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Synthesis and Structural Elucidation of Organotin (IV) Complexes with 2-Aminothiophenol and 2-Aminophenol

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Abstract

Synthesis and structural elucidation of organotin(IV) complexes with 2-aminothiophenol(ATP) and 2-aminophenol(AP) of composition $[SnA_3L]$ and $[SnA_2L_2]$ (A =C_6H_5 or $C_6H_5CH_2$, L= monobasic bidentate anion of ATP or AP) having trigonal bipyramidal and octahedral structure respectively have been reported. The complexes have been characterized by analytical, conductance, IR, UV-vis and ^1H NMR Spectral data.

Key words: Organotin(IV), 2-aminothiophenol, 2-aminophenol, spectroscopic studies.

Introduction

Organotin(IV) complexes possess anti-tumor properties[1-5] and analogous to Carboplatin[6-8]. These compounds have unique and interesting insights into structure, bonding and bio-activities[9]. We have reported synthesis, characterization and biological elucidation of some organotin(IV) compounds ligated by anthranilic acid[10] and heterocyclic thioamides[11] in our earlier communications. The present study aims at synthesis, characterization and structural investigations of some organotin(IV) complexes ligated by 2-aminothiophenol and 2-aminophenol.

Experimental

All chemicals used were AR grade or CP grade. Solvents were dried before use. Tribenzyltin (IV) chloride were prepared according to the literature method[12,13]. All the reagents and solvents were purchased commercially and used without any further purification. The diphenyltin (IV) dichloride (Aldrich), Triphenyltin(IV) hydroxide(Merck), 2-aminothiophenol (ATP) (sch-ucharolt, Munchen) and 2-aminophenol(AP) (Ward Blenkinsop, London) were used without further purification. Tin was determined gravimetrically by igniting a known quantity of each complex to SnO_2.

Preparation of Complexes :

All complexes were prepared using desired molar ratio of organotin(IV) compound and ligand(ATP/AP) in acetone or in methanol using our previous method reported in literature[11].

Analysis:

Sl. No. 1 : [Ph_3SnL](L = ATP/AP)(yellow): Calculated (%) for $C_{24}H_{21}SNSn$ (473.7): C = 60.79; H = 4.43; N = 2.95; Sn = 25.05; Found (%) : C= 60.80; H = 4.45; N = 2.85; Sn= 25.12

Sl. No. 2 : [Ph_3SnL](L = AP)(light yellow): Calculated (%) for $C_{24}H_{21}ONSn$(457.7): C=62.92; H = 4.58; N = 3.05 Sn = 25.93; Found (%) : C = 63.01; H = 4.62; N = 2.96; Sn = 26.11

Sl. No. 3 : [Bz_3SnL](L = ATP)(yellow) : Calculated (%) for $C_{27}H_{27}SNSn$(515.7): C = 62.82; H = 5.23; N = 2.71; Sn = 23.01; Found (%) C = 62.93; H = 5.43; N = 2.75; Sn = 23.16.

Sl. No. 4 : [Bz_3SnL](L = AP)(yellow) : Calculated (%) for $C_{27}H_{27}ONSn$(499.7): C = 64.83; H = 5.40; N = 2.80; Sn = 23.75; Found (%) : C= 64.90; H = 5.55; N = 2.75; Sn = 23.85

Sl. No. 5 : [Ph_2SnL_2](L = ATP)(yellow) : Calculated (%) for $C_{24}H_{22}S_2N_2Sn$(520.7): C =55.31; H = 4.22; N = 5.37; Sn = 22.79; Found(%): C= 55.47; H = 4.32; N = 5.42; Sn = 22.82

Sl. No. 6 : [Ph_2SnL_2](L = AP)(light yellow): Calculated (%) for $C_{24}H_{22}O_2N_2Sn$ (488.7): C =58.93; H = 4.50; N = 5.72; Sn = 24.28; Found(%) : C = 56.01; H = 4.48; N = 5.88; Sn = 24.55

The, C, H and N analysis, IR, UV-vis, H'NMR spectra and molar conductance data were obtained as reported elsewhere[11].

Results and Discussion

The analytical data consistent with the proposed stoichiometeries of the complexes. All isolated products were stable solid and soluble in DMF and DMSO and molar conductance were found in the range of 10.2 - 12.5 Ω^{-1} cm^2 mol^{-1} indicating their non- electrolytic nature of the compounds[14]. Molecular weight determination of complexes suggested their monomeric nature. The free 2-aminothiophenol exhibited two absorption maxima around 310 nm and 328 nm assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. These bands are observed at 360-362 nm as broad band on complexation indicating the presence of coordinated ligand and assigned due to charge transfer.

IR Spectra :

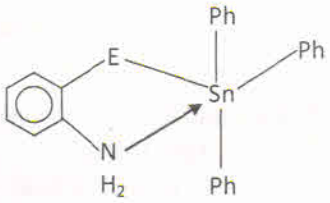
IR bands of free ligands and complexes are elaborated and elucidated for comparison. The free 2-aminothiophenol exhibits characterstic bands, υSH(2530 cm^{-1}), υasym NH_2 (3460 cm^{-1}), υsym NH_2(3340 cm^{-1}) undergo major change on complexation to Sn(IV). The first band was not observed in the spectra of complexes and / other two bands undergo red shift of lower frequency about 45-50 cm^{-1} and

55-60 cm^{-1} respectively indicating of simultaneous formation of Sn-S and Sn-N bond[15].

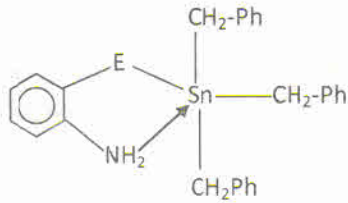
The other ligand, 2- aminophenol exhibits υOH(3480 cm^{-1}) υasym NH_2(3380 cm^{-1}), υsym NH_2(3300 cm^{-1}), υC-O(1220 cm^{-1}) and out of plane CH bonding (740 cm^{-1}). The OH band was not observed in complexes indicates the formation of Sn-O bond which is further supported by non-ligand bands at 500-510 cm^{-1} assigned to Sn-O stretching modes[16]. The formation of Sn-N bond with ligand is also indicated by red shift of υasym NH_2 and υsym NH_2 (Table-1) to lower frequency. New bands in complexes around 430-490 cm^{-1} and 370-380 cm^{-1} are assigned to Sn-N[17] and Sn-S[18] stretching modes consistent with previous literature[17-18]. Thus, 2-aminothiophenol and 2-aminophenol acts as mononegative bidentate anion in all complexes.

'H NMR Spectra :

The free ligands AP and ATP exhibit signals at δ8.89 PPM and δ3.38 PPM respectively due to intramolecularly hydrogen bonded phenolic and thiol proton. These protons disappeared from the spectra of complexes indicating their replacement by Sn(IV) ion during complexation[19-21]. The aryl proton signals are observed in the range of δ6.42-6.68 PPM (AP) and δ6.64-7.30 PPM(ATP) as complex multiplet are down field shifted and appeared at δ6.78 (AP) and δ7.43 PPM (ATP). the observed down field shift of the phenyl ring protons resonances may be rationalized in terms of deshielding of these protons due to drainage of electron density from aromatic ring to tin metal, which is in agreement with the previous report of Clark and co-workers[22]. The



(TBP- Str.)
(E = O/S)



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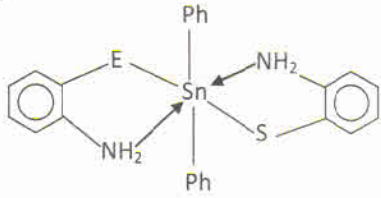

(Oh- Str.)
(E = O/S)

Table 1. Major IR and ^{1}H NMR Spectral data of ligands and complexes

Compounds	IR (cm^{-1})				^{1}H NMR (δPPM)		
ATP (ligand)	υasym NH_2/ (υsym.NH_2) 3460 m (3340 m)	υSn-O -	υSn-N -	υSn-S -	Amino protons 3.68	Phenyl protons 6.64-7.30 (Multiplet)	SH/(OH) protons 3.66 (-)
[Ph_3Sn(ATP)]	3415 m (3305 m)	-	430 m	370 w	3.56	7.43-7.45 multiplat	- (-)
[$Ph_3Sn(ATP)_2$]	3410 m (3300 m)	-	490 m	380 w	3.60	7.45-7.55 multiplat	- (-)
AP(ligand)	3405 m (3305 m)	-	-	-	4.40	6.42-6.68 multiplet	- (8.89)
[Ph_3Sn(AP)]	3410 m (3295 m)	500 m	435 m	-	4.12-4.41 (Split)	6.77-7.88 multiplat	- (-)
[$Ph_3Sn(AP)_2$]	3410 m (3000 m)	510 m	485 m	-	4.42		- (-)

integration of signals due to phenyl protons supported the stoichiometric formulation of the complexes.

The amino protons of A.P. (δ4.40 PPM) and ATP (δ3.688 PPM) are low field shifted on complexation and the integrated intensities of the signals agree well with the assigned structures (Str. I, II & III). These observations are consistent with conclusion drawn from IR Spectral data.

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