Synthesis and structural studies of some organotin(IV) complexes with macrocyclic ligands

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Six five-coordinated complexes of diorganotin(IV) with general formula [Ph₂SnL]X₂ where L = 1,4,8,11-tetraaza tetradeca-5,7,12,14-tetraene or 1,4,8,11-tetradeca-2,3,9,10-dibenzocyclotetradeca-5,7,12,14-tetraene and X = ClO₄, BF₄, NO₃ have been prepared and characterised through elemental analysis and molar conductance data. The IR and ¹H NMR spectra show that only three out of the four nitrogens of ligand L and the two phenyl groups are coordinated to tin atom leading to trigonal-bipyramidal structure for the complexes.

Recently, several metal derivatives of a wide variety of macrocyclic ligands have been synthesised and characterised¹-⁴, but corresponding organometallic derivatives of these ligands have not been synthesised so far. The studies on the reactivity of a large number of compounds indicate that many organometallics with balancing anions of large size may act as simple dipositive cations having a tendency to undergo template reactions with macrocyclic ligands to yield a novel series of compounds. In this report, we describe the synthesis and spectroscopic studies of several new complexes of organotin(IV) with macrocyclic ligands derived from acetylacetone and ethylenediamine or o-phenylenediamine.

Experimental
SnCl₄ and Ph₂Sn were obtained from M/s Aldrich Chemicals (USA). Ethylenediamine, acetylacetone, o-phenylenediamine and potassium cyanide were BDH reagents. Other commercially available reagent grade chemicals were purified by standard methods⁵. All the reactions were carried out under dry nitrogen. Diphenyltin dichloride was prepared by the standard method⁶. Ph₂SnX₂ (X = ClO₄, BF₄, NO₃) were prepared by simple metathetical reactions of Ph₂SnCl₂ with AgX/NaX in methanol. All the tin complexes were prepared by the non-template method as described below:

Preparation of macrocyclic ligand
The reported reaction of acetylacetone with ethylenediamine or o-phenylenediamine in 2:2 ratio in the presence of NiCl₂.6H₂O was used to obtain complexes of formula [Ni(L₁)]Cl₂ or [Ni(L₂)]Cl₂ where L₁ = 1,4,8,11-tetraaza tetradeca-5,7,12,14-tetraene (C₁₄H₂₄N₄) and L₂ = 1,4,8,11-tetradeca-2,3,9,10-dibenzocyclotetradeca-5,7,12,14-tetraene (C₂₂H₂₄N₄). From these the free ligand was extracted by the following method. Ni(II) complex (0.01 mol) was dissolved in methanol and treated with KCN (0.04 mol). The solution was continuously refluxed for 20 hr. The precipitate of K₂[Ni(CN)₄] was removed by running the reaction mixture over a silica column and eluting with benzene and testing the elute for nickel qualitatively. This process was repeated several times and when the elute failed to give the test for nickel it was concentrated and run over TLC plates till completely pure. The free macrocycle was then crystallised using petroleum ether and analysed (Table 1).

<table>
<thead>
<tr>
<th>Complexes</th>
<th>M.P. (°C)</th>
<th>Elemental analysis Found (Calc,%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Sn</td>
</tr>
<tr>
<td>[C₁₄H₂₄N₄(L₁)]ClO₄</td>
<td>85</td>
<td>67.7</td>
</tr>
<tr>
<td>[C₁₂H₂₄N₄(L₂)]ClO₄</td>
<td>90</td>
<td>76.1</td>
</tr>
<tr>
<td>Ph₂Sn(C₁₄H₂₄N₄)(ClO₄)₂</td>
<td>*</td>
<td>16.4</td>
</tr>
<tr>
<td>Ph₂Sn(C₁₂H₂₄N₄)(BF₄)₂</td>
<td>&gt; 250</td>
<td>17.0</td>
</tr>
<tr>
<td>Ph₂Sn(C₁₂H₂₄N₄)(NO₃)₂</td>
<td>&gt; 250</td>
<td>18.4</td>
</tr>
<tr>
<td>Ph₂Sn(C₂₂H₂₄N₄)(ClO₄)₂</td>
<td>*</td>
<td>14.5</td>
</tr>
<tr>
<td>Ph₂Sn(C₂₂H₂₄N₄)(BF₄)₂</td>
<td>&gt; 250</td>
<td>15.1</td>
</tr>
<tr>
<td>Ph₂Sn(C₂₂H₂₄N₄)(NO₃)₂</td>
<td>&gt; 250</td>
<td>16.0</td>
</tr>
</tbody>
</table>

* Explodes before melting  
** Due to explosive character and presence of fluorine, C, H analyses were not possible.
stirred at room temperature under nitrogen for 8 hr, at the end of which period a pale yellow precipitate of the tin complex settled down. This was filtered, washed repeatedly with methanol and solvent ether and dried over P2O5.

The IR spectra were recorded in CsI on a Perkin-Elmer model 521 spectrophotometer. 1H NMR spectra of the complexes were recorded in DMSO-d6 using TMS as the internal standard on a Varian A 90D spectrometer. Elemental analyses were carried out at the semimicro scale at the CDRI, Lucknow. Molar conductances of 10-3 molar solutions in anhydrous DMSO were measured at 30°C by a Philips magic eye conductivity bridge model PR 9500 using dip type conductivity cell.

Results and Discussion

The above synthetic procedure gave six new complexes; their analytical data are summarized in Table 1 which show the molecular formula to be [Ph2Sn(L)]Cl2 or [L2]Cl2 where \( L_1 = C_{14}H_{24}N_4 \); \( L_2 = C_{22}H_{24}N_8 \) and \( X = ClO_4^{-} \), NO3 and BF4. The complexes, which are crystalline solids, are white in colour for ligand L1 and white to grey for ligand L2. Their molar conductances in DMSO are in the range 40-60 ohm^{-1}cm^{2}mol^{-1} corresponding to 1:2 electrolytes.

In the IR spectra (4000-200 cm^{-1}) of the free ligands L1 and L2, the absence of NH stretching, the usual CO stretching modes of absorptions and presence of a strong band at 1660 cm^{-1} due to \( C = N \) stretching provide strong evidence for the presence of a closed cyclic product containing Schiff base linkages. In case of \( L_2 \) four additional bands located at 1614, 1591, 1492 and 1448 cm^{-1} correspond to the vibrational modes of benzene ring.

A comparison of the spectra of free macrocyclic ligands L1 and L2 with those of their nickel and tin complexes indicates that the \( C = N \) stretching undergoes significant changes on complexation. The shift of \( C = N \) from 1660 cm^{-1} in the free ligands to 1580 ± 10 cm^{-1} in the above complexes may be due to the presence of strongly coordinated and conjugated \( C = N \) groups. The substituted benzene ring vibrations remain unaltered on complexation of the ligand. Two absorptions of weak intensities identified at 426 ± 6 and 364 ± 6 cm^{-1} in the spectra of tin complexes, which are absent in the spectra of free macrocycle, may be attributed to vSn-N vibration. A single weak band at 290 ± 6 cm^{-1} identified in the spectra of all the complexes is assigned to Sn-C (Ph) stretching mode indicating the presence of two phenyl groups at axial positions. As reported earlier, these vibrations are insensitive to complexation and occur almost in the same range as in diphenyltin dichloride.

The absorptions associated with anions in these complexes are identified at 1085, 621, 412 cm^{-1} for chlorate, at 1050, 620, 420 cm^{-1} for tetrafluoroborate and at 1360, 810, 230 cm^{-1} for nitrate; these positions show the presence of uncoordinated anions.

In the 1H NMR spectrum of free ligand L1, all the CH3 protons (as these are equivalent) appear as a singlet at 6 1.75 (12H) while the two types of methylene protons give singlets at 6 2.30 (4H) and 6 2.70 (8H). In the spectrum of \( L_2 \) the CH3 and CH2 protons give singlets at 6 1.70 (12H) and 6 2.40 (4H), respectively, while the phenyl protons appear as a multiplet in the range 6 6.70-7.10 (8H).

In the spectra of complexes [Ni(L1)]Cl2, the CH3 protons appear as a singlet at 6 1.90 (12H) while the two types of methylene groups show singlets at 6 2.92 (4H) and 6 3.12 (8H). In the spectrum of the complex [Ni(L2)]Cl2, three signals are observed, all as singlets, at 6 1.80 (12H), 6 3.20 (4H) and 6 7.32 (8H) corresponding to CH3, CH2 and phenyl protons, respectively. The shift of the signals toward lower field is an indication of the coordination of macrocycle while the fact that all the signals appear as singlets suggests that all the four nitrogens have coordinated to the same Ni(II) ion resulting in a square-planar structure for the complexes as shown below (Ia and Ib).

In the 1H NMR spectrum of the complexes [Ph2Sn(L1)]Cl2, three types of CH3 protons are observed instead, all as singlets, at 6 1.80 (6H), 6 1.93 (3H) and 6 3.10 (3H) in a 2:1:1 ratio. All the CH2 protons are observed as a broad signal centered at 6 3.30 (12H). The phenyl ring protons are observed as a very broad signal in the range 6 7.10-7.80.

In the 1H NMR spectra of the complexes [Ph2Sn(L2)]Cl2, the CH3 protons appear in 2:1:1 ratio, similar to the signals in the complexes of \( L_1 \), at 6 1.83 (6H), 6 1.90 (3H) and 6 2.16 (3H) CH2 protons were observed as two singlets at 6 3.40 (2H) and 6 3.60 (2H). The phenyl ring protons gave a multiplet at 6 7.30-7.70.

The presence of three types of CH3 protons in the spectra of both types of complexes suggests that the macrocycle coordinates through only three of its nitrogens to the tin atom, while the fourth one remains uncoordinated.
free (structures IIa and IIb). This type of coordination is expected to give five types of CH$_2$ protons in structure IIa, which appear to have merged together into one broad signal at $\delta$3.30, and two type of CH$_2$ protons in structure IIb, which appear at $\delta$3.40 and $\delta$3.60. The complexes are thus assigned five coordinated trigonal bipyramidal geometry with the phenyl groups occupying axial positions, as drawn above.

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**References**