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**Research Article** 

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# Inventive Triorgano Tin (IV) Complexes of Biologically Potent Schiff Base Derivatives

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# ABSTRACT

The reaction of triphenyltin chloride and trimethyltin chloride with the hydrazinecarboxamide and hydrazinecarbothioamide ligands of Schiff bases in 1:1 stoichiometry afford complexes having general formula  $[M_3Sn(L_1)]$ ,  $[M_3Sn(L_2)]$ ,  $[M_3Sn(L_3)]$ ,  $[M_3Sn(L_4)]$ , where M = triphenyl and trimethyl. New series of bio potent organotin, (IV) complexes were isolated as coloured solids soluble in most of the organic solvents. The coordination behaviour and bonding pattern of these compounds are discussed by the support of electronic, infrared and multinuclear magnetic resonance ( ${}^{1}H$ ,  ${}^{13}C$  and  ${}^{119}Sn NMR$ ) spectral studies. These analyses suggest that the ligands act in a bidentate manner, coordinating metal through the oxygen/sulphur and nitrogen atoms. Trigonal bipyramidal geometry is assigned for 1:1 metal complexes. Their molecular weight determinations show that the complexes are monomeric in nature. Conductivity measurement values in DMF lie in the range of 10-12 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> indicate them to be non-electrolyte. All the schiff base ligands and their corresponding organotin complexes have also been screened for their antifungal and antibacterial activities against Gram-positive bacterial strain (Staphylococcus aureus) and Gram-negative bacterial strain (Escherichia coli).

Key words: Triorganotin (IV) complexes; thio- and semi-ligands; spectral studies; biochemical studies

# INTRODUCTION

Organometallic compounds containing lead, tin and mercury are all commercially significant [1]. Organotins with three organic groups can be powerful fungicides and their demand increased the worldwide production of organotin compounds with a novel Schiff base ligand during the last 50 years [2]. Schiff bases represent an important group of compounds in organic chemistry because they are starting materials in the synthesis of industrial products where carbon-nitrogen bonds are present [3]. In particular, this N–C bond is involved in several biological functions allowing the Schiff bases to behave, for instance, as antimicrobial, anti-inflamatory, antitumour, or antiviral drugs [4]. The design of organotin derivatives with biologically important ligands like antibiotics [5-6], anticancer drugs [7] and some other biologically relevant substrates [8] has been explored in the past years [9].

A close review of metal coordination complexes of Schiff bases have been suggested as antibacterial, antifungal, cytotoxic, anti-inflammatory and Cytostatic agents [10-13]. In order to widen the scope of investigations on the coordination behavior of various donor ligands including Schiff base towards organo metallics, number of investigations are carried out and established their bioactivities [14-17]. The number and diversity of nitrogen and sulfur chelating agents used to prepare new coordination and organometallic compounds has increased rapidly during the past few years [18]. The dithiocarbazate ( $NH_2NHCS_2^-$ ) and its substituted derivatives have been investigated [19]. These compounds have received much attention for further studies as (i) they provide an interesting series of ligands whose properties can be greatly modified by introducing different organic substituents, thereby causing a variation in the ultimate donor properties, (ii) the interaction of these donors with metal ions gives complexes of different geometries and properties, and (iii) these complexes are potentially biologically active.

During the last few decades, significant attention has been paid to the bioactive diorganotin(IV) compounds with similar antitumor activity to cisplatin against several human tumors such as gastric carcinoma, immature granulocyte leukemia, henrietta carcinoma and urinary bladder [20-21]. These diorganotin(IV) compounds are active against

cancer cells *via* different molecular mechanisms [22-23]. As an extension of all the review of organotin compounds, herein, an explanation of the synthesis, characterization and bactericidal activity of some Schiff base metal complexes is presented.

# EXPERIMENTAL

# **Physical Measurements**

Before starting the chemical reaction, all the chemicals were dried and purified and the reactions were carried out with a distillation assembly, fitted with condensor and protected from moisture. Nitrogen was estimated by the Kjeldahl's method and sulphur was estimated by the Messenger's method. Tin was determined gravimetrically as  $SnO_2$  with the help of silica crucible. The conductance was measured by conductivity bridge type 304 Systronics model and the molecular weights were determined by the Rast Camphor method. <sup>1</sup>H and <sup>19</sup>F NMR spectra were recorded in DMSO-D<sub>6</sub>, <sup>13</sup>C and <sup>119</sup>Sn spectra were recorded in methanol, using TMS as the internal standard.  $C_6F_6$  was used as the external reference for the <sup>19</sup>F NMR spectra and tetramethyl tin is used as external reference for <sup>119</sup>Sn NMR spectra. IR spectra were recorded on FTIR spectrophotometer; model IR-550 as nujol mulls using KBr optics.

## Synthesis of the Ligands, $L_1H$ , $L_2H$ , $L_3H$ and $L_4H$

Ligands ( $L_1H$  and  $L_2H$ ) were prepared by the condensation of heterocyclic ketones 1,3-dihydro-3-[2-(phenyl)-2-oxoethylidene]-2H-indol-2-one (5.2g) and 2-phenyl-3-(3-phenyl-3-oxoprop-1-enyl)-indol (6.5g) with hydrazine carboxamide (1.57g and 1.51g respectively) in the presence of sodium acetate in equimolar ratio (1:1) in absolute ethanol.

Ligand ( $L_3H$ ) was prepared by the condensation of heterocyclic ketone 1,3-dihydro-3 [2-(4-fluoro-3-methylphenyl)-2-oxo-ethylidene]2H-indol-2-one (5.5g) with hydrazinecarboxamide (1.47g) in the presence of sodium acetate in equimolar ratio (1:1) in absolute alcohol.

Ligand ( $L_4H$ ) was prepared by the condensation of 1,3-dihydro-3-[2-( 4-fluoro-3-methylphenyl)-2-oxo-ethylidene]-2H-indol-2-one (6.7g) with hydrazinecarbothioamide (2.17g) in 1:1 molar ratio in alcoholic medium.

These mixtures were heated under reflux for 45 minutes. The solvent was then removed and the residue was dried in vacuum under reduced pressure. The products were purified by recrystallization from the same solvent. The analysis and physical properties of these ligands are enlisted in (Table-1).

Compound	Colour and state	Molar	M.P.	Analysis (%) Found (Calcd.)					
Compound	Colour and state	ratio	(°C)	С	Н	Ν	S	Sn	
$L_1 H C_{17} H_{14} N_4 O_2$	Red Crystalline Solid		180-181	66.51 (66.66)	4.56 (4.61)	18.08 (18.29)	-	-	
$Me_{3}Sn(L_{1}) C_{20}H_{22}N_{4}O_{2}Sn$	Orange solid	1:1	152-153	51.08 (51.2)	4.53 (4.73)	11.81 (11.94)	-	25.19 (25.3)	
Ph <sub>3</sub> Sn(L <sub>1</sub> ) C <sub>35</sub> H <sub>28</sub> N <sub>4</sub> O <sub>2</sub> Sn	Orange solid	1:1	160-162	64.08 (64.15)	4.21 (4.31)	8.39 (8.55)	-	18.02 (18.11)	
L <sub>2</sub> H C <sub>24</sub> H <sub>20</sub> N <sub>4</sub> O	Red Crystalline Solid		176-178	75.61 (75.77)	5.18 (5.30)	14.60 (14.73)		-	
$Me_{3}Sn(L_{2}) C_{27}H_{28}N_{4}OSn$	Orange solid	1:1	158-160	59.59 (59.69)	5.11 (5.19)	10.14 (10.31)	-	21.68 (21.85)	
$Ph_3Sn(L_2) C_{42}H_{34}N_4OSn$	Orange solid	1:1	165-167	69.05 (69.15)	4.59 (4.70)	7.53 (7.68)	-	16.17 (16.27)	
$L_{3}H$ $C_{18}H_{15}N_{4}O_{2}F$	Orange Crystalline Solid		160-161	63.60 (63.90)	4.31 (4.47)	16.48 (16.56)			
Me <sub>3</sub> Sn(L <sub>3</sub> ) C <sub>21</sub> H <sub>28</sub> N <sub>4</sub> O <sub>2</sub> FSn	Brown solid	1:1	156-157	49.61 (49.83)	5.45 (5.58)	11.02 (11.07)		23.23 (23.45)	
Ph <sub>3</sub> Sn(L <sub>3</sub> ) C <sub>36</sub> H <sub>29</sub> N <sub>4</sub> O <sub>2</sub> FSn	Reddish brown solid	1:1	198-199	62.71 (62.91)	4.18 (4.25)	8.09 (8.15)		17.12 (17.27)	
L4H C18H15N4OSF	Orange Solid		165-167	60.92 (61.0)	4.19 (4.27)	15.72 (15.81)	9.01 (9.05)		
Me <sub>3</sub> Sn(L <sub>4</sub> ) C <sub>21</sub> H <sub>28</sub> N <sub>4</sub> OSFSn	Brown solid	1:1	186-187	48.21 (48.3)	5.30 (5.40)	10.61 (10.73)	6.08 (6.14)	22.59 (22.73)	
Ph <sub>3</sub> Sn(L <sub>4</sub> ) C <sub>36</sub> H <sub>29</sub> N <sub>4</sub> OSFSn	Brown solid	1:1	192-194	61.31 (61.40)	4.10 (4.16)	7.86 (7.96)	4.45 (4.56)	16.72 (16.88)	

Table -1 Physical	Properties of th	e Ligands and their	Organotin (IV	) Complexes

# Synthesis of the Complexes

A calculated amount of the sodium salt of the ligand in dry methanol was added to the weighed amounts of  $Me_3SnCl$ and  $Ph_3SnCl$  in a round bottom flask in 1:1 molar ratios The reaction was refluxed over a ratio-head for 16-18 hours and the white precipitate of sodium chloride obtained, was removed. Compounds were dried under reduced pressure for 3-4 hours. These were purified by repeated washing with n-hexane and methanol. All the compounds were isolated as powdered solids. The details of these reactions and the analysis of the resulting products are recorded in (Table-1).

#### **RESULTS AND DISCUSSION**

Reactions of triorganotin (IV) halides with monobasic bidentate ligands in 1:1 molar ratio in methanol may be represented by the following equations:

$$\begin{array}{c} \text{Me}_{3}\text{SnCl} + \overset{}{\text{N}} \text{S.Na} & \xrightarrow{1:1} & \text{Me}_{3}\text{Sn}(\overset{}{\text{N}} \text{S}) + & \text{NaCl} \\ \text{Ph}_{3}\text{SnCl} + \overset{}{\text{N}} \text{S.Na} & \xrightarrow{1:1} & \text{Ph}_{3}\text{Sn}(\overset{}{\text{N}} \text{S}) + & \text{NaCl} \\ \text{Me}_{3}\text{SnCl} + \overset{}{\text{N}} \text{O.Na} & \xrightarrow{1:1} & \text{Me}_{3}\text{Sn}(\overset{}{\text{N}} \text{O}) + & \text{NaCl} \\ \text{Ph}_{3}\text{SnCl} + \overset{}{\text{N}} \text{O.Na} & \xrightarrow{1:1} & \text{Ph}_{3}\text{Sn}(\overset{}{\text{N}} \text{O}) + & \text{NaCl} \\ \text{(where, } \overset{}{\text{N}} \text{S and } \overset{}{\text{N}} \text{O} = \text{donar set of the ligands)} \end{array}$$

## **IR Spectra**

The infrared spectra of the ligands and their tin complexes were recorded and important features may be summarized as follows:

The IR spectra of the ligands show broad and medium intensity bands in region 3280-3100cm<sup>-1</sup> due to vNH mode. These disappear in the spectra of metal complexes thereby showing the deprotonation of the group. The IR spectra of fluorohydrazines show two sharp bands around 3450 and 3350 cm<sup>-1</sup> due to vasym and vsym NH<sub>2</sub> vibrations, respectively, which remain almost at the same positions in the metal complexes, showing non-involvement of this group in the complexation.

The bands of medium intensity appearing in the region 3300 cm<sup>-1</sup> and 2700 cm<sup>-1</sup> may be assigned to vNH [24] and vSH vibrations, respectively, which suggest that the ligands exist as in keto-enol tautomerism. These disappear in the corresponding tin complexes.

The band due to >C=N of free azomethine group in the ligands get shifted to the lower wave number ( $\Delta v$ = 15–20 cm<sup>-1</sup>) in the tin complexes indicating coordination through azomethine nitrogen [25]. The vC=O band in hydrazinecarboxamide and vC=S in hydrazinecarbothioamide appear at 1690 cm<sup>-1</sup> and 1035 cm<sup>-1</sup>, respectively. These bands disappear on complexation, which is due to the covalent bond formation of the ligand with the tin atom through the oxygen or sulphur atoms. Several new bands in the complexes at 530, 420 and 325 cm<sup>-1</sup>, are due to v(Sn-O), v(Sn-N) and v(Sn-S) respectively, which are absent in the spectrum of the ligand, further supporting the participation of the oxygen/sulphur atom and the azomethine nitrogen in complexation.

#### **UV Spectra**

A band due to the >C=N chromophore in the spectrum of the ligand at 365 nm shifts to a higher wavelength in the tin complexes. This clearly indicates the coordination of the azomethine nitrogen to the tin atom. Such a shift in n- $\pi$  \* transition band is probably due to the donation of lone pair of electrons by the nitrogen of the ligand to the central metal atom indicating the delocalization of the electronic charge within the chetate ring and thus stabilizing of the resulting complexes. Further, two bands at 260 nm and 305 nm are due to  $\pi$ - $\pi$  \* transitions, these are assigned to the benzenoid ring and (>C=N) band of the azomethine group respectively. The K band  $\pi$ - $\pi$  \* showed a red shift due to the overlap of the central metal d-orbital with the p-orbital of the donor atom, which causes an increase in conjugation and the B-band undergoes a hypsochromic shift in the complexes.

# <sup>1</sup>H NMR Spectra

The proton magnetic resonance spectra [26] of the ligands and their corresponding tin complexes were recorded in DMSO-d<sub>6</sub> using TMS as the internal standard. The chemical shift values ( $\delta$ , ppm) of the different protons are given in (Table 2). The <sup>1</sup>H NMR spectra of the ligands exhibit peaks around of  $\delta$  value 11.24–10.12 (1H) were characteristic of –NH of the isatin ring. The peaks found around  $\delta$  value 7.74–6.36 (7H) may be due to aromatic protons, while that observed at  $\delta$  value 10.08–10.04 (1H) due to –NH of thiosemicarbazone/semicarbazone. The disappearance of signal which is due to –NH of thiosemicarbazone/semicarbazone in the tin derivatives indicate the coordination of the azomethine nitrogen atom as well as covalent bond formation between tin and sulphur/oxygen due to deprotonation of the ligands. In the spectra of the complexes, a downfield shift in the position of -CH<sub>3</sub> and aromatic protons indicate deshielding, as well as the coordination of azomethine nitrogen to the tin atom. This is probably due to the donation of the lone pair of electrons by the nitrogen to the central tin atom, resulting in the formation of a coordinate linkage (Sn  $\leftarrow$ -N). The appearance of a signal around 2.98–2.56  $\delta$  value due to –NH<sub>2</sub>

group at the same positions in the ligand and its tin complexes, showing non-involvement of this group in coordination. A peak was observed at  $\delta$  value 2.46 (3H) due to  $-CH_3$  protons attached to the phenyl ring. The  ${}^2J$  [<sup>1</sup>H,<sup>119</sup>Sn] values for various tri organotin compounds indicate that the compounds have 5-coordinated environment [27] around them.

Compound	-NH ring(bs)	-NH free(bs)	-NH <sub>2</sub> (bs)	=CH-C=N (s)	Aromatic (indole ring) (m)	$\frac{\text{Sn-Me/Ph}}{{}^{2}J({}^{1}H-{}^{119}Sn)}$	CH <sub>3</sub> -Ph (s)	Aromatic (CH <sub>3</sub> -Ph) (m)/ Phenyl
$L_1H$	12.32	10.08	2.36	8.08	7.24-6.08	-	-	7.38-7.01
$Me_3Sn(L_1)$	12.12	-	2.28	8.12	7.36-6.16	1.14 ² <b>J [64.2]</b>	-	7.45-7.32
$Ph_3Sn(L_1)$	12.24	-	2.30	8.16	8.08-6.94	6.08	-	7.90-7.40
$L_2H$	11.04	9.08	2.55	8.24	7.94-6.16	-	-	7.40-7.25
Me <sub>3</sub> Sn(L <sub>2</sub> )	11.64	-	2.48	8.63	7.98-6.36	1.08 ² <b>J [65.5]</b>	-	7.95-7.54
$Ph_3Sn(L_2)$	11.72	-	2.60	8.77	8.08-7.12	6.24	-	8.12-7.73
$L_3H$	10.12	10.08	2.98	8.08	7.68-6.65	-	2.25	7.48-7.11
Me <sub>3</sub> Sn(L <sub>3</sub> )	10.16	-	3.04	8.16	7.72-6.54	0.84 ² <b>J [67.5]</b>	2.36	7.58-7.22
$Ph_3Sn(L_3)$	10.22	-	3.08	8.32	7.98-6.55	6.36	2.43	8.02-7.72
$L_4H$	11.12	10.04	2.64	8.12	7.72-6.34	-	2.29	7.45-7.28
Me <sub>3</sub> Sn(L <sub>4</sub> )	11.22	-	2.78	8.24	7.74-6.36	0.98 <sup>2</sup> <b>J</b> [68.2]	2.34	7.96-7.58
Ph <sub>3</sub> Sn(L <sub>4</sub> )	11.32	-	2.74	8.36	8.16-6.54	6.34	2.45	7.68-7.48

Table -2<sup>1</sup>H NMR Spectra Data of the Ligands and their Organotin (IV) Complexes

 Table -3 <sup>13</sup>C NMR Spectra Data of the Ligands and their Organotin (IV) Complexes

		Chemical Shift Values (δ, ppm)							
Compound	Amido	Azomethine	-NH-C=O/ - NH-C-Ph	Aromatic * (indole ring)	Sn-Me/Ph	Phenyl ring * Phenyl/ (Ph-H <sub>3</sub> )			
$L_1H$	170.52	159.92	165.86	141.24, 140.22, 126.16, 128.94, 129.94, 125.12, 124.08, 139.66	-	137.12, 128.29, 125.56, 131.15,130.05			
$Me_3Sn(L_1)$	165.94	154.16	163.98	143.36, 142,01, 127.08, 129.92, 130.12, 126.72, 125.44, 140.11	14.98	139.98, 134.59 130.25, 132.25 130.23			
$L_2H$	169.88	156.51	162.16	143.68, 142.28, 128.34, 123.34, 127.85, 125.66, 121.56, 141.92	-	140.93, 133.95 130.25, 133.51 130.75			
Ph <sub>3</sub> Sn(L <sub>2</sub> )	166.58	151.36	163.32	146.72, 146.12, 129.38 125.11, 130.36,130.98, 125.72, 148.23	131.68, 130.16, 128.11, 127.58	144.11, 139.82 132.95, 136.95 133.09			
L <sub>3</sub> H	170.20	160.24	159.98	143.66, 140.22, 127.85, 123.32, 122.36, 117.32, 120.66, 140.66	-	138.1, 129.9, 128.5, 132.5,130.5			
Me <sub>3</sub> Sn(L <sub>3</sub> )	166.12	156.73	159.23	146.73, 142,01, 128.11, 127.63, 124.08, 119.32 123.36, 141.11	16.38	139.23, 132.19 128.25, 132.25 131.95			
$L_4H$	172.52	155.12	164.58	147.24, 144.28, 135.72, 130.22, 129.71, 120.55, 121.56, 136.92	-	139.91, 130.95 129.5, 134.5 131.85			
Ph <sub>3</sub> Sn(L <sub>4</sub> )	169.68	150.51	164.38	148.12, 145.36, 137.08 136.89, 132.52, 130.42, 128.72, 145.52	131.23, 134.48, 135.68, 138.19	140.81, 133.12 130.15, 134.65 131.85			

For compound  $Ph_3Sn(L_4)$   ${}^{1}J({}^{13}C^{-119}Sn) = 487.6Hz - 489.5Hz$ , 476.9Hz - 480.5Hz

$${}^{2}J({}^{13}C-{}^{119}Sn) = 35.5Hz-36.7Hz$$

$${}^{5}J({}^{15}C-{}^{119}Sn) = 48.5Hz - 50.6 Hz$$

$$^{4}J(^{13}C-^{119}Sn) = 13.6Hz - 10..6 Hz$$

\* Detailed Values of aromatic and phenyl carbons are given in below table -4.

# <sup>13</sup>C NMR Spectra

The <sup>13</sup>C NMR spectra of the ligands and their corresponding tin complexes were also recorded in dry MeOH. Substantial shifts in the positions of carbon atoms attached to the azomethine nitrogen, thiolic sulphur or amido oxygen support the proposed coordination in these complexes. The heterocyclic moiety carbon signals, especially those of the carbon atoms directly bonded to the heteroatom, undergo slight upfield shifts relative to the other carbon atoms which remain almost undisturbed. The shift towards upfield in the signal of the thiolo carbon and azomethine carbon in the complexes suggest participation of these groups in coordination to the tin atom. The heteronuclear coupling constant values viz  ${}^{1}J$  [ ${}^{13}C$ ,  ${}^{119}Sn$ ],  ${}^{2}J$  [ ${}^{13}C$ ,  ${}^{119}Sn$ ],  ${}^{3}J$  [ ${}^{13}C$ ,  ${}^{119}Sn$ ] and  ${}^{4}J$  [ ${}^{13}C$ ,  ${}^{119}Sn$ ] for few compounds are also scrutinized which are very useful in providing the information regarding the geometry [28-29] of organotin complexes. The different  $\delta$  values of all the carbon atoms of aromatic and phenyl group along with (Sn–CH<sub>3</sub>) and (Sn–C<sub>6</sub>H<sub>5</sub>) [30] signals are listed in (Table 3and 4).

Table -4 Values of Aromatic and Pheny									ons				
Compound	C <sub>2</sub>	C <sub>3</sub>	$C_4$	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	C <sub>8</sub>	C <sub>9</sub>	C <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub>	C <sub>13</sub>	C <sub>14</sub>
$L_3H$	143.66	140.22	127.85	123.32	122.36	117.23	120.66	140.66	138.9	140.2	131.0	130.8	131.5
Me <sub>3</sub> Sn(L <sub>3</sub> )	146.73	142,01	128.11	127.63	124.08	119.32	123.36	141.11	139.23	132.19	128.25	132.25	131.95
$L_4H$	147.24	144.28	135.72	136.22	129.71	120.55	121.56	136.92	139.6	141.0	131.0	130.8	130.9
Ph <sub>3</sub> Sn(L <sub>4</sub> )	148.12	145.36	137.08	136.89	132.52	130.42	128.72	145.52	140.81	133.12	130.15	134.65	131.85
								14		13 12 10			

# <sup>19</sup>F NMR Spectra

The <sup>19</sup>F NMR spectrum [31] of the ligands  $L_3H$  and  $L_4H$  display a sharp singlet at  $\delta$ -114.36 ppm,  $\delta$ -120.36 ppm. Their organotin (IV) complexes does not show any change in the position of the signal and thus supporting the non-involvement of fluorine in complexation.

#### <sup>119</sup>Sn NMR Spectra

In the case of the tin complexes  $Ph_3Sn(L_3)$  and  $Me_3Sn(L_4)$  signals at  $\delta$ —181.7 ppm and  $\delta$ -145.5 ppm for 1:1 complexes, respectively which stated for coordination number five [32-33] around the tin atom. On the basis of the above spectral studies, possible trigonal bipyramidal geometry has been suggested for pentacoordinated state for all the 1:1 metal complexes (Figure 1).

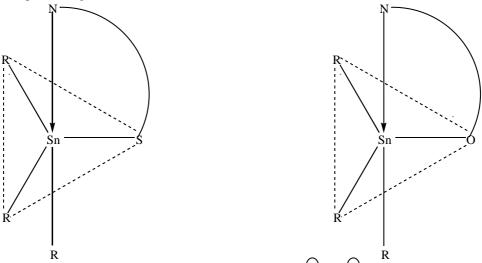


Fig. 1 Suggested structures for the complexes; R= Me or Ph and N (S) and N (O) = donar set of the ligands)

# MICROBIAL EXAMINATION

Bioefficacies of the Schiff base ligands and their complexes were tested in *in vitro*, as well as in *in vivo*. The paper disc method [34] has been used for the antibacterial activity and percent disease incidence (PDI) [35] for antifungal screening.

#### Antibacterial Screening (in vitro)

Bacterial strains, *Staphylococcus aureus*(+) and *Escherichia coli* (-) are selected for this study and the technique used is paper disc method [36]. In this technique sterilized hot nutrient agar and paper disc of Whatman No.1 were used. The discs having a diameter of 5 mm were soaked in the solutions of test compounds in methanol (500 and 1000 ppm concentrations). These discs were placed on agar medium previously seeded with bacterial suspension in petri plates and stored in an incubator at  $30 \pm 1^{\circ}$ C. The inhibition zone around each disc was measured after 24-30 hours. Results have been recorded in the form of inhibition zones (diameter, mm) reported in (Table 5).

Compound	Diameter of inhibition zone (mm)							
Compound	Staphylococcus	aureus (+) (Concentration in ppm)	Escherichia coli S(-) Concentration in pp					
	500	1000	500	1000				
$L_1H$	7	10	6	10				
$Ph_3Sn(L_1)$	9	13	8	12				
$L_3H$	8	11	6	10				
$Me_3Sn(L_3)$	10	14	10	14				
$L_4H$	9	12	7	11				
$Ph_3Sn(L_4)$	14	17	12	15				
Streptomycin	15	17	17	18				

#### Table -5 Bactericidal Screening Data of the Ligands and Their Tin Complexes

#### Antifungal Screening (in vivo)

The chemicals, found most effective against fungal and bacterial strains which were tested in *in vitro*, were also tested in field for controlling the *Guar blight* in *Guar (Cyamopsis tetragonoloba)* caused by *Alternaria yamopsidae*. Field experiments were laid out in randomized block design plots with three replications. The crops (20 plants) were raised in each plot. Compounds with a standard fungicide, Bavistin, [2-(methoxycarbamyl) benzimidazole] were tried. After sowing of 45 days, the plants were inoculated artificially by spraying the conidial suspension. The suspension was prepared by crushing the infected leaves in water. The first spray of the respective fungicide was given, when lesions were first seen and were repeated after ten days. Disease intensity was analysed for statistical significance and (%) disease control on test compounds was worked out.

Sum of score of infected plants x 100

Total number of plants observed x Maximum rating of score (10)

The effectiveness of the chemicals were calculated using the following formula

PDI in treated plants – PDI in untreated plants

% Disease control =

PDI in untreated plants The results of these findings are given in (Table 6).

Table -6 Efficacies of the compounds against Guar blight was evaluated using the Percent Disease Incidence Technique (PDI)

Compound	PDI in treated plants	% Disease control
L <sub>1</sub> H	12	57.1
$Me_3Sn(L_3)$	7	75.0
L <sub>2</sub> H	9	67.8
$Ph_3Sn(L_2)$	5	82.1
L <sub>3</sub> H	12	57.1
$Me_3Sn(L_3)$	7	75.0
L <sub>4</sub> H	11	60.7
$Ph_3Sn(L_4)$	4	85.7
Bavistin	3	89.3

#### **Mode of Action**

Metal based fungicides inhibit a wide range of enzymes involved in various metabolic pathways, ultimately causing cell death. Early work on the mode of action of fungicides showed that these compounds inhibit cell division. It was later [37] shown that the specific site of action is  $\beta$ -tubuline, a polymeric protein found in microtubules - an essential component of the cytoskeleton. Phenyl and amine groups in the complexes affect nucleic acid, synthesis and mitochondrial electron transport also.

This activity might be due to the presence of a hydroxyl and phenyl groups [38]. The increased activity in the organotin complexes may be due to the coordination and polarity of a tin (IV) atom with oxygen of the ligand [39]. The order of increasing activities is; ligand<Me<sub>3</sub>SnL<Ph<sub>3</sub>SnL, the results matched with the previously reported data for the biological activity of organotin complexes [40]. Further, it has been concluded that the organotin compounds are more active than the free ligands, which indicate that metallation increases antibacterial activity which is in accordance with earlier reports [41]. The novel synthesized compounds are cost effective and are easy to synthesize. It is likely that the new complexes might be more environments friendly. There have been several reports dealing with the impact of organotin chemistry in the biosphere.

We might then expect at least the following regulatory processes to be operative. Chelation theory [42-43] accounts for the increased activity of the metal complexes. Chelation reduces the polarity of the metal atom, mainly because of partial sharing of its positive charge with the donor groups and possible  $\pi$  electron delocalisation within the whole chelate ring. The chelation increases the lipophilic nature of the central atom, which subsequently favours its

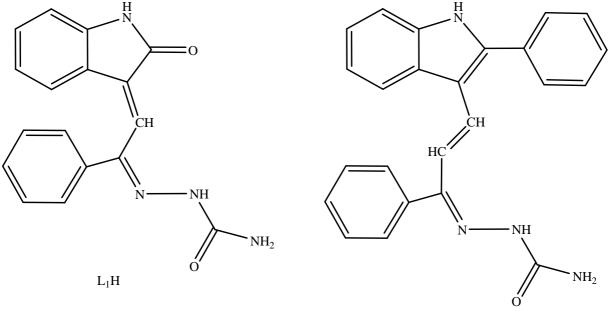
permeation through the lipid layer of the cell membrane. An additional theory is based on penetration of cell wall [44]. It suggests chitinases and a another compound,  $\beta$ -1,3-glucanase, defense system of the plants, hydrolyze fungal cell walls and inhibit the rapid growth of fungal pathogens.

### CONCLUSION

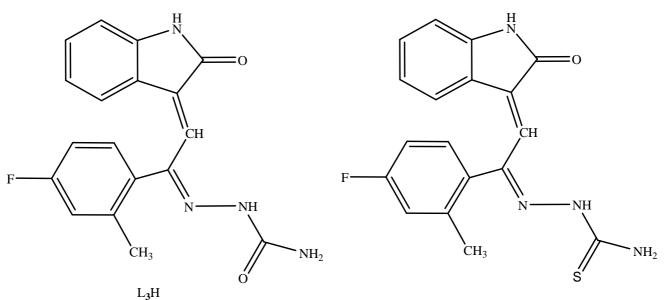
The results of fungicidal and bactericidal screening of the tin complexes against some pathogenic fungi and bacteria are recorded in Tables 5 and 6. The results show that the activity is enhanced on undergoing chelation. It is a well-known fact that the concentration plays a vital role in increasing the degree of inhibition. Hence as the concentration increases, the activity also increases.

The screening results have shown that the triorganotin(IV) complexes have better antibacterial activity than the free ligands. Furthermore, it has been shown that the triphenyltin(IV) derivatives exhibit significantly better activities than the trimethyltin(IV) derivatives.

#### Structure of the Ligands







L<sub>4</sub>H

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