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Hydrogen bonding and π - π stacking interaction in the coordination of sulfur and nitrogen donor heterocycle to organotin(IV): syntheses and crystal structures of di- and triorganotin(IV) derivatives with 1-(4-hydroxyphenyl)-1*H*-tetrazole-5-thiol

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Abstract

A series of organotin(IV) complexes with 1-(4-hydroxyphenyl)-1*H*-tetrazole-5-thiol of the type, $R_n Sn[S(C_7H_5N_4O)]_{4-n} \cdot L$ (n = 3, L = 0: R = Me (1), n-Bu (2), Ph (3); n = 3, $L = 0.5C_2H_5OH \cdot 0.5H_2O$, $R = PhCH_2$ (4); n = 2, $L = H_2O$, R = Me (5); n = 2, L = 0: R = n-Bu (6), Ph (7), PhCH₂ (8)) have been synthesized. All the complexes 1–8 have been characterized by elemental, IR and ¹H NMR analyses. Among them complexes 3, 4, 5 and 6 have also been characterized by X-ray crystallography diffraction analyses, which revealed the 1D ribbons of complexes 3 and 5 and the 2D network of complex 6 due to the versatile intermolecular hydrogen bonds O–H···X (X = O, N, S) in the crystallographic structures. Moreover, strong π - π stacking interactions are found in complexes 4 and 5.

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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], especially that of some organotin(IV) derivatives from heterocyclic thionates containing a nitrogen atom (or more) and an adjacent, exocyclic thioketo group [2–4]. In our previous work, we studied the coordination chemistry of two ligands of such kind: 2-mercaptonicotinic acid (Hmnc) and 2,5dimercapto-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 act as thiol form but the primary bond of the latter to the tin atom varies dramatically according to distinct R of the precursor $R_n SnCl_{4-n}$ [5,6]. These results indicate there are 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: 1-(4-Hydroxyphenyl)-1H-tetrazole-5-thiol, which possesses one -SH and one -OH group, through which primary bonds to tin atoms are likely formed. Moreover, the three potential coordination nitrogen atoms of tetrazole make the ligand act as a fulcrum about which lattice construction is orchestrated in one or more dimensions.

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In this paper, we report some details of the syntheses and characterizations of a series of organotin(IV) complexes with the ligand of the type $R_n Sn[S(C_7-H_5N_4O)]_{4-n} \cdot L$ (n = 3, L = 0: R = Me (1), n-Bu (2), Ph (3); n = 3, $L = 0.5C_2H_5OH \cdot 0.5H_2O$, $R = PhCH_2$ (4); n = 2, $L = H_2O$, R = Me (5); n = 2, L = 0: R = n-Bu (6), Ph (7), PhCH₂ (8)). X-ray crystallography of complexes 3, 4, 5 and 6 show that all the complexes contain the thiol form of the ligand, i.e. the ligand is linked to the organometal moiety primarily through sulfur, resembling as Hmnc and 1-phenyl-1*H*-tetrazole-5-thiol [5,7]. Interestingly, the versatile hydrogen bonding, $O-H \cdots X$ (X = O, N, S), and strong π - π stacking interactions are found.

2. Experimental

2.1. Materials and measurements

Trimethyltin chloride, tri-*n*-butyltin chloride, triphenyltin chloride, dimethyltin dichloride, di-*n*-butyltin dichloride, diphenyltin dichloride and 1-(4-hydroxyphenyl)-1*H*-tetrazole-5-thiol were commercially available, and they were used without further purification. Tribenzyltin chloride and dibenzyltin chloride were prepared by a standard method reported in the literature [8]. The melting points were obtained with Kofler micro melting point apparatus and are uncorrected. Infraredspectra were recorded on a Nicolet-460 spectrophotometer using KBr disks and sodium chloride optics. ¹H NMR spectra were obtained on a JEOL-FX-90Q spectrometer, chemical shifts were given in ppm relative to Me₄Si in CDCl₃ solvent. Elemental analyses were performed with a PE-2400II apparatus.

2.2. Syntheses of the complexes 1–8

2.2.1. $Me_3Sn[S(C_7H_5N_4O)]$ (1)

The reaction was carried out under nitrogen atmosphere. The 1-(4-hydroxyphenyl)-1*H*-tetrazole-5-thiol (0.194 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 add Me₃SnCl (0.199 g, 1 mmol) to the mixture, continuing the reaction for 12 h at 45 °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. White crystal was formed. Yield, 65%. m.p. 118–120 °C. *Anal.* Calc. for C₁₀H₁₄N₄OSSn: C, 33.64; H, 3.95; N, 15.69. Found: C, 33.68; H, 3.95; N, 15.70%. ¹H NMR (90 MHz, CDCl₃): δ 7.23–7.38 (m, 4H,C₆H₄–N), 0.75 (s, 9H, Sn–CH₃) ppm. IR (KBr, cm⁻¹): v(C=N) 1600, $v(Sn-C)_{as}$ 536, $v(Sn-C)_{s}$ 504, v(Sn-S) 312.

2.2.2. $(n-Bu)_3 Sn[S(C_7H_5N_4O)]$ (2)

The synthesis procedure was the same as 1. 1-(4-Hydroxyphenyl)-1*H*-tetrazole-5-thiol (0.194 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol) and (n-Bu)₃SnCl (0.326 g, 1 mmol), reaction time 12 h, temperature 45 °C. Recrystallized from ether–petroleum. White crystal was formed. Yield, 74%. m.p. 67–69 °C. *Anal.* Calc. for C₁₉H₃₂N₄OSSn: C, 47.22; H, 6.67; N, 11.59. Found: C, 47.26; H, 6.57; N, 11.70%. ¹H NMR (90 MHz, CDCl₃): δ 7.25–7.38 (m, 4H,C₆H₄–N), 0.84–1.71 (m, 27H, Sn–C₄H₉) ppm. IR (KBr, cm⁻¹): v(C=N) 1601, v(Sn–C)_{as} 445, v(Sn–C)_s 425, v(Sn–S) 309.

2.2.3. $Ph_3Sn[S(C_7H_5N_4O)]$ (3)

The synthesis procedure was the same as 1. 1-(4-Hydroxyphenyl)-1*H*-tetrazole-5-thiol (0.194 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol) and Ph₃SnCl (0.385 g, 1 mmol), reaction time 12 h, temperature 45 °C. Recrystallized from hexane-dichloromethane. White crystal was formed. Yield, 72%. m.p. 184–186 °C. *Anal.* Calc. for C₂₅H₂₀N₄OSSn: C, 55.27; H, 3.71; N, 10.31. Found: C, 55.31; H, 3.76; N, 10.32%. ¹H NMR (90 MHz, CDCl₃): δ 7.18–7.37 (m, 4H,C₆H₄–N), 7.46–7.79 (m, 15H, Sn–C₆H₅) ppm. IR (KBr, cm⁻¹): v(C=N) 1599, v(Sn–C)_{as} 444, v(Sn–C)_s 409, v(Sn–S) 310.

2.2.4. $(PhCH_2)_3 Sn[S(C_7H_5N_4O)] \cdot 0.5C_2H_5OH \cdot 0.5H_2O$ (4)

The synthesis procedure was the same as 1. 1-(4-Hydroxyphenyl)-1*H*-tetrazole-5-thiol (0.194 g, 1 mmol), sodium ethoxide (0.068 g, 1 mmol) and (PhCH₂)₃SnCl (0.427 g, 1 mmol), reaction time 12 h, temperature 45 °C. Recrystallized from dichloromethane. White crystal was formed. The crystal suitable for X-ray diffraction was grown from ethanol (95%). Yield, 78%. m.p. 124–126 °C. *Anal.* Calc. for C₂₉H₃₀N₄O₂SSn: C, 56.42; H, 4.90; N, 9.08. Found: C, 56.47; H, 4.86; N, 9.14%. ¹H NMR (90 MHz, CDCl₃): δ 7.30 (m, 4H,C₆H₄–N), 6.88–7.15 (m, 15H, Sn–CH₂C₆H₅), 3.74 (m, 1H, CH₃CH₂-OH), 2.78 (s, 6H, Sn–CH₂C₆H₅), 1.25 (t, 1.5H, CH₃CH₂OH) ppm. IR (KBr, cm⁻¹): v(C=N) 1599, v(Sn–C)_{as} 450, v(Sn–C)_s 427, v(Sn–S) 309.

2.2.5. $Me_2Sn[S(C_7H_5N_4O)]_2 \cdot H_2O(5)$

The synthesis procedure was the same as 1. 1-(4-Hydroxyphenyl)-1*H*-tetrazole-5-thiol (0.388 g, 2 mmol), sodium ethoxide (0.136 g, 2 mmol) and Me₂SnCl₂ (0.220 g, 1 mmol), reaction time 12 h, temperature 45 °C. Recrystallized from ether–petroleum. White crystal was formed. The crystal suitable for X-ray diffraction was grown from ethanol (95%). Yield, 70%. m.p. 126–128 °C. *Anal.* Calc. for C₁₆H₁₈N₈O₃S₂Sn: C, 34.74; H, 3.28; N, 20.26. Found: C, 34.84; H, 3.23; N, 20.07%. ¹H

NMR (90 MHz, CDCl₃): δ 7.26–7.40 (m, 8H,C₆H₄–N), 1.42 (s, 6H, Sn–CH₃) ppm. IR (KBr, cm⁻¹): v(C=N) 1600, v(Sn–C)_{as} 476, v(Sn–C)_s 450, v(Sn–S) 310.

2.2.6. $(n-Bu)_2 Sn[S(C_7H_5N_4O)]_2$ (6)

The synthesis procedure was the same as **1**. 1-(4-Hydroxyphenyl)-1*H*-tetrazole-5-thiol (0.388 g, 2 mmol), sodium ethoxide (0.136 g, 2 mmol) and $(n-Bu)_2SnCl_2$ (0.304 g, 1 mmol), reaction time 12 h, temperature 45 °C. Recrystallized from ether–petroleum. White crystal was formed. Yield, 76%. m.p. 128–130 °C. *Anal.* Calc. for C₂₂H₂₈N₈O₂S₂Sn: C, 42.66; H, 4.56; N, 18.09. Found: C, 42.75; H, 4.49; N, 18.20%. ¹H NMR (90 MHz, CDCl₃): δ 7.20–7.37 (m, 8H,C₆H₄–N), 0.86–2.12 (m, 18H, Sn–C₄H₉) ppm. IR (KBr, cm⁻¹): *v*(C=N) 1600, *v*(Sn–C)_{as} 441, *v*(Sn–C)_s 425, *v*(Sn–S) 315.

2.2.7. $Ph_2Sn[S(C_7H_5N_4O)]_2$ (7)

The synthesis procedure was the same as **1**. 1-(4-Hydroxyphenyl)-1*H*-tetrazole-5-thiol (0.388 g, 2 mmol), sodium ethoxide (0.136 g, 2 mmol) and Ph₂SnCl₂ (0.344 g, 1 mmol), reaction time 12 h, temperature 50 °C. Recrystallized from ether–petroleum. White crystal was formed. Yield, 67%. m.p. 168–170 °C. *Anal.* Calc. for C₂₆H₂₀N₈O₂S₂Sn: C, 47.36; H, 3.06; N, 17.00. Found: C, 47.48; H, 2.91; N, 17.12%. ¹H NMR (90 MHz, CDCl₃): δ 7.20–7.33 (m, 8H,C₆H₄–N), 7.46–7.79 (m, 10H, Sn–C₆H₅) ppm. IR (KBr, cm⁻¹): v(C=N) 1601, v(Sn–C)_{as} 444, v(Sn–C)_s 415, v(Sn–S) 309.

2.2.8. $(PhCH_2)_2 Sn[S(C_7H_5N_4O)]_2$ (8)

The synthesis procedure was the same as 1. 1-(4-Hydroxyphenyl)-1*H*-tetrazole-5-thiol (0.388 g, 2 mmol), sodium ethoxide (0.136 g, 2 mmol) and (PhCH₂)₂SnCl₂ (0.372 g, 1 mmol), reaction time 12 h, temperature 45 °C. Recrystallized from ether–petroleum. White crystal was formed. Yield, 79%. m.p. 112–114 °C. *Anal.* Calc. for C₂₈H₂₄N₈O₂S₂Sn: C, 48.92; H, 3.52; N, 16.30. Found: C, 49.02; H, 3.59; N, 16.39%. ¹H NMR (90 MHz, CDCl₃): δ 7.17–7.42 (m, 8H, C₆H₄–N), 6.82–7.05 (m, 10H, Sn–CH₂C₆H₅), 3.52 (s, 4H, Sn–CH₂C₆H₅) ppm. IR (KBr, cm⁻¹): v(C=N) 1600, v(Sn–C)_{as} 440, v(Sn–C)_s 421, v(Sn–S) 310.

2.3. X-ray crystallographic studies of complexes 3, 4, 5 and 6

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 K α 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 SHELXL-97 and refined against F^2 by full-matrix least-squares using SHELXL-97. Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in Table 1.

Table 1

Crystal data and structure refinement parameters for complex 3, 4, 5 and $\boldsymbol{6}$

Complexes	3	4	5	6
Empirical formula	C25H20N4OSSn	$C_{29}H_{30}N_4O_2SSn$	$C_{16}H_{18}N_8O_3S_2Sn$	$C_{22}H_{28}N_8O_2S_2Sn$
Formula weight	543.20	617.32	553.19	619.33
Crystal system	triclinic	triclinic	orthorhombic	monoclinic
Space group	$P\overline{1}a$	$P\overline{1}$	Pnma	$P2_{1}/n$
Unit cell dimensions				
a (Å)	9.517(5)	10.533(5)	7.223(13)	14.964(12)
b (Å)	14.348(8)	12.313(6)	22.09(4)	9.548(8)
<i>c</i> (Å)	18.953(11)	24.147(11)	16.76(3)	20.233(16)
α (°)	107.796(8)	86.956(6)	90	90
β (°)	100.726(8)	88.200(7)	90	111.703(9)
γ (°)	102.442(8)	71.827(6)	90	90
V (Å ³)	2316(2)	2971(2)	2674(8)	2686(4)
Ζ	4	4	4	4
$D_{\rm c}~({\rm Mgm^{-3}})$	1.558	1.380	1.374	1.532
Absorption coefficient (mm ⁻¹)	1.218	0.961	1.140	1.142
F(000)	1088	1256	1104	1256
Crystal size (mm)	$0.32 \times 0.15 \times 0.11$	$0.55 \times 0.33 \times 0.25$	$0.29 \times 0.23 \times 0.16$	$0.41 \times 0.35 \times 0.09$
θ range (°)	1.56-25.03	1.69-25.03	1.84-25.02	2.39-25.02
Independent reflections	$8093 \ (R_{\rm int} = 0.0281)$	10345 ($R_{\rm int} = 0.0254$)	2323 ($R_{\rm int} = 0.1932$)	4652 ($R_{\rm int} = 0.0462$)
Data/restraints/parameters	8093/0/577	10345/5/675	2323/3/147	4652/0/316
Goodness-of-fit on F^2	0.925	1.063	0.904	0.956
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0408,$	$R_1 = 0.0413,$	$R_1 = 0.0706,$	$R_1 = 0.0537,$
	$wR_2 = 0.0937$	$wR_2 = 0.0981$	$wR_2 = 0.1319$	$wR_2 = 0.1317$
R indices (all data)	$R_1 = 0.0704,$	$R_1 = 0.0662,$	$R_1 = 0.1526,$	$R_1 = 0.0838,$
	$wR_2 = 0.1143$	$wR_2 = 0.1139$	$wR_2 = 0.1563$	$wR_2 = 0.1492$



Scheme 1.

3. Results and discussion

3.1. Syntheses of the complexes 1–8

The synthesis procedure is given in Scheme 1.

3.2. IR spectroscopic studies of the complexes 1-8

The explicit feature in the IR spectra of the eight complexes 1-8 is the absence of the band in the region $2550-2430 \text{ cm}^{-1}$, which appears in the free ligand as the v(S-H) vibration, thus indicating metal-ligand bond formation through this site. In the far-IR spectra, the absorption about 310 cm^{-1} region for all complexes 1–8, 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 $(300-400 \text{ cm}^{-1})$ [9,10]. In organotin compounds, the IR spectra can provide useful information concerning the geometry of the SnC_n moiety [11]. In the case of our compounds, for both di- and triorganotin(IV) derivatives, two bands were assigned to asymmetric and symmetric Sn-C vibrations. Thus suggesting nonlinear SnC₂ units for diorganotins and non-planar SnC₃ fragments for triorganotins, respectively. The middle intensity bands observed at about 1600 cm^{-1} in the spectra of all complexes have been assignable to v(C=N) according

to literatures [12,13], which suggested the coordinates of free ligand to these complexes is through sulfur atoms via thiol form.

3.3. ¹H NMR data of the complexes 1-8

¹H 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 ¹H NMR spectra show that the chemical shifts of the phenyl group $(Sn-C_6H_5)$ in complexes 3 and 7, 7.46-7.79 ppm, and those of methylene connected directly with tin in complexes 2, 4, 6 and 8, 1.71–3.52 ppm, upfield shift as compared with those of their corresponding precursors. All these data are similar to those cases appear in literature [14], 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 phenyl group connected with nitrogen atom and hydroxyl group (N–C₆H₄–OH) appears at 7.17–7.42 ppm for all complexes 1-8.

3.4. Crystal structures of complexes 3, 4, 5 and 6

3.4.1. $Ph_3Sn[S(C_7H_5N_4O)]$ (3)

For complex **3**, the asymmetric unit contains two monomers A and B (Fig. 1), which are crystallographically nonequivalent. The conformations of the two independent molecules A and B are almost the same, with only small differences in bond lengths and bond angles (see Table 2). The compound is formed by discrete molecules in which the tin atom is indeed bound to the sulfur atom of the tetrazolate, which together with the phenyl groups defines a distorted tetrahedron around



Fig. 1. Molecular structure of the complex 3.

Table 2 Selected bond lengths (Å) and bond angles (°) for complex ${\bf 3}$

Molecule A		Molecule B	
Bond lengths			
Sn(1)-C(8)	2.128(6)	Sn(2)–C(39)	2.122(6)
Sn(1)-C(20)	2.136(6)	Sn(2)-C(45)	2.129(5)
Sn(1)-C(14)	2.152(5)	Sn(2)-C(33)	2.138(6)
Sn(1)-S(1)	2.4760(17)	Sn(2)–S(2)	2.4726(17)
$Sn(1) \cdot \cdot \cdot N(4)$	3.330(6)	$Sn(2) \cdot \cdot \cdot N(8)$	3.487(6)
N(4)-C(1)	1.313(7)	N(8)-C(26)	1.315(7)
S(1)–C(1)	1.740(5)	S(2)–C(26)	1.727(6)
Bond angles			
C(8) - Sn(1) - C(20)	112.4(2)	C(39)-Sn(2)-C(45)	112.1(2)
C(8)-Sn(1)-C(14)	110.1(2)	C(45)–Sn(2)–C(33)	110.3(2)
C(20)-Sn(1)-C(14)	111.9(2)	C(39)-Sn(2)-C(33)	111.2(2)
C(8)-Sn(1)-S(1)	119.28(15)	C(39)–Sn(2)–S(2)	119.55(15)
C(20)-Sn(1)-S(1)	104.81(15)	C(33)–Sn(2)–S(2)	108.24(16)
C(14)-Sn(1)-S(1)	97.31(15)	C(45)-Sn(2)-S(2)	94.07(14)
C(1)-S(1)-Sn(1)	99.83(18)	C(26)-S(2)-Sn(2)	105.8(2)
N(4)-C(1)-S(1)	126.9(4)	N(8)-C(26)-S(2)	126.9(4)

the tin atom. There is also an intramolecular tin-nitrogen short contact $(Sn(1) \cdots N(4) 3.330(6))$ Å for A and $Sn(2) \cdots N(8)$ 3.487(6) Å for B), shorter than the sum of the van der Waals radii (3.75 A) [15]. The C-Sn-C bond angles are close to the theoretical tetrahedral angle but the C-Sn-S bond angles more acute or obtuse than it, largest deviations occurring in C(8)-Sn(1)-S(1)119.28(15)° for A and C(39)–Sn(2)–S(2) 119.55(15)° for B; C(14)–Sn(1)–S(1) 97.31(15)° for A and C(45)–Sn(2)– S(2) 94.07(14)° for B. This is possibly due to the secondary interaction $(Sn(1) \cdots N(4) \text{ for } A \text{ and } Sn(2) \cdots N(8))$ for B). The Sn–S bond length (Sn(1)–S(1) 2.4760(17) Å)for A and Sn(2)–S(2) 2.4726(17) Å for B) lies toward the middle of the range reported for triphenyltin heteroarenethiolates (2.405–2.481 Å) [16,17] and approach the sum of the covalent radii of tin and sulfur (2.42 A) [18]. In the tetrazolate, the C–S bond distance (C(1)-S(1))1.740(5) Å for A and C(26)–S(2) 1.727(6) Å for B) lies between the average value for 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) [19], suggesting that the C-S bond has some double-bond character in the deprotonated tetrazole.

Moreover, the discrete molecules of complex 3 associate in a 1D ribbon by hydrogen bonds (O(1)– H(1)···N(3) 2.911 Å, O(1)–H(1)–N(3) 157.88° for A; O(2)–H(2)···N(7) 2.857 Å, O(1)–H(1)–N(3) 148.77° for B). A view of the extended ribbon is shown in Fig. 2.

3.4.2. $(PhCH_2)_3 Sn[S(C_7H_5N_4O)] \cdot 0.5C_2H_5OH \cdot 0.5H_2O$ (4)

The X-ray diffraction investigation of complex 4 has shown two independent molecules in the unit cell, which are alternatively associated in a polymeric chain through intermolecular dative $N \rightarrow Sn$ bonds. The differences in the bond lengths and angles within the two molecules



Fig. 2. perspective view showing the 1D ribbon of the complex 3.

might be the result of packing effects in the crystal. The molecular structure of complex **4** is shown in Fig. 3. Selected bond lengths and angels are listed in Table 3.

In the monomeric units the tetrazolethiolato ligand is primarily coordinated through the sulfur atom: Sn(1)-S(1) 2.5812(14) A, Sn(2)-S(2) 2.6260(15) A. They are slightly longer than the sum of the covalent radii (2.42 A) [18]. This is consistent with the thiol form of the ligand in the previously reported molecular structure of Bz₃SnSCN₄Ph [7c], and in contrast to the primary coordination suggested on the basis of IR data. It is similar to the complex 3, there are also secondary intramolecular tin-nitrogen short contacts $(Sn(1) \cdots N(4) 3.289(4))$ A and $Sn(2) \cdots N(8) 3.311(4)$ A), shorter than the sum of the van der Waals radii (3.75 A) [15]. In the crystal, the molecules of complex 3 associated in polymeric chains through intermolecular, dative tin-nitrogen bonds (Sn(1)–N(7A) 2.604(4) Å and Sn(2)–N(3) 2.557(4) Å). This leads to an increase in the tin coordination number to 5. The coordination polyhedron around the central tin atom can be described as distorted trigonal bipyramidal. The methylene carbons are in equatorial positions and the axial ones are occupied by the sulfur atom of the ligand and a nitrogen atom of a neighboring molecule, respectively.

The component $(PhCH_2)_3Sn[S(C_7H_5N_4O)]$ crystallizes with 0.5 molecules of ethanol and 0.5 molecules of water while the water molecule shows no short contacts, the ethanol is involved in two hydrogen bonds, both as a donor (O(3)-H(3A)···O(2) 2.735 A, O(3)-H(3A)-O(2) 169.33°) and as an acceptor $(O(2)-H(33)\cdots O(3) 2.735)$ A, O(2)-H(33)-O(3) 168.41°). Moreover, the polymeric chain in the unit cell associates in a dimeric form with another chain through the $O(1)-H(5)\cdots S(1)$ ($O(1)\cdots$ S(1) 3.338 A, O(1)-H(5)-S(1) 155.93°) hydrogen bond. The crystal structure of 4 shows ring-stacking interactions, each hydroxyphenyl group involved O-H···S hydrogen bond is arrange face-to-face at a distance of 3.744 A and shows significant π - π stacking interactions, as reported in the literatures [20]. A view of the unit cell of 4 showing hydrogen bonds and $\pi-\pi$ stacking interactions is given in Fig. 4.



Fig. 3. Molecular structure of the complex 4.

Table 3											
Selected	bond	lengths	(Å)	and	bond	angles	(°)	for	comple	x 4	4

Intramolecular			
Bond lengths			
Sn(1)–C(8)	2.144(5)	Sn(2)–C(36)	2.154(5)
Sn(1)–C(15)	2.149(4)	Sn(2)–C(43)	2.159(5)
Sn(1)–C(22)	2.166(5)	Sn(2)–C(50)	2.163(5)
Sn(1)-S(1)	2.5812(14)	Sn(2)–S(2)	2.6260(15)
$Sn(1) \cdot \cdot \cdot N(4)$	3.289(4)	$Sn(2) \cdot \cdot \cdot N(8)$	3.311(4)
N(4)-C(1)	1.326(5)	N(8)–C(29)	1.327(6)
S(1)–C(1)	1.729(4)	S(2)–C(29)	1.706(5)
Bond angles			
C(8)-Sn(1)-C(15)	116.3(2)	C(36)-Sn(2)-C(43)	127.6(2)
C(8)-Sn(1)-C(22)	124.16(19)	C(36)-Sn(2)-C(50)	116.0(2)
C(15)-Sn(1)-C(22)	114.9(2)	C(43)-Sn(2)-C(50)	115.2(2)
C(8)-Sn(1)-S(1)	96.32(15)	C(36)-Sn(2)-S(2)	94.09(14)
C(15)-Sn(1)-S(1)	95.73(14)	C(43)-Sn(2)-S(2)	97.19(15)
C(22)-Sn(1)-S(1)	99.43(14)	C(50)–Sn(2)–S(2)	89.04(14)
C(1)-S(1)-Sn(1)	98.41(15)	C(29)-S(2)-Sn(2)	100.00(16)
N(4)-C(1)-S(1)	128.0(3)	N(8)-C(29)-S(2)	126.1(4)
Intermolecular			
Bond lengths			
Sn(1)–N(7A)	2.604(4)	Sn(2)–N(3)	2.557(4)
Bond angles			
N(7A) - Sn(1) - C(8)	85.04(18)	N(3)-Sn(2)-C(36)	87.85(17)
N(7A)-Sn(1)-C(15)	80.05(17)	N(3)-Sn(2)-C(43)	83.69(17)
N(7A)-Sn(1)-C(22)	83.06(17)	N(3)-Sn(2)-C(50)	87.72(16)
N(7A)–Sn(1)–S(1)	175.73(10)	N(3)–Sn(2)–S(2)	176.71(9)

3.4.3. $Me_2Sn[S(C_7H_5N_4O)]_2 \cdot H_2O(5)$ and $(n-Bu)_2Sn-[S(C_7H_5N_4O)]_2$ (6)

Selected bond lengths and bond angles for 5 and 6 are given in Tables 4 and 5, respectively. The molecular structures of 5 and 6 are shown in Figs. 5 and 6. In contrast with the triorganotin derivatives mentioned above, the coordination of diorganotin derivatives is different. In both complexes 5 and 6, the tin atom establishes covalent bonds with the two heterocyclic sulfur

atoms, apart from the two methyl or methylene carbons, and interacts intramolecularly with the unsubstituted nitrogen atoms of the ring thioamide moiety (N(4), N(4A) for **5** and N(4), N(8) for **6**). The Sn–C bond lengths (2.050(15) and 2.111(14) Å in **5**; 2.134(6) and 2.150(7) Å in **6**) are quite close to those previously described in the literature [6]. The Sn–S bond distances (2.505(4) Å in **5**; 2.4740(19) and 2.4716(19) Å in **6**) are very close to the sum of the corresponding covalent radii



Fig. 4. Packing diagram of complex 4, showing hydrogen bonds and π - π stacking interactions.

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

Bond lengths			
Sn(1)–C(9)	2.050(15)	Sn(1)–N(4)	2.704(8)
Sn(1)–C(8)	2.111(14)	N(4)–C(1)	1.287(10)
Sn(1)–S(1)	2.505(4)	S(1)–C(1)	1.724(9)
Bond angles			
C(9)-Sn(1)-C(8)	134.8(6)	S(1A)-Sn(1)-N(4)	151.95(16)
C(9)-Sn(1)-S(1)	103.6(3)	S(1)–Sn(1)–N(4)	60.59(18)
C(8)-Sn(1)-S(1)	107.5(3)	C(1)-N(4)-Sn(1)	89.9(5)
S(1A)-Sn(1)-S(1)	91.50(17)	C(1)-S(1)-Sn(1)	88.1(3)
C(9)-Sn(1)-N(4)	87.0(2)	N(4)-C(1)-S(1)	121.3(6)
C(8)-Sn(1)-N(4)	80.72(19)		

(2.42 Å) [18], and is similar to the distances found in other Sn(IV) complexes of the terazolethiolato with metal-sulfur primary bonds, viz. 2.474(3)-2.614(5) Å. It





Fig. 5. Molecular structure of the complex 5.

is worth noting that in complex 5 the Sn–N bond length is shorten (2.704(8) Å) than those reported in analogous diorganotin derivatives of 1-phenyl-1*H*-tetrazole-5-



Fig. 6. Molecular structure of the complex 6.



Fig. 7. perspective view showing the 2D network of the complex 5.

thilato (2.975(5) [7a] and 2.947(4) Å [7b]). But in complex **6** the Sn–N bond lengths are longer (3.154(5) Å and 3.175(5) Å), although they all lie within the sum of their respective van der Walls radii (3.75 Å).

The establishment of such intramolecular tin-nitrogen interactions brings the present structure rather far from a regular tetrahedron, i.e. despite the fact that the complexes' core angles (S(1)-Sn(1)-C(9)) $103.6(3)^{\circ}$ and S(1)–Sn(1)–C(8) $107.5(3)^{\circ}$ for 5; S(1)– Sn(1)-C(15) 107.78(18)°, S(1)-Sn(1)-C(19) 107.83(17)°, S(2)-Sn(1)-C(15) 108.55(17)° and S(2)-Sn(1)-C(19) $109.64(17)^{\circ}$ for 6) are close the expected tetrahedral value, the C-Sn-C angle (134.8(6)° for 5 and 129.2(3)° for 6) is more obtuse due to the occurrence of the Sn-N secondary interactions in a plane bisecting it, with the concomitant decrease of the S-Sn-S angle $(91.50(17)^{\circ} \text{ for } 5 \text{ and } 84.87(8)^{\circ} \text{ for } 6)$. The geometry around the metal may thus be viewed, alternatively, as a distorted trapezoidal bipyramid, with the two methyl or methylene carbons in bent axial positions and the trapezoidal plane being defined by the two Sn-S covalent bonds and the two Sn-N secondary interactions.

In the complex 5, the hydrogen bonding between the hydroxyl of ligand and nitrogen atom adjacent molecule (O(1)-H(1)···N(3) 2.750 Å, O(1)-H(1)-N(3) 167.89°) is recognized, which contributes to construct the 2D network of **5** (see Fig. 7). It is worthy noting that no short contacts have been found though the main component Me₂Sn[S(C₇H₅N₄O)]₂ crystallizes with one water molecule. Moreover, ring-stacking interactions are shown in the complex **5**. The orientation is such that the phenyl ring substituents 'face' other phenyl ring on neighboring layer at a distance of 3.677 Å and show significant π - π stacking interactions [20]. A view of the crystal packing along the *a* axis is shown in Fig. 8. As for **6**, the hydrogen bonds are also found (O(1)–H(1)···N(3) 2.892 Å, O(1)–H(1)– N(3) 138.73° and O(2)–H(2)···N(7) 2.886 Å, O(1)– H(1)–N(3) 139.08°) and its discrete molecules are



Fig. 8. Packing diagram of complex 5, showing π - π stacking interactions.



Fig. 9. perspective view showing the 1D ribbon of the complex 6.

connected to 1D ribbon through hydrogen bonding (see Fig. 9).

4. Conclusions

A series of organotin(IV) complexes based on 1-(4-hydroxyphenyl)-1H-tetrazole-5-thiol have been synthesized and characterized. Detailed studies on the structures and spectra of these complexes indicate that there exist such an inclination that the structures of those dialkyltin complexes are likely to construct distorted trapezoidal bipyramidal geometry and those trialkyltin complexes are apt to have diverse geometry. The complex 3 is formed by discrete molecules but the molecules of complex 4 associates in polymeric chains through intermolecular, dative $N \rightarrow Sn$ bonds. Such differences may attribute to the fact that the stereoconstraints of PhCH₂-groups are smaller than that of Ph-groups. Consequently, it can be concluded 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-220182, 222015, 222017, 220175. 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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