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Synthesis, characteristic spectral studies and anti-bacterial activity of a novel stannane

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ABSTRACT

This research paper reports the synthesis of a novel Stannane. The synthesized complex was characterized by various spectroscopic techniques.The Ultraviolet-visible spectra depicted a bathochromic shift from the electronic transitions taking place in ligand as a result of complex formation.[1]HNMR, [13]CNMR and [119]SnNMR were recorded which duly confirms the successful synthesis of complex by the above quoted method. The synthesized complexes thus obtained were screened for antibacterial activity against gram positive bacterial strains ***Bacillus subtilis*MTCC121**, ***Micrococcus luteus* MTeC106** and gram negative strains ***Escherichia coli* 1610**, ***Pseudomonas aeruginosa*1934**. The zone of inhibition of the complex was compared with starting material and the control, the stannane has better antibacterial activities. The novel complex thus synthesized, characterized and analysed could have various applications in the different fields for a synthetic chemistry.

Key Words: Stannane, synthesis, spectroscopy , antibacterial activity, synthetic chemistry.

1. INTRODUCTION

Organotin oxides react with inorganic or organic acids, alcohols, mercaptanes etc. with ligand exchange. These reactions are equilibrium reactions which are driven to completion by removal of water, often by azeotropic distillation with a solvent. Stannanes are chemical compounds containing tin bonded to the hydrocarbons. Since tin atom has large size and low-lying empty 5d atomic orbitals consequently various examples of coordination number greater than four are located. Despite the fact that carbon to tin bond is weaker than carbon-carbon or carbon-silicon bond, it is relatively non-polar having high stability in air and moisture as well as in the presence of many nucleophilic species. (Tabassum S and Pettinari. C, 2006; Beltran H.I, 2007; Muhammad N, 2009, Gleeson B, 2008).

Since 1930, the extensive use of Organotin compounds has started in the field of PVC stabilization. As PVC is fundamentally thermally unstable and could not stand high extrusion temperature without stabilization therefore degradation occurs but the Organotin stabilizers traps any HCl released which results in rapid degradation and also it functions as an antioxidant.

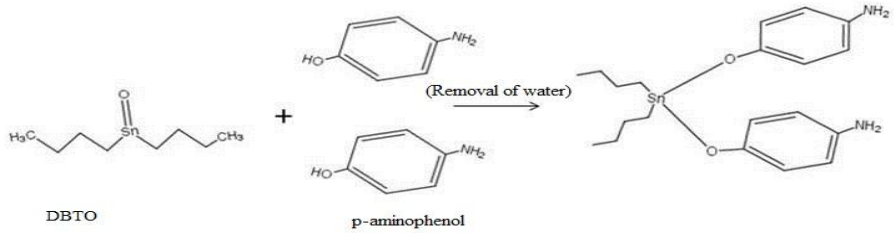
Stannanes have various catalytic applications. A mechanism has been proposed involving coordination of tin with –OH containing compounds and possibly the other reactants. Also tin catalysts can find vast applications in the field of condensation reactions for preparing room temperature vulcanized silicones. The tin catalyst forms an intermediate with cross-linker to form a -Sn-O-Si- bond. Other applications include biocidal activity in antifouling paints, wood preservatives and agriculture (Biunden S J, 1984; Cima F, 2003). Stanannes are also advantageous in the form of tin oxide coatings; used on bottles to for breakage on a line and on window-panes as heat reflective coatings. (Yousif, 2009; Y.Win, 2012)

2.MATERIALS AND METHOD

2**.1 Materials and Physical Measurements:** All the chemicals used were of Analytical Grade and obtained from commercial sources(Merck specialitics,Spectrochem, Qualigen and Fischer scientific). Solvents used for the synthesis were dried and purified by standard procedures[W.L.F. Armarego and D.D. Perrin (1996)]the instrument used wasRotatory Vaccum Evaporator (Khera Instruments Pvt Ltd,pressure range 0-30 in Hg/0 to -760 mmHg. The complex was synthesized according to the reported method.The UV visible spectra studies were measured usingUV instrument SHIMADZU UV 1800, 200-600 in ethanol. The ^{1}H NMR spectra (in DMSO –d6 solution) of Organotin (IV) complexes were recorded on BRUKER AVANCE II 400 NMR Spectrometer SAIF Panjab University, Chandigarh. TMS was used as internal standard. The NMR spectra were processed by JEOL Delta^{TM}NMR data processing software. The ^{13}C NMR and^{119}Sn spectra (in DMSO –d^{6} solution) of Organotin (IV) complexes were also recorded on BRUKER AVANCE II 400 NMR Spectrometer SAIF Panjab University, Chandigarh. $CDCl_3$ was used as internal standard.The instrument used for sterilizing purpose in Antimicrobial study was Khera laboratory autoclave, Khera Instrumentation (pressure range 0-30 lb/in 2 or 0-2.1 kg/cm 2) and Incubator used was Orbital shaker, PSN Instrumentation PVT Ltd.

2.2. Experiment: Weighed 1 mmol of starting material, Dibutyltinoxide and dissolved in 60 mL of AR grade dry benzene) and 20 mL absolute ethanol mixture.The mixture was refluxed azeotropically over a heating mantle for about 10 -15 minutes. The dibutyltinoxide goes into the mixture giving a clear solution. After this step, 2 mmol of the ligand (4-Aminophenol) was added into this mixture ,the metal-ligand molar ratio was 1:2, the reaction was refluxed azeotropically further for 5-6 hours which results in azeotropic removal of the water. The extra solvent was dismissed by reducing the pressure in a Rotatory Vaccum Evaporator and the solid left behind was washed with 10 mL AR grade chloroformand further removal of solvent was done by using the Rotatory Vaccum evapourator, the product obtained thus was filtered ,reported the yield and a small fraction was recrystallized using ethanol.Reported the melting point of the obtained product. (Mala Nath , 2003; Jose S, 2004).

REACTION SEQUENCE : Reaction of Dibutyltinoxide with p-aminophenol:



Scheme: Reaction pathway for the formation of Dibutyltin (IV) complexes of above shown ligand

The above reaction was found to be facile and was complete within 5-6 hours of refluxing. The resulting complex was obtained in **good yield (0.3785 g, 82%) and was mehroon coloured solid soluble in dimethyl sulphoxide and ethanol.**

2.3 Antibacterial test: The ligand and its organotin(IV) complex was screened for their antibacterial activity using the agar well diffusion method[Rahman A ,et al,(2001)] The wells were dug(6mm) in the media with a sterile metallic borer and 18-24 h bacterial inoculums containing 0.1658 OD was spread on the surface of the nutrient agar using a sterile cotton swab. The sample in the concentration of 0.02 g/100 mL in ethanol was introduced into the respective wells. Other wells containing Ethanol and the reference antibacterial drug served as negative and positive controls respectively. The plates were incubated immediately at 37 ℃ for 18-24 h. The activity was determined by measuring the diameter of the inhibition zone (in mm).The results were compared with the control (Streptomycin).[Mala Nath (1997),Mala Nath(1999),Tushar S Basu(2008)]

3.RESULTS

3.1. Electronic absorption spectra: The Ligand showed band at λ_{max} 306.50 nm; Absorbance0.147781.After the formation of complex, the value of the wavelength of stannane was changed to λ_{max} 316.0nm; Absorbance0.0638280(Refer Table 1 for electronic absorption spectrum data).It is observed that there is a shift of absorption maxima to longer wavelength, known as "Bathochromic shift or Red shift ".It may be due to the presence of non-bonding electron pair as they become available for interaction with metal ion.This gives an evidence of complex formation of ligand with dibutyl tin oxide. [Leovac et al(2007), Norrihen San (2012)] (Refer figure 1 for Overlay graph of ligand (4-Aminophenol) and synthesized Stannane)

3.2.^{1H} NMR Spectra: The ^{1}H NMR spectra (in d^{6}DMSO solution) of Organotin(IV)complexes were registered on BRUKER AVANCE II which was running at 400 frequency on NMR Spectrometer at SAIF situated at in Panjab University, Chandigarh. TMS was used as internal standard.

DISCUSSION

Resonance signals were observed at δ(ppm): 0.9061 (Methyl $-CH_3$ of n- butyl group); 1.6051, 1.2944(Methylene $-CH_2$of n- butyl group); 4.0734(proton of p-Amine NH_2 group); 6.5095, 6.46650(Aromatic Hydrogen, –CH/butyl group protons). (Refer figure 2 for ^{1}H NMR spectra of synthesized Stannane)

The absence of -OH proton signal in the ^{1}H NMR spectra of the organotin(IV) complexes [Jose S and Casas (2004)] indicated that the phenolic oxygen is coordinated to the Sn(IV) atom after de-protonation. [Uche B. Eke (2010)]

3.3 ^{13}CNMR Spectra: The ^{13}C NMR spectra (in d^{6}DMSO) of Organotin (IV) complexes were registered on BRUKER AVANCE II which was running at 400 frequencieson NMR Spectrometer at SAIF placed in Panjab University, Chandigarh. TMS was used as internal standard. Numbers of peaks were found same as the number of non-equivalent carbon atom.

DISCUSSION

Resonance signals were observed at δ(ppm):13.50 (Methyl carbon $-CH_3$ of n- butyl group); 39.20, 39.07, 30.06(methylene carbon $-CH_2$ of n- butyl group); 115.47, 115.49 p (Carbons adjacent to $-NH_2$ group), 148.57(carbon adjacent to Sn-O bond).(Refer figure 3 for ^{13}C NMR of synthesized stannane)

3.4 ^{119}Sn NMR SPECTRA

DISCUSSION

The geometry of the novel tin complexes can be predicted by observing tin NMR spectra as ^{119}Sn nucleus is one of the most attractive nuclei for NMR analysis because of the wide chemical shift range and relatively simple spectral interpretation. The ^{119}Sn NMR chemical shift is very sensitive to complexation. The shielding of tin nucleus increases markedly with an increase in coordination number around tin. Also the electron releasing power of the alkyl groups makes tin atom progressively more shielded. Therefore the delta values in tin NMR move to a higher field with changes in geometry. The significant peaks at +16.26 and +46.01 ppm indicate octahedral geometry around central tin atom, coordination no.6. (Refer figure 4 for ^{119}SnNMR of synthesized Stannane)

3.5 ANTIBACTERIAL STUDIES

DISCUSSION

The synthesized complex was found to be more toxic toward Gram positive strains than Gram negative strains due to difference in the structures of the cell walls. The walls of Gram negative cells are more complex than those of Gram positive cells. Lip polysaccharides form an outer lipid membrane and contribute to the complex antigenic specificity of Gram negative cells. Since the complex inhibited the growth of microorganisms, it has been assumed that the production of an enzyme is being affected; hence, the organisms were less able to metabolize nutrients and, consequently, growth ceased. Those enzymes that require free sulfydryl groups (-SH) for activity, appear to be especially susceptible to deactivation by ions of the complex. (Refer Table 2: Antibacterial activity $_{a,b}$ of the free ligands and its organotin(IV) complexes (inhibition zone in mm).(Refer figure 5,6,7 for Graph showing antibacterial action of synthesized stannane against different bacterial strains used)

Table.1.Electronic absorption data

Sample	Wavelength (nm)	Absorbance
Ligand (4-Aminophenol)	306.50	0.147781
Stannane	316.0	0.063828
Stannane (dilution 1)	318.0	0.033463
Stannane(dilution 2)	315.0	0.007797

Table 2: Antibacterial activity $_{a,b}$ of the free ligands and its organotin(IV) complexes (inhibition zone in mm).

	Clinical implication	Dilutions	Zone of Inhibition (mm)			
		g/L	DBTO	L	C	R
***Bacillus subtilis* MTCC121**	notable food spoiler, causing ropiness in bread and related food, causesfood poisoning	0.02	12	9	17	14
		0.01	-	-	14	
	REPORTED MIC-5×10^{3}ppm	0.005	-	-	9	
Escherichia coli 1610	Infection of wounds, urinary tract, and dysentery	0.02	1.3	8	10	29
		0.01	-	-	-	-
	REPORTED MIC-20×10^{3}ppm	0.005	-	-	-	-
***Micrococcus luteus* MTeC106**	skin infections, or chronic cutaneous infections, colonizes mouth, mucosae, oropharynx and upper respiratory tract	0.02	20	9	16	41
		0.01	-	-	14	
	REPORTED MIC-5×10^{3}ppm	0.005		-	9	
***Pseudomonas aeruginosa* 1934**	Pneumonia, infections of the lungs , bone, or urinary tract	0.02	-	-	-	18
		0.01	-	-	-	
	REPORTED MIC- NIL	0.005	-	-	-	

R –Reference, streptomycin, L – ligand(4-Aminophenol), DBTO- Dibutyl tin oxide, C –Complex(stannane of 4-Aminophenol) ,MIC-Minimum Inhibition Concentration.

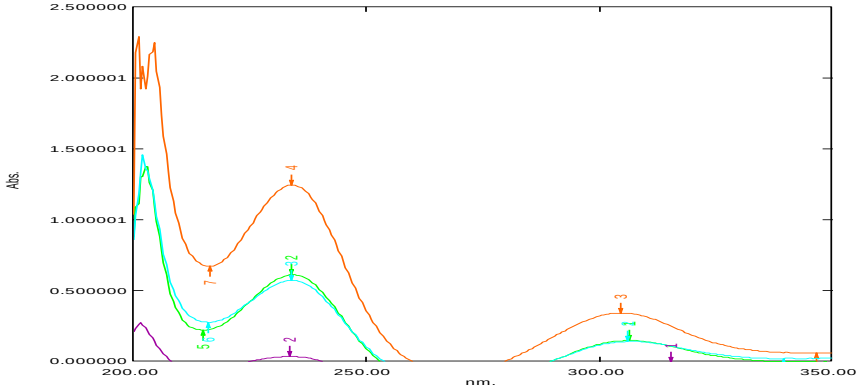


Figure.1.Overlay graph of ligand (4-Aminophenol) and synthesized Stannane

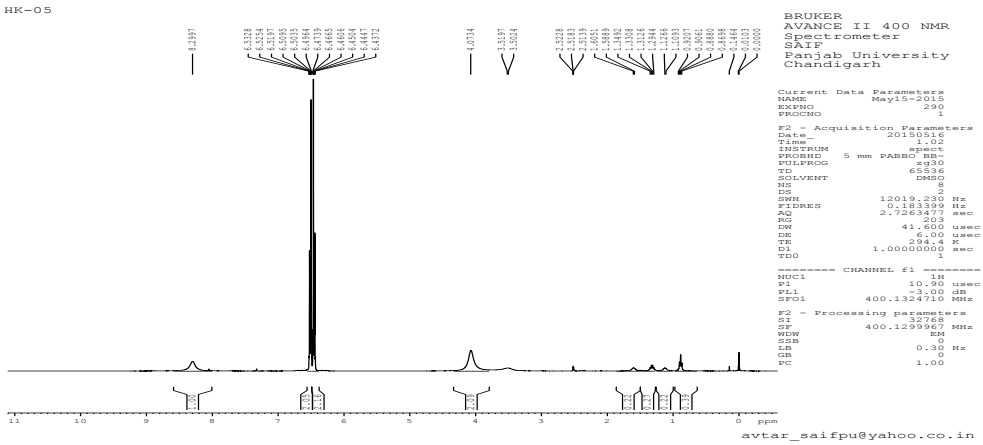


Figure.2.^{1}H NMR SPECTRA of synthesized Stannane of 4-Aminophenol

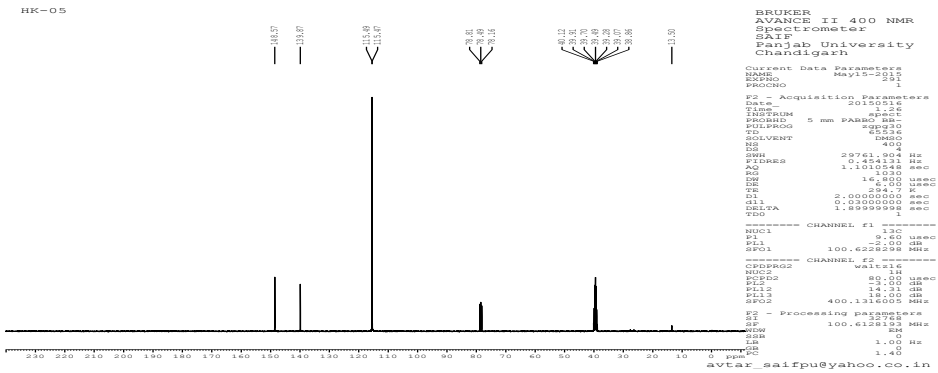


Figure.3.^{13}CNMR of synthesized Stannane of 4-Aminophenol

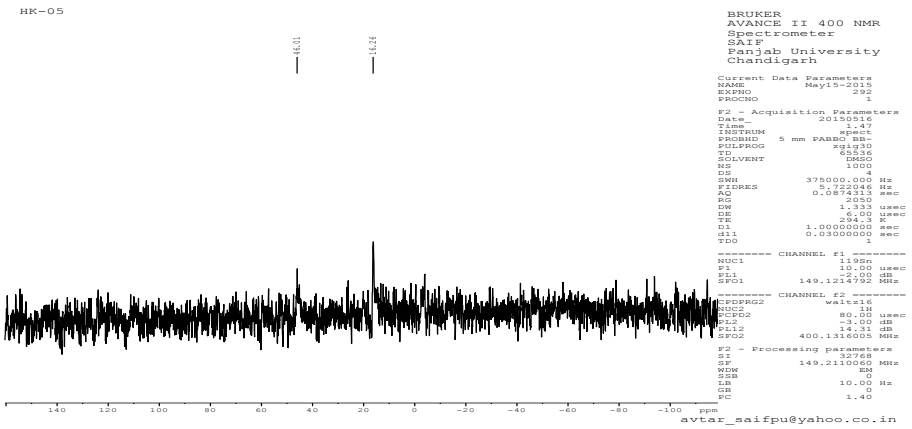


Figure.4.^{119}SnNMR of synthesized Stannane

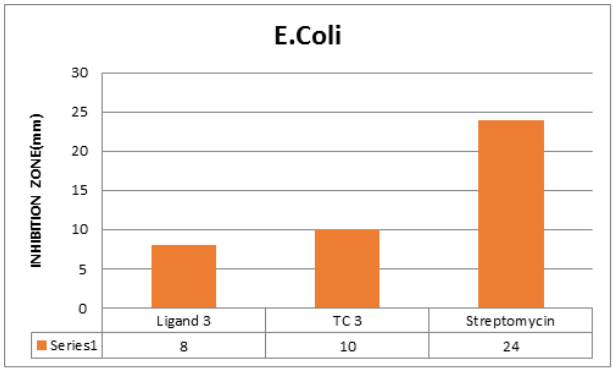
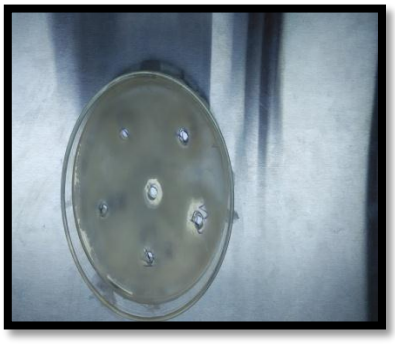


Figure.5.Graph showing antibacterial action of synthesized stannane against *Escherichia coli 1610*



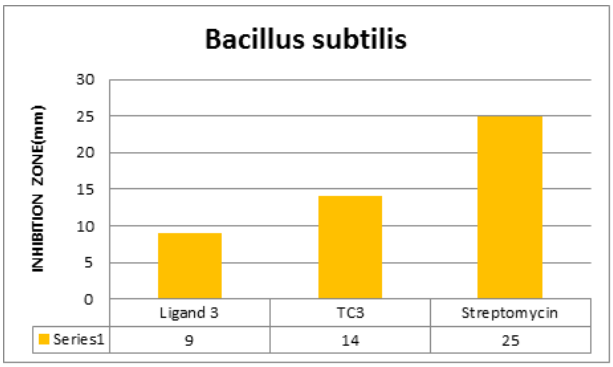


Figure.6.Graph showing antibacterial action of synthesized stannane against *Bacillus subtilis* MTCC121

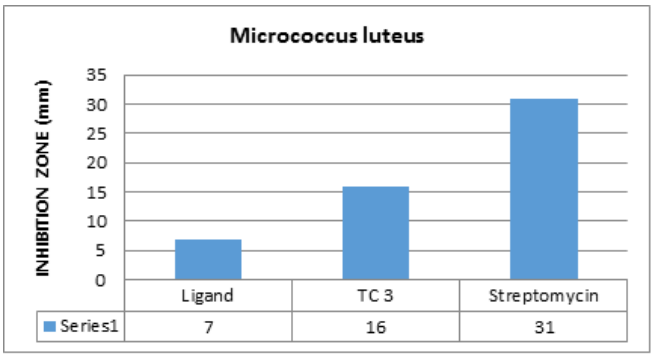


Figure.7.Graph showing antibacterial action of synthesized stannane against *Micrococcus luteus MTeC106*

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SCOPE

In view of the antibacterial activity of synthesized complex, it can have potential uses in the field of anti-bio fouling agents, bactericides and other fields of synthetic chemistry.

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