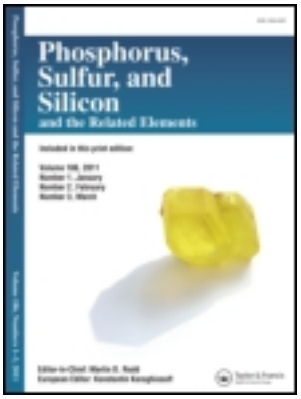

Phosphorus, Sulfur, and Silicon and the Related Elements

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Synthesis, Characterization, Thermal, and Antibacterial Studies of Organotin(Iv) Complexes of Indole-3-Butyric Acid and Indole-3-Propionic Acid

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SYNTHESIS, CHARACTERIZATION, THERMAL, AND ANTIBACTERIAL STUDIES OF ORGANOTIN(IV) COMPLEXES OF INDOLE-3-BUTYRIC ACID AND INDOLE-3-PROPIONIC ACID

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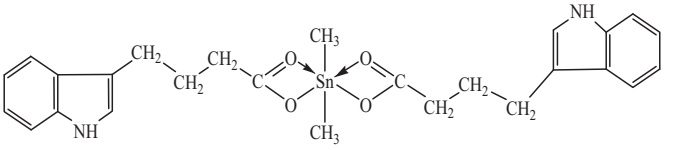
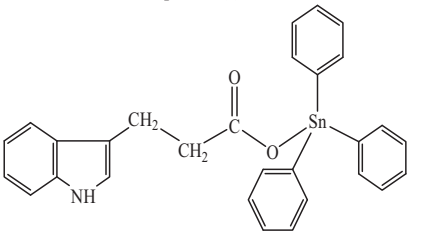
GRAPHICAL ABSTRACT



Compound: (1)



Compound: (6)

Abstract *Six organotin(IV) complexes of type Me_2SnL_2, Bu_2SnL_2, and Ph_3SnL [where* L = *indole-3-butyric acid (1, 2 and 3) or indole-3-propionic acid (4, 5 and 6)] have been synthesized by the reactions of the corresponding diorganotin(IV) oxide and triphenyltin(IV) hydroxide with respective indole-3-butyric acid (IBH) or indole-3-propionic acid (IPH) in the desired molar ratios of 1:2/1:1. All of the compounds have been characterized by elemental analysis, IR, ^1H NMR, ^{13}C NMR, and ^{119}Sn NMR spectroscopy. Thermal studies of all synthesized complexes have been carried out using thermogravimetry (TG) technique under a nitrogen atmosphere. The thermal decompositions for compounds Me_2SnL_2 and Bu_2SnL_2 occurred in two steps, whereas in compounds Ph_3SnL, it exhibited as three steps decomposition and resulted into the formation of pure SnO_2. The complexes were also screened against three gram-positive (*Staphylococcus aureus, Staphylococcus epidermidis, *and* Micrococcus luteus*) and three gram-negative (*Escherichia coli, Pseudomonas aeruginosa, *and* Enterobacter aerogenes*) bacteria*

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using minimum inhibition concentration (MIC) method, and all of these complexes showed significant antibacterial activity.

[Supplementary materials are available for this article. Go to the publisher's online edition of Phosphorus, Sulfur, and Silicon and the Related Elements *for the following free supplemental files: Additional text, tables, and figures.]*

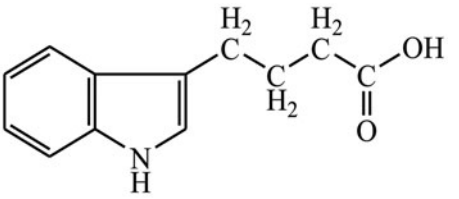
Keywords Diorganotin(IV) oxide; triphenyltin(IV) hydroxide; spectroscopic analysis; thermal decomposition; antibacterial activity

INTRODUCTION

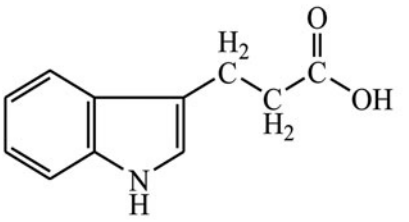
Organotin(IV) compounds have been receiving increasing attention owing to a variety of industrial and agricultural applications.[1,2] In view of the diverse fields of applications, numerous articles and reviews are available in the literature.[3,4] The coordination chemistry of tin is extensive with various geometries and coordination numbers known for both inorganic and organometallic complexes.[5] Considerable efforts have been made to synthesize and characterize organotin compounds having heterodonor atoms (O, N, and S) which have different applications[6] and stabilities depending on the number, type, and arrangement of ligands about tin;[7] many studies have been focused on their structure-activity correlations.[8,9] The organotin(IV) derivatives of donor ligands are also of considerable interest as they have been suggested to possess mild to good biological activities.[10]

Among the organotin compounds, organotin(IV) carboxylates have been widely studied due to their structural diversity[2] and wide range of applications,[11] such as biocides, wood preservatives, antifouling agents, catalysts, and stabilizers.[12–14] In general, the biochemical activity of organotin(IV) complexes is greatly influenced by the molecular structures and coordination number of the tin atom.[7,15] Tri-organotin(IV) compounds display better biological activity than their diorganotin and mono-organotin analogs.[16] This has been attributed to their ability to bind proteins.[17] Therefore, their synthesis and structural chemistry is well documented in the literature.[18] However, thermokinetic parameters required to assess the functional stability of an organotin compound for its particular end usage are yet to be explored. The thermal properties can easily be evaluated by using thermogravimetry analysis (TGA). TGA scans recorded at a certain heating rate and under nitrogen atmosphere can be utilized for the evaluation of degradation processes of a compound. It has further been suggested that the biological activity of organotin(IV) compounds will be considerably enhanced if acids containing an indole ring is bound with metals.[19]

Hence, it is considered worthwhile to design and synthesize new organotin carboxylates using indole-3-butyric acid (IBH) and indole-3-propionic acid (IPH) as ligands and to study their thermal stability and biological assays. In view of this, we have synthesized six organotin(IV) complexes of dimethyltin, dibutyltin, and triphenyltin esters of IBH or IPH. These complexes have been characterized by elemental analysis, infrared, multinuclear (^{1}H, ^{13}C, ^{119}Sn) NMR spectroscopy. Thermal analysis was performed for the complexes to study their thermal degradation and they were also screened against three gram-positive (*Staphylococcus aureus*, *Staphylococcus epidermidis*, and *Micrococcus luteus*) and three gram-negative (*Escherichia coli*, *Pseudomonas aeruginosa*, and *Enterobacter aerogenes*) bacteria to establish their antibacterial activity.



Indole-3 butyric acid (IBH)



Indole-3 propionic acid (IPH)

Figure 1 Structure and acronyms of indole-3-butyric acid and indole-3-propionic acid.

RESULTS AND DISCUSSION

General Procedure for the Synthesis of the Complexes 1–6

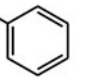
The structures and acronyms of IBH and IPH used for the preparation of complexes are given in Figure 1. The six organotin(IV) complexes were synthesized by azeotropic removal of water from the reaction between the diorganotin(IV) oxide/triphenyltin(IV) hydroxide and indole-3-butyric acid and indole-3-propionic acid in 1:2/1:1 molar ratio (Scheme 1). Some representative experiments to illustrate the synthesis of the above complexes are given subsequently.

$$Me_2SnO + 2HL \xrightarrow[\text{Reflux, 2h, r.t.}]{\text{MeOH}} Me_2Sn(L)_2 + 2H_2O \quad (1)$$

$$Bu_2SnO + 2HL \xrightarrow[\text{Reflux, 3h, r.t.}]{\text{Acetonitrile}} Bu_2Sn(L)_2 + 2H_2O \quad (2)$$

$$Ph_3SnOH + HL \xrightarrow[\text{Reflux, 2h, r.t.}]{\text{Acetonitrile}} Ph_3SnL + H_2O \quad (3)$$

where,

Me = $-CH_3$, Bu = $-CH_2CH_2CH_2CH_3$, Ph = 

HL = IBH or IPH

Scheme 1 Synthesis of organotin(IV) complexes.

Structural Characterization and Elemental Analysis

The compounds were of white to light brown in color. They were soluble in organic solvents such as dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) but insoluble

Table 1 Analytical data of organotin(IV) complexes

Comp.	Compound designation	Molecular formula	Yield %	FMW g mol^{-1}	Elemental analysis% Found (Calc.)			
					Sn	C	H	N
1	$Me_2Sn(IB)_2$	$C_{26}H_{30}N_2O_4Sn$	71	553.24	21.10 (21.45)	55.07 (56.44)	4.97 (5.46)	5.11 (5.06)
2	$Bu_2Sn(IB)_2$	$C_{32}H_{42}N_2O_4Sn$	70	637.40	18.95 (18.62)	59.81 (60.29)	6.90 (6.64)	4.53 (4.39)
3	Ph_3SnIB	$C_{30}H_{27}NO_2Sn$	82	552.25	21.63 (21.49)	65.33 (65.24)	5.13 (4.92)	2.71 (2.53)
4	$Me_2Sn(IP)_2$	$C_{24}H_{26}N_2O_4Sn$	70	525.18	22.47 (22.60)	55.10 (54.88)	4.85 (4.98)	4.92 (5.33)
5	$Bu_2Sn(IP)_2$	$C_{30}H_{38}N_2O_4Sn$	74	609.35	19.55 (19.48)	59.27 (59.13)	6.31 (6.28)	4.68 (4.59)
6	Ph_3SnIP	$C_{29}H_{25}NO_2Sn$	80	538.23	21.91 (22.05)	64.65 (64.71)	4.77 (4.68)	2.51 (2.60)

in water, carbon tetrachloride, and hexane. The yields were in the range of 70% to 82%. The analytical data are listed in Table 1. The calculated values of C, H, N, and Sn agreed well with the experimentally determined values.

FTIR Spectra

The IR spectra of organotin(IV) complexes have been recorded as KBr discs in the range of 400 to 4000 cm^{-1} and are summarized in Table 2. The bands in the range of 421 to 460 cm^{-1} and 548 to 578 cm^{-1} indicate the Sn–O and Sn–C bonds, respectively.[17,20] A strong band due to ν(N–H) was observed at 3370 to 3423 cm^{-1}. The compounds **1** to **6** do not show the broad ν(OH) band at 2600 to 3000 cm^{-1}, indicating the deprotonations of the carboxylic group of ligands due to the formation of the oxygen-tin bond.[11]

In organotin(IV) complexes, when there are interactions between the carbonyl oxygen atoms of the carboxylate groups and the tin atom, the asymmetric absorption vibration frequencies ν_{as}(COO) of carboxylate groups decreases and the symmetric absorption frequencies ν_s(COO) increases.[21] In the IR spectra of the complexes **1** to **6**, the two absorption bands in the ranges of 1585 to 1615 cm^{-1} and 1319 to 1458 cm^{-1} can be assigned to ν_{as}(COO) and ν_s(COO), respectively. The $\Delta\nu$ values [$\Delta\nu = \nu_{as}(COO) - \nu_s(COO)$] has been also used to predict the bonding mode of the ligand.[22] As reported earlier,[23] in complexes where $\Delta\nu$ is below 200 cm^{-1}, the ligand behaves as a bidentate carboxylate and in the complexes where $\Delta\nu$ is above 200 cm^{-1} the ligand behaves as a monodentate carboxylate. There is donation of charge density from C=O: $\rightarrow$ to the electropositive tin metal, which slightly increase the C=O bond length, hence, the absorption frequency decreases

Table 2 FTIR spectral data of organotin(IV) complexes

Comp.	Compound designation	ν_{as}(COO)	ν_s(COO)	$\Delta\nu$	ν(NH)	ν(SnO)	ν(Sn–C)
1	$Me_2Sn(IB)_2$	1615 (s)	1432 (s)	183	3370 (s)	421 (s)	563 (m)
2	$Bu_2Sn(IB)_2$	1613 (s)	1433 (s)	180	3370 (w)	430 (s)	570 (m)
3	Ph_3SnIB	1585 (s)	1319 (m)	265	3385 (m)	438 (s)	564 (w)
4	$Me_2Sn(IP)_2$	1610 (s)	1456 (s)	154	3400 (s)	458 (m)	560 (s)
5	$Bu_2Sn(IP)_2$	1599 (s)	1458 (m)	141	3408 (s)	460 (s)	578 (s)
6	Ph_3SnIP	1588 (s)	1330 (w)	258	3423 (s)	455 (m)	548 (m)

ν was measured as wave number in cm^{-1}.
Abbreviations: s, strong; m, medium; w, weak.

and carboxylate acts as bidentate ligand in the solid state.[24] Complexes **1**, **2**, **4,** and **5** showed that the magnitude of $\Delta\nu$ is comparable to the sodium salt of the acid indicating bidentate bonding of the carboxylate group to tin(IV) atom in the solid state. For complexes derived from triphenyltin(IV) hydroxide, the magnitude of $\Delta\nu$ below 200 cm^{-1} would be expected for bridging or chelating carboxylates, but greater than 200 cm^{-1} is for the monodentate bonding carboxylate anions.[8,21] Hence, carboxylate group in complexes **3** (265 cm^{-1}) and **6** (258 cm^{-1}) would be expected to bond to the tin atom in monodentate manner since the $\Delta\nu$ is above 200 cm^{-1}. As a result, the complexes **1**, **2**, **4,** and **5** exhibit six-coordinated tin atom and complexes **3** and **6** exhibit four-coordinated tin atom. The IR spectra of complexes **3** and **6** are shown in Figure S1 and complex **5** is shown in Figure S2 (Supplemental Materials).

^{1}H NMR Spectra

The ^{1}H NMR spectra of the derivatives were recorded in DMSO-d_6. The ^{1}H NMR spectra of the 3-indole carboxylates, due to the protons of indole ring, exhibited the resonances between δ 6.51 to 7.61 ppm. The heterocyclic –NH protons appeared at δ 10.10 to 10.81 ppm and there is no appreciable change in its position in the metal complexes confirming that heteronitrogen atom is not involved in coordination. The methylene protons i.e. $–CH_2CH_2CH_2–$ of IBH and $–CH_2CH_2–$ of IPH are observed in the range of δ 1.20 to 2.61 ppm. In the studied complexes, the –COOH resonance of the ligand at δ 12.00 to 13.00 ppm was absent, which suggests the replacement of the carboxylic proton by the organotin(IV) moiety.[25]

In ^{1}H NMR spectra of six complexes, all protons have been identified by intensity and multiplicity patterns. The upfield regions of the ^{1}H NMR spectra of the complexes **1** and **4** showed the signal of the methyl protons as singlet in the range of δ 0.89 ppm and δ 0.91 ppm, and complexes **2** and **5** showed the signal of the butyl protons as multiplet in the range of δ 0.81 to 1.57 ppm. The resonances due to the tin-phenyl protons in the studied complexes **3** and **6** were observed as multiplet in the region of δ 7.18 to 7.44 ppm with integration values of 9:6, respectively, ascribed to the aromatic protons of the phenyl group.[26] Generally, upon complexation, the magnitude of $^{n}J(^{119}Sn–^{1}H)$ varies depending on the stereochemistry at the tin atom and on the nature of the ligand. The larger coupling constant indicates the higher coordination number of tin.[27] The proton integration area was consistent with the molecular formula. The chemical shift values of ^{1}H NMR spectra are given in Table 3.

^{13}C NMR Spectra

The ^{13}C NMR characteristic resonance peaks of the complexes were recorded in DMSO-d_6 and the chemical shifts of the characterized carbons of organotin(IV) derivatives are listed in Table 4. The carboxylate carbon shifts to a lower field region in all the complexes, indicating the participation of the carboxyl group in the coordination to tin.[17] The indole ring carbons are observed in the range of δ 111.2 to 137.7 ppm and the other resonance lines in the spectrum fall into three regions, i.e., δ 5.9 to 34.4 ppm for aliphatic carbons, δ 127.6 to 138.2 ppm for carbons of phenyl group (**3** and **6**), and δ 179 $\pm$ 2 ppm for carbonyl carbon of the carboxyl group.

Table 3 ^{1}H NMR data (ppm) of organotin(IV) complexes of indole-3-butyric acid and indole-3-propionic acid

		δ ^{1}H[a]				
Comp.	Compound designation	–NH	Indole ring protons	–$(CH_2)_n$–	–CH_3/–$(CH_2)_3CH_3$ protons	Phenyl ring protons
1	$Me_2Sn(IB)_2$	10.10 (s)	7.51–6.81 (m)	2.51 (m), 1.60 (m), 1.33 (m)	0.89 (s, 7.2) [78.4][b]	—
2	$Bu_2Sn(IB)_2$	10.81 (s)	7.55–6.96 (m)	2.60 (m), 1.53 (m), 1.20 (m)	1.57–1.33 (m), 0.82 (t, 7.3)	—
3	Ph_3SnIB	10.70 (s)	7.55–6.71 (m)	2.42 (m), 1.61 (m), 1.30 (m)	–	7.44–7.18 (m)
4	$Me_2Sn(IP)_2$	10.11 (s)	7.50–6.51 (m)	2.71 (m), 1.40 (m)	0.91 (s, 7.2) [68.0]	—
5	$Bu_2Sn(IP)_2$	10.64 (s)	7.45–6.94 (m)	2.60 (m), 1.52 (m)	1.54–1.30 (m), 0.81 (t, 7.1)	—
6	Ph_3SnIP	10.69 (s)	7.61–6.66 (m)	2.61 (m), 1.60 (m)	–	7.44–7.26 (m)

[a]Multiplicity is given as: s, singlet; t, triplet; m, multiplet.

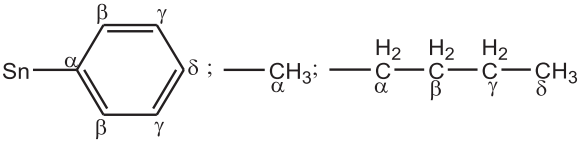
[b]Chemical shifts (δ) in ppm. $^{n}J[^{119}Sn–^{1}H]$ and $^{3}J(^{1}H–^{1}H)$ in Hz are listed in square brackets and parenthesis, respectively.

Table 4 ^{13}C NMR data (ppm) of organotin(IV) complexes of indole-3-butyric acid and indole-3-propionic acid

		δ ^{13}C[a]					
Comp.	Compound designation	–COO–	Indole ring carbons	– $(CH_2)_n$–	–CH_3/CH_2 $(CH_2)_2CH_3$ carbons	Phenyl ring carbons	δ ^{119}Sn[a]
1	$Me_2Sn(IB)_2$	178.9	136.2–112.0	32.0, 25.5, 24.1	5.9 [723.1][b]	—	-349
2	$Bu_2Sn(IB)_2$	180.1	136.3–111.3	33.8, 25.7, 24.2	25.3 [584.0], 26.8 [38.6], 26.3 [98.3], 13.6	—	-351
3	Ph_3SnIB	181.0	136.8–111.2	33.2, 25.6, 23.7	—	136.2 (C_α) [640.0], 136.8 (C_β) [48.1], 127.6 (C_γ) [64.8], 129.1 (C_δ)	102
4	$Me_2Sn(IP)_2$	179.6	135.9–112.0	34.1, 20.5	6.0 [754.0]	—	—
5	$Bu_2Sn(IP)_2$	178.1	136.3–111.3	34.3, 21.0	25.5 [568.2], 27.1 [34.7], 26.6 [87.5], 14.0	—	—
6	Ph_3SnIP	180.0	137.7–112.0	34.4, 20.7	—	138.2(C_α) [647.1], 137.7 (C_β) [54.3], 129.0 (C_γ) [69.2], 130.2 (C_δ)	99

[a]Chemical shifts (δ) in ppm.

[b]$^{n}J[^{119}Sn–^{13}C]$ in Hz are listed in square brackets.



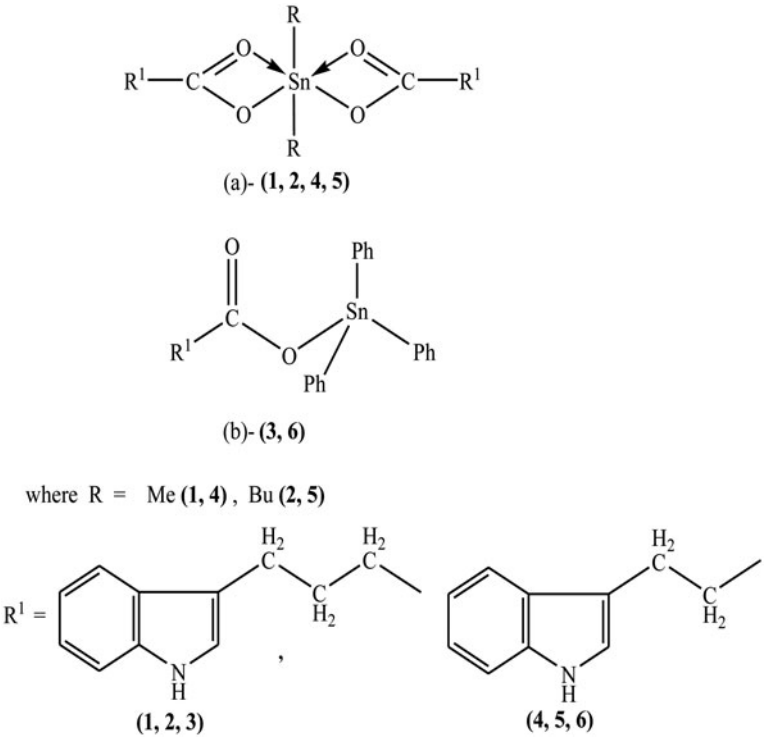


Figure 2 Suggested structures of organotin(IV) complexes: (a) Octahedral geometry of complexes **1**, **2**, **4**, and **5**, and (b) Tetrahedral geometry of complexes **3** and **6**.

The magnitudes of the coupling constants $^{1}J(^{119}Sn–^{13}C)$ for tri-organotin complexes (**3** and **6**) suggested the tetrahedral geometry around the tin atom in solution, diorganotin(IV) complexes (**1**, **2**, **4**, and **5**) are expected to be octahedral in solution as well as in the solid state[17] (Figure 2).

^{119}Sn NMR Spectra

The characteristic resonance peaks in the ^{119}Sn NMR spectra of all of the studied derivatives were recorded in DMSO-d_6. The ^{119}Sn chemical shifts of the organotin(IV) compounds covered a range $\delta \pm 600$. As the electron releasing power of the alkyl group bonded to tin increases, the tin atom becomes progressively more shielded and the δ (^{119}Sn) value moves to a higher field.[28] It was reported earlier that ^{119}Sn NMR is also a powerful technique and the value of δ (^{119}Sn) is directly linked to the coordination number of the central tin atom.[29]

The ^{119}Sn chemical shifts of organotin(IV) derivatives are listed inTable 4 and their values indicates that the complexes **1** and **2** were hexa-coordinated and the complexes **3** and **6** were tetra-coordinated.[28] Due to insufficient solubility of the diorganotin(IV) complexes **4** and **5**, it was not possible to record the ^{119}Sn NMR spectra.

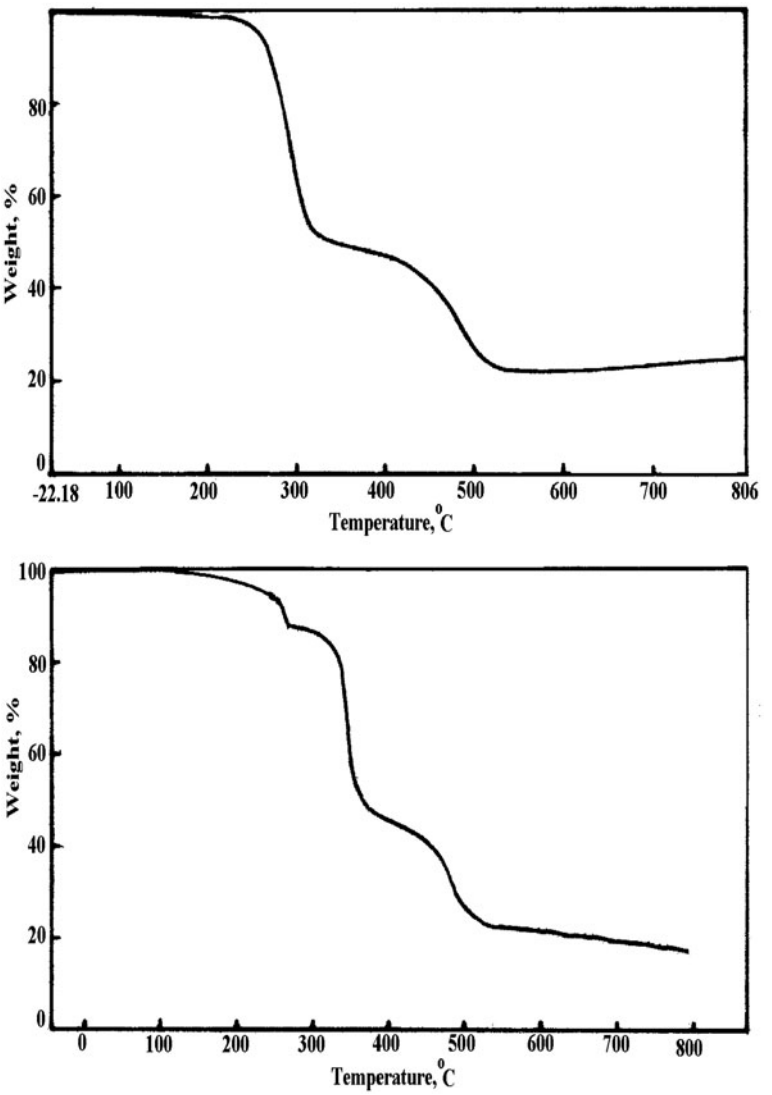


Figure 3 TG curves of organotin(IV) complexes: (a) $Bu_2Sn(IB)_2$ (**2**) and (b) Ph_3SnIP (**6**).

Thermal Analysis of Organotin(IV) Complexes

The thermogravimetric (TG) curves of the organotin(IV) derivatives were obtained in the dynamic nitrogen atmosphere and the TG curves of complexes **4** and **6** are shown in Figure 3. The thermogravimetric (TG) analyses were used to describe thermal behavior of the synthesized complexes **1 to 6**. The thermogravimetric analysis curves of diorganotin(IV) complexes *viz*., **1**, **2**, **4**, and **5** show two consecutive steps of decomposition. The first step of decomposition corresponds to the loss of the two alkyl groups attached to tin in the temperature range 210 to 345°C. Similarly, the second step of decomposition corresponds to the loss of ligand moiety along with the formation of SnO_2 as final residue in the temperature range 345 to 600°C. The TG study for the complexes **3** and **6** shows three steps

of decomposition. The first step of decomposition corresponds to the loss of three phenyl groups in the temperature range 142 to 280°C. The second step has been attributed to the loss of ligand moiety in the temperature range 280 to 408°C, and third step of decomposition corresponds to the formation of the SnO_2 in the temperature range 408 to 798°C. The end product (SnO_2) obtained by the decomposition of all of the synthesized complexes has been analyzed by the presence of ν(Sn–O) at 620 ± 2 cm^{-1} in the IR spectrum of the residue.[9]

The higher slope of the TG curve of **3** and **6**, suggests that their decomposition rate is higher than **1**, **2**, **4**, and **5**.

Antibacterial Activity

The antibacterial activity of synthesized organotin(IV) complexes (**1–6**), together with the standard antibacterial drug, *viz*., chloramphenicol was evaluated against three gram-positive (*S. aureus*, *S. epidermidis*, and *M. luteus*) and three gram-negative (*E. coli*, *P. aeruginosa*, and *E. aerogenes*) bacterial strains, using the minimum inhibition concentration (MIC) method and the results are listed in Table S1 (Supplemental Materials). The results revealed that all the synthesized compounds showed moderate to good bacterial inhibition. The screening results exhibited by triphenyltin(IV) complexes **3** and **6** showed high activities against all the bacterial strains, due to the presence of the phenyl groups, which facilitate binding to biological molecules by π–π interactions[30] and more lipophilic character, which favors the permeation of the complexes through the lipid layer of the cell membrane. Compounds **1**, **2**, **4**, and **5** displayed moderate antibacterial activity against all the strains.

It was found that the synthesized compounds were more active against gram-positive than gram-negative bacteria and this can be attributed to the difference in the structure of the cell walls. The walls of gram-negative cells are more complex than those of gram-positive cells.[31] The enhancement in activity upon complexation may be due to the increasing of lipophilic nature of these complexes resulted from the metal chelation.[32] The chelation of metal ion and sharing of electrons with donor atom reduces polarity of metal ion. The reduction of polarity causes blockage of binding sites in the enzymes of pathogens and enhances penetration of complexes into the lipid membrane. Therefore, the presence of different organic groups in organotin(IV) complexes has played a significant role in their growth inhibitory activity. The phenomenon of protein synthesis is blocked by interference of complexes with the respiration processes of cell and as a result further growth of pathogens is restricted.[33] In addition, the antimicrobial activity might be due to the presence of the NH group in the ligand;[30] this group is believed to impart the transformation reaction in the biological system.

The antibacterial effects of these complexes have been compared with a standard reference drug, chloramphenicol and it is concluded that the synthesized compounds showed higher antibacterial activity than the standard reference drug.

EXPERIMENTAL

Materials and Methods

All manipulations were carried out under nitrogen atmosphere, using standard Schlenk techniques.[34] Dimethyltin dichloride, dibutyltin oxide, and triphenyltin hydroxide were procured from Sigma Aldrich (New Delhi, India) and were used without further purification. Indole-3-butyric acid and indole-3-propionic acid were purchased from Merck (New Delhi, India) and were used as received. Acetonitrile and methanol were purchased

from Spectrochem (New Delhi, India). Methanol was dried over sodium wire and distilled. Acetonitrile was dried over $CaCl_2$ for overnight followed by distillation. Ethanol was purchased from Merck and dried over sodium pieces and distilled. It was followed by refluxing with Mg turnings and a crystal of iodine and redistilled.

Preparation of Dimethyltin(IV) Oxide and Sodium Salts of Acids

Dimethyltin(IV) dichloride (Me_2SnCl_2) was dissolve in distilled water and stirred for overnight. Colorless solution was obtained. Ammonia solution (60%) was added into the colorless solution and finally fine white precipitate was obtained and filtered. The precipitate was dried in oven (60°C) for a day until dry white yellow precipitate of dimethyltin(IV) oxide was obtained.

The sodium salts of acids were synthesized by heating under reflux a 1:1 molar mixture of NaOH (0.12 g, 3 mmol) and indole-3-butyric acid (0.61 g, 3 mmol) or indole-3-propionic acid (0.57 g, 3 mmol) in ethanol (50 mL) for 2 h. The resulting clear solution was filtered and evaporated to dryness. Recrystallization of the light yellow residue from alcohol gave a white solid. Yield: 86%; IR (KBr, cm^{-1}); IBH: ν_{as}(COO) 1570 s, ν_s(COO) 1420 s; IPH: ν_{as}(COO) 1560 s, ν_s(COO) 1410 s.

$Me_2Sn(IB)_2$ and $Me_2Sn(IP)_2$ Complexes (1 and 4)

Complexes **1** and **4** were prepared by heating a 1:2 molar mixture of dimethyltin(IV)oxide (0.49 g, 3 mmol) and indole-3-butyric acid (1.22 g, 6 mmol) or indole-3-propionic acid (1.13 g, 6 mmol) in methanol (50 mL) under a nitrogen atmosphere. The reaction mixture was refluxed for 2 h with a Dean-Stark apparatus, and then allowed to cool at room temperature. A clear light yellow (**1**) or brown (**4**) transparent solution was separated by filtration and kept in a bottle. After 4 days, pale yellow solid (**1**) or brown solid (**4**) was obtained. The products were then recrystallized from absolute ethanol.

$Bu_2Sn(IB)_2$ and $Bu_2Sn(IP)_2$ Complexes (2 and 5)

Complexes **2** and **5** were prepared by heating under reflux a 1:2 molar mixture of dibutyltin(IV) oxide (0.75 g, 3 mmol) and indole-3-butyric acid (1.22 g, 6 mmol) or indole-3-propionic acid (1.13 g, 6 mmol) in acetronitrile (50 mL) for 3 h with a Dean-Stark apparatus. A clear light yellow (**2**) or brown (**5**) transparent solution was isolated by filtration and kept in a bottle. After two weeks, pale yellow crystalline solid (**2**) or brown solid (**5**) was collected. The products were then recrystallized from methanol.

Ph_3SnIB and Ph_3SnIP Complexes (3 and 6)

Complexes **3** and **6** were prepared by heating under reflux a 1:1 molar mixture of triphenyltin(IV) hydroxide (1.10 g, 3 mmol) and indole-3-butyric acid (0.61 g, 3 mmol) or indole-3-propionic acid (0.57 g, 3 mmol) in acetronitrile (50 mL) for 2 h with a Dean-Stark apparatus. A clear transparent solution of light yellow (**3**) or light brown (**6**) was isolated by filtration and kept in a bottle. After 8 days, white solid (**3**) or light brown solid (**6**) was collected. The products were then recrystallized from methanol.

Characterization

The structural characterization of all six diorganotin(IV) derivatives was done by using IR, ^{1}H NMR, ^{13}C NMR, and ^{119}Sn NMR spectroscopic techniques. Elemental analysis was carried out using EURO EA 3000 elemental analyzer. The tin content in the complexes synthesized was determined gravimetrically as SnO_2.[35] IR spectra were recorded in KBr pellets using Shimadzu FTIR 8300 spectrometer. NMR spectra were recorded on a Bruker 300 spectrophotometer in DMSO-d_6 using tetramethylsilane (TMS) as an internal standard (^{1}H, ^{13}C) and tetramethyltin as an external standard (^{119}Sn).

Thermal Studies

The TG curves in the range of 25 to 700°C were recorded using a Perkin Elmer Diamond TG/DTA instrument having TG 1500 module at a heating rate of 20 °C min^{-1} in nitrogen atmosphere. Powdered samples having weights ranging from 8 to 10 mg were used in each experiment.

Determination of Antibacterial Activity

The synthesized organotin(IV) complexes were tested against six bacterial strains; three gram-positive: *S. aureus*, *S. epidermidis* and *M. luteus* and three gram-negative: *E. coli*, *P. aeruginosa*, and *E. aerogenes*. Antibacterial activity was performed by employing Broth Microdilution MIC method.[36]

CONCLUSIONS

The synthesized compounds were characterized by suitable analytical techniques, *i.e.*, IR, ^{1}H NMR, ^{13}C NMR, ^{119}Sn NMR, and elemental analysis. The data obtained were in full agreement with the proposed structures. The thermal stability of the complexes **3** and **6** is higher as compared to compounds **1**, **2**, **3**, and **4**. All the synthesized compounds were screened for their in vitro antibacterial activity against standard strains of *S. aureus*, *S. epidermidis, M. luteus, P. aeruginosa*, *E. coli*, and *E. aerogenes*, and data revealed that compounds showed moderate to good activity. Compounds **3** and **6** were exhibited as a strong activity against all the tested bacterial strains. The results provided evidence that the studied compounds reported in this paper could serve as potential sources of microbial agents.

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