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Synthesis, Characterization, Biological Activity and Pharmaceutical Applications of Organotin Complexes

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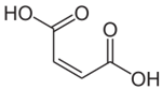
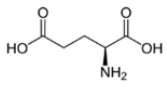
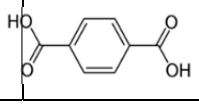
Abstract—*Various organotin complexes have broad scope as potential drugs due to the presence of metal ion which would help in target drug delivery and high activity of a particular drug. The mechanism of action of these drugs on our biological system can be studied. In this research work the organotin complexes of three ligands (maleic acid, l-glutamic acid and Terephthalic acid) have been synthesized successfully by the reported method in benzene-ethanol medium. The synthesis was carried out by azeotropic removal of water molecule in benzene-ethanol medium, in a reaction system. The refluxing with Dean-Stark attachment was carried out initially for 3-4 hours followed by the use of Rotatory Vacuum Evaporator for the removal of any solvent left in the system. A dry product was obtained. Analyzed for its melting point and UV-Vis absorption was recorded. Characterization of novel product was done using FTIR technology and ^{1}H NMR, ^{13}C NMR and ^{119}Sn NMR studies. According to these results these novel organotin complexes may interact with the biological system. A clear bathochromic shift is observed in UV spectra indicating the successful complexation of ligand with tin atom. The dominant peaks in FTIR spectra are identified which corresponds to various functional groups present in the suggested tin complex, as shown in the reaction sequence. Also many organotin complexes have wide applications as antifouling agents and as biocides thus further studies of their anti-microbial activity are under progress.*

1. INTRODUCTION

Introduction of Ligands

Ligand	Molar Mass (g/mol)	Structure
L_1(Maleic) Acid	116.07	
L_2(L-Glutamic acid)	147.13	
L_3(Terephthalic) acid	166.13	

2. LITERATURE REVIEW

Stannanes are achieving incredible intrigue due to its wide application in natural and potential action in the region of inorganic and metal natural science. It is used broadly in ventures, for example, marine hostile to biofouling paints, additives, fungicides, bactericides and fire retardants. Progresses in the utilization of stannane or organotin (IV) mixes in pharmacological as antibacterial, antifungal, hostile to tuberculosis and cytotoxic operators and better natural activity as an anticancer medication when contrasted with other conventional substantial metals, have increased significant intrigue. These complexes are broadly thought about on account of their coordination geometries and also auxiliary differences. Physiochemical properties of the organometallic complex are tranquil selective and now being broadly utilized as a part of restorative inorganic science. The after effects of research work experienced till now are very amazing, a portion of the organometallic complexes have as of now entered clinical trials. Stannanes have picked up an edge over different organometallics attributable to their bioavailability in biological system and passageway into the natural way of life, the reality they are less hazardous to the earth and their pharmaceutical applications. So by remembering the different uses of stannane/organotin (IV) edifices and further continuation of our work, we here report the synthesis, characterization and anti-bacterial activity of novel stannanes.

3. EXPERIMENTAL

Drying and Distillation of Solvents

Desired amount of benzene is treated with benzophenone, which is used to remove the thiophene content present in the given benzene. Sodium pellets were introduced into the reaction mixture to remove the water content from the solvent. Reflux the contents for around 2-3 hours. After filtration a

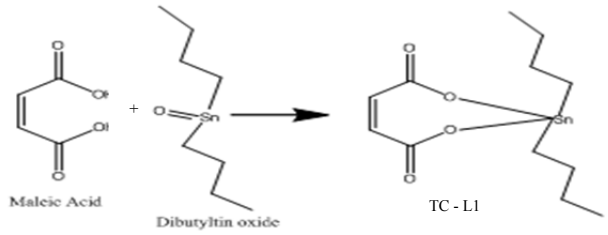
distillation unit was established to achieve pure amount of benzene.

Synthesis of Complexes

(i) Dibutyltin oxide with L_1

Weighed 4 moles of starting material Dibutyltin oxide in weighing machine and dissolved in benzene-ethanol mixture. The mixture was refluxed azeotropically over a heating mantle for 25-30 minutes. Dbto goes into the mixture giving a clear solution. After that 4 moles of the ligand Maleic acid was added, the metal-ligand ratio was 1:1, the contents were refluxed for further 5-6 hours which results in azeotropical removal of water. The excess of solvent was removed under reduced pressure in a Rotatory Vacuum Evaporator and the solid left has been washed with chloroform.

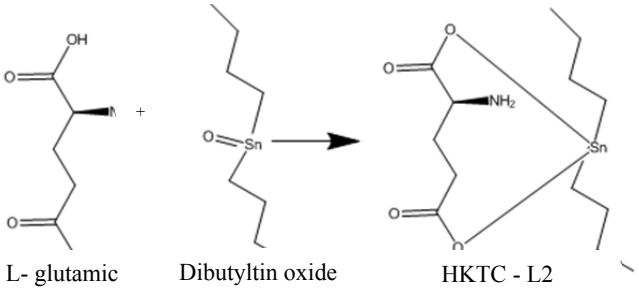
Reaction Sequence



Dibutyltin oxide with L_2

Weighed 4 moles of starting material Dibutyltin oxide in weighing machine and dissolved in benzene-ethanol mixture. The mixture was refluxed azeotropically over a heating mantle for 25-30 minutes. Dbto goes into the mixture giving a clear solution. After that 4 moles of the ligand L-glutamic acid was added, the metal-ligand ratio was 1:1, the contents were refluxed for further 5-6 hours which results in azeotropical removal of water. The excess of solvent was removed under reduced pressure in a Rotatory Vacuum Evaporator and the solid left has been washed with chloroform.

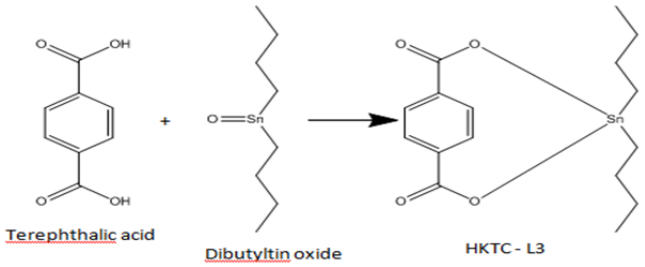
Reaction Sequence



Dibutyltin oxide with L_3

Weighed 4 moles of starting material Dibutyltin oxide in weighing machine and dissolved in benzene-ethanol mixture. The mixture was refluxed over a heating mantle for 25-30 minutes. Dbto goes into the mixture giving a clear solution. After that 4 moles of the ligand terephthalic acid was added, the metal-ligand ratio was 1:1, the removal was refluxed further for 5-6 hours which results in azeotropical removal of water. The excess of solvent was removed under reduced pressure in a Rotatory Vacuum Evaporator and the solid left has been washed with chloroform.

Reaction Sequence



4. RESULTS AND DISCUSSIONS

Physical Analysis

S. No.	Molecular Formula	Molecular Weight	Color
1.	$C_{12}H_{20}O_4Sn$	347g/mol	Dark Brown
2.	$C_{13}H_{25}NO_4Sn$	378.3g/mol	Chocolate Brown
3.	$C_{16}H_{22}O_4Sn$	397g/mol	Creamish yellow

5. CHARACTERIZATION STUDIES

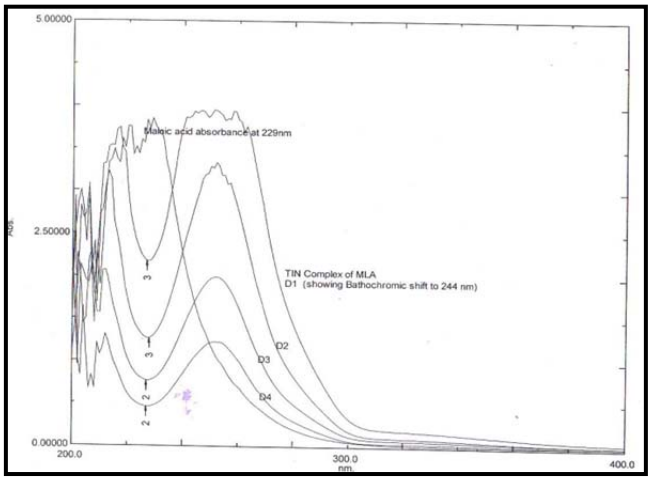
1. UV-Vis Spectroscopy

Theory

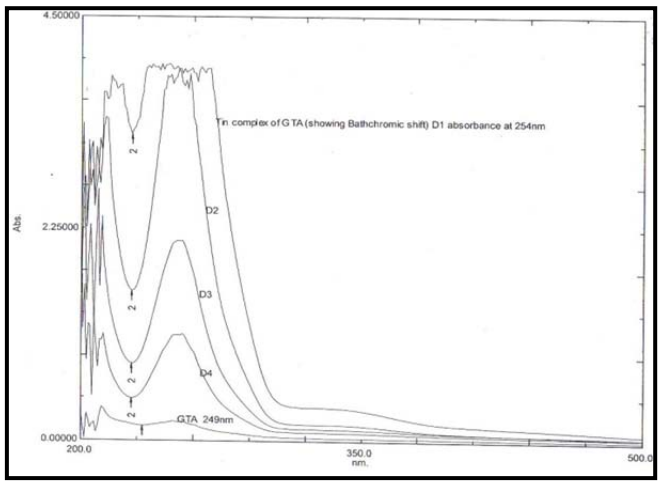
UV light can be consumed by atoms to energize higher energy (most approximately bound) electrons from lower energy states to higher states. Such moves can be considered broadly to comprehend the coupling energies of the comparing electrons experiencing move. Since π-electrons are most loosely bound in a natural atom, UV spectroscopy yields a great deal of data about the level of unsaturation in a particle. At the point when the wavelength of the transition surpasses the UV range, in view of a similar guideline, even the colors of molecules can be clarified on the basis of absorption of visible light.

Results

(i) TC-L_1



(ii) TC-L_2



Compound	Wavelength(nm)	Absorbance
Ligand	249	0.20041
Complex	254	3.95279

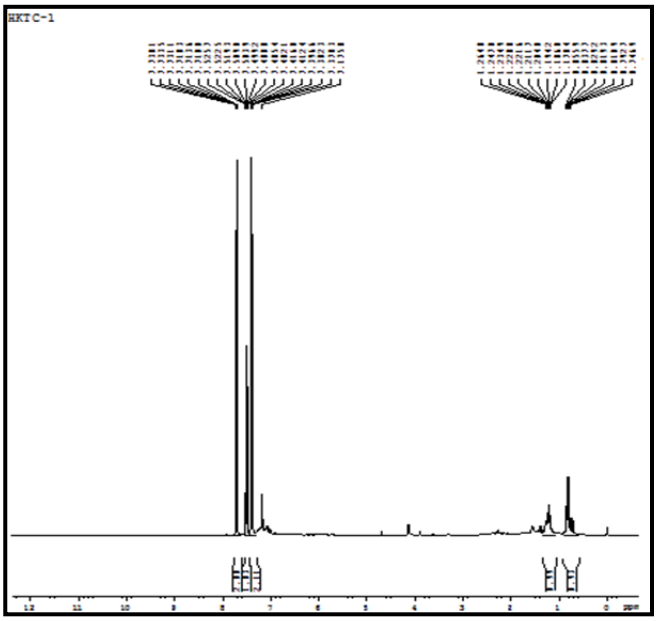
Compound	Wavelength(nm)	Absorbance
Ligand	229	3.85263
Complex	244	3.98890

Upon comparison the wavelength of absorption peaks in UV/Vis spectra of starting material with its tin complex, it is observed that there is a shift of absorption maxima to longer wavelength, known as "Bathochromic shift". This gives an evidence of complex formation of ligand with DBTO.

2. NMR Studies

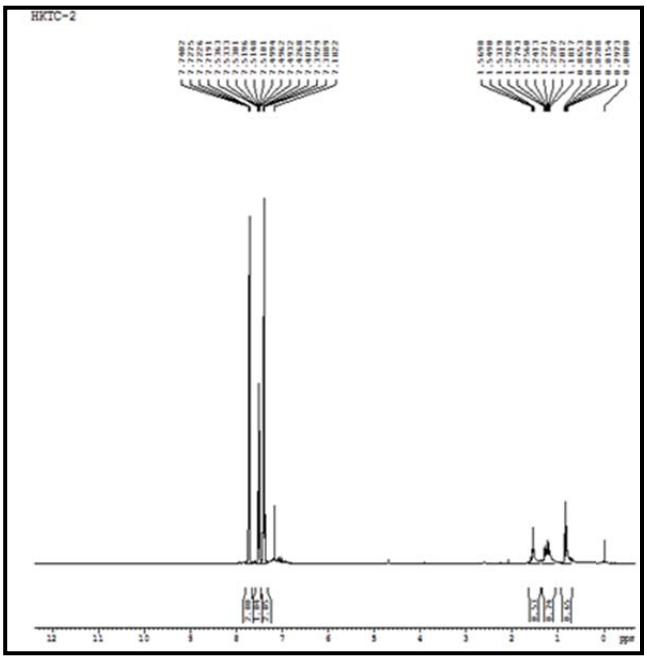
(i) ^{1}H NMR

- **TC-L_1**



Groups	Chemical Shifts (ppm)
N-butyl group protons	0.7469 – 1.2648
Protons adjacent to carbonyl carbon	7.71 – 7.7381

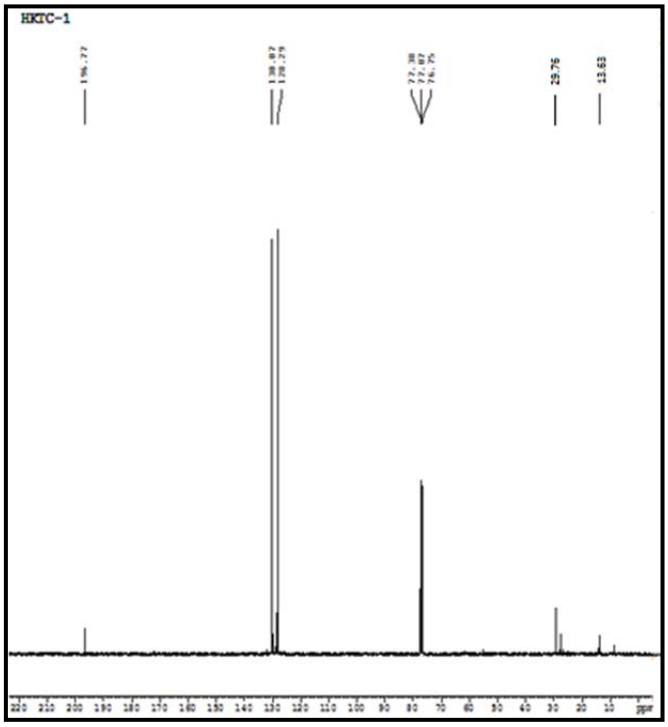
- **TC-L_2**



Groups	Chemical Shifts (ppm)
N-butyl group protons	0.7973 – 1.5678
Protons on carbon $-CH_2$	7.38
Protons adjacent to carbonyl carbon $-CH_2$	7.4938 – 7.5363
Protons attached to carbon linked with amine group	7.71 – 7.74
Amine $-NH_2$	7.1822

(i) ^{13}C NMR

- **TC-L_1**



Groups	Chemical Shifts (ppm)
N-butyl/ aliphatic carbon $-CH_3$	13.63
N-butyl/ aliphatic carbon $-CH_2$	29.76
Carbonyl carbon	196.77
CH=CH	128.29 – 130.07

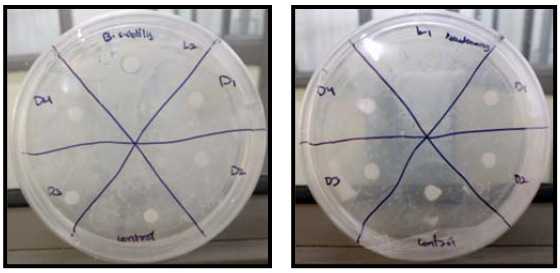
3. Antibacterial Studies

Purpose: To compare the antibacterial activity of various complexes with their ligands.

Strains Used: Gram Positive: Bacillus subitilis.

Gram Negative: Pseudomonas sp.

These bacterial strains were selected because they are recommended for great quality assurance purposes.



6. CONCLUSION

In this research work the organotin complexes of four ligands (maleic acid, l-glutamic acid and terephthalic acid) have been synthesized successfully by the reported method in benzene-ethanol medium. The products thus obtained were characterized by their physical analysis, UV-Vis spectroscopy FTIR and nuclear magnetic resonance spectroscopic studies for proton, carbon and tin nuclei. A clear bathochromic shift is observed in UV spectra indicating the successful complexation of ligand with tin atom. The dominant peaks in IR spectra are identified which corresponds to various functional groups present in the suggested tin complex, as shown in the reaction sequence.

7. SCOPE

Great researches have led to the design of organotin-containing molecules to one of the most common therapeutic applications, anti-neoplastic agents. Other applications are related to corrosion inhibition coupled with their biocide activities. Due to these kind of applications a regular development of new organotin-containing molecules is taking place. Lead-induced biochemical alterations can be significantly done by tin compounds. Various organotin complexes have broad scope as potential drugs due to the presence of metal ion which will help in target drug delivery and high activity of particular drug. These can be used as antifouling agents in paints due to their biocidal activity. Thus the mechanism of action of these drugs on our biological system can be studied. The interaction of organotin compounds with biological system permits the tracking of these drugs in our body. Compare to other organometallic reagents, the organotin compounds surprisingly are more specific towards the biological receptors. According to the chemical structure of organotin compounds, they interact with real and model cell membranes locating them in specific regions depending on their physicochemical properties.

8. ACKNOWLEDGEMENT

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