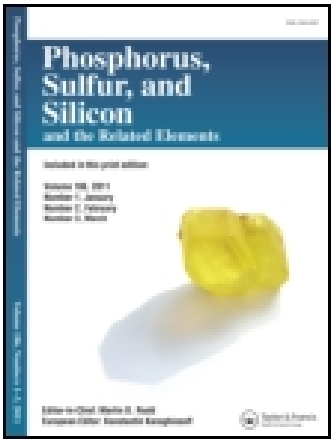


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# Synthesis and Characterization of Diorganotin (IV) Complexes with Tridentate Schiff Base Ligand Pyridoxal Aroylhydrazones

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# SYNTHESIS AND CHARACTERIZATION OF DIORGANOTIN (IV) COMPLEXES WITH TRIDENTATE SCHIFF BASE LIGAND PYRIDOXAL AROYLHYDRAZONES

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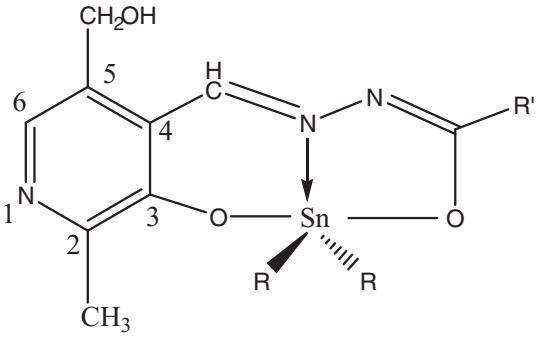
## GRAPHICAL ABSTRACT




R = Me,Bu, Ph

R' = 2-pyridyl, 2-thenyl, 1-naphthyl

**Abstract** *Dichlorodiorganotin (IV) $R_2SnCl_2$ (where R = Me, Bu, or Ph) on reaction with substituted hydrazones ($H_2L$) derived from the condensation of pyridoxal hydrochloride with substituted acid hydrazides, $H_2$pydx-inh ($L_I$), $H_2$pydx-th ($L_{II}$), or $H_2$pydx-nh ($L_{III}$) (pydx = pyridoxal, inh = isonicotinoyl hydrazone, th = 2-thiophene carboxyl hydrazone, nh = 1-naphthoyl hydrazone), dry benzene give pentacoordinated complexes of the type $R_2SnL_{(I\text{-}III)}$. In the solution of isolated complexes the ligand acted in a tridentate manner (O,O,N), co-ordinating through a phenolic oxygen, oxygen of keto group after enolization, and nitrogen of azomethine group. The synthesized complexes were characterized by elemental analyses, molar conductance, molecular weight determination, and infrared (IR) and nuclear magnetic resonance (NMR; $^1H$, $^{13}C$, and $^{119}Sn$) spectral data. The ligands and their tin complexes were evaluated for antifungal and antibacterial activities, and the results indicate that they exhibit significant antimicrobial properties.*

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**Keywords** Diorganotin (IV) complexes; pyridoxal aroylhydrazone; Schiff base



## INTRODUCTION

Schiff bases continue to be of paramount importance in coordination chemistry; in addition to their biomedical applications, they form stable complexes with most transition metals that can serve as models for studying a wide range of biological reactions that are catalyzed by enzymes.[1,2] Pyridoxal is the biological active form of vitamin $B_6$ acting as a coenzyme in several biosynthetic, metabolic, or regulatory processes. Schiff bases derived from pyridoxal and amines or their derivatives are of great interest because they have been found to be more effective than the individual pyridoxal or amino derivatives and are considered promising for the treatment of diabetic complications.[3] Hydrazones of pyridoxal (Figure 1), viz. those derived from hydrazides of benzoic, p-methoxybenzoic, m-fluorobenzoic, and 2-fluroylhydrazone, were highly effective in mobilizing $^{59}$Fe from $^{59}$Fe-labeled hepatocytes in vitro.[4] It is noteworthy that the biological activity of Schiff bases is significantly enhanced on coordination with suitable metal ions.[5,6]

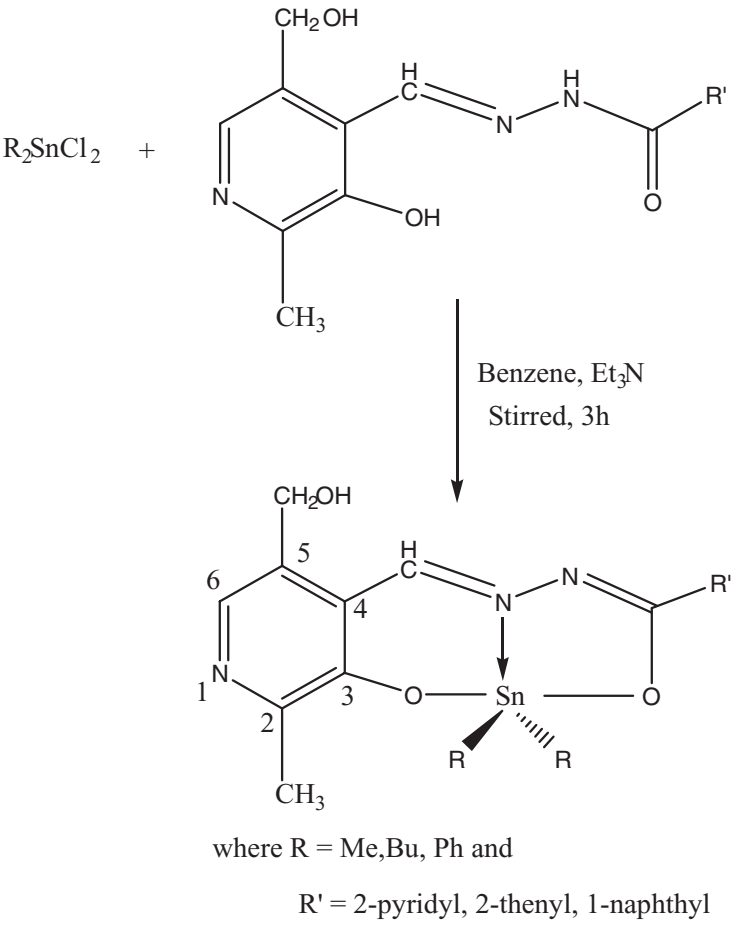
Organotin compounds show a wide spectrum of biological activity,[7,8] which essentially is determined by the number and the nature of the donor atoms of the ligands attached to the tin moiety. Diorganotin (IV) complexes exhibit higher biological activity than the corresponding mono/triorganotin (IV) complexes. The activity also depends upon the nature of the alkyl group attached to the tin atom and the highest activity is extended when R is ethyl or phenyl in organotin complexes.[9,10] Keeping this in mind, we have synthesized complexes (Scheme 1) obtained by the interaction of the organotin moiety with nitrogen/sulfur donor ligands and studied the effect of coordination on biocidal activity in order to explore their use as potential biocidal agents.

## RESULTS AND DISCUSSION

Pyridoxal-substituted hydrazones ($H_2L_I$–$H_2L_{III}$) were prepared by the condensation of pyridoxal hydrochloride with substituted acid hydrazides. The progress of the reaction was regularly monitored by thin-layer chromatography (TLC). The reaction of dichlorodiorganotin (IV) $R_2SnCl_2$ (R=Me, Bu, and Ph) with ligands ($H_2L_I$–$H_2L_{III}$) in a 1:1 molar ratio at room temperature afforded the complexes that were characterized by elemental analyses, infrared (IR) and $^1$H−, $^{13}$C−, and $^{119}$Sn-NMR. All of the complexes were obtained as solids, insoluble in most organic solvents. The low values of molar conductivity (7.0–15.0 ohm$^{-1}$ cm$^2$ mol$^{-1}$) of the complexes in dry dimethyl formamide (DMF) indicate their nonelectrolytic nature.

### IR Spectra

Coordination sites were ascertained on the basis of shifts in the frequency of various groups and/or from the intensity lowering on comparison of the infrared spectra of the ligands with that of the complexes. Infrared spectra of the ligands showed two bands in the region of 3210–3250 and 1673–1678 cm$^{-1}$ assigned to $\nu$ (N−H) and $\nu$ (C=O), respectively, indicating their ketonic nature in the solid state. In the complexes, the bands attributed to




**Scheme 1** Synthesis of organotin (IV) complexes.



$\nu$ NH and $\nu$ C=O disappeared, and two new bands in these complexes appeared in the region 1350 $cm^{-1}$, 1220 $cm^{-1}$ due to $\nu$ (NCO) and $\nu$ (C—O), which suggested enolization of the ligand after deprotonation when coordinated to the tin atom. The C=N band of the ligand at 1617–1632 $cm^{-1}$ shifts to 1603–1620 $cm^{-1}$ in the spectra of complexes and suggested coordination of imine nitrogen to the tin atom.[11] Of the two nitrogens of the azomethine group, coordination through the N(2) nitrogen of terminal isonicotinic acid hydrazide is suggested because it gives rise to a stable five-membered ring that would be formed on coordination through the other nitrogen. The broad band at 3240–3280 $cm^{-1}$ assignable to the $\nu$ (OH) group disappeared in the complexes, indicating the possible loss of protons on complexation and subsequent formation of an M—O bond. Involvement of nitrogen and oxygen in coordination was supported by the appearance of new bands in the regions 445–459 and 530–561 $cm^{-1}$ in the complexes, assigned to $\nu$ (Sn—N) and $\nu$ (Sn—O) modes.[12]

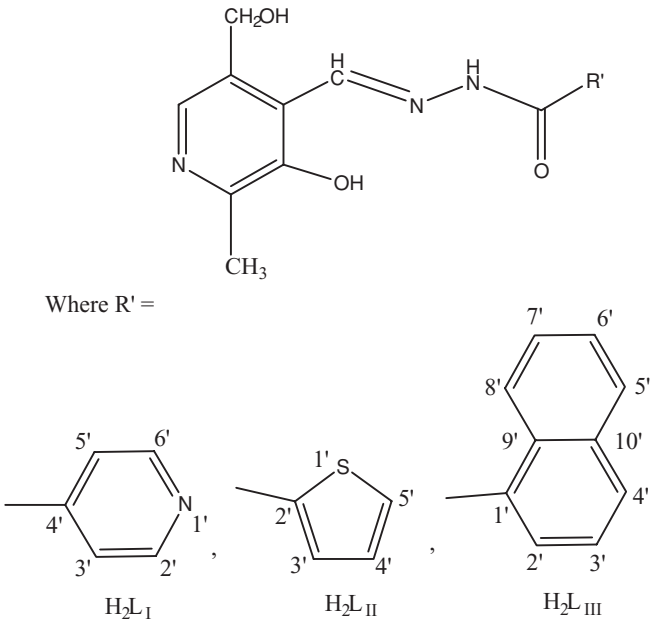



**Figure 1** Structure of Schiff base ligands.

## NMR Spectra

The coordinating modes of the ligands were confirmed by comparing $^1$H-NMR patterns of the ligands and their tin complexes (Table 1). In the $^1$H-NMR spectra of ligands, the chemical shift of the proton due to phenolic hydroxyl that appeared as a broad singlet around $\delta$ 12.27–12.62 was absent in the spectra of complexes, thereby indicating the involvement of pyridoxal –OH in coordination after deprotonation. The singlet at $\delta$ 8.94–9.08 showed a significant downfield shift ($\Delta\delta = 0.38$–$0.20$) relative to the corresponding ligands, confirming that the coordination has indeed taken place through azomethine nitrogen.[12] The absence of proton signal at 12.08 assigned to the NH group coupled with the shift of the proton of the OH group of the $-CH_2OH$ moiety from $\delta$ 5.06 to 5.59 suggested the cleavage of hydrogen bonding between hydrogen of the NH group and oxygen of the OH group (viz. N-H . . . O-H), and coordination occurred through an enolate oxygen atom. These results

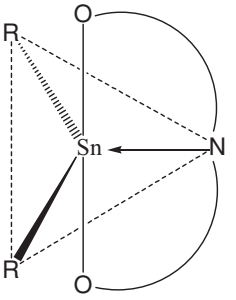



**Figure 2** Suggested structure of the complexes and $\widehat{ONO}$ donor site of the ligand.

**Table 1** $^{1}$H- and $^{119}$Sn—NMR spectral data ($\delta$) of ligands and their metal complexes

| Compound | $C_3$-O**H** (Phenolic) | -C**H**=N- (Azomethine) | $C_5$-C**H**$_2$-OH (Methylene) | $C_2$-C**H**$_3$ (Methyl) | $C_5$-O**H** (Alcoholic) | $C_6$-**H** | Aromatic | R | $^{119}$Sn |
|---|---|---|---|---|---|---|---|---|---|
| $H_2L_I$ | 12.62 (br, 1H) | 9.08 (s, 1H) | 4.68 (s, 2H) | 2.57 (s, 3H) | 5.27 (br, 1H) | 7.95 (s, 1H) | 7.89 (d, 2H, $C_3'$-H, $C_5'$-H, $J = 4.72$ Hz) 8.78 (d, 2H, $C_2'$-H, $C_6'$-H, $J = 3.52$ Hz) | — | — |
| $H_2L_{II}$ | 12.27 (br, 1H) | 9.01 (s, 1H) | 4.69 (s, 2H) | 2.51 (s, 3H) | 5.06 (br, 1H) | 7.95 (s, 1H) | 7.63 (d, 1H, $C_3'$-H, $J = 4.68$ Hz) 7.17 (dd, 1H, $C_4'$-H, $J = 3.96$ Hz) 7.92 (dd, 1H, $C_5'$-H, $J = 3.72$ Hz) | — | — |
| $H_2L_{III}$ | 12.62 (br, 1H) | 8.94 (s, 1H) | 4.68 (s, 2H) | 2.57 (s, 3H) | 5.33 (br, 1H) | 8.94 (s, 1H) | 8.36 (d, 1H, $C_2'$-H, $J = 6.82$ Hz) 7.56–7.61 (m, 3H, $C_3'$-H, $C_6'$-H, $C_7'$-H) 7.95 (m, 1H, $C_4'$-H) 7.82 (d, 1H, $C_5'$-H, $J = 6.36$ Hz) 8.06 (d, 1H, $C_8'$-H, $J = 8.20$ Hz) | — | — |
| $Me_2Sn$ ($L_I$) | — | 9.42 (s, 1H) | 4.71 (s, 2H) | 2.60 (s, 3H) | 5.29 (br, 1H) | 7.67 (s, 1H) | 7.64 (d, 2H, $C_3'$-H, $C_5'$-H, $J = 5.56$ Hz) 7.92 (d, 2H, $C_2'$-H, $C_6'$-H, $J = 5.32$ Hz) | 1.47 (s, 6H) | −185.3 |
| $Bu_2Sn$ ($L_I$) | — | 9.42 (s, 1H) | 4.78 (s, 2H) | 2.41 (s, 3H) | 5.29 (br, 1H) | 7.64 (s, 1H) | 7.92 (d, 2H, $C_3'$-H, $C_5'$-H, $J = 5.48$ Hz) 8.68 (s, 2H, $C_2'$-H, $C_6'$-H) | 0.86 (t, 3H, $C_1$-H, $J = 14.6$ Hz) 1.40 (m, 2H, $C_2$-H) 1.66 (m, 2H, $C_3$-H) | −187.3 |
| $Ph_2Sn$ ($L_I$) | — | 9.42 (s, 1H) | 4.78 (s, 2H) | 2.69 (s, 3H) | 5.29 (br, 1H) | 7.68 (s, 1H) | 7.68 (d, 2H, $C_3'$-H, $C_5'$-H, $J = 5.68$ Hz) 7.92 (d, 2H, $C_2'$-H, $C_6'$-H, $J = 5.24$ Hz) | 1.70 (t, 3H, $C_4$-H, $J = 7.96$ Hz) 6.85–7.79 (m, 7H) | −334.8 |
| $Me_2Sn$ ($L_{II}$) | — | 9.21 (s, 1H) | 4.67 (s, 2H) | 2.57 (s, 3H) | 5.33 (br, 1H) | 7.20 (s, 1H) | 7.62 (d, 1H, $C_3'$-H, $J = 5.08$ Hz,) 7.11 (s, 1H, $C_4'$-H) 7.70 (dd, 1H, $C_5'$-H, $J = 5.84$ Hz) | 1.41 (s, 6H) | −189.3 |

*(Continued on next page)*

**Table 1** $^{1}$H- and $^{119}$Sn—NMR spectral data ($\delta$) of ligands and their metal complexes *(Continued)*

| Compound | $C_3$-O**H** (Phenolic) | -C**H**=N- (Azomethine) | $C_5$-C**H**$_2$-OH (Methylene) | $C_2$-C**H**$_3$ (Methyl) | $C_5$-O**H** (Alcoholic) | $C_6$-**H** | Aromatic | R | $^{119}$Sn |
|---|---|---|---|---|---|---|---|---|---|
| $Bu_2Sn$ ($L_{II}$) | — | 9.21 (s, 1H) | 4.77 (s, 2H) | 2.38 (s, 3H) | 5.38 (br, 1H) | 7.11 (s, 1H) | 7.63 (d, 1H, $C_3'$-H, $J = 5.24$ Hz)<br>7.16(s, 1H, $C_4'$-H)<br>7.92 (dd, 1H, $C_5'$-H, $J = 5.16$ Hz) | 0.87 (t, 3H, $C_1$-H, $J = 14.3$ Hz)<br>1.41 (m, 2H, $C_2$-H) 1.63 (m, 2H, $C_3$-H) | −203.8 |
| $Ph_2Sn$ ($L_{II}$) | — | 9.21 (s, 1H) | 4.70 (s, 2H) | 2.59 (s, 3H) | 5.33 (br, 1H) | 7.16 (s, 1H) | 7.62 (d, 1H, $C_3'$-H, $J = 5.28$ Hz)<br>7.14 (s, 1H, $C_4'$-H)<br>7.77 (dd, 1H, $C_5'$-H, $J = 5.56$ Hz) | 1.89 (t, 3H, $C_4$-H, $J = 7.59$ Hz)<br>6.75–7.72 (m, 7H) | −335.4 |
| $Me_2Sn$ ($L_{III}$) | — | 9.32 (s, 1H) | 4.85 (s, 2H) | 2.60 (s, 3H) | 5.56 (br, 1H) | 7.59 (s, 1H) | 8.23 (m, 1H, $C_2'$-H)<br>7.53–7.60 (m, 3H, $C_3'$-H, $C_6'$-H, $C_7'$-H)<br>7.90 (m, 1H, $C_4'$-H)<br>7.80 (d, 1H, $C_5'$-H, $J = 8.12$ Hz)<br>8.00 (d, 1H, $C_8'$-H, $J = 8.56$ Hz) | 1.43 (s, 6H) | −186.5 |
| $Bu_2Sn$ ($L_{III}$) | — | 9.32 (s, 1H) | 4.85 (s, 2H) | 2.63 (s, 3H) | 5.57 (br, 1H) | 7.59 (s, 1H) | 8.23 (m, 1H, $C_2'$-H)<br>7.53–7.60 (m, 3H, $C_3'$-H, $C_6'$-H, $C_7'$-H)<br>7.90 (m, 1H, $C_4'$-H)<br>7.80 (d, 1H, $C_5'$-H, $J = 8.12$ Hz)<br>8.00 (d, 1H, $C_8'$-H, $J = 8.56$ Hz) | 0.84 (t, 3H, $C_1$-H, $J = 14.1$ Hz)<br>1.40 (m, 2H, $C_2$-H)<br>1.65 (m, 2H, $C_3$-H)<br>1.84 (t, 3H, $C_4$-H, $J = 7.32$ Hz) | −207.8 |
| $Ph_2Sn$ ($L_{III}$) | — | 9.32 (s, 1H) | 4.83 (s, 2H) | 2.69 (s, 3H) | 5.59 (br, 1H) | 7.60 (s, 1H) | 8.23 (m, 1H, $C_2'$-H)<br>7.53–7.60 (m, 3H, $C_3'$-H, $C_6'$-H, $C_7'$-H)<br>7.90 (m, 1H, $C_4'$-H)<br>7.80 (d, 1H, $C_5'$-H, $J = 8.12$ Hz)<br>8.00 (d, 1H, $C_8'$-H, $J = 8.56$ Hz) | 6.79–7.80 (m, 7H) | −336.4 |

are consistent with those reported in the literature.[13] The methylene and methyl protons of pyridoxal moiety of the ligands resonate at $\delta$ 4.68–4.69 and $\delta$ 2.51–2.57, and these signals appeared in the complexes with slight shifts in their positions. All of these data are consistent with the conclusions drawn from the IR spectral studies and support the dibasic tridentate ONO coordination mode. Examples of the spectra for $H2L_I$ and $Bu_2Sn(L_I)$ are shown in the Supplemental Materials (Figures S1–S5, available online).

The $^{13}$C-NMR spectra of the ligands and their organotin (IV) complexes were recorded in $CDCl_3$ and dry DMSO-$d_6$ (Table 2). The signals due to methyl and butyl groups attached to the tin atom appeared at 10.3–10.9 and $\delta$ 26.8, 22.6, 19.5, 13.5, respectively, and the carbons of the phenyl group attached to tin appeared at $\delta$ 149.8, 135.5, 128.5, 130.2. The peaks at $\delta$ 155.0–156.9 and $\delta$ 162.9–169.7 are due to the carbon of azomethine (C=N) and carbon of carbonyl (C=O). The peaks observed at $\delta$ 59.1–61.5 were assignable to the methine carbons of pyridoxal groups. The signals of aromatic carbons for pyridyl group were observed in the range of $\delta$ 158.9–159.8 for ($C_2'$, $C_6'$), $\delta$ 121.7–122.5 for ($C_3'$, $C_5'$), and $\delta$ 140.3–140.9 for ($C_4'$). In the case of 2-thenyl these signals were in the range of $\delta$ 153.0–153.7, 136.4–139.1, 127.3–129.2, and 134.2–135.4 for ($C_1'$), ($C_2'$), ($C_3'$), and ($C_4'$) carbons, respectively. For the 1-napthyl group it was observed in the range of 151.2–151.9, 139.1–140.7, 132.4–132.9, 136.0–136.7, 124.6–125.3, 128.6–129.6, 127.0–127.7, 129.2–130.2, 133.5–134.9, and 136.2–137.4 for ($C_1'$) to ($C_{10}'$) carbons in the complexes. The spectra of all tin complexes showed a significant downfield shift of all carbon resonances compared with the free ligand. The shift was a consequence of an electron density transfer from the ligand to the acceptor, which is consistent with that reported in the literature.[14]

The $^{119}$Sn chemical shift values of tin complexes were found to be in the range of $\delta$ −185.3 to −207.8 for the complexes where R = methyl or butyl and $\delta$ −334.8 to −336.4 when R = phenyl.[15] The appearance of chemical shift values in this region indicated a penta-coordinated environment around the central tin atoms in these complexes. The chemical shift of $^{119}$Sn is affected by (i) the nature of the R group directly attached to the tin atom and (ii) the type of donor atom of the ligand. In cases when R = phenyl, the localized system of this group allows for p$\pi$-d$\pi$ interaction to dominate shielding of the $^{119}$Sn values.[16] The coupling constant $^1J(^{119}Sn-^{13}C)$ was observed in the range of 562–598.5 Hz for methyl derivatives and for phenyl it was observed in the range of 614.4–627.6 Hz. The parameters of $^{119}$Sn−NMR spectra, that is, values of the chemical shift, confirm the five coordination of complexes.[17,18]

## EXPERIMENTAL

All of the operations were carried out in an inert atmosphere using dry nitrogen on a vacuum line. The solvent used was dried by conventional methods. Sn and Cl contents in the complexes were estimated gravimetrically. Elements (C, H, N, and S) were analyzed on a Perkin-Elmer 2400 instrument. The Fourier transform infrared (FTIR) spectra (4000–400 $cm^{-1}$) were obtained in KBr pellets on a Perkin-Elmer spectrum RX1 instrument. $^1$H-, $^{13}$C-, and $^{119}$Sn−NMR spectra were determined on a Bruker Avance II 400 MHz NMR spectrometer in $CDCl_3$ and DMSO-$d_6$ using tetramethylsilane (TMS) as an internal standard at Chandigarh, India. Molecular weights of the complexes were determined by cryoscopic method in dry nitrobenzene. Molar conductance measurements were carried out using a model 306 Systronics conductivity bridge in dimethyl sulfoxide (DMSO) solvent.

**Table 2** $^{13}C$ NMR spectral data ($\delta$) of the ligands and their metal complexes

| Compound | >**C**=N | **C**=O | -**C**$H_2$OH | Methyl/Butyl/Phenyl | Aromatic **C** |
|---|---|---|---|---|---|
| $H_2L_I$ | 157.7 | 162.4 | 62.5 | — | 151.2 ($C_2'$, $C_6'$), 120.0 ($C_3'$,$C_5'$) 140.2 ($C_4'$) |
| $H_2L_{II}$ | 154.4 | 161.2 | 64.0 | — | 150.0 ($C_1'$), 134.4 ($C_2'$), 124.8 ($C_3'$), 131.3 ($C_4'$) |
| $H_2L_{III}$ | 158.7 | 164.3 | 62.3 | — | 150.2 ($C_1'$), 132.8 ($C_2'$), 127.3 ($C_3'$), 134.0 ($C_4'$), 124.9 ($C_5'$), 126.2 ($C_6'$), 135.5 ($C_7'$), 124.2 ($C_8'$), 130.1 ($C_9'$), 131.9 ($C_{10}'$) |
| $Me_2Sn$ ($L_I$) | 156.2 | 168.6 | 61.2 | 10.3 | 159.1 ($C_2'$, $C_6'$), 122.3 ($C_3'$,$C_5'$), 140.4 ($C_4'$) |
| $Bu_2Sn$ ($L_I$) | 155.0 | 168.2 | 60.2 | 26.8, 22.6, 19.5, 13.5 | 159.8 ($C_2'$, $C_6'$) 121.7 ($C_3'$,$C_5'$) 140.9 ($C_4'$) |
| $Ph_2Sn$ ($L_I$) | 156.4 | 165.5 | 60.9 | 149.8, 135.5, 128.5, 130.2 | 158.9 ($C_2'$, $C_6'$) 122.5 ($C_3'$,$C_5'$) 140.3 ($C_4'$) |
| $Me_2Sn$ ($L_{II}$) | 155.0 | 162.9 | 59.5 | 10.5 | 153.7 ($C_1'$), 136.4 ($C_2'$), 128.2 ($C_3'$), 134.2 ($C_4'$) |
| $Bu_2Sn$ ($L_{II}$) | 156.3 | 165.8 | 59.1 | 26.3, 24.0, 19.3, 13.3 | 153.0 ($C_1'$), 136.8 ($C_2'$), 127.3 ($C_3'$), 135.4 ($C_4'$) |
| $Ph_2Sn$ ($L_{II}$) | 156.9 | 165.9 | 59.2 | 149.5, 137.7, 126.3, 130.1 | 153.4 ($C_1'$), 139.1 ($C_2'$), 129.2 ($C_3'$),134.8 ($C_4'$) |
| $Me_2Sn$ ($L_{III}$) | 155.3 | 169.3 | 60.5 | 10.9 | 151.6 ($C_1'$), 139.2 ($C_2'$), 132.7 ($C_3'$), 136.7 ($C_4'$), 124.6 ($C_5'$), 128.6 ($C_6'$), 127.0 ($C_7'$), 129.2 ($C_8'$), 133.5 ($C_9'$), 136.2 ($C_{10}'$) |
| $Bu_2Sn$ ($L_{III}$) | 155.0 | 169.7 | 60.2 | 26.5, 22.5, 19.7, 13.4 | 151.9 ($C_1'$), 140.7 ($C_2'$), 132.4 ($C_3'$), 136.0 ($C_4'$), 125.3 ($C_5'$), 128.8 ($C_6'$), 127.3 ($C_7'$), 129.2 ($C_8'$), 134.9 ($C_9'$), 137.4 ($C_{10}'$) |
| $Ph_2Sn$ ($L_{III}$) | 155.2 | 168.3 | 61.5 | 147.5, 135.2, 128.2, 13.2 | 151.2 ($C_1'$), 139.1 ($C_2'$), 132.9 ($C_3'$), 136.6 ($C_4'$), 125.0 ($C_5'$), 129.6 ($C_6'$), 127.7 ($C_7'$), 130.2 ($C_8'$), 134.7 ($C_9'$), 136.6 ($C_{10}'$) |

**Table 3** Analytical data of the ligands and their metal complexes

| Ligands/Complexes | m.p. (°C) | Color | Yield (%) | Analysis (%) Found (Calcd.) | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | C | H | N | S | Sn |
| $H_2L_I$ | 261–263 | Orange | 82 | 58.53 (58.73) | 4.72 (4.93) | 19.24 (19.57) | — | — |
| $H_2L_{II}$ | 255 d[a] | Pale yellow | 84 | 51.45 (51.14) | 4.09 (4.29) | 17.99 (18.35) | 10.17 (10.50) | — |
| $H_2L_{III}$ | 280 d[a] | Light brown | 77 | 66.21 (66.10) | 5.09 (5.27) | 15.10 (15.42) | — | — |
| $Me_2Sn$ ($L_I$) | 272–275 | Orange | 75 | 44.10 (44.38) | 3.98 (4.19) | 12.66 (12.94) | — | 27.08 (27.41) |
| $Bu_2Sn$ ($L_I$) | 280–281 | Yellow | 65 | 50.79 (51.09) | 5.66 (5.85) | 10.56 (10.83) | — | 22.56 (22.95) |
| $Ph_2Sn$ ($L_I$) | 292–294 | Light yellow | 75 | 55.78 (56.05) | 3.81 (3.98) | 9.88 (10.06) | — | 20.89 (21.31) |
| $Me_2Sn$ ($L_{II}$) | 110–112 | Yellow | 72 | 40.79 (41.12) | 3.76 (3.91) | 9.37 (9.59) | 7.07 (7.32) | 26.72 (27.10) |
| $Bu_2Sn$ ($L_{II}$) | 122–125 | Pale yellow | 68 | 47.99 (48.30) | 5.28 (5.60) | 7.86 (8.05) | 5.95 (6.14) | 22.40 (22.73) |
| $Ph_2Sn$ ($L_{II}$) | 158–160 | Light yellow | 74 | 53.68 (53.41) | 3.51 (3.76) | 7.26 (7.47) | 5.51 (5.70) | 20.76 (21.11) |
| $Me_2Sn$ ($L_{III}$) | 212–215 | Light brown | 72 | 53.46 (53.15) | 4.79 (4.87) | 8.22 (8.45) | — | 23.51 (23.88) |
| $Bu_2Sn$ ($L_{III}$) | 234–238 | Light brown | 67 | 57.37 (57.75) | 6.14 (6.40) | 7.02 (7.22) | — | 20.02 (20.39) |
| $Ph_2Sn$ ($L_{III}$) | 250–252 | Brown | 70 | 61.44 (61.76) | 4.47 (4.70) | 6.54 (6.75) | — | 18.81 (19.08) |

[a]d = Decomposition temperature.

### Preparation of Schiff Base Ligands

Pyridoxal isonicotinoyl hydrazone was synthesized by dissolving pyridoxal hydrochloride (3 g, 15 mmol) in distilled water (30 mL) with continuous stirring. Isonicotinic acid hydrazide (2.1 g, 15 mmol) was separately dissolved in 50% of ethanol (30 mL). The two reactants were mixed with continuous stirring followed by the addition of a solution of sodium acetate (1.2 g) in distilled water (15 mL). The reaction mixture was refluxed in a steam bath for 1 h and the solution was kept overnight at room temperature. The orange solid product so obtained was recrystallized from the mixture of benzene and methanol in a 2:1 ratio. A similar procedure was adopted for 2-thiophenecarboxylic acid hydrazide and 1-naphthoic acid hydrazides with pyridoxal hydrochloride.

### Preparation of Complexes

A solution of dichlorodialkyltin (IV) (10 mmol) in dry benzene (20 mL) was added dropwise with constant stirring to a solution of pyridoxal-substituted hydrazone (10 mmol) and triethylamine (10 mmol) in the same solvent 30 mL under a dry nitrogen atmosphere at room temperature. The reaction mixture was stirred for 3 h and the white precipitate of triethylammonium chloride obtained was filtered off. The excess solvent was removed under vacuum. The yellow solid complex was washed with $CH_2Cl_2$/petroleum ether (30–60 °C) to ensure the purity of the product and finally dried under vacuum. The analytical data of the resulting complexes are recorded in Table 3.

### Biological Activities

**Antibacterial and Antifungal Activity.** The in vitro antibacterial and antifungal activity of ligands and their organotin (IV) complexes were studied against the phytopathogenic fungi *Candida albicans* and *Aspergillus niger* and the bacteria *Bacillus subtilis*, *Escherichia coli*, and *Staphylococcus aureus* by adopting the same procedure as reported earlier[19] by dissolving the compounds in DMSO to give a concentration of 100 $\mu$g/mL and used as a stock solution (see Supplemental Materials, Table S1).

**Antimicrobial Activity.** The ligands and their corresponding dichlorodiorganotin (IV) complexes were subjected to in vitro antimicrobial studies. Antibacterial activity was done by the serial dilution method on the following strains: *Bacillus subtilis* (MTCC no. 2063), *Staphylococcus aureus* (MTCC no. 2901), and *Escherichia coli* (MTCC no. 1652), under the standard conditions of temperature of 37 °C ± 1 °C and relative humidity of 40 ± 5% for 24 h.

## CONCLUSION

Dichlorodiorganotin (IV) complexes of pyridoxal aroylhydrazones were synthesized, characterized, and screened against pathogenic bacteria and fungi. The presence of a toxophorically important group -CON < & -CSN < was found to be responsible for antimicrobial activity of the ligands.[20] Dichlorodiorganotin (IV) complexes show a higher antimicrobial activity compared to the free ligands. On complexation, the in vitro antimicrobial activity of the ligands was enhanced, which may be explained on the basis of chelation theory. This reduces the polarity of the central metal ion, thereby increasing the lipophilic nature of the metal complex, which susequently favors its permeation through

the lipid layer of the cell membrane of the microorganism and results in interference with normal cell processes.

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