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

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Abstract

A series of organotin (IV) complexes with 6-amino-1,3,5-triazine-2,4-dithiol of the type $[(R_nSnCl_{4-n})_2 (C_3H_2N_4S_2)]$ ($n = 3$: R = Me **1**, *n*-Bu **2**, PhCH$_2$ **3**, Ph **4**; $n = 2$: R = Me **5**, *n*-Bu **6**, PhCH$_2$ **7**, Ph **8**) have been synthesized. All the complexes **1–8** have been characterized by elemental analysis, IR, ^{1}H and ^{13}C NMR spectra. Among them complexes **1**, **4**, **5** and **8** have also been characterized by X-ray crystallography diffraction analyses, which revealed that the tin atoms of complexes **1**, **4**, **5** and **8** are all five-coordinated with distorted trigonal bipyramid geometries.

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1. Introduction

Organotin (IV) complexes are attracting more and more attention for their potential industrial applications and biological activities [1]. Recently, increasing investigation on organotin (IV) complexes has been focused on acquiring well-state structures to learn the nature of their versatile bonding modes [2], especially those of some organotin (IV) derivatives from heterocyclic thionates [3]. Heterocyclic thionates are ligands derived form heterocyclic thiones that contain at least one deprotonated heterocyclic thioamide group $(N–C–S)^-$ and can act as monodentate, chelating and bridging ligands. In our previous work, we studied the coordination chemistry of three ligands of such kind: 6-thiopurine, 1-(4-hydroxyphenyl)-1*H*-tetrazole-5-thiol and 2,5-dimercapto-1,3,4-thiodiazole (bismuthiol-I), which possessed one or two deprotonated heterocyclic thioamide group, respectively [4–6]. The X-ray analyses revealed that

there are several factors that can influence the topologies of the organotin (IV) derivatives from heterocyclic thionates such as the special geometries of ligand, the spatial resistant from R, etc. To continue our studies in this field, we choose another fascinating heterocyclic thionate: 6-amino-1,3,5-triazine-2,4-dithiol, which possesses two –SH groups, through which primary bonds to tin atoms are likely formed. Moreover, the three potentially coordinating nitrogen atoms of triazine make the ligand act as a fulcrum about which lattice construction is orchestrated in one or more dimensions.

In this paper, we report some details of the syntheses and characterizations of a series of organotin (IV) complexes with the ligand of the type $[(R_nSnCl_{4-n})_2 (C_3H_2N_4S_2)]$ ($n = 3$: R = Me **1**, *n*-Bu **2**, PhCH$_2$ **3**, Ph **4**; $n = 2$: R = Me **5**, *n*-Bu **6**, PhCH$_2$ **7**, Ph **8**). The X-ray crystallography of complexes **1**, **4**, **5** and **8** show that all the complexes contain the thiolate form of the ligand, i.e. the ligand is linked to the organometal moiety primarily through sulfur, resembling as Hmnc and 1-phenyl-1*H*-tetrazole-5-thiol [3,7]. Interestingly, the versatile hydrogen bonding, N–H···X (X = N, S, Cl) are found.

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2. Experimental

2.1. Materials and measurements

Trimethyltin chloride, tri-n-butyltin chloride, triphenyltin chloride, dimethyltin dichloride, di-n-butyltin dichloride, diphenyltin dichloride and 6-amino-1,3,5-triazine-2,4-dithiol were commercially available, and they were used without further purification unless otherwise noted. Tribenzyltin chloride and dibenzyltin dichloride were prepared by a standard method reported in the literature [8]. The melting points were obtained with Kofler micro-melting point apparatus and were uncorrected. Infrared-spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. ^{1}H, ^{13}C NMR spectra were recorded on Varian Mercury Plus 400 spectrometer operating at 400 and 100.6 MHz, respectively. The spectra were acquired at room temperature (298 K) unless otherwise specified; ^{13}C spectra are broadband proton decoupled. The chemical shifts were reported in ppm with respect to the references and were stated relative to external tetramethylsilane (TMS) for ^{1}H and ^{13}C NMR. Elemental analyses (C, H, N) were performed with a PE-2400II apparatus.

2.2. Syntheses of the complexes 1–8

Complexes **1**–**8** were obtained following a procedure, which is here reported for complex **1**.

2.2.1. [Me₃Sn(S–C₃H₂N₄–S)SnMe₃] · 0.5C₂H₅OH (1)

The reaction was carried out under dry nitrogen atmosphere. The 6-amino-1,3,5-triazine-2,4-dithiol (0.160 g, 1 mmol) and sodium ethoxide (0.136 g, 2 mmol) was added to benzene (20 ml) in a Schlenk flask, and the mixture was stirred for 10 min, then add Me₃SnCl (0.396 g, 2 mmol) to the mixture, the reaction mixture was stirred for 12 h at 45 °C. After cooling down to the room temperature, the solution was filtered. The solvent of the filtrate was gradually removed by evaporation under vacuum until solid product was obtained. The solid was then recrystallized from ethanol. Yield, 72%: m.p. 102–104 °C. Anal. Calc. for C₂₀H₄₆N₈OS₄Sn₄: C, 23.60; H, 4.56; N, 11.01. Found: C, 23.68; H, 4.53; N, 11.09%. ^{1}H NMR (CDCl₃–D₂O, ppm): δ 0.73 (s, 9H, $^2J_{SnH}$ = 58 Hz), δ 0.76 (s, 36H, Sn–CH₃), 3.74 (m, 1H, CH₃CH₂OH), 1.25 (t, 3H, CH₃CH₂OH), 2.00 (t, 1H, CH₃CH₂OH), 4.00 (s, 2H, C–NH₂). ^{13}C NMR (CDCl₃): δ 178.8 (C–NH₂), 197.7 (C–S), 197.7 (C–S), 1.9 (Sn–Me). IR (KBr, cm^{-1}): v(C=N) 1630, v(Sn–C)$_{as}$ 532, v(Sn–C)$_s$ 503, v(Sn–N) 561, v(Sn–S) 312.

2.2.2. (n-Bu)₃Sn(S–C₃H₂N₄–S)Sn(n-Bu)₃ (2)

Yield, 68%: m.p. 70–72 °C. Anal. Calc. for C₂₇H₅₆N₄S₂Sn₂: C, 43.92; H, 7.65; N, 7.59. Found: C, 43.85; H, 7.66; N, 7.55%. ^{1}H NMR (CDCl₃, ppm): δ 0.84–1.71 (m, 54H, Sn–C₄H₉), 4.00 (s, 2H, C–NH₂). ^{13}C

NMR (CDCl₃, ppm): δ 178.8 (C–NH₂), 197.7 (C–S), 197.7 (C–S), 17.4, 28.1, 26.6, 13.8 (n-Bu). IR (KBr, cm^{-1}): v(C=N) 1632, v(Sn–C)$_{as}$ 528, v(Sn–C)$_s$ 502, v(Sn–N) 567, v(Sn–S) 311.

2.2.3. (PhCH₂)₃Sn(S–C₃H₂N₄–S)Sn(PhCH₂)₃ (3)

Yield, 75%: m.p. 130–132 °C. Anal. Calc. for C₄₅H₄₄N₄S₂Sn₂: C, 57.35; H, 4.71; N, 5.95. Found: C, 57.39; H, 4.66; N, 5.99%. ^{1}H NMR (CDCl₃, ppm): δ 7.45–7.78 (m, 30H, Sn–CH₂C₆H₅), 2.82 (s, 12H, CH₂C₆H₅), 4.00 (s, 2H, C–NH₂). ^{13}C NMR (CDCl₃, ppm): δ 178.8 (C–NH₂), 197.7 (C–S), 197.7 (C–S), 15.9 (CH₂–Ph), 142.8 (i-C), 129.1 (o-C), 128.7 (m-C), 125.8 (p-C). IR (KBr, cm^{-1}): v(C=N) 1631, v(Sn–C)$_{as}$ 460, v(Sn–C)$_s$ 435, v(Sn–N) 564, v(Sn–S) 314.

2.2.4. Ph₃Sn(S–C₃H₂N₄–S)SnPh₃ (4)

Yield, 74%: m.p. 177–179 °C. Anal. Calc. for C₃₉H₃₂N₄S₂Sn₂: C, 54.58; H, 3.76; N, 6.53. Found: C, 54.56; H, 3.71; N, 6.56%. ^{1}H NMR (CDCl₃, ppm): δ 7.46–7.79 (m, 30H, Sn–C₆H₅), 4.00 (s, 2H, C–NH₂). ^{13}C NMR (CDCl₃, ppm): δ 178.8 (C–NH₂), 197.7 (C–S), 197.7 (C–S), 129 (i-C), 137.5 (o-C), 128.8 (m-C), 128.8 (p-C). IR (KBr, cm^{-1}): v(C=N) 1631, v(Sn–C)$_{as}$ 464, v(Sn–C)$_s$ 429, v(Sn–N) 561, v(Sn–S) 312.

2.2.5. [Me₂SnCl(S–C₃H₂N₄–S)SnClMe₂] · 0.5C₈H₂₄Cl₄O₂Sn₄ (5)

Yield, 74%: m.p. 118–120 °C. Anal. Calc. for C₃₆H₈₀Cl₁₂N₁₆O₂S₈Sn₁₂: C, 15.04; H, 2.80; N, 7.79. Found: C, 15.01; H, 2.85; N, 7.84%. ^{1}H NMR (CDCl₃, ppm): δ 0.95 (s, 6H, $^2J_{SnH}$ = 72 Hz), δ 1.42 (s, 48H, Sn–CH₃), 4.00 (s, 2H, C–NH₂). ^{13}C NMR (CDCl₃, ppm): δ 178.8 (C–NH₂), 197.7 (C–S), 197.7 (C–S), 2.5 (Me). IR (KBr, cm^{-1}): v(C=N) 1633, v(Sn–C)$_{as}$ 525, v(Sn–C)$_s$ 498, v(Sn–N) 564, v(Sn–S) 311.

2.2.6. (n-Bu)₂SnCl(S–C₃H₂N₄–S)SnCl(n-Bu)₂ (6)

Yield, 69%: m.p. 117–119 °C. Anal. Calc. for C₃₈H₇₆Cl₄N₈S₄Sn₄: C, 32.84; H, 5.51; N, 8.06. Found: C, 32.80; H, 5.56; N, 8.13%. ^{1}H NMR (CDCl₃, ppm): δ 0.86–1.75 (m, 72H, Sn–C₄H₉), 4.00 (s, 2H, C–NH₂). ^{13}C NMR (CDCl₃, ppm): δ 178.8 (C–NH₂), 197.7 (C–S), 197.7 (C–S), 13.7, 25.2, 25.8, 13.8 (n-Bu). IR (KBr, cm^{-1}): v(C=N) 1632, v(Sn–C)$_{as}$ 530, v(Sn–C)$_s$ 504, v(Sn–N) 558, v(Sn–S) 315.

2.2.7. (PhCH₂)₂SnCl(S–C₃H₂N₄–S)SnCl(PhCH₂)₂ (7)

Yield, 76%: m.p. 108–110 °C. Anal. Calc. for C₃₁H₃₀Cl₂N₄S₂Sn₂: C, 46.61; H, 4.49; N, 6.39. Found: C, 46.67; H, 4.53; N, 16.37%. ^{1}H NMR (CDCl₃, ppm): δ 6.80–7.05 (m, 20H, Sn–CH₂C₆H₅), 3.52 (s, 8H, CH₂C₆H₅), 4.00 (s, 2H, C–NH₂). ^{13}C NMR (CDCl₃, ppm): δ 178.8 (C–NH₂), 197.7 (C–S), 197.7 (C–S), 19.1 (CH₂–Ph), 142.8 (i-C), 129.1 (o-C), 128.7 (m-C), 125.8 (p-C). IR (KBr, cm^{-1}): v(C=N) 1634, v(Sn–C)$_{as}$ 465, v(Sn–C)$_s$ 434, v(Sn–N) 561, v(Sn–S) 315.

Table 1
Crystal data and structure refinement parameters for complexes **1** and **4**

Complex	**1**	**4**
Empirical formula	$C_{20}H_{46}N_8OS_4Sn_4$	$C_{39}H_{32}N_4S_2Sn_2$
Formula weight	1017.65	858.19
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2(1)/n$
Unit cell dimensions		
a (Å)	11.689(2)	9.632(3)
b (Å)	13.436(3)	57.269(18)
c (Å)	13.932(3)	14.093(4)
α (°)	70.346(3)	90
β (°)	85.406(3)	96.758(6)
γ (°)	86.479(3)	90
V (Å³)	2052.6(7)	7720(4)
Z	2	8
μ (mm⁻¹)	2.632	1.433
$F(000)$	988	3408
Reflections collected	10728	40439
Independent reflections [R_{int}]	7133 [0.0179]	13498 [0.1095]
Data/restraints/parameters	7133/4/337	13498/0/847
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0331$	$R_1 = 0.0761$
	$wR_2 = 0.0888$	$wR_2 = 0.1701$
R indices (all data)	$R_1 = 0.0506$	$R_1 = 0.1730$
	$wR_2 = 0.0992$	$wR_2 = 0.2220$
Goodness-of-fit	0.998	1.026
Θ Range for data collection (°)	1.83–25.03	2.03–25.03

Table 2
Crystal data and structure refinement parameters for complexes **5** and **8**

Complex	**5**	**8**
Empirical formula	$C_{36}H_{80}Cl_{12}N_{16}O_2S_8Sn_{12}$	$C_{27}H_{22}Cl_2N_4S_2Sn_2$
Formula weight	2875.32	774.89
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions		
a (Å)	11.308(2)	9.266(2)
b (Å)	15.540(3)	11.129(4)
c (Å)	17.815(3)	16.863(4)
α (°)	108.664(2)	99.015(2)
β (°)	92.226(2)	103.315(2)
γ (°)	108.424(3)	98.996(2)
V (Å³)	2779.9(9)	1637.4(8)
Z	1	2
μ (mm⁻¹)	3.114	1.837
$F(000)$	1356	756
Reflections collected	14234	7536
Independent reflections [R_{int}]	9474 [0.0194]	5289 [0.0426]
Data/restraints/parameters	9474/0/388	5289/0/334
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0359$	$R_1 = 0.0582$
	$wR_2 = 0.0850$	$wR_2 = 0.1385$
R indices (all data)	$R_1 = 0.0591$	$R_1 = 0.0797$
	$wR_2 = 0.1002$	$wR_2 = 0.1561$
Goodness-of-fit	1.000	0.992
Θ Range for data collection (°)	2.91–25.03	2.05–25.03

2.2.8. $Ph_2SnCl(S–C_3H_2N_4–S)SnClPh_2$ (**8**)

Yield, 71%: m.p. 159–161 °C. Anal. Calc. for $C_{27}H_{22}Cl_2N_4S_2Sn_2$: C, 41.85; H, 2.86; N, 7.23. Found: C, 41.88; H, 2.83; N, 7.29%. ^1H NMR (CDCl$_3$, ppm): δ 7.46–7.79 (m, 20H, Sn–C$_6$H$_5$), 4.00 (s, 2H, C–NH$_2$). ^{13}C NMR (CDCl$_3$, ppm): δ 178.8 (C–NH$_2$), 197.7 (C–S), 197.7 (C–S), 129 (*i*-C), 137.5 (*o*-C), 128.8 (*m*-C), 128.8 (*p*-C). IR (KBr, cm⁻¹): v(C=N) 1635, v(Sn–C)$_{as}$ 460, v(Sn–C)$_s$ 425, v(Sn–N) 561, v(Sn–S) 317.

2.3. X-ray crystallographic studies of complexes 1, 4, 5 and 8

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. Correction for semi-empirical from equivalents was applied. And the structure was solved by direct methods and refined by a full-matrix least-squares procedure based on F^2 using the SHELXL-97 program system [9]. The positions of hydrogen atoms were calculated, and their contributions were included in structural factor calculations. Crystal data and experimental details of the structure determinations are listed in Tables 1 and 2.

3. Results and discussion

3.1. Syntheses of the complexes 1–8

The synthesis procedure is given in Scheme 1.

3.2. IR spectroscopic studies of the complexes 1–8

The explicit feature in the IR spectra of the eight complexes **1**–**8** is the absence of the band in the region 2550–2430 cm⁻¹, which appears in the free ligand as the v(S–H) vibration, thus indicating metal–ligand bond formation through this site. While in the far-IR spectra, a strong absorption appears in the range 285–344 cm⁻¹ in the spectra of complexes **1**–**8**, which is absent in the spectrum of the ligand, is assigned to the Sn–S stretching mode of the vibration and all the values are consistent with that detected in a number of organotin (IV)–sulfur derivatives [10].

Furthermore, in organotin complexes, the IR spectra can provide useful information concerning the geometry of the SnC$_n$ moiety [11]. In the case of our complexes, two bands were assigned to SnC$_2$ asymmetric (460–530 cm⁻¹) and symmetric (425–504 cm⁻¹) vibrations of diorganotin (IV) derivatives and to SnC$_3$ asymmetric (460–532 cm⁻¹) and symmetric (429–503 cm⁻¹) vibrations of triorganotin (IV) derivatives. Thus, suggesting nonlinear SnC$_2$ units for diorganotins and non-planar SnC$_3$ fragments for triorganotins, respectively. The middle intensity bands observed at about 1600 cm⁻¹ in the spectra of all complexes have been assignable to v(C=N) according to the literatures [12,13], which suggested the coordinates of free ligand to these complexes is through sulfur atoms via thiolate form.

Scheme 1.

3.3. ^1H and ^{13}C NMR data of the complexes 1–8

^{1}H NMR data showed that the signal of the –SH proton in the spectrum of the ligand is absent in all of the complexes **1–8**, indicating the removal of the –SH proton and the formation of Sn–S bonds. The formation accords well with what the IR data have revealed. Moreover, the ^{1}H NMR spectra show that the chemical shifts of the phenyl group (Sn–C$_6$H$_5$) in complexes **4** and **8**, 7.46–7.79 ppm, and those of methylene connected directly with tin in complexes **1**, **2**, **3**, **5**, **6** and **7**, 1.71–3.52 ppm, upfield shift as compared with those of their corresponding precursors.

Fig. 1. Crystal structure of the complex **1**.

Fig. 2. Perspective view showing the 1D polymer of complex **1**.

Fig. 3. Crystal structure of the complex **4**.

The structural changes occurring in ligand upon deprotonation and coordination to the Sn atom should be reflected by the changes in the ^{13}C NMR spectra of our complexes. If the ligand chelate tin through thiolate form, C–S should be further low frequency in the spectra of all complexes compared with those in free ligands. As shown above, the chemical shifts of C–S in complexes **1–8** are shifted by 8 ppm to low frequency compared with the free ligand (δ 176.2 ppm), indicating that the ligands involved

in these complexes act as thiolate form. All of the above analyses are confirmed by X-ray diffraction.

3.4. Crystal structures of complexes 1, 4, 5 and 8

The crystal structures or perspective view of complexes **1, 4, 5** and **8** are shown in Figs. 1–8. All H atoms have been omitted for the purpose of clarity. Tables 1 and 2 list the crystal data and structure refinement parameters for com-
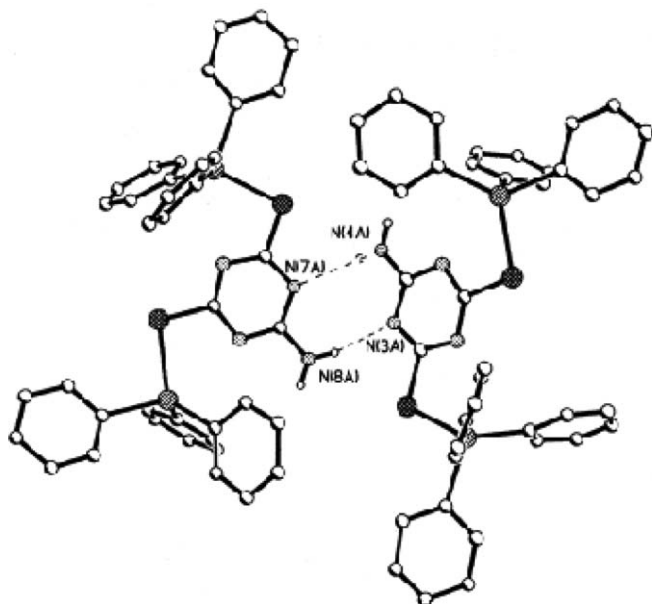

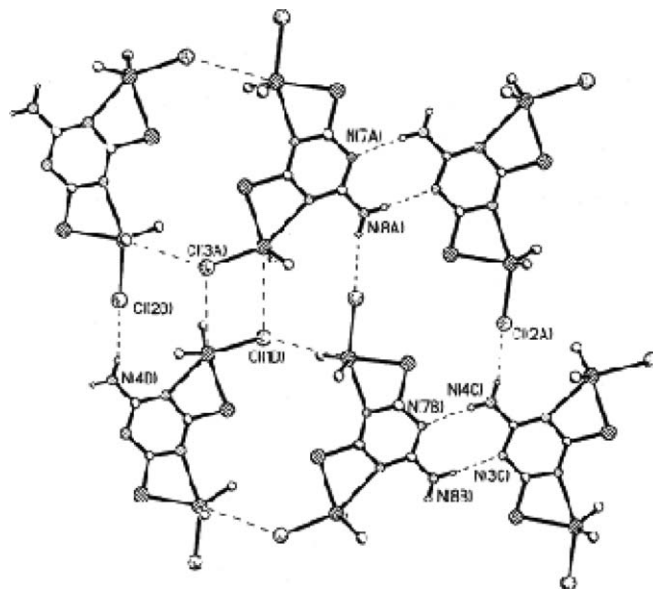Fig. 4. The dimer of the complex **4**.

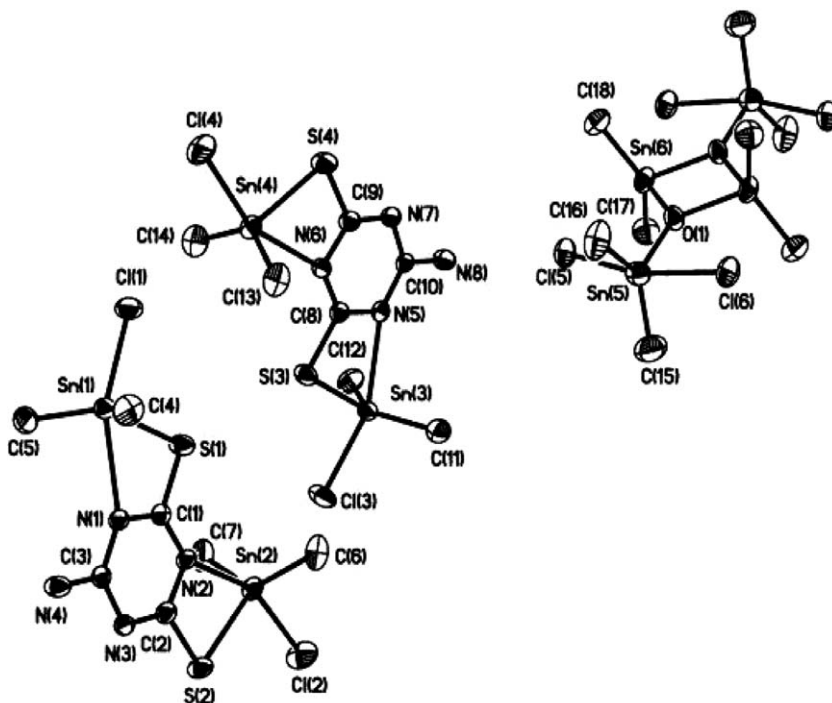Fig. 6. Perspective view showing the 2D network of the complex **5**.

Fig. 5. Molecular structure of the complex **5**.
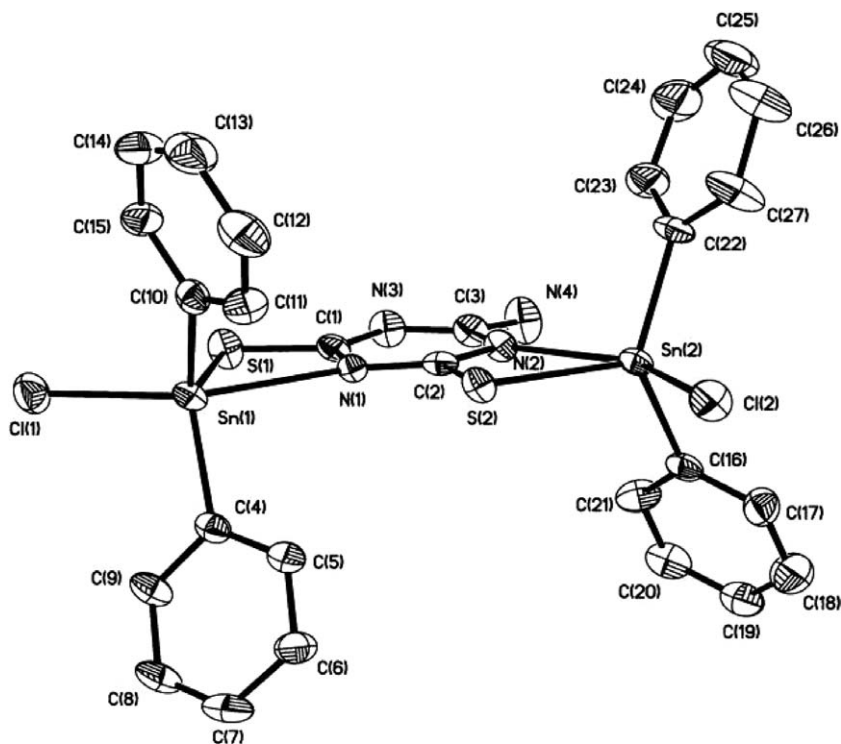
Fig. 7. Crystal structure of complex **8**.
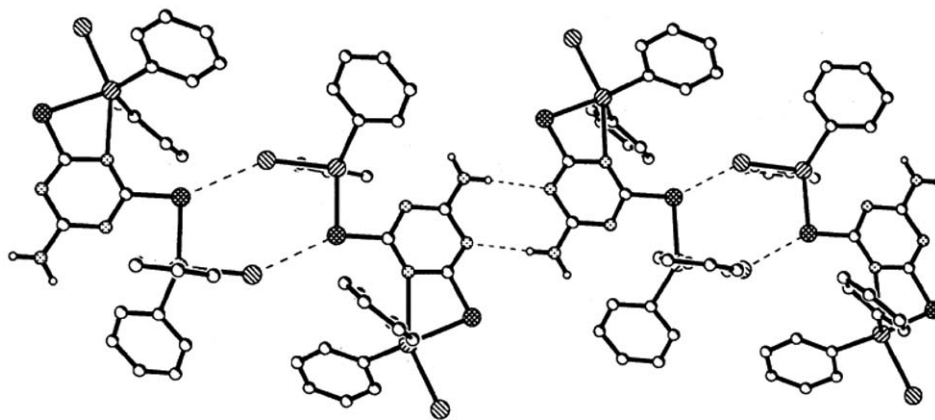
Fig. 8. Perspective view showing the 1D polymer of complex **8**.

plexes **1**, **4**, **5** and **8** and their selected bond lengths and angles are shown in Tables 3–6, respectively.

3.4.1. $[(Me_3Sn)_2(C_3H_2N_4S_2)] \cdot 0.5C_2H_5OH$ (**1**) and $[(Ph_3Sn)_2(C_3H_2N_4S_2)]$ (**4**)

Selected bond lengths and bond angles for complexes **1** and **4** are given in Tables 3 and 4 and their molecular structures are shown in Figs. 1–4, respectively. For complex **1** and **4**, the asymmetric units both contain two monomers A and B, which are different from a crystallographically point of view. The conformations of the two independent molecules A and B are almost the same, with only small differences in bond lengths and bond angles.

As exhibited, the compounds are formed by discrete molecules in which the tin atoms are indeed bound to the sulfur atoms of the triazine, which together with the methyl (or phenyl) groups defines a distorted tetrahedron around the tin atoms.

For complex **1**, the four Sn–S bond lengths lie toward the middle of the range reported for trialkyltin heteroarenethiolates (2.405–2.481 Å) and approach the sum of the covalent radii of tin and sulfur (2.42 Å) [5,14,15]. Besides, there exist intramolecular Sn–N interactions, common observed in trialkyltin heteroarenethiolates [16]. The distance of four Sn–N bonds are midway between the sums of the van der Walls radii and covalent radii of tin and nitrogen (2.15–3.74 Å) [17] and can be regarded as weak

Table 3
Selected bond lengths (Å) and bond angles (°) for complex **1**

Molecule A		Molecule B	
Bond lengths (Å)			
Sn(1)–C(6)	2.129(7)	Sn(3)–C(14)	2.109(7)
Sn(1)–C(5)	2.132(6)	Sn(3)–C(13)	2.112(7)
Sn(1)–C(4)	2.144(7)	Sn(3)–C(15)	2.123(6)
Sn(1)–S(1)	2.4462(16)	Sn(3)–S(3)	2.4501(16)
Sn(1)···N(1)	2.950(4)	Sn(3)···N(7)	2.953(4)
Sn(2)–C(7)	2.117(6)	Sn(4)–C(16)	2.114(8)
Sn(2)–C(8)	2.117(7)	Sn(4)–C(17)	2.123(8)
Sn(2)–C(9)	2.137(7)	Sn(4)–C(18)	2.162(7)
Sn(2)–S(2)	2.4632(15)	Sn(4)–S(2)	2.4727(15)
Sn(2)···N(2)	2.929(4)	Sn(4)···N(2)	2.853(4)
Bond angles (°)			
C(6)–Sn(1)–C(5)	116.2(3)	C(14)–Sn(3)–C(13)	117.7(3)
C(6)–Sn(1)–C(4)	111.2(3)	C(14)–Sn(3)–C(15)	110.6(3)
C(5)–Sn(1)–C(4)	110.5(3)	C(13)–Sn(3)–C(15)	109.3(3)
C(6)–Sn(1)–S(1)	112.7(2)	C(14)–Sn(3)–S(3)	109.6(2)
C(5)–Sn(1)–S(1)	104.81(15)	C(13)–Sn(3)–S(3)	109.6(2)
C(4)–Sn(1)–S(1)	98.0(2)	C(15)–Sn(3)–S(3)	98.3(2)
C(6)–Sn(1)–N(1)	84.7(3)	C(14)–Sn(3)–N(7)	79.7(2)
C(5)–Sn(1)–N(1)	76.9(2)	C(13)–Sn(3)–N(7)	82.6(2)
C(4)–Sn(1)–N(1)	154.8(2)	C(15)–Sn(3)–N(7)	156.0(2)
S(1)–Sn(1)–N(1)	57.74(9)	S(3)–Sn(3)–N(7)	57.74(8)
C(7)–Sn(2)–C(8)	114.5(3)	C(16)–Sn(4)–C(17)	114.6(3)
C(7)–Sn(2)–C(9)	111.5(3)	C(16)–Sn(4)–C(18)	111.4(4)
C(8)–Sn(2)–C(9)	111.3(3)	C(17)–Sn(4)–C(18)	111.4(4)
C(7)–Sn(2)–S(2)	108.3(2)	C(16)–Sn(4)–S(4)	114.0(2)
C(8)–Sn(2)–S(2)	110.3(2)	C(17)–Sn(4)–S(4)	107.8(2)
C(9)–Sn(2)–S(2)	100.0(2)	C(18)–Sn(4)–S(4)	96.2(2)
C(7)–Sn(2)–N(2)	78.3(2)	C(16)–Sn(4)–N(5)	79.9(2)
C(8)–Sn(2)–N(2)	80.2(2)	C(17)–Sn(4)–N(5)	82.1(2)
C(9)–Sn(2)–N(2)	157.8(2)	C(18)–Sn(4)–N(5)	154.3(2)
S(2)–Sn(2)–N(2)	57.82(8)	S(2)–Sn(2)–N(2)	58.32(9)

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

Molecule A		Molecule B	
Bond lengths (Å)			
Sn(1)–C(10)	2.108(14)	Sn(3)–C(49)	2.091(12)
Sn(1)–C(16)	2.120(14)	Sn(3)–C(55)	2.118(13)
Sn(1)–C(4)	2.153(13)	Sn(3)–C(43)	2.164(112)
Sn(1)–S(1)	2.453(4)	Sn(3)–S(3)	2.452(3)
Sn(1)···N(1)	2.850(10)	Sn(3)···N(5)	2.943(10)
N(1)–C(1)	1.324(14)	N(5)–C(40)	1.321(13)
S(1)–C(1)	1.789(14)	S(3)–C(40)	1.770(12)
Sn(2)–C(34)	2.109(13)	Sn(4)–C(73)	2.103(14)
Sn(2)–C(28)	2.116(14)	Sn(4)–C(67)	2.103(14)
Sn(2)–C(22)	2.120(14)	Sn(4)–C(61)	2.124(13)
Sn(2)–S(2)	2.433(3)	Sn(4)–S(2)	2.442(3)
Sn(2)···N(2)	2.915(10)	Sn(4)···N(2)	2.898(9)
N(2)–C(2)	1.339(13)	N(6)–C(41)	1.356(13)
S(2)–C(2)	1.754(12)	S(4)–C(41)	1.715(12)
Bond angles (°)			
C(10)–Sn(1)–C(16)	106.2(5)	C(49)–Sn(3)–C(55)	112.4(5)
C(10)–Sn(1)–C(4)	108.4(5)	C(49)–Sn(3)–C(43)	112.9(4)
C(16)–Sn(1)–C(4)	113.6(5)	C(55)–Sn(3)–C(43)	108.4(5)
C(10)–Sn(1)–S(1)	115.1(4)	C(49)–Sn(3)–S(3)	110.6(3)
C(16)–Sn(1)–S(1)	96.2(4)	C(55)–Sn(3)–S(3)	116.2(4)
C(4)–Sn(1)–S(1)	116.7(4)	C(43)–Sn(3)–S(3)	95.2(3)
C(10)–Sn(1)–N(1)	84.6(4)	C(49)–Sn(3)–N(5)	85.8(4)
C(16)–Sn(1)–N(1)	154.1(4)	C(55)–Sn(3)–N(5)	81.0(4)
C(4)–Sn(1)–N(1)	83.9(4)	C(43)–Sn(3)–N(5)	152.0(4)
S(1)–Sn(1)–N(1)	58.1(2)	S(3)–Sn(3)–N(5)	57.76(19)
C(34)–Sn(2)–C(28)	112.8(5)	C(73)–Sn(4)–C67)	120.2(5)
C(34)–Sn(2)–C(22)	108.4(5)	C(73)–Sn(4)–C(61)	107.2(5)
C(28)–Sn(2)–C(22)	107.2(6)	C(67)–Sn(4)–C(61)	109.4(5)
C(34)–Sn(2)–S(2)	113.9(3)	C(73)–Sn(4)–S(4)	109.8(4)
C(28)–Sn(2)–S(2)	116.7(4)	C(67)–Sn(4)–S(4)	111.2(3)
C(22)–Sn(2)–S(2)	96.0(4)	C(61)–Sn(4)–S(4)	96.3(3)
C(34)–Sn(2)–N(2)	86.0(4)	C(34)–Sn(4)–N(6)	82.8(4)
C(28)–Sn(2)–N(2)	85.6(5)	C(28)–Sn(4)–N(6)	83.7(4)
C(22)–Sn(2)–N(2)	154.0(4)	C(22)–Sn(4)–N(6)	154.5(4)
S(2)–Sn(2)–N(2)	58.0(2)	S(4)–Sn(4)–N(6)	58.3(2)

coordination bonds. All above information suggests that the primary bonds of the 6-amino-1,3,5-triazine-2,4-dithiol to tin atoms are through sulfur atoms via its thiolate form. The same coordination mode occurs in complex **4**.

The C–S bond distances of complexes **1** and **4** (1.745(5) and 1.757(12) Å) are close to C–S single bond (1.730 Å) in triphenyltin derivatives with thiolate ligands [16], Which indicates C–S existing as single bond and further proves indirectly the 6-amino-1,3,5-triazine-2,4-dithiol bonding to tin atoms via thiolate form, which keeps accordance with the result from the IR spectral data.

Including the tin–nitrogen interactions, the geometry at tin atoms in both complexes **1** and **4** become distorted *cis*-trigonal bipyramid with the axial-tin-axial angles N(1)–Sn(1)–C(4) of 154.8(2)° for complex **1** and N(1)–Sn(1)–C(16) of 154.1(4)° for complex **4**.

There exist two kinds of hydrogen bonds in the crystal of complex **1**. One strong H-bond is N–H···N, N(4)–H···N(3A) 2.984 Å and N(8A)–H···N(4) 3.245 Å. And the other weak H-bond is N–H···S, N(4)–H···S(4A) 3.573 Å. Those two kinds of hydrogen bonds help the construction of 1D polymer for complex **1**. For complex **4** only strong intermolecular hydrogen bonding N(4A)–H···N(7A) 2.964 Å and N(3A)–H···N(8A) 3.088 Å is rec-

ognized, which associates the discrete molecule into a dimer. Those hydrogen bonds play an important role in the stabilization of the polymers.

Besides, for complex **1**, the co-crystallized solvent ethanol molecule is found with the molar ratio of [(Me$_3$Sn)$_2$(C$_3$H$_2$N$_4$S$_2$)]:EtOH is 2:1.

3.4.2. [(Me$_2$SnCl)$_2$(C$_3$H$_2$N$_4$S$_2$)] · 0.5C$_8$H$_{24}$Cl$_4$O$_2$Sn$_4$ (**5**) and [Ph$_2$SnCl]$_2$(C$_3$H$_2$N$_4$S$_2$)] (**8**)

Selected bond lengths and bond angles for complex **5** and **8** is given in Tables 5 and 6 and their molecular structures are shown in Figs. 5–8.

In contrast with the triorganotin derivatives mentioned above, diorganotin dichlorides have two chlorine atoms that can be substituted. Together with the particular stereochemistry of the 6-amino-1,3,5-triazine-2,4-dithiol, their reaction may form special cyclic or polymeric complexes such as reported in our previous work [18]. However, when large stereo-constraint functions, the situation may change and this is the case of complexes **5** and **8**, which are dinuclear complexes as shown in Figs. 5–8.

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

Molecule A		Molecule B	
Bond lengths (Å)			
Sn(1)–C(4)	2.103(7)	Sn(3)–C(11)	2.103(7)
Sn(1)–C(5)	2.112(6)	Sn(3)–C(12)	2.111(7)
Sn(1)–Cl(1)	2.4375(18)	Sn(3)–Cl(3)	2.4267(18)
Sn(1)–S(1)	2.4695(18)	Sn(3)–S(3)	2.4739(17)
Sn(1)–N(1)	2.555(5)	Sn(3)–N(5)	2.588(5)
Sn(2)–C(7)	2.100(7)	Sn(4)–C(14)	2.091(7)
Sn(2)–C(6)	2.111(8)	Sn(4)–C(13)	2.097(7)
Sn(2)–Cl(2)	2.4472(19)	Sn(4)–Cl(4)	2.4417(19)
Sn(2)–S(2)	2.4942(18)	Sn(4)–S(4)	2.4836(19)
Sn(2)–N(2)	2.418(4)	Sn(4)–N(6)	2.428(4)
Bond angles (°)			
C(4)–Sn(1)–C(5)	131.7(3)	C(11)–Sn(3)–C(12)	131.9(3)
C(4)–Sn(1)–Cl(1)	102.6(2)	C(11)–Sn(3)–Cl(3)	102.2(2)
C(5)–Sn(1)–Cl(1)	101.4(2)	C(12)–Sn(3)–Cl(3)	101.8(2)
C(4)–Sn(1)–S(1)	110.3(2)	C(11)–Sn(3)–S(3)	109.1(2)
C(5)–Sn(1)–S(1)	111.0(2)	C(12)–Sn(3)–S(3)	111.7(2)
Cl(1)–Sn(1)–S(1)	89.96(6)	Cl(3)–Sn(3)–S(3)	90.66(6)
C(4)–Sn(1)–N(1)	88.9(3)	C(11)–Sn(3)–N(5)	88.7(2)
C(5)–Sn(1)–N(1)	88.6(2)	C(12)–Sn(3)–N(5)	88.3(2)
Cl(1)–Sn(1)–N(1)	152.42(11)	Cl(3)–Sn(3)–N(5)	152.90(11)
S(1)–Sn(1)–N(1)	62.47(11)	S(3)–Sn(3)–N(5)	62.27(10)
C(7)–Sn(2)–C(6)	132.0(4)	C(14)–Sn(4)–C(13)	131.7(3)
C(7)–Sn(2)–Cl(2)	99.7(2)	C(14)–Sn(4)–Cl(4)	99.8(2)
C(6)–Sn(2)–Cl(2)	100.5(2)	C(13)–Sn(4)–Cl(4)	100.1(2)
C(7)–Sn(2)–S(2)	108.0(2)	C(14)–Sn(4)–S(4)	111.0(2)
C(6)–Sn(2)–S(2)	114.3(2)	C(13)–Sn(4)–S(4)	111.5(2)
Cl(2)–Sn(2)–S(2)	91.95(7)	Cl(2)–Sn(2)–S(2)	91.95(7)
C(7)–Sn(2)–N(2)	89.6(2)	C(14)–Sn(4)–N(6)	89.6(2)
C(6)–Sn(2)–N(2)	89.8(2)	C(13)–Sn(4)–N(6)	89.7(2)
Cl(3)–Sn(2)–N(2)	124.37(12)	Cl(4)–Sn(4)–N(6)	155.83(12)
S(2)–Sn(2)–N(2)	63.32(12)	S(4)–Sn(4)–N(6)	63.69(11)

Table 6
Selected bond lengths (Å) and bond angles (°) for complex **8**

Bond lengths (Å)			
Sn(1)–C(4)	2.112(7)	Sn(2)–C(22)	2.135(7)
Sn(1)–C(10)	2.125(8)	Sn(2)–C(16)	2.157(8)
Sn(1)–Cl(1)	2.410(2)	Sn(2)–Cl(2)	2.4065(19)
Sn(1)–S(1)	2.470(2)	Sn(2)–S(2)	2.453(2)
Sn(1)–N(1)	2.544(5)	Sn(2)–N(2)	2.641(5)
S(1)–C(1)	1.745(7)	S(2)–C(2)	1.739(7)
N(1)–C(1)	1.359(8)	N(1)–C(1)	1.340(9)
Bond angles (°)			
C(4)–Sn(1)–C(10)	121.6(3)	C(22)–Sn(2)–C(16)	129.0(3)
C(4)–Sn(1)–Cl(1)	102.4(2)	C(22)–Sn(2)–Cl(2)	99.9(2)
C(10)–Sn(1)–Cl(1)	99.1(2)	C(16)–Sn(2)–Cl(2)	97.8(2)
C(4)–Sn(1)–S(1)	117.7(2)	C(22)–Sn(2)–S(2)	113.4(2)
C(10)–Sn(1)–S(1)	115.5(2)	C(16)–Sn(2)–S(2)	113.8(2)
Cl(1)–Sn(1)–S(1)	90.94(8)	Cl(2)–Sn(2)–S(2)	90.98(7)
C(4)–Sn(1)–N(1)	93.5(2)	C(22)–Sn(2)–N(2)	93.9(3)
C(10)–Sn(1)–N(1)	90.6(2)	C(16)–Sn(2)–N(2)	91.3(2)
Cl(1)–Sn(1)–N(1)	153.08(12)	Cl(2)–Sn(2)–N(2)	153.02(13)
S(1)–Sn(1)–N(1)	62.31(11)	S(2)–Sn(2)–N(2)	62.19(13)

For complexes **5** and **8**, two Sn–S and Sn–N bonds are basically identical, respectively. Both of the Sn–S bond lengths (Sn(1)–S(1) 2.4695(18) Å and Sn(2)–S(2) 2.4942(18) Å) for complex **5** and (Sn(1)–S(1) 2.470(2) Å and Sn(2)–S(2) 2.453(2) Å) for complex **8** approach the covalent radii of Sn and S (2.42 Å) [19]. Concerning the Sn–N bonds lengths, though there are small differences between them, they are both midway between the sums of the covalent radii and van der Waals radii of tin and nitrogen (2.15–3.74 Å) [19]. As the case for complexes **1** and **4**, the primary bonds of the 6-amino-1,3,5-triazine-2,4-dithiol to the tin atoms in complexes **5** and **8** are through sulfur atoms and the 6-amino-1,3,5-triazine-2,4-dithiol appears mainly as thiolate form when reacting with dialkyltin dichloride. There also two Sn–Cl bonds (Sn(1)–Cl(1) 2.4375(18) Å and Sn(1)–Cl(1) 2.4472(19) Å) in complex **5** and two (Sn(1)–Cl(1) 2.410(2) Å and Sn(1)–Cl(1) 2.4065(19) Å) in complex **8**, which are typical Sn–Cl bond lengths (2.32–2.58 Å) found in chloroorganotin (IV) complexes in general [20]. Thus, the geometry at tin atoms of complex **5** and **8** become distorted trigonal bipyramidals with C(4)–C(5)–S(1) and C(4), C(10), S(1) atoms occupying the equatorial planes and the axial angles, Cl(1)–Sn(1)–N(1) is 152.42(11)° and Cl(1)–Sn(1)–N(1) is 153.08(12)°, respectively.

The X-ray diffraction investigation of complex **8** has shown that the asymmetric unit also contains two monomers A and B as complexes **1** and **4**, which are different from a crystallographic point of view, and the molecules A and B of complex **8** are associate in polymeric chains through intermolecular, dative N → Sn bonds. In addition, there exist intramolecular Sn–N interactions. The distance of two Sn–N bonds are midway between the sums of the van der Waals radii and covalent radii of tin and nitrogen (2.15–3.74 Å) [18] and can be regarded as weak coordination bonds.

Two kinds of hydrogen bonds are recognized in complex **5**. One strong H-bond is N–H⋯N, N(7B)–H⋯N(4C) 3.012 Å and N(8B)–H⋯N(3C) 3.007 Å. And the other weak H-bond is N–H⋯Cl, N(4)–H⋯Cl(2A) 3.381 Å. Besides, there exist Sn⋯Cl weak interactions, Sn(4)⋯Cl(1) 3.637 (2) Å. Those interactions help the construction of a 2D network for complex **5**. For complex **8**, there exist intermolecular hydrogen bonding and S⋯Cl non-bonded weak interactions [12]. The former is N(4A)–H⋯N(3) 3.090 Å and N(4)–H⋯N(3A) 3.090, the later is S⋯Cl 3.545 Å. As far as bond lengths, bond angles, intermolecular hydrogen bonding and Cl⋯S non-bonded interaction are concerned, the supramolecular structure of complex **8** is constructed as a 1D polymer.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure analysis of complexes **1**, **4**, **5** and **8** have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 262019, 262018, 262017 and 262020. Copies of these information can 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 http://www.ccdc.cam.ac.uk).

Acknowledgements

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