Synthesis, Spectral, Thermal, and Biological Studies of Adducts of Organotin(IV) Halides with Schiff Bases Derived from 2-Amino-5-(*o*-methoxyphenyl)-1,3,4-thiadiazole

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Some new organotin(IV) complexes of the general formula, $R_nSnCl_{4-n}\cdot L$ [where $n=3$, $R=CH_3$ or C_6H_5; $n=2$, $R=C_6H_5$; L = Schiff bases derived from the condensation of 2-amino-5-(*o*-methoxyphenyl)-1,3,4-thiadiazole with salicylaldehyde (L-1), 2-hydroxy-1-naphthaldehyde (L-2), 2′-hydroxyacetophenone (L-3), benzyl methyl ketone (L-4), acetylacetone (L-5), and 2-furancarbaldehyde (L-6)] have been synthesized and characterized by elemental analyses, molar conductances, electronic, infrared, far-infrared, ^1H and ^{119}Sn NMR and Mössbauer spectral studies. Thermal studies of three complexes, viz., Ph_3SnCl(L-2), Me_3SnCl(L-4), and Ph_3SnCl(L-5) have been carried out in the temperature range 25—1000 °C using TG, DTG, and DTA techniques. All these complexes decompose gradually with the formation of SnO_2 as an end product. In vitro antimicrobial activity of the ligands and their complexes has also been determined against *Streptococcus faecalis*, *Klebsiella pneumoniae*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus* Penicillin resistance (2500 units), *Candida albicans*, *Cryptococcus neoformans*, *Sporotrichum schenckii*, *Trichophyton mentagrophytes*, and *Aspergillus fumigatus*.

Thiadiazole ring is reported to display fungicidal property by virtue of –N=C–S– linkage, which is a possible toxophore in many pesticides.[1] 2,5-Disubstituted 1,3,4-thiadiazole moieties have been found to possess herbicidal, radioprotective, diuretic, and bacteriostatic properties.[1—3] Acetamide derivatives of 2-(benzoylaminomethyl)-1,3,4-thiadiazole have been found to possess antiarrhythmic, antimetastatic, psychoneurosis, schistosomicidal, fungicidal, herbicidal, and pesticidal activities.[3] There are a few reports on transition metal complexes of Schiff bases derived from 2-amino-5-aryl-1,3,4-thiadiazoles.[4—7] Hitherto no effort has been made to synthesize non-transition metal complexes of these versatile ligands. The present communication is a part of a programme to study such complexes and deals with the synthesis and structural features of organotin(IV) complexes of the Schiff bases derived from 2-amino-5-(*o*-methoxyphenyl)-1,3,4-thiadiazole and different aldehydes or ketones [Fig. 1]. The antimicrobial activity of the ligands and of the corresponding organotin complexes are also reported here in.

Experimental

Materials. Triphenyltin chloride (Fluka), diphenyltin dichloride, trimethyltin chloride (Aldrich chemicals), salicylaldehyde, 2-hydroxynaphthaldehyde, 2′-hydroxyacetophenone, benzyl methyl ketone, acetylacetone, 2-furancarbaldehyde (Fluka), and iron(III) chloride hexahydrate (S.D.S) were used as received. Ethanol and methanol were refluxed over magnesium turnings for several hours and then distilled and stored under nitrogen.

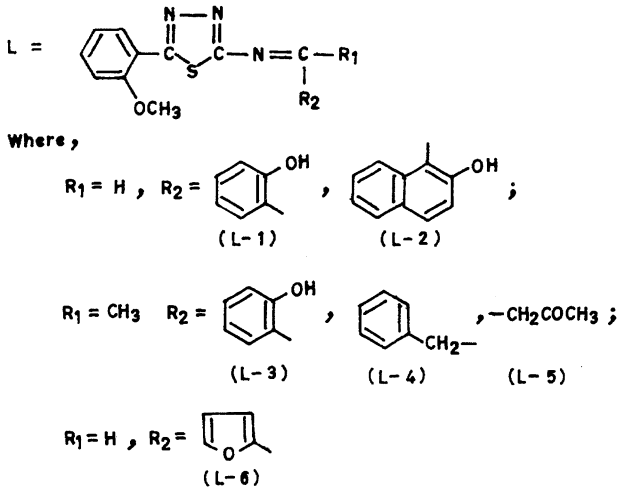

Fig. 1. General formula of the ligand.

Measurements. Carbon and Hydrogen were determined on a Perkin–Elmer, CHN-rapid elemental analyzer at the Indian Institute of Technology, New Delhi. The tin content of the compounds was determined gravimetrically by hydrolysing a weighed amount of the compound (ca. 0.1 g) with a few drops of concd H_2SO_4 followed by a mixture of concd HNO_3 and H_2SO_4. After evaporation of the acids on a low flame, the residue was ignited and weighed as SnO_2.[8] Molar conductance, electronic spectra, infrared, far-infrared, and thermal measurements were carried out on the same instruments as previously reported.[9] ^1H and ^{119}Sn NMR spectra were recorded on a FX-100 JEOL FT NMR spectrometer using $CDCl_3$ as the solvent

and tetramethyl silane (TMS) as the internal standard at the Indian Institute of Petroleum, Dehradun. The ^{119}Sn Mössbauer spectra were measured at 80 K on a Mössbauer spectrometer Model MS-900 (Ranger Scientific Co., Burelson, TX) in the acceleration mode with a moving source geometry using a liquid nitrogen Cryostat (CYRO Industries of America, Inc., Salem, NH). The samples were mounted in teflon holders. The source was 15 mCi Ca $^{119m}SnO_3$, and the velocity was calibrated at ambient temperature using a composition of $BaSnO_3$ and Sn foil (splitting = 2.52 mm s^{-1}). The resultant spectra were analysed by a least-square fit to Lorenzian shaped lines. Antimicrobial activities of the ligands and their organotin-(IV) complexes were carried out at microbial section of the Central Drug Research Institute (CDRI), Lucknow using two fold serial dilution techniques.

Synthesis of the Ligands. 2-Amino-5-(*o*-methoxyphenyl)-1,3,4-thiadiazole was prepared by oxidative cyclisation of 2-methoxybenzaldehyde thiosemicarbazone.[10] The Schiff bases were prepared by refluxing 2-amino-5-(*o*-methoxyphenyl)-1,3,4-thiadiazole (1 mol) and aldehyde or ketone (1 mol) in distilled ethanol (50 ml) for 2 h. The colored solid was obtained on cooling after the removal of excess of solvent by distillation. It was recrystallized from the same solvent and dried under vacuum.

Synthesis of the Organotin(IV) Complexes. To 4.00 mmol of tri- or diorganotin(IV) chloride in hot absolute methanol (ca. 20 ml) was added 4.00 mmol of Schiff base in minimum amount of absolute methanol in a dry atmosphere with constant stirring. The solution was stirred for 0.5 h and then refluxed for 3—4 h. The excess of solvent was removed by distillation and the product was dried under vacuum. The resulting crude solid was crystallized from the same solvent and dried under vacuum.

Results and Discussion

The reaction of R_nSnCl_{4-n} with various Schiff bases (L) led to the formation of 1 : 1 molar adducts.

$$R_nSnCl_{4-n} + L \xrightarrow[\text{Reflux for 3—4 h.}]{\text{methanol}} R_nSnCl_{4-n}\cdot L$$

[where n=3, R=CH_3 or C_6H_5; n=2, R=C_6H_5; L=(L-1) to (L-6), as indicated in Fig. 1].

All the newly synthesized complexes are colored solids and soluble in common organic solvents. The colors, yields, melting points, elemental analyses, and molar conductances of the complexes are presented in Table 1. The analytical data are in good agreement with the proposed stoichiometry of the complexes. Molar conductance values of 10^{-3} M solutions (M=mol dm^{-3}) of the complexes are in the range of 15.10—35.20 Ω^{-1} cm^2 mole^{-1} indicating their slightly polar nature due to the electrolytic behavior of chlorine in organotin(IV) moiety.[11]

The electronic spectral data of the ligands and of their organotin complexes are depicted in Table 2. In the spectra of the ligands and of their organotin(IV) complexes, two bands are observed in the region 216—250 and 272—309 nm which may be assigned to π–π^* transition of the benzenoid and of the >C=N chromophore, respectively. A band in the region 355—428 nm in the spectra of the ligands and complexes is likely to be the secondary band of benzene ring coupled with the intramolecular charge-transfer transition taking place within ligand moiety. Further, there were sharp bands observed in the region 311—339 nm in the spectra of the complexes which could be assigned to the charge-transfer transition from ligand to tin.[12]

The characteristic infrared frequencies of the ligands and their organotin(IV) complexes are summarized in Table 3. The infrared spectra of Schiff bases derived from 2-hydroxybenzaldehyde (L-1), 2-hydroxynaphthaldehyde (L-2), and 2′-hydroxyacetophenone (L-3) exhibit a band at ca. 2940 cm^{-1} characteristic of hydrogen-bonded phenolic νOH vibrations.[6] It is shifted to higher frequency side ca. 3100 cm^{-1} in the complexes. The appearance of azomethine νC=N vibrations in all the Schiff bases at lower frequencies (1637±9 cm^{-1}) in comparison with the normal position (1675 cm^{-1}) indicates the involvement of the azomethine nitrogen atoms in hydrogen bonding (Fig. 2). This band suffers a negative shift (1622±13 cm^{-1}) on complex formation suggesting coordination of the azomethine nitrogen to tin. Other characteristic IR bands observed in the spectra of the Schiff bases at 1599±3, 1022±2, and 676±2 cm^{-1} have been assigned[5] to the ν >C=N–N=C< (cyclic), ν N–N and ν C–S–C modes of vibrations, respectively, of the thiadiazole ring. In the spectra of all the complexes the ν >C=N–N=C< (cyclic) and ν N–N vibrations remain almost unchanged indicating, thereby, non-involvement of the ring nitrogen in coordination. The ν C–S–C undergoes a negative shift in the complexes indicating the coordination of ring sulfur to tin. The coordination through the azomethine nitrogen and sulfur is further supported by the occurrence of new bands at 447±16 and 330±18 cm^{-1} in the spectra of the complexes which may be assigned[13] to ν Sn←N and ν Sn←S vibration, respectively. The far-IR spectra of Ph_3SnCl·L (L=Schiff bases as abbreviated in Fig. 1) show bands at 267±7 and 229±11 cm^{-1} which may be assigned[13,14] to the ν_{as} Sn–C and ν_s Sn–C, respectively, whereas the corresponding vibrations at 563±3 and 517±7 cm^{-1} have also been assigned[13] in the spectra of Me_3SnCl·L. Only one Sn–C stretching frequency has been observed at 235±3 cm^{-1} in six-coordinated Ph_2SnCl_2·L, suggesting an octahedral geometry with a *trans* arrangement of phenyl groups.[15] A strong band in the region 215—250 cm^{-1} has been assigned to the ν Sn–Cl in R_3SnCl·L (R=Me or Ph), but multiple ν Sn–Cl frequencies have been assigned[13] in the region 244—281 cm^{-1} in the spectra of Ph_2SnCl_2·L.

The ^{1}H NMR spectral data of a few ligands and of their complexes are presented in Table 4. The spectra of the Schiff bases, viz., (L-2) and (L-3) show a signal at δ=8.60±0.10 due to the intramolecularly hydrogen-bonded phenolic proton[5,6] which remains unaltered in their complexes indicating the non-involvement of the phenolic (OH) group in coordination.

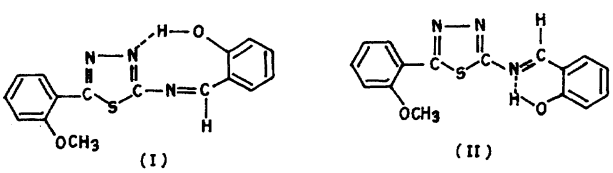

Fig. 2. Hydrogen-bonded structures of (L′H-1).

Table 1. Physical Characteristics and Analytical Data of Ligands and Their Organotin(IV) Complexes

SI. No.	Ligand/Complex (Empirical formula)	Color (Yield/%)	Mp °C	Elemental analysis/% Obsd (Calcd) Sn	S	C	H	Molar conductance Ω^{-1} cm^2 mole^{-1}
1.	(L-1)	Yellow	151—152	—	10.23	61.63	4.17	—
	($C_{16}H_{13}O_2N_3S$)	(80)			(10.30)	(61.72)	(4.21)	
2.	Ph_3SnCl(L-1)	Cream	103—105	16.95	4.54	58.57	4.01	23.75
	($C_{34}H_{28}O_2N_3SSnCl$)	(80)		(17.03)	(4.60)	(58.61)	(4.05)	
3.	Me_3SnCl(L-1)	White	180—182	23.17	6.20	44.61	4.25	31.25
	($C_{19}H_{22}O_2N_3SSnCl$)	(60)		(23.25)	(6.28)	(44.69)	(4.34)	
4.	Ph_2SnCl_2(L-1)	Cream	114—115	18.04	4.82	51.29	3.47	28.70
	($C_{28}H_{23}O_2N_3SSnCl_2$)	(85)		(18.12)	(4.89)	(51.33)	(3.54)	
5.	(L-2)	Dark yellow	118—120	—	8.76	66.41	4.07	—
	($C_{20}H_{15}O_2N_3S$)	(90)			(8.87)	(66.47)	(4.18)	
6.	Ph_3SnCl(L-2)	Yellow	159—160	15.87	4.19	61.03	4.02	27.80
	($C_{38}H_{30}O_2N_3SSnCl$)	(73)		(15.89)	(4.29)	(61.11)	(4.05)	
7.	Me_3SnCl(L-2)	Dark yellow	98—100	21.08	5.67	49.18	4.28	35.20
	($C_{23}H_{24}O_2N_3SSnCl$)	(60)		(21.17)	(5.72)	(49.27)	(4.31)	
8.	Ph_2SnCl_2(L-2)	Greenish yellow	93—95d[a]	16.75	4.49	54.43	3.49	15.10
	($C_{32}H_{25}O_2N_3SSnCl_2$)	(75)		(16.83)	(4.55)	(54.50)	(3.57)	
9.	(L-3)	White	109—110	—	9.81	62.69	4.61	—
	($C_{17}H_{15}O_2N_3S$)	(85)			(9.85)	(62.75)	(4.65)	
10.	Ph_3SnCl(L-3)	Light pink	104—105	16.63	4.47	59.07	4.19	18.00
	($C_{35}H_{30}O_2N_3SSnCl$)	(62)		(16.70)	(4.51)	(59.14)	(4.25)	
11.	Me_3SnCl(L-3)	White	183—185	22.54	6.07	45.87	4.53	18.00
	($C_{20}H_{24}O_2N_3SSnCl$)	(60)		(22.62)	(6.11)	(45.79)	(4.61)	
12.	Ph_2SnCl_2(L-3)	White	114—115	17.67	4.71	52.00	3.71	17.30
	($C_{29}H_{25}O_2N_3SSnCl_2$)	(65)		(17.74)	(4.79)	(52.05)	(3.77)	
13.	(L-4)	Creamish yellow	119—120	—	9.88	66.79	5.24	—
	($C_{18}H_{17}ON_3S$)	(60)			(9.91)	(66.85)	(5.30)	(75)
14.	Ph_3SnCl(L-4)	Cream	104—105	16.67	4.48	60.91	4.48	25.40
	($C_{36}H_{32}ON_3SSnCl$)	(70)		(16.74)	(4.52)	(61.00)	(4.55)	
15.	Me_3SnCl(L-4)	Creamish brown	148—150	22.62	6.09	48.21	4.96	32.50
	($C_{21}H_{26}ON_3SSnCl$)	(68)		(22.71)	(6.13)	(48.26)	(5.01)	
16.	Ph_2SnCl_2(L-4)	Cream	124—125	17.69	4.73	53.91	4.01	16.30
	($C_{30}H_{27}ON_3SSnCl_2$)	(65)		(17.79)	(4.81)	(54.00)	(4.08)	
17.	(L-5)	Brown	158—160	—	11.01	58.04	5.17	—
	($C_{14}H_{15}O_2N_3S$)	(78)			(11.08)	(58.11)	(5.22)	
18.	Ph_3SnCl(L-5)	Steel grey	102—103	17.50	4.68	56.91	4.42	28.70
	($C_{32}H_{30}O_2N_3SSnCl$)	(70)		(17.59)	(4.75)	(56.96)	(4.48)	
19.	Me_3SnCl(L-5)	Dark brown	163—165	24.19	6.50	41.70	4.88	29.00
	($C_{17}H_{24}O_2N_3SSnCl$)	(67)		(24.29)	(6.56)	(41.79)	(4.95)	
20.	Ph_2SnCl_2(L-5)	Brown	138—140d[a]	18.64	5.00	49.27	3.90	19.00
	($C_{26}H_{25}O_2N_3SSnCl_2$)	(64)		(18.75)	(5.06)	(49.32)	(3.98)	
21.	(L-6)	Brown	148—150	—	11.17	58.88	3.83	—
	($C_{14}H_{11}O_2N_3S$)	(79)			(11.24)	(58.94)	(3.89)	
22.	Ph_3SnCl(L-6)	Light grey	94—95	17.60	4.71	57.21	3.80	34.85
	($C_{32}H_{26}O_2N_3SSnCl$)	(75)		(17.69)	(4.78)	(57.30)	(3.91)	
23.	Me_3SnCl(L-6)	Brown	163—165	24.41	6.52	42.09	4.07	19.00
	($C_{17}H_{20}O_2N_3SSnCl$)	(50)		(24.49)	(6.62)	(42.14)	(4.16)	
24.	Ph_2SnCl_2(L-6)	Light brown	233—235	18.81	5.02	49.59	3.28	23.90
	($C_{26}H_{21}O_2N_3SSnCl_2$)	(65)		(18.87)	(5.10)	(49.64)	(3.36)	

a) d, decomposition temperature.

The signals due to the azomethine (–C(H)=N–) and methyl (–C(CH_3)=N–) protons in the ligands appear as a singlet at δ=7.05 and 1.60, respectively indicating that the azomethine nitrogen is hydrogen bonded.[5,6] In the complexes, these signals shifted downfield (δ=1.75—1.95 for methyl and δ=8.15 for methine protons) as compared to their positions in the free ligands owing to the coordination of the azomethine nitrogen to tin.[5,6] The signal at δ=4.57±0.03 in the ligands has been assigned to the –OCH_3 protons which remains unaltered on complexation and thus clearly indicates the non-involvement of this group in complex formation. Due to the complex nature of multiplet observed in the region δ=7.10—9.30 in all the complexes, the signals for the phenyl groups bonded to tin are indistinguishable from those of the aromatic ligand protons, however, the integration takes their presence into account. Methyl protons attached to the tin in

Table 2. Electronic Spectral Bands (in nm) and Their Assignments in Ligands and Their Organotin(IV) Complexes

SI. No.	Ligand/Complex[a)]	π–π^* (benzenoid)	π–π^* (C=N)	Charge-transfer band from ligand to tin	Secondary band of benzene ring coupled with intramolecular charge transfer
1.	(L-1)	223	293	—	372
2.	Ph_3SnCl(L-1)	228	286	313	388
3.	Me_3SnCl(L-1)	232	280	324	390
4.	Ph_2SnCl_2(L-1)	250	290	321	393
5.	(L-2)	219	309	—	355, 428
6.	Ph_3SnCl(L-2)	250	280	339	412
7.	Me_3SnCl(L-2)	223	293	318	377
8.	Ph_2SnCl_2(L-2)	230	290	315, 325	360sh[a)]
9.	(L-3)	222	294sh[a)]	—	388
10.	Ph_3SnCl(L-3)	228	293	314	390
11.	Me_3SnCl(L-3)	233	293	314	380
12.	Ph_2SnCl_2(L-3)	227	288	313	370
13.	(L-4)	218	292	—	377
14.	Ph_3SnCl(L-4)	223	285	314	368
15.	Me_3SnCl(L-4)	225	272	318, 329	392
16.	Ph_2SnCl_2(L-4)	231	287	311	369
17.	(L-5)	216	293	—	370
18.	Ph_3SnCl(L-5)	228	283	318	392
19.	Me_3SnCl(L-5)	217	290	314	394
20.	Ph_2SnCl_2(L-5)	220	302	336	372
21.	(L-6)	223	294	—	380
22.	Ph_3SnCl(L-6)	228	285	314	390
23.	Me_3SnCl(L-6)	227	275	315	388
24.	Ph_2SnCl_2(L-6)	217	290	314	381

a) sh, shoulder; a, in methanol.

Me_3SnCl(L-4) have also been assigned[16–18] as a singlet at $\delta=1.50$. A singlet in the region $\delta=4.00$—5.03 due to the $-CH_2$ protons has also been observed in the complexes of the ligand (L-4). The number of protons of various groups calculated from the integration curves and those calculated for the expected molecular formula agrees with each other.

The tin shielding in ^{119}Sn NMR spectra increases markedly with increase in coordination number from $\delta=-50$——100 for 4-coordinate to $\delta=-200$ for 5-coordinate to $\delta=-330$ for 6-coordinate alkyl tin compounds.[19] Tin shifts are normally higher with phenyl compared to alkyl substituents.[19] The compounds, Ph_3SnCl (L-6), Me_3SnCl (L-3), and Ph_2SnCl_2 (L-2) give sharp signals in the ^{119}Sn NMR spectra at $\delta=-478.2$, -332.7, and -485.3, respectively and these are in accordance with the proposed six-coordinated structures.

^{119}Sn Mössbauer spectral data of the complexes are presented in Table 5. The complexes of the types $R_3SnCl\cdot L$ and $Ph_2SnCl_2\cdot L$ (where R=CH_3 or C_6H_5, L=Schiff bases, as shown in Fig. 1) are six-coordinated having neutral bidentate ligands which coordinate through the azomethine nitrogen and thiadiazole ring sulfur atoms as revealed from the infrared spectral data. Octahedral cationic,[20] neutral,[20–22] and anionic[22] complexes containing two organic residues and four electronegative ligands possess a mutually *trans* geometry for the tin–carbon bonds with few exceptions. In this context, the magnitude of the ^{119}Sn Mössbauer quadrupole splitting (Δ) is a useful parameter. Point charge calculations[22–24] for octahedral SnX_4Y_2 systems predict that the Δ for the *trans* isomer (ca. 4.00 mm s^{-1}) will be twice that of the *cis* isomer (ca. 2.00 mm s^{-1}). The Mössbauer spectrum of Ph_2SnCl_2 (L-3) shows an isomeric shift (δ) value of 1.20 mm s^{-1} and a Δ of 3.45 mm s^{-1} which indicate *trans*-configuration of the phenyl groups in a distorted octahedral geometry as shown in Fig. 3. The *trans*-configuration is further supported by the appearance of a single infrared band at 235±3 cm^{-1} attributable to the Sn–C stretching vibration.

The observed Δ (2.52—2.55 mm s^{-1}) and δ (1.15—1.32 mm s^{-1}) values of the complexes $R_3SnCl\cdot L$ [R=CH_3, L=(L-4); R=C_6H_5, L=(L-2) and (L-5)] suggested the existence of *fac-cis*-R_3Sn(IV) moieties in a distorted octahedral arrangement around tin atom for these complexes (Fig. 4). The gross distortions in these octahedral structures may be due to the asymmetry of the bidentate ligands with N and S donor

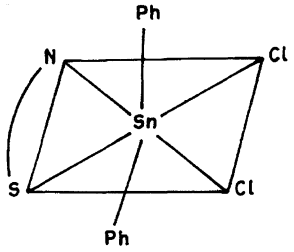

Fig. 3. *trans*-Octahedral structure of $Ph_2SnCl_2\cdot L$ (L=$\widehat{NS}$).

Table 3. Structurally Important IR Absorption Bands (cm^{-1}) of Ligands and Their Organotin(IV) Complexes[b)]

SI.[a)] No.	ν C=N (azomethine)	ν >C=N–N=C<	ν C–O	ν C–S–C	ν Sn←N	ν Sn←S	ν Sn–Cl	ν_{as}, ν_s Sn–C
1.	1632m	1600vs	1258m	678m	—	—	—	—
2.	1620m	1598vs	1260s	622m	448s	336vs	245m	264m 228m
3.	1618m	1599vs	1258s	630s	452m	339m	220m	560m 521s
4.	1625m	1598s	1260s	600m	450s	338s	280m 262m	232m
5.	1628m	1596vs	1256s	675m	—	—	—	—
6.	1614m	1595vs	1256s	637s	462s	348s	218s	263m 230m
7.	1612m	1596vs	1256s	623vs	448vs	339m	215s	565m 515m
8.	1609m	1596vs	1256s	630vs	431s	333m	281m 263m	238m
9.	1630m	1602vs	1250vs	677s	—	—	—	—
10.	1614m	1603vs	1250vs	637m	444s	337s	240m	262m 218vs
11.	1612m	1603vs	1250vs	648vs	437vs	348m	218m	560s 510m
12.	1617m	1602vs	1250s	653vs	445s	315s	280s, 264s, 251sh	235vs
13.	1645m	1600vs	—	676s	—	—	—	—
14.	1630m	1600vs	—	645s	438vs	342m	239m	260m 225m
15.	1632m	1600vs	—	660s	459s	339s	229s	560s 520m
16.	1635m	1599vs	—	652m	454s	347vs	272m 244m	235w
17.	1630m	1598vs	—	676s	—	—	—	—
18.	1622m	1598vs	—	622w	446s	336vs	244m	274m 239m
19.	1618m	1598vs	—	633s	456vs	346vs	223m	565m 524s
20.	1620m	1598vs	—	642s	454s	312m	265m 251m	235m
21.	1643m	1600vs	—	677s	—	—	—	—
22.	1618m	1600vs	—	652vs	435s	329s	250s	268m 230s
23.	1620m	1601vs	—	627s	453m	342m	220s	564vs 519m
24.	1621m	1599vs	—	638vs	437vs	330s	267m 245m	233m

a) SI. Nos. are those as indiated in Table 1. b) sh, shoulder; m, medium; s, strong; vs, very strong; w, weak.

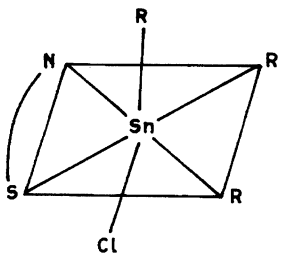

Fig. 4. *fac-cis*-Octahedral structure of $R_3SnCl{\cdot}L$ (R=CH_3 or C_6H_5; L=$\widehat{NS}$).

atoms. Further it has been reported[25)] that the bidentate ligands which have relatively large "normalised bite" (the distance between the two donor atoms of the same ligand, $b \approx 1.2$—1.5) are expected to form the undistorted *trans*-octahedral structure. This is in agreement with the structure of $[Sn(MeCOCHCOMe)_2Me_2]$. As the "normalised bite" is decreased, the structure becomes distorted *trans*-octahedral or *cis*-octahedral. Therefore, it has been concluded that the small normalised bite of the Schiff bases derived from 2-amino-5-(*o*-methoxyphenyl)-1,3,4-thiadiazole in which two dissimilar donor atoms such as the ring sulfur and the azomethine nitrogen are involved in coordination may result the gross distortions in the octahedral geometries of the organotin(IV) complexes of the ligands (Figs. 3 and 4).

Antimicrobial activity of the ligands and their complexes show (Table 6) that all the ligands are active against fungal

Table 4. ^{1}H NMR Chemical Shifts (δ/ppm) of the Ligands and Their Organotin(IV) Complexes[a)]

Ligand/Complex	–CH=/–C(CH$_3$)=	Sn–C$_6$H$_5$/–phenyl (ligand)/Sn–CH$_3$	–OCH$_3$	–OH	–CH$_2$
[HO·C$_{10}$H$_6$·CH : N·C : N·N : C(C$_6$H$_4$OCH$_3$)·S]	7.05 (s,1H)	7.15—7.20 (m,10H)	4.55 (s,3H)	8.50 (s,1H)	—
Ph$_3$SnCl[HO·C$_{10}$H$_6$·CH : N·C : N·N : C(C$_6$H$_4$OCH$_3$)·S]	8.15 (s,1H)	7.40—8.00 (m,25H)	4.55 (s,3H)	8.50 (s,1H)	
[HO·C$_6$H$_4$·C(CH$_3$) : N·C : N·N : C(C$_6$H$_4$OCH$_3$)·S]	1.60 (s,3H)	7.35—7.70 (m,8H)	4.60 (s,3H)	8.70 (s,1H)	—
Ph$_2$SnCl$_2$(HO·C$_6$H$_4$·C(CH$_3$) : N·C : N·N : C(C$_6$H$_4$OCH$_3$)·S]	1.95 (s,3H)	7.40—8.40 (m,18H)	4.60 (s,3H)	8.70 (s,1H)	—
Ph$_3$SnCl[C$_6$H$_5$·CH$_2$·C(CH$_3$) : N·C : N·N : C(C$_6$H$_4$OCH$_3$)·S]	1.75 (s,3H)	7.10—9.30 (m,24H)	4.45 (s,3H)	— —	4.00 (s,2H)
Me$_3$SnCl[C$_6$H$_5$·CH$_2$·C(CH$_3$) : N·C : N·N : C(C$_6$H$_4$OCH$_3$)·S]	1.80 (s,3H) 1.50 (s,9H)	7.90—8.40 (m,9H)	4.48 (s,3H)	— —	5.03 (s,2H)

a) s, singlet; m, multiplet; solvent CDCl$_3$ (at 100 MHz).

Table 5. The ^{119}Sn Mössbauer Spectroscopic Data of Organotin(IV) Complexes at 80 K vs. Ba $^{119m}SnO_3$

Complex	Δ/mm s^{-1}	δ/mm s^{-1}	Line Widths	
			τ_1/mm s^{-1}	τ_2/mm s^{-1}
Ph$_3$SnCl(L-2)	2.52±0.03	1.32±0.01	0.67±0.03	0.63±0.03
Ph$_2$SnCl$_2$(L-3)	3.45±0.03	1.20±0.02	0.49±0.04	0.77±0.06
Me$_3$SnCl(L-4)	2.54±0.04	1.15±0.01	0.74±0.03	0.64±0.06
Ph$_3$SnCl(L-5)	2.55±0.02	1.30±0.01	0.51±0.02	0.51±0.02

strains 6 to 10 only. Among all the ligands, (L-2) was found to be the most active. The ligands (L-1) and (L-2) were found to be active against fungal strains 6, 7, 8, and 10, and (L-3) was active against fungal strain 7 only, viz., *Cryptococcus neoformans*. Ligand (L-4) was active against *Sporotrichum schenckii* and *Aspergillus fumigatus*. The Ligands (L-5) and (L-6) were active against *Sporotrichum schenckii* only.

As evident from the Table 6, complexes Ph$_3$SnCl(L-1) and Ph$_2$SnCl$_2$(L-6) are very active against all the bacteria and fungi used and show lower MIC values in comparison to the ligands while Me$_3$SnCl(L-4) and Me$_3$SnCl(L-5) are completely inactive against all the bacteria and fungi used. Rest of the complexes also show greater bactericidal and fungicidal activities as compared to their corresponding ligands and show lower MIC values than those of the ligands. Thus the results clearly indicate that the organotin(IV) complexes possess moderate bactericidal and fungicidal activities.

Thermal decomposition of three complexes, viz., Ph$_3$SnCl(L-2), Me$_3$SnCl(L-4), and Ph$_3$SnCl(L-5) has been studied using TG, DTG, and DTA techniques. All the complexes decompose gradually with the formation of SnO_2 as an end product.

As evident from the data compiled in Table 7, the complex Ph$_3$SnCl(L-2) decomposes in two steps. The observed weight loss (50.00%) in the first step of decomposition in the temperature range 157—535 °C corresponds to the loss of all the phenyl groups and chlorine attached to tin together with the loss of $CH_3OC_6H_4$ group of the ligand moiety. The tentative composition ($C_{13}H_8N_3OSSn$) assigned to the intermediate (I) has been confirmed by the elemental analyses. [Found: C, 41.72; H, 2.03; Sn, 31.73%. Calcd for: C, 41.86; H, 2.16; Sn, 31.82%; for intermediate (I)]. The second step of decomposition occurs between 584—743 °C to give SnO_2 as end product. The observed weight loss was 30.00% as against the calculated value (29.76%), and corresponds to the loss of remaining skeleton of the ligand moiety. The residue (SnO_2) has been characterized by powder X-ray diffraction analyses[26)] and tin determination ['*d*' values Obsd: 3.40, 2.62, 1.78, and 2.34; Obsd: Sn, 78.63%]. The corresponding DTA and DTG peaks are listed in Table 7.

The complex Me$_3$SnCl(L-4) was stable up to 80 °C and decomposed in two steps in the temperature range 80 to 556

Table 6. Results of Antimicrobial Activity of the Ligands and Their Organotin(IV) Complexes[a)]

Sl. No.	Ligand/ Complex	Minimum inhibitory concn (MIC)[b)] in μg ml^{-1} against Bacteria					Fungi				
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
1.	(L-1)	-	-	-	-	-	50	50	50	-	50
2.	Ph_3SnCl(L-1)	25	12.5	25	50	<12.5	<12.5	<12.5	<12.5	<12.5	<12.5
3.	Ph_2SnCl_2(L-1)	25	-	50	-	50	<12.5	<12.5	<12.5	25	<12.5
4.	(L-2)	-	-	-	-	-	50	25	25	-	25
5.	Ph_3SnCl(L-2)	<12.5	-	-	-	<12.5	<12.5	<12.5	50	-	-
6.	Ph_2SnCl_2(L-2)	25	50	25	-	<12.5	50	<12.5	25	50	25
7.	(L-3)	-	-	-	-	-	-	50	-	-	-
8.	Ph_3SnCl(L-3)	<12.5	<12.5	25	-	<12.5	<12.5	<12.5	<12.5	<12.5	<12.5
9.	Me_3SnCl(L-3)	-	-	-	-	-	-	50	-	-	-
10.	Ph_2SnCl_2(L-3)	25	-	50	-	25	<12.5	<12.5	50	-	25
11.	(L-4)	-	-	-	-	-	-	-	25	-	50
12.	Ph_3SnCl(L-4)	50	-	50	-	25	<12.5	<12.5	<12.5	<12.5	<12.5
13.	Me_3SnCl(L-4)	-	-	-	-	-	-	-	-	-	-
14.	Ph_2SnCl_2(L-4)	50	-	50	-	50	<12.5	<12.5	<12.5	50	<12.5
15.	(L-5)	-	-	-	-	-	-	-	50	-	-
16.	Ph_3SnCl(L-5)	<12.5	-	50	-	<12.5	<12.5	<12.5	<12.5	<12.5	<12.5
17.	Me_3SnCl(L-5)	-	-	-	-	-	-	-	-	-	-
18.	Ph_2SnCl_2(L-5)	50	-	50	-	50	<12.5	<12.5	50	50	<12.5
19.	(L-6)	-	-	-	-	-	-	-	50	-	-
20.	Ph_3SnCl(L-6)	<12.5	<12.5	25	-	<12.5	<12.5	25	<12.5	<12.5	50
21.	Me_3SnCl(L-6)	25	-	50	-	<12.5	-	<12.5	25	-	<12.5
22.	Ph_2SnCl_2(L-6)	<12.5	<12.5	<12.5	50	<12.5	<12.5	<12.5	25	50	<12.5

a) **1**. *Streptococcus faecalis*, **2**. *Klebsiella pneumoniae*, **3**. *Escherichia coli*, **4**. *Pseudomonas aeruginosa*, **5**. *Staphylococcus aureus* Penicillin resistance (2500 units), **6**. *Candida albicans*, **7**. *Cryptococcus neoformans*, **8**. *Sporotrichum schenckii*, **9**. *Trichophyton mentagrophytes*, **10**. *Aspergillus fumigatus*. b) The compounds were not tested below 12.5 μg ml^{-1}; solvent used, DMSO.

Table 7. Thermal Analysis Data of the Organotin(IV) Complexes.

Complex	Step	Temp range from TG	Peak temp in DTG	Temp range in DTG	Peak temp in DTA (Nature of the peak)/°C	Temp range in DTA	Loss of mass (%) from TG
		°C	°C	°C		°C	Obsd (Calcd)
Ph_3SnCl(L-2)	I	157—535	237	181—310	438 (exothermic)	258—521	50.00 (50.06)
	II	584—743	649	597—755	637 (exothermic)	579—763	30.00 (29.76)
Me_3SnCl(L-4)	I	80—127	114	58—127	114 (endothermic)	51—145	17.64 (17.44)
	II	163—556	336	266—466	181 (endothermic)	169—198	54.90 (53.73)
		—	606	521—671	602 (exothermic)	484—713	—
Ph_3SnCl(L-5)	I	145—275	226	151—269	232 (exothermic)	157—258	38.17 (39.53)
	II	300—697	461	360—535	512 (exothermic)	414—566	39.28 (38.14)
		—	654	584—722	654 (exothermic)	588—679	—

°C. The first plateau was obtained at 127 °C and extended up to 163 °C. The observed weight loss (17.64%) corresponds to the loss of benzyl group of the ligand. Both DTA and DTG curves show a peak at 114 °C. The observed elemental analyses (C, 39.21; H, 4.31; Sn, 27.69%) of the residue obtained by isothermal heating of Me_3SnCl(L-4) at 130±5 °C are in good agreement with the calculated values (C, 38.97; H, 4.44; Sn, 27.50%) for the intermediate (I) having the tentative composition $C_{14}H_{19}N_3OSSnCl$. The second step of decomposition started from 163 °C and extended up to 556 °C to give SnO_2 as end product. The observed weight loss was 54.90% as against the calculated value (53.73%) required for the loss of remaining organic groups of the ligand together with the loss of methyl groups and chlorine attached to tin. The observed '*d*' values in the residue left were 3.38, 2.66, 1.79 and 2.30 and Obsd: Sn was 78.67%. The

DTA and DTG curves show peaks at 181 °C (endothermic), 602 °C (exothermic), and 336 °C, 606 °C, respectively but no distinct plateau has been observed in TG curve in the temperature range 163—556 °C.

The complex Ph_3SnCl(L-5) decomposed in the temperature range 145—697 °C giving SnO_2 as end product of decomposition. The observed weight loss (38.17%) as against the calculated value (39.53%) in the first step (145—275 °C) of decomposition corresponds to the loss of all the phenyl groups and chlorine attached to tin. The corresponding DTA and DTG peaks are observed at 232 °C (exothermic) and 226 °C, respectively. The observed per centages of C, H, and Sn in the residue obtained by isothermal heating of the complex at 280±5 °C support the intermediate (I) having the tentative composition $C_{14}H_{15}N_3O_2SSn$ [Obsd: C, 41.11; H, 3.61; Sn, 28.89%; Calcd: C, 41.21; H, 3.71; Sn, 29.09% for $C_{14}H_{15}N_3O_2SSn$]. The second step corresponds to the loss of ligand moiety resulting in the formation of SnO_2 as residue. Although two peaks were obtained in DTA and DTG, but no distinct plateau was obtained in TG in the temperature range 300—697 °C. The observed '*d*' values in the powder X-ray spectrum of the residue were 3.32, 2.61, 1.77, 2.33 and Obsd: Sn was 78.75%, which are very close to those for SnO_2.[26]

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