Titanium(IV) & Organotin(IV) Chelates of S-Benzyl-β-N-(2-hydroxyphenyl)methylene Dithiocarbazate†

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S-Benzyl-β-N-(2-hydroxyphenyl)methylene dithiocarbazate forms stable titanium derivatives, \(\text{LTiCl}_2\), \(\text{L}_2\text{Ti}\) and \(\text{L}_3\text{Ti}^+\) when reacted with titanium tetrachloride, isopropyl titanate and bis-chelated diisopropoxytitanium respectively. Salicylaldehyde, benzoylacetone, benzoylphenylhydroxylamine and salicylaldazine are the chelating ligands used. \(\text{LSnCl}_2\) has been prepared from stannic chloride and the sodo-derivative of the ligand. Organotin oxide/hydroxide reacts with the ligand giving organo-tin chelated derivatives. Synthesis and structure of these compounds have been discussed based on their molecular weights, infrared, PMR and ultraviolet spectra.

Materials and Methods

Reactions were carried out under dry nitrogen atmosphere. Solids were separated from solutions either by centrifuging or by filtering in sintered glass apparatus using a positive pressure of nitrogen.

S-Benzyl-β-N-(2-hydroxyphenyl) methylene dithiocarbazate (LH₂) — The ligand was prepared by the procedure reported in literature, from hydrizine hydrate, salicylaldehyde, carbon disulphide and benzyl chloride. The yield was above 90%. The white crystals when recrystallized from benzene melted at 184° (reported 185°).

Preparation of \(\text{LTiCl}_2\cdot\text{HCl}\) — The ligand (0.604 g; 0.002 mol) was dissolved in benzene (50 ml) and cooled in ice. To this was added TiCl₄ (0.38 g; 0.002 mol) in benzene (10 ml). The colour of the solution changed to red, and the HCl formed was removed by refluxing for 2 hr in a current of nitrogen. The solid separated was filtered, washed with benzene and dried in vacuo; yield 0.68 g (75%). The brown solid, m.p. 192°, was soluble in ethanol only undergoing partial decomposition [Found : Ti, 10.43; Cl, 23.03; C, 39.32; H, 2.37. (C₁₅H₁₂N₂S₂O) TiCl₂.HCl requires Ti, 10.50; Cl, 23.35; C, 39.55; H, 2.86%].

Preparation of \(\text{L}_2\text{Ti}\) — The ligand (3.02 g; 0.01 mol) dissolved in benzene (50 ml) was mixed with isopropyl titanate (1.42 g; 0.005 mol) in benzene (25 ml) and refluxed mildly in an oil-bath using a partial take off condenser. The liberated isopropanol was estimated using a gas chromatograph. The reaction was over in about 2 hr. The benzene solution was then concentrated to get a black crystalline solid which was purified by washing with hexane followed by drying at 60° in vacuo; yield 2.59 g (80%). The black shining crystals, m.p. 245°, were soluble in benzene.

Attempts to prepare the diisopropoxide, \(\text{LTI}(\text{OPr})_2\), using different molar ratios of the reactants, were unsuccessful; only \(\text{L}_2\text{Ti}\) was obtained.

Preparation of bis-salicylaldehydo \(\text{TiL}^+\) — The ligand (0.302 g; 0.001 mol) was dissolved in benzene (50 ml) and added to a benzene solution of bis-salicylaldehydo-diisopropoxytitanium (0.408 g; 0.001 mol) and refluxed. The colour of the solution turned dark red. The isopropanol liberated was removed azeotropically and estimated using gas chromatographic method. The benzene solution upon concentration, to crystallisation gave a black crystalline product which was washed with hexane and dried in vacuo at 60°; yield 0.46 g (78%). The substance m.p. 262°, was soluble in benzene.

Derivatives of benzoylacetone, benzoylphenylhydroxylamine and salicylaldazine were prepared similarly from the corresponding chelated diisopropoxytitaniums (Table 1).

Preparation of \(\text{LSnCl}_2\) — Sodium methoxide, prepared from sodium (0.046 g; 0.002 mol) and methanol (10 ml), was reacted with the ligand (0.302 g; 0.001 mol) in benzene (50 ml) to give the sodo derivative of the ligand. To this was added stannic chloride (0.261 g; 0.001 mol) and refluxed for 2 hr...
TABLE 1 — CHELATED TITANIUM AND TIN COMPLEXES OF S-BENZYL-β-N-(2-HYDROXYPHENYL) METHYLENEDITHIOCARBAZATE [C₁₅H₁₅N₂S₂O]

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Product</th>
<th>Colour</th>
<th>m.p. °C</th>
<th>Found (calc) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiCl₄</td>
<td>(C₁₅H₁₅N₂S₂O)TiCl₂·HCl</td>
<td>Brown</td>
<td>192</td>
<td>10.43/9.32</td>
</tr>
<tr>
<td>Ti(OPr)₄</td>
<td>(C₁₅H₁₅N₂S₂O)Ti</td>
<td>Black</td>
<td>245</td>
<td>7.39/53.07</td>
</tr>
<tr>
<td>Bis-Salicylaldehyde Ti(OPr)₄</td>
<td>(C₁₅H₁₅N₂S₂O)Ti(Cl(C₇H₈O)₃)</td>
<td>Black</td>
<td>262</td>
<td>8.23/58.67</td>
</tr>
<tr>
<td>Bis-Benzoylacetone Ti(OPr)₄</td>
<td>(C₁₅H₁₅N₂S₂O)Ti(C₇H₈O)₃</td>
<td>Black</td>
<td>247</td>
<td>7.02/62.37</td>
</tr>
<tr>
<td>Bis-Benzoyl phenylhydroxylamino-Ti(OPr)₄</td>
<td>(C₁₅H₁₅N₂S₂O)Ti(Cl(C₇H₈O)₃)</td>
<td>Orange</td>
<td>112</td>
<td>6.20/63.65</td>
</tr>
<tr>
<td>Salicyladazino Ti(OPr)₄</td>
<td>(C₁₅H₁₅N₂S₂O)Ti(Cl(C₇H₈O)₃)</td>
<td>Black</td>
<td>252</td>
<td>7.98/59.13</td>
</tr>
<tr>
<td>SnCl₄</td>
<td>(C₁₅H₁₅N₂S₂O)SnCl₄</td>
<td>Yellow</td>
<td>190</td>
<td>24.12/36.55</td>
</tr>
<tr>
<td>Dimethyltin oxide</td>
<td>(CH₃)₂Sn(C₁₅H₁₅N₂S₂O)</td>
<td>Yellow</td>
<td>115</td>
<td>26.23/45.12</td>
</tr>
<tr>
<td>Dibutyltin oxide</td>
<td>(C₂H₅)₂Sn(C₁₅H₁₅N₂S₂O)</td>
<td>Yellow</td>
<td>45</td>
<td>22.34/51.55</td>
</tr>
<tr>
<td>Dioctyltin oxide</td>
<td>(C₁₃H₂₇)₂Sn(C₁₅H₁₅N₂S₂O)</td>
<td>Yellow</td>
<td>35</td>
<td>18.13/57.45</td>
</tr>
<tr>
<td>Tributyltin oxide</td>
<td>[(C₁₃H₂₇)₂Sn(C₁₅H₁₅N₂S₂O)]</td>
<td>Yellow</td>
<td>Low melting</td>
<td>18.65/59.10</td>
</tr>
<tr>
<td>Trioctyltin oxide</td>
<td>[(C₁₃H₂₇)₂Sn(C₁₅H₁₅N₂S₂O)]</td>
<td>Yellow</td>
<td>-do-</td>
<td>23.52/61.19</td>
</tr>
<tr>
<td>Triphenyltin hydroxide</td>
<td>[(C₁₃H₂₇)₃Sn(C₁₅H₁₅N₂S₂O)]</td>
<td>Yellow</td>
<td>40</td>
<td>23.74/61.24</td>
</tr>
</tbody>
</table>

Results and Discussion

The ligand S-benzyl-β-N-(2-hydroxyphenyl) methylenedithiocarbazate exists in thione and thiol forms. It forms stable titanium and tin compounds by replacing chlorine or isopropoxy groups attached to these metals. In these reactions the ligand behaves as dibasic tridentate. It forms monochelated titanium dichloride (as hydrochloride) with the elimination of one molecule of HCl (Eq. 1).

\[
\text{TiCl}_4 + \text{C}_{15}\text{H}_{15}\text{N}_2\text{S}_2\text{O} \rightarrow \text{[C}_{15}\text{H}_{15}\text{N}_2\text{S}_2\text{O}]\text{TiCl}_3\text{HCl} + \text{HCl.} \quad \ldots \ (1)
\]

However, when the disodium salt reacts with stannic chloride, the chelated tin compound, LSnCl₄ is obtained. Other chelated titanium derivatives of the ligand containing bidentate and tridentate chelates such as salicylaldehyde, benzoylaceton, benzoylphenyldihydroxylamine and salicylaldazine have been prepared by the elimination of isopropoxy groups of substituted isopropoxy titaniurns, as isopropanol. However, the organotin chelates are obtained by the elimination of water in the reaction between an organotin oxide/hydroxide and the ligand in benzene. The compounds are listed in Table 1.

The new tin and titanium compounds are all stable and well-defined by chemical analysis. They are in general soluble in benzene (except the chloro-titanium compound) and are monomeric in that solvent (ebullioscopy).

The IR spectrum of the ligand in nujol shows a strong N-H band around 3090. The hydrogen bonded O-H stretching frequency is not observed in spectrum taken in nujol or in hexachlorobutadiene. However, in hexachlorobutadiene, a band around 2900 is seen. The ν (C = N) of the Schiff base is seen at 1622. A strong band at 1040 may be attributed to ν (C-S) since the ligand exists in thio keto form in solid state. The ν (N - N) is found in the ligand as a medium band around 945.

The chelated dichlorotitanium hydrochloride, L[TiCl₂HCl₂] shows the protonated ν (N-H) band around 3150. The ν(C = N) is shifted to a lower frequency by about 25 cm⁻¹. Both the (C = N) groups absorb as a single peak suggesting their coordinated nature. The ν(C = S) in this compound is seen at 1622 indicating the thio form. The ν(N-N) band is observed at 1000 indicating the thio form. The ν(N-N) band

\[\nu_{\text{max}} \text{ in cm}^{-1} \text{ throughout the paper.}\]
at 945 is split and is seen as medium bands at 920, 935 and 955, which suggests chelate formation with the titanium atom.

The dichelated titanium compound, L₂Ti, shows complete absence of ν(O-H) and ν(N-H) and this suggests the dibasic nature of the ligand. The ν(C=N) is shifted downwards and absorbs along with (C=C) around 1590; the ν(C=S) is seen around 1000 as a strong band. The splitting of ν(N—N) is more prominent in this compound as indicated by the appearance of two strong bands at 970 and 915. An identical phenomenon has been observed in chelated tin dichloride, alkyl and aryl tin chelates of the ligand also. In the chelated tin dichloride, the tin atom attains a coordination number five. In the case of alkyl and aryl tin chelates the shift in ν(C=N) is less compared to the titanium complexes, as expected. The mixed chelates of titanium, for example, bis-salicylaldehydotitanium complex, exhibits coordination of both the carbonyl groups to titanium. The ν(C=N) of the ligand is not easily detected due to ν(C=O) and ν(C=C) in the same region. In these compounds the titanium atom might have a distorted octahedral geometry with weak (C=N) coordination, but this has to be confirmed by further studies.

The electronic spectra of the ligand and its tin compounds were studied in acetonitrile and in CCl₄ solutions. In acetonitrile, the spectrum of the ligand exhibits the high intensity band at 220 nm (ε 27000) corresponding to the β band of benzene. A hump is seen at 297 nm (ε 16800) and two long wavelength bands are seen at 320 (ε 19800) and 350 nm (ε 26200). The long wavelength band at 350 nm with increased intensity is the secondary band of benzene (at 256 nm) red shifted due to the chromophore —C=N—N=C—. In CCl₄ solution the three long wavelength absorption bands suffer slight bathochromic shift with reduction in their intensities, 301 (ε 13000), 328 (ε 15000) and 360 nm (ε 24000). In the case of organotin chelates and chelated tin dichloride in acetonitrile, the high intensity band at 220 nm remains in the same position. The other long wavelength absorptions of the ligand give a broad band between 340-350 nm. A new band is observed around 401 nm in acetonitrile and 417 nm in CCl₄ with medium intensities in all the tin complexes. This may be due to the ligand metal charge transfer band and this is a clear indication that a stable complex has been formed.

The electronic spectra of the new titanium compounds could not be studied because of the insolubility in acetonitrile and CCl₄.

The PMR spectrum of the ligand was studied in DMSO as solvent due to solubility reasons. The spectrum of the ligand exhibited the-CH₂-proton signal (chemical shift in δ, ppm) at 4.50, aromatic proton signals around 6.60—7.00 and 7.00—7.60, azomethine proton at 8.43, a broad signal due to δ N-H proton at 10.10 and phenolic proton signal at 13.10 in the ratio 2 : 9 : 1 : 1 : 1. The three and five protons of the salicylidine ring absorbed slightly upfield compared to the other aromatic protons in the ratio 2 : 7, as expected. Both N-H and O-H proton signals disappeared on deuteration. In the spectrum of the chelated tin dichloride in the same solvent, complete absence of the hydroxyl proton and the N-H proton is suggestive of the dibasic nature of the ligand. The azomethine proton suffers some deshielding and gives a signal at 9.13 which indicates the coordination of the azomethine nitrogen to tin. The three and five protons of the hydroxy substituted ring also absorb in the low field as expected (6.60—7.16). The dimethyltin chelate also show similar shift in the absorption of azomethine proton. The NMR spectra of titanium compounds could not be studied due to poor solubility of these compounds in common solvents.

References