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Synthesis, spectral and thermal studies of some organotin(IV) derivatives of 5-amino-3H-1,3,4-thiadiazole-2-thione

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Abstract

Some tri- and diorganotin(IV) compounds of the general formula, R_nSnL_{4-n} (where $n = 2$, R = Me, *n*-Bu and Ph; $n = 3$, R = Me, *n*-Bu, *n*-Pr and Ph; HL = 5-amino-3H-1,3,4-thiadiazole-2-thione) have been synthesized by the reaction of R_nSnCl_{4-n} (where $n = 2$ or 3, R = Me, *n*-Bu, *n*-Pr and Ph) and the sodium salt of the ligand. Oct_2SnL_2 was obtained by the reaction of Oct_2SnO with HL in a 1:2 molar ratio under azeotropic removal of water. The bonding and coordination behavior in these derivatives are discussed on the basis of IR, Far-IR, multinuclear (^1H, ^{13}C and ^{119}Sn) NMR and ^{119}Sn Mössbauer spectroscopic studies. These investigations suggest that in all the compounds the ligand acts as monoanionic bidentate coordinating through ring N(3) and exocyclic S. Thermal studies of five compounds, viz., Ph_3SnL, Me_2SnL_2, *n*-Bu_2SnL_2, Oct_2SnL_2 and Ph_2SnL_2 have been carried out in the temperature range 25–1000 °C using TG, DTG and DTA techniques under an atmosphere of dry nitrogen.

Keywords: Thiadiazole; Organotin(IV); TG; DTA; ^{119}Sn Mössbauer

1. Introduction

1,3,4-Thiadiazoles are a group of heterocycles whose derivatives are important in industry, medicine and agriculture [1–10]. Thiadiazole ring displays a broad spectrum of biocidal activities possibly by virtue of >N=C–S– toxophoric moiety. Its derivative 2-amino-1,3,4-thiadiazole is a cyclic analogue of thiosemicarbazone, which often displays diverse physiological activites. 2,5-Disubstituted-1,3,4-thiadiazole derivatives have been found to possess biocidal activities including antifungal [1–4], antibacterial [2–4], anti-inflammatory [5], antituberculosis [6], anticonvulsant [4,7], radioprotective [8] and anticancer [9,10] activity.

The metal coordination of substituted 1,3,4-thiadiazole is of current interest especially because of its relevance to metal interactions with biological molecules. Among the metals forming coordination compounds with these derivatives most are d-block metals [11–17]. However, relatively few investigations have involved coordination to organotin(IV) derivatives [18–21]. The organotin(IV) complexes with biologically important ligands have been of interest for the past few decades [22–24] owing to their possible use as potential metallopharmaceuticals. Since the mode of biological action of the organotin(IV) complexes, or even the parent organotin(IV) compounds, have not yet been completely understood and may vary from one compound to another [22–24]. Nevertheless, it has been proposed that the biological activity of these molecules may depend on the number of leaving groups available around Sn and consequently on geometry or on the strength of Sn–S and/or Sn–N bonds of the complexes [22]. Moreover, from structural viewpoint, the organotin(IV) derivatives of the ligands containing thioamide groups are interesting on account of the diversity of the coordination modes that stem from the presence of the –N=C=S– moiety. At least, four bonding modes between ligand and tin are conceivable (Fig. 1). Coordination with the exocyclic sulfur (Fig. 1a) can be found in every kind of monomeric structure. Coordination with only the endocyclic nitrogen (Fig. 1b)

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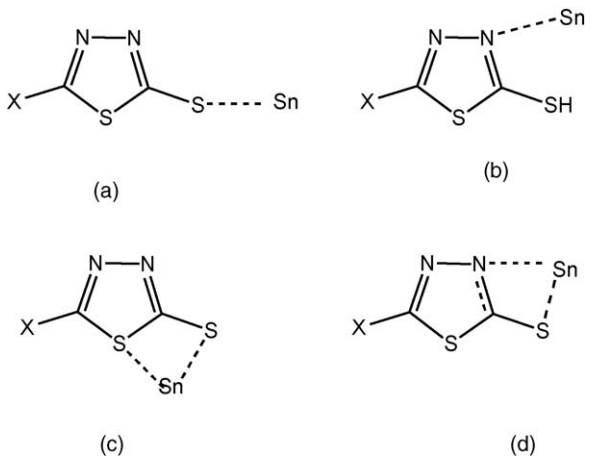


Fig. 1. Possible modes of coordination of heterocyclic ring containing thioamide group.

is not common for tin compounds, but it is often found for zinc derivatives [25]. Chelation by both S atoms (Fig. 1c) is to our knowledge unknown, but N, S chelation (Fig. 1d) is commonly observed in dialkyltin(IV) compounds [20,21]. In addition, bridging between different molecules via the heterocycles rather than chelation and/or distortion from regular geometry may also be possible.

Here, we report the synthesis and characterization of some tri- and diorganotin(IV) complexes of the heterocyclic thioamide such as 5-amino-3H-1,3,4-thiadiazole-2-thione.

2. Experimental

2.1. Materials and methods

All reactions were carried out in an anhydrous nitrogen atmosphere. Solvents were dried before use. Triphenyltin(IV) chloride, trimethyltin(IV) chloride, tri-*n*-propyltin(IV) chloride, tri-*n*-butyltin(IV) chloride, diphenyltin(IV) dichloride, dimethyltin(IV) dichloride, di-*n*-butyltin(IV) dichloride, dioctyltin(IV) oxide and 5-amino-3H-1,3,4-thiadiazole-2-thione (Merck-Schuchardt) were used as received.

2.2. Synthesis of organotin(IV) thiadiazolates

The tri- and diorganotin(IV) derivatives of 5-amino-3H-1,3,4-thiadiazole-2-thione have been synthesized by using following two methods.

2.2.1. Synthesis by sodium chloride method

5-Amino-3H-1,3,4-thiadiazole-2-thione (1.10 g, 8.0 mmol) was dissolved in the minimum amount (∼20 ml) of dry methanol and was added to sodium methoxide, prepared by dissolving sodium (0.18 g, 8.0 mmol) in dry methanol (∼10 ml). The resulting solution was stirred for 8 h at room temperature under inert atmosphere of dry nitrogen. To this methanol solution of triorganotin(IV) chloride (8.0 mmol)/diorganotin(IV) dichloride (4.0 mmol) was added dropwise with constant stirring and stirring was further continued for another 30–35 h at room temperature. It was centrifuged and filtered in order to remove sodium chloride. Excess of solvent was gradually removed by evaporation under vacuum until solid product was obtained. The solid was then recrystallized from dichloromethane-hexane (2:1, v/v) or dichloromethane-methanol (2:1, v/v) mixture.

2.2.2. Synthesis by azeotropic removal of water method

The dioctyltin(IV) derivative of 5-amino-3H-1,3,4-thiadiazole-2-thione was prepared by a dropwise addition of methanol solution (∼40 ml) of 5-amino-3H-1,3,4-thiadiazole-2-thione (0.80 g, 6.0 mmol) to the suspension of dioctyltin(IV) oxide (1.10 g, 3.0 mmol) in methanol (∼30 ml) with constant stirring at room temperature under inert atmosphere of dry nitrogen. The mixture obtained was stirred for 40 h at 35 °C. The water formed during the reaction was removed azeotropically. The solution was filtered, and the excess of solvent was gradually removed by evaporation under vacuum until solid product was obtained. The solid was then recrystallized from dichloromethane–methanol (2:1, v/v) mixture.

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 and sulfur were analyzed on 'Elementar Analyser systeme VarioEL' CHNS analyzer. UV–vis spectra of the compounds were recorded on a Shimadzu UV-1601, UV–vis spectrophotometer. IR and Far-IR spectra of the solid compounds were recorded on a Perkin-Elmer 1600 series FTIR in the range 4000–400 cm^{-1} in KBr discs and 500–200 cm^{-1} in CsI discs. Molar conductance measurements were carried out on the same instrument as reported previously [26]. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-300 (300 MHz FTNMR) spectrometer at the Central Drug Research Institute, Lucknow, India, using tetramethylsilane as internal standard. ^{119}Sn NMR spectra were recorded on a Mercury Varian 300 MHz, instrument at Regional Sophisticated Instrumentation Center, Indian Institute of Technology Bombay, India, using tetramethyltin as internal standard. ^{119}Sn Mössbauer spectra were recorded on a Mössbauer spectrometer model MS-900 according to the procedure reported previously [26], at the Department of Chemistry and Physics, University of The District of Columbia, Washington, DC. Thermal measurements were carried out on a Perkin-Elmer (Pyris Diamond) thermal analyzer under dry nitrogen (200 ml/min) atmosphere in the temperature range 25–1000 °C with heating rate 10 °C/min in a platinum crucible using alumina powder as a reference material.

3. Results and discussion

The reactions of triorganotin(IV) chloride/diorganotin(IV) dichloride with the sodium salt of 5-amino-3H-1,3,4-thiadiazole-2-thione {formed according to Eq. (1a)} led to the formation of the compounds according to Eqs. (1b) and (2). The reaction of dioctyltin(IV) oxide with 5-amino-3H-1,3,4-thiadiazole-2-thione in a 1:2 molar ratio resulted the product under azeotropic removal of water according to Eq. (3).

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

$$NaL + R_3SnCl \rightarrow R_3SnL + NaCl \quad (1b)$$

(where R = Me, *n*-Pr, *n*-Bu and Ph)

$$2NaL + R_2SnCl_2 \rightarrow R_2SnL_2 + 2NaCl \quad (2)$$

(where R = Me, *n*-Bu and Ph)

$$2HL + Oct_2SnO \rightarrow Oct_2SnL_2 + H_2O \quad (3)$$

(where HL = 5-amino-3H-1,3,4-thiadiazole-2-thione)

All of the synthesized compounds are yellow coloured and obtained in good yield (50–90%). All of the compounds are stable towards air and moisture. The triorganotin(IV) derivatives of 5-amino-3H-1,3,4-thiadiazole-2-thione are soluble in common organic solvents, whereas the diorganotin(IV) derivatives are insoluble in MeOH and $CHCl_3$ but sparingly soluble in DMSO. The analytical data of the compounds are presented in Table 1. The molar conductance of $\approx 10^{-3}$ M solutions of the synthesized compounds in DMSO observed in the range 7.0−10.0 $ohm^{-1}\,cm^2\,mol^{-1}$, indicating their non-electrolytic nature.

Table 2
Electronic spectral bands (nm) of 5-amino-3H-1,3,4-thiadiazole-2-thione and its organotin(IV) derivatives

Ligand/compound	Solvent	$\pi \rightarrow \pi^*$ (ε in $l\,mol^{-1}\,cm^{-1}$)	$n \rightarrow \pi^*$ (ε in $l\,mol^{-1}\,cm^{-1}$)
HL	MeOH	237 (3562)	316 (16690)
HL	DMSO	256 (1920)	322 (12700)
Me_3SnL	MeOH	230 (3250)	314 (11115)
n-Pr_3SnL	DMSO	224 (18181)	311 (7069)
n-Bu_3SnL	DMSO	258 (1667)	318 (6703)
Ph_3SnL	MeOH	217 (17181)	318 (12011)
Me_2SnL_2	DMSO	258 (4000)	318 (15653)
n-Bu_2SnL_2	DMSO	258 (4000)	318 (13915)
Ph_2SnL_2	DMSO	252 (2704)	319 (9141)
Oct_2SnL_2	DMSO	259 (4128)	318 (15653)

3.1. Electronic spectral studies

The electronic spectral bands (in nm) together with their ε (molar extinction coefficient) values of the ligand and its organotin(IV) derivatives are presented in Table 2. The spectra of the uncoordinated ligand and its organotin(IV) derivatives exhibit two absorption bands at 256 ± 2 and 318 ± 4 nm, which may be assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively, of the chromophor (>C=N–) present in thiadiazole ring [4]. These bands undergo a hyperchromic shift upon complexation indicating participation of >C=N– group in coordination.

3.2. Infrared spectral studies

The characteristic infrared frequencies and their assignments of the ligand and its organotin(IV) derivatives are presented in Table 3. It has been reported [27] that 5-amino-3H-1,3,4-thiadiazole-2-thione exhibts thione-thiol tautomerism

Table 1
Characteristic properties of organotin(IV) derivatives of 5-amino-3H-1,3,4-thiadiazole-2-thione

Compound (empirical formula)	Yield (%)	M.P. (°C)	Colour and physical State	Analysis (%): found (calculated)				
				C	H	N	S	Sn
Me_3SnL $[C_5H_{11}N_3S_2Sn]$	75	138–140	Yellow solid	20.27 (20.29)	3.65 (3.74)	14.11 (14.20)	21.57 (21.66)	40.10 (40.10)
n-Pr_3SnL $[C_{11}H_{23}N_3S_2Sn]$	55	–	Yellow semi-solid	34.66 (34.75)	5.97 (6.10)	10.98 (11.05)	16.77 (16.87)	31.00 (31.23)
n-Bu_3SnL $[C_{14}H_{29}N_3S_2Sn]$	60	–	Yellow semi-solid	39.56 (39.82)	6.83 (6.92)	9.68 (9.95)	14.98 (15.19)	27.99 (28.11)
Ph_3SnL $[C_{20}H_{17}N_3S_2Sn]$	84	198–200	White solid	49.56 (49.81)	3.33 (3.55)	8.58 (8.71)	12.86 (13.30)	24.31 (24.62)
Me_2SnL_2 $[C_6H_{10}N_6S_4Sn]$	64	178–182	Yellow solid	17.40 (17.44)	2.38 (2.44)	20.25 (20.34)	30.77 (31.04)	28.69 (28.73)
n-Bu_2SnL_2 $[C_{12}H_{22}N_6S_4Sn]$	90	131–133	Yellow solid	28.95 (28.98)	4.40 (4.46)	16.81 (16.90)	25.68 (25.79)	23.85 (23.87)
Oct_2SnL_2 $[C_{20}H_{38}N_6S_4Sn]$	80	130–135	Yellow solid	39.38 (39.41)	6.21 (6.28)	13.68 (13.79)	20.88 (21.04)	19.38 (19.48)
Ph_2SnL_2 $[C_{16}H_{14}N_6S_4Sn]$	51	188–191	Yellow solid	35.65 (35.77)	2.57 (2.63)	15.51 (15.64)	23.69 (23.87)	22.12 (22.09)

Table 3
Characteristic IR frequencies (cm^{-1}) of 5-amino-3H-1,3,4- thiadiazole-2-thione and its organotin(IV) derivatives[a]

Assignments	HL	Me_3SnL	n-Pr_3SnL	n-Bu_3SnL	Ph_3SnL	Me_2SnL_2	n-Bu_2SnL_2	Oct_2SnL_2	Ph_2SnL_2
ν_{as} (NH_2)	3347 m 3323 sh	3270 br	3354 m 3326 m	3317 w 3271 w	3281 m	3300 m 3280 m	3335 m 3261 m	3338 m 3252 m	3344 m
ν_s (NH_2)	3244 m 3222 w	3066 br	3192 m 3080 w	3156 w 3116 w	3160 w	3213 vw	3127 s	3134 mbr	3268 w 3224 m
ν_{as} (N(3)─H)	3108 s	–	–	–	–	–	–	–	–
ν_s (N(3)─H)	2923 m	–	–	–	–	–	–	–	–
ν_s (S─H)	2622 vw 2542 vw	–	–	–	–	–	–	–	–
δ (N─H) + ν (C═N)	1604 vs	1632 s	1611 sh	1624 s	1605 s	1633 vs	1607 vs	1610 vs	1608 vs
ν (C═N)/ring mode	1547 vs 1476 vs	1496 vs 1410 w	1589 s 1457 s	1510 vs 1459 w	1513 vs 1422 s	1505 s –	1502 vs 1461 m	1553 vs 1471 vs	1505 vs 1424 m
ν (C═N) + δ (N─H)	1365 m 1326 m 1166 w	1320 w – 1126 s	1377 s 1333 sh 1154 w	1369 m 1328 vw 1131 w	1312 w 1267 sh 1133 w	1373 s – 1132 s	1363 vs 1143 m	1363 s 1329 m 1130 w	1369 w 1136 w
ν (C═S)	1240 w	1196 w	1193 w	1183 w	1188 w	1197 w	1183 w	1175 w	1200 vw
ν (N─N)	1058 m 1030 s	1032 vs	1030 s	1032 vs	1046 vs	1040 s	1031 vs	1059 vs 1035 s	1042 vs
δ (N─H) + ring-in-plane bending	750 m 719 m	780 vs	703 vw	733 vw	726 s 694 s	784 m	752 m	755 s 716 m	727 m
Ring torsion + ν (C─S) (ring) + ν (C─S) (exocyclic)	672 w	678 sh	583 vw	594 w	594 vw	685 sh	679 s	665 m	695 m
	634 w 534 s	–	538 w 489 sh	539 vw 511 m	550 w 494 w	– –	–	643 m	539 m
ν_{as} (Sn─C)	–	605 m	670 m	674 s	265 vs	635 w	603 s	603 s	264 s
ν_s (Sn─C)	–	537 s	607 m	594 w	242 s	571 s	559 s	566 s	242 s
ν (Sn─N)	–	426 vs	436 s	435 m	444 s	430 s	434 vs	432 s	451 s
ν_s (Sn─S)	–	345 w	359 m	332 m	339 s	362 s	341 m	350 s	339 m

[a] νs, very strong; s, strong; m, medium; w, weak; vw, very weak; sbr, singlet broad; sh, shoulder.

(Fig. 2a and b) and both forms coexist in the solid state but thione form is the dominant one.

In the uncoordinated ligand two bands have been observed at 2622 and 1240 cm^{-1} which can be assigned to the ν(S–H) and ν(C=S) vibrational modes, respectively, indicating the coexistence of both thione and thiol forms in the solid state. In the spectra of the organotin(IV) compounds, the ν(S–H) is not observed which indicates the deprotonation of thiol form and the ν(C=S) undergoes a downward shift by 53 ± 13 cm^{-1} indicating the coordination of thione sulfur to tin.

In the uncoordinated ligand spectrum two bands at 3347 and 3244 cm^{-1} are assigned to $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ modes, respectively. Two additional bands at 3108 and 2923 cm^{-1} are attributable to the N(3)–H stretching of thione tautomer, these bands appear at low frequencies due to the intramolecular hydrogen bond N(3)–H $\cdots$ $S_{exocyclic}$ [27]. In the spectra of compounds studied, the $\nu(NH_2)$ absorption bands undergo a downward shift by ~30–90 cm^{-1} when compared to the free ligand, but a downward shift by 200–300 cm^{-1} would require for the coordination of the ligand through the amino group [28]. Therefore, the observed downward shift in $\nu(NH_2)$ is mainly due to the involvement of the amino group in inter-and/or intramolecular hydrogen bonding. Further, the N(3)–H stretching vibrational modes are not observed in the spectra of the compounds studied indicating the deprotonation of N(3)–H of the ligand.

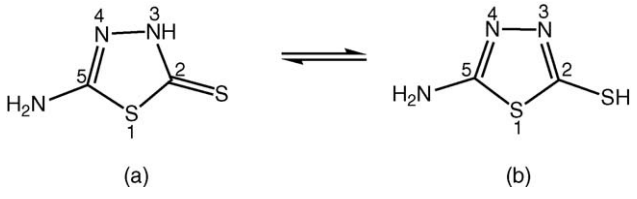


Fig. 2. Thione and thiol tautomers of 5-amino-3H-1,3,4-thiadiazole-2-thione.

Two bands observed in the spectrum of the ligand at 1547 and 1365 cm^{-1}, which may be assigned to the combination bands [δ(NH)(major) + ν(C=N)(minor)] and [δ(NH)(minor) + ν(C=N) (major)] [11], respectively, are shifted towards lower wave numbers in the organotin(IV) compounds, indicating that the ring nitrogen N(3) is coordinated to the central tin atom. Further, most of the ring band shifts observed in this region are in agreement with the ring structural changes occurred after the coordination of ring nitrogen N(3) to tin [12]. The above mode of coordi-

nation of the 5-amino-3H-1,3,4-thiadiazole-2-thione through N(3) and exocyclic sulfur is further confirmed by the appearance of two new bands at 439 ± 13 and $347 \pm 15\,cm^{-1}$ in the spectra of the organotin(IV) compounds, which are assigned to ν(Sn–N) [26] and ν(Sn ← S) [28], respectively. The ν_{as}(Sn–C) and ν_s(Sn–C) bands in all the tri- and dialkyltin(IV) derivatives have been observed at 639 ± 36 and $572 \pm 35\,cm^{-1}$, respectively, whereas the corresponding vibrational bands in tri- and diphenyltin(IV) analogues are observed at 265 and 242 cm^{-1}, respectively [22].

3.3. Solution NMR spectral studies

The ^1H and ^{13}C NMR chemical shifts of the uncoordinated ligand [29] and its organotin(IV) derivatives, are presented in Table 4. It has been reported [29] that ring N(3)–H in the uncoordinated ligand is clearly observed at δ 13.2 ppm instead of the aromatic SH in the region δ 2.0–5.0 ppm; indicating that the ligand exists in thione form rather than the thiol form in DMSO-d_6 solution. Further, the absence of the thiol SH proton resonances in the ^1H NMR spectra of the organotin(IV) compounds confirms the thione tautomer as the dominant species of the ligand in all of its organotin(IV) compounds in solution. The resonances of NH_2 protons in the ^1H NMR spectra of the organotin(IV) compounds become sharp and shift slightly to up field as compared to the uncoordinated ligand (sbr, 7.0 ppm) due to the formation of the Sn ← S bond, and the extent of N–H $\cdots$ $S_{(exocyclic)}$ hydrogen bonding is greatly reduced [28]. In the ^{13}C NMR spectrum of the uncoordinated ligand C(2) and C(5) are reported [29] at δ 181.2 and 161.6 ppm, respectively. Further, in the ^{13}C NMR spectra of the organotin(IV) compounds the signal of C(5) is shifted to lower field whereas that of C(2) is shifted to higher field upon complexation, as expected for a process involving deprotonation of N(3) and a partial evolution of the thione form at C(2) into a thiolate form [30]. All magnetically non-equivalent protons and carbons of the alkyl or phenyl groups attached to tin have been identified and their chemical shift values are in close agreement with the reported values [22].

The ^{119}Sn NMR chemical shift is very sensitive to complexation and is usually shifted downfield or upfield on bonding to a Lewis base. Typical ranges of tin chemical shifts have been proposed [31] for coordination number five (δ −90 to −330 ppm) and six (δ −125 to −515 ppm) for organotin(IV) compounds in $CDCl_3$ solution. The ^{119}Sn chemical shift values in Ph_3SnL and Me_3SnL at δ −368.5 and −211.2 ppm, respectively, suggest that Ph_3SnL and Me_3SnL are five-coordinated in CD_3OD solution. The ^{119}Sn NMR spectra of diorganotin(IV) compounds were not recorded because of their low solubility in common organic solvents.

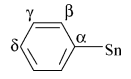
3.4. ^{119}Sn Mössbauer spectral studies

^{119}Sn Mössbauer spectral data of all the compounds are given in Table 5. Mössbauer spectra of all the triorganotin(IV) derivatives of 5-amino-3H-1,3,4-thiadiazole-2-thione viz. R_3SnL (where R = Me, *n*-Pr, *n*-Bu and Ph) exhibit a well resolved doublet centered in the isomer shift (I.S.) value range 1.36–1.45 mm s^{-1}. The quadruple splitting (Q.S.) values in the range 2.05–3.51 mm s^{-1} for R_3SnL compounds indicate that the electric field gradient around the tin nucleus is produced by the inequalities in the tin-ligand σ bond and is also due to the geometric distortions. The ρ(Q.S./I.S.) value of 1.50 in triphenyltin(IV) derivative and 1.90–2.17 in trialkyltin(IV) derivatives indicate a coordination number 4 and

Table 4
^1H and ^{13}C NMR spectral data of 5-amino-3H-1,3,4- thiadiazole-2-thione and its organotin(IV) derivatives[a]

Compound	Solvent	δ (ppm)
HL[b]	DMSO-d_6	7.00 (sbr, 2H, NH_2), 13.20 (s, 2H, N(3)—H)). C-2: 181.2; C-5: 161.6
Me_3SnL	DMSO-d_6	C-α: −2.0; C-2: 172.0; C-5: 169.1
n-Pr_3SnL	$CDCl_3$	1.38 (t, 6H, 8 Hz, H-α); 1.79 (m, 6H, H-β)[c]; 1.08 (t, 9H, 7 Hz, H-γ); 6.33 (s, 2H, NH_2)
	$CDCl_3$ + DMSO-d_6	C-2: 167.6; C-5: 165.4; C-α:21.3; C-β: 19.4 [26][d]; C-γ: 18.6 [75][d]
n-Bu_3SnL	$CDCl_3$	1.33 (m, 12H, H-α, H-γ)[e]; 1.61 (m, 6H, H-β)[f]; 0.9 (t, 9H, 7 Hz, H-δ); 5.38 (s, 2H, NH_2) C-2: 168.0; C-5: 157.0; C-α:16.0; C-β: 28.34 [45][d]; C-γ: 26.9 [63][d]; C-δ:13.5
Ph_3SnL	$CDCl_3$	7.70 (d, 6H, 3 Hz, H-β) [61/51][d]; 7.39 (dd, 9H, 3, 3 Hz, H-γ and H-δ); 5.90 (s, 2H, NH_2) C-2: 169.0; C-5: 167.1; C-α: 138.3; C-β: 136·3 [45][d]; C-γ: 128.4 [60][d]; C-δ: 129.3
Me_2SnL_2	DMSO + 1drop $CDCl_3$	1.18 (s, 6H, H-α); 0.87 (s, 6H, H-α)[g] [66][d]; 6.37 (sbr, 4H, NH_2) C-2: 163.0; C-5: 156.0; C-α: 0.91
n-Bu_2SnL_2	DMSO-d_6	1.25 (m, 8 H, H-α and H-γ); 1.52 (mbr, 4H, H-β); 0.82 (t, 6H, 6 Hz, H-δ); 6.80 (sbr, 4H, NH_2) C-2: 170.6; C-5: 162.8; C-α: 26.4; C-β: 27.1; C-γ: 26.6; Cδ:13.6
Ph_2SnL_2	DMSO-d_6	7.83 (d, 4H, 6 Hz, H-β) [70/57][d]; 7.39 (dd, 6H, 6, 7 Hz, H-γ and H-δ); 6.67 (sbr, 4H, NH_2) C-2: 171.0; C-5: 164.7; C-α: 142.1; C-β: 136.3 [45][d]; C-γ 128.3 [60][d]; C-δ: 128.9

α γ β α δ γ β α
H_3C–Sn; H_3C–H_2C–H_2C–Sn; H_3C–H_2C–H_2C–H_2C–Sn;



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[a] s, singlet; d, doublet; dd, double doublet; t, triplet; m, multiplet; sbr, singlet broad.
[b] Ref. [29].
[c] Strongly overlapping pattern of quartet and triplet.
[d] $^nJ[^1H$-$^{119/117}Sn]/^nJ[^{13}C$-$^{119/117}Sn]$.
[e] Strongly overlapping patterns
[f] Overlapping pattern of triplets
[g] Peak of trimethyltin–dimethylsulfoxide complex formed.

Table 5
^{119}Sn Mössbauer data (80 K) of the organotin(IV) derivatives of 5-amino-3H-1,3,4-thiadiazole-2-thione[a]

Compound	Q.S. (mm s^{-1})	I.S. (mm s^{-1})	ρ (Q.S./I.S.)	τ (L)	τ (R)
Me_3SnL	2.58	1.36	1.90	1.90	1.10
n-Pr_3SnL	3.51	1.45	2.17	1.22	1.39
n-Bu_3SnL	3.00	1.40	2.14	1.51	1.83
Ph_3SnL	2.05	1.36	1.51	1.15	0.94
Me_2SnL_2	2.86	1.11	2.58	1.12	1.48
n-Bu_2SnL_2	2.99	1.23	2.43	1.11	1.27
Oct_2SnL_2	2.10	0.98	2.14	1.03	1.20
Ph_2SnL_2	1.73	0.65	2.66	1.48	1.88

[a] Q.S., quadrupole splitting; I.S., isomeric shift relative to $BaSnO_3$ and tin foil (splitting 2.52 mm s^{1}); τ (L): Half line-width left doublet component; τ (R): half line-width right doublet component.

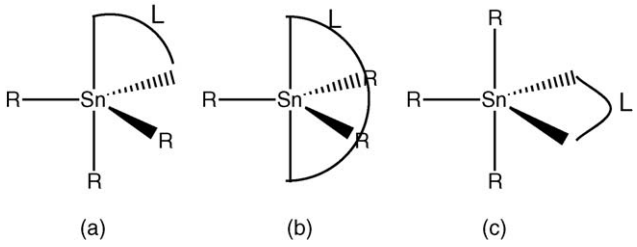

Fig. 3. Three possible isomers for R_3SnL.

5, respectively [32]. The low value of Q.S. for Ph_3SnL is due to greater polarizibility of the phenyl groups.

The observed Q.S. value of 2.58 mm s^{-1} for Me_3SnL is substantially lower than those typical for *trans*-trigonal bipyramidal configuration (Fig. 3b) of tin as found in R_3SnO_2 fragments (3.00–4.00 mm s^{-1}) of triorganotin(IV) carboxylates, but slightly higher than those for *cis*-trigonal bipyramidal (1.70–2.40 mm s^{-1}) (Fig. 3a) and pseudotetrahedral (1.00–2.40 mm s^{-1}) arrangements [33]. Therefore, a highly distorted tetrahedral structure involving weak interaction between N(3) and Sn or a distorted *cis*-trigonal bipyramidal structure (Fig. 4) has been tentatively proposed for Me_3SnL. The geometric distortion is due to the formation of four membered Sn, S, C, N chelate ring [30]. This structure is further supported by ^{119}Sn NMR in solution CD_3OD where ^{119}Sn chemical shift value (δ −211.20 ppm) clearly indicates the coordination number greater than four. The observed Q.S. value of 2.05 mm s^{-1} for Ph_3SnL lies in the

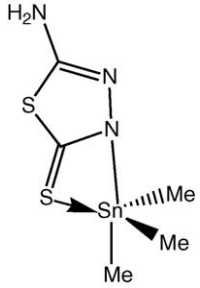

Fig. 4. Proposed structure of trimethyltin(IV) derivative of 5-amino-3H-1,3,4-thiadiazole-2 thione.

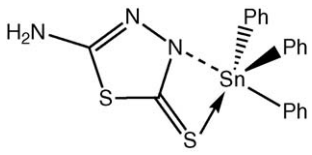

Fig. 5. Proposed structure of triphenyltin(IV) derivative of 5-amino-3H-1,3,4-thiadiazole 2 thione.

range typical of *cis*-trigonal bipyramidal configuration of tin as found in R_3SnO_2 fragments of triorganotin(IV) carboxylates (Fig. 3a) or pseudotetrahedral configuration but the ρ value 1.51 suggests four coordination number of tin. Therefore, the most probable geometry around tin in Ph_3SnL may be pseudotetrahedral (Fig. 5) because of the bigger size of phenyl groups and steric strain introduced in the molecule, involving weak Sn–N(3) interactions. But ^{119}Sn chemical shift value of (δ −368.55 ppm) in its ^{119}Sn NMR spectrum is clearly indicative of five coordination of tin in solution. The proposed structure is also in good agreement with the structure determined [18] by Ng et al. by single crystal X-ray diffraction. On the other hand, the Q.S. values 3.00 and 3.50 mm s^{-1} observed for n-Bu_3SnL and n-Pr_3SnL, respectively, suggest a severely distorted polymeric *trans*-trigonal bipyramidal geometry around tin (Fig. 3b) in which the equatorial positions are occupied by n-butyl or n-propyl groups and exocyclic S and N(3) from the adjacent molecule occupy the apical positions (Fig. 6).

The spectra of all the diorganotin(IV) derivatives of 5-amino-3H-1,3,4-thiadiazole-2-thione, viz. R_2SnL_2 (where R = Me, n-Bu, Ph and Oct), exhibit a doublet centered in the isomer shift value range 0.65–1.23 mm s^{-1} and Q.S. values in the range 1.73–2.99 mm s^{-1}. The ρ(Q.S./I.S.) values (2.14–2.66) in R_2SnL_2 compounds indicate a coordination number greater than four with either 5- or 6-coordinated tin [32]. The Q.S. values for *trans*- and *cis*-octahedral $[R_2SnX_4]^{-2}$ are around 4.00 and 2.00 mm s^{-1}, respectively [33]. Further, it has been reported [33] that I.S. values for *cis*-$[R_2SnX_4]^{-2}$ are less than 1.00 mm s^{-1}

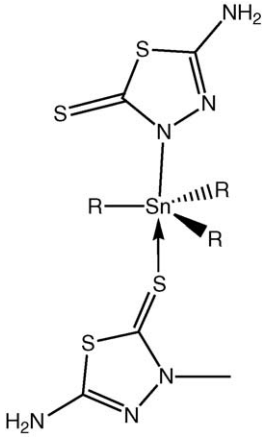

Fig. 6. Proposed structure of R_3Sn(IV) derivatives of 5-amino-3H-1,3,4-thiadiazole-2-thione where R = n-Pr and n-Bu.

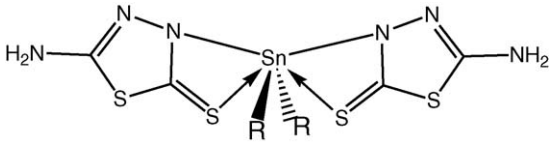

Fig. 7. Proposed structure of $R_2Sn(IV)$ derivatives of 5-amino-3H-1,3,4-thiadiazole-2-thione, where R = Me and *n*-Bu.

while those for *trans*- are approximately 1.2–1.3 mm s^{-1}. The observed values of Q.S. and I.S. of R_2SnL_2 are substantially lower than the values for *trans*-octahedral configuration and slightly higher than the values for *cis*-octahedral configuration. Further, the ∠C–Sn–C for the dimethyltin(IV) derivative is calculated by using Parish's relationship [34]: $Q.S. = 4[R][1 - 3/4 \sin^2 2\theta]^{1/2}$, where ∠C–Sn–C is $(180 - 2\theta)^\circ$ and $R = -1.03$ mm s^{-1}, is the partial quadruple splitting for methyl groups bonded to tin. The calculated value of ∠C–Sn–C in Me_2SnL_2 is 124°, which is again intermediate between the corresponding *cis*-octahedral with ∠C–Sn–C = 90° and *trans*-octahedral with ∠C–Sn–C = 180°. Thus, the structure of Me_2SnL_2 and *n*-Bu_2SnL_2 are best described by the highly distorted square bipyramidal/skew trapezoidal bipyramidal configuration [35,36] (Fig. 7), with the two organic groups (Me or *n*-Bu) in bent axial positions and trapezoidal plane being defined by the two Sn–S coordination and the two Sn–N(3) interactions. A similar structure has also been reported [37] for $Bu_2Sn(mbo)_2$ (where Hmbo is 1,2-mercaptobenzoxazole). The observed Q.S. values 1.73–2.10 mm s^{-1} and I.S. values 0.65–0.98 mm s^{-1} for Ph_2SnL_2 and Oct_2SnL_2 lie in the range typical of *cis*-octahedral structure (Fig. 8).

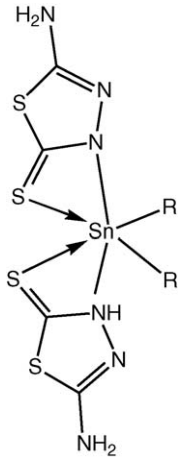

Fig. 8. Proposed structure of $R_2Sn(IV)$ derivatives of 5-amino-3H-1,3,4-thiadiazole-2-thione where R = Oct and Ph.

3.5. Thermal studies

The thermal decomposition behavior of Ph_3SnL, Me_2SnL_2, *n*-Bu_2SnL_2, Oct_2SnL_2 and Ph_2SnL_2 have been studied using TG, DTG and DTA techniques under an inert atmosphere of dry nitrogen. The DTG, DTA and TG temperature ranges, peak temperatures in DTA and DTG, percent weight loss as well as enthalpy of DTA peaks are presented in Table 6.

Ph_3SnL melts at 199 °C as evident by an endothermic peak in its DTA curve and decomposes in three steps. The weight loss in the first step of decomposition, which extends from 180 to 225 °C, corresponds to the loss of ligand moiety

Table 6
Thermal analysis data of organotin(IV) derivatives of 5-amino-3H-1,3,4-thiadiazol-2-thione

Compound	Step no.	Temperature range in TG (°C)	Temperature range in DTG (°C)	Peak temperature in DTG (°C)	Temperature range in DTA (°C)	Peak temperature in DTA (°C)	Enthalpy (mJ/mg)	% Wt. loss of mass obsd. (calcd.)
Ph_3SnL	I	180–225	200–225	217	181–205	199 (endothermic)	40.3	27.01 (27.41)
					205–225	216 (exothermic)	−115	
	II	225–350	283–350	320	–	Broad exothermic	–	17.94 (15.99)
	III	350–1000	761–839	800	674–833	782 (endothermic)	579	30.60 (31.98)
Me_2SnL_2	I	110–282	188–282	216	182–206	200 (endothermic)	25.5	32.45 (32.00)
					206–209	215 (exothermic)	−64.4	
	II	282–665	605–635	627	–	Broad exotherm	–	25.00 (24.23)
	III	665–900	750–831	808	765–950	871 (endothermic)	478	7.43 (7.28)
n-Bu_2SnL_2	I	55–330	125–142	132	–	Broad exotherm	–	46.57 (46.71)
			200–330	219, 302				
	II	330–711	590–610	597	–	Broad exotherm	–	22.70 (22.97)
Oct_2SnL_2	I	174–333	195–330	231, 272	195–237	227 (endothermic)	60.1	44.25 (43.37)
	II	333–537	330–370	343	–	Broad exotherm	–	18.25 (18.58)
	III	537–828	595–620	613	–	Broad exotherm	–	18.20 (18.58)
			815–828	819				
Ph_2SnL_2	I	150–241	186–229	204	194–229	209 (exothermic)	−50.4	22.86 (24.60)
	II	241–644	475–645	622	–	Broad exotherm	–	35.0 (32.99)
	III	644–900	859–882	864	781–819	801 (endothermic)	23.2	20.00 (20.32)
					852–879	865 (endothermic)	29.7	

($C_2H_2N_3S_2$; wt. loss obsd. 25.94%: calcd. 27.41%). Thereafter one phenyl group is lost (wt. loss obsd.17.94%: calcd. 15.99%) in the second step with subsequent loss of other two phenyl groups (wt. loss obsd. 30.60%: calcd. 31.98%) in the third step of decomposition leaving 2.439 mg (24.39%) residue (relative to 10.0 mg of sample taken) up to 1000 °C (maximum temperature recorded).

The diorganotin(IV) derivatives viz., Me_2SnL_2 and Ph_2SnL_2 decompose in three steps. The weight losses in the first step of decomposition correspond to the loss of ligand moiety ($C_2H_2N_3S_2$) leaving the intermediates of tentative compositions $C_4H_8N_3S_2Sn$ and $C_{14}H_{12}N_3S_2Sn$, respectively, which undergo slow decomposition of a part of ligand moiety ($C_2H_2N_3S$; wt. loss obsd. 25.00%: calcd. 24.23%) in case of Me_2SnL_2 and a part of ligand moiety together with a phenyl group ($C_2H_2N_3S + C_6H_5$; wt. loss obsd. 35.00%: calcd. 32.99%) in case of Ph_2SnL_2. In case of Me_2SnL_2, two methyl groups are lost in the third step of decomposition yielding SnS, whereas in case of Ph_2SnL_2 the observed weight loss (20.00%) corresponds to the loss of one phenyl group and sulfur atom leaving 2.00 mg (relative to 10.00 mg of sample taken) residue. *n*-Bu_2SnL_2 decomposes in two steps in the temperature range 55–711 °C. The first step of its decomposition (55–330 °C) corresponds to the loss of two ligand moieties ($C_4H_4N_6S_3$; wt. loss obsd. 46.57%: calcd. 46.71%) yielding an intermediate having tentative composition $C_8H_{18}SnS$ which decomposes in the temperature range 330–711 °C with the loss of two butyl groups (wt. loss obsd. 22.70%: calcd. 22.97%) giving 2.837 mg (relative to 10.0 mg of sample taken) of SnS. It has been recently reported that SnS is formed in the thermal decomposition of diphenyltin(IV) derivatives of 2-mercaptobenzothiazole [38]. Oct_2SnL_2 decomposes in three steps with the loss of two ligand moieties (wt. loss obsd. 44.25%: calcd. 43.37%) in the first step followed by slow decomposition of two octyl groups in the second and third step of decomposition. The respective DTG and DTA peaks are presented in Table 6.

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