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Spectral and Antibacterial Studies of Organotin (IV) Complexes Ligated by 2-Thiobarbituric Acid

Chemistry

KEYWORDS : Organotin (IV)-Chelates, 2-thiobarbituric acid, six-coordination, Spectra Bonding.

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ABSTRACT

Some new organotin(IV)-chelates of 2-thiobarbituric acid were prepared and characterized by elemental analysis, conductometric, IR, Uv-vis and 'H NMR spectral studies. IR Spectral Studies provides strong evidence in support bidentate (N, O) coordination of deprotonated mono negative anion of ligand in octahedral structure. The ligand and metal chelates were screened for their anti-microbial activity against the gram-negative bacteria, Escherichia coli and gram-positive bacteria, Staphyllococcus aureus. All tin(IV)-chelates exhibit more activity than free ligand.

INTRODUCTION

A Survey of the literature reveals that organotin(IV) compounds are analogous to carboplatin(1-3) and possess anti-tumor activities(4-6). Thiobarbituric acid play an important role in Biological system(7-9) and a Well-known reagent in use for the determination of the lipid peroxidation(10-11). This bioactive molecule contains thioamide group and coordination behaviour are reported(12-14). Our interest in this category of ligands(15-16), the present communication reports synthesis, spectral characterization and antibacterial studies of some organotin(iv) complex ligated by 2-thiobarbituric acid in continuation of our previous report(17-18).

EXPERIMENTAL

All solvents used were of reagent grade. The precursors organotin(iv) compounds, diphenyltin dichloride, triphenyltin(iv) hydroxide, tribenzyltin(iv) chloride and tri-n-butyltin(iv) chloride were commercially available and used without any further purification. 2-thiobarbituric was also available from (E.Merck) and its purity was checked from 'H NMR and infrared spectral studies.

PREPARATION OF COMPLEXES

The metal complexes were prepared by the same general method. A solution of the precursors compound(0.01 mol) were suspended in equimolar amount of El_3N and 2-thiobarbituric (0.02 mol.) in 150 ml methanol and stirred on magnetic stirrer for 1 hr. It was further heated under reflex for 3 hrs. A clear yellow solution was isolated by filteration and concentrated to ~10 m*l* and kept in a covered beaker for few days. The yellow crystals were collected and dried over anhydrous $CaCl_2$ in a Vaccuo desiccators. (yield = 65-66%)

Analysis :

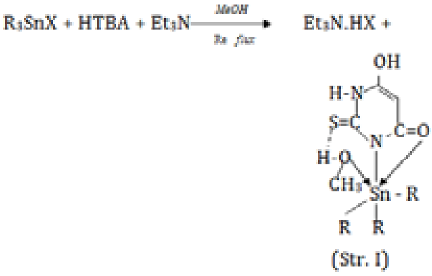
1. $[Ph_3Sn(TBA)(MeOH)]$ (light yellow): Calculated (%) for- $\mathbf{SnC_{23}H_{22}N_2O_3S}$ (524.7): C = 52.60; H=4.19; N = 5.33; Sn = 22.62;
   Found(%) : C = 52.56; H = 4.20; N = 5.40; Sn = 22.52
2. $[Bz_3Sn(TBA)MeOH]$(yellow) : Calculated (%) for $\mathbf{SnC_{26}H_{28}N_2O_3S}$ (566.70) : C = 55.05; H = 4.94; N = 4.94; Sn = 20.94;
   Found(%): C = 54.96; H = 5.01; N = 4.85; Sn = 20.86
3. $[n\text{-}Bu_3Sn(TBA)(MeOH)]$(yellow) : Calculated(%) for $\mathbf{SnC_{17}H_{34}N_2O_3S}$ (464.70) : C = 4.89; H = 3.65; N = 6.02; Sn = 25.54;
   Found (%) : C = 44.01; H = 3.81; N = 6.00; Sn = 25.31
4. $[Ph_2Sn(TBA)(MeOH)Cl]$(dull yellow) : Calculated (%) for $\mathbf{SnC_{17}H_{17}N_2O_3SCl}$ (483.2) : C = 42.21; H = 3.51; N = 5.79; Sn = 24.56
   Found (%): C = 42.11; H = 3.52; N = 5.80; Sn = 24.44

Tin was determined gravimetrically by igniting a known quantity of each complex to SnO_2 Carbon, hydrogen and nitrogen analysis were done at the micro analytical section of CDRI, Lucknow. The IR spectra of ligand and complexes were recorded with Perkin Elmer models 577 spectrophoto-meter in the range of 4000-200 cm^{-1} as KBr pellets. Electronic Spectra were recorded with zeiss(Jena) model and molar conductance of complexes were measured in DMF(10^{-3}M) using Wiss-Wekstatter Weitheim obb type LBR conductivity meter. 'H NMR Spectra were obtained with Varian EM 390 MHz NMR Spectro photometer.

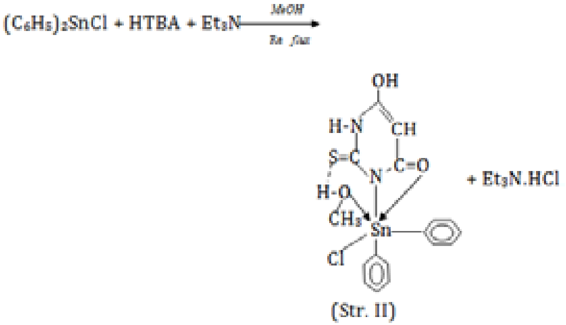
RESULTS AND DISCUSSION

Methanolic solution of ligand (HTBA) and R_3SnX (R= C_6H_5/ $C_6H_5CH_2$/ n- Bu; X = Cl/OH) in presence of Et_3N yielded solid products with formula $[R_3Sn(TBA)(MeOH)]$ (Scheme- I). Under similar conditions $(C_6H_5)_2SnCl_2$ reacts with ligand (HTBA) giving yellow solid with molecular formula $[(C_6H_5)_2SnCl(TBA)(MeOH)]$ (Scheme- II) and the ligand acts as deprotonated mononegative bidentate anion as :

Scheme 1 :



Scheme 2 :



All isolated products were insoluble in most of organic solvents but soluble in DMF and DMSO. The conductivity values were found in the range 6.85-8.35$\wedge^{-1}cm^2$ mol^{-1} indicating their non-electrolytic nature(19). Electronic Spectra of complexes exhibit a single broad band between 24390-24100 cm^{-1} due to charge transfer of coordinated ligand.

IR SPECTRA

The IR Spectra of free ligand (HTBA) and complexes are elaborated and elucidated for comparison which brings out the following facts to light :

(i) The υNH of free ligand are observed at 3100(m)cm^{-1} and 3020(m)cm^{-1} undergoes a major change in intensity and position. The first band disappears and the second band was observed at 3025 cm^{-1} indicating deprotonation of one of two NH groups and the ligand exist as [TBA] before complexation. New bands of medium intensity due to Sn-N stretching mode at 490-495 cm^{-1} provides a strong evidence for the formation of Sn(iv)-N bond(20).

(ii) The carbonyl absorption band C=O of the free ligand at 1710 cm^{-1} and 1680 cm^{-1}either disapplared, weakened or shifted to lower frequency in chelates complexes indicating that at least one of the two carbonyl groups of the ligand is coordinated. New bands at 500-510 cm^{-1} due to stretching mode in far- IR Spectra of complexes also provides strong evidence for the formation of Sn-O bond on complexation(21).

(iii) The presence of a broad band at 3410 cm^{-1} and decrease of C-O (alcoholic) stretch of MeOH from 1035cm^{-1} to lower frequency by 60-65 cm^{-1} in complexes indicated the involvement of oxygen atom of MeOH in coordination(22).

(iv) There is no change in intensity as well as position of thioamide ban IV(23-24) (830 cm^{-1}), on complexation. No coordination through sulphur may be assumed. Thus, the ligand acts as bidentate anion having simultaneous bonding through N and O atoms.

‘H NMR SPECTRA

The ‘H NMR Spectrum of HTBA shows a sharp signal at δ12.2 PPM with integration corresponds to two NH and one OH protons as a result of C_5-C_6 enolization and δ4.9 PPM (S, H-C), δ3.5 PPM (S, H-C) shifted at δ10.8 PPM (S, H-N) and at δ4.2 PPM (S, H-C) on complenation. The signal at δ3.5 PPM (S, H-C) could not be observed in the ‘H NMR of the complexes. Resonance signal at δ1.56 PPM(t), δ1.30 PPM(M), δ1.08 PPM(m) and at δ0.91 PPM(t) were assigned to the (H-C) protons of the n-butyl group in corresponding complex. The protons resonances originating from methanol molecule occurred around δ3.42 PPM based on the integration, only one molecule was present in complexes. The methanol molecule was coordinated to Sn(IV) atom during formation of complexes(25). The aromatic protons in complexes were found at δ6.88- 7.2 PPM.

Thus, the correlation of the experimental data and valence requirement allows assigning octahedral stereochemistry (Str. I & II) to all the reported complexes.

ANTIBACTERIAL ACTIVITY

All isolated solid complexes and ligand (HTBA) were tested against gram positive bacteria S. Aurens and gram negative bacteria E. Coli using paper disc method described in literature (26) Muller Hinton Agar was used to culture the test bacteria. The microbial culture were grown at 37° C for 24 hrs and then appropriately diluted with sterile 0.8% saline solution. The concentration of test drug was kept 200 µg/ML in DMF using streptomycin as standard drug for comparison.

The results obtained show that the synthesized compounds have higher activity than the corresponding ligand but lower activity than the standard drug.

Table 1 : Major IR, ‘H NMR and Electronic Spectral data of HTBA and Complexes.

Compd.	IR Spectra (cm^{-1})					λmax (cm^{-1})
	υN-H	υC=O	Thio-amide Band IV (υC=S)	υSn-O	υSn-N	
HTBA (ligand)	3100(m) 3025(m)	1710(sb) 1680(s)	830(m)	-	-	35085 42550
[Ph$_3$Sn (TBA) MeOH]	3025(m)	1700(s)	832(s)	510(m)	490(m)	24390 (CT Band)
[Bz$_3$Sn (TBA) (MeOH)]	3030(m)	1705(s)	830(s)	520(m)	495(m)	24100 (CT Band)
[(n-B$_u$)$_3$ Sn (TBA) (MeOH)]	3025(m)	1705(s)	835(m)	500(m)	490(m)	24050 (CT Band)
[Ph$_2$Sn (TBA) (MeOH) Cl]	3035 (m)	1700 (m)	830 (m)	505 (m)	485(m)	24400 (CT Band)

Table 2 : ‘H NMR Spectra (δPPM) of ligand (HTBA) and complexes.

Comp.	N-H+OH Protons	CH Protons	Methanol ofProtons	Arene Protons	n-butyl protons	Benzyl Protons
HTBA	12.2	4.9 3.5	-	-	-	
[Ph$_3$Sn (TBA) MeOH]	10.8	4.2	3.42	6.88-7.2 (multiplet)	-	-
[Bz$_3$Sn (TBA) (MeOH)]	11.2	4.2	3.45	6.86-7.46 (multiplet)	-	7.15 7.32 2.78
[(n-Bu)$_3$ Sn (TBA) (MeOH)]	11.4	4.3	3.28	-	1.56 1.30 1.08 0.91	-
[Ph$_2$Sn (TBA) (MeOH) Cl]	11.6	4.2	3.42	7.11-7.88 (multiplet)	-	7.2-7.80 (multiplet)

Table 3 : The zone of inhibition (mm) of ligand and complexes.

Comp.	Zone of inhibition ψ (mm) E Coli		S. aurens	
	100	200	100	200
HTBA (ligand)	16	22	18	20
[Ph$_3$Sn(TBA)MeOH]	16	23	19	22
[Bz$_3$Sn(TBA)(MeOH)]	17	23	19	22
[(n-By)$_3$Sn(TBA)(MeOH)]	17	22	18	21
[Ph$_2$Sn(TBA)(MeOH)Cl]	17	23	18	23
Streptomycin (Stand. Drug)	26		26	

ψ : Solution are µg/ml

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