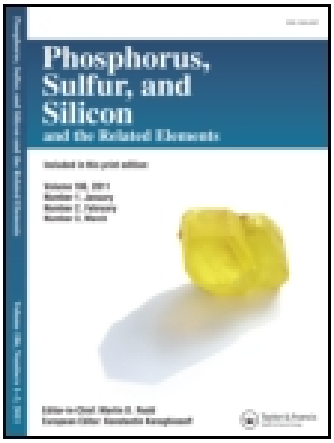

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Bioactive Penta-Coordinated Diorganotin(Iv) Complexes of Pyridoxalimine Schiff Bases

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BIOACTIVE PENTA-COORDINATED DIORGANOTIN(IV) COMPLEXES OF PYRIDOXALIMINE SCHIFF BASES

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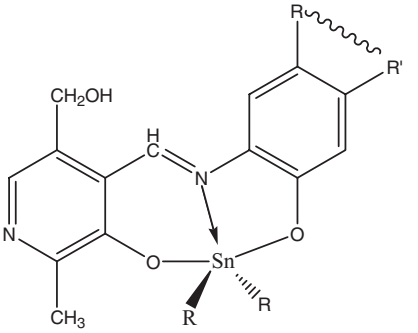
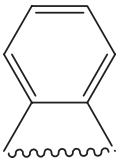
GRAPHICAL ABSTRACT



R = Me, Bu, Ph



	R	R'
H_2L^1 =	-H	- H
H_2L^2 =	$-CH_3$	-H
H_2L^3 =	-Cl	-H
H_2L^4 =	$-NO_2$	-H
H_2L^5 =		

Abstract *Diorganotin(IV) complexes of an extended system derived from the condensation of pyridoxal hydrochloride with 2-amino phenol (H_2L^1), 2-amino-4-methyl phenol (H_2L^2), 2-amino-4-chloro phenol (H_2L^3), 2-amino-4-nitro phenol (H_2L^4), 1-amino-2-naphthol hydrochloride (H_2L^5) have been synthesized by the reaction of dichlorodiorganotin(IV) in a 1:1 molar ratio with these ligands. Spectral studies (IR, ^1H, ^{13}C, ^{119}Sn NMR) along with physical data evidenced the formation of penta-coordinated species with the ligands acting as tridentate (ONO) with oxygen occupying the axial positions, and nitrogen at one of the equatorial positions. The ligands and their organotin complexes have been evaluated for antimicrobial activity against phytopathogenic fungi Candida albicans and Aspergillus niger at 25 ± 1 °C and bacteria Bacillus subtilis, Escherichia coli, and Staphylococcus aureus at 37 ± 1 °C. The activities of the ligands have been enhanced on complexation and the results indicate that they exhibit significant antimicrobial properties.*

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Keywords Schiff base; pyridoxal hydrochloride; diorganotin (IV) complexes

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INTRODUCTION

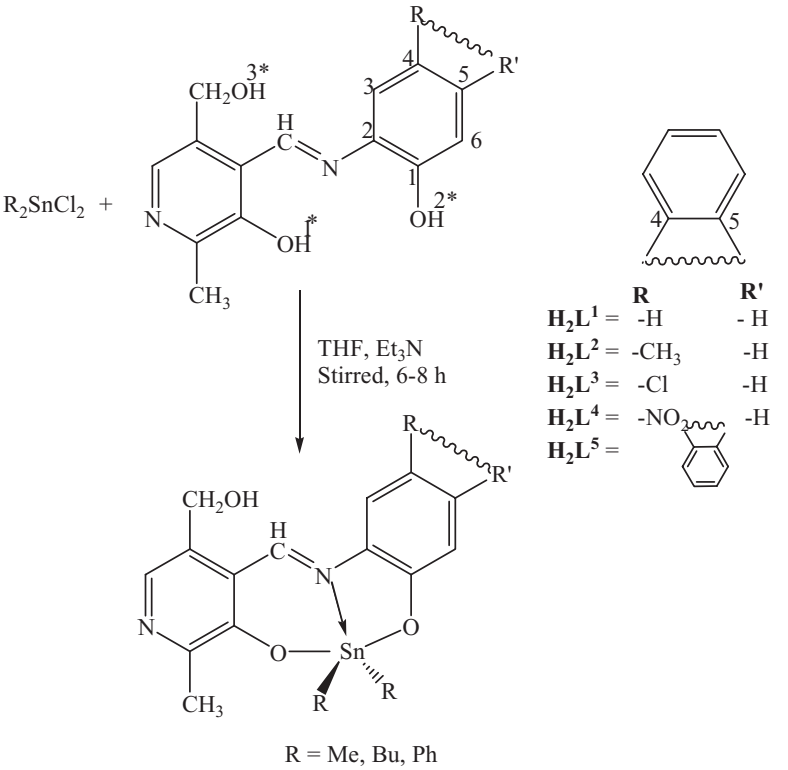
Considerable importance has been given to pyridoxal having a pyridine ring, hydroxyl, and hydroxymethyl substituents, which may help to balance hormonal changes in women and aid the immune system and account of other different biological properties.[1] Lack of pyridoxine may cause anemia, nerve damage, seizures, skin problems, and sores in the mouth.[2] A wide variety of biological effects have been shown by organotin complexes including bactericidal, acaricidal, fungicidal,[3,4] antiinflammatory,[5] anti-HIV,[6] anticancer,[7] and antitumor agents.[8,9] A great amount of attention has been given to the biological activity of organotin(IV) complexes with tridentate Schiff bases which are of particular interest for existing in lactum or lactim tautomeric forms, giving variations to their donating properties. It has been reported that these compound showed remarkable enhancement in biological activities when combined to organotinhalides.[10] We are more concerned with the antimicrobial activity of organotin(IV) compounds, keeping this in mind and in continuation of our work, on the synthesis of biologically active compounds containing N, O, S, and their organotin/silicon complexes.[11–14] We report the synthesis of new complexes of Schiff bases derived from the condensation of pyridoxal hydrochloride with derivatives of aminophenol and studied the effect of introducing tin on the activity of the ligand.

RESULTS AND DISCUSSION

Pyridoxal-substituted imines (H_2L^1– H_2L^5) have been prepared by the condensation of pyridoxal hydrochloride with substituted aminophenols. The progress of reaction was regularly monitored by thin layer chromatography. The reaction of dichlorodiorganotin(IV) R_2SnCl_2 (R = Me, Bu, and Ph) with ligands (H_2L^1– H_2L^5) in 1:1 molar ratio at room temperature afforded the complexes which were characterized by elemental analyses, IR, ^1H, ^{13}C, and ^{119}Sn NMR. All the complexes have been obtained as solids, insoluble in most organic solvents. The low values of molar conductivity (7.0–15.0 Ω^{-1} cm^2 mol^{-1}) of the complexes in dry dimethylformamide indicate their nonelectrolytic nature (see Scheme 1).

IR Spectra

The strong broad band due to ν(O-H) appeared at approximately 3155–3180 cm^{-1} in the ligands showing hydrogen bonding with the nitrogen of the azomethine group. The intensity of which was considerably reduced in the spectra of complexes indicating the deprotonation of hydroxyl group of the ligands and involvement of both phenolate oxygens in bonding to tin, which was further authenticated by the appearance of new band in the spectra of complexes at 1264–1280 cm^{-1} assigned to ν(C-O) band. In all the tin complexes of pyridoxal substituted imines, the ν(C=N) band, appeared at 1603–1612 cm^{-1} was shifted toward lower frequencies as compared to the parent Schiff base confirming the coordination through azomethine nitrogen to diorganotin(IV) moiety due to electron density transfer from nitrogen to tin atom, thus resulting in the weakening of the C=N bond.[15] In the spectra, some new bands assigned in the region 517–577 cm^{-1}, 616–742 cm^{-1}, and 446–529 cm^{-1} were due to Sn-O, Sn-C, and Sn-N bonds that were absent in the precursors, further indicated formation of complexes.[12]



Scheme 1

^{1}H NMR Spectra

In ^{1}H NMR, chemical shift assignments of ligands and their diorganotin(IV) complexes were assigned on the basis of multiplicity patterns and/or resonance intensities. Broad singlets were observed for both phenolic O-H appeared at δ 12.13–15.00 (OH-1*) and δ 9.54–10.14 (OH-2*). A singlet of azomethine proton appeared in the range of δ 9.24–9.36. Alcoholic proton as a singlet of (CH_2-O**H**) group was observed at δ 5.12–5.38 in the ligands while methylene and methyl proton of pyridoxal moiety appeared at δ 4.60–4.79 and δ 2.45–2.54, respectively.

The ^{1}H NMR data of the ligands and their diorganotin(IV) complexes is given in Tables 1 and 2. The absence of the O-H(1* & 2*) proton signal in the complexes showed deprotonation when attached to tin atom. The downfield shift of ≈0.3 ppm was observed in chemical shift values of azomethine CH=N proton with ^{3}J (^{119}Sn, ^{1}H) coupling constant value in the range 39–47 Hz[16] supported the involvement of azomethine nitrogen in coordination. On complexation, not much variation is observed in the chemical shift value of methylene, methyl proton, and proton of OH of CH_2OH group of pyridoxal moiety. The spectra showed that the chemical shifts of the butyl group attached to tin appeared as a multiplet in the region δ 0.77–1.88 where as protons due to phenyl ring and methyl appeared as a multiplet in the region δ 6.68–7.94 and a singlet in the region δ 1.34–1.51, respectively. The ^{2}J [^{119}Sn, ^{1}H] coupling constants were in the range (76–81 Hz) for Me_2SnL complexes and supported a trigonal bipyramidal geometry.[17] The integrated proton ratio

Table 1 ^{1}H NMR spectral characteristics (δ) of pyridoxalimine Schiff bases

Ligand	C−OH$^{*(1)}$	C−OH$^{*(2)}$	−CH=N−	CH_2−OH	C−CH_3	C−OH$^{*(3)}$	C_6−H	Aromatic ring protons
H_2L^1	15.00(bs)	10.14(bs)	9.24(s)	4.60(s)	2.50(s)	5.12(bs)	7.94(s)	7.69 (d, 1H, C_3'- H, J = 7.8 Hz) 6.83 (t, 1H, C_4'-H,) 7.13 (t, 1H, C_5'- H,) 6.83 (d, 1H, C_6'- H, J = 8.0 Hz)
H_2L^2	14.70(bs)	9.54(bs)	9.26(s)	4.76(s)	2.46(s)	5.38(bs)	8.01(s)	7.16 (s, 1H, C_3'- H) 6.96 (d, 1H, C_5'-H, J = 8.1 Hz) 6.90 (d,1H, C_6'- H, J = 8.1 Hz)
H_2L^3	14.31(bs)	9.54(bs)	9.24(s)	4.78(s)	2.45(s)	5.23(bs)	8.14(s)	7.94 (s, 1H, C_3'- H) 7.51 (d, 1H, C_5'-H, J = 8.0 Hz) 7.14 (d, 1H, C_6'- H, J = 8.0 Hz)
H_2L^4	14.22(bs)	9.65(bs)	9.24(s)	4.78(s)	2.52(s)	5.17(bs)	8.34(s)	8.06 (s, 1H, C_3'- H) 7.71 (d, 1H, C_5'-H, J = 9.0 Hz) 7.08 (d, 1H, C_6'- H, J = 9.0 Hz)
H_2L^5	12.13(bs)	9.84(bs)	9.36(s)	4.79(s)	2.54(s)	5.20(bs)	8.15(s)	7.61–8.50 (m, 6H)

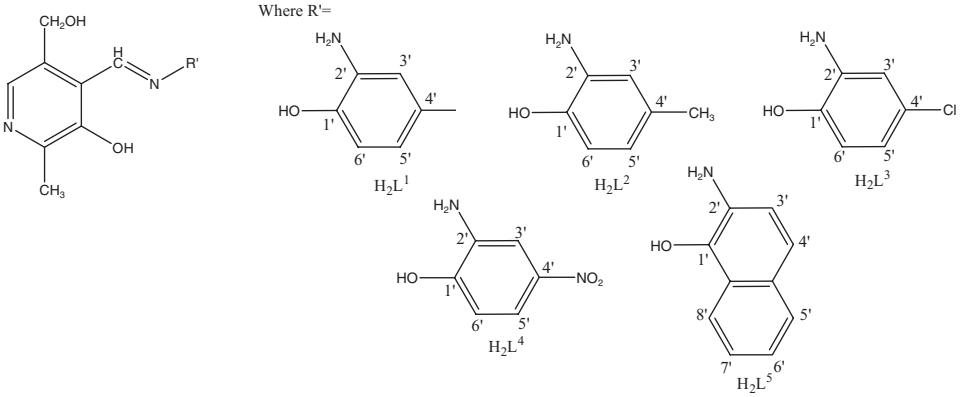
*OH group attached to different carbon atoms as in Scheme 1.

Table 2 ^{1}H NMR spectral characteristics $^{*}(\delta)$ of diorganotin (IV) complexes of pyridoxalimine Schiff bases

Complexes	−CH=N− ^{3}J[^{119} Sn,^{1}H] in [Hz]	CH_2-OH	$C-CH_3$	$C-OH^{*(3)}$	C−H	Aromatic ring protons	Me/Bu/Ph-Sn, ^{2}J[^{119} Sn,^{1}H] in [Hz]
$Me_2Sn(L^1)$	9.44(s)[45]	4.73(s)	2.52(s)	5.45(bs)	8.12(s)	7.71 (d, 1H, C_3'- H, J = 6.8 Hz) 6.80 (t, 1H, C_4'-H) 7.15 (t, 1H, C_5'- H) 6.93 (d, 1H, C_6'- H, J = 8.0 Hz)	1.40 (s, 6H) [79]
$Bu_2Sn(L^1)$	9.43(s)[39]	4.78(s)	2.68(s)	5.35(bs)	8.14(s)	7.75 (d, 1H, C_3'- H, J = 7.4 Hz) 6.83 (t, 1H, C_4'-H) 7.13 (t, 1H, C_5'- H) 6.83 (d, 1H, C_6'- H, J = 7.2 Hz)	0.89–1.78 (m, 18H)
$Ph_2Sn(L^1)$	9.32(s)[47]	4.88(s)	2.60(s)	5.29(bs)	8.02(s)	7.75 (d, 1H, C_3'- H, J = 7.4 Hz) 6.83 (t, 1H, C_4'-H) 7.13 (t, 1H, C_5'- H) 6.83 (d, 1H, C_6'- H, J = 7.2 Hz)	6.80–7.69 (m, 10H)
$Me_2Sn(L^2)$	9.50(s)[45]	4.87(s)	2.63(s)	5.47(bs)	8.05(s)	7.19 (s, 1H, C_3'- H) 6.96 (d, 1H, C_5'-H, J = 8.2 Hz) 6.95 (d,1H, C_6'- H, J = 8.2 Hz)	1.47 (s, 6H) [80]
$Bu_2Sn(L^2)$	9.45(s)[46]	4.80(s)	2.61(s)	5.29(bs)	8.11(s)	7.18 (s, 1H, C_3'- H) 7.02 (d, 1H, C_5'-H, J = 7.8 Hz) 6.96 (d,1H, C_6'- H, J = 7.8 Hz)	0.95–1.88 (m, 18H)
$Ph_2Sn(L^2)$	9.41(s)[39]	4.74(s)	2.51(s)	5.33(bs)	8.13(s)	7.19 (s, 1H, C_3'- H) 6.96 (d, 1H, C_5'-H, J = 8.2 Hz) 6.95 (d,1H, C_6'- H, J = 8.2 Hz)	6.68–7.80 (m, 10H)
$Me_2Sn(L^3)$	9.43(s)[49]	4.77(s)	2.66(s)	5.44(bs)	8.16(s)	7.94 (s, 1H, C_3'- H) 7.55 (d, 1H, C_5'-H, J = 7.4 Hz) 7.19 (d, 1H, C_6'- H, J = 7.4 Hz)	1.51 (s, 6H) [81]
$Bu_2Sn(L^3)$	9.35(s)[45]	4.85(s)	2.62(s)	5.49(bs)	8.04(s)	7.98 (s, 1H, C_3'- H) 7.54 (d, 1H, C_5'-H, J = 7.8 Hz) 7.17 (d, 1H, C_6'- H, J = 7.8 Hz)	0.81–1.75 (m, 18H)
$Ph_2Sn(L^3)$	9.51(s)[47]	4.86(s)	2.63(s)	5.50(bs)	8.05(s)	7.94 (s, 1H, C_3'- H) 7.55 (d, 1H, C_5'-H, J = 7.4 Hz) 7.19 (d, 1H, C_6'- H, J = 7.4 Hz)	6.70–7.94 (m, 10H)
$Me_2Sn(L^4)$	9.54(s)[45]	4.82(s)	2.60(s)	5.30(bs)	8.13(s)	8.10 (s, 1H, C_3'- H) 7.75 (d, 1H, C_5'-H, J = 8.2 Hz) 7.10 (d, 1H, C_6'- H, J = 8.2 Hz)	1.34 (s, 6H) [76]
$Bu_2Sn(L^4)$	9.43(s)[46]	4.74(s)	2.51(s)	5.57(bs)	8.11(s)	8.12 (s, 1H, C_3'- H) 7.70 (d, 1H, C_5'-H, J = 8.4 Hz) 7.15 (d, 1H, C_6'- H, J = 8.4 Hz)	0.77–1.69 (m, 18H)
$Ph_2Sn(L^4)$	9.47(s)[39]	4.79(s)	2.67(s)	5.59(bs)	8.16(s)	8.12 (s, 1H, C_3'- H) 7.70 (d, 1H, C_5'-H, J = 8.4 Hz) 7.15 (d, 1H, C_6'- H, J = 8.4 Hz)	6.72–7.90 (m, 10H)
$Me_2Sn(L^5)$	9.35(s)[45]	4.88(s)	2.62(s)	5.62(bs)	8.04(s)	7.55–8.57 (m, 6H)	1.49 (s, 6H) [80]
$Bu_2Sn(L^5)$	9.55(s)[47]	4.85(s)	2.66(s)	5.65(bs)	8.07(s)	7.72–8.55 (m, 6H)	0.85–1.78 (m, 18H)
$Ph_2Sn(L^5)$	9.54(s)[39]	4.81(s)	2.60(s)	5.62(bs)	8.10(s)	7.70–8.62 (m, 6H)	6.77–7.53 (m, 10H)

*Chemical shift (δ) in ppm. Multiplicity is given as s = singlet; d = doublet; m = multiplet; and bs = broad singlet.

Table 3 ^{13}C NMR spectral characteristics (δ) of pyridoxalimine Schiff bases



Ligand	>C=N	$-CH_2OH$	Aromatic C
H_2L^1	163.7	58.8	148.8 (C_1'), 136.7 (C_2'), 127.8 (C_3'), 124.8 (C_4'), 128.6 (C_5'), 118.4 (C_6')
H_2L^2	157.7	58.8	149.1 (C_1'), 137.2 (C_2'), 132.5 (C_3'), 128.3 (C_4'), 129.3 (C_5'), 119.6 (C_6')
H_2L^3	159.5	58.5	148.5 (C_1'), 137.6 (C_2'), 123.3 (C_3'), 127.7 (C_4'), 128.1 (C_5'), 119.1 (C_6')
H_2L^4	161.0	58.4	153.6 (C_1'), 138.7 (C_2'), 124.6 (C_3'), 145.5 (C_4'), 124.6 (C_5'), 119.8 (C_6')
H_2L^5	160.4	60.1	146.7 (C_1'), 138.3 (C_2'), 121.5 (C_3'), 133.2 (C_4'), 127.5 (C_5'), 124.5 (C_6'), 125.9 (C_7'), 126.3 (C_8'), 130.9 (C_9'), 111.0 (C_{10}')

for each group was in agreement with the proposed structures. All these data are consistent with the conclusions drawn from the IR spectral studies and support the dibasic tridentate ONO coordination mode of the ligands.

^{13}C NMR Spectra

^{13}C NMR spectra of ligands as well as their complexes were recorded with dimethyl sulfoxide (DMSO)-d_6 (Tables 3 and 4). The spectra of all tin complexes showed a significant downfield shift of all carbon resonances as compared to 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 literature.[11]

The signals due to methyl groups attached to the tin atom appeared at δ 10.3–10.9. The butyl group can be supported via the four bands due to carbon 1 to 4 in (Sn-$^1CH_2$ $^2CH_2$ $^3CH_2$ $^4CH_3$) at δ 28.3–32.8, δ 26.2–26.9, δ 19.3–19.7, and δ 13.3–13.7. The carbons of the phenyl group attached to tin appeared at δ 145.8–148.5, 135.2–136.7, 125.3–129.3, and 130.4–132.2. A downfield shift in the value of azomethine HC=N proton from 157.7–163.7 to 162.9–169.7 was observed on complexation. The peak observed at δ 60.2–62.1 was assignable to the carbon of CH_2OH group of pyridoxal.

Table 4 ^{13}C and ^{119}Sn NMR characterization (δ) of diorganotin(IV) complexes of pyridoxalimine Schiff bases

Complexes	>C=N	$-CH_2OH$	Aromatic C	Sn-Me/Bu/Ph	^{119}Sn
$Me_2Sn(L^1)$	168.6	61.2	149.2 (C_1'), 138.0 (C_2'), 126.7 (C_3'), 124.9 (C_4'), 128.7 (C_5'), 119.4 (C_6')	10.3	−185.3
$Bu_2Sn(L^1)$	168.2	60.2	148.8 (C_1'), 137.7 (C_2'), 127.8 (C_3'), 125.0 (C_4'), 128.8 (C_5'), 118.5 (C_6')	32.8, 26.5, 19.3, 13.3	−203.8
$Ph_2Sn(L^1)$	165.5	60.9	149.0 (C_1'), 136.7 (C_2'), 128.0 (C_3'), 124.9 (C_4'), 128.0 (C_5'), 118.7 (C_6')	145.8, 135.5, 127.5, 131.2	−331.6
$Me_2Sn(L^2)$	162.9	61.5	150.1 (C_1'), 137.4 (C_2'), 127.8 (C_3'), 125.1 (C_4'), 128.8 (C_5'), 118.5 (C_6')	10.5	−180.7
$Bu_2Sn(L^2)$	165.8	62.1	150.2 (C_1'), 137.5 (C_2'), 126.6 (C_3'), 125.2 (C_4'), 128.8 (C_5'), 119.2 (C_6')	28.9, 26.9, 19.3, 13.5	−190.3
$Ph_2Sn(L^2)$	165.9	61.2	150.5 (C_1'), 136.8 (C_2'), 126.6 (C_3'), 124.7 (C_4'), 128.8 (C_5'), 119.0 (C_6')	148.5, 135.7, 125.3, 130.5	−333.2
$Me_2Sn(L^3)$	169.3	60.5	148.6 (C_1'), 135.4 (C_2'), 127.9 (C_3'), 123.6 (C_4'), 128.8 (C_5'), 119.2 (C_6')	10.9	−189.3
$Bu_2Sn(L^3)$	169.7	60.2	149.2 (C_1'), 137.2 (C_2'), 127.7 (C_3'), 124.8 (C_4'), 128.9 (C_5'), 119.7 (C_6')	29.3, 26.2, 19.7, 13.7	−334.8
$Ph_2Sn(L^3)$	168.3	61.5	148.3 (C_1'), 136.5 (C_2'), 127.8 (C_3'), 125.2 (C_4'), 128.8 (C_5'), 118.6 (C_6')	146.5, 135.2, 126.2, 131.5	−335.7
$Me_2Sn(L^4)$	168.6	61.2	149.1 (C_1'), 138.0 (C_2'), 127.8 (C_3'), 125.0 (C_4'), 128.6 (C_5'), 119.0 (C_6')	10.3	−184.4
$Bu_2Sn(L^4)$	168.2	60.2	148.5(C_1'), 137.0 (C_2'), 127.8 (C_3'), 125.9 (C_4'), 128.6 (C_5'), 118.8 (C_6')	28.6, 26.8, 19.5, 13.5	−185.3
$Ph_2Sn(L^4)$	165.5	60.9	150.2 (C_1'), 138.1 (C_2'), 127.9 (C_3'), 124.8 (C_4'), 128.6 (C_5'), 118.5 (C_6')	147.8, 136.5, 126.5, 132.2	−337.5
$Me_2Sn(L^5)$	162.9	60.5	150.4 (C_1'), 137.1 (C_2'), 127.8 (C_3'), 124.8 (C_4'), 128.6 (C_5'), 118.6 (C_6') 125.9 (C_7'), 126.3 (C_8'), 130.6 (C_9'), 111.4 (C_{10}')	10.5	−189.8
$Bu_2Sn(L^5)$	165.8	61.1	150.7 (C_1'), 137.7 (C_2'), 127.7 (C_3'), 125.1 (C_4'), 128.7 (C_5'), 118.6 (C_6') 125.9 (C_7'), 126.3 (C_8'), 130.9 (C_9'), 112.54 (C_{10}')	28.3, 26.3, 19.3, 13.3	−210.3
$Ph_2Sn(L^5)$	165.9	61.2	150.9 (C_1'), 138.1 (C_2'), 127.8 (C_3'), 124.9 (C_4'), 128.7 (C_5'), 118.4 (C_6') 125.9 (C_7'), 126.3 (C_8'), 131.9 (C_9'), 111.3 (C_{10}')	146.5, 136.7, 129.3, 130.4	−340.7

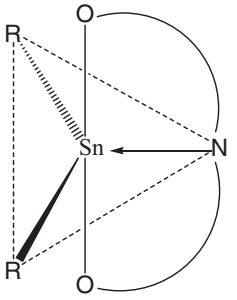


Figure 1 Suggested structure of the complexes and donor site of the ligand.

^{119}Sn NMR Spectra

The chemical shift of ^{119}Sn is affected by several factors, (i) the nature of R group directly attached to the tin atom if R is phenyl, the localized system of this group allows for $p\pi$-$d\pi$ interaction to dominate shielding of the ^{119}Sn values.[18] (ii) The type of donor atom of the ligand. (iii) The geometry around tin atom. The ^{119}Sn NMR spectra of organotin(IV) complexes show only one sharp singlet indicating the formation of single tin species. The ^{119}Sn chemical shift values of tin complexes R_2SnL were found to be in the range of δ –180.7 to –210.3 for the complexes, where R = methyl or butyl and δ –331.6 to –340.7, where R = phenyl (Table 4). The parameters of ^{119}Sn NMR spectra, i.e., values of chemical shift confirm the penta-coordinated environment around the central tin atoms in these complexes (see Fig. 1).

EXPERIMENTAL

All the operations were carried out in an inert atmosphere using dry nitrogen on a vacuum line. The solvent used were dried by the conventional methods. Dimethyltindichloride, dibutyltindichloride, and diphenyltindichloride were obtained through Aldrich and were used as such without any further purification. Tin content was estimated gravimetrically. Elements (C, H, and N) were analyzed on Perkin-Elmer 2400 instrument (Waltham, Massachusetts). The FT-IR spectra (Perkin Elmer, New Jersey) [4000–400 cm^{-1}] were obtained in KBr pellets on Perkin-Elmer spectrum RX1 instrument. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were determined on Bruker Avance II 400 MHz NMR Spectrometer (Bruker, Switzerland) in DMSO-d_6 using tetramethylsilane as an internal standard at SAIF Chandigarh. 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 (Mumbai, India) in DMSO solvent.

Synthesis of Schiff Base Ligands

The pyridoxal hydrochloride (2.03 g, 10 mmol) was dissolved in methanol (25 mL) and added to a solution of sodium methoxide (0.54g, 10 mmol) in the same solvent. A solution of 2-amino-4-methyl phenol (2.72g, 10 mmol) in methanol (10 mL) was added dropwise to the above reaction mixture. The suspension was refluxed for 6–8 h and the mixture was kept for overnight at room temperature. The orange to dark red solids isolated

Table 5 Physical and analytical data of diorganotin(IV)complexes of pyridoxalimine Schiff bases

Compound g (mmol)	Ligand g (mmol)	$(C_2H_5)_3N$ g (mmol)	Molar ratio	Product	Yield (%)	Mp (°C)	Analytical data,% found (calculated)				Molecular weight found (calculated)
							C	H	N	Sn	
Me_2SnCl_2 1.15 (5.24)	H_2L^1 1.35 (5.24)	$(C_2H_5)_3N$ 1.06 (10.48)	1:1:2	$Me_2Sn(L_1)$	90	270–272 d	47.80 (47.45)	4.84 (4.48)	7.25 (6.92)	29.68 (29.31)	412.50 (405.04)
Bu_2SnCl_2 1.67 (5.50)	H_2L^1 1.42 (5.50)	$(C_2H_5)_3N$ 1.11 (11.0)	1:1:2	$Bu_2Sn(L_1)$	72	280–282 d	51.96 (51.64)	6.92 (6.50)	6.39 (6.02)	25.74 (25.52)	453.11 (465.17)
Ph_2SnCl_2 2.11 (6.12)	H_2L^1 1.58 (6.12)	$(C_2H_5)_3N$ 1.22 (12.24)	1:1:2	$Ph_2Sn(L_1)$	86	297–298 d	59.42 (59.01)	4.35 (4.19)	5.55 (5.29)	22.91 (22.43)	516.55 (529.17)
Me_2SnCl_2 1.33 (6.06)	H_2L^2 1.65 (6.06)	$(C_2H_5)_3N$ 1.22 (12.12)	1:1:2	$Me_2Sn(L_2)$	78	271–274 d	49.10 (48.72)	5.05 (4.81)	6.95 (6.68)	28.15 (28.33)	422.10 (419.06)
Bu_2SnCl_2 1.46 (4.83)	H_2L^2 1.31 (4.83)	$(C_2H_5)_3N$ 0.96 (9.66)	1:1:2	$Bu_2Sn(L_2)$	70	302–304 d	55.49 (54.90)	6.79 (6.41)	5.89 (5.57)	23.82 (23.59)	494.43 (503.22)
Ph_2SnCl_2 2.03 (5.93)	H_2L^2 1.61 (5.93)	$(C_2H_5)_3N$ 1.20 (11.86)	1:1:2	$Ph_2Sn(L_2)$	81	261–265 d	60.05 (59.70)	4.30 (4.45)	5.50 (5.16)	22.15 (21.85)	557.60 (543.20)
Me_2SnCl_2 1.48 (6.78)	H_2L^3 1.98 (6.78)	$(C_2H_5)_3N$ 1.36 (13.56)	1:1:2	$Me_2Sn(L_3)$	93	288–290	39.70 (39.58)	3.85 (3.53)	8.97 (8.66)	24.87 (24.45)	498.32 (485.49)
Bu_2SnCl_2 1.41 (4.65)	H_2L^3 1.36 (4.65)	$(C_2H_5)_3N$ 0.94 (9.30)	1:1:2	$Bu_2Sn(L_3)$	85	296–298 d	46.72 (46.39)	5.49 (5.13)	7.70 (7.38)	21.10 (20.84)	582.45 (569.65)
Ph_2SnCl_2 1.60 (4.68)	H_2L^3 1.36 (4.68)	$(C_2H_5)_3N$ 0.94 (9.36)	1:1:2	$Ph_2Sn(L_3)$	88	278–280 d	51.45 (51.22)	3.89 (3.47)	6.60 (6.89)	19.77 (19.47)	620.23 (609.63)
Me_2SnCl_2 1.39 (6.33)	H_2L^4 1.91 (6.33)	$(C_2H_5)_3N$ 1.28 (12.66)	1:1:2	$Me_2Sn(L_4)$	71	265–267	42.97 (42.70)	4.10 (3.81)	9.65 (9.34)	26.70 (26.38)	444.15 (450.03)
Bu_2SnCl_2 1.75 (5.78)	H_2L^4 1.75 (5.78)	$(C_2H_5)_3N$ 1.16 (10.56)	1:1:2	$Bu_2Sn(L_4)$	69	277–279 d	49.27 (49.46)	5.74 (5.47)	8.09 (7.87)	22.10 (22.22)	551.54 (534.19)
Ph_2SnCl_2 2.12 (6.18)	H_2L^4 1.87 (6.18)	$(C_2H_5)_3N$ 1.24 (12.36)	1:1:2	$Ph_2Sn(L_4)$	92	310–314 d	54.47 (54.39)	3.42 (3.69)	7.75 (7.32)	20.95 (20.67)	555.67 (547.17)
Me_2SnCl_2 1.21 (5.55)	H_2L^5 1.71 (5.55)	$(C_2H_5)_3N$ 1.12 (11.10)	1:1:2	$Me_2Sn(L_5)$	85	290–292	52.05 (52.78)	4.87 (4.43)	6.55 (6.16)	26.45 (26.08)	448.78 (455.05)
Bu_2SnCl_2 1.71 (5.63)	H_2L^5 1.73 (5.63)	$(C_2H_5)_3N$ 1.12 (1.26)	1:1:2	$Bu_2Sn(L_5)$	84	297–299 d	58.15 (57.91)	6.30 (5.98)	5.65 (5.19)	22.50 (22.01)	547.94 (539.25)
Ph_2SnCl_2 2.15 (6.26)	H_2L^5 1.93 (6.26)	$(C_2H_5)_3N$ 1.26 (12.52)	1:1:2	$Ph_2Sn(L_5)$	76	325–326 d	62.55 (62.21)	4.08 (4.18)	4.70 (4.84)	20.84 (20.49)	590.21 (579.23)

were filtered, washed with small amount of water to remove sodium chloride, followed by diethyl ether, and then dried. A similar procedure was adopted to isolate other ligands.

Synthesis of Dimethyltin(IV) Complex of 2-Amino-4-Methyl Phenol (H_2L^2)

The complexes were prepared by the reaction of diphenyltindichloride (2.03 g, 5.93 mmol) taken in dry tetrahydrofuran (20 mL) and 5-hydroxymethyl-4-[(2-hydroxy-5-methyl-phenylimino)-methyl]-2-methyl-pyridin-3-ol] (1.61 g, 5.93 mmol) (H_2L^2) and triethylamine (1.20g, 11.86 mmol) taken in a same solvent, at the room temperature under a dry nitrogen atmosphere. The reaction mixture was stirred for 6–8 h. Triethylamine hydrochloride formed was filtered off and excess of the solvent was removed under vacuum. The solid obtained was dried under reduced pressure. The compound was then washed with a mixture of chloroform and n-hexane (50–50 v/v) and finally dried over vacuum. The physical and analytical data of complexes are given in Table 5.

Antimicrobial Activity

Antimicrobial activity of the pyridoxalimine and their corresponding dichlorodiorganotin(IV) complexes are given in Table S1 (online Supplementary Materials). Antibacterial and antifungal activity was carried out by the serial dilution method on the following strains, i.e., *Bacillus subtilis* [Microbial type cultural collection (MTCC) no. 2063], *Staphylococcus aureus* (MTCC no. 2901), *Escherichia coli* (MTCC no. 1652), *Aspergillus niger* (MTCC no1344), and *Candida albicans* (MTCC no.183).

It has been observed that biocidal activity of the ligands was enhanced on complexation with organotin. In general, complexes where phenyl attached to tin were found to be more potent compared to other complexes. The order of inhibiting activity was Sn-Ph > Sn-Bu > Sn-Me and is in agreement with the reported data. The activity of the compounds, was compared with standard drugs and the results and additional experimental details are presented in Figure S1 (online Supplementary Materials).[4,13,19]

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