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Synthesis, Spectral and Antimicrobial Activity of Organotin (IV) Compounds Ligated by Anthranilic acid

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Abstract

Synthesis, characterization and anti-microbial activity of some novel di and triphenyltin(IV) complexes of anthranilic acid are reported. The infrared, ^{1}H NMR, elemental analysis and other physico-chemical data are made for structural determination. Spectroscopic data reveals that anthranilic acid acts as mono negative bidentate anion and bonding occurs through both amino nitrogen and carbohydrate oxygen. On the basis of spectroscopic data octahedral geometry is proposed for synthesized compounds. The synthesized compounds have been tested against various microorganisms and the synthesized compounds have higher activity than parent anthranilic acid.

Key words: Organotin(IV) Chelates, triphenyltin, activity, spectra.

Introduction

Organotin(IV) complexes are analogous to carboplatin[1-3] having significant anti-tumor properties[4-6]. Gielen *et al.*[7] and Xanthopoulon and co-workers[8] have reported anti-tumor activities of many organotin(IV) complexes in terms of chemistry it has been well established and the study of its biological properties against bacterial, fungal and cancer cells line also have been expanded[9]. As part of our interest and research on organotin (IV) compounds we have synthesized and characterized organotin(IV) carboxylate complexes of anthranilic acid. The metal complexes were tested in vitro against three types of pathogenic bacteria microorganism (*staphylococcus, klebsiella spp* and *Bacillas*) to assess their antimicrobial properties.

Experimental

All the reagents and solvents were purchased commercially and used without any further purification. The diphenyltin (IV) dichloride, Triphenyltin(IV) hydroxide (Merck) and anthranilic acid (B.D.H.) were used as

such and diphenyltin (IV) oxide dichloride with NaOH as described in literature[8]. Tin was determined gravimetrically by igniting a known quantity of each complex to SnO_2.

Preparation of Sodium Salt and Complexes:

The sodium salt of anthranilic acid was prepared by heating under reflux an equimolar (1:1) mixture of acid and sodium hydroxide in ethanol (50mL) for 2 hrs. After few days, white precipitate was obtained.

Preparation of Complexes:

All complexes were prepared using a general method. The equimolar mixture of triphenyltin (IV) hydroxide(2mmol) or diphenyltin (IV) dichloride (2 mmol) were suspended in acetone (50 mL) or in methanol (100 mL) containing sodium salt of anthranilic acid and mixture was heated under reflux for 2 hrs. A clear yellow solution was isolated by filtration and kept in a covered beaker for few days. The yellow crystals were collected and dried over anhydrous $CaCl_2$ in a vacuo desiccators. (Yield = 65-68%).

Analysis:

1. $[Ph_3SnA]$(yellow) (A= anthranilate ion)
   Calculated (%) for $C_{25}H_{22}O_2NSn$: C=61.63; H= 4.52;N= 2.87;Sn= 24.38;
   Found(%) : C= 61.65; H= 4.53; N= 3.01;Sn= 24.30;

2. $[Ph_2SnA_2]$(yellow)
   Calculated(%) for $C_{26}H_{24}N_2O_4Sn$: C=57.06; H= 4.38;N= 5.12;Sn= 21.71;
   Found(%) : C=57.11; H= 4.40; N=5.31;Sn= 21.75;

3. $[Ph_2SnA(MeOH)]$(yellow)
   Calculated (%) for $C_{20}H_{21}O_3NSn$:C= 54.33; H= 4.75;N= 3.16;Sn= 26.87;
   Found(%) : C= 54.35; H= 4.81; N= 3.18;Sn= 26.88;

4. $[Ph_2SnOA]_2$(yellow)
   Calculated (%) for $C_{38}H_{34}N_2O_6Sn_2$:C= 53.55; H= 3.99;N= 3.28;Sn= 27.88;
   Found(%) : C= 53.66; H= 4.01; N= 3.33;Sn= 27.92;

The C, H, N analysis, IR spectra, electronic spectra, ^1H NMR spectra and molar conductance were obtained as reported elsewhere[10].

Results and Discussion

The micro-elemental analysis for C,H,N, and Sn data obtained were in agreement with proposed formula for complexes . The υ O-H bands of the parent acid was absent in the infrared spectra of sodium salt and the complexes indicating the deprotonation and coordination of the carboxylate anion. The υ_{asym} COO(1665 cm^{-1}) and υ_{asym} COO(1555 cm^{-1}) suffered a major change to lower frequency and observed at 1660-1613 cm^{-1} and 1405-1365 cm^{-1} (table 1) respectively in complexes suggest the unidentate carboxylato group[11-12]. The Δυ below would be expected for bridging or chelating carboxylates but greater than 200 cm^{-1} for monodentate bonding of carboxylate anion[12].

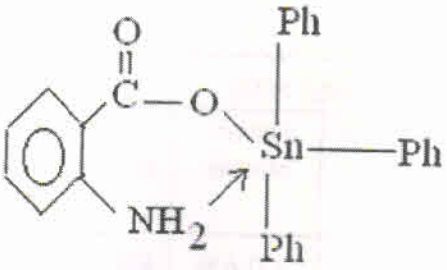
The presence of a broad band at 3410 cm^{-1}

Table 1. Selected IR(cm^{-1}) and ^1H NMR Spectral data(δ PPH) of ligand (AH) and Complexes.

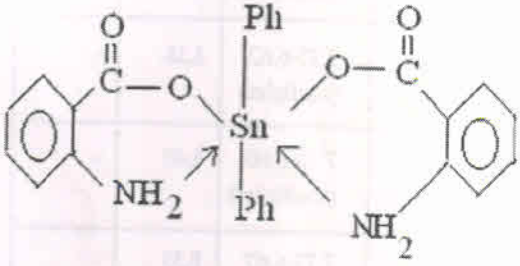
IR (cm^{-1})				^1H NMR(δ PPM)			
Compound	υNH_2	$\upsilon_{asym}COO$ / υ_{asym} COO	Δυ	υSn-O/ υSn-N	Phenyl protons	Amino protons	O-H protons
AH(ligand)	3325(m) 3240(m)	1665(s) 1555(m)	110	- -	7.71-6.56 (multiplet)	8.45	3.6
$[Ph_3SnA]$	3304(m) 3120(m)	1660(s) 1410(m)	250	470(m) 520(m)	7.70-6.66 (multiplet)	8.40	-
$[Ph_3SnCl(A)(MeOH)]$	3315(m) 3120(m)	1635(s) 1370(m)	265	480(m) 535(m)	7.72-6.62 (muliplet)	8.38	-
$[Ph_2SnA_2]$	3290(s) 3130(m)	1625(s) 1375(s)	250	450(m) 510(m)	7.70-6.60 (multiplet)	8.40	-
$[Ph_2SnOA]_2$	3310(s) 3125(m)	1613(s) 1365(m)	248	445(m) 510(m)	7.77-6.67 (multiplet)	8.35	-

Table 2. Inhibition circle diameter in millimeter for the bacteria after 24 hrs. incubation paid and 37°C for compounds.

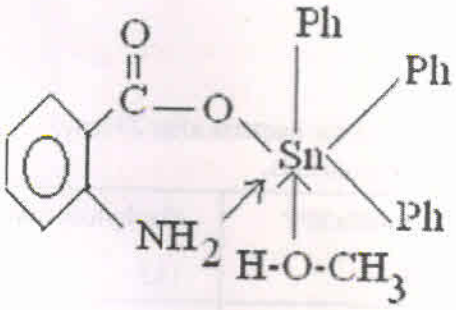
Compond	Bacillus	Klebsiella SPP	Staphylococcus
Control DMSO	11.1	10.0	13.5
AH	18.3	14.0	20.8
$[Ph_3SnA]$	20.2	17.3	20.1
$[Ph_3SnCl(A)(MeOH)]$	20.3	15.2	21.3
$[Ph_2SnA_2]$	20.1	17.1	20.1
$[Ph_2SnOA]_2$	20.3	15.1	21.2



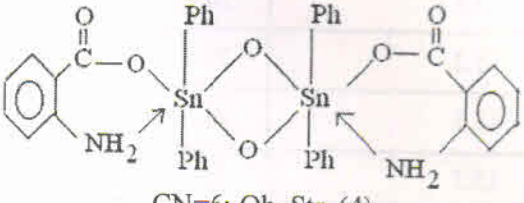
CN=5, TBP str. (1)



CN=6, Oh- Str. (2)



CN=6, Oh-Str. (3)



CN=6; Oh. Str. (4)

and the decrease of υ C-O (alcoholic) stretch of MeOH from 1034 cm^{-1} to lower energy by 64 cm^{-1} in [Ph_2SnCl (A) MeOH] indicate the involvement of O atom of MeOH towards coordination[13].

The $\upsilon_{asym}(NH_2)$ and $\upsilon_{sym}(NH_2)$ in free anthranilic acid were observed at 3325 and 3240 cm^{-1} red shift to lower frequency by 21-15 cm^{-1} and 120 cm^{-1} respectively indicating the formation of Sn - N band. This is also corroborated by the presence of new band in the range of 520-535 cm^{-1} due to metal – N stretching mode[14]. The non- ligand band at 470-480 cm^{-1} in complexes also suggest the formation of Sn-O bond and tentatively assigned to υSn-O mode[15]. New band at 635 cm-1 assigned υSn-O-Sn mode in dimeric complex (4) is in agreement with previous literature[16].

^1H NMR Spectra:

The free anthranilic acid exhibits signals at δ 7.72-6.52(multiplets) ppm, δ8.4 ppm and δ3.6 ppm due to phenyl protons, amino protons and protons of –O-H group respectively. The amino proton signals are low field shifted on complexation and the integrated intensities of the signals agree with the assigned structure of complexes (str.1 to str. 4) . The –OH proton signals are not present in complexes indicating deprotonation. The resonances appeared as two well separated sets of multiplets in the region centering around δ=7.50 and 7.85 ppm (downfield) with integration values 9.6 respectively ascribed to the aromatic protons

of phenyl group[17]. The protons resonances originating from methanol molecule occurred around δ= 3.48 ppm and based on the integration, only one molecule was present in complex (3). The methanol molecule was believed to coordinate to Sn(IV) atom during the formation of complex[16].

On the basis of analytical data valence requirements, the infrared spectral studies and ^{1}H NMR data, it is proposd that anthranilic acid acts as bidentate anion in octahedral structure of complexes.

Antimicrobial activities:

Antimicrobial activities of ligand and complexes was carried out against three types of pathogenic bacteria using nutrient agar medium by disc diffusion method[18]. The test solution were prepared in DMSO and soaked in filter paper of 5 mm diameter and 1 mm thickness. These discs were placed on the already seeded plates and incubated at 37^{0}C for 24 hours[19]. The zone of inhibition of bacterial growth is given in Table 2.

The antibacterial activity results revealed that the ligand and complexes show weak activity when compared to the control (DMSO)[20]. The complexes have more pronounced activities than ligand due to chelation[21-23].

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