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Syntheses and Crystal Structures of Triorganotin(IV) Complexes of Schiff Base Derived from 4-Amino-5-phenyl-4*H*-1,2,4-trizole-3-thiol

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ABSTRACT: *Four triorganotin complexes of the types* $[(Ph_3Sn)(C_{15}H_{10}FN_4S)]$ (**3**), $[(CH_3)_3Sn(C_{15}H_{10}FN_4S)]_n$(**4**), $[(Ph_3Sn)(C_{13}H_9FN_4S_2)]$ (**5**), *and* $[(CH_3)_3Sn(C_{13}H_9FN_4S_2)]_n$ (**6**) *have been obtained by Schiff base compound* **1** *(derived from 4-fluorobenzaldehyde) and compound* **2** *(derived from thiophene-2-carboxadehyde) with triorganotin chloride in the presence of sodium ethoxide. All the complexes were characterized by elemental analysis, IR, and NMR spectroscopies, and X-ray diffraction analyses, which revealed that complexes* **3** *and* **5** *are mononuclear structures, complex* **4** *and* **6** *are one-dimensional zigzag infinite chains via N → Sn and S → Sn bonding interactions.* © 2008 Wiley Periodicals, Inc. Heteroatom Chem 19:583–591, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20481

INTRODUCTION

The Schiff base derived from various heterocycles was reported to possess cytotoxic, anticonvulsant, antiproliferative, anticancer, and antifungal activities [1–4]. Organotin(IV) Schiff base ligands have potential applications in organic synthesis, catalysis, medicinal chemistry, and biotechnology [5–12]. Among them, the organotin complexes of Schiff bases derived from heterocyclic thiol also display a broad range of biological activity, showing potential applications as antitumor, antibacterial, antifungal, and antiviral agents [13–14]. In our previous work, we reported some interesting organotin(IV) structures of Schiff base derived from heterocyclic thiones [15,16]. As an extension of this research program and combined with the development of organotin(IV) Schiff base chemistry, we selected another fascinating ligand 4-amino-5-phenyl-4*H*-1,2,4-trizole-3-thiol to synthesize Schiff base ligands with 4-fluorobenzaldehyde and thiophene-2-carboxadehyde. 4-Amino-5-phenyl-4*H*-1,2,4-trizole-3-thiol was chosen because it is 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. We use these Schiff base ligands to a reaction with triorganotin complexes and got four triorganotin Schiff base complexes. Here we report the syntheses, characterization, and crystal structure of these triorganotin Schiff base complexes.

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EXPERIMENT

Materials and Measurements

All reagents were commercially available, and they were used without further purification. 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 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 (C,H,N) were performed with a PE-2400II apparatus.

Syntheses of Schiff Base Compounds **1–2** *and Triorganotin Schiff Base Complexes* **3–6**

$C_{15}H_{11}FN_4S$ **1**. The reaction was carried out under nitrogen atmosphere, with the use of standard Schlenk technique, 4-amino-5-phenyl-4*H*-1,2,4-trizole-3-thiol (1.153, 6 mmol) was added to the solution of dry ethanol (30 mL) and then added 4-fluorobenzaldehyde (0.745 g, 6 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. mp >200°C. Yield: 89%. Anal. Found: C, 60.01; H, 3.41; N, 19.07. Calcd. for $C_{15}H_{11}FN_4S$: C, 60.39; H, 3.72, N, 18.78%. IR (KBr, cm^{-1}): ν(S—H) 2718, ν(C=N) 1667, ν(S—C=N) 1578, ν(C—S) 988. ^{1}H NMR (CDCl$_3$. ppm): 8.57 (s, 1H, CH=N), 7.69–7.88 (m, 9H, Ar—H), 2.41 (s, 1H, S—H).

$C_{13}H_{10}N_4S_2$ **2**. The procedure was the same as in the Schiff base compound **1**. 4-Amino-5-phenyl-4*H*-1,2,4-trizole-3-thiol (1.153, 6 mmol) and thiophene-2-carboxadehyde (0.673 g, 6 mmol) added to ethanol of 30 mL, refluxing for 6 h, the yellow precipitate was collected by filtration, washed with ether–petroleum, and dried at the nitrogen atmosphere. mp >200°C. Yield: 81%. Found: C, 54.20; H, 3.81; N, 19.20. Calcd. for $C_{13}H_{10}N_4S_2$: C, 54.52; H, 3.52, N, 19.56%. IR (KBr, cm^{-1}): ν(S—H) 2787, ν(C=N) 1689, ν(S—C=N) 1573, ν(C—S) 970. ^{1}H NMR (CDCl$_3$. ppm): 8.85 (s, 1H, CH=N), 7.61–7.85 (m, 8H, Ar—H), 2.47 (s, 1H, S—H).

$(Ph_3Sn)(C_{15}H_{10}FN_4S)$ **3**. The reaction was carried out under nitrogen atmosphere. The Schiff base compound **1** (0.298 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol), and Ph$_3$SnCl (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, and yellow crystals were formed. Yield: 77%. mp 158–162°C. Anal. Found: C 61.63, H 3.55, N 8.31. Calcd. for $C_{33}H_{25}FN_4SSn$: C 61.23, H 3.89, N 8.65%. IR (KBr, cm^{-1}): ν(C=N), 1614; ν(S—C=N), 1557; ν(C—S), 967; ν(Sn—S), 328. ^{1}H NMR [(CD$_3$)$_2$SO, ppm] δ : 8.48 (s, 1H, CH=N), 7.33–7.58 (m, 24H, Ar—H). ^{13}C NMR (CDCl$_3$. ppm): 167.1 (C—S—Sn), 153.2 (CH=N), 149.7 (Ph—C—N), 137.6, 137.1, 137.0, 136.7, 135.2, 135.1, 134.9, 134.8, 130.7, 130.5, 130.1, 129.4 (Ar—C); ^{119}Sn NMR (CDCl$_3$, ppm): 61.5

$[(CH_3)_3Sn(C_{15}H_{10}FN_4S)_n$ **4**. The procedure is similar to that of complex **3**. The Schiff base compound **1** (0.298 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol), and Me$_3$SnCl (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, and yellow crystals were formed. Yield: 73%. mp 137–141°C. Anal. Found: C 46.53, H 4.38, N 11.87. Calcd. for $C_{18}H_{19}FN_4SSn$: C 46.88, H 4.15, N 12.15%. IR (KBr, cm^{-1}): ν(C=N), 1656; ν(S—C=N), 1549; ν(C—S), 943; ν(Sn—S), 354; ν(Sn—N) 442. ^{1}H NMR [(CD$_3$)$_2$SO, ppm] δ : 8.36 (s, 1H, CH=N), 7.32–7.83 (s, 9H, Ar—H), 0.87 (9H, CH$_3$, $^2J_{^{119}\mathrm{Sn},^1\mathrm{H}} = 81.2$ Hz). ^{13}C NMR (CDCl$_3$. ppm): 168.4 (C—S—Sn), 154.9 (CH=N), 148.1 (Ph—C—N), 136.2, 135.5, 135.0, 134.8, 130.9, 130.2, 129.3, 128.6 (Ar—C), 14.1 (CH$_3$) ($^1J_{^{119}\mathrm{Sn},^{13}\mathrm{C}} = 497$ Hz). ^{119}Sn NMR (CDCl$_3$, ppm): −116.7.

$(Ph_3Sn)(C_{13}H_9N_4S_2)$ **5**. The procedure is similar to that of complex **3**. The Schiff base compound **2** (0.287 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol), and Ph$_3$SnCl (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, and yellow crystals were formed. Yield: 81%. mp 155–157°C. Anal. Found: C 58.29, H 3.50, N 9.12. Calcd. for $C_{31}H_{24}N_4S_2Sn$: C 58.60, H 3.81, N 8.82%. IR (KBr, cm^{-1}): ν(C=N), 1664; ν(S—C=N), 1552; ν(C—S), 951; ν(Sn—S), 343. ^{1}H NMR [(CD$_3$)$_2$SO, ppm] δ : 8.44 (s, 1H, CH=N), 7.01–7.76 (m, 20H, Ar—H), 7.35 (d, $J_{\mathrm{H,H}} = 3.6$ Hz, 1H), 7.12 (dd, $J_{\mathrm{H,H}} = 4.8$ Hz, 1H), 7.37 (d, 1H), ^{13}C NMR (CDCl$_3$. ppm): 161.8 (C—S—Sn), 152.4 (CH=N), 140.1 (Ph—C—N), 136.2, 134.5, 132.1, 130.6, 129.7, 128.9, 128.6, 126.6 (Ar—C), 122.1, 119.4, 117.5, 110.2 (thiophene ring-C). ^{119}Sn NMR (CDCl$_3$, ppm): 53.2.

$(CH_3)_3Sn(C_{13}H_9N_4S_2)$ **6**. The procedure is similar to that of complex **3**. The Schiff base compound

TABLE 1 Crystal Data and Refinement Details for Complexes **3–6**

Complexes	3	4	5	6
Empirical formula	$C_{33}H_{25}FN_4SSn$	$C_{18}H_{19}FNSSn$	$C_{31}H_{24}N_4S_2Sn$	$C_{16}H_{18}N_4S_2Sn$
Formula weight	647.32	461.12	635.35	449.15
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group	*Pna*2(1)	*P*21/*c*	*Pbca*	*Cc*
		Unit cell dimensions		
a (Å)	19.824(5)	11.031(7)	9.796(5)	16.477(2)
b (Å)	9.716(2)	10.369(6)	17.382(9)	16.642(2)
c (Å)	15.515(4)	20.946(10)	33.942(18)	28.101(2)
α (°)	90	90	90	90
β (°)	90	121.78(2)	90	90.083(2)
γ (°)	90	90	90	90
V (Å^3)	2988.3(13)	2037(2)	5779(5)	7705.5(15)
Z	4	4	8	16
Dc (mg m^{-3})	1.439	1.504	1.460	1.549
Absorption coefficient (mm^{-1})	0.959	1.373	1.055	1.546
F(0 0 0)	1304	920	2560	3584
Crystal size (mm)	0.45 × 0.35 × 0.20	0.48 × 0.32 × 0.27	0.46 × 0.43 × 0.35	0.65 × 0.58 × 0.49
θ range (°)	2.05–25.00	2.17–25.02	2.34–25.01	1.74–25.01
Reflections collected	14382	8699	28424	19016
Independent reflections	5082	3520	5095	6773
Data/restraints/parameters	5082/19/361	3520/0/226	5095/0/343	6773/2/829
Goodness-of-fit on *F*2	1.002	1.003	1.004	1.008
Final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0174, wR2 = 0.0441	R1 = 0.0674, wR2 = 0.1472	R1 = 0.0538, wR2 = 0.2032	R1 = 0.0444, wR2 = 0.1181
R indices (all data)	R1 = 0.0184, wR2 = 0.0447	R1 = 0.1479, wR2 = 0.2271	R1 = 0.0766, wR2 = 0.2283	R1 = 0.0672, wR2 = 0.1375

2 (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, and yellow crystals were formed. Yield: 80%. mp 176–178°C. Anal. Found: C 42.45, H 4.41, N 12.11. Calcd. for $C_{16}H_{18}N_4S_2Sn$: C 42.78, H 4.04, N 12.47%. IR (KBr, cm^{-1}): ν(C=N), 1665; ν(S—C=N), 1557; ν(C—S), 962; ν(Sn—N) 448;. ^{1}H NMR [$(CD_3)_2SO$, ppm] δ : 8.59 (s, 1H, CH=N), 7.32–7.85 (m, 5H, Ar—H), 7.48 (d, $J_{H,H} = 3.6$ Hz, 1H), 7.26 (dd, $J_{H,H} = 5.2$ Hz, 1H), 7.42 (d, 1H), 0.85 (9H, CH_3,$^2J_{^{119}Sn,^1H} = 83$ Hz); ^{13}C NMR ($CDCl_3$. ppm): 164.4 (C—S—Sn), 150.7 (CH=N), 141.9 (Ph—C—N), 133.7, 131.7, 129.6, 128.4 (Ar—C), 125.5, 121.2, 118.7, 110.2 (thiophene ring—C), 15.6 (CH_3); ($^1J_{^{119}Sn,^{13}C} = 512$ Hz). ^{119}Sn NMR ($CDCl_3$, ppm): 57.1.

X-Ray Crystallography

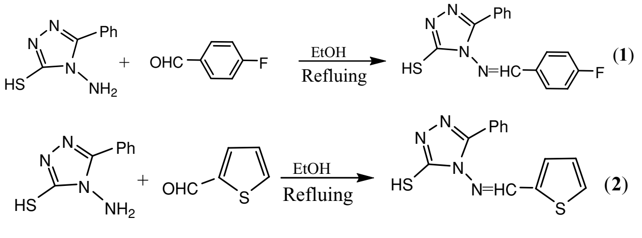
Data were collected at 298 K on a Bruker SMART CCD 1000 diffractometer fitted with Mo Kα radiation. The structures were solved by direct methods and refined by a full-matrix least squares procedure based on *F*2, using the SHELXL-97 program system. All non-hydrogen atoms were included in the model at 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

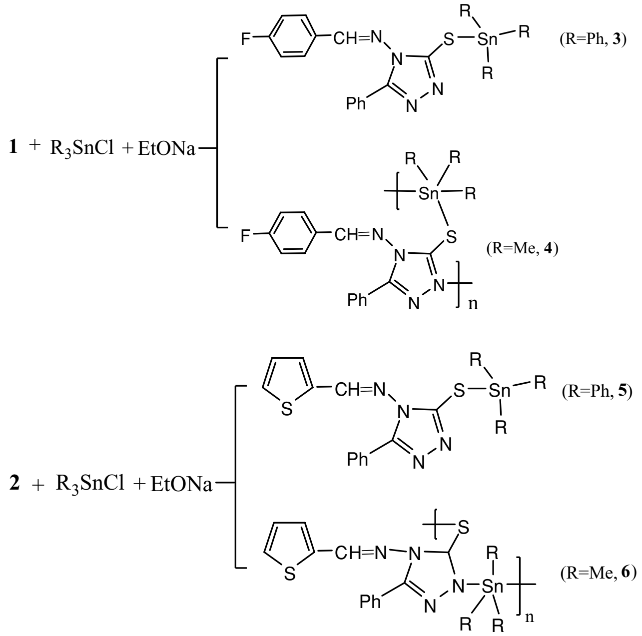
The syntheses procedures for compounds **1–2** are shown in Scheme 1 and for complexes **3–6** are shown in Scheme 2.

IR Spectroscopic Studies of Complexes **3–6**

The stretching frequencies of interest are those associated with the Sn—S and Sn—N groups. The explicit features in the infrared spectra of complexes **3–5** strong absorption, appearing in the range of



SCHEME 1



SCHEME 2

328–354 cm^{-1} in respective of the complexes, which are absent in compounds **1–2**, are assigned to the Sn—S stretching mode [17]. Although in complexes **4** and **6**, new bands at 442^{-} and 448 cm^{-1}appear in the spectra of the organotin(IV) complexes, which are assigned to ν(Sn—N), showing an N atom from the ligand moiety is coordinated to the central tin atom [18].

NMR Data of Complexes 3–6

The ^{1}H NMR data showed that the signal of the —SH proton in the spectrum of compounds **1–2** is absent in complexes **3–6**, indicating the removal of the —SH proton and the formation of Sn—S bonds. The structural changes occurring in the ligand upon deprotonation and coordination to the Sn atom should be reflected by the changes in the ^{13}C NMR spectra of complexes **3–6**; the ^{13}C NMR spectra of all complexes **3–6** show a downfield shift of all carbon resonances compared with Schiff base compounds **1–2**. It might result from some degree of paramagnetic contribution of tin—Carbon bonds. The ^{119}Sn NMR spectra of complexes **3–6** show resonances between 53.2 and −116.7 ppm. As reported in the literature [19], values of δ (^{119}Sn) in the range −210 to −400, −90 to −190, and 200 to −60 ppm are associated with six-, five-, and four-coordinated tin centers, respectively. On this basis, we can conclude that complexes **3** and **5** are typical of four- coordinated and complex **4** is five coordinated. These data were confirmed by the X-ray crystal structures of complexes **3–5**; whereas complex **6** has the signals in 57.1 ppm, thus indicating four-coordinated environment around the tin atoms for complex **6**; which is not accordance with the structure in the solid state. It can reasonably be assumed that the Sn—S bond of complex **6** is probably rupture in the solution.

Crystal Structure of Complexes 3 *and* 5

The molecular structure of complexes **3** and **5** are illustrated in Figs. 1 and 2, respectively; the 1D chain structure of complex **5** is illustrated in Fig. 3, and selected bond lengths and bond angles are given in Tables 2 and 3, respectively. These complexes have common structural property with a monomeric coordination structure. All the tin atoms are four-coordinated tetrahedral geometry. The Sn—S bond lengths are 2.4917(7) for **3** and 2.458(2) for **5**, which approach the range reported for triphenyltin heteroarenethiolates (2.405–2.481 Å), and the sum of the covalent radii of tin and sulfur (2.42 Å) [20], which prove that sulfur atoms coordinated to the tin atom by strong chemical bonds. Besides, the Sn(1)—N(4) distance (2.876 Å for **3** and 2.900 Å for **5**) is longer than that of complex [(Bu$_2$Sn)$_2$O(EtO)(L$_1$)]$_2$ (L$_1$ is a Schiff base ligand derived from 3-alkyl-4-amino-1,2,4-triazole-5-thi-one [21], but much shorter than the sum of the van der Waals radii of tin and nitrogen (3.74 Å) [22].

Furthermore, the C—H···N hydrogen bond is found in complex **5**, which connects the adjacent molecules to give rise to a one-dimensional (1D) infinite chain, the N(3)···H(16) and C(16)—H(16) distances are 2.696 and 0.930 Å, respectively, and the C—H···N angle is 151.70° . These data are similar to other triorganotin complexes that we have reported in [15].

Crystal Structure of Complexes 4 *and* 6

The molecular structure of complexes **4** and **6** are illustrated in Figs. 4 and 5, respectively; the 1D chain structure of complexes **4** and **6** are illustrated in Figs. 6 and 7, respectively; and selected bond lengths and bond angles are given in Tables 4 and 5, respectively. Complex **4** exhibit an infinite 1D polymeric chain structure via the S and N atoms from the triazole moiety coordinating to the Sn. All the Sn atoms are five-coordinated geometry with slight distortions from an ideal trigonal bipyramidal. The distortion lies the angle of N(1)—Sn(1)—S(1)#1 is 169.7(3)°, which slightly deviate from the normal angle of 180°.

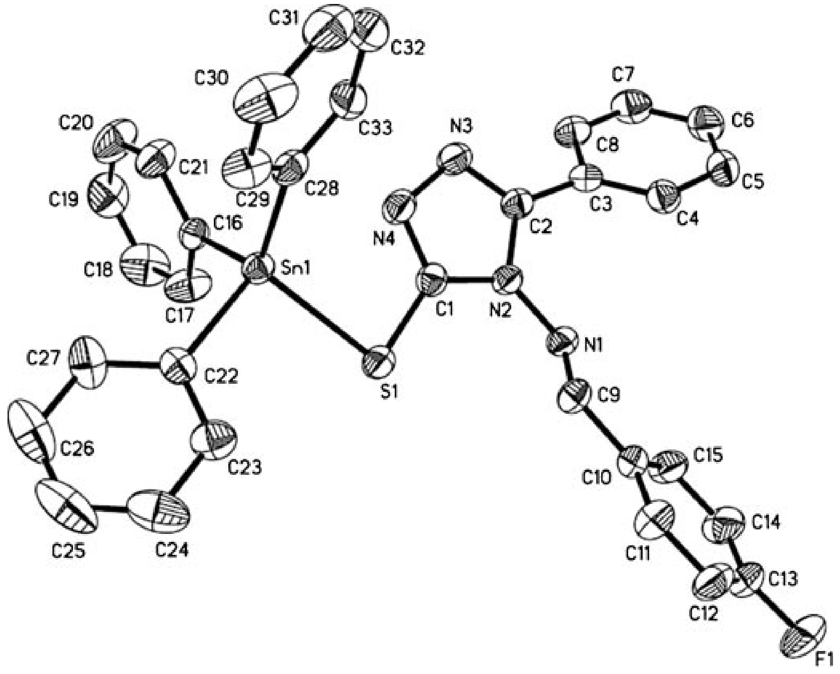


FIGURE 1 The molecular structure of complex **3.**

Three methyl groups defined the equatorial plane and the axial positions are occupied by the S and N atoms from the triazole moiety. The bond length of Sn(1)—S(1)#1 is 2.797(4) Å, which is longer than the sum of the covalent radii of tin and sulfur (2.42) [20], but much shorter than the sum of the van der Waals radii of tin and sulfur (4.0 Å) [20]. The Sn(1)—N(1) bond length (2.353(10) Å) is little longer than the covalent radii of tin and nitrogen (2.15 Å) [22] but shorter than that found in other similar triorganotin complexes as reported in [23,24], which suggest that Sn(1)—N(1) is a strong chemical bond.

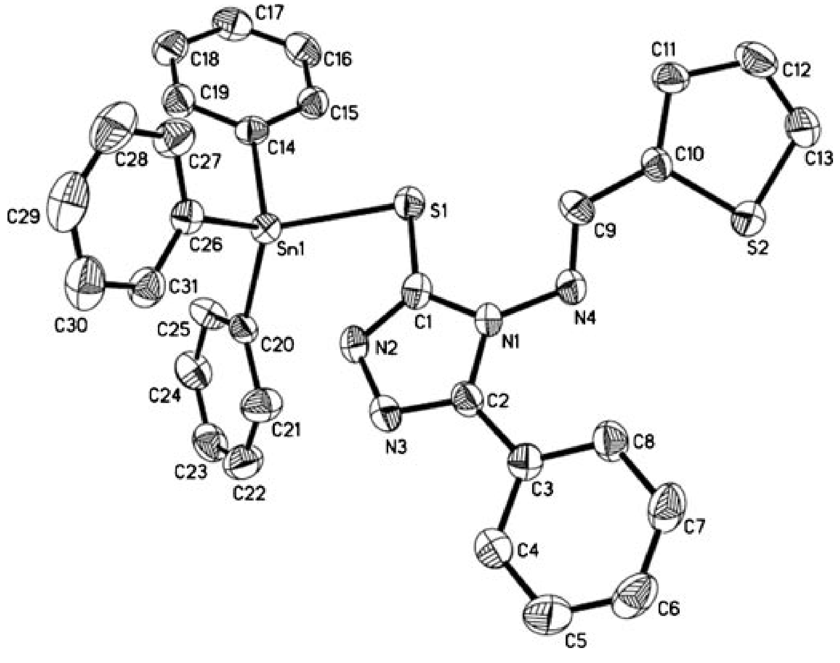


FIGURE 2 The molecular structure of complex **5**.

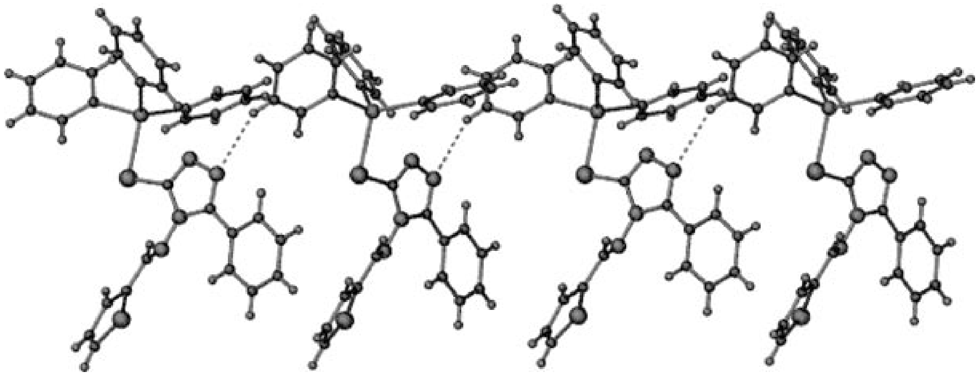


FIGURE 3 The 1D chain of complex **5**, propagation via intermolecular C—H···N hydrogen bond interactions.

TABLE 2 Selected Bond Lengths (Å) and Bond Angles (°) for **3**

	Bond lengths		
Sn(1)—C(16)	2.1332(19)	Sn(1)—C(22)	2.150(3)
Sn(1)—C(28)	2.141(2)	Sn(1)—S(1)	2.4917(7)
	Bond angles		
C(16)—Sn(1)—C(28)	118.84(8)	C(28)—Sn(1)—S(1)	112.98(6)
C(16)—Sn(1)—C(22)	105.54(10)	C(22)—Sn(1)—S(1)	96.21(7)
C(28)—Sn(1)—C(22)	108.91(10)	C(1)—S(1)—Sn(1)	91.60(8)
C(16)—Sn(1)—S(1)	111.58(6)		

TABLE 3 Selected Bond Lengths (Å) and Bond Angles (°) for **5**

	Bond Lengths		
Sn(1)—C(26)	2.115(8)	Sn(1)—C(20)	2.144(8)
Sn(1)—C(14)	2.139(8)	Sn(1)—S(1)	2.458(2)
	Bond Angles		
C(26)—Sn(1)—C(14)	110.7(3)	C(26)—Sn(1)—S(1)	110.1(2)
C(26)—Sn(1)—C(20)	114.5(3)	C(14)—Sn(1)—S(1)	97.2(2)
C(14)—Sn(1)—C(20)	106.0(3)	C(20)—Sn(1)—S(1)	116.7(2)

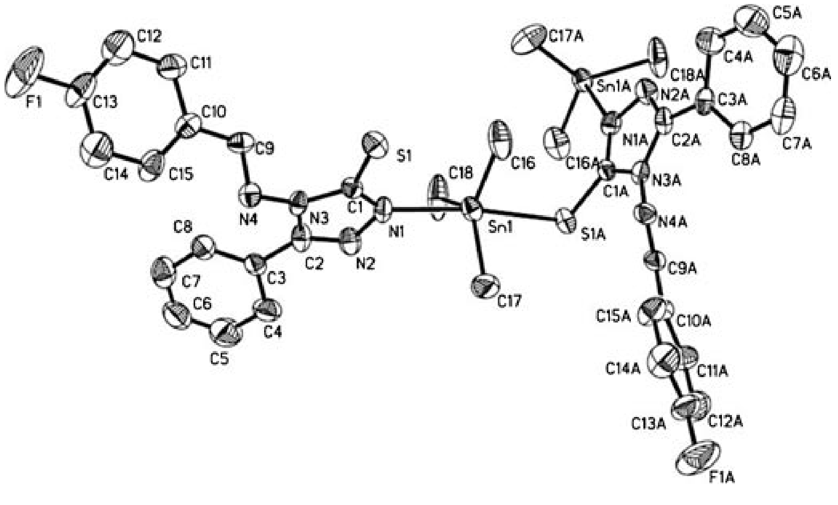


FIGURE 4 The molecular structure of complex **4**.

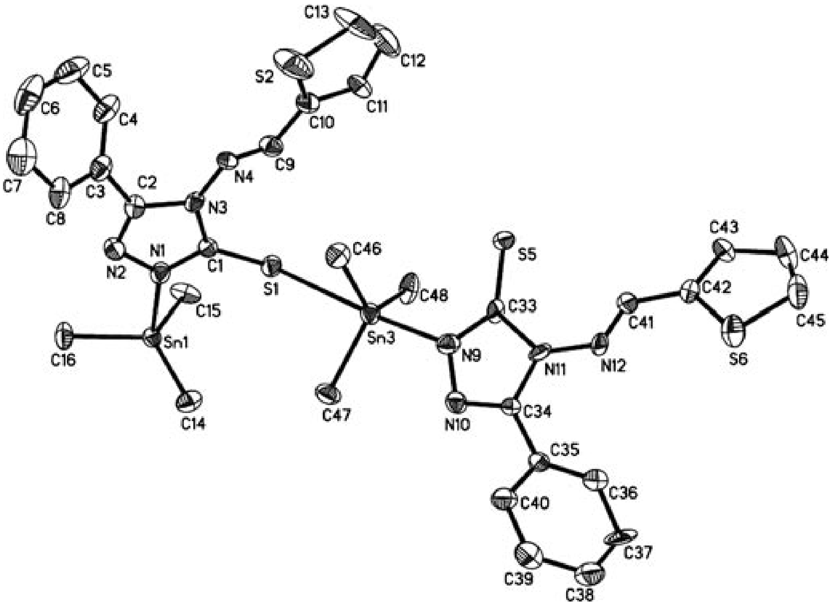


FIGURE 5 The molecular structure of complex **6** (only one molecular of complex **6** has been labeled for clarity).

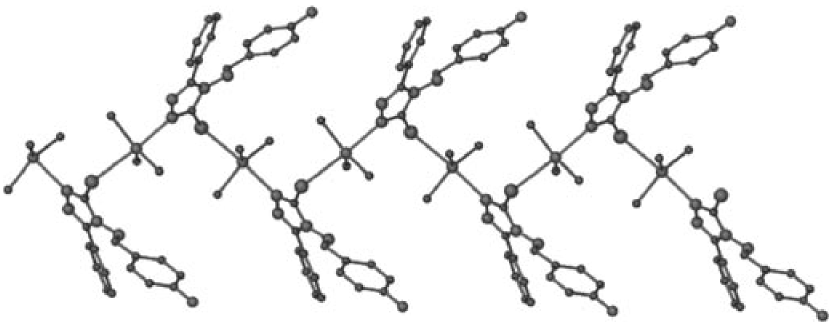


FIGURE 6 The 1D zigzag chain of complex **4**.

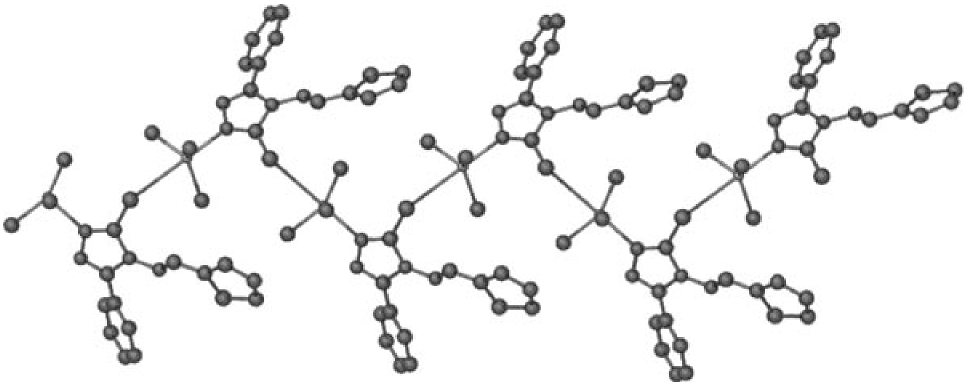


FIGURE 7 The 1D zigzag chain of complex **6**.

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

	Bond Lengths		
Sn(1)—C(16)	2.086(16)	Sn(1)—N(1)	2.353(10)
Sn(1)—C(17)	2.089(15)	Sn(1)—S(1)#1	2.797(4)
Sn(1)—C(18)	2.104(14)		
	Bond Angles		
C(16)—Sn(1)—C(17)	117.3(7)	C(18)—Sn(1)—N(1)	87.4(5)
C(16)—Sn(1)—C(18)	118.4(8)	C(16)—Sn(1)—S(1)#1	93.4(4)
C(17)—Sn(1)—C(18)	124.2(9)	C(17)—Sn(1)—S(1)#1	88.7(5)
C(16)—Sn(1)—N(1)	96.6(5)	C(18)—Sn(1)—S(1)#1	85.6(4)
C(17)—Sn(1)—N(1)	88.9(5)	N(1)—Sn(1)—S(1)#1	169.7(3)

TABLE 5 Selected Bond Lengths (Å) and Bond Angles (°) for **6**

	Bond Lengths		
Sn(1)—C(14)	2.089(15)	Sn(3)—C(48)	2.105(15)
Sn(1)—C(16)	2.145(14)	Sn(3)—C(47)	2.125(14)
Sn(1)—C(15)	2.149(15)	Sn(3)—C(46)	2.135(14)
Sn(1)—N(1)	2.210(11)	Sn(3)—N(9)	2.185(12)
Sn(2)—C(31)	2.101(16)	Sn(4)—C(64)	2.112(14)
Sn(2)—C(30)	2.133(16)	Sn(4)—C(63)	2.115(17)
Sn(2)—C(32)	2.135(15)	Sn(4)—C(62)	2.125(16)
Sn(2)—N(5)	2.226(12)	Sn(4)—N(13)	2.204(12)
	Bond Angles		
C(14)—Sn(1)—C(16)	115.5(7)	C(48)—Sn(3)—C(47)	117.1(7)
C(14)—Sn(1)—C(15)	126.9(7)	C(48)—Sn(3)—C(46)	125.4(7)
C(16)—Sn(1)—C(15)	114.1(8)	C(47)—Sn(3)—C(46)	113.0(7)
C(14)—Sn(1)—N(1)	97.3(5)	C(48)—Sn(3)—N(9)	97.7(6)
C(16)—Sn(1)—N(1)	93.3(5)	C(47)—Sn(3)—N(9)	96.0(5)
C(15)—Sn(1)—N(1)	97.5(5)	C(46)—Sn(3)—N(9)	97.2(5)
C(31)—Sn(2)—C(30)	113.1(7)	C(64)—Sn(4)—C(63)	116.7(7)
C(31)—Sn(2)—C(32)	129.1(7)	C(64)—Sn(4)—C(62)	125.8(7)
C(30)—Sn(2)—C(32)	115.1(7)	C(63)—Sn(4)—C(62)	113.7(7)
C(31)—Sn(2)—N(5)	96.7(6)	C(64)—Sn(4)—N(13)	97.3(6)
C(30)—Sn(2)—N(5)	93.8(6)	C(63)—Sn(4)—N(13)	96.3(6)
C(32)—Sn(2)—N(5)	95.6(5)	C(62)—Sn(4)—N(13)	95.7(6)

For complex **6**, the asymmetric unit contains three infinite 1D polymeric chain structure via the S and N atoms from the triazole moiety coordinating to the Sn, which are crystallographically nonequivalent. The conformations of the three independent molecules are almost the same, with only small differences in bond lengths and bond angles. All the tin atoms are five-coordinated trigonal bipyramidal geometry. The Sn—N bond length (2.185(12)–2.226(12) Å) is shorter than other similar triorganotin complexes and approaches to the sum of the covalent radii of tin and nitrogen (2.42 Å) [22], which proves that nitrogen atoms coordinated to the tin atom by strong coordinate bonds. The Sn—S bond lengths (3.224–3.246 Å) are longer than other similar triorganotin complexes, which we have reported in our previous works [16,23], but considerably less than the van der Waals radii of tin and sulfur (4.0 Å) [20], so the Sn—S bonds in complex **6** should be considered as weak coordinate bonds.

CONCLUSIONS

A series of triorganotin Schiff base complexes derived from 4-amino-5-phenyl-4*H*-1,2,4-trizole-3-thiol have been synthesized and characterized. Both the spectra and crystal structures show that stereoresistance from the R groups of trialkyltin chloride has great influence on the crystal structures. When the Schiff base ligands reacted with trimethyltin chloride, the 1D polymeric chain organotin structures were formed; whereas when the Schiff base ligands reacted with triphenyltin chloride the monomer organotin structures were formed. The reasoning for this result should be the stereoresistance of phenyl prevents complexes **3** and **5** from forming 1D polymeric chain structures.

SUPPLEMENTARY DATA

Atomic coordinates, thermal parameters, and bond lengths and angles for complexes **3–6** have been deposited in the Cambridge Crystallographic Data Center, CCDC nos. CCDC 679532, 679531, 679533, and 679534. 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).

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