

1.1 Organotin Compounds: General Introduction

The chemistry of organotin compounds originated with the discovery of diethyltin diiodide [Et₂SnI₂] by Frankland in 1849. The tremendous growth in the field was witnessed after the discovery of the Grignard reagent, which had a significant role in the early development of Sn-C bond containing compounds (Scheme 1.1).



Scheme 1.1

Since this application of the Grignard reagent in the synthesis, many different types of organotin compounds have been prepared, namely R₄Sn, R₃SnX, R₂SnX₂, and RSnX₃.

Organotin compounds became increasingly attractive because of their industrial applications as catalysts [Ni et al., 2020], PVC stabilizers [Piver, 1973], wood preservatives [Dacosta et al., 1971], biocides [Mehmood et al., 2019], and antifouling paints [Champ et al., 1996]. Among organotin compounds, tetraorganotin compounds with an organic substituent of the tin as n-butyl, n-octyl, and phenyl are used as reagents in the Stille reaction [Zhou et al., 2009]. Triorganotin compounds are known for their excellent biological properties, such as biocides [Mehmood et al., 2019], fungicides [Joshi et al., 2020], and bactericides [Huedo et al., 2019]. For example, tri-n-butyltin compounds are used in antifouling paints. In general, it is observed that the biological activity of these compounds depends on the number and type of the organic substituent attached to the Sn center. Some of the diorganotin compounds have found applications in the production of silicone rubber [Cervantes et al., 2012].

Many organotin compounds, including organotin oxides and organotin sulfides, have been explored as precursors to preparing advanced nanomaterials [Ramasamy et al., 2013; Sharps et al., 2019]. In recent years, organotin compounds have been investigated as molecular materials, which includes reports on the selective ion sensing using Schiff base decorated diorganotin carboxylates [Vinayak et al., 2019b], antibacterial activity based on coumarin substituted triorganotin carboxylates via two-photon absorption phenomenon [Wang et al., 2017a], diorganotin dithiocarbamate as a single-source precursor to SnS using aerosol-assisted chemical vapour deposition [Ramasamy et al., 2013], IR light to broad white light photon up-conversion using adamantane based monoorganotin sulfide [(RSn)₄S₆] (R = 4-(CH₂=CH)-C₆H₄) [Rosemann et al., 2016a], an optoelectronic device made up of diorganotin carboxylate-PEDOT:PSS based composites [Sánchez-vergara et al., 2021], etc.

1.2 Structural Aspects of Organotin Compounds

Organotin compounds display a vast amount of structural diversity resulting from various reaction pathways and ligand systems employed for their synthesis. Two major categories of organotin compounds studied in this thesis are; Sn-O and Sn-S units containing organotin compounds. Depending on the type of ligands used for synthesis, these compounds can be further divided into various other subgroups.

Organotin compounds have been extensively investigated with unreactive organic substituents on the tin center (Me, Et, Bu, Ph, etc.) and the structural chemistry of these compounds are well documented in the literature [Gielen, 2008]. However, organotin compounds involving substituents with intramolecular coordination are significantly less explored. Various unique structural forms have been isolated using the intramolecular coordination approach in the past. Recently, we have utilized the N→Sn intramolecular coordination of 2-phenylazophenyl substituent on the tin center and reported various interesting organotin assemblies both with Sn-S and Sn-O units in their structure.

1.2.1 Sn-O unit containing Organotin Compounds

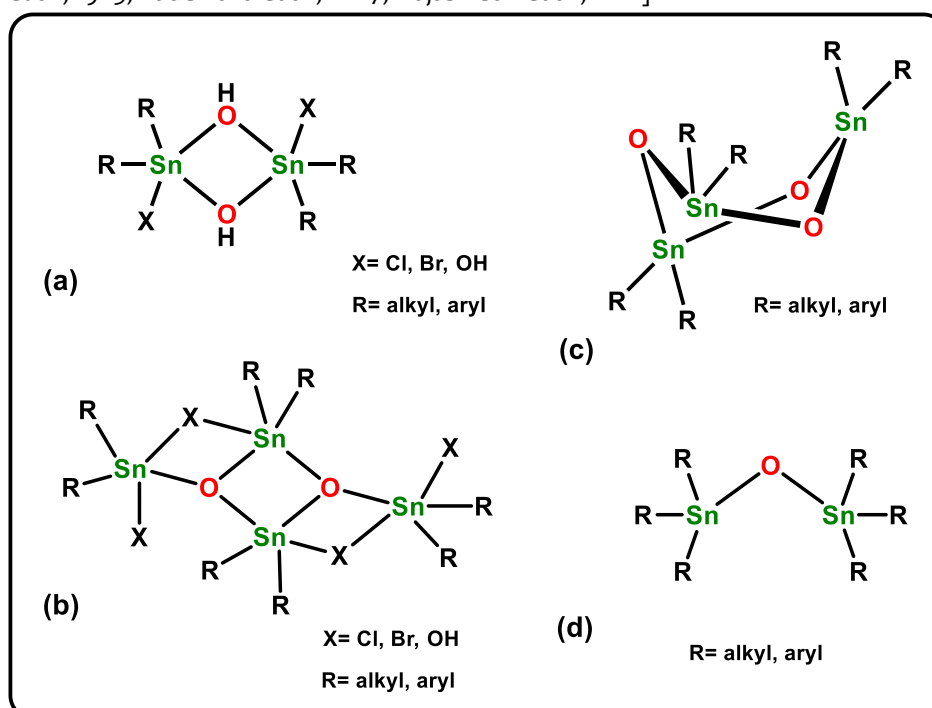
All the organotin compounds that contain Sn-O units in their structures are considered in this category. These compounds are generally known as organostannoxanes in the literature. This is the most studied class of organotin compounds and has a remarkable structural diversity amongst organotin compounds. We will discuss the structural aspects of different types of organostannoxanes in the upcoming subsections.

- **Organotin oxides/hydroxides**

Organotin oxides/hydroxides are primarily obtained by the hydrolysis of corresponding organotin halides. This class of organotin compounds exists mainly in both polymeric and discrete forms. The nature of the product is dependent on the nature of the R group present on the tin center. In general, sterically bulky substituents result in the formation of discrete compounds. Numerous structures have been isolated and structurally characterized by using single-crystal x-ray diffraction studies in the past [Chandrasekhar et al., 2002b].

Partial as well as complete hydrolysis of diorganotin dihalides have been observed to result in discrete structures. Controlled partial hydrolysis in the presence of base leads to the formation of two different products depending on the nature of the base and steric bulk of the organic substituent; one is diorganotin hydroxy halide $[\text{R}_2\text{Sn}(\mu_2\text{-OH})\text{X}]_2$, in which Sn centers are bridged through two μ_2 -hydroxo ligands [Beckmann et al., 2002] [Chart 1.1 (a)], and other is dimeric tetraorganodistannoxane $[(\text{R}_2\text{Sn})_2(\mu_3\text{-O})(\mu_2\text{-X})\text{X}]_2$ (ladder-like structure) which contains two μ_3 -oxo and two μ_2 -halido bridging ligands [Rojas-León et al., 2021] [Chart 1.1 (b)]. The latter has two different sets of Sn centers, which can be identified with

Chart 1.1: Representative examples of di- and triorganotin oxides/hydroxides [Beckmann et al., 2002; Masamune et al., 1983; Padělková et al., 2007; Rojas-León et al., 2021].

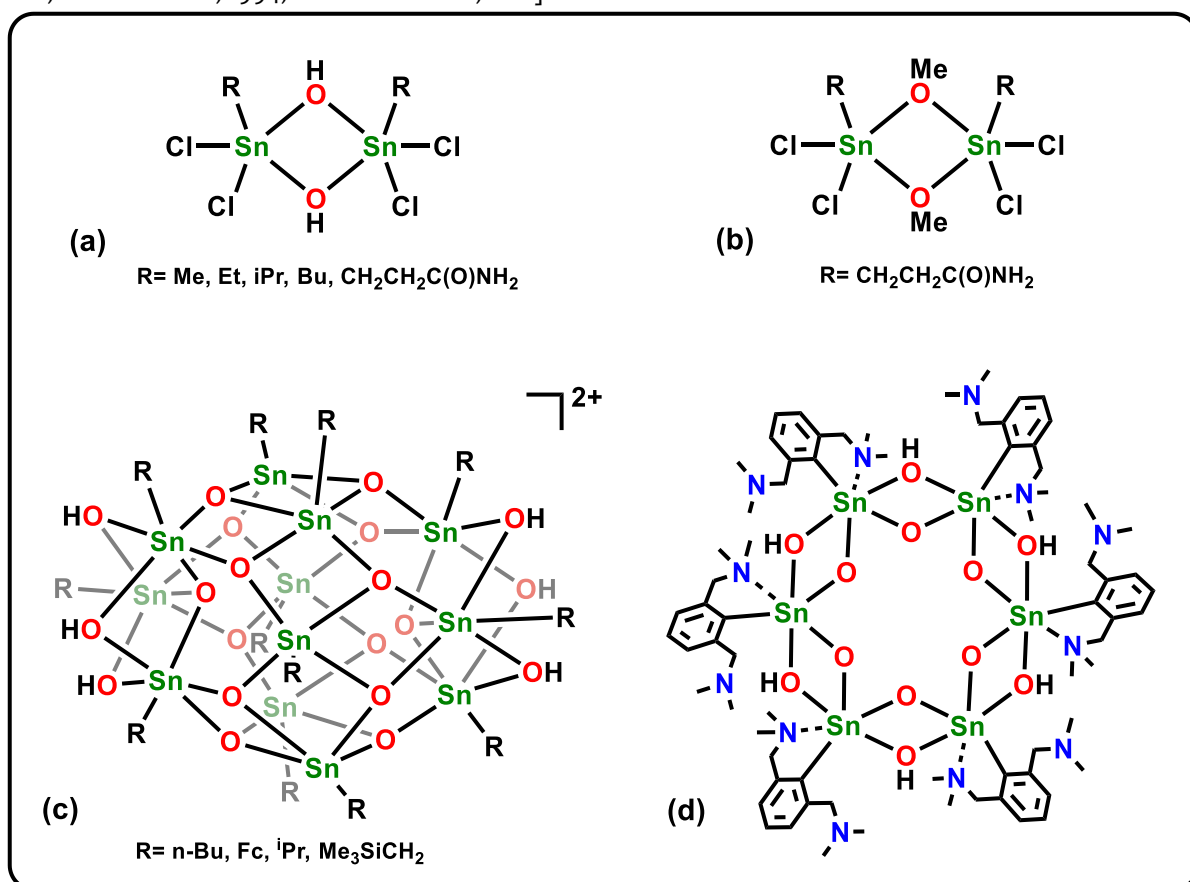


the help of ^{119}Sn NMR. However, diorganotin dihalides on complete hydrolysis were found to show a six-membered macrocycle $[\text{R}_2\text{Sn}(\mu_2\text{-O})]_3$ formed by the three repeating units of R_2SnO [Masamune et al., 1983] [Chart 1.1 (c)]. The hydrolysis chemistry for triorganotin compounds is generally restricted to limited structures due to the steric hindrance and the less availability of reactive sites. The hydrolysis of triorganotin halides generally yields a dinuclear compound bridged through μ_2 -oxo ligand [Padělková et al., 2007] [Chart 1.1 (d)]. Chart 1.1 represents a few prominent structures obtained as the result of hydrolysis of di- and triorganotin halides.

The partial hydrolysis of monoorganotin halides generally leads to the formation of cyclic four-membered monoorganostannoxane that contains a Sn_2O_2 ring consisting of either bridging μ_2 -OH or μ_2 -OMe ligands. Interestingly although there are a large number of compounds reported possessing μ_2 -hydroxo bridging ligands, very few structures are known with μ_2 -OMe bridging ligands [Howie et al., 2011; Johnson et al., 1994] [Chart 1.2 (a) and (b)].

Complete hydrolysis of monoorganotin trihalides achieved in an alkaline medium leads to the formation of organostannoic acid $[\text{RSn}(\text{O})(\text{OH})]_n$. Structural aspects of organostannoic acid have been attracting continuous interest in organotin chemistry for a long time. Lambourne *et al.*, in 1922, proposed the cyclic or chain-like structure for methylstannonic acid $[\text{MeSn}(\text{O})(\text{OH})]$ [Lambourne, 1922]. The exact structure of routinely used starting precursor n-butylstannonic acid is still not known, and it is proposed to have a structure similar to dicationic dodecanuclear organotin oxo-hydroxo $[(\text{RSn})_{12}(\mu_3\text{-O})_{14}(\mu_2\text{-OH})_6]^{2+}$ cage [Dong et al., 2015; Kundu et al., 2014b; Plasseraud et al., 2011] [Chart 1.2 (c)]. The Sn_{12} oxo-hydroxo cage is known as football cage in the literature, whose equator position consists of six pentacoordinated Sn centers, whereas the pole position consists of six hexacoordinated Sn centers constituting two trimeric subunits called o-capped clusters $[(\text{RSn})_3(\mu_3\text{-O})(\mu_2\text{-OH})_3]$.

Chart 1.2: Representative examples of monoorganotin oxides/hydroxides [Bouška et al., 2009; Howie et al., 2011; Johnson et al., 1994; Plasseraud et al., 2011].



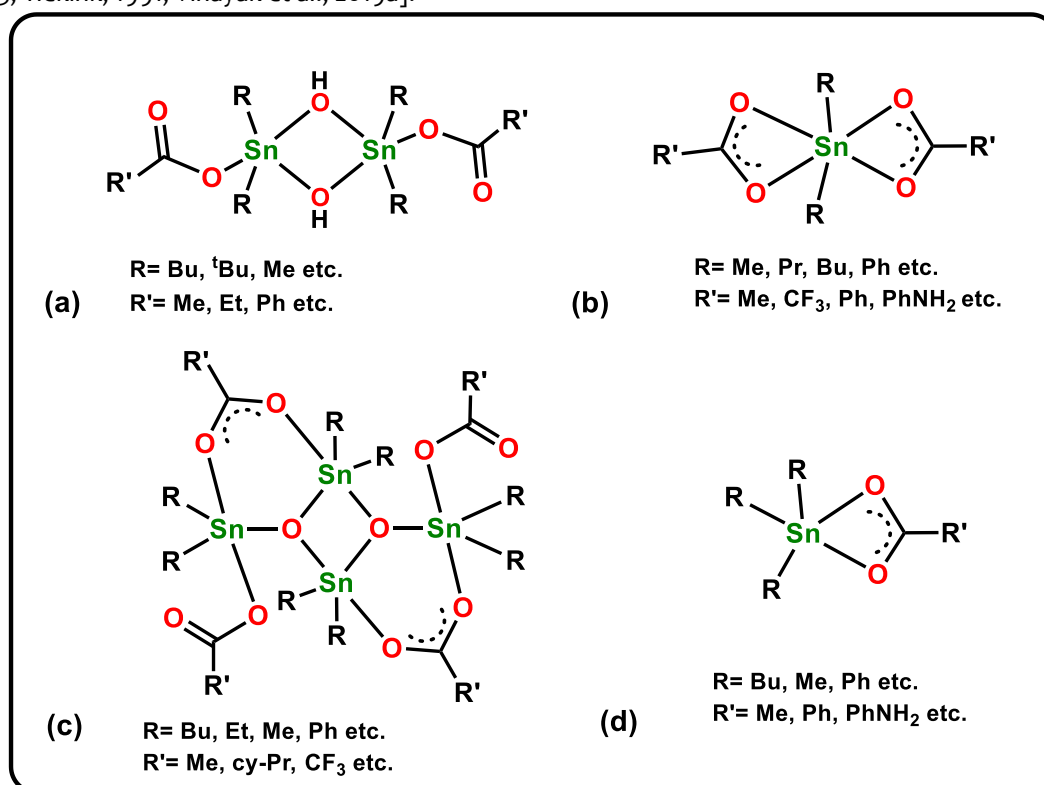
Recently, Bouška *et al.* have reported a hexanuclear structure for N→Sn intramolecularly coordinated organostannic acid $[\text{R}_2\text{Sn}(\text{O})(\text{OH})]_6$; {R= N,C,N-pincer ligand $[\text{2,6-(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]$ } [Bouška *et al.*, 2009]. The structure is unexpectedly different from the previously reported football cage. The molecular structure of this organostannic acid shows a macrocyclic ring made up of six Sn atoms and each pair of adjacent Sn atoms is bridged through $\mu_2\text{-O}$ and $\mu_2\text{-OH}$ ligands [Chart 1.2 (d)]. Additionally, there is no o-capped cluster found in the structure of hexanuclear organostannic acid.

• Organotin carboxylates

Organotin carboxylates are an important class of organotin compounds and are known to display rich structural diversity [Tiekink, 1991]. Various structural forms like simple mononuclear compounds to complex polynuclear cages and polymeric structures are reported for this class of compounds. Organotin precursors such as organotin halides and organotin oxides-hydroxides on reaction with carboxylic acid ligands yield corresponding organotin carboxylates. Among organotin carboxylates, in di- and triorganotin carboxylates compounds, the predominant structures found in the literature are chain and polymeric structures, although some discrete structures, including some macrocycles, have also been isolated and structurally characterized [Chandrasekhar *et al.*, 2002b].

Diorganotin carboxylates exhibit a range of diverse structures. These are generally obtained utilizing the reactions of diorganotin oxides $[\text{R}_2\text{SnO}]_n$ with carboxylic acids by the subtle variation in stoichiometry and reaction conditions. The equimolar reaction undergoes the nucleophilic addition $[\text{R}_2\text{Sn}(\text{OH})(\text{O}_2\text{CR}')]_2$ followed by dimerization to yield a dinuclear organotin carboxylate $[\text{R}_2\text{Sn}(\text{O}_2\text{CR}')(\mu_2\text{-OH})]_2$ [Chart 1.3 (a)] whereas reaction with two equivalent of carboxylic acid leads to a mononuclear compound resulting into the substitution of both halides with two carboxylate ligands [Kundu *et al.*, 2015a] [Chart 1.3 (b)]. In certain instances, equimolar reactions are known to undergo self-condensation to form $[\text{R}_2\text{Sn}(\text{O}_2\text{CR}')(\mu_2\text{-O})(\text{O}_2\text{CR}')\text{SnR}_2]$, which on further dimerization leads to the formation of tetranuclear ladder-type structure $[\text{R}_2\text{Sn}(\text{O}_2\text{CR}')(\mu_2\text{-O})(\mu_2\text{-O}_2\text{CR}')(\text{O}_2\text{CR}')]_2$ [Vinayak *et al.*, 2019a] [Vinayak *et al.*, 2019a] shown in Chart 1.3 (c). The chemistry of diorganotin

Chart 1.3: Representative examples of di- and triorganotin carboxylates [Dakternieks *et al.*, 2003; Tian *et al.*, 2005; Tiekink, 1991; Vinayak *et al.*, 2019a].

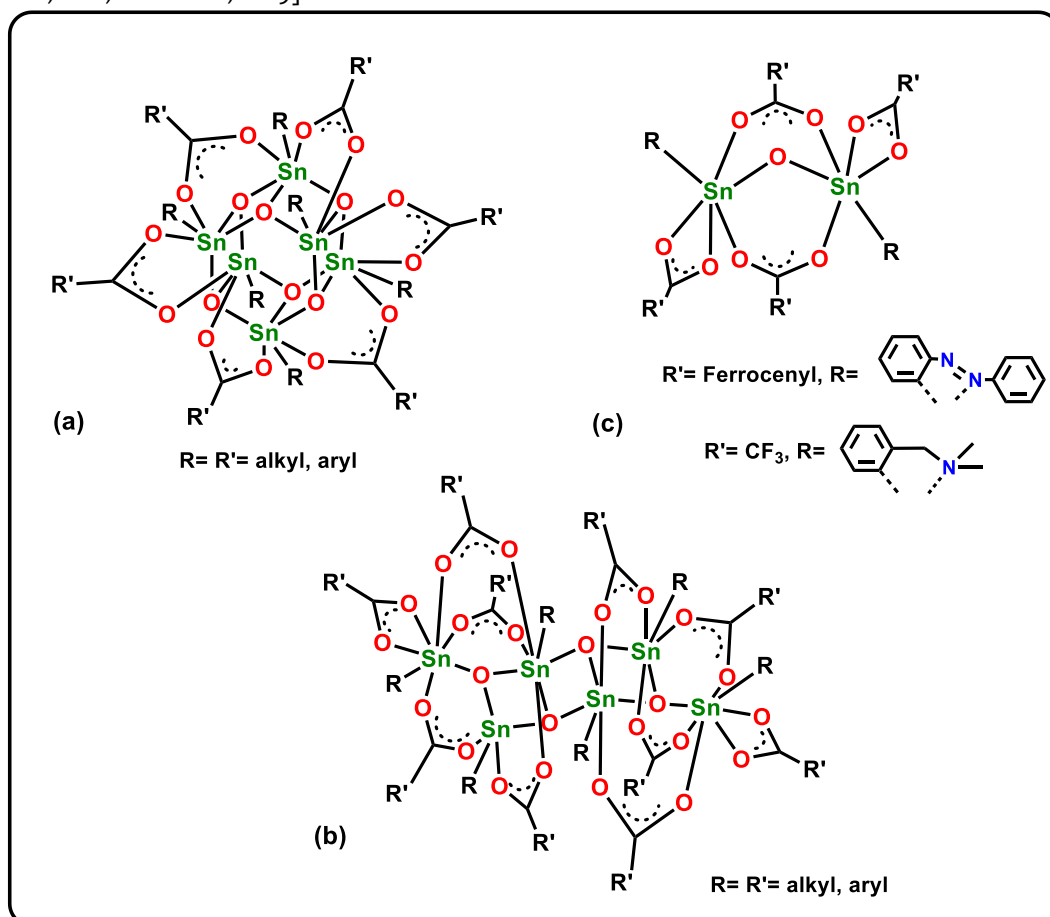


carboxylates has been reviewed in the past by Tiekink and others [Dakternieks et al., 2003; Tiekink, 1991]. The formation of different structural products from the same stoichiometric reactions depends on the type of carboxylic acid and organic substituent present on the tin center.

Triorganotin carboxylates are generally obtained by the reactions of R_3SnX ($X = Cl, Br, I$), R_3SnOH , or $(R_3Sn)_2O$ with a carboxylic acid $RCOOH$. These compounds usually possess structures of the type such as chain structures, discrete structures, and polymeric structures. Discrete structures are known in the literature for compounds of the type Ar_3SnO_2CR ($Ar = Aryl$) [Tian et al., 2005] [Chart 1.3 (d)].

Monoorganotin carboxylates have been relatively less explored compared to the di- and triorganotin carboxylates. The synthetic route to obtain monoorganotin carboxylates include reactions of organostannic acid with carboxylic acids in different molar ratio or reactions of monoorganotin halides with carboxylic acids in the presence of an appropriate base in different molar ratios. There are two extensively found monoorganotin carboxylates in the literature; one is hexanuclear compound $[R_3Sn(\mu_3-O)(\mu_2-O_2CR')]_6$ that has a drum-like Sn-O skeleton [Guan et al., 2018; Sharps et al., 2019; Xiao et al., 2019] [Chart 1.4 (a)], whereas the other is hexanuclear compound $\{[R_3Sn(\mu_2-O)(\mu_2-O_2CR')]_2[(R_3Sn(\mu_2-O_2CR')]_2(\kappa^2-O_2CR')]\}_2$ that has ladder-like Sn-O core [Chandrasekhar et al., 1987] [Chart 1.4 (b)]. The drum-like structure contains two Sn_3O_3 rings over to each other linked through a Sn-O bond, and a carboxylate ligand is bridging over two Sn atoms of both the Sn_3O_3 rings. Interestingly, these Sn_3O_3 rings are not entirely planar but in a chair-like conformation. Also, it is a highly symmetric framework that has six repeating units of $[R_3Sn(\mu_3-O)(\mu_2-O_2CR')]$. While the ladder-like framework is constituted of three fused Sn_2O_2 rings with an extended Sn center supported by three bridging μ_2-O_2CR' units and one isodentate κ^2-O_2CR' unit on each side. Unlike the drum framework, it has three distinct Sn centers and has symmetry around the central Sn_2O_2 ring. As evident from the literature, organotin carboxylates have been

Chart 1.4: Representative examples of monoorganotin carboxylates [Chandrasekhar et al., 1987, 2013a; Švec et al., 2011; Xiao et al., 2019].



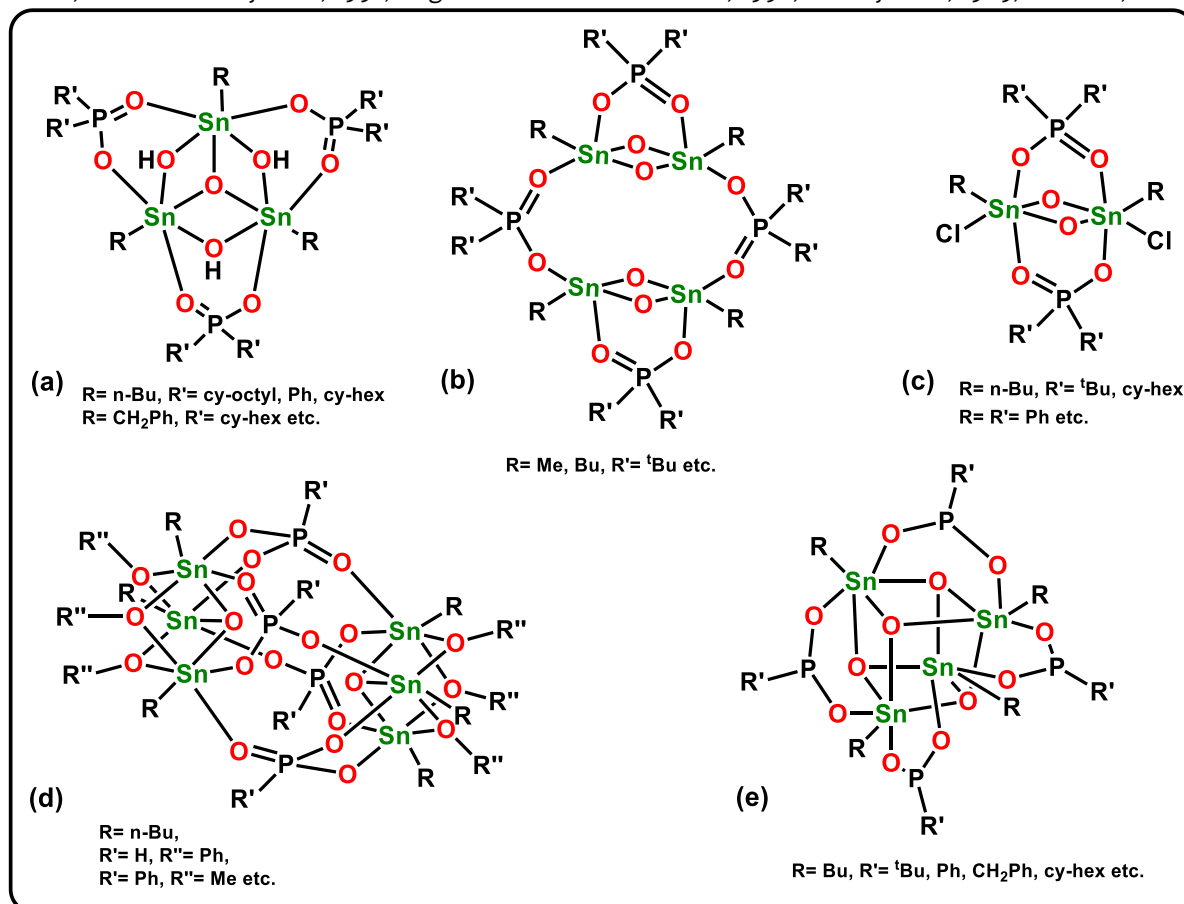
extensively investigated with many unreactive organic substituents on the tin center (such as Me, Et, Bu, Ph, etc.). However, organotin carboxylates involving substituents having the ability to show intramolecular coordination are significantly less reported. The presence of intramolecular coordination can significantly increase the stability of the compounds and present the opportunity to isolate various unique structural forms. Literature reports show only a few intramolecularly N→Sn coordinated organotin carboxylates with distinct dinuclear structures. Molecular structure of one of the organotin carboxylates of this class $[(\text{RSn})_2(\mu_2\text{-O})(\mu_2\text{-O}_2\text{CR}')_2(\kappa^2\text{-O}_2\text{CR}')_2)]_2$ {R = 2-phenylazophenyl, 2-(N,N-dimethylaminomethyl)phenyl-}, R' = Fc, CF₃} revealed the presence of rare unsupported Sn-O-Sn motif [Chandrasekhar et al., 2013a; Švec et al., 2011] [Chart 1.4 (c)]. We have recently reported a similar unsupported Sn-O-Sn core substituted with 2-phenylazophenyl group on tin utilizing a different reaction strategy [Mishra et al., 2021a].

• Organotin phosphonates/phosphinates

In this thesis, among Sn-O units containing organotin compounds, we mainly deal with the clusters/cages of organotin oxide-hydroxide and carboxylates. For the sake of completion, other classes of Sn-O containing compounds such as organotin phosphonates/phosphinates are mentioned briefly.

Organotin phosphonates/phosphinates are also known in the literature for their structural diversity. The ubiquitous Sn₂O₂ unit has been a prominent building block of this class of organotin compounds. Reactions of RSn(O)(OH) with organophosphates, phosphonic or phosphinic acid are known to show a variety of structures such as o-capped cluster [Nagabrahmanandachari et al., 1998], crown cluster [Kumara Swamy et al., 1992], butterfly [Swamy et al., 1989], cube [Chandrasekhar et al., 2002b], extended cluster [Xie et al., 2010] etc. [Chart 1.5]. Slight variation in the stoichiometry ends up in the formation of various

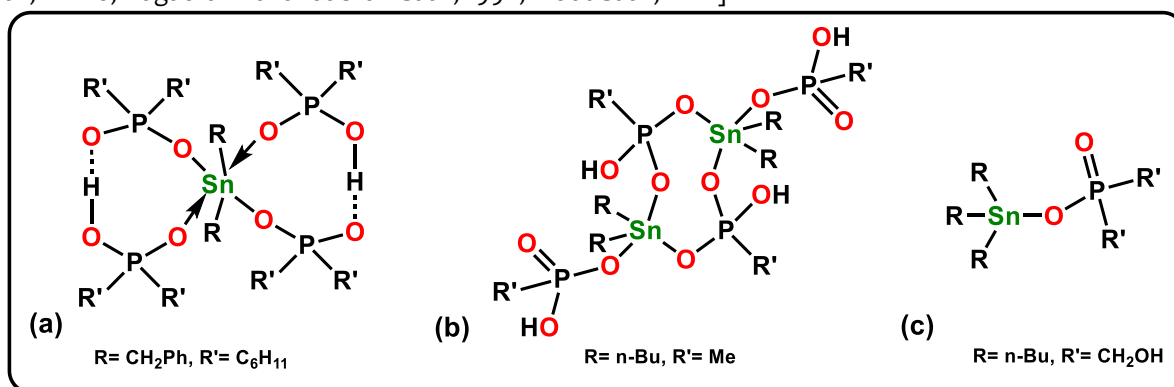
Chart 1.5: Representative examples of monoorganotin phosphonates/phosphinates [Chandrasekhar et al., 2002b; Kumara Swamy et al., 1992; Nagabrahmanandachari et al., 1998; Swamy et al., 1989; Xie et al., 2010].



clusters; 3:4 molar reactions of RSn(O)(OH) with $\text{R}'_2\text{P(O)(OH)}$ turn out to produce an o-capped cluster [Chart 1.5 (a)], 4:5 molar reaction produces crown cluster [Chart 1.5 (b)], 1:2 molar reaction turns out to form butterfly structure [Chart 1.5 (c)], while reactions with phosphonic acid [$\text{R}'\text{P(O)(OH)}_2$] in different stoichiometry generates extended cluster and cube clusters [Chart 1.5 (d) and (e)]. Interestingly, many of these compounds can rearrange and interconvert themselves. In some cases, the formation of the product is accompanied with the cleavage of the Sn-C bond.

It has been observed that diorganotin phosphonates/phosphinates are restricted to limited structures so far. Chart 1.6 shows two representative examples, which are the results of reactions of R_2SnCl_2 with phosphonic acid and phosphonic acid in 1:4 and 2:4 stoichiometry, respectively [Nagabrahmanandachari et al., 1998; Ribot et al., 2001]. The formation of the first compound [Chart 1.6 (a)] occurs by involving hydrogen bonding in two units of phosphonic acids producing an eight-membered cyclic ring on each side of the organotin moiety. While the second compound [Chart 1.6 (b)] shows the presence of an eight-membered macrocycle made up of Sn and P moieties bridging together through μ_2 -oxo ligand along with the unidentate coordination of one phosphonate unit on each organotin moiety. Triorganotin compounds generally form a mononuclear structure with a unidentate linkage of phosphinate ligand [Chandrasekhar et al., 2002b], as shown in Chart 1.6 (c).

Chart 1.6: Representative examples of di- and triorganotin phosphonates/phosphinates [Chandrasekhar et al., 2002b; Nagabrahmanandachari et al., 1998; Ribot et al., 2001].



1.2.2 Sn-S unit containing Organotin Compounds

Here in this section, a background to the organotin compounds containing Sn-S linkage will be discussed. There are several sulfur-based ligands that have been used to generate organotin compounds with Sn-S units in the structure. Depending upon the type of sulfur-based ligands used, these compounds can be further categorized into organotin- sulfides (S^{2-}), thiols (RS), dithiocarbamates (R_2NCS_2^-), thiosemicarbazones $\{\text{RNC}(\text{NNR})\text{S}\}$, thiophosphines (R_2PS_2), xanthates (ROCS_2^-), thiocarboxylates (RCOS) etc.

The class of organotin compounds containing the Sn-S unit has emerged intensively in the last decade. Compounds of this class have demonstrated intriguing biological [Adeyemi et al., 2018], catalytic [Dasgupta et al., 2020], and photophysical applications [Geringer et al., 2021]. Unlike organostannoxanes, class of Sn-S unit containing compounds is still less explored and is relatively not well documented in the literature. In a recent development, exploration of various photophysical properties of these compounds has been successfully demonstrated by Dehnen *et al.*, where they have reported $[(\text{RSn})_4\text{S}_6]$ ($\text{R} = 4\text{-(CH}_2=\text{CH)-C}_6\text{H}_4$), which shows photon up-conversion phenomenon thereby converting IR light into a broad white light spectrum [Rosemann et al., 2016a]. In another report, the role of an organotin sulfide cation was favorably investigated for the rearrangement of NHC group to abnormal NHC group [Wagner et al., 2013]

In addition to searching for a new synthetic approach to novel structures, one important aspect of current research in this area is focused on the development of new molecular materials

in this class of compounds. Designing and optimization of new molecular materials with desired property involves the required structural modification, which can be achieved either by functionalizing the organic substituent on the tin center or by extending the inorganic core to make ternary compounds. Jurkschat and coworkers probed the N→Sn intramolecular coordination on molecular systems affording Sn-S unit in the early 90s [Jurkschat et al., 1992]. Dehnen and coworkers recently have expanded the field of organotin sulfides by exploiting various facets of intramolecular N→Sn and O→Sn coordination [Eußner et al., 2013, 2014, 2015; Fard et al., 2009b, 2009a; Geringer et al., 2020, 2021; Halvagar et al., 2010; Leusmann et al., 2015, 2016]. The intramolecular coordination approach is known to be crucial for the stabilization of unusual structural motifs in these classes of compounds.

- **Organotin sulfides**

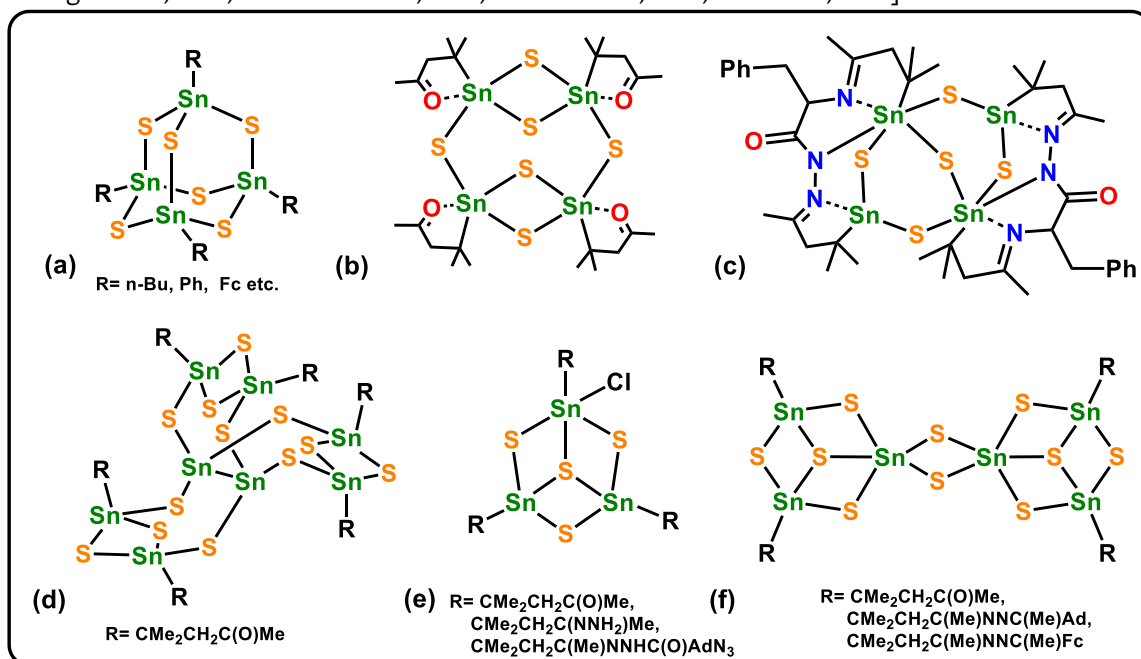
Among organotin sulfides, monoorganotin sulfides have been a subject of immense interest because of their tremendous structural diversity. These compounds can be synthesized from the reaction of monoorganotin halide precursor with a Sulfide (S^{2-}) ligand source. Structural diversity in monoorganotin sulfides can be achieved by either functionalizing the organic group attached to the organotin moiety or expanding the core by changing the molar ratios of the reactants and reaction conditions. Unlike organostannoxanes, mostly discrete structures with varying nuclearity have been isolated for organotin sulfides.

The more common and well-established compound in monoorganotin sulfide is $[(RSn)_4S_6]$ with Sn_4S_6 core, which can be synthesized by reacting a monoorganotin halide ($RSnCl_3$) with sodium sulfide. It is observed that Sn_4S_6 core may exist in two different structural forms, i.e., adamantane (AD) and double-decker (DD) type cage [Chart 1.7 (a) and (b)]. Interestingly, the structural type of Sn_4S_6 core depends on the type of organic substituent present on the Sn center. The monodentate substituent on the Sn center results into formation of an adamantane structure, whereas the bidentate substituent on the Sn center produces a double-decker cage [Berwe et al., 1987; Fard et al., 2009b; Leusmann et al., 2016; Rosemann et al., 2018]. These structural types (AD or DD) can be further distinguished by their x-ray crystal structures, where a double-decker cage is characterized by the presence of a Sn_2S_2 ring while an adamantane cage is characterized by the presence of a Sn_3S_3 ring. Another prominent feature observed is the difference in the local environment of the Sn center; in the case of adamantane structure, it was found to be distorted tetrahedral, whereas, in a double-decker, it was found to be distorted TBP geometry.

Dehnen and coworkers have reported a double-decker cage $[(RSn)_4S_6]$ involving a reactive carbonyl group bearing substituent $[R = CMe_2CH_2C(O)Me]$ on organotin moiety [Fard et al., 2009b]. The carbonyl group in $[(RSn)_4S_6]$ ($R = CMe_2CH_2C(O)Me$) provides a number of possibilities for further modification. Functionalization with hydrazine and its derivatives resulted in several high nuclearity clusters such as $[(RSn)_2SnS_4]_2(\mu-S)_2$, $\{R = CMe_2CH_2C(O)Me\}$ [Eußner et al., 2013]; $[(RSn)_2(\mu-S)_6]$, $\{R = (CMe_2CH_2CMeNNH)_2CO\}$ [Halvagar et al., 2010]; $[R'_2Sn_4S_5]$, $\{R' = (CMe_2CH_2C(Me)-N_2C(O)CH(CH_2Ph)NC(Me)CH_2CMe_2)\}$ [Rinn et al., 2016]; $[(RSn^{IV})_6Sn^{III}_2S_{12}]$, $\{R = CMe_2CH_2C(O)Me\}$ [Eußner et al., 2013] (Chart 1.7). In certain instances, trimethylsilyl sulfide $[(Me_3Si)_2S]$ was used as a source of sulfide ligand. $RSnCl_3$ on reacting with trimethylsilyl sulfide $[(Me_3Si)_2S]$ produces $[(RSn)_3S_4Cl]$ which on further derivatization afforded clusters of varying nuclearity. [Eußner et al., 2013].

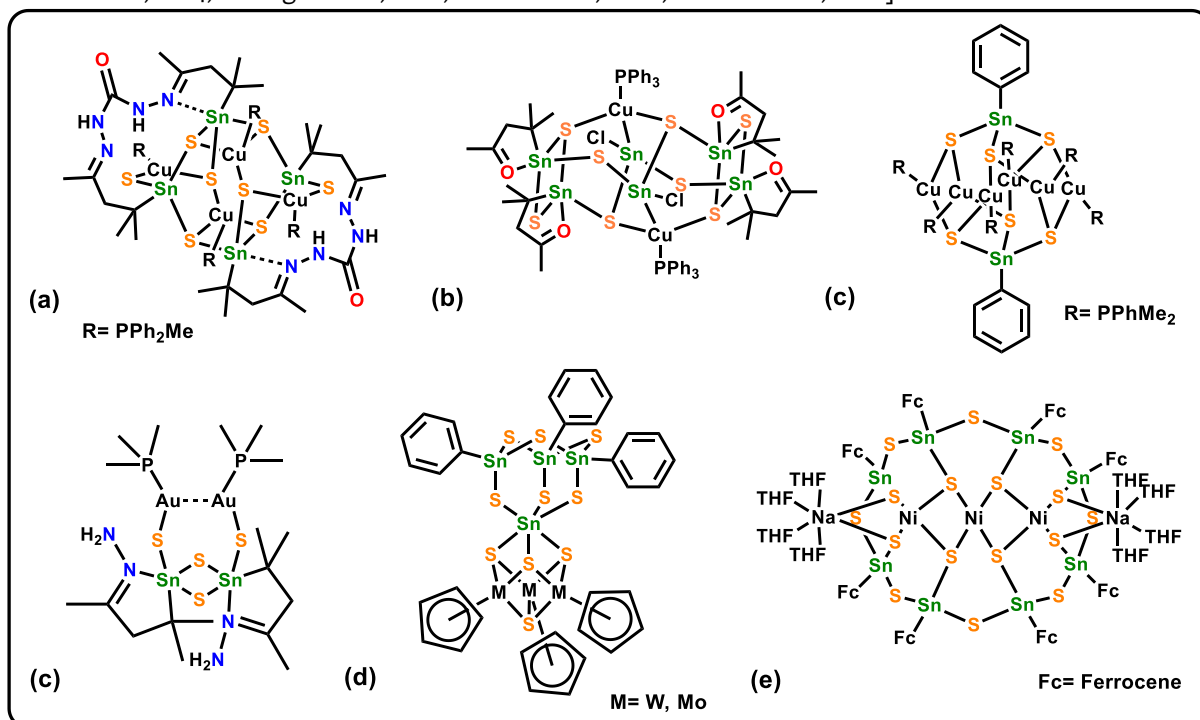
Another interesting route to functionalize monoorganotin sulfides is the introduction of transition metal ions in the inorganic SnS core. The inclusion of transition metal ions leads to a wide range of structures with exciting properties such as optical, photoconductive, photovoltaics etc. [Geringer et al., 2020; Dornsiepen et al., 2017; Eichhöfer et al., 2017]. Such compounds can be synthesized generally in two ways. In one method, the organotin sulfide cluster is directly reacted with the transition metal salt/complex, which results in the rearrangement of the inorganic SnS core. In another method, the organotin sulfide cluster is treated with the excess sulfide ligands followed by a transition metal ion source [Dornsiepen et al., 2019c; Eußner et al., 2014].

Chart 1.7: Representative examples of monoorganotin sulfides [Eußner et al., 2013; Fard et al., 2009a; Halvagar et al., 2010; Leusmann et al., 2016; Pöhlker et al., 2010; Rinn et al., 2016].



In most of the transition metal ion functionalized organotin sulfide clusters, generally, in a first step the organotin sulfide core R₄Sn₄S₆ reacts with excess sulfide ligands to generate an intermediate anion RSnS₃³⁻ which is found to be highly reactive towards various transition metal ions [Fard et al., 2009b]. Among transition metal ions, copper has shown a higher affinity towards monoorganotin sulfides. Cu(I) was observed to be very common in such

Chart 1.8: Representative examples of monoorganotin ternary sulfides [Dornsiepen et al., 2017, 2019b; Eußner et al., 2014; Halvagar et al., 2010; Hauser et al., 2002; Pöhlker et al., 2010].

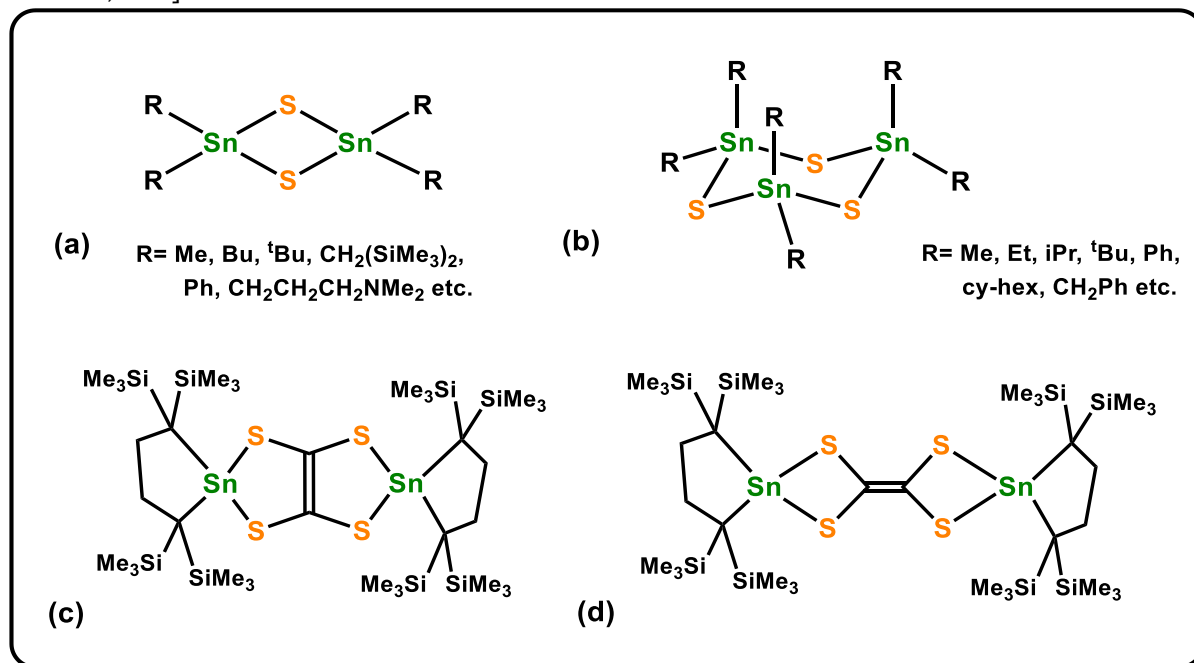


ternary monoorganotin Cu/Sn/S clusters, but a rare example of Cu in +II oxidation state is recently isolated [Dornsiepen et al., 2019c]. The reduction of Cu(II) to Cu(I) was observed routinely in these compounds due to the reductive character of sulfide ligands. More

recently, these ternary organotin sulfides have also been isolated with various coinage metal ions such as Ag, Au, Zn, and other transition metals such as Mo, W, Pt, Ni etc. [Barth et al., 2013; Dornsiepen et al., 2019b; Eußner et al., 2014; Geringer et al., 2018; Pöhlker et al., 2010] (Chart 1.8).

The structure of diorganotin sulfides mainly depends on the organic group attached directly to the Sn center. Generally, these are synthesized by the direct reaction of diorganotin halides (R_2SnCl_2) with sodium sulfide in different stoichiometric ratios. Reaction in 1:1 molar ratio affords $(R_2SnS)_2$ [Leung et al., 2000] [Chart 1.9 (a)] type product whereas 2:1 reaction affords $ClR_2SnSSnR_2Cl$ type compound [Beckmann et al., 2001]. In another method, initially, it was proposed to synthesize these dinuclear diorganotin sulfides $ClR_2SnSSnR_2Cl$ from the reaction of R_2SnS with appropriate diorganotin precursor R_2SnCl_2 , which was later isolated by Beckmann and group. Diorganotin sulfides compounds are known to show distinct structures like cyclic trimers $(R_2SnS)_3$ {R=Me, Ph} [Chart 1.9 (b)] having a six-membered Sn_3S_3 ring [Lange et al., 2002], cyclic dimer $(R_2SnS)_2$ having four-membered Sn_2S_2 ring [Dostál et al., 2007], polymeric chain $(iPr_2SnS)_n$ [Puff et al., 1978] etc. The size of the ring also depends on the bulk of the substituent present on the tin center. Four membered Sn_2S_2 rings in these compounds can also be stabilized using organic ligands with intramolecular coordination or chelating groups on the tin precursor [Dostál et al., 2007; Leung et al., 2000]. Recently, Yan and coworkers reported two diorganotin sulfide compounds that were isolated as $R_2SnS_2C=CS_2SnR_2$ and $[R_2Sn]_2(\mu^2-S_2C=CS_2)$ { $R_2=C(SiMe_3)_2CH_2CH_2C(SiMe_3)_2$ } as a result of a reaction between diorganostannylene with CS_2 in the presence of elemental sulfur [Yan et al., 2016] [Chart 1.9 (c) and (d)]. The activation of CS_2 was observed in the reaction leading to the formation of fused five and four-membered rings along with a C-C double bond.

Chart 1.9: Representative examples of di- and triorganotin sulfides [Dostál et al., 2007; Lange et al., 2002; Yan et al., 2016].



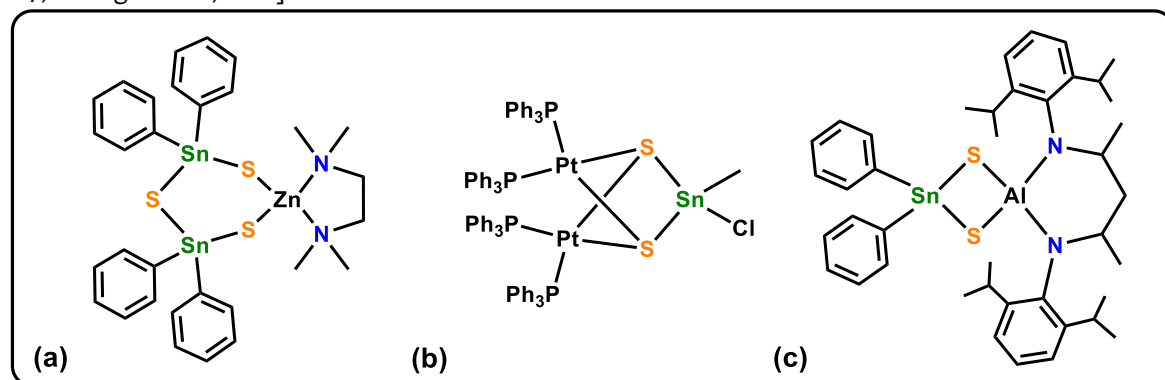
Because of the fewer coordination sites available for the derivatization, diorganotin compared to monoorganotin sulfides, display a limited variety of ternary sulfide-based structures [Yang et al., 2006].

However, few novel structures for diorganotin ternary sulfides are reported, where a diorganotin precursor was reacted with a ligand-protected transition metal sulfide compound. A six-membered Zn/Sn/S compound [Chart 1.10 (a)] was synthesized by the reaction of in-situ prepared TMEDA protected zinc sulfide with Ph_2SnCl_2 . The six-membered Sn_2ZnS_3 core is in twist boat-like conformation with both Sn and Zn atoms

present in distorted Td geometry [Fuhrmann et al., 2017]. In another example, an ionic compound of Pt/Sn/S [Chart 1.10 (b)] is reported where the Sn center is bridged by the two μ_2 -S of the Pt₂S₂ ring possessing TBP geometry. In this instance, phosphine-protected platinum sulfide was reacted with Me₂SnCl₂ followed by NH₄PF₆ [Audi Fong et al., 2001].

Triorganotin halides having more bulky groups tend to form low nuclearity compounds [Dostál et al., 2007; Singh et al., 2009, 2011]. Due to the presence of three organic substituents present on the tin atom, three of the coordination sites are occupied and only allow to form compounds with distorted Td geometry.

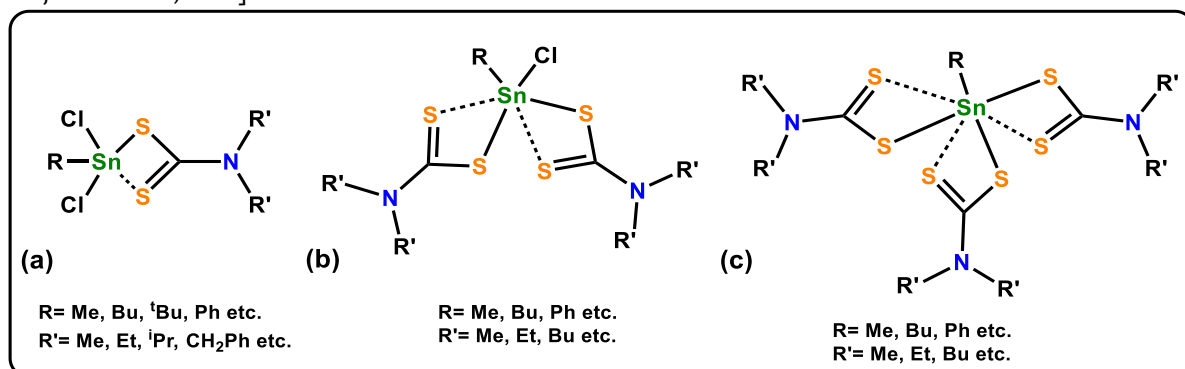
Chart 1.10: Representative examples of diorganotin ternary sulfides [Audi Fong et al., 2001; Fuhrmann et al., 2017; Geringer et al., 2018].



• Organotin dithiocarbamates

Dithiocarbamates (DTCs) belong to the carbamate family of ligands obtained by the replacement of two oxygen atoms with two sulfur atoms. These ligands are denoted as R₂NCS₂ and are easily prepared from the reaction of a secondary amine with carbon disulfide in the presence of a base. These sulfur-based ligands have a higher affinity to bind with the different metal ions. Organotin DTCs are considered to be an important class of organotin compounds due to their stereospecific synthesis and various biological applications [Adeyemi et al., 2018]. These compounds are well known for their stability arising from their resonating structures. X-ray crystal structures of the previously reported organotin DTCs include majorly the mononuclear products, i.e., RSn(S₂CNR'₂)Cl₂, RSn(S₂CNR'₂)₂Cl, RSn(S₂CNR'₂)₃ obtained by different stoichiometric reactions of RSnCl₃ with DTC ligands [Kellö et al., 1995; Li et al., 2005; Sirajuddin et al., 2016] (as shown in Chart 1.11). DTC ligands attached to the organotin moiety are generally arranged asymmetrically in space. The coordination geometry of the Sn center in these compounds depends upon the coordinating modes of the DTC ligand.

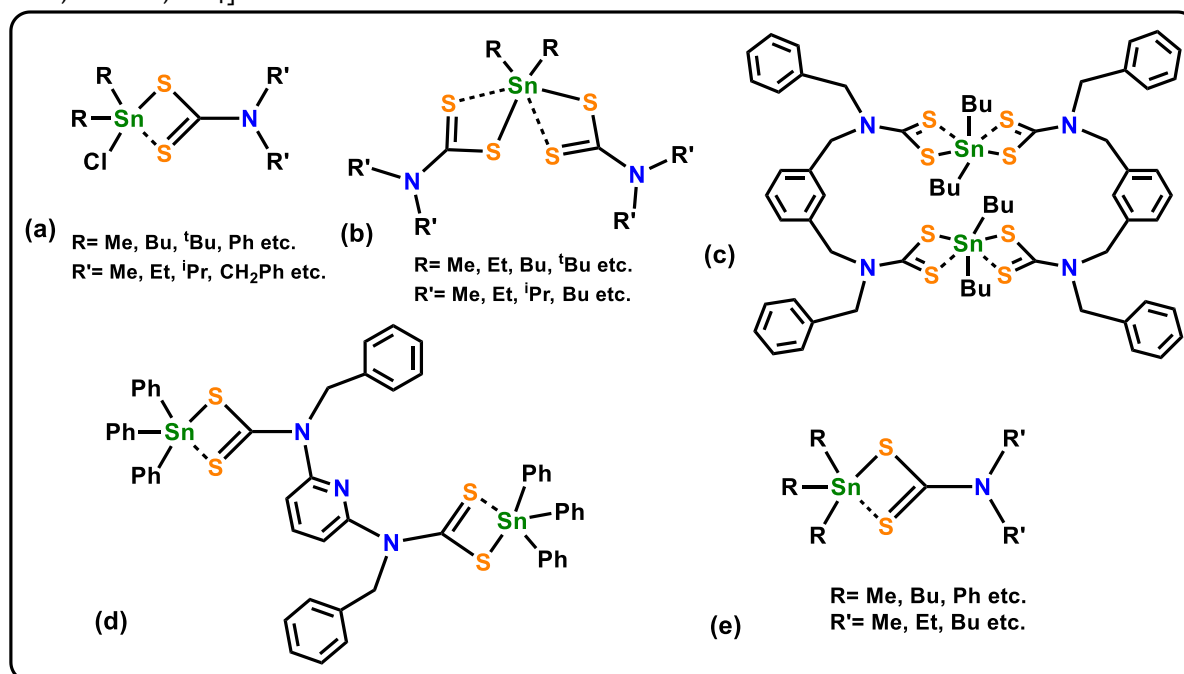
Chart 1.11: Representative examples of monoorganotin dithiocarbamates [Kellö et al., 1995; Li et al., 2005; Sirajuddin et al., 2016].



Diorganotin derivatives of DTC are the most studied and explored compounds in this category. These compounds are obtained by two different stoichiometric reactions of

R_2SnCl_2 and DTC ligand, which yield products with the generic formula $R_2Sn(S_2CNR'_2)_2$ and $R_2Sn(S_2CNR'_2)Cl$ [Yin et al., 2006] [Chart 1.12 (a) and (b)]. Depending on the bulk of the organotin substituent, $R_2Sn(S_2CNR'_2)_2$ was found to exist in either cis or trans geometries accordingly. Different structural motifs originate from the difference in the coordinating modes of the DTC ligand. In contrast, the triorganotin DTC compounds show only one type of structure, $R_3Sn(S_2CNR'_2)$ [Kana et al., 2001] [Chart 1.12 (e)]. Recently, Yu *et al.* reported diamine functionalized DTC compounds of di- and triorganotin precursors where they have observed the formation of an interesting macrocyclic and open-chain structure [Yu et al., 2014] [Chart 1.12 (c) and (d)].

Chart 1.12: Representative examples of di- and triorganotin dithiocarbamates [Kana et al., 2001; Yin et al., 2006; Yu et al., 2014].

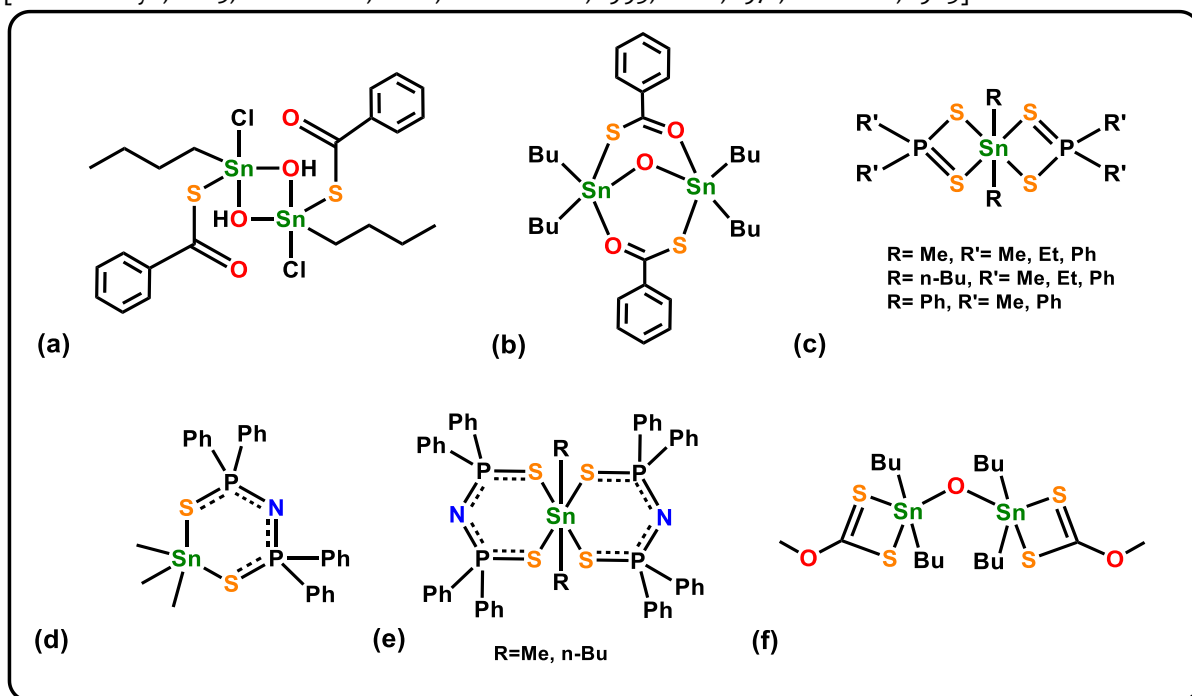


• Organotin thiocarboxylates/thiols/thiophosphinates/xanthates

Numerous reports on Sn-S unit containing organotin compounds, which originate from different types of sulfur-based ligands such as thiocarboxylates, thiols, thiophosphonates and xanthates are known in the literature. These ligands can be represented by the general formula $RC(O)S^-$, ROS^- , $R_2PS_2^-$, and $ROCS_2^-$ respectively. All the ligand systems are monoanionic but differ in their coordinating modes with metal center. The general reaction scheme for organotin thiocarboxylate proceeds through the chloride exchange with the thiocarboxylate ligand.

A few representative examples are shown in Chart 1.13. An example of a monoorganotin derivative constituting a Sn_2O_2 ring along with unidentate thiocarboxylate coordination [Bhattacharya, 2005] as well as a diorganotin derivative having a Sn-O-Sn motif supported with two κ^2 -thiocarboxylate bridgings are reported [Hoch, 1971]. While organotin dithiophosphinates in general shows mononuclear structure whereas, reactions of imido-substituted dithiophosphinates with organotin precursor results in the formation of metal-containing inorganic heterocycles [Casas et al., 2000]. As shown in Chart 1.13, only two such structures are known; a six-membered heterocycle capturing a triorganotin moiety [Chart 1.13 (d)], the other example is of a diorganotin moiety linking two six-membered heterocycles [Chart 1.13 (e)] [Haiduc et al., 1993]. Xanthates ($ROCS_2^-$), on the other hand, are the extended class of DTCs that are synthesized by the reaction of a primary alcohol with carbon disulfide in the presence of a base [Rao et al., 1983]. The structural chemistry of organotin xanthates is similar to that of organotin DTCs [Chart 1.13 (f)].

Chart 1.13: Representative examples of organotin thiocarboxylates/thiols/thiophosphonates/xanthates [Bhattacharya, 2005; Casas et al., 2000; Haiduc et al., 1993; Hoch, 1971; Rao et al., 1983].



1.3 Materials and Biological Applications of Organotin Compounds containing Sn-O and Sn-S units.

Organotin compounds have been finding their use in various materials and biological applications for the last few decades. Various applications of organotin compounds, including materials and biological applications, have been reviewed in great detail in the past [Adeyemi et al., 2018; Ali et al., 2018; Gao et al., 2019; Lanza et al., 2019]. This section will mainly present here the recent applications of molecular organotin compounds containing Sn-O and Sn-S units. For the sake of better clarity, we will discuss the materials and biological applications of organotin compounds as two separate subheadings.

1.3.1 Materials Applications

Organotin compounds have been widely explored for their applications in materials science. Due to their structural diversity, organotin compounds can be further modified structurally in order to get desired property. Various materials applications of organotin compounds containing Sn-S as well as Sn-O units are discussed in this section.

- **Application in Resistive Switching Materials**

Over the past few decades, the concept of resistive switching memory gained attention due to the increasing demand for data storage and energy-efficient data processing. Resistive switching materials are widely used in various devices such as non-volatile memory, information security, molecular switching, and artificial neural networks. The resistive switching phenomena in the materials can occur due to the charge trapping/detrapping, oxygen exchange, or electrochemical redox reactions [Shi et al., 2021]. Various materials such as NiO, CoO, TiO₂, ZnO, TaO, Sb₂S₃, SnO₂ etc. [Inoue et al., 2013; Perla et al., 2021; Prakash et al., 2013; Simanjuntak et al., 2016; Yanagida et al., 2013; Boratto et al., 2017; Wu et al., 2014; Yun et al., 2021] have been investigated as resistive switching materials in the past.

Rahmani *et al.* have shown memristive behavior of SnO₂ deposited over Zinc Tin Oxide (ZTO) on the TiN substrate [Rahmani et al., 2020]. The primary device structure was W/SnO₂/TiN, where the thin film of SnO₂ has sandwiched between TiN and W electrodes.

In a comparative study, it was observed that the device W/SnO₂/ZTO/TiN had a lower reset voltage and a larger memory window than the device W/SnO₂/TiN. The deposition of ZTO film on the TiN substrate had a crucial role in the improvement of device memory behavior, which was attributed to the oxygen ion migration in the SnO₂/ZTO matrix. Yuan *et al.* have demonstrated the self-rectified memory behavior of SnO₂ using various metal-based top electrodes on a new prototypical device structure of metal/SnO₂/FTO (fluorinated tin oxide) [Yuan *et al.*, 2020]. Among various metal electrodes, the aluminium (Al) and gold (Au) top electrodes showed the self-improved resistive switching characteristics of the device compared to silver (Ag) electrode. The conduction mechanism in this device was explained on the basis of the migration of the oxygen vacancies.

Recently, there has been increasing interest in resistive switching devices based on molecular complexes. Molecular complexes may present various advantages such as solubility, flexibility, light weight, and ease of processing etc. In the pioneering work, Goswami *et al.* have successfully reported two azo-substituted dianionic complexes of [RhL₃][CF₃SO₃] {L= (4-chlorophenylazo)pyridine} and [RuL₃][PF₆]₂ {L= (2-phenylazo)pyridine} as the active material for the resistive switching memory device [Goswami *et al.*, 2017b; Paul *et al.*, 2012]. In the detailed mechanistic study, it was observed in the case of [RhL₃][CF₃SO₃] complex, two out of the three ligands exhibited non-innocent behavior in the complex, which was considered to be the key feature of memristive behavior. The device showed consistent response over 100 cycles without degradation of the material and also exhibited the ON/OFF ratio of 10³. In the case of ruthenium (II) [RuL₃][PF₆]₂ {L= (2-phenylazo)pyridine} the device exhibited an excellent memory behavior with high repeatability (~350 devices), long retention (~10¹² cycles), and stability up to 10⁶ sec. Utilizing different techniques such as in-situ Raman, Uv-Vis spectroscopy, and spectro-electrochemistry, it was demonstrated the role of redox-active ligand L= (2-phenylazo)pyridine, in the switching mechanism of the device.

Another report by Hong *et al.* presented a phosphole oxide containing organogold (III) complex, which exhibited interesting ternary resistive switching memory characteristics [Hong *et al.*, 2016]. The device structure contained the organogold (III) complex as the active material sandwiched between ITO stripped glass substrate and Al electrode. The device worked at a low threshold voltage with an exceptionally high OFF/ON1/ON2 ratio of 1:10³:10⁷. It was proposed that, two charge-trapping sites located in the cyclometalated ligand and the benzophosphole oxide moiety in organogold (III) complex play a role in the observed multilevel memory properties.

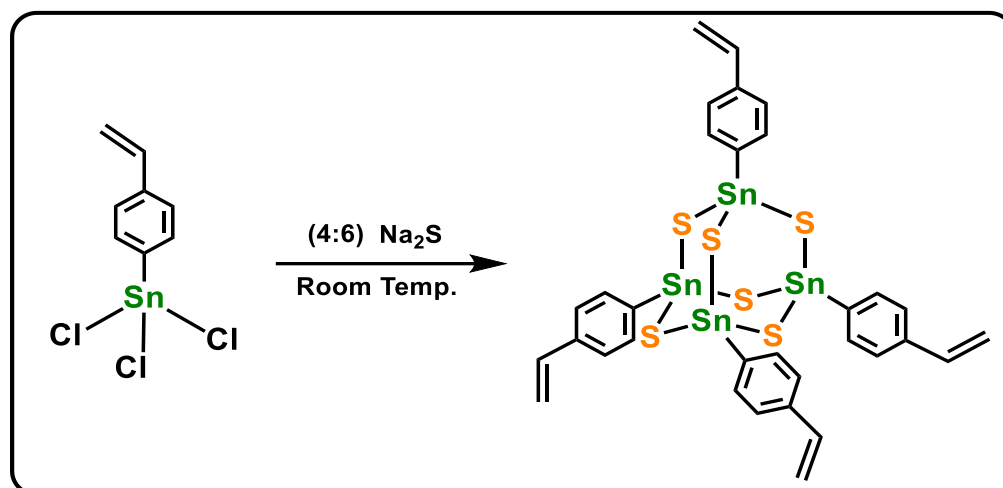
Very recently, our research group has designed, synthesized and structurally characterized a tetranuclear organotin sulfide cage with 2-phenylazophenyl substitution on the tin center and utilized it as the active material for the resistive memory device. The complex exhibited an excellent memory behavior at a low threshold write voltage of -1.4 V and a good ON/OFF ratio of 10³ with high retention over 10000s [Mishra *et al.*, 2020]. We have further reported the synthesis of a hydroxo-methoxo bridged dinuclear organostannoxane [Mishra *et al.*, 2021b] and a non-football type dodecanuclear organostannoxane [Mishra *et al.*, 2022b]. These complexes were successfully employed as the active material for NDR (negative differential resistance) device.

• Non-linear Optical (NLO) Materials

Non-linear optical properties have been reported since a very long ago for organometallic complexes; surprisingly, only a few investigations of NLO properties for organotin complexes have been reported [Dornsiepen *et al.*, 2019a; García-López *et al.*, 2016; Luo *et al.*, 2022; Rivera *et al.*, 2006; Rosemann *et al.*, 2016b, 2018]. The possibility of a large structural derivatization amongst organotin complexes makes this further desirable to study such applications. The present section will present a few recent investigations on molecular organotin complexes as NLO materials.

Very recently, Rosemann *et al.* have reported a tetranuclear organotin sulfide cage [(RSn)₄S₆]; R = 4-(CH₂=CH)-C₆H₄ [Scheme 1.2], which has an adamantane type Sn₄S₆

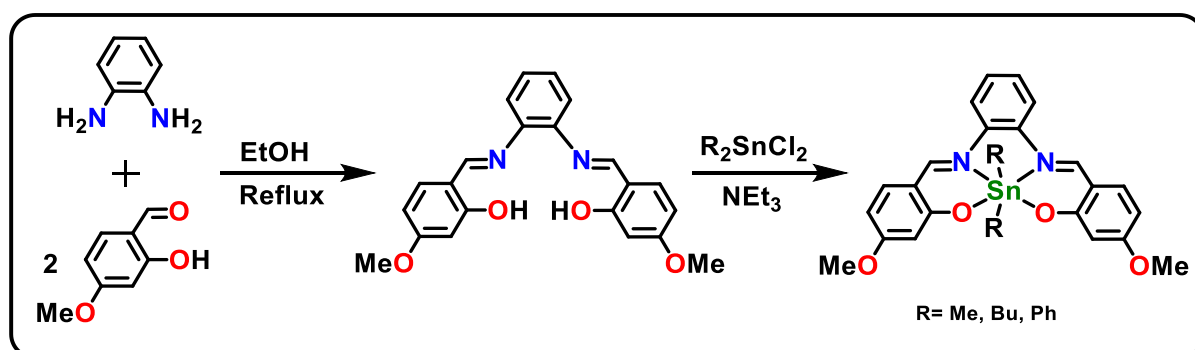
core[Rosemann et al., 2016a]. The complex was isolated as an amorphous material with an inorganic core decorated with well π -conjugated organic substituent. Also, the complex was found to be air and thermally stable up to 200°C. The central core $[\text{Sn}_4\text{S}_6]$ of the complex acts as a non-linear medium. The device fabricated using $[(\text{R}\text{Sn})_4\text{S}_6]$, on excitation of a continuous wave laser of $\lambda=800\text{nm}$ (near IR) on the matrix emitted a warm white light.



Scheme 1.2: Synthetic scheme of $[(\text{R}\text{Sn})_4\text{S}_6]$; R = 4-(CH₂=CH)-C₆H₄ exhibiting NLO property [Rosemann et al., 2016a].

Dornsiepen *et al.* have extended non-linear optical studies of organotin complex $[(\text{R}\text{Sn})_4\text{S}_6]$ with various aromatic substitutions [R=phenyl, cyclopentadienyl, cyclohexyl, benzyl, CH₂CH₂(C₆H₄)CO₂Et] [Dornsiepen et al., 2019a]. The adamantane type Sn₄S₆ core is known to behave as a non-linear medium when irradiated with an IR laser diode to produce highly directional white light. The comparative NLO studies with various substituents have found that organotin complexes of the class $[(\text{R}\text{Sn})_4\text{S}_6]$ generate white light with similar emissions. This observation counters the previous assumption of having aromatic substitution as the essential condition for a white-light generation; instead, it is now proposed to be the presence of cyclic substituent on the Sn center.

There are also few reports of organotin complexes in the literature whose NLO behavior is computed theoretically [Jiménez et al., 2018]. Muñoz-Flores *et al.* have reported a series of diorganotin derivatives of Schiff bases [Scheme 1.3] that estimated interesting second-order non-linear optical properties [Muñoz-Flores et al., 2014]. NLO properties calculated for the organotin complexes using the EFISH technique are comparable with that of previously reported nickel-based complexes. Feng *et al.* have documented a series of dinuclear monoorganotin carboxylates $[(n\text{BuSn})_2(\text{TEOA})_2\text{L}_2]$ {TEOA= triethanolamine, L= monocarboxylates} synthesized using the solvothermal method and successfully demonstrated their potential candidature in third-order NLO properties [Feng et al., 2021].



Scheme 1.3: Synthetic scheme of diorganotin Schiff base complex exhibiting NLO property [Muñoz-Flores et al., 2014].

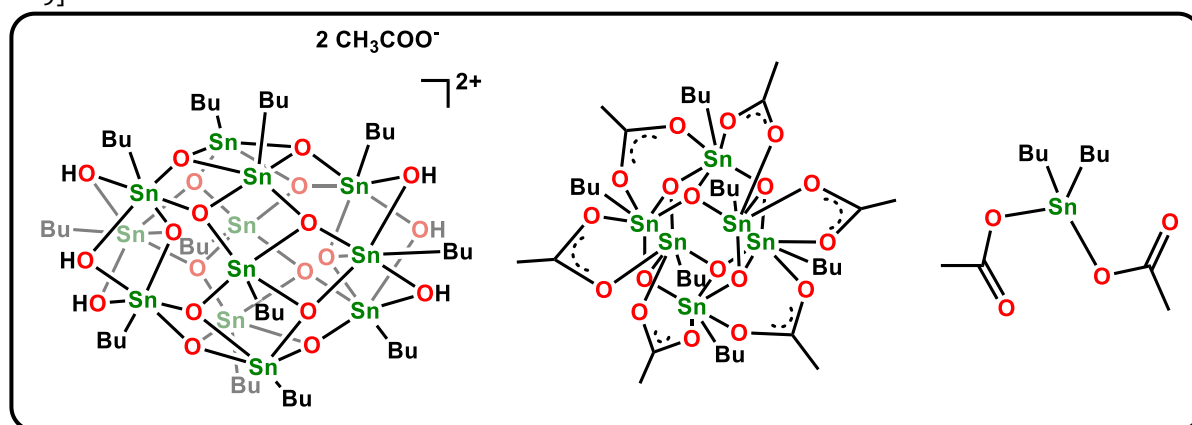
Other reports on NLO properties of organotin complexes include organotin Schiff base complexes by Rivera et al. [Rivera et al., 2006] and diorganotin based polyoxotungstate systems by Guan and coworkers [Guan et al., 2006].

• Application in Photoresist Materials

Molecular organometallic complexes have always been a preferred choice of candidates for highly dense integrated circuits. Organometallic complexes have been explored as a photoresist for extreme-ultraviolet lithography (EUVL), in which organic substituents on the metal center generally direct the formation of the resultant metal oxide network [Satyanarayana et al., 2014; Yu et al., 2021].

Sharps *et al.* have synthesized three organotin complexes with the same organic ligand, i.e., dodecanuclear n-butyl stannic acid $[(\text{BuSn})_{12}\text{O}_{14}(\text{OH})_6]^{2+}(\text{CH}_3\text{COO}^-)_2$, hexanuclear drum $[\text{BuSn}(\text{O})\text{O}_2\text{CCH}_3]_6$ and dibutyltin diacetate $\text{Bu}_2\text{Sn}(\text{O}_2\text{CCH}_3)_2$ [Chart 1.14] and used them as photoresist for extreme-ultraviolet lithography [Sharps et al., 2019]. On exposure to UV photons, the chemical transformation occurs in the film, leading to the decomposition of the organic part resulting in the formation of the insoluble metal oxide network. The product patterning generally depends on the coordination of metal as well as the ligand arrangement in the complex.

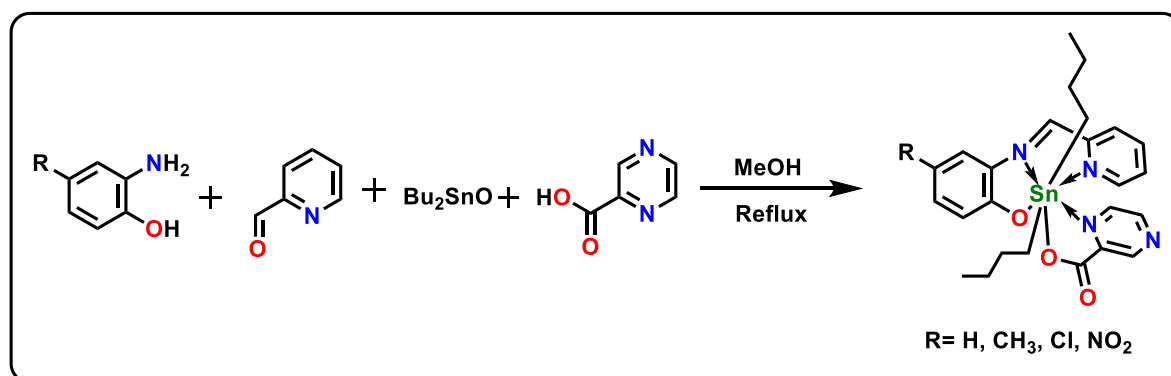
Chart 1.14: Representative examples of organostannoxanes for photoresist application [Sharps et al., 2019].



• Optoelectronic Application

Next-generation electronics demand easily processable, flexible, thermally stable and low-cost efficient materials. Metal-Semiconductor-Metal (MSM) devices are simple and sustainable devices to fabricate in which a semiconducting layer is sandwiched between two metal contacts. These metal contacts are considered according to their flexibility, transparency, and thermal stability [Jou et al., 2015].

Sánchez-vergara *et al.* have reported Schiff base, and pyrazine carboxylic acid derived four organotin complexes involving multidentate coordination [Scheme 1.4] and analyzed the effect of different substituents on the tin for their the optoelectronic properties [Sánchez-vergara et al., 2021]. The complexes have shown a good band gap (1.23-1.40eV) suitable for electronic applications. ITO was replaced with PEDOT:PSS and zinc-hexadecafluoro-phthalocyanine (ZnPcF_{16}), which acts as hole and electron carriers, respectively. Due to the highly π rich character of ZnPcF_{16} , the charge generated on the molecule gets delocalized easily throughout the film. The complex with the lowest band gap is found to exhibit better optoelectronic response compared to others at a low voltage of $<1.5\text{mV}$.



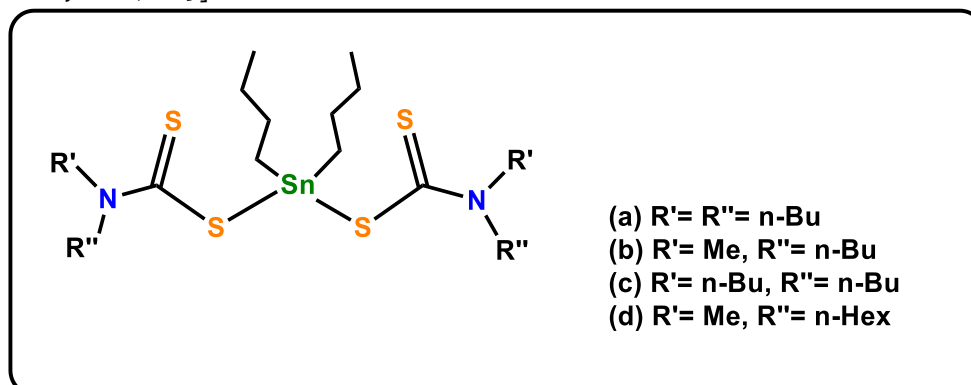
Scheme 1.4: Synthetic scheme of dibutyltin Schiff base complexes used in optoelectronic application [Sánchez-vergara et al., 2021].

• Single Source Precursor to Nanomaterial

Numerous methods to synthesize nanomaterials are known in the literature, such as chemical vapour deposition (CVD) [Huang et al., 2015], spray pyrolysis [Yassin et al., 2015], hot injection method [Huang et al., 2017], atomic layer deposition [Pyeon et al., 2018], thermal evaporation [Lei et al., 2020], hydrothermal method [Zhang et al., 2011], solvothermal method [Mishra et al., 2017] etc. The use of single-source molecular precursor in the above-mentioned methods is gaining increasing importance for synthesizing nanomaterials. Literature reports a plethora of molecular organotin complexes having Sn-S and Sn-O units that have been used as single-source precursors for the formation of various nanoscale entities such as SnO, SnO₂, SnS, SnS₂ etc. [Adeyemi et al., 2020; Butt et al., 2018; Kana et al., 2001; Kumar et al., 2011; Mahon et al., 2005; Menezes et al., 2010; Nath et al., 2009b; Okuya et al., 2001; Řičica et al., 2015]. Three phases of tin sulfides, SnS, SnS₂ and Sn₂S₃, have a band gap of 1.3, 2.18 and 0.95 eV falling in the semiconducting range and being well suitable for electrical and electronic applications [Gedi S, Reddy VRM, 2019; Jethwa et al., 2021; Kuepper et al., 2003; Urbaniak et al., 2017; Voznyi et al., 2016; Wang et al., 2017b].

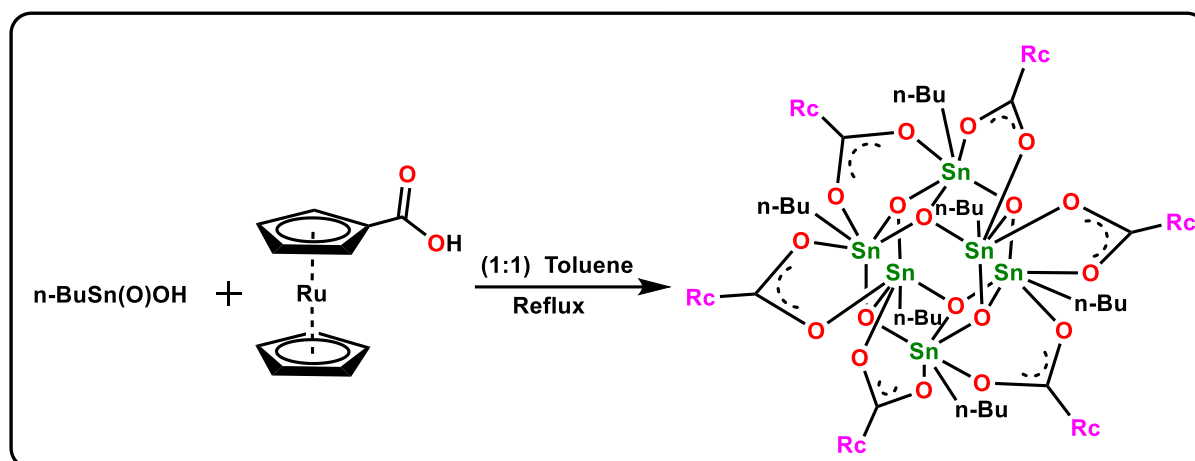
Ramasamy *et al.* have reported eight diorganotin dithiocarbamates with a different substituent on the tin as well as on dithiocarbamate ligands (Chart 1.15) [Ramasamy et al., 2013]. All the complexes were thermally stable up to 200°C. The conversion of four out of these eight complexes to the corresponding nanostructures was carried out using the aerosol-assisted chemical vapour deposition (AACVD) technique. The deposition of SnS thin films was optimized at a temperature between 400 to 530°C. Characterization of the films reveals the formation of an orthorhombic phase of SnS nanostructure.

Chart 1.15: Representative examples of dibutyltin dithiocarbamate used as a single source precursor [Ramasamy et al., 2013].



Kundu *et al.* have reported a series of mono- and diorganotin derivatives of ruthenocene carboxylic acid [Kundu et al., 2014a]. One of the six organotin carboxylates, hexanuclear organostannoxane [n-BuSn(O)OOCRC]₆ {RC = ruthenocene} [Scheme 1.5] was converted to the binary (RuSn)O₂ phase by heating in the presence of oxygen. The binary (RuSn)O₂ phase

was formed at a temperature of 400°C, whereas on continuous heating to 700°C, it was observed that two binary oxide phases of RuO₂ and SnO₂ got separated.



Scheme 1.5: Synthetic scheme of ruthenocene substituted hexanuclear organostannoxane used as single source precursor [Kundu et al., 2014a].

1.3.2 Biological Applications

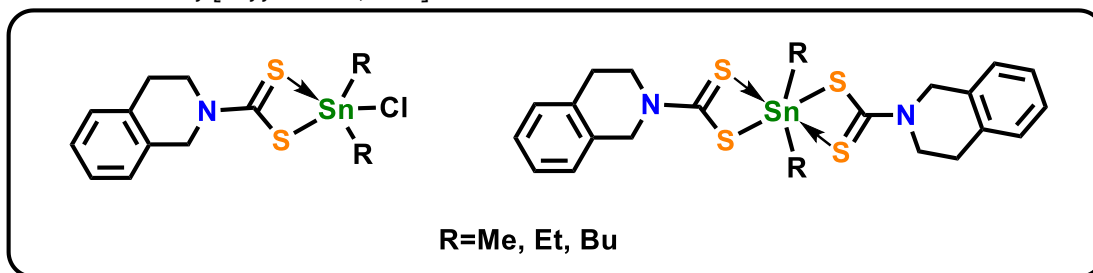
Among the organometallic compounds, organotin compounds are the most widely studied for their biological properties. Furthermore, organotin compounds have shown a wide range of biological activities such as antibacterial [Nath et al., 2006], antioxidant [Antonenko et al., 2020; Etaiw et al., 2018], anti-inflammatory [Nath et al., 2009a], amoebicidal [Saxena et al., 1982], anti-leishmanial [Ahmad et al., 2020], etc. in the past. Various Biological properties of organotin compounds have been reviewed earlier in great detail [Adeyemi et al., 2018; Hadi et al., 2019]. This section will present a recent literature review of some biologically active organotin compounds.

- **Antibacterial Activity**

Bacterial infection, as well as contamination, is still a challenge for the world. Even though a number of antibiotics have been discovered for different bacterial infections, millions of infectious illnesses are being reported every year from antibiotic-resistant bacteria. Many studies have been carried out in the past few decades to overcome this issue by discovering new antibacterial drugs for medicinal use as well as new materials for antibacterial surface coatings to stop the spread of infection. In general, the antibacterial activity of tri- and diorganotin complexes is found to be significantly better compared to the monoorganotin complexes.

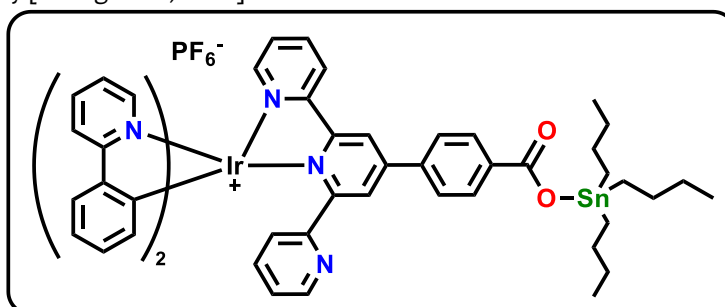
Hu *et al.* have reported two triorganotin carboxylates derived from coumarin functionalized carboxylic acid [Hu et al., 2018]. Interestingly, the coumarin-based ligand was substituted with the cyano group making it easier to bind with organotin moiety. As these complexes have shown two-photon absorption in the near IR region, antibacterial studies were carried out using two-photon fluorescence imaging, which indicated the interaction between the complex and bacterial membrane resulting in cell death. The complexes were found to inhibit both gram-positive (*B. subtilis*) and gram-negative (*E. coli*) bacteria efficiently at very low concentrations. Fayyaz *et al.* have reported a series of diorganotin chlorodithiocarbamates/dithiocarbamates R_2SnCIL & R_2SnL_2 [L= 3,4-dihydroisoquinoline-2-(1H)-carbodithioate] and demonstrated the role of Me, Et and Bu substituent and chloro- group on the antibacterial potency of these complexes [Fayyaz et al., 2021] [Chart 1.16]. Organotin derivatives with methyl substituents, due to their higher diffusive property found to be more potent towards antibacterial activity.

Chart 1.16: Representative example of diorganotin chlorodithiocarbamate/dithiocarbamate exhibiting antibacterial activity [Fayyaz et al., 2021].



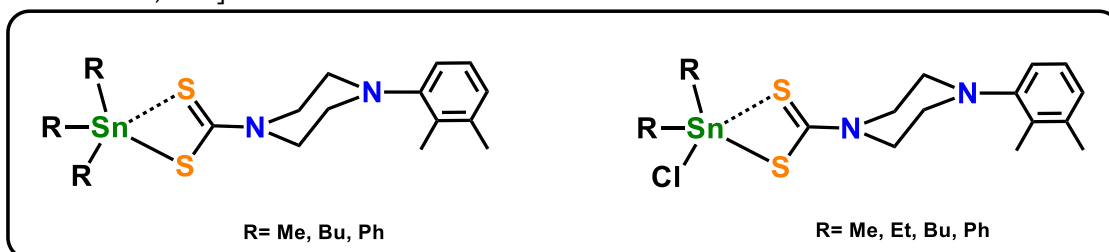
Zhang *et al.* have reported a cyclometallated iridium(III)-organotin(IV) complex showing antibacterial properties towards *S. aureus* than *E. coli* bacteria (Chart 1.17) [Zhang et al., 2020]. Interestingly, the complex was also found to exhibit the three-photon phosphorescence in the near IR region.

Chart 1.17: Representative example of cyclometallated iridium(III)-organotin(IV) complex exhibiting antibacterial activity [Zhang et al., 2020].



Shaheen *et al.* have reported a series of di- and triorgano thiocarbamates [Chart 1.18] that exhibited potential antibacterial activity against *S. aureus*, *B. subtilis*, *P. aeruginosa* and *E. coli* [Shaheen et al., 2012]. These complexes have shown better inhibition against the bacteria compared to the free ligand and standard antibiotic drug ampicillin. Triorganotin derivatives were found to be more active than corresponding diorganotin derivatives.

Chart 1.18: Representative examples of di- and triorganotin DTCs exhibiting antibacterial activity [Shaheen et al., 2012].



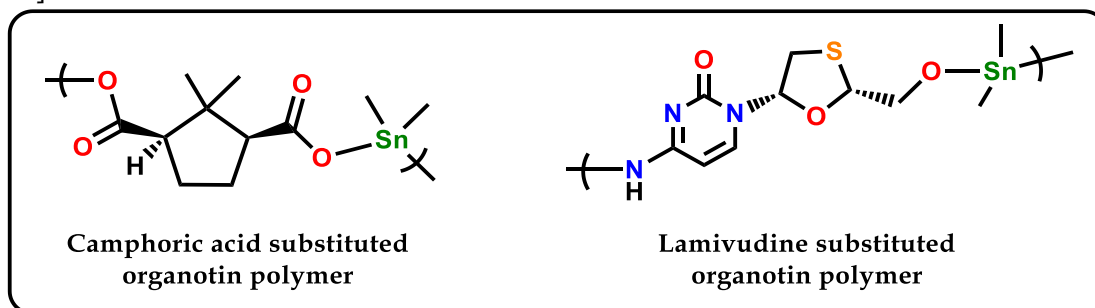
• Antiviral Activity

The current situation of the COVID-19 pandemic is an example of the seriousness of the threat emerging from the viral infection. Organotin-based polymers are found to be effective against viral infections by inhibiting DNA replicated cells. The first antiviral organotin polymer reported was derived from trialkyl (methyl, ethyl) esters of poly(methylmethacrylate) [PMMA] and poly(vinylalcohol). Demonstration of the antiviral compounds towards DNA viruses like herpes simplex type I ,type II, vaccinia virus, Zika virus and RNA viruses like vesicular stomatitis virus, parainfluenza virus type III, HIV etc. have been well documented. A number of organotin polymers with potential antiviral applications have been discussed in the review by Carraher Jr's

group. Two mononuclear diorganotin additives of o-phenanthroline and 2-(2-pyridyl)benzimidazole were tested successfully for the antiviral activities for Herpes simplex virus type I and type II (HSV-I and HSV-II) [Carraher et al., 2014].

Roner *et al.* have reported two polymeric diorganotin derivatives of camphoric acid and lamivudine (Chart 1.19) [Roner et al., 2020]. These polymers are effective towards inhibition of the Zika virus completely at a minimal concentration. These polymers were also found to inhibit the Vaccinia virus to some extent.

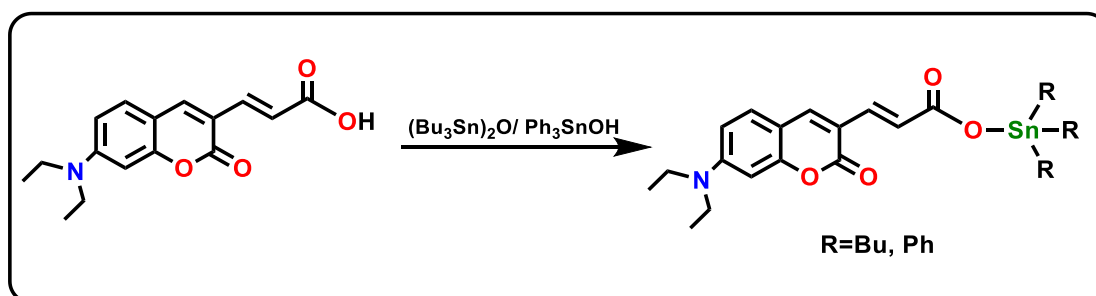
Chart 1.19: Representative examples of diorganotin polymers exhibiting antiviral activity [Roner et al., 2020].



• Anticancer Activity

Cancer is the most deadly disease and requires continuous research in the improvement of anticancer drugs. Cis-platin was the first organometallic compound to be successfully prompted for chemotherapy. The fusion of metal and organic ligands in organometallic compounds helps it in interacting with nucleotides, amino acids, and DNA, thereby facilitating intercalation. The development of anticancer agents based on organotin carboxylates has seen remarkable growth over the past few decades [Devi et al., 2018; Ullah et al., 2019]. The photon absorption/fluorescence phenomenon associated with the complexes helps to visualize the action of the complex on targeted cancer cells. Photon absorption fluorescence microscopy is currently the state of the art technique for biomedical applications.

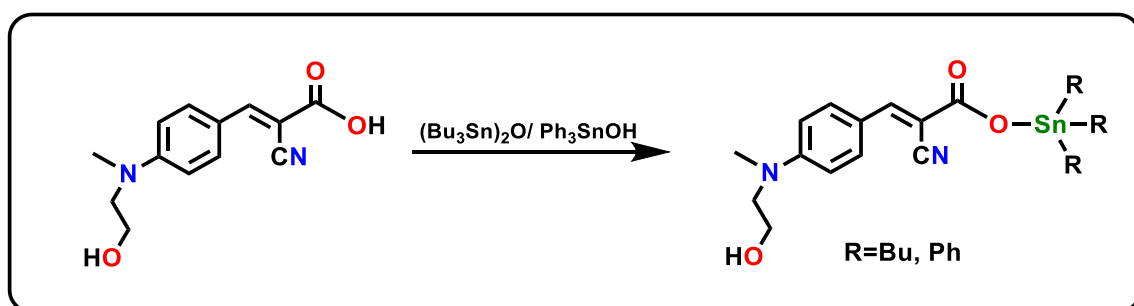
Wang *et al.* have reported two new organotin carboxylates incorporating coumarin unit in the carboxylate ligands (Scheme 1.6) [Wang et al., 2017a]. Two-photon fluorescence microscopy of the complexes revealed the significant penetration strength of these complexes into the cancer cells. Cytotoxicity of the complexes was observed to be higher when compared to cis-platin. Also, a higher selectivity was detected between the cancerous and non-cancerous cells making these complexes potential candidates for chemotherapy agents.



Scheme 1.6: Synthetic scheme of coumarin substituted triorganotin carboxylate exhibiting anticancer activity [Wang et al., 2017a].

Zhang *et al.* reported two triorganotin carboxylates with cyano substitution on carboxylate ligand. Cyano substitution adjacent to carboxylic acid [Scheme 1.7] promotes the deprotonation of carboxylic acid by improving the acidic character [Zhang et al., 2019]. Two-photon absorption phenomena of these complexes was utilized by

two-photon fluorescence microscopy to visualize the penetration of the complex into the cell membrane. The inhibition of selective cancer cells was demonstrated using these complexes on a mouse model successfully, which favors the potential of these organotin complexes as anticancer agents.



Scheme 1.7: Synthetic scheme of triorganotin carboxylates exhibiting anticancer activity [Zhang et al., 2019].

1.4 Scope of the Thesis

This thesis describes the chemistry of organotin compounds leading to the synthesis of cages, macrocycles, and discrete structures containing Sn-O and Sn-S units. The utility of these Sn-S and Sn-O containing organotin compounds as molecular materials in resistive switching devices and antibacterial agents have been studied. This work is described in the following order.

- i) Utilizing the synthetic strategy of the intramolecular N→Sn coordination approach, we have prepared organotin sulfide assemblies.
- ii) Utilizing a similar synthetic strategy of the intramolecular N→Sn coordination approach, we have also prepared and structurally characterized various organostannoxane assemblies.
- iii) We have demonstrated the utility of an organotin sulfide cage as molecular material for the molecular memory device.
- iv) We have also designed and synthesized transition metal ion functionalized organotin sulfide compound and have studied theoretical aspects of the complex.
- v) We have demonstrated an interesting application of a resistive switching device, Negative differential resistance (NDR), utilizing hydroxo-methoxy bridged dinuclear organostannoxanes. Synthesis, structural characterization, and theoretical studies have also been explored.
- vi) By employing a simple synthetic protocol, we have isolated a dodecanuclear organostannoxane with an unprecedented non-football cage type structure. The synthesis, structural characterization, and NDR device studies of this complex have been carried out.
- vii) Finally, we have also studied the antibacterial properties of di- tetra and hexanuclear organostannoxanes as well as some organotin sulfide complexes.

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