CHAPTER - IV

Organotin(IV) Derivatives of Catecholyl Borate
4.1 INTRODUCTION

The organoborate chemistry has been extensively explored in the past two decades\(^1\)-\(^3\). Interaction of KBH\(_4\) with pyrazole, indazole, imidazole\(^4\) and indole\(^5\) have been shown to yield a variety of ligands which have been exploited mainly in the synthesis of transition metal complexes. The organoborates containing B-O bonds have relatively, been less studied\(^6\),\(^7\), especially with group (IV) elements\(^8\),\(^9\) mainly because of the difficulties in handling of the material.

Although organotin (IV) chelates with oxygen and nitrogen donor ligands such as carboxylates, glycolates, urea, pyrrolidine, phenanthroline,\(^10\)-\(^13\) have been widely studied,\(^1\) there seems to be no report on organotin (IV) borates containing a boron-oxygen-tin linkage. Since diphenoxy spiroborate anion may form a strong coordinate bond with any metal ion, it was worth attempting the syntheses of its chelates with organotin (IV) chlorides in order to study the nature of bonding and shape of molecule with the help of the characteristic infra red active B-O, Sn-O and Sn-C stretching frequencies and NMR signals.

4.2 PURIFICATION OF SOLVENTS AND THE STARTING MATERIALS:

The aromatic dioles, potassium borohydride (BDH) and organotin (IV) chloride (E. Merck or Fluka) were used without further purification. The solvents were dried and deoxygenated before use. All the experiments were done under dry nitrogen atmosphere to prevent oxygen and moisture.
4.3 PHYSICAL AND SPECTRAL MEASUREMENTS OF THE TITLE COMPOUNDS:

The melting points were determined using an electro-thermal melting point apparatus and are uncorrected. Molar conductance was measured in DMSO on Elico conductivity bridge type CM 82 T. Infra red spectra were recorded on a Perkin-Elmer model 621 spectrometer using CsI window. The proton NMR spectra were run in D$_2$O or DMSO d$^6$ solution on a Varian A 60D spectrometer. Tin was analysed as SnO$_2$ gravimetrically.

4.4 SYNTHESIS OF LIGAND

The synthetic route employed under this project for the synthesis of the ligands is an improvement over Hermans$^{14}$ and Boesken$^{15}$ method as reflected by its quantitative yield. Catechol (30 m mol, 3.3 g) dissolved in ethanol (25 ml) was added to potassium borohydride (10 m mol, 0.54 g) suspension in ethanol (25 ml) in a flask fitted with a condenser connected to a gas collecting device. The mixture was refluxed for 5 h till hydrogen gas ceased to evolve. It was cooled and filtered through air tight filtration assembly, washed several times with ethanol and dry ether. The greyish white solid was dried in vacuum desiccator over CaCl$_2$. The solid turned brown on standing for a few days. The yield was 85%, mp > 300°C. The observed % of C, H was 54.33, respectively while calculated % for K[B(C$_6$H$_4$O$_2$)$_2$] are C, 54.13 and H, 3.01 respectively. The molar conductance in 1 m molar solution in methanol was found 70 mho cm$^2$mol$^{-1}$. 
4.5 PREPARATION OF THE TITLE COMPOUNDS

4.5.1 R₂SnL₂ Type :

4.5.1.1 Di [bis (catecholyl) borate] dimethylnit (IV) :

0.8 g (1 m mol) of dimethylnit(IV) dichloride in ethanol was mixed into an ethanolic suspension of 0.6 g (4 m mol) of potassium bis catecholyl borate under anaerobic condition in a 100 ml flask. The content of the flask was refluxed for about 4 h till the ligand suspension was nearly dissolved. Subsequently, it was cooled and the unreacted mass was filtered off alongwith the precipitate of KCl. The filtrate was dried in vacuo and washed several times with diethylether. The white powdered solid thus obtained was again dried over CaCl₂ giving 40% yield of the compound, m.p. > 300°C.

Analysis observed, C, 51.63, H, 3.70, Sn, 19.60 and calculated for Me₂Sn[B(C₆H₄O₂)₂]₂; C, 51.7, H, 3.65, Sn, 19.73. Molar conductance in 1 m molar solution of CH₃OH was found to be 14 ohm⁻¹ cm² mol⁻¹. The formula of the compound may be represented as follows:

 Me₂SnCl₂ + 2K[B(C₆H₄O₂)₂] --> Me₂Sn[B(C₆H₄O₂)₂]₂ + 2KCl

4.5.1.2 Di[bis(Catecholyl)borate]dibutyltin(IV):-

An ethanolic solution of 0.6 g (2 m mol) of butyl tin(IV) dichloride was mixed with a suspension of 1.06 g (4 m mol) of potassium bis(catecholyl)borate in the same solvent in an inert atmosphere. The reaction mixture was refluxed for about 4 h until the suspension converted into a clear solution which was cooled
after which the KCl white precipitated and was filtered off. The filtrate was dried in vacuo leaving behind white solid which was washed several times with ether. The yield was 35%, m.p. was observed above 300°C and the 1 m molar methanolic solution gave 15 ohm⁻¹ cm² mol⁻¹ as the molar conductance. For Bu₂Sn[B(C₆H₄O₂)₂]₂ the calculated C, 55.90, H, 4.95 and Sn 17.32% and found C, 55.88, H, 3.70, and Sn, 17.20% respectively.

The following chemical equation depicts the formation of the complex:

\[
\text{Bu}_2\text{SnCl}_2 + 2\text{K[B(C}_6\text{H}_4\text{O}_2\text{)}_2]} \rightarrow \text{Bu}_2\text{Sn[B(C}_6\text{H}_4\text{O}_2\text{)}_2]} + 2\text{KCl}
\]

4.5.1.3 Di[bis(Catecholyl)borate] diphenyl tin(IV):

This complex was prepared by refluxing an ethanolic solution of 0.68 g (2 m mol) of diphenyl tin(IV) dichloride with 1.06 g (4 m mol) of the ligand in ethyl alcohol. The reaction mixture was cooled down and the precipitate of KCl was filtered off. The filtrate was evaporated to a dry white powdery mass. The product was washed 3 to 4 times with dry ether. The yield was 35%. The compound did not melt upto 300°C and the elemental analysis showed the observed percentage as C, 58.94, H, 3.6, Sn, 17.20, the calculated percentage for Ph₂Sn[(B(C₆H₄O₂)_2)_2] being; C, 59.94, H, 3.60 and Sn, 17.20 1 m molar solution of this compound shows molar conductance as 14 ohm⁻¹ cm² mol⁻¹. The equation for the complex formation may be written as:

\[
\text{Ph}_2\text{SnCl}_2 + 2\text{K[B(C}_6\text{H}_4\text{O}_2\text{)}_2]} \rightarrow \text{Ph}_2\text{Sn[B(C}_6\text{H}_4\text{O}_2\text{)}_2]} + 2\text{KCl}
\]
4.5.2 \textbf{R}_3\text{SnL Type :}

4.5.2.1 \textbf{[Bis (catecholyl) borate] tributyltin (IV)}:

To a solution of 0.65 g (2 m mol) of tri butyltin (IV) chloride was added in ethanolic suspension of 0.53 g (2 m mol) of the ligand. The reaction mixture was refluxed for about 4 h, cooled down and the precipitate was filtered off as KCl. The filtrate so obtained was evaporated yielding a white powdered product with 35% yield, m.p. >300°C. Observed % of C, H and Sn was 55.30, 6.86 and 22.80, respectively; while that calculated for Bu$_3$Sn[B(C$_6$H$_4$O$_2$)$_2$]$_2$ is 55.70, 6.77 and 23.02, respectively. The molar conductance measured in 1 molar solution in CH$_3$OH is 12-20 mho cm$^2$ mol$^{-1}$. The following equation is suggested for this complex formation:

\begin{align*}
\text{Bu}_3\text{SnCl} + \text{K}[\text{B(C}_6\text{H}_4\text{O}_2)_2] & \rightarrow \text{Bu}_3\text{Sn}[\text{B(C}_6\text{H}_4\text{O}_2)_2] + \text{KCl}
\end{align*}

4.5.2.2 \textbf{[Bis (catecholyl) borate] tri phenyl tin (IV)}:

A freshly prepared solution of 0.77 g (2 mmol) of triphenyl tin (IV) chloride was refluxed for 4 h with 0.53 g (2 m mol) of the same ligand in ethanol. The white powdery solid was isolated in the manner as described for the earlier complexes. Percentage yield being 30, m.p. >300°C. The observed percentage values being C, 62.28, H, 4.05, Sn, 20.40 % and those calculated for Ph$_3$Sn[B(C$_6$H$_4$O$_2$)$_2$] are 62.39, 3.99 and 20.62, for C, H and Sn, respectively. Molar conductance measured in 1 molar solution in CH$_3$OH was obtained as 12 ohm$^{-1}$ cm$^2$ mol$^{-1}$. The equation may be as follows:

\begin{align*}
\text{Ph}_3\text{SnCl} + \text{K}[\text{B(C}_6\text{H}_4\text{O}_2)_2] & \rightarrow \text{Ph}_3\text{Sn}[\text{B(C}_6\text{H}_4\text{O}_2)_2] + \text{KCl}
\end{align*}
4.6 RESULTS AND DISCUSSION:

Though potassium bis-(catecholyl) borate is thermally stable it is slightly sensitive to oxidation by air and moisture. On exposure to air it turned brown without any change in composition.

The NMR spectrum of the filtrate showed two signals owing to aromatic protons at (6.4 - 6.8) and at 6.47 ppm. This aromatic proton signal is lost when deuterated, suggesting that the filtrate may contain catechol. The Muelenhoff's free acid (MFA) may be one of the products obtained during the course of the reaction which may not be distinguished from free catechol. Since the filtrate immediately turns brown it is believed that there is a small quantity of Muelenhoff's acid in the filtrate which was rejected.

![Fig. 4.1 Proposed structure of Muelenhoff's free acid.](image)

Its metal chelates are soluble in ethanol and DMSO. They are covalent as evidenced by their reaction and molar conductance (12-20 ohm\(^{-1}\) cm\(^2\)/mol) measured in DMSO at ambient temperature.

4.6.1 IR SPECTRA:

The B-O frequency depends on the geometry of the boron atom, the (B-O) stretching frequency lies in 1340 ± 10 cm\(^{-1}\) range if
Table - 7.

Melting Points, Molar Conductivity and Analytical data of Organotin Complexes of Bis (catecholyl) Borate.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Yield (%)</th>
<th>Melting point (°C)</th>
<th>Analysis Found (Calcd.) %</th>
<th>Molar conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>K[B(cat)$_2$]</td>
<td>85</td>
<td>&gt;300</td>
<td>54.33</td>
<td>3.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(54.13)</td>
<td>(3.01)</td>
</tr>
<tr>
<td>1. Me$_2$Sn[B(cat)$_2$]$_2$</td>
<td>40</td>
<td>&gt;300</td>
<td>51.63</td>
<td>3.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(51.74)</td>
<td>(3.65)</td>
</tr>
<tr>
<td>2. Bu$_2$Sn[B(cat)$_2$]$_2$</td>
<td>35</td>
<td>&gt;300</td>
<td>55.88</td>
<td>3.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(55.90)</td>
<td>(4.95)</td>
</tr>
<tr>
<td>3. Ph$_2$Sn[B(cat)$_2$]$_2$</td>
<td>32</td>
<td>&gt;300</td>
<td>58.94</td>
<td>3.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(59.42)</td>
<td>(3.58)</td>
</tr>
<tr>
<td>4. Bu$_3$Sn[B(cat)$_2$]$_2$</td>
<td>35</td>
<td>&gt;300</td>
<td>55.30</td>
<td>6.86</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(55.70)</td>
<td>(6.77)</td>
</tr>
<tr>
<td>5. Ph$_3$Sn[B(cat)$_2$]$_2$</td>
<td>30</td>
<td>&gt;300</td>
<td>62.28</td>
<td>4.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(62.39)</td>
<td>(3.99)</td>
</tr>
</tbody>
</table>

cat = (catecholyl); Me = methyl, Bu = butyl, Ph = phenyl
Table - 8.

Characteristic Infra Red Bands (cm⁻¹) for Organotin Complexes of Bis (Catecholyl) Borate and their assignments

<table>
<thead>
<tr>
<th>Complexes</th>
<th>B-O</th>
<th>C-O</th>
<th>Sn-O</th>
<th>Sn-C</th>
<th>C-C</th>
<th>C-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>K[B(cat)₂]</td>
<td>1340s</td>
<td>1260vs</td>
<td>--</td>
<td>--</td>
<td>1500vs</td>
<td>3045m</td>
</tr>
<tr>
<td>1. Me₂Sn[B(cat)₂]</td>
<td>1330m</td>
<td>1250vs</td>
<td>670w</td>
<td>587m</td>
<td>1495vs</td>
<td>3040m</td>
</tr>
<tr>
<td>2. Bu₂Sn[B(cat)₂]</td>
<td>1340m</td>
<td>1250vs</td>
<td>670m</td>
<td>600s</td>
<td>1495vs</td>
<td>3035m</td>
</tr>
<tr>
<td>3. Ph₂Sn[B(cat)₂]</td>
<td>1340w</td>
<td>1245vs</td>
<td>677sb</td>
<td>272m</td>
<td>1505vs</td>
<td>3040m</td>
</tr>
<tr>
<td>4. Bu₃Sn[B(cat)₂]</td>
<td>1330m</td>
<td>1250vs</td>
<td>680m</td>
<td>600wb</td>
<td>1485vs</td>
<td>3040m</td>
</tr>
<tr>
<td>5. Ph₃Sn[B(cat)₂]</td>
<td>1330w</td>
<td>1250vs</td>
<td>680s</td>
<td>271.245m</td>
<td>1485vs</td>
<td>3045m</td>
</tr>
</tbody>
</table>

s, strong; m, medium; w, weak; b, broad; v, very.
boron is trigonal planar BO\(_3\) while for tetrahedral BO\(_4^-\) unit\(^{18}\) B-O shows prominent bands at 914 and 518 cm\(^{-1}\) corresponding to \(\nu_3\) and \(\nu_4\) absorptions, respectively. These infrared bands are highly sensitive to the substituent R in B(-OR)\(_4\). Of the several normal modes of the planar XY\(_4\) molecule, only \(\nu_3\), \(\nu_6\) and \(\nu_7\) are IR active\(^{19}\). Since boron in bis-(catecholyl)borate achieves square planar geometry, it is expected to display three bands corresponding to the above modes. The following bands obtained correspond to 1340 ± 10 cm\(^{-1}\) which is symmetrical bending vibration [6] due to the movement of boron atom above and below the plane of oxygen atoms (Fig. 4.2). The other frequencies observed at 950 and 923 cm\(^{-1}\) also agree with a symmetrical square planar geometry of the BO\(_4^-\) group.

\[
\begin{array}{c}
\begin{array}{c}
\text{(i)} \\
\text{[O-O-B-O]} \\
\text{(ii)}
\end{array}
\end{array}
\]

*Fig. 4.2* + & - signs indicate upward and downward motions for the oxygen and boron in complexes respectively.

The \(\nu(C-O)\) in aromatic dioles ranges from 1280-1230 cm\(^{-1}\)\(^{20}\) but slightly varies with increasing ring size and substituent on the ring. When such alcohols form an alkoxide there occurs a significant decrease in C-O due to M-O bond formation\(^{21}\). The present case is similar to that of an alkoxide where the formation of M-O bond causes a decrease in C-O frequency as a consequence of electrons being pulled away from the C-O bond.
It is important to note that in borate esters and metal alkoxides, the metal-oxygen stretching frequency is the key evidence of the bonding. A distinction between covalent and ionic Sn-O may be made on the basis of Sn-O stretching frequency. For a covalent Sn-O bond the Sn-O falls in the region 680 ± 10 cm⁻¹ while for an ionic or weakly bonded tin compounds the Sn-O appears in the very narrow range of 300 ± 10 cm⁻¹. Since the organotin borates under consideration exhibit only one band 680 ± 10 cm⁻¹, it is believed that Sn-O bond is covalent. It has been reported that if the organotin (IV) borate undergoes polymerization it would exhibit a sharp absorption band in 665-670 cm⁻¹ region. As there is no such band in the above range the possibility of the polymerization of organotin(IV) borate complex is ruled out.

The symmetrical and unsymmetrical nature of SnC₃/SnC₂ moiety may be distinguished from (Sn-C) stretching frequency. The presence of both the symmetric and asymmetric (Sn-C) stretching frequencies indicate nonlinear or bent C-Sn-C configuration while only asymmetric (Sn-C) would suggest a planar structure for Sn-C moiety. Mesubi and Enemo have suggested that the presence of two such bands would imply a cis-configuration while according to Kitching both these bands may be due to considerable distortion from a regular geometry. In aryltin (IV) the Sn-C bands are observed at a relatively lower frequency region (235-274 cm⁻¹). However, in alkyl tin(IV) both these bands fall in the 620-480 cm⁻¹ region. Due to the presence of twin Sn-C bands in triphenyl tin(IV) catecholyl borate, a non-linear arrangement of the phenyl groups around tin atom may be proposed which is also
In agreement with the findings of Mesubi and Enemo. In $R_3SnL$ and $R_2SnL_2$ ($R =$ alkyl) complexes only one asymmetric (Sn-C) band has been observed which implies that the alkyl groups are planar irrespective of the gross stereochemistry of the complex.

4.6.2 $^1H$ NMR spectra:

The proton magnetic resonance of the parent diols show a sharp signal at $\delta$ 6.6 for the aromatic protons while -OH proton can appear as a broad signal at $\delta$ 7.8 which was absent in the ligand indicating the formation of B-O bond. The ring proton of phenoxy borate gives a multiplet at $\delta$ 6.4-6.8. The chemical shift observed in these ligand protons due to the drain of the electrons of the ring towards electron deficient centre. The shifting of the signal depends upon the nature of the boron and groups attached to it. As the electrophilicity of the boron increases, the diol proton signals shift towards downfield. It has also been observed that the ring protons in the ligand show two sets of the signals. The stronger one is due to the original ring protons and the weaker one is mainly due to the hydrolysis of the ligand by the presence of a little amount of water in the NMR solvent as was also observed by Okamoto et al. In the organotin diolato compound minor shift occurs in the position of the ligand protons after coordination which is quite reasonable. The signals due to organotin protons are observed in the usual position without any significant shift after chelation. However, the Sn-R resonance in the $Me_2Sn[B(C_6H_4O_2)_2]_2$, occurred at $\delta$ 1.2 as a singlet flanked by $^{117}Sn$, $^{119}Sn$ satellites which appeared on either side of the main signal, while the Sn-R signals which appeared at
about $\delta$ 1.8 - .9 and $\delta$ 1.7 - 0.8 for the Bu$_2$Sn[B(C$_6$H$_4$O$_2$)$_2$]$_2$ and Bu$_3$Sn[B(C$_6$H$_4$O$_2$)$_2$] complexes, respectively.
Table - 9.

Observed Proton NMR signals for the Potassium Bis (catecholyl) Borate and its Organotin Complexes.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Solvent</th>
<th>Signal of Organotin Protons</th>
<th>Signal of Ligand Protons</th>
</tr>
</thead>
<tbody>
<tr>
<td>K[B(cat)₂]</td>
<td>D₂O</td>
<td>--</td>
<td>6.40 - 6.8</td>
</tr>
<tr>
<td>1. Me₂Sn[B(cat)₂]</td>
<td>DMSO d₆</td>
<td>1.13</td>
<td>6.57 - 6.90</td>
</tr>
<tr>
<td>2. Bu₂Sn[B(cat)₂]</td>
<td>DMSO d₆</td>
<td>1.8 - 0.9</td>
<td>6.55 - 6.90</td>
</tr>
<tr>
<td>3. Ph₂Sn[B(cat)₂]</td>
<td>DMSO d₆</td>
<td>8.0 - 7.2</td>
<td>6.52 - 6.90</td>
</tr>
<tr>
<td>4. Bu₃Sn[B(cat)₂]</td>
<td>DMSO d₆</td>
<td>1.7 - 0.8</td>
<td>6.66 - 6.77</td>
</tr>
<tr>
<td>5. Ph₃Sn[B(cat)₂]</td>
<td>DMSO d₆</td>
<td>8.0 - 7.3</td>
<td>6.60 - 6.76</td>
</tr>
</tbody>
</table>

Chemical shift (δ) are measured in ppm from internal TMS.
4.7 References:


