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Investigation on coordination modes of organotin(IV) complexes with 6-thiopurine and related ligands

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Abstract

The organotin(IV) complexes $R_2Sn(tpu)_2 \cdot L$ [L = 2MeOH, R = Me (**1**); L = 0: R = *n*-Bu (**2**), Ph (**3**), $PhCH_2$ (**4**)], $R_3Sn(Hthpu)$ [R = Me (**5**), *n*-Bu (**6**), Ph (**7**), $PhCH_2$ (**8**)] and $(R_2SnCl)_2(dtpu) \cdot L$ [L = H_2O, R = Me (**9**); L = 0: R = *n*-Bu (**10**), Ph (**11**), $PhCH_2$ (**12**)] have been synthesized, where tpu, Hthpu and dtpu are the anions of 6-thiopurine (Htpu), 2-thio-6-hydroxypurine (H_2thpu) and 2,6-dithiopurine (H_2dtpu), respectively. All the complexes **1**–**12** have been characterized by elemental, IR, ^1H, ^{13}C and ^{119}Sn NMR spectra analyses. And complexes **1**, **2**, **7** and **9** have also been determined by X-ray crystallography, complexes **1** and **2** are both six-coordinated with R_2Sn coordinated to the thiol/thione S and heterocyclic N atoms but the coordination modes differed. As for complex **7** and **9**, the geometries of Sn atoms are distorted trigonal bipyramidal. Moreover, the packing of complexes **1**, **2**, **7** and **9** are stabilized by the hydrogen bonding and weak interactions.

Keywords: 6-Thiopurine; Organotin(IV); Coordination modes

1. Introduction

Organotin(IV) compounds 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-defined solid-state structures to learn the nature of their versatile bonding modes [2], especially that of some organotin(IV) derivatives from heterocyclic thionates [3]. Heterocyclic thionates are ligands derived from heterocyclic thiones that contain at least one deprotonated heterocyclic thioamide group $(N–C–S)^-$ and can act as monodentate, chelating and bridging ligands. Among them, due to the versatile coordination modes and effective biological activities, derivatives from purine caught our attractions [4], for example, 6-thiopurine (Htpu), 2-thio-6-hydroxypurine (H_2thpu) and 2,6-dithiopurine (H_2dtpu) (see Scheme 1).

Htpu, which is an anticancer antimetabolite (*inter alia*) proved to be clinically effective against human leukemias [5]. The Htpu ligand is interesting also because of it has multiple binding sites such as N^1, N^3, S^6, N^7 and N^9, when it coordinates to tin atom, the coordination modes are certainly versatile (see Scheme 2). If coordination occurs through the S site, there may be two isomerism between thiol and thione form (mode **A** and **B**) [6]. While if as a N,S-chelating ligand, two nitrogen atoms (N^1 and N^7) will compete to involve the coordination to the center tin atom. The final structure will depend on the stability of the N^1/S^6 (mode **C**) or S^6/N^7 (mode **D**) and different alkyl groups of organotin compounds [6,7]. For instance, in $Me_3Sn(tpu)$, Htpu adopted mode **E** to coordinate to tin atoms, and formed a polymeric trigonal bipyramidal structure [6]. While in

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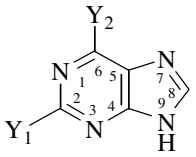


	Y_1	Y_2
Htpu	H	SH
H_2thpu	SH	OH
H_2dtpu	SH	SH

Scheme 1.

$Bz_3Sn(tpu)SnBz_3OMe$, Htpu adopted mode **F** to coordinate to tin atoms, and displayed a binuclear structure [3e]. As far as in n-$Bu_2Sn(tpu)_2$, Htpu adopted mode **D** to coordinate to tin atom [6].

In our previous work, we have studied the coordination behavior of five- and six-membered thiol/thione heterocycles to organotin(IV) [8,9]. As an extension of this research program and in connection with our current interest in the coordination chemistry of organotin(IV) compounds with heterocyclic thionates, we choose three fascinating ligands: Htpu, H_2thpu and H_2dtpu. We synthesized a series of complexes, $R_2Sn(tpu)_2 \cdot L$ [L = 2MeOH, R = Me (**1**); L = 0: R = n-Bu (**2**), Ph (**3**), $PhCH_2$ (**4**)], $R_3Sn(Hthpu)$ [R = Me (**5**), n-Bu (**6**), Ph (**7**), $PhCH_2$ (**8**)] and $(R_2SnCl)_2(dtpu) \cdot L$ [L = H_2O, R = Me (**9**); L = 0: R = n-Bu (**10**), Ph (**11**), $PhCH_2$ (**12**)]. All the complexes **1**–**12** have been characterized by elemental, IR, ^1H, ^{13}C and ^{119}Sn NMR spectra analyses. And complexes **1**, **2**, **7** and **9** have also been determined by X-ray crystallography.

2. Results and discussion

2.1. Syntheses

The organotin(IV) derivatives were obtained by reacting stoichiometric amounts of the thiopurine, sodium methoxide and corresponding organotin chlorides. The syntheses procedure is given in Scheme 3.

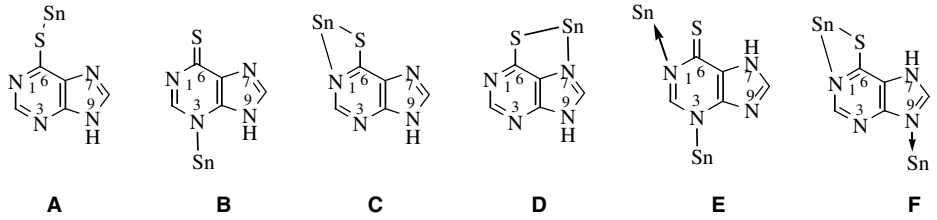
As shown in above Scheme, complexes **1**–**4** were synthesized by using a 1:2:2 molar ratio of R_2SnCl_2:Htpu:MeONa. When using a 1:1:1 molar ratio of R_3SnCl:H_2thpu:MeONa, complexes **5**–**8** were obtained. It is worthy to note that despite using a 1:1:2 molar ratio of R_2SnCl_2:H_2dtpu:MeONa in the syntheses of complexes **9**–**12**, we obtained 2:1 (R_2SnCl_2:H_2dtpu) products with only one chloride atom of R_2SnCl_2 replaced.

2.2. IR spectra

The IR spectra of organotin complexes **1**–**12** are summarized in Table 1. The data show that the medium absorption at 1150 cm^{-1} in free ligands due to the C=S is absent in spectra of all complexes **1** and **3**–**12**, while new absorption appears 700–800 cm^{-1} region which have been assignable to ν(C–S) according to literature [3d], suggesting the coordinates of ligands involved in these complexes are through sulfur atoms via thiolate form. However, the two absorptions at 1224 and 782 cm^{-1} coexist in the spectrum of the complex **2**, which have been assigned to ν(C=S) and ν(C–S), respectively, indicating that the two chelating ligand act as thiol and thione forms, respectively. In the far-IR spectra, the absorption in 305–312 cm^{-1} region for all complexes **1**–**12**, which is absent in the spectra of the free ligands, is assigned to the ν(Sn–S) and all the values are located within the range for Sn–S vibration observed in common organotin derivatives of thiolate (300–400 cm^{-1}) [10]. The ν(Sn–Cl) absorption at about 290 cm^{-1} in complexes **9**–**12** is close to that found in (S-dimethylchlorostannyl)-1-phenyl-5-thiotetrazole (300 cm^{-1}) [11], which suggests the incomplete substituent of chloride atoms of R_2SnCl_2. In organotin compounds, the IR spectra can provide useful information concerning the geometry of the SnC_n moiety [12]. In the case of our complexes, for both di- and triorganotin(IV) derivatives, two bands were assigned to asymmetric and symmetric Sn–C vibrations. Thus suggesting non-linear SnC_2 units for diorganotins and non-planar SnC_3 fragments for triorganotins, respectively.

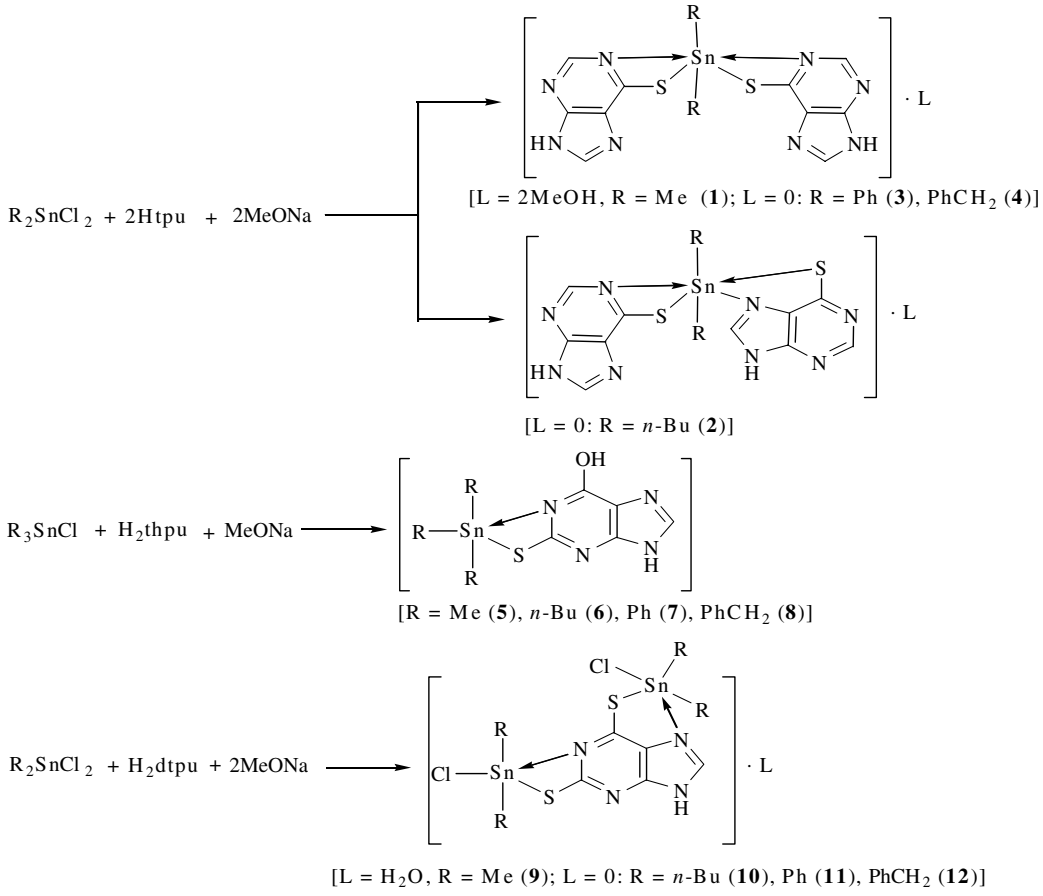
2.3. NMR spectra

The ^1H, ^{13}C and ^{119}Sn NMR spectral data are collected in Table 2. The ^1H NMR data show that the chemical shifts of the phenyl group (Sn–C_6H_5) in complexes **3**, **7** and **11**, 7.36–7.80 ppm, and those of methyl or methylene connected directly with tin in other complexes, 0.74–3.61 ppm, low frequency shift as compared



A B C D E F

Scheme 2.



Scheme 3.

Table 1
Some relevant infrared spectral data (cm^{-1}) for organotin(IV) complexes of Htpu, H_2thpu and H_2dtpu

Complex	ν(C–S)	ν_{as}(Sn–C)	ν_s(Sn–C)	ν(Sn–S)	Others
$Me_2Sn(tpu)_2 \cdot 2MeOH$ (**1**)	757	550	517	305	3427, ν(O–H)
$(n\text{–}Bu)_2Sn(tpu)_2$ (**2**)	782	442	424	310	1224, ν(C=S)
$(Ph)_2Sn(tpu)_2$ (**3**)	750	532	507	311	–
$(PhCH_2)_2Sn(tpu)_2$ (**4**)	732	452	427	307	–
$Me_3Sn(Hthpu)$ (**5**)	704	535	504	305	3429, ν(O–H)
$(n\text{–}Bu)_3Sn(Hthpu)_2$ (**6**)	712	449	425	310	3425, ν(O–H)
$Ph_3Sn(Hthpu)$ (**7**)	704	543	525	305	3430, ν(O–H)
$(PhCH_2)_3Sn(Hthpu)$ (**8**)	697	535	461	312	3426, ν(O–H)
$(Me_2SnCl)_2(dtpu) \cdot H_2O$ (**9**)	791	558	519	312	3429, ν(O–H); 289, ν(Sn–Cl)
$(n\text{–}Bu_2SnCl)_2(dtpu)$ (**10**)	789	551	525	310	286, ν(Sn–Cl)
$(Ph_2SnCl)_2(dtpu)$ (**11**)	790	555	500	305	285, ν(Sn–Cl)
$[(PhCH_2)_2SnCl]_2(dtpu)$ (**12**)	790	543	514	308	281, ν(Sn–Cl)

with those of their corresponding precursors. All these data are similar to those cases appear in literature [13], indicating coordination of the ligand to tin atom occurred for all the complexes **1**–**12**.

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 initial thione form of ligand changes to the thiolate on complexation, C^2 and/or C^6 should be further low frequency in the spectra of all complexes compared with those in free ligands, the shielding effect of the C=N bond being greater than that of the C=S bond [14]. As shown in Table 2, C^6 atom of complex **2** shows two signals (δ 170.7, 160.5), one is similar to that of free ligand (δ 169.5) and the other is shifted by 9 ppm to low frequency compared with it, indicating that two tpu act as thiolate and thione forms, respectively. Moreover, C^2 and/or C^6 atom signals of

Table 2
^1H, ^{13}C and ^{119}Sn NMR spectral data (δ) for organotin(IV) complexes of Htpu, H_2thpu and H_2dtpu

Complex	^{13}C NMR		^1H NMR		^{119}Sn NMR
	Purine ring	R_n–Sn	Purine ring	R_n–Sn	
$Me_2Sn(tpu)_2 \cdot 2MeOH$ (**1**)	151.2 (C^2), 144.7 (C^4), 127.8 (C^5), 162.1 (C^6), 144.4 (C^8)	8.1, 49.9 (CH_3OH)	8.22 (s, 2H), 8.01 (s, 2H)	1.43 (s, 6H), 3.40 (s, 6H, CH_3OH)	68.3
(n-Bu)$_2$Sn(tpu)$_2$ (**2**)	149.2 (C^2), 144.8, 151.3 (C^4), 127.7, 136.5 (C^5), 170.7, 160.5 (C^6), 144.5, 147.4 (C^8)	28.2, 27.6, 26.0, 13.4	8.21 (s, 2H), 8.00 (s, 2H)	0.91–2.10 (m, 18H)	50.8
(Ph)$_2$Sn(tpu)$_2$ (**3**)	150.2 (C^2), 144.8 (C^4), 127.5 (C^5), 165.0 (C^6), 144.5 (C^8)	138.9 (C_o), 135.5 (C_m), 129.2 (C_p), 131.8 (C_i)	8.19 (s, 2H), 8.02 (s, 2H)	7.47–7.80 (m, 10H)	−82.1
(PhCH$_2$)$_2$Sn(tpu)$_2$ (**4**)	150.6 (C^2), 145.1 (C^4), 127.3 (C^5), 160.6 (C^6), 142.2 (C^8)	123.5 (C_o), 128.2 (C_m), 128.9 (C_p), 138.1 (C_i), 23.6	8.25 (s, 2H), 8.01 (s, 2H)	6.95–7.32 (m, 10H), 3.50 (s, 4H)	63.1
Me_2Sn(Hthpu) (**5**)	171.5 (C^2), 152.0 (C^4), 117.8 (C^5), 166.5 (C^6), 136.1 (C^8)	8.12	8.05 (s, 1H)	0.74 (s, 9H)	119.4
(n-Bu)$_2$Sn(Hthpu)$_2$ (**6**)	172.6 (C^2), 151.8 (C^4), 117.3 (C^5), 167.2 (C^6), 136.4 (C^8)	28.3, 27.5, 26.4, 13.5	8.14 (s, 1H)	0.86–1.70 (m, 27H)	120.3
Ph_3Sn(Hthpu) (**7**)	171.6 (C^2), 152.5 (C^4), 117.6 (C^5), 166.9 (C^6), 136.4 (C^8)	136.4 (C_o), 128.6 (C_m), 129.2 (C_p), 148.2 (C_i)	8.05 (s, 1H)	7.45–7.80 (m, 15H)	−63.4
(PhCH$_2$)$_3$Sn(Hthpu) (**8**)	172.2 (C^2), 153.5 (C^4), 116.4 (C^5), 167.0 (C^6), 136.4 (C^8)	123.8 (C_o), 128.1 (C_m), 128.8 (C_p), 138.2 (C_i), 24.7	8.07 (s, 1H)	6.85–7.17 (m, 15H), 2.68 (s, 6H)	96.6
(Me_2SnCl)$_2$(dtpu) $\cdot$ H_2O (**9**)	170.3 (C^2), 156.7 (C^4), 130.1 (C^5), 162.1 (C^6), 148.9 (C^8)	7.7	8.03 (s, 1H)	1.35 (s, 12H)	−77.9
(n-Bu$_2$SnCl)$_2$(dtpu) (**10**)	170.6 (C^2), 155.0 (C^4), 131.2 (C^5), 161.1 (C^6), 148.8 (C^8)	28.2, 27.7, 25.9, 13.5	7.89 (s, 1H)	0.83–2.15 (m, 36H)	−72.3
(Ph_2SnCl)$_2$(dtpu) (**11**)	172.3 (C^2), 157.6 (C^4), 132.0 (C^5), 162.3 (C^6), 148.5 (C^8)	134.8 (C_o), 128.7 (C_m), 129.3 (C_p), 148.6 (C_i)	8.08 (s, 1H)	7.36–7.79 (m, 20H)	−84.8
[(PhCH$_2$)$_2$SnCl]$_2$(dtpu) (**12**)	170.5 (C^2), 155.7 (C^4), 132.0 (C^5), 163.4 (C^6), 147.5 (C^8)	127.5 (C_o), 127.3 (C_m), 128.5 (C_p), 138.7 (C_i), 26.3	8.25 (s, 1H)	6.85–7.22 (m, 20H), 3.61 (s, 8H)	−65.7

complexes **1** and **3**–**12** are shifted by 5–15 ppm to low frequency compared with those of free ligands, suggesting the ligands involved in these complexes act as thiolate form.

From the ^{13}C NMR spectra, we can also obtain useful information about the actual linkage isomerism of ligands. According to the literature, if the thiopurine coordinate to tin atom by the mode **D**, the signal of the C^5 atom will high frequency shift compared with that of free ligand [15]. For complexes **1**, **3** and **4**, the C^5 signals are located at δ 127.3–127.8 region, much close to that of free Htpu (δ 128.4), suggesting no mode **D** involved in these complexes. While, for the complex **2**, two signals for C^5 appear at δ 127.7 and 136.5. Together with the signal of C^4 (δ 144.8 and 151.3), the information indicates that N^7 atoms in complex **2** exist in two different environment, one is similar to that in free ligand and the other is consistent with that adopts coordination mode **D**. Both the C^5 and C^4 signals of complexes **9**–**12** (as shown in Table 2) are shifted by 10–20 ppm to high frequency compared with that of H_2dtpu. This fact means that complexes **9**–**12** all adopt the chelating mode **D**. All of above analyses are confirmed by X-ray diffraction.

As reported in literatures [16], values of $\delta(^{119}Sn)$ in the ranges −210 to −400, −90 to −190 and 200 to −60 ppm have been associated with six-, five- and four-coordinate tin centers, respectively. The $\delta(^{119}Sn)$ values of **1**–**4** [68.3 (**1**), 50.8 (**2**), −82.1 (**3**) and 63.1 (**4**)] are intermediate between those of four-coordinated diorganotin dithiolates [$\delta(^{119}Sn)$ 122–144 ppm] and six-coordinated diorganotin bis(dithiocarbamates) [e.g., $Me_2Sn(SCSNEt_2)_2$, $\delta(^{119}Sn)$ −336 ppm] [17]. All these revealed expanded coordination geometry about tin in solution. The ^{119}Sn NMR spectra of **5**–**8** show only one sharp signal, and the δ values found (119.4, 120.3, −63.4 and 96.6 ppm, respectively) are consistent with a tetrahedral and monomeric structure in solution. Besides, the ^{119}Sn NMR chemical shifts of **9**–**12** are in accordance with those of five coordinate diorganotin(IV) halides complexes involving halide or phosphine ligands [18], as well as chelating S-donors and O-donors complexes [19,20]. Thus, the $\delta(^{119}Sn)$ values of **9**–**12** [−77.9 (**9**), −72.3 (**10**), −84.8 (**11**) and −65.7 (**12**)] suggest that the Sn–N interactions probably survive in solution and that five-coordinate species is maintained.

2.4. Description of crystal structures

2.4.1. $Me_2Sn(tpu)_2 \cdot 2MeOH$ (**1**)

The molecular structure of complex **1** is shown in Fig. 1, selected bond lengths and angles are given in Table 3. There exists crystallographic twofold axe in the complex **1**. Thus, two Sn–S and Sn–N bonds are identical, respectively, due to the symmetric operation. The tin atom establishes covalent bonds with the two thiolate sulfur

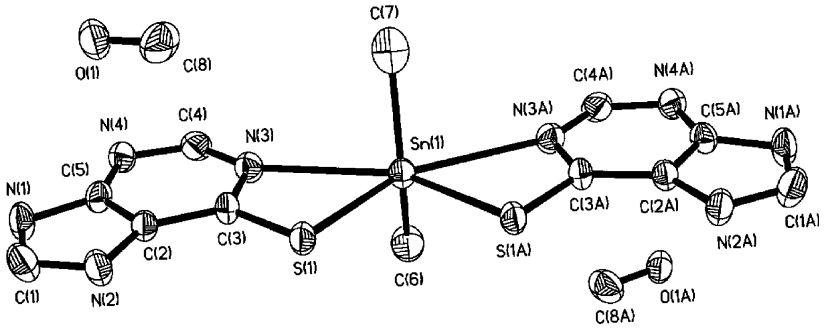


Fig. 1. Molecular structure of the complex **1**.

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

Sn(1)–C(6)	2.104(7)	N(3)–C(4)	1.330(7)
Sn(1)–C(7)	2.109(7)	N(3)–C(3)	1.337(6)
Sn(1)–S(1)	2.497(2)	N(4)–C(5)	1.319(10)
Sn(1)–N(3)	2.718(6)	N(4)–C(4)	1.329(6)
N(1)–C(1)	1.349(7)	O(1)–C(8)	1.390(7)
N(1)–C(5)	1.377(7)	S(1)–C(3)	1.733(6)
N(2)–C(1)	1.319(7)	C(2)–C(5)	1.392(8)
N(2)–C(2)	1.372(6)	C(2)–C(3)	1.408(8)
C(6)–Sn(1)–C(7)	130.5(4)	S(1)–Sn(1)–S(1A)	87.27(10)
C(6)–Sn(1)–S(1)	106.5(3)	C(6)–Sn(1)–N(3)	85.05(13)
C(7)–Sn(1)–S(1)	108.73(19)	C(7)–Sn(1)–N(3)	83.09(12)
C(6)–Sn(1)–S(1A)	106.5(3)	S(1)–Sn(1)–N(3)	60.67(14)
C(7)–Sn(1)–S(1A)	108.73(19)	S(1A)–Sn(1)–N(3)	147.94(12)

atoms and weak connections with two heterocyclic nitrogen atoms (N(3), N(3A)) of the ligand (mode **C**). The Sn–S bond distances (2.497(2) Å) are very close to the sum of the corresponding covalent radii (2.42 Å) [21], similar to the distances found in other Sn(IV) complexes of the terazolethiolato with metal–sulfur primary bonds, viz. 2.474(3)–2.614(5) Å [11,22]. The Sn–N bond lengths are markedly shorter [Sn(1)–N(3) 2.718(6) Å] than those reported in diorganotin derivatives of 1-phenyl-1*H*-tetrazole-5-thilato (2.975(5) [22c] and 2.947(4) Å [23]), all of which lie within the sum of their respective van der Walls radii (3.74 Å) [24]. These information suggests that the ligand Htpu adopts mode **C** to coordinate tin atom.

Including the intramolecular tin–nitrogen interactions, the geometry of center tin atom thus becomes skew-trapezoidal bipyramidal with the two methyl carbons in bent axial positions and the plane being defined by the two Sn–S covalent bonds and the two Sn–N secondary interactions. The C–Sn–C angle is 130.5(4)°. The two sulfur atoms occupy *cis*-positions with the S–Sn–S angle, 87.27(10)°.

It is worth to note that the component $Me_2Sn(tpu)_2$ crystallizes with two molecules of methanol and through the hydrogen bonding between them the supramolecular structure of complex **1** becomes a 2D network (Fig. 2). The methanol molecules involve in two hydrogen bonds, acting as a donor (O(1)–H(1B)···N(2) 2.741(6) Å, O(1)–H(1B)–N(2) 164.13°) as well as an acceptor (N(1)–H(1A)···O(1) 2.724(6) Å, N(1)–H(1A)–O(1) 171.77°).

2.4.2. *(n-Bu)$_2$Sn(tpu)$_2$ (**2**)*

For complex **2**, the asymmetric unit contains two monomers A and B (see Fig. 3), which are crystallographically non-equivalent. The conformations of the two independent molecules A and B are almost the same, with only small differences in bond lengths and bond angles (see Table 4). The geometry at tin atom in the complex **2** is distorted octahedral with the two methylene carbons in axial positions and the equatorial plane being defined by two S atoms and two N atoms. Two Sn–S bonds and two Sn–N bonds form around each tin atom but the two Sn–S bond lengths are much distinct and the same case occurs for Sn–N bond lengths. The shorter Sn–S bond (Sn(1)–S(1) 2.529(2) Å for A and Sn(2)–S(3) 2.514(2) Å for B) is close to the sum of the covalent radii of tin and sulfur atoms (2.42 Å) [21],

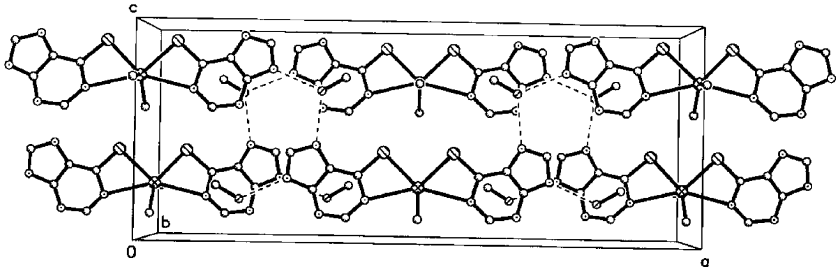


Fig. 2. Perspective view showing the 2D network of the complex **1**.

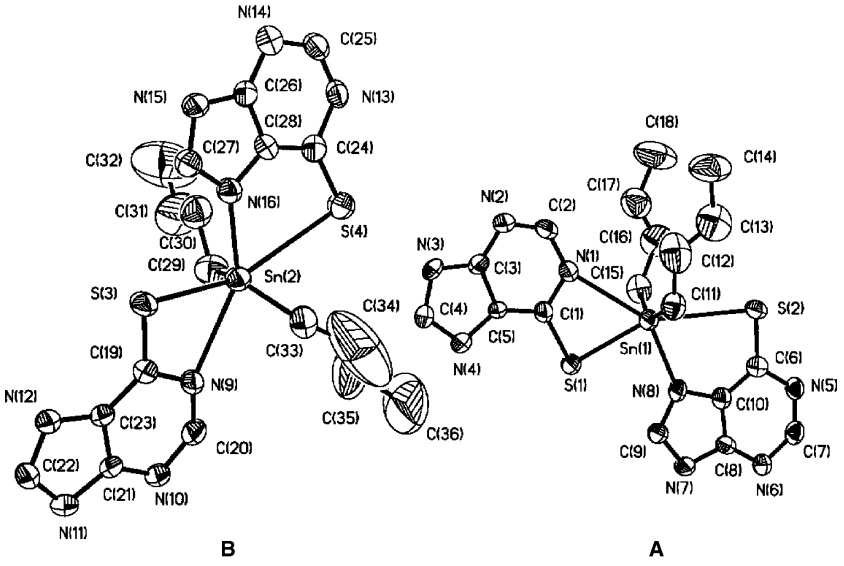


Fig. 3. Molecular structure of the complex **2**.

Table 4
Selected bond lengths (Å) and bond angles (°) for **2**

Molecule A		Molecule B	
Sn(1)–C(11)	2.117(8)	Sn(2)–C(33)	2.095(9)
Sn(1)–C(15)	2.147(8)	Sn(2)–C(29)	2.137(8)
Sn(1)–N(8)	2.196(5)	Sn(2)–N(16)	2.209(5)
Sn(1)–S(1)	2.529(2)	Sn(2)–S(3)	2.514(2)
Sn(1)–N(1)	2.725(5)	Sn(2)–N(9)	2.660(5)
Sn(1)–S(2)	3.123(2)	Sn(2)–S(4)	3.128(2)
N(1)–C(1)	1.336(8)	N(9)–C(20)	1.328(8)
N(1)–C(2)	1.361(8)	N(9)–C(19)	1.339(8)
N(2)–C(2)	1.290(8)	N(10)–C(21)	1.331(7)
N(2)–C(3)	1.334(8)	N(10)–C(20)	1.302(8)
N(3)–C(4)	1.308(8)	N(11)–C(22)	1.320(8)
N(3)–C(3)	1.355(8)	N(11)–C(21)	1.372(8)
N(4)–C(4)	1.342(8)	N(12)–C(22)	1.341(8)
N(4)–C(5)	1.373(7)	N(12)–C(23)	1.361(8)
N(5)–C(7)	1.327(8)	N(13)–C(25)	1.295(9)
N(5)–C(6)	1.414(8)	N(13)–C(24)	1.396(9)
N(6)–C(7)	1.322(8)	N(14)–C(25)	1.335(9)
N(6)–C(8)	1.347(8)	N(14)–C(26)	1.342(8)
N(7)–C(9)	1.316(8)	N(15)–C(27)	1.308(8)
N(7)–C(8)	1.341(7)	N(15)–C(26)	1.337(7)
N(8)–C(9)	1.336(8)	N(16)–C(27)	1.328(8)
N(8)–C(10)	1.358(7)	N(16)–C(28)	1.350(8)
S(1)–C(1)	1.732(6)	S(3)–C(19)	1.740(6)
S(2)–C(6)	1.681(7)	S(4)–C(24)	1.659(8)
C(11)–Sn(1)–C(15)	143.7(3)	C(33)–Sn(2)–C(29)	139.3(4)
C(11)–Sn(1)–N(8)	103.1(3)	C(33)–Sn(2)–N(16)	106.5(3)
C(15)–Sn(1)–N(8)	104.4(3)	C(29)–Sn(2)–N(16)	105.0(3)
C(11)–Sn(1)–S(1)	102.0(2)	C(33)–Sn(2)–S(3)	103.3(3)
C(15)–Sn(1)–S(1)	103.9(2)	C(29)–Sn(2)–S(3)	104.0(3)
N(8)–Sn(1)–S(1)	84.40(14)	N(16)–Sn(2)–S(3)	86.06(14)
C(11)–Sn(1)–N(1)	84.3(3)	C(33)–Sn(2)–N(9)	85.6(3)
C(15)–Sn(1)–N(1)	87.0(3)	C(29)–Sn(2)–N(9)	81.6(3)
N(8)–Sn(1)–N(1)	144.29(17)	N(16)–Sn(2)–N(9)	147.27(18)
S(1)–Sn(1)–N(1)	59.93(12)	S(3)–Sn(2)–N(9)	61.38(12)
C(11)–Sn(1)–S(2)	84.8(2)	C(33)–Sn(2)–S(4)	82.6(3)
C(15)–Sn(1)–S(2)	82.0(2)	C(29)–Sn(2)–S(4)	83.5(3)
N(8)–Sn(1)–S(2)	71.31(14)	N(16)–Sn(2)–S(4)	71.65(14)
S(1)–Sn(1)–S(2)	155.69(5)	S(3)–Sn(2)–S(4)	157.68(5)
N(1)–Sn(1)–S(2)	144.38(11)	N(9)–Sn(2)–S(4)	140.94(12)

while the longer one (Sn(1)–S(2) 3.123(2) Å for A and Sn(2)–S(4) 3.128(2) Å for B) is near to the sum of the van der Waals radii of the two atoms (4.0 Å) [24]. Similarly, the shorter and the longer Sn–N bond lengths (Sn(1)–N(8) 2.196(5) Å and Sn(1)–N(1) 2.725(5) Å for A, Sn(2)–N(16) 2.209(5) Å and Sn(2)–N(9) 2.660(5) Å for B) approach to the sum of the covalent radii (2.15 Å) and the van der Waals radii of tin and nitrogen atoms (3.74 Å) [24], respectively. Furthermore, there are differences between two C–S bonds (S(2)–C(6) 1.681(7) Å and S(1)–C(1) 1.732(6) Å for A, S(4)–C(24) 1.659(8) Å and S(3)–C(19) 1.740(6) Å for B). The shorter C–S bond length is near to that in thioureas (1.681 Å), suggesting its role as C=S double bond. While the longer lies between the average value for the double C=S bond in thioureas (1.681 Å) and the single C–S bond in the C–S–Me fragment (1.789 Å) [25], so that it can be regarded as C–S single bond and also suggesting that it has some double-bond character. All these remarkable differences in Sn–S, Sn–N and C–S bond lengths reveal that the thiol and thione forms may be concurrent in the Htpu when it reacts with *n*-Bu_2SnCl_2. Thus we can conclude that two S,N-chelating ligand asymmetrically coordinate to the center tin atom, different from that of complex **1**, which adopts modes **C** and **D** simultaneously. And the conclusion is complementary to Barbieri's prediction according to the data of infrared and Mössbauer spectroscopy [9].

In addition, intermolecular hydrogen bonding (N(7)–H(7)···N(4) 2.766(7) Å, N(7)–H(7)–N(4) 164.87° for A and N(15)–H(15)···N(12) 2.867(7) Å, N(15)–H(15)–N(12) 164.35° for B) is recognized, which associates the discrete molecule into a dimer. Besides, both the hydrogen bonding and intermolecular non-bonded N···N interactions are noted in the complex **2**, which help the construction of the 2D network (Fig. 4). The

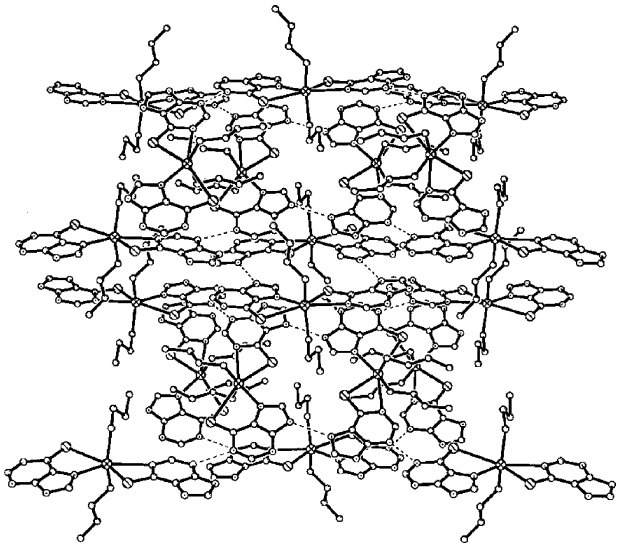


Fig. 4. Perspective view showing the 2D network of the complex **2**.

non-bonded N···N distances (N(2)···N(13) 2.772(8) Å and N(5)···N(10) 2.794(8) Å) are shorter than the sum of the van der Waals radii of nitrogen and nitrogen (3.08 Å) [21].

2.4.3. $Ph_3Sn(Hthpu)$ (7)

The molecular structure of complex **7** is shown in Fig. 5, selected bond lengths and angles are collected in Table 5. As expected, when the Htpu was replaced by the H_2thpu ligand, we found that the bonding is through the deprotonated SH rather than the OH group and the ligand adopts N^1/S^2 mode to coordinate to tin atom. The bond length of Sn(1)–S(1) (2.4661(17) Å) approaches to the sum of the covalent radii of tin and sulfur (2.42 Å) [21]. The bond distance of Sn(1)–N(1) (2.653(5) Å) is midway between the sums of the van der Waals and covalent radii of tin and nitrogen (2.15, 3.74 Å) [24], and approaches to the Sn–N length in the complex **1**. The C–S bond distance (C(2)–S(1) 1.740(6) Å) is similar to the longer C–S bond in complex **2**, also suggesting that the single C–S bond has some double-bond character in the deprotonated H_2thpu. Including the Sn(1)–N(1) interaction, the geometry at Sn(1) atom becomes distorted *cis*-trigonal bipyramidal with the axial–tin–axial angle N(1)–Sn(1)–C(6) of 159.03(19).

Table 5
Selected bond lengths (Å) and bond angles (°) for **7**

Sn(1)–C(18)	2.127(6)	N(3)–C(3)	1.350(7)
Sn(1)–C(12)	2.134(6)	N(3)–C(4)	1.368(8)
Sn(1)–C(6)	2.165(6)	N(4)–C(4)	1.311(8)
Sn(1)–S(1)	2.4661(17)	N(4)–C(5)	1.383(8)
Sn(1)–N(1)	2.653(5)	O(1)–C(1)	1.343(7)
N(1)–C(2)	1.341(7)	S(1)–C(2)	1.740(6)
N(1)–C(1)	1.343(7)	C(1)–C(5)	1.398(8)
N(2)–C(2)	1.332(7)	C(3)–C(5)	1.375(8)
N(2)–C(3)	1.345(7)		
C(18)–Sn(1)–C(12)	115.3(2)	C(6)–Sn(1)–S(1)	99.43(16)
C(18)–Sn(1)–C(6)	106.7(2)	C(18)–Sn(1)–N(1)	78.38(19)
C(12)–Sn(1)–C(6)	106.6(2)	C(12)–Sn(1)–N(1)	88.6(2)
C(18)–Sn(1)–S(1)	115.86(17)	C(6)–Sn(1)–N(1)	159.03(19)
C(12)–Sn(1)–S(1)	111.11(17)	S(1)–Sn(1)–N(1)	60.92(10)

There recognized two kind of hydrogen bonding in the crystal of complex **7**. One exists between the N(3)–H(3) and the N(2) derive from a neighboring molecule (N(3)–H(3)···N(2) 2.804(7) Å, N(3)–H(3)–N(2) 166.45°). And the other exists between O(1)–H(1) and the N(4) of a third molecule (O(1)–H(1)···N(4) 2.883(7) Å, O(1)–H(1)–N(4) 143.39°). Thus the supramolecular structure of complex **7** is constructed as a 1D polymer (Fig. 6).

2.4.4. $(Me_2SnCl)_2(dtpu)\cdot H_2O$ (9)

The molecular structure of complex **9** is shown in Fig. 7, selected bond lengths and angles are given in Ta-

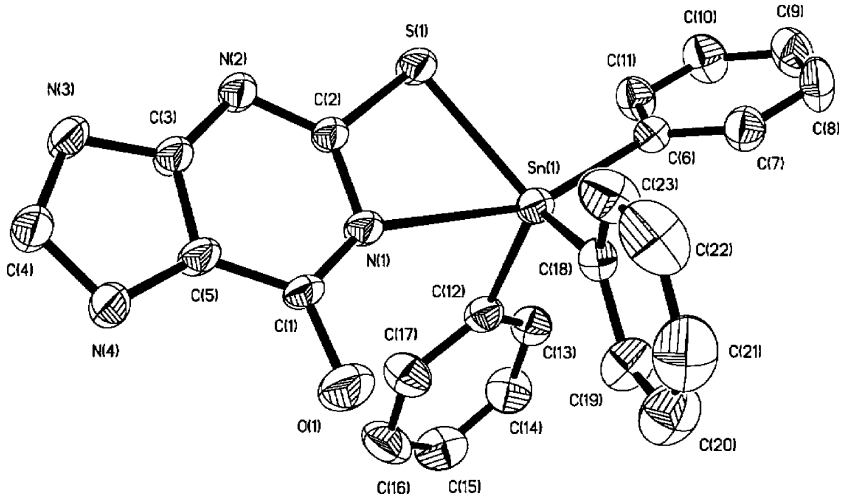


Fig. 5. Molecular structure of the complex **7**.

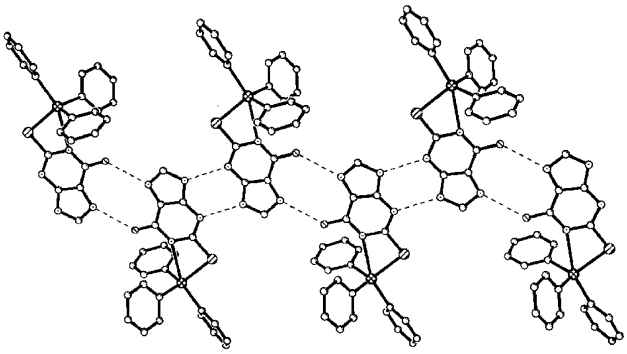


Fig. 6. Perspective view showing the 1D polymer of the complex **7**.

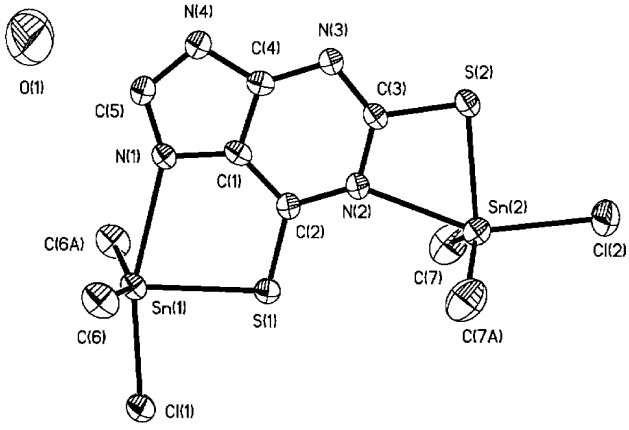


Fig. 7. Molecular structure of the complex **9**.

Table 6
Selected bond lengths (Å) and bond angles (°) for **9**

Sn(1)–C(6)	2.101(5)	N(2)–C(2)	1.348(8)
Sn(1)–Cl(1)	2.430(2)	N(2)–C(3)	1.375(8)
Sn(1)–S(1)	2.524(2)	N(3)–C(3)	1.322(8)
Sn(1)–N(1)	2.597(5)	N(3)–C(4)	1.365(8)
Sn(2)–C(7)	2.091(7)	N(4)–C(5)	1.329(9)
Sn(2)–Cl(2)	2.434(3)	N(4)–C(4)	1.352(9)
Sn(2)–S(2)	2.484(2)	S(1)–C(2)	1.709(7)
Sn(2)–N(2)	2.428(5)	S(2)–C(3)	1.730(7)
N(1)–C(5)	1.304(9)	C(1)–C(4)	1.391(9)
N(1)–C(1)	1.374(8)	C(1)–C(2)	1.392(9)
C(6A)–Sn(1)–C(6)	147.2(4)	C(7A)–Sn(2)–C(7)	131.5(4)
C(6)–Sn(1)–Cl(1)	99.70(17)	C(7)–Sn(2)–Cl(2)	101.9(2)
C(6)–Sn(1)–S(1)	103.85(17)	C(7)–Sn(2)–S(2)	110.9(2)
Cl(1)–Sn(1)–S(1)	85.33(8)	Cl(2)–Sn(2)–S(2)	89.40(9)
C(6)–Sn(1)–N(1)	84.24(16)	C(7)–Sn(2)–N(2)	88.9(2)
Cl(1)–Sn(1)–N(1)	164.19(12)	Cl(2)–Sn(2)–N(2)	152.57(14)
S(1)–Sn(1)–N(1)	78.86(13)	S(2)–Sn(2)–N(2)	63.16(14)

ble 6. There exists crystallographic symmetry in the complex **1**. Thus, two Sn–C bonds are identical, respectively. As shown in Fig. 7, when we choose the H_2dtpu ligand to react with Me_2SnCl_2, the complex **9** is obtained. Which is a binuclear and the H_2dtpu adopts N^1/S^2 and S^6/N^7 modes. Both of the Sn–S bond lengths

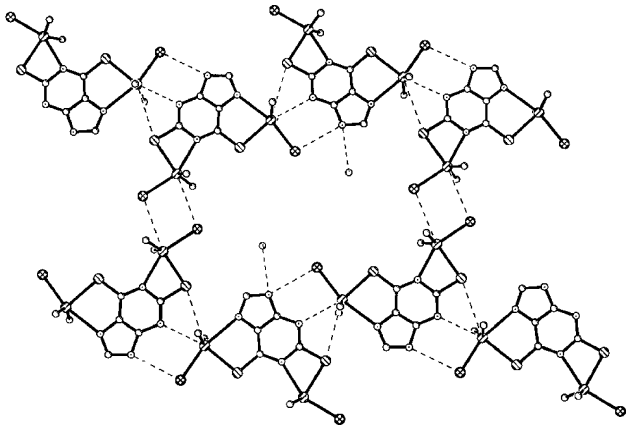


Fig. 8. Perspective view showing the 2D network of the complex **9**.

(Sn(1)–S(1) 2.524(2) Å and Sn(2)–S(2) 2.484(2) Å) approach the sum of the covalent radii of Sn and S (2.42 Å) [21]. Concerning the Sn–N bond lengths, though Sn(1)–N(1) bond length (2.597(5) Å) is little longer than that of Sn(2)–N(2) (2.428(5) Å), they are both midway between the sums of the van der Waals and covalent radii of tin and nitrogen (2.15–3.74 Å) [24]. Two Sn–Cl bonds (Sn(1)–Cl(1) 2.430(2) Å and Sn(2)–Cl(2) 2.434(3) Å) are typical Sn–Cl bond lengths found in chloroorganotin(IV) complexes in general [12,25]. Thus, the geometry at tin atoms become distorted trigonal bipyramidal with C(6), C(6A) and S(1) atoms for Sn(1), C(7), C(7A) and S(2) atoms for Sn(2) occupying the equatorial plane. And the axial angle Cl(1)–Sn(1)–N(1) and Cl(2)–Sn(2)–N(2) are 164.19(12) and 152.57(14), respectively.

The supramolecular structure of complex **9** is a 2D network (Fig. 8) linked by all kinds of weak interactions such as Sn···Cl, Sn···S, Sn···N and N–H···Cl. The Sn···Cl distance is 3.580(8) Å, shorter than the sum of the van der Waals' radii of Sn and Cl (3.85 Å) [24]. The Sn···S and Sn···N are 3.675(7) Å and 2.907(8) Å, respectively. For the hydrogen bond, the N(4)–H(4)···Cl(1) and N(4)–H(4)–Cl(1) are 3.278(7) Å and 143.16°, respectively. All of them benefit the construction of the 2D network.

Besides, it should be noted that the component $(Me_2SnCl)_2$(dtpu) crystallizes with one molecule of water that acts as an acceptor in the hydrogen bond (N(4)–H(4)···O(1) 2.933(6) Å, N(4)–H(4)–O(1) 126.05°).

3. Experimental details

3.1. Materials and measurements

Trimethyltin chloride, tri-*n*-butyltin chloride, triphenyltin chloride, dimethyltin dichloride, di-*n*-butyltin dichloride, diphenyltin dichloride, and all of the

thiopurine were commercially available, and they were used without further purification. Tribenzyltin chloride and dibenzyltin dichloride were prepared by a standard method reported in the literature [26]. The melting points were obtained with Kofler micro melting point apparatus and are uncorrected. Infrared-spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Bruker AMX-300 spectrometer operating at 300, 75.3 and 93.28 MHz, respectively. The TMS and Me_4 Sn were used as internal standards. The chemical shifts were given in ppm in $CDCl_3$ or CD_3Cl–D_2O solvent. Elemental analyses were performed with a PE-2400II apparatus.

3.2. Synthesis

The general route of synthesis is shown in the following. The reaction was carried out under nitrogen atmosphere with use of standard Schlenk technique. Thiopurine (Htpu, H_2thpu or H_2dtpu) ligand and the sodium methoxide were added to the solution of methanol, the mixture was stirred for 10 min, and then added organotin chlorides to the mixture, continuing the reaction about 12 h at 40 °C. After cooling down to room temperature, filtered it. The solvent of the filtrate was gradually removed by evaporation under vacuum until solid product was obtained. The solid was then recrystallized from methanol and the elemental analyses of all products are shown in Table 7.

Table 7
Physical and analytical data for organotin(IV) complexes of Htpu, H_2thpu and H_2dtpu

Complex[a,b]	m.p. (°C)	Yield (%)	Analysis Found (Calc.) (%)		
			C	H	N
$Me_2Sn(tpu)_2 \cdot 2MeOH$ (**1**)	142–144	73	32.44(32.64)	3.74(3.91)	21.71(21.75)
$(n\text{-}Bu)_2Sn(tpu)_2$ (**2**)	268–270	78	40.33(40.39)	4.54(4.52)	21.03(20.93)
$(Ph)_2Sn(tpu)_2$ (**3**)	168–171	69	46.09(45.93)	2.85(2.80)	19.38(19.48)
$(PhCH_2)_2Sn(tpu)_2$ (**4**)	123–124	81	47.96(47.78)	3.41(3.34)	18.45(18.57)
$Me_3Sn(Hthpu)$ (**5**)	122–124	75	29.23(29.03)	3.68(3.65)	17.09(16.93)
$(n\text{-}Bu)_3Sn(Hthpu)_2$ (**6**)	75–77	65	44.78(44.66)	6.65(6.61)	12.33(12.25)
$Ph_3Sn(Hthpu)$ (**7**)	212–215	84	53.35(53.41)	3.41(3.51)	10.79(10.83)
$(PhCH_2)_3Sn(Hthpu)$ (**8**)	142–143	87	54.47(54.26)	3.75(3.79)	10.40(10.55)
$(Me_2SnCl)_2(dtpu) \cdot H_2O$ (**9**)	116–118	70	19.05(19.01)	2.68(2.84)	10.05(9.85)
$(n\text{-}Bu_2SnCl)_2(dtpu)$ (**10**)	148–150	74	34.94(35.08)	5.33(5.33)	7.64(7.79)
$(Ph_2SnCl)_2(dtpu)$ (**11**)	140–143	85	43.72(43.59)	2.56(2.78)	7.15(7.01)
$[(PhCH_2)_2SnCl]_2(dtpu)$ (**12**)	124–125	71	46.14(46.35)	3.61(3.54)	6.67(6.55)

[a] All complexes are pale yellow.
[b] Solvent of recrystallization: methanol.

Table 8
Crystal data and structure refinement parameters for **1**, **2**, **7** and **9**

	1	**2**	**7**	**9**
Empirical formula	$C_{14}H_{20}N_8O_2S_2Sn$	$C_{18}H_{24}N_8S_2Sn$	$C_{23}H_{18}N_4OSSn$	$C_9H_{16}Cl_2N_4OS_2Sn_2$
M	515.19	535.26	517.16	568.66
T (K)	293(2)	298(2)	298(2)	298(2)
Crystal system	Orthorhombic	Monoclinic	Triclinic	Orthorhombic
Space group	$Cmc2_1$	$P2_1/c$	$P\bar{1}$	$Cmca$
a (Å)	27.28(3)	13.589(8)	9.431(3)	10.827(8)
b (Å)	7.383(8)	23.021(14)	9.487(3)	26.875(18)
c (Å)	10.597(12)	15.498(9)	15.866(5)	16.320(11)
α (°)	90	90	88.172(5)	90
β (°)	90	103.308(9)	78.842(6)	90
γ (°)	90	90	74.973(5)	90
V (Å^3)	2134(4)	4718(5)	1344.9(8)	4749(6)
Z	4	8	2	8
μ (mm^{-1})	1.418	1.281	1.045	2.504
Reflections collected	4270	23,856	7123	11,483
Independent reflections	1601	8116	4661	2121
R_{int}	0.0403	0.0537	0.0399	0.0357
Goodness-of-fit on F^2	0.985	0.941	0.928	1.026
R_1, wR_2 [$I > 2\sigma(I)$]	0.0274, 0.0606	0.0491, 0.1067	0.0544, 0.1267	0.0351, 0.0941
R_1, wR_2 (all data)	0.0301, 0.0618	0.1054, 0.1323	0.0800, 0.1371	0.0480, 0.1033

3.3. 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). A semi-empirical absorption correction was applied to the data. The structure was solved by direct-methods using SHELXL-97 and refined against F^2 by full-matrix least squares using SHELXL-97. The positions of hydrogen atoms were calculated, and their contributions in structural factor calculations were included. Crystal data and experimental details of the structure determinations are listed in Table 8.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper (**1**, **2**, **7** and **9**) have been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication Nos. CCDC-220163, 222016, 223775, 223782. Copies of the data can be obtained free of charge on application to 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).

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