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SYNTHESIS AND CHARACTERISATION OF SOME DI & TRIORGANOTIN(IV) DERIVATIVES OF SCHIFF BASES

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Twenty novel compounds of di and triorganotin (IV) derivatives with two Schiff base ligands derived from furan-2-aldehyde with aniline (L_1) and from p-toluidine with glyoxal (L_2), have been prepared possessing formulae such as: $[Ph_2Sn(L_1 \text{ or } L_2)X_2]$; $[Ph_2Sn(L_1 \text{ or } L_2)_2]Y_2$; $[Ph_3Sn(L_1 \text{ or } L_2)X]$; $[Ph_3Sn(L_1 \text{ or } L_2)]Y$, where X = Cl^-, SCN^-, Y =ClO_4^-, BF_4^-, NO_3^-. These are assigned six coordinate octahedral or five coordinate trigonal bipyramidal structures respectively on the basis of analytical and spectral studies.

INTRODUCTION

Numerous Schiff base and macrocyclic compounds of transition metal cations, oxometal cations and some organotin derivatives have so far been reported from this laboratory[1–4]. In the present paper we report the synthesis followed by characterization of some octahedral and trigonal bipyramidal di- and triorganotin (IV) complexes with two new Schiff base ligands viz. 2-furfuraldene-aniline (L_1) and N,N bistoludeneglyoxal (L_2), using a variety of coordinating and non-coordinating anions. The structures of these compounds have been assigned on the basis of elemental analysis, molar conductance, IR & ^{1}H NMR spectral studies.

EXPERIMENTAL

All the reactions were carried out under dry nitrogen atmosphere and reactants and products were purified on TLC plates.

I. Preparation of 2-furfuraldeneaniline (L_1) and N, N-bistoluideneglyoxal (L_2)

A solution of furan-2-aldehyde (0.01 mole) 1.65 ml or glyoxal (0.01 mol, 0.45 g) in methanol (25 ml) was added slowly and dropwise to a solution of aniline (0.01 mole, 1.82 ml for L_1) or p- toluidene (0.002 mole, 2.14 gm for L_2) respectively and the reaction mixture was refluxed for 10-12 hrs. At the end of this period a brown solution was obtained from which methanol was distilled off, and the brown liquid so obtained was run over TLC plates and the ligands were crystallised out from the light brown fraction using petroleum ether and characterised.

L_1—$C_{11}H_9NO$	Found C = 76.48%; H = 5.50%; N = 8.25%; Calcd C = 76.85%; H = 5.70%; N = 8.52%
L_2—$C_{16}H_{16}N_2$	Found C = 81.36%; H = 6.78%; N = 11.86%; Calcd C = 81.62%; H = 7.00%; N = 12.08%

II. Preparation of di and triorganotin salts

Diphenyltin dichloride and triphenyl tin chloride were prepared by standard methods[5]. Replacement of chloride by ClO_4^-, BF_4^-, NO_3^- and SCN^- was done by simple metathetical reactions using silver or sodium salts as follows: Calculated amount (0.01 mole) of di or triphenyltin chlorides were suspended in dry methanol (20 ml) and were stirred with silver perchlorate/nitrate/thiocyanate or sodium tetrafluoroborate in 1:2 molar ratio for eight hrs. The precipitated Ag/Na chloride was filtered off and the organotin (IV) salts were crystallized out from the solution.

III. Preparation of Complexes

0.01 Mole of the organotin (IV) salts were dissolved in methanol (20 ml) and treated with 0.02 mole of ligand L_1 or L_2 also dissolved in methanol (25 ml). The reaction mixture was refluxed for 14 hrs when it assumed a brown colour; this solution was concentrated and run over TLC plates using chloroform/acetone as running solvent. The organotin (IV) derivatives were separated out from the top dark maroon layer and recrystallized using solvent ether.

RESULTS AND DISCUSSION

The analytical and conductance data suggest the formulae of the complexes to be $[Ph_2Sn(L_1 \text{ or } L_2)X_2]$; $[Ph_2Sn(L_1 \text{ or } L_2)_2]Y_2$; $Ph_3Sn(L_1 \text{ or } L_2)X]$ and $[Ph_3Sn(L_1 \text{ or } L_2)]Y$. The two ligands L_1 and L_2 can offer bidentate N, O or N, N coordination to organotin (IV). Thus smaller anions like Cl^- or SCN^- which can be favourably coordinated, form non-electrolytic complexes, while bigger anions like ClO_4^-, NO_3^- or BF_4^- do not coordinate. The coordination number is therefore either six or five depending upon the triorganotin (IV) derivatives and ligand.

In the IR spectra of free ligands a few sharp bands are seen in the range 1600–1450 cm^{-1} due to phenyl groups, while a very sharp band at 1660 ± 10 cm^{-1} is due to azomethine stretch. In the spectra of complexes the former set of bands undergoes positive and later negative shift due to coordination[6–9]. The two absorptions of weak intensities at 530 ± 5 cm^{-1} and at 436 ± 4 cm^{-1} are attributed to be due to $Sn \leftarrow 0$ and $Sn \leftarrow N$ frequency, while another weak band at 292 ± 5 cm^{-1} corresponds to Sn-phenyl groups[10-13].

In the IR spectra of chloro complexes sharp bands at 350 ± 10; 410 ± 10 and 505 ± 10 cm^{-1} correspond to coordinated chloride ion[11–14], while in thiocyanato complexes bands at 2000 ± 4 cm^{-1} are due to $\rangle C{=}N$, at 450 ± 10 cm^{-1} due to ν N–C–S and at 810 ± 20 cm^{-1} due to C–S stretching and these correspond to coordinated thiocyanate ion[17]. In the spectra of perchlorato complexes the presence of uninegative perchlorate and in tetrafluoroborate complexes the presence of tetrafluoroborate ions is indicated by bands at 1120, 650 and 1016 and 529 cm^{-1} respectively which corresponds to ν_3 and ν_4 modes of vibrations of the uncoordinated ions[18]. The presence of ionic nitrate is shown in nitrato complexes by two bands at 1360 and 810 cm^{-1}.

In ^{1}H NMR spectra of ligand L_1, CH^- protons appear as singlet at δ 2.05 (2H) whereas the heterocyclic and phenyl ring protons merge together and appear as a broad, multiplet in the region δ 6.10–7.10 (8H). Both of these singlets shift and are observed in complexes at δ 2.20 and 7.90. Similarly in the ^{1}H NMR spectra of ligand L_2 a triplet centred at δ 2.30 (6H) which is due to CH_3 protons and a singlet at δ 3.50 (2H) due to C–H proton is observed. A broad multiplet at δ 7.10 (8H) is accounted for phenyl protons of ligands. The spectra of complexes show CH_3 and CH protons as singlets at δ 2.45 and δ 3.65 while the phenyl protons appear as a broad multiplet at δ 7.50. This shift towards high field of the different signals in complexes is on account of coordination.

On the basis of above discussion octahedral and trigonal bipyramidal structures are being suggested for these complexes.

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