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Syntheses, Characterizations, and Crystal Structures of Tri- and Diorganotin (IV) Derivatives with 2-Mercapto-5-methyl-1,3,4-thiadiazole

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ABSTRACT: *A series of organotin(IV) complexes with 2-mercapto-5-methyl-1,3,4-thiadiazole (HL) of the type $R_3Sn(L)$ ($R = Me$* **1***; Bu* **2***; Ph* **3***; $PhCH_2$* **4***) and $R_2Sn(L)_2$ ($R = CH_3$* **5***; Ph* **6***; $PhCH_2$* **7***; Bu* **8***) have been synthesized. All complexes* **1–8** *were characterized by elemental analysis, IR, ^1H, ^{13}C, and ^{119}Sn NMR spectra. Among these, complexes* **1**, **3**, **4**, *and* **7** *were also determined by X-ray crystallography. The tin atoms of complexes* **1**, **3**, *and* **4** *are all penta-coordinated and the geometries at tin atoms of complexes* **3** *and* **4** *are distorted trigonal–bipyramidal. Interestingly, complex* **1** *has formed a 1D polymeric chain through Sn and N intermolecular interactions. The tin atom of complex* **7** *is hexa-coordinated and its geometry is distorted octahedral.* © 2006 Wiley Periodicals, Inc. Heteroatom Chem 17:353–364, 2006; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20215

INTRODUCTION

Metal thiolato complexes have been extensively studied because of their ability to adopt various nuclearities and their relevance in biology, since these form the inorganic part of the biologically active centers of some metalloproteins and enzymes [1–3]. Much work has focused on the synthesis and characterization of novel thiolate complexes that involve heavier group elements of lower valencies [4,5]. The potential in C–S bond cleavages and in desulfurizations [6–8], and their use as precursors of ceramic materials [9] have also been reported. Recently, attention has been paid to the coordination chemistry of heterocyclic thiol/thione donors, which can give potential access to new complexes with unusual structures and reactivities [10]. For example, triazyl- and tetrazole-thiol organometallic derivatives have been reported. A related class of such complexes is thiosemicarbazones in which the structure unit HS—C—N—N or S=C—N—N can bond to metal ions through S or N or both atoms [11–14].

In our previous work, we studied the coordination chemistry of organotin(IV) with two ligands: 2-mercaptonicotinic acid (Hmnc) and 2,5-dimercapto-1,3,4-thiodiazole (bismuthiol-I), which possess one and two deprotonated heterocyclic thioamide group $(N—C—S)^-$, respectively. The X-ray analyses revealed that the former acts as thiol form but the primary bond of the latter to the tin atom varies dramatically according to distinct R of the precursor R_nSnCl_{4-n} [15]. These results indicate there are several factors that can influence the topologies of the organotin(IV) derivatives from heterocyclic thionates such as the special geometries

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of ligand, the special resistant from R, etc. As a result of our continuing interest in the coordination of organotin(IV) with S, N ligands [16], we choose another fascinating ligand 2-mercapto-5-methyl-1,3,4-thiadiazole, which possesses one—SH group, through which primary bonds to tin atoms are likely formed. Furthermore, the potential coordination nitrogen and sulfur atoms of the thiadiazole ring make the ligand act as a fulcrum through which lattice construction is orchestrated in one or more dimensions.

In this paper, we report some details of the syntheses and characterizations of eight organotin(IV) complexes with the ligand 2-mercapto-5-methyl-1,3,4-thiadiazole of the type $R_3Sn(L)$ (R = Me **1**; Bu **2**; Ph **3**; $PhCH_2$ **4**) and $R_2Sn(L)_2$(R = CH_3 **5**; Ph **6**; $PhCH_2$ **7**; Bu **8**). All complexes **1–8** were characterized by elemental analysis, IR, ^1H, ^{13}C, and ^{119}Sn NMR spectra. Among these, complexes **1, 3, 4**, and **7** were also determined by X-ray crystallography. The tin atoms of complexes **1, 3**, and **4** are all penta-coordinated and the geometries at tin atoms of complexes **3** and **4** are distorted trigonal–bipyramidal. Interestingly, complex **1** has formed 1D polymeric chains through Sn and N intermolecular interactions. The tin atom of complex **7** is hexa-coordinated and its geometry is distorted octahedral.

EXPERIMENTAL

Materials and Measurements

Trimethyltin chloride, tributyltin chloride, triphenyltin chloride, and 2-mercapto-5-methyl-1,3,4-thiadiazole were commercially available, and these were used without further purification. Tribenzyltin chloride and dibenzyltin dichloride were prepared by a standard method reported in the literature [17]. 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. ^1H, ^{13}C, and ^{119}Sn NMR spectra were recorded on Varian Mercury Plus 400 spectrometer operating at 400, 100.6, and 149.2 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 for ^1H and ^{13}C NMR and Me_4Sn for ^{119}Sn NMR. Elemental analyses were performed with a PE-2400II apparatus.

Syntheses of Complexes **1–8**

$Me_3Sn[S(C_3H_3N_2S)]$ **1**. The reaction was carried out under nitrogen atmosphere. The 2-mercapto-5-methyl-1,3,4-thiadiazole (0.132 g, 1 mmol) was added to the solution of ethanol (20 mL) with sodium ethoxide (0.068 g, 1 mmol), and the mixture was stirred for 10 min, then added Me_3SnCl (0.199 g, 1 mmol) to the mixture, continuing the reaction for 12 h at 40°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 ether–petroleum. Colorless crystal was formed. Yield 70%; mp 124–126°C. Anal. Cacl. for $C_6H_{12}N_2S_2Sn$: C, 24.43; H, 4.10; N, 9.50. Found: C, 24.41; H, 4.09; N, 9.53%. ^1H NMR ($CDCl_3$) δ: 2.63 (s, 3H, CH_3—C), 0.60–0.74 (s, 9H, Sn—CH_3) ppm. ^{13}C NMR ($CDCl_3$) δ: 170.20 (C-2 ligand), 164.86 (C-5), 24.23 (CH_3), 15.81 (CH_3—Sn) ppm. IR (KBr, cm^{-1}): ν(C=N) 1584, $\nu(Sn—C)_{as}$ 530, $\nu(Sn—C)_s$ 504, ν(Sn—S) 313, ν(Sn—N) 486. ^{119}Sn NMR ($CDCl_3$, 298 K) δ: −86.5 ppm.

$Bu_3Sn[S(C_3H_3N_2S)]$ **2**. The synthesis procedure was the same as complex **1**. 2-Mercapto-5-methyl-1,3,4-thiadiazole (0.132 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol), and Bu_3SnCl (0.325 g, 1 mmol), reaction time 12 h, temperature 40°C. Recrystallized from ether–petroleum. Colorless crystal was formed. Yield 77%; mp 86–88°C. Anal. Cacl. for $C_{15}H_{30}N_2S_2Sn$: C, 42.77; H, 7.18; N, 6.65. Found: C, 42.75; H, 7.16; N, 6.66. ^1H NMR ($CDCl_3$) δ: 2.46 (s, 3H, CH_3), 0.84–1.71 (m, 27 H, Sn—C_4H_9) ppm. ^{13}C NMR ($CDCl_3$) δ: 170.12 (C-2 ligand), 164.66 (C-5), 24.20 (CH_3), 13.6, 26.4, 27.6, 29.7 (^{n}Bu) ppm. IR (KBr, cm^{-1}): ν(C=N) 1583, $\nu(Sn—C)_{as}$ 535, $\nu(Sn—C)_s$ 510, ν(Sn—S) 311, ν(Sn—N) 483. ^{119}Sn NMR ($CDCl_3$, 298 K) δ: −81.5 ppm.

$Ph_3Sn[S(C_3H_3N_2S)]$ **3**. The synthesis procedure was the same as complex **1**. 2-Mercapto-5-methyl-1,3,4-thiadiazole (0.132 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol), and Ph_3SnCl (0.385 g, 1 mmol), reaction time 12 h, temperature 40°C. Recrystallized from *n*-hexane-dichloromethane. Colorless crystal was formed. Yield 74%; mp 112–114°C. Anal. Cacl. for $C_{21}H_{18}N_2S_2Sn$: C, 52.41; H, 3.77; N, 5.82. Found: C, 52.39; H, 3.76; N, 5.85%. ^1H NMR ($CDCl_3$) δ: 7.46–7.79 (m, 5H, C_6H_5—C), 2.44 (s, 3H, CH_3—C) ppm. ^{13}C NMR ($CDCl_3$) δ: 171.02 (C-2 ligand), 166.60 (C-5), 28.32 (CH_3), 128.26 (*m*-C), 131.54 (*p*-C), 127.06 (*o*-C), 124.22 (*i*-C) ppm. IR (KBr, cm^{-1}):

ν(C=N) 1582, ν(Sn—C)$_{as}$ 444, ν(Sn—C)$_s$ 409, ν(Sn—S) 314, ν(Sn—N) 493. ^{119}Sn NMR ($CDCl_3$, 298 K) δ: −57 ppm.

$(PhCH_2)_3Sn[S(C_3H_3N_2S)]$ **4**. The synthesis procedure was the same as complex **1**. 2-Mercapto-5-methyl-1,3,4-thiadiazole (0.132 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol), and $(PhCH_2)_3SnCl$ (0.427 g, 1 mmol), reaction time 12 h, temperature 40°C. Recrystallized from *n*-hexane-dichloromethane. Colorless crystal was formed. Yield 76%; mp 106–108°C. Anal. Cacl. for $C_{24}H_{24}N_2S_2Sn$: C, 55.08; H, 4.62; N, 5.35. Found: C, 55.03; H, 4.61; N, 5.36%. ^{1}H NMR ($CDCl_3$) δ: 6.91–7.17 (m, 15H, Sn—$CH_2C_6H_5$), 2.76 (s, 6H, Sn—$CH_2C_6H_5$), 2.48 (s, 3H, CH_3—C) ppm. ^{13}C NMR ($CDCl_3$) δ: 170.15 (C-2 ligand), 165.62 (C-5), 28.42 (CH_3), 36.45 (PhC-Sn), 127.46 (*m*-C), 132.58 (*p*-C), 128.07 (*o*-C), 125.24 (*i*-C) ppm. IR (KBr, cm^{-1}): ν(C=N) 1584, ν(Sn—C)$_{as}$ 450, ν(Sn—C)$_s$ 425, ν(Sn—S) 311, ν(Sn—N) 490. ^{119}Sn NMR ($CDCl_3$, 298 K) δ: −51 ppm.

$Me_2Sn[S(C_3H_3N_2S)]_2$ **5**. The synthesis procedure was the same as complex **1**. 2-Mercapto-5-methyl-1,3,4-thiadiazole (0.264 g, 2 mmol), sodium ethoxide (0.136 g, 2 mmol), and Me_2SnCl_2 (0.220 g, 1 mmol), reaction time 12 h, temperature 40°C. Recrystallized from ether–petroleum. Colorless crystal was formed. Yield 75%; mp 125–127°C. Anal. Cacl. for $C_8H_{12}N_4S_4Sn$: C, 23.37; H, 2.94; N, 13.63. Found: C, 23.36; H, 2.93; N, 13.64%. ^{1}H NMR ($CDCl_3$) δ: 1.42 (s, 6H, Sn—CH_3), 2.52 (s, 3H, CH_3—C) ppm. ^{13}C NMR ($CDCl_3$) δ: 170.10 (C-2 ligand), 164.71 (C-5), 24.23 (CH_3), 10.9 (CH_3—Sn) ppm. IR (KBr, cm^{-1}): ν(C=N) 1585, ν(Sn—C)$_{as}$ 525, ν(Sn—C)$_s$ 475, ν(Sn—S) 445, ν(Sn—N) 498. ^{119}Sn NMR ($CDCl_3$, 298 K) δ: −121 ppm.

$Ph_2Sn[S(C_3H_3N_2S)]_2$ **6**. The synthesis procedure was the same as complex **1**. 2-Mercapto-5-methyl-1,3,4-thiadiazole (0.264 g, 2 mmol), sodium ethoxide (0.136 g, 2 mmol), and Ph_2SnCl_2 (0.344 g, 1 mmol), reaction time 12 h, temperature 40°C. Recrystallized from *n*-hexane-dichloromethane. Colorless crystal was formed. Yield 79%; mp 168–170°C. Anal. Cacl. for $C_{18}H_{16}N_4S_4Sn$: C, 40.39; H, 3.01; N, 10.47. Found: C, 40.38; H, 3.00; N, 10.48%. ^{1}H NMR ($CDCl_3$) δ: 7.45–7.78 (m, 10H, Sn—C_6H_5), 2.53 (s, 3H, CH_3—C) ppm. ^{13}C NMR ($CDCl_3$) δ: 170.16 (C-2 ligand), 164.77 (C-5), 24.25 (CH_3), 128.69 (*m*-C), 129.43 (*p*-C), 134.57 (*o*-C), 146.56 (*i*-C) ppm. IR (KBr, cm^{-1}): ν(C=N) 1589, ν(Sn—C)$_{as}$ 445, ν(Sn—C)$_s$ 418, ν(Sn—S) 315, ν(Sn—N) 497. ^{119}Sn NMR ($CDCl_3$, 298 K) δ: −129 ppm.

$(PhCH_2)_2Sn[S(C_3H_3N_2S)]_2$ **7**. The synthesis procedure was the same as complex **1**. 2-Mercapto-5-methyl-1,3,4-thiadiazole (0.264 g, 2 mmol), sodium ethoxide (0.136 g, 2 mmol), and $(PhCH_2)_2SnCl_2$ (0.427 g, 1 mmol), reaction time 12 h, temperature 40°C. Recrystallized from ether–petroleum. Colorless crystal was formed. Yield 77%; mp 170–172°C. Anal. Cacl. for $C_{20}H_{20}N_4S_4Sn$: C, 42.64; H, 3.58; N, 9.94. Found: C, 42.44; H, 3.48; N, 9.98%. ^{1}H NMR ($CDCl_3$) δ: 7.02–7.27 (m, 10H, Sn—$CH_2C_6H_5$), 3.06–3.26 (s, 4H, Sn—$CH_2C_6H_5$), 2.50 (s, 3H, CH_3—C) ppm. ^{13}C NMR ($CDCl_3$) δ: 170.42 (C-2 ligand), 164.74 (C-5), 24.21 (CH_3), 35.68 (PhC-Sn), 129.19 (*m*-C), 134.43 (*p*-C), 129.07 (*o*-C), 126.26 (*i*-C) ppm. IR (KBr, cm^{-1}): ν(C=N) 1596, ν(Sn—C)$_{as}$ 440, ν(Sn—C)$_s$ 421, ν(Sn—S) 313, ν(Sn—N) 491. ^{119}Sn NMR ($CDCl_3$, 298 K)δ: − 205 ppm.

$Bu_2Sn[S(C_3H_3N_2S)]_2$ **8**. The synthesis procedure was the same as complex **1**. 2-Mercapto-5-methyl-1,3,4-thiadiazole (0.264 g, 2 mmol), sodium ethoxide (0.136 g, 2 mmol), and Ph_2SnCl_2 (0.304 g, 1 mmol), reaction time 12 h, temperature 40°C. Recrystallized from *n*-hexane-dichloromethane. Colorless crystal was formed. Yield 78%; mp 128–130°C. Anal. Cacl. for $C_{14}H_{24}N_4S_4Sn$: C, 33.95; H, 4.88; N, 11.31. Found: C, 33.84; H, 4.87; N, 11.27%. ^{1}H NMR ($CDCl_3$) δ: 2.56 (s, 3H, CH_3—C), 0.86–2.12 (m, 18H, Sn—C_4H_9) ppm. ^{13}C NMR ($CDCl_3$) δ: 171.14 (C-2 ligand), 164.65 (C-5), 23.45 (CH_3), 13.6, 26.4, 27.6, 29.7 (^{n}Bu) ppm. IR (KBr, cm^{-1}): ν(C=N) 1579, ν(Sn—C)$_{as}$ 517, ν(Sn—C)$_s$ 441, ν(Sn—S) 425, ν (Sn—N) 499. ^{119}Sn NMR ($CDCl_3$, 298 K)δ: −82 ppm.

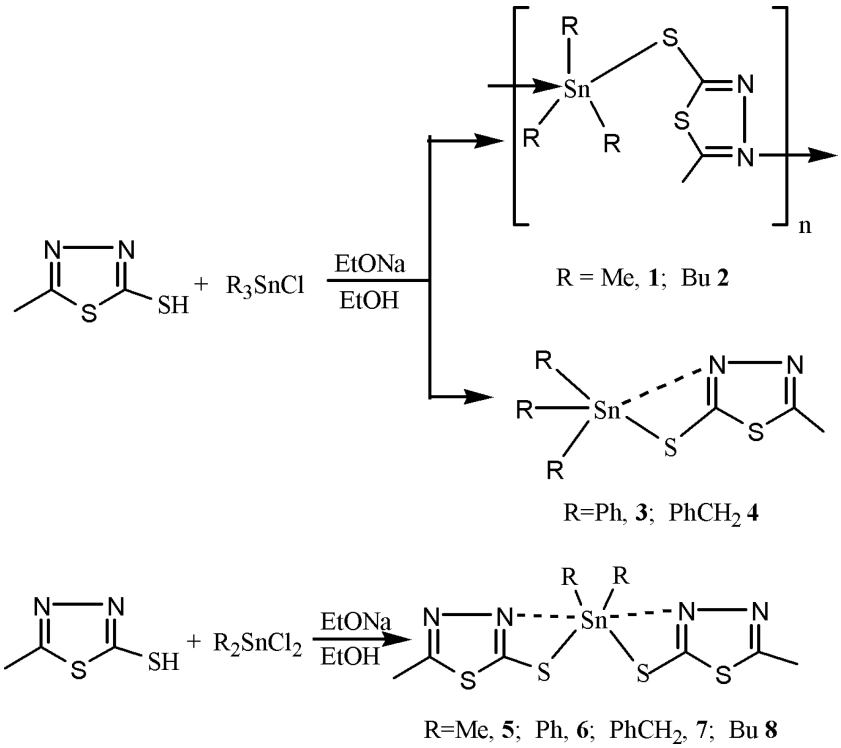
X-ray Crystallography

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 atoms were placed in calculated positions.

RESULTS AND DISCUSSION

Syntheses of Complexes **1–8**

The synthesis procedure is given in Scheme 1.



SCHEME 1

IR Spectroscopic Studies of Complexes **1–8**

Comparing the IR spectra of the free ligand with complexes **1–8**, the band at 2550–2430 cm^{-1}, which appears in the spectra of the free ligand as the ν(S—H) vibration, is absent in those of complexes **1–8**, thus indicating metal–ligand bond formation through this site. In the far-IR spectra, the absorption band at 305–317 cm^{-1} region for all 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 located within the range for Sn—S vibration observed in common organotin derivatives of thiolate (300–400 cm^{-1}) [18,19]. In organotin complexes, the IR spectra can provide useful information concerning the geometry of the SnC_n moiety [20]. 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 nonlinear SnC_2 units for diorganotins and nonplanar SnC_3 fragments for triorganotins, respectively. The middle intensity bands observed at about 1600 cm^{-1} in the spectra of all complexes have been assigned to ν(C=N) according to literatures [21,22], which suggested that the coordinates of free ligand to these complexes were through sulfur atoms via thiol form.

^{1}H, ^{13}C, and ^{119}Sn NMR Data of 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, indicating the removal of the —SH protons and the formation of Sn—S bonds. The formation accord 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_6H_5) in complexes **3** and **6**, 7.45–7.79 ppm, and those of methylene connected directly with tin in complexes **4** (2.76 ppm) and **7** (3.06–3.26 ppm), upfield shift as compared with those of their corresponding precursors. All these data are similar to those cases appear in literature [23], indicating there may exist novel coordination of the ligand to tin atom for all the eight complexes **1–8**. In addition, the resonance of the methyl group connected with the thiadiazole ring (CH_3—$C_2N_2S_2$) appears at 2.44–2.63 ppm for all complexes **1–8**.

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 chelates the tin through thiolate form, C—S should be further low frequency in the spectra of all complexes compared with those in free ligand. As shown above, the chemical shifts of C—S in complexes **1–8** are shifted

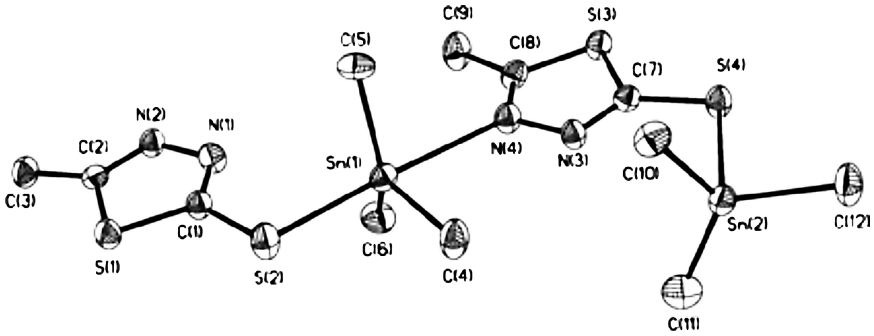


FIGURE 1 The molecular structure of complex **1**.

by 8–9 ppm to low frequency compared with the free ligand ($\delta = 179.2$ ppm), indicating that the ligand involved in these complexes acts as thiolate form.

As reported in literatures [24], values of δ (^{119}Sn) in the ranges −210 to −400, −90 to −190, and 200 to −60 ppm have been associated with hexa-, penta-, and tetra-coordinate tin centers, respectively. On this basis, the signals of ^{119}Sn NMR spectra (−86.5, −81.5, −57, and −51 ppm, respectively) of organotin(IV) derivatives **1–4** are consistent with trigonal–bipyramidal and tetrahedral structure caused by the weaker Sn—N bond. Contrarily, ^{119}Sn NMR chemical shifts of complexes **5–8** (−121, −129, −205, and −82, respectively) are not informative enough to discriminate penta- or weakly hexa-coordinated diorganotin(IV) complexes [25,26]. All the above analyses are confirmed by X-ray diffraction.

Crystal Structures

The crystal data and structure refinement parameters for complexes **1, 3, 4**, and **7** are listed in Table 1. The crystal structures, polymeric chain or unit cells of complexes **1, 3, 4**, and **7** are shown in Figs. 1–8. Selected bond lengths and bond angles of complexes **1, 3, 4**, and **7** are listed in Tables 2–5, respectively.

Crystal Structure of Complex **1**. For complex 1, the X-ray diffraction investigation has shown that it formed a 1D polymeric chain through intermolecular Sn—N bonds. The central tin atoms in complex 1 are penta-coordinated with the *trans*-trigonal–bipyramidal geometries. The methyl carbons in complex **1** are in equatorial positions and the axial positions are occupied by sulfur and nitrogen atoms derived from the neighboring molecule, respectively. The sum of equatorial angles are 356.8° (C(5)—Sn(1)—C(6) (122.3(3)°), C(5)—Sn(1)—C(4) (118.8(3)°), and C(6)—Sn(1)—C(4) (115.7(3)°)) in complex **1**. It is a little less than 360°, indicating that the corresponding atoms are almost in the same plane. But the axial angles are S(2)—Sn(1)—N(4) (175.34(11)°) in complex 1, slightly deviating from 180°, thus it is distorted trigonal–bipyramidal geometry.

The Sn—S bond length in Sn(1)—S(2) (2.5708(19) Å) for complex **1** is a little longer than the sum of covalent radii of Sn and S (2.42 Å) [27,28], and quite shorter than that of the van der Waals radii of Sn and S (4.00 Å). The Sn—N bond length in Sn(1)—N(4) (2.709(5) Å) is slightly greater than the sum of the covalent radii of tin and nitrogen atoms (2.15 Å), but considerably less than that of the van der Waals radii of the two atoms (3.74 Å) [29] and cannot be regarded as weak coordination bonds.

Crystal Structures of Complexes **3** *and* **4**. The structures of both complexes **3** and **4** are penta-coordinated with R_3Sn coordinated to the thiol S

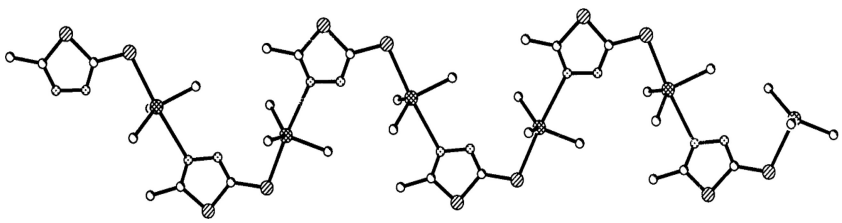


FIGURE 2 Perspective view showing the 1D polymeric chain of complex **1**.

TABLE 1 Crystal Data and Structure Refinement Parameters for Complexes **1, 3, 4**, and **7**

	1	**3**	**4**	**7**
Empirical formula	$C_6H_{12}N_2S_2Sn$	$C_{21}H_{18}N_2S_2Sn$	$C_{24}H_{24}N_2S_2Sn$	$C_{20}H_{20}N_4S_4Sn$
Formula weight	294.99	481.18	523.26	563.21
Crystal system	Triclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	*P*-1	*Pbca*	$P2_1/n$	$C2/c$
Unit cell dimensions				
a(Å)	9.765(4)	12.027(3)	14.009(2)	27.060(7)
b(Å)	10.530(4)	17.230(4)	9.7873(17)	5.9617(16)
c(Å)	11.935(5)	20.338(4)	17.195(3)	16.949(5)
α (°)	108.019(5)	90	90	90
β (°)	95.985(5)	90	98.841(2)	124.685(3)
γ (°)	100.520(6)	90	90	90
V (Å^3)	1130.2(8)	4214.6(16)	2329.6(7)	2249.1(10)
Z	4	8	4	4
D_c (mg m^{-3})	1.734	1.517	1.492	1.474
Absorption coefficient (mm^{-1})	2.580	1.417	1.288	1.333
F(0 0 0)	576	1920	1056	1000
Crystal size (mm)	0.42 × 0.37 × 0.24	0.49 × 0.42 × 0.35	0.39 × 0.33 × 0.24	0.38 × 0.17 × 0.14
θ range (°)	2.09–25.02	2.00–25.02	2.04–25.03	2.41–25.02
Reflections collected	5351	20840	11925	5506
Independent reflections	3605 [$R_{int} = 0.0209$]	3725 [$R_{int} = 0.0313$]	4119 [$R_{int} = 0.0354$]	1984 [$R_{int} = 0.0285$]
Data/restraints/parameters	3605/0/199	3725/0/235	4119/0/262	1984/0/132
Goodness-of-fit on F^2	1.001	1.004	1.007	1.003
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0393$, $wR_2 = 0.1093$	$R_1 = 0.0376$, $wR_2 = 0.1165$	$R_1 = 0.0317$, $wR_2 = 0.0763$	$R_1 = 0.0273$, $wR_2 = 0.0756$
R indices (all data)	$R_1 = 0.0456$, $wR_2 = 0.1141$	$R_1 = 0.0566$, $wR_2 = 0.1466$	$R_1 = 0.0488$, $wR_2 = 0.0879$	$R_1 = 0.0382$, $wR_2 = 0.0855$

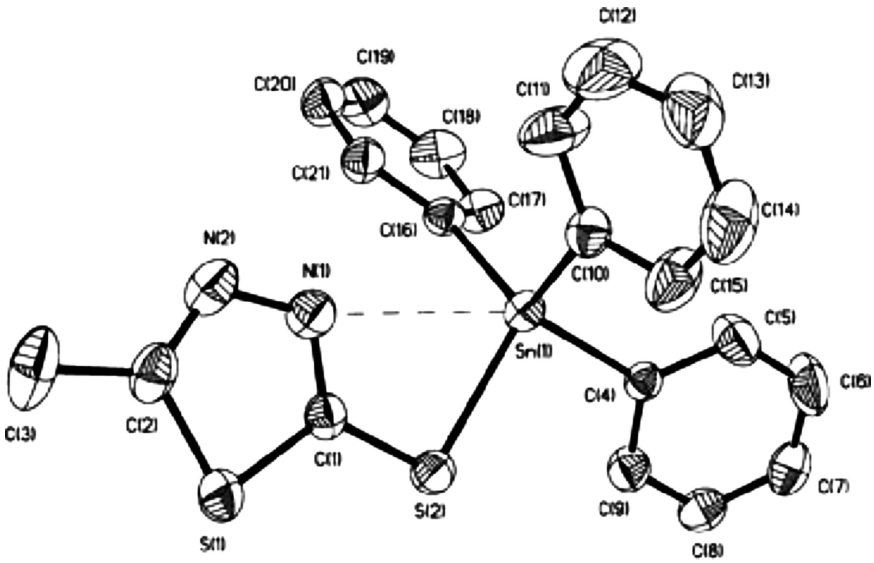


FIGURE 3 The molecular structure of complex **3**.

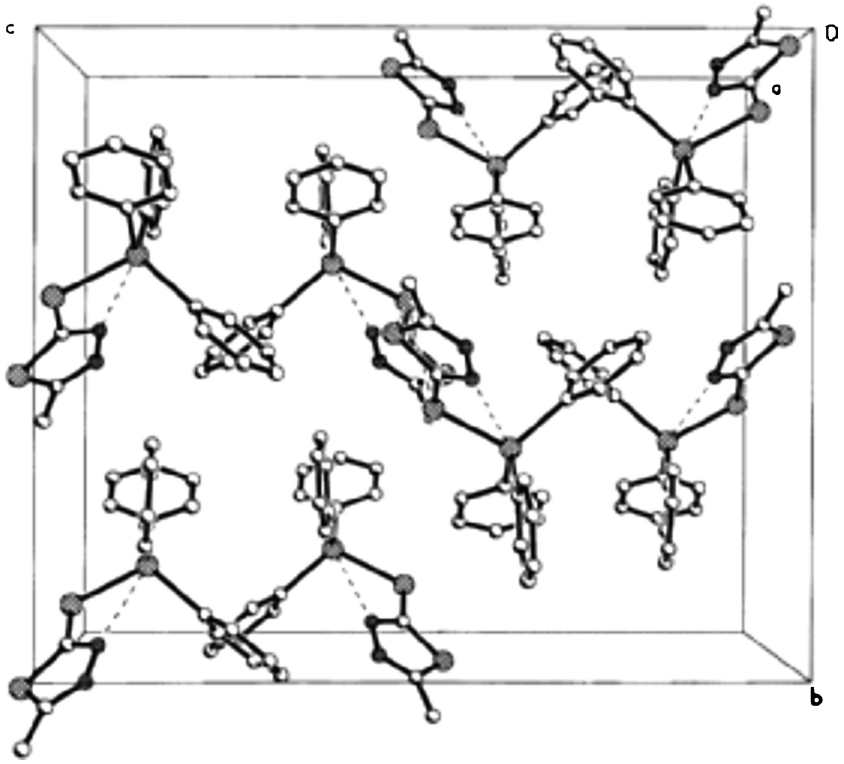


FIGURE 4 The unit cell of complex **3**.

and heterocyclic N atoms of the same ligand, and the structural distortion for each is a displacement from tetragonal toward trigonal–bipyramidal geometry.

For complex **3**, the central tin atom forms four primary bonds: three to phenyl groups and one to the sulfur atom. In addition, there is a weak intramolecular Sn—N interaction, the Sn(1)—N(1) bond length (3.072(4) Å) is longer than the sum of covalent radii (2.15 Å), but is considerably shorter than the sum of van der Waals radii of Sn and N atoms (3.74 Å) [29]. This bond length is almost equal to that in $Ph_3Sn(MBZ)$ (3.07 Å) [30], but is

TABLE 2 Selected Bond Lengths (Å) and Bond Angles (°) for Complex **1**

Bond lengths			
Sn(1)—C(4)	2.127(7)	Sn(2)—S(4)	2.5816(18)
Sn(1)—C(5)	2.11(6)	Sn(2)—N(2)#1	2.708(5)
Sn(1)—C(6)	2.114(7)	C(1)—S(2)	1.741(6)
Sn(1)—S(2)	2.5708(19)	C(7)—S(4)	1.722(6)
Sn(1)—N(4)	2.709(5)		
Bond angles			
C(5)—Sn(1)—C(6)	122.3(3)	C(6)—Sn(1)—C(4)	115.7(3)
C(5)—Sn(1)—C(4)	118.8(3)	S(4)—Sn(2)—N(2)#1	175.38(11)
C(5)—Sn(1)—S(2)	98.1(2)	C(8)—N(4)—Sn(1)	129.4(4)
C(5)—Sn(1)—N(4)	83.2(2)	N(3)—N(4)—Sn(1)	116.4(3)
S(2)—Sn(1)—N(4)	175.34(11)	C(1)—S(2)—Sn(1)	102.1(2)
C(10)—Sn(2)—S(4)	97.91(19)	C(7)—S(4)—Sn(2)	101.75(19)
C(10)—Sn(2)—N(2)#1	85.0(2)		

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

Bond lengths			
Sn(1)—C(10)	2.128(5)	Sn(1)—S(2)	2.4505(14)
Sn(1)—C(4)	2.137(5)	Sn(1)—N(1)	3.072(4)
Sn(1)—C(16)	2.1742(5)	C(1)—S(2)	1.733(5)
Bond angles			
C(10)—Sn(1)—C(4)	108.48(18)	C(16)—Sn(1)—N(1)	82.52(16)
C(10)—Sn(1)—C(16)	114.27(19)	S(2)—Sn(1)—N(1)	56.66(9)
C(4)—Sn(1)—C(16)	111.1(2)	C(1)—N(1)—Sn(1)	82.2(3)
C(10)—Sn(1)—S(2)	110.49(15)	N(2)—N(1)—Sn(1)	165.6(3)
C(4)—Sn(1)—S(2)	96.19(12)	C(1)—S(2)—Sn(1)	96.93(17)
C(16)—Sn(1)—S(2)	114.72.5(12)	C(5)—C(4)—Sn(1)	121.2(4)
C(10)—Sn(1)—N(1)	85.12(16)	C(11)—C(10)—Sn(1)	122.8(4)
C(4)—Sn(1)—N(1)	152.80(14)	C(21)—C(16)—Sn(1)	123.5(4)

TABLE 4 Selected Bond Lengths (Å) and Bond Angles (°) for Complex **4**

Bond lengths			
Sn(1)—C(11)	2.152(3)	Sn(1)—S(2)	2.455(3)
Sn(1)—C(18)	2.166(3)	Sn(1)—N(1)	2.657(1)
Sn(1)—C(4)	2.179(3)	S(2)—C(1)	2.657(1)
Bond angles			
C(11)—Sn(1)—C(18)	115.41(19)	C(18)—Sn(1)—N(1)	81.13(14)
C(11)—Sn(1)—C(4)	110.65(15)	C(4)—Sn(1)—N(1)	157.65(13)
C(18)—Sn(1)—C(4)	109.89(17)	S(2)—Sn(1)—N(1)	57.06(7)
C(11)—Sn(1)—S(2)	110.47(12)	C(1)—N(1)—S(1)	83.3(2)
C(18)—Sn(1)—S(2)	108.80(12)	N(1)—C(1)—S(2)	124.0(3)
C(4)—Sn(1)—S(2)	100.60(11)	C(5)—C(4)—Sn(1)	113.4(2)
C(11)—Sn(1)—N(1)	79.81(13)	C(12)—C(11)—Sn(1)	112.5(3)

shorter than that of triphenyl-(5-mercapto-1-phenyl-1,2,3,4-tetrazolato) tin(IV) (3.28 Å) [31] and is little longer than that reported in $Ph_3Sn(Me_2dmt)$ (2.835(7) Å) [32]. Thus, complex **2** has a distorted *cis*-trigonal–bipyramidal geometry with the sulfur (S(2)) atom and two carbon atoms (C(10)) and (C(16)) occupying the equatorial plane, whereas the nitrogen (N(1)) and another carbon (C(4)) are in axial positions. The sum of the equatorial angles around the tin atom (C(10)—Sn(1)—C(16), C(10)—Sn(1)—S(2), C(16)—Sn(1)—S(2)) is 339.4(8)° and the axial—Sn—axial angle (C(4)—Sn(1)—N(1)) is 152.8(0)°. This significant distortion is mainly due to the rigidity of the chelate ring (N(1)—Sn(1)—S(2):

TABLE 5 Selected Bond Lengths (Å) and Bond Angles (°) for Complex **7**

Bond lengths			
Sn(1)—C(4)	2.146(3)	Sn(1)—S(2)	2.4873(11)
Sn(1)—C(4)#1	2.146(3)	Sn(1)—N(1)	2.818(3)
Sn(1)—S(2)#1	2.4873(11)	S(2)—C(1)	1.734(4)
Bond angles			
C(4)—Sn(1)—C(4)#1	124.8(2)	C(4)#1—Sn(1)—N(1)	85.66(12)
C(4)—Sn(1)—S(2)#1	113.99(10)	S(2)#1—Sn(1)—N(1)	145.50(7)
C(4)#1—Sn(1)—S(2)#1	105.75(11)	S(2)—Sn(1)—N(1)	59.86(7)
C(4)—Sn(1)—S(2)	105.75(12)	C(1)—N(1)—Sn(1)	86.8(2)
C(4)#1—Sn(1)—S(2)	113.99(10)	N(2)—N(1)—Sn(1)	157.6(2)
S(2)#1—Sn(1)—S(2)	86.01(5)	C(1)—S(2)—Sn(1)	90.17(13)
C(4)—Sn(1)—N(1)	82.62(12)	C(5)—C(4)—Sn(1)	115.5(2)

56.6(7))°, together with the large covalent radius of tin(IV). The Sn(1)—S(2) bond length (2.450(5) Å) is just outside the range (2.39–2.44 Å) found in tetra-coordinated R_3SnSR'[33], but similar to that reported in the penta-coordinated organotin complex Ph_3Sn(MTS) (2.47 Å) [30].

Complex **4** has a distorted *cis*-trigonal–bipyramidal geometry with a Sn—N intramolecular interaction similar to complex **3**. The chelate bite angle of N(1)—Sn(1)—S(2) is 57.06(7)°. The Sn(1)—S(2) bond length is 2.4705(11) Å, which lies in the normal range for those higher-than-tetra-coordinated organotin structures and is slightly shorter than that reported in tribenzyl(2-thiolatopyridine-*N*-oxide) tin(IV) (2.58 Å) [34]. Concerning the Sn—N bonds, the bond length of Sn(1)—N(1) (3.039(3) Å) is just between the sum of the van der Waals and covalent radii of Sn and N (3.74 and 2.15 Å) and is similar to that in complex **3** (3.072(4) Å). It is worth to note that both the Sn—N bond lengths of complexes **3** and **4** are consistent with the average Sn—N bond length (>2.39 Å) [35] of Sn complexes having antitumor activity.

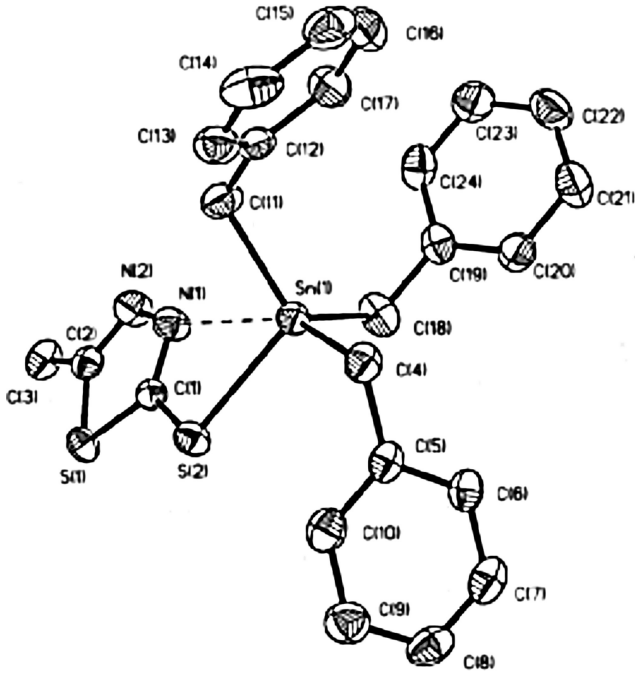


FIGURE 5 The molecular structure of complex **4**.

Crystal Structure of Complex **7**. Complex **7** contains a hexa-coordinate tin atom, thus the geometry around the Sn center is a distorted octahedron. In this case, two carbon atoms and two sulfur atoms are covalently linked to Sn atom. The valence extension is performed via the nitrogen atoms. The two chelating nitrogen atoms occupy *trans* positions (N(1)—Sn(1)—N(1)#1 148.1°), whereas the cases for the sulfur bonding vary and these occupy *cis* positions (S(2)—Sn(1)—S(2)#1 186.0(2)°). In addition, on each side of the Sn atom, the sulfur and nitrogen equatorial ligating atoms belong to the same moiety (S(2)—Sn(1)—N(1), 59.8(7)°), so their positions are fixed and the S—Sn—N angles can only admit very little deformation.

The Sn—C bond lengths (2.146(3) Å and 2.146(3) Å) are quite close to those previously described in the literature [36]. For complex **7**, the Sn—N bond length is 2.818(3) Å, which coincide well with the values in the literature but which are still little longer than those of the type $SnCl_2N_2C_2$ recorded in the Cambridge Crystallographic Database [36] (2.27–2.58 Å), but is slightly shorter than that in complexes **3** and **4**. This may be caused by the different coordination mode of the Sn centers. Concerning the Sn—S bond lengths (2.4873(11) Å) in complex **7**, we may note that these are slightly longer than the sum of the atomic radii (2.44 Å) [37].

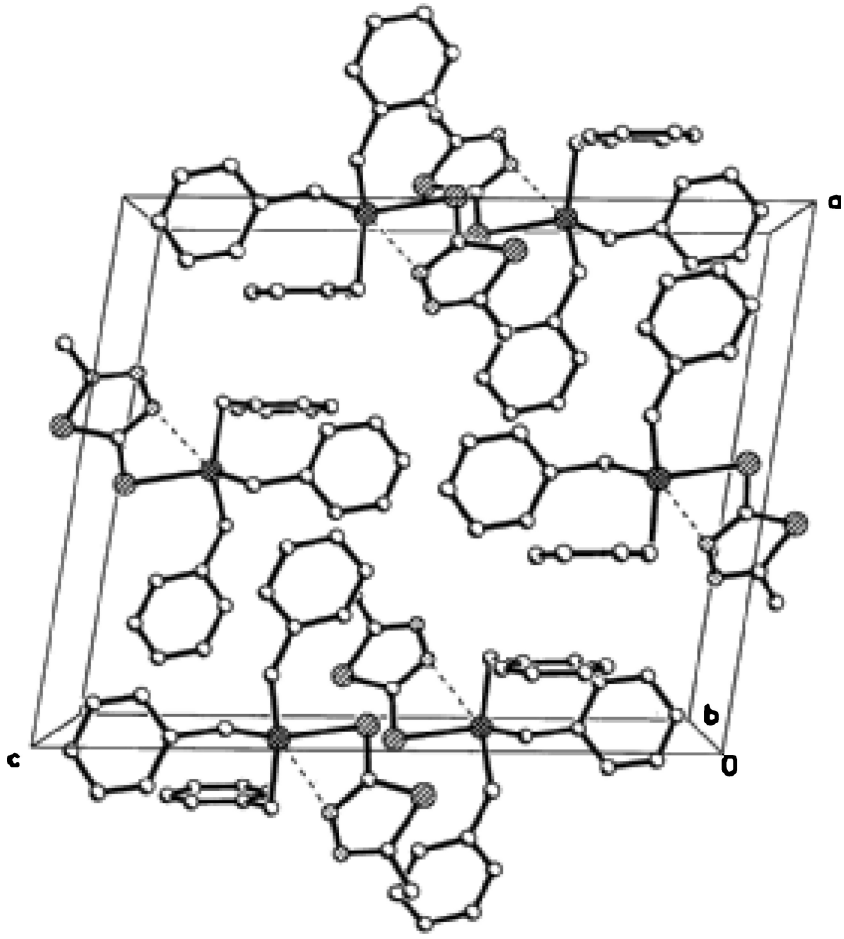


FIGURE 6 The unit cell of complex **4**.

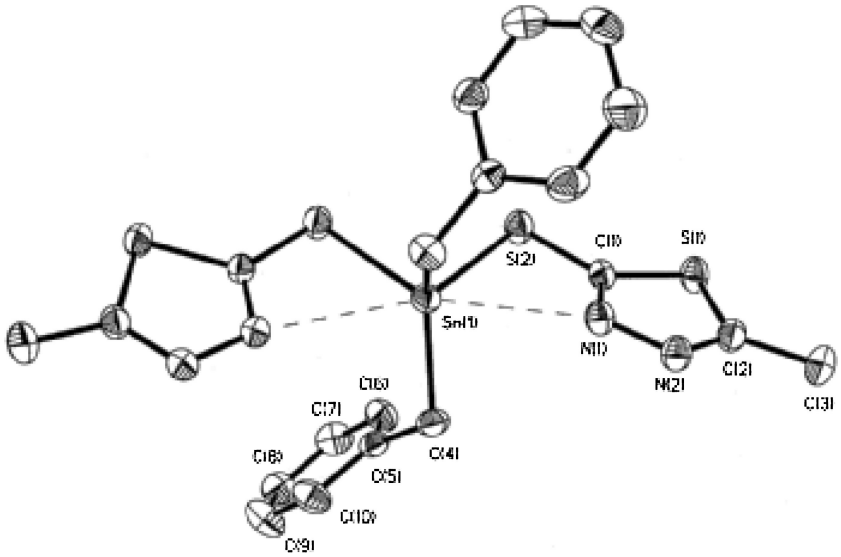


FIGURE 7 The molecular structure of complex **7**.

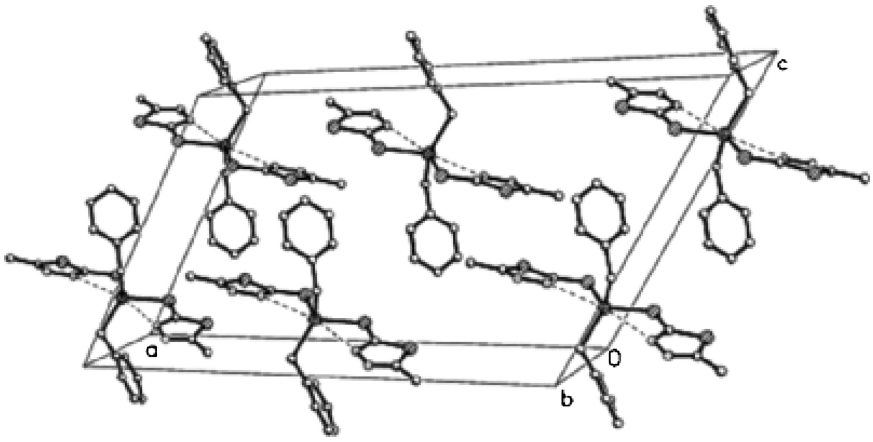


FIGURE 8 The unit cell of complex **7**.

CONCLUSIONS

A series of organotin(IV) complexes based on 2-mercapto-5-methyl-1,3,4-thiadiazole have been synthesized and characterized. Detailed studies on the structures and spectra of these complexes indicate that the stereo-constraints from the R groups of trialkyltin chloride have great influence on the final coordination mode and crystal structures. Methyl has the smaller spatial resistance, consequently, complex **1** has formed 1D polymeric chains through intermolecular Sn—N bonds. In contrast, phenyl and benzyl respectively have the greater stereo-constraints to prevent additional intermolecular ligand chelation to the central tin atom of complexes **3** and **4** forming 1D polymeric chain. Moreover, the effects of analogous stereo-constraints worked on complex **7** to give hexa-coordinated organotin(IV) structure. Therefore, we conclude that the differences in molecular structures of complexes **1, 3,** and **4** may be due to the fact that the stereo-constraints of methyl are smaller than that of phenyl and benzyl, and the decrease of stereo-constraints may benefit the coordination of nitrogen atoms.

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