Synthesis, spectroscopic and structural features of diorganotin(IV) oximes derived from 9,10-phenanthrenequinone monooxime

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Reactions of monofunctional 9,10-phenanthrenequinone monooxime with dialkyl/diaryl-tin dichloride in desired molar ratios in refluxing benzene affords corresponding dialkyl-diaryl-tin(IV) oximates, which have been characterized by elemental analyses (C, H, N and Sn), IR, multinuclear (1H, 13C and 119Sn) NMR and mass spectroscopy. On the basis of calculation of C-Sn-C bond angle from coupling constant, trigonal-bipyramidal and octahedral geometries are proposed for the chelates 5a-5e and 6a-6e. Semiempirical studies have been carried out to understand the tautomeric and conformational behaviour of the ligand.

Organometallic and organotin compounds are an active area of research owing to rich variety of biological (antitumorantitumor, antifungal and biocidal) activity and coordination behaviour of tin(IV) analogues. The use of organotin compounds in organic synthesis and in homogeneous catalysis has prompted the synthesis and characterization of many novel organotin compounds. Unabated activity of many organotin complexes has enhanced the use of internally functionalized oximes. A recent review describes the synthesis and structural features of oxime derivatives. Keeping in view the synthetic and structural significance of organotin compounds and continuing our research work in organotin, organoboron and titanium chelates, we herein report the synthesis, characterization and structural features of tin oximates.

Experimental

All the reactions were carried out under nitrogen atmosphere excluding moisture rigorously. Analytical grade chemicals were used to prepare the ligand and complexes. Dialkyl-alkyl-tin(IV) chlorides and 9,10-phenanthrenequinone were used as supplied by Fluka/Lancaster. The solvents were dried by standard methods. Tin was estimated as tin oxide and nitrogen was estimated as reported. IR spectra were recorded on Nicolet DX FTIR spectrophotometer in the range 4000-200 cm$^{-1}$, $^1$H (CDCl$_3$, 300 MHz), $^{13}$C (CDCl$_3$, 75.5 MHz) and $^{119}$Sn (C$_2$D$_6$, 111.9 MHz) NMR spectra of the complexes were recorded on a JEOL 300 AL FT NMR spectrometer using TMS as an internal standard and tetramethylsilane as an external standard. Mass spectra were recorded using FAB-LSIMS on a Finnigan Mat 95 or MAT 900 spectrometer. Elemental analyses were performed on Perkin-Elmer 2400 model. M.ps were recorded on perfit MP apparatus model 1013 and are uncorrected. All semiempirical calculations were carried out using MOPAC6 quantum chemical program.

The desired ligand 9,10-phenanthrenequinone monooxime (m.pt. 161-162°C) was prepared, as reported already and purified by column chromatography by elution using chloroform.

To a freshly prepared methanolic solution of sodium methoxide (0.27 g, 5.0 mmol), a solution of 9,10-phenanthrenequinone monooxime (1.12 g, 5.0 mmol) in methanol was added dropwise under nitrogen atmosphere and the mixture was refluxed for 4 h. Removal of solvent under reduced pressure afforded orange-brown solid almost quantitatively (1.06 g, 95%).

Representative method for synthesis of metal oximates

Synthesis of chlorodiethylstannyl(IV)-9,10-phenanthrenequinone monooximate (5a) — To the alcoholic solution of sodium salt of ligand (1.0 g, 5.0 mmol) in methanol, benzene solution of dimethyl dichloride (1.09 g, 5.0 mmol) was added at room temperature. The reaction mixture was then refluxed for 5 h. It was then cooled to room temperature and precipitated sodium chloride filtered off. The filtrate was concentrated under reduced pressure to afford brownish powder, which was recrystallized from methylene dichloride/hexane (2:3) to afford yellow crystals (1.56 g, 75%, m.pt. 164°C).

All other metal oximates of the type R$_2$Sn(L)$_2$Cl were prepared analogously. The metal oximates of the type R$_3$Sn(L)$_2$ were also prepared similarly by taking the metal halide and ligand in 1:2 molar ratio.
Physical and analytical data of tin oximates (5a-5c) and (6a-6c) are given in Table 1.

Results and discussion

The concerned ligand system (equation 1) was synthesized\(^{18}\) and the diaryl-diaryl-tin complexes of general formula \(\text{R}_2\text{Sn}(\text{L})\text{Cl}\) and \(\text{R}_2\text{SnL}_2\) were prepared by reacting corresponding diaryl-/diaryl-tin(IV) chloride with conjugate base of ligand (prepared using sodium methoxide and oxime in 1:1 molar ratio) in 1:1 and 1:2 molar ratios, respectively according to Eqs (2) and (3).

All the organotin(IV) complexes are soluble in common organic solvents like \(\text{C}_6\text{H}_6\), \(\text{CHCl}_3\), \(\text{CH}_2\text{Cl}_2\), etc. Molecular weight determinations in freezing benzene demonstrate these complexes to be monomeric.

The IR spectra of ligand exhibit a broad band in the region 3225-3104 cm\(^{-1}\), assignable to vOH of the \(=\text{N.OH}\) group due to strong intramolecular hydrogen bonding\(^{19}\). This intramolecular hydrogen bonding has also been substantiated by the optimized geometry of the ligand, which gives hydrogen bond distance of 1.612 Å. \(\nu\text{C}=\text{O}\) absorption band observed at 1672 cm\(^{-1}\) in free ligand, shifts towards lower wave number on complexation, and observed at 1660-1642 cm\(^{-1}\) in all the complexes, indicating the participation of carbonyl group in chelation\(^{12}\) to give penta-hexa coordination around central tin atom. The \(\nu\text{C}=\text{N}\) absorption bands (in free ligand observed at 1521 cm\(^{-1}\)) in complexes have been observed in the region 1508-1497 cm\(^{-1}\). The \(\nu\text{N}=\text{O}\) absorption band in oximes is very intensive\(^{20}\) usually appearing in the range 960-930 cm\(^{-1}\). However, this characteristic \(\nu\text{N}=\text{O}\) absorption in 1,2-monoxime is shifted towards higher frequency due to conjugation with carbonyl group\(^{21}\), observed in free oxime at 985 cm\(^{-1}\) and on complexation observed in the region 971-958 cm\(^{-1}\).

The appearance of new medium intensity band in the region 512-471 cm\(^{-1}\) indicates deprotonation of \(=\text{N.OH}\) group and concomitant Sn-O bond\(^{22}\)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Empirical formula</th>
<th>Molecular weight</th>
<th>Yield (%)</th>
<th>M.p. (°C)</th>
<th>Physical state</th>
<th>Found (Calc.) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>5a</td>
<td>(\text{C}<em>{16}\text{H}</em>{14}\text{N}_0\text{2SnCl})</td>
<td>405.50</td>
<td>67</td>
<td>164</td>
<td>Brown solid</td>
<td>47.27 (47.34)</td>
</tr>
<tr>
<td>5b</td>
<td>(\text{C}<em>{22}\text{H}</em>{26}\text{N}_0\text{2SnCl})</td>
<td>489.50</td>
<td>65</td>
<td>272</td>
<td>Yellow solid</td>
<td>52.87 (53.93)</td>
</tr>
<tr>
<td>5c</td>
<td>(\text{C}<em>{22}\text{H}</em>{26}\text{N}_0\text{2SnCl})</td>
<td>529.50</td>
<td>70</td>
<td>209</td>
<td>Light brown powder</td>
<td>58.88 (58.92)</td>
</tr>
<tr>
<td>6a</td>
<td>(\text{C}<em>{26}\text{H}</em>{26}\text{N}_0\text{2Sn})</td>
<td>592.00</td>
<td>72</td>
<td>219 (dec)</td>
<td>Dark brown solid</td>
<td>60.78 (60.81)</td>
</tr>
<tr>
<td>6b</td>
<td>(\text{C}<em>{30}\text{H}</em>{26}\text{N}_0\text{2Sn})</td>
<td>676.00</td>
<td>69</td>
<td>187</td>
<td>Light mustard solid</td>
<td>63.76 (63.90)</td>
</tr>
<tr>
<td>6c</td>
<td>(\text{C}<em>{26}\text{H}</em>{26}\text{N}_0\text{2Sn})</td>
<td>716.00</td>
<td>74</td>
<td>192</td>
<td>Yellow brown solid</td>
<td>66.92 (67.03)</td>
</tr>
</tbody>
</table>
formation. The vSn-C band gives medium absorption in the region 624-572 cm⁻¹.

The ¹H and ¹³C[N¹H] NMR spectra of all complexes exhibit characteristic multiplicities and signals for R-Sn, ligand protons and carbon atoms. The hydroxyl proton resonance appears in the free oxime at δ 17.02 ppm, is absent in ¹H NMR spectra of all the complexes, indicating the deprotonation of the -OH group and formation of Sn-O bond. The methyl proton signals of the [Sn(CH₂)₃CH₃] appear as a triplet at δ 0.62 and 0.69 ppm and the methylene proton signals for [Sn(CH₂)₂CH₃] in 5b and 6b appear to be partially buried within the signal in the region 0.83-1.61 and 0.89-1.74 ppm, respectively. The methyl protons of 5a and 6a appear as a sharp singlet at 0.78 and 0.86 ppm, respectively and the presence of single set of Sn-Me protons indicates that both methyl groups reside in identical environment. The ²J values have been found in the range 71±2 and 87±2 Hz for 5a-c and 6a-c, respectively, suggesting the higher (five or six) coordination around tin atom.

¹³C NMR spectra exhibit expected number of signals. A slight downfield shifting (δ 0.5 to 3.1 ppm) is observed for the C=N carbon, ruling out the possibility of coordination through N-atom. However, the appreciable downfield shifting of carbonyl carbon by about 12-17 ppm in all the complexes suggests the participation of carbonyl group in chelation. The resonance due to aryl moiety of ligand (2) appearing in the free oxime at 121.9-128.9 ppm, is slightly affected in all the complexes, suggesting the monofunctional bidentate behaviour of ligand.

The ¹J ([¹⁹Sn-¹³C]) values have been found in the range of five- and six-coordinated tin atom. The C-Sn-C bond angle may be calculated from ¹J and ²J values using following relationship.

\[ \theta(C-Sn-C) = 11.4 \frac{0}{(¹J(¹⁹Sn-¹³C))²} + 87.5 \]

The ¹⁹Sn NMR signals for the compounds (5a-5c and 6a-6c) have been found in the regions δ -195.4 to -240.2 and δ 338.2 to 360.3 ppm, respectively suggesting the penta- and hexa-coordination around tin. Spectral data of the diorganotin(IV) oximates (5a-5c) and (6a-6c) are given in Table 2.

The conclusive evidence for the structure of metal chelates was obtained from the FAB Mass fragmentation of two metal chelates, 5a and 6c. For mono-chelate (5a), molecular ion peak was observed
Table 2 — Spectral data of diorganotin(IV) oximates (5a-c) and (6a-c)

<table>
<thead>
<tr>
<th>Compd</th>
<th>IR (cm⁻¹)</th>
<th>vC=O</th>
<th>vC=N</th>
<th>vSn-O</th>
<th>vSn-C</th>
<th>¹H</th>
<th>¹¹⁷Sn¹H</th>
<th>¹¹⁸Sn¹H</th>
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<tr>
<td>5a</td>
<td>1658</td>
<td>1497</td>
<td>502</td>
<td>572</td>
<td></td>
<td>0.78</td>
<td>14.2</td>
<td>27.74</td>
</tr>
<tr>
<td>5b</td>
<td>1640</td>
<td>1502</td>
<td>471</td>
<td>596</td>
<td></td>
<td>0.62</td>
<td>12.71</td>
<td>27.74</td>
</tr>
<tr>
<td>5c</td>
<td>1652</td>
<td>1508</td>
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<td>589</td>
<td></td>
<td>0.83</td>
<td>14.2</td>
<td>27.74</td>
</tr>
<tr>
<td>6a</td>
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<td>1493</td>
<td>512</td>
<td>614</td>
<td></td>
<td>0.78</td>
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<td>603</td>
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<td>12.71</td>
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<td>6c</td>
<td>1656</td>
<td>1506</td>
<td>496</td>
<td>624</td>
<td></td>
<td>0.78</td>
<td>14.2</td>
<td>27.74</td>
</tr>
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</table>

Scheme 1

Phenanthrenequinone monooxime may exist in two tautomeric forms, viz. oxime A and nitroso B. The oxime tautomer may further exist in two conformational forms: syn-A₁ and anti-A₂.

Applying energy minimization, the energy difference between both isomers syn-oxime A₁ and anti-oxime A₂, was found to be 1.387 Kcal/mol. The barrier of tautomerization (A₁→B₁) is predicted to be 13.94 Kcal/mol and the rotational barrier (A₁→A₂) is found to be 8.26 Kcal/mol. If it does happen, the latter process should be favoured and this explains why tautomerization does not occur. The barrier height of A₁→B₁ is higher than A₁→A₂. The data obtained clearly indicate the presence of the ligand in its oxime form only and the monooxime predominantly exists in syn form. The carbonyl group and =N.O group in syn-isomer (A₁) are oriented in such a way that the chelation may occur through carbonyl group.
Acknowledgement

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References

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