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Investigation on steric effect in the coordination of S, N and O donor heterocycle to organotin(IV): Syntheses and crystal structures of triorganotin(IV) derivatives with 5-phenyl-1,3,4-oxadiazole-2-thiol

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Abstract

A series of organotin(IV) complexes with 5-phenyl-1,3,4-oxadiazole-2-thiol of the type $R_3Sn[S(C_8H_5N_2O)]$ (R = Me **1**, *n*-Bu **2**, $PhCH_2$ **3**, Cy **4**, Ph **5**) have been synthesized. All the complexes **1**–**5** have been characterized by elemental, IR, ^1H NMR, ^{13}C NMR analyses and X-ray crystallography. Among them, the central tin atoms of complexes **1**–**5** are all five-coordinated with distorted trigonal bipyramidal geometry. Interestingly, complexes **1**–**4** exhibit 1D polymeric chains through Sn and N intermolecular interactions.

Keywords: 5-Phenyl-1,3,4-oxadiazole-2-thiol; Triorganotin(IV); Crystal structures; Steric effect

1. Introduction

Increasing investigation of organotin(IV) complexes has been focused on acquiring well-defined solid-state structures to learn the nature of their versatile coordination chemistry [1–3], especially those organotin(IV) derivatives from heterocyclic thionates containing a nitrogen atom (or more) and an adjacent, exocyclic thioketo group [4–6]. A characteristic feature of these complexes in the solid state is that the ligands chelate the tin atom through S and N atoms. In our previous work, we studied the coordination chemistry of three ligands of such kind: 2-mercaptonicotinic acid, 1-(4-hydroxyphenyl)-1*H*-tetrazole-5-thiol and 2,5-dimercapto-1,3,4-thiodiazole which possess one or two deprotonated heterocyclic thioamide group $(N–C–S)^-$. The X-ray analyses have revealed that the former act as thiol form but the primary bond of the latter two ligands to the tin atom varies dramatically according to distinct R of the precursor R_nSnCl_{4-n} [7–10]. These results indicate that several factors can influence the topologies of the organotin derivatives from heterocyclic thionates such as the special geometries of ligand, the spacial resistant from R, etc. To continue our studies in this field, we choose another fascinating heterocyclic thionate: 5-phenyl-1,3,4-oxadiazole-2-thiol, which possesses one –SH group, through which primary bonds to tin atoms are likely formed. Furthermore, the potential coordination nitrogen and oxygen atoms of the oxadiazole 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 five triorganotin(IV) complexes with the ligand of the type $R_3Sn[S(C_8H_5N_2O)]$

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(R = Me **1**, *n*-Bu **2**, $PhCH_2$ **3**, Cy **4**, Ph **5**). The X-ray crystallography data show that the tin atoms of complexes **1**–**5** are all five-coordinated with distorted trigonal bipyramidal geometry. Interestingly, complexes **1**–**4** exhibit 1D polymeric chains through Sn and N intermolecular interactions.

2. Experimental

2.1. Materials and measurements

Trimethyltin chloride, tri-*n*-butyltin chloride, triphenyltin chloride, tricyclohexyltin chloride and 5-phenyl-1,3,4-oxadiazole-2-thiol were commercially available, and they were used without further purification. Tribenzyltin chloride was prepared by a standard method reported in the literature [11]. 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 and ^{13}C NMR spectra were recorded on Varian Mercury Plus 400 spectrometer operating at 400 and 100.6 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 (TMS) for ^{1}H and ^{13}C NMR. Elemental analyses were performed with a PE-2400II apparatus.

2.2. Syntheses of the complexes *1*–*5*

The general route of synthesis is shown in the following. The reaction was carried out under nitrogen atmosphere. The 5-phenyl-1,3,4-oxadiazole-2-thiol (1 mmol) was added to the solution of benzene 20 ml with sodium ethoxide (1 mmol), then add R_3SnCl (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 dichloromethane-*n*-hexane. Colorless crystal was formed.

2.2.1. $Me_3Sn[S(C_8H_5N_2O)]$ (*1*)

Yield, 70%; m.p. 116–118 °C. *Anal.* Calc. for $C_{11}H_{14}N_2OSSn$: C, 38.74; H, 4.14; N, 8.21. Found: C, 38.65; H, 4.04; N, 8.10%. ^{1}H NMR ($CDCl_3$): δ 7.24–7.83 (m, 5H,C_6H_5–C), 0.76 (s, 9H, Sn–CH_3) ppm. ^{13}C NMR: δ 145.7 (C-1 ligand), 136.6 (C-2), 136.6 (C-2′), 128.4 (C-3), 128.4 (C-3′), 129.5 (C-4), 168.2 (C–S), 168.7 (C–Ph), 8.11 (Me) 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.

2.2.2. $(n\text{-}Bu)_3Sn[S(C_8H_5N_2O)]$ (*2*)

Yield, 74%; m.p. 69–72 °C. *Anal.* Calc. for $C_{20}H_{32}N_2OSSn$: C, 51.41; H, 6.90; N, 6.00. Found: C, 51.50; H, 6.70; N, 6.22%. ^{1}H NMR ($CDCl_3$): δ 7.25–7.82 (m, 5H, C_6H_5–C), 0.85–1.68 (s, 27H, Sn–C_4H_9) ppm. ^{13}C NMR: δ 145.6 (C-1 ligand), 136.5 (C-2), 136.5 (C-2′), 128.3 (C-3), 128.3 (C-3′), 129.4 (C-4), 168.3 (C–S), 168.8 (C–Ph), 13.5, 26.3, 27.5, 29.2 (*n*-Bu) ppm. IR (KBr, cm^{-1}): ν(C=N) 1586, $\nu(Sn–C)_{as}$ 528, $\nu(Sn–C)_s$ 502, ν(Sn–S) 315, ν(Sn–N) 485.

2.2.3. $(PhCH_2)_3Sn[S(C_8H_5N_2O)]$ (*3*)

Yield, 76%; m.p. 125–127 °C. *Anal.* Calc. for $C_{29}H_{26}N_2OSSn$: C, 61.18; H, 4.60; N, 4.92. Found: C, 61.05; H, 4.41; N, 4.80%. ^{1}H NMR ($CDCl_3$): δ 7.31–7.47 (m, 5H, C_6H_5–C), 6.91–7.17 (m, 15H, Sn–$CH_2C_6H_5$), 2.76 (s, 6H, Sn–$CH_2C_6H_5$). ^{13}C NMR: δ 145.5 (C-1 ligand), 136.4 (C-2), 136.4 (C-2′), 128.2 (C-3), 128.2 (C-3′), 129.3 (C-4), 168.1 (C–S), 168.6 (C–Ph), 37.4 (CH_2–Ph), 127.5 (*m*-C), 128.7 (*p*-C), 127.6 (*o*-C), 124.5 (*i*-C) ppm. IR (KBr, cm^{-1}): ν(C=N) 1596 $\nu(Sn–C)_{as}$ 460, $\nu(Sn–C)_s$ 437, ν(Sn–S) 308, ν(Sn–N) 484.

2.2.4. $Cy_3Sn[S(C_8H_5N_2O)]$ (*4*)

Yield, 77%; m.p. 120–121 °C. *Anal.* Calc. for $C_{26}H_{38}N_2OSSn$: C, 57.26; H, 7.02; N, 5.14. Found: C, 57.15; H, 7.11; N, 5.05%. ^{1}H NMR ($CDCl_3$): δ 7.21–7.41 (m, 5H, C_6H_5–C), 0.82–1.65 (m, 33H, Sn–C_6H_{33}). ^{13}C NMR: δ 145.3 (C-1 ligand), 136.2 (C-2), 136.2 (C-2′), 128.2 (C-3), 128.2 (C-3′), 129.2 (C-4), 168.3 (C–S), 168.6 (C–Ph), 26.6 (*m*-C), 26.5 (*p*-C), 26.8 (*o*-C), 27.5 (*i*-C) ppm. IR (KBr, cm^{-1}): ν(C=N) 1592, $\nu(Sn–C)_{as}$ 450, $\nu(Sn–C)_s$ 427, ν(Sn–S) 307, ν(Sn–N) 483.

2.2.5. $Ph_3Sn[S(C_8H_5N_2O)]$ (*5*)

Yield, 75%; m.p. 185–187 °C. *Anal.* Calc. for $C_{26}H_{20}N_2OSSn$: C, 59.23; H, 3.82; N, 5.31. Found: C, 59.11; H, 3.71; N, 5.22%. ^{1}H NMR ($CDCl_3$): δ 7.21–7.42 (m, 5H, C_6H_5–C), 7.45–7.76 (m, 15H, Sn–C_6H_5) ppm. ^{13}C NMR: δ 145.2 (C-1 ligand), 136.3 (C-2), 136.3 (C-2′), 128.1 (C-3), 128.1 (C-3′), 129.1 (C-4), 168.0 (C–S), 168.5 (C–Ph), 127.9 (*m*-C), 129.0 (*p*-C), 136.4 (*o*-C), 148.5 (*i*-C) ppm. IR (KBr, cm^{-1}): ν(C=N) 1590, $\nu(Sn–C)_{as}$ 464, $\nu(Sn–C)_s$ 429, ν(Sn–S) 311.

2.3. X-ray crystallographic studies of complexes *1*–*5*

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 (λ = 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

Table 1
Crystal data and structure refinement parameters for complexes **1**–**5**

Complexes	**1**	**2**	**3**	**4**	**5**
Empirical formula	$C_{11}H_{14}N_2OSSn$	$C_{20}H_{32}N_2OSSn$	$C_{29}H_{26}N_2OSSn$	$C_{26}H_{38}N_2OSSn$	$C_{26}H_{20}N_2OSSn$
Formula weight	340.99	467.23	569.27	543.32	527.19
Crystal system	monoclinic	triclinic	orthorhombic	monoclinic	monoclinic
Space group	$P2_1/m$	$P\bar{1}$	$P2_12_12_1$	$P2_1/c$	$P2_1/n$
Unit cell dimensions					
a (Å)	6.891(3)	10.56(1)	6.789(2)	12.603(1)	10.82(4)
b (Å)	7.509(4)	12.55(1)	19.326(6)	12.549(1)	12.97(5)
c (Å)	13.354(7)	18.31(2)	19.896(6)	19.818(1)	16.43(6)
α (°)	90	88.42(1)	90	90.00	90
β (°)	104.723(5)	75.27(1)	90	125.503(4)	101.92
γ (°)	90	87.48(1)	90	90.00	90
V (Å^3)	668.2(6)	2345(5)	2610(1)	2551.5(4)	2257(1)
Z	2	4	4	4	4
D_c (Mg m^{-3})	1.695	1.324	1.449	1.414	1.552
Absorption coefficient (mm^{-1})	2.050	1.188	1.082	1.103	1.245
F(0 0 0)	336	960	1152	1120	1056
Crystal size (mm)	$0.37 \times 0.28 \times 0.21$	$0.48 \times 0.46 \times 0.16$	$0.44 \times 0.25 \times 0.21$	$0.20 \times 0.18 \times 0.13$	$0.48 \times 0.41 \times 0.36$
θ Range (°)	3.06–25.02	1.62–25.03	1.47–25.03	2.298–27.983	2.07–25.05
Reflections collected	2792	11 766	13 718	28 636	10 466
Independent reflections [R_{int}]	1028 [0.0203]	8112 [0.0309]	4571 [0.0294]	5812 [0.0274]	3638 [0.1630]
Data/restraints/parameters	1028/9/100	8112/30/451	4571/0/307	5812/0/0280	3638/0/280
Goodness-of-fit onF^2	1.026	0.997	1.002	1.045	1.008
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0503$	$R_1 = 0.0491$	$R_1 = 0.0263$	0.0343	$R_1 = 0.0739$
	$wR_2 = 0.1392$	$wR_2 = 0.1154$	$wR_2 = 0.0526$	0.0858	$wR_2 = 0.1483$
R indices (all data)	$R_1 = 0.0508$	$R_1 = 0.0963$	$R_1 = 0.0312$	0.0410	$R_1 = 0.1120$
	$wR_2 = 0.1400$	$wR_2 = 0.1438$	$wR_2 = 0.0547$	0.0906	$wR_2 = 0.1722$

positions. Crystal data and experimental details of the structure determinations are listed in Table 1.

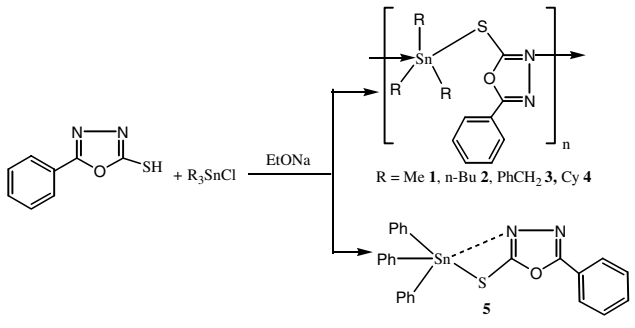
3. Results and discussion

3.1. Syntheses of complexes 1–5

The synthesis procedure is given in Scheme 1.

3.2. IR spectroscopic studies of complexes 1–5

Comparing the IR spectra of the free ligand with complexes **1**–**5**, the band at 2560–2430 cm^{-1}, which appears in the spectra of the free ligand as the ν(S–H) vibration, is absent in those of complexes **1**–**5** thus indicating metal–ligand bond formation through this site. In the far-IR spectra, the absorption about 310 cm^{-1} region for all complexes **1**–**5**, 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}) [12,13]. In organotin complexes, the IR spectra can provide useful information concerning the geometry of the SnC_n moiety [14]. In the case of our complexes, for triorganotin(IV) derivatives, two bands were assigned to asymmetric and symmetric Sn–C vibrations. Thus suggesting non-planar SnC_3 fragments for triorganotins. The middle intensity bands observed at about 1600 cm^{-1} in the spectra of all complexes have been assignable to ν(C=N) according to the literatures [15,16], which suggested the coordination of free ligand to these complexes is through sulfur atoms via thiol form.



Scheme 1.

3.3. ^1H and ^{13}C NMR data of complexes 1–5

^{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 proton and the formation of Sn–S bonds. The formation accords 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 complex **5**,

7.45–7.76 ppm, and those of methylene connected directly with tin in complex **3**, 2.76 ppm, upfield shift as compared with those of their corresponding precursors. All these data are similar to those cases in literature [17], indicating there may exist novel coordination of the ligand to tin atom for all the five complexes **1**–**5**. In addition, the resonance of the phenyl group connected with the oxadiazole ring (C–C_6H_5) appears at 7.21–7.83 ppm for all complexes **1**–**5**.

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 chelate tin through thiolate form, C–S should be further low frequency in the spectra of all complexes compared with those in free ligands. As shown above, the chemical shifts of C–S in complexes **1**–**5** are shifted by 8 ppm to low frequency compared with the free ligand (δ 176.2 ppm), indicating that the ligands involved in these complexes act as thiolate form. All of the above analyses are confirmed by X-ray diffraction.

3.4. Crystal structures of complexes *1*–*5*

The crystal structures and polymeric chains of complexes **1**–**4** are shown in Figs. 1–8, respectively. And the crystal structure and cell packing diagram of complex **5** are shown in Figs. 9 and 10. All H atoms have been omitted for the purpose of clarity. Table 1 lists the crystal data and structure refinement parameters for complexes **1**–**5** and their selected bond lengths and angles are shown in Tables 2–6, respectively.

3.4.1. $Me_3Sn[S(C_8H_5N_2O)]$ (*1*), $(n\text{-}Bu)_3Sn[S(C_8H_5N_2O)]$ (*2*), $(PhCH_2)_3Sn[S(C_8H_5N_2O)]$ (*3*) and $Cy_3Sn[S(C_8H_5N_2O)]$ (*4*)

For complexes **1**–**4**, the X-ray diffraction investigation has shown that they exhibit 1D polymeric chains through intermolecular Sn–N bonds. The central tin atoms in complexes **1**–**4** are all five-coordinate with the *trans*-trigonal–bipyramidal geometry. The methyl carbons in complex **1**, the methylene carbons which are next to tin in complex **2**, the methylene carbons in complex **3** and the –CH– carbons in complex **4** are in equatorial positions and the axial positions are occupied by the sulfur atom and the nitrogen atom of a neighboring molecule, respectively. The sum of equatorial angles are 359.4° (C(10)#1–Sn(1)–C(10) (123.4(5)°), C(10)#1–Sn(1)–C(9) (118.0(3)°) and C(9)–Sn(1)–C(10) (118.0(3)°)), in complex **1**; 359.9° (C(25)–Sn(1)–C(21) (118.7(5)°), C(25)–Sn(1)–C(17) (124.7(6)°) and C(21)–Sn(1)–C(17) (116.5(5)°)), in complex **2**; 358.04° (C(23)–Sn(1)–C(9) (116.42(14)°), C(23)–Sn(1)–C(16) (111.64(14)°) and C(9)–Sn(1)–C(16) (129.98(13)°)), in complex **3**; 359.86° (C(7)–Sn(1)–C(13) (122.50(14)°), C(7)–Sn(1)–C(1) (121.21(12)°) and C(13)–Sn(1)–C(1) (116.15(13)°)), in complex **4**, respectively. They are all

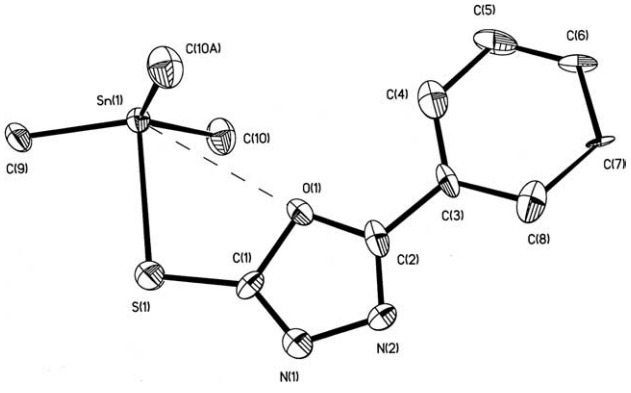


Fig. 1. Molecular structure of the complex **1**.

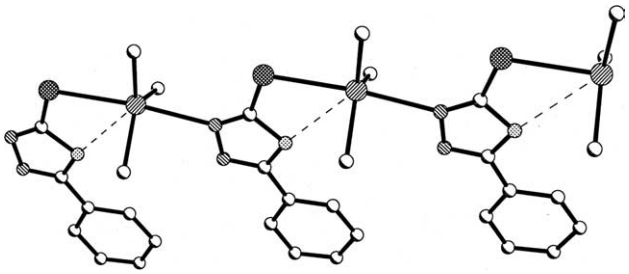


Fig. 2. Perspective view showing the 1D polymeric chain of the complex **1**.

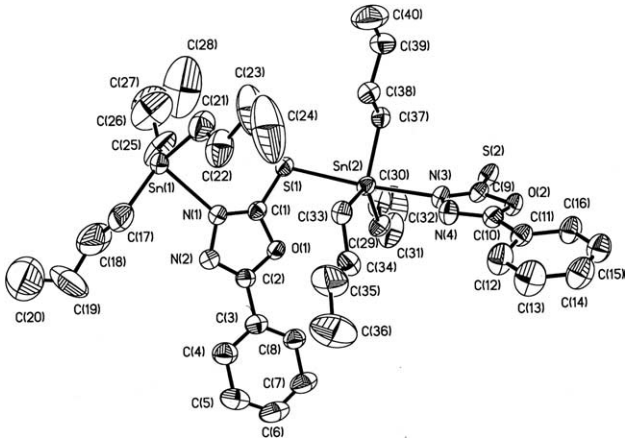


Fig. 3. Molecular structure of the complex **2**.

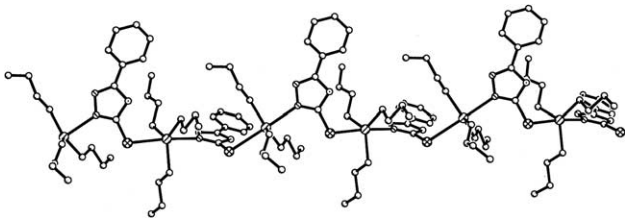


Fig. 4. Perspective view showing the 1D polymeric chain of the complex **2**.

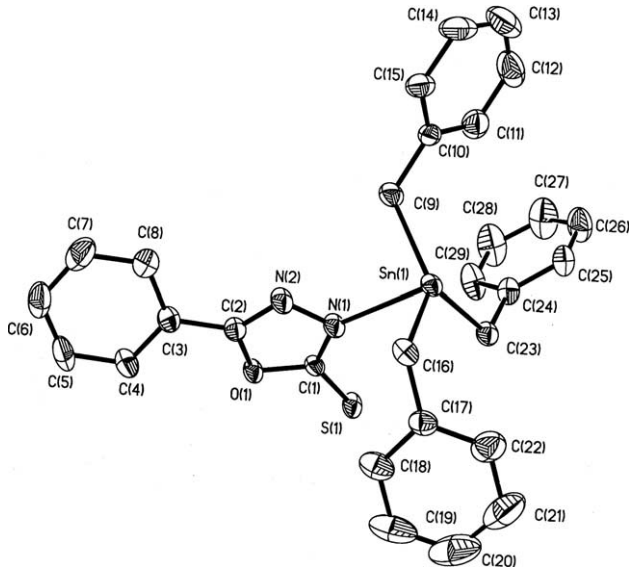


Fig. 5. Molecular structure of the complex **3**.

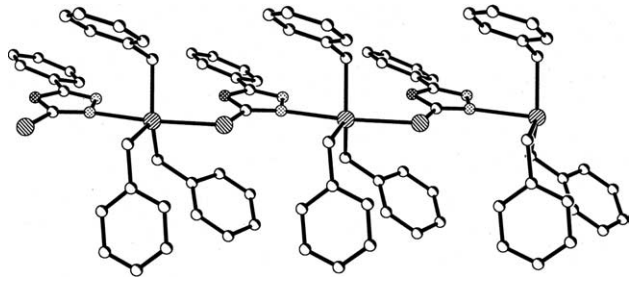


Fig. 6. Perspective view showing the 1D polymeric chain of the complex **3**.

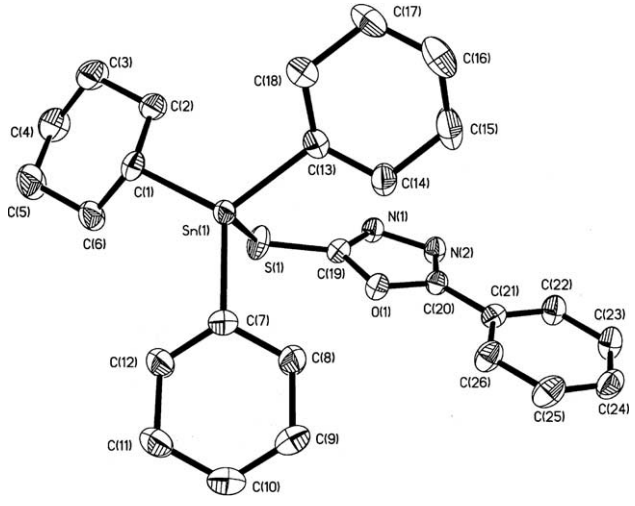


Fig. 7. Molecular structure of the complex **4**.

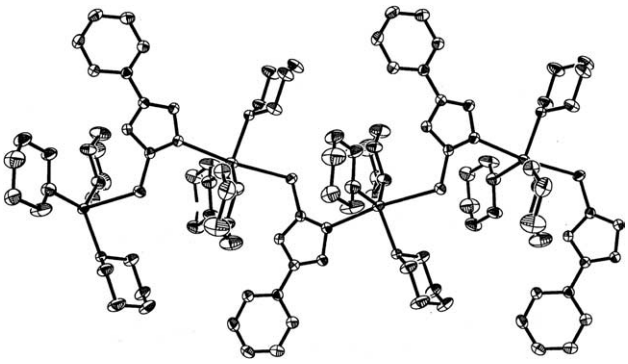


Fig. 8. Perspective view showing the 1D polymeric chain of the complex **4**.

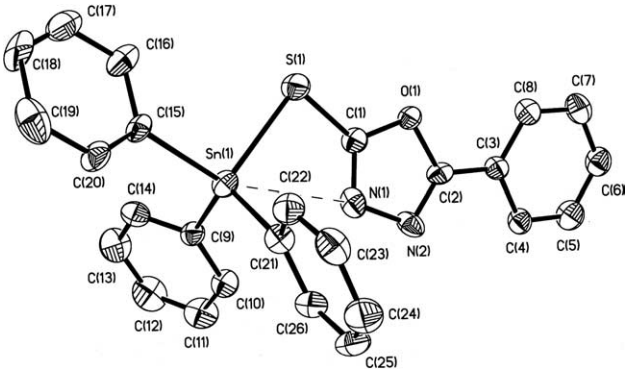


Fig. 9. Molecular structure of the complex **5**.

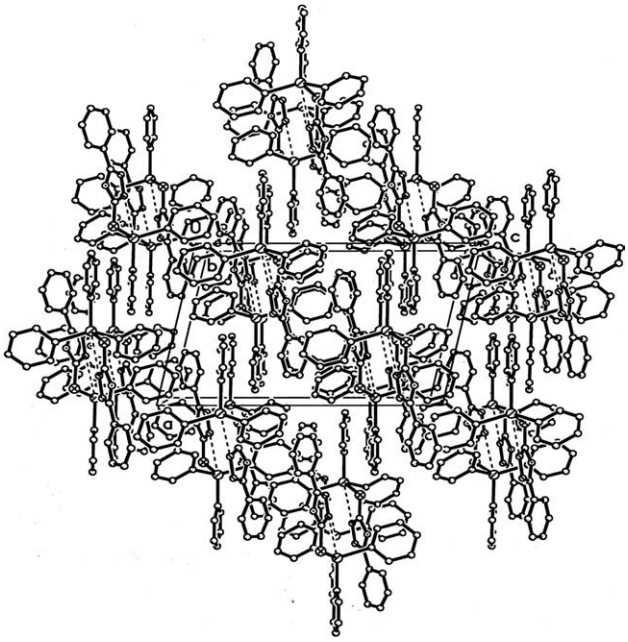


Fig. 10. Packing diagram of complex **5**.

a little less than 360°, indicating that the corresponding atoms are almost in the same plane. But the axial angles are S(1)–Sn(1)–N(1)#2 (173.0(2)°) in complex **1**; N(1)–Sn(1)–S(2)#1 (177.49(15)°) in complex **2**; N(1)–Sn(1)–S(1)#1 (174.51(7)°) in complex **3**; N(1)–Sn(1)–S(1) (172.36(6)°) in complex **4**, respectively, slightly

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

Bond lengths	
Sn(1)–C(10)	2.125(9)
Sn(1)–S(1)	2.713(4)
Sn(1)–C(9)	2.13(1)
Sn(1)···O(1)	3.278(9)
Bond angles	
C(10)#1–Sn(1)–C(10)	123.4(5)
C(9)–Sn(1)–S(1)	91.0(4)
C(10)#1–Sn(1)–C(9)	118.0(3)
N(1)#2–Sn(1)–S(1)	173.0(2)
C(10)–Sn(1)–C(9)	118.0(3)
C(10)#1–Sn(1)–O(1)	70.3(3)
C(10)#1–Sn(1)–N(1)#2	83.6(4)
C(10)–Sn(1)–O(1)	70.3(3)
C(10)–Sn(1)–N(1)#2	83.6(4)
C(9)–Sn(1)–O(1)	143.0(4)
C(9)–Sn(1)–N(1)#2	96.0(4)
N(1)#2–Sn(1)–O(1)	121.0(3)
C(10)#1–Sn(1)–S(1)	93.1(3)
S(1)–Sn(1)–O(1)	52.0(1)
C(10)–Sn(1)–S(1)	93.1(3)

Table 3
Selected bond lengths (Å) and bond angles (°) for complex **2**

Bond lengths	
Sn(1)–C(25)	2.11(1)
Sn(2)–C(37)	2.144(7)
Sn(1)–C(21)	2.11(1)
Sn(2)–N(3)	2.440(6)
Sn(1)–C(17)	2.17(1)
Sn(2)–S(1)	2.773(3)
Sn(1)–N(1)	2.415(6)
Sn(2)···O(1)#1	3.461(3)
Sn(1)–S(2)#1	2.765(3)
Sn(1)···N(2)	3.310(3)
Sn(2)–C(33)	2.131(6)
Sn(2)···N(4)	3.389(3)
Sn(2)–C(29)	2.140(7)
Bond angles	
C(25)–Sn(1)–C(21)	118.7(5)
C(33)–Sn(2)–C(29)	121.4(3)
C(25)–Sn(1)–C(17)	124.7(6)
C(33)–Sn(2)–C(37)	118.0(3)
C(21)–Sn(1)–C(17)	116.5(5)
C(29)–Sn(2)–C(37)	120.4(3)
C(25)–Sn(1)–N(1)	88.4(3)
C(33)–Sn(2)–N(3)	85.8(2)
C(21)–Sn(1)–N(1)	90.9(3)
C(29)–Sn(2)–N(3)	91.7(3)
C(17)–Sn(1)–N(1)	88.5(3)
C(37)–Sn(2)–N(3)	87.9(3)
C(25)–Sn(1)–S(2)#1	89.6(3)
C(33)–Sn(2)–S(1)	93.1(2)
C(21)–Sn(1)–S(2)#1	91.4(3)
C(29)–Sn(2)–S(1)	93.5(2)
C(17)–Sn(1)–S(2)#1	91.5(3)
C(37)–Sn(2)–S(1)	87.8(2)
N(1)–Sn(1)–S(2)#1	177.5(2)
N(3)–Sn(2)–S(1)	174.4(1)

Table 4
Selected bond lengths (Å) and bond angles (°) for complex **3**

Bond lengths	
Sn(1)–C(23)	2.152(3)
Sn(1)–N(1)	2.455(3)
Sn(1)–C(9)	2.166(3)
Sn(1)–S(1)#1	2.657(1)
Bond angles	
C(23)–Sn(1)–C(9)	116.4(1)
C(23)–Sn(1)–S(1)#1	91.01(9)
C(23)–Sn(1)–C(16)	111.6(1)
C(9)–Sn(1)–S(1)#1	99.3(1)
C(9)–Sn(1)–C(16)	130.0(1)
C(16)–Sn(1)–S(1)#1	92.8(1)
C(23)–Sn(1)–N(1)	93.6(1)
N(1)–Sn(1)–S(1)#1	174.51(7)
C(9)–Sn(1)–N(1)	81.2(1)
C(1)–S(1)–Sn(1)#2	98.2(1)
C(16)–Sn(1)–N(1)	82.8(1)

Table 5
Selected bond lengths (Å) and bond angles (°) for complex **4**

Bond lengths	
Sn(1)–C(7)	2.160(3)
Sn(1)–N(1)	2.524(2)
Sn(1)–C(13)	2.163(3)
Sn(1)–S(1)	2.8108(8)
Sn(1)–C(1)	2.173(3)
Bond angles	
C(7)–Sn(1)–C(13)	122.5(1)
C(7)–Sn(1)–S(1)	96.1(1)
C(7)–Sn(1)–C(1)	121.2(1)
C(13)–Sn(1)–S(1)	92.1(1)
C(13)–Sn(1)–C(1)	116.2(1)
C(1)–Sn(1)–S(1)	85.19(8)
C(7)–Sn(1)–N(1)	84.8(1)
N(1)–Sn(1)–S(1)	172.36(6)
C(13)–Sn(1)–N(1)	93.9(1)
C(1)–Sn(1)–N(1)	87.85(9)

Table 6
Selected bond lengths (Å) and bond angles (°) for complex **5**

Bond lengths	
Sn(1)–C(21)	2.105(9)
Sn(1)–S(1)	2.476(8)
Sn(1)–C(9)	2.12(1)
Sn(1)···N(1)	2.90(1)
Sn(1)–C(15)	2.14(1)
S(1)–C(1)	1.71(1)
Bond angles	
C(21)–Sn(1)–C(9)	120.9(4)
C(21)–Sn(1)–N(1)	78.5(3)
C(21)–Sn(1)–C(15)	108.2(3)
C(9)–Sn(1)–N(1)	82.8(3)
C(9)–Sn(1)–C(15)	109.6(3)
C(15)–Sn(1)–N(1)	157.9(3)
C(21)–Sn(1)–S(1)	107.3(3)
S(1)–Sn(1)–N(1)	59.2(2)
C(9)–Sn(1)–S(1)	109.7(2)
C(1)–N(1)–Sn(1)–	83.3(6)
C(15)–Sn(1)–S(1)	98.9(2)
N(2)–N(1)–Sn(1)	169.2(6)

deviating from 180°, thus they are all distorted trigonal–bipyramidal geometry.

All the Sn–S bond lengths Sn(1)–S(1)#1 (2.713(4) Å) for complex **1**; Sn(1)–S(2)#1 (2.765(3) Å) for complex **2**; Sn(1)–S(1)#1 (2.6565(11) Å) for complex **3**; Sn(1)–S(1) (2.8108(8) Å) for complex **4**, are a little longer than the covalent radii of Sn and S (2.42 Å) [18,19], and quite shorter than the van der Waals radii of of Sn and S (4.00 Å) [20]. Concerning Sn–N bond lengths, the values are Sn(1)–N(1)#2 (2.450(12) Å) for complex **1**; Sn(1)–N(1) (2.415(6) Å) for complex **2**; Sn(1)–N(1) (2.455(3) Å) for complex **3**; Sn(1)–N(1) (2.524(2) Å) for complex **4**, respectively. All these lie in the range recorded in the Cambridge Crystallographic Database from 2.27 to 2.58 Å [21b], slightly greater than the sum of the covalent radii of tin and nitrogen atoms (2.15 Å) but considerably less than the van der Waals radii of the two atoms (3.74 Å) [21a].

The intramolecular interaction distances of Sn, N(2)#1 and/or Sn, O(1)#1 are: 3.158 and 3.278(9) Å for complex **1**; 3.310 and 3.583 Å for complex **2**; 3.206 and 3.127 Å for complex **3**; 3.397 Å for complex **4**, respectively. All the bond distances are within the van der Waals radii of Sn and N atoms (3.74 Å) [21a] and Sn and O atoms (3.68 Å) [22a]. But they are much longer than the values recorded in the Cambridge Crystallographic Database (Sn–N 2.27–2.58 Å) [21b] and Sn–O (2.61–3.02 Å) [22b,c], and cannot be regarded as weak coordination bonds.

Further, most Sn–S and Sn–N bond lengths in complexes **1**–**4** are comparable with those in organotin(IV) derivatives from heterocyclic thionates containing a nitrogen atom (or more), such as organotin thiotetrazoles complexes (Sn–S 2.477(4)–2.614(5) Å and Sn–N 2.464(5)–2.810(7) Å) [6,10a]. To some extent, our ligand has some resemblance with thiotetrazoles. Due to the multidentate nature of the oxadiazole and tetrazole ring, both of them have the possibility to act as a fulcrum through which lattice construction is orchestrated in one or more dimensions [23]. And polymeric chains of complexes **1**–**4** in this paper are covalently linked through intermolecular Sn–N bonds, while organotin thiotetrazoles complexes prefer to adopt both covalent bond and all kinds of hydrogen bonding to construct polymeric chain, 2D zigzag sheets and 3D arrays [24].

3.4.2. $Ph_3Sn[S(C_8H_5N_2O)]$ (**5**)

For complex **5**, the central tin atom forms four primary bonds: three to the phenyl groups and one to the sulfur atom. The Sn–S bond length (2.476(8) Å) lies toward the middle of the range reported for triphenyltin heteoarenethiolates (2.405–2.481 Å) [18,19]. This bond length is a little longer than the sum of covalent radii of Sn and S atoms (2.42 Å) [18,19], but is considerably shorter than the sum of van der Waals radii of Sn and S atoms (4.00 Å) [20]. And it is similar to that found in $Ph_3Sn[S(C_7H_5N_4O)]$ (2.4760(17) Å) [9] and $Ph_3Sn(S–C_2SN_2–S)SnPh_3$ (2.467(2) Å) [8]. Besides, there exist intramolecular Sn···N weak interaction, common observed in triphenyltin heteroarenethiolates [25]. The Sn···N bond length (2.896(12) Å) is midway between the sums of the covalent radii and van der Waals radii of tin and nitrogen (2.15–3.74 Å) [21a] and can be regarded as weak coordination bond. Including the Sn···N weak interaction, the geometry at tin in complex **5** becomes distorted *cis*-trigonal–bipyramidal with the axial-tin-axial angle C(15)–Sn(1)–N(1) (157.9(3)°). As a result of the Sn···N weak coordination bond, though the C–Sn–C bond angles are close to the theoretical tetrahedral angle, the C–Sn–S bond angles are more acute or obtuse than it, largest deviations occurring in C(9)–Sn(1)–S(1) 109.7(2)°, C(15)–Sn(1)–S(1) 98.9(2)° and C(21)–Sn(1)–S(1) 107.3(3)°. In the oxadiazole, the C–S bond distance (C(1)–S(1) 1.708(11) Å) lies between the average value of the double C=S bond in thioureas (1.681 Å) and the single C–S bond in the C–S–Me fragment (1.789 Å) [26], suggesting that the C–S bond has some double-bond character in the deprotonated oxadiazole.

4. Conclusions

A series of organotin(IV) complexes based on 5-phenyl-1,3,4-oxadiazole-2-thiol 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, *n*-butyl, benzyl, cyclohexyl have the smaller spatial resistance, consequently, complexes **1**–**4** adopt the same coordination modes and exhibit 1D polymeric chains through Sn and N intermolecular interactions, respectively. But, phenyl has the bigger stereo-constraints and prevents another ligand chelating the central tin atom, so, complex **5** does not form a 1D polymeric chain. Therefore, we conclude that the decrease of stereo-constraints may benefit the coordination of nitrogen atoms.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-257756 for **1**, 238959 for **2**, 257755 for **3**, 261920 for **4** and 238958 for **5**. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK,

fax: +44 1223 336033, e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

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