Organotin(IV) triazolates: Synthesis and their spectral characterization

Mala Nath [a,*], Sulaxna [a], Xueqing Song [b], George Eng [b]

[a] *Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247667, India*
[b] *Department of Chemistry and Physics, University of The District of Columbia, Washington, DC 20008, USA*

Abstract

Some organotin(IV) triazolates of general formula $R_nSn(L)_{4-n}$ (where R = Me, *n*-Bu and Ph for $n = 2$; R = Me, *n*-Pr and *n*-Bu for $n = 3$ and HL = 3-amino-5-mercapto-1,2,4-triazole) have been synthesized by the reaction of R_2SnCl_2/R_3SnCl with NaL in 1:2/1:1 molar ratio. Whereas, Oct_2SnL_2 has been synthesized azeotropically by the reaction of Oct_2SnO and HL in 1:2 molar ratio. As good single crystals were not obtained, a large number of experimental techniques, viz. UV/Vis, IR, far-IR, multinuclear (^{1}H, ^{13}C and [119]Sn) NMR and [119]Sn Mössbauer spectroscopic studies, were used to accomplish a definitive characterization and determination of their most probable structures. In these compounds triazole acts as a monoanionic bidentate ligand, coordinating through S_{exo} and N(4). The IR and [119]Sn Mössbauer spectroscopic studies allow us to deduce a highly distorted *cis*-trigonal-bipyramidal structure for R_3SnL and a distorted skew trapezoidal-bipyramidal structure for R_2SnL_2, in the solid state. However, ^{1}H, ^{13}C and ^{119}Sn NMR spectral studies revealed that weak bonding between tin and N(4) is further weakened in the solution leading to pseudo-tetrahedral/tetrahedral structure.
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Keywords: 1,2,4-Triazole; Organotin(IV) compounds; NMR solution studies; [119]Sn Mössbauer

1. Introduction

1,2,4-Triazole and its derivatives constitute an interesting class of heterocycles, which gained considerable attention in recent years [1] because 1,2,4-triazole represents a hybrid of pyrazole and imidazole with regards to the arrangement of ring nitrogens. They also possess a broad spectrum of biological activities including antimicrobial and antifungal activities [2–6], e.g., triazole antifungal agents, fluconazole and itraconazole, have been extensively used for the treatment of prophylaxis and a variety of fungal infections since a decade ago [7]. Several new triazole agents are in various phases of preclinical and clinical trials [7] and may be available for human use in the near future. Further, they show a versatile coordinating ability, especially when the triazole nucleus is substituted with additional donor groups [1]. In addition, 1,2,4-triazole and, in particular, its derivatives exhibit a strong property of acting as bridging ligands between two metal centers [1] and can provide 1,2-bridging as well as 2,4-bridging form in case of 4-unsubstituted 1,2,4-triazoles. Though, triazoles have their non-biological origin but their 2,4-bridging form is similar to 1,3-imidazolate bridging found in enzymes [8], which has made triazoles and their metal complexes much sought after compounds to mimic natural processes, and they are also used to mimic imidazoles in model compounds for such processes [9]. A large number of reports have been appeared on their metal complexes involving d-block metals [1,10–17], however, only a few reports have been cited on tin and organotin derivatives of triazoles [18–20].

Increasing industrial uses of organotin compounds containing Sn–S bond, especially as stabilizers of polyvinyl chloride [21], and recognition of the importance of this bond for the biological properties of organotin compounds [22], have together spurred to study organotin(IV) thiolates. Recently, the organotin complexes of heterocyclic thioamides, which are interesting owing to their different

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* Corresponding author. Tel.: +91 1332 285797; fax: +91 1332 273560.
 E-mail address: malanfcy@iitr.ernet.in (M. Nath).

coordination modes, have attracted great attention. Moreover, they can give a better insight to understand the interaction of organotin compounds with sulfur containing molecules present in biological system [23].

In view of this, here we report the synthesis of seven new organotin(IV) derivatives of heterocyclic thioamide, viz. 3-amino-5-mercapto-1,2,4-triazole (HL), and their spectral characterization by using UV/Vis, IR, far-IR, ^{1}H, ^{13}C and ^{119}Sn NMR and ^{119}Sn Mössbauer spectroscopic techniques.

2. Experimental

2.1. Materials

All the syntheses were carried out under anhydrous nitrogen atmosphere and the precautions to avoid the presence of oxygen were taken at every stage. Solvents were dried and distilled before use. All the di-/triorganotin(IV) chlorides/oxide (except diphenyltin(IV) dichloride) and 3-amino-5-mercapto-1,2,4-triazole were purchased from Merck–Schuchardt and were used as received. Diphenyltin(IV) dichloride was synthesized by the literature method [24].

2.2. Synthesis of organotin(IV) derivatives of 3-amino-5-mercapto-1,2,4-triazole (HL)

2.2.1. Synthesis of R$_2$SnL$_2$ (where R = Me (1), n-Bu (2) and Ph (4)) and R$_3$SnL (where R = Me (5), n-Pr (6) and n-Bu (7)) by sodium chloride method

The methanolic solution ($\sim$30 ml) of HL (0.47 g, 4.0 mmol) was added under dry nitrogen to sodium methoxide, prepared by dissolving sodium (0.1 g, 4.2 mmol) in dry methanol ($\sim$5 ml). The resulting solution was stirred for $\sim$8 h at room temperature under dry nitrogen. To this was added a methanolic solution of R$_3$SnCl (4 mmol)/R$_2$SnCl$_2$ (2 mmol) dropwise with constant stirring, and it was further stirred for 30–35 h at room temperature. The reaction mixture was centrifuged and filtered in order to remove sodium chloride, and the volatiles were removed in vacuo. The solid obtained was recrystalized from a mixture of methanol and dichloromethane (1:2 v/v).

Me$_2$SnL$_2$ (1): Pale yellow solid; m.p. 171–174 °C. Anal. Calc. for C$_6$H$_{12}$N$_8$S$_2$Sn: C, 19.0; H, 3.19; N, 29.56; S, 16.92; Sn, 31.77. Found: C, 18.95; H, 3.16; N, 29.49; S, 16.88; Sn, 31.76%. UV/Vis: $\pi \rightarrow \pi^*$ at λ 209 nm (ε: 11839 l mol^{-1} cm^{-1}); n $\rightarrow \pi^*$ at λ 258 nm (ε: 13842 l mol^{-1} cm^{-1}) (in MeOH). Molar conductance: 3.0 Ω^{-1} cm^2 mol^{-1} (in MeOH).

n-Bu$_2$SnL$_2$ (2): Pale yellow solid; m.p. 221–224 °C. Anal. Calc. for C$_{12}$H$_{24}$N$_8$S$_2$Sn: C, 31.26; H, 5.22; N, 24.19; S, 13.85; Sn, 25.63. Found: C, 31.21; H, 5.19; N, 24.16; S, 13.79; Sn, 25.57%. UV/Vis: $\pi \rightarrow \pi^*$ at λ 204 nm (ε: 10075 l mol^{-1} cm^{-1}); n $\rightarrow \pi^*$ at λ 259 nm (ε: 25751 mol^{-1} cm^{-1}) (in MeOH). Molar conductance: 5.0 Ω^{-1} cm^2 mol^{-1} (in MeOH).

Ph$_2$SnL$_2$ (4): Pale yellow solid; m.p. 195–199 °C. Anal. Calc. for C$_{16}$H$_{16}$N$_8$S$_2$Sn: C, 38.19; H, 3.20; N, 22.27; S, 12.75; Sn, 23.59. Found: C, 38.15; H, 3.14; N, 22.23; S, 12.69; Sn, 23.55%. UV/Vis: $\pi \rightarrow \pi^*$ at λ 208, 216 nm (ε: 23983; 28721 l mol^{-1} cm^{-1}); n $\rightarrow \pi^*$ at λ 258 nm (ε: 4026 l mol^{-1} cm^{-1}) (in MeOH). Molar conductance: 3.0 Ω^{-1} cm^2 mol^{-1} (in MeOH).

Me$_3$SnL (5): Pale yellow solid; m.p. 180–184 °C. Anal. Calc. for C$_5$H$_{12}$N$_4$SSn: C, 21.53; H, 4.34; N, 20.09; S, 11.50; Sn, 42.56. Found: C, 20.51; H, 4.30; N, 20.01; S, 11.44; Sn, 42.51%. UV/Vis: $\pi \rightarrow \pi^*$ at λ 209 nm (ε: 2907 l mol^{-1} cm^{-1}); n $\rightarrow \pi^*$ at λ 260 nm (ε: 6726 l mol^{-1} cm^{-1}) (in MeOH). Molar conductance: 4.0 Ω^{-1} cm^2 mol^{-1} (in MeOH).

n-Pr$_3$SnL (6): Yellow semi-solid. Anal. Calc. for C$_{11}$H$_{24}$N$_4$SSn: C, 36.39; H, 6.66; N, 15.43; S, 8.83; Sn, 32.70. Found: C, 36.38; H, 6.61; N, 15.41; S, 8.72; Sn, 32.61%. UV/Vis: $\pi \rightarrow \pi^*$ at λ 208 nm (ε: 12403 l mol^{-1} cm^{-1}); n $\rightarrow \pi^*$ at λ 260 nm (ε: 11453 l mol^{-1} cm^{-1}) (in MeOH). Molar conductance: 8.0 Ω^{-1} cm^2 mol^{-1} (in MeOH).

n-Bu$_3$SnL (7): Yellow semi-solid. Anal. Calc. for C$_{14}$H$_{30}$N$_4$SSn: C, 41.51; H, 7.46; N, 13.83; S, 7.91; Sn, 29.30. Found: C, 41.48; H, 7.41; N, 13.75; S, 7.85; Sn, 29.24%. UV/Vis: $\pi \rightarrow \pi^*$ at λ 209 nm (ε: 8670 l mol^{-1} cm^{-1}); n $\rightarrow \pi^*$ at λ 261 nm (ε: 8356 l mol^{-1} cm^{-1}) (in MeOH). Molar conductance: 6.0 Ω^{-1} cm^2 mol^{-1} (in MeOH).

2.2.2. Synthesis of dioctyltin(IV) bis(triazolate) (3) by azeotropic removal of water method

To the suspension of dioctyltin(IV) oxide (0.72 g, 2.0 mmol, in $\sim$35 ml methanol) a methanol solution of HL (0.47 g, 4.0 mmol) was added dropwise with constant stirring at room temperature under dry nitrogen. The resulting mixture was further stirred for another 40 h at $\sim$40 °C. The water formed during the reaction was recovered azeotropically and the excess of solvent was removed in vacuo. The solid obtained was washed with dichloromethane and recrystallized from methanol. Pale yellow solid; m.p. 168–172 °C. Anal. Calc. for C$_{20}$H$_{40}$N$_8$S$_2$Sn: C, 41.75; H, 7.00; N, 19.47; S, 11.15; Sn, 20.63. Found: C, 41.68; H, 6.91; N, 19.41; S, 11.10; Sn, 20.60%. UV/Vis: $\pi \rightarrow \pi^*$ at λ 205 nm (ε: 9168 l mol^{-1} cm^{-1}); n $\rightarrow \pi^*$ at λ 260 nm (ε: 7097 l mol^{-1} cm^{-1}) (in MeOH). Molar conductance: 5.0 Ω^{-1} cm^2 mol^{-1} (in MeOH).

2.2.3. Attempted synthesis of triphenyltin(IV) triazolate

Triphenyltin(IV) chloride (1.16 g, 3.0 mmol) was dissolved in $\sim$30 ml of methanol. It was added slowly, with constant stirring, to the performed sodium salt of HL in methanol (as described in Section 2.2.1) in a 1:1 molar ratio. The resulting reaction mixture was further stirred for $\sim$40 h at room temperature/at 40 °C, but the unreacted reactants were recovered in each case. Another attempt to synthesize this compound was made by adding a methanol solution of triphenyltin hydroxide (1.10 g, 3.0 mmol) to a

methanol solution of HL (0.35 g, 3.0 mmol) with constant stirring and the mixture was heated at 40 °C for ∼40 h, but no complexation took place.

2.3. Measurements

The melting points of the synthesized compounds were determined on a Toshniwal capillary melting point apparatus and were uncorrected. Carbon, hydrogen, nitrogen, sulfur and tin were determined as reported previously [25]. UV–Vis spectra and molar conductance measurements of the compounds were recorded in MeOH on the same instruments as reported previously [25]. IR and far-IR spectra of the solid compounds were recorded on a Perkin–Elmer 1600 series FT-IR in the range 4000–200 cm^{-1} from CsI discs. ^1H NMR spectra were recorded on a Bruker Avance 500 MHz (at 296.3 K) at the Indian Institute of Technology Roorkee, Roorkee. ^1H (of HL) and ^{13}C NMR (at 300.0 K) spectra were recorded at the Central Drug Research Institute, Lucknow, India and ^{119}Sn NMR spectra were recorded at the Regional Sophisticated Instrumentation Center, Indian Institute of Technology Bombay, India using the same instruments as reported previously [25]. ^{119}Sn Mössbauer spectra were recorded on a Mössbauer spectrometer model MS-900 according to the procedure reported previously [25], at the Department of Chemistry and Physics, University of the District of Columbia, Washington, DC.

3. Results and discussion

The reactions of di-/triorganotin(IV) chloride with sodium salt of 3-amino-5-mercapto-1,2,4-triazole (HL) {formed according to Eq. (1)} led to the formation of the compounds according to Eq. (2). In these compounds HL acts as a mono deprotonated bidentate ligand with the negative charge residing on the sulfur atom of the resulting aromatic tautomer [26]. The reaction of dioctyltin(IV) oxide with HL in a 1:2 molar ratio yielded the product under azeotropic removal of water according to Eq. (3).

$$HL + NaOMe \rightarrow NaL + MeOH \quad (1)$$

$$mNaL + R_nSnCl_{(4-n)} \rightarrow R_nSn(L)_m + mNaCl \quad (2)$$
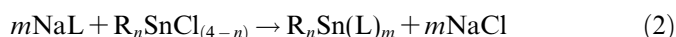
(where $m = 1$, $n = 3$, R = Me, n-Pr and n-Bu; $m = 2$, $n = 2$, R = Me, n-Bu and Ph; HL = 3-amino-5-mercapto-1,2,4-triazole)

$$2HL + Oct_2SnO \rightarrow Oct_2SnL_2 + H_2O \quad (3)$$
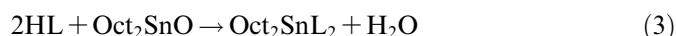
The reactions involved in the synthesis of di- and triorganotin(IV) triazolates were found to be quite feasible and required 30–35 h of stirring at room temperature except Oct_2SnL_2 which requires 40 h stirring at 40 °C. However, even prolonged stirring for ∼40 h at 40 °C of the mixture of Ph_3SnCl/Ph_3SnOH with NaL/HL in methanol did not result in complexation.

All of the synthesized compounds are light yellow powder and soluble in DMSO and MeOH, but insoluble in $CHCl_3$, except n-Pr_3SnL and n-Bu_3SnL. Me_2SnL_2 and Ph_2SnL_2 are hygroscopic in nature and decomposed on exposure in air. The analytical data of the complexes are in agreement with the proposed stoichiometry. The compounds are non-electrolytes as suggested by the low molar conductance values (3.0–8.0 $\Omega^{-1}\, cm^2\, mol^{-1}$) of 10^{-3} M solution in MeOH.

3.1. Electronic spectral studies in solution

The ultraviolet spectrum of HL exhibits two strong bands at 207 and 260 nm, which have been assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of (C=N) chromophore [27], respectively. For organotin(IV) triazolates a corresponding shift is observed in these bands.

3.2. Infrared spectral studies

The characteristic IR bands of HL and its organotin(IV) derivatives assigned with the help of the following general references [28,29] and of other related molecules [14,18,30,31] are presented in Table 1. In the spectrum of HL, several medium intensity bands are observed in the region 3382–2704 cm^{-1}, mainly due to NH stretching vibrations [31,32]. The bands, particularly, at 3382 and 3299 cm^{-1} are assigned to v_{as}(N–H) and v_s(N–H), respectively, of NH_2 group [31]. The remaining bands in the region 3382–2704 cm^{-1} are assigned to v(N–H) of N_{ring}–H [31] as HL exhibits thione-thiol tautomerism (Fig. 1) in the solid state [14]. In the complexes the coordination via NH_2 group would require a downward shift in the sensitive NH stretching frequencies by 200–300 cm^{-1} [32]. On the contrary, the studied organotin(IV) triazolates reveal an upward shift by 10–70 cm^{-1} relative to the frequencies of HL. The upward shift as well as the position and character of the v(NH) bands is indicative of the weakening of extensive H-bonding that was originally present in the crystal lattice of HL, upon complexation.

A medium intensity band at 2618 cm^{-1} attributable to v(SH) of HL [32] disappears in all the studied complexes and confirms the deprotonation of thiol group. The bands at 1485 and 1399 cm^{-1} are assigned to v(CN) vibrations (i.e., thioamide bands I and II, respectively) of the thioamide group, whereas the bands at 1141 and 1030 cm^{-1} are assigned to v(CS) vibrations (i.e., thioamide bands III and IV, respectively) of the thioamide group of HL [23]. In the studied organotin(IV) triazolates, these bands shift to lower wave numbers indicating the coordination of L^- through S_{exo} and N_{ring}. The observed shifts in these thioamide bands might be due to the evolution of partial double bond character in the (—N═C═S—) group after its deprotonation [26] and subsequent coordination to tin. In addition to this, the bands observed in the region 1650–800 cm^{-1} in the spectra of the organotin(IV) triazolates, show a shift in their position, some of them shift to

Table 1
IR spectral bands[a] of 3-amino-5-mercapto-1,2,4-triazole and its organotin(IV) compounds

HL	Me$_2$SnL (1)	n-Bu$_2$SnL$_2$ (2)	Oct$_2$SnL$_2$ (3)	Ph$_2$SnL$_2$ (4)	Me$_3$SnL (5)	n-Pr$_3$SnL (6)	n-Bu$_3$SnL (7)	Assignments
3382s	3330brs	3456brw	3439w	3430wsh	3419m	3386mbr	3425m	
3299m	3144w	3330brw	3382w	3384wsh	3375m	3300mbr	3317m	
3267m	2852w	3213w	3213w	3013w	3301m	3170mbr	3230w	
3216m	2787vw	2869s	3182w	2952w	3213w	2866s	3182w	
3170m		2857s	3095w	2923m	3104m		3113w	ν(N–H)
3107m			2853s	2858m	2767m			
3019m			2765vw		2708m			
2909m			2704vw					
2858m								
2761w								
2704w								
	2922s	2958s	2965s	3064s	2982m	2957s	2957s	ν(C–H)
		2925s	2923s	3043s	2907m	2926s	2922s	
2618m	–	–	–	–	–	–	–	ν(S–H)
1646vs	1669s	1624s	1645s	1643s	1623s	1652s	1633s	
1586s	1638s	1529s	1593m	1587wsh	1549s	1578s	1578m	δ(N–H)
1544s	1541s		1543m	1539w				
1485s	1430m	1466s	1466m	1429vs	1440s	1461m	1464s	Thioamide band (I)
1399m	1364m	1377s	1364m	1301m	1327s	1332m	1377s	Thioamide band (II)
1141s	1096m	1078s	1108m	1077vs	1101s	1109m	1077s	Thioamide band (III)
1030s	1023s	1024m	1056s	1024m	1024s	1023m	1022s	Thioamide band (IV)
–	574m	596m	608m	275s	552m	615w	543wsh	ν_{as}(Sn–C)
–	557shw	570m	574m	228m	543s	600w	507s	ν_s(Sn–C)
–	474m	474m	466s	449s	445s	470m	465m	ν(Sn ← N)
–	325w	302m	324m	376s	392s	386m	353m	ν(Sn–S)

[a] s: strong; m: medium; w: weak; vw: very weak; brs: broad strong; sh: shoulder.
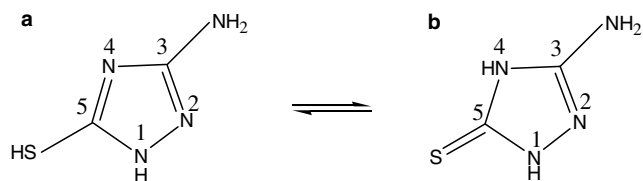

Fig. 1. Thiol (a) and thione (b) tautomer of 3-amino-5-mercapto-1,2,4-triazole.

higher wave numbers while others to lower wave numbers as compared to those of the non-coordinated HL. But assignment of these bands in terms of localized vibrations could not possible because the ring atoms are involved in several vibrational modes.

In the region 600–200 cm^{-1}, a few new bands are observed due to ν_{as}(Sn–C) and ν_s(Sn–C), which suggest a non-planar arrangement of C–Sn–C moiety. All of the complexes display new bands of medium intensity in the region 470–400 cm^{-1} and 390–310 cm^{-1}, which are assigned to ν(Sn ← N) and ν(Sn–S) modes [23,32], respectively. These new bands further confirm the complexation of tin via S$_{exo}$ and N$_{ring}$. For the triazole ring Johnson et al. [33] and Vasnin et al. [19] reported that N(4) is the potential donor site among the ring nitrogens. These spectral investigations along with the literature data reveal that the coordination of triazolate anion (L$^-$) occurs through S$_{exo}$ and ring N(4), whereas N(1)H and NH$_2$ groups participate in intermolecular H-bonding of NH···N type [17,18].

3.3. ^{119}Sn Mössbauer spectral studies

The ^{119}Sn Mössbauer spectra of the organotin(IV) triazolates are shown in Fig. 2 and the spectral data are presented in Table 2. The spectral data show a small lowering in the isomer shift (I.S.) values as compared to the corresponding organotin(IV) chlorides because the 5s orbital electron density of tin atom is reduced upon complexation. The quadrupole splitting (Q.S.) values in the range 2.02–2.93 mm s^{-1} show that the electric field gradient around the tin nucleus is produced by the inequalities in the tin-sulfur/nitrogen bonds and is also due to geometric distortions. The ρ (Q.S./I.S.) values in the range 1.96–2.72 for these studied derivatives indicate a coordination number greater than four with either a five- or six-coordinated tin.

Octahedral cationic [36], neutral [36,37] and anionic [38] tin(IV) complexes containing two organic residues and four electronegative ligands possess a mutually *trans*-geometry for the tin-carbon bonds (with a few exceptions). In this context, the magnitude of the ^{119}Sn Mössbauer Q.S. is a useful parameter. The point charge calculations [39] for octahedral diorganotin(IV) derivatives predict that the Q.S. for the *trans*-isomer will be twice (~4.0 mm s^{-1}) that of the *cis*-isomer (~2.0 mm s^{-1}). However, the observed Q.S. values (2.02–2.93 mm s^{-1}) of the studied diorganotin(IV) bis(triazolate) lie in the intermediate range i.e., higher than that of *cis*-octahedral, but substantially lower than that of *trans*-octahedral arrangement. Indeed, where the other ligands have higher electronegativity, the Q.S. is
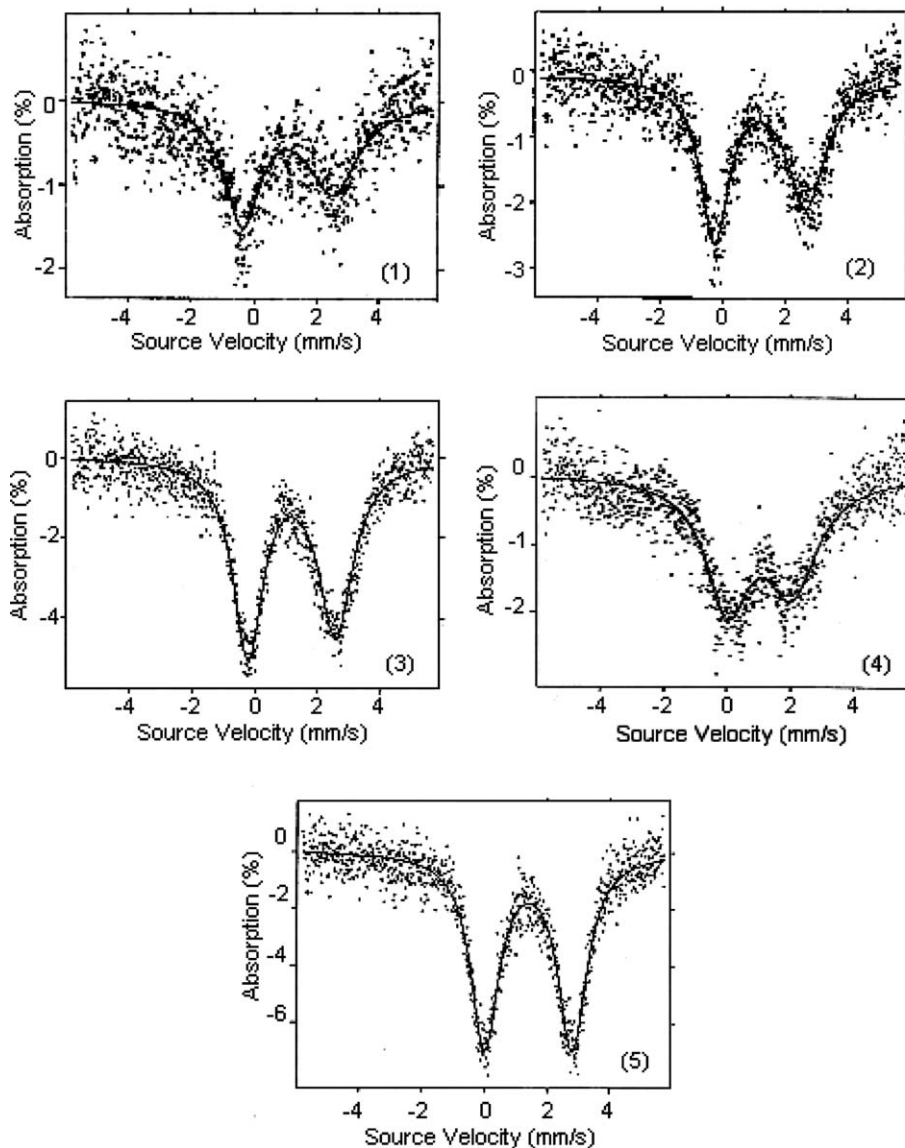
Fig. 2. [119]Sn Mössbauer spectra of compounds **1**–**5**.

mainly governed by C–Sn–C bond angle [40], and the distortion from regular six coordination can give values similar to those reported [41] for highly distorted square bipyramidal/skew trapezoidal-bipyramidal structure. Further, it has been reported [42] that I.S. value for *cis*-$[R_2SnX_4]^{2-}$ are less than 1.00 mm s^{-1} while *trans*-compounds have I.S. values approximately 1.20–1.30 mm s^{-1}. In the studied diorganotin(IV) bis(triazolate) the I.S. value are observed in the range 1.03–1.21 mm s^{-1} and the angle ∠C–Sn–C lies in the range 121.91–124.84° (Table 2), which are close to the average of the two extremes, in which the organic substituents do not adopt either *cis*- or *trans*-geometry about the tin center [41]. Therefore, the observed [119]Sn Mössbauer parameters of the studied diorganotin(IV) bis(triazolate) are best interpreted in terms of a highly distorted skew trapezoidal-bipyramidal geometry in which equatorial positions are occupied by two sulfur and two

N(4) atoms, whereas the two organic groups occupy the axial positions (Fig. 3). The proposed structure is similar to the structures reported for Bu$_2$SnL$_2$ (where L = mercaptobenzoxazole [43] and 2-thio-5-nitro-pyridine [44]). The distortion in these studied compounds is significant due to the formation of four membered (Sn–S–C–N) chelate rings as shown in Fig. 3. Further, the pronounced line asymmetry (Goldanskii–Karyagin effect) observed in the [119]Sn Mössbauer spectra (Fig. 2, spectra (1)–(4)) of these compounds suggests the intermolecularly associated crystal lattice [45] and also explains the low solubility of these compounds.

The [119]Sn Mössbauer spectrum of Me$_3$SnL could be taken as representative for the assignment of structure of the studied triorganotin(IV) triazolates. The spectra of *n*-Pr$_3$SnL and *n*-Bu$_3$SnL could not be recorded because of their semi-solid nature. The [119]Sn Mössbauer spectrum

Table 2
^{119}Sn Mössbauer spectral data[a] of organotin(IV) derivatives of 3-amino-5-mercapto-1,2,4-triazole

Compound	I.S. (mm s^{-1})	Q.S. (mm s^{-1})	ρ (Q.S./I.S.)	τ (L)	τ (R)	∠C–Sn–C[b]
Me$_2$SnCl$_2$[c]	1.66	3.56				
n-Bu$_2$SnCl$_2$[c]	1.75	3.50				
Ph$_2$SnCl$_2$[c]	1.45	2.76				
1	1.07	2.90	2.72	1.386	1.988	124.84
2	1.20	2.81	2.34	1.166	1.346	122.36
3	1.21	2.93	2.42	1.127	1.488	121.91
4	1.03	2.02	1.96	1.683	1.991	–
5	1.40	2.79	1.99	1.103	1.120	125.79

[a] Compound numbers according to Table 1; Q.S. quadrupole splitting; I.S. isomeric shift; τ (L) half line-width left doublet component; τ (R) half line-width right doublet component.
[b] Ref. [34].
[c] Ref. [35].
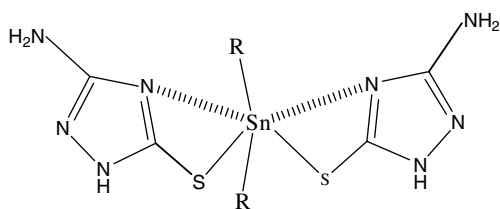
Fig. 3. Proposed structure for R$_2$SnL$_2$ (where R = Me, *n*-Bu, Oct and Ph).

Fig. 5. Proposed structure for R$_3$SnL (where R = Me, *n*-Pr and *n*-Bu).

of Me$_3$SnL exhibits Q.S. at 2.79 mm s^{-1} and I.S. at 1.40 mm s^{-1}. It has been reported [46] that the three conceivable (Fig. 4) five coordinate isomers of R$_3$SnXY (where X or Y = N/O/S; XY are the donor sites of the bidentate ligand) have different Q.S. value ranges, for isomer (a) 1.70–2.30 mm s^{-1}; for (b) 3.0–3.90 mm s^{-1}; and for (c) 3.50–4.10 mm s^{-1}.

The observed value of Q.S. (2.79 mm s^{-1}) in Me$_3$SnL is higher than that for isomer (a) and considered to be compatible with *trans*-structure which is the conventional one (follows Bent's rule) found in organotin chemistry. But the observed v_{as}(Sn–C) and v_s(Sn–C) stretching vibrations in the IR spectra of the studied triorganotin(IV) triazolates indicate a non-planar SnC$_3$ fragment and rule out the possibility of *trans*-isomer 4(b). Therefore, the most plausible structure for Me$_3$SnL is a highly distorted *cis*-trigonal-bipyramidal as shown in Fig. 5, which is intermediate between 4(a) (*fac*) and 4(c) (*mer*) *cis*-trigonal-bipyramidal structures. A similar structure has been reported for the

closely related compound Me$_3$SnL (where L = pyridine-2-thiolate) [47], which was considered to have a *cis*-trigonal-bipyramidal arrangement having Sn–S–C–N ring. Furthermore, a similar structure as shown in Fig. 5 has also been suggested for *n*-Pr$_3$SnL and *n*-Bu$_3$SnL.

3.4. ^{1}H, ^{13}C and ^{119}Sn NMR solution spectral studies

The ^{1}H NMR spectral data of the ligand (HL) and its organotin complexes are given in Table 3. The ^{1}H NMR

Fig. 4. Three possible isomers of R$_3$Sn(XY) [46].

Table 3
^{1}H NMR spectral data[a] of organotin(IV) compounds[b] of 3-amino-5-mercapto-1,2,4-triazole

Compound	(δ/ppm)
HL (DMSO-d_6 + CDCl$_3$)	SH: 2.58; N(1)–H: 12.19; N(4)–H: 11.79; NH$_2$: 5.31
1 (CD$_3$OD)	NH$_2$: 5.14; H$_\alpha$: 2.18 s
3 (DMSO-d_6)	NH$_2$: 5.14; H$_{\alpha\ to\ \mu}$ 2.99–1.83 m;[c] H$_\omega$: 0.85 t
4 (CD$_3$OD)	NH$_2$: 5.14; H$_o$: 7.74;[d] H$_{m+p}$: 7.44[d]
5 (CD$_3$OD)	NH$_2$: 5.36; H$_\alpha$: 0.47 [64.20/61.55][e]
6 (CDCl$_3$)	NH$_2$: 4.30; H$_\alpha$: 1.29; H$_\beta$: 1.69–1.64 m; H$_\gamma$: 0.97 t (10 Hz)[f]
7 (CDCl$_3$)	NH$_2$: 4.59; H$_{\alpha+\gamma}$: 1.34–1.28 m; H$_\beta$: 1.65–1.57 m; H$_\delta$: 0.87 t (10 Hz)[f]

[a] Compound numbers according to Table 1.
[b] For N(1)–H: broad and weak signals is observed; s: singlet; t: triplet; m: multiplet.
[c] Unassigned due to overlapping patterns.
[d] Broad peaks.
[e] $^2J(^1$H–$^{119/117}$Sn).
[f] $^3J(^1$H–^{1}H).

spectrum of HL exhibits two signals at δ 12.19 and 11.79 ppm which may be assigned to N(1)–H and N(4)–H, respectively, whereas a signal of less than half intensity at δ 2.58 ppm has been assigned to –SH. Therefore, it is concluded that thiol–thione equilibrium is fast on the NMR timescale and predominant species may be thione form of HL in solution. A signal observed at δ 5.31 ppm is also assigned to –NH$_2$ group. In the organotin(IV) triazolates the signal due to N(1)–H is observed as a broad singlet centered at δ ~12 ppm, whereas –SH/N(4)–H resonances are absent in the organotin(IV) triazolates, indicating the deprotonation of the ligand and its coordination to tin. The signal of NH$_2$ is observed in the range δ 5.36–4.30 ppm. The characteristic signals for all the magnetically non-equivalent alkyl- or phenyl-protons of the organotin moieties have also been assigned, which are in good agreement with reported values [17]. The observed $^2J(^1H-^{119/117}Sn)$ for Me$_3$SnL is 64.20/61.55 Hz (Fig. 6a). The angle $\angle$Me–Sn–Me calculated by using Lockhart and Manders [48] equation ($\theta = 0.0161|^2J|^2 - 1.32|^2J| + 133.4$) is 114.83°, which indicates pseudotetraheral arrangement.

The ^{13}C and ^{119}Sn NMR spectral data are presented in Table 4. In the ^{13}C NMR spectrum of HL, three signals are observed at δ 173.62, 161.72 and 151.14 ppm; as the ligand exists in thiol–thione tautomeric forms (Fig. 1), these signals are assigned to C(5) of thione form, C(3) thione/thiol form and C(5) of thiol form, respectively, on the basis of the literature values reported for the related molecules [19,31,49,50]. In the ^{13}C NMR spectra of organotin(IV) triazolates, C(3) and C(5) are observed in the range δ 158.11–159.0 and 160.70–164.15 ppm, respectively. A small shift to lower δ value of C(3) signals may be due to the weakening of hydrogen bonding that occurs via NH$_2$ group, while a shift in δ value of C(5) signal is because of the evolution of thiolate ion on deprotonation of HL which participates in bond formation with organotin moiety [49]. The characteristic signals for all the magnetically non-equivalent alkyl- or phenyl-carbons of the organotin moieties have also been assigned, which are in good agreement with reported values [17]. For triorganotin(IV) derivatives viz. Me$_3$SnL, n-Pr$_3$SnL (Fig. 6b) and n-Bu$_3$SnL, the observed $^1J(^{13}C-^{119/117}Sn)$ values (~353–397 Hz) lie in the range of pseudotetrahedral arrangement as reported for other R$_3$Sn(XY) (where X or Y = O/N/S; XY are the donor sites of the bidentate ligand) [48,51]. For n-Bu$_2$SnL$_2$ the value of $^1J(^{13}C-^{119}Sn)$ is 397.13 Hz, which indicates a tetracoordinated tin. Moreover, the calculated values of $\angle$C–Sn–C using the observed $^1J(^{13}C-^{119}Sn)$ values in the equation given by Lockhart and Manders [48] ($|^1J| = 11.4\theta - 875$) are in the range of 108.0–111.6° (Table 3) indicating a distorted tetrahedral/pseudotetrahedral geometry for R$_2$Sn(S$_{exo}$)$_2$/R$_3$SnS$_{exo}$.

The ^{119}Sn NMR chemical shifts are very sensitive to coordination number of tin and are greatly shifted upfield
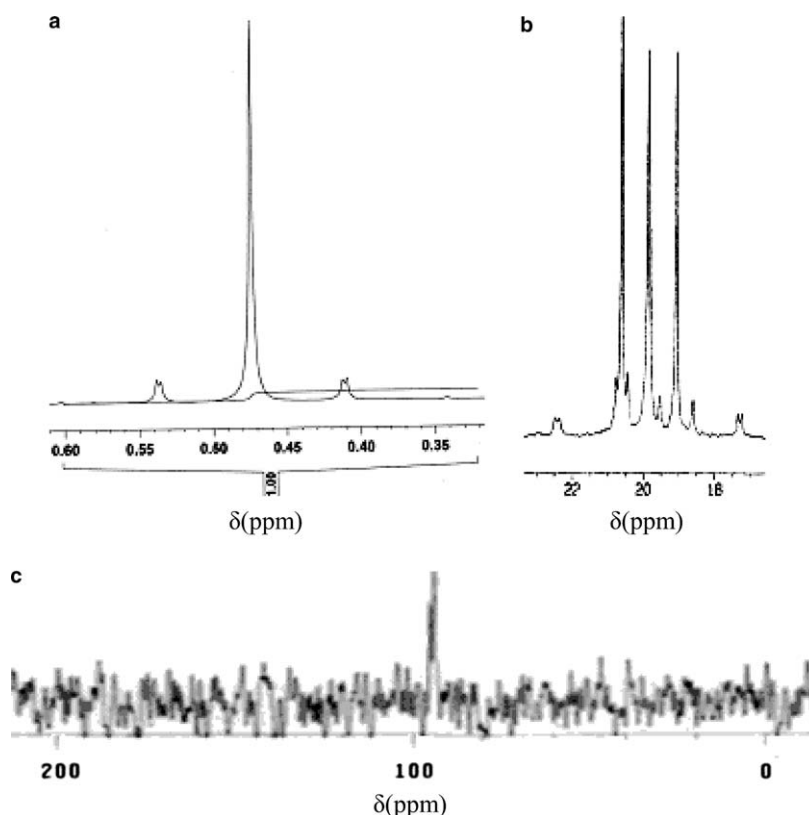

Fig. 6. (a) ^{1}H NMR spectrum of Me$_3$SnL; (b) ^{13}C NMR spectrum of n-Pr$_3$SnL; and (c) ^{119}Sn NMR spectrum of Me$_2$SnL$_2$.

Table 4
^{13}C and ^{119}Sn NMR spectral data[a] of organotin(IV) compounds of 3-amino-5-mercapto-1,2,4-triazole (in CD$_3$OD, if not indicated otherwise)

Ligand/compound (solvent)	δ ^{119}Sn (ppm)	δ ^{13}C (ppm)	$\angle$C–Sn–C (°)
HL (DMSO-d_6 + CDCl$_3$)		C(3): 161.72; C(5): 173.62 (thione); C(5): 151.14 (thiol)	–
1	96.0	C(3): 158.26; C(5): 164.15; C$_\alpha$: 1.94	–
2	–	C(3) + C(5): 160.0; C$_\alpha$: 24.27 [397.13];[b] C$_\beta$: 28.92 [28.69];[c] C$_\gamma$: 28.10 [46.06];[d] C$_\delta$: 14.11	111.60[e]
3 (CD$_3$OD + CDCl$_3$)	–	C(3): 158.47; C(5): 163.27; C$_\alpha$: 23.44; C$_\beta$: 34.97; C$_\gamma$: 26.15; C$_\delta$: 32.78, 32.73; C$_\theta$: 30.13; C$_\lambda$: 24.91; C$_\mu$: 21.33; C$_\omega$: 14.43	–
4	–	C(3): 159.0; C(5): 163.0; C$_\alpha$: 139.90; C$_\beta$: 137.70; C$_\gamma$: 129.70; C$_\delta$: 130.60	–
5	–	C(3): 158.72; C(5): 160.70; C$_\alpha$: −3.26 [353.0][b]	108.0[e]
6 (CDCl$_3$)[f]	92.18	C(3): 158.71; C(5): 162.49; C$_\alpha$: 19.86 [397.0/379.0];[b] C$_\beta$: 20.62 [24.16];[c] C$_\gamma$: 19.07 [70.22][d]	111.50[e]
7 (CDCl$_3$)[f]	94.36	C(3): 158.54; C(5): 162.86; C$_\alpha$: 16.85 [379.0/365.0];[b] C$_\beta$: 29.40 [23.41];[c] C$_\gamma$: 28.10 [66.44][d] C$_\delta$: 14.06	110.0[e]

$$\overset{\alpha}{\text{Sn-CH}_3}; \quad \overset{\alpha}{\text{Sn-CH}_2}\overset{\beta}{\text{CH}_2}\overset{\gamma}{\text{CH}_3}; \quad \overset{\alpha}{\text{Sn-CH}_2}\overset{\beta}{\text{CH}_2}\overset{\gamma}{\text{CH}_2}\overset{\delta}{\text{CH}_3}; \quad \overset{\alpha}{\text{Sn-CH}_2}\overset{\beta}{\text{CH}_2}\overset{\gamma}{\text{CH}_2}\overset{\delta}{\text{CH}_2}\overset{\theta}{\text{CH}_2}\overset{\lambda}{\text{CH}_2}\overset{\mu}{\text{CH}_2}\overset{\omega}{\text{CH}_3};$$

[a] Compound numbers according to Table 1.
[b] $^1J(^{13}$C–$^{119/117}$Sn).
[c] $^2J(^{13}$C–^{119}Sn).
[d] $^3J(^{13}$C–^{119}Sn).
[e] For $^1J(^{13}$C–^{119}Sn).
[f] For ^{119}Sn NMR.

on bonding to Lewis base. The ^{119}Sn NMR spectra of sufficiently soluble compounds, viz. Me$_2$SnL$_2$, n-Pr$_3$SnL and n-Bu$_3$SnL were recorded in CD$_3$OD or CDCl$_3$ in order to obtain additional support for the conclusions drawn by ^{1}H and ^{13}C NMR. The ^{119}Sn NMR spectrum of Me$_2$SnL$_2$ is shown in Fig. 6c. For Me$_2$SnL$_2$, n-Pr$_3$SnL and n-Bu$_3$SnL, the ^{119}Sn chemical shifts are observed at δ 96.0, 92.18 and 94.36 ppm, respectively. As reported in the literature [52], the values of ^{119}Sn chemical shifts in the ranges 200 to −60, −90 to −190 and −210 to −400 ppm have been associated with four-, five- and six-coordinate tin centers, respectively. The observed ^{119}Sn chemical shifts of the studied compounds are in the range of four-coordinate tin compounds and show an upward shift as compared to the reactants Me$_2$SnCl$_2$ ($\delta = 137$ ppm) and n-Bu$_3$SnCl ($\delta = 154$ ppm) [53].

Therefore, ^{119}Sn, ^{1}H and ^{13}C NMR spectral data reveal that the weak interaction between central tin and N(4) (as existing in the solid state supported by IR and ^{119}Sn Mössbauer) weakens further in the solution, leading to the distorted tetrahedral R$_2$Sn(S$_{exo}$)$_2$/pseudo-tetrahedral R$_3$SnS$_{exo}$ moiety.

4. Conclusions

Di- and triorganotin(IV) derivatives of 3-amino-5-mercapto-1,2,4-triazole (HL) possess hexa- and penta-coordination around tin, respectively, in the solid state. The diorganotin(IV) bis(triazolate) are proposed to have a distorted skew trapezoidal-bipyramidal structure in which the axial positions are occupied by the alkyl-/phenyl groups and the equatorial positions are occupied by the S$_{exo}$ and N(4). Whereas for triorganotin(IV) triazolates, a highly distorted *cis*-trigonal-bipyramidal structure has been proposed which is intermediate between *fac*- and *mer-cis*-trigonal-bipyramidal structures, in the solid-state. However, in

the solution the bonding between tin and N(4), becomes weaker leading to the distorted tetrahedral/pseudo-tetrahedral geometry.

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