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# Organtin Complexes of 2,5-Dithiobiurea ($H_2$dtbu): The Crystal Structures of ($Ph_3Sn)_2$(dtbu) and [(*n*-Bu)$_2$SnCl]$_2$(dtbu)

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ABSTRACT: *A series of organotin(IV) complexes of two types, $[R_3Sn]_2$(dtbu) (R = $PhCH_2$* **1**, *Ph* **2**, *n-Bu* **3**, *$H_2$dtbu = 2,5-dithiobiurea), $[R_2SnCl]_2$(dtbu) (R = $PhCH_2$* **4**, *Ph* **5**, *n-Bu* **6**) *have been synthesized and characterized by elemental analysis, IR, and NMR ($^1H$, $^{119}Sn$) spectroscopy. The structures of* **2** *and* **6** *have been determined by X-ray crystallography. Crystal structures show that both complexes* **2** *and* **6** *are the symmetric dinuclear unit. Interestingly, supramolecular structures show that complex* **2** *has formed a linear chain through N—H···S hydrogen bonding and* **6** *has formed a two-dimensional network in perfect bc plane connected through N—H···Cl hydrogen bonding and nonbonded S···S interactions.* © 2008 Wiley Periodicals, Inc. Heteroatom Chem 19:435–442, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20456

## INTRODUCTION

Although organotin complexes were found to exhibit the potential industrial applications and biological activities [1,2], numerous studies on adduct formation by organotin(IV) halides with a variety of nitrogen and thiol/thione donors have been carried out. For example, triazine-, triazyl-, and tetrazolethiol organotin derivatives have been reported [3–6]. A related class of such complexes is thiosemicarbazones in which the structure unit HS—C=N—N or S=C—NH—N can bond to metal ions through S or N or both atoms [7].

In our previous work, we have reported a five-membered chelate ring complex $Ph_3SnSN_4C_{13}H_{11}$ with 1,5-diphenyl thiocarbazone [8] and a series of N,S,S-bonded diorganotin complexes with 2,5-dithiobiurea [9]. Although the reactions of diorganotin and 2,5-dithiobiurea had been researched with 1:1:2 molar ratio of $LH_2$:$R_2SnCl_2$:EtONa at 60°C and obtained four monomeric compounds of the type $R_2$Sn(dtbu) [R = Me **1**, *n*-Bu **2**, Ph **3**, $PhCH_2$ **4**], now, we have changed the conditions of the reactions, with 1:2:2 molar ratio of $LH_2$:$R_2SnCl_2$:EtONa at 40°C and obtained three new organotin complexes of type $[R_2SnCl]_2$(dtbu) (R = $PhCH_2$ **4**, Ph **5**, *n*-Bu **6**); we also studied the reactions of triorganotin with 2,5-dithiobiurea with 1:2:2 molar ratio of $LH_2$:$R_3SnCl$:EtONa at 40°C and obtained three new organotin complexes of type $[R_3Sn]_2$(dtbu) (R = $PhCH_2$ **1**, Ph **2**, *n*-Bu **3**).

## EXPERIMENTAL

### Materials and Measurements

Tri-*n*-butyltin chloride, triphenyltin chloride, di-*n*-butyltin dichloride, diphenyltin dichloride, and 2,5-dithiobiurea are commercially available, and they

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were used without further purification. Dibenzyltin dichloride and tribenzyltin chloride were prepared by a standard method reported in the literature [10]. The melting points were obtained with X-4 digital micromelting point apparatus and were uncorrected. Infrared spectra were recorded on a Nicolet-6700 spectrophotometer using KBr disks and sodium chloride optics. $^1$H and $^{119}$Sn NMR spectra were recorded on a Varian Mercury Plus 400 spectrometer operating at 400 and 149.2 MHz, respectively. The spectra were acquired at 298 K. The chemical shifts were reported in ppm with respect to the references and were stated relative to external tetramethylsilane (TMS) for $^1$H NMR and neat tetramethyltin for $^{119}$Sn NMR. Elemental analyses were performed with a PE-2400II apparatus.

### *Syntheses of the Complexes* **1–6**

*[(PhCH$_2$)$_3$Sn]$_2$(dtbu)* **1**. The reaction was carried out under nitrogen atmosphere with the use of the standard Schlenk technique. H$_2$dtbu (0.150 g, 1 mmol) was added to the solution of ethanol (20 mL) with sodium ethoxide (0.136 g, 2 mmol) and stirred for 10 min, and then added (PhCH$_2$)$_3$SnCl (0.854 g, 2 mmol) to the mixture. The mixture was stirred at 40°C for 12 h and then filtered. The solvent was gradually removed by evaporation under vacuum until a solid product was obtained. The solid was then recrystallized from ethanol. mp 142–144°C. Yield (0.717 g, 0.77 mmol) 77%. Anal. Calcd for $C_{44}H_{46}N_4S_2Sn_2$: C, 56.68; H, 4.97; N, 6.01. Found: C, 56.46; H, 4.87; N, 5.76. IR (KBr, cm$^{-1}$): $\nu$(NH$_2$) 3431 m, 3045, $\nu$(C=N) 1600s, $\nu_{as}$(Sn—C) 553 m, $\nu_s$ (Sn—C) 451 m, $\nu$(Sn—S) 307. $^1$H NMR (CDCl$_3$): $\delta$ 7.73 (s, 4H, NH$_2$), 6.81–7.23 (m, 30H, Sn—CH$_2$C$_6$H$_5$), 3.40 (s, 12H, Sn—CH$_2$C$_6$H$_5$) ppm. $^{119}$Sn NMR (CDCl$_3$, ppm): $\delta = -50.17$.

*(Ph$_3$Sn)$_2$(dtbu)* **2**. The procedure is similar to that of complex **1** by adding Ph$_3$SnCl (0.771 g, 2 mmol) to H$_2$dtbu (0.150 g, 1 mmol) and sodium ethoxide (0.136 g, 2 mmol). The solid was recrystallized from ethanol, and colorless crystals were formed. mp 159–161°C. Yield (0.763 g, 0.90 mmol) 90%. Anal. Calcd for $C_{38}H_{34}N_4S_2Sn_2$: C, 53.81; H, 4.04; N, 6.60. Found: C, 53.65; H, 4.15; N, 6.44. IR (KBr, cm$^{-1}$): $\nu$(NH$_2$) 3442 m, 3063, $\nu$(C=N) 1637s, $\nu_{as}$(Sn—C) 564 m, $\nu_s$(Sn—C) 546 m, $\nu$(Sn—S) 310. $^1$H NMR (CDCl$_3$): $\delta$ 7.48 (s, 4H, NH$_2$), 7.23–7.40 (m, 30H, Sn—C$_6$H$_5$) ppm. $^{119}$Sn NMR (CDCl$_3$, ppm): $\delta = -107.42$.

*[(n-Bu)$_3$Sn]$_2$(dtbu)* **3**. The procedure is similar to that of complex **1** by adding (*n*-Bu)$_3$SnCl (0.651 g, 2 mmol) to H$_2$dtbu (0.150 g, 1 mmol) and sodium ethoxide (0.136 g, 2 mmol). The solid was recrystallized from ethanol. mp 112–114°C. Yield (0.509 g, 0.70 mmol) 70%. Anal. Calcd for $C_{26}H_{58}N_4S_2Sn_2$: C, 42.88; H, 8.03; N, 7.69. Found: C, 42.67; H, 7.84; N, 7.48. IR (KBr, cm$^{-1}$): $\nu$(NH$_2$) 3380 m, 3050, $\nu$(C=N) 1610s, $\nu_{as}$(Sn—C) 546 m, $\nu_s$(Sn—C) 525 m, $\nu$(Sn—S) 304. $^1$H NMR (CDCl$_3$): $\delta$ 7.62 (s, 4H, NH$_2$), 0.84–2.23 (m, 54H, Sn—C$_4$H$_9$) ppm. $^{119}$Sn NMR (CDCl$_3$, ppm): $\delta = -63.73$.

*[(PhCH$_2$)$_2$SnCl]$_2$(dtbu)* **4**. The procedure is similar to that of complex **1** (PhCH$_2$)$_2$SnCl$_2$ (0.742 g, 2 mmol) to H$_2$dtbu (0.150 g, 1 mmol) and sodium ethoxide (0.136 g, 2 mmol). The solid was recrystallized from ethanol. mp 166–168°C. Yield (0.641 g, 0.78 mmol) 78%. Anal. Calcd for $C_{30}H_{32}N_4S_2Cl_2Sn_2$: C, 43.88; H, 3.93; N, 6.82. Found: C, 43.76; H, 4.10; N, 6.73. IR (KBr, cm$^{-1}$): $\nu$(NH$_2$) 3429 m, 3040, $\nu$(C=N) 1602s, $\nu_{as}$(Sn—C) 454 m, $\nu_s$(Sn—C) 423 m, $\nu$(Sn—S) 311, $\nu$(Sn—Cl) 280.. $^1$H NMR (CDCl$_3$): $\delta$ 7.65 (s, 4H, NH$_2$), 6.86–7.26 (m, 20H, Sn—CH$_2$C$_6$H$_5$), 3.39 (m, 8H, Sn—CH$_2$C$_6$H$_5$) ppm. $^{119}$Sn NMR (CDCl$_3$, ppm): $\delta = -82.38$.

*(Ph$_2$SnCl)$_2$(dtbu)* **5**. The procedure is similar to that of complex **1** Ph$_2$SnCl$_2$ (0.688 g, 2 mmol) to H$_2$dtbu (0.150 g, 1 mmol) and sodium ethoxide (0.136 g, 2 mmol). The solid was recrystallized from ethanol. mp 179–181°C. Yield (0.611 g, 0.80 mmol) 80%. Anal. Calcd for $C_{26}H_{24}N_4S_2Cl_2Sn_2$: C, 40.82; H, 3.16; N, 7.32. Found: C, 40.78; H, 3.10; N, 7.47. IR (KBr, cm$^{-1}$): $\nu$(NH$_2$) 3420 m, 3024, $\nu$(C=N) 1577s, $\nu_{as}$(Sn—C) 448 m, $\nu_s$(Sn—C) 411 m, $\nu$(Sn—S) 313, $\nu$(Sn—Cl) 284. $^1$H NMR (CDCl$_3$): $\delta$ 7.88 (s, 4H, NH$_2$), 6.94–7.67 (m, 20H, Sn—C$_6$H$_5$) ppm. $^{119}$Sn NMR (CDCl$_3$, ppm): $\delta = -80.11$.

*[(n-Bu)$_2$SnCl]$_2$(dtbu)* **6**. The procedure is similar to that of complex **1** (*n*-Bu)$_2$SnCl$_2$ (0.608 g, 2 mmol) to H$_2$dtbu (0.150 g, 1 mmol) and sodium ethoxide (0.136 g, 2 mmol). The solid was recrystallized from ethanol. mp 152–154°C. Yield (0.514 g, 0.75 mmol) 75%. Anal. Calcd for $C_{18}H_{40}N_4S_2Cl_2Sn_2$: C, 31.56; H, 5.89; N, 8.18. Found: C, 31.48; H, 5.81; N, 8.10. IR (KBr, cm$^{-1}$): $\nu$(NH$_2$) 3389 m, 3039, $\nu$(C=N) 1587s, $\nu_{as}$(Sn—C) 530 m, $\nu_s$(Sn—C) 506 m, $\nu$(Sn—S) 318, $\nu$(Sn—Cl) 287. $^1$H NMR (CDCl$_3$): $\delta$ 7.75 (s, 4H, NH$_2$), 0.78–2.15 (m, 36H, Sn—C$_4$H$_9$) ppm. $^{119}$Sn NMR (CDCl$_3$, ppm): $\delta = -95.62$.

### *X-Ray Crystallography*

Data were collected at 298 K on a Bruker SMART CCD 1000 diffractometer fitted with Mo K$\alpha$

**TABLE 1** Crystal Data and Refinement Details for Complexes **2** and **6**

| *Complex* | **2** | **6** |
|---|---|---|
| Empirical formula | $C_{38}H_{34}N_4S_2Sn_2$ | $C_{18}H_{40}Cl_2N_4S_2Sn_2$ |
| Formula weight | 848.19 | 684.94 |
| Crystal system | Monoclinic | Orthorhombic |
| Space group | $P2(1)/c$ | Cmca |
| Unit cell dimensions | | |
| $a$ (Å) | 13.928(6) | 17.789(8) |
| $b$ (Å) | 19.501(8) | 8.992(4) |
| $c$ (Å) | 13.676(6) | 17.576(7) |
| $\alpha$ (°) | 90 | 90 |
| $\beta$ (°) | 92.307(5) | 90 |
| $\gamma$ (°) | 90 | 90 |
| $V$ (Å$^3$) | 3712(3) | 2811(2) |
| Z | 4 | 4 |
| $Dc$ (mg m$^{-3}$) | 1.518 | 1.618 |
| Absorption coefficient (mm$^{-1}$) | 1.489 | 2.127 |
| $F$(0 0 0) | 1688 | 1368 |
| Crystal size (mm) | 0.38 × 0.34 × 0.26 | 0.50 × 0.46 × 0.40 |
| $\theta$ range (°) | 1.80–25.01 | 2.29–25.00 |
| Reflections collected | 18,373 | 6524 |
| Independent reflections | 6429 | 1285 |
| Data/restraints/parameters | 6429/0/415 | 1285/59/74 |
| Goodness-of-fit on $F$ 2 | 1.005 | 1.000 |
| Final $R$indices [$I > 2\sigma(I)$] | $R_1 = 0.0551$, $wR_2 = 0.1372$ | $R_1 = 0.0391$, $wR_2 = 0.1331$ |
| $R$ indices (all data) | $R_1 = 0.1033$, $wR_2 = 0.2059$ | $R_1 = 0.0407$, $wR_2 = 0.1358$ |

radiation. The structures were solved by direct methods and refined by a full-matrix least-squares procedure based on $F^2$ using the SHELXL-97 program system. All non-Hydrogen atoms were included in the model at their calculated positions. 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 1.

## *RESULTS AND DISCUSSION*

### *Syntheses of the Complexes* **1–6**

The syntheses procedure is shown in Scheme 1.

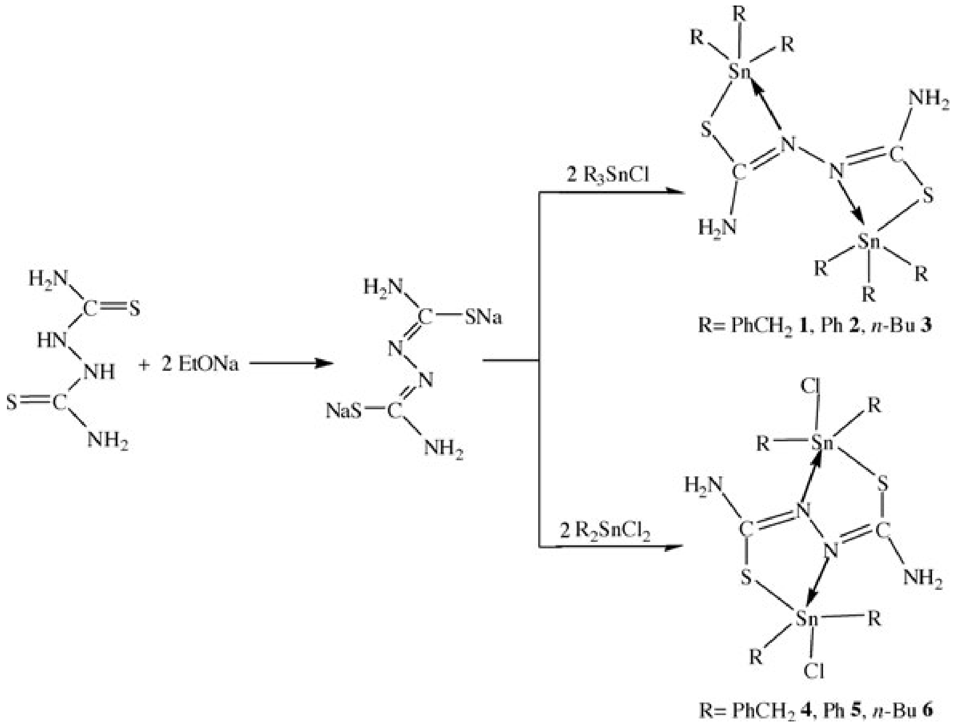
### *IR Spectroscopic Studies of the Complexes* **1–6**

The most significant IR bands are listed in the experimental section. The data suggest that the coordination mode of dtbu$^{2-}$ with triorganotin is same in the complexes as is shown for the phenyl derivatives by the X-ray diffraction study, and the coordination mode of dtbu$^{2-}$ with diorganotin is same in the complexes as shown for the *n*-butyl derivatives. The three high frequency bands of the free ligand, centered at 3355, 3272, and 3171 cm$^{-1}$, are attributed to $\nu$(N—H) stretching. The spectra of all complexes lack bands located at about 3272 cm$^{-1}$, as a result of the ligand deprotonation, indicating that this absorption refers to the $\nu(N_{\text{hydrazinic}}\text{—H})$ vibration. In organotin complexes, the IR spectra can provide useful information concerning the geometry of the $SnC_n$ moiety [11]. The absorption about 304–318 cm$^{-1}$ region for all complexes **1–6**, 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 located within the range for Sn—S vibration observed in common organotin derivatives of thiolate (300–400 cm$^{-1}$) [12].

### *$^1$H NMR and $^{119}$Sn NMR Data of the Complexes* **1–6**

The NH proton signals of the ligand $H_2$dtbu were not observed in the $^1$H NMR spectra of the complexes due to the double deprotonation of $H_2$dtbu. Nevertheless, the most prominent feature of these spectra is behavior of the $NH_2$ groups. The sharp resonances appear at 7.48–7.88 ppm in all complexes **1–6**, indicating existence of the $NH_2$ groups.

The $^{119}$Sn NMR chemical shift is very sensitive to complexation, and usually greatly shifted downfield or upfield on bonding to a Lewis base. The chemical shift for **2** shows only one signal (−107.42 ppm), which has been found in accordance with those of four-coordinate triphenyltin(IV) compounds [13];



**SCHEME 1**

Complexes **1** and **3** (−50.17 and −63.73 ppm, respectively) are four-coordinate according to the literature for $(PhCH_2)_3Sn(SC_5H_5N_2)$ (−55 ppm) and $(n\text{-}Bu)_3Sn(SC_5H_5N_2)$ (−51 ppm) complexes [14]. Thus, the values of **1–3** suggest that weak Sn←N interactions may disappear in the solution. The chemical shifts of **4–6** are in accordance with those of five-coordinate diorganotin(IV) halide complexes involving halide or phosphine ligands [15], as well as chelating S-donor and O-donor complexes [16,17]. Thus, the values of **4–6** (−82.38, −80.11, and −96.52 ppm) suggest that the Sn←N interactions probably survive in the solution and a five-coordinate species is maintained.

### *Crystal Structure of Complex* 2

Selected bond lengths and bond angles for **2** are shown in Table 2. A perspective view of the molecular structure of **2** is shown in Fig. 1.

**TABLE 2** Selected Bond Lengths (Å) and Bond Angles (°) for **2**

| | | | |
|---|---|---|---|
| | *Bond lengths* | | |
| Sn(1)–C(9) | 2.128(9) | Sn(2)–S(2) | 2.438(3) |
| Sn(1)–C(15) | 2.129(9) | N(2)–C(1) | 1.283(11) |
| Sn(1)–C(3) | 2.148(9) | N(2)–N(3) | 1.429(10) |
| Sn(1)–S(1) | 2.450(3) | N(3)–C(2) | 1.275(11) |
| Sn(2)–C(21) | 2.123(9) | S(1)–C(1) | 1.780(9) |
| Sn(2)–C(33) | 2.125(9) | S(2)–C(2) | 1.764(9) |
| Sn(2)–C(27) | 2.158(9) | | |
| | Bond angles | | |
| C(9)–Sn(1)–C(15) | 113.8(3) | C(21)–Sn(2)–C(27) | 103.9(4) |
| C(9)–Sn(1)–C(3) | 104.7(3) | C(33)–Sn(2)–C(27) | 106.5(3) |
| C(15)–Sn(1)–C(3) | 108.1(3) | C(21)–Sn(2)–S(2) | 111.3(3) |
| C(9)–Sn(1)–S(1) | 112.1(3) | C(33)–Sn(2)–S(2) | 119.6(3) |
| C(15)–Sn(1)–S(1) | 117.4(3) | C(27)–Sn(2)–S(2) | 97.2(2) |
| C(3)–Sn(1)–S(1) | 98.7(3) | C(1)–N(2)–N(3) | 113.2(7) |
| C(21)–Sn(2)–C(33) | 115.2(4) | C(2)–N(3)–N(2) | 113.0(7) |

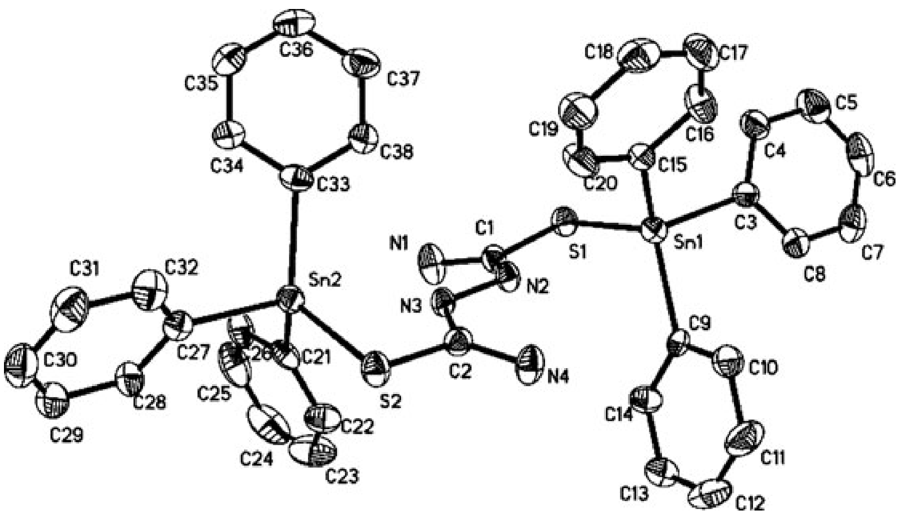


**FIGURE 1** Molecular structure of complex **2**.

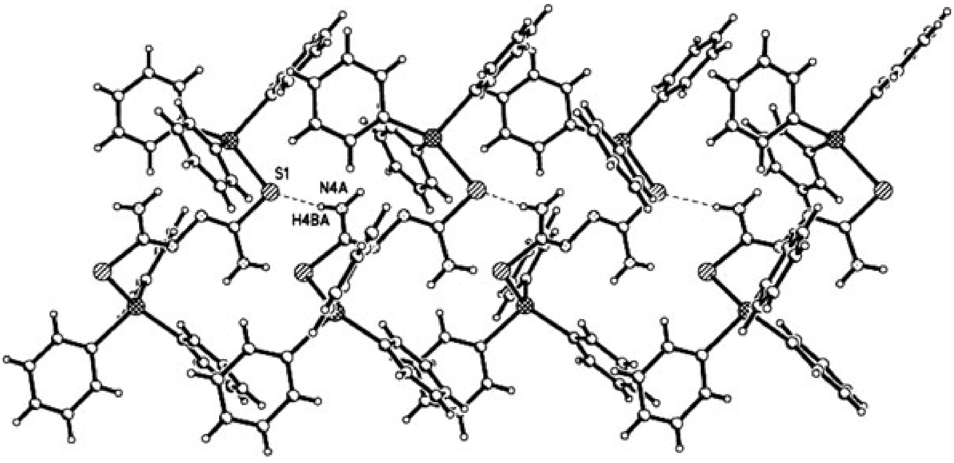


**FIGURE 2** One-dimensional chain of complex **2** along *c* axis.

The symmetric unit is a dinuclear tin moiety. Each tin atom is a four-coordinated tetrahedron. The four primary bonds to Sn are three phenyl groups and one sulfur atom, and there is a weak Sn←N bond. Take the weak Sn←N bond into consideration each tin atom in the complex is a five-coordinated distorted trigonal bipyramid. Furthermore, there is only a little difference of two tin atoms in bond lengths and bond angles (see Table 2).

The Sn(1)←N(2) and Sn(2)←N(3) bond lengths are 2.800 and 2.719 Å, respectively, longer than the sum of covalent radii (2.15 Å), but is considerably shorter than $Ph_3Sn(Me_2Pymt)$ (2.835 Å) [18]. The Sn—S bond lengths [2.438(4) and 2.449(6) Å] consist of the sum of the covalent radii of Sn and S (2.44 Å) [19], within the range (2.405–2.481 Å) for triphenyltin(IV) thiolate complexes $R_3SnL$ reported before in [20].

It should be noted that intermolecular N—H· · ·S hydrogen bonding (see Table 4) made the discrete molecules into being a linear chain (as shown in Fig. 2).

## *Crystal Structure of Complex* 6

Selected bond lengths and bond angles for **6** are shown in Table 3. The crystal structure of **6** is shown in Fig. 3.

Different from complex **2**, only one chlorine atom of $n$-$Bu_2SnCl_2$ is replaced; the five primary bonds to Sn are two butyl groups, one sulfur atom, one chlorine atom, and one nitrogen atom. Complex **6** is the symmetric dinuclear unit made up of two distorted coordination trigonal bipyramids. The coordination mode, bond lengths, and bond angles of the two Sn atoms of complex **6** are completely same. Take (Sn(1)), for example, the trigonal equatorial

**TABLE 3** Selected Bond Lengths (Å) and Bond Angles (°) for **6**

| | | | |
|---|---|---|---|
| | *Bond lengths* | | |
| Sn(1)–C(2)#1 | 2.127(7) | S(1)–C(1) | 1.735(8) |
| Sn(1)–C(2) | 2.127(7) | S(1)–Sn(1)#2 | 2.419(2) |
| Sn(1)–N(2) | 2.347(6) | N(2)–N(2)#2 | 1.407(12) |
| Sn(1)–S(1)#2 | 2.419(2) | N(2)–C(1) | 1.284(10) |
| Sn(1)–Cl(1) | 2.561(2) | | |
| | Bond angles | | |
| C(2)#1–Sn(1)–C(2) | 134.3(4) | N(2)–Sn(1)–Cl(1) | 162.3(16) |
| C(2)#1–Sn(1)–N(2) | 93.6(2) | S(1)#2–Sn(1)–Cl(1) | 84.9(8) |
| C(2)–Sn(1)–N(2) | 93.6(2) | C(1)–S(1)–Sn(1)#2 | 100.4(3) |
| C(2)#1–Sn(1)–S(1)#2 | 112.8(2) | C(1)–N(2)–N(2)#2 | 116.9(8) |
| C(2)–Sn(1)–S(1)#2 | 112.8(2) | C(1)–N(2)–Sn(1) | 125.3(5) |
| N(2)–Sn(1)–S(1)#2 | 77.4(16) | N(2)#2–N(2)–Sn(1) | 117.8(6) |
| C(2)#1–Sn(1)–Cl(1) | 93.3(2) | N(2)–C(1)–S(1) | 127.5(7) |
| C(2)–Sn(1)–Cl(1) | 93.3(2) | | |

#1 = $-x + 1$, $y$, $z$.
#2 = $-x + 1$, $-y + 1$, $-z + 1$.

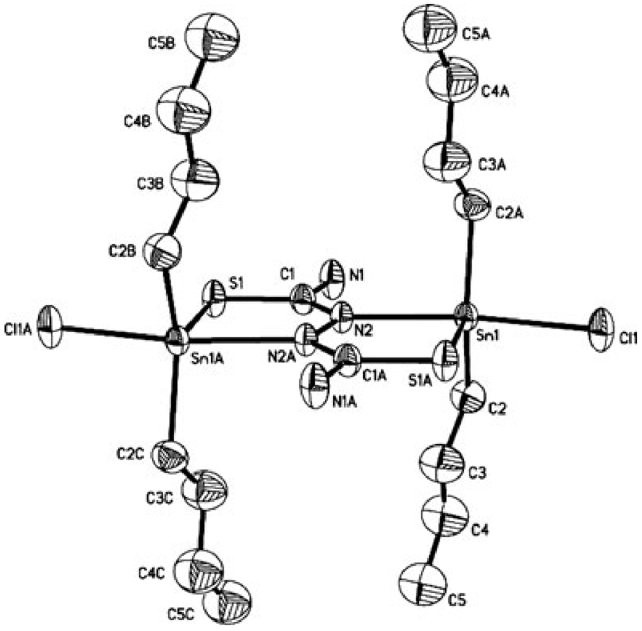


**FIGURE 3** Molecular structure of complex **6**.

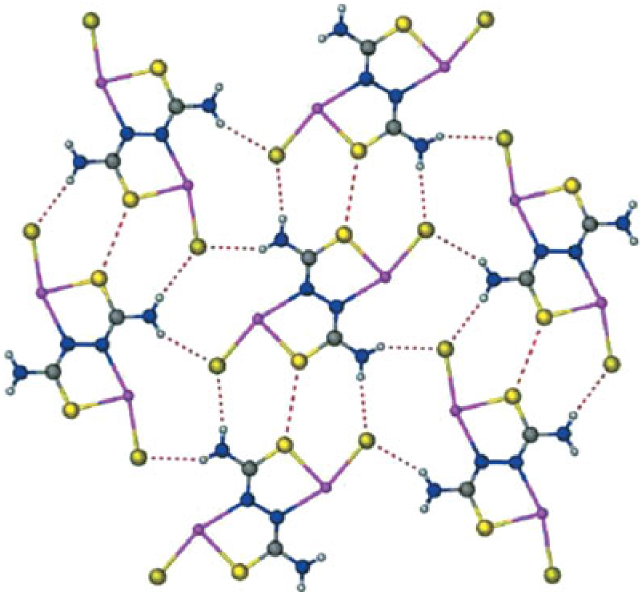


**FIGURE 4** Perspective view showing the two-dimensional network of the complex **6** in *bc* plane connected through N—H···Cl hydrogen bonding, nonbonded S···S contacts, unattached hydrogen atoms, and carbon atoms of the Sn-butyl groups have been omitted for clarity.

**TABLE 4** N—H···S and N—H···Cl hydrogen bonds of complexes **2** and **6**

| | *N—H···S and N—H···Cl hydrogen bonds* | | | | |
|---|---|---|---|---|---|
| | | *Lengths (Å)* | | | *Angles (°)* |
| *Complex* | *N—H···X* | *N—H* | *N···X* | *H···X* | *N—H···X* |
| **2** | N(4)—H(4)B···S1#1 | 0.859 | 3.550 | 2.710 | 166.30 |
| **6** | N(1)—H(1)B···Cl1#2 | 0.861 | 3.472 | 2.619 | 171.37 |
| | N(1)—H(1)A···Cl1#3 | 0.859 | 3.426 | 2.647 | 151.43 |

#1 = $x$, $y$, $1 + z$.
#2 = $x$, $-1 + y$, $z$.
#3 = $1 - x$, $-1/2 + y$, $1/2 - z$.

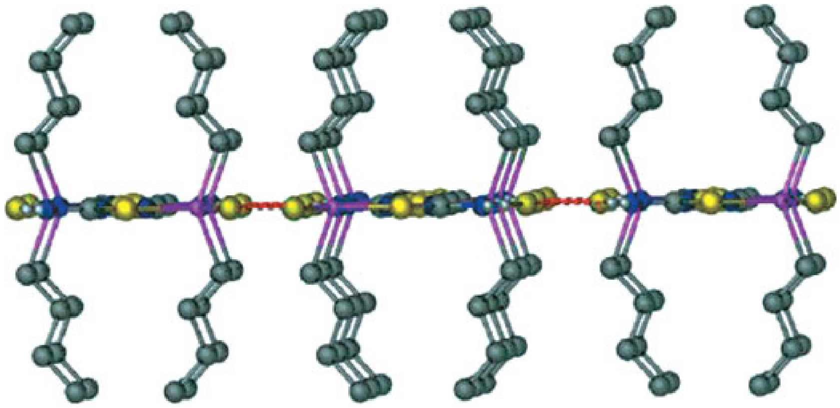


**FIGURE 5** Perspective view showing the two-dimensional network in perfect *bc* plane.

plane is occupied by the sulfur (S(1)) atom and two carbon atoms (C(2) and (C(2)#1) (#1 = $-x + 1$, $y$, $z$), whereas the axial positions were located by nitrogen (N(2)) and another chlorine atom (Cl(1)) with the axial-Sn-axial angle (Cl(1)–Sn(1)–N(2)), 162.27°. The sum of the equatorial angles around the (Sn(1)) atom, (C(2)–Sn(1)–S(1), (C(2)#1)–Sn(1)–S(1), and C(2)–Sn(1)–(C(2)#1) is 359.93°. In this way, the ligand behaves as a bidentate species and chelates the tin atom by the means of nitrogen and sulfur. The consequence is the formation of a five-membered ring with an S–SN–N bite angle (77.40(16)°), which is bigger than those found in $[Me_2Sn(2\text{-SpyO})_2]$ (72.0(1)°) [21].

The Sn(1)←N(2) bond length (2.346 Å) is shorter than that in complex **2** (2.800 and 2.719 Å) and $Me_2Sn(2\text{-SPy})_2$ (2.702(5) Å) [22], but is longer than the sum of covalent radii (2.15 Å). The Sn(1)–S(1) bonds length (2.419(2) Å) is shorter than complex **2** and the sum of the covalent radii of Sn and S (2.44 Å) [19]. The Sn(1)–Cl(1) bond length is 2.561(2) Å, consists of $Ph_2SnCl$(acpm) (2.556 Å) [23], longer than $Bu_2SnCl$(Spym) (2.388 Å) [24], but shorter than $Ph_2Sn(Hapt)Cl\cdot H_2O$ (2.601 Å) [25].

The discrete molecules are connected through N—H· · ·Cl hydrogen bonding (see Table 4) into a two-dimensional network (as shown in Figs. 4 and 5). This structure was further stabilized by nonbonded S· · ·S interactions. The S· · ·S distance (3.497 Å) is less than the sum of the van der Waals radii of S and S (3.70 Å) [26].

## SUPPLEMENTARY DATA

Atomic coordinates, thermal parameters, and bond lengths and angles for complexes **2** and **6** have been deposited in the Cambridge Crystallographic Data Center, CCDC nos. CCDC 646688, 646690. Copies of this information may be obtained free of charge from the Director, CCDC, 2 Union Road, Cambridge CB2 1EZ, UK on request (fax: +44–1223-336–033; e-mail: deposit@ccdc.cam.ac.uk or URL: http://www.ccdc.cam.ac.uk), quoting the deposition numbers for **2** and **6**.

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