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Synthesis, spectral, 3D molecular modeling and antibacterial studies of dibutyltin (IV) Schiff base complexes derived from substituted isatin and amino acids

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ABSTRACT

New dibutyltin (IV) complexes of Schiff base derived from 5-chloroindoline-2,3-dione, indoline-2,3-dione with amino acids (tryptophan, alanine and valine) were synthesized and characterized by elemental analysis, IR, electronic spectra, conductance measurements, and biological activity. The analytical data showed that the Schiff base ligand acts as bidentate towards metal ions via the azomethine nitrogen and carboxylate oxygen by a stoichiometric reaction of M:L (1:2) to form metal complexes. NMR (^{1}H, ^{13}C and ^{119}Sn) spectral data of the ligands and metal complex agree with proposed structures. The conductivity values between 14 - 27 ohm^{-1}·cm^{2}·mol^{-1} in DMF imply the presence of non-electrolyte species. 3D molecular modeling and analysis of bond lengths and bond angles have also been conducted for a representative compound, [$Bu_2Sn(L^2)_2$], to substantiate the proposed structures. Antibacterial results indicate that the metal complexes are more active than the free ligands.

Keywords: Schiff Base; Isatins; Amino Acids; Dibutyltin (IV) Complexes; Spectral Studies; Antimicrobial Activity

1. INTRODUCTION

Isatin, possessing an indole nucleus having both the keto and lactam moiety has aroused tremendous curiosity due to its diverse biological and pharmacological studies. From literature survey it is well known that isatin heterocycles exhibit manifold importance in the field of medicinal chemistry as a potent chemotherapeutic agent. Schiff base complexes have been extensively investigated for more than a century and employed in areas that include pharmaceutical, medicinal and coordination chemistry [1-7]. Schiff bases are potentially biologically active compounds and have been reported to possess antibacterial, antifungal, antitumor and anticancer activities [8-12]. Schiff bases have also been employed as ligands for complexation of metal ions [13]. On the industrial scale, they have wide range of applications such as dyes and pigments [14]. Schiff base metal complexes are more biologically active than uncoordinated Schiff base molecules [15]. Amino acid Schiff bases are an important class of ligands because such ligands and their metal complexes have a variety of application including biological, clinical, analytical and industrial in addition to their important role in catalysis and organic synthesis. It is well known that organotin (IV) complexes exhibit high biological activity such as antitumor and antimicro- bial activity [16-20]. The interest in organotin compounds in general and organotin carboxylates in particular continues to grow because of their biological activity and potential antineoplastic, antituberculosis agents [21,22]. Among those compounds dibutyltin derivatives have displayed both higher activity and lower toxicity [23]. Organotin complexes derived from carboxylic acids are among the most extensively studied class of compounds owing to their rich structural chemistry. The diverse structural motifs known in this family of compounds are attributed to the ambidentate character of the carboxylate ligands [24]. Steric and electronic attributes of organic substituents on tin and/or the carboxylate moiety impart significant influence on the structural characteristics in tin carboxylates. Therefore, synthesis of new organotin carboxylates with different structural features will be beneficial in the development of pharmaceutical organotin and in other properties and application.

Keeping in view the structural and biological diversity of organotin carboxylates and in connection with our

interest in coordination chemistry of organotin compounds with different amino acids, herein we report the synthesis, characterization and biological studies of organotintin (IV) derivatives with Schiff base to widen their scope in biological applications. The structures of the ligands are shown in **Figure 1**.

2. EXPERIMENTAL AND METHODS

2.1. Chemicals and General Methods

All chemicals and organotin precursors used were procured from Aldrich and Merck. All the solvents were dried before use by the literature methods [25] and moisture was excluded from the glass apparatus using $CaCl_2$ drying tubes. The melting points were determined in an open glass capillary and were uncorrected.

2.2. Analytical Methods and Spectral Measurements

Tin was estimated gravimetrically as SnO_2. Nitrogen was estimated by Kjeldahl's methods. Molar conductance measurements were made in anhydrous dimethylformamide at 25˚C ± 5˚C using a Systronics conductivity bride model 305. Molecular weight determinations were carried out by the Rast camphor method.

The electronic spectra were recorded in DMSO on a Thermo UV1 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer RX1 FTIR spectrometer in the region 4000 - 400 cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded on BRUKER AVANCE II (400 MHz) FTNMR spectrometer at the SAIF, Punjab University, Chandigarh, using DMSO-d_6 as the solvent and tetramethylsilane (TMS) as an internal standard. The ^{119}Sn NMR spectra with proton noise decoupling were recorded on a BRUKER Avance II spectrometer using dry DMSO as the solvent and tetramethyltin (TMT) as an external standard. The 3D molecular modeling of a representative compound was carried out on a CS Chem. 3D Ultra Molecular Modeling and analysis program.

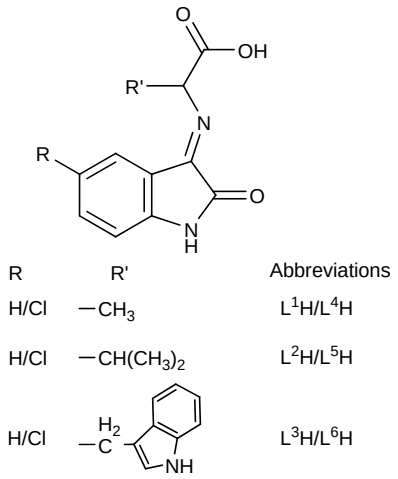


Figure 1. Proposed structure of the ligands.

2.3. Syntheses of Schiff Base Ligands

The ligands were synthesized by the condensation of indoline-2,3-dione (0.231 g; 1.57 mmole), 5-chloroindoline-2,3-dione (0.285 g; 1.57 mmole) with amino acids (0.140 - 0.321 g; 1.57 mmole) (tryptophan, alanine and valine) in 1:1 molar ratio using methanol (100 mL) as the reaction medium and were then, it was refluxed for 6 - 8 hours. After this it was put on cooling at room temperature and the solid products were obtained. The excess solvent was removed on a rotary evaporator. It was dried further and then purified by recrystallization from same solvent (**Table 1**).

2.4. Syntheses of Organotin (IV) Complexes

Dibutyltin (IV) oxide (0.280 g; 1.125 mmole) was added to the calculated amount of the ligands (0.491 - 0.829 g; 2.250 mmole) in 1:2 molar ratio in dry benzene (80 mL), methanol (25 mL) mixture as reaction medium. The contents were refluxed on a fractionating column for about 6 - 8 hours. The water librated in the reaction was removed azeotropically with benzene. On completion of the reaction, the resulting products were rendered free from solvent and then washed repeatedly with dry cyclohexane. The crystalline solids were separated out and purified by recrystallization from the same solvent. The products so formed were finally dried in vacuum at 40˚C ± 5˚C for 2 - 3 hours. The purity of the complexes was checked by TLC using silica gel-G as adsorbent. Their physical properties and analytical data were recorded in **Table 2**.

2.5. Antibacterial Assay

Synthesized compounds were screened for their antibacterial activity against *Bacillus cereus* (MTCC 0430) and *Enterobacter aerogenes* (MTCC 2824) at various concentrations 25, 50 and 100 µg by the agar Well Diffusion method [26]. 5 ml aliquot of nutrient broth was inoculated with the test organisms and incubated at 37˚C for 24 hours. Sterile nutrient agar plates were also prepared and holes of 5 mm diameter were cut using a sterile cork borer ensuring proper distribution. The test organisms after 24 hours of incubation were spread onto separate agar plates. The chemical compounds were dissolved in DMSO were poured into appropriately labeled holes using a pipette in aseptic conditions. A hole containing DMSO served as a control. Triplicate plate of each bacterial strain was prepared. The plates were incubated aerobically at 37˚C for 24 h. The antimicrobial

Table 1. Analytical and physical data of the ligands.

Ligands	Colour	Yield (g)	M.P. ˚C (d)	Elemental Analysis			Mol. Wt. Found (Calcd.)
				%C	%H	%N	
2-(2-oxoindolin-3-ylideneamino)propanoic acid ($C_{11}H_{10}N_2O_3$) L^1H	Pink	0.292 gm 85.26%	106 - 107	60.64 (60.55)	4.56 (4.62)	12.89 (12.84)	228.71 (218.21)
3-methyl-2-(2-oxoindolin-3-ylideneamino)butanoic acid ($C_{13}H_{14}N_2O_3$) L^2H	Brownish red	0.190 gm 68.1%	104 - 105	63.28 (63.40)	5.68 (5.73)	11.31 (11.38)	239.33 (246.26)
3-(1*H*-indol-3-yl)-2-(2-oxoindolin-3-ylideneamino) propanoic acid ($C_{19}H_{15}N_3O_3$) L^3H	Light brown	0.272 gm 76.97%	128 - 130	68.55 (68.46)	4.46 (4.54)	12.58 (12.61)	338.65 (333.34)
2-(5-chloro-2-oxoindolin-3-ylideneamino)propanoic acid ($C_{11}H_9ClN_2O_3$) L^4H	Light yellow	0.150 gm 70.7%	140	52.17 (52.29)	3.51 (3.59)	11.19 (11.09)	243.68 (252.65)
2-(5-chloro-2-oxoindolin-3-ylideneamino)-3-methyl-but anoic acid ($C_{13}H_{13}ClN_2O_3$) L^5H	Yellow	0.140 gm 67.0%	150 - 152	55.47 (55.62)	4.62 (4.67)	9.89 (9.98)	293.36 (280.71)
2-(5-chloro-2-oxoindolin-3-ylideneamino)-3-(1*H*-indol-3-yl)propanoic acid ($C_{19}H_{14}ClN_3O_3$) L^6H	Brown	0.280 gm 89.4%	149 - 150	61.98 (62.05)	3.82 (3.84)	11.46 (11.43)	372.69 (367.79)

Table 2. Analytical and physical data of the organotin (IV) complexes.

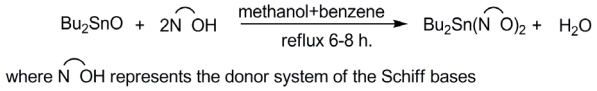
S. No	Reactants		Molar ratio	Products & Colour	M.P. ˚C (d)	Yield (g)	Elemental Analysis				Mol. Wt. Found (Calcd.)
	Metal	Ligands					%Sn	%C	%H	%N	
1	Bu_2SnO 0.34 g	$C_{11}H_{10}N_2O_3$ 0.59 g	1:2	$C_{30}H_{36}N_4O_6Sn$ Red	174	0.64 g 70.22%	17.57 (17.79)	53.81 (53.99)	5.40 (5.44)	8.18 (8.40)	658.51 (667.34)
2	Bu_2SnO 0.28 g	$C_{13}H_{14}N_2O_3$ 0.55 g	1:2	$C_{34}H_{44}N_4O_6Sn$ Brown	250	0.66 g 81.11%	16.56 (16.41)	56.36 (56.45)	6.18 (6.13)	7.83 (7.74)	732.92 (723.45)
3	Bu_2SnO 0.25 g	$C_{19}H_{15}N_3O_3$ 0.67 g	1:2	$C_{46}H_{46}N_6O_6Sn$ Red	140	0.80 g 88.75%	13.01 (13.23)	61.68 (61.55)	5.11 (5.17)	9.26 (9.36)	881.43 (897.60)
4	Bu_2SnO 0.25 g	$C_{11}H_9ClN_2O_3$ 0.51 g	1:2	$C_{30}H_{34}Cl_2N_4O_6Sn$ Dark Brown	260	0.56 g 75.68%	16.25 (16.12)	48.76 (48.94)	4.60 (4.65)	7.49 (7.61)	747.77 (736.23)
5	Bu_2SnO 0.24 g	$C_{13}H_{13}ClN_2O_3$ 0.54 g	1:2	$C_{34}H_{42}Cl_2N_4O_6Sn$ Brown	274	0.57 g 74.63%	14.78 (14.98)	51.43 (51.54)	5.27 (5.34)	6.94 (7.07)	784.50 (792.34)
6	Bu_2SnO 0.21 g	$C_{19}H_{14}ClN_3O_3$ 0.61 g	1:2	$C_{46}H_{44}Cl_2N_6O_6Sn$ Dark Brown	172	0.59 g 72.21%	12.03 (12.28)	57.24 (57.16)	4.46 (4.59)	8.72 (8.70)	951.12 (966.49)

activity was determined by measuring the diameter of the zone (mm) showing complete inhibition with respect to control (DMSO).

3. RESULTS AND DISCUSSION

The Schiff base (HL) and metal complexes are subjected to elemental analysis. The results of elemental analysis (C, H and N) with molecular formula and the melting points are presented in experimental part. The results obtained are in good agreement with those calculated for suggested formula. New organotin (IV) complexes were synthesized by the reaction of dibutyltin (IV) oxide with Schiff bases have been carried out in 1:2 molar ratios using anhydrous benzene and absolute methanol in 3:1 ratio as solvent. These reactions proceed with the liberation of water, which were azeotropically removed. The scheme of the Organotin (IV) complexes preparation is given by **Scheme 1**.

The above reactions were found to be quite facile and could be completed in 3 - 4 h of stirring. All these complexes are intensively coloured and solids. They are soluble in common organic solvents, DMF and DMSO. The compounds were dissolved in DMF and molar conductance 10^{-3} M of solution at 25˚C was measured. The molar conductance valves of the complexes fall in the range 14.85 to 26.14 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ indicating that these compounds are non-electrolytes. The elemental analyses data (**Table 1**) agree with the proposed formulae for the ligands and also confirmed the Bu_2SnL_2 (**Figure 2**) composition of the diorganotin (IV) complexes.



Scheme 1. The scheme of the Organotin (IV) complexes preparation.

3.1. IR Spectra

The IR spectra of the complexes were compared with those of the free ligands (**Table 3**) in order to determine

Table 3. Important IR spectral data (cm^{-1}) of Schiff bases and their corresponding organotin (IV) complexes.

Compounds	ν(OH)	ν(C=N$^-$)	ν(C=O)	ν(COO)$_{asym}$	ν(COO)$_{sym}$	Δν	ν(Sn-C)	ν(Sn←N)	ν(Sn-O)
L^1H	3105 - 2790 br	1635 s	1730 s	-	-	-		-	-
$Bu_2Sn(L^1)_2$	-	1622 s	1728 s	1590 s	1320 m	270	644 w	542 s	425 m
L^2H	3100 - 2795 br	1632 s	1726 s	-	-	-		-	-
$Bu_2Sn(L^2)_2$	-	1620 s	1727 s	1595 s	1330 m	265	625 w	545 w	422 w
L^3H	3108 - 2795 br	1630 s	1725 s	-	-	-		-	-
$Bu_2Sn(L^3)_2$	-	1615 s	1724 s	1585 vs	1325 s	260	635 w	540 m	430 w
L^4H	3095 - 2790 br	1630 s	1720 s	-	-	-		-	-
$Bu_2Sn(L^4)_2$	-	1618 s	1722 s	1590 s	1328 vs	262	640 w	555 m	428 w
L^5H	3105 - 2810 br	1632 s	1725 s	-	-	-		-	-
$Bu_2Sn(L^5)_2$	-	1618 s	1728 s	1600 s	1332 m	268	628 w	540 w	425 m
L^6H	3110 - 2800 br	1640 s	1728 s	-	-	-		-	-
$Bu_2Sn(L^6)_2$	-	1625 s	1726 s	1588 s	1316 m	272	630 w	550 s	435 w

br = broad; vs = very sharp; v = sharp; m = medium; w = weak.

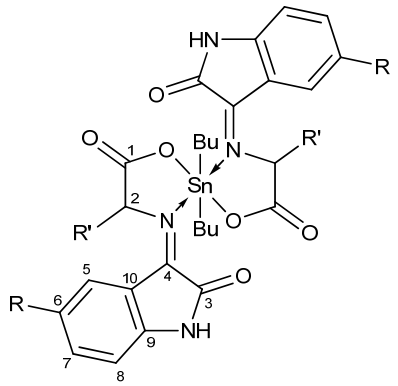


Figure 2. Structure of organotin (IV) complexes.

the coordination sites that may be involved in chelation. The position and the intensities of these peaks are expected to be changed on chelation. New peaks and quasi-peaks are also a guide to chelation. The IR spectra of all the ligands [27] show the absence of band at 3450 and 1750 cm^{-1} due to ν(NH_2) group of amino acids and ν (C=O) of isatin. Instead, a new prominent band at 1635 ± 5 cm^{-1} due to azomethine ν(C=N) linkage appeared in all the ligands [28,29] indicating that condensation between ketone moiety of isatin and that of amino group of amino acid has take place resulting into the formation of the desired ligands (L^1H - L^6H). Moreover, on comparison of the IR spectra of the ligands with their organotin (IV) complexes showed a major shift to lower wave numbers by 12 - 20 cm^{-1} in azomethine ν(C=N) at 1620 ± 5 cm^{-1} suggesting the involvement of the azomethine nitrogen with the organotin (IV) ion [30,31]. The new bands appeared in the region of 545 ± 10 cm^{-1} in the spectra of the complexes, are assigned to stretching frequencies of ν(Sn←N) [31] bond formations.

The spectra of the ligands contain a broad absorption band appeared in the region 3110 - 2790 cm^{-1} which is assigned to hydrogen bonded ν(OH). This band disappears on complexation, suggesting chelation of the oxygen to the tin atom [32]. The infrared spectra of complexes revealed that the $\nu_{asym}(COO^-)$ was shifted to a lower wave number compared to the parent ligands which signify that the coordination took place via the oxygen atom of the carboxylate anion. Complexes showed the $\nu_{asym}(COO^-)$ and $\nu_{sym}(COO^-)$ are in the range of 1600 - 1585 and 1330 - 1316 cm^{-1}, respectively [33,34].

Upon complexation, the structures of the ligands are altered, all alterations can be observed through the shift of the characteristic bands. The remarkable change is the disappearance of ν(OH) (3110 - 2790 cm^{-1}). This is attributable to $\nu_{asym}(COO^-)$ and $\nu_{sym}(COO^-)$ existing in the spectra of all the complexes, thus supporting the deportonation of carboxylic group and coordination of its carboxylic oxygen to the tin(IV) ion. The magnitude of $\Delta\nu = [\nu_{asym}(COO^-) - \nu_{sym}(COO^-)]$ for the complexes falls in the range of 272 - 260 cm^{-1}, indicating the carboxyl group in all the complexes is bound in monodentate manner [35]. Moreover, for complexes Δν below 200 cm^{-1} would be expected for bridging or chelating carboxylate, but greater than 200 cm^{-1} for the monodentate bonding carboxylate anions. Further evidence for the coordination to tin via oxygen atom was revealed by the presence of the ν(Sn-O) [36] stretching bands in the spectra of complexes (1 - 6) in the region of 422 - 435

cm^{-1}. New band appear in the complexes at 630 ± 5 cm^{-1} is probably due to ν(Sn-C) [37] stretching.

3.2. Electronic Spectra

The spectra of the ligands and their complexes were recorded in dry DMSO. The various bands observed were assigned to interligand and charge transfer of n-π^* transition according to their energies and intensities. Electronic spectra of the complexes exhibit three bands in the region 200 - 235, 250 - 345 and 365 - 430 nm, which may be due to the π-π^* transition of benzenoid, π-π^* transition of COO and π-π^* transition of the >C=N chromophore, respectively. Further, there was a sharp band observed in the 250 ± 5 nm regions in the spectra of the complexes, which could be assigned as a charge transfer band. It has been reported that a metal is capable of forming dπ-pπ^* bonds with ligands containing nitrogen or oxygen as the donor atoms. Since tin atom has its 5d orbitals completely vacant, L-M bonding can take place by the acceptance of a pair of electrons from nitrogen or oxygen atoms of the ligands.

3.3. ^{1}H NMR Spectra

All the protons were found as to be in their expected regions (**Table 4**). The conclusions drawn from these studies lend further support to the mode of bonding discussed in their IR spectra. In the spectra of organotin (IV) complexes, coordination of the ligands via azomethine nitrogen and carboxylate oxygen was established by the downfield shifting of these signals in the organotin (IV) complexes, because of the increased conjugation and coordination [38]. The number of protons calculated from the integration curves and those obtained from the values of the expected CHN analyses agree with each other. It was observed that DMSO had no coordinating effect either on the spectra of the ligands or on its metal complexes. In the proton magnetic resonance spectra of the ligands, give an OH proton signals at δ 11.25 - 11.50 ppm (s) which is absent from the spectra of the corresponding lead complexes, showing thereby chelation of the ligand moiety through the deprotonated carboxylate oxygen. The ligands give a complex multiplet signal in the region δ 6.95 - 7.89 ppm (m) for the aromatic protons and these remain almost at the same position in the spectra of the metal complexes. The appearance of signals due to NH protons at the same positions in the ligand and its complexes show the non-involvement of this group in coordination. The complexes, however, show additional signals at δ 0.72 - 1.90 ppm owing to the protons of the

Table 4. ^{1}H NMR spectral data[a] of the ligands and their corresponding organotin (IV) complexes.

Compounds	Chemical Shift (δ ppm)				
	COOH	N-CH-C	NH	Aromatic	Sn-Bu
L^1H	11.25 (s, 1H)	4.72 (q, 1H, 8.4)	8.34 (s, 1H)	7.82 (t, H-5, 7.7), 7.21 (dd, H-6, 7.4, 7.3), 7.34 (dd, H-7, 7.3, 7.4), 7.64 (t, H-8, 7.8)	-
$Bu_2Sn(L^1)_2$	-	4.76 (q, 2H, 8.3)	8.36 (s, 2H)	7.80 (t, H-5, 7.7), 7.20 (dd, H-6, 7.4, 7.3), 7.35 (dd, H-7, 7.3, 7.4), 7.63 (t, H-8, 7.8)	0.81 (t, 6H, 7.2), 1.32 - 1.82 (m, 12H)
L^2H	11.32 (s, 1H)	4.28 (d, 1H, 6.9)	8.47 (s, 1H)	7.81 (t, H-5, 7.6), 7.18 (dd, H-6, 7.3, 7.3), 7.25 (dd, H-7, 7.3, 7.2), 7.50 (t, H-8, 8.0)	-
$Bu_2Sn(L^2)_2$	-	4.30 (d, 2H, 6.9)	8.46 (s, 2H)	7.80 (t, H-5, 7.6), 7.16 (dd, H-6, 7.3, 7.4), 7.25 (dd, H-7, 7.4, 7.5), 7.48 (t, H-8, 8.0)	0.85 (t, 6H, 7.4), 1.30 - 1.85 (m, 12H)
L^3H	11.46 (s, 1H)	4.39 (t, 1H, 8.3)	8.09 (s, 1H)	7.85 (t, H-5, 7.6), 7.18 (dd, H-6, 7.5,2.4), 7.34 (dd, H-7, 2.4, 7.8), 7.65 (t, H-8, 7.8)	-
$Bu_2Sn(L^3)_2$	-	4.38 (t, 2H, 8.3)	8.12 (s, 2H)	7.83 (t, H-5, 7.6), 7.17 (dd, H-6, 7.5, 7.5), 7.34 (dd, H-7, 7.5, 7.6), 7.64 (t, H-8, 7.8)	0.76 (t, 6H, 7.1), 1.25 - 1.88 (m, 12H)
L^4H	11.32 (s, 1H)	4.14 (q, 1H, 8.8)	7.98 (s, 1H)	7.76 (s, H-5), 7.45 (t, H-7, 7.9), 7.58 (t, H-8, 7.9)	-
$Bu_2Sn(L^4)_2$	-	4.16 (q, 2H, 8.7)	7.96 (s, 2H)	7.75 (s, H-5), 7.43 (t, H-7, 7.6), 7.56 (t, H-8, 8.0)	0.80 (t, 6H, 7.0), 1.20 - 1.88 (m, 12H)
L^5H	11.41 (s, 1H)	4.08 (d, 1H, 6.2)	8.52 (s, 1H)	7.83 (s, H-5), 7.38 (t, H-7, 7.4), 7.66 (t, H-8, 8.1)	-
$Bu_2Sn(L^5)_2$	-	4.11 (d, 2H, 6.2)	8.54 (s, 2H)	7.80 (s, H-5), 7.38 (t, H-7, 7.5), 7.64 (t, H-8, 8.0)	0.78 (t, 6H, 6.9), 1.30 - 1.78 (m, 12H)
L^6H	11.50 (s, 1H)	4.20 (t, 1H, 8.1)	8.15 (s, 1H)	7.78 (s, H-5), 7.31 (t, H-7, 7.8), 7.15 (t, H-8, 8.0)	-
$Bu_2Sn(L^6)_2$	-	4.15 (t, 2H, 8.1)	8.14 (s, 2H)	7.77 (s, H-5), 7.30 (t, H-7, 7.8), 7.13 (t, H-8, 8.1)	0.80 (t, 6H, 6.8), 1.29 - 1.90 (m, 12H)

[a]Chemical shift (δ) in ppm. $^nJ(^1H,H^1)$, vales are given in Hz are listed in square brackets, respectively. Multiplicity is given as: s = singlet, d = doublet, t = triplet, q = quartet, m = complex pattern.

butyl group. The CH_3 protons of dibutyltin compounds are significant as a triplet at 0.78 - 82 ppm with $^3J_{HH}$ = 7.4 Hz, while $–CH_2$-protons appear as a multiplet. The most important information obtained from ^{1}H NMR values in these compounds, demonstrates that diorganotion complexes show the coordination number greater than four, probably six, in non coordinating solvent.

3.4. ^{13}C NMR Spectra

The ^{13}C NMR spectral data for L^1H, L^2H, L^4H and its corresponding tin complexes have been recorded in dry DMSO (**Table 5**). The formations of the complexes were evident from the δ(COO) value in the ^{13}C NMR spectra. All the complexes exhibited a δ(COO) signal in the range of 172 - 178 ppm. The ^{13}C NMR spectra of complexes showed that the chemical shift of the δ(COO) signal in each complexes was shifted downfield compared to that of their parent ligands (~δ 175 ppm), indicating the participation of the carboxylate anion in the coordination to the tin atom. The occurrence of resonances in the range of 110 - 150 ppm in the ^{13}C NMR spectra of the complexes and ligands defined as benzene signals. The carbon of the butyl group is observed at (δ ~ 26.6, 27.8, 26.0, 14.3 ppm) position comparable to other similar compounds. The R group attached to tin displays resonance for chemically equivalent carbon; however, the butyl compounds display three resonances. Coordination of the tin atom has been related to $^1J(^{119}Sn\text{-}^{13}C)$ coupling constants. The $^nJ(^{119}Sn\text{-}^{13}C)$ coupling constant values (n = l, 925 Hz; n = 2, 40.6 Hz; and n = 3, 126.1 Hz) obtained for the synthesized complexes are indicative of hexa coordination of dibutyltin complexes. The carbons of alkyl groups attached to tin are observed at position comparable with other, similar compounds [39, 40].

3.5. ^{119}Sn NMR Spectra

The value of $\delta(^{119}Sn)$ define the coordination number of the central tin atom. The results are listed in **Table 5**. All the complexes, ^{119}Sn NMR spectra show only a sharp singlet indicating the formation of a single species. For diorganotin(IV) complexes, the $\delta(^{119}Sn)$ value for four-coordinated complexes fall in the range between δ + 200 to δ − 60 ppm; for five-coordinated complexes fall in the range between δ − 90 to δ − 190 ppm and for six-coordinated complexes fall in the range between δ − 210 to δ − 400 ppm. Complexes 1 - 6 derivatives of dibutyltin(IV) exhibited $\delta(^{119}Sn)$ values at ~δ − 360 ppm which lie in the range of δ − 210 to δ − 400 ppm, hence, indicating that the tin atom in all the complexes have six-coordinated and have a distorted octahedral geometry [41-43].

On the basis of the above mentioned different spectral studies, it is suggested that the bonding through the azomethine nitrogen and carboxylate oxygen atoms to the tin atom. Finally, distorted octahedral geometries around the tin atom have been proposed as shown in **Figure 2**.

3.6. Molecular Modeling and Analysis

In view of the hexa-coordination of the present tin complexes, $[Bu_2Sn(L^1)_2]$, the molecular modeling of the compound as a representation, is based on its octahedral structure and all the 237 measurements are obtained (bond angles, 155 in numbers and the bond lengths, 82 in numbers). In most of the cases, the actual bond angles and lengths are close to the optimal values, and thus the proposed structure of the compound is acceptable (**Figure 3**). In compound $[Bu_2Sn(L^1)_2]$, the Sn atom is 2.01 and 3.9 Å away from the oxygen's of the carboxylic group. The two long Sn-O bond being Trans to each other. The C-O bonds are nearly (1.39 and 1.21 Å). The two butyl groups are equidistant from Sn (2.10 Å) and complete the

Table 5. ^{13}C and ^{119}Sn NMR spectral data[a] of the ligands and their corresponding organotin (IV) complexes.

Compounds	Chemical Shift in (δ ppm)							
	^{119}Sn	C-1/C-7	C-2/C-8	C-3/C-9	C-4/C-10	C-5/C-11	C-6/C-12	Sn-$CH_2CH_2CH_2CH_3$
L^1H	-	172.6 133.8	63.5 110.9	155.8 148.5	159.9 121.3	130.4 20.2	129.5 -	-
$Bu_2Sn(L^1)_2$	−360	183.3 134.1	64.8 111.3	160.2 148.3	153.4 120.6	130.8 20.7	129.4 -	27.2 (C-*α*, 928 Hz), 28.4 (C-β, 40.2 Hz), 26.9 (C-*γ*, 125.8 Hz), 13.7 (C-δ)
L^2H	-	175.7 140.6	68.3 120.5	161.3 150.8	160.5 121.5	131.5 31.4	123.1 19.2	-
$Bu_2Sn(L^2)_2$	−358	182.7 141.3	71.1 120.6	161.5 150.0	151.5 121.9	132.1 31.2	123.1 20.1	27.5 (C-*α*, 928 Hz), 28.9 (C-*β*, 39.9 Hz), 26.3 (C-*γ*, 126.2 Hz), 14.1 (C-δ)
L^4H	-	177.5 134.2	65.1 115.3	160.2 145.7	162.4 121.0	131.2 20.2	129.7 -	-
$Bu_2Sn(L^3)_2$	−355	184.1 138.5	65.7 116.5	160.1 145.2	154.6 120.8	131.5 20.8	129.4 -	28.4 (C-*α*, 925 Hz), 29.2 (C-*β*, 40.6 Hz), 27.7 (C-*γ*, 126.1 Hz), 14.6 (C-δ)

[a]Chemical shift (δ) in ppm. $^nJ(^{119}Sn\text{-}^{13}C)$, vales are given in Hz are listed in square brackets.

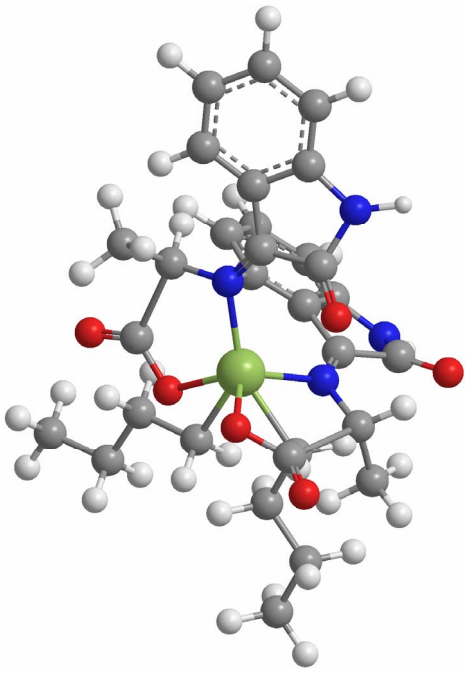


Figure 3. 3D structure of the $[Bu_2Sn(L^1)_2]$ complexes.

coordination sphere of Sn. The Bu(C)-Sn-(C)Bu angles are 162.1˚. The O-Sn-O and N-Sn-N angle are 109.5 and is 110.5˚, respectively for both the carboxylic ligands.

3.7. Antimicrobial Results

In vitro antibacterial activity of the ligands and their corresponding organotin complexes was tested against Gram-positive and Gram-negative (*Enterobacter aerogenes* and *Bacillus cereus*) bacteria. The agar well-diffusion method was used in these assays and each experimental was performed in triplicate. The zone of inhibition value represents the mean value of three readings, which are shown in **Table 6**. The results show that all compounds exhibit antibacterial activity and in many case, the organotin complexes are more potent in their inhibition properties than the free ligands. This can be explained in terms of the greater lipid solubility and cellular penetration of the complexes [44]. It is clear that the coordination enhances the antibacterial activity and clearly indicates that the newly synthesized complexes in the present studies are more active against Gram-positive than Gram-negative bacteria. The preliminary results achieved have led us to conclude that these types of complexes should be studied in detail for their applications in diverse areas.

The screening data of a particular ligand and its metal complexes show that the former has greater activity than the latter from the biochemical point of view. On comparing the results in general, it may be concluded that the organotin (IV) complexes have greater inhibiting power than the free ligands against all the microbes. Although it is difficult to make out an exact structure-activity relationship between the antimicrobial activity and the structure of these complexes, it can possibly be concluded that the chelation as well as the addition of a substrate enhance the activity of the complexes. The variation in the toxicity of different antibacterial agents against various organisms depends on either the impermeability of the cell or differences in site of action or ability to cause mutations in the microorganism. Though the results suggest that the ligands have a remarkable toxic property, their complexes of tin inhibit the growth of microorganisms to a greater extent. This is in accordance with earlier reports [45]. Further, the greater activity of the complexes can also be explained on the basis of their higher solubility of the particles.

Table 6. Antibacterial and antifungal activity of ligands and their organotin (IV) complexes.

Compounds	Zone of inhibition (mm)*					
	Bacillus cereus (MTCC 0430)			*Enterobacter aerogenes* MTCC 2824		
	25 µg	50 µg	100 µg	25 µg	50 µg	100 µg
L^1	4.5	11.9	14.6	3.6	7.5	11.7
$Bu_2Sn(L^1)_2$	4.4	15.6	19.7	4.8	10.1	15.9
L^2	5.5	12.3	15.5	5.55	10.2	14.5
$Bu_2Sn(L^2)_2$	6.9	16.5	20.2	7.2	13.6	17.8
L^3	7.2	9.5	15.0	5.66	8.28	15.0
$Bu_2Sn(L^3)_2$	8.8	12.6	18.8	7.5	11.3	16.9

*The zone of inhibition was measured with respect to control. DMSO (Dimethyl sulfo-oxide was taken as control and as well as solvent).

4. CONCLUSION

The newly synthesized Schiff bases act as bidntate ligands coordinating to metal ion through azomethine nitrogen, and carboxylate oxygen atom. Distorted octahedral geometries have been proposed for diorganotin (IV) complexes with the help of different spectral studies like IR, UV, ^1H, ^{13}C and ^{119}Sn NMR. The Schiff bases and their metal complexes were found to be active against some of the antibacterial and antifungal species. The activity is significantly increased on coordination.

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