Synthesis and structural elucidation of diorgano(chloro)tin(IV) complexes of heterocyclic dithiocarbamates

Jyoti Sharma, Yashpal Singh & Audhesh Kumar Rai*
Department of Chemistry, University of Rajasthan, Jaipur 302 004, India
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Some new diorganochlorotin(IV) complexes of the composition \( \text{R}_2\text{CISnS}_2\text{CNCH}_2\text{CH}_2\text{XCH}_2\text{CH}_2 \) (where \( X = >\text{CH}_2, >\text{CH}-\text{CH}_3, >\text{N}-\text{CH}_3, >\text{O}, \text{R} = -\text{CH}_3 \), and \( n-\text{C}_4\text{H}_9 \)) have been synthesized by the interaction of diorganotin dichloride with the sodium salt of the corresponding ligands in 1:1 stoichiometric ratio. These complexes have been characterized on the basis of elemental analyses, molecular weight measurements and spectral studies like IR and NMR \( ^1\text{H}, ^13\text{C} \) and \(^{119}\text{Sn} \).

Triorganotin derivatives of bidentate ligands have been extensively studied and are reported to have tetrahedral\(^{1,2}\) or trigonal bipyramidal\(^{3-6}\) (TBP) geometry depending upon the nature of organo group as well as the electronegativity of the atoms attached with central tin atom\(^2\). Replacement of one of the organo groups by more electronegative atom e.g. Cl leads to the TBP geometry around central tin atom\(^2\).

Recently, we have reported that in \( \text{Me}_2\text{SnS}d\text{tc} \) (dctc = cyclic-dithiocarbamate)\(^9\), the central tin atom acquires tetrahedral geometry, whereas in \( \text{Ph}_3\text{Sn}d\text{tc} \) trigonal bipyramidal geometry is preferred. On the other hand in \( \text{Me}_2\text{Sn}(d\text{tc})_2 \) (ref. 10) an octahedral geometry around central tin atom has been reported.

In the present note we are reporting the synthesis and characterisation of some \( \text{R}_2\text{ClS}n\text{dtc} \) type of complexes (\( \text{R} = -\text{CH}_3 \) & \( n-\text{C}_4\text{H}_9 \)).

**Experimental**

The ligands used in the synthesis were prepared by the literature method\(^{11}\). \( \text{Me}_2\text{SnCl}_2 \) and \( \text{Bu}_2\text{SnCl}_2 \) (BDH) were distilled before use. Tin and sulphur were estimated gravimetrically as tin oxide and barium sulphate\(^{12}\) respectively. Molecular weights were determined with a “Knauber Vapour Pressure Osmometer”, using chloroform solutions at 45°C. Infrared spectra were recorded in the range 4000-200 cm\(^{-1}\) on a Perkin-Elmer 577 spectrophotometer using KBr pellets \(^1\text{H} \) and \(^{13}\text{C} \) NMR spectra were recorded in CDCl\(_3\) and CHCl\(_3\) solutions respectively on 90 MHz JEOL FX 90Q spectrometer using TMS as an internal reference. \(^{119}\text{Sn} \) NMR spectra of the complexes were recorded in CHCl\(_3\) solution using Me\(_4\)Sn as an external reference. \(^{13}\text{C} \) NMR spectra of four samples (\( \text{R} = -\text{CH}_3 \)) were recorded on a Bruker WH 270 MHz spectrometer in CDCl\(_3\) solution using TMS as an internal reference.

Since similar procedure was adopted for the synthesis of the complexes, experimental details of only one compound is being discussed. The analytical results of other derivatives are summarised in Table 1.

**Synthesis**

\( \text{(CH}_2)_2\text{ClSnS}_2\text{CNCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \)

A benzene solution (\( ~30 \text{ ml} \)) of the ligand piperdinedithiocarbamate (1.44 g, 6.57 mmol) was added dropwise to the benzene solution (\( ~20 \text{ ml} \)) of \( \text{Me}_2\text{SnCl}_2 \) (1.40 g, 6.37 mmol). The reaction mixture was stirred for ~4 h at room temperature and then refluxed for ~6 h. NaCl thus formed was filtered off, and the excess solvent was removed under reduced pressure. The crude product was recrystallised from chloroform-hexane solution. Analysis: Sn, 34.38; S, 18.20; Req. for \( \text{C}_{4}\text{H}_{16}\text{NS}_2\text{ClSn}: \) Sn, 34.45%; S, 18.61%.

**Results and discussion**

The reactions of diorganotin dichloride with the sodium salt of heterocyclic dithiocarbamates in 1:1 molar ratio in benzene solution yield the corresponding diorganochlorotin(IV) derivatives.

\[
\text{R}_2\text{SnCl}_2 + \text{CH}_2\text{CH}_2(X)\text{CH}_2\text{CH}_2\text{NCS}_2\text{Na} \rightarrow \text{R}_2\text{ClSnS}_2\text{CNCH}_2\text{CH}_2(X)\text{CH}_2\text{CH}_2 + \text{NaCl} \]

(\( \text{X} = >\text{CH}_2, >\text{CH}-\text{CH}_3, >\text{N}-\text{CH}_3, >\text{O}; \text{R} = -\text{CH}_3 \) and \( n-\text{C}_4\text{H}_9 \))

After filtering off the precipitated sodium chloride and stripping off the volatile components from the filtrate, crystalline solids having sharp melting points are obtained in case of dimethyltin derivatives whereas corresponding dibutyl tin derivatives are found to be viscous in nature. All these derivatives are soluble in common organic
Table 1—Analytical and physical data of heterocyclic dithiocarbamate complexes of diorganochloro tin (IV) complexes

<table>
<thead>
<tr>
<th>Reactants in g</th>
<th>Mol. form. (%) yield</th>
<th>M.pt. (±1°C)</th>
<th>Found (Calcd), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaS₂CNCH₂CH₂XCH₂CH₂ R₂SnCl₂</td>
<td>C₇H₄N₂SnCl</td>
<td>100</td>
<td>340</td>
</tr>
<tr>
<td>X = &gt;CH₂</td>
<td>R = -CH₃</td>
<td>(344.48)</td>
<td>(34.45)</td>
</tr>
<tr>
<td>1.27</td>
<td>92%</td>
<td>(359)</td>
<td>(33.10)</td>
</tr>
<tr>
<td>1.83</td>
<td>95%</td>
<td>(359.49)</td>
<td>(33.01)</td>
</tr>
<tr>
<td>X = &gt;CH-CH₃</td>
<td>R = -CH₃</td>
<td>(346.45)</td>
<td>(34.25)</td>
</tr>
<tr>
<td>1.90</td>
<td>95%</td>
<td>(359)</td>
<td>(33.10)</td>
</tr>
<tr>
<td>X = &gt;N-CH₃</td>
<td>R = -CH₃</td>
<td>(343.65)</td>
<td>(34.25)</td>
</tr>
<tr>
<td>1.36</td>
<td>89%</td>
<td>(346.66)</td>
<td>(34.25)</td>
</tr>
<tr>
<td>X = &gt;O</td>
<td>R = -CH₃</td>
<td>(340.61)</td>
<td>(27.56)</td>
</tr>
<tr>
<td>2.11</td>
<td>96%</td>
<td>(346.66)</td>
<td>(34.25)</td>
</tr>
</tbody>
</table>

Vapour pressure Osmometric molecular weight measurements in chloroform solution at 45°C indicate their monomeric nature.

The IR spectra of these derivatives exhibit a strong band in the region 1470±20 cm⁻¹ which may be attributed to ν(C=N) mode. The presence of one intense absorption band at 990±20 cm⁻¹ assigned to ν(C=S) indicates the bidentate nature of ligand moiety. The presence of a new band at 380±20 cm⁻¹ which has been assigned to ν(Sn-S) supports the bonding of central tin atom with sulphur. The ν(Sn-S) (refs 15, 16) band was observed at 320±10 cm⁻¹.

The ¹H NMR spectra of the complexes show characteristic signals due to -CH₃ ring >CH₂, >N-CH₃, >CH-CH₃, >CH₂O-CH₂- and -CH₂N-CH₂- protons. Butyl protons attached with tin atom are observed as a complex multiplet in the range δ 0.88-2.17 ppm, whereas methyl protons (CH₃-Sn) appear as a singlet at δ 1.20-1.30 ppm.

In ¹³C NMR spectra of dibutyl tin (IV) complexes, the signals at ~13.0, 26.0, 27.0, 28.0 ppm may be assigned to butyl carbons attached to tin. In case of dimethyl tin (IV) complexes, a singlet for methyl carbon was observed in the range δ 9.74-9.91 ppm. The tin carbon coupling constants, ¹J(¹¹⁹Sn, ¹³C) were observed in the range of 553-573 Hz, which indicates pentacoordination environment around the central tin atom. A correlation between ¹J(¹¹⁹Sn, ¹³C) values and C-Sn-C bond angle (θ) in dimethyl tin (IV) complexes is given by

\[ ¹J = 11.4 \theta - 875 \]

or \[ \theta = 0.0877 (¹J) + 76.7543 \]

The C-Sn-C bond angles thus calculated are in the range of 125-127°. These are similar to the observed C-Sn-C (127-128°) bond angles in the compounds [PhBuCISn(S₂CNEt₂)] (ref. 19) and Me₂CISn(S₂CNMe₂) (ref. 20). Remembering that tin atom is bound to five atoms (two carbons of methyl groups, chlorine and two sulphur atoms of the ligand moiety) and noting the Bent's rule, the most probable spatial arrangement of chelate complexes seems to be cis-trigonal bipyramidal with organic substituents in the equatorial plane. This has been supported by the C-Sn-C bond angles also. Generally in metal complexes, the dithiocarbamate moiety is bonded to central metal atom, through two different M-S bond (M-S=C and M-S-C bond). This accounts for the deformation from ideal shape.

![Diagram](image)
The five coordination around tin atom has also been supported by their $^{119}\text{Sn}$ NMR spectra in which, $^{119}\text{Sn}$ signals are found to be in the range of $\delta - 187$ to $-203$ ppm.

Acknowledgement

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References