Synthesis and characterization of novel chiral organotin complexes

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Novel chiral complexes of organotin have been synthesized using amino acids as chiral auxiliary and 1,10-phenanthroline as a secondary ligand. A series of di- and tri-organotin (IV) [LSnR.L'[ complexes where n = 2 or 3, L=l-amino acids like tryptophan, leucine and valine and L'=1,10-phenanthroline, have been prepared and characterized by conventional methods. Structure elucidation has been done by IR, UV, 1H, 13C, 119Sn NMR spectroscopy. All the complexes are air stable and non-electrolytic in nature.

On the basis of spectral evidences, it has been concluded that the carboxylic acid of the l-amino acid is behaving as a monodentate ligand in all these complexes and the complexes are octahedral in shape with a coordination number six around the tin atom.

Asymmetric synthesis has been a thrust area of organic chemistry. Metal based chiral complexes have invoked interest to many researchers primarily due to their use as catalysts and has led to a challenging new subarea-inorganic asymmetric synthesis. Synthetic routes to asymmetric complexes are still very important and require a new approach which includes the choice of chiral auxiliary, chiral reagents or chiral pool.

In this work we have chosen amino acids as a source of chiral stereogenic center firstly as they are cheap and home chiral and secondly they serve as excellent building blocks and lead to optically pure conformation in good yield. There is an increased interest in synthesis of tin based antitumour drugs and activity of these complexes is closely related to their structure. Thus the chiral complexes may have wide spread application in the field of medicine as antitumour, anti HIV agents, as catalysts and also as enzyme model systems. Here we report the novel route for the synthesis of chiral complexes of organotin where amino acids and 1,10-phenanthroline have been used as ligands. This route yields the optically active complexes in good yield (Table 1) and will serve as a most reliable and versatile method for the synthesis of optically active catalysts.

Experimental

L-tryptophan, L-valine (Sisco research lab), L-leucine (loba chemic), dibutyl, dimethyl and triphenyltin chlorides, (Fluka chemical) and 1,10-phenanthroline (CDH) were used as such. The IR spectra (4000-200 cm⁻¹) were recorded on a Carl-Ziess Specord M-80 spectrophotometer in nujol mulls. Microanalysis were obtained on a Carl-Erba Analyser Model 1106. UV/vis spectra were run on a spectronic 119. The NMR spectra were recorded in CDCl₃ on a amx500. The optical rotation of the complexes were recorded on ASI, India polarimeter.

Synthesis of the complexes [2-amino-3-(3-indolyl)propionato (N,N-1,10-phenanthroline)] triphenyl tin(IV) [C₃₁H₃₄N₃O₂Sn], [2-amino-3-(3-indolyl)propionato (N,N-1,10-phenanthroline)] dibutyl tin(IV) chloride [C₃₅H₃₇N₄O₂SnCl] and [2-amino-3-(3-indolyl)propionato (N,N-1,10-phenanthroline)] dimethyl tin(IV) chloride [C₂₅H₃₅N₄O₂SnCl].

To a solution of L-tryptophan (0.204 g, 1 mmol) in hot dry methanol (25 ml) was added a solution of 1,10-phenanthroline (0.198 g, 1 mmol) in the same solvent. The resultant mixture was refluxed for 20 h after adding a solution of triphenyltin chloride (0.398 g, 1mmol) in hot methanol. The mixture was allowed to stand overnight in refrigeration. The solid product obtained was isolated by filtration, washed with ether and dried in vacuo (Fig. 1).

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Fig. 1—Proposed structure of [2-amino-3-(3-indolyl)propionate (N,N-1,10-phenanthroline)](triphenyltin)
Table 1—Analytical data, M.P., yield and \([\alpha]\) of the complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>M.P. (°C)</th>
<th>% Yield</th>
<th>Analysis (% Calc. (Found)</th>
<th>[\alpha]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}<em>{41}\text{H}</em>{34}\text{N}<em>{3}\text{O}</em>{2}\text{Sn})</td>
<td>190-193</td>
<td>72</td>
<td>68.5 (68.3) 4.71 (4.69) 5.8 (5.70)</td>
<td>11±1 in DMSO</td>
</tr>
<tr>
<td>(\text{C}<em>{31}\text{H}</em>{32}\text{N}<em>{4}\text{O}</em>{2}\text{SnCl})</td>
<td>195-198</td>
<td>80</td>
<td>57.2 (57.08) 5.69 (5.68) 8.61 (8.50)</td>
<td>13±1 in MeOH</td>
</tr>
<tr>
<td>(\text{C}<em>{25}\text{H}</em>{32}\text{N}<em>{4}\text{O}</em>{2}\text{SnCl})</td>
<td>230-233</td>
<td>75</td>
<td>52.96 (52.95) 4.41 (4.31) 9.89 (9.88)</td>
<td>12±1 in MeOH</td>
</tr>
<tr>
<td>(\text{C}<em>{36}\text{H}</em>{34}\text{N}<em>{3}\text{O}</em>{2}\text{Sn})</td>
<td>231-233</td>
<td>78</td>
<td>65.2 (65.5) 5.31 (5.31) 6.37 (6.37)</td>
<td>20±1 in CHCl</td>
</tr>
<tr>
<td>(\text{C}<em>{26}\text{H}</em>{38}\text{N}<em>{3}\text{O}</em>{2}\text{SnCl})</td>
<td>210-212</td>
<td>75</td>
<td>54.02 (54.01) 6.58 (6.48) 7.27 (7.26)</td>
<td>5±1 in CHCl</td>
</tr>
<tr>
<td>(\text{C}<em>{30}\text{H}</em>{36}\text{N}<em>{3}\text{O}</em>{2}\text{SnCl})</td>
<td>286-289</td>
<td>76</td>
<td>48.63 (48.62) 5.27 (5.26) 8.51 (8.50)</td>
<td>10±1 in MeOH</td>
</tr>
<tr>
<td>(\text{C}<em>{19}\text{H}</em>{24}\text{N}<em>{3}\text{O}</em>{2}\text{SnCl})</td>
<td>335-338</td>
<td>74</td>
<td>50.61 (50.51) 5.33 (5.32) 9.32 (9.31)</td>
<td>12±1 in CHCl</td>
</tr>
</tbody>
</table>

Similarly the synthesis of complexes using dibutyl and dimethyl group was carried out yielding white crystalline product.

Synthesis of the complexes [2-amino-4-methyl-valerato (N,N-1,10-phenanthroline)] triphenyl tin(IV) \([\text{C}_{36}\text{H}_{35}\text{N}_{3}\text{O}_{2}\text{Sn}]\), [2-amino-4-methyl-valerato (N,N-1,10-phenanthroline)] dibutyl tin(IV) chloride \([\text{C}_{26}\text{H}_{38}\text{N}_{3}\text{O}_{2}\text{SnCl}]\), and [2-amino-4-valerato (N,N-1,10-phenanthroline)] dimethyl tin(IV) chloride \([\text{C}_{19}\text{H}_{24}\text{N}_{3}\text{O}_{2}\text{SnCl}]\).

The complexes were prepared by adding a solution of 1-leucine (0.131 g, 1 mmol) in methanol (20 ml) and two/three drops of dimethyl amine to the solution of 1,10-phenanthroline (0.198 g, 1 mmol) in methanol. The above mixture was refluxed for ca. 1 h. and to this mixture a solution of triphenyltin chloride/dibutyltin dichloride/dimethyltin dichloride in hot methanol (20 ml) was added. The solution was refluxed for ca. 30 h. On refrigeration coloured crystalline product was isolated. The crystals were washed with ether and dried in vacuo.

Similarly the synthesis of \([\text{L(R)}\text{SnCl}_2\text{L'}]\) was performed by reaction of 1,10-phenanthroline, amino acid and organotin chloride in 1:1:1 ratio. Physical and analytical data for all new complexes are given in (Table 1). All the complexes are air stable and nonelectrolytes in chloroform.

(1) \(\text{1,10-Phenanthroline}+\text{R}_3\text{SnCl} \rightarrow [\text{R}_3\text{SnCl}_2\text{L'}]\) \(\text{L'}\) 
\(\text{[L']R}_2\text{SnCl}_2 \rightarrow \text{[R}_2\text{SnCl}_3\text{L'}]\)

(II) \([\text{R}_3\text{SnCl}_2\text{L'}]+\text{Amino acid} \rightarrow [\text{LR}_3\text{SnL'}]\) 
\([\text{R}_2\text{SnCl}_3\text{L'}]+\text{Amino acid} \rightarrow [\text{LR}_2\text{SnCl}_3\text{L'}]\)

where \(\text{L}=1\)-amino acid as \(\text{1-tryptophan, 1-leucine and 1-valine} \text{ L'} = 1,10-phenanthroline and \text{ R=phenyl, dibutyl or dimethyl.} \)

Results and discussion

The complexes were characterized by IR, UV, \(^1\text{H}, \(^{13}\text{C}, \(^{119}\text{Sn}\) NMR spectroscopy. The \(\text{1-amino acids exhibit v(OH)}\) band of the carboxylate group at ca. 3200 cm\(^{-1}\). However the IR spectrum of \([\text{C}_{41}\text{H}_{34}\text{N}_{3}\text{O}_{2}\text{Sn}]\) does not show this band indicating the deprotonation of the carboxylic group. This is further supported by appearance of a new medium intensity band in far IR region 440-460 cm\(^{-1}\) attributed to Sn-O stretching vibration indicating the coordination of metal through oxygen. No splitting has been observed in the band at ca. 1650 cm\(^{-1}\) due to \((\text{COO})_{2}\text{asym and (COO)}_{\text{sym}}\) which clearly indicates the monodentate nature of the carboxylate group. The electronic spectra of complex \([\text{C}_{41}\text{H}_{34}\text{N}_{3}\text{O}_{2}\text{Sn}]\) was recorded in DMSO. Two prominent peaks observed at 220 and 264 nm in UV region are assigned \(\pi\) to \(\pi^*\) transition due to MLCT.
The $^1$H NMR was recorded in CDCl$_3$ on an instrument amx 500. A singlet was observed in the high field at δ 2.9 due to-CH$_2$ protons of tryptophan. A sharp signal was observed at δ 6.9 due to the tryptophan group (–CH–NH–) protons which are also associated with NH protons. It is, however, difficult to identify NH protons as they lie in the same range. The phenyl protons signals appear in the range of 7-8 ppm. Proton signals due to 1,10-phenanthroline appear at δ 8.45-8.51. Protons at δ 8.51 overlap with R-CO-NH$_2$ group therefore exact position of -NH$_2$ remains unassigned. Since-COOH proton signal is absent in $^1$H NMR spectra it confirms the coordination through carbonyl group which is further supported by Sn-O peak in the far IR spectrum. Our $^1$H NMR data for all other amino acids and organotin derivatives are quite comparable with the results reported earlier.  

$^{13}$C NMR spectra of the complex [C$_4$H$_{34}$N$_2$O$_2$Sn], recorded in CDCl$_3$, exhibit the carboxylic carbon signal at 4.17 ppm (showing upfield shift than the free amino acid) attributed to the monodentate nature of the carboxylic group. The bands due to phenyl carbon attached to tin are observed at 126-128 ppm. The carbons of 1,10-phenanthroline (heterocyclic carbons) are observed at 126, 136 and 145 ppm respectively. On the basis of spectral evidences, it may be inferred that the carboxylic acid of the l-amino acid is behaving as monodentate in these complexes and the complexes are octahedral in shape with a coordination number six around the tin atom.

$^{119}$Sn NMR spectrum of all the complexes have been run in DMSO $D_6$. $^{119}$Sn chemical shift at δ 280.931 indicates that tin is in octahedral environment in the complex [C$_4$H$_{34}$N$_2$O$_2$Sn] while the value of tin in complex [C$_4$H$_{34}$N$_2$O$_2$SnCl] is in lower field δ 260.9 also indicates the six coordinate geometry around the tin atom. The somewhat higher value for the triphenyl complex in comparison to other alkyltin complex may be accounted for the increased polarizability of the phenyl groups and chelate effects. Our results are fully consistent with the six coordinated as reported by Smith et.al.

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References