

Organotin(IV) Complexes of Some 2-Pyrazoline Derivatives, Part I: R_3SnCl and R_2SnCl_2 Complexes

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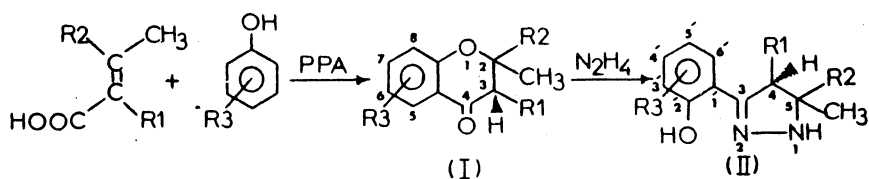
Triorganotin(IV) and diorganotin(IV) compounds react with 3-aryl-5-methyl-2-pyrazoline, 3-aryl-4,5-dimethyl-2-pyrazoline and 3-aryl-5,5-dimethyl-2-pyrazoline derivatives (L) in 1:1 molar ratio to give complexes of the general formula $R_3SnCl \cdot L$ and $R_2SnCl_2 \cdot L$ ($R = Me, Bu^n, Ph$) respectively. The complexes obtained have been characterised physico-chemically and spectroscopically. As revealed from the IR and 1H NMR spectral data, the 2-pyrazoline derivative coordinates with tin of R_3SnCl as a monodentate ligand via one of the active donor sites, either N_2 or OH, to give penta-coordinate tin species, whereas it coordinates with tin of R_2SnCl_2 in a bidentate fashion via both sites (N_2 and OH) to give six member chelate ring with tin of hexa-coordination number. All the complexes prepared showed no conductivity in both solvents, acetonitrile and DMF, indicating the non-ionic species, $[R_3Sn(L)Cl]$ and $[R_2Sn(L)Cl_2]$.

INTRODUCTION

In the past few years, we have been interested in the study of the coordination behaviour of organotin(IV) compounds with several ligands containing oxygen, sulphur and nitrogen as donor sites¹⁻³. Some of the complexes obtained were found to have significant biological activities against certain types of bacteria and tumour cells⁴⁻⁷.

As a continuation of our comprehensive investigation in this field of coordination chemistry, we have chosen, in the present work, the 2-pyrazoline derivative ligands as containing more than one donating site. We have already shown in a separate work⁸, that some of these ligands coordinate with platinum metal in a bidentate fashion to give complexes structurally analogous to *cis*-platin, the anti-tumour agent⁹. However, we carried out here the reaction of these 2-pyrazolines, IIa-j (Scheme-1) with the organotin(IV) compounds R_3SnCl and R_2SnCl_2 ($R = Me, Bu^n, Ph$) in order to examine the type of interaction between these ligands and the tin metal, which to our best of knowledge have not been previously attempted.

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| | R ₁ | R ₂ | R ₃ | |
|------|-----------------|-----------------|----------------|--|
| | | | I | II |
| (a): | H | H | 5,7- | or 4',6'-(CH ₃) ₂ |
| (b): | H | H | 6,7- | or 4',5'-(CH ₃) ₂ |
| (c): | H | H | 6,7- | or 4',5'-(OCH ₃) ₂ |
| (d): | H | CH ₃ | 6,7- | or 4',5'-(CH ₃) ₂ |
| (e): | H | CH ₃ | 6,8- | or 3',5'-(CH ₃) ₂ |
| (f): | H | CH ₃ | 7,8- | or 3',4'-(CH ₃) ₂ |
| (g): | H | CH ₃ | 7- | or 4'-OCH ₃ |
| (h): | H | CH ₃ | 5,7- | or 4',6'-(OCH ₃) ₂ |
| (i): | H | CH ₃ | 5,6,7- | or 4',5',6'-(OCH ₃) ₃ |
| (j): | CH ₃ | H | — | H |

SCHEME 1

The preparation route of the chroman-4-one intermediates (Ia-j) and their corresponding pyrazolines (IIa-j); used in coordination with organotin(IV) compounds

EXPERIMENTAL

General

The ¹H NMR spectra were recorded at Basrah University, Basrah, Iraq, on a Jeol, JNM-Ex-90 FT NMR using CDCl₃ as a solvent, unless otherwise stated, with TMS as an internal standard. IR spectra were recorded on a Perkin-Elmer 580B infrared spectrophotometer in the range 4000–200 cm⁻¹ using Nujol Mull and CsI discs. Analyses of the complexes were carried out at the College of Science, University of Mosul, Mosul, Iraq, using a CHN Analyser, Type 1106 (Carlo Erba). Electronic spectra were recorded on a UV/vis. spectrophotometer model 160 Shimadzu Kyoto (Japan), using DMF as a solvent and quartz cell of 1 cm width. Conductivity measurements were done for 10⁻³ M solutions of the complexes in DMF and CH₃CN at room temperature (25°C), using a conductivity meter, model 4070 (Jenway).

Preparation of starting materials

The compounds Ph_3SnCl , Bu_3SnCl and Bu_2SnCl_2 were commercial products (Fluka). The compounds Me_3SnCl , Me_2SnCl_2 and Ph_2SnCl_2 were prepared by standard methods^{10, 11}.

The ligands, 2-pyrazoline derivatives (IIa-j) were prepared in our laboratories by a standard method¹², by the successive conversions of β - β -acrylic acid or techlic acid or crotonic acid and phenol derivatives into the chroman-4-one intermediates (Ia-j), then into the 2-pyrazoline derivatives (IIa-j) (Scheme 1). The structure of the chromon-4-ones (Ia-j) together with the corresponding 2-pyrazolines (IIa-j) were determined by physico-chemical methods. The yield of the 2-pyrazoline ligands obtained was varied from 65 to 85%.

Preparation of the complexes $\text{R}_3\text{SnCl}\cdot\text{L}$ and $\text{R}_2\text{SnCl}_2\cdot\text{L}$

The complexes were prepared according to the following standard method which is outlined in general format.

The ligand (0.5 mmol) was dissolved in an organic solvent; CHCl_3 or EtOH or acetone (according to its solubility). To this was added a solution of the organotin(IV) compounds (0.5 mmol) in the corresponding solvent (5 mL) with vigorous stirring under moderate heating for *ca.* 30 min. The resulting solution was evaporated to *ca.* 1/2 its original volume, then petroleum spirit (40–60°C) was added until turbidness and the total mixture was kept in the refrigerator for several hours. The resulting crystalline product was filtered, washed several times with pet. spirit and dried under vacuum for several hours. When the product was an oil, it was separated from the mother liquor by decantation, washed with light petroleum, and dried. The oil could be solidified when stirred with light petroleum overnight, and then could be treated as for the solids above. The yield of the complexes $\text{R}_3\text{SnCl}\cdot\text{L}$ and $\text{R}_2\text{SnCl}_2\cdot\text{L}$ ranged between 60 to 90%.

RESULTS AND DISCUSSION

The physical properties of triorganotin(IV) and diorganotin(IV) complexes are listed in Table-1 and the ^1H NMR spectral data of some selected complexes are listed in Table-2. The elemental composition of the complexes prepared is clearly assigned to a 1:1 molar ratio of organotin compound to ligand, *i.e.*, $\text{R}_3\text{SnCl}\cdot\text{L}$ and $\text{R}_2\text{SnCl}_2\cdot\text{L}$.

Spectral data and structure

The triorganotin(IV) and diorganotin(IV) complexes were subjected to IR and ^1H NMR spectral studies for structural elucidation and establishing the mode of bonding.

We have previously reported that tin of R_3SnCl forms as high as five coordination number, while tin of R_2SnCl_2 forms as high as six coordination number, when reacted with various donating ligands¹⁻⁷. Since 2-pyrazoline ligands (Scheme 1) possess more than one donor site, hence R_3SnCl compounds form penta-coordinate tin species, regioselectively, with one of the donor sites, while R_2SnCl_2 compounds form hexa-coordinate tin species, most likely, via.

TABLE-1
THE PHYSICAL PROPERTIES AND ANALYSES OF THE ORGANOTIN(IV)—COMPLEXES R₃SnCl·L and R₂SnCl₂·L

| Ligand L(II) | Complex | Colour | m.p. (°C) | Analyses, Found (Calcd.) % | | | | Selected IR* bands (cm ⁻¹) | | | | UV/vis λ _{max} (nm) | |
|---------------------------------------|---------------------------------------|--------------|----------------|----------------------------|--------------|--------------|-----------------|--|---------|---------|----------|---------------------------------|---------------|
| | | | | C | H | N | | v(C=N) (Δν)† | v(Sn—O) | v(Sn—N) | v(Sn—Cl) | | v(Sn—C) |
| a | Ph ₃ SnCl·La | yellow | 115–116 | — | — | — | — | 1605 m | — | — | — | — | 233, 271, 361 |
| | | yellow-green | 187–190 | 60.9 (61.1) | 5.4 (5.2) | 4.6 (4.7) | — | 1605 m (0) | 430 m | — | 272 s | 252 w | 233, 281, 339 |
| | Me ₂ SnCl ₂ ·La | yellow | 189–190 | 39.7 (39.7) | 5.2 (5.2) | 6.7 (6.6) | — | 1527 m (-27) | 398 m | 418 m | 270 m | 554 m | 235, 280, 345 |
| | | brown | 208–210 | 52.5 (52.6) | 4.8 (4.7) | 5.2 (5.1) | — | 1582 m (-23) | 350 m | 425 s | 293 m | 238 w | 234, 282, 371 |
| b | Bu ₂ SnCl ₂ ·La | brown | 200–202 | 46.1 (47.3) | 6.5 (6.7) | 5.4 (5.5) | — | 1573 m (-32) | 405 m | 432 m | 305 w | 534 m, b | 235, 282, 337 |
| | | yellow | 126 | — | — | — | 1613 s, b | — | — | — | — | — | 235, 276, 316 |
| | Me ₃ SnCl·Lb | yellow | 206–208 | 44.5 (44.7) | 6.0 (6.2) | 7.1 (6.9) | — | 1613 s (0) | 391 m | — | 276 m | 554 m | — |
| | | yellow | 191–194 | 60.4 (61.1) | 5.8 (5.2) | 4.6 (4.7) | — | 1578 s (-35) | — | 449 s | 268 s | 246 w | 234, 276, 317 |
| Me ₂ SnCl ₂ ·Lb | yellow | 213–215 | 39.6 (39.7) | 5.1 (5.2) | 6.7 (6.6) | — | 1573 m (-40) | 391 w | 400 s | 285 m | 554 m | 234, 280, 347 | |
| | yellow | 209–211 | 52.3 (52.6) | 5.0 (4.7) | 5.0 (5.1) | — | 1578 m (-35) | 350 w | 418 w | 302 s | 260 m | 235, 277, 347 | |
| c | Bu ₂ SnCl ₂ ·Lb | yellow | 218–219 | 47.0 (47.3) | 6.5 (6.7) | 5.6 (5.5) | — | 1573 m (-40) | 384 m | 418 m | 276 m | 534 w | 237, 279, 337 |
| | | yellow | 115–116 | — | — | — | 1614 s, b | — | — | — | — | — | 231, 273, 326 |
| Ph ₃ SnCl·Lc | pale-yellow | 226–228 | 58.1 (58.0) | 5.2 (5.0) | 4.4 (4.5) | — | 1614 s (0) | 405 w | — | 285 m | 248 w | 273, 325 | |

| Ligand L(II) | Complex | Colour | m.p. (°C) | Analyses, Found (Calcd.) % | | | Selected IR* bands (cm ⁻¹) | | | | UV/vis λ _{max} (nm) | |
|-----------------|---------------------------------------|----------------------|--------------------|----------------------------|--------------|--------------|--|---------------|------------|------------|---------------------------------|---------------------------|
| | | | | C | H | N | v(C=N) (Δν)† | v(Sn—O) | v(Sn—N) | v(Sn—Cl) | | v(Sn—C) |
| | Me ₂ SnCl ₂ :Lc | yellow | 237–239 | 36.8 (36.9) | 4.9 (4.8) | 6.1 (6.1) | 1578 s (-36) | 384 m | 450 m | 285 s | 554 m | 235, 272, 369 |
| | Ph ₂ SnCl ₂ :Lc | orange | 230–232 | 50.0 (49.7) | 4.6 (4.5) | 4.7 (4.8) | 1587 m (-27) | 357 m | 425 s | 286, 297 m | 275 w | 277, 367 |
| | Bu ₂ SnCl ₂ :Lc | brown | 226–228 | 44.1 (44.5) | 6.0 (6.3) | 5.3 (5.2) | 1560 m (-54) | 391 w | 412 w | 305 m, b | 520 m | 235, 276, 383 |
| d | Me ₃ SnCl:Ld | off-white yellow | 132–134 251–254 | — (46.0) | — (6.5) | — (6.7) | 1600 m, sh 1600 m, sh (0) | — 338 m, b | — 271 m | — 560 m | — 560 m | 232, 276, 318 264, 356 |
| | Me ₂ SnCl ₂ :Ld | brown | 227–230 | 40.8 (41.1) | 5.7 (5.5) | 6.2 (6.4) | 1578 m, sh (-22) | 391 m | 449 s | 282, 320 w | 561 m | 230, 280, 346 |
| | Ph ₂ SnCl ₂ :Ld | brown | 204–206 | 53.2 (53.4) | 5.0 (5.0) | 4.8 (5.0) | 1570 m (-30) | 422 w | 443 s | 302 m, b | 276 w | 230, 280, 346 |
| e | Bu ₂ SnCl ₂ :Ld | yellow | 250–253 | 48.1 (48.3) | 6.7 (6.9) | 5.2 (5.4) | 1573 s, sh (-27) | 391 m | 429 w | 276, 310 w | 541 w | 230, 278, 359 |
| | Ph ₃ SnCl:Le | yellow | 100–101 | — | — | — | 1605 m, sh | — | — | — | — | 232, 282, 345 |
| | Me ₂ SnCl ₂ :Le | yellow | 208–211 | 61.1 (61.7) | 5.3 (5.5) | 4.4 (4.6) | 1605 w (0) | 398 m | — | 276 m | 212 w | 232, 276, 345 |
| f | Me ₂ SnCl ₂ :Le | brown | 220–222 | 41.2 (41.1) | 5.4 (5.5) | 6.5 (6.4) | 1573 m, sh (-32) | 401 m | 425 m | 275 m | 552 w | 235, 273, 257 |
| | Ph ₂ SnCl ₂ :Le | brown | 148–150 | 53.4 (53.4) | 4.9 (5.0) | 5.1 (5.0) | 1582 m (-23) | 388 s | 418 w | 298 s | 230 w | 234, 283, 345 |
| | Bu ₂ SnCl ₂ :Le | brown | 231–234 | 48.2 (48.3) | 6.8 (6.9) | 5.8 (5.4) | 1570 m, sh (-35) | 395 s | 429 w | 302 w | 517 m, b | 229, 273, 345 |
| | Me ₃ SnCl:Lf | white light brown | 103–105 140–143 | — (46.0) | — (6.3) | — (6.5) | 1600 s 1560 s (-40) | — — | — 446 s | — 255 s | — 531 m | 230, 268, 328 235, 271 |

| Ligand L(II) | Complex | Colour | m.p. (°C) | Analyses, Found (Calcd.) % | | | | Selected IR* bands (cm ⁻¹) | | | | UV ^{vis} λ _{max} (nm) | |
|-----------------|---------------------------------------|------------------|--------------------|----------------------------|-------------------|-------------------|---|--|---------------|----------|------------|--|--------------------------------|
| | | | | C | H | N | | v(C=N) (Δv)† | v(Sn—O) | v(Sn—N) | v(Sn—Cl) | | v(Sn—C) |
| g | Bu ₃ SnCl:Lf | yellow | 160–162 | 55.0 (55.2) | 8.3 (8.3) | 5.0 (5.1) | — | 1587 m (-13) | 395 s | — | 251 m | 531 m | 232, 271, 346 |
| | Me ₂ SnCl ₂ :Lf | yellow | 88–91 d | 41.0 (41.1) | 5.4 (5.5) | 6.2 (6.4) | — | 1560 s, sh (-40) | 381 m | 439 s | 251, 272 s | 527 m | 232, 270, 346 |
| | Ph ₂ SnCl ₂ :Lf | yellow | 45–48 | 53.4 (53.4) | 4.8 (5.0) | 5.0 (5.0) | — | 1570 m, sh (-30) | 388 m | 436 s | 256 m | 233 w | 231, 354 |
| h | Me ₂ SnCl ₂ :Lg | brown yellow | 118–120 140–143 | — 37.9 (38.2) | — 5.1 (5.0) | — 6.5 (6.4) | — | 1596 s, sh 1578 s (-18) | — 390 w, b | — | — | — | 230, 278, 336 229, 278, 347 |
| | Ph ₂ SnCl ₂ :Lg | yellow-brown | 92–94 | 50.9 (51.1) | 4.8 (4.6) | 4.8 (5.0) | — | 1578 s (-18) | 395 m | 446 m, b | 282, 301 s | 264 m, sh | 230, 270, 349 |
| | Bu ₂ SnCl ₂ :Lg | brown | 167 | 45.2 (45.8) | 6.2 (6.5) | 5.1 (5.3) | — | 1570 m, sh (-26) | 284 m | 439 m | 302 s, b | 520 w | 232, 276, 356 |
| i‡ | Ph ₃ SnCl:Lh | yellow yellow | 124–125 176–179 | — 58.3 (58.6) | — 5.2 (5.2) | — 4.2 (4.4) | — | 1600 m 1587 s (-13) | — | — | — | — | 230, 285 229, 344 |
| | Me ₂ SnCl ₂ :Lh | orange | 141–144 | 39.0 (38.3) | 5.2 (5.1) | 5.9 (6.0) | — | 1595 s (-5) | 391 s | 432 s | 225, 251 m | 534 m | 227, 335 |
| | Ph ₂ SnCl ₂ :Lh | yellow | 152–154 | 50.2 (50.6) | 4.8 (4.7) | 4.9 (4.7) | — | 1570 m, sh (-30) | 408 s | 425 m | 285, 306 m | 293 w | 230, 233 |
| i‡ | Bu ₂ SnCl ₂ :Lh | orange | 118–120 | 46.0 (45.5) | 6.4 (6.5) | 5.0 (5.0) | — | 1570 m (-30) | 395 m | 418 w | 268 m, b | 548 m | 230, 232 |
| | Me ₃ SnCl:Li | yellow | 206–208 179–181 | 59.9 (60.0) | 7.4 (7.1) | 10.1 (10.0) | — | 1595 s | — | — | — | — | 230, 279, 345 |
| | | | | 42.0 (42.6) | 5.9 (6.0) | 5.6 (5.8) | — | 1595 s (0) | 384 w | — | 242 m | 514 m | 256, 271, 382 |

| Ligand L(II) | Complex | Colour | m.p. (°C) | Analyses, Found (Calcd.) % | | | Selected IR* bands (cm ⁻¹) | | | | UV/vis λ_{\max} (nm) | |
|-----------------|---------------------------------------|--------|--------------|----------------------------|--------------|----------------|--|---------------------------|---------------------------|----------------------------|---------------------------------|---------------------------|
| | | | | C | H | N | $\nu(\text{C}=\text{N})$ ($\Delta\nu$)† | $\nu(\text{Sn}-\text{O})$ | $\nu(\text{Sn}-\text{N})$ | $\nu(\text{Sn}-\text{Cl})$ | | $\nu(\text{Sn}-\text{C})$ |
| j‡ | Ph ₃ SnCl·Li | yellow | 183-185 | 57.5 (57.7) | 5.4 (5.2) | 4.0 (4.2) | 1595 s (0) | 384 m | — | 263 s | 251 m | 233, 274, 357 |
| | Me ₂ SnCl ₂ ·Li | yellow | 112-115 | 38.0 (38.4) | 5.3 (5.2) | 5.4 (5.6) | 1578 (-17) | 391 m | 405 m | 255 m | 534 m | 230, 280, 346 |
| | Ph ₂ SnCl ₂ ·Li | yellow | 146-148 | 49.8 (50.0) | 4.6 (4.8) | 4.3 (4.5) | 1578 (-17) | 398 m | 418 m | 276 s | 247 m | 230, 281, 346 |
| j‡ | Me ₃ SnCl·Lj | yellow | 100-101 | 69.3 (69.5) | 7.4 (7.4) | 14.5 (14.7) | 1605 s, b | — | — | — | — | 237, 276, 364 |
| | Ph ₃ SnCl·Lj | yellow | 182-185 | 42.9 (43.2) | 5.6 (5.9) | 7.2 (7.2) | 1605 s (0) | 422 m | — | 282 m | 517 m | 236, 292, 335 |
| | Me ₂ SnCl ₂ ·Lj | yellow | 100-102 | 60.0 (60.5) | 5.4 (5.0) | 4.5 (4.9) | 1605 s, b (0) | 416 s | — | 271 s | 252 w | 274, 369 |
| j‡ | Ph ₂ SnCl ₂ ·Lj | yellow | 180-182 | 37.9 (38.1) | 5.0 (4.9) | 6.6 (6.8) | 1587 s, b (-18) | 425 s | 442 m, b | 306, 327 s | 541 m | 232, 271, 334 |
| | Ph ₂ SnCl ₂ ·Lj | yellow | 184-186 | 51.8 (51.7) | 4.4 (4.5) | 5.3 (5.2) | 1580 s, b (-25) | 391 w | 450 s | 290, 305 m | 275 w | 234, 274, 335 |
| | Bu ₂ SnCl ₂ ·Lj | orange | 234-236 | 46.1 (46.2) | 6.4 (6.5) | 5.7 (5.7) | 1560 m, sh (-45) | 418 w | 446 m, b | 305 m | 520 m | 280, 351 |

*In Nujol Mulls

† $\Delta\nu$ equal to $\nu(\text{complex}) - \nu(\text{ligand})$.‡These are new ligands, not reported previously¹².

TABLE-2
 ^1H NMR DATA, δ (ppm) AND J (Hz) FOR SOME SELECTED $\text{R}_3\text{SnCl}\cdot\text{L}$ AND $\text{R}_2\text{SnCl}_2\cdot\text{L}$ COMPLEXES

| Compound | $\delta\text{Me/Ph}$ ($2J(^{119}\text{Sn}-\text{CH})$) | Ligand (LII) assignments* | | | | | | $\delta(\text{NH})$ |
|--|---|---------------------------------|-----------------------|-----------------------|--|---|--------|---------------------|
| | | $\delta(\text{CH}_3\text{C}-5)$ | $\delta(\text{HC}-4)$ | $\delta(\text{HC}-5)$ | $\delta(\text{R}_3-\text{H})$ | $\delta(\text{Ar}-\text{H})$ | | |
| $\text{Me}_2\text{SnCl}_2\cdot\text{La}$ | 1.20 s (92) | 1.44 s | 3.08 s | 3.83 m | 2.15 s, 3H(CH ₃) 2.36 s, 3H(CH ₃) | 6.60 b, HC-3' 8.24 b, HC-5' | 5.06 b | |
| $\text{Me}_2\text{SnCl}_2\cdot\text{Lb}$ | 1.20 s (86) | 1.50 d $J = 7.3$ | 3.45 dq | 4.20 m | 2.20 s, 6H(CH ₃) ₂ | 6.70 s, HC-3' 6.90 s, HC-6' | ‡ | |
| $\text{Ph}_3\text{SnCl}\cdot\text{Lc}$ | 7.37-7.82 m | 1.46 d $J = 0.7$ | 2.72 dd | 4.16 m | 3.85 s, 3H(OCH ₃) 3.90 s, 3H(OCH ₃) | 6.45 s, HC-3' 7.20 s, HC-6' | 5.90 b | |
| $\text{Me}_2\text{SnCl}_2\cdot\text{Lc}$ | 1.20 s (90) | 1.45 d $J = 0.7$ | 3.46 dq | 4.25 m | 3.90 s, b, 6H(CH ₃) ₂ | 6.45 s, HC-3' 7.60 s, HC-6' | ‡ | |
| $\text{Me}_2\text{SnCl}_2\cdot\text{Ld}$ | 1.20 s (81) | 1.40 s | 2.96 s | — | 2.27 s, 6H(CH ₃) ₂ | 6.70 s, HC-3' 7.88 s, HC-6' | 5.40 b | |
| $\text{Me}_2\text{SnCl}_2\cdot\text{Lf}$ | 1.18 s (90) | 1.25 s | 2.33 s | — | 2.08 s, 3H(CH ₃) 2.15 s, 3H(CH ₃) | 6.75 d, HC-5' 7.58 d, HC-6' $J = 8.0$ | 5.10 b | |
| $\text{Me}_2\text{SnCl}_2\cdot\text{Lg}$ | 1.20 s (80) | 1.43 s | 2.15 s | — | 3.82 s, 3H(OCH ₃) | 6.54 d, HC-3' 6.60 d, HC-5' 8.14 d, HC-6' $J = 7.0, 7.2, 10$ | 6.40 b | |
| $\text{Ph}_3\text{SnCl}\cdot\text{Lh}$ | 7.50-7.75 m | 1.46 s | 2.32 s | — | 3.88 s, 3H(OCH ₃) 4.16 s, 3H(OCH ₃) | 6.18 d, HC-3' 6.08 d, HC-5' $J = 1.0$ | 5.40 b | |
| $\text{Me}_2\text{SnCl}_2\cdot\text{Lh}$ | 1.28 s (85) | 1.48 s | 2.80 s | — | 3.88 s, 3H(OCH ₃) 4.00 s, 3H(OCH ₃) | 6.18 m | 5.30 b | |

| Compound | $\delta_{\text{Me/Ph}}$ ($2J(^{119}\text{Sn}-\text{CH})$) | Ligand (LII) assignments* | | | | | $\delta(\text{NH})$ |
|---------------------------------------|--|----------------------------------|-----------------------|-----------------------|---|---|---------------------|
| | | $\delta(\text{CH}_3\text{-C-5})$ | $\delta(\text{HC-4})$ | $\delta(\text{HC-5})$ | $\delta(\text{R}_3-\text{H})$ | $\delta(\text{Ar}-\text{H})$ | |
| Li | — | 1.39 s | 2.54 s | — | 3.83 s, 6H(OCH ₃) ₂ 3.90 s, 3H(OCH ₃) | 6.24 s, HC-3' | 5.28 b |
| Me ₃ SnCl·Li | 1.15 s (70) | 1.40 s | 3.10 s | — | 3.80 s, 6H(OCH ₃) ₂ 3.85 s, 3H(OCH ₃) | 6.20 s, HC-3' | ‡ |
| Ph ₂ SnCl ₂ ·Li | 7.25–7.92 m | 1.42 s | 2.98 s | — | 3.85 s, 6H(OCH ₃) ₂ 3.92 s, 3H(OCH ₃) | 6.20 s, HC-3' | 5.35 b |
| Me ₂ SnCl ₂ ·Li | 1.20 s (91) | 1.48 s | 2.80 s | — | 3.90 s, 6H(OCH ₃) ₂ 4.60 s, 3H(OCH ₃) | 6.29 s, HC-3' | 5.10 b |
| Lj† | — | 1.40 d J = 9.0 | 2.80 m | 3.35 m | — | 6.80 s, HC-3',4' 7.70 d, HC-5' 8.05 d, HC-6' J = 9.0 | 5.05 b |
| Me ₃ SnCl·Lj† | 1.10 s (70) | 1.35 d J = 9.0 | 2.80 m | 3.30 m | — | 6.85 s, HC-3',4' 7.60 d, HC-5' 8.10 d, HC-6' J = 9.0 | 5.00 b |

*Downfield from internal TMS using CDCl₃ as a solvent. For the abbreviations, s, Singlet; d, doublet; dd, doublet of doublet; dq, doublet of quartet; m, multiplet and b, broad signals.

†Methanol-d₄ was used as a solvent; $\delta(\text{CH}_3\text{-C-4}) = 1.25$ d, J = 9.0.

‡Not very well resolved signals.

N_2 —OH linkage. These facts were mainly demonstrated by IR and 1H NMR spectral data (*vide infra*).

IR spectra

The routine IR spectral measurements showed that coordination of tin with these ligands had taken place. The IR bands appearing in the region 430–350 cm^{-1} and 450–400 cm^{-1} are tentatively assigned to $\nu(Sn-O)$ and $\nu(Sn-N)$ respectively, which serve as a good indicator of coordination *via* O and N sites^{3,4}. It is more likely that N_2 site rather than N_1 site of the 2-pyrazoline derivatives would be involved in the coordination with organotin(IV) compounds. This was supported by the drastic decrease ($\Delta\nu = 13-50\text{ cm}^{-1}$) of the $\nu(C=N)$ value on going from the free ligand to its complex^{6,7}. It is, therefore, concluded that R_3SnCl compounds coordinate with 2-pyrazoline derivatives *via* either N_2 or OH site of the ligand, whereas R_2SnCl_2 compounds coordinate with these ligands in a bidentate fashion *via* N_2 —OH linkage to form six-membered chelate ring. This was confirmed by the 1H NMR spectral data of $Me_2SnCl_2 \cdot L$ complexes (*vide infra*).

Furthermore, the IR spectra of the complexes showed also other bands: a band in the region 325–225 cm^{-1} which is attributed to $\nu(Sn-Cl)$ modes and a band in the region 275–220 cm^{-1} and 560–520 cm^{-1} (usually as a weak band) which is attributed to $\nu(Sn-C)$ modes for both $Sn-Ph$ and $Sn-Me$ (or Bu^n) respectively^{2,6,13}. The bands due to $\nu(OH)$ and $\nu(NH)$ usually interfered with each other and appeared in the region 3380–3150 cm^{-1} as broad bands and could not be distinguished.

NMR spectra

The NMR spectral data of the free ligands (L) (Scheme 1) were extensively discussed in our previous articles¹². The 1H NMR spectra of some selected $R_3SnCl \cdot L$ and $R_2SnCl_2 \cdot L$ complexes were recorded in $CDCl_3$. In the case of the complexes, where $R = Bu^n$ or Ph , the 1H NMR spectral data showed no significant differences than those of the free ligands, apart from the presence of some new signals related to the Bu^n and Ph protons. We have shown in many articles that $^{119}Sn-CH$ coupling constant serves as a very good indicator to evaluate the coordination number of tin in its methyl complexes^{1,2}. It is very clear from the $2J(^{119}Sn-CH)$ values of $Me_3SnCl \cdot L$ complexes (*ca.* 70 Hz) (Table-2), that 2-pyrazoline derivatives coordinate with tin in a monodentate fashion *via* the most reactive donor site to give penta-coordinate tin species^{4,14}. In the contrary, the $2J(^{119}Sn-CH)$ values of $Me_2SnCl_2 \cdot L$ complexes which ranged between 80 to 92 Hz, assign that these ligands coordinate with tin in a bidentate mode *via* the N_2 —OH linkage to give hexa-coordinate species¹⁻⁴. This is a good support to the idea suggested by the IR studies, in which 2-pyrazoline derivatives coordinate with R_3SnCl and R_2SnCl_2 compounds in a mono- and bidentate forms respectively.

Electronic spectra

UV/vis spectral data for the complexes (Table-1) showed absorption bands attributed to the ligand in its complexes¹⁵. The absorption band appearing in the

region 229–237 nm is attributed to $\pi \rightarrow \pi^*$ electronic transitions in the aryl ring, the band appearing in the region 268–282 nm is attributed to $\pi \rightarrow \pi^*$ electronic transitions in the C=N group, and the band appearing in the region 332–382 nm is due to $n \rightarrow \pi^*$ electronic transitions in the C=N group too. Bands due to d-d transitions in the d-orbitals of the tin atom were too weak to be observed.

Conductivity measurements

The conductivity measurements for 10^{-3} molar solutions of both complexes $R_3SnCl \cdot L$ and $R_2SnCl_2 \cdot L$ at room temperature in both solvents DMF and acetonitrile fall in the range 3–29 and 2–38 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$, respectively. It was reported that 1:1 conductivity compounds in these solvents usually fall in the range 65–90 and 120–160 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$, respectively¹⁶. Therefore, the conductivity figures obtained, in both solvents, for the complexes studied are for non-conductive species, *i.e.*, nonionic complexes, $[R_3Sn(L)Cl]$ and $[R_2Sn(L)Cl_2]$, respectively.

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