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Synthesis, Characterization and Biological Studies of Some Organotin Compounds: (A-Review)

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ABSTRACT

Significant attention has been given to organotin (IV) amino acids compounds in recent years. Organometallic compounds are better known for their potentiality to stabilize peculiar stereochemistry of their complexes and application in agriculture, catalysis and as single source precursors. Due to the better stability and diverse molecular structures the complexes own a wide range of biological activities. These individual properties create an alliance of action in the hybrid complex. In this review, we discuss the chemistry of organotin (IV) complexes and their different aspects in various fields. The aim of the present review is to evaluate the synthesis, characterization and biological activities of organotin compounds.

Keywords: Organotin complexes, Amino acid, Antimicrobial, Anticancer.

INTRODUCTION

Organotin compounds or stannanes are globally used as they possess a huge variety of manufacturing and farming applications although these compounds are comprehensively used for their natal properties like anticancer, antimicrobial, antiviral etc. These compounds are generally systemized with tin and covalently insured with hydrocarbon substituent. The tin atom in these compounds is generally four-coordinated or six coordinated with extensive existence in the solid form that is favored to be the most secure form[1-2]. Organotin (IV) complexes and their derivatives exhibit a vital role in many spheres like fungicides, pesticides, anti-fouling coating materials, polymer stabilizers and wood preservatives[3-5]. The first organotin compound prepared in a laboratory was diethyltindiiodide, produced by Frankland in 1849. In due course it was proved that the natal exercise of the central tin atom bet on the softening of organic groups attached[6].

Amino acids and their compounds with various metals ions play a vital role in pharmaceutical industries. Amino acids are possibly bidentate ligands which can join to the metals, and therefore, empower the exchange and transport mechanisms to detect metal ions in the human body[7-10]. Organotin (IV) complexes of amino acids that are being researched as available biocides and as medium in peptide fusion[11]. The organotin esters of amino as

well as N-protected amino acids by adding benzene or toluene as a solvent along with Tri-n-butyltin-N-acetyl-valinate when synthesized from $(Bu_3Sn)_2O$, Et_3N, acetic anhydride and valine[12]. Anthranilic acid (2-aminobenzoic acid), aminobenzoic acid (3-aminobenzoic acid), p-aminobenzoic acid (4-aminobenzoic acid) and their off-shoots that consist of supplementary functional groups, aliphatic, aromatic or halogen constituents are widely used in many areas of industry and chemistry[13-16].

Synthesis

This literature analysis is taken into account in which different aspects for the isolation of organotin complexes have been considered through various processes.

From Organotin halides

Organotin halides grapple a pivotal place in organometallic chemistry. To synthesize halide complexes of organotin, various methods are practiced

1. Redistribution reaction
2. Direct synthesis by reaction between metallic tin and alkyl halide
3. Cleavage Reaction
4. Condensation Reaction

Most of the di-triorganotin complexes have been synthesized under aerobic conditions using appropriate solutions of ligands and metal salts. Zhu *et al.,*[17] have synthesized penta-coordinated with trigonal bipyramid geometry derivatives compounds by the reactions of ferrocene carboxylic acid with Bu_3SnCl and Bu_2SnCl_2. The synthesized complexes exhibit supramolecular behavior through C–H…O and O–H…N weak interactions.

Pena-Hueso *et al.,*[18] have isolated hexa-coordinated derivatives by reacting potassium 4-thioxo-3-thia-1,4,9-triazafluorene-2-thiolate with Ph_3SnCl. It has been noticed that the process took place under metathesis reaction with the addition of THF as a solvent.

The reaction was targeted for the Alteration of bis(pyrazol-1-yl) methanes with organotin halides, where it was observed thatBis(3,5-dimethylpyrazol-1-yl) (iododiphenylstannyl) methane was being steered by the tabbed cleavage of the $Sn–Csp_2$ bond at room temperature in good return[19]. According to Tarassoli and coworkers[20], the organotin (IV) chlorides Bu_2SnCl_2, Ph_2SnCl_2 reacts with 2-amino-1-cyclopentene-1-carbodithioic acid to form organotin (IV) derivatives. It has been noticed that the complexes formed exhibit penta-coordinated geometry.

Furthermore, diorganotin (IV) complexes are synthesized by reacting with corresponding diorganotin(IV) dichlorides with the ligand, 3-(2-hydroxyphenylimino)-1-phenylbutan-1-one. It was analyzed that the central tin atom implements distorted trigonal–bipyramidal geometry whereas it was justified that in discrete molecule of dimethyltin compound, the coordination geometry was found to be square-pyramidal[21]. Reaction of sodium salt of ligand, R'COONa and organotin compound reacted to form organotin (IV) carboxylates Dibutyltin (IV) bis(4-nitrophenylethanoate), Diethyltin(IV) bis(4-nitrophenylethanoate), Tributyltin(IV) 4-nitrophenyl ethanoate, Trimethyltin(IV) 4-nitrophenylethanoate)[22]. The reaction between $[2\text{-}(Et_2NCH_2)C_6H_4]Li$ with $SnCl_4$ synthesized a Hyper coordinated through Halide-exchange route. It has been observed that the complexes unveil distorted octahedral geometry[23].

Dibutyltindichloride and sodium methacrylate when are reacted together at room temperature gave the Acetoxy dibutyltin methacrylate complex. When Ph_2SnCl_2 is added it was observed that diblock copolymer vesicles to nano-particle or cross-linked nano-composite were shaped[24]. Transmetallation process was inspected by the reactions that appeared between pyruvic acid hydrazone and different salts of organotin. Schiff base ligands of pyruvic acid series have been used as starting materials and get bridged with two neighboring tin atoms. The same reaction has been observed when $PhSnMe_3$ and $PhSnnBu_3$ reacted with $[AuCl(PPh_3)]$ and $[AuCl(AsPh_3)]$[25-26]. The synthesis of dihydride was used as starting material dibenzyltin dichloride. Alkylation of dichloride formation reacted with neophyl magnesium chloride led to dineophyldibenzyltin[27].

Ruan *et al.,* and Alan *et al.,*[28-29] have been observed that Hexa-coordinate remains of $(H_2NCOCH_2CH_2\text{-}CO)\ SnCl_3$, has been synthesized by the reaction between anhydrous $SnCl_2$. HCl and acrylamide ($H_2C= CHCONH_2$) in Et_2O. The reactions between organotin halides (R_2SnCl_2R= Me, Bu, Ph)

and dithiocarbamate ligand in different molar ratio synthesizes new organotin complexes[30-34]. Organotin compounds were prepared by the reaction between butyl tin trichloride and ammonium hydroxide or sodium sulfide[35-37].

Moreover, it has also been studied that organotin (IV) complexes were synthesized by the reaction of organotin (IV) halides with different carboxylates as a ligand[38-39]. Reaction of dihydrazone ligands, with R_2SnCl_2 virtue towards the synthesis of new organotin complexes[40-41]. Reaction of Me_2SnCl_2 with 6,6′-dithionicotinic acid and 4,4-bipy in a 1:1:1 ratio and 1,10 phenanthroline were taken to proceed the reaction which granted seven-coordinate organotin complexes[42]. Triphenyltin(IV) chloride treated with ligand which was further synthesized by using benzoyl chloride and N-methylhydroxyl-amine that was accomplished by condensation method with the respective organotin(IV) chlorides using a molar ratio of 1:1to proceed the reaction[43]. Me_2Cl_2Sn reacted with distinctive phosphoric triamide in which CH_3CN solvent was added to stir under reflux for 16 days for the synthesis of organotin compounds[44]. Penta-coordinated and trigonal bipyramidal tin complexes were formed by reacting triethyl, tributyl, triphenyl or tribenzyltin chloride with schiffs base formulated by adenine and hydroxyl benzaldehyde. This reaction mixture was refluxed for 6–8 h under nitrogen atm[45]. Homobimetallic organotin (IV) complexes were supplied by reacting dibutyltin (IV) dichloride with N,N-bis(5-bromo-2-hydroxy benzylidene) adipodihydrazide[46]. The synthesis of the Schiff bases was achieved by reacting 2-hydroxysalicylaldehyde derivative with 1, 2-phenylenediamine in ethanol and was refluxed after which it reacted with organotin halides to obtain organotin complexes in good returns[47]. The reaction of the assigned Schiff base and R_2SnCl_2 (R= Me, Bu, or Ph) in triethylamine supported the corresponding organotin compounds which were Chiral organotin complexes and showed nonlinear optical properties[48].

According to Khodayar *et al.,* and Muhammad *et al.,*[49-50] Organotin chloride ($SnMe_2Cl_2$, $SnPh_3Cl$, $SnPh_2Cl_2$ or $SnPhCl_3$) when reacted with carboxylate complexes in 1:1, 2:1 and 1:1 molar ratio, synthesized organotin complexes.

Diorganotin complexes were created by reacting organotin halides with mandelic acid salt as a ligand, this reaction is carried by using conventional thermal method that is microwave-assisted method[51]. Di and triorganotin (IV) nitrates and nitrites were synthesized by reacting organotin halides with $AgNO_3$ and treated in the air with $AgNO_3$ or $NaNO_2$ in biphasic systems (diethyl ether/ water or CH_2Cl_2/water) to give C, N-chelated organotin (IV) nitrates and nitrites as outcomes. The reaction between organotin (IV) compounds bearing the 2-(N,N-dimethylaminomethyl)phenyl as a C,N-chelating ligand could have been observed[52]. Organotin (IV) chloride reacted with $[Ph_3SnL_1]$, $[Bu_2Sn(L_1)_2]$, $[Ph_2Sn(L_1)Cl]$, $[Ph_2Sn(L_1)_2]$, $[Ph_2Sn(L_2)_2]$ and $[Ph_3Sn(L_2)]$ where L1 = thiomorpholine-4-carbodithiolate and L2 = 2,6-dimethylmorpholine-4-carbodithiolate have been synthesized in a very good outcome[53].

Diorganotin(IV) and triphenyltin(IV) derivatives of L-proline were synthesized by microwave-assisted method; the solvent being used was methanol54. Sodium 2-(4-methoxy-2-nitrophenylcarbamoyl)benzoate reacted with R_3SnCl and organotin(IV) carboxylates were synthesized with good results[55].

Shaheen *et al.,* carried out a metathesis process for the preparation of Organotin (IV) derivatives by the reaction of 4-(benzo[1,3]dioxol-5-ylmethyl)piperazine-1-carbodithioate with the corresponding di and triorganotin compounds[56].

Dibutyltindichloride when reacted with different amino acids synthesize complexes as Bu_2Sn (AA)Cl (AA = glycine, DL = valine and L = leucine) and $Bu_2SnPhen_2$ (Phen = DL-phenylalanine) which were having trigonal bipyramidal geometry[57]. Organotin (IV) derivativeshave been synthesized when organotin chlorides salts reacted with different carboxylate ligands having distorted trigonal bipyramidal geometry[58-60].

From organotin(IV) oxides or hydroxides

Various compounds of the type R_3SnAA, where R=alkyl or aryl, and AA is the anion of the amino acids or glycylglycine (Gly-Gly) have been prepared by condensation reactions and an azeotropic distillation of water from methanol or toluene solutions of the corresponding stannol or bis(triorganyltin)oxide and the amino acids or Gly-Gly(R=H (Gly)[61]. Di- and tri-organotin(IV)

diphenyldithiophosphinates were prepared by reaction of the corresponding organotin chlorides or oxides with diphenyldithiophosphinic acid[62]. Novel p-aminobenzenesulfonate organotin complexes, were synthesized by reaction of p-aminobenzenesulfonic acid with tributyltin oxide, dibutyltin oxide, dimethyltin oxide and monobutyltin oxide, respectively[63]. Fewn-Bu_2Sn(IV) derivatives were also synthesized by the reaction of Bu_2SnO with amino acid/peptides under azeotropic removal of water[64].

Organotin carboxylates were synthesized with the efficient removal of the water produced in the condensation reaction between an organotin acid/oxide to give oligomeric organotin carboxylate complexes. It could have been notified that it is a microwave assisted reaction in benzene were refluxed for 24 h in which removal of H_2O took place under azeotropic reaction which gave diphenyltin (IV) complex[65-67].

Gerbino *et al.,*[68] have worked over the synthesis of organotin benzoates which have been synthesized by the reaction between aryl and hetero aryl bromides with bis(tri-n-butyltin) oxide in THF. Salam *et al.,*[69] have processed by SonochemicalMethod,the reaction of organotin(IV) chloride(s) with 2-hydroxy-5methoxybenzaldehyde-N(4)-methyl thiosemicarbazone in the presence of stable solvent to give derivatives of organotin compounds. Ariadna *et al.,* Singh *et al.,* and Vieira *et al.,*[70-72] have isolated the new series of organotin (IV) complexes by reacting Schiff bases derived from amino acids (phenylalanine, isoleucine, glycine and L-histidine) and the corresponding tin(IV) derivatives: di-n-methyltin oxide, di-n-butyltin oxide, di-n-phenyltin oxide, bis-tri-n-butyltin oxide, or triphenyltin hydroxide. By the condensation or protonolytic reactions of organotin(IV) oxide or hydride with catechol and reduction of a quinone by distannane, organotin(IV) hydride tri-, di- and monoorganotin(IV) catecholates were prepared with good yield[73].

Diorganotin(IV) derivatives were prepared by Malhotra et al.74 by treating organotin compounds with of the Schiff bases which was attained by the condensation of methyl/ethyl pyruvate with substituted acid hydrazides in ethanol as solvent[74]. When hydrazide/hydrazones and the corresponding diorganotin oxide reacted with microwaves assisted method, organotin complexes were synthesized in good yields having penta-coordinated geometry[75-78].

From organotin(IV) alkoxides and ligands

The alkoxides $R_2Sn(OMe)_2$ have been synthesized under nitrogen from sodium methoxide and R_2SnCl_2 in methanol[78] where (R=Me, H_2L=Gly-Ala, Gly-Met and Gly-Tyr; R=Ph, H_2L=Gly-Val).The ring-opening polymerization of L-lactide, to give poly-L-lactide by $R_2Sn(OPri)_2$ compounds, where R = Bu and p-XC_6H_4 (X = CF_3, F, H, Me and OMe) were studied in benzene over a temperature range[79].

Molecular Structure and association

Triclinic and monoclinic forms have been observed in organotin complexes. The central tin atom adopts distorted trigonal–bipyramidal coordination geometry whereas in dimeric it is distorted octahedral when including the intermolecular Sn–O(phenolic) bond[19,21-22,23,25,31,43]. Intramolecular coordination of N and O with Sn thus resulting in distorted octahedral[55,67,84] shown in Fig. 1, 5, 9. Trigonal bipyramidal[21,23,58] geometry in Fig. 2,3,4,8 and in few complexes tetrahedral geometry[27] have been seen in Figure 6,7.

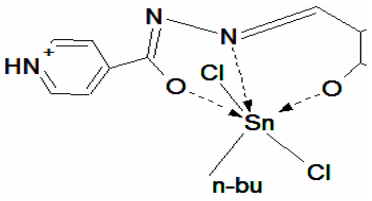

Fig. 1

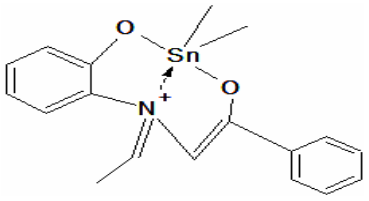

Fig. 2

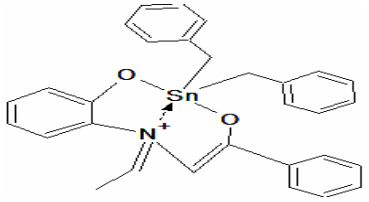

Fig. 3

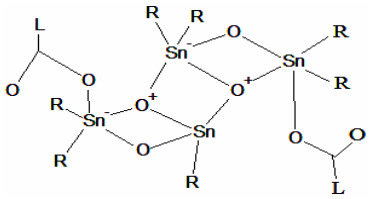

Fig. 4

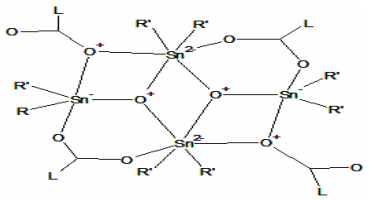

Fig. 5

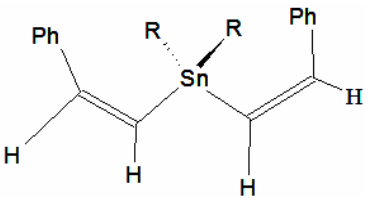

Fig. 6

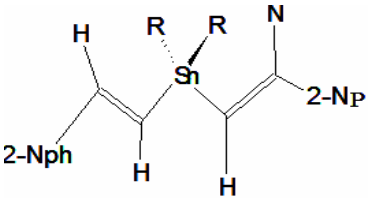

Fig. 7

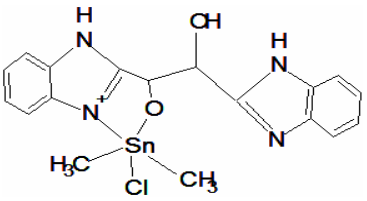

Fig. 8

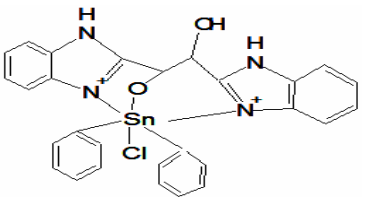

Fig. 9

Spectrochemical properties

IR spectra

Valuable information regarding the structures of the compounds in the solid state is provided by the Infrared spectra of the complexes of organotin (IV) moieties. After the IR done of any compound its functional groups can be portrayed and the disposition of nitrogen or oxygen present in the amino group can also be apprehended to exhibit how it is bonded with tin compound.

Characteristic absorption at 1596–1615 cm^{-1} in the spectra of these compounds indicate the presence of C=N-N=C group, thus pointing out the ligands coordinated to the tin[25,33]. In the IR spectrum of the strong bands at 3147 cm^{-1} and 3088 cm^{-1} are assigned to the asymmetric asymmetric mode of terminal NH_2.The intense bands of the amide observed at 1651 cm^{-1} and 1671 cm^{-1}, 1648 cm^{-1}.

The position and intensity of ν(N-H) bands are influenced by hydrogen bonding, and by coordination of the nitrogen to tin[20,26]. In all the organotin(IV) derivatives of amino acid/peptides, very intense absorption bands in the range 3266-2958 cm^{-1} due to the ν(N-H)amino undergo a substantial lowering in comparison to the non-coordinated amino acid/peptides (3288-3017 cm^{-1}), indicating coordination by the amino group to the tin atom[17,25,28,54,64,66]. The IR spectra of the three organotin(IV) complexes indicate the complete disappearance of the stretching vibration bands of O-H of their free ligand[67]. In the IR spectra of the ligands the -OH and -NH frequencies are present as a broad envelope in the region from 3450 cm^{-1} to 3199 cm^{-1} due to intermolecular hydrogen bonding NH and OH groups[80-83].

Nuclear (^1H, ^{13}C and 119Sn) magnetic resonance spectral studies

In case of ^1H NMR spectra, deprotonation of the carboxyl group is evidenced by the loss of the signal from hydrogen or hydroxyl group in the carboxyl group[17,35,37,22,39,48,51,55,58,72]. The sharp singlet observed for the single proton. Also, it is observed that downfield shifts in proton suggest that carboxyl moiety is coordinated with tin in the amino group[54,64,70,72].

Biological activities

Particular attention is focused to the organotin complexes with their natal biological properties. A complete summary has been made on this subject; it has been proved that organotin complexes display a range of biological activities. The most common are tested for Antifungal activity[41,34,50,86] anticancer activity[22,87] antitumor activity[17,67,69,39,76,88] antiproliferative activity[39,66] antileishmanial[38] and antibacterial activity[36,38,41,43,46,50,55,56, 70,71,80,87].

CONCLUSION

Literature have revealed that till date so may organotin derivatives compounds have been isolated from different organotin compounds (dibutyltindichloride, diphenyltindichloride, dibutyltinoxides and dibutyltinhydroxides) using so many ligands. The molecular structures of different organotin compounds have also been studies under this review. The derivatives isolated possess various biological activities like antimicrobial, cytotoxic, anticancer, antioxidant, Antileishmanial, Antifungal activities etc.

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Conflict of Interest

There is no conflict of interest among the authors regarding the publication of this manuscript.

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