparison with data for solutions of organotin thiotetrazoles [δ(^{119}Sn), R = Ph, from −65.0 to −69.4; R = alkyl 109.8–122.8 ppm] [6, 10] or organotin trithiotriazines [δ(^{119}Sn), R = alkyl, 68.3–74.4; R = Ph, −100.5 ppm] [22] is in agreement with this interpretation.

3.4. *X-ray crystallographic studies*

3.4.1. Crystal structure of 1. The molecular structure of **1** is illustrated in figure 1. Selected bond lengths (Å) and angles (°) are listed in table 2.

Complex **1** is a monomer with one ligand coordinated to two trimethyltin moieties. Each tin has four primary bonds, three methyl groups and one sulfur atom, and a weak Sn ← N bond. With the weak Sn ← N bond, each tin is five-coordinate trigonal bipyramidal geometry. The ligand thiol sulfur and heterocyclic nitrogen coordinate to tin. The equatorial plane is defined by S(1), C(10) and C(17) for Sn(1), S(2), C(12) and C(13) for Sn(2) with the sum of 335.8° (S(1)–Sn(1)–C(10) 111.8(3)°, C(24)–Sn(1)–S(1) 106.0(3)°, C(10)–Sn(1)–C(24) 117.9(4)°) and 336.5° (C(12)–Sn(2)–S(2) 111.0(3)°, C(13)–Sn(2)–S(2) 111.5(4)°, C(12)–Sn(2)–C(13) 113.9(5)°). The axial positions are

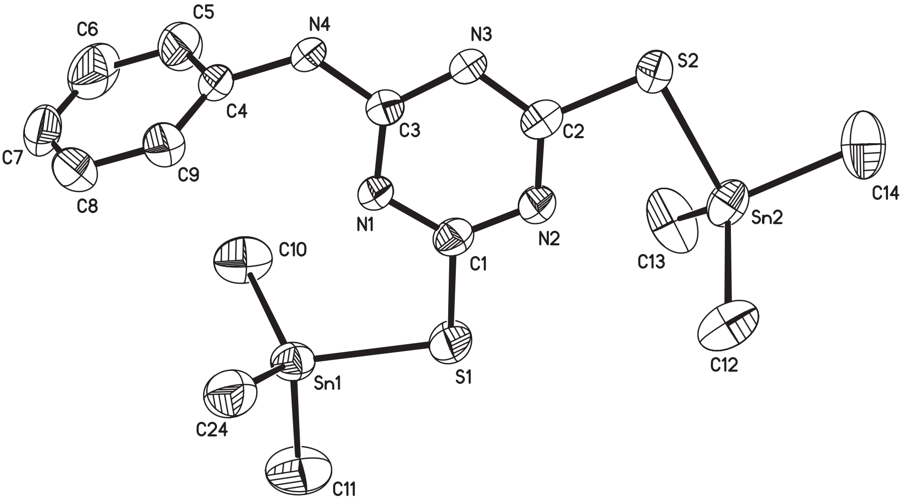


Figure 1. Molecular structure of **1**; ellipsoids at 30% probability; hydrogen atoms have been removed for clarity.

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

Sn(1)–C(10)	2.10(9)	Sn(2)–C(12)	2.10(10)
Sn(1)–C(24)	2.11(10)	Sn(2)–C(13)	2.14(9)
Sn(1)–C(11)	2.14(9)	Sn(2)–C(14)	2.16(10)
Sn(1)–S(1)	2.44(3)	Sn(2)–S(2)	2.45(2)
C(10)–Sn(1)–C(24)	117.9(4)	C(12)–Sn(2)–C(13)	113.9(5)
C(10)–Sn(1)–C(11)	109.2(4)	C(12)–Sn(2)–C(14)	111.8(4)
C(24)–Sn(1)–C(11)	111.1(5)	C(13)–Sn(2)–C(14)	109.9(4)
C(10)–Sn(1)–S(1)	111.8(3)	C(12)–Sn(2)–S(2)	111.0(3)
C(24)–Sn(1)–S(1)	106.0(3)	C(13)–Sn(2)–S(2)	111.5(4)
C(11)–Sn(1)–S(1)	99.2(4)	C(14)–Sn(2)–S(2)	97.5(3)

occupied by C(11), N(1) for Sn(1), and C(14), N(2) for Sn(2) with angles of 154.1° and 156.0°.

The Sn–S and Sn–N bond lengths are Sn(1)–S(1) 2.44(3) Å, Sn(2)–S(2) 2.45(2) Å, Sn(1)–N(1) 3.11 Å and Sn(2)–N(2) 2.84 Å, consistent with [$Me_3Sn(S–C_3H_2N_4–S)SnMe_3$] [15], and the Sn–S bond lengths (2.44(3) Å, 2.45(2) Å) lie in the range reported for trialkyltin heteroarethiolates (2.405–2.481 Å) [23], approaching the sum of the covalent radii of tin and sulfur (2.42 Å), which proves that sulfur coordinates to tin atom by strong covalent bonds.

There exists one strong intermolecular hydrogen bond N(4)–H(4)···N(3), which associates the discrete molecule into a dimer (see figure 2).

3.4.2. Crystal structure of 2 and 4.

Perspective views of the molecular structures of **2** and **4** are illustrated in figures 3 and 4. Selected bond lengths (Å) and angles (°) are listed in tables 3 and 4.

X-ray crystal structure analysis reveals that **2** and **4** are monomers with one ligand bonding to two tin atoms through Sn–S bonds. The four primary bonds to Sn are three

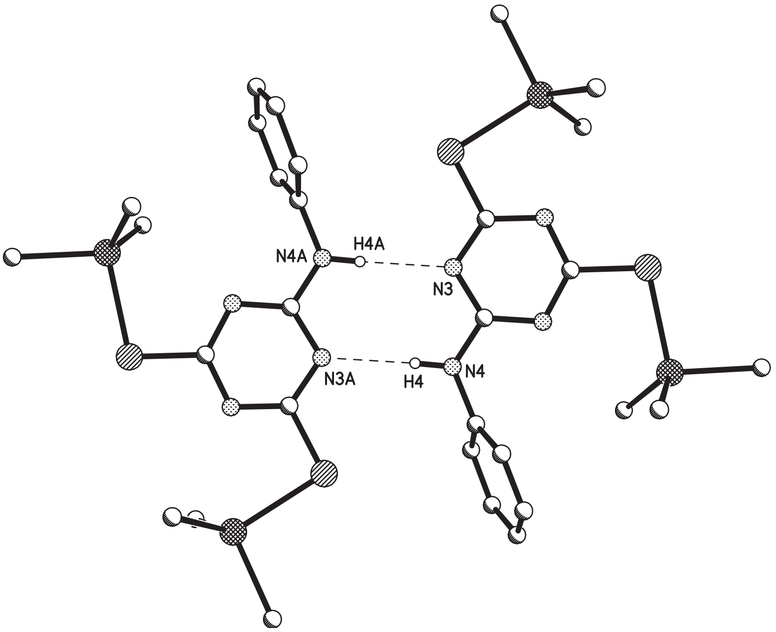


Figure 2. Dimer of **1** connected by N–H $\cdots$ N intermolecular hydrogen bonds.

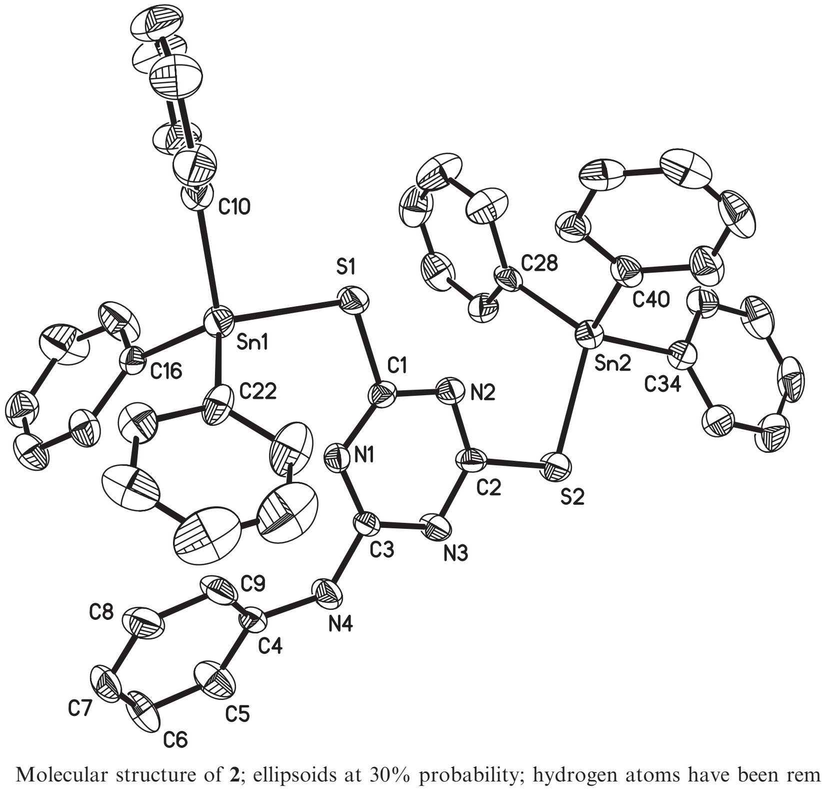


Figure 3. Molecular structure of **2**; ellipsoids at 30% probability; hydrogen atoms have been removed for clarity.

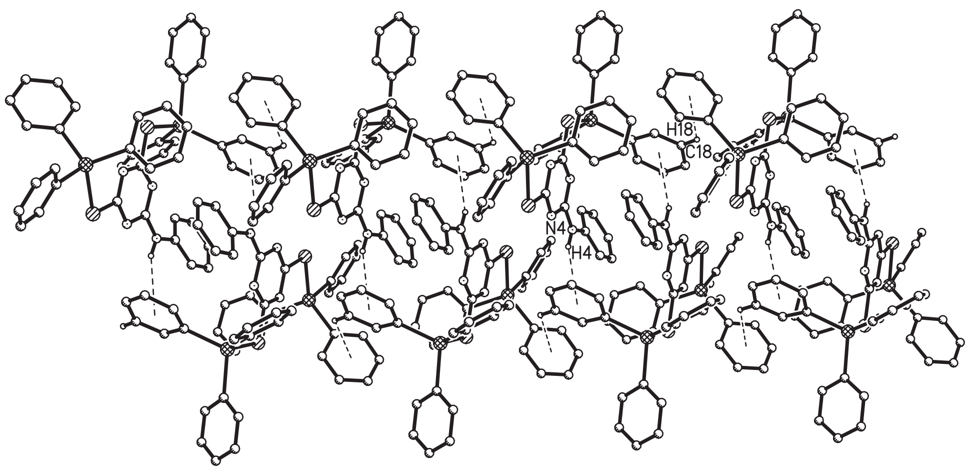


Figure 4. Molecular structure of **4**; ellipsoids at 30% probability; hydrogen atoms have been removed for clarity.

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

Sn(1)–C(16)	2.11(8)	Sn(2)–C(40)	2.12(10)
Sn(1)–C(22)	2.13(10)	Sn(2)–C(28)	2.12(10)
Sn(1)–C(10)	2.13(9)	Sn(2)–C(34)	2.15(9)
Sn(1)–S(1)	2.43(2)	Sn(2)–S(2)	2.43(2)
C(16)–Sn(1)–C(22)	110.2(3)	C(40)–Sn(2)–C(28)	113.4(3)
C(16)–Sn(1)–C(10)	111.3(3)	C(40)–Sn(2)–C(34)	109.6(4)
C(22)–Sn(1)–C(10)	110.7(4)	C(28)–Sn(2)–C(34)	108.1(3)
C(16)–Sn(1)–S(1)	113.4(2)	C(40)–Sn(2)–S(2)	116.6(2)
C(22)–Sn(1)–S(1)	114.1(3)	C(28)–Sn(2)–S(2)	111.4(2)
C(10)–Sn(1)–S(1)	96.5(3)	C(34)–Sn(2)–S(2)	96.2(2)

Table 4. Selected bond lengths (Å) and angles (°) for **4**.

Sn(1)–C(18)	2.13(8)	Sn(2)–C(42)	2.08(7)
Sn(1)–C(12)	2.13(8)	Sn(2)–C(36)	2.12(10)
Sn(1)–C(24)	2.14(8)	Sn(2)–C(30)	2.13(6)
Sn(1)–S(1)	2.44(2)	Sn(2)–S(2)	2.43(2)
C(18)–Sn(1)–C(12)	112.7(3)	C(42)–Sn(2)–C(36)	116.9(5)
C(18)–Sn(1)–C(24)	113.6(3)	C(42)–Sn(2)–C(30)	109.0(3)
C(12)–Sn(1)–C(24)	106.1(3)	C(36)–Sn(2)–C(30)	109.3(4)
C(18)–Sn(1)–S(1)	112.1(2)	C(42)–Sn(2)–S(2)	110.3(3)
C(12)–Sn(1)–S(1)	96.2(2)	C(36)–Sn(2)–S(2)	110.2(4)
C(24)–Sn(1)–S(1)	114.8(3)	C(30)–Sn(2)–S(2)	99.6(3)

phenyl groups and one sulfur for both complexes. The Sn–S bond lengths Sn(1)–S(1) 2.43(2) Å, Sn(2)–S(2) 2.43 (2) Å for **2** and Sn(1)–S(1) 2.44 (2) Å, Sn(2)–S(2) 2.43(2) Å for **4** are slightly less than the sum of the covalent radii of Sn and S (2.44 Å) [24]. There are also weak Sn ← N bonds in **2** and **4**. Sn(1)–N(1) 3.288 Å, Sn(2)–N(2) 3.109 Å for **2** and Sn(1)–N(1) 3.00 Å, Sn(2)–N(2) 3.057 Å for **4** similar to **1**. Each tin is five-coordinate trigonal bipyramidal geometry with the equatorial plane of **2** defined by S(1), C(16) and C(22) for Sn(1), S(2), C(28) and C(40) for Sn(2) with the sum of 337.7°

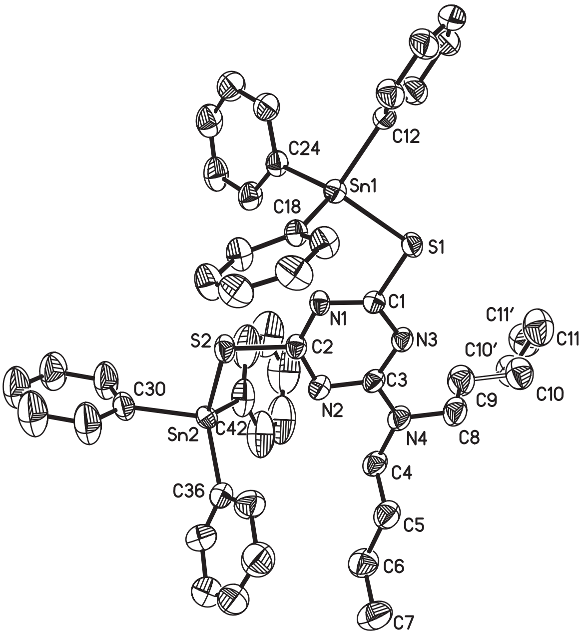


Figure 5. Linear chain structure of **2** connected through point-to-face C–H ··· π and N–H ··· π interactions.

(S(1)–Sn(1)–C(16) 113.4(2)°, C(22)–Sn(1)–S(1) 114.1(3)°, C(16)–Sn(1)–C(22) 110.2(3)°) and 341.4° (C(28)–Sn(2)–S(2) 111.4(2)°, C(40)–Sn(2)–S(2) 116.6(2)°, C(28)–Sn(2)–C(40) 113.4(3)°). The axial positions are occupied by C(10), N(1) for Sn(1), and C(34), N(2) for Sn(2) with the angles of 149.6° and 151.9°. The equatorial plane of **4** is defined by S(1), C(18) and C(24) for Sn(1), S(2), C(36) and C(42) for Sn(2) with the sum of 340.5° (S(1)–Sn(1)–C(18) 112.1(2)°, C(24)–Sn(1)–S(1) 114.8(3)°, C(18)–Sn(1)–C(24) 113.6(3)°) and 337.4° (C(36)–Sn(2)–S(2) 110.2(4)°, C(42)–Sn(2)–S(2) 110.3(3)°, C(36)–Sn(2)–C(42) 116.9(5)°). The axial positions are occupied by C(12), N(1) for Sn(1), and C(30), N(2) for Sn(2) with the angles of 153.6° and 155.3°.

The complexes exhibit interesting intermolecular interactions as shown in figures 5 and 6. Molecules of **2** are connected *via* edge- or point-to-face C–H ··· π and N–H ··· π interactions into a linear chain. The C(18)–H is directed towards the symmetry related ($1+x$, y, z) aromatic ring containing the C(40a)–C(45a) atoms. The C(18) ··· π(centroid) and H(18) ··· π(centroid) distances are 3.82 and 3.23 Å, respectively. The angle of C(18)–H(18) ··· π(centroid) is 128.3°. The N(4)–H is directed towards the symmetry related ($2-x$, $-y$, $-z$) aromatic ring containing C(16a)–C(21a) with N(4) ··· π(centroid) and H(4) ··· π(centroid) distances of 3.73 and 2.92 Å, respectively. The angle of N(4)–H(4) ··· π(centroid) is 159.6°. These values are consistent with the literature [25].

Molecules of **4** are connected via edge or point-to-face C–H ··· π interactions into a dimer (as shown figure 6).

3.4.3. Crystal structure of 3.

Perspective view of molecular structure of complex **3** is illustrated in figure 7. Selected bond lengths (Å) and angles (°) are listed in table 5.

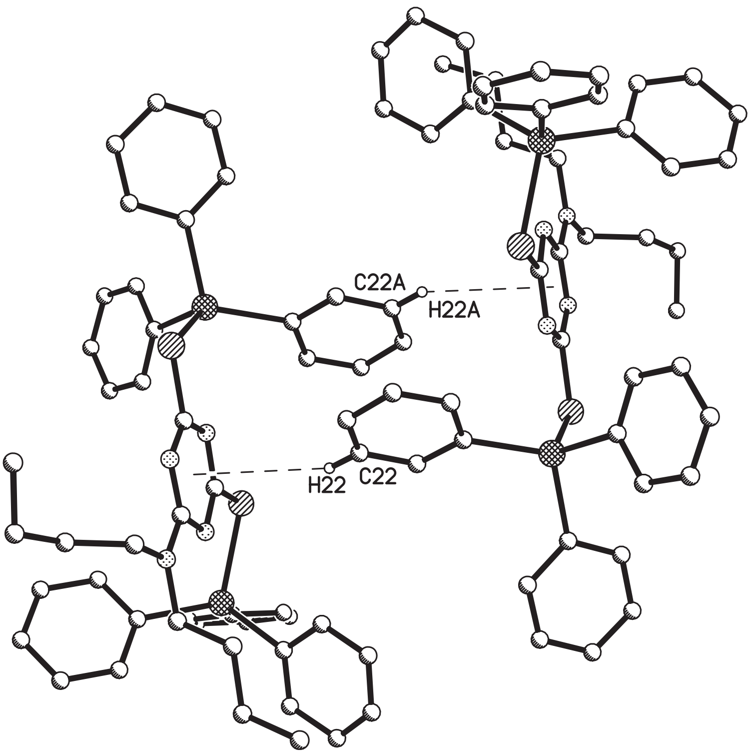


Figure 6. Dimer structure of **4** connected by C–H $\cdots \pi$ interactions.

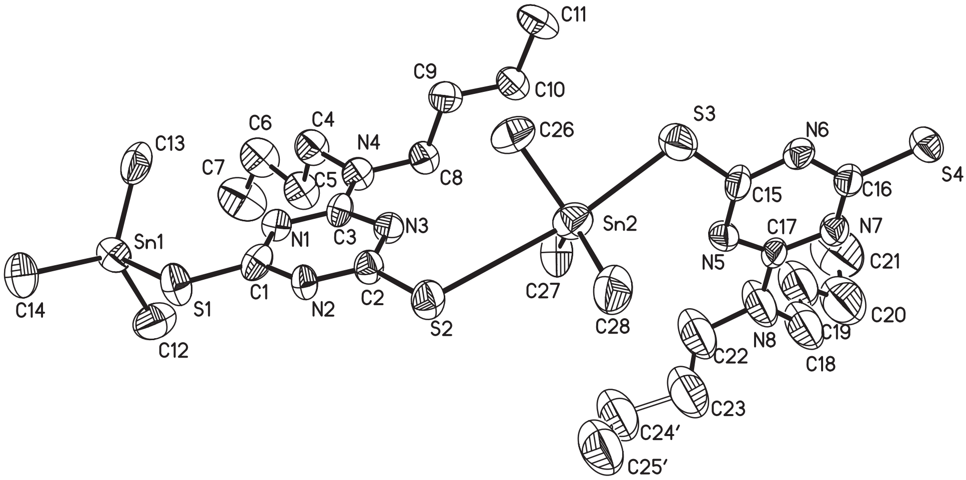


Figure 7. Molecular structure of **3**; ellipsoids at 30% probability; hydrogen atoms have been removed for clarity.

The coordination mode, bond lengths and bond angles of the two Sn atoms of complex **3** are slightly different. Take Sn(2) for example: it is directly bonded to the thiol (C(15)–S(3)) and is further coordinated intermolecularly by the thione (C(2)–S(2)) of a neighboring molecule. So the ligand can be described as unsymmetrical S(2),

Table 5. Selected bond lengths (Å) and angles (°) for **3**.

Sn(1)–C(13)	2.00(17)	Sn(2)–C(27)	2.14(16)
Sn(1)–C(14)	2.11(15)	Sn(2)–C(26)	2.14(14)
Sn(1)–C(12)	2.14(17)	Sn(2)–S(3)	2.58(4)
Sn(1)–S(1)	2.58(4)	Sn(2)–S(2)	3.25(4)
Sn(2)–C(28)	2.06(18)		
C(13)–Sn(1)–C(14)	116.8(7)	C(28)–Sn(2)–C(26)	118.1(8)
C(13)–Sn(1)–C(12)	117.8(8)	C(27)–Sn(2)–C(26)	117.1(7)
C(14)–Sn(1)–C(12)	119.9(8)	C(28)–Sn(2)–S(3)	96.2(5)
C(13)–Sn(1)–S(1)	102.9(4)	C(27)–Sn(2)–S(3)	106.0(4)
C(14)–Sn(1)–S(1)	90.1(4)	C(26)–Sn(2)–S(3)	88.6(5)
C(12)–Sn(1)–S(1)	100.5(5)	C(28)–Sn(2)–S(2)	84.0(5)
C(28)–Sn(2)–C(27)	120.4(8)	C(27)–Sn(2)–S(2)	84.0(4)
S(3)–Sn(2)–S(2)	168.0(12)	C(26)–Sn(2)–S(2)	80.8(5)

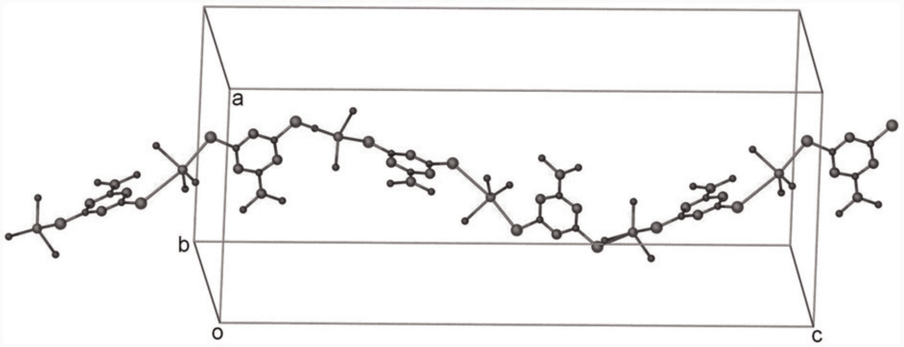


Figure 8. Left-handed helical structure of **3** along the *c*-axis, unattached hydrogen atoms and α-, β- and γ-carbon atoms of the Sn-butyl groups have been omitted for clarity.

S(3)–bidentate bridging and the structure of **3** can be described as a left-handed helix [26] containing a trigonal bipyramidal S_2SnC_3 (see figure 8), consistent with the spectral data. All S–Sn–S and C–Sn–C angles [168.0(12) and 116.8(7)–119.9(8)°, respectively] support this description.

The two Sn–S bonds are of different lengths. Thus, the Sn(2)–S(3), Sn(1)–S(1) distances [2.58(4) Å, 2.58(4) Å, respectively], although slightly longer than the corresponding bonds of **1**, **2** and **4** [2.43(2)–2.45(2) Å], are comparable with Sn–S bond lengths found for organotin thiotetrazoles [2.48(4)–2.61(5) Å] [6, 10]. The intermolecular Sn(2)–S(2) distance [3.25(4) Å], though long, falls in the range proposed for secondary Sn $\cdots$ S coordination [2.79–3.81 Å] [4].

Supplementary material

Crystallographic data for the structure analysis of the compounds have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 655982 **1**, 655983 **2**, 659523 **3**, 659522 **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (http://www.ccdc.cam.ac.uk; Fax: + 44-1223-336033).

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