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Synthesis and spectral studies of organotin(IV) 4-amino-3-alkyl-1,2,4-triazole-5-thionates: *In vitro* antimicrobial activity

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Abstract

Some di- and triorganotin(IV) triazolates of general formula, $R_{(4-n)}SnL_n$ (where $n = 2$; R = Me, *n*-Bu and Ph; $n = 1$; R = Me, *n*-Pr, *n*-Bu and Ph and HL = 4-amino-3-methyl-1,2,4-triazole-5-thiol (HL-**1**); and 4-amino-3-ethyl-1,2,4-triazole-5-thiol (HL-**2**)) were synthesized by the reaction of $R_{(4-n)}SnCl_n$ with sodium salt of HL-**1** and HL-**2**. The bonding and coordination behavior in these derivatives have been discussed on the basis of IR and ^{119}Sn Mössbauer spectroscopic studies in the solid state. Their coordination behavior in solution is discussed by multinuclear (^{1}H, ^{13}C and ^{119}Sn) NMR spectral studies. The IR and ^{119}Sn Mössbauer spectroscopic studies indicate that the ligands, HL-**1** and HL-**2** act as a monoanionic bidentate ligand, coordinating through S^-_{exo} and N_{ring}. The distorted skew trapezoidal-bipyramidal and distorted trigonal bipyramidal geometries have been proposed for R_2SnL_2 and R_3SnL, respectively, in the solid state. *In vitro* antimicrobial screening of some of the newly synthesized derivatives and of some di- and triorganotin(IV) derivatives of 3-amino-1,2,4-triazole-5-thiol (HL-**3**) and 5-amino-3H-1,3,4-thiadiazole-2-thiol (HL-**4**) along with two standard drugs such as fluconazole and ciprofloxacin have been carried out against the bacteria, viz. *Staphylococcus aureus* and *Escherichia coli*, and against some fungi, viz. *Aspergillus fumigatus, Candida albicans, Candida albicans* (ATCC 10231), *Candida krusei* (GO_3) and *Candida glabrata* (HO_5) by the filter paper disc method. The studied organotin(IV) compounds show mild antifungal activity as compared to that of fluconazole, however, they show almost insignificant activity against the studied Gram-positive (*Staphylococcus aureas*) and Gram-negative (*Escherichia coli*) bacteria as compared to that of standard drug, ciprofloxacin.

Keywords: 1,2,4-Triazole; 1,3,4-Thiadiazole; Organotin(IV) compounds; Antifungal activity; Antibacterial activity

1. Introduction

Organotin compounds have emerged as potentially active compounds among non-platinum chemotherapeutic metallopharmaceuticals in the last two decades. Some organotin(IV) derivatives have been found to exhibit antitumor activity against a number of tumor cell lines of human origin [1–4]. Organotin compounds are formulated as wettable and flowable powders for use mainly as fungicides to control blights on field crops and orchard trees, and as molluscicides, acaricides and in marine antifouling paints [5]. Besides this, the organotin(IV) compounds, viz. Brestan (Ph_3SnOAc) and Duter (Ph_3SnOH) are commercially used as antifungal agents [6], therefore, several studies have been carried out to explore their antimicrobial activity [7–11]. Many *in vitro* studies have been performed in order to explain the mechanism which is responsible for the biological activity of organotin compounds. Although, the mode of biological action of organotin compounds is not completely understood, but it has been revealed from the literature that the biocidal properties of organotin(IV) compounds are dependent on both the organic group and the ligand attached to tin. In this context, the interaction of organotins has been extensively studied with a variety of ligands having their biological origin [3,12] and with other hetero (N/S/O) donor ligands [9–12]. The coordination of organotins with heterocyclic thionates is of current interest because thionates can coordinate to the metal ions in different coordinating modes [13]. Moreover, heterocyclic thionates can (a) mimic cysteine sulfur coordination in metalloenzymes, (b)

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show electronic and structural properties of the active sites in copper blue proteins involving S, N-coordination, (c) comprise purine and pyrimidine bases [14,15].

Among N-heterocyclic thionates, thiadiazoles and triazoles, in particular, are interesting compounds because of their chemistry and biological activity. The biocidal activities, e.g., antifungal [16,17], antibacterial [16,17], antiinflammatory [18], antituberculosis [19], anticonvulsant [17,20] and anticancer [21] activities, of thiadiazole derivatives are possibly by virtue of >N=C–S– toxophoric moiety. However, 1,2,4-triazole represents a hybrid of pyrazole and imidazole with regard to the arrangement of ring nitrogens [22]. 1,2,4-Triazole and their derivatives possess a broad range of biological activities including antimicrobial and antifungal activities [23,24]. Examples of such compounds bearing the 1,2,4-triazole moieties are fluconazole, a powerful antifungal agent [25] and *N*-nucleoside ribavirin, a potent antiviral compound [26]. Several new triazole derivatives are in various phases of preclinical and clinical trials [27] and may be available for human use in the near future. In addition to this, the derivatives of thiadiazoles and triazoles have been broadly applied in the area of pharmaceutical, agricultural, industrial, and polymer chemistry [22].

In the present paper, we report the synthesis and characterization of organotin(IV) derivatives of HL-**1** and HL-**2**. The *in vitro* antibacterial and antifungal activities of the ligands, viz. 4-amino-3-methyl-1,2,4-triazole-5-thiol (HL-**1**), 4-amino-3-ethyl-1,2,4-triazole-5-thiol (HL-**2**), 3-amino-1,2,4-triazole-5-thiol (HL-**3**) and 5-amino-3H-1,3,4-thiadiazole-2-thiol (HL-**4**) (Scheme 1) and some of their organotin(IV) derivatives against the bacteria, *S. aureus* and *E. coli*, and against the fungi, viz. *A. fumigatus, C. Albicans, C. albicans* (ATCC 10231), *C. krusei* (GO_3) and *C. glabrata* (HO_5), carried out by the filter paper disc method, have also been reported. The synthesis and characterization of tri- and diorganotin(IV) derivatives of HL-**3** and HL-**4** have been reported previously in [28,29].

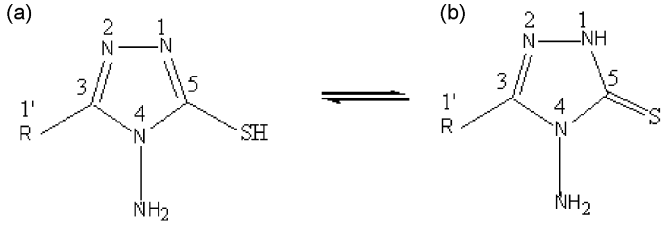
2. Experimental

2.1. Materials and methods

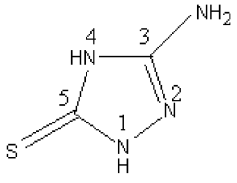
All the syntheses were carried out under an anhydrous nitrogen atmosphere and the precautions to avoid the presence of oxygen were taken at every stage. Solvents were dried and stored under nitrogen before use. Dimethyltin(IV) dichloride, di-*n*-butyltin(IV) dichloride, trimethyltin(IV) chloride, tri-*n*-propyltin(IV) chloride, tri-*n*-butyltin(IV) chloride and triphenyltin(IV) chloride (Merck-Schuchardt), tetraphenyltin(IV) (Sigma–Aldrich), tin tetrachloride (Farmitalia Carlo Erba), thiocarbohydrazide (Fluka), acetic acid (Merck), propionic acid (Aldrich), nutrient agar (Qualigen) and sabouraud dextrose agar (Himedia) were used as received. Diphenyltin(IV) dichloride was synthesized according to the reported method [5]. The ligands 4-amino-3-methyl-1,2,4-triazole-2-thiol (HL-**1**) and 4-amino-3-ethyl-1,2,4-triazole-2-thiol (HL-**2**) were synthesized by the reported method [30].

2.1.1. Synthesis by sodium chloride method

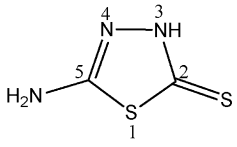
A methanolic solution (∼30 ml) of HL-**1**/HL-**2** (4.0 mmol) was added to sodium methoxide (prepared by dissolving sodium (4.2 mmol) in dry methanol (∼5 ml)) under dry nitrogen. The reaction mixture was immediately turned to orange-red color, which was stirred for another ∼8 h at room temperature. To this, a methanol (∼30 ml) solution of R_2SnCl_2 (2.0 mmol)/R_3SnL (4.0 mmol) was added dropwise with constant stirring, and stirred for 30–35 h at room temperature. The reaction mixture was centrifuged and filtered in order to remove sodium chloride,



Thiol-thione tautomers of 4-amino-3-R-1,2,4-triazole-5-thiol
(Where R = CH_3 (HL-**1**) and CH_2CH_3 (HL-**2**))



3-Amino-1,2,4-triazole-5-thiol (HL-**3**)



5-Amino-3H-1,3,4-thiadiazole-2-thiol (HL-**4**)

Scheme 1.

and the volatiles were removed in vacuo. The solid obtained was recrystallized from methanol.

2.2. Measurements and antimicrobial studies

All the physico-chemical and spectral measurements were carried out using the same methods and instruments reported previously [28,29], except (^{1}H, ^{13}C and ^{119}Sn) NMR spectra of a few compounds were recorded on a Bruker Avance 500 MHz NMR spectrometer at the Indian Institute of Technology Roorkee, Roorkee.

2.2.1. In vitro antimicrobial activity

The *in vitro* antibacterial and antifungal activities of the ligands (HL-**1** to HL-**4**) and some of their soluble organotin(IV) derivatives were performed against the bacteria, *viz*. *Staphyloccus aureus* (209p) (Gram-positive) and *Escherischia coli* (ESS 2231) (Gram-negative), and against the fungi, *viz*. *Aspergillus fumigatus*, *Candida albicans*, *Candida albicans* (ATCC 10231), *Candida krusei* (GO_3) and *Candida glabrata* (HO_5), by filter paper disc method [31]. The observed screening results of the test compounds were compared with that of the reference drugs, *viz*. ciprofloxacin for antibacterial and fluconazole for antifungal activity. The results of biological screening are mentioned in mm, showing diameter of inhibition zone (i.z.) and these are categorized as, 0–6 mm for mild, 7–13 mm for moderate and 14–26 mm for potential efficacy at the tested dose.

2.2.1.1. In vitro antibacterial activity. The bacteria were cultured in nutrient agar medium (peptone 10 g, meat extract 10 g, NaCl 5 g and Agar 10 g in distilled water, at pH 7.5 ± 0.1) and used as inoculums. The solvent used in control was 10% DMSO in methanol. Whatmann filter paper discs (diameter 6.5 mm) were sterilized by dry heat at 140 °C for 1 h and saturated with the solution of test compound (concentration: 250 μg ml^{-1}) or reference drug, ciprofloxacin (concentration: 50 μg ml^{-1}). These discs were air-dried at room temperature to remove any residual solvent, which might interfere with the determination. These discs were then placed on the surface of a sterilized agar nutrient medium that was inoculated with test organism (by using a sterile swab) and air-dried to remove the surface moisture. The thickness of the agar medium was kept equal in all Petri dishes. A control disc (saturated with solvent) without the test compound was similarly treated. Before incubation, Petri dishes were placed for 1 h in a cold room (5 °C) to allow diffusion of the compound from the disc into the agar plate. Thereafter, the discs were incubated at 37 ± 1 °C for 20–24 h. The zone of inhibition of growth was measured, which indicates the inhibitory activity of the compounds on the growth of the microorganism.

2.2.1.2. In vitro antifungal activity. For antifungal screening, spore suspension (5 ml) of each test microorganisms (72 h culture) was added to sterilized sabouraud dextrose agar medium at 35–40 °C with shaking. The Petri dishes were seeded with the mixture and the filter paper discs of test compound (prepared as mentioned in Section 2.2.1.1) and reference drug, fluconazole (concentration 50 μg ml^{-1}) were placed in the same manner as in antibacterial activity determination. These Petri dishes were incubated at 30 ± 1 °C for 48 h. The zone of inhibition of growth was considered as an indicator for the antifungal activity. A control disc (saturated with solvent) without the test compound was similarly treated.

3. Results and discussion

It has been reported [30] that 4-amino-3-alkyl-1,2,4-triazole-5-thiones exhibit thione-thiol tautomerism (Scheme 1) and both forms coexist in the solid-state but thione form is the dominant one in the solid-state and equilibrium shifts to thiol form in solution. The reactions of diorganotin(IV) dichlorides and triorganotin(IV) chloride with sodium salt of HL in methanol (where HL = 4-amino-3-methyl-1,2,4-triazole-5-thiol (HL-**1**) and 4-amino-3-ethyl-1,2,4-triazole-5-thiol (HL-**2**)) {formed according to Eq. (1)} in 1:2 and 1:1 molar ratios, respectively, led to the formation of the compounds according to Eq. (2). In the resulting organotin(IV) triazolates, HL acts as a mono deprotonated bidentate ligand with the negative charge residing on the sulfur atom of the aromatic thiol tautomer.

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

$$n\mathrm{NaL} + \mathrm{R}_{(4-n)}\mathrm{SnCl}_n \rightarrow \mathrm{R}_{(4-n)}\mathrm{SnL}_n + n\mathrm{NaCl} \quad (2)$$

(where n = 2, R = Me, *n*-Bu and Ph; n = 3, R = Me, *n*-Pr, *n*-Bu and Ph; HL = 4-amino-3-methyl-1,2,4-triazole-5-thiol (HL-**1**) and 4-amino-3-ethyl-1,2,4-triazole-5-thiol (HL-**2**)).

The reactions involved in the synthesis of di- and triorganotin(IV) derivatives were found to be quite feasible and required 30–35 h of stirring at room temperature. All of the synthesized organotin(IV) derivatives are white powder, except *n*-Pr_3Sn(L-**1**/L-**2**) and *n*-Bu_3Sn(L-**1**/L-**2**), which are semisolid. The diorganotin(IV) derivatives are sparingly soluble in MeOH and DMSO, whereas triorganotin(IV) derivatives have good solubility in MeOH and $CHCl_3$, but all of the synthesized compounds are insoluble in water and other organic solvents. All of the synthesized compounds are obtained in good yield (41–63%) and are stable towards atmospheric air and moisture. The analytical data of the synthesized compounds together with those of HL-**1** and HL-**2** are given in Table 1, and correspond to the proposed stoichiometry. The molar conductances of the studied compounds in methanol (10^{-3} M) lie in the range 5.0–70.0 ohm^{-1} cm^2 mol^{-1}, indicating their non-electrolytic nature.

3.1. IR spectral studies

The characteristic infrared absorption frequencies (in cm^{-1}) and their assignments for HL-**1**, HL-**2** and their organotin(IV) derivatives are presented in Table 2. The IR spectra of HL-**1** and HL-**2** exhibit a weak ν(S–H) band at 2704 and 2671 cm^{-1}, respectively, which is not observed in all of the organotin(IV) derivatives studied, indicating the deprotonation of thiol group of the ligands and their subsequent coordination to tin. In the IR spectra of HL-**1** and HL-**2**, there are several medium intensity bands due to ν(N–H) and ν(C–H), in the region

Table 1
Analytical data of HL-**1**, HL-**2** and their organotin(IV) derivatives

Ligand/compound (empirical formula)	Yield (%)	Color and physical state	m.p. (°C)	Analysis (%): found (calculated)				
				C	H	N	S	Sn
Ligands								
HL-**1** [$C_3H_6N_4S$]	65	White solid	202–203 (203)[a]	27.65 (27.68)	4.64 (4.65)	43.00 (43.03)	24.59 (24.64)	–
HL-**2** [$C_4H_8N_4S$]	58	White solid	148–149 (149)[a]	33.29 (33.32)	5.54 (5.59)	38.79 (38.84)	22.18 (22.24)	–
Diorganotin(IV) derivatives								
Me_2Sn(L-**1**)2 [$C_8H_{16}N_8S_2Sn$]	38	White solid	210 (dec)	23.55 (23.60)	3.94 (3.96)	27.48 (27.52)	15.64 (15.75)	29.10 (29.16)
n-Bu_2Sn(L-**1**)$_2$ [$C_{14}H_{28}N_8S_2Sn$]	57	White solid	178–180	34.18 (34.23)	5.73 (5.75)	22.76 (22.81)	12.98 (13.05)	24.13 (24.16)
Ph_2Sn(L-**1**)$_2$ [$C_{18}H_{20}N_8S_2Sn$]	48	White solid	168–170	40.60 (40.69)	3.74 (3.79)	21.01 (21.09)	12.02 (12.07)	22.30 (22.35)
Me_2Sn(L-**2**)$_2$ [$C_{10}H_{20}N_8S_2Sn$]	52	White solid	280 (dec)	27.54 (27.60)	4.60 (4.63)	25.68 (25.75)	14.69 (14.74)	27.25 (27.28)
n-Bu_2Sn(L-**2**)$_2$ [C16H32N8S2Sn]	59	White solid	110–111	36.96 (37.01)	6.16 (6.21)	21.52 (21.58)	12.31 (12.35)	22.83 (22.86)
Triorganotin(IV) derivatives								
Me_3Sn(L-**1**) [$C_6H_{14}N_4SSn$]	50	White solid	125–127	24.55 (24.60)	4.76 (4.82)	19.07 (19.12)	10.88 (10.95)	40.47 (40.52)
n-Pr_3Sn(L-**1**) [$C_{12}H_{26}N_4SSn$]	44	Light yellow Semi-solid	–	38.17 (38.22)	6.89 (6.95)	14.81 (14.86)	8.44 (8.50)	31.41 (31.48)
n-Bu_3Sn(L-**1**) [$C_{15}H_{32}N_4SSn$]	60	Light yellow Semi-solid	–	42.92 (42.98)	7.63 (7.69)	13.33 (13.37)	7.59 (7.65)	28.29 (28.32)
Ph_3Sn(L-**1**) [$C_{21}H_{20}N_4SSn$]	55	White solid	117–120	52.58 (52.64)	4.17 (4.21)	11.64 (11.69)	6.63 (6.69)	24.75 (24.77)
Me_3Sn(L-**2**) [$C_7H_{16}N_4SSn$]	63	White solid	128–130	27.34 (27.39)	5.20 (5.25)	18.19 (18.25)	10.38 (10.45)	38.61 (38.67)
n-Pr_3Sn(L-**2**) [$C_{13}H_{28}N_4SSn$]	41	Light yellow Semi-solid	–	39.88 (39.92)	7.15 (7.21)	14.28 (14.32)	8.16 (8.20)	30.29 (30.35)
n-Bu_3Sn(L-**2**) [$C_{16}H_{34}N_4SSn$]	53	Light yellow semi-solid	–	44.32 (44.36)	7.88 (7.91)	12.89 (12.93)	7.36 (7.40)	27.37 (27.40)
Ph_3Sn(L-**2**) [$C_{22}H_{22}N_4SSn$]	57	White solid	300 (dec)	53.53 (53.57)	4.46 (4.49)	11.33 (11.36)	6.44 (6.50)	24.00 (24.07)

[a] Ref. [30].

3272–2946 cm^{-1}, but it is difficult to differentiate between the N–H and C–H stretching vibrations with certainty. However, bands at 3270 ± 2 and $3158 \pm 20\,cm^{-1}$ may be assigned to ν_{as}(N–H) and ν_s(N–H) [20,32], respectively, of NH_2 group. In the IR spectra of most of the organotin(IV) derivatives studied the (N–H) stretching absorption bands undergo a small shift to lower wave numbers (ν_{as}(N–H): $3289 \pm 24\,cm^{-1}$ and ν_s(N–H): $3158 \pm 42\,cm^{-1}$) as compared to that of free ligands, but a downward shift by 200–300 cm^{-1} would require for the coordination of the ligand through the amino group [3,32,33]. Therefore, the observed shift in ν(N–H) vibration mode may be due to the participation of NH_2 group in weak inter-/intramolecular hydrogen bonding. In the IR spectrum of HL-**1**/HL-**2**, the thioamide bands I and II (due to ν(C=N) vibrations) have been assigned at 1475/1487 and 1379/1398 cm^{-1}, respectively, whereas the thioamide bands III and IV (due to ν(C=S) vibrations) are observed at 1287/1241 and 1038/1022 cm^{-1}, respectively [34]. In the IR spectra of the organotin(IV) derivatives, these thioamide bands shift to lower wave numbers (by 5–78 cm^{-1}), which may be due to the evolution of partial double bond character in the thioamide group (–N=C=S–) after its deprotonation [13] and subsequent coordination to tin via S_{exo} and N(1). This mode of coordination of the 4-amino-3-alkyl-1,2,4-triazole-5-thiols is further confirmed by the appearance of two medium intensity bands at $452 \pm 37\,cm^{-1}$ and $341 \pm 39\,cm^{-1}$ in the far-IR spectra of the organotin(IV) compounds which are assigned to the ν(Sn ← N) and ν(Sn–S) vibrational modes, respectively [3,28,29,32–34]. In all of the compounds, the ν_{as}(Sn–C) and ν_s(Sn–C) bands are also observed in the range 505–604 cm^{-1} for alkyltin and 220–278 cm^{-1} for aryltin compounds [28,29], which suggest a non-planar arrangement of C–Sn–C moiety.

3.2. *^{119}Sn Mössbauer spectral studies*

The ^{119}Sn Mössbauer spectral data of the synthesized organotin(IV) derivatives are presented in Table 3. The ^{119}Sn Mössbauer spectra of the studied organotin(IV) derivatives exhibit a doublet centered in the isomer shift (I.S.) value range 0.97–1.33 mm s^{-1}. The quadruple splitting (Q.S.) values in the range 2.25–3.33 mm s^{-1} for R_3SnL/R_2SnL_2 compounds show that the electric field gradient around the tin nucleus is produced by the inequalities in the tin-sulfur/-nitrogen σ bonds and is also due to geometric distortions. The ρ (Q.S./I.S.) values (2.32–2.94) for these studied compounds indicate a coordination number superior than four with either a 5- or 6-coordinated tin.

The point charge calculations for octahedral diorganotin(IV) derivatives $[R_2SnX_4]^{2-}$ predict that the Q.S values for the *trans*-isomer will be twice (~4.0 mm s^{-1}) that of the *cis*-isomer (2.0 mm s^{-1}), [35]. Further, it has been reported [36] that I.S. values for *cis*-$[R_2SnX_4]^{2-}$ are less than 1.0 mm s^{-1} while those for *trans*-compounds are approximately 1.20–1.30 mm s^{-1}. However, the observed Q.S. and I.S. values of the diorganotin(IV) derivatives studied (Table 3) are intermediate between the two geometries, i.e., the observed values are slightly

Table 2
IR frequencies[a] (in cm^{-1}) of HL-**1**, HL-**2** and their organotin(IV) derivatives

Ligand/compound	ν(N–H), ν(C−H)	ν(S–H)	Thioamide bands I, II, III, IV	ν_{as} (Sn–C), ν_s (Sn–C)	ν(Sn ← N), ν(Sn–S)
Ligands					
HL-**1**	3272vs, 3178vs, 3114vs, 2946s	2704w	1475s, 1379vs, 1287m, 1038s	–	–
HL-**2**	3268m, 3139sbr, 3054m, 2982w, 2957m	2671w	1487vs, 1398s, 1241vs, 1022s	–	–
Diorganotin(IV) derivatives					
$Me_2Sn(L\text{-}\mathbf{1})_2$	3265m, 3178w, 3113m, 2948m	–	1474m, 1381vs, 1213s, 1039s	531w, 523w	425s 350m
$n\text{-}Bu_2Sn(L\text{-}\mathbf{1})_2$	3269w, 3178w, 3113w, 2956m, 2935m	–	1470m, 1379s, 1211s, 1040s	568s	476s 313m
$Ph_2Sn(L\text{-}\mathbf{1})_2$	3274m, 3178m, 3108m, 2952w	–	1477m, 1380vs, 1211s, 1039s	250s, 220vw	426s 350m
$Me_2Sn(L\text{-}\mathbf{2})_2$	3270m, 3139s, 2985s, 2939sh, 2916s, 2804vs	–	1471vs, 1365s, 1257s, 1028m	556vs, 520w	419m 352m
$n\text{-}Bu_2Sn(L\text{-}\mathbf{2})_2$	3268m, 3145vs, 3054w 2957s, 2922s, 2870m	–	1487vs, 1381m, 1288s, 1022s	547s, 532s	418m 346m
Triorganotin(IV) derivatives					
$Me_3Sn(L\text{-}\mathbf{1})$	3274w, 3117w, 2995m, 2913m	–	1474m, 1378s, 1283m, 1046s	548vs, 513w	468vs 326w
$n\text{-}Pr_3Sn(L\text{-}\mathbf{1})$	3265w, 3182w,3117m, 2961s, 2926m, 2865m	–	1456w, 1383vs, 1256w, 1035m	540s, 531m	475s 351m
$n\text{-}Bu_3Sn(L\text{-}\mathbf{1})$	3270m, 3178m, 3115m, 2957vs, 2922s, 2855m	–	1460s, 1377vs, 1291w, 1037m	540s, 533w	419s 318w
$Ph_3Sn(L\text{-}\mathbf{1})$	3270m, 3178w, 3116m, 3059s	–	1476s, 1378w, 1263w, 1020m	275m, 229w	447s 303s
$Me_3Sn(L\text{-}\mathbf{2})$	3312s, 3269w, 3200vs, 2985s, 2939m, 2917m	–	1480vs, 1396vs, 1254m, 1036vs	543vs, 522s	414m 356w
$n\text{-}Pr_3Sn(L\text{-}\mathbf{2})$	3269w, 3148w, 2956s, 2922m, 2866s	–	1486m, 1374s, 1239w, 1023m	515w, 505w	460m 331w
$n\text{-}Bu_3Sn(L\text{-}\mathbf{2})$	3289m, 3162m, 2956vs, 2917vs, 2859s	–	1457vs, 1372vs, 1289s, 1018w	604m 528m	456w 326m
$Ph_3Sn(L\text{-}\mathbf{2})$	3313mbr, 3061s, 3048s, 3017w, 2987m	–	1478vs, 1397m 1251m, 1040s	278m 228m	447m 303s

[a] vs, very strong; s, strong; m, medium; w, weak; br, broad; sh, shoulder.

higher than the values for *cis*-octahedral configuration, but substantially lower than the values for *trans*-octahedral configuration. Indeed, where the other donor groups of the ligands have higher electronegativity, the Q.S. is mainly governed by C–Sn–C bond angle [37], and the distortion from the regular six coordination can give values similar to those reported [38] for highly distorted square-bipyramidal/ skew trapezoidal-bipyramidal structure. Therefore, a distorted skew-trapezoidal bipyramidal structure is proposed for R_2SnL_2 compounds, which is also supported by the calculated values of the angle ∠C–Sn–C (105–137°) as given in Table 3, which are close to the average of the two extremes, in which the organic substituents do not adopt either *cis*- or *trans*-geometries about the tin center [38].

The most probable structure for R_2SnL_2, which is in agreement with all the spectral observations and the observed Goldanskii-Karyagin effect [39] is shown in Fig. 1, in which the ligands, HL-**1**/HL-**2**, act as monoanionic bidentate coordinating through (S_{exo}) and N(1) in the equatorial positions and two

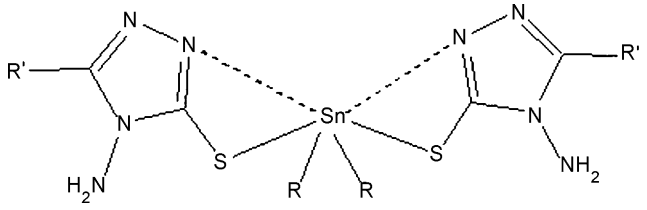


Fig. 1. Proposed structure for R_2SnL_2 (where R = Me, *n*-Bu and Ph).

organic groups occupy the axial positions. The solution NMR spectral studies suggest that in R_2SnL_2 compounds, the primary bonding occurs through $(S_{exo})^-$, however, Sn ← N(1) interactions are very weak and may easily be disrupted in solution (discussed later in NMR).

The ^{119}Sn Mössbauer spectra of R_3SnL exhibit Q.S. in the range 2.74–3.33 mm s^{-1} and in the range I.S. 1.09–1.33 mm s^{-1}. It has been reported [40] that the three conceivable (Fig. 2) five coordinate isomers of R_3SnXY (where X or Y = N/O/S; XY are the donor sites of the bidentate ligand) have different

Table 3
^{119}Sn Mössbauer spectral data (80 K) of synthesized compounds[a]

Compound	I.S. (mm s^{-1})	Q.S. (mm s^{-1})	ρ (Q.S./I.S.)	τ_1 (L)	τ_2 (R)	∠C–Sn–C[b]
Diorganotin(IV) derivatives						
$Me_2Sn(L\text{-}\mathbf{1})_2$	1.03	3.03	2.94	–	–	129
$n\text{-}Bu_2Sn(L\text{-}\mathbf{1})_2$	0.97	2.25	2.32	1.12	1.14	105
$Me_2Sn(L\text{-}\mathbf{2})_2$	1.05	2.81	2.68	1.36	1.47	122
$n\text{-}Bu_2Sn(L\text{-}\mathbf{2})_2$	1.16	2.89	2.48	1.27	1.54	125
Triorganotin(IV) derivatives						
$Me_3Sn(L\text{-}\mathbf{1})$	1.26	3.33	2.63	1.07	1.22	137
$Ph_3Sn(L\text{-}\mathbf{1})$	1.14	2.98	2.61	1.24	1.09	127
$Me_3Sn(L\text{-}\mathbf{2})$	1.33	3.19	2.40	1.44	1.52	133
$Ph_3Sn(L\text{-}\mathbf{2})$	1.09	2.74	2.52	1.72	1.93	120

[a] Q.S.: quadruple splitting; I.S.: isomer shift relative to $BaSnO_3$ and tin foil (splitting: 2.52 mm s^{-1}); τ_1 (L): half line-width left doublet component; τ_2 (R): half line-width right doublet component.

[b] Calculated by using Parish's relationship [37]: $Q.S. = 4[R][1 - 3/4\sin^2 2\theta]^{1/2}$; ∠C–Sn–C = 180–2θ°.

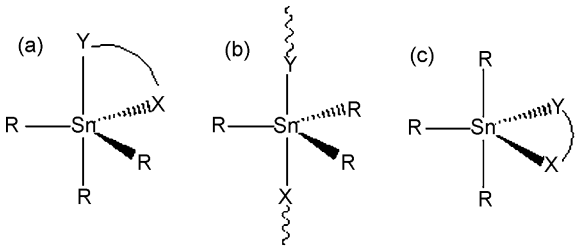


Fig. 2. Three possible isomers of $R_3Sn(XY)$ [40].

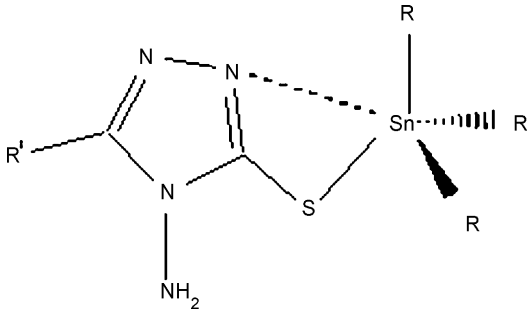


Fig. 3. Proposed structure for R_3SnL (where, R = Me, *n*-Pr, *n*-Bu and Ph; R' = Me or Et).

Q.S. value ranges; for isomer (a) 1.70–2.40 mm s^{-1}; for (b) 3.0–4.0 mm s^{-1}; and for (c) 3.50–4.10 mm s^{-1}.

The observed Q.S. values (2.74–3.33 mm s^{-1}) of R_3Sn(L-**1**/L-**2**) (R = Me and Ph) are higher than that for isomer (a) as shown in Fig. 2, and considered to be compatible with *trans*-structure, i.e., isomer (b) as shown in Fig. 2. But the observed ν_{as}(Sn–C) and ν_s(Sn–C) stretching vibrations in the IR spectra of the triorganotin(IV) derivatives studied indicate a non-planar SnC_3 fragment and rule out the possibility of *trans*-isomer as shown in Fig. 2b. Therefore, a highly distorted *cis*-trigonal-bipyramidal structure (Fig. 3), which is intermediate between *fac* (Fig. 2a) and *mer* (Fig. 2c) *cis*-trigonal bipyramidal structures is proposed for these triorganotin(IV) derivatives, in the solid state. On the basis of IR spectral interpretations, a similar structure (as shown in Fig. 3) has been tentatively proposed for *n*-Pr_3SnL and *n*-Bu_3SnL because their ^{119}Sn Mössbauer spectra could not be recorded as they are semisolid.

3.3. Multinuclear (^1H, ^{13}C and ^{119}Sn) NMR spectral studies in solution

^{1}H and ^{13}C NMR spectral data of HL-**1**, HL-**2** and their organotin(IV) derivatives (except those, which do not have enough solubility) are given in Table 4 and 5, respectively. In the ^{1}H NMR spectra of HL-**1** and HL-**2**, the –SH resonance is observed at $\delta \sim 1.30$ ppm, which is absent in all of the studied organotin(IV) derivatives, indicating deprotonation of thiol group of

Table 4
^{1}H NMR spectral data of HL-**1**, HL-**2** and their organotin(IV) derivatives (recorded in CD_3OD unless otherwise reported)

Ligand/compound (solvent)	∠C–Sn–C[a] (°)	δ[b] (ppm)
Ligands		
HL-**1**[c]	–	1.30 (s, 1H, SH); 2.35 (s, 3H, H-1′); 5.40 (s, 2H, NH_2).
HL-**2**[c]	–	2.80–2.73 (q, 2H, 7.5 Hz, H-1′); 1.30 (*t*, 3H, 7.5 Hz, H-2′ + SH); 5.40 (s, 2H, NH_2).
Diorganotin(IV) derivatives		
Me_2Sn(L-**1**)$_2$[d]	–	2.35 (s, 6H, H-1′); 5.33 (s, 4H, NH_2); 0.92 (s, 6H, H-α).
n-Bu_2Sn(L-**1**)$_2$[d]	–	2.35 (s, 6H, H-1′); 5.28 (s, 4H, NH_2); 1.59 (br, 4H, H-α); 1.70 (brm, 4H, H-β); 1.44–1.36 (m, 4H, H-γ); 0.93 (t, 6H, 7.0 Hz, H-δ).
Ph_2Sn(L-**1**)$_2$[d]	–	2.30 (s, 6H, H-1′); 5.29 (s, 4H, NH_2); 7.81 (m, 4H, 7.5 Hz, H-β); 7.45 (m, 6H, H-γ, H-δ).
Me_2Sn(L-**2**)$_2$[d]	–	2.65–2.61 (q, 4H, 7.5 Hz, H-1′); 1.18 (*t*, 6H, 7.5 Hz, H-2′); 5.53 (s, 4H, NH_2); 2.51 (s, 6H, H-α).
Triorganotin(IV) derivatives		
Me_3Sn(L-**1**)[c]	115.62	2.33 (s, 3H, H-1′); 5.40 (s, 2H, NH_2); 0.51 (s, 9H, H-α) [$^2J(^1H\text{-}^{119}Sn)$ = 65 Hz].
n-Pr_3Sn(L-**1**)[c]	–	2.33 (s, 3H, H-1′); 5.40 (s, 2H, NH_2); 1.31 (*t*, 6H, 7.5 Hz, H-α); 1.76–1.63 (m, 6H, H-β); 0.98 (*t*, 9H, 7.5 Hz, H-γ).
n-Bu_3Sn(L-**1**)[c]	–	2.34 (s, 3H, H-1′); 5.40 (s, 2H, NH_2); 1.43–1.30 (m, 12H, H-α, H-γ)[e]; 1.70–1.60 (m, 6H, H-β); 0.92 (*t*, 9H, 7.2 Hz, H-δ).
Ph_3Sn(L-**1**)[d]	–	2.26 (s, 3H, H-1′); 7.78 (d, 6H, 6.6 Hz, H-β) [$^3J(^1H\text{-}^{119/117}Sn)$ = 61/58 Hz]; 7.51–7.41 (m, 9H, H-γ, H-δ)[e].
Me_3Sn(L-**2**)[c] ($CDCl_3$)	111.56	2.76–2.69 (q, 2H, 7.5 Hz, H-1′); 1.28 (t, 3H, 7.5 Hz, H-2′); 0.75 (s, 9H, H-α) [$^2J(^1H\text{-}^{119}Sn)$ = 59 Hz].
n-Pr_3Sn(L-**2**)[c]	–	2.80–2.72 (q, 2H, 7.5 Hz, H-1′); 1.33–1.23 (m, 9H, H-2′ + H-α); 1.76–1.66 (m, 6H, H-β); 1.02 (*t*, 9H, 7.2 Hz, H-γ).
n-Bu_3Sn(L-**2**)[c] ($CDCl_3$)	–	2.73–2.66 (q, 2H, 7.5 Hz, H-1′); 1.25 (*t*, 3H, 7.5 Hz, H-2′); 4.62 (s, 2H, NH_2); 1.40–1.30 (m, 12H, H-α, H-γ)[e]; 1.68–1.58 (m, 6H, H-β); 0.90 (*t*, 9H, 7.2 Hz, H-δ).
Ph_3Sn(L-**2**)[c]	–	2.76–2.62 (q, 2H, 7.5 Hz, H-1′); 1.28 (*t*, 3H, 7.5 Hz, H-2′); 7.82 (d, 6H, 6.0 Hz, H-β)) [$^3J(^1H\text{-}^{119/117}Sn)$ = 61/58 Hz]; 7.51–7.44 (m, 9H, H-γ, H-δ).

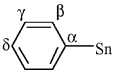
[a] Ref. [41]
[b] s, singlet; d: doublet; dd: double doublet; t: triplet; q: quartet; m: multiplet; br: broad; the signal of NH_2 group is weak and broad and sometimes not observed.
[c] Spectrum recorded on a Bruker DRX 300 MHz, FTNMR spectrometer.
[d] Spectrum recorded on a Bruker Avance 500 MHz, FTNMR spectrometer.
[e] Strongly overlapping multiplets.

α α β γ α β γ δ γ β
$Sn\text{-}CH_3$; $Sn\text{-}CH_2CH_2CH_3$; $Sn\text{-}CH_2CH_2CH_2CH_3$; δ α Sn

Table 5
^{13}C NMR spectral data of HL-**1**, HL-**2** and their organotin(IV) derivatives (recorded in CD_3OD unless otherwise reported)

Ligand/compound (solvent)	∠C–Sn–C[a]	δ (ppm)
Ligands		
HL-**1**[b]	–	C-1′: 10.55; C-3: 151.0; C-5: 163.0.
HL-**2**[b]	–	C-1′: 19.30; C-2′: 10.70; C-3: 155.70; C-5: 167.70.
Diorganotin(IV) derivatives		
Me_2Sn(L-**1**)$_2$[c]	–	C-1′: 9.25; C-3: 149.83; C-5: 165.0; C-α: 1.61.
Ph_2Sn(L-**1**)$_2$[c]	–	C-1′: 9.21; C-3: 150.39; C-5: 165.50; C-α: 139.50; C-β: 136.26 [$^2J(^{13}C\text{-}^{119}Sn)$ = 43 Hz]; C-γ: 128.38 [$^3J(^{13}C\text{-}^{119}Sn)$ = 64 Hz]; C-δ: 129.23 [$^4J(^{13}C\text{-}^{119}Sn)$ = 13 Hz].
Me_2Sn(L-**2**)$_2$[c]	–	C-1′: 17.95; C-2′: 9.36; C-3: 154.29; C-5: 167.80; C-α: 3.78.
Triorganotin(IV) derivatives		
Me_3Sn(L-**1**)[b]	119.12	C-1′: 10.60; C-3: 151.70; C-5: 168.50; C-α: −3.40 [$^1J(^{13}C\text{-}^{119/117}Sn)$ = 483/468 Hz].
n-Pr_3Sn(L-**1**)[b]	113.07	C-1′: 10.75; C-3: 151.40; C-5: 166.20; C-α: 19.90 [$^1J(^{13}C\text{-}^{119/117}Sn)$ = 414/ 396 Hz]; C-β: 20.51 [$^2J(^{13}C\text{-}^{119}Sn)$ = 25 Hz]; C-γ: 19.06 [$^3J(^{13}C\text{-}^{119}Sn)$ = 73 Hz].
n-Bu_3Sn(L-**1**)[b]	112.81	C-1′: 10.72; C-3: 151.90; C-5: 167.30; C-α: 17.0 [$^1J(^{13}C\text{-}^{119/117}Sn)$ = 411/393 Hz]; C-β: 29.24 [$^2J(^{13}C\text{-}^{119}Sn)$ = 25 Hz]; C-γ: 28.08 [$^3J(^{13}C\text{-}^{119}Sn)$ = 72 Hz]; C-δ: 14.04.
Ph_3Sn(L-**1**)[c]	–	C-1′: 9.21; C-3: 160.49; C-5: 165.50; C-α: 139.55; C-β: 136.26 [$^2J(^{13}C\text{-}^{119}Sn)$ = 43 Hz]; C-γ: 128.38 [$^3J(^{13}C\text{-}^{119}Sn)$ = 64 Hz]; C-δ: 129.23 [$^4J(^{13}C\text{-}^{119}Sn)$ = 50 Hz].
Me_3Sn(L-**2**)[b] ($CDCl_3$)	116.49	C-1′: 18.70; C-2′: 10.90; C-3: 155.10; C-5: 167.0; C-α: −3.70 [$^1J(^{13}C\text{-}^{119}Sn)$ = 453 Hz].
n-Pr_3Sn(L-**2**)[b]	113.25	C-1′: 18.51; C-2′: 11.07; C-3: 155.20; C-5: 167.50; C-α: 19.42 [$^1J(^{13}C\text{-}^{119}Sn)$ = 416 Hz]; C-β: 20.50 [$^2J(^{13}C\text{-}^{119}Sn)$ = 26 Hz]; C-γ: 18.99 [$^3J(^{13}C\text{-}^{119}Sn)$ = 69 Hz].
n-Bu_3Sn(L-**2**) [b]($CDCl_3$)	–	C-1′: 18.69; C-2′: 10.75; C-3: 154.90; C-5: 171.60; C-α: 15.68; C-β: 27.82 [$^2J(^{13}C\text{-}^{119}Sn)$ = 20 Hz]; C-γ: 26.85 [$^3J(^{13}C\text{-}^{119}Sn)$ = 65 Hz]; C-δ: 13.46.
Ph_3Sn(L-**2**)[b]	–	C-1′: 19.50; C-2′:11.90; C-3: 155.30; C-5: 164.60; C-α: 140.90; C-β: 137.60 [$^2J(^{13}C\text{-}^{119}Sn)$ = 38 Hz]; C-γ: 129.70 [$^3J(^{13}C\text{-}^{119}Sn)$ = 60 Hz]; C-δ: 130.60.

[a] Ref. [41].
[b] Spectrum recorded on a Bruker DRX 300 MHz, FTNMR spectrometer.
[c] Spectrum recorded on a Bruker Avance 500 MHz, FTNMR spectrometer.

α α β γ α β γ δ
Sn-CH_3; Sn-$CH_2CH_2CH_3$; Sn-$CH_2CH_2CH_2CH_3$; 

the ligands, and its subsequent coordination to tin. The absence of an appreciable shift in NH_2 proton resonance indicates its non-involvement in coordination to the organotin(IV) moiety. In the ^{13}C NMR spectra of HL-**1** and HL-**2**, the C-5 resonance is observed at δ 163.0 and 167.70 ppm, respectively, which is shifted downfield in all of the organotin(IV) derivatives studied (see Table 5), indicating the coordination of the deprotonated ligands to tin via $(S_{exo})^-$ attached to C-5 carbon. The heteronuclear coupling constants, viz. $^2J(^1H\text{–}^{119}Sn)$ and $^1J(^{13}C\text{–}^{119}Sn)$ are very useful as they provide important information about the coordinating environment of tin. In a few compounds studied, the satellites are resolved and the observed coupling constants, $^2J(^1H\text{–}^{119}Sn)$ and $^1J(^{13}C\text{–}^{119/117}Sn)$ are 62 ± 3 Hz and $447 \pm 36/429 \pm 36$ Hz (Table 4 and 5), respectively, indicating pseudotetrahedral or distorted tetrahedral arrangement around tin. The angle, ∠C–Sn–C calculated by the Lockhart and Manders equation [41] using the observed $^2J(^1H\text{–}^{119}Sn)$ and $^1J(^{13}C\text{–}^{119}Sn)$ values, is $115.34 \pm 3.78°$, which also suggests a distorted tetrahedral/pseudotetrahedral environment around tin [41] in solution. However, in other compounds studied, the $^2J(^1H\text{–}^{119}Sn)$ and $^1J(^{13}C\text{–}^{119}Sn)$ coupling constants could not be resolved successfully. The resonances of the magnetically non-equivalent protons and carbons of alkyl/phenyl groups of the organotin moiety and of ligands have also been given in Tables 4 and 5.

The ^{119}Sn NMR spectral data for all of the studied compounds except *n*-Bu_2Sn(L-**1**/L-**2**)$_2$ are given in Table 6. The ^{119}Sn NMR chemical shifts are very sensitive to coordination number of tin and are generally shifted upfield on bonding to Lewis base. It has been reported [42] that the ^{119}Sn chemical shifts in the ranges 200 to −60, −90 to −190 and −210 to −400 ppm are associated with four-, five- and six-coordinated alkyltin(IV) compounds and these ^{119}Sn shifts are higher with aryltin(IV) compounds. In the ^{119}Sn NMR spectra of Me_3Sn(L-**1**), *n*-Pr_3Sn(L-**2**) and

Table 6
^{119}Sn NMR spectral data of synthesized compounds

Compound	Solvent	δ (ppm)
Diorganotin(IV) derivatives		
Me_2Sn(L-**1**)$_2$[a]	CD_3OD	−264.25
Ph_2Sn(L-**1**)$_2$[a]	CD_3OD	−383.40
Me_2Sn(L-**2**)$_2$[b]	DMSO-d_6	−30.84
Triorganotin(IV) derivatives		
Me_3Sn(L-**1**)[a]	$CDCl_3$	105.37
n-Pr_3Sn(L-**1**)[a]	CD_3OD	−174.63
Ph_3Sn(L-**1**)[a]	CD_3OD	−384.94
Me_3Sn(L-**2**)[b]	$CDCl_3 + CD_3OD$[c]	−0.50
n-Pr_3Sn(L-**2**)[b]	$CDCl_3$	86.29
n-Bu_3Sn(L-**2**)[b]	$CDCl_3$	90.46
Ph_3Sn(L-**2**)[b]	CD_3OD	−175.28

[a] NMR spectrum recorded on Mercury Varian 300 MHz, FTNMR spectrometer.
[b] NMR spectrum recorded on a Bruker Avance 500 MHz, FTNMR spectrometer.
[c] A drop of solvent was added.

Table 7
Results of antimicrobial (antibacterial and antifungal) activity of ligands and their organotin(IV) derivatives[a]

Compound	Zone of inhibition (z.i.) in mm						
	Bacteria		Fungi				
	S. aureus (209p)	*E. coli* (ESS 2231)	*A. fumigatus*	*C. albicans*	*C. albicans* (ATCC 10231)	*C. krusei* (GO_3)	*C. glabrata* (HO_5)
HL-**1**	7	6	25	26	24	21	22
HL-**2**	1	3	20	22	26	20	21
HL-**3**	7	3	23	24	25	23	24
HL-**4**	5	3	24	25	26	22	23
Me_2Sn(L-**1**)$_2$	11	7	23	20	21	18	19
n-Bu_2Sn(L-**1**)$_2$	12	3	21	22	23	20	21
n-Bu_3Sn(L-**1**)	10	6	20	21	22	23	19
Me_2Sn(L-**2**)$_2$	8	6	10	12	14	23	24
n-Bu_2Sn(L-**2**)$_2$	9	5	11	13	15	25	22
Me_3Sn(L-**2**)	1	1	12	13	14	18	19
n-Bu_3Sn(L-**2**)	15	18	13	14	15	19	22
Ph_3Sn(L-**2**)	5	5	14	15	16	21	23
n-Oct_2Sn(L-**3**)$_2$	9	6	22	18	21	21	20
Ph_2Sn(L-**3**)$_2$	7	7	18	19	20	18	22
Me_3Sn(L-**3**)	8	6	20	18	19	22	19
Me_2Sn(L-**4**)$_2$	8	5	18	21	22	20	22
n-Bu_2Sn(L-**4**)$_2$	7	6	20	21	22	21	21
n-Oct_2Sn(L-**4**)$_2$	6	6	21	22	23	24	25
Ph_2Sn(L-**4**)$_2$	7	6	19	20	21	23	20
Me_3Sn(L-**4**)	7	7	18	19	20	20	22
n-Bu_3Sn(L-**4**)	7	6	17	18	19	19	20
Ph_3Sn(L-**4**)	6	7	18	19	20	21	22
Ciprofloxacin[b]	20	20	–	–	–	–	–
Fluconazole[b]	–	–	29	29	25	19	15
10% DMSO in Methanol	0	0	0	0	0	0	0

[a] Concentration used: test compounds = 250 μg ml^{-1}; standard drugs = 50 μg ml^{-1}.
[b] Standard drugs.

n-Bu_3Sn(L-**2**) recorded in $CDCl_3$, the ^{119}Sn chemical shifts are observed at δ 105.37, 86.29 and 90.46 ppm, respectively, which lie in the range of four-coordinated tin [42]. This indicates that the six-coordinated and five-coordinated structure of di-/ and triorganotin(IV) derivatives, respectively, found in the solid-state, do not exist in solution. It seems that the weak coordination between Sn and N(1) as found in the solid-state, is easily disrupted in the solution giving rise to the distorted tetrahedral R_2SnL_2/R_3SnL monomeric unit in solution. However, for all other compounds (recorded in MeOH-d_6/DMSO-d_6) the ^{119}Sn chemical shifts are observed in the range: δ −0.50 to −384.94 ppm, which suggest a five-coordinated tin [42]. The ^{119}Sn NMR is more sensitive to structural changes as compared to ^1H and ^{13}C NMR. The observed ^{119}Sn chemical shifts of these compounds suggest that the nature of the solvent plays an important role in these compounds, and it is proposed that one molecule of coordinating solvent (DMSO or MeOH) is coordinated to tin in these compounds in the solution, yielding a distorted trigonal-bipyramidal geometry around tin.

3.4. Antimicrobial studies

The antimicrobial activities of the ligands (HL-**1** to HL-**4**) and some of their organotin(IV) derivatives having good solubility are presented in Table 7. The observed screening results suggest that the ligands as well as their organotin(IV) derivatives (except *n*-Bu_3Sn(L-**2**)) (concentration: 250 μg ml^{-1}) show almost insignificant activity against the bacteria, viz. *Staphylococcus aureus* and *Escherichia coli*, as compared to ciprofloxacin (concentration: 50 μg ml^{-1}) used as standard drug. However, *n*-Bu_3Sn(L-**2**) shows mild antibacterial activity (Table 7). The screening results of the ligands (HL-**1** to HL-**4**) and their organotin(IV) derivatives against the fungi, viz. *A. fumigatus*, *C. albicans*, *C. albicans* (*ATCC 10231*), *C. krusei* (*GO_3*) and *C. glabrata* (*HO_5*) (Table 7) suggest that the ligands and their organotin(IV) derivatives (concentration: 250 μg ml^{-1}) (except for the organotin(IV) derivatives of HL-**2**, which show mild activity) show moderate antifungal activity as compared to the reference drug, fluconazole (concentration: 50 μg ml^{-1}). However, no significant difference is observed in the di- and triorganotin(IV) derivatives of a given ligand. The ligands are more active than the corresponding organotin(IV) derivatives.

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ing ^{119}Sn NMR spectral facilities. One of the authors (Ms. Sulaxna) is thankful to the Council of Scientific and Industrial Research, New Delhi, India, for awarding Senior Research Fellowship. Financial support for ^{119}Sn Mössbauer work from the National Institute of Biomedical Research Support Program (MBRS/SCORE, GM08005) is gratefully acknowledged. Thanks are also extended to the Microbiology Department, L.L.R.M. Medical College, Meerut for biological studies.

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