**119Sn Mössbauer Spectroscopic Study of Novel β-Carbomethoxyethyltin(IV) Compounds**

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The Mössbauer parameters are presented for β-carbomethoxyethyltrichlorotin and bis-β-carbomethoxyethyl-dichlorotin, their substitution products of the type RSnCI.L, RSnCIL₂, RSnL₃, R₂SnL₄ and molecular addition compounds of the trichloro derivative with neutral donor molecules. The chelating ligands used are 8-hydroxyquinoline, acetylacetone, dibenzoylmethane, 2-hydroxy-4-methoxybenzophenone, salicylaldazine, 1,10-phenanthroline, 2,2'-bipyridyl and hexamethylphosphortriamide. On the basis of observed isomer shift and quadrupole splitting data, possible structural assignments have been made for these compounds.

**Materials and Methods**

Reactions were carried out under dry nitrogen atmosphere. Solvents and chemicals used were of AR grade.

The Mössbauer spectra were taken using a MBS-35 spectrometer (Electronic Corporation of India) operated in the constant acceleration mode coupled to a ND 100 multichannel analyser. The spectrometer was calibrated with 1 mil natural iron foil using a 4 mCi ⁶⁰Co in a Pd matrix. All the spectra were recorded with 2 mCi Ba ¹¹⁹SnO₄ matrix (New England Nuclear Corporation). The absorbers were prepared by spreading well ground powder of each sample between two thin Al foils of 1 inch radius, sandwiched between two brass rings. The thickness of the absorber was so adjusted that it contained about 40 mg/cm² of natural tin. In all the cases 10⁶ counts were collected in each channel.

The IR spectra were recorded on a Perkin-Elmer model 221 or 599 B spectrophotometer using sodium chloride or caesium iodide optics.

**Results and Discussion**

The Mössbauer spectrum of bis-β-carbomethoxyethyl-dichlorotin shows an isomer shift (δ) value of 1.28 mm/sec and a quadrupole splitting (ΔEQ) of 3.46 mm/sec, the magnitude of which indicates trans configuration of the organic groups as shown in structure (I). For an octahedral complex containing two organic groups the point charge treatment predicts a ΔEQ value of 2 mm/sec for cis isomer and 4 mm/sec for trans isomer. The trans-configuration is further supported by the appearance of single infrared band at 578 cm⁻¹ attributable to νSn-C. In all its substitution products with bidentate ligands (except in the case of the 8-hydroxyquinoline complex), the geometry around tin is trans-octahedral since the ΔEQ values fall between 3.04 and 3.97 mm/sec. The δ-values of the above complexes are

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TABLE 1 — THE MOSSBAUER SPECTROSCOPIC DATA FOR β-CARBOMETHOXYETHYL Tin COMPOUNDS

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>Colour</th>
<th>8±0.03 (mm/sec)</th>
<th>ΔE0/8</th>
<th>A.E0/8 (mm/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>RSnCl</td>
<td>White</td>
<td>1.28</td>
<td>3.28</td>
<td>2.5625</td>
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<tr>
<td>2</td>
<td>RSn(dibenzoxy)methanolate</td>
<td>Orange</td>
<td>1.21</td>
<td>3.97</td>
<td>3.2810</td>
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<tr>
<td>3</td>
<td>RSn(acetylacetone)</td>
<td>White</td>
<td>1.21</td>
<td>3.97</td>
<td>3.2810</td>
</tr>
<tr>
<td>4</td>
<td>RSn(2-oxo-4-methoxy-benzophenone)</td>
<td>Yellow</td>
<td>1.15</td>
<td>3.04</td>
<td>2.6435</td>
</tr>
<tr>
<td>5</td>
<td>RSn(salicylaldazine)</td>
<td>Yellow</td>
<td>1.09</td>
<td>2.81</td>
<td>2.5780</td>
</tr>
<tr>
<td>6</td>
<td>RSn(8-hydroxyquinolinato)</td>
<td>Yellow</td>
<td>0.82</td>
<td>2.08</td>
<td>2.5366</td>
</tr>
<tr>
<td>7</td>
<td>RSnCl</td>
<td>White</td>
<td>0.95</td>
<td>1.95</td>
<td>2.0526</td>
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<tr>
<td>8</td>
<td>RSnCl(8-hydroxyquinolinato)</td>
<td>Yellow</td>
<td>0.92</td>
<td>1.90</td>
<td>2.0652</td>
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<td>9</td>
<td>RSnCl(8-hydroxyquinolinato)</td>
<td>Yellow</td>
<td>0.71</td>
<td>1.53</td>
<td>2.2836</td>
</tr>
<tr>
<td>10</td>
<td>RSn(8-hydroxyquinolinato)</td>
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<td>0.70</td>
<td>1.50</td>
<td>2.1429</td>
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<td>RSnCl(1,10-phenanthroline)</td>
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<td>1.45</td>
<td>1.7242</td>
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<tr>
<td>12</td>
<td>RSnCl₂,2,2’-bipyridyl</td>
<td>Pink</td>
<td>0.82</td>
<td>1.26</td>
<td>1.5366</td>
</tr>
<tr>
<td>13</td>
<td>RSnCl₃(hexamethylphosphorramid)</td>
<td>White</td>
<td>0.77</td>
<td>2.19</td>
<td>2.8442</td>
</tr>
</tbody>
</table>

R = β-carbomethoxyethyl group.

between 1.15 and 1.21 mm/sec. This close resemblance between the isomer shifts of bis-β-carbomethoxyethyl dichlorotin and its chelated complexes suggests almost the same s-electron density at tin nucleus.

In contrast to the above findings, bis-β-carbomethoxyethyltin-bis-8-hydroxyquinolinato has a cis-octahedral arrangement of organic groups as revealed by ΔE0 = 2.08 mm/sec. This cis-complex, like other di-organotin bis-chelates, shows a considerably lower δ-value of 0.82 mm/sec than their trans-analogues due to a decrease in the 5r character in the Sn-C σ-bonds in the cis-position. In all the bis-chelates examined, the δ values fall between 2.50 and 3.28 suggesting a six-coordinated tin atom.

In the salicylaldazine complex with bis-β-carbomethoxyethyltin, the possible geometry around tin is trigonal bipyramidal as it is monomeric in benzene. The non-coordinating nature of the ester carbonyl and coordination of C = N group of the ligand are confirmed from IR and PMR data. The quadrupole splitting observed is 2.81 mm/sec and the δ value is above 2.10. The possible arrangements of organic groups around tin are shown in structures (II) and (III).

From a study of the five-coordinated organotin complexes of the type [Me₅SnCl₃, terpyridyl]⁺ [Me₅SnCl₃]⁻ it was concluded that ΔE0 value for equatorial arrangement of ligands in trigonal bipyramidal structure was not very different from that for trans-octahedral R₃SnL₄ species. An example for a five-coordinated tin complex with cis-phenyl groups is (C₆H₅)₂SnNCS(8-hydroxyquinolinate). Mullins and Curran obtained ΔE0 values for this compound and similar other compounds in the range 2.4 - 2.5 mm/sec and concluded that the phenyl groups are in cis-position. Poller and Ruddick found the corresponding values five-coordinated cis-complexes of the type Et₅SnX (8-hydroxy-quinolinato) to be between 3.10 and 2.85 mm/sec. In the light of the above findings, the possible arrangement of organic groups in the salicylaldazine compound will be a cis disposition of the monodentate ester group since ΔE0 value of 2.81 mm/sec is in same range. The corresponding value for Bu₄SnNCS (8-hydroxyquinolinato) with trans butyl groups is 3.25 mm/sec (see ref. 1).

Mössbauer isomer shift values (Table 1) demonstrate that bis-β-carbomethoxyethyl dichlorotin (δ = 1.28 mm/sec) is a weaker Lewis acid than the corresponding trichlorotin compound (δ = 0.95 mm/sec) as expected. This decrease in δ-value of the trichloro compound suggests greater σ-electron withdrawing power of chlorine atom due to inductive effect.

A decrease in asymmetry of electron cloud around tin atom in β-carbomethoxyethyltrichlorotin compared to the dichloro derivative is evident from lower ΔE0 value. The decrease may also be due to the small difference in the polarity of Sn-C and Sn-Cl bonds. The new molecular addition complexes of β-carbomethoxyethyltrichlorotin of the type RSnCl₃.L or RSnCl₃.L.L, where L is a mono- or bi-dentate ligand give δ-values in the range 0.77 to 0.84 mm/sec (Fig. 1) which are smaller than the value for the trichloro compound itself. This decrease may be interpreted in terms of change in the hybridization at tin from sp³d² to sp³d³ thereby reducing the σ-electron density at the tin nucleus due to the shielding effect of occupied 5d orbitals. Further the polarity of Sn-O bond in β-carbomethoxyethyltrichlorotin-hexamethylphosphoramide dduct is more than that of Sn-N in nitrogen heterocyclics as seen from lower δ-values for the former. The ΔE0 values for these complexes fall in the range 1.26 to 2.19 mm/sec.
This is a much wider range when compared to cis- or trans-octahedral complexes of the type R₂SnL₄ and may be due to higher order of distortion from perfect octahedral symmetry.⁠¹⁵-¹⁶

The stepwise substitution products of 8-carboxyethyltrichlorotin with one, two and three 8-hydroxyquinoline groups contain hexa-coordinated tin. In 8-carboxyethylarachichlorotin-8-hydroxyquinolinate adduct, the ester group is acting as a bidentate moiety as seen from its IR spectrum whereas in other two compounds ester carboxyl is non-coordinating. The 8-values decrease gradually from the trichloro derivatives to the chlorine-free compound (from 0.95 to 0.70 mm/sec). This decrease may arise by the replacement of chlorine by bidentate ligands or due to extra-nuclear shielding caused by higher hybridization at tin, sp³d² or sp³d³ as in BuSn-(8-hydroxyquinolinate)₃ (ref. 17).

References