Spectral Studies and In Vitro Antimicrobial Activity of New Organotin(IV) Complexes of Schiff Bases Derived from Amino Acids

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Some new di- and triphenyltin(IV) complexes of the general formulae Ph_2SnL and Ph_3SnL', where H_2L/HL' = Schiff bases derived from the condensation of 2-hydroxy-1-naphthaldehyde (H_2L) and benzaldehyde (HL') with glycine (H_2L-1/HL'-1), DL-α-alanine (H_2L-2/HL'-2), L-methionine (H_2L-3/HL'-3), DL-valine (H_2L-4/HL'-4), D-phenylalanine (H_2L-5/HL'-5), 2-aminobutyric acid (H_2L-6/HL'-6), and L-leucine (H_2L-7/HL'-7), have been synthesized and characterized by elemental analyses, molar conductance, electronic, infrared and far-infrared, multinuclear magnetic resonance (^1H, ^{13}C, and ^{117}Sn), and ^{119}Sn Mössbauer studies. Thermal decomposition of a few complexes using TG, DTG, and DTA techniques indicates the formation of SnO_2 as a residue. The complexes have also been tested in vitro against bacteria [*Streptococcus faecalis*, *Klebsiella pneumoniae*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus* Penicillin resistance (2500 units)] and fungi [*Candida albicans*, *Cryptococcus neoformans*, *Sporotrichum schenckii*, *Trichophyton mentagrophytes*, and *Aspergillus fumigatus*]. All of the complexes show remarkable activity.

The chemistry of the metal complexes of amino acids has recently developed not only from an inorganic point of view, but also because of possible biological interest. Transition-metal complexes of Schiff bases in which amino groups are provided by amino acids have received considerable attention during the last two decades due to their possible use as potential *N*-pyridoxylidene amino acid systems.[1—9] The pyridoxal (vitamin B_6 aldehyde)–amino acid Schiff bases are believed to be intermediate in biologically important amination processes.[10]

In contrast to transition-metal complexes, some work has been reported on the organotin(IV) complexes of these biologically important Schiff bases.[11—13] Organotin derivatives of amino acids have been of interest as possible biocides;[14] for example, tricyclohexyltin alaninate has been found to be active as a fungicide and bactericide for seeds and plants.[15] In view of this, it was considered of interest to synthesize new organotin complexes of Schiff bases derived from amino acids, and to study their biological activity. The results of these investigations are reported in this paper.

Experimental

Materials: All of the reactions were carried out under an anhydrous and oxygen-free nitrogen atmosphere. The solvents were purified, dried, and stored under nitrogen. Anal R grade (Fluka) 2-hydroxy-1-naphthaldehyde and benzaldehyde were used as received. The di- and triphenyltin chloride (Merck), glycine (Richie Renolds Chemicals Inc.), DL-α-alanine and DL-valine (B.D.H.), L-methionine (Sisco Research Laboratory, India), L-leucine (Sigma), D-phenylalanine and 2-aminobutyric acid (Fluka) were used as received.

Synthesis of Sodium Salt of Schiff Bases: Schiff bases were prepared by the condensation of 2-hydroxy-1-naphthaldehyde or benzaldehyde (3.50 mmol) and the various amino acids (3.50 mmol) in a minimum amount (25 ml) of absolute methanol. The solution was refluxed for 2—3 h with constant stirring. To this was added sodium methoxide prepared by dissolving sodium (0.10 g, 4.50 mmol) in absolute methanol (10 ml) under dry nitrogen; mixture was again refluxed for 2—3 h. Any excess of the solvent was removed by distillation. The thus-obtained viscous oils were purified by repeated washings with petroleum ether (bp 40—60 °C). The mixture was kept in a freezer for crystallization. When, occasionally, no crystallization occurred, the solvent was completely removed under reduced pressure and underwent repeated treatment of the remaining viscous mass with a low boiling-point solvent; e.g. hexane or petroleum ether (40—60 °C), followed by evaporation, yielded a yellow-to-brown solid crystallizable residue. The crystals were washed and dried in vacuo.

Synthesis of Di- and Triphenyltin(IV) Complexes: The complexes were prepared under anhydrous conditions by the slow addition of a dry, hot methanol solution of the diphenyltin(IV) dichloride (1.16 g, 3.00 mmol) or triphenyltin(IV) chloride (1.03 g, 3.00 mmol) in ca. 1 : 1 molar ratio to a solution of the sodium salt of the Schiff base (3.50 mmol) in hot absolute methanol (35 ml). The mixture was refluxed with constant stirring, giving a clear solution in half an hour; refluxing was then continued for 3—4 h. It was centrifuged and filtered to remove any sodium chloride and excess of the sodium salt of the Schiff base. The excess of the solvent was removed under reduced pressure. The thus-obtained semi-solid product was solidified and purified by trituration with petroleum ether (bp 40—60 °C). The complexes were recrystallized from methanol and a petroleum ether (bp 40—60 °C) mixture.

Measurements: The melting points were determined on a Toshniwal capillary melting-point apparatus, and were uncorrected.

Tin, nitrogen and sulfur in the complexes were determined by gravimetric, Kjeldahl's and Messenger's methods, respectively.[16,17] The details concerning the molar-conductance measurements were similar to those reported previously.[16] Infrared and far-infrared spectra were recorded on an FTIR spectrophotometer model FTS 165, 4000—400 cm^{-1} in KBr discs: 600—200 cm^{-1} in CsI discs, respectively, at the Institute of Exploration and Petroleum, Dehradun. ^{1}H-, ^{13}C-, and ^{117}Sn NMR spectra were recorded on Bruker VM - 400 MHz and Bruker 250 MHz spectrophotometers at the Central Drug Research Institute (CDRI), Lucknow, and Indian Institute of Technology, Bombay, using $CDCl_3$ as the solvent and tetramethylsilane as the internal standard. The electronic spectra were recorded on a Beckman DU-6 spectrophotometer. The details of the ^{119}Sn-Mössbauer spectra[18] and the antimicrobial activity[16] of the complexes were similar to those reported previously. Thermal measurements were carried out using a Stanton Redcroft Thermal Analyzer (STA-780 series), which simultaneously recorded DTA, DTG, and TG curves. Samples of 10 mg were heated at a rate of 5 °C min^{-1} in a platinum crucible to a temperature of 1000 °C in dry nitrogen. Alumina was used as a standard reference material. A thermobalance with 0.01 mg sensitivity was used and the chart speed was maintained at 20 cm h^{-1}.

The analytical data, molar conductance (ohm^{-1} cm^2 mol^{-1}), electronic spectral data (nm), ^{1}H NMR and ^{13}C NMR chemical shift (δ/ppm) of the complexes in $CDCl_3$ are given below:

1. Ph_2SnL-1, $(C_6H_5)_2SnOC_{10}H_6CH{=}NCH_2C(O)O$: Dark brown; % yield, 90; mp, 105—112 °C. Found: Sn, 23.27; N, 2.30%. Calcd for $C_{25}H_{19}NO_3Sn$: Sn, 23.73; N, 2.80%. Molar conductance in DMF, 48.0; UV-vis in $CHCl_3$, 210 (14000), 230 (14200) π–π^* (benzenoid)/n–π^* (COO); 331 (24400) π–π^* (>C=N–); 403 (18600) secondary band of the naphthalene ring; ^{1}H NMR δ = 8.68 (s, 1H (–CH=N–), 8.10—7.30 (m, 16H, [$C_{10}H_6$ + 2(C_6H_5) of tin]), 3.98 (s, 2H, (CH_2)) and ^{13}C NMR (C-1 to C-10 of $C_{10}H_6$) δ = 108.78, 133.92, 124.05, 124.98, 129.35, 128.24, 127.03, 139.98, 118.35, 170.30; (–CH=N–), 166.25; (–NCH_2), 60.38; (C(O)O), 174.20; (C-α to C-δ of C_6H_5 of tin) 138.20, 135.10, 128.94, 130.25.

2. Ph_3SnL'-1, $(C_6H_5)_3SnC_6H_5CH{=}NCH_2C(O)O$: Yellow; % yield, 40; mp, 120—124 °C. Found: Sn, 21.19; N, 2.33%. Calcd for $C_{27}H_{23}NO_2Sn$: Sn, 22.55; N, 2.73%. Molar conductance in DMF, 65.0; UV-vis in CH_3OH, 215 (13500), 223 (18800) π–π^* (benzenoid)/n–π^* (COO); 260 (12500) π–π^* (>C=N–); ^{1}H NMR δ = 8.15 (s, 1H, (–CH=N–)), 8.00—7.37 (m, 20H, [C_6H_5 + 3(C_6H_5) of tin]), 4.05 (s, 2H, (CH_2)); ^{13}C NMR (C-1 to C-4 of C_6H_5) δ = 136.18, 133.34, 127.22, 128.99; (–CH=N–) 166.70; (–NCH_2) 59.41; (C(O)O) 174.30; (C-α to C-δ of C_6H_5 of tin) 140.44, 136.40, 128.50, 129.49.

3. Ph_2SnL-2, $(C_6H_5)_2SnOC_{10}H_6CH{=}N\overset{\alpha}{C}H(\overset{\beta}{C}H_3)C(O)O$: Dark brown; % yield, 99; mp, 165—170 °C. Found: Sn, 23.03; N, 2.52%. Calcd for $C_{26}H_{21}NO_3Sn$: Sn, 23.08; N, 2.72. Molar conductance in DMF, 66.0; UV-vis in $CHCl_3$, 220 (11200), 230 (11500) π–π^* (benzenoid)/n–π^* (COO); 329 (19600) π–π^* (>C=N–); 396 (15300) secondary band of the naphthalene ring; ^{1}H NMR δ = 8.59 (s, 1H, (–CH=N–)), 8.25—7.39 (m, 16H, [$C_{10}H_6$ + 2(C_6H_5) of tin]), 4.08 (m, 1H, [=NCH(α)]), 1.35 (m, 3H, [CH_3(β)]).

4. Ph_3SnL'-2, $(C_6H_5)_3SnC_6H_5CH{=}N\overset{\alpha}{C}H(\overset{\beta}{C}H_3)C(O)O$: Dark yellow; % yield, 98; mp, 121—125 °C. Found: Sn, 23.07; N, 2.16%. Calcd for $C_{28}H_{25}NO_2Sn$: Sn, 23.17; N, 2.66%. Molar conductance in CH_3OH, 90.0; UV-vis in CH_3OH, 210 (10800), 221 (17400) π–π^* (benzenoid)/n–π^* (COO); 258 (19200) π–π^* (>CH=N–); ^{1}H NMR δ = 8.10 (s, 1H, (–CH=N–)), 8.00—7.32 (m, 20H, [C_6H_5 + 3(C_6H_5) of tin]), 4.21 (m, 1H, [=NCH(α)]), 1.30 (m, 3H, [CH_3(β)]).

5. Ph_2SnL-3, $(C_6H_5)_2SnOC_{10}H_6CH{=}N\overset{\alpha}{C}H(\overset{\beta}{C}H_2\overset{\gamma}{C}H_2\overset{\delta}{S}CH_3)C(O)O$: Brown: % yield, 99; mp, 145—150 °C. Found: Sn, 19.06; N, 2.14; S, 5.56%. Calcd for $C_{28}H_{25}NO_3SnS$: Sn, 20.66; N, 2.44; S, 5.58%. Molar conductance in DMF, 67.0; UV-vis in $CHCl_3$, 230 (28300), 236 (29100) π–π^* (benzenoid)/n–π^* (COO); 336 (15700) π–π^* (>C=N–); 369 (13500), 405 (18700) secondary band of naphthalene ring; ^{1}H NMR δ = 9.28 (s, 1H, (–CH=N–)), 8.09—7.30 (m, 16H, [$C_{10}H_6$ + 2(C_6H_5) of tin]), 4.55, 4.54 (d of d, 1H, [=NCH(α)]), 2.58 (q, 2H, [CH_2(γ)], 2.34, 2.01 (m, 2H, [CH_2(β)]), 1.92 (s, 3H, [SCH_3(δ)]).

6. Ph_3SnL'-3, $(C_6H_5)_3SnC_6H_5CH{=}N\overset{\alpha}{C}H(\overset{\beta}{C}H_2\overset{\gamma}{C}H_2\overset{\delta}{S}CH_3)C(O)O$: Yellow; % yield, 80; mp, 123—128 °C. Found: Sn, 19.97; N, 2.05; S, 5.45%. Calcd for $C_{30}H_{29}NO_2SnS$: Sn, 20.24; N, 2.39; S, 5.47%. Molar conductance in CH_3OH, 95.0; UV-vis in CH_3OH, 200 (17500), 222 (27800) π–π^* (benzenoid)/n–π^* (COO); 260 (10900) π–π^* (>C=N–); ^{1}H NMR δ = 8.75 (s, 1H, (–CH=N–)), 8.02—7.38 (m, 20H, [C_6H_5 + 3(C_6H_5) of tin]), 4.58, 4.57 (d of d, 1H, (=NCH(α)]), 2.60 (q, 2H, [CH_2(γ)]), 2.30, 2.01 (m, 2H, [CH_2(β)]), 1.91 (s, 3H, [SCH_3(δ)]).

7. Ph_2SnL-4: Dark brown; % yield, 99; mp, 140—145 °C. Found: Sn, 21.42; N, 2.40%. Calcd for $C_{28}H_{25}NO_3Sn$: Sn, 21.89; N, 2.58%. Molar conductance in DMF, 84.0; UV-vis in CH_3OH, 225 (22000), 232 (24400) π–π^* (benzenoid)/n–π^* (COO); 311 (14900) π–π^* (>C=N–); 364 (18800), 429 (28900) secondary band of the naphthalene ring.

8. Ph_3SnL'-4: Cream; % yield, 90; mp, 150—154 °C. Found: Sn, 20.47; N, 2.45%. Calcd for $C_{30}H_{29}NO_2Sn$: Sn, 21.41; N, 2.53%. Molar conductance in CH_3OH, 100.0; UV-vis in CH_3OH, 200 (21200), 228 (18100) π–π^* (benzenoid)/n–π^* (COO); 255 (10500) π–π^* (>C=N–).

9. Ph_2SnL-5, $(C_6H_5)_2SnOC_{10}H_6CH{=}N\overset{\alpha}{C}H(\overset{\beta}{C}H_2C_6H_5)C(O)O$: Brown; % yield, 98; mp, 152—155 °C. Found: Sn, 19.82; N, 2.30%. Calcd for $C_{32}H_{25}NO_3Sn$: Sn, 20.10; N, 2.37%. Molar conductance in DMF, 66.0; UV-vis in $CHCl_3$, 228 (27700), 235 (29300) π–π^* (benzenoid)/n–π^* (COO); 344 (16900) π–π^* (>C=N–); 374 (14300), 410 (24900) secondary band of the naphthalene ring; ^{1}H NMR δ = 8.80 (s, 1H, (–CH=N–)), 8.05—7.30 (m, 21H, [$C_{10}H_6$ + C_6H_5 of ligand and 2(C_6H_5) of tin]), 5.00 (m, 1H, [=NCH(α)]), 3.90, 2.88 (d, 2H, [CH_2(β)]); ^{13}C NMR (C-1 to C-10 of $C_{10}H_6$) δ = 107.90, 133.72, 123.79, 124.45, 129.28, 128.56, 127.14, 139.88, 118.29, 172.47; (–CH=N–) 166.17; (=NCH(α)) 70.74; (CH_2(β)) 42.02; (C-11 to C-14 of C_6H_5 attached to CH_2) 136.03, 130.79, 127.42, 128.92; (C(O)O) 173.59; (C-α to C-δ of C_6H_5 of tin) 137.30, 135.30, 128.23, 129.94.

10. Ph_3SnL'-5, $(C_6H_5)_3SnC_6H_5CH{=}N\overset{\alpha}{C}H(\overset{\beta}{C}H_2C_6H_5)C(O)O$: Light yellow; % yield, 90; mp, 200 °C. Found: Sn, 18.80; N, 2.25%. Calcd for $C_{34}H_{29}NO_2Sn$: Sn, 19.70; N, 2.32%. Molar conductance in CH_3OH, 98.0; UV-vis in CH_3OH, 200 (16700), 220 (21700) π–π^* (benzenoid)/n–π^* (COO); 252 (16900) π–π^* (>C=N–); ^{1}H NMR δ = 8.06 (s, 1H, (–CH=N–)), 7.80—7.10 (m, 25H, [2(C_6H_5) of ligand + 3(C_6H_5) of tin]), 5.38 (1H, [=NCH(α)]), 3.96, 2.60 (d, 2H, [CH_2(β)]).

11. Ph_2SnL-6: Dark brown; % yield, 99; mp, 150—155 °C. Found: Sn, 21.06; N, 2.50%. Calcd for $C_{27}H_{23}NO_3Sn$: Sn, 22.47; N, 2.65%. Molar conductance in DMF, 72.0; UV-vis in CH_3OH, 220 (19500), 226 (21100) π–π^* (benzenoid)/n–π^* (COO); 339 (15600) π–π^* (>C=N–); 402 (17400), 416 (17500) secondary band of the naphthalene ring.

12. Ph_3SnL'-6: Yellow; % yield, 95; mp, 128—130 °C.

Found: Sn, 20.75; N, 2.45%. Calcd for $C_{29}H_{27}NO_2Sn$: Sn, 21.97; N, 2.59%. Molar conductance in CH_3OH, 102.0; UV-vis in CH_3OH, 205 (18500), 220 (16900) π–π^* (benzenoid)/n–π^* (COO); 250 (10200) π–π^* (>C=N–).

13. Ph_2SnL-7, $(C_6H_5)_2SnOC_{10}H_6CH{=}N\overset{\alpha}{C}H[\overset{\beta}{C}H_2\overset{\gamma}{C}H(\overset{\delta}{C}H_3)_2]C(O)O$: Brown; % yield, 98; mp, 155—162 °C. Found: Sn, 21.26; N, 2.30%. Calcd for $C_{29}H_{27}NO_3Sn$: Sn, 22.33; N, 2.52%. Molar conductance in DMF, 60.0; UV-vis in $CHCl_3$, 200 (18900), 224 (19200) π–π^* (benzenoid)/n–π^* (COO); 336 (15800) π–π^* (>C=N–); 405 (14400), 414 (14500) secondary band of the naphthalene ring; ^{1}H NMR δ = 8.69 (s, 1H, (–CH=N–)), 8.05—6.83 (m, 16H, [$C_{10}H_6$ + 2(C_6H_5)]), 4.34, 4.32 (d of d, 1H, [=NCH(α)]), 3.56, 3.54 (d of d, 2H, [CH_2(β)]), 2.78 (m, 1H, [CH(γ)]), 1.27, 0.88 (m, 6H, {[CH_3]$_2$(δ)}).

14. Ph_3SnL'-7, $(C_6H_5)_3SnC_6H_5CH{=}N\overset{\alpha}{C}H[\overset{\beta}{C}H_2\overset{\gamma}{C}H(\overset{\delta}{C}H_3)_2]C(O)O$: Cream; % yield, 90; mp, 125—128 °C. Found: Sn, 17.76; N, 2.25%. Calcd for $C_{31}H_{31}NO_2Sn$: Sn, 22.88, N, 2.46%. Molar conductance in DMF, 63.0; UV-vis in CH_3OH, 200 (17900), 222 (18300) π–π^* (benzenoid)/n–π^* (COO); 250 (10200) π–π^* (>C=N–); ^{1}H NMR, δ = 8.42 (s, 1H, (–CH=N–)), 8.00—7.25 (m, 20H, [C_6H_5 of ligand + 3(C_6H_5) of tin]), 4.32, 4.30 (d of d, 1H, [=NCH(α)]), 3.48, 3.46 (d of d, 2H, [CH_2(β)]), 2.65 (m, 1H, [CH(γ)]), 1.23, 0.90 (m, 6H, {[CH_3]$_2$(δ)}).

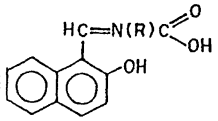
Results and Discussion

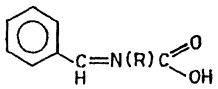
Di- and triphenyltin(IV) derivatives of the Schiff bases, respectively, derived from the condensation of 2-hydroxy-1-naphthaldehyde and benzaldehyde with different amino acids (H_2L/HL′), have been synthesized by the reactions of the corresponding diphenyltin and triphenyltin chlorides with the sodium salt of the Schiff bases in ca. 1 : 1 molar ratios.

$$H_2L/HL' + 2NaOMe/NaOMe = Na_2L/NaL' + 2MeOH/MeOH \quad (1)$$

$$Ph_2SnCl_2 + Na_2L = Ph_2SnL + 2NaCl \quad (2)$$

$$Ph_3SnCl + NaL' = Ph_3SnL' + NaCl \quad (3)$$

Where H_2L =  and

HL′ = 

Where R = –CH_2– H_2L-1 ; HL′-1
= >CH–CH_3 H_2L-2 ; HL′-2
= >CH–CH_2–CH_2–SCH_3 H_2L-3 ; HL′-3
= >CH–CH(CH_3)$_2$ H_2L-4 ; HL′-4
= >CH–CH_2–C_6H_5 H_2L-5 ; HL′-5
= >CH–CH_2–CH_3 H_2L-6 ; HL′-6
= >CH–CH_2–CH(CH_3)$_2$ H_2L-7 ; HL′-7

The above reactions were found to be quite facile, and completed within 7—8 h of refluxing. The resulting complexes, obtained in good yields, were colored solids, stable in air and soluble in methanol and chloroform, but sparingly soluble in DMF and DMSO. In every instance the resulting complexes crystallized with 1 : 1 stoichiometry, regardless of the proportions of the Schiff bases and di- and triphenyltin chloride used. The analytical data are in good agreement with the proposed stoichiometry of the complexes. The molar conductance values of 10^{-3} M (1 M=1 mol dm^{-3}) solutions of the complexes in dimethylformamide or methanol are in the range of 48—102 ohm^{-1} cm^2 mol^{-1}, indicating their nonelectrolytic nature.

The electronic spectra of the complexes exhibit three bands in the regions 200—236, 250—344, and 364—429 nm, which may be due to the π–π^* transition of the benzenoid/π–π^* COO, π–π^* transition of the (>C=N–) chromophore and the secondary band of the naphthalene ring,[11] respectively. Further, there was a sharp band observed in the 252±4 nm region in the spectra of the complexes, which could be assigned as a charge-transfer band. It has been reported[19] that a metal/metalloid is capable of forming dπ–pπ bonds with ligands containing nitrogen or oxygen as the donor atoms. Since tin atom has its 5d orbitals completely vacant, L→M bonding can take place by the acceptance of a pair of electrons from nitrogen or oxygen donor atoms of the ligands.

Important infrared frequencies (in cm^{-1}) and their assignments are tabulated in Table 1. It has been reported[8] that Schiff base derived from glycine and 1-(2-hydroxy-4-methylphenyl)-1-ethanone exists predominantly in iminium form, as represented in Fig. 1, on the basis of the appearance of an infrared band around 3400 cm^{-1} due to NH vibration. Two bands at 1675 and 1610 cm^{-1} were also assigned[8] to the –COO asymmetric stretch and the C=N/C=C ring stretching modes of vibration, respectively.

The infrared spectra of all the organotin(IV) complexes do not show a strong band in the 3500—3300 cm^{-1} region, due to $\nu_{OH/NH}$,[7] indicating the deprotonation of the phenolic and carboxylic oxygen of the Schiff bases upon complexation with tin metal, as expected. It has further been confirmed by the appearance of a sharp band at 528—580 cm^{-1} in the spectra of the complexes assignable to the Sn–O stretching vibration.[11]

In the sodium salts of the Schiff bases H_2L/HL′ two bands at 1675±10 and 1585±10 cm^{-1} were observed and assigned to the –COO asymmetric stretch and the C=N/C=C ring stretching modes of vibrations, respectively. In the spectra of the organotin(IV) complexes, the asymmetric –COO stretch is shifted to a lower frequency (1620±15 cm^{-1}), whereas the C=N/C=C ring stretch is slightly shifted to a higher frequency (1591±11 cm^{-1}), indicating coordination of the ligand through the carboxyl oxygen and the imino nitrogen to tin. The symmetric stretch of the –COO group suffers a high-frequency shift from a well-defined peak at 1372±18 cm^{-1}, indicating the possibility of metal–oxygen bond formation through the –COO group. Furthermore, the separation between the asymmetric and symmetric vibrations

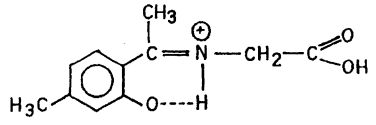


Fig. 1. Structure of Schiff base derived from glycine and 1-(2-hydroxy-4-methylphenyl)-1-ethanone.

Table 1. Infrared Frequencies (in cm^{-1}) of Ph_2SnL and Ph_3SnL' Complexes

Sl. No.[a)]	ν_{as}(COO)	ν(C=N) / ν(C=C)	ν_s(COO)	$\Delta\nu$(COO)	ν_{as}(Sn–C)	ν_s(Sn–C)	ν(Sn–O)	ν(Sn←N)
1	2	3	4	5	6	7	8	9
1	1610s	1580vs	1362m	248	268m	230w	541w	453vs
2	1625s	1595vs	1375s	250	271m	233w	555m	435s
3	1605mbr	—	1339s	266	265m	225w	531m	447vs
4	1620vs	1593s	1365s	255	276m 270sh	231w	565w	420m
5	1625s	1590s	1369s	256	273m	223w	552m	430s
6	1620s	1588s	1360s	260	267m	219w	548w	437s
7	1625m	1595vs	1370s	255	259m	220w	550m	432s
8	1609s	1600vs	1350vs	259	280vs 265m	235m	530m	420m
9	1628vs	1598s	1370s	258	260m	221w	550m	433s
10	1635vs	1600s	1375s	260	275m	227w	555m	435s
11	1628s	1601vs	1378s	250	264m	226w	550w	430s
12	1615s	1600vs	1395vs	220	269wsh	220w	580w	420m
13	1635s	1602s	1380s	255	268m	232w	549m	438s
14	1608sbr	—	1380s	228	266m	231w	528vs	439vs

a) Sl. Nos. are those as indicated in experimental; vs, very strong; s, strong; m, medium; w, weak; br, broad; sh, shoulder.

is about ca. 243±23 cm^{-1}, indicating the covalent nature of the metal–oxygen bond.[8)] Ionic bonding and also bridging or chelation can therefore be excluded, and carboxylic groups bonding tin unidentatily must be assumed.[20)]

The conclusions drawn above are further supported by the presence of a new band in the far-I.R. spectra of the complexes, at ca. 437±17 cm^{-1}, which may be assigned to Sn←N.[18)]

Five-coordinate complexes of the MX_3Y_2 type may assume either of the three trigonal bipyramidal arrangements, A, B, and C of D_{3h}, C_{2v}, and C_4 symmetry, respectively [Fig. 2]. It is apparent from an examination of the available data for five- and six-coordinate organotin complexes that the preferred geometries are, respectively, trigonal bipyramidal with *cis* (equatorial) organic moieties and octahedral with a *trans* arrangement of organic groups, seemingly independent of any charge carried by the complex. The far-I.R. spectra of Ph_3SnL'-1 to Ph_3SnL'-7 depict two Sn–C stretching frequencies at 273±7 and 227±8 cm^{-1}. This indicates that the three phenyl groups are not in equatorial positions, and that the two donor atoms, viz. oxygen and nitrogen in the ligands, are not in the axial positions, as one would expect from the steric properties of the bidentate ligands.[18)] Further, the far-I.R. spectra of Ph_2SnL-1 to Ph_2SnL-7 (where L-1 to L-7 are tridentate biionic anions of Schiff bases) also show two Sn–C stretching frequencies at 266±7 at 226±6 cm^{-1}, which suggest the presence of two *cis* phenyl groups in the equatorial positions of the trigonal bipyramidal structure.[11)]

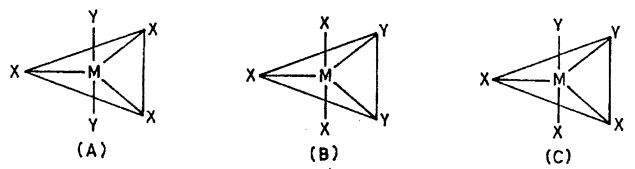


Fig. 2. Possible geometries for MX_3Y_2.

The chemical shifts (δ in ppm) of various protons in all of the complexes, except for the complexes of sl. nos. 7, 8, 11, and 12 because of their insufficient solubility in $CDCl_3$ and DMSO-d_6, are given in Experimental. The absence of a signal due to the –OH proton at δ=12.00—13.00 ppm suggests deprotonation of the phenolic/carboxylic oxygen atoms of the ligands upon complexation.[11)] The signal at δ=8.67±0.61 ppm has been assigned to the azomethine (–N=CH–). Due to the complex nature of multiplets observed in the δ=8.25—6.83 ppm region in all of 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.

The signals corresponding to $-CH_2$, –CH, and $-CH_3$ of the ligand moieties were also given in Experimental. The number of protons of the various groups, calculated from the integration curves, and those calculated for the expected molecular formula agree with each other. ^{13}C NMR data of three complexes have been recorded and given in Experimental. The various types of carbon have been successfully assigned. The tin shielding in the $^{117}Sn/^{119}Sn$ NMR spectra increases markedly alongwith an increase in the coordination number from δ=−50 to −100 ppm for 4-coordinate to δ=−200 ppm for 5-coordinate to δ=−330 ppm for 6-coordinate alkyltin compounds.[21)] Tin shifts are normally higher with phenyl compared to that of alkyl substituent.[21)] Ph_2SnL-1, Ph_2SnL-2, Ph_2SnL-5, Ph_3SnL'-1, and Ph_3SnL'-2 show sharp signals at δ=−334.8, −342.2, −340.7, −330.9, and −335.7 ppm, respectively. These are in accordance with the proposed five coordinated structures. These compounds give a ρ value (ρ=Q.S./C.S.) of 2.31±0.11 (Table 2) which indicates a coordination number greater than four.[22)] The chemical-shift values indicate the presence of tin in the +IV oxidation state, and the presence of a quadrupole splitting

Table 2. ^{117}Sn NMR Chemical Shifts (in δ/ppm) and ^{119}Sn Mössbauer Spectral Data at (77 K) vs. Ba $^{119m}SnO_3$

Sl. No.	Complexes	^{119}Sn shifts ppm	Q.S. mm s^{-1} ±0.06	C.S. mm s^{-1} ±0.03	δ=Q.S/C.S.	τ_1	τ_2
1	Ph_2SnL-1	−334.8	2.82	1.23	2.29	1.14	1.10
2	Ph_2SnL-2	−342.2	—	—	—	—	—
3	Ph_2SnL-4	—	2.38	1.06	2.34	1.45	1.58
4	Ph_2SnL-5	−340.7	—	—	—	—	—
5	Ph_3SnL'-1	−330.9	—	—	—	—	—
6	Ph_3SnL'-2	−335.7	2.54	1.15	2.20	0.74	0.64
7	Ph_3SnL'-6	—	2.72	1.12	2.42	0.76	0.75

shows that the EFG around the tin nucleus is produced by the inequalities in the tin-ligand σ bond.[19,23] The possible geometry around tin in the complexes of the type Ph_2SnL (where L=L-1 to L-7, are the bianions of Schiff bases derived from the condensation of 2-hydroxy-1-naphthaldehyde with various amino acids) is distorted trigonal bipyramidal, in which the ligands are bifunctional tridentate coordinating through the ONO donor set derived from the phenolic oxygen, azomethine nitrogen and carboxyl oxygen.

The observed values of the quadrupole splitting (Q.S.) and chemical shift (C.S.) of the complexes are in the 2.82—2.38 mm s^{-1} and 1.23—1.06 mm s^{-1} range, respectively. A number of workers obtained a Q.S. value in the 2.40—3.10 mm s^{-1} range for R_2Sn(8-quinolinolate), where R=C_6H_5 or C_2H_5, X=halogen, and for other similar compounds and concluded that the organic groups are in *cis* position.[24—26] In light of the above findings, the possible arrangement of the phenyl groups in Ph_2SnL will be a *cis*, since the observed

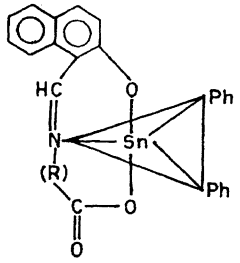


Fig. 3. Structure of Ph_2SnL.

Q.S. values are in the same range and represented in Fig. 3. The proposed structure is also consistent with the observed multiple ν_{Sn-C} (phenyl) vibrations in the far-infrared spectra (Table 1).

The Ph_3SnL' complexes (where, L'=L'-1 to L'-7 are the monoanion of bidentate Schiff bases derived from the condensation of benzaldehyde with various amino acids) have been tentatively proposed to have a distorted trigo-

Table 3. Results of Antimicrobial Activity of Ph_2SnL and Ph_3SnL' Complexes

Complexes	Minimum inhibitory concentration (MIC)[a] in μg ml^{-1} against									
	Bacteria					Fungi				
	1	2	3	4	5	6	7	8	9	10
Ph_3SnL'-1	<12.5	20	<12.5	I	<12.5	<12.5	<12.5	<12.5	<12.5	<12.5
Ph_3SnL'-2	<12.5	25	<12.5	50	<12.5	<12.5	<12.5	<12.5	25	<12.5
Ph_3SnL'-3	<12.5	50	<12.5	I	<12.5	<12.5	<12.5	25	25	<12.5
Ph_3SnL'-5	<12.5	25	<12.5	I	<12.5	<12.5	<12.5	25	25	<12.5
Ph_3SnL'-7	<12.5	50	<12.5	I	<12.5	<12.5	25	I	50	50
Ph_2SnL-2	<12.5	I	<12.5	I	<12.5	25	50	25	25	<12.5
Ph_2SnL-3	<12.5	I	<12.5	I	<12.5	25	25	25	25	<12.5
Ph_2SnL-4	<12.5	50	<12.5	50	<12.5	25	25	25	50	<12.5
Ph_2SnL-6	<12.5	50	<12.5	25	<12.5	<12.5	25	25	25	<12.5
Ph_2SnL-7	<12.5	50	25	I	<12.5	25	50	I	I	<12.5
Ph_3SnCl	I	I	12.5	I	6.25	12.5	1.56	6.25	3.925	3.125
Ph_2SnCl_2	25	I	25	I	12.5	I	25	I	25	I
Amphotericin-B	—	—	—	—	—	0.20	0.39	1.0	0.42	0.76
5,Flucytosine	—	—	—	—	—	1.20	0.59	—	0.39	—
Sofaclonzo	—	—	—	—	—	—	—	—	—	0.78
Norflox	—	12.5	6.2	12.5	3.0	—	—	—	—	—
Cap.flox	1.5	3.1	1.5	0.78	0.78	—	—	—	—	—

a) The samples were not screened below 12.5 μg ml^{-1}; I. Inactive; solvent used, DMSO 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*.

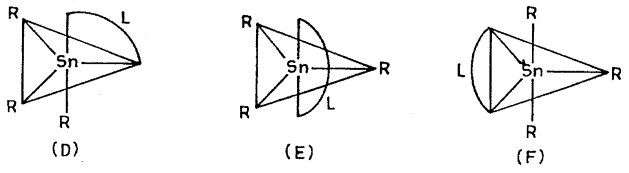


Fig. 4. The possible isomers of R_3SnL.

nal bipyramidal geometry around tin. The three possible R_3SnL (L=bidentate ligand) isomers are shown in Fig. 4. Each of these possible isomers would be expected to show a different quadrupole splitting (Q.S.) value in the Mössbauer spectrum.[27,28] For an isomer of type D, the range of Q.S. is 1.7—2.3 mm s^{-1} for type E, 3.0—3.9 mm s^{-1} and for type F, 3.5—4.1 mm s^{-1}. The observed values of Q.S. in Ph_3SnL'-2 and Ph_3SnL'-6 are 2.54 and 2.72 mm s^{-1}, respectively, supporting the structure D. Further, the steric requirements for the bidentate Schiff-base anions (L′-1 to L′-7) along with the I.R. evidence rule out structure E. Bancroft et al. have reported similar results for five-coordinate β-diketonatotriorganotin compounds.[28]

As evident from Table 3, the parent organotin compounds, viz. Ph_3SnCl and Ph_2SnCl_2, as well as their individually screened derivatives exhibit varying degrees of inhibitory effects on the growth of a wide spectrum of bacteria and fungi. All of the complexes were very active against all of the bacteria and fungi used. The inhibitory effects of the complexes were found to be fairly greater than those of the limiting effects of the parent organotin compounds, signifying a greater activity of the complexes. As evident from Table 3, the bactericidal and fungicidal activities of the organotin complexes under the experimental conditions decreased in the following order: triphenyltin complex > diphenyltin complex. Thus, the results clearly show that the organotin(IV) complexes possess moderate bactericidal and fungicidal activities.

Thermal Studies. The thermal decomposition of some complexes, viz. Ph_3SnL'-4, Ph_3SnL'-5, Ph_3SnL'-6, Ph_2SnL-2, and Ph_2SnL-7, have been studied using TG, DTG, and DTA techniques. All of the complexes gradually decomposed with the formation of SnO_2 above 700 °C. As is evident from the data compiled in Table 4, all of the complexes, except for Ph_3SnL'-6 and Ph_2SnL'-2, gradually decompose in the temperature range 25—890 °C with two inflection points in TG, although no sharp distinct plateau has been observed for the loss of ligand or phenyl groups attached to tin. Ph_2SnL-2 decomposes in a single step in the 70—960 °C temperature range, giving SnO_2 as an end product of the decomposition. The observed percent weight loss (70.00%) was in good agreement with the calculated percent weight loss (71.69%). It has been observed that a rapid loss occurred in the 107—350 °C temperature range, thereafter, the complex decomposed very slowly. DTA shows two peaks at 428 °C (exothermic) and 796 °C (endothermic). Ph_2SnL-7 decomposed in the 114—890 °C temperature range with two inflection points at 270 and 765 °C. The observed weight loss (28.57%) up to the first inflection point indicated the

Table 4. Thermal Analysis Data of the Complexes

Sl. No.	Temp range (°C) from TG	Peak temp in DTG (°C)	Temp range in DTG (°C)	Peak temp in DTA (°C) [Nature of peak]	Temp range in DTA (°C)	Loss of mass % from TG obsd (calcd)	Total % wt. loss obsd (calcd)
Ph_3SnL'-4	94—705 with two inflection points at 250 and 300	226	215—248	120 (endothermic)	107—134	21.50 upto 1st (21.50) point	73.00 (72.81)
		279	248—300	227 (exothermic) followed by endotherm	169—248	24.50 upto 2nd (27.50) point	
		312	300–350	312 (endothermic)	287—322	27.00 remaining (23.81) loss	
Ph_3SnL'-5	25—722 with two inflection points at 151 and 290	114	95—133	107br (endothermic)	87—157	12.00 upto 1st (12.30) point	74.50 (74.98)
		279	193—310	V.broad endotherm	220—302	40.00 upto 2nd (38.91) point	
		345	325—378	V.broad endotherm	350—438	22.50 remaining (23.77) loss	
Ph_3SnL'-6	85—835 with inflection point at 215	192	145—220	107 (endothermic)	80—181	17.35 upto 1st (14.01) point	73.46 (72.11)
		278	237–409	395 (exothermic)	271—456	56.11 remaining (58.10) loss	
				503 (exothermic)	456—580		
Ph_2SnL-2	70—960	269 (V.broad)	192—360	Initial upward start from 65	350—539	—	70.00 (71.69)
				428 (exothermic broad hump)	790—807	—	
				796 (endothermic)			
Ph_2SnL'-7	114—890 with two inflection points at 270 and 765	250	120—310	Initial start from 40 upward 428 (exothermic broad)	235—523	28.57 upto 1st (27.72) point	72.45 (72.91)
		388	370—409	584 (broad exothermic)	523—725	30.61 upto 2nd (32.41) point	
		812	787—835	796 (endothermic)	788—805	13.27 remaining (12.78) loss	

loss of both phenyl groups attached to tin, for which the calculated weight loss was 27.72%. The observed weight loss (30.61%) up to 765 °C corresponds to a loss of the naphthalene ring ($C_{10}H_6$) and the C_4H_6 moiety of the ligand, giving intermediate II, which undergoes a further loss of 13.27%, giving SnO_2 as a residue. DTG shows three peaks corresponding to a three-step decomposition of the complex; in DTA, however, there is an initial exothermic reaction, giving the peak temperature at 428 °C (as broad exotherms) followed by another broad exotherm at 584 °C and a sharp endothermic peak at 796 °C.

Complexes Ph_3SnL'-4 and Ph_3SnL'-5 show two inflection points in the TG curves. The observed percent weight losses in Ph_3SnL'-4 up to these inflection points (250 and 300 °C), corresponding to the loss of the $-C_6H_5$ group attached to the tin $+C_3H_6$ moiety of the ligand, and a further loss of two C_6H_5 groups attached to tin, respectively, give an intermediate which undergoes decomposition with the loss of the remaining portion of the ligand moiety, giving SnO_2 as a residue. The percent weight loss in Ph_3SnL'-5 corresponds to the first inflection point, indicating the loss of one phenyl group attached to the tin or phenyl group attached to the $-CH_2$ group of the amino acid moiety, whereas the weight loss up to the second inflection point (290 °C) indicates the loss of two C_6H_5 groups attached to tin. The remaining part of the ligand was lost from 290—680 °C, giving SnO_2 as a residue. The corresponding DTG and DTA peaks are given in Table 4. Ph_3SnL'-6 undergoes a two-step decomposition, and is stable up to 85 °C. The first step from 85—215 °C corresponds to the loss of one phenyl group attached to tin, followed by the loss of the other two phenyl groups attached to tin together with the loss of the ligand moiety, resulting in the formation of the SnO_2 residue. DTG shows two peaks at 192 and 278 °C, whereas three peaks are observed in DTA, as given in Table 4. The residues in all cases have been characterized by X-ray analysis and tin determination. All of the '*d*' values observed in the residues were in good agreement with the reported '*d*' values for SnO_2.[29]

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