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FULL PAPER

Synthesis, characterization and antimicrobial activity of triorganotin(IV) derivatives of some bioactive Schiff base ligands

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Triorganotin(IV) complexes of the type $Me_3Sn[OC(R^1):CH(CH_3)C:NR^2OH]$ and $Ph_3Sn[OC(R'):CH(CH_3)C:NR''OH]$ ($R' = -CH_3$, $-C_6H_5$; $R'' = -(CH_2)_2-$, $-(CH_2)_3-$) have been synthesized by the reactions of trimethyl/phenyltin(IV) chloride with the sodium salt of corresponding Schiff base ligands in unimolar ratio in refluxing tetrahydrofuran. All these compounds have been characterized using elemental analyses and their probable structures have been proposed on the basis of infrared, ^{1}H NMR, ^{13}C NMR, ^{119}Sn NMR and mass spectroscopic studies. In the trimethyltin(IV) derivatives the central tin atom is tetracoordinated, whereas in the analogous triphenyltin(IV)derivatives the central tin atom is pentacoordinated. All these ligands, metal precursors and corresponding triorganotin(IV) complexes have been screened for antimicrobial activities. A comparison of activities of the ligands and their corresponding triorganotin(IV) derivatives has been made. Attempts have also been made to relate the activity to the structure of these compounds.

KEYWORDS

antimicrobial activities, ^{1}H, ^{13}C, ^{119}Sn NMR spectroscopy, mass spectral data, tetracoordinated and pentacoordinated tin, triorganotin(IV) Schiff base derivatives

1 | INTRODUCTION

Various types of Schiff bases have been synthesized and extensively studied because of their antifungal, antiviral, antibacterial, anti-tumour and anti-inflammatory properties as well as their industrial and medicinal utility.[1–18] Organotin(IV) complexes of β-diketones,[19–21] heterocyclic β-diketones,[22] Schiff bases,[23–25] oximes,[26,27] amino acids,[28] sulfa drugs,[29] etc., have been reported in the literature due to their potential industrial and biological applications.[30–34] Organotin(IV) complexes of Schiff bases have attracted considerable interest owing to their biocidal[35] and anti-tumour activities[36] and potential applications in organic synthesis,[37] catalysis,[38,39] medicinal chemistry[40] and biotechnology.[41] In general, triorganotin(IV) compounds exhibit more bioefficiency than their di- and monoorganotin(IV) analogues.[42] Structural modification of organic molecules has considerable biological relevance and coordination of metal atoms in complexes also alters their toxicity. Triphenyltin(IV) compounds are widely used as biocides in agriculture whereas tributyltin species are the best additives for paints applied on the outer covering of vessels to protect them from marine microorganism corrosion.[42] Some triaryltin benzoates have also shown good anti-tumour activity.[43] Moreover, trialkyl and triphenyl compounds exhibit interesting structural diversity.[44–46]

In view of the above, we have synthesized and characterized some new triorganotin(IV) complexes with bioactive Schiff bases derived from β-diketones and amino alcohols. These compounds have been screened for antimicrobial activities. The antimicrobial activities of these tin compounds have been compared with those of the corresponding free Schiff bases and metal precursors. Structural modification of organic molecules has considerable biological relevance and coordination of metal atoms in complexes also alters their toxicity which has also been observed in the present case.

2 | EXPERIMENTAL

All the reactions were carried out under anhydrous conditions. Solvents were purified and dried by standard

procedures.[47] Schiff bases (L^1H_2–L^4H_2) were prepared using a literature method.[48] Trimethyltin(IV) chloride and triphenyltin(IV) chloride (Aldrich) were distilled before use. Tin was estimated gravimetrically as oxide.[49] C, H and N were analysed using an Eager Xperience. Melting points of the triorganotin(IV) complexes were determined in sealed capillaries.

Infrared (IR) spectra of the complexes were recorded with Shimadzu 840 840 FT-IR spectrophotometer as nujoll mull on KBr disc in the range 400–4000 cm^{-1}. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ solution with a Bruker FT 400 MHz spectrometer using tetramethylsilane as an internal reference. ^{119}Sn NMR spectra of the complexes were recorded using Me_4Sn as an external reference. Mass spectra of the complexes were recorded with a Shimadzu GC–MS QP 2010 ULTRA spectrometer.

2.1 | Syntheses of complexes

All the organotin complexes, R_3SnLH, were synthesized using the same procedure. Therefore, the synthetic procedure for one representative compound is discussed in detail. The analytical as well as preparative details for all of the compounds are summarized in Table 1.

2.1.1 | Synthesis of complex Me_3SnL^1H

Trimethyltin chloride (1.564 g, 5.15 mmol) and the freshly prepared sodium salt of Schiff base ligand Na[$OC(CH_3)$:$CH(CH_3)C$:NCH_2CH_2OH] (1.036 g, 5.15 mmol) were mixed in tetrahydrofuran (THF; *ca* 50 ml) and the reaction mixture was refluxed for *ca* 6 h. NaCl thus precipitated was filtered off. The solvent was removed under reduced pressure to yield a brownish viscous compound. The compound was recrystallized from THF–*n*-hexane mixture. The compound on analyses (%) was found to have: Sn, 38.76; C, 39.24; H, 6.90; N, 4.55; calculated (%): Sn, 38.79; C, 39.25; H, 6.91; N, 4.57.

2.2 | Antimicrobial activity

Antimicrobial activities of complexes and ligands were studied against bacterial and fungal strains. Two bacterial and two fungal strains were selected for primary screening. Streptomycin was used as positive control for antibacterial activity and clotrimazol for antifungal activity. Dimethylsulfoxide (DMSO) was used as negative control for antimicrobial activity of the complexes.

2.2.1 | Microorganisms used

Clinical laboratory bacterial isolates of *Bacillus subtilis* and *Escherichia coli* and fungal isolates of *Aspergillus niger* and *Fusarium oxysporum* were collected from stock cultures of the Microbiology Laboratory, SMS Medical College, Jaipur, India.

TABLE 1 Synthetic and analytical data for new triorganotin(IV) Schiff base derivatives

Complex	Reactants, g (mmol)		NaCl in g: found (calcd)	Empirical formula (yield, %)	Colour, physical state (m. p., °C)	Analyses, %: found (calcd)			
	R_3SnCl	LH_2				Sn	C	H	N
Me_3SnL^1H	1.3024 (6.535)	0.9357 (6.535)	0.3811 (0.3819)	$C_{10}H_{21}O_2NSn$ (83)	Creamish white, solid (155)	38.77 (38.79)	39.23 (39.25)	6.90 (6.91)	4.54 (4.57)
Me_3SnL^2H	1.2453 (6.249)	0.9824 (6.249)	0.3654 (0.3652)	$C_{11}H_{23}O_2NSn$ (79)	Dark brown ,viscous liquid	37.06 (37.09)	41.28 (41.28)	7.23 (7.24)	4.36 (4.37)
Me_3SnL^3H	1.0827 (5.433)	1.1152 (5.433)	0.3167 (0.3175)	$C_{15}H_{23}O_2NSn$ (78)	Creamish white, solid (162)	32.21 (32.25)	48.94 (48.95)	6.27 (6.29)	3.81 (3.80)
Me_3SnL^4H	1.0430 (5.234)	1.1471 (5.234)	0.3053 (0.3058)	$C_{16}H_{25}O_2NSn$ (76)	Dark brown, viscous liquid	31.06 (31.07)	50.30 (50.29)	6.56 (6.59)	3.63 (3.66)
Ph_3SnL^1H	1.566 (4.062)	0.5817 (4.062)	0.2370 (0.2374)	$C_{25}H_{27}O_2NSn$ (82)	Light brown, solid (168)	24.11 (24.12)	61.04 (61.01)	5.53 (5.53)	2.82 (2.84)
Ph_3SnL^2H	1.5229 (3.950)	0.6211 (3.950)	0.2310 (0.2308)	$C_{26}H_{29}O_2NSn$ (81)	Brown, viscous liquid	23.45 (23.44)	61.70 (61.69)	5.76 (5.77)	2.77 (2.76)
Ph_3SnL^3H	1.3900 (3.607)	0.7405 (3.607)	0.2102 (0.2108)	$C_{30}H_{29}O_2NSn$ (78)	Brown, solid (171)	21.40 (21.42)	65.02 (65.01)	5.30 (5.27)	2.55 (2.53)
Ph_3SnL^4H	1.3565 (3.519)	0.7717 (3.519)	0.2048 (0.2056)	$C_{31}H_{31}O_2NSn$ (75)	Brown, viscous liquid	20.85 (20.89)	65.51 (65.52)	5.49 (5.50)	2.45 (2.46)

2.2.2 | Culture and maintenance of bacteria

Pure cultures obtained from SMS Medical College were used as indicator organisms. These bacteria were grown in nutrient agar medium (prepared by autoclaving 8% nutrient agar of Difeco Laboratories, Detroit, USA, in distilled water at 15 psi for 25–30 min) and incubated at 37°C for 48 h. Each bacterial culture was further maintained on the same medium after every 48 h of transferring. A fresh suspension of test organism in saline solution was prepared from a freshly grown agar slant before every antimicrobial assay.

2.2.3 | Antibacterial assay

In vitro antibacterial activity of the complexes was studied against Gram-positive and Gram-negative bacterial strains by the agar well diffusion method.[50] Mueller–Hinton agar no. 2 (Hi Media, India) was used as the bacteriological medium. The test solutions were diluted in 100% DMSO at a concentration of 5 mg ml^{-1}. The Mueller–Hinton agar was melted and cooled to 48–50°C and a standardized inoculum (1.5×10^8 CFU ml^{-1}, 0.5 McFarland) was then added aseptically to the molten agar and poured into sterile Petri dishes to give a solid plate. Wells were prepared in the seeded agar plates. The test compound (100 µl) was introduced in the well (6 mm). The plates were incubated overnight at 37°C. The antimicrobial spectrum of the extract was determined for the bacterial species in terms of zone sizes around each well. The diameters of zones of inhibition produced by the agent were compared with those produced by the commercial control antibiotic streptomycin. For each bacterial strain, controls were maintained where pure solvents were used instead of the extract. The control zones were subtracted from the test zones and the resulting zone diameter was measured with an antibiotic zone reader to the nearest millimetre. The experiment was performed three times to minimize the error and the mean values are presented.

2.2.4 | Antifungal assay

Antifungal activity of the complexes was investigated using the agar well diffusion method.[51] The yeasts and saprophytic fungi were subcultured onto Sabouraud's dextrose agar SDA (Merck, Germany) and incubated at 37°C for 24 h and 25°C for 2–5 days, respectively. Suspensions of fungal spores were prepared in sterile phosphate-buffered saline and adjusted to a concentration of 106 cells ml^{-1}. A sterile swab was dipped into the fungal suspension and rolled on the surface of the agar medium. The plates were dried at room temperature for 15 min. Wells of 10 mm in diameter and about 7 mm apart were punctured in the culture media using a sterile glass tube. An amount of 0.1 ml of several dilutions of fresh extracts was administered to fullness for each well. Plates were incubated at 37°C. After 24 h of incubation, bioactivities were determined by measuring the diameter of inhibition zones (in millimetres). All experiments were made in triplicate and means were calculated.

3 | RESULTS AND DISCUSSION

3.1 | Syntheses of triorganotin(IV) derivatives

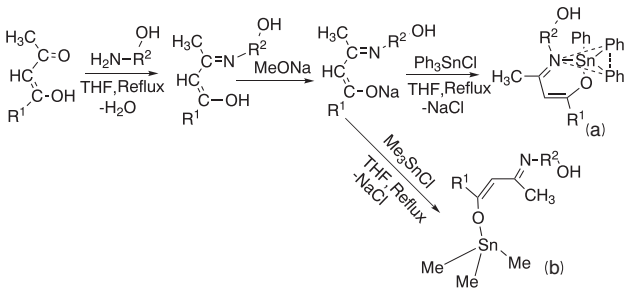
Ligands were synthesized by the condensation reaction of β-diketones and selected amino alcohols using a literature method.[48] Sodium salts of the ligands were prepared by the reaction of Schiff bases and freshly prepared sodium methoxide in unimolar ratio. The reactions of R_3SnCl with sodium salts of Schiff bases (LHNa) in unimolar ratio in refluxing THF yield triorganotin(IV) complexes (Scheme 1).

3.2 | IR spectra

In the IR spectra of these derivatives the disappearance of the broad band observed in the spectra of parent ligands at 2700–3000 cm^{-1} and assigned[52] to enolic ─OH indicates the deprotonation of ─OH group. This is supported by the appearance of a new band at 512–536 cm^{-1} due to ν(Sn─O) stretching vibrations.[53] In the IR spectra of free ligands the azomethine ν(>C═N) band present at 1617–1625 cm^{-1} is shifted to 1571–1602 cm^{-1} in the spectra of the complexes Ph_3SnL^1H–Ph_3SnL^4H. Considerable shifts to lower wavenumber in its position may be due to the involvement of >C═N group nitrogen in coordination with tin atom. The appearance of a new band in the region 441–448 cm^{-1} due to ν(Sn─N) supports the formation of Sn─N bond[54] in complexes Ph_3SnL^1H–Ph_3SnL^4H. However, no significant shift is observed in the position of ν(>C═N) band in the spectra of Me_3SnL^1H–Me_3SnL^4H which rules out the involvement of this group in the bonding. A broad band observed for aminol group ν(C─OH) at 3300–3600 cm^{-1} in the spectra of ligands does not show any appreciable shift in its position for all the complexes which rules out the involvement of this group in the bonding.

3.3 | ^{1}H NMR spectra

In the ^{1}H NMR spectra (Table 2) of the ligands both enolic and aminol ─OH signals are observed at 11.3–12.2 and



Where, R'	R"	Ligands	R= -CH_3	R= -C_6H_5
-CH_3	-$(CH_2)_2$-	L_1H_2	Me_3SnL_1H	Ph_3SnL_1H
-CH_3	-$(CH_2)_3$-	L_2H_2	Me_3SnL_2H	Ph_3SnL_2H
-C_6H_5,	-$(CH_2)_2$-	L_3H_2	Me_3SnL_3H	Ph_3SnL_3H
-C_6H_5,	-$(CH_2)_3$-	L_4H_2	Me_3SnL_4H	Ph_3SnL_4H

SCHEME 1 Synthetic route for bifunctional tridentate Schiff bases (L^1H_2–L^4H_2) and their triorganotin(IV) derivatives: (A) triphenyltin(IV) complexes; (B) trimethyltin(IV) complexes

TABLE 2 ^{1}H NMR and ^{119}Sn NMR spectral data (δ, ppm) of Schiff bases and their corresponding new triorganotin(IV) derivatives

Ligand/compound	^{1}H NMR									^{119}Sn NMR
	–*OH* Inolic, alcoholic	$-C_6H_5$	–*CH*CO	$-CH_2O$	$-CH_2N$	$-CH_2-CH_2-CH_2-$	$-CH_3CO$	$-CH_3CN$	$-CH_3Sn$	
L^1H_2	11.37, 3.85	—	5.521(s)	3.284(t) J = 7.41 Hz	3.115(t) J = 6.1 Hz	—	2.010(s)	1.854(s)	—	—
L^2H_2	11.51, 3.45	—	5.534(s)	3.301(t) J = 7.4 Hz	3.202(t) J = 6.8 Hz	3.212(m)	2.035(s)	1.915(s)	—	—
L^3H_2	12.04, 3.64	7.152–7.741(m)	5.539(s)	3.421(t) J = 7.47 Hz	3.315(t) J = 6.32 Hz	—	—	1.714(s)	—	—
L^4H_2	12.17, 4.35	7.251–7.811(m)	5.540(s)	3.654(t) J = 7.61 Hz	3.299(t) J = 6.12 Hz	3.201(m)	—	1.762(s)	—	—
Me_3SnL^1H	—, 3.91	—	5.544(s)	3.313(t) J = 7.44 Hz	3.212(t) J = 6.4 Hz	—	2.056(s)	1.969(s)	1.727(s)^2J(^{119}Sn–^{1}H) = 54 Hz	–40.4
Me_3SnL^2H	—, 3.62	—	5.582(s)	3.472(t) J = 7.44 Hz	3.370(t) J = 7.21 Hz	3.204(m)	1.997(s)	1.742(s)	1.216(s)^2J(^{119}Sn–^{1}H) = 54.7 Hz	–52
Me_3SnL^3H	—, 3.70	7.192–7.811(m)	5.554(s)	3.714(t) J = 7.8 Hz	3.352(t) J = 6.5 Hz	—	—	1.777(s)	0.774(s)^2J(^{119}Sn–^{1}H) = 56.1 Hz	–50.8
Me_3SnL^4H	—, 4.11	7.265–7.396(m)	5.591(s)	3.691(t) J = 7.9 Hz	3.404(t) J = 6.14 Hz	3.389(m)	—	1.827(s)	1.812(s)^2J(^{119}Sn–^{1}H) = 55.8 Hz	–47.2
Ph_3SnL^1H	—, 3.67	7.148–7.245(m)	4.909(s)	3.680(t) J = 7.4 Hz	3.356(t) J = 7.1 Hz	—	1.920(s)	1.908(s)	—	–141
Ph_3SnL^2H	—, 3.56	7.312–7.775(m)	4.887(s)	3.316(t) = 7.44 Hz	3.204(t) J = 6.78 Hz	3.003(m)	1.910(s)	1.874(s)	—	–153.5
Ph_3SnL^3H	—, 3.73	7.336–7.753(m)	5.535(s)	3.684(t) J = 7.9 Hz	3.332(t) J = 6.8 Hz	—	—	1.969(s)	—	–169
Ph_3SnL^4H	—, 3.98	7.139–7.656(m)	5.134	3.589(t) J = 7.71 Hz	3.271(t) J = 6.5 Hz	2.998(m)	—	1.969(s)	—	–176.1

3.4–4.4 ppm, respectively. Absence of the signal for enolic ─OH in the spectra of all the triorganotin(IV) derivatives reveals the deprotonation and involvement of this group in bonding with tin atom. But the signal for aminol ─OH group is present in the spectra of ligands as well as of complexes. The position of the signal does not show any significant shift even after complexation which shows that aminol group does not take part in bonding and is present as free ─OH group. Aromatic protons appear as a multiplet in the region 7.3–7.9 ppm in the spectra of ligands as well as of organotin complexes.

In the spectra of Me_3SnL^1H–Me_3SnL^4H the Sn─CH_3 protons appear as a singlet in the range 0.36–0.81 ppm which indicates that all three methyl groups are in the same chemical environment. The $^2J(^1H–^{119}Sn)$ coupling constants, which provide important information about the coordination environment, were also determined and are given in Table 2. For triphenyltin(IV) complexes it is not possible to distinguish between signals due to aromatic ligand protons and those linked to tin, but integration takes their presence into account. The $^2J(^1H–^{119}Sn)$ values are in the range 54–56.1 Hz for Me_3SnLH-type complexes. The C─Sn─C bond angle calculated using Lockhart and Manders equations[55,56] is in the range 109.06–110.12° for these complexes. These coupling constant values correspond to tetracoordination and the bond angles clearly indicate tetrahedral geometry[55] in complexes Me_3SnL^1H–Me_3SnL^4H.

3.4 | ^{13}C NMR spectra

The ^{13}C NMR spectral data for these derivatives are summarized in Table 3. The spectra of all the triorganotin(IV) complexes as well as their corresponding ligands exhibit a signal for >C─O─ enolic group carbon[57] in the range 187.5–195.8 ppm. A small downfield shift is observed in the position of this signal as compared to the corresponding free ligands. This shift is slightly more downfield in case of triphenyltin(IV) complexes as compared to trimethyltin(IV) complexes. Signal for >C═N imine group carbon is observed in the range 162.9–165.9 ppm. A downfield shift of *ca* 2–5 ppm is been observed for triphenyltin(IV) complexes (Ph_3SnL^1H–Ph_3SnL^4H) as compared to its position in the spectra of corresponding free Schiff base ligands. However, for trimethyltin(IV) derivatives no appreciable shift in this signal is observed. This shift in the positions of the signal of carbon atom adjacent to the imine group nitrogen suggests that nitrogen is involved in coordination with tin in triphenyltin(IV)complexes only. While in trimethyltin(IV) complexes this group does not take part in the bonding. The signal for CH_2O─ group carbon appears in the range 60.7–68.3 ppm in spectra of Schiff bases and the corresponding tin complexes. The spectra of complexes Me_3SnL^1H–Me_3SnL^4H exhibit a signal for CH_3─Sn group carbon in the range 7.4–8.1 ppm. The $^1J(^{119}Sn–^{13}C)$ coupling constant values are found to be in the range 369.7–381.3 Hz for these

TABLE 3 ^{13}C NMR spectral data (δ, ppm) of new triorganotin(IV) Schiff base derivatives

Ligand/compound	=*C*–OH	>*C*=N	–C_6H_5	Alkylene carbon
L^1H_2	191.1	162.6		94.9 (=*C*H–), 62.2 (*C*H_2O), 58.0 (*C*H_2N), 33.9 (*C*H_3CO), 26.3 (*C*H_3CN)
L^2H_2	193.5	163.4		96.6 (=*C*H–), 68.3 (*C*H_2O), 51.3 (*C*H_2N), 41.2 (*C*H_2), 31.2 (*C*H_3CO), 24.3 (*C*H_3CN)
L^3H_2	188.2	161.7	126.1–140.4	95.6 (=*C*H–), 67.6 (*C*H_2O), 52.4 (*C*H_2N), 27.4 (*C*H_3CN)
L^4H_2	192.9	163.8	126.4–140.2	92.2 (=*C*H–), 70.1 (*C*H_2O), 59.5 (*C*H_2N), 39.9 (*C*H_2), 26.4 (*C*H_3CN)
Me_3SnL^1H	191.9	164.4		95.2 (=*C*H–), 63.4 (*C*H_2O), 58.4 (*C*H_2N), 34.6 (*C*H_3CO), 26.7 (*C*H_3CN)
Me_3SnL^2H	192.5	165.7		96.9 (=*C*H–),68.7 (*C*H_2O),51.6 (*C*H_2N),41.0 (*C*H_2),31.5 (*C*H_3CO), 24.8 (*C*H_3CN)
Me_3SnL^3H	193.5	164.8		95.3 (=*C*H–),68.2 (*C*H_2O),57.9 (*C*N),34.7 (*C*H_3CO),28.7 (*C*H_3CN) 20.3 (*C*H_3)
Me_3SnL^4H	194.1	164.3		95.8 (=*C*H–), 68.4 (*C*H_2O), 52.8 (*C*H_2N), 27.7 (*C*H_3CN)
Ph_3SnL^1H	193.9	165.1	126.7–140.8	92.7 (=*C*H–), 69.3 (*C*H_2O), 60.4 (*C*H_2N), 38.2 (*C*H_2), 26.6 (*C*H_3CN)
Ph_3SnL^2H	194.2	165.4	126.2–140.1	94.3 (=*C*H–), 61.2 (*C*H_2O), 52.2 (*C*N), 27.9 (*C*H_3CN), 24.6–19.7 (CH_3)
Ph_3SnL^3H	195.8	164.9	126.4–140.3	95.3 (=*C*H–),68.2 (*C*H_2O),57.9 (*C*N),34.7 (*C*H_3CO),28.7 (*C*H_3CN) 20.3 (*C*H_3)
Ph_3SnL^4H	195.4	165.2	127.4–140.6	95.8 (=*C*H–), 68.4 (*C*H_2O), 52.8 (*C*H_2N), 27.7 (*C*H_3CN)

complexes, which is consistent with tetracoordination in trimethyltin(IV) complexes.[55,56]

3.5 | ^{119}Sn NMR spectra

^{119}Sn NMR spectra can be used as an indicator of coordination number of the tin atom. ^{119}Sn chemical shift also shows a variation with a change in coordination number. The ^{119}Sn NMR chemical shifts for all the organotin(IV) complexes are given in Table 2. Holecek et al.[58] reported $\delta(^{119}Sn)$ for four-coordinate and five-coordinate compounds in the range − 40 to −120 and −180 to −260 ppm, respectively. Chemical shifts in the range − 90 to −330 ppm in $CDCl_3$ solution have been reported for five-coordinate organotin(IV) chelates by Otera.[59] The ^{119}Sn NMR spectra of complexes Me_3SnL^1H–Me_3SnL^4H show only one singlet at −40.4 to −52 ppm which is in the normal range for four-coordinate tin complexes,[60] further supported by a value of −47 ppm for tetrahedral Ph_3SnL (L = heterocyclic β-diketone).[61] The spectra of complexes Ph_3SnL^1H–Ph_3SnL^4H exhibit only one singlet at −141 to −176.1 ppm which is in the normal range for five-coordinate complexes.[43,59,60]

3.6 | Mass spectra

The mass spectra of all the newly synthesized complexes were recorded and the characteristic mass peaks of one representative complex, Me_3SnL^1H, are summarized in Table 4. Molecular ion peaks and other characteristic peaks indicate the monomeric nature of these complexes. Mass peaks indicate the formation of a variety of fragments bearing tin atom in the course of decomposition. Molecular ion peaks of complexes Me_3SnL^1H–Me_3SnL^4H are observed at *m/z* 306, 304, 352 and 366, respectively. For complexes Ph_3SnL^2H and Ph_3SnL^4H low abundant molecular ion peaks are observed at *m/z* 490 and 538. In complexes Ph_3SnL^1H and Ph_3SnL^4H no molecular ion peaks are observed. For all these compounds molecular ion peaks are not base peaks. In all these compounds the fragmentation initiates in same manner by the loss of ethylenic (=CH) carbon followed by the decomposition of ligand and the R–Sn]$^+$ fragment is formed as a final decomposition product showing strong bonding of tin atom by alkyl/phenyl group.

3.7 | Antimicrobial activity

The triorganotin(IV) complexes and their corresponding free Schiff bases (L^1H_2–L^4H_2) were screened against bacteria (Table 5) and fungi (Table 6) to examine their growth inhibitory potential towards the test organisms. The results for antimicrobial activity are summarized in the following points.

i. All the compounds (ligands as well as complexes) are more toxic towards Gram-positive strain (*B. subtilis*) than Gram-negative strain (*E. coli*).The reason probably lies in the difference between the structures of the cell

TABLE 4 Fragmentation mode of complex Me_3SnL^1H

Fragment	*m/z*	Relative abundance (%)
$(CH_3)_3Sn[OC(CH_3):CH\ (CH_3)C:N(CH_2CH_2)OH]^{+\cdot}$	306	6
$(CH_3)_3Sn[OC(CH_3):C(CH_3):N(CH_2CH_2)OH]^{+\cdot}$	293	100
$(CH_3)_3Sn[OC(CH_3):N(CH_2CH_2)OH]^{+\cdot}$	267	18
$(CH_3)_3Sn[N(CH_2CH_2)OH]^{+\cdot}$	223	37
$(CH_3)_3Sn[CH_2\text{-}OH]^{+\cdot}$	195	23
$(CH_3)_3Sn]^{+\cdot}$	164	19
$(CH_3)Sn]^{+\cdot}$	134	41

TABLE 5 Antibacterial studies of ligands and corresponding triorganotin (IV) Schiff base derivatives

Compound	Concentration (mg ml^{-1})	Inhibition zone diameter (mm)			
		S. aureus	*B. subtilis*	*E. coli*	*P. aeruginosa*
L^1H_2	2	7	6	6	5
	4	8	9	8	7
L^2H_2	2	7	7	5	6
	4	10	10	9	9
L^3H_2	2	9	8	8	7
	4	12	11	10	10
L^4H_2	2	6	7	5	7
	4	8	9	7	9
Me_3SnL^1H	2	7	8	6	8
	4	10	10	9	10
Me_3SnL^2H	2	6	7	6	7
	4	8	12	8	11
Me_3SnL^3H	2	7	9	7	9
	4	11	14	10	12
Me_3SnL^4H	2	11	9	8	7
	4	14	15	13	11
Ph_3SnL^1H	2	13	12	11	10
	4	17	15	16	14
Ph_3SnL^2H	2	10	12	10	9
	4	13	16	13	12
Ph_3SnL^3H	2	14	13	12	8
	4	17	17	16	11
Ph_3SnL^4H	2	12	12	12	9
	4	17	19	13	13

TABLE 6 Antifungal studies of ligands and corresponding triorganotin(IV) Schiff base derivatives

Compound	Concentration (mg ml^{-1})	Inhibition zone diameter (mm)			
		F. oxysporum	T. reesei	P. funiculosum	*A. niger*
L^1H_2	2	7	6	6	5
	4	8	9	8	7
L^2H_2	2	9	8	7	6
	4	11	12	11	10
L^3H_2	2	11	10	9	8
	4	13	12	13	12
L^4H_2	2	6	5	5	6
	4	7	9	8	9
Me_3SnL^1H	2	7	8	6	7
	4	9	11	9	10
Me_3SnL^2H	2	8	7	7	8
	4	10	11	10	11
Me_3SnL^3H	2	7	9	7	8
	4	11	12	12	10
Me_3SnL^4H	2	8	7	8	9
	4	12	11	10	13
Ph_3SnL^1H	2	10	9	14	13
	4	13	12	16	17
Ph_3SnL^2H	2	11	13	11	14
	4	15	14	15	16
Ph_3SnL^3H	2	12	15	16	17
	4	15	18	20	20
Ph_3SnL^4H	2	11	11	13	14
	4	13	14	17	19

walls. The relatively more complex cell walls of Gram-negative strains may prevent the diffusion of chemicals into the cytoplasm of the organisms, which may not be the case in Gram-positive strains.

ii. The results indicate that the metal chelates have higher activity than the free ligands. This increased activity of the metal chelates can be explained by Tweedy's chelation theory[62] and Overtone's concept. According to Overtone's concept of cell permeability, the lipid membrane that surrounds the cell favours passage of only lipid-soluble material due to liposolubility which is an important factor that controls antimicrobial activity. On chelation, the polarity of the metal ions is reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor group. Enhanced activity may be due to the coordination of ligand to tin leading to electron delocalization and therefore increasing the lipophilic character and efficient diffusion of the metal complexes into bacterial cells.

iii. It is important to mention that the antimicrobial activity for ligands derived from benzoyl acetone (L^3H_2 and L^4H_2) and their corresponding metal complexes (Me_3SnL^3H, Me_3SnL^4H, Ph_3SnL^3H and Ph_3SnL^4H) is greater than the ligands derived from acetyl acetone (L^1H_2 and L^2H_2) and their corresponding metal complexes (Me_3SnL^1H, Me_3SnL^2H, Ph_3SnL^1H and Ph_3SnL^2H). Moreover, the triphenyltin(IV) complexes of all the ligands are more active than the corresponding trimethyltin(IV) derivatives. Thus, it may be concluded that the presence of phenyl group in the ligand as well as at the tin centre enhances the activity which may be due to the electron-withdrawing nature of the phenyl group.

iv. The concentration of compounds is another important factor which affects the inhibition of growth. At lower concentration (2 mg ml^{-1}) growth will be slowed down, while at higher concentration more enzymes will become inhibited leading to a quicker death of the organism.

3.8 | Structural elucidation

For all the complexes, aminol ─OH is not deprotonated and deprotonation of only enolic group indicates the monofunctional nature of the ligands. In triphenyltin(IV) complexes (Ph_3SnL^1H–Ph_3SnL^4H), the >C═N group takes part in coordination as indicated by the significant shift in the position of >C═N group carbon signal in ^{13}C NMR spectra. Thus the ligands behave as monofunctional bidentate moieties.

In view of the above, we propose structures in which the central tin atom acquires tetracoordination (Figure 1B) and

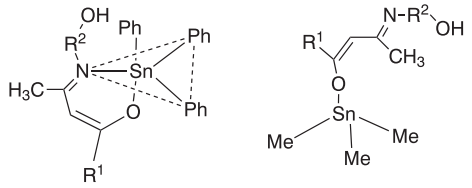


FIGURE 1 Proposed structures for the complexes: (A) Ph_3SnL^1H–Ph_3SnL^4H; (B) Me_3SnL^1H–Me_3SnL^4H

pentacoordination (Figure 1A) in trimethyltin(IV) complexes (Me_3SnL^1H–Me_3SnL^4H) and triphenyltin(IV) complexes (Ph_3SnL^1H–Ph_3SnL^4H), respectively, which is supported by the $^2J(^1H–^{119}Sn)$ and $^1J(^{119}Sn–^{13}C)$ coupling constants and ^{119}Sn NMR chemical shift values.

4 | CONCLUSIONS

In triorganotin(IV) derivatives of chelating ligands, the denticity of ligands and geometry of complexes are found to be different in trimethyltin(IV) and triphenyltin(IV) complexes. One explanation for this behaviour may be that in trimehtyltin(IV) complexes the central tin atom is less electron deficient due to the presence of electron-releasing group as compared to the triphenyltin(IV) derivatives where electron-withdrawing phenyl groups are present. We observed similar behaviour of ligand and different geometries around the central tin atom for trimethyltin(IV) and triphenyltin(IV) compounds. In the compounds Me_3SnLH, the ligand, which usually behaves as a bifunctional tridentate moiety,[63] is a monofunctional monodentate moiety and the geometry around the central tin atom is tetrahedral. Whereas in the compounds Ph_3SnLH, the ligand behaves as a monofunctional bidentate moiety and the geometry of the compounds is trigonal bipyramidal.

We have also observed a structure–activity relationship in the ligands and the newly synthesized complexes. The presence of the phenyl group enhances the toxicity of the ligands and the complexes.

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