Preparation and characterization of organotin(IV) complexes with some schiff bases

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Some triorganotin(IV) complexes with the general formula, \( \text{Ph}_3\text{SnL} \) [where \( \text{LH} = \) semi- and thiosemi-carbazones of 2-acetylthiophene, 2-acetylfuran and 2-acetyl-naphthalene] have been prepared and characterized on the basis of elemental analyses, molecular weight, conductivity and infrared, \(^1\text{H}\) NMR and \(^{13}\text{C}\) NMR spectral data. The IR and \(^1\text{H}\) NMR spectral data suggest that the ligands act in a monofunctional bidentate manner coordinating through nitrogen and sulphur atoms. A pentacoordinate trigonal-bipyramidal structure is tentatively proposed for the complexes.

Organotin compounds of the type \( \text{R}_3\text{SnX}_4 \) have been found to possess significant biological and pharmacological activities and are used as fungicides\(^1\text{,}^2\), bactericides and antitumour agents\(^3\). Several reports have appeared on the complexes of di- and tri-organotin halides with various nitrogen and oxygen/sulphur containing ligands\(^4\text{,}^5\), but studies on the schiff base derivatives of triorganotin compounds are comparatively limited. Therefore, in continuation of our work on the synthesis of biologically active ligands and their metal complexes, we report here some such Sn(IV) complexes.

Experimental

The chemicals and solvents used were dried and purified by standard methods and moisture was excluded from glass apparatus using \( \text{CaCl}_2 \) guard tubes.

Preparation of ligands

Semicarbazones and thiosemicarbazones were prepared by the condensation of 2-acetylfuran [(1.88g; 0.017 mol), (2.93g; 0.026 mol)], 2-acetyltioliphene [(2.42g; 0.019 mol), (2.73g; 0.022 mol)] or 2-acetyl-naphthalene [(2.75g; 0.016 mol), (3.25g; 0.019 mol)] with semicarbazide hydrochloride [(1.90g; 0.017 mol), (1.74g; 0.019 mol) and (1.80g; 0.016 mol)] or thiosemicarbazide [(2.43g; 0.026 mol), (1.97g; 0.022 mol) & (1.74g; 0.019 mol)], respectively in boiling ethanol. On cooling the solution after 30 min of refluxing the semi- and thiosemi-carbazones separated out as crystalline solids. These were finally recrystallized from the same solvent and dried \( \textit{in vacuo} \) (yield, \( \sim 80\% \)). 2-Acetyltioliphene semicarbazone (2-AcThiop.ScHzH), white solid, m.p. 180°C; 2-acetylfuran semicarbazone (2-AcFur.ScHzH), yellow solid, m.p. 148°C; 2-acetyl-naphthalene semicarbazone (2-AcNaphth.ScHzH), white solid, m.p. 214°C; 2-acetyltioliphene thiosemicarbazone (2-AcThiop.TscHzH), light yellow solid, m.p. 155°C; 2-acetylfuran-thiosemicarbazone (2-AcFur.TscHzH), brown solid, m.p. 168°C and 2-acetyl-naphthalene thiosemicarbazone (2-AcNaphth.TscHzH), white solid, m.p. 144°C.

Preparation of complexes

A calculated amount (2 mmol) of SCH base in dry methanol (40 ml) was allowed to react with sodium methoxide (2 mmol). The sodium salt of the SCH base thus obtained in the solution was added to \( \text{Ph}_3\text{SnCl} \) (2 mmol) in dry benzene (20 ml). The reaction mixture was refluxed for 15-16 hr and sodium chloride so precipitated was separated by filtration. Benzene was added to the filtrate and the mixture was again refluxed and filtered. This process of refluxing and filtration was repeated two or three times until all of the sodium chloride was precipitated and separated out. The excess of solvent was removed \( \textit{in vacuo} \). The resulting complexes were washed with n-hexane and finally dried \( \textit{in vacuo} \) under reduced pressure.

Carbon and hydrogen analyses were performed at the Microanalytical Laboratory of our Department. Nitrogen and sulphur were estimated by the Kjeldahl's and Messenger's methods, respectively. Tin was estimated gravimetrically as SnO\(_2\). Molecular weights were determined ebullioscopically in boiling benzene. The IR spectra were recorded in KBr on a Perkin Elmer 577 grating spectrophotometer. \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra were recorded on a Jeol FX-90Q spectrometer.

Results and discussion

\( \text{Ph}_3\text{SnCl} \) reacts with the sodium salt of schiff bases in 1:1 molar ratio in benzene-methanol mixture according to the following equations:

\[ \text{Ph}_3\text{SnCl} + \text{NO.Na} \rightarrow \text{Ph}_3\text{Sn(NO)} + \text{NaCl} \]
NOTES

Table 1—Analytical data and physical properties of tin(IV) complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>m.p., °C (yield, %)</th>
<th>Found (Calc.)</th>
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<tbody>
<tr>
<td></td>
<td>C%</td>
<td>H%</td>
</tr>
<tr>
<td>Ph₃Sn(2-AcThiop.Scz)</td>
<td>165 (65)</td>
<td>56.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(56.42)</td>
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<tr>
<td>Ph₃Sn(2-AcFur.Scz)</td>
<td>120 (58)</td>
<td>57.92</td>
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<tr>
<td></td>
<td></td>
<td>(58.08)</td>
</tr>
<tr>
<td>Ph₃Sn(2-AcNaphth.Scz)</td>
<td>186 (62)</td>
<td>64.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(64.61)</td>
</tr>
<tr>
<td>Ph₃Sn(2-AcThiop.Tscz)</td>
<td>98 (70)</td>
<td>54.49</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(54.76)</td>
</tr>
<tr>
<td>Ph₃Sn(2-AcFur.Tscz)</td>
<td>135 (61)</td>
<td>56.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(56.42)</td>
</tr>
<tr>
<td>Ph₃Sn(2-AcNaphth.Tscz)</td>
<td>105 (72)</td>
<td>62.71</td>
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<td></td>
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<td>(62.86)</td>
</tr>
</tbody>
</table>

Ph₃SnCl + NS.Na → Ph₃Sn(NS) + NaCl

(where NO and NS are the donor sets of semi- and thiosemi-carbazones, respectively).

The analytical data of all the complexes are listed in Table 1. All the complexes are coloured solids, partially soluble in chloroform and methanol but readily soluble in DMSO, DMF and THF. These are monomeric and non-electrolytic in nature.

IR spectra of semicarbazones and thiosemicarbazones show a strong band around 3300 and 2700 cm⁻¹ due to v(NH)/v(OH) and v(SH), respectively. In the spectra of metal complexes, these bands are absent indicating deprotonation of NH/OH/SH groups followed by coordination. The band observed at 1610 ± 5 cm⁻¹ in the spectra of free ligands, attributable to v(C = N) vibrations, gets shifted to 1620 ± 5 cm⁻¹ in the spectra of complexes indicating the participation of this group in coordination.

New bands observed at ~ 420, ~ 325, ~ 533 and ~ 275 cm⁻¹ may be assigned to v(Sn – N)⁹, v(Sn – S), v(Sn – O)¹⁰ and v(Sn – Ph)¹¹, respectively.

The ¹H NMR spectra of 2-AcThiop.TsczH, 2-AcNaphth.TsczH, 2-AcNaphth.SczH and the corresponding metal complexes were recorded in DMSO-d₆. The spectra of free ligands exhibit the signals due to –NH and –CH₃ protons at δ 10.69, 2.12 ppm (2-AcThiop.TsczH), δ 10.65, 2.26 ppm (2-AcNaphth.TsczH) and δ 10.64, 2.29 ppm (2-AcNaphth.SczH). A complex multiplet due to the aromatic protons appears in the region δ 8.96–7.56 ppm. In the spectra of the corresponding metal complexes, the signal due to NH proton disappears and the signals due to –CH₃ protons get shifted to δ 2.32, 2.41 and 2.48 ppm, respectively. The multiplet is, however, observed in the region δ 9.12–7.52 ppm. The disappearance of NH proton signals and the shifting of –CH₃ and aromatic proton signals in the spectra of metal complexes support the coordination through nitrogen atom.

¹³C NMR spectra of 2-acetylthiophene thiosemicarbazone and its metal complex were also recorded in dry DMSO. The shifting of the signals due to carbons attached to the azomethine nitrogen and thiolic sulphur in the spectrum of the complex (from δ 145.36 to δ 153.40 and from 178.62 to 186.96 ppm, respectively) further supports the involvement of these groups in complexation.

Thus, on the basis of above studies, it becomes clear that the ligands are behaving in a monofunctional bidentate manner coordinating through azomethine nitrogen and ketonic oxygen or thiolic sulphur. Therefore, a pentacoordinated environment around tin may be tentatively proposed in the resulting complexes. However, a single crystal could not be grown inspite of our best efforts and, hence, X-ray studies could not be carried out. On the basis of spectral studies and reports already available in the literature¹²,¹³, a trigonal-bipyramidal geometry with the Sn-N bond occupying the axial position (structure I) has been proposed for the present complexes.
Acknowledgement

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References