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Synthesis and Applications of Organotin (IV) Compounds: Mini Review

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Abstract: Organotin (IV) compounds have seen a marked increase in industry utilization over the years and exhibited enormous economic benefits as well as environmental costs due to their numerous industrial, medical, and agricultural uses and other applications. The present review is a continuation of a series of reviews on the use of organotin (IV), chemicals, synthesis, characteristics and geometry as well as the industrial and biological applications.

Keywords: Organotin (IV), industrial, medical, agricultural, application

1. Introduction

The first organotin compounds were synthesised in the mid-nineteenth century in 1849 by the British scientist Edward Frankland, who synthesised crystals of diethyltin (IV) diiodide ((C₂H₅)₂SnI₂) by heating ethyl iodide with Sn [1]. Also, after a few years in 1852, Carl Löwig observed the formation of alkyltin compounds when alkyl halides reacted with the tin-sodium alloy [2]. However, these compounds were limited in the laboratory for over a century without any recognized industrial applications. In the 1950s, Organotin captured researchers' attention due to the discovery of industrial applications for organotin in the late 1940s. Organotin compounds overheard arose in large part as the plastics sector expanded and the impact of polyvinyl chloride (PVC) became clear especially when using organotin compounds as thermal and light stabilizers in the plastics sector, in addition to catalysts to polyurethane

foams and silicones [3]. Following the events in London in 1981, the Sn market began to expand commercially. Nowadays, the widespread industrial and medicinal uses of organometallic derivatives, particularly organotin (IV) compounds, have seen a growth in production on a global scale [4].

1.1 Organotin Compounds: Chemistry, Synthesis, and Characterizes

The origin of organic Sn chemistry lies in the synthesis; for example, this synthesis was sufficient for many of the pioneers of this branch of chemistry in the nineteenth century [5]. However, some of these chemists were able to make important theoretical advances by looking at known compounds. The general formula for these substances is R_nSnX_{4-n} , where R is an alkyl group which refers in this review to a methyl, butyl, or phenyl group, X is an anionic species, such as an oxide, chloride, hydroxide, or another functional group, and $(n = 1 - 4)$ [5]. The electronic configuration of Sn: $[Kr] 4d^{10}5s^25p^2$ and exhibits two stable oxidation states which are Sn^{+4} and Sn^{+2} . Organotin (II) compounds oxidize easily to form more stable organotin (IV) compounds. Organotin compounds are classified as mono-, di-, tri-, or tetraorganotins based on the number of organic moieties [6].

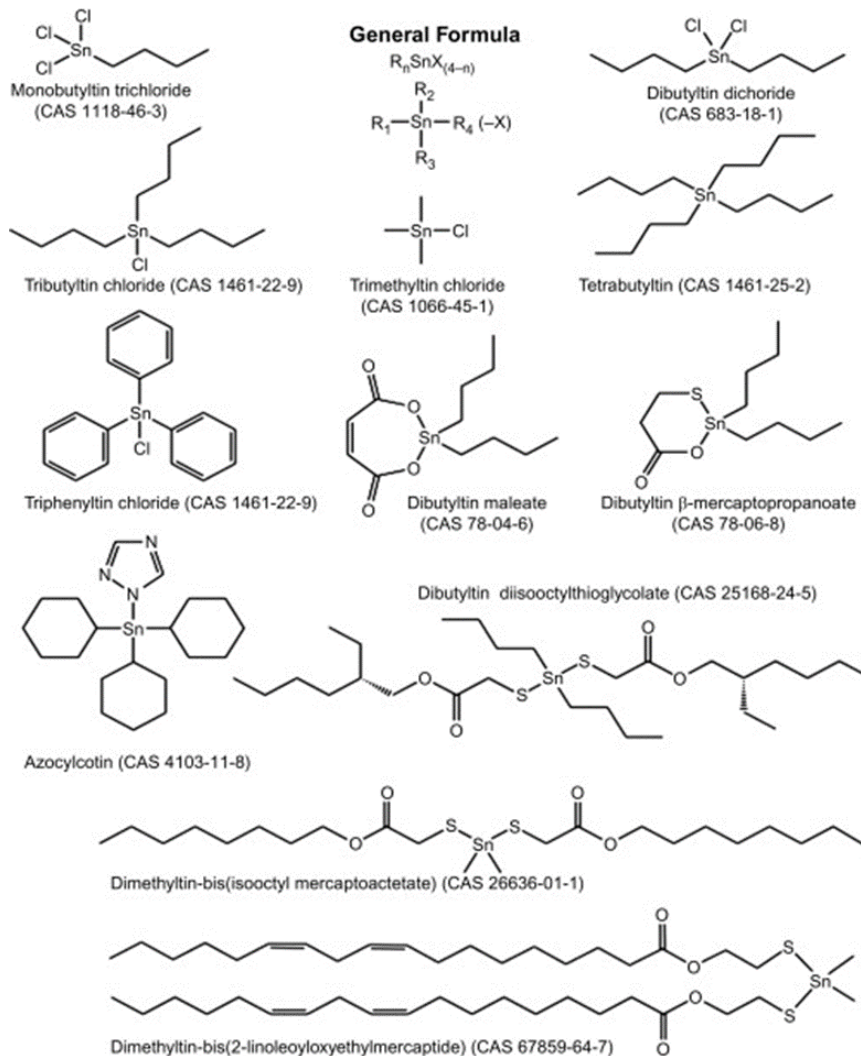


Fig. 1 - An example of organotin derivatives [7]

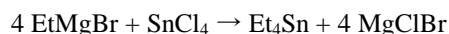
The first reports of the existence of "organic bodies of Sn", as they were then known, appeared in 1852 [7, 8]. One was by Carl Lowig (1803-1890) [8], and the other was by Edward Frankland (1825-1899) [7].

Frankland's additional descriptions of 1852 [7] were expanded upon in later publications of 1853 and 1854 [6]. Frankland was a very distinguished chemist who introduced modern graphical compound formulas, coined the terms "bond" and "organometallic" and recognized that atoms have different binding capacities, leading to the concept of valence [7].

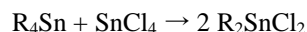
Diethylzinc was used by Buckton to make metal chlorides more alkaline, which was a significant contribution to the development of organometallic chemistry. As a result, in 1857, he was admitted to the Fellowship of the Royal Society.

After the Grignard reagents, which are useful for creating Sn-C bonds, were discovered, the field expanded quickly in the 1900s. The field continues to be rich with a variety of applications in business and ongoing activity in the research lab [2].

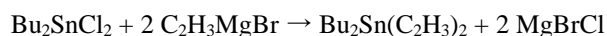
The synthesis of tetraethyltin provides an example of this:



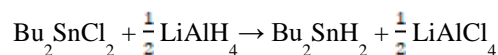
Redistribution processes can then transform the symmetrical tetraorganotin compounds, particularly tetraalkyl derivatives, into different mixed chlorides (also known as the "Kocheshkov comproportionation" in the case of organotin compounds):



A similar technique was initiated by Seyferth, Dietmar in 1959 which combines Sn halides and oxoaluminium compounds to produce dibutyldivinyltin [6]:



Two decays later John Eisch synthesised the organotin hydrides by reducing the mixed alkyl chlorides. For instance, dibutyltin dichloride and lithium aluminum hydride are combined to produce dibutyltin dihydride, a colorless distillable oil [17]:



Generally, methods of producing organotin compounds are displayed in Fig. 2. These organotin (IV) chlorides can be used to create further Sn (IV) derivatives [8-12].

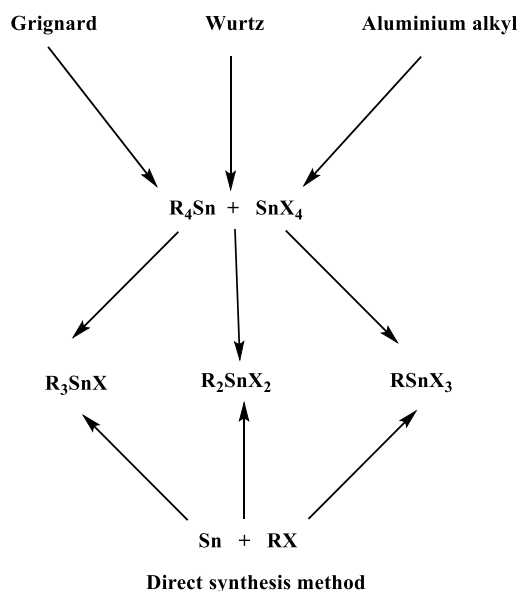


Fig. 2 - General synthesis methods of organotin (IV) compounds [7]

Organotin (IV) compounds have varied greatly of chemical and physical characteristics, corresponding mostly to the type and number (n) of the R groups, but also to the type of ligand (X). For instance, when the quantity and length of organic substituents increase, the solubility of organotin compounds in water decreases [13].

However, the kind of ligand can also have a role. Organotin toxicity varies widely and is largely impacted by the amount and kind of organic groups. While trisubstituted compounds have the maximum. In order to achieve the electrical configuration of xenon, it can either lose the two 5p electrons and produce Sn²⁺ ions or share all four electrons with other atoms [14].

1.2 Geometry Structures of Organotin Compounds

The Sn atom contains two electrons in the 5s and 2 electrons in the 5p in its valence shell. As a result, it can either lose the two 5p electrons and form Sn^{2+} ions or share all four electrons with other atoms to gain the electrical configuration of xenon [14]. Sn (II) compounds are mostly bent, pyramidal, or deformed structures due to a lone pair electron that does not participate in bonding and exhibits stereochemical activity [15]. Sn (IV) compounds form tetrahedral, trigonal-bipyramidal or octahedral (Fig. 3) [16].

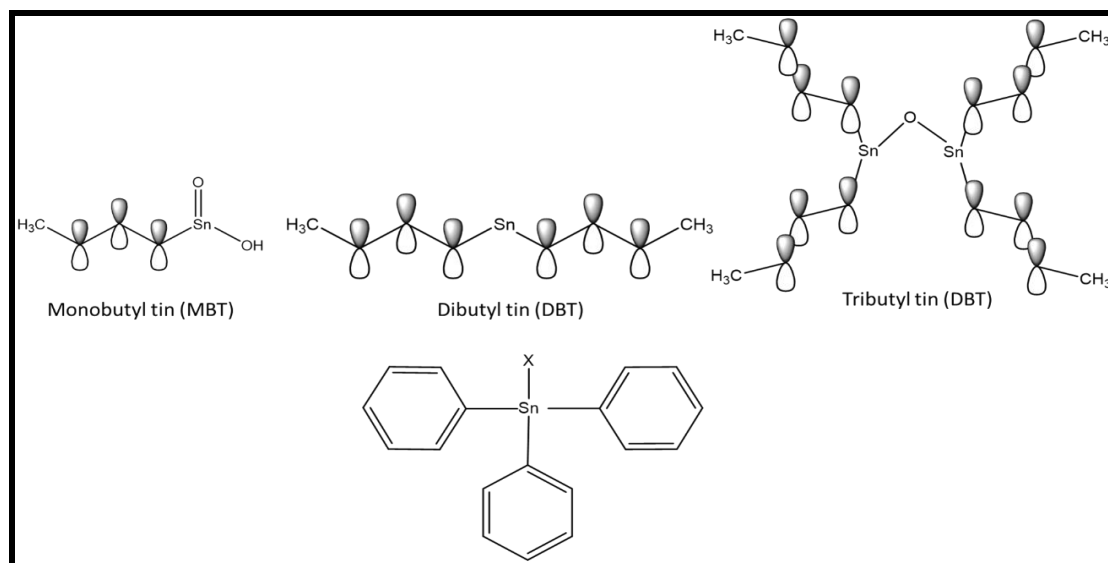


Fig. 3 - The principal coordination geometries of Sn (II) and Sn (IV) [17]

Toxicological activity, inorganic Sn is typically non-toxic. Inorganic and cyclic organic Sn compounds are insoluble and are therefore very poorly absorbed such as triorganotin compounds [18-22]. Organotin (IV) compounds are the most frequently utilized organometallic chemical family, with an estimated yearly output of over 60,000 tons [23-26]. Except for methyltins, which are created naturally by bacteria, all organotin (IV) compounds are anthropogenic [27-29].

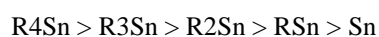
2. Applications of Organotin (IV) Compounds

Numerous industries, including those in the biological sciences, utilize organotin (IV) compounds in various applications [30-33]. Hence, it can be divided into three major fields of utilization: as thermal stabilizers to prevent degradation of several chlorinated substances, including transformer oils, polyvinyl chloride, chlorinated rubbers, paraffin, and modified plastics; industrial catalysts for a variety of chemical processes, such as the production of polyurethane foam goods and vulcanizing agents for silicone rubbers; and as biocidal properties for utilizing as agricultural fungicides, herbicides, bactericides such as hospital-use disinfectants and other applications [34, 35].

2.1 Checking Biological Activity

Organotin compounds (IV) with oxygen (O) and nitrogen (N) donor atoms play a significant role in the industry, medicine, and biology by demonstrating their use in coordination and bioinorganic chemistry with both chemical and biological properties [36]. In 1954 Van der Kerk and Luijten discovered the biocidal action of triorganotin compounds, which was afterwards explored by Kaars Sijpesteyn *et al.* in 1962. Tripropyltin, tributyltin, and triphenyltin compounds displayed good fungicidal and bactericidal characteristics [37,38].

Organotin (IV) complexes containing Schiff bases have been intensively researched for biomedical applications such as antimalarial, anticancer, antitumor, and antibacterial [39, 40]. Based on structural variety, type, quantity, and arrangement of donor atoms linked to the tin metal, Schiff bases with biologically reactive donor atoms are in high demand due to their better solubility and simplicity of production [41, 42]. The biological activity of unsymmetrical habitats of Schiff base ligands with continuous stoichiometry and varied methods of coordination is also facilitated by the Schiff bases, which continue to have a wide range of analytical and therapeutic applications [43, 44]. The toxicity of alkylorganostannanes is highly dependent on the alkyl group, and the quantity of alkyl groups reduces activity as follows for Sn (IV) compounds, with no impact on the activity from anionic group [45]:



The interaction of diorganotin (IV) complexes (Bu_2SnL_2 , Me_2SnL_2 , and Ph_2SnL_2) with the ligand (L) benzamidophenylalanine revealed that the complexes exhibit high fungicidal activity against fungi such as *Gibberella*, *Cercospora*, *arachidicola*, *Physalospora piricola*, and *Fusarium oxysporum* [45]. The complex structure is shown in Fig. 4. Furthermore, Ph_2SnL_2 has a larger proportion of inhibition than diorganotin carboxylate [46].

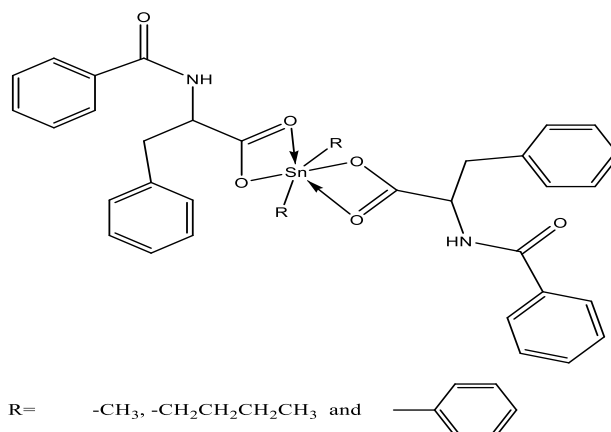


Fig. 4 - Diorganotin (IV) complexes [47]

2.2 As Stabilizer for Poly (Vinyl Chloride)

Poly (vinyl chloride) is the least weather-resistant of the major industrial polymers utilized in outdoor applications today. In reality, when exposed to sunlight, atmospheric air, wetness, contamination, and temperature, this polymer suffers severe chemical modifications that cause brittleness, discoloration, and a lack of gloss [48]. Hence, to prevent the decomposition of PVC, it must incorporate stabilizers, and organotin (IV) complexes are considered one of the main ways to stabilize PVC against UV light [49].

The effect of the organic (IV)-tri- and di-tin (IV) complexes (Ph_3SnL , Bu_3SnL , Ph_2SnL_2 and Bu_2SnL_2) with benzamidoleucine as PVC photostabilizers was investigated, the complex structure of which is shown in Fig. 5. Ph_3SnL complex was the most efficient photostabilizer possibly because of its high aromatic content as shown previously in Fig. 3 [50]. For instance, photolysis of TBT may be hindered leading to the accumulation and preservation in sediment. As stabilizers for PVC light, additional aromatic organotins were employed. Triphenyltin (IV) molecule, for instance, demonstrated the highest light stabilizing effect. In several methods, this substance can slow down PVC's photodegradation. Sn can be employed as an additional stabilizer because it is acidic. Because of this, it can remove the hydrogen chloride that is created during the dehydrochlorination process (i.e., hydrogen chloride scavenger). Similar findings for several PVC light stabilizers containing aromatic moieties have been reported [18,45,51-54].

In general, organotin (IV) complexes are present, in the following order:

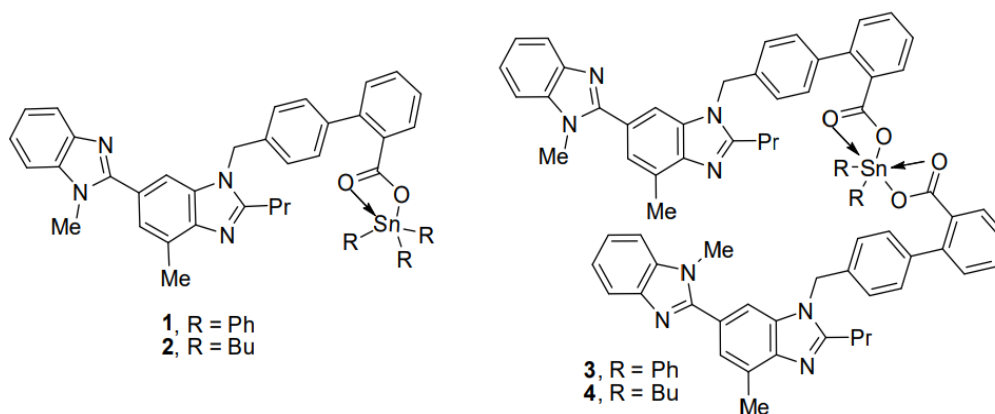
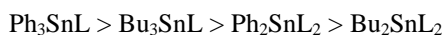


Fig. 5 - Tri- and di-organotin (IV) complexes [54]

2.3 As Antifouling Paints

Organotin compounds (IV), especially tributyltin (TBT), are major components of organotin antifouling paints. Antifouling paints serve to avoid 'fouling' organisms from growing on marine buildings and boats. Antifouling paints continue to function for the duration of their useful lives either through the direct leaching of tin-containing anti-foulants from the paint or by the continuous erosion of the paint surface, revealing active antifouling compounds. The "target" creatures for the paints are typically aquatic organisms like barnacles, mussels, and algae. These organisms on vessel hulls have a negative impact on ship movement in the sea, leading to higher fuel prices and trip lengths for the shipping sector [55-56].

2.4 Wood Preservation

Typically, tributyltin compounds which is an organotin (IV) compounds are used to treat wood in the form of a 1-3% solution in an organic solvent like kerosene in order to guard against fungal and insect attacks. The protector is usually used to process wood in specially built impregnation chambers that use an alternating vacuum and pressure cycles. It can be applied by brushing or spraying for restorative work. It has been hypothesized that organotins condense on hydroxyl groups in terminal locations of cellulose and are chemically attached to the active centers of cellulose in wood rather than directly attacking mold [57-59]. These closed-system processes are unlikely to be deteriorated by external causes. The tributyltin compound is securely held inside the wood's structure after the solvent evaporates [60].

3. Conclusion

Organotin compounds have a larger range of technological, biological, and therapeutic uses than organic metal compounds. Contrary to the Sn load employed, several of these applications necessitate extensive and ongoing research in polymer chemistry. As a result, the chemistry of three significant families of frequently used organometallic compounds based on Sn, silicon, and aluminum was investigated in this research. The chemistry, coordination geometries, coordination numbers, and adaptability of the ligands to engage in various modes of chelation, from monodentate to bidentate and tridentate, are some characteristics that contribute to the structural diversity of these compounds. It has also been discussed to use of organotin (IV) to photo-stabilize PVC products. Finally, organotin (IV) chemicals produce remarkable outcomes in sectors like wood preservation and antifouling coating.

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Synthesis and Applications of Organotin (IV) Compounds: Mini Review

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Abstract: Organotin (IV) compounds have seen a marked increase in industry utilization over the years and exhibited enormous economic benefits as well as environmental costs due to their numerous industrial, medical, and agricultural uses and other applications. The present review is a continuation of a series of reviews on the use of organotin (IV), chemicals, synthesis, characteristics and geometry as well as the industrial and biological applications.

Keywords: Organotin (IV), industrial, medical, agricultural, application

1. Introduction

The first organotin compounds were synthesised in the mid-nineteenth century in 1849 by the British scientist Edward Frankland, who synthesised crystals of diethyltin (IV) diiodide ((C₂H₅)₂SnI₂) by heating ethyl iodide with Sn [1]. Also, after a few years in 1852, Carl Löwig observed the formation of alkyltin compounds when alkyl halides reacted with the tin-sodium alloy [2]. However, these compounds were limited in the laboratory for over a century without any recognized industrial applications. In the 1950s, Organotin captured researchers' attention due to the discovery of industrial applications for organotin in the late 1940s. Organotin compounds overheard arose in large part as the plastics sector expanded and the impact of polyvinyl chloride (PVC) became clear especially when using organotin compounds as thermal and light stabilizers in the plastics sector, in addition to catalysts to polyurethane

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foams and silicones [3]. Following the events in London in 1981, the Sn market began to expand commercially. Nowadays, the widespread industrial and medicinal uses of organometallic derivatives, particularly organotin (IV) compounds, have seen a growth in production on a global scale [4].

1.1 Organotin Compounds: Chemistry, Synthesis, and Characterizes

The origin of organic Sn chemistry lies in the synthesis; for example, this synthesis was sufficient for many of the pioneers of this branch of chemistry in the nineteenth century [5]. However, some of these chemists were able to make important theoretical advances by looking at known compounds. The general formula for these substances is $R_nSnX_{(4-n)}$, where R is an alkyl group which refers in this review to a methyl, butyl, or phenyl group, X is an anionic species, such as an oxide, chloride, hydroxide, or another functional group, and $(n = 1-4)$ [5]. The electronic configuration of Sn: $[Kr] 4d^{10}5s^25p^2$ and exhibits two stable oxidation states which are Sn^{+4} and Sn^{+2} . Organotin (II) compounds oxidize easily to form more stable organotin (IV) compounds. Organotin compounds are classified as mono-, di-, tri-, or tetraorganotins based on the number of organic moieties [6].

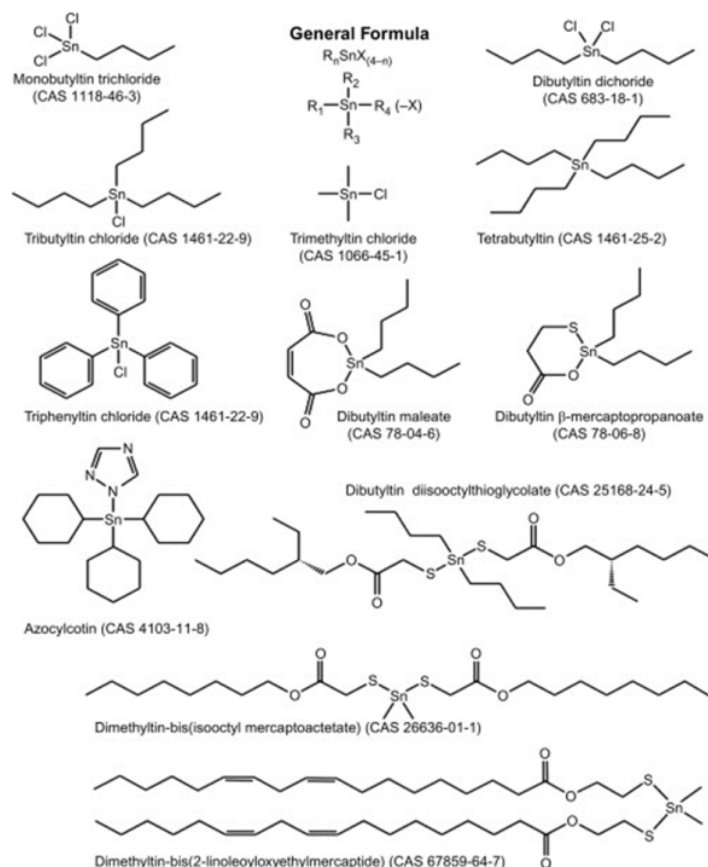


Fig. 1 - An example of organotin derivatives [7]

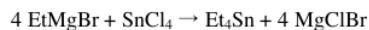
The first reports of the existence of "organic bodies of Sn", as they were then known, appeared in 1852 [7, 8]. One was by Carl Lowig (1803-1890) [8], and the other was by Edward Frankland (1825-1899) [7].

Frankland's additional descriptions of 1852 [7] were expanded upon in later publications of 1853 and 1854 [6]. Frankland was a very distinguished chemist who introduced modern graphical compound formulas, coined the terms "bond" and "organometallic" and recognized that atoms have different binding capacities, leading to the concept of valence [7].

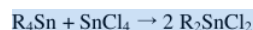
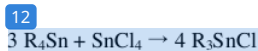
Diethylzinc was used by Buckton to make metal chlorides more alkaline, which was a significant contribution to the development of organometallic chemistry. As a result, in 1857, he was admitted to the Fellowship of the Royal Society.

After the Grignard reagents, which are useful for creating Sn-C bonds, were discovered, the field expanded quickly in the 1900s. The field continues to be rich with a variety of applications in business and ongoing activity in the research lab [2].

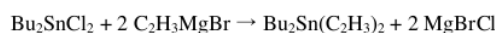
The synthesis of tetraethyltin provides an example of this:



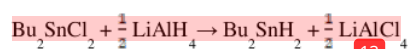
Redistribution processes can then transform the symmetrical tetraorganotin compounds, particularly tetraalkyl derivatives, into different mixed chlorides (also known as the "Kocheshkov comproportionation" in the case of organotin compounds):



A similar technique was initiated by Seyferth, Dietmar in 1959 which combines Sn halides and oxoaluminium compounds to produce dibutyldivinyltin [6]:



Two decades later John Eisch synthesised the organotin hydrides by reducing mixed alkyl chlorides. For instance, dibutyltin dichloride and lithium aluminium hydride are combined to produce dibutyltin dihydride, a colorless distillable oil [17]:



Generally, methods of producing organotin compounds are displayed in Fig. 2. These organotin (IV) chlorides can be used to create further Sn (IV) derivatives [8-12].

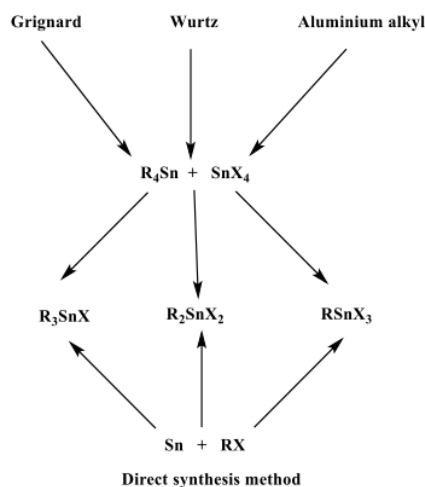


Fig. 2 - General synthesis methods of organotin (IV) compounds [7]

Organotin (IV) compounds have varied greatly of chemical and physical characteristics, corresponding mostly to the type and number (n) of the R groups, but also to the type of ligand (X). For instance, when the quantity and length of organic substituents increase, the solubility of organotin compounds in water decreases [13].

However, the kind of ligand can also have a role. Organotin toxicity varies widely and is largely impacted by the amount and kind of organic groups. While trisubstituted compounds have the maximum. In order to achieve the electrical configuration of xenon, it can either lose the two 5p electrons and produce Sn²⁺ ions or share all four electrons with other atoms [14].

1.2 Geometry Structures of Organotin Compounds

The Sn atom contains two electrons in the $5s$ and two electrons in the $5p$ in its valence shell. As a result, it can either lose the two $5p$ electrons and form Sn^{2+} ions or share all four electrons with other atoms to gain the electrical configuration of xenon [14]. Sn (II) compounds are mostly bent, pyramidal, or deformed structures due to a lone pair electron that does not participate in bonding and exhibits stereochemical activity [15]. Sn (IV) compounds form tetrahedral, trigonal-bipyramidal or octahedral (Fig. 3) [16].

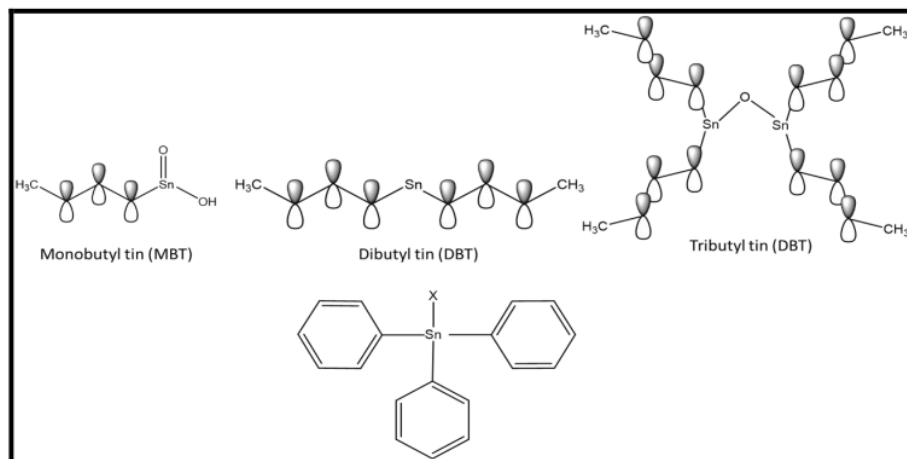


Fig. 3 - The principal coordination geometries of Sn (II) and Sn (IV) [17]

Toxicological activity, inorganic Sn is typically non-toxic. Inorganic and cyclic organic Sn compounds are insoluble and are therefore very poorly absorbed such as organotin compounds [18-22]. Organotin (IV) compounds are the most frequently utilized organometallic chemical family, with an estimated yearly output of over 60,000 tons [23-26]. Except for methyltins, which are created naturally by bacteria, all organotin (IV) compounds are anthropogenic [27-29].

2. Applications of Organotin (IV) Compounds

Numerous industries, including those in the biological sciences, utilize organotin (IV) compounds in various applications [30-33]. Hence, it can be divided into three major fields of utilization: as thermal stabilizers to prevent degradation of several chlorinated substances, including transformer oils, polyvinyl chloride, chlorinated rubbers, paraffin, and modified plastics; industrial catalysts for a variety of chemical processes, such as the production of polyurethane foam goods and vulcanizing agents for silicone rubbers; and as biocidal properties for utilizing as agricultural fungicides, herbicides, bactericides such as hospital-use disinfectants and other applications [34, 35].

2.1 Checking Biological Activity

Organotin compounds (IV) with oxygen (O) and nitrogen (N) donor atoms play a significant role in the industry, medicine, and biology by demonstrating their use in coordination and bioinorganic chemistry with both chemical and biological properties [36]. In 1921 Van der Kerk and Luijten discovered the biocidal action of triorganotin compounds, which was afterwards explored by Kaars Sijpesteijn *et al.* in 1962. Tripropyltin, tributyltin, and triphenyltin compounds displayed good fungicidal and bactericidal characteristics [37,38].

Organotin (IV) complexes containing Schiff bases have been intensively researched for biomedical applications such as antimalarial, anticancer, antitumor, and antibacterial [39, 40]. Based on structural variety, type, quantity, and arrangement of donor atoms linked to the tin metal, Schiff bases with biologically reactive donor atoms are in high demand due to their better solubility and simplicity of production [41, 42]. The biological activity of unsymmetrical habitats of Schiff base ligands with continuous stoichiometry and varied methods of coordination is also facilitated by the Schiff bases, which continue to have a wide range of analytical and therapeutic applications [43, 44]. The toxicity of alkylorganostannanes is highly dependent on the alkyl group, and the quantity of alkyl groups reduces activity as follows for Sn (IV) compounds, with no impact on the activity from anionic group [45]:



The interaction of diorganotin (IV) complexes (Bu_2SnL_2 , Me_2SnL_2 , and Ph_2SnL_2) with the ligand (L) benzamidophenylalanine revealed that the complexes exhibit high fungicidal activity against fungi such as *Gibberella*, *Cercospora*, *arachidicola*, *Physalospora pircola*, and *Fusarium oxysporum* [45]. The complex structure is shown in Fig. 4. Furthermore, Ph_2SnL_2 has a larger proportion of inhibition than diorganotin carboxylate [46].

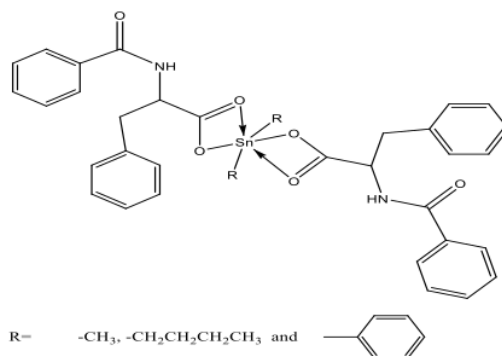


Fig. 4 - Diorganotin (IV) complexes [47]

2.2 As Stabilizer for Poly (Vinyl Chloride)

Poly (vinyl chloride) is the least weather-resistant of the major industrial polymers utilized in outdoor applications today. In reality, when exposed to sunlight, atmospheric air, wetness, contamination, and temperature, this polymer suffers severe chemical modifications that cause brittleness, discoloration, and a lack of gloss [48]. Hence, to prevent the decomposition of PVC, it must incorporate stabilizers, and organotin (IV) complexes are considered one of the main ways to stabilize PVC against UV light [49].

The effect of the organic (IV)-tri- and ditin (IV) complexes (Ph_3SnL , Bu_3SnL , Ph_2SnL_2 and Bu_2SnL_2) with benzamidophenylalanine as PVC photostabilizers was investigated, the complex structure of which is shown in Fig. 5. Ph_3SnL complex was the most efficient photostabilizer possibly because of its high aromatic content as shown previously in Fig. 3 [50]. For instance, photolysis of TBT may be hindered leading to the accumulation and preservation in sediment. As stabilizers for PVC light, additional aromatic organotins were employed. Triphenyltin (IV) molecule, for instance, demonstrated the highest light stabilizing effect. In several methods, this substance can slow down PVC's photodegradation. Sn can be employed as an additional stabilizer because it is acidic. Because of this, it can remove the hydrogen chloride that is created during the dehydrochlorination process (i.e., hydrogen chloride scavenger). Similar findings for several PVC light stabilizers containing aromatic moieties have been reported [18,45,51-54].

In general, organotin (IV) complexes are present, in the following order:

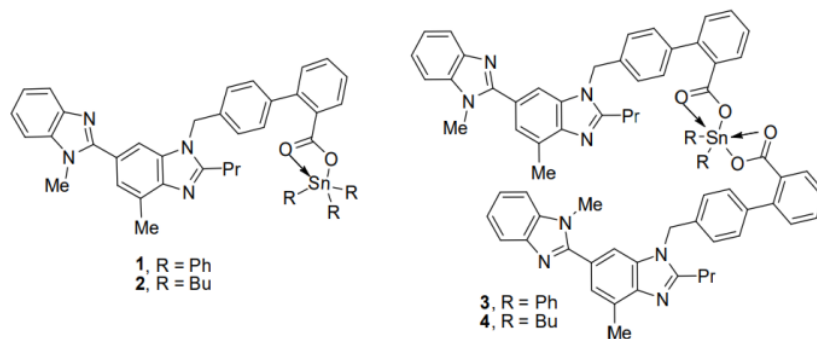


Fig. 5 - Tri- and di-organotin (IV) complexes [54]

2.3 As Antifouling Paints

Organotin compounds (IV), especially tributyltin (TBT), are major components of organotin antifouling paints. Antifouling paints serve to avoid 'fouling' organisms from growing in marine buildings and boats. Antifouling paints continue to function for the duration of the useful lives either through the direct leaching of tin-containing anti-foulants from the paint or by the continuous erosion of the paint surface, revealing active antifouling compounds. The "target" creatures for the paints are typically aquatic organisms like barnacles, mussels, and algae. These organisms on vessel hulls have a negative impact on ship movement in the sea, leading to higher fuel prices and trip lengths for the shipping sector [55-56].

2.4 Wood Preservation

Typically, tributyltin compounds which is an organotin (IV) compounds are used to treat wood in the form of a 1-3% solution in an organic solvent like kerosene in order to guard against fungal and insect attacks. The protector is usually used to process wood in specially built impregnation chambers that use an alternating vacuum and pressure cycles. It can be applied by brushing or spraying for restorative work. It has been hypothesized that organotins condense on hydroxyl groups in terminal locations of cellulose and are chemically attached to the active centers of cellulose in wood rather than directly attacking mold [57-59]. These closed-system processes are unlikely to be deteriorated by external causes. The tributyltin compound is securely held inside the wood's structure after the solvent evaporates [60].

3. Conclusion

Organotin compounds have a larger range of technological, biological, and therapeutic uses than organic metal compounds. Contrary to the Sn load employed, several of these applications necessitate extensive and ongoing research in polymer chemistry. As a result, the chemistry of three significant families of frequently used organometallic compounds based on Sn, silicon, and aluminum was investigated in this research. The chemistry, coordination geometries, coordination numbers, and adaptability of the ligands to engage in various modes of chelation, from monodentate to bidentate and tridentate, are some characteristics that contribute to the structural diversity of these compounds. It has also been discussed to use of organotin (IV) to photo-stabilize PVC products. Finally, organotin (IV) chemicals produce remarkable outcomes in sectors like wood preservation and antifouling coating.

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