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Triorganotin(IV) complexes of Schiff base derived from 6-amino-2-mercaptobenzothiazole: Synthesis, characterization and X-ray crystal structures

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Abstract

Nine triorganotin(IV) complexes of the type R_3SnL (L = L1 R = Me **1**, Ph **2**, $PhCH_2$ **3**; L = L2 R = Me **4**, Ph **5**, $PhCH_2$ **6**; L = L2 R = Me **7**, Ph **8**, $PhCH_2$ **9**) have been obtained by reaction of new Schiff base HL1, HL2 or HL3 with triorganotin(IV) chloride in the presence of sodium ethoxide. All the complexes **1**–**9** were characterized by elemental, IR and NMR spectra analyses. Except for complexes **3**, **4**, **6**, **9**, the others were also characterized by X-ray crystallography diffraction analyses, which revealed that complexes **1**, **2**, **5**, **7**, **8** were four coordinated and displayed a capped tetrahedron.

Keywords: Triorganotin(IV); Schiffbase; 6-Amino-2-mercaptobenzothiazole; Crystal structure

1. Introduction

In recent years, organotin(IV) complexes have received much attention both in academic and applied research because of the ability tin to afford stable bonds with carbon as well as with other hetero atoms. Heterocyclic thiones that contain at least one deprotonated heterocyclic thioamide group $(N–C–S)^-$ has been subject for their versatile coordination modes and effective biological activities. Recently, some organotin(IV) derivatives from heterocyclic thionates have been reported [1–5]. Our research group has been focused on this area for many years and reported many interesting structures [3,4,6–12]. Schiff base derived from various heterocycles were reported to possess cytotoxic, anticonvulsant, antiproliferative, anticancer and antifungal actives [13–16]. However, the majority of work that has been reported so far involves complexes of these ligands with transition metal ions. Complexes of non-transition metal ions such as tin have received less attention. Since organotin(IV) Schiff base ligands have potential applications in organic synthesis, catalysis, medicinal chemistry and biotechnology [17–20] and very little work has been done on organotin(IV) complexes of Schiff base derived from heterocyclic thiones. As an extension of this research program and in connection with our current interest in the coordination chemistry of organotin(IV) complexes with heterocyclic thionates, and combined with the development of organotin(IV) Schiff base chemistry, we select the ligand: 6-amino-2-mercaptobenzothiazole as raw material, synthesis the Schiff base HL1, HL2, HL3 and nine new organotin(IV) complexes **1**–**9** of the Schiff base. The HL1, HL2 and HL3 have been characterized by the elemental, IR and ^1H NMR spectra analyses. All the complexes **1**–**9** have been characterized by the elemental, IR, ^1H, ^{13}C and ^{119}Sn NMR spectra analyses. The complexes **1**, **2**, **5**, **7** and **8** were also characterized by X-ray crystallography.

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2. Experimental

2.1. Materials and measurements

All reagents were commercially available, and were used without further purification. 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 obtained on a Varian Mercury Plus 400 spectrometer operating at 400, 101 and 149.2 MHz, respectively. The chemical shifts were given in ppm with respect to the references and were stated relative to Me_4Si for ^{1}H and ^{13}C NMR, and to neat Me_4Sn for ^{119}Sn NMR. Elemental analyses were performed with a PE-2400II apparatus. The synthetic experiments of new Schiff base HL1, HL2, HL3 were shown in Scheme 1.

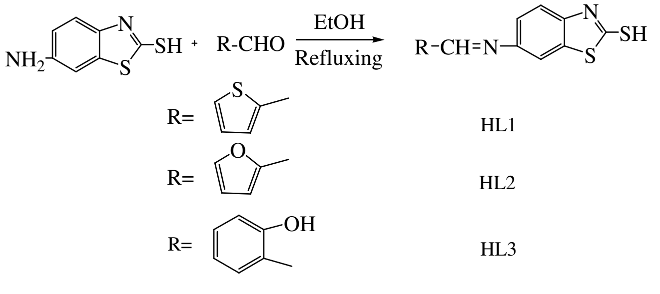
2.2. Synthesis of new Schiff base HL1, HL2 and HL3

2.2.1. Synthesis of HL1

The reaction was carried out under nitrogen atmosphere with use of standard Schlenk technique. The 6-amino-2-mercaptobenzothiazole (0.550 g, 3 mmol) was added to the solution of ethanol 30 ml, and then added thiophene-2-carboxaldehyde (0.400 g, 3.5 mmol) to the solution, continuing the reaction for 6 h at refluxing. The yellow precipitate was collected by filtration, washed with ether-petroleum, and dried at the nitrogen atmosphere. M.p. >200 °C. Yield: 0.514 g, 72%. *Anal.* Calc. for $C_{13}H_9NS_3$: C, 56.69; H, 3.29; N, 5.09. Found: C, 57.01; H, 3.41; N, 4.89%. IR (KBr, cm^{-1}): ν (S–H) 2734, ν (C=N) 1653, ν (S–C=N) 1583 (C–S) 972. ^{1}H NMR ($CDCl_3$, ppm): δ 8.85 (CH=N), 7.72–7.99 (Ar–H), 2.41 (S–H).

2.2.2. Synthesis of HL2

The produce was the same as the HL1, The 6-amino-2-mercaptobenzothiazole (0.550 g, 3 mmol) and 2-furaldehyde (0.336 g, 3.5 mmol) added to ethanol 30 ml, refluxing 6 h. The yellow precipitate was collected by filtration, washed with ether-petroleum, and dried at the nitrogen atmosphere. M.p. >200 °C. Yield: 0.515 g, 68%. *Anal.* Calc. for $C_{13}H_9NOS_2$: C, 60.20; H, 3.50; N, 5.40. Found: C, 59.92; H, 3.22; N, 5.13%. IR (KBr, cm^{-1}): ν (S–H) 2730, ν (C=N) 1650, ν (S–C=N) 1584, (C–S) 962. ^{1}H NMR ($CDCl_3$, ppm): δ 8.91 (CH=N), 2.52 (S–H).



Scheme 1.

2.2.3. Synthesis of HL3

The produce was the same as the HL1, The 6-amino-2-mercaptobenzothiazole (0.550 g, 3 mmol) and salicylaldehyde (0.430 g, 3.5 mmol) added to ethanol 30 ml, refluxing 6 h. The yellow precipitate was collected by filtration, washed with ether-petroleum, and dried at the nitrogen atmosphere. M.p. >200 °C. Yield: 0.545 g, 70%. *Anal.* Calc. for $C_{15}H_{11}NOS_2$: C, 63.13; H, 3.89; N, 4.91. Found: C, 63.41; H, 3.48; N, 4.66%. IR (KBr, cm^{-1}): ν (S–H) 2727, ν (C=N) 1650, ν (S–C=N) 1571, (C–S) 963. ^{1}H NMR ($CDCl_3$, ppm): δ 9.23 (CH=N), 2.61 (S–H).

2.3. Synthesis of complexes **1**–**4**

2.3.1. Synthesis of [Me_3SnL1] (**1**)

The reaction was carried out under nitrogen atmosphere. The HL1 (0.276 g, 1 mmol) was added to the solution of absolute benzene (20 ml) with sodium ethoxide (0.068 g, 1 mmol), and the mixture was stirred for 15 min, then added trimethyltin chloride (0.199 g, 1 mmol) to the mixture, continuing the reaction for 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 ether. Yellow crystal was formed. Yield: 72%. M.p.: 100–102 °C. *Anal.* Calc. for $C_{15}H_{16}N_2S_3Sn$: C, 41.02; H, 3.67; N, 6.38. Found: C, 41.14; H, 3.59; N, 6.21%. IR (KBr, cm^{-1}): ν (C=N) 1609, ν (S–C=N) 1578, (C–S) 973, (Sn–S) 318. ^{1}H NMR ($CDCl_3$, ppm): δ 8.63 (CH=N), 7.14–7.72 (Ar–H), 1.23 (Sn–CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 167.4 (C–S–Sn) 152.1, 151.9, 147.6, 142.8, 138.4, 132.4, 130.5, 127.9, 120.9, 119.9, 112.8, 11.3. ^{119}Sn NMR ($CDCl_3$, ppm): 108.2.

2.3.2. Synthesis of [Ph_3SnL1] (**2**)

The procedure is similar to that of complex **1**. The HL1 (0.276 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol) and Ph_3SnCl (0.385 g, 1 mmol) were added to the solution of benzene (20 ml), continuing the reaction for 12 h at 40 °C. The solid was recrystallized from ether-petroleum, and yellow crystals were formed. M.p.: 176–178 °C. *Anal.* Calc. for $C_{30}H_{22}N_2S_3Sn$: C, 57.62; H, 3.55; N, 4.48. Found: C, 57.60; H, 3.38; N, 4.52%. IR (KBr, cm^{-1}): ν (C=N) 1611, ν (S–C=N) 1582, (C–S) 996, (Sn–S) 338. ^{1}H NMR ($CDCl_3$, ppm): δ 8.62 (CH=N), 7.25–7.76 (Ar–H). ^{13}C NMR ($CDCl_3$, ppm): δ 167.2 (C–S–Sn) 151.8, 147.1, 137.3, 136.4, 136.2, 136.0, 130.6, 129.5, 129.2, 128.9, 120.1, 119.7, 119.1, 117.5, 113.4. ^{119}Sn NMR ($CDCl_3$, ppm): −117.2.

2.3.3. Synthesis of [$(PhCH_2)_3SnL1$] (**3**)

The procedure is similar to that of complex **1**. The HL1 (0.276 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol) and $(PhCH_2)_3SnCl$ (0.427 g, 1 mmol) were added to the solution of benzene (20 ml), continuing the reaction for 12 h at 40 °C. The solid was recrystallized from ether-petroleum, and yellow crystals were formed. M.p.: 165–167 °C. *Anal.* Calc. for $C_{33}H_{28}N_2S_3Sn$: C, 59.38; H, 4.23; N, 4.19. Found: C, 59.05; H, 4.38; N, 4.49%. IR (KBr, cm^{-1}): *v* (C=N) 1610, *v* (S–C=N) 1579, (C–S) 995, (Sn–S) 332. ^1H NMR ($CDCl_3$, ppm): δ 8.62 (CH=N), 7.25–7.76 (Ar–H). ^{13}C NMR ($CDCl_3$, ppm): δ 167.9 (C–S–Sn) 152.4, 147.9, 137.1, 136.1, 135.8, 135.6, 130.2, 129.3, 129.0, 128.7, 120.0, 119.5, 118.7, 117.1, 113.0, 38.4 (CH_2–Ph). ^{119}Sn NMR ($CDCl_3$, ppm): −98.5.

2.3.4. Synthesis of [Me_3SnL2] (**4**)

The procedure is similar to that of complex **1**. The HL2 (0.260 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol) and Me_3SnCl (0.199 g, 1 mmol) were added to the solution of benzene (20 ml), continuing the reaction for 12 h at 40 °C. The solid was recrystallized from ether-petroleum, and yellow crystals were formed. M.p.: 104–106 °C. *Anal.* Calc. for $C_{62}H_{50}N_4O_3S_4Sn_2$: C, 58.88; H, 3.98; N, 4.43. Found: C, 58.56; H, 3.77; N, 4.68%. IR (KBr, cm^{-1}): *v* (C=N) 1606, *v* (S–C=N) 1579, (C–S) 970, (Sn–S) 320. ^1H NMR ($CDCl_3$, ppm): δ 8.64 (CH=N), 7.16–7.78 (Ar–H), 1.25 (Sn–CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ167.0 (C–S–Sn) 152.0, 151.6, 147.3, 142.7, 138.3, 132.1, 130.2, 127.7, 120.6, 119.8, 112.7, 11.2. ^{119}Sn NMR ($CDCl_3$, ppm): 106.5.

2.3.5. Synthesis of [Ph_3SnL2] (**5**)

The procedure is similar to that of complex **1**. The HL2 (0.260 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol) and Ph_3SnCl (0.385 g, 1 mmol) were added to the solution of benzene (20 ml), continuing the reaction for 12 h at 40 °C. The solid was recrystallized from ether-petroleum, and yellow crystals were formed. M.p.: 150–152 °C. *Anal.* Calc. for $C_{30}H_{22}N_2OS_2Sn$: C, 59.13; H, 3.64; N, 4.60. Found: C, 59.40; H, 3.89; N, 4.33%. IR (KBr, cm^{-1}): *v* (C=N) 1611, *v* (S–C=N) 1583, *v* (C–S) 998, (Sn–S) 340. ^1H NMR ($CDCl_3$, ppm): δ 8.62 (CH=N), 7.24–7.75 (Ar–H). ^{13}C NMR ($CDCl_3$, ppm): δ167.1 (C–S–Sn) 151.7, 147.2, 137.1, 136.3, 136.1, 135.9, 130.5, 129.3, 129.1, 128.7, 120.0, 119.6, 119.0, 117.3, 113.2. ^{119}Sn NMR ($CDCl_3$, ppm): −118.1.

2.3.6. Synthesis of [$(PhCH_2)_3SnL2$] (**6**)

The procedure is similar to that of complex **1**. The HL1 (0.276 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol) and $(PhCH_2)_3SnCl$ (0.427 g, 1 mmol) were added to the solution of benzene (20 ml), continuing the reaction for 12 h at 40 °C. The solid was recrystallized from ether-petroleum, and yellow crystals were formed. M.p.: 148–150 °C. *Anal.* Calc. for $C_{33}H_{26}N_2OS_2Sn$: C, 61.03; H, 3.41; N, 4.31. Found: C, 61.33; H, 3.65; N, 4.63%. IR (KBr, cm^{-1}): *v* (C=N) 1607, *v* (S–C=N) 1581, (C–S) 997, (Sn–S) 330. ^1H NMR ($CDCl_3$, ppm): δ 8.62 (CH=N), 7.25–7.76 (Ar–H). ^{13}C NMR ($CDCl_3$, ppm): δ 167.9 (C–S–Sn) 152.3, 147.7, 137.0, 136.0, 135.5, 135.3, 130.0, 129.1, 129.0, 128.5, 119.8, 119.5, 118.6, 116.9, 112.9, 38.3 (CH_2–Ph). ^{119}Sn NMR ($CDCl_3$, ppm): −97.2.

2.3.7. Synthesis of [Me_3SnL3] (7)

The procedure is similar to that of complex **1**. The HL3 (0.287 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol) and Me_3SnCl (0.199 g, 1 mmol) were added to the solution of benzene (20 ml), continuing the reaction for 12 h at 40 °C. The solid was recrystallized from ether-petroleum, and yellow crystals were formed. M.p.: 106–108 °C. *Anal.* Calc. for $C_{17}H_{18}N_2OS_2Sn$: C, 45.46; H, 4.04; N, 6.23. Found: C, 45.32; H, 3.97; N, 6.18%. IR (KBr, cm^{-1}): *v* (C=N) 1612, *v* (S–C=N) 1568, (C–S) 978, (Sn–S) 325. ^1H NMR ($CDCl_3$, ppm): δ 13.22 (–OH), 8.68 (CH=N), 6.98–7.84 (Ar–H) 0.98 (Sn–CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 168.3 (C–S–Sn), 162.1, 161.1, 152.4, 144.6, 138.6, 132.3, 121.1, 119.8, 119.3, 119.2, 117.3, 113.1, 14.2. ^{119}Sn NMR ($CDCl_3$, ppm): 111.3.

2.3.8. Synthesis of [Ph_3SnL3] (**8**)

The procedure is similar to that of complex **1**. The HL3 (0.287 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol) and Ph_3SnCl (0.385 g, 1 mmol) were added to the solution of benzene (20 ml), continuing the reaction for 12 h at 40 °C. The solid was recrystallized from ether-petroleum, and yellow crystals were formed. M.p.: 142–144 °C. *Anal.* Calc. for $C_{32}H_{24}N_2OS_2Sn$: C, 60.49; H, 3.81; N, 4.41. Found: C, 60.40; H, 3.90; N, 4.25%. IR (KBr, cm^{-1}): *v* (C=N) 1615, *v* (S–C=N) 1570, *v* (C–S) 997, (Sn–S) 342. ^1H NMR ($CDCl_3$, ppm): δ 13.22 (–OH), 8.67 (CH=N), 6.95–7.74 (Ar–H). ^{13}C NMR ($CDCl_3$, ppm): δ 167.3 (C–S–Sn), 162.4, 161.1, 151.7, 144.8, 139.3, 138.8, 137.1, 136.8, 136.6, 133.3, 132.3, 129.9, 129.7, 129.2, 128.9, 128.8, 128.6, 120.7, 120.1, 119.3, 117.3, 113.2. ^{119}Sn NMR ($CDCl_3$, ppm): −108.2.

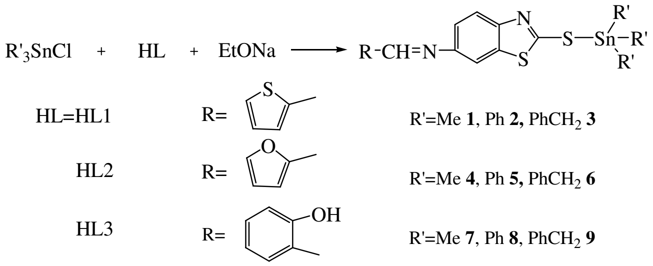
2.3.9. Synthesis of [$(PhCH_2)_3SnL3$] (**9**)

The procedure is similar to that of complex **1**. The HL2 (0.287 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol) and $(PhCH_2)_3SnCl$ (0.427 g, 1 mmol) were added to the solution of benzene (20 ml), continuing the reaction for 12 h at 40 °C. The solid was recrystallized from ether-petroleum, and yellow crystals were formed. M.p.: 150–152 °C. *Anal.* Calc. for $C_{35}H_{30}N_2OS_2Sn$: C, 62.61; H, 3.60; N, 4.17. Found: C, 62.33; H, 3.87; N, 4.35%. IR (KBr, cm^{-1}): *v* (C=N) 1614, *v* (S–C=N) 1569, *v* (C–S) 996, (Sn–S) 336. ^1H NMR ($CDCl_3$, ppm): δ 13.18 (–OH), 8.73 (CH=N), 7.05–7.86 (Ar–H), 3.26 (CH_2–Ph). ^{13}C NMR ($CDCl_3$, ppm): δ 172.8 (C–S–Sn), 168.5, 164.2, 156.7, 148.2, 140.3, 138.5, 137.6, 136.8, 135.4, 134.1, 132.8, 130.5, 129.8, 129.0, 128.7, 128.1, 121.3, 120.7, 119.8, 118.1, 113.9, 37.5 (CH_2–Ph). ^{119}Sn NMR ($CDCl_3$, ppm): −95.7.

3. Result and discussion

3.1. Synthesis of complexes **1–9**

The synthesis procedure was shown in Scheme 2.



Scheme 2.

3.2. IR

The stretching frequencies of interest are those associated with the Sn—S and S—C=N groups. The spectra of all the complexes **1**–**9** show some common characters. The explicit features in the infrared spectra of all complexes **1**–**9**, strong absorption appearing in the range of 318–342 cm^{-1} in respective of the complexes, which are absent in the free ligands, are assigned to the Sn–S stretching mode of vibration. All these values are consistent with that detected in a number of organotin(IV)-sulfur derivative [21]. The v (S—C=N), occurring at 1578 cm^{-1} for **1**, 1582 cm^{-1} for **2**, 1580 cm^{-1} **3**, 1579 cm^{-1} **4**, 1583 cm^{-1} **5**, 1581 cm^{-1} **6**, 1568 cm^{-1} for **7**, 1570 cm^{-1} for **8**, 1569 cm^{-1} for **9** is shift a littler lower frequencies compare with that of the HL1 (1583 cm^{-1}), HL2 (1584 cm^{-1}) and HL3 (1571 cm^{-1}), confirming the very weak coordination of the heterocyclic N to the tin. This can be further confirmed by the X-ray crystallography.

3.3. NMR

In the ^{1}H NMR spectrums of the complexes **1**–**9**, the ^{1}H NMR spectra show the expected integration and peak multiplicities. In the spectra of the HL1, HL2 and HL3 ligands, the resonances observed at 2.41, 2.52 and 2.61 ppm, which are absent in the spectra of the complexes, indicate removal of the SH protons and formation of Sn–S bonds. This conclusion accords well with the IR data. Moreover, the ^{1}H NMR spectroscopic data show that the chemical shifts of the phenyl groups in complexes **2**, **5**, **8**, the methyl groups in complexes **1**, **4**, and **7**, and the methyl groups in complexes **3**, **6** and **9** undergo an up field shift relative to those of their precursors.

The ^{13}C NMR spectra of all complexes **1**–**9** show a significant downfield shift of all carbon resonances compared with the free ligand (HL1, HL2 and HL3) because of an electron-density transfer from the ligand to the metal atom. The ^{119}Sn NMR spectroscopic data shown only one signals for complexes **1**–**9** ($\delta = 108.2$ ppm for **1**, −117.2 ppm for **2**, −98.5 ppm for **3**, 106.5 ppm for **4**, −118.1 ppm for **5**, −97.2 ppm for **6**, 111.3 ppm for **7**, −108.2 ppm for **8**, −95.7 ppm for **9**) are in the normal range for four-coordinate tin complexes [22].

3.4. Description of crystal structures of *1, 2, 5, 7 and 8*

Selected bond lengths and bond angles for **1**, **2**, **5**, **7** and **8** are given in Tables 1–3, respectively, and their crystal molecular structures are given in Figs. 1–5, respectively.

From the structures we can see that there exist four primary bonds to the central tin atom in complexes **1**, **2**, **5**, **7** and **8**, three carbons from the methyl (for complexes **1** and **7**), phenyl groups (for complexes **2**, **5** and **8**), and one S from the HL1, HL2 or HL3. Thus, the complexes **1**, **2**, **5**, **7** and **8** are all display tetrahedral coordination sphere with six angles ranging from 95.30(18)° to 118.1(2)°. The Sn–S bond lengths [between 2.4281(14) and 2.4877(14) Å] are a little longer than the covalent radii of tin and sulfur atoms

Table 1
Selected bond lengths (Å) and bond angles (°) of complex **1** and **2**

Complex **1**		Complex **2**	
Bond lengths		*Bond lengths*	
Sn(1)–C(15)	2.101(15)	Sn(1)–C(13)	2.120(5)
Sn(1)–C(13)	2.131(14)	Sn(1)–C(25)	2.124(5)
Sn(1)–C(14)	2.143(13)	Sn(1)–C(19)	2.130(5)
Sn(1)–S(2)	2.455(4)	Sn(1)–S(2)	2.4281(14)
Sn(1)–N(1)	3.005	Sn(1)–N(1)	3.381
Bond angles		*Bond angles*	
C(15)–Sn(1)–C(13)	111.5(8)	C(13)–Sn(1)–C(25)	110.07(19)
C(15)–Sn(1)–C(14)	115.9(7)	C(13)–Sn(1)–C(19)	114.39(19)
C(13)–Sn(1)–C(14)	111.8(7)	C(25)–Sn(1)–C(19)	108.73(18)
C(15)–Sn(1)–S(2)	107.4(5)	C(13)–Sn(1)–S(2)	110.27(13)
C(13)–Sn(1)–S(2)	100.4(5)	C(25)–Sn(1)–S(2)	96.69(14)
C(14)–Sn(1)–S(2)	108.5(5)	C(19)–Sn(1)–S(2)	115.21(14)

Table 2
Selected bond lengths (Å) and bond angles (°) of complex **5**

Bond lengths			
Sn(1)–C(13)	2.129(7)	Sn(1)–C(25)	2.133(7)
Sn(1)–C(19)	2.135(6)	Sn(1)–S(2)	2.460(2)
Bond angles			
C(13)–Sn(1)–C(25)	112.7(2)	C(13)–Sn(1)–C(19)	112.6(2)
C(25)–Sn(1)–C(19)	109.5(3)	C(13)–Sn(1)–S(2)	112.1(2)
C(25)–Sn(1)–S(2)	113.45(17)	C(19)–Sn(1)–S(2)	95.30(18)

Table 3
Selected bond lengths (Å) and bond angles (°) of complex **7** and **8**

Complex **7**		Complex **8**	
Bond lengths		*Bond lengths*	
Sn(1)–C(16)	2.110(4)	Sn(1)–C(27)	2.127(5)
Sn(1)–C(17)	2.132(5)	Sn(1)–C(21)	2.143(4)
Sn(1)–C(15)	2.139(4)	Sn(1)–C(15)	2.143(4)
Sn(1)–S(2)	2.4877(14)	Sn(1)–S(2)	2.447(3)
Sn(1)–N(1)	3.073(3)	Sn(1)–N(1)	3.049
Bond angles		*Bond angles*	
C(16)–Sn(1)–C(17)	118.1(2)	C(27)–Sn(1)–C(21)	116.54(16)
C(16)–Sn(1)–C(15)	114.99(18)	C(27)–Sn(1)–C(15)	108.90(17)
C(17)–Sn(1)–C(15)	112.5(2)	C(21)–Sn(1)–C(15)	110.21(17)
C(16)–Sn(1)–S(2)	105.42(14)	C(27)–Sn(1)–S(2)	111.52(12)
C(17)–Sn(1)–S(2)	103.56(15)	C(21)–Sn(1)–S(2)	111.27(11)
C(15)–Sn(1)–S(2)	99.26(14)	C(15)–Sn(1)–S(2)	96.56(13)

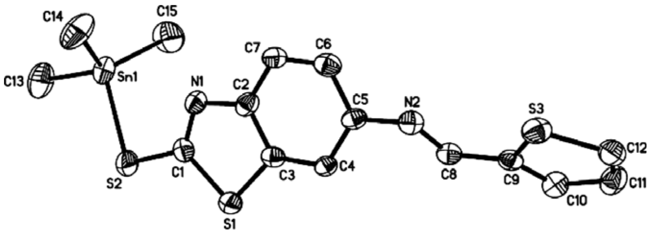


Fig. 1. The molecular structure of complex **1**.

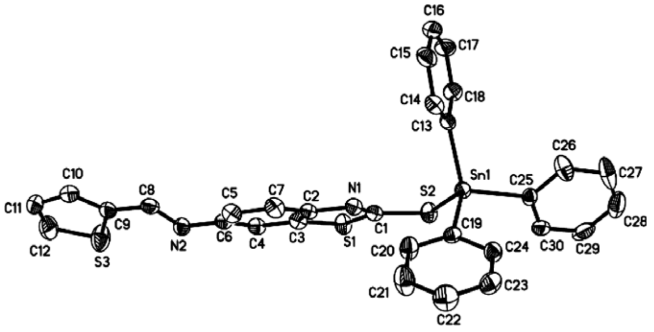


Fig. 2. The molecular structure of complex **2**.

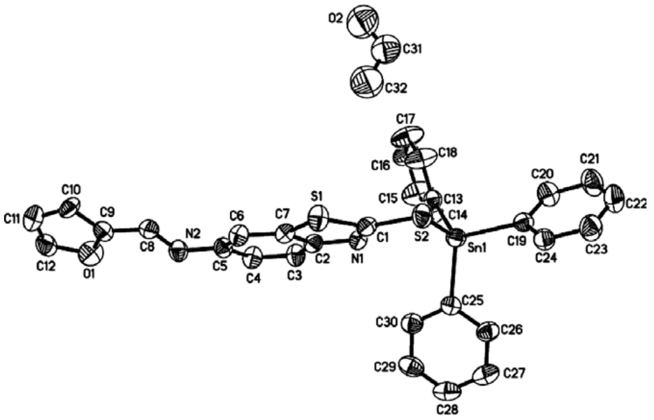


Fig. 3. The molecular structure of complex **5**.

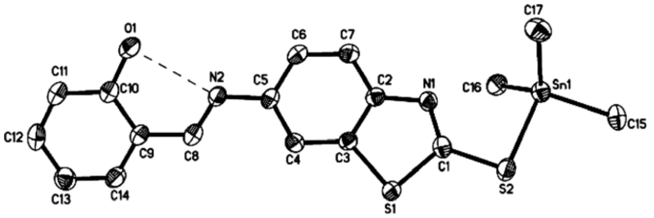


Fig. 4. The molecular structure of complex **7**.

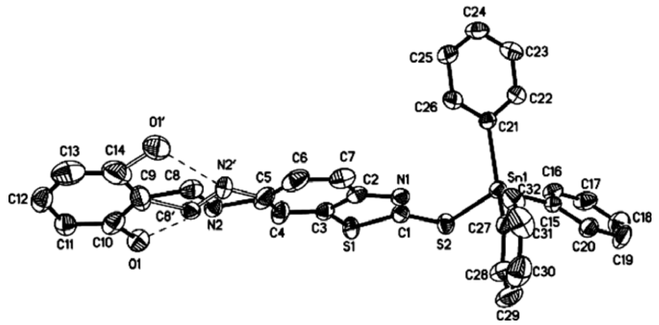


Fig. 5. The molecular structure of complex **8**.

(2.42 Å) [23] and within the range from 2.41 to 2.48 Å on the whole that reported in triphenyltin(IV) heteroarenethiolates [24]. The Sn–C bond lengths fall in a narrow range from 2.101(15) to 2.143(13) Å for complexes **1**, **2**, **5**, **7** and **8**, typical for organotin(IV) derivatives. Five complexes are different distinctly from each other with regards to their weak intramolecular Sn···N interactions [Sn(1)–N(1): 3.005 Å **1**, 3.381 Å **2**, 2.992 Å **5**, 3.073(3) Å **7**, 3.049 Å **8**, respectively], they are all longer than the sum of the covalent radii of tin and nitrogen atoms (2.15 Å), but still lie within the sum of the van der Walls radii of the two atoms (3.74 Å) [23]. As the N atoms of the heterocycle are involved in a weak coordinative interaction with tin along one of the tetrahedral faces, the structure distortion for the tin atom in **1**, **2**, **5**, **7** and **8** is best described as a capped tetrahedron. For complexes **7** and **8** there is different from **1**, **2** and **5** is that an intramolecular hydrogen bonds between the oxygen of the hydrogen and nitrogen of the CH=N was identified as can be seen from the Figs. 4 and 5 and the values are list in Table 4.

Further analysis of the supramolecular structure of the complexes **1**, **2**, **5**, **7** and **8**, only find the complexes **1** and **7** have more important intermolecular interactions. The supramolecular structure of **1** is dominated by 1D chain linked by intermolecular C(8)–H(8)···S(3) [H(8)···S(3) 2.961 Å, C(8)···S(3) 3.857 Å, C(8)–H(8)···S(3) 162.35°] as can be seen from the Fig. 6. The H(8)···S(3) distance is much close to the literature report for the H and S weak interaction (2.959 Å) [25].

The supramolecular structure of complex **7** is dominated by intermolecular Sn···O, C–H···π and C–H···S interactions. An important Sn···O interaction along the *b* axis was found from the crystal packing of complex **7** (Fig. 7), and link the discrete molecular into a 1D chain. Though the Sn···O distance (Sn(1)···O(1) = 3.296 Å) is considerably longer than the normal Sn–O covalent bond, they are much shorter than the van der Waals radii of Sn and O (3.68 Å). The C–H···π interaction has identified between the C7A and the ring of benzothiazole. This can be considered as a pair of bifurcated intermolecular C–H···π interaction [C(7)–H(7 A)···Cg1 (Cg1 cent of the C2–C7, H(7A)···Cg1 2.783 Å, 3.671 Å, 160.18°) and C(7)–H(7A)···Cg2 (Cg2 cent of the C(1)–N(1)–C(2)–C(3)–S(1) 3.169 Å, 3.790 Å, 125.98°)] as shown in Fig. 8, all these distances are reasonable as an intermolecular action according to the literature reported [26]. The pair of C–H···π interactions further reinforces the 1D chain as can be seen from the Fig. 9. In the direction of *a* axis an intermolecular C–H···S (C12–H12···S2 2.862 Å, 3.635 Å, 141.26 °) interaction link these 1D chain together and 2D network was formed in the *bc* plane (Fig. 9).

Table 4
Hydrogen bonds and C–H···π interaction for the complexes **7** and **8**

	D–H···A	*d*(D–H) (Å)	*d*(H...A) (Å)	*d*(D...A) (Å)	∠DHA (°)
Complex 7	O1–H1···N2	0.820	1.887	2.617	147.68
Complex 8	O1–H1_a···N2_a	0.820	1.861	2.618	152.98
	O1′–H1′_b···N2′_b	0.820	1.973	2.762	161.21
	C–H···π	H···Cg (Å)	C···Cg (Å)	C–H···Cg	
	C(7)–H(7A)···Cg(1)	2.783	3.671	160.18	
	C(7)–H(7A)···Cg(2)	3.169	3.790	125.98	

Cg(1) and Cg(2) are referred to the centroids of C(2)–C(3)–C(4)–C(5)–C(6)–C(7), C(1)–N(1)–C(2)–C(3)–S(1).

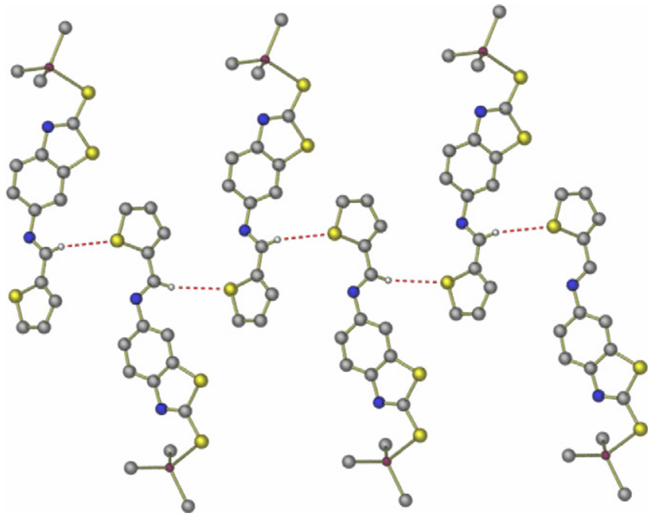


Fig. 6. 1D chain was connected by intermolecular C–H···S interaction of complex **1**.

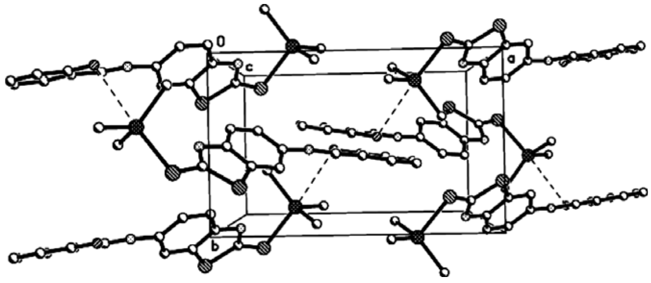


Fig. 7. The crystal packing of complex **7**.

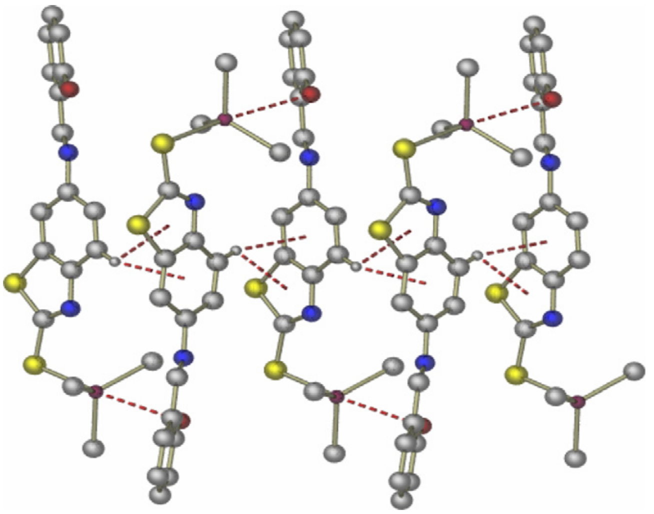


Fig. 8. The 1D chain linked by intermolecular Sn···O and C–H···π interaction of complex **7**.

4. 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 structure was solved by direct methods using SHELXS-97 and refined against F^2 by full-matrix least squares using SHELXL-97. Hydrogen

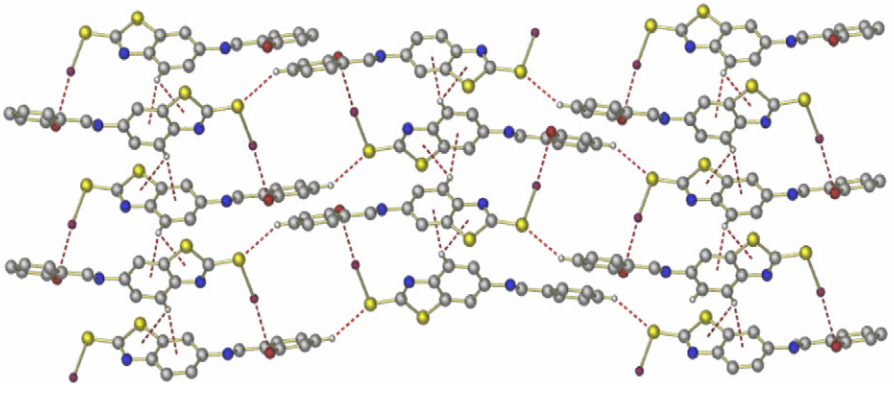


Fig. 9. The 2D network connected by intermolecular Sn···O, C–H···π and C–H···S interaction of complex **7**. The non-interaction hydrogen atoms and the methyl group have been omitted for clarity.

Table 5
Crystal data and structure refinement parameters for complexes **1**, **2**, **5**, **7** and **8**

Complex	**1**	**2**	**5**	**7**	**8**
Empirical formula	$C_{15}H_{16}N_2S_3Sn$	$C_{120}H_{88}N_8S_{12}Sn_4$	$C_{62}H_{50}N_4O_3S_4Sn_2$	$C_{17}H_{18}N_2OS_2Sn$	$C_{32}H_{24}N_2OS_2Sn$
Formula weight	439.17	2501.46	1264.68	449.14	635.34
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	orthorhombic	monoclinic	triclinic	monoclinic	triclinic
Space group	*Pccn*	*P*2(1)/*n*	$P\bar{1}$	*P*2(1)/*c*	$P\bar{1}$
a (Å)	44.779(2)	9.5234(16)	9.685(2)	11.755(5)	9.547(9)
b (Å)	10.786(3)	29.597(5)	13.204(3)	7.337(3)	11.792(13)
c (Å)	7.502(3)	10.1657(17)	13.323(3)	21.838(10)	14.644(16)
α (°)	90	90	68.117(4)	90	113.141(14)
β (°)	90	107.927(2)	76.261(4)	93.108(6)	94.362(16)
γ (°)	90	90	75.145(4)	90	101.25(2)
V (Å^3)	3623.4(18)	2726.2(8)	1508.8(6)	1880.6(15)	1465(3)
Z	8	1	1	4	2
D_{calc} (Mg m^{-3})	1.610	1.524	1.392	1.586	1.440
F(000)	1744	1256	638	896	640
Absorption coefficient (mm^{-1})	1.750	1.189	1.012	1.585	1.041
Crystal size (mm)	0.42 × 0.39 × 0.16	0.53 × 0.49 × 0.48	0.21 × 0.16 × 0.11	0.38 × 0.27 × 0.21	0.57 × 0.51 × 0.48
θ Range for data collection (°)	1.82–25.01	1.38–25.01	1.94–25.01	1.73–25.01	1.90–25.01
Index ranges	$-53 \leqslant h \leqslant 47$, $-12 \leqslant k \leqslant 12$, $-6 \leqslant l \leqslant 8$	$-10 \leqslant h \leqslant 11$, $-32 \leqslant k \leqslant 35$, $-11 \leqslant l \leqslant 12$	$-11 \leqslant h \leqslant 11$, $-15 \leqslant k \leqslant 15$, $-15 \leqslant l \leqslant 8$	$-11 \leqslant h \leqslant 13$, $-8 \leqslant k \leqslant 8$, $-25 \leqslant l \leqslant 22$	$-10 \leqslant h \leqslant 11$, $-12 \leqslant k \leqslant 14$ $-17 \leqslant l \leqslant 17$
Reflections collected	16673	14089	8021	9413	7580
Unique reflections	3105	4794	8021	3312	5072
Maximum/minimum transmission	0.7671/0.5268	0.5991/0.5714	0.8968/0.8156	0.7319/0.5842	0.6349/0.5883
Data/restraints/parameters	3105/0/190	4794/0/325	5267/39/353	3312/0/208	5072/11/371
Goodness of fit on F^2	1.009	1.000	1.001	1.000	1.003
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0756$, $wR_2 = 0.1969$	$R_1 = 0.0447$, $wR_2 = 0.1094$	$R_1 = 0.0525$, $wR_2 = 0.1282$	$R_1 = 0.0323$, $wR_2 = 0.0728$	$R_1 = 0.0346$, $wR_2 = 0.0870$
R indices (all data)	$R_1 = 0.1087$, $wR_2 = 0.2246$	$R_1 = 0.0631$, $wR_2 = 0.1200$	$R_1 = 0.0960$, $wR_2 = 0.1572$	$R_1 = 0.0498$, $wR_2 = 0.0848$	$R_1 = 0.0501$, $wR_2 = 0.1001$

atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are list in Table 5.

5. Supplementary material

CCDC 627615, 627613, 627616 and 627614 contain the supplementary crystallographic data for **1**, **2**, **7** and **8**. 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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