

Syntheses and crystal structures of four new organotin complexes with Schiff bases containing triazole

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Abstract

Four new organotin complexes, namely $[(\text{Bu}_2\text{Sn})_2\text{O}(\text{EtO})(\text{L1})]_2$ (**1**), $[(\text{Bu}_2\text{Sn})_2\text{O}(\text{EtO})(\text{L2})]_2$ (**2**), $[(\text{Bu}_2\text{Sn})_2\text{O}(\text{EtO})(\text{L3})]_2$ (**3**) and $[\text{Ph}_3\text{Sn}(\text{L4})] \cdot 0.5\text{H}_2\text{O}$ (**4**), were obtained by reactions of Bu_2SnO and Ph_3SnOH with 4-phenylideneamino-3-methyl-1,2,4-triazole-5-thione (HL1), 4-furfuralideneamino-3-methyl-1,2,4-triazole-5-thione (HL2), 4-(2-thienylideneamino)-3-ethyl-1,2,4-triazole-5-thione (HL3) and 4-(3,5-di-*t*-butylsalicylideneamino)-3-ethyl-1,2,4-triazole-5-thione (HL4). Compounds **1–4** were characterized by elemental analysis, IR spectra and their structures were determined by single-crystal X-ray diffraction methods. Complexes **1–3** show similar structures containing a Sn_4O_4 ladder skeleton in which each of the *exo* tin atoms is bonded to the N atom of a corresponding thione-form deprotonated ligand. Complex **4** shows a mononuclear structure in which the tin atom of triphenyltin group is coordinated by the S atom of a thiol-form L4^- anion.

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Keywords: Triazole; Organotin; Schiff base

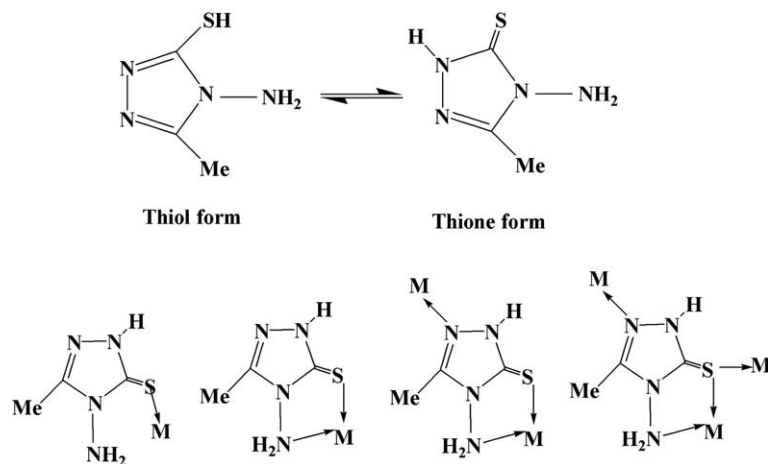
1. Introduction

The organotin complexes have been of great interest for many years because of their versatile bonding modes and biological perspective [1,2] as well as their industrial and agricultural applications [3,4]. A variety of organotin complexes are now known to show antitumor activity [5] and some others are well established for use as fungicides, biocides and pesticides [6–8]. Triazole derivatives also display a broad range of biological activity, showing potential applications as antitumor, antibacterial, antifungal and antiviral agents [9,10]. One representative compound for this class is 3-alkyl-4-amino-1,2,4-triazole-5-thione (HAATT) which presents in solution thione–thiol tautomerism whereas in the solid state it presents only the thione

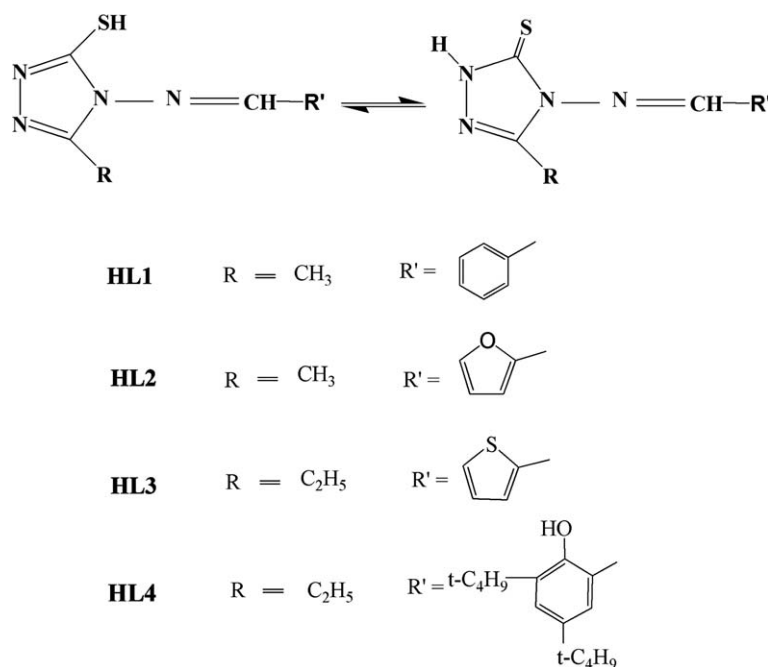
form [11]. As shown in Scheme 1, this ligand can act as monodentate mode through the sulfur atom, or bidentate chelating mode through the sulfur and the amine nitrogen atoms, or tridentate chelating N,S and bridging through the endocyclic nitrogen atom, and finally μ_3 -bridging mode [11,12]. Based on the biological activity and versatile bonding modes of HAATT, further functionalization of the amine or R groups can modify the activity of the compound. The syntheses and the coordination chemistry of the Schiff bases condensed from 3-alkyl-4-amino-1,2,4-triazole-5-thione and various aldehydes have been studied, and the crystal structures of several Schiff bases were determined [13], but there have been no reports on the crystal structures of the metal complexes. In this work, four Schiff bases that differ in the identity of the alkyl R group on the triazole ring and the R' group on the amine substituent have been synthesized (Scheme 2), and their reactions with organotin have been studied.

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Scheme 1.



Scheme 2.

Four novel diorganotin and triorganotin complexes were obtained. All complexes were characterized by elemental analysis, IR spectra and X-ray crystallography.

2. Experimental

2.1. Materials and measurements

All reagents were commercially available, and were used without further purification. Elemental analyses were carried out with a Perkin–Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in range 4000–400 cm⁻¹ on a Mattson Alpha-Centauri spectrometer.

2.1.1. Synthesis of thiocarbohydrazide

Thiocarbohydrazide was prepared according to the reported procedure [14].

2.1.2. Synthesis of 4-amino-3-methyl-1,2,4-triazole-5-thione [15,16]

A mixture of thiocarbohydrazide (3.18 g, 0.03 mol) in glacial acetic acid (10 ml) was heated under reflux for 4 h. The left glacial acetic acid was removed. After cooling down to room temperature, the solid product was separated, and recrystallized from water (yield 70%).

2.1.3. Synthesis of 4-amino-3-ethyl-1,2,4-triazole-5-thione

The synthesis procedure was the same as Section 2.1.2. Yield 75%.

2.1.4. Synthesis of HL1, HL2, HL3 and HL4

Synthesis of HL1. Concentrated sulfuric acid (0.75 ml) was added to a mixture of 4-amino-3-methyl-1,2,4-triazole-5-thione (0.13 g, 1 mmol) and benzaldehyde (0.11 g, 1 mmol) in ethanol (20 ml). After stirring for 1 h, the yellow

precipitate was collected by filtration, washed with ethanol, and dried at room temperature.

HL2, HL3 and HL4 were synthesized analogously.

2.1.5. Synthesis of organotin complexes

2.1.5.1. Synthesis of $[(Bu_2Sn)_2O(EtO)(L1)]_2$ (1**).** After a mixture of *n*-Bu₂SnO (248 mg, 1 mmol) and HL1 (109 mg, 0.5 mmol) in a mixed solvent of benzene (20 ml) and ethanol (10 ml) had been heated under reflux for 8 h, the resulting solution was filtered. Yellow crystals of **1** were obtained by evaporating the filtrate at room temperature. Yield 50%. Analysis: Found (Calc. for $[(Bu_2Sn)_2O(EtO)(L1)]_2$): C, 45.11 (45.19); H, 6.71 (6.77); N, 7.56 (7.53)%.

2.1.5.2. Synthesis of $[(Bu_2Sn)_2O(EtO)(L2)]_2$ (2**).** **2** was prepared according to the method for **1** by a reaction of *n*-Bu₂SnO (248 mg, 1 mmol) and HL2 (104 mg, 0.5 mmol). Yield 45%. Analysis: Found (Calc. for $[(Bu_2Sn)_2O(EtO)(L2)]_2$): C, 42.44 (42.54); H, 6.53 (6.59); N, 7.61 (7.63)%.

2.1.5.3. Synthesis of $[(Bu_2Sn)_2O(EtO)(L3)]_2$ (3**).** **3** was also prepared according to the method for **1** by a reaction of *n*-Bu₂SnO (248 mg, 1 mmol) and HL3 (119 mg, 0.5 mmol). Crystals of **3** were obtained by recrystallization from a mixture of petroleum ether and ethanol. Yield 53%. Analysis: Found (Calc. for $[(Bu_2Sn)_2O(EtO)(L3)]_2$): C 42.41(42.44), H 6.53(6.59), N 7.39(7.33)%.

2.1.5.4. Synthesis of $[Ph_3Sn(L4)] \cdot 0.5H_2O$ (4**).** After a mixture of Ph₃SnOH (371 mg, 1 mmol) and HL4 (359 mg, 1 mmol) in benzene was refluxed for 8 h, the resulting yellow solution was filtered. Yellow crystals of **4** were obtained by evaporating the filtrate at room temperature. Yield 62%. Analysis: Found (Calc. for $[Ph_3Sn(L4)] \cdot 0.5H_2O$): C, 61.16 (61.85); H, 6.18 (6.03); N, 7.75 (7.80)%.

2.2. X-ray crystallographic studies of **1**, **2**, **3** and **4**

Experimental details of the X-ray analyses are provided in Table 1. Diffraction intensities for **1–4** were collected on a Bruker Apex CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å). The structures were solved by direct methods using SHELXS-97 [17] and refined with full-matrix least-squares techniques using the SHELXL-97 [18] program within WINGX [19]. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms on carbon atoms were generated geometrically.

3. Results and discussion

3.1. Synthesis and spectra

When *n*-Bu₂SnO was treated with 0.5 equiv. of HL1, HL2 and HL3 in a mixture of benzene and ethanol (2:1), $[(Bu_2Sn)_2O(EtO)(L1)]_2$ (**1**), $[(Bu_2Sn)_2O(EtO)(L2)]_2$ (**2**) and $[(Bu_2Sn)_2O(EtO)(L3)]_2$ (**3**) were isolated, respectively. The suitable crystals for X-ray analysis were obtained by evaporating the corresponding solutions at room temperature. $[Ph_3Sn(L4)] \cdot 0.5H_2O$ (**4**) was obtained by the reaction of Ph₃SnOH with equivalent of HL4.

Each of the IR spectra of **1**, **2** and **3** shows absorption at 1254–1259 cm⁻¹ which can be attributed to N=N=C vibration. The bands of $\nu(N-H)$ occurring at about 3100 cm⁻¹ in free ligands disappear, indicating metal–ligand bond formation through this site. The absorptions at about 1250 cm⁻¹ can be assigned to $\nu(C=S)$. Their existences also indicate that the primary bonds of the ligand to tin atoms are through N atom on the triazole ring. The strong absorptions at 2955 cm⁻¹ are ascribed to the vibration of –CH₂– groups. In the IR spectrum of **4**, the $\nu(C=S)$ vibration of HL4 in about 1250 cm⁻¹ disappears, and the new absorption at 729 cm⁻¹ can be assigned to $\nu(C=S)$, indicating that L4⁻ is coordinated to tin atom through sulfur atom via thiolate form [20].

Table 1
Crystal data for compounds **1–4**

	1	2	3	4
Empirical formula	C ₅₆ H ₁₀₀ N ₈ O ₄ S ₂ Sn ₄	C ₅₂ H ₉₆ N ₈ O ₆ S ₂ Sn ₄	C ₅₄ H ₁₀₀ N ₈ O ₄ S ₄ Sn ₄	C ₃₇ H ₄₃ N ₄ O _{1.5} SSn
Formula weight	1488.32	1468.25	1528.42	718.50
Crystal size (mm)	0.278 × 0.185 × 0.068	0.316 × 0.184 × 0.122	0.356 × 0.234 × 0.178	0.289 × 0.248 × 0.146
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	12.6661(5)	12.6881(5)	24.389(4)	9.397(5)
<i>b</i> (Å)	15.9642(7)	15.7729(7)	11.519(2)	13.252(5)
<i>c</i> (Å)	17.8316(8)	17.5699(8)	25.179(4)	14.815(5)
α (°)	90	90	90	83.351(5)
β (°)	106.441(1)	107.642(5)	90.503(2)	82.450(5)
γ (°)	90	90	90	80.757(5)
Volume (Å ³)	3458.2(3)	3351(2)	7074(2)	1797(1)
<i>Z</i>	2	2	4	2
<i>R</i> _{int}	0.0629	0.0599	0.0826	0.0535
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0336	0.0339	0.0851	0.0539
<i>wR</i> ₂ (all data)	0.0661	0.0686	0.2654	0.1469

3.2. Crystal structures

Selected bond lengths and bond angles for **1–4** are given in Table 2. The structures of **1–3** are shown in Figs. 1–3, respectively. Compounds **1–3** possess similar Sn₄O₄ ladder structures. The ladder structure contains two kinds of Sn atoms. The *exo* Sn center shows a five-coordinate trigonal bipyramidal geometry composed of two C atoms, one μ_3 -O²⁻ atom, one μ_2 -EtO⁻ group and one N atom from L⁻ anion. The EtO⁻ and the N of L⁻ occupy the axial sites of the distorted trigonal bipyramidal geometry. For the *endo* Sn center, there is a weak interaction between another N atom on the triazole ring and the *endo* tin atom. So the *endo* Sn atom can be regarded as a six-coordinate center, showing distorted octahedral geometry.

For compound **1**, the axial–Sn–axial angle of *exo* Sn atom is O(1)–Sn(1)–N(1) 159.02°. The Sn(1)–N(1) bond length of 2.248 Å is similar to the reported values in the related compounds [21]. The distance of *endo* Sn(2)–N(2A) (2.837 Å) is midway between the sums of the covalent radii and van der Waals radii of tin and nitrogen (2.15–3.74 Å) [22,23], and this interaction can be regarded as a weak coordination bond. In addition, the C–S distance of 1.675 Å is similar to the reported C=S bond length [24]. All above information shows that the primary bond of the ligand to the tin atom is through the amido N atom, but the sulfur atom does not coordinate to any tin atoms.

For compound **2**, the ligand is not substantially different in the triazole moiety, however the amine substituent on the triazole is different. The bond length of Sn(1)–N(3) of 2.259 Å is slightly longer than that of **1** (2.248 Å), and the interatomic distance between Sn(2A) and N(4) is 2.800 Å. Like compound **1**, the *exo* Sn atom is five-coordinate, showing a distorted trigonal bipyramidal geometry with O(2)–Sn(1)–N(3) being 159.11°.

As exhibited in Fig. 3, HL3 differs from HL1 and HL2 in having an ethyl group not methyl group on the triazole ring and having a thienyl group on the substituted amino group, and there are two kinds of **3** molecules in the crystal structure. The structures of these two molecules are almost the same with slight differences in bond lengths and bond angles. The axial–Sn–axial angles of the *exo* Sn atoms are O(1)–Sn(1)–N(4) 160.0° and O(3)–Sn(3)–N(8) 159.3° respectively, showing the distorted trigonal bipyramidal geometry. The Sn(*exo*)–N bond lengths of the two molecules are Sn(1)–N(4) (2.227 Å) and Sn(3)–N(8) (2.249 Å). The Sn(*endo*)–N interatomic distances are 2.928 and 2.824 Å, respectively. Furthermore, there are remarkable differences between the C–S bond distances of the two molecules (1.678 and 1.705 Å).

Several compounds containing dimeric tetraorganodis-tannoxane skeleton [R₂Sn(μ-X)OR₂Sn(Y)]₂ (X and Y = univalent anions) have been reported [25]. For compounds where X = OH, Cl, I or NCS; Y = OH, Cl or EtO, their structures are shown in Scheme 3 [26]. Each of compounds **1–3** has a similar structure, and compounds

1–3 are the first examples of this type containing amido and ethoxide groups.

As shown in Fig. 4, compound **4** shows a mononuclear structure. In contrast to compounds **1–3**, L₄⁻ anion exists in thiol form in **4**, and coordinates to tin atom through the thiol S atom not the nitrogen atom on the triazole ring. The tin atom shows a distorted tetrahedral geometry. The angles C(26)–Sn(1)–C(24), C(26)–Sn(1)–S(2) and C(24)–Sn(1)–S(2) are wider than the ideal tetrahedral angle; and C(26)–Sn(1)–C(32), C(24)–Sn(1)–C(32) and especially C(32)–Sn(1)–S(2) are narrower than the ideal tetrahedral angle. The deviation from the regular tetrahedral geometry may result from steric hindrance and different electronegativities of the ligand attached to the tin atom. The Sn(1)–S(2) bond distance (2.459 Å) is similar to the reported values for triphenyltin thiolates [27,28]. The C(34)–S(2) distance (1.726 Å) is consistent with the values in triphenyltin derivatives with thiolate ligands [29]. In addition, there exist lattice water molecules in the structure of **4**. The water and hydroxyl group of the ligand are potential hydrogen-bonding sites. There is an intramolecular O–H···N hydrogen bond, and the lattice water molecule is hydrogen-bonded to one N atom on the triazole ring. The hydrogen bond distances are listed in Table 3.

The coordination modes of 3-alkyl-4-amino-1,2,4-triazole-5-thione (HAATT) with the divalent first row transition metals Mn–Zn have been studied in detail [11,12]. HAATT tends to coordinate to the metal ion in bidentate chelating mode via the thione and amine substituents on the triazole ring. Since most syntheses were carried out in acidic media, HAATT presents as neutral thione form in the complexes. No complexes containing deprotonated [AATT]⁻ ligand have been reported. It is very interesting to investigate the coordination chemistry of larger triazole derivatives, such as the four molecules in this study, that have organic functional groups on the amine N atom. As shown in Scheme 2, ligand in this work (HL) presents in solution thione–thiol tautomerism whereas in the solid state it presents only the thione form [13]. In principle, HL can coordinate to metal ion in neutral form (HL) or deprotonated form (L⁻), and both neutral form and deprotonated form can exist in thiol or thione form (Schemes 2 and 4). There are various possible coordination modes for both thiol and thione ligands (Scheme 5). Thus single crystal structure determination is necessary to investigate the true coordination modes of the ligands. Although the coordination interaction between such ligands and transition metals has been studied [13], no crystal structures have been determined. In this work, due to the basicity of organotin reactants, ligands exist as deprotonated anions in compounds **1–4**. For compounds **1–3**, L⁻ anions exist in thione-form. There are two possible coordination modes for thione-form L⁻ anions: I-a and I-b (Scheme 5). The crystal structures reveal that L⁻ anions coordinate to tin atom in a monodentate mode (I-a in Scheme 5). Like the structures of free Schiff base ligands [13], in each case of **1–3** the conformation adopted by the L⁻ ligand in the solid

Table 2
Selected bond distance (Å) and bond angles (°) for **1** and **2**^a

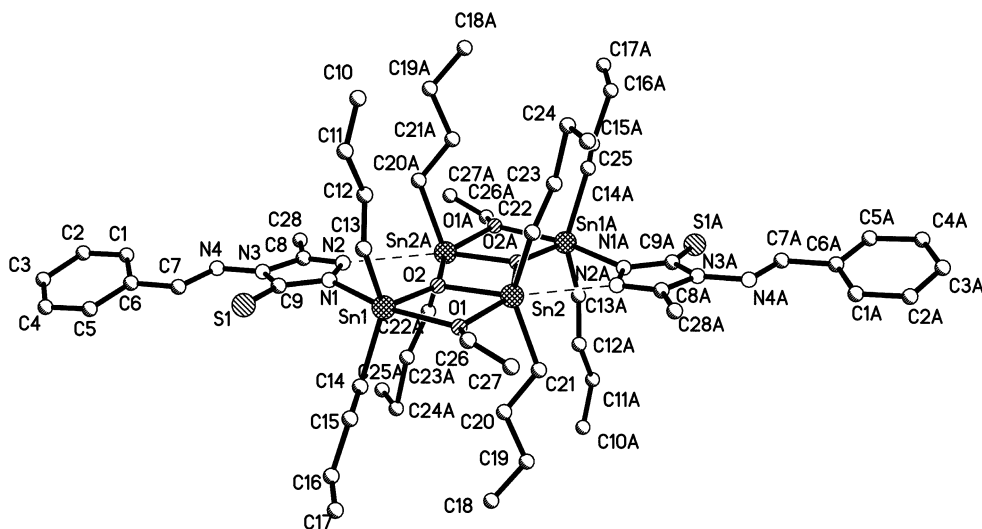
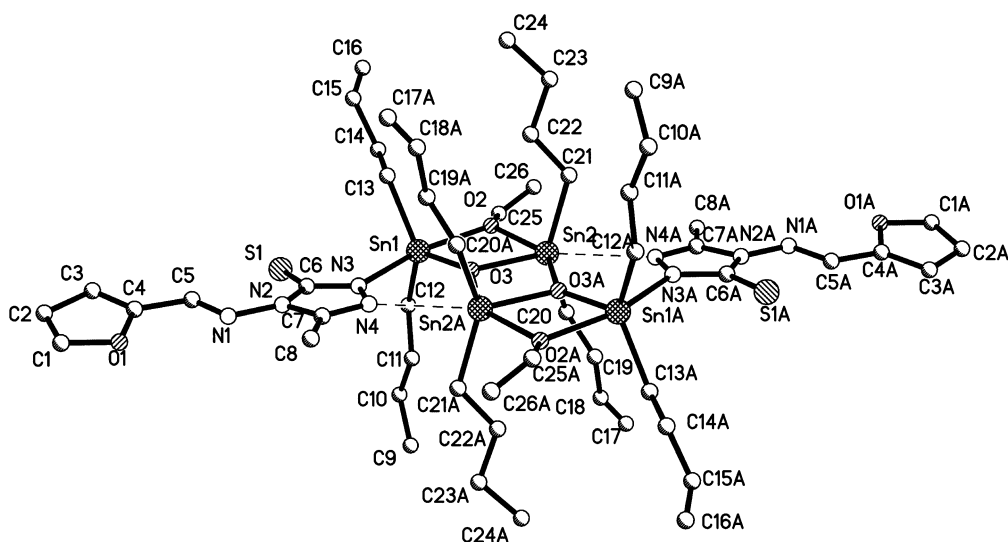
<i>Compound 1</i>			
C(9)–S(1)	1.675(4)	N(1)–N(2)	1.375(4)
N(3)–N(4)	1.393(4)	C(13)–Sn(1)	2.104(5)
C(14)–Sn(1)	2.155(4)	C(21)–Sn(2)	2.130(4)
C(22)–Sn(2)	2.119(4)	O(1)–Sn(1)	2.188(2)
O(2)–Sn(1)	2.032(2)	O(1)–Sn(2)	2.237(2)
O(2)–Sn(2)	2.078(2)	Sn(2)–O(2)#1	2.115(2)
N(1)–Sn(1)	2.248(3)		
O(2)–Sn(1)–C(13)	114.08(16)	O(2)–Sn(1)–C(14)	112.59(14)
C(13)–Sn(1)–C(14)	133.22(19)	O(2)–Sn(1)–O(1)	74.31(9)
C(13)–Sn(1)–O(1)	94.41(14)	C(14)–Sn(1)–O(1)	94.96(13)
O(2)–Sn(1)–N(1)	84.73(10)	C(13)–Sn(1)–N(1)	95.09(15)
C(14)–Sn(1)–N(1)	92.09(14)	O(1)–Sn(1)–N(1)	159.02(10)
O(2)–Sn(2)–C(22)	108.08(13)	O(2)–Sn(2)–O(2)#1	74.38(9)
C(22)–Sn(2)–O(2)#1	101.23(13)	O(2)–Sn(2)–C(21)	111.47(13)
C(22)–Sn(2)–C(21)	138.82(17)	O(2)#1–Sn(2)–C(21)	99.96(13)
O(2)–Sn(2)–O(1)	72.41(8)	C(22)–Sn(2)–O(1)	89.10(13)
O(2)#1–Sn(2)–O(1)	146.79(9)	C(21)–Sn(2)–O(1)	92.08(13)
<i>Compound 2</i>			
S(1)–C(6)	1.668(5)	N(2)–N(1)	1.390(4)
N(3)–N(4)	1.387(4)	Sn(1)–C(12)	2.093(5)
Sn(1)–C(13)	2.128(5)	Sn(2)–C(20)	2.102(5)
Sn(2)–C(21)	2.118(4)	Sn(1)–O(3)	2.023(2)
Sn(1)–O(2)	2.184(3)	Sn(2)–O(3)	2.087(2)
Sn(2)–O(3)#1	2.112(2)	Sn(2)–O(2)	2.246(3)
Sn(1)–N(3)	2.259(3)		
O(3)–Sn(2)–C(20)	106.70(15)	O(3)–Sn(2)–O(3)#1	74.62(10)
C(20)–Sn(2)–O(3)#1	101.91(16)	O(3)–Sn(2)–C(21)	111.57(15)
C(20)–Sn(2)–C(21)	139.51(19)	O(3)#1–Sn(2)–C(21)	100.44(14)
O(3)–Sn(2)–O(2)	71.14(9)	C(20)–Sn(2)–O(2)	88.13(16)
O(3)#1–Sn(2)–O(2)	146.75(9)	C(21)–Sn(2)–O(2)	91.30(15)
O(3)–Sn(1)–C(12)	114.91(19)	O(3)–Sn(1)–C(13)	113.04(14)
C(12)–Sn(1)–C(13)	131.9(2)	O(3)–Sn(1)–O(2)	74.66(10)
C(12)–Sn(1)–O(2)	94.10(17)	C(13)–Sn(1)–O(2)	94.87(15)
O(3)–Sn(1)–N(3)	84.48(12)	C(12)–Sn(1)–N(3)	95.66(18)
C(13)–Sn(1)–N(3)	92.28(16)	O(2)–Sn(1)–N(3)	159.11(12)
<i>Compound 3</i>			
S(2)–C(6)	1.678(12)	S(4)–C(33)	1.705(12)
Sn(1)–C(13)	2.124(12)	Sn(3)–C(40)	2.124(12)
Sn(1)–C(14)	2.136(12)	Sn(3)–C(41)	2.151(13)
Sn(2)–C(22)	2.097(12)	Sn(4)–C(49)	2.096(13)
Sn(2)–C(21)	2.121(12)	Sn(4)–C(48)	2.133(13)
Sn(1)–O(2)	2.017(7)	Sn(3)–O(4)	2.017(7)
Sn(1)–O(1)	2.182(8)	Sn(3)–O(3)	2.172(8)
Sn(2)–O(2)	2.060(7)	Sn(4)–O(4)	2.063(7)
Sn(2)–O(2)#1	2.138(7)	Sn(4)–O(3)	2.231(9)
Sn(2)–O(1)	2.196(7)	Sn(4)–O(4)#2	2.131(7)
N(1)–N(2)	1.402(12)	N(5)–N(6)	1.392(13)
N(3)–N(4)	1.407(12)	N(7)–N(8)	1.392(13)
Sn(1)–N(4)	2.227(9)	Sn(3)–N(8)	2.249(9)
O(2)–Sn(1)–C(13)	114.1(4)	O(4)–Sn(3)–C(40)	114.7(4)
O(2)–Sn(1)–C(14)	115.8(4)	O(4)–Sn(3)–C(41)	115.5(5)
C(13)–Sn(1)–C(14)	129.5(5)	C(40)–Sn(3)–C(41)	129.5(5)
O(2)–Sn(1)–O(1)	72.8(3)	O(4)–Sn(3)–O(3)	73.9(3)
C(13)–Sn(1)–O(1)	95.3(4)	C(40)–Sn(3)–O(3)	95.2(5)
C(14)–Sn(1)–O(1)	92.5(4)	C(41)–Sn(3)–O(3)	93.4(4)
O(2)–Sn(1)–N(4)	87.2(3)	O(4)–Sn(3)–N(8)	85.4(3)
C(13)–Sn(1)–N(4)	93.4(4)	C(40)–Sn(3)–N(8)	93.7(5)
C(14)–Sn(1)–N(4)	95.7(5)	C(41)–Sn(3)–N(8)	95.3(5)
O(1)–Sn(1)–N(4)	160.0(3)	O(3)–Sn(3)–N(8)	159.3(3)
O(2)–Sn(2)–C(22)	112.3(5)	O(4)–Sn(4)–C(49)	107.1(6)

(continued on next page)

Table 2 (continued)

O(2)–Sn(2)–C(21)	111.9(4)	O(4)–Sn(4)–O(4)#2	74.6(3)
C(22)–Sn(2)–C(21)	135.3(6)	C(49)–Sn(4)–O(4)#2	99.5(5)
O(2)–Sn(2)–O(2)#1	74.6(3)	O(4)–Sn(4)–C(48)	111.2(5)
C(22)–Sn(2)–O(2)#1	100.2(5)	C(49)–Sn(4)–C(48)	140.5(7)
C(21)–Sn(2)–O(2)#1	97.3(4)	O(4)#2–Sn(4)–C(48)	99.3(4)
O(2)–Sn(2)–O(1)	71.7(3)	O(4)–Sn(4)–O(3)	71.8(3)
C(22)–Sn(2)–O(1)	93.8(5)	C(49)–Sn(4)–O(3)	92.6(5)
C(21)–Sn(2)–O(1)	93.8(4)	O(4)#2–Sn(4)–O(3)	146.2(3)
O(2)#1–Sn(2)–O(1)	146.3(3)	C(48)–Sn(4)–O(3)	90.6(4)
Compound 4			
C(34)–S(2)	1.726(6)	N(1)–N(2)	1.403(6)
N(3)–N(4)	1.398(6)	O(5)–H(5)	0.893(10)
S(2)–Sn(1)	2.4592(17)	C(24)–Sn(1)	2.121(6)
C(26)–Sn(1)	2.110(6)	C(32)–Sn(1)	2.142(6)
C(26)–Sn(1)–C(24)	115.4(2)	C(26)–Sn(1)–C(32)	108.3(3)
C(24)–Sn(1)–C(32)	108.9(3)	C(26)–Sn(1)–S(2)	114.28(15)
C(24)–Sn(1)–S(2)	110.18(16)	C(32)–Sn(1)–S(2)	98.34(18)

^a Symmetry operations: for **1** (#1) $1 - x, -y, 2 - z$; for **2** (#1) $1 - x, -y, 1 - z$; for **3** (#1) $1 - x, -y, -z$; (#2) $2 - x, 1 - y, -z$.

Fig. 1. Molecular structure of **1**.Fig. 2. Molecular structure of **2**.

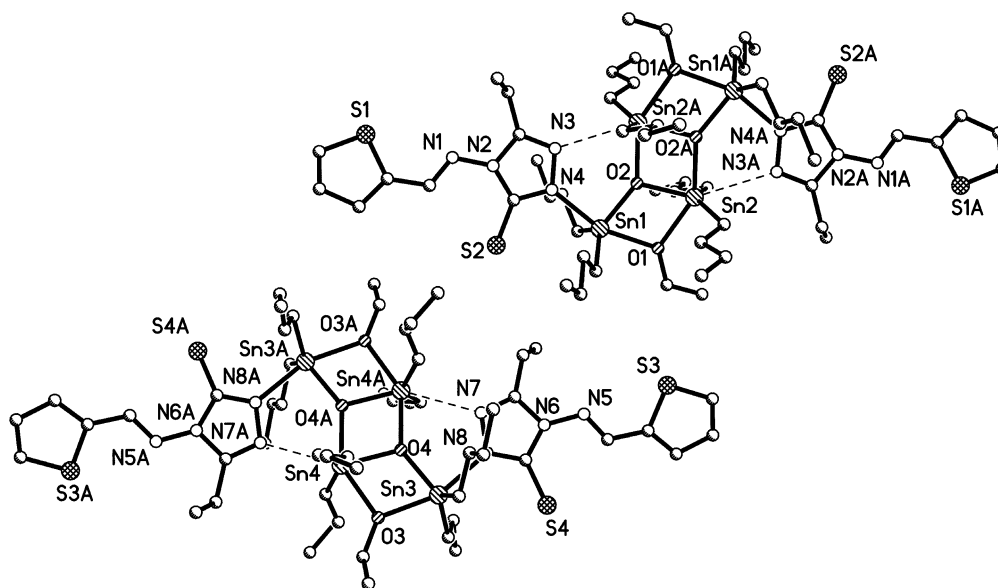
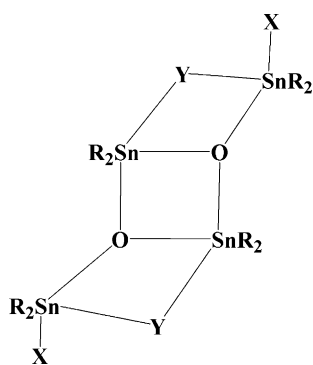


Fig. 3. Molecular structure of 3.



Scheme 3.

Table 3
Hydrogen-bond geometries for compound 4^a

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	∠D–H···A (°)
OW1–H(1A) ···N(2)#1	0.850(10)	2.02(4)	2.810(14)	155(9)
O(5)–H(5) ···N(4)	0.893(10)	2.09(8)	2.588(6)	114(7)

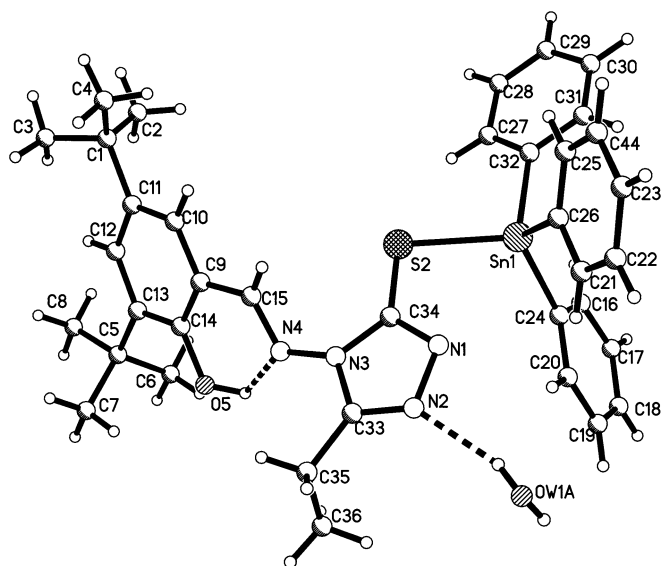
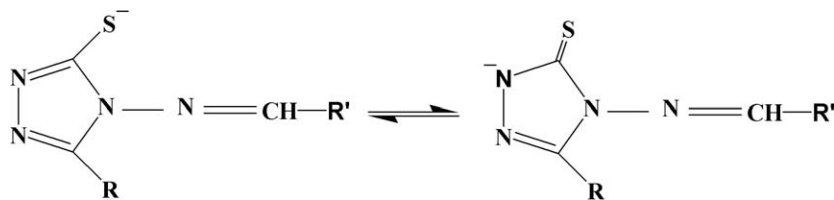
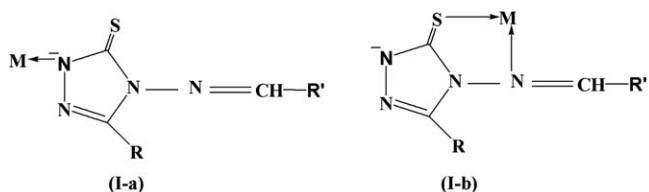
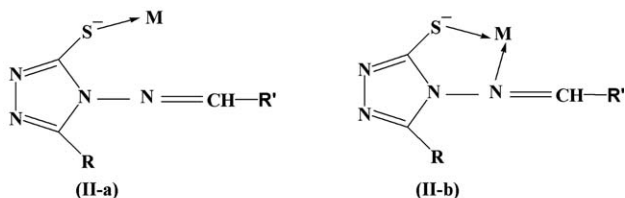
^a Symmetry operations: (#1) $-x + 1, -y, -z$.

Fig. 4. The structure of 4.

state places the organic group attached to N atom on the same side of the N–N bond as the S atom. Thus the C atom is blocking the N from chelating a metal ion together with the S atom, and the chelating mode (I-b in Scheme 5) which exists in the metal complexes of HAATT [11,12] cannot occur for 1–3. The ability of L⁻ anions to adopt conformations more suitable to chelating modes depends in part on the ease of rotation about the N–N bond. In contrast with 1–3, L⁻ anion adopts a thiol form not a thione form in compound 4. Thiol form L⁻ anion may coordinate to metal ion in two modes: II-a and II-b in Scheme 5. Base on the same steric hindrance for compound 1–3, L⁻ anion coordinates to tin atom in the monodentate mode (II-a in Scheme 5) in 4.

From the structures of 1–3, it can be seen that the substituted group at the amino position has little influence on the structures of the complexes. In 1–3, the tin atom is coordinated by the N atom on the triazole ring; while the tin atom of 4 is coordinated by the S atom. This may result from the steric repulsion of three phenyl groups which is strong enough to prevent the ligand from coordinating to tin atom through the N atom on the triazole ring. The bulkier the organic groups of the organotin are, the more difficult the coordination through the N atom on the triazole ring is.

Scheme 4. Thiol-thione tautomerism of L^- anions.Possible coordination modes of thione L^- Possible coordination modes of thiol L^- Scheme 5. Possible coordination modes of deprotonated L^- .

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Appendix A. Supplementary material

CCDC 602386–602389 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033)). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2006.05.002](https://doi.org/10.1016/j.jorganchem.2006.05.002).

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