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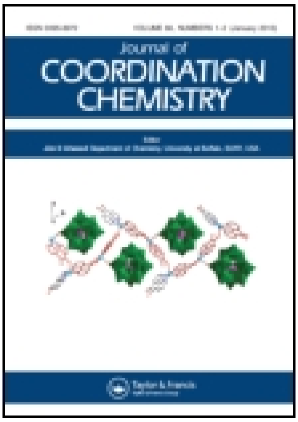

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Review: structural diversity in organotin(IV) dithiocarboxylates and carboxylates

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Review: structural diversity in organotin(IV) dithiocarboxylates and carboxylates

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Organotin(IV) complexes are known for their outstanding structural diversity and applications. Organotin(IV) carboxylates and dithiocarboxylates form an important class of organotin(IV) compounds. The structural diversity of these compounds emanates from several features including flexibility in coordination geometries, coordination numbers, and versatility of the ligands to engage in different modes of chelation from monodentate to bidentate. Triorganotin(IV) complexes with various ligands mostly demonstrate tetrahedral or trigonal bipyramidal symmetry with some distortions, while diorganotin(IV) and chlorodiorganotin(IV) complexes have variation of geometries and coordination numbers. Some monoorganotin(IV) complexes have also been reported with pentagonal bipyramidal geometries.

Keywords: Organotin(IV); Dithiocarboxylates; Carboxylates; XRD; Structural diversity

1. Introduction

Major structural issues in organotin(IV) chemistry are induced by the high coordination ability of tin, more specifically its ability to be involved in either weak or strong intra- or intermolecular coordination [1]. This is because of the availability of empty 5d-orbitals of suitable energy in tetravalent tin. Organotin dithiocarboxylates/carboxylates exhibit a wide variety of structural types [2–7] as the effective nuclear charge on tin increases due to the introduction of electronegative substituents. It is not uncommon that coordination characteristics of tin and hence the structure of an organotin compound differ dramatically in solution and solid states. This occurs when a nucleophilic group is present in the tin moiety or when an organic group linked by a Sn–C bond bears additional functionality with donor properties [8]. Consequently, it leads to modifications in Sn–C cleavage reactivity with respect to analogous organotin compounds where such functionalities are absent [9]. Organotin cluster chemistry also offers some challenging structural issues [10].

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The aim of this review is to summarize categories of organotin(IV) complexes [11–13] in order to illustrate the diverse modes of coordination/association of the dithiocarboxylate/carboxylates, as determined by crystallographic methods.

2. Organotin(IV) dithiocarboxylates

This class of compounds comprises organotin compounds containing Sn–S bond formed via CSS^- group. Di and triorganotin dithiocarboxylates have been widely studied due to their wide range of applications in industry and agriculture and structural diversity.

Based on the available crystal structures, organotin(IV) dithiocarboxylates can be categorized into the following three classes:

(1) Triorganotin(IV) dithiocarboxylates
(2) Chlorodiorganotin(IV) dithiocarboxylates
(3) Diorganotin(IV) bis(dithiocarboxylates)

2.1. *Triorganotin(IV) dithiocarboxylates*

The prototype structure for the majority of complexes in this category, that is, with general formula $R_3Sn(S_2CNR')$, is shown in figure 1 for $Ph_3Sn[S_2CN(C_{12}H_{16})]$ [14]. Here, the tin is coordinated by an asymmetrically coordinating dithiocarboxylate and three carbons from the organic substituents.

In more precisely determined structures, the $Sn–S_{short}$ bond distances fall in the narrow range 2.45–2.48 Å. Similarly, the $Sn–S_{long}$ bond distances fall in the range 2.92–3.24 Å. The longer $Sn–S_{long}$ bond distances are generally found with bulky tin-bound substituents,

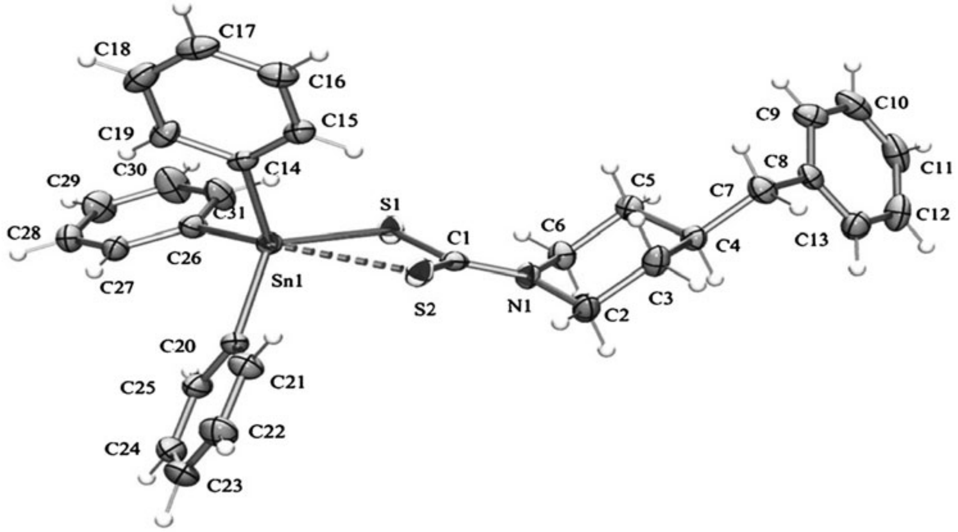


Figure 1. Molecular structure of triphenyltin(IV) 4-benzylpiperidine-1-carbodithioate serving as an example for structures of the general formula $R_3Sn(S_2CNR')$ [14].

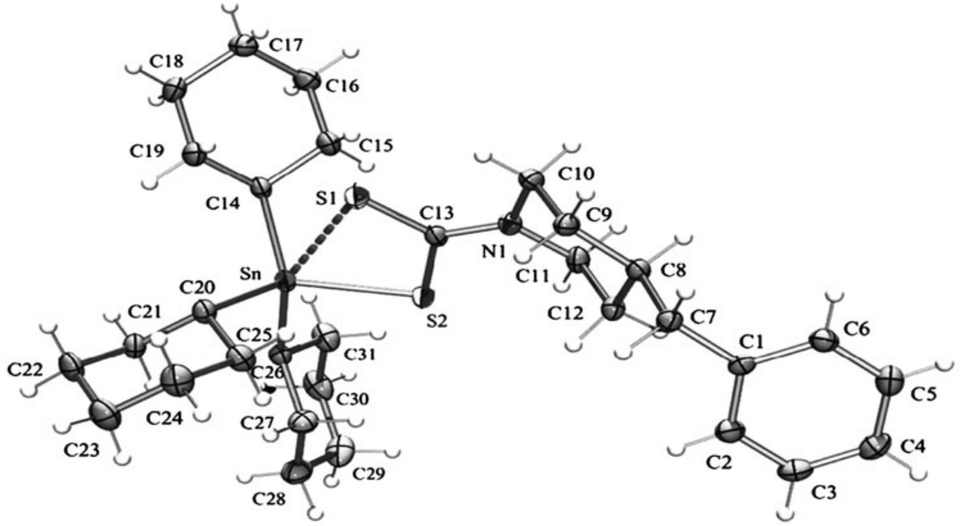


Figure 2. Molecular structure of tricyclohexyltin(IV) 4-benzylpiperidine-1-carbodithioate serving as an example for structures of the general formula $R_3Sn(S_2CNR')$ [14].

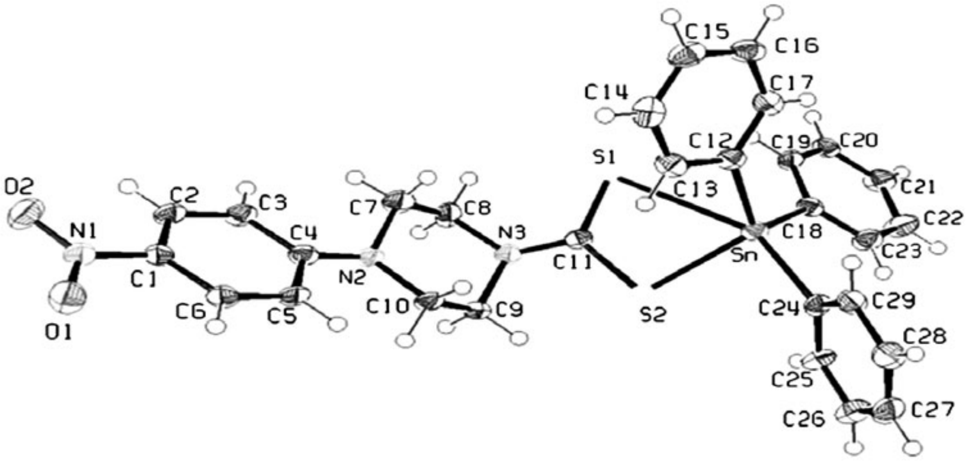


Figure 3. Molecular structure of $Ph_3Sn(C_{11}H_{12}N_3S_2O_2)$, highlighting the trigonal bipyramidal geometry for tin [19].

for example, cyclohexyl [14], shown in figure 2, indicating a possible steric influence upon distances.

The coordination geometry is best described as based on distorted trigonal bipyramidal geometry with sulfur involved in forming longer Sn–S bonds occupying one of the axial positions. Based on the values of τ [15], the structure has a coordination environment for tin more closely resembling trigonal bipyramidal geometry.

There are two $R_3Sn(S_2CNR'_2)$ structures in which one of the tin-bound *R* groups carries additional donors capable of coordination to tin, for example, 2-(4,4-dimethyl-2-oxazolinyl)-3-thienyl group provides an additional nitrogen as donor (Sn–N is 2.723(3) Å), so that the

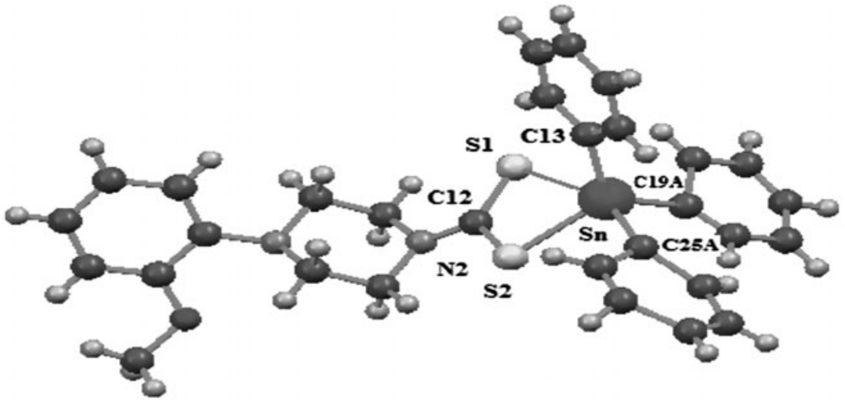


Figure 4. Molecular structure of $Ph_3Sn[C_{30}H_{30}N_2OS_2]$, highlighting the distorted trigonal bipyramidal geometry for tin [12].

coordination number of the tin atom increases to six, based on a skewed trapezoidal bipyramidal geometry [16].

The second example conforming to this type is that of $Ph_2(2\text{-}NC_5H_4CH_2CH_2)Sn(S_2CNMe_2)$ [17]. The dithiocarboxylate is monodentate and the Sn–N bond distance is considerably shorter, that is, 2.486(7) Å, as compared with the previous structure [16]. The coordination geometry is based on a trigonal bipyramid with the axial positions occupied by the more tightly bound sulfur and the nitrogen; the axial S–Sn–N angle is 169.6(2)°.

The structure of $Ph_3Sn[S_2CN(CH_2CH_2)_2NCS_2]SnPh_3$ features the bi-functional, dinegative dithiocarboxylate, $^{-}S_2CN(CH_2CH_2)_2NCS_2^{-}$, and bridges the triorganotin centers, defining coordination geometries almost indistinguishable from those described above for mononuclear $R_3Sn(S_2CNR')$, with asymmetrically coordinating dithiocarboxylate ligands and approximate trigonal bipyramidal geometries [12, 18–23] as shown in figures 3 and 4.

2.2. *Chlorodiorganotin(IV) dithiocarboxylates*

The first class of mononuclear diorganotin dithiocarboxylate structures conforms to the general formula $R_2Sn(S_2CNR')X$, where X is usually chloride. The prototype structures are Bz_2Sn(2-amino-1-cyclopentene-1-carbodithioates)Cl, Et_2Sn(4-(2-methoxyphenyl)piperazine-1-carbodithioate)Cl, and Ph_2SnCl(piperidine-1-carbodithioate) [12, 24, 25]. The tin is five-coordinate, being chelated by an asymmetrically coordinating dithiocarboxylate, a halide and two organic substituents. The Sn–S bond distances, approximately *trans* to the halide, are always longer than the other Sn–S bond distance. The coordination geometry is almost intermediate between square pyramidal and trigonal bipyramidal with the majority of the structures having a small bias toward the former, at least based on the values of τ that generally lie in the range 0.40–0.60. However, there are several structures with values of τ [15] less than 0.40. In the structure of $Ph_2Sn(S_2CNMe_2)Br$ [26], $\tau = 0.38$, which contrasts with $\tau = 0.59$ and 0.57 in structures of $Ph_2Sn(S_2CNEt_2)X$ for X = Cl [27] and X = I [28], respectively.

More tangible explanations are available for the deviation of the coordination geometries toward square pyramidal in $[MeO(O{=})CCH_2CH_2]_2Sn(S_2CNMe_2)Cl$ [29], Me_2Sn [4-ethoxylcarbonylpiperazine-1-carbodithioate]Cl [30] and $Me_2Sn(S_2Cpiperidine)Cl$ [31]. In $[MeO(O{=})CCH_2CH_2]_2Sn(S_2CNMe_2)Cl$ [29], with $\tau = 0.29$, there are two intramolecular Sn–O contacts formed by the carbonyl-oxygens, that is, 2.949(5) and 3.147(5) Å and in the case of Me_2Sn [4-ethoxylcarbonylpiperazine-1-carbodithioate]Cl [30] with $\tau = 0.35$, the lower value of τ is due to the presence of intramolecular interactions.

Finally, in the structure of chlorodimethyltin(IV) 4-benzylpiperidine-1-carbodithioate [14], the presence of intermolecular secondary Sn–S interactions led to formation of a supramolecular zig-zag chain, figure 5, which accounts for variation in coordination geometry. Although, it is likely that it is the more symmetric mode of coordination for the dithiocarboxylates in $R_2Sn(S_2CNR')X$ type structures as reported [22, 25, 32] and shown in figures 6–8.

2.3. *Diorganotin(IV) bis(dithiocarboxylates)*

In terms of crystallographic analysis, the diorganotin bis(dithiocarboxylates), $R_2Sn(S_2CNR')_2$, are the best studied and arguably the most interesting in terms of the observed structural diversity. A systematic analysis of these structures shows that there are four distinct structural motifs. The most prevalent is illustrated in figure 9 for dibutyltin(IV) bis[4-benzylpiperidine-1-carbodithioate] [14].

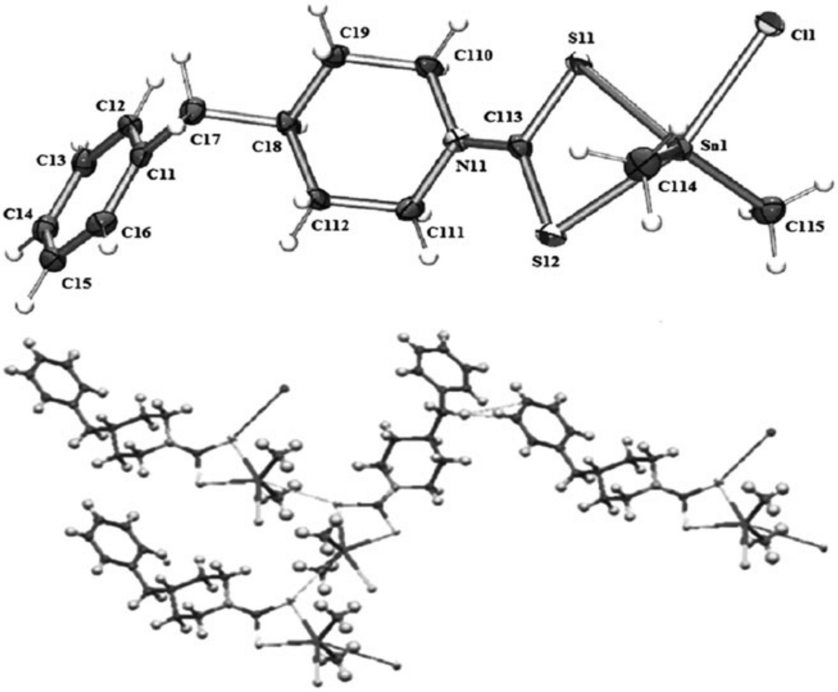


Figure 5. Supramolecular zig-zag chain in the structure of chlorodimethyltin(IV) 4-benzylpiperidine-1-carbodithioate mediated by secondary Sn–S and benzyl C–H interactions [14].

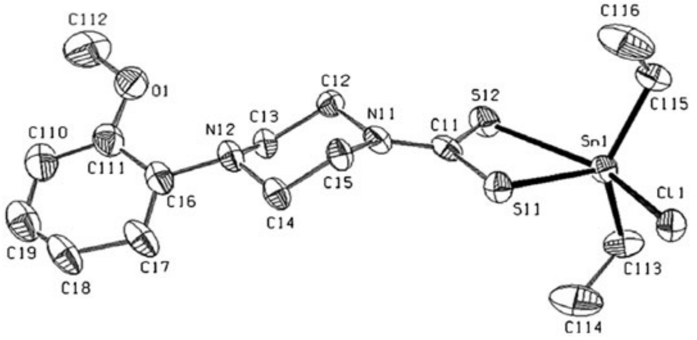


Figure 6. Molecular structure of Et_2Sn, serving as an example for structures of the general formula $R_2Sn(S_2CNR')X$ [24].

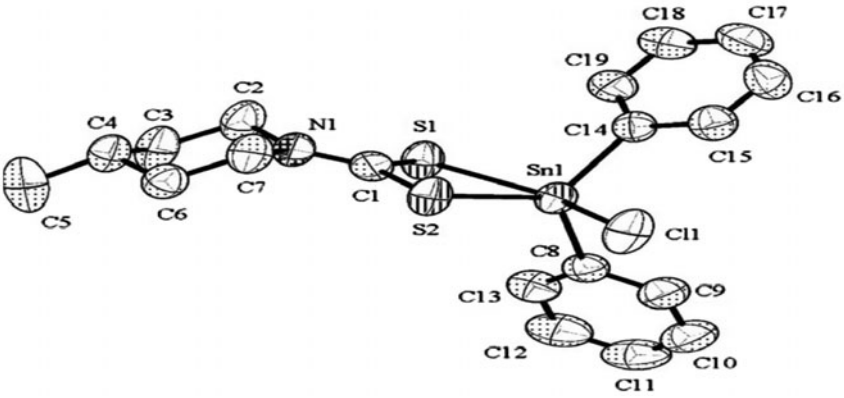


Figure 7. Molecular structure of Ph_2SnCl (4-methylpiperidine-1-carbodithioate), serving as an example for structures of the general formula $R_2Sn(S_2CNR')X$ [25].

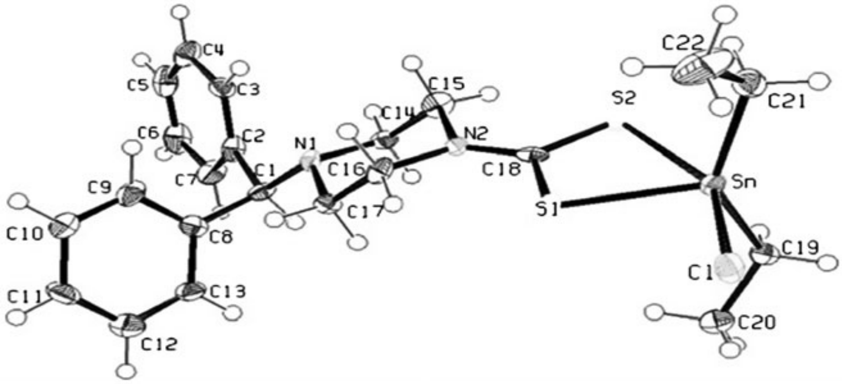


Figure 8. Molecular structure of chlorodiethyltin(IV) 4-benzhydrylpiperazine-1-carbodithioate, serving as an example for structures of the general formula $R_2Sn(S_2CNR')X$ [32].

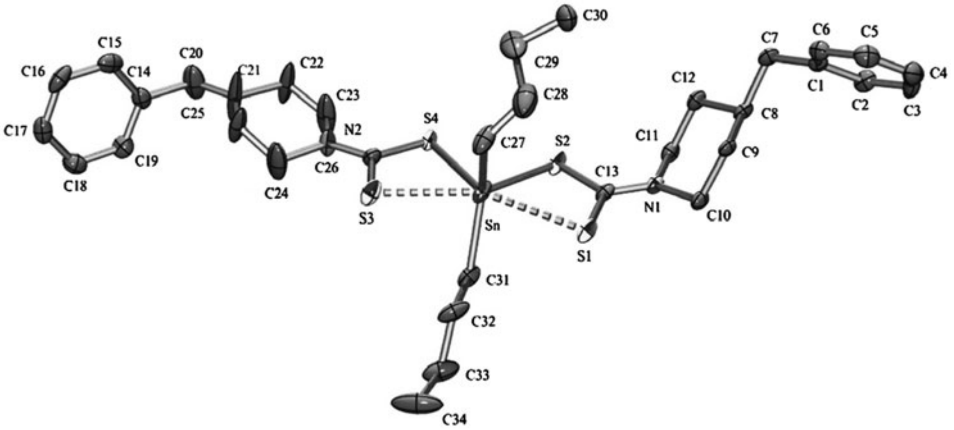


Figure 9. Molecular structure of dibutyltin(IV) bis[4-benzylpiperidine-1-carbodithioate], serving as an example of motif I for structures of the general formula $R_2Sn(S_2CNR')_2$ [14].

Motif I features two asymmetrically coordinating dithiocarboxylate ligands that define a skewed trapezoidal plane and two tin-bound butyl groups that lie over the weaker Sn–S interactions so that the coordination geometry is best described as being skewed trapezoidal bipyramidal. There is a great deal of homogeneity in the geometric parameters describing these structures. The short Sn–S bond distances lie in the relatively narrow range 2.48–2.57 Å with the longer distances found in structures with bulky tin-bound groups, for example, *t*-butyl, cyclohexyl and *o*-$ClC_6H_4CH_2$. The longer distances are 2.81–3.08 Å. The structures uniformly have sulfur forming the shorter Sn–S bonds to one side of the SnS_4 plane and hence the skewed-trapezoidal planar description. With one exception, the S_{short}–Sn–S_{short} bond angles always lie in the range 78–88° and the S_{long}–Sn–S_{long} angles are always 140–154°; normally the values are midway between these extremes. The exception is that of (*o*-$ClC_6H_4CH_2)_2Sn[S_2C$(4-methylpiperidine)$]_2$ [33], for which the S_{short}–Sn–S_{short} and S_{long}–Sn–S_{long} angles are 95.33(4) and 131.37(4)°, respectively. The presence of an intramolecular Sn–Cl interaction of 3.901(2) Å may be responsible for broadening of the S_{short}–Sn–S_{short} angle and concomitant narrowing of the S_{long}–Sn–S_{long} angle in this structure.

The second motif for $R_2Sn(S_2CNR')_2$ compounds is adopted exclusively by R = Ph derivatives. This observation supports the view that, relative to their alkyl (and vinyl) counterparts, phenyls are less electropositive/more electronegative so that the resulting $Ph_2Sn(S_2CNR'_2)_2$ structures are octahedral. The representative example for motif II is $Ph_2Sn(S_2CNEt_2)_2$, which highlights the distorted octahedral geometry and the *cis*-disposition of the tin-bound phenyl groups [34].

No obvious reason can be offered for the appearance of motif III, adopted by $Bz_2Sn(ACDA)_2$ [23]. This structure is quite readily related to the skewed trapezoidal bipyramidal geometry for motif I. As a starting point, the structure of the diethyldithiocarboxylate analog, that is, (t-Bu)$_2Sn(S_2CNEt_2)_2$ [35], is considered. Simply, there is a twist about one of the short Sn–S bonds so that the weakly coordinated dithiocarboxylate-sulfur is moved to a position approximately orthogonal to the original SnS_4 plane. As a result, the Sn–S bond distance expands to 3.5319(11) Å, clearly showing non-bonding character. Both Sn–S bond distances of the remaining chelating dithiocarboxylate decrease significantly and the C–Sn–C angle contracts to 119.1(1)°. The resulting coordination geometry is intermediate between square pyramidal and trigonal bipyramidal as confirmed by $\tau = 0.47$ [15]. There are several examples in the literature, where the difference between structures is found solely in the nature of the nitrogen-bound substituent but the structures of $(t\text{-Bu})_2\text{Sn}(\text{S}_2\text{CNR}_2)_2$, R = Me [35], and Et [36] are the only examples where such a profound difference in the molecular structure is observed.

The fourth and final motif for $\text{R}_2\text{Sn}(\text{S}_2\text{CNR}'_2)_2$ structures is also readily related to motif I. The molecular structure of $[\text{MeO(O=)CCH}_2\text{CH}_2)_2\text{Sn}(\text{S}_2\text{CNMe}_2)_2]$ [38] shows that tin-bound groups carry additional donors for coordination and one of these, in fact, forms an intramolecular Sn–O interaction. To a first approximation, the coordination geometry can be thought of as a skewed trapezoidal bipyramidal as for motif I. The carbonyl-oxygen of one $\text{MeO(O=)CCH}_2\text{CH}_2$ group approaches the tin in the SnS_4 plane. The Sn–O separation is 2.75(2) Å and this association results in formation of a five-membered SnC_3O chelate ring. As expected, there are some geometric consequences of the close association of the carbonyl-oxygen. The $\text{S}_{\text{long}}\text{–Sn–S}_{\text{long}}$ angle opens up by about 5° compared with motif I but, interestingly, the $\text{S}_{\text{short}}\text{–Sn–S}_{\text{short}}$ angle of 81.91(9)° falls in the range of $\text{S}_{\text{short}}\text{–Sn–S}_{\text{short}}$ angles, although at the lower end. This suggests that the sulfurs forming $\text{Sn–S}_{\text{short}}$ bond distances cannot get any closer for steric reasons. In order to accommodate the incoming oxygen, these sulfurs elongate their Sn–S bonds as compared with those of motif I and, concomitantly, one of the $\text{Sn–S}_{\text{long}}$ distances has contracted [2.847(4) Å] and the other is at the lower end of the $\text{Sn–S}_{\text{long}}$ range [2.914(5) Å].

When these interactions are weak they fall within the sum of the van der Waals radii of tin and sulfur, taken as 4.0 Å [38]. While there is a dominance of dibenzyl derivatives, the lack of systematic trends for such Sn–S secondary interactions is highlighted by the fact that they are observed in the triclinic form of $\text{Me}_2\text{Sn}(\text{S}_2\text{CNEt}_2)_2$ [39], but neither in the orthorhombic [40] nor in the monoclinic forms [41]. Some dithiocarboxylates carry hydrogen-bonding functionality so that, while the sulfurs of the dithiocarboxylate ligands rarely engage in supramolecular aggregation, certainly not to form extended arrays, the substituents might [42].

The structure of $[\text{PhSn}(\text{S}_2\text{CNEt}_2)(\text{S})(\text{CH}_2\text{CH}_2\text{CH}_2)\text{SnPh}(\text{S}_2\text{CNEt}_2)]$ [43] has two fold symmetry and a bridging organic ligand connecting the two tins. Each tin is chelated by an asymmetrically chelating dithiocarboxylate, a bridging sulfide, and two carbons derived from organic substituents. Indeed, this structure can be readily related to the $\text{R}_2\text{Sn}(\text{S}_2\text{CNR}')\text{X}$ type structures with X now a sulfur and one of the tin-bound R groups is on one end of a bridging organic ligand. The pattern of Sn–S bond distance is consistent with this concept, with the longer distance occupying a position approximately *trans* to the bridging sulfur. The coordination geometries are distinct, however, based on a comparison of the values of τ, the geometries for the tin in the dinuclear compound are trigonal bipyramidal.

The dinuclear and centrosymmetric structure of $(t\text{-Bu})_2\text{Sn}(\text{S}_2\text{CN(H)CH}_2\text{CH}_2\text{N(H)CS}_2)_2\text{Sn}(t\text{-Bu})_2$, isolated as a THF di-solvate [44], features two tins bridged by a pair of bi-functional dithiocarboxylates. The coordination geometry comprises one asymmetrically coordinating dithiocarboxylate, a monodentate ligand [Sn–S is 3.607(3) Å] and two organic substituents. The coordination geometry is almost identical to that observed for motif III of $\text{R}_2\text{Sn}(\text{S}_2\text{CNR}')_2$ structures, represented by $\text{Bz}_2\text{Sn(ACDA)}_2$. Examples are shown in figures 10 and 11 [45, 46].

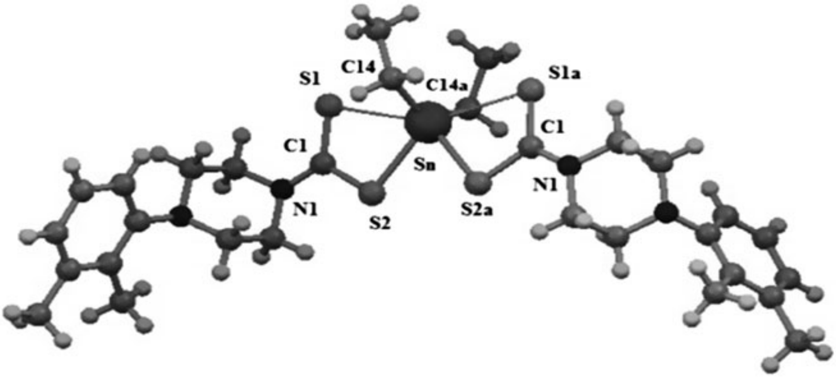


Figure 10. Molecular structure of diethylstannyl bis[N-(2,3-dimethylphenyl)piperazine-1-carbodithioate], serving as an example of motif II for structures of the general formula $R_2Sn(S_2CNR')_2$ [45].

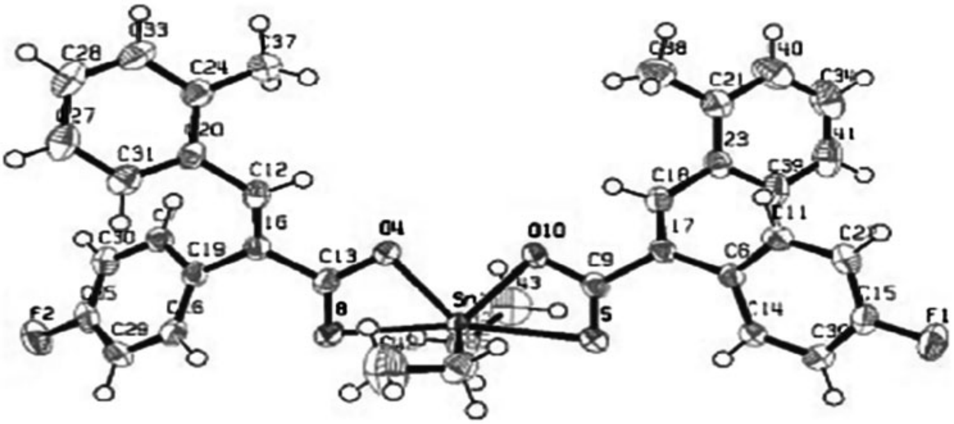


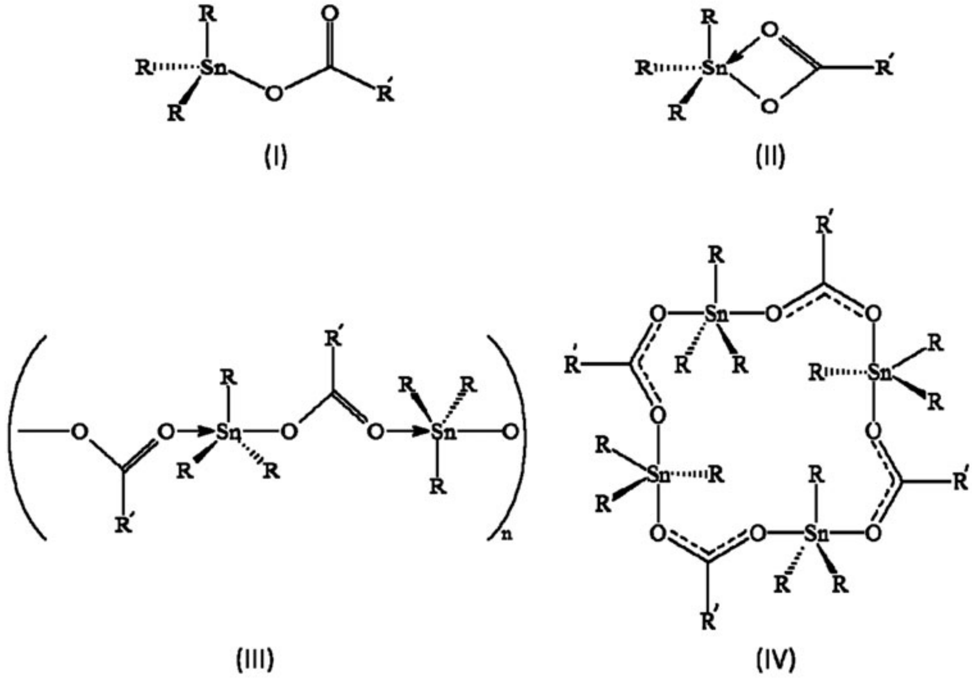
Figure 11. Molecular structure of diethyltin(IV) bis[3-(2-methylphenyl)-2-(4-fluorophenyl)acrylate] [46].

3. Organotin(IV) carboxylates

This class of compounds comprises organotins containing Sn–O bonds formed through COO^- group. Organotin(IV) carboxylates are widely studied organotin compounds due to their structural diversity and pharmaceutical applications, especially with reference to their antitumour activity [47]. These compounds also exhibit a number of interesting structural features because of the tendency of the anionic group to coordinate inter or intra-molecularly [48]. Therefore, organotin carboxylates have been studied extensively.

Based on the available crystal structures, organotin(IV) carboxylates can generally be categorized into the following four classes:

(1) Triorganotin(IV) carboxylates
(2) Diorganotin(IV) dicarboxylates
(3) Monoorganotin tricarboxylates
(4) Chlorodiorganotin(IV) carboxylates



(I) (II) (III) (IV)

Figure 12. Four structural classes for compounds of the type $R_3SnOCOR'$.

3.1. *Triorganotin(IV) carboxylates*

Triorganotin carboxylates in the solid state show four types of structures [49, 50]. The structure of $R_3SnOCOR'$ depends upon the size of *R* attached to tin and can be categorized ideally (figure 12) as follows:

3.1.1. Type I (Tetrahedral geometry). This structure has a four-coordinate distorted tetrahedral tin. Recent examples are triphenyltin(IV)12-(4-methylbenzoyl)-9,10-dihydro-9,10-ethanoanthracene-11-carboxylic acid [51], triphenyltin(IV)-2-hydroxybenzoate [52] and triphenyltin(IV)(4-chloro-3,5-dinitrobenzoate) [53] (figure 13), in which the tin-oxygen bonding distance is 2.065(2) Å, in agreement with the value for triphenyltin salicylate [57], dimethylstannyl bis[3-amino-4-chlorophenylcarboxylate] [54] (figure 14) and triphenyltin (IV) [2-(2,3-dimethylanilino)nicotinate] [55] (figure 15).

3.1.2. Type II (Trigonal bipyramidal monomeric geometry). Type II contains a five-coordinate tin with a bidentate carboxylate. This geometry is based on a distorted trigonal bipyramid with carboxylate oxygens spanning one apical and one equatorial position.

Examples are triphenyltin(IV) [*p*-tolylacetate], $Et_3Sn\{O_2CC_6H_3\text{-p-OH}[N{=}N(C_6H_4\text{–}4\text{-}CH_3)\}]OH_2$ and triphenyltin(IV) 2,5-dimethylfuran 3-carboxylate [$SnPh_3$(DMFU)] [56–58] in which the two bonding tin-oxygen distances are 2.564(7) and 2.115(6) Å, respectively. Both type I and II structures are monomeric. Triphenyl stannyl 2-(2,3,6-trimethylphenyla-

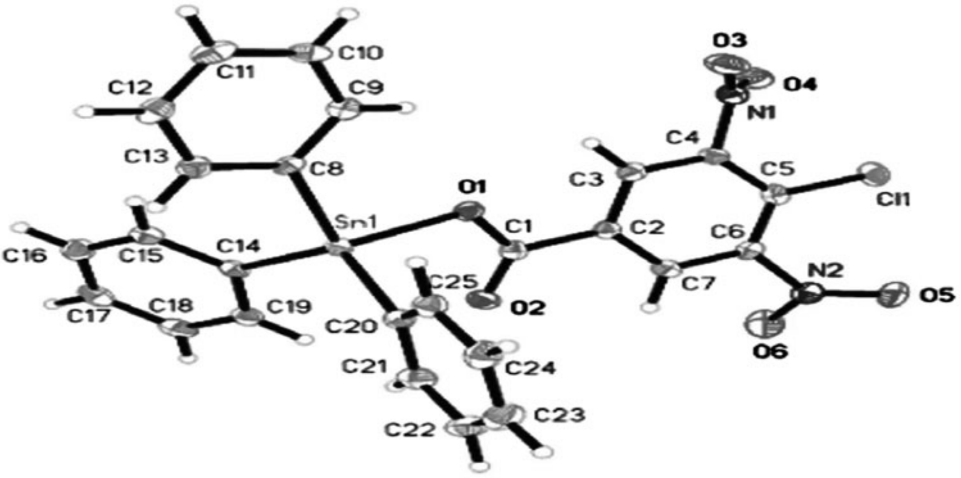


Figure 13. The molecular structure of triphenyltin(IV)-(4-chloro-3,5-dinitrobenzoate) [53].

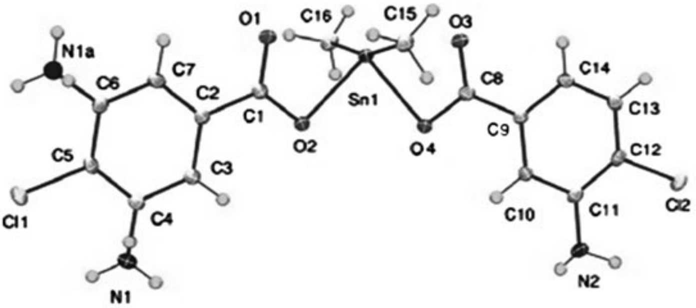


Figure 14. The molecular structure of dimethylstannyl bis[3-amino-4-chlorophenylcarboxylate] [54].

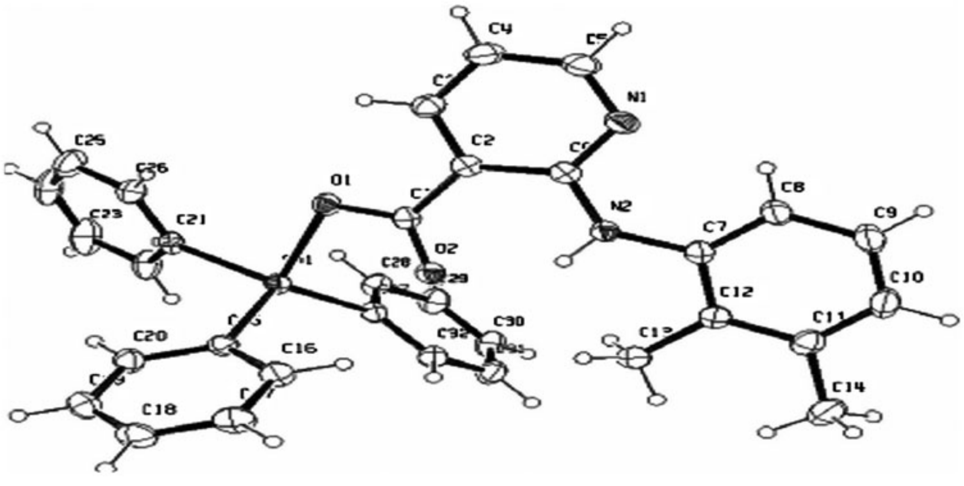


Figure 15. The molecular structure of triphenyltin(IV) [2-(2,3-dimethylanilino)nicotinate] [55].

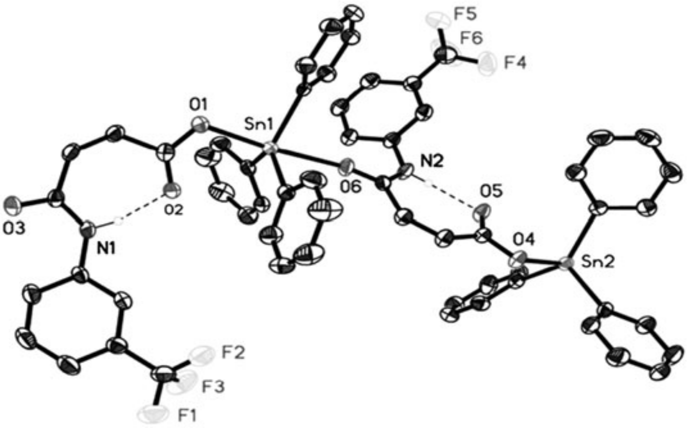


Figure 16. The molecular structure of di-phenylstannyl bis[(E)-4-oxo-4-((3-trifluoromethyl)phenyl)amino)but-2-enoate] [60].

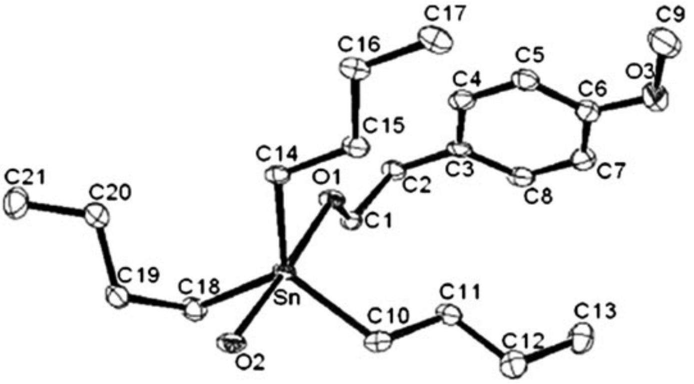


Figure 17. The molecular structure of tributyltin(IV) 4-methoxyphenylethanoate [65].

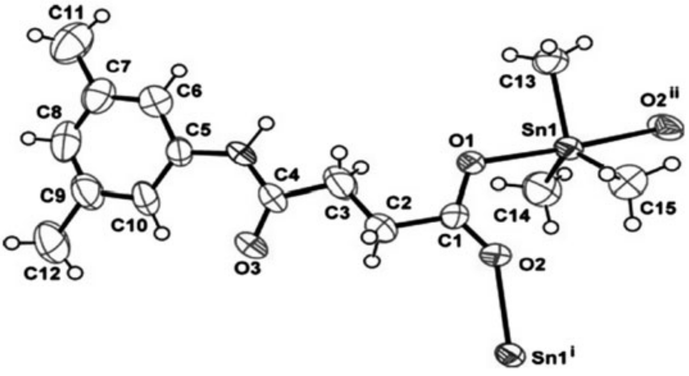


Figure 18. The molecular structure of trimethyltin(IV) 3-[(′3,′5-dimethylphenylamido)]propanoates [66].

mino)benzoate [Ph_3(Meclo)Sn] [59] is characterized by a quite long coordination bond (2.823(3) Å) as compared to that of the dimethylamino analog (2.564(7) Å) due, in part, to the presence of an intermolecular hydrogen bond between the carbonyl-oxygen and the NH-group. Example of this type is diphenylstannyl bis[(E)-4-oxo-4-((3-trifluoromethyl) phenyl)amino)but-2-enoate] [60] as shown in figure 16.

3.1.3. Type III (Linear polymeric geometry). The type III compounds exhibit polymeric trans-R_3SnO_2 structural motif, in which adjacent SnR_3 moieties are bridged by a single bidentate carboxylate. Each Sn has slightly distorted trigonal bipyramidal coordination with equatorial alkyl groups and the carboxylate oxygens from two different carboxylates occupying axial positions [61].

These molecules adopt an infinite 1-D polymeric chain structure. One oxygen of the carboxylate group remains uncoordinated and the oxygen, bonded directly to the phenyl ring, bonds to the other tin. As one coordinating site of the ligand is on one end of the molecule and the other site is on the other end, it gives a linear polymeric arrangement to the complex. Such structures depend upon the size of R attached to Sn [62].

A typical example is 3,4,5,6-tetrachlorophenyl-1,2-dicarboxylatobis[trimethyltin(IV)] [52] with one axial tin-oxygen bond much longer than the other axial tin–oxygen bond [2.4010(17) and 2.2214(16) Å]. The O-Sn-O angle is 170.87(1)° and very similar to that of $\{[(n\text{-Bu})_3Sn]_2[(C_8H_{10})(COO)_2]\}_n$ [63]. The distortion of triorganotin carboxylate from ideal geometry is not only influenced by the type of organic groups on tin but also dictated by steric and electronic effects [64]. Two more examples of this type are tributyltin(IV) 4-methoxyphenylethanoate and trimethyltin(IV) 3-[(3′,5′-dimethylphenylamido)]propanoates (figure 17) [65].

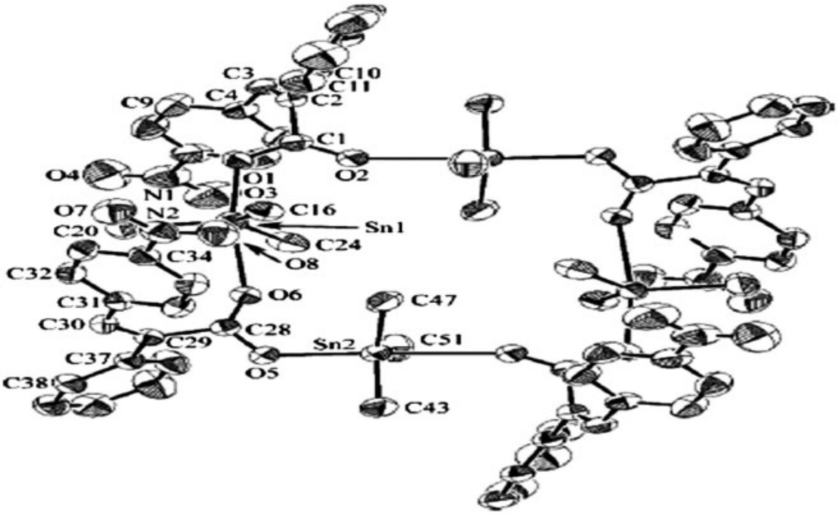


Figure 19. Molecular structure for cyclotetrameric n-Bu_3SnL [67].

3.1.4. Type IV (Polymeric triorganotin(IV) carboxylates). Type IV has a macrocyclic tetramer, which contains four units of five-coordinate tin with bidentate carboxylate moieties. An example is trimethyltin(IV) 3-[('3,'5-dimethylphenylamido)]propanoates (figure 18) [66] and tri-*n*-butyltin(IV) (*Z*)-3-(4-nitrophenyl)-2-phenyl-2-propenoate (figure 19) [67] in which carboxylates bridge two neighboring tins such that the Sn–O bonds formed by the bridging ligands are asymmetric with values of 2.186(4) and 2.514(4) Å. These are comparable with linear polymers of Type III, where oxygens occupy the apical position of the trigonal bipyramidal tin, with O–Sn–O angles of 175.2(1)°. The three equatorial *n*-butyl groups and the tin are nearly coplanar, the sum of the equatorial C–Sn–C angles being 357.7(4)°. Intermolecular interactions between the tetramers appear to be exclusively van der Waals in nature. Example is tetrabutylbis(4,5-dimethoxy-2-nitrobenzoato) [68] (figure 20).

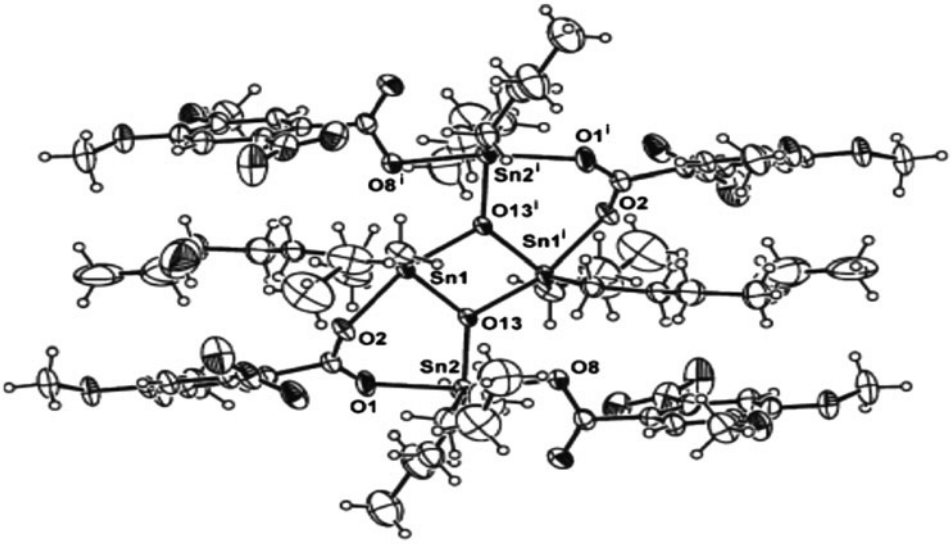


Figure 20. Molecular structure for tetrabutylbis(4,5-dimethoxy-2-nitrobenzoato) [68].

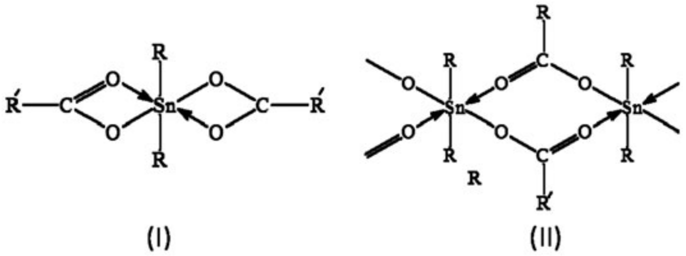


Figure 21. Two major structure classes of diorganotin(IV) compounds.

3.2. *Diorganotin(IV) dicarboxylates*

Diorganotin dicarboxylates adopt a variety of structural modes (figure 21) depending on the nature of organic substituents at the tin and/or carboxylate.

3.2.1. Type I (Octahedral geometry, monomeric structure).

Two longer and two shorter tin-oxygen bonds form the tetrahedron. As in [n-$Bu_2Sn(O_2CC_4H_4NOS_2)_2$] and Oct_2Sn-5-[(E)-2-(aryl)-1-diazenyl]-2-hydroxybenzoic acid, the C–Sn–C angle is 147.2(7)° and the largest O–Sn–O angle is 165.3(3)°, while the two short tin-oxygen bond lengths are 2.156(9), 2.128(8) and two long ones are 2.510(1), 2.510(9) Å, respectively [69, 70]. Several other structures exhibiting similar geometry around tin and an anisobidentate mode of coordination of the carboxylate ligands as found in dimethyltin dibenzoate are also reported [71–75].

This is exemplified by the structure given in figure 22 [76], described as highly distorted octahedral or bicapped tetrahedron. The two carboxylates are bonded to tin in an anisobidentate fashion.

3.2.2. Type II (Trigonal bipyramidal geometry).

The structure of dimethyltin(IV) (9-anthracene-carboxylate)·CH_3OH [$Me_2Sn(OCOC_{14}H_9)_2 \cdot CH_3OH$] has distorted trigonal bipyramidal geometry. This is due to extensive crowding by the bulky anthracene groups, preventing the carboxylates to make a coordinate bond intra- or intermolecularly with tin. In this structure, the three carboxylates are bonded by one oxygen. The other two positions

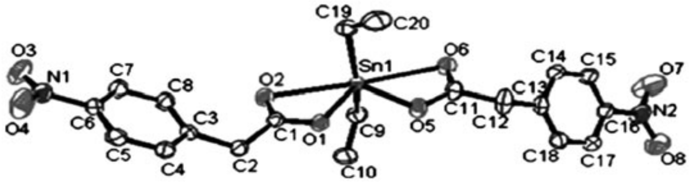


Figure 22. Molecular structure for diethyltin(IV) bis(4-nitrophenylethanoate) [76].

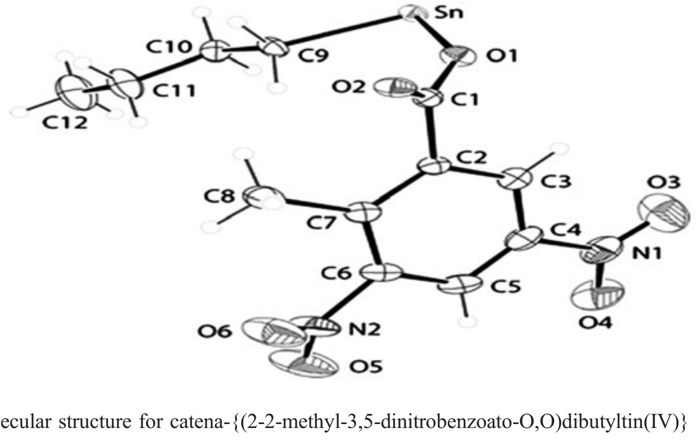


Figure 23. Molecular structure for catena-{(2-2-methyl-3,5-dinitrobenzoato-O,O)dibutyltin(IV)} [77].

are occupied by two methyls. Overall this gives a trigonal bipyramidal monomeric geometry (figure 23) [65, 77].

3.2.3. Type III (Polymeric geometries; stannoxanes).

There are three possible geometries in stannoxanes.

(1) 1-D infinite polymeric chain structures
(2) 2-D polymeric structures
(3) Irregular 3-D frameworks

These are discussed as:

(1) 1-D infinite polymeric chain structure [78]. This complex is dimeric dicarboxylatotetraorganodistannoxane which consists of a central planar $(Me_2Sn)_2O_2$ four-membered ring and two peripheral Me_2Sn units, each bridging oxygen in the Sn_2O_2 ring is attached to three Me_2Sn units and as a result these oxygens are tri-coordinated. The geometries of all the tins can be classified into five-coordinate tin (Sn1) and six-coordinate tin (Sn2).
(2) 2-D polymeric structure [78] shows that all 2-D organotin polymers are made up of dimeric tetraorganodistannoxane and bridging dicarboxylates. The geometries of all tins can be classified into five-coordinate tin (Sn2) and six-coordinate tin (Sn1) types. Sn2 may be viewed as slightly distorted trigonal bipyramidal and Sn1 may be viewed as distorted octahedral.
(3) Irregular 3-D frameworks.

The molecular structure of $\{(Me_2Sn)_2[\mu_4\text{-}(C_{10}H_{14}O_4)](\mu_3\text{-}O)\}_n$ [78] is a tetranuclear centrosymmetric dimer. The geometries of all tins can also be classified into five-coordinate tin (Sn2) and six-coordinate tin (Sn1).

3.3. *Monoorganotin tricarboxylates*

Monoorganotin(IV) tricarboxylates are monomeric in solution [79]. In the structure, there are three carboxylic ligands attached to tin, each bidentate and one organic group attached through carbon. There are two types of ligands, 2-pyridinecarboxylate and 2-chlorobenzoxylate, which are found to be chelating bidentate to the Sn. The coordination number of tin is seven.

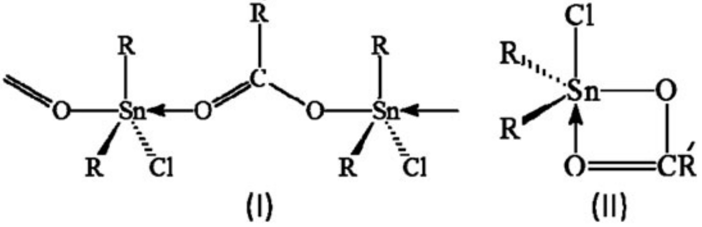


Figure 24. Two major structure classes of chlorodiorganotin(IV) compounds.

3.4. *Chlorodiorganotin(IV) carboxylates*

Dialkylchlorotin carboxylates $R_2Sn(OCOR)Cl$ possess similar inter- and intramolecularly chelated structures (figure 24) in the solid state and solution, respectively [80].

Tin with a trigonal bipyramidal cis-R_2SnX_3 geometry has been confirmed by X-ray crystallography for R = Me [81]. Other compound(s) in this class reveal the polymeric $RXSnO_2$ structural motif; a typical example is $MeSn(C_6H_4O_3)Cl$ with one axial tin-oxygen bond much longer than the other axial tin-oxygen bond [2.4010 and 2.2214 Å]. The O–Sn–R angle is 110.87°, very similar to that of distorted tetrahedral environment. The distortion of chlorodiorganotin carboxylates from ideal geometry is influenced by the type of organic groups on tin and by steric and electronic effects.

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