

Synthesis, Characterization and Antimicrobial Activities of Di- and Tri Organotin (IV) Schiff Base Complexes

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Abstract

2-Thiophenecarboxylic acid hydrazide has been treated with benzaldehyde in 1:1 molar ratio at room temperature in the presence of a suitable solvent to yield Schiff base. Then it has been treated with R_2SnCl_2/R_3SnCl in 1:1 molar ratio to synthesize organotin (IV) complexes under reflux conditions. Organotin (IV) complexes have been characterized by FT-IR and semi-empirical study. FT-IR data explains the tetrahedral arrangement of sulphur donor ligand with tin metal which is further confirmed by semi-empirical study. Least value of dipole moment of complex 3 explain the trans orientation of chlorine atom around tin metal. The complexes along with ligand have also been screened for their antibacterial and antifungal activities. Organotin (IV) complexes exhibited antibacterial activities with few exceptions as compared to free ligand. Complex 4 has been found potent antibacterial agent among all complexes.

Key words: *Organo tin compounds, Schiff base, 2-Thiophenecarboxylic acid hydrazide, Benzaldehyde*

Introduction

Organostannic or organotin compounds are substances composed of tin directly bound to number of organic groups. They are characterized by the presence of strong carbon to tin bond and have the general formula of $R_xSnL_{(4-x)}$ where R is any organic alkyl or aryl group, L is singly charged anion or an anionic organic group, Sn the central tin atom and x is 1-2 [1]. R is usually a butyl, octyl or phenyl group and X is commonly chloride, fluoride, oxide, hydroxide, carboxylate or thiolate. On the basis of number of organic substituents (R) organotins are designated as mono-, di-, tri- and tetra-organotin compounds and their formula are $RSnX_3$, R_2SnX_2 , R_3SnX and R_4Sn , respectively [2].

Expansion of organotin compounds had geared up in full-fledged, cause of this, was the accessibility of Grignard reagents when alkylating and arylating agent. The Grignard reagents were vital in the enlargement of organotin compounds due to high electropositivity of Mg which permits the relocation of hydrocarbon radicals to main group metal [3]. Organotin compounds are highly soluble in common organic solvents such as ethers, alcohols and halogenated hydrocarbons. However their solubility in water is of the order of 50 mg/L at ambient temperature. Experimentally determined data explains that aqueous solubilities range for Me_2SnCl_2 is 20 mg/L for readily soluble to 1 mg/L for sparingly

soluble phenyl, cyclohexyl and octyltin compounds [4].

Organotin compounds are mostly liquids or solids and are thermally stable up to 200 °C. These compounds do not react immediately with air or water; but very slowly changed into inorganic tin compounds. Their melting points commonly depend on the type of organic group connected to tin and vary over a wide range [5]. Organotin compounds are very reactive and have many applications in biological field as well as in industrial field. The most efficient heat stabilizers are those containing Sn-S bond particularly dimercaptides such as isooctylthioglycollates and are used often in combination with corresponding monoalkyltin compound [4]. Organic and inorganic tin compounds can be used as fire retardants [6]. A variety of organotin compounds were used as catalysts in industry, e.g., in the reaction of phthalic anhydride with iso octanol to form di-n-octyl phthalate [7].

Tin(IV) sulfate is most commonly used compounds in electroplating for the production of range of deposits containing tin, generally on a metallic surface [8]. Thin coating of tin(IV) oxide on glass are used to strengthen glassware, returnable bottles and jars [9]. One of the major uses of organotin compounds is as the antifungal agents. The first compound that was used as antifungal agent was triphenyltin acetate [10].

Organotin(IV) compounds had been used as anthelmintic. For example a drug named wormal which contains piperazine, phenothiazine, and dibutyltin dilaurate was used for such purpose [11]. A higher concentration of organotin compounds can even prevent the attack by insects [12]. A number of triorganotin compounds have been developed as agrochemicals and they are successfully used in specialized applications [4]. The later study showed that tributyltin compounds had deleterious effects on the development of the pacific oysters [13].

Chemicals and Instrumentation

Analytical grade all organic solvents were procured from Merck, Germany were used for research work. 2-Thiophene carboxylic acid hydrazide, R_2SnCl_2 , R_3SnCl were purchased from Aldrich (USA). Benzaldehyde was purchased from Fluka (Germany). Yeast extract was of Lab M, (UK) origin, Casine was of Uni-chem. Dextrose was of Daejung (Korea). Nutrient broth, nutrient agar and potato dextrose agar were of Oxoid (UK) origin. Solvent was dried by standard procedure [14]. Melting points of all the compounds were determined using electrothermal melting point

apparatus, MP-D Mitamura Riken Kogyo (Japan). IR spectra of the compounds were recorded as KBr disc using Perkin Elmer FT-IR-100 spectrophotometer in the range of 4000-250 cm^{-1} . Molecular modelling was carried out by MOPAC 2007 program in gas phase by using PM3 method. Biological activities were performed by using autoclave, laminar air flow, (Dalton, Japan) and incubator of (Sanyo, Germany).

General procedure for the synthesis of complexes

2-Thiophenecarboxylic acid hydrazide (1 mmol) was dissolved in dried ethanol (50 mL) in round bottom flask (250 mL) on continuous stirring at room temperature. Then benzaldehyde (1 mmol) was added dropwise to above solution. The reaction mixture was refluxed for 2 hours. Then R_2SnCl_2/R_3SnCl (1 mmol) was added as solid in the portions to the above reaction mixture and refluxed it for 4 hours. Solvent was evaporated through rotary evaporator under reduced pressure. Solid product obtained was recrystallized in Methanol: Pet. ether. Purity of the compound was also checked by TLC.

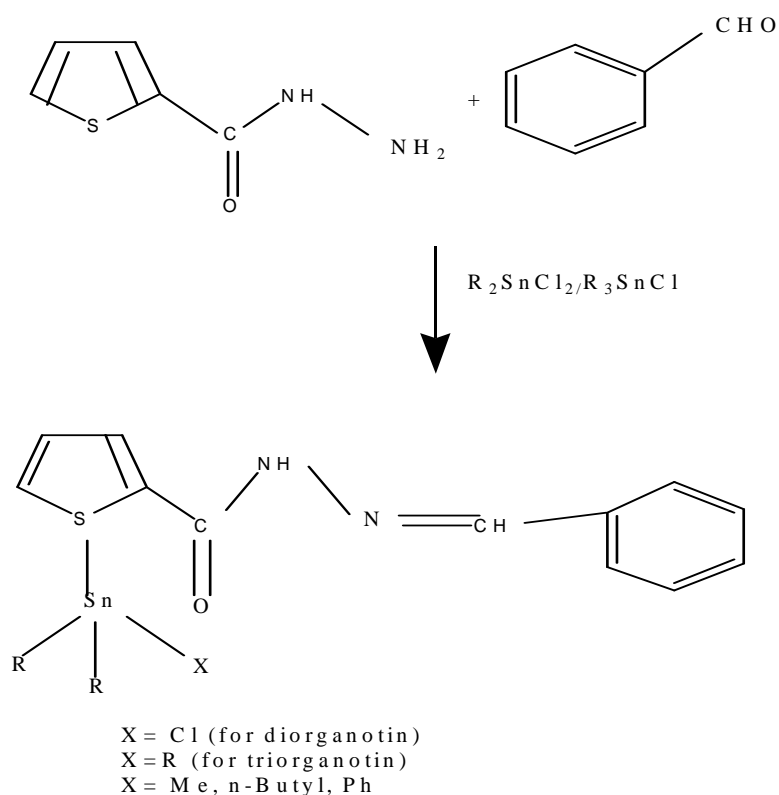


Fig. A: Synthetic reaction

Biological activities

Antibacterial activity

The synthesized complexes were screened for their *in vitro* antibacterial activity against four bacterial strains such as *E. coli*, *B. cerus* and *Nitrospora* by measuring inhibition zones using disc diffusion method [15].

Nutrient agar (2.8%)

Nutrient agar 2.8 g was dissolved in appropriate amount of distilled water and then volume of the solution was made up to 100 mL by adding water. The prepared nutrient agar medium was autoclaved for 15 min at 121 °C. This medium was used to culture the bacterial strains.

Bacterial growth medium, culture and inoculums preparation

Pure cultures were maintained on nutrient agar medium in petri plates. For the inoculum preparations, 13 g of nutrient broth was suspended in 1 L distilled water, mixed well and autoclaved. 10 µL of pure culture of a bacterial strain was mixed in medium and placed in shaker for 24 h at 27 °C. The inocula were stored at 0 °C in refrigerator.

Disc diffusion method

Nutrient agar, 28 g was suspended in 1 L distilled water, mixed well and distributed homogeneously. The medium was sterilized by autoclaving at 121 °C for 15 min. Before the medium was transferred to petri plates; inoculums (100 µL/100 mL) were added to the medium and poured in sterilized petri plates. After this, small filter paper discs were laid flat on growth medium containing 100 µL of sample. The recommended concentration 100 µL of the test sample (2 mg/mL in DMSO) was introduced into the respective wells. The petri plates were then incubated at 37 °C for 24 hrs, for the growth of bacteria. The complexes having antibacterial activity inhibited the bacterial growth and clear zones were formed. The zones of inhibition were measured in millimeters using zone reader.

3.7.2. Antifungal activity

The synthesized complexes were screened for their *in vitro* antifungal activity against four fungal strains such as *A. niger*, *C. vulgana* and *P. ostreatus*, using disc diffusion method [16]. Pure culture of the fungi was maintained on potato dextrose agar (PDA) medium in petri plates that were presterilized in hot air oven at 100 °C for 3 h.

Nutrient broth (1.3%)

Nutrient broth (1.3 g) was dissolved in 25 ml of distilled water and made the volume upto 100 mL. The prepared nutrient medium was autoclaved for 15 min at 121 °C. This medium was used to culture the fungus.

Potato dextrose agar (3.9%)

Potato dextrose was dissolved in 25 mL of distilled water and made the volume up to 100 mL. The prepared medium was autoclaved for 15 min at 121 °C. This medium was used for activity of fungal strains.

Growth medium, culture and inoculums preparation

The fungus was cultured on potato dextrose agar medium in petri plates. These culture plates were incubated at 28 °C for 2 days for the multiplication of fungal strains. The prepared sterilized growth medium was transferred to the sterilized petri plates. The petri plates were then incubated at 28 °C for 48 h, for the growth of fungus [17].

Disc diffusion method

Small filter paper discs were laid flat on growth medium having fungal growth and 100 µL of sample was applied on each disc. The petri plates were again incubated. The sample having antifungal activity exhibited zones around the discs. The zones of inhibition were measured in mm against reference ampicilline using zone reader [18].

Results and Discussion

The ligand and its synthesized complexes are solid and stable in air. They have sharp melting points. The physical data of ligand and synthesized complexes (1-5) is summarized in Table 1.

Infrared spectroscopy

IR spectroscopy is one of most frequently employed technique used for characterization of organotin(IV) compounds [19]. IR spectra of free ligand (HL) and its synthesized organotin (IV) complexes (1-5) were recorded as KBr pellets in range of 4000-250 cm⁻¹.

The IR spectrum of free ligand (HL) was compared with spectra of synthesized complexes (1-5) to study binding mode of sulphur to tin(IV). The characteristic infrared absorption frequencies (cm⁻¹) for ligand and synthesized complexes are listed in Table 2.

The IR spectrum of free ligand (HL) exhibited a sharp band at 3310 cm⁻¹ which was attributed to the $\nu(\text{NH}_2)$ stretching mode. Formation of Schiff base in complexes was confirmed by absence of $\nu(\text{NH}_2)$ vibrational frequency in all complexes (1-5) which can be clearly observed at 3310 cm⁻¹ in spectrum of free ligand (HL). Presence of $\nu(\text{C}=\text{N})$ in the range of 1514-1512 cm⁻¹ in all complexes (1-5) further confirms formation of Schiff base by the attachment of benzaldehyde with ligand (HL). No shift of band of $\nu(\text{C}=\text{N})$ toward higher wave number in all complexes (1-5) confirms that there is no increase and decrease in carbon to nitrogen bond [20].

The $\nu(\text{NH})$ band was observed at 3113 cm^{-1} and $3160\text{-}3158\text{ cm}^{-1}$ for ligand (**HL**) and synthesized complexes (**1-5**), respectively. The absence of large systematic shifts of $\nu(\text{NH})$ band in spectra of complexes indicates that there is no interaction between (NH) group and tin metal [21].

Spectrum of ligand (**HL**) and complexes (**1-5**) exhibited absorption band at 1738 cm^{-1} and $1748\text{-}1730\text{ cm}^{-1}$ that were attributed to $\nu(\text{C}=\text{O})$ stretching mode. The presence of $\text{C}=\text{O}$ frequency both in ligand and complexes confirms that complexation does not occur through oxygen atom of carbonyl group.

A strong absorption band in the range of $440\text{-}434\text{ cm}^{-1}$ confirms the formation of $\nu(\text{Sn-S})$ bond in complexes (**1-5**). This absorption band is not found in spectrum of ligand [22]. The $\nu(\text{Sn-C})$ bond was appeared in range of $560\text{-}558\text{ cm}^{-1}$ in all synthesized complexes (**1-5**) that also confirms the complexation and $\nu(\text{Sn-Cl})$ in the range of $327\text{-}328\text{ cm}^{-1}$ in diorganotin complexes (**3-4**) [23].

4.2. Semi-empirical Analysis

Semi-empirical analysis shows that tin(IV) shows four co-ordinated tetrahedral geometry in all five complexes and observed bond lengths and bond angles of newly synthesized complexes are in accordance with previous studies [24].

For newly synthesized organotin(IV) complexes **1**, **3**, **5** the Sn atom is asymmetrically attached to sulfur atom having bond length in range of $2.43\text{-}2.44\text{ \AA}$ respectively. Other bonds including shorter Sn-Cl and Sn-C are also correctly estimated. The slightly larger C-O bond corresponding to strong bond having same bond length 1.22 \AA in synthesized complexes **1**, **3** and **5**. The bond distance between C-S groups are almost similar within complexes in range of $1.79\text{-}1.80\text{ \AA}$ [25]. The C-N bond distances are shorter than C-S bond distances, lies in the range of $1.30\text{-}1.43\text{ \AA}$. The N-N bond length is similar in all three complexes lies at 1.37 \AA which is accordance with earlier reports.

The C-Sn-C angles of methyl and phenyl groups appear in range of $89.9\text{-}90.1^\circ$ [26]. The C-Sn-Cl bond angle was only observed in complex **3** in range of $104.3\text{-}107.3^\circ$ due to presence of chlorine. Selected bond angles and bond length of optimized structure of complexes **1**, **3** and **5** are given in Table 3 and 4. Geometry optimized structure are given in Figures 1-3.

The low value of dipole moment of complex **3** is due to the trans orientation of chlorine atom on the tin metal atom [27]. This indicates the symmetrical structure of complex **3**. The computed dipole moment of organotin(IV) complexes is given in Table 5. The electrostatic surface map (ESP) map of complexes **1**, **3** and **5** showed that there is possibility of nucleophilic

attack on complexes. As the red colour in the ESP map indicates the density upon which a nucleophile can attack.

Biological activities

Antibacterial activity

The parent acid and its synthesized complexes were screened for *in vitro* antibacterial activity against three bacterial strains such as *Bacillus cerus*, *Nitrospora* and *Escherichia coli*, respectively. The results revealed that all the newly synthesized complexes (**1-5**) show greater antibacterial activity than the parent acid **HL** and less than the standard drug except complex **5**. Complex **5** showed greatest activity than standard drug. Ampicilline was used as standard drug (Positive control).

Complexes **2** and **4** showed greatest antibacterial activity against *Nitrospora*, moderate activity against *Bacillus cerus* and lowest activity against *Escherichia coli*. Complex **5** show highest antibacterial activity against all bacterial strains. Among all synthesized complexes, trimethyltin complex **5** show higher activity than the standard drug. It was clear from the data that antimicrobial activity varied according to presence of bulky alkyl groups on metal ion and increase in bulkiness on the Sn(IV) enhances antibacterial activity [29, 28, 23].

On comparing with the data in literature the synthesized complexes show variable activities due to difference in the structure of cell wall. The walls of gram negative cells are more complex than those of gram positive cells [22]. The lipopolysaccharides form an outer lipid membrane and contribute to complex antigenic specificity for gram negative cells [30] causing decrease in antibacterial activity of complexes **2**, **4** and **5** against *Escherichia coli* as compared to other bacterial strains such as *Basillus cerus* and *Nitrospora* which show greater activities than *Escherichia coli* [31].

The variation in the toxicity of different antibacterial agents against different organisms depend either on the impermeability of the cells [10], or differences in ribosomes to the antimicrobial agents [32].

From the data it can be suggested that tri-organotin complexes were usually more effective against bacteria than diorganotin complexes [33]. The antibacterial data of ligand and synthesized complexes is given in Table 6 and Figure 4.

Antifungal activity

Antifungal activity of parent acid and complexes is determined against three fungal strains such as *Aspergillus niger*, *C. vulgana* and *P. ostreatus*, respectively. The results revealed that all the newly synthesized complexes show greater

activity than the parent acid but negligible activity as compared to standard drug. It is evident from tabulated data that the parent acid as well as the synthesized complexes exhibit varying degree of fungicidal activity against the fungi used. Complex **2** showed least antifungal activity against all fungal strains as compared to other complexes. Complexes **4, 5** showed minor activities against fungal strains, greater than complex **2** but negligible as compared to standard drug. From results it can be suggested that organotin(IV) complexes were found to be less potent against antifungal activity as compared to antibacterial activity. Further research on these synthesized complexes as fungicidal agents against other different fungal strains could lead to more interesting results in future. Antifungal data of ligand and synthesized complexes is given in Table 7 and Figure 5.

Ampicilline was used as standard drug (Positive control)

Conclusion

Organotin (IV) complexes have been synthesized in good quantitative yield by refluxing the synthesized Schiff base and respective organotin (IV) chlorides in dry ethanol for 5-6 hours. FT-IR spectral data clearly demonstrate that organotin (IV) moiety reacts with sulfur [S] of ligand. Semi-empirical study shows that in the complexes **1-5**, the tin atom is asymmetrically attached to the sulfur. Low value of dipole moment of complex **3** is due to the trans orientation of chlorine atom on tin metal atom. Ligand and its synthesized complexes exhibited biological activities with few exceptions. The antimicrobial assay of ligand and synthesized complexes against different bacterial and fungal strains show that antibacterial activity of complex **4** is greater among all complexes

Table 1: Physical data of organotin (IV) complexes

Compound Code	Molecular Formula	Molecular Weight (g/mol)	Melting Point (°C)	Yield (%)	Solubility
HL	C ₅ H ₆ N ₂ OS	142.18	136-139	-	DMSO
1	C ₃₀ H ₂₅ N ₂ OSSn	580.27	160-161	72.21	DMSO
2	C ₂₄ H ₃₇ N ₂ OSSn	520.31	170-172	48.72	DMSO
3	C ₁₄ H ₁₆ ClN ₂ OSSn	414.53	166-167	65.51	DMSO
4	C ₂₀ H ₂₈ ClN ₂ OSSn	498.69	163-164	88	DMSO
5	C ₁₅ H ₁₉ N ₂ OSSn	394.07	168-169	62.31	DMSO

Table 2: IR spectral data^a (cm⁻¹) of organotin (IV) complexes

Χομπουνδ Ν ο.	ν(X=N)	ν(N-H)	ν(NH ₂)	ν(X=O)	ν(Σν-X)	ν(Σν-Σ)
HL	-	3113w	3310s	1738s	-	-
1	1514s	3158w	-	1743m	560m	440s
2	1512s	3160w	-	1748w	558s	435s
3	1512s	3160w	-	1730w	5559s	438m
4	1512s	3160w	-	1743m	560m	436s
5	1512s	3159w	-	1740w	560s	434s

^as = strong; m = medium; w = weak

Table 3: Selected bond angles (°) of the organotin (IV) complexes

Bond Angles	1	3	5
C-S-C	90	89.9	90.1
C-Sn-C	111.3, 112.6, 111.0	115.0	110.7, 110.6, 112.
C-Sn-Cl		107.7, 104.3	-

Table 4: Selected bond lengths (Å) of the organotin(IV) complexes

Bond Lengths	1	3	5
Sn-S	2.43	2.43	2.44
C-O	1.22	1.22	1.21
C-S	1.80, 1.80	1.79, 1.80	1.79, 1.79
C-N	1.43, 1.31	1.42, 1.30	1.43, 1.30
N-N	1.37	1.37	1.37

Table 5: Computed dipole moment (debye) of organotin (IV) complexes

Complex No.	Dipole moments (debye)
1	4.345
3	2.641
5	5.042

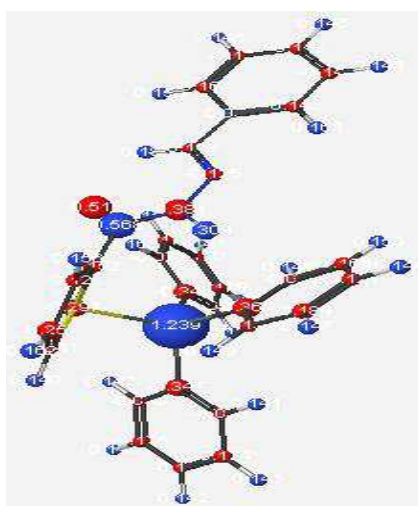


Figure 1: Dipole moment and Partial charges of complex 1

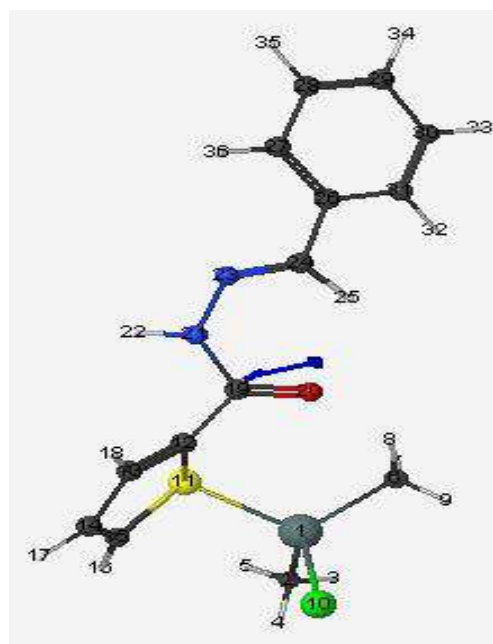


Figure 2: Dipole moment and Partial charges of complex 3

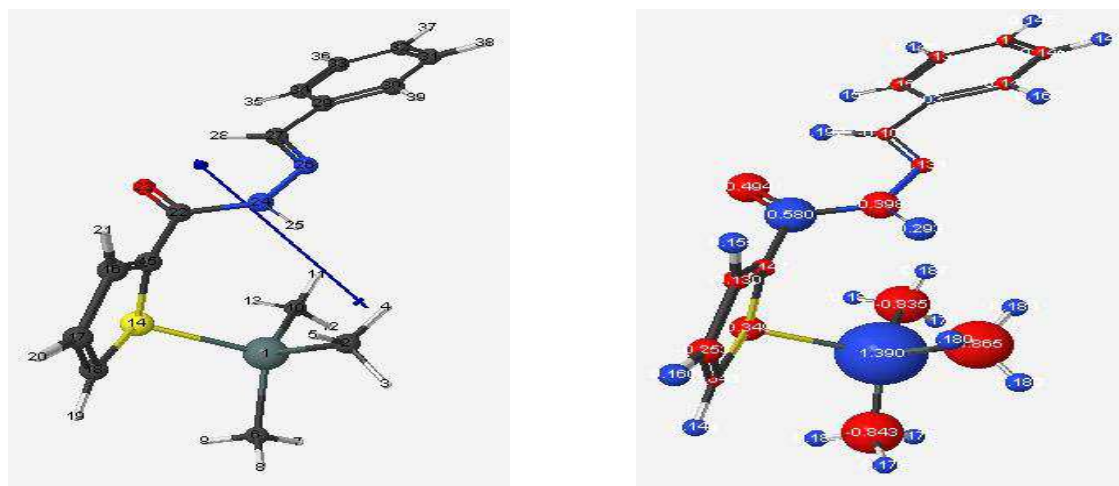


Figure 3: Dipole moment and Partial charges of complex 5

Table 6: Antibacterial activity of organotin(IV) complexes^{a-c}

Compound No.	Inhibition zone (mm)		
	<i>E. coli</i>	<i>B. cerus</i>	<i>Nitospora</i>
	Mean	Mean	Mean
HL	0	0	0
1	40	20	40
2	30	40	50
3	0	0	0
4	20	30	50
5	30	60	60
Standard drug	10	30	40

^aStandard Drug, Ampicilline

^bConcentration 1 mg/mL in DMSO

^cValues are mean of three samples analyzed individually in triplicate

Table 7: Antifungal activity of organotin(IV) complexes^{a-c}

Compound No.	Inhibition zone (mm)		
	<i>A. niger</i>	<i>C. vulgana</i>	<i>P. ostreatus</i>
	Mean	Mean	Mean
HL	0	0	0
1	0	0	0
2	2	3	3
3	0	0	0
4	5	4	3
5	2	3	5
Standard drug	10	30	40

^aStandard Drug, Chloramphocinol

^bConcentration 1 mg/mL in DMSO

^cValues are mean of three samples analyzed Individually in triplicate

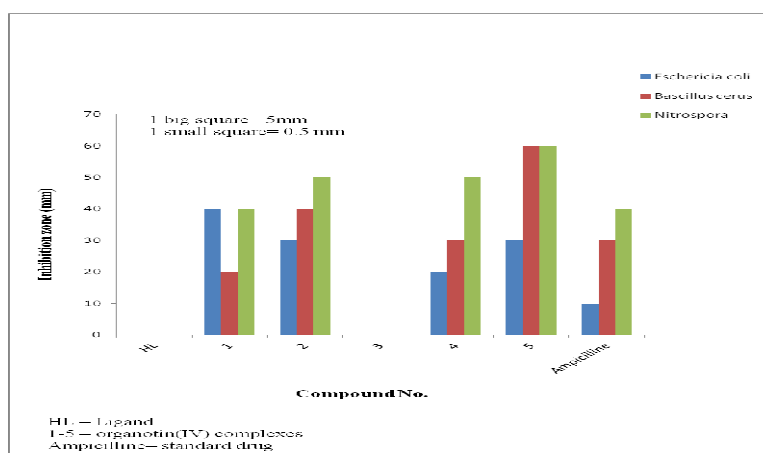


Figure 4: Antibacterial activity of organotin(IV) complexes

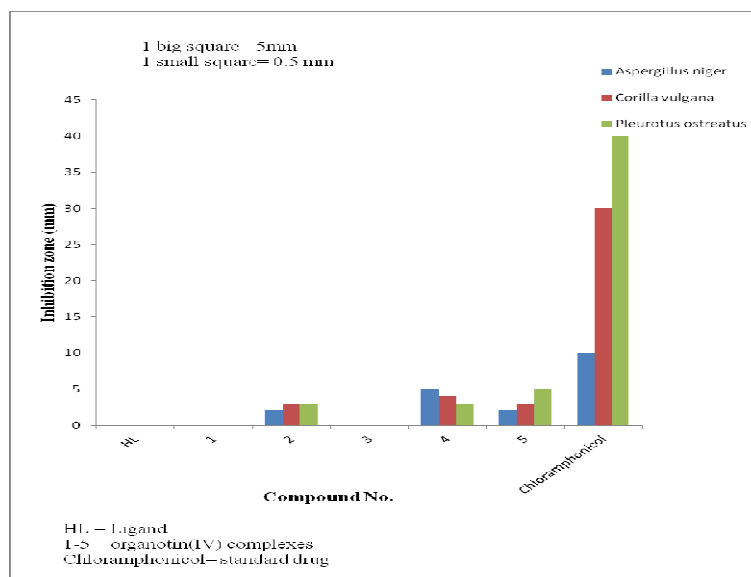


Figure 5: Antifungal activity of organotin(IV) complexes

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