

Triorganotin(IV) Complexes with Biologically Potent Schiff Bases: Infrared, ^{119}Sn Spectral Characteristics and Antimicrobial Applications

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Abstract: This review paper has attempted information specific to the title compound. This survey of the literature data provides useful information about the design and stabilities of the triorganotin with biologically active ligands. Up to now, considerable efforts have been made to synthesize and characterize triorganotin(IV) schiff base complexes with the general formulae R_3SnL [R = organic group, M: Sn and L: schiff base] and many studies have been focused in order to understand bioassay results. Users with an interest in this substance are strongly encouraged for future research that this is still a very open field.

Keywords: Triorganotin(IV), Schiff base, IR, NMR, Antimicrobial activity.

1. INTRODUCTION

This review document has attempted to acquire the effect of schiff base ligands upon the behavior of triorganotin complexes. It has been chosen to pay attention to the synthesis, characterization and biological applications [1]. The variety of possible organotin schiff base complexes with wide choice of ligands, and coordination environments, has prompted us to undertake review in this area [2]. Since the early 1980s, there has been substantial interest in the synthesis and properties of organotin, with the majority of attention focused on triorganotin schiff base complexes [3]. However, a comprehensive review of the triorganotin(IV) schiff base complexes [R_3SnL] is not yet available [4]. Baul *et al.*, 2009 have been extensively deal with the characterization of triorganotin(IV) schiff bases complexes with general formulae R_3SnL and it is found that antimicrobial activities of R_3SnL is possibly superior to that of R_2SnL_2 and RSnL_2 [5]. Chandrasekhar *et al.*, 2009 have studied schiff base ligands and their complexes of Sn(IV) and its effect as antibacterial and antifungal activities [6]. Ma *et al.*, 2007 have studied same types of the complexes; however they did not investigate their biological activities [7]. In view of these findings it appeared of interest to understand the design, selection and processing of organotin compounds for their wide range of biocidal and industrial applications [8]. Schiff base ligands provide the opportunity to design new systems selective to specific metal ions [9]. The first organotin compound was *diethyltindiodide*, discovered by *Edward Frankland* in 1849 [10]. Recently, large number of new triorganotin species has led to renewed interest in organotin complexes [11]. Some examples are mentioned later. R_3SnL with the general formulae R_3ML [R = organic group, M: Sn and L: schiff base] have been

reviewed in this present studies. These complexes have been characterized by IR and NMR spectral methods. R_3ML have been tested against a number of plant and animal pathogens and found to be very much active in this respect. It is found that they possess significant antimicrobial activity and effect of Ph_3SnL is possibly superior over all R_3SnL [12]. R_3ML have displayed comparable or slightly better activity against different bacteria and fungi populations than the reference drugs [13]. The tetrahedral geometry around the tin atom is proposed for the R_3SnL [14]. R_3SnL mainly those bearing oxygen and nitrogen donor atoms in particular offer variations of coordination mode which may give rise to oligomeric or polymeric structures [15]. Very little work has however been carried out on the formation of R_3SnL [16]. Recently, the discovery R_3SnL that are used commercially has led to considerable attention in organotin complexes [17]. Bacterial and fungal diseases pose a greater threat; hence the need to find cheap and effective antibacterial and antifungal agents is necessary [18]. Keeping in view, considerable success has been attained in the use of R_3SnL to control economically important diseases. Finally, more and more experimental data are collected in order to understand the spectral characteristics and biological activities of R_3SnL .

2. TRIORGANOTIN(IV) SCHIFF BASE COMPLEXES [R_3SNL] TESTED FOR THEIR ANTIMICROBIAL ACTIVITY

Schiff base is a functional group that contains a carbon-nitrogen double bond with a general formula $\text{R}_1\text{R}_2\text{C}=\text{NR}_3$. Triorganotin(IV) schiff base complexes have been reviewed in this present studies with the general structure:



Where R = organic group

Sn = the central tin atom in the oxidation state +4

L = schiff base [an anionic organic group]

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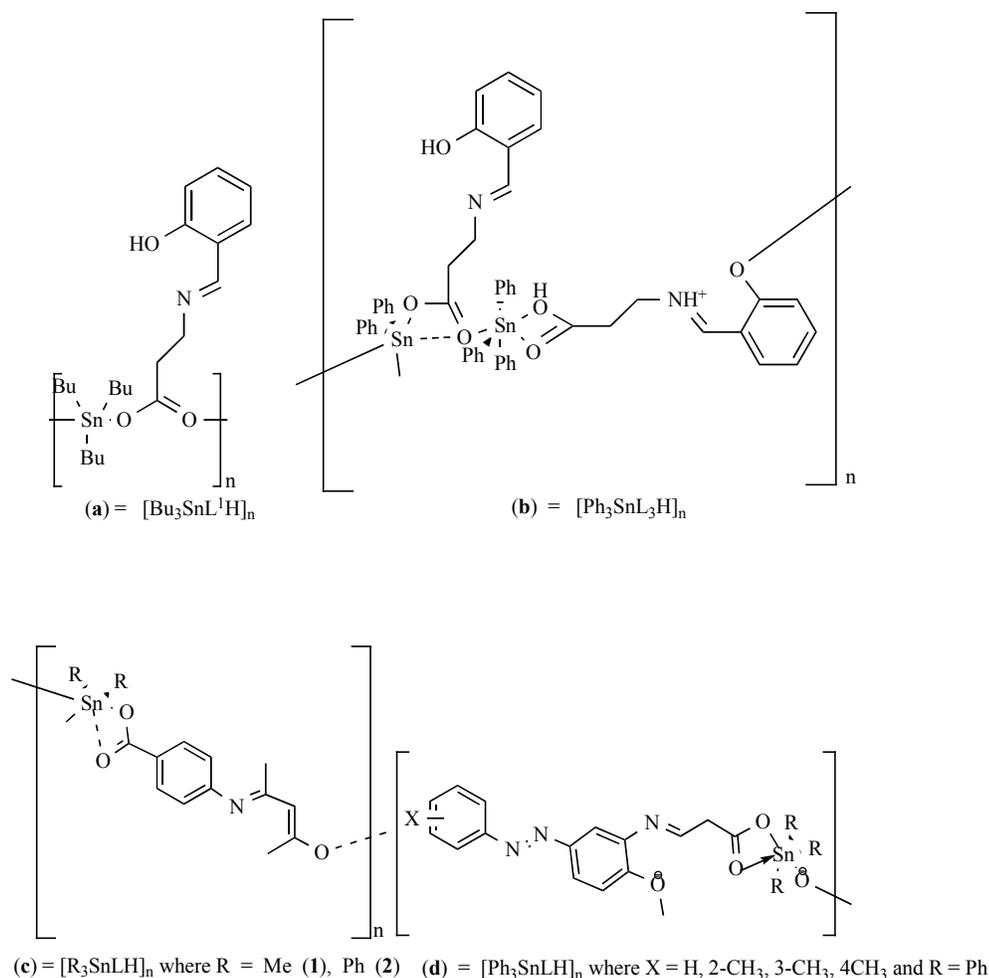


Fig. (1). (a-d) Structures of R_3SnL where an overview showing the coordination.

A large number of organotin(IV) schiff base complexes $[R_3SnL]$ has been investigated and is used widely in synthetic chemistry in the past 15 years [19]. Recently, organotin have attracted considerable attention owing to their potential applications in medicinal chemistry and biotechnology [20]. Structural aspects of the organotin (IV) schiff base complexes have received much attention [21]. Nuclear magnetic resonance (1H , ^{13}C and ^{119}Sn) spectral studies have been carried out to throw light on the structures of the complexes in solution [22]. On the other hand, Infrared studies elucidate the structures of these compounds in the solid state [23]. In line with these developments, several attempts of R_3SnL have been published. According to literature, the presence of schiff base in triorganotin(IV), modifies the antimicrobial properties of the complexes [24]. The compounds drawn on these bases are being summarized below. Baul *et al.*, 2006 have been reported the synthesis and characterization of some triorganotin(IV) schiff base complexes, Ph_3SnL^1H , Ph_3SnL^2H , Ph_3SnL^4H , Bu_3SnL^1H , $Bu_2SnL^2H_2O_2$ and $Bu_2SnL^3H_2O_2$, where L^1 and L^3 , L^2 and L^4 are schiff bases [25]. Fig. (1a) shows the structure of $[Bu_3SnL^1H]_n$. This complex has been characterized by spectroscopic techniques in combination with 1H , ^{13}C , ^{119}Sn NMR and IR spectroscopy. In the solid state, the above compounds are a one-dimensional polymer while on

the basis of NMR [1H , ^{13}C and ^{119}Sn] spectral studies; a tetrahedral geometry around the tin atom is proposed, which revealed that the polymeric structure found in the solid state is lost upon dissolution. Baul *et al.*, 2007 have been reported synthesis, structural characterization and biological applications of R_3SnL with the general formulae R_3SnL , where R = Bu, Bz and Ph. It is found that antimicrobial effect of triphenyltin(IV) derivative is possibly superior to that of other triorganotin schiff bases [26]. Fig. (1b) shows the structure of $[Ph_3SnL_3H]_n$. As a continuation of his previous work in this area, Baul *et al.*, 2009 have reported the characterization of another two R_3SnL viz., $[Me_3Sn(LH)]_n$ and $[Ph_3Sn(LH)]_n$ [27]. Fig. (1c) shows the general structure $[R_3SnLH]_n$. Baul *et al* 2010 have studied synthesis, characterization and structure analysis of some tetrameric tributyltin(IV) $[Bu_3SnLH]$ and triphenyltin(IV) $[Ph_3SnLH]$ schiff base complexes which are sterically crowded [28]. Fig. (1d) shows the general structure of $[Ph_3SnLH]_n$. These complexes have been characterized by spectroscopic methods including multinuclear ^{119}Sn NMR and IR spectroscopy. The structures of trialkyltin(IV) complexes showing a macrocyclic structure involving a tetrameric tin assembly bridged by carboxylate oxygen connectors.

During the last few decades, the current investigative efforts and the state of the art in the field of antimicrobial agents have been reported in the literature. Furthermore, it has been reported that among the various types of organotin, generally triorganotin(IV) (R_3SnL) and diorganotin(IV) (R_2SnL_2) have been investigated in greater extent for their antimicrobial potential [29]. Xie *et al.*, 2010 have been interested in the antifungal activity of triorganotin(IV) schiff base complexes with additional carboxylates groups [30]. These triorganotin derivatives display remarkably different coordination modes. The complexes display cyclohexameric and polymeric chain by the unsymmetric bridging carboxylate group and the Sn-N coordination bond. All these complexes exhibit significant antifungal activities. Fig. (2) shows the general structure of triorganotin 1 H-tetrazolyl-1-acetates.

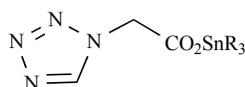


Fig. (2). Structure of triorganotin 1 H-tetrazolyl-1-acetates, where R = Ph, p-tolyl, cyclohexyl, n-Bu and Et.

Previously, a number of semi synthetic antibiotics of organotin(IV) moieties had been prepared in the laboratory. In recent years, more and more investigations have focused on the synthesis of organotin(IV) functionalized with additional oxygen, sulfur or nitrogen donor groups [31]. Li *et al.*, 2009 have discussed some triazols, such as azocyclotin, that have also been commercially available as antifungal agents and successfully reported a new series of antifungal triorganotin(IV) triazol derivatives as shown in Fig. (3) [32]. These complexes display a polymeric chain by the intermolecular Sn-N interactions. All these complexes have been shown good antifungal activities *in vitro*. Structural diversity of the organotin(IV) schiff base complexes is well documented and a variety of coordination geometries leading to monomeric-, dimeric-, trimeric-, tetrameric-, oligomeric- and polymeric structures have been reported.

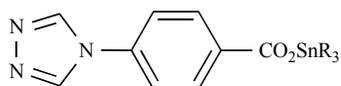


Fig. (3). Synthesis of triorganotin (4H-1,2,4-triazol-4-yl)benzoates where R = Et, n-Bu, Ph, p-tolyl, cyclohexyl.

Data from the present study suggests that further investigation as a new drug and may be suitable candidate for modification in order to improve biocidal properties [33]. Zhang *et al.*, 2009 have been obtained eight R_3SnL derived from 4-amino-5-phenyl-4H-1,2,4-triazole-3-thiol and 5-amino-1,3,4-thiadiazole-2-thiol ligands [34]. These complexes were characterized by spectroscopic technique including IR and NMR spectra analyses, which reveal that complexes display dinuclear, network and macrocyclic structures. Here is reported the generic structure of complex 1, 2 and 3 (Fig. 4).

One of the most important goals of triorganotin schiff base complexes research is the search for new molecular structures which exhibit effective antimicrobial activities

[35]. It is well established that R_3SnL are very important in antimicrobial drugs [36]. Ma *et al.*, 2007 have been obtained nine R_3SnL of the type R_3SnL by reaction of schiff bases with triorganotin(IV) chloride in the presence of sodium ethoxide [37]. All the complexes 1-9 were characterized by IR and NMR spectra analyses, which revealed that complexes were four coordinated and displayed a capped tetrahedron. The general structure of these complexes is shown in Fig. (5).

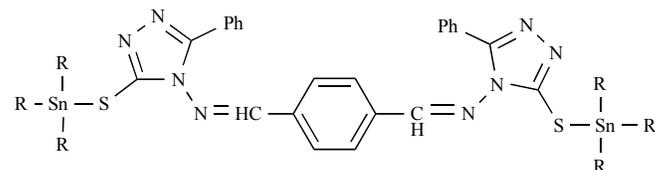


Fig. (4). The generic structure of the complexes, where R = Ph, Bu, CH_3OH .

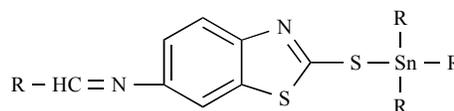
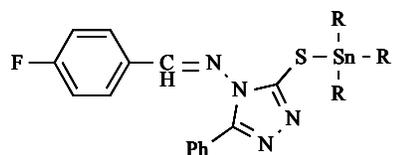
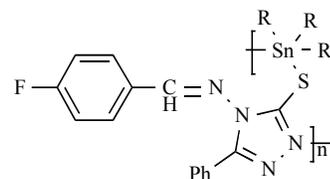


Fig. (5). General structure of the complexes, where R = Me, Ph, $PhCH_2$.

In view of our continuing interest in the synthesis, characterization, biological applications and structure analysis of R_3SnL , we have documented a series of new organotin(IV) derivatives. Ma *et al.*, 2008 reported and characterized another fascinating four types of R_3SnL derived from 4-amino-5-phenyl-4H-1,2,4-triazole-3-thiol schiff base ligand as shown in the Fig. (6) [38]. Triphenyltin complexes (Fig. (6a)) have been displayed monomer organotin structures while trimethyltin (Fig. (6b)) were formed one dimensional polymeric chain.



(a) = Monomer organotin structure



(b) = Polymeric chain organotin structure

Fig. (6). General structure of the complexes, where R = Ph, Me.

Deyab *et al.*, 2010 have been developed new technique for the preparation of a triorganotin complexes substituted α -anilinomethylphosphonates [39] as shown in the Fig. (7).

Khan *et al.*, 2010 have been generated biologically active moiety with the general formulae R_3ML [R: alkyl (Et, Ph and Bz), M: Sn and L: 1,3-bis(2-hydroxybenzylidene)thiourea

(Fig. (8a)) and 1,3-bis(2-hydroxybenzylidene)urea (Fig. (8b)) [40]. This report supported the previous findings. These findings add new insights that antimicrobial activity of compounds has even more potency with respect to the inhibition of microbes.

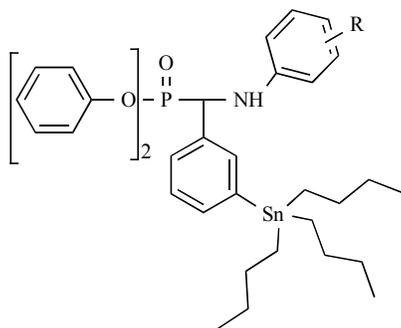
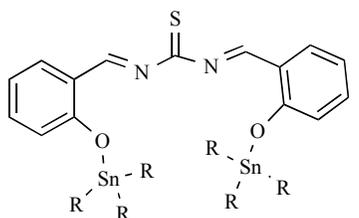
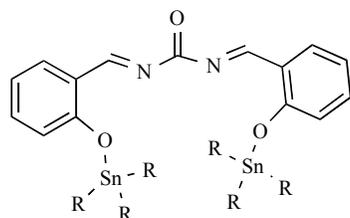


Fig. (7). Structure of organotin substituted-anilinomethylphosphonate.



(a) = Triorganotin(IV) thiourea derivatives



(b) = Triorganotin(IV) urea derivatives

Fig. (8). Structure of complexes, where R: Et, Ph, Bz.

On the other hand, with the R_3SnL , schiff base in bidentate fashion have been documented. Claudio *et al.*, 2001 reported in the literature that in R_3SnL bidentate schiff base the (C=N) band is considerably shifted towards lower frequencies with respect to that of the free schiff base owing to the delocalization of electron cloud from N to Sn atom (Fig. 9) [41].

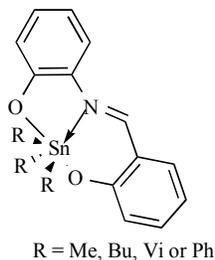


Fig. (9). R_3SnL bidentate schiff base complex.

Rufen *et al.*, 2009 characterized all such types of complexes by IR and NMR spectra analyses which confirmed that complexes are bidentate in structures (Fig. 10) [42].

It has been revealed that many series of the R_3SnL and indeed, significant structural diversity and biological applications are found despite similarities in chemical formulae. Such a study is essential, as bibliographic surveys. This has driven inorganic and organometallic chemists to look for new R_3SnL with good activities, preferably against bacteria and fungi that are responsible for various diseases in plants and animals [43]. Further research on triorganotin(IV) amino acid, and DNA schiff base complexes were also investigated [44]. R_3SnL are a widely studied class of metal-based antimicrobial drugs and their intensive investigation has led to the discovery of compounds with excellent *in vitro* antimicrobial activity.

3. SPECTRAL CHARACTERISTICS

3.1. ^{119}Sn IR Spectra

Practically R_3SnL have been characterized in detail by recording their IR spectra. Spectroscopic technique IR provided useful information concerning the stabilities of the R_3SnL complexes containing O, N, S and P etc donor atoms. The IR spectra of all the R_3SnL show some common characters [45]. A common feature of IR spectra in R_3SnL derivatives is the absence of an absorption band in a region assigned to a particular functional group can usually be taken as an evidence for the absence of functional group [46]. While in complexes new bands at $400-600\text{ cm}^{-1}$ in the spectra of respective R_3SnL , which are assigned to Sn-stretching mode of vibration, showing that ligand moiety is coordinate to the central tin atom is indicative of complex formation [47]. IR spectra of the complexes have been recorded in the range $4000-400\text{ cm}^{-1}$. The characteristic absorption frequencies *e.g.*, $\nu(Sn-O)$, $\nu(Sn-S)$, and $\nu(Sn-N)$ etc provide valuable information about the formation of complex and coordination mode of ligand [48]. Various efforts have been made to correlate the values of characteristic vibration frequencies with their precursors and literature reports predict the structures of synthesized compound [49]. Siang *et al.*, documented that all R_3SnL possess a unidentate Sn-O and Sn-N coordination modes and the bonding modes were observed by means of ^{119}Sn IR spectra [50]. According to the IR data, the R_3SnL adopt a bridged structure in the solid state, gradual opening of the C.Sn.C was proposed from tetrahedral to octahedral environments around the tin atom. This procedure also distinguished the different structures [51]. As far as polymeric R_3SnL has also been reported.

3.2. ^{119}Sn NMR Spectroscopy

The ^{119}Sn NMR spectroscopy is one of the most powerful tools for the characterization of R_3SnL in solution and in the solid state [52]. According to literature, ^{119}Sn NMR spectra of the R_3SnL show signals between 200 ppm and 60 ppm, while in some cases ^{119}Sn chemical shift of R_3ML cover a range of 600 ppm [53]. The data shows a significant shift of the resonance peaks to higher/lower fields upon chelation with the triorganotin(IV) moiety. These

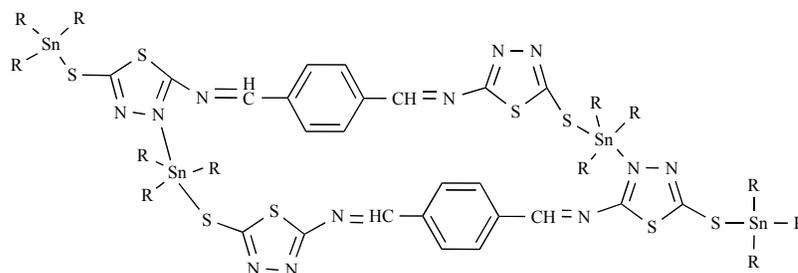


Fig. (10). Synthetic R_3SnL bidentate schiff base complex.

values are dependent on the nature of L and electrophilic character of Sn atom in R_3SnL [54]. ^{119}Sn NMR plays a significant role in determining the geometry around the tin atom. The prediction of geometry can be assigned by coupling that corresponds to the hydrogen atom. In some reports such coupling are not observed in complexes due to overlapping of signals [55]. The coupling constant, $^nJ[^{119}Sn]$ is important parameter for the structure characterization of R_3SnL . This value depends upon the nature and orientation of the organic groups attached to tin [56]. The ^{119}Sn NMR data for the R_3SnL fall in different coordination ranges, i.e., The R_3SnL , compounds are clearly in the 4-coordination environment [57]. Hence, ^{119}Sn chemical shifts reports of R_3SnL describing tetrahedral monomeric geometry in non-coordinating solvent. Han *et al.*, 2005 suggested hexacoordination environment around the central tin atoms [58]. ^{119}Sn NMR results confirmed that the ^{119}Sn group participates in complex formation. Different coordination environments are observed in R_3SnL derivatives. Penta (115-150 ppm) and hexa (220-300 ppm) coordination environments have also been observed [59].

4. ANTIMICROBIAL APPLICATIONS

4.1. Antibacterial Activities

The present communication describes to focus specifically on the scientific challenges of antimicrobial research around the world. The results indicate that the R_3SnL have a profound antibacterial activity [60]. The antibacterial activity of the R_3SnL has been tested against different pathogenic gram positive and gram-negative bacteria [61]. The different concentrations of the test compounds have been used to study %age inhibitory effect on one or more types of bacteria [62]. It can be noted that compounds with phenyl groups attached in triorganotin(IV) schiff base complexes show the high inhibitory effect as compared to other groups in the same position, generally at concentrations below 0.05 millimeter but complete inhibition was observed at a 1 millimeter concentration under both aerobic and anaerobic conditions [63]. This activity of R_3SnL depends upon the coordination and polarity of a tin (IV) atom [64]. The potential of antimicrobial action of R_3SnL has not yet been completely clarified and may vary from one complex to another [65]. Results of bioassay reveal that R_3SnL verified them to be vigorous and may be devised as new Sn-based drugs in future.

4.2. Antifungal Activities

R_3SnL have broad-spectrum antifungal applications. Recently, considerable attention has been paid to organotins,

owning to their high *in vitro* antifungal activities against some medically important fungi [66]. Keeping in view the damages caused by fungi, the use of R_3SnL as antifungal agents is of fundamental interest [67]. Preliminary *in vitro* tests for fungicidal activity of complexes have been carried out by the fungi growth inhibition method. R_3SnL with three organic groups can be significant fungicides depending on the organic group. Similarly, the R_3SnL having carbohydrates and amino acid groups have also been investigated as possible antifungal agents [68]. In addition from the results of biological activity of the R_3SnL depict high to moderate antifungal activity with respect to the inhibition of microbes. Ph_3SnL shows the highest inhibition percentage. The results obtained show the order of the antimicrobial activity of R_3SnL as: $n-Ph_3SnL > n-Bz_3SnL > Bu_3SnL > Et_3SnL > Me_3SnL$ [69]. The improve activity of $n-Ph_3SnL$ is most likely due to less number of coordination sites, which make easy the formation of $Ph_3Sn(IV)L$ moiety as a part of inhibition. The presence of NH and OH groups etc in R_3SnL is also responsible for the rise of toxicity. Attempts to get better the bioavailability of the R_3SnL by the formation of water soluble complexes have also been obtained. R_3SnL are strongly related to the interactions between cellulose and amino acid and are based on the good microbial activity. Antimicrobial properties of R_3SnL are strongly related to the interactions of organotin(IV) cation. Several R_3SnL DNA complexes have also been reported. The analytical data indicated that how the R_3SnL influence with DNA [70]. Unfortunately, the high phytotoxicity of these compounds towards many plants/animals has restricted their practical use [71]. It is concluded that, there is a direct relationship between the biocidal activity and the coordination environment of the Sn. The activity varies with variation of R groups, attached with the Sn [72]. The most probable reason is the association of the activity with the length of R group. As the length of the R group increases, activity also increases [73]. In conclusion, R_3SnL showed high fungistatic activities against different species of fungi. Finally, more and more experiments are needed to be conducted in order to understand the antifungal activity of R_3SnL .

CONCLUDING REMARKS

R_3SnL adopt a tetrahedral geometry in solution and solid states and exhibit significant *in vitro* and *vivo* antimicrobial activity with encouraging results [74]. Although the mechanism of this antimicrobial activity is not well established, it has been suggested that R_3SnL wield antimicrobial effects through binding to thiol groups of the

proteins [75]. It is most probably due to the availability of the free coordination positions around tin(IV) atoms and the occurrence of relatively stable ligand-Sn bond [76]. The present study evaluated the spectral characteristics and antimicrobial applications of R_3SnL ; the results provided evidence that the studied complexes might indeed be potential sources of antimicrobial agents and this is still a very open field [77]. R_3SnL are cost effective and are easy to synthesize and it is likely that the complexes might be more environments friendly [78-79].

CONFLICT OF INTEREST

Declared none.

ACKNOWLEDGEMENTS

One of us, Dr. Wajid Rehman is highly acknowledge Prof Dr. Joachim Heinicke, Ernst-Moritz-Arndt-University Greifswald, Department of Biochemie-Inorganic Chemistry for his valuable cooperation though out the stay of author at Greifswald Germany.

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