Chapter Five

Synthesis and Structural studies of dibutyltin compounds

5.1 Experimetal

Dibutyltin oxide, *ortho*-hydroxybenzoic acid, meta-hydroxybenzoic acid, *para*-hydroxybenzoic acid, salicylic acid, salicylaldehyde, 5-chlorosalicylaldehyde, 5-bromosalicylaldehyde, 5-nitrosalicylaldehyde, tris(hydroxymethyl)aminomethane were purchased from Fluka and were used without any purification. Other chemicals and solvents with high purity from Merck were used.

Elemental analyses were determined on a CHN elemental analyzer in the Elemental Analysis laboratory in National University of Malaysia, Bangi , Selangor. The melting points of the complexes were determined on a eletrothermal digital melting apparatus and were uncorrected. The infrared spectra were recorded in the region between 400 to 4000 cm^{-1} with a Perkin Elmer Spectrum RX1 spectrophotometer. The samples were prepared as nujol mull in between KBr cells. The ^{1}H and ^{13}C NMR spectra of selected compounds were recorded at ambient temperature on a JEOL JNM-FX400 FT-NMR spectrometer operating at 399.65 MHz for ^{1}H and 100.4 MHz for ^{13}C. The solutions were prepared with a concentration of 0.05 g/ml in $CDCl_3$ for ^{1}H NMR and as saturated solutions for ^{13}C NMR. The ^{1}H and ^{13}C NMR chemical shifts were quoted relative to tetramethylsilane and $CGCl_3$, respectively. The ^{119}Sn NMR for the organotin compounds were recorded on the same instruments.

The X-ray crystallographic intensity data were measured using Mo-Kα radiation (graphite crystal monochromator, λ = 0.71069 Å). The data were collected by using a

Bruker APEX2 CCD area detector diffractometer at the X-ray Crystallographic laboratory, University of Malaya.

5.2 Synthesis

5.2.1 Synthesis of dibutyltin(IV) esters of hydroxybenzoic acid:

The synthesis of dibutyltin esters of hydroxybenzoic acid was performed as followed:

Synthesis of dibutyltin(IV) ester of ortho-hydroxybenzoic acid

2.76 g (0.02 mole) of *ortho*-hydroxybenzoic acid was mixed with 2.48 g (0.01 mole) dibutytin oxide in 50 ml toluene in a round bottom flask fitted with a Dean and Stark apparatus and was refluxed for two hours in order to separate the azeotropic mixture. The resulting solution was then filtered and left at room temperature for crystallization. The solid product obtained was washed with distilled water and dried in oven.

Synthesis of dibutyltin(IV) ester of meta-hydroxybenzoic acid

2.76 g (0.02 mole) *meta*-hydroxybenzoic acid was mixed with 2.48 g (0.01 mole) dibutytin oxide in 50 ml toluene in a round bottom flask fitted with a Dean and Stark apparatus and was refluxed for two hours in order to separate the azeotropic mixture. The resulting solution was then filtered and left at room temperature for crystallization. The solid product obtained was washed with distilled water and dried in oven.

Synthesis of dibutyltin(IV) ester of para-hydroxybenzoic acid

2.76 g (0.02 mole) *para*-hydroxybenzoic acid was mixed with 2.48 g (0.01 mole) dibutytin oxide in 50 ml toluene in a round bottom flask fitted with a Dean and Stark apparatus and was refluxed for two hours in order to separate the azeotropic mixture. The resulting solution was then filtered and left at room temperature for crystallization. The solid product obtained was washed with distilled water and dried in oven.

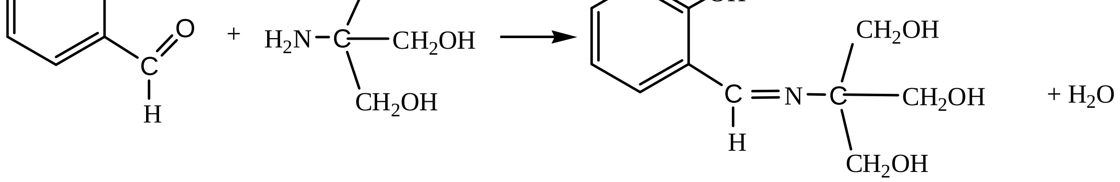
5.2.2 Synthesis of Schiff base ligands and their butyltin complexes

The synthesis of Schiff base ligands and their dibutyltin complexes are described in details as follows:

Syntheses of 2- salicylideniminato-2-(hydroxymethyl)-1, 3-dihydroxypropane (Saltris)

1.21 g (0.01 mole) of salicylaldehyde in ethanol was added to 1.22 g (0.01 mole) of tris(hydroxymethyl)aminomethane in ethanol and the reaction mixture was refluxed for two hours, then it was cooled to room temperature, where yellow crystal was obtained.

Using the same procedure, the following substituted saltris ligands: 5-chlorosaltris, 5-bromosaltris and 5-nitrosaltris were prepared by using 5-chlorosalicylaldehyde, 5-bromosalicylaldehyde and, 5-nitrosalicylaldehyde, respectively (Syamal et al., 1973; Mishtu D., 2003; Gerbay Asgedum, 1996; Hapipah et al., 2007).



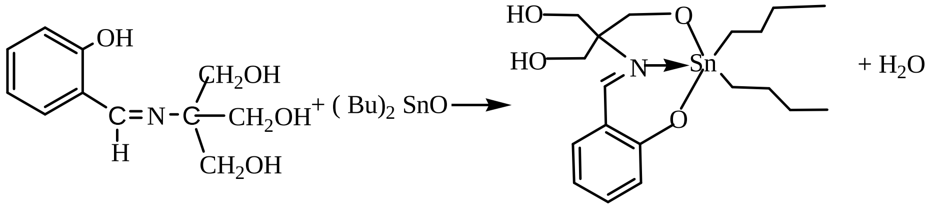
Salicylaldehyde tris(hydroxymethyl)aminomethane saltris

5.2.3 Synthesis of dibutyltin Schiff base complexes:

The preparation of the dibutyltin Schiff base complexes of saltris and substituted saltris ligands were carried by using a Dean and Stark apparatus to remove the water produced during the reaction.

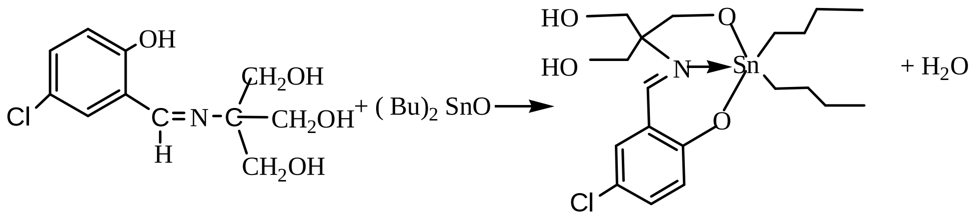
Synthesis of dibutyltin(IV) complex of saltris

2.48 g (0.01 mole) of dibutyltin oxide (Bu_2SnO) and 2.25 g (0.01 mole) saltris were dispersed in 50 ml of toluene in a flask fitted with a Dean and Stark apparatus and the mixture was refluxed for two hours to separate azeotropic mixture The solution mixture was then filtered and left at room temperature for crystallization.



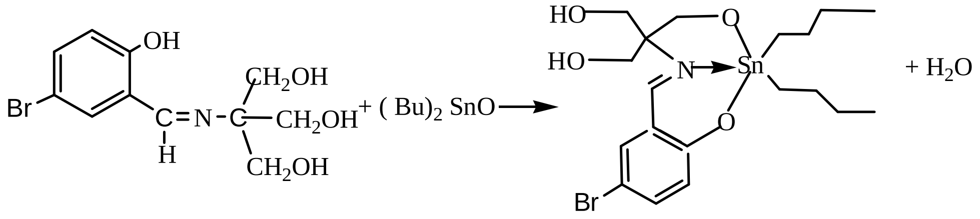
Synthesis of 5-Clsaltris complex of dibutyltin(IV)

2.48 g (0.01 mole) dibutyltin oxide (Bu_2SnO) and 2.60 g (0.01 mole) 5-chlorosaltris ligand were dispersed in 50 ml of toluene in a flask fitted with a Dean and Stark apparatus and the mixture was refluxed for two hours to separate azeotropic mixture. The solution mixture was then filtered and left at room temperature for crystallization.



Synthesis of 5-Brsaltris complex of dibutyltin(IV):

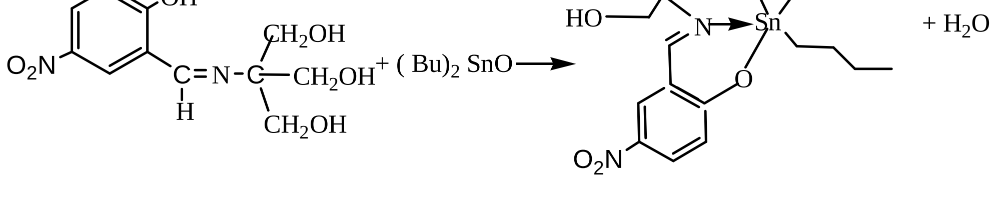
2.48 g (0.01 mole) dibutyltin oxide (Bu_2SnO) along with 3.05 g (0.01 mole) 5-bromo saltris ligand were dispersed in 50 ml of toluene in a flask fitted with a Dean and Stark apparatus and the mixture was refluxed for two hours to separate azeotropic mixture The solution mixture was then filtered and left at room temperature for crystallization.



Synthesis of 5-NO₂saltris complex of dibutyltin(IV):

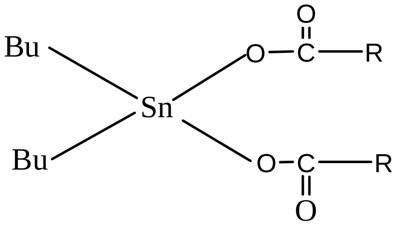
2.48 g (0.01 mole) dibutyltin oxide (Bu_2SnO) and 2.7 g (0.01 mole) 5- nitrosaltris

were dispersed in 50 ml of toluene in a flask fitted with a Dean and Stark apparatus and the mixture was refluxed for two hours to separate azeotropic mixture The solution mixture was then filtered and left at room temperature for crystallization.

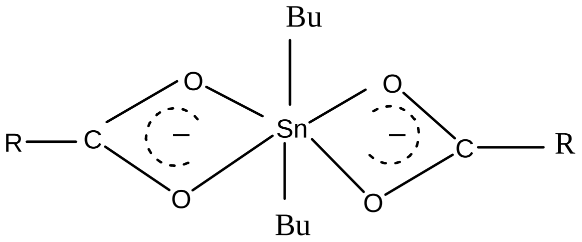


5.3 Characterization of dibutyltin(IV) complexes of hydroxybenzoic acid

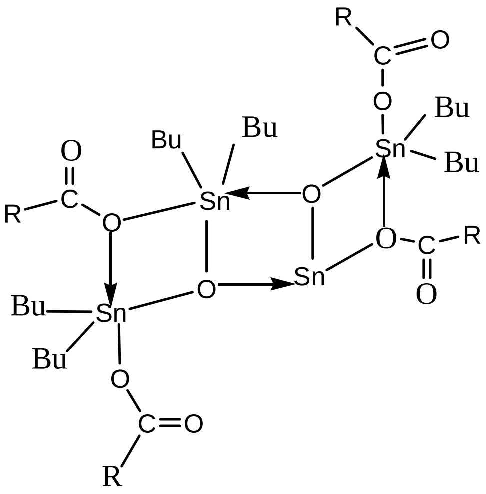
Diorganotin oxide are known to react with carboxylic acid in a similar manner as an acid-base reaction. Hence, the reaction of dibutyltin(IV) oxide with *ortho*-hydroxybenzoic acid, *meta*-hydroxybenzoic acid and *para*-hydroxybenzoic acid are expected to produce diorganotin dicarboxylates with various structural motif as shown below.



monodentate



bidentate



distannoxane

The products obtained were found to be white solids with melting points as shown in Table 5.1. The melting points of the free acids are found to be different from the products obtained upon reacting with dibutyltin oxide. This clearly indicates that reactions had proceeded to give the carboxylates as the major products. The dibutyltin carboxylates were further characterized by various instrumental techniques such as FT-IR , ^{1}H , ^{13}C and ^{119}Sn NMR spectroscopies. In the case of dibutyltin carboxylate of *o*-hydroxybenzoic acid, suitable crystals were selected and its structure was determined by single-crystal X-ray diffractometry.

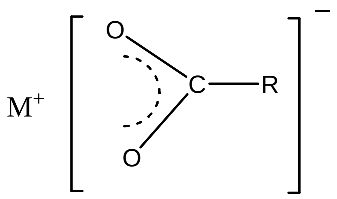
Table 5.1: Melting points and elemental data for hydroxybenzoic acids and their dibutyltin(IV) complexes

Compound	m.p	%C (calcd)	%H (calcd)
o- Hydroxybenzoic acid	158-161	-	-
m- Hydroxybenzoic acid	201- 205	-	-
p- Hydroxybenzoic acid	214-216	-	-
Dibutyltin ester of o-Hydroxybenzoic acid	77-79	46.8(47.5)	6.11(6.07)
Dibutyltin ester of m-Hydroxybenzoic acid	136-138	46.5(47.5)	6.20(6.07)
Dibutyltin ester of	119-120	47.1(47.5)	6.18(6.07)

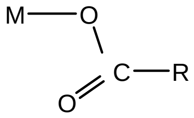
p-Hydroxybenzoic acid			

5.3.1 IR spectroscopic analysis of hydroxybenzoic acids and dibutyltin carboxylates of hydroxybenzoic acids

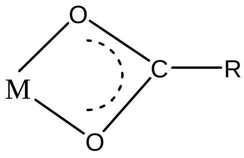
Most carboxylic acids are able to form bonds with metal ions *via* the following coordination modes:



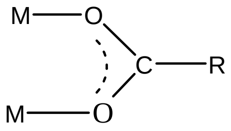
Free ion



Monodentate



Bidentate (chelate)



Bidentate (bridge)

The characteristics of each of the above coordination modes can be studied by using FT-IR spectroscopic technique. The IR spectral data of the hydroxybenzoic acids and their dibutyltin carboxylates are tabulated in Table 5.2. Inspection of the IR spectral data of the compounds (Table 5.2) shows that the peak intensity at the region around 3300 cm^{-1} had decreased indicating that the acid ligand was bonded to tin. The presence of a weaker peak at 3300 cm^{-1} for the three dibutyltin carboxylates are due to the presence of the hydroxyl group at the *ortho, meta* and *para* position of the phenyl ring. It was also found that the $\bar{\nu}$ of COO (asymmetric) of the free carboxylic acids tends to shift to lower frequencies after the formation of COO-Sn bond as shown for dibutyltin carboxylate of *o*-hydroxybenzoic acid where the $\bar{\nu}$ of COO (asymmetric) values which is found in the region around 1680 cm^{-1} are shifted to 1629 cm^{-1}. On the other hand, the $\bar{\nu}$ of COO (symmetric) tends to shift to higher frequencies, that is from 1296 cm^{-1} to 1310 cm^{-1}. This indicates that the COO bond character of the carboxylate group of the free acid had decreased due to the significant interaction of the carbonyl oxygen with the tin atom upon forming the COO-Sn bond. This observation was also found in the other two dibutyltin carboxylates of hydroxybenzoic acids (Table 5.3). The above results showed that the carboxylate groups act as bidentate ligand by forming a chelate ring with the tin atom. However, inspection of the IR data revealed that an additional peak at the region around 1600 cm^{-1} was observed for all the three dibutyltin carboxylates, indicating the existence of two type of carboxylate coordination, that is a bidentate and a monodentate carboxylate. The involvement of carbonyl oxygen coordination with the tin atom can be obtained from the difference between the $\bar{v}$ of COO (symmetric) and $\bar{v}$ of COO (asymmetric) or $\Delta\bar{v}$ which is usually smaller than 200 cm^{-1} when the carbonyl oxygen of the carboxylate group is bonded to the tin atom. However, the observed values of $\Delta\bar{v}$ for the three dibutyltin carboxylates are in the range of 264 cm^{-1} to 319 cm^{-1}, thus the evidence for carbonyl oxygen interaction with the tin atom cannot be established in this case. In addition, the appearance of peaks at 420-480 cm^{-1} and 520-580 cm^{-1} that belongs to $\bar{v}$(Sn-O) and $\bar{v}$(Sn-C) are evidenced for complex formation (Shahidi et al. 2005; Siang Guan Teoh et al,1997; Szorcsrik et al., 2003; Bonire et al., 1998).

Table 5.2 : IR Stretching frequencies of hydoxybenzoic acids and their dibutyltin carboxylates.

Compound	IR stretching frequencies (cm^{-1})
***o*-hydroxybenzoic acid**	3239m, 1658s, 1613s, 1444s, 1296s, 1249m, 1156s, 1030s, 965m, 892m, 852s, 785s, 759s, 698s, 659s, 567s, 532s, 464s
Dibutyltin carboxylate of *o*-hydroxybenzoic acid	3145w, 1629s, 1586m, 1560w, 1483s, 1310s, 1251m, 1159m, 1091s, 1030s, 997m, 955s, 877s, 824s, 808s, 752s, 701m,671m, 582s, 562s, 529s, 461w, 434s
***m*-hydroxybenzoic acid**	3288m, 1720s, 1603s,1508m, 1463s, 1361s, 1270s, 1166m, 1114s, 1080m, 1000m, 924s, 886s, 821s, 797s, 763s, 747m, 675s, 653, 634s, 558s, 534m, 513s, 460s
Dibutyltin carboxylate of *m*-hydroxybenzoic acid	3364m, 1718s, 1605w, 1498m, 1455s, 1400m, 1341m, 1260m, 1237m, 1156m, 1113s, 1080s, 1019m, 999s, 938s, 924m, 904w, 888m, 876m, 821s, 765s, 678s, 567w, 528m, 464s, 416m
***p*-hydroxybenzoic acid**	3393s, 1676s, 1608s, 1595s, 1509m, 1448m, 1424s, 1364w, 1317s, 1291s, 1245s, 1169s, 1128w, 1101m, 1012m, 930s, 854s, 769s, 693m, 641m, 619s, 547m, 504m
Dibutyltin carboxylate of *p*-hydroxybenzoic acid	3448w, 1663m, 1593s, 1509w, 1396w, 1319s, 1282m, 1166s, 915w, 853s, 785m, 770m, 626s, 546m, 503m

Table 5.3: Selected stretching frequencies

Compound	ν(OH)	ν(C=O)	ν(C-O)	ν(Sn-O)
***o*-hydroxybenzoic acid**	3239m	1658s, 1613s	1296s	464s
Dibutyltin carboxylate of *o*-hydroxybenzoic acid	3145w	1629s, 1586m	1310s,	434s
***m*-hydroxybenzoic acid**	3288m	1720s, 1603s	1361s	460s
Dibutyltin carboxylate of *m*-hydroxybenzoic acid	3364m	1718s, 1605w	1341m	464s
***p*-hydroxybenzoic acid**	3393s	1676s, 1608s	1317s	504m
Dibutyltin carboxylate of *p*-hydroxybenzoic acid	3448w	1663m, 1593s	1319s	503m

5.3.2 NMR Spectroscopic study

The ^{1}H NMR and ^{13}C NMR of hydroxybenzoic acids and their respective dibutyltin complexes were recorded and their data are given in Tables 5.4 and 5.5. In addition, the ^{119}Sn NMR data for the dibutyltin carboxylates were also secured and tabulated in Table 5.6. As shown in the ^{1}H NMR chemical shifts data of the hydroxybenzoic acids, the aryl protons are located in the region between 6.82 – 8.63 ppm, whereas the hydroxyl functional group on the benzoic acid occurs at 9.75 to 10.59 ppm. The proton chemical shift of the carboxylic proton (-COOH) is variable but usually found at the region of 10.00 ppm. The presence of signal in the region between 0.89 to 1.85 ppm indicates that the formation of the dibutyltin carboxylates.

The ^{119}Sn NMR chemical shift of organotin compounds covers a wide range of 600 ppm and is quoted relative to tetramethyltin with downfield shift from reference compound toward positive sign. As the electron releasing of the alkyl groups in $R_{4-n}SnX_4$ increase the Sn atom becomes progressively more shielded and Sn chemical shift value moves to a higher field. The chemical shift values also dependent on the nature of X groups and generally moves to a lower field as the electronegativity of the latter increases. One of the most important features of the Sn chemical shift is that an increase in the coordination number of Sn atom usually produces a large upfield shift. Chemical shift about -90 to -330 ppm and -125 to -515 ppm was reported for 5 and 6 coordinated compounds, respectively. When the coordination number changes from 4 to 5, the chemical shift moved upfield by 60-150 ppm and from five to six and upfield by 130- 200 ppm is obtained. In our case, the ^{119}Sn NMR chemical shift of the three dibutyltin carboxylates clearly indicated a 4-coordinate tin structure in non donor solvent, similar to that obtained for di-n-butyl bis(2,4-dihydroxybenzoate) tin(IV) (-128 ppm) [Siang- Guan Teoh, 1997]. However, when the tin-119 NMR of dibutyltin carboxylates were analysed in MeOH-d^5 and pyridine-d^5, higher than four coordination at tin was observed as can be seen from the large upfield shift to -255 ppm for both dibutyltin o- and m-hydroxybenzoate. In the case of dibutyltin bis(p-hydroxybenzoate), the tin-119 chemical shift in pyridine-d^5 showed a even larger upfield shift to -347 ppm indicating a stronger coordination bond between the pyridyl nitrogen and the tin atom. On the basis of their ^{13}C and ^{119}Sn NMR data, the dibutyltin carboxylates can be best interperated in terms of the common diorganotin dicarboxylate structure i.e. the tin atom adopts a six coordinated with two bis–chelated carboxylate ligands in the solution state.

Table 5.4: ^{1}H NMR data of hydroxybenzoic acid ligands, and their dibutyltin(IV) complexes

Compound	^{1}H NMR Chemical shifts (ppm)
***o*-hydroxybenzoic acid**	6.91-7.82 (aryl proton), 9.83(OH), 12.79 (COOH)
Dibutyltin *o*-hydroxybenzoate	0.89 (CH_3), 1.38-1.85 (CH_2), 6.92-7.99 (aryl proton), 10.59 (OH)
***m*-hydroxybenzoic acid**	6.82-7.40 (aryl proton) 9.75(OH), 12.81 (COOH)
Dibutyltin *m*-hydroxybenzoate	0.79-0.82 (CH_3), 1.31-1.70 (CH_2), (6.84-7.88) (aryl)
***p*-hydroxybenzoic acid**	6.81-7.90(aryl proton), 10.23 (OH),12.43(COOH)
Dibutyltin *p*-hydroxybenzoate	0.85-0.89 (CH_3) 1.25-1.75(CH_2) 7.14-8.63 (aryl proton)

Table 5.5. ^{13}C NMR chemical schift for hydroxybenzoic acid and their dibutyltin(IV) complex

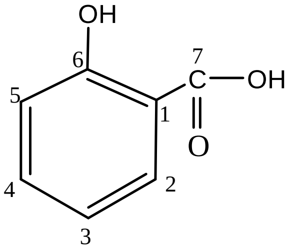
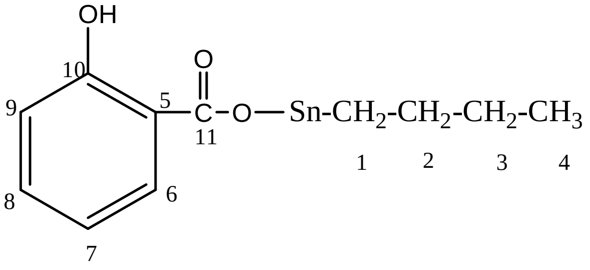
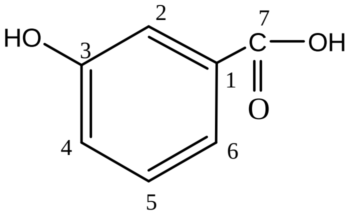
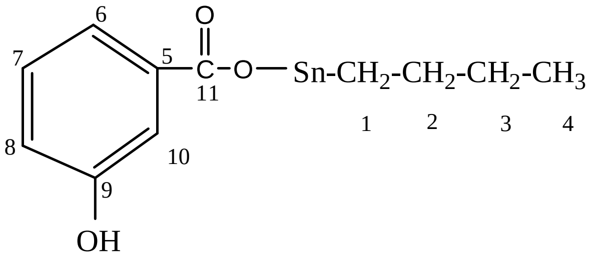
Compound	^{13}C NMR chemical shift(ppm)	
	C1 C2 C3 C4 C5 C6 C7	135.7 119.2 113 130.3 114.1 161.1 172
	C1 C2 C3 C4 C5 C6 C7 C8 C9 C10 C11	30 26.8 26.5 13.7 112.5 131.8 117.7 119.6 136.5 161.9 177.2
	C1 C2 C3 C4 C5 C6 C7	132 129.6 157.4 120 119.8 115.8 167.3
	C1 C2 C3 C4 C5 C6 C7 C8 C9 C10 C11	30 26.8 25.8 13.7 117.1 123.0 130 131.4 156 120.8 175.9

Table 5.5. Continued:

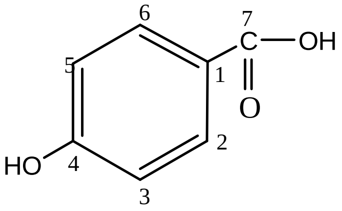
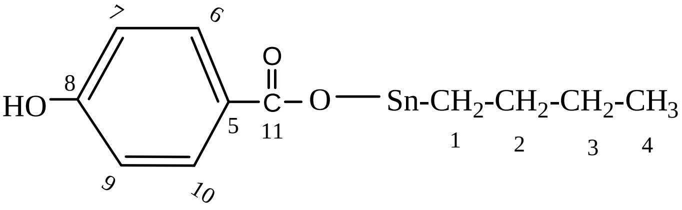
Compound	^{13}C NMR chemical shift (ppm)	
	C1	121.3
	C2	115.1
	C3	131.5
	C4	161.6
	C5	131.5
	C6	115.1
	C7	167.2
	C1	32.3
	C2	27.9
	C3	26.2
	C4	13.6
	C5	115.9
	C6	135.9
	C7	135.4
	C8	163.2
	C9	149.5
	C10	123.4
	C11	175.6

Table 5.6: ^{119}Sn NMR chemical shift of dibutyltin(IV) hydroxybenzoic acid complexes

Compounds	Solvent	^{119}Sn NMR chemical shift (ppm)
Dibutyltin carboxylate of *o*-hydroxybenzoic acid	chloroform-d	-121.9
Dibutyltin carboxylate of *o*-hydroxybenzoic acid	methanol-d^3	-255.0
Dibutyltin carboxylate of *m*-hydroxybenzoic acid	methanol-d^3	-255.5
Dibutyltin carboxylate of *p*-hydroxybenzoic acid	pyridine-d^5	-347.0

5.3.3 X-ray Crystallographic study of dibutyltin ester of *o*-hydroxybenzoic acid

The X-ray crystallographic study of dibutyltin carboxylate of *o*-hydroxybenzoic acid was carried out in order to determine the structural motif of the of the dibutyltin hydroxybenzoate and hence to confirm the structural information derived from the spectroscopic analysis in the previous section. Quite unexpectedly, the X-ray analysis showed that two structural motifs were adopted by dibutyltin carboxylate of *o*-hydroxybenzoic acid , that is a dibutyltin bis(o-hydroxybenzoate) and a tetranuclear distannoxane as discussed in the following sections.

5.3.4 X-ray structure of dibutyltin bis(*o*-hydroxybenzoate)

Diorganotin carboxylates, in particular dibutyltin carboxylates are known to form monomeric dibutyltin bis(carboxylate) in which the carboxylate group is anisobidentate and the tin adopts the octahedral geometry in solid state. In the present study, the X-ray structure of dibutyltin bis(o-hydroxybenzoate) is found to compose of discrete monomeric molecules in which the tin atom lie on a crystallographic two-fold axis such that only half of the asymmetric unit is generated (Fig. 5.1). The six-coordinated tin atom is bonded to four oxygen atoms of the two o-hydroxybenzoic acids and forms the equatorial plane. The remaining two position are occupied by the two butyl groups [C—Sn—C = 140.1(3)^o]. This highly distorted octahedral geometry is best described as a skew-trapezoidal planar geometry. The symmetry related o-hydroxybenzoate units are asymmetrically coordinated to the tin atom, with Sn-O bond distances of 2.107(6) and 2.090(5) Å. These Sn-O bond distances are similar to those reported for other skew-trapezoidal bipyramidal diorganotin carboxylates such as $Me_2Sn(O_2CMe)_2$ [Lockhart, et. Al., 1987], $Bu_2Sn(OCOC_6H_4Br\text{-}p)_2$ [Ng, 1987] and $Bu_2Sn(OCOCH_2SC_6H_5)_2$ [Sandhu et al., 1989]. The carbonyl oxygen atoms form weak bonds with the tin atom as can be seen from their relatively longer Sn-O bond distances [Sn1-O2 2.561(6) and 2.646(6) Å]. The anisobidentate mode of coordination of the carboxylate ligand is also reflected by the C-O bond distances, that for the weakly coordinate oxygen atom ,O5- C16 (1.24 Å) is shorter than the C-O bond distance associated with the strongly bonded atom, O4- C16 (1.29 Å) (Siang- Guan Teoh et al., 1996).

The molecular structure also shows (figure 5.2) that both the butyl group adopts a W conformation, unlike the case of another structural modification in which one *n*-butyl group was in a *W* conformation and the other in a U conformation. The Sn-C bond distances are 2.118(8) and 2.116(8) Å. It was also noted that the phenolic oxygen of the ligand is not involved in any coordination to the tin atom. However, intramolecular hydrogen bonding is observed between the hydroxyl group with one of the carboxylate oxygen [O-H….O 2.599(9) and 2.62698) Å].

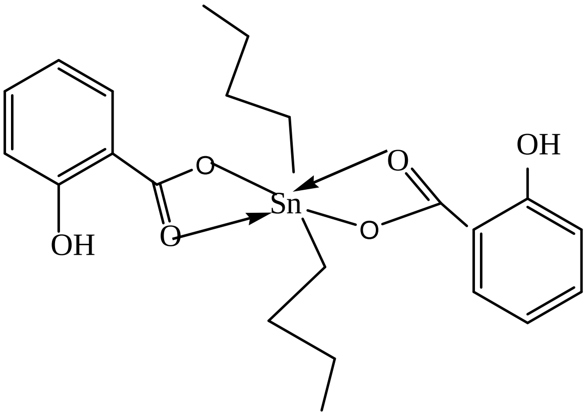


Figure 5.1 Structural formula of di-n-butyl bis(*o*-hydroxybenzoato)tin(IV)

Single crystal data, atomic coordinate, bond distances and angles of this complex are shown in tables 5.7 to 5.9.

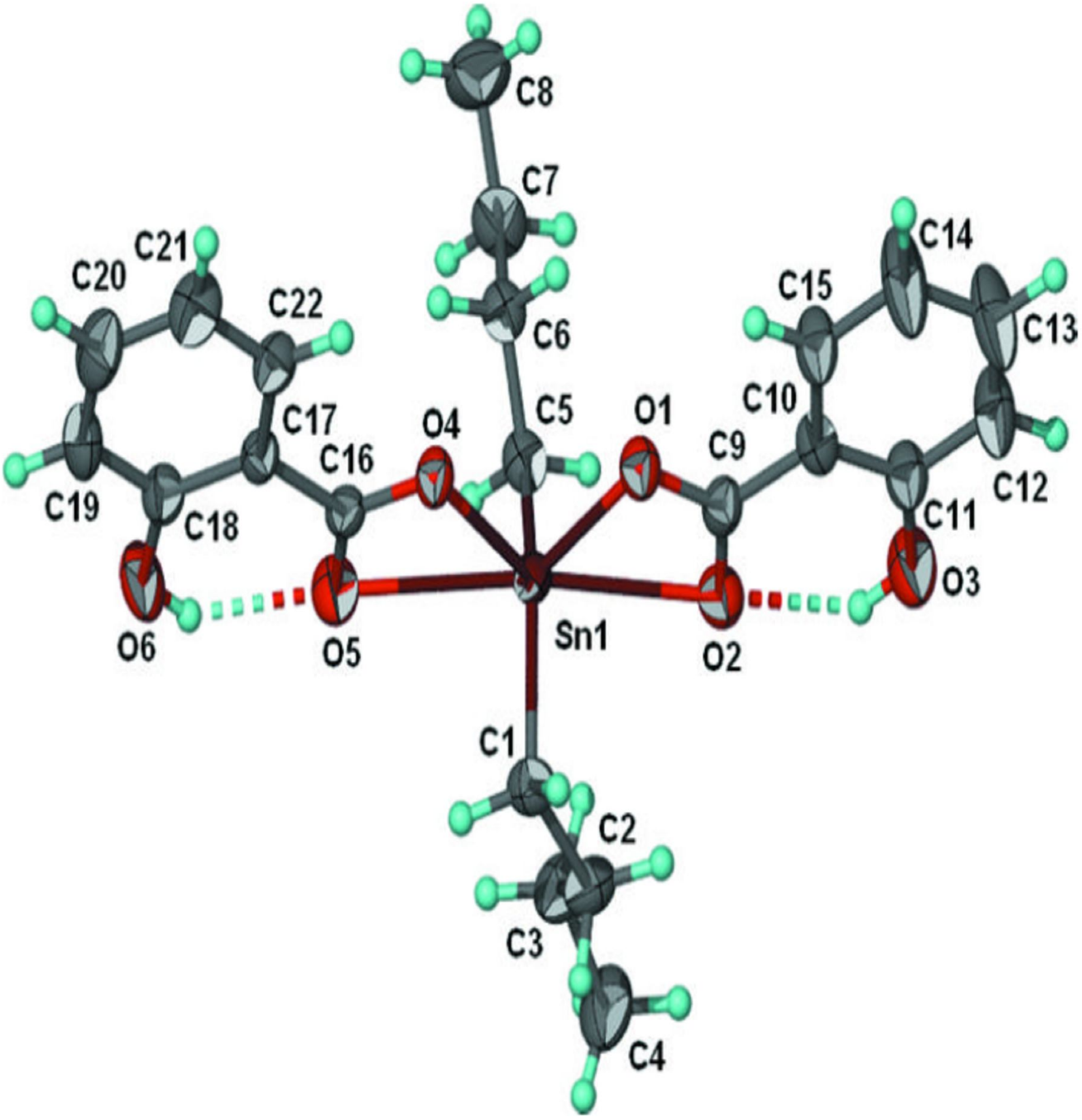


Figure 5.2 Molecular structure of di-n-butyl bis(*o*-hydroxybenzoato)tin(IV)

5.3.5 Single crystal data for bis[1,1,3,3-tetrabutyl-1,3-bis[2-hydroxybenzoato) 1,3-distannoxane]

In the second structural motif of the same dibutyltin carboxylate of *o*-hydroxybenzoic acid, the molecular structure as depicted in Fig. 5.3 reveals the formation of two dibutyldicarboxylato stannoxane which associated to form a dimer. Hence, the compound was renamed bis[1,1,3,3-tetrabutyl-1,3-bis[2-hydroxybenzoato)1,3-distannoxane] and was found to crystallize in the triclinic P-1 space group with cell dimention together with other crystallographic information as given in the Table 5.10.

The dimeric molecule was formed through the Sn-O linkages resulting in the formation of a centrosymmetric Sn_2O_2 centre. The dimer incorporates two types of carboxylates , one effectively isobidentate and the other one nearly unidentate. This resulted in one of the two independent Sn atoms is five-coordinate in a *cis*-C_2SnO_3 trigonal-bipyramidal geometry [C—Sn—C = 142.7 (1) ^{o}]; the geometry is distorted with O1-Sn1-O2 167.0296)^{o}, owing to a long Sn--O (double bond) [Sn--O = 2.862 (1) A°]. The other Sn atom has a bent R_2Sn skeleton [C—Sn—C = 144.0 ^{o}(1)], but the geometry is best regarded as being a *trans*-C_2SnO_4 octahedron as the Sn–O (single bond) interaction is shorter [Sn-O = 2.674 A° (1)]. The isobidentate nature of the carboxylate group was supported by the smaller difference between the two C-O bond distances [C24-O1 1.254 Å vs C24-O2 1.272 Å]. In constrast, the two C-O bond distances differ significantly [C17-O4 1.290 Å vs C17-O5 1.249 Å] for the monodentate carboxylate group, indicating one of the C-O have higher double bond character. The internal angles of the Sn_2O_2 ring are 102.82^{o} and 77.15^{o} indicating the 4-membered ring is planar. The range of internal angles are in good agreement with most of the dimeric dicarboxylate stannoxane reported in the literature [Tiekink, 1991]. In addition, it was found that the *ortho*-hydroxyl substituent of benzoate group is also involved in hydrogen bonding with the free carbonyl oxygen O3—H3---O2 2.638(2) Å and

O6—H6----O5 2.548(2)Å. The atomic coordinates and equivalent isotropic displacement parameters is given in Table 5.11. A list of the bond distances and bond angles for bis[1,1,3,3-tetrabutyl-1,3-bis[2-hydroxybenzoato)1,3-distannoxane] is given in Table 5.12

.

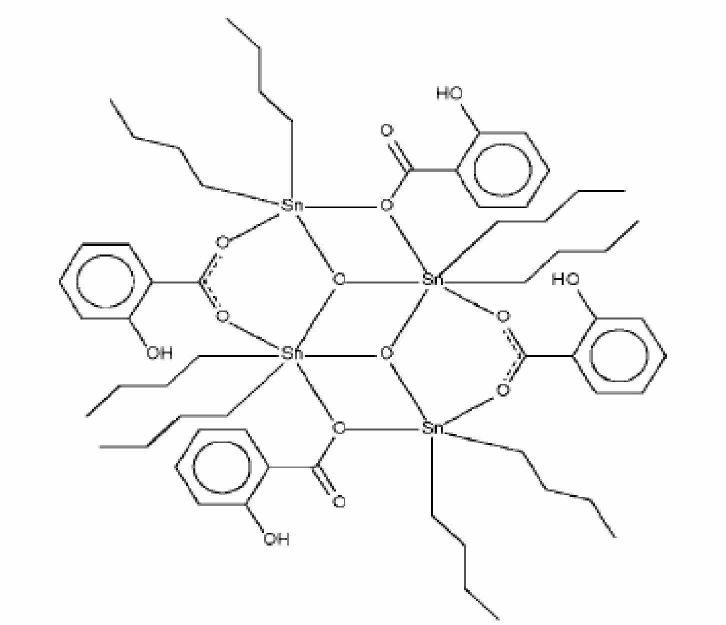


Figure 5.3 Structural formula of bis[1,1,3,3-tetrabutyl-1,3-bis[2-hydroxybenzoato)1,3-distannoxane

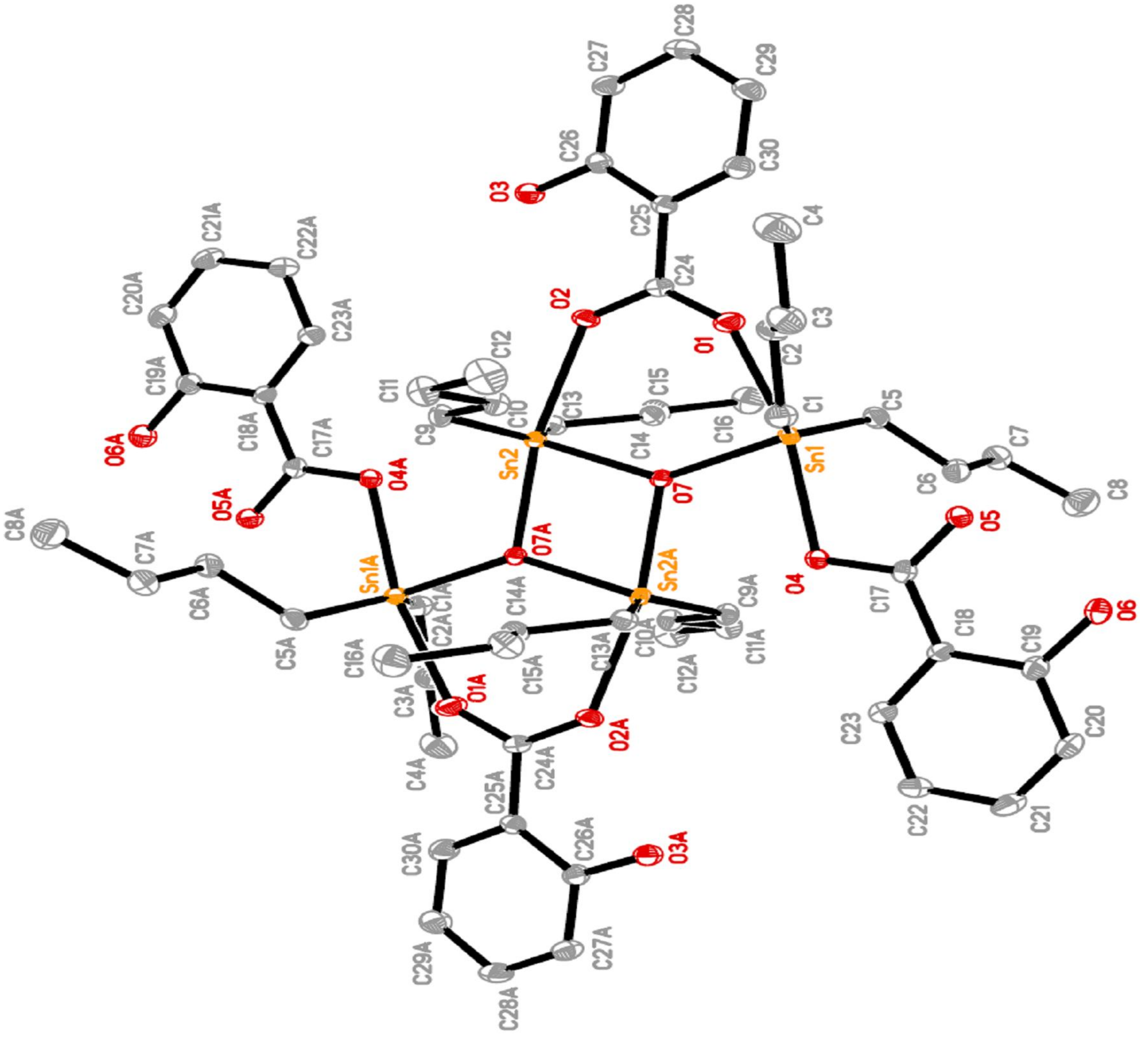


Figure 5.4: Molecular structure of bis[1,1,3,3-tetrabutyl-1,3-bis[2-hydroxybenzoato)1,3-distannoxane]

Table 5.7: Crystal data and structure refinement for di-n butyl bis(o-hydroxybenzoato)tin(IV)

Empirical formula	$C_{22} H_{28} O_6 Sn$
Formula weight	507.13
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, P-1
Unit cell dimensions	a = 9.1652(2) Å b = 11.2111(2) Å c = 12.2620(2) Å alpha = 94.7590(10) ^{o} beta = 106.8720(10) ^{o} gamma = 108.5860(10) ^{o}
Volume	1121.24(4) $Å^{3}$
Z, Calculated density	2, 1.502 Mg/m^{3}
Absorption coefficient	1.173 mm^{-1}
F(000)	516
Crystal size	0.25 x 0.20 x 0.15 mm
Theta range for data collection	1.77 to 27.50 deg.
Limiting indices	-11<=h<=7, -14<=k<=14, -15<=l<=15
Reflections collected / unique	11666 / 5068 [R(int) = 0.0338]
Completeness to theta = 27.50	98.3 %
Max. and min. transmission	0.8437 and 0.7581
Refinement method	Full-matrix least-squares on F^{2}
Data / restraints / parameters	5068 / 2 / 262
Goodness-of-fit on F^2	1.194
Final R indices [I>2sigma(I)]	R1 = 0.0593, wR2 = 0.1853
R indices (all data)	R1 = 0.0633, wR2 = 0.1878
Largest diff. peak and hole	2.571 and -1.405 e. $Å^{-3}$

Table 5.8: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å x 10^3) for di-n-butyl bis(2-hydroxybenzoato)tin(IV).

	X	Y	Z	U_{iso}/U_{eq}
Sn1	0.50157 (6)	0.34322 (5)	0.64132 (4)	0.03511 (17)
O1	0.6039 (7)	0.5445 (5)	0.6922 (5)	0.0424 (11)
O2	0.4303 (7)	0.4748 (5)	0.7850 (5)	0.0495 (13)
O3	0.4148 (9)	0.6313 (7)	0.9462 (6)	0.0687 (19)
O4	0.6470 (6)	0.3786 (5)	0.5355 (4)	0.0391 (11)
O5	0.5384 (8)	0.1687 (6)	0.5037 (5)	0.0535 (14)
O6	0.5995 (9)	0.0298 (5)	0.3515 (6)	0.0634 (18)
C1	0.2603 (9)	0.2912 (8)	0.5242 (7)	0.0452 (17)
C2	0.1264 (10)	0.2505 (8)	0.5755 (8)	0.0512 (19)
C3	0.1281 (12)	0.1422 (9)	0.6398 (9)	0.059 (2)
C4	−0.0260 (15)	0.0841 (11)	0.6719 (11)	0.077 (3)
C5	0.6353 (10)	0.2839 (7)	0.7842 (7)	0.0429 (16)
C6	0.8165 (10)	0.3455 (7)	0.8106 (7)	0.0423 (16)
C7	0.9178 (12)	0.3068 (9)	0.9151 (8)	0.059 (2)
C8	1.0967 (13)	0.3666 (13)	0.9401 (10)	0.079 (3)
C9	0.5369 (9)	0.5664 (7)	0.7668 (6)	0.0391 (15)
C10	0.5867 (10)	0.6976 (7)	0.8301 (6)	0.0391 (15)
C11	0.5246 (11)	0.7235 (8)	0.9170 (7)	0.0466 (18)
C12	0.5768 (15)	0.8474 (9)	0.9784 (8)	0.066 (3)
C13	0.6896 (18)	0.9447 (9)	0.9535 (11)	0.085 (4)
C14	0.7559 (19)	0.9206 (9)	0.8676 (11)	0.091 (5)
C15	0.7029 (12)	0.7971 (8)	0.8060 (8)	0.053 (2)
C16	0.6292 (8)	0.2670 (7)	0.4830 (6)	0.0350 (14)
C17	0.7181 (8)	0.2616 (7)	0.4013 (6)	0.0344 (14)
C18	0.6975 (10)	0.1431 (7)	0.3404 (7)	0.0420 (16)
C19	0.7814 (12)	0.1408 (9)	0.2613 (7)	0.052 (2)
C20	0.8863 (13)	0.2521 (10)	0.2488 (8)	0.061 (2)
C21	0.9105 (12)	0.3695 (9)	0.3108 (8)	0.056 (2)

Table 5.9: Selected bond distances (Å) and bond angles (^{o}) for

di-n-butyl bis(2-hydroxybenzoato)tin(IV)

Sn(1)-O(1)	2.107(5)
Sn (1)-C(5)	2.116(8)
Sn(1)-C(1)	2.118(8)
Sn (1)-O(1)	2.106(5)
Sn(1)-O(2)	2.561(6)
Sn(1)-O(4)	2.090(5)
Sn(1)-O(5)	2.646(6)
O(1)-C(9)	1.289(9)
O(2)-C(9)	1.258(9)
O(3)-C(11)	1.350(10)
O(4)-C(16)	1.296(9)
O(5)-C(16)	1.248(9)
O6)-C(18)	1.347(9)
C(1)-C(2)	1.500(11)
C(2)-C(3)	1.503(12)
C(3)-C(4)	1.534(13)
C(5)-C(6)	1.504(11)
C(6)-C(7)	1.534(11)
C(7)-C(8)	1.484(15)
C(9)-C(10)	1.467(10)
C(10)-C(15)	1.396(11)
C(10)-C(11)	1.396(11)
C(11)-C(12)	1.385(12)
C(12)-C(13)	1.368(15)
C(14)-C(15)	1.380(12)
C(16)-C(17)	1.472(9)
C(17)-C(22)	1.382(10)
C(17)-C(18)	1.397(10)
C(18)-C(19)	1.406(11)
O(4)-Sn(1)-O(1)	82.2(2)
O(4)-Sn(1)-C(5)	104.7(3)
O(1)-Sn(1)-C(5)	102.1(3)
O(4)-Sn(1)-C(1)	104.1(3)
O(1)-Sn(1)-C(1)	108.7(3)
C(5)-Sn(1)-C(1)	140.1(3)
O(4)-Sn(1)-O(2)	137.43(19)
O(1)-Sn(1)-O(2)	55.25(19)
O(4)-Sn(1)-O(5)	53.64(18)
C(5)-Sn(1)-O(2)	88.1(3)
C(1)-Sn(1)-O(2)	89.0(3)
O(4)-Sn(1)-O(5)	53.64(18)
O(1)-Sn(1)-O(5)	135.77(19)

Table 5.10: Crystal data and structure refinement for bis[1,1,3,3-tetrabutyl-1,3-bis [2-hydroxybenzoato)1,3-distannoxane]

Empirical formula	$C_{17} H_{24} O_5 Sn$
Formula weight	427.08
Temperature	100(2)K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, P-1
Unit cell dimensions	a = 11.4549(2) Å b = 121610(2) Å c = 13.4436(2) Å alpha = 106.300(1) ^{o} beta = 92.532(1) ^{o} gamma = 115.204(1) ^{o}
Volume	1597.18(5) Å^{3}
Z, Calculated density	1, 1.572 Mg/m^{3}
Absorption coefficient	1.601 mm^{-1}
F(000)	764.0
Crystal size	0.183 x 0.297 x 0.383 mm
Theta range for data collection	1.6 to 27.50 deg.
Limiting indices	-14<=h<=14, -15<=k<=15, 17<=l<=17
Reflections collected / unique	9253 / 7210 [R(int) = 0.008]
Completeness to theta	1.6 - 27.50^{o}
Max. and min. transmission	0.761 and 0.587
Refinement method	Full-matrix least-squares on F^{2}
Data / restraints / parameters	7210 / 0 / 352
Goodness-of-fit on F^{2}	1.17
Final R indices [I>2sigma(I)]	R1 = 0.018, wR2 = 0.067
R indices (all data)	R1 = 0.0227, wR2 = 0.0505
Largest diff. peak and hole	0.91 and -0.86 ($e_{\text{Å}}{}^{-3}$)

Table 5.11 : Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å x 10^3) for bis[1,1,3,3-tetrabutyl-1,3-bis[2-hydroxybenzoato)1,3-distannoxane].

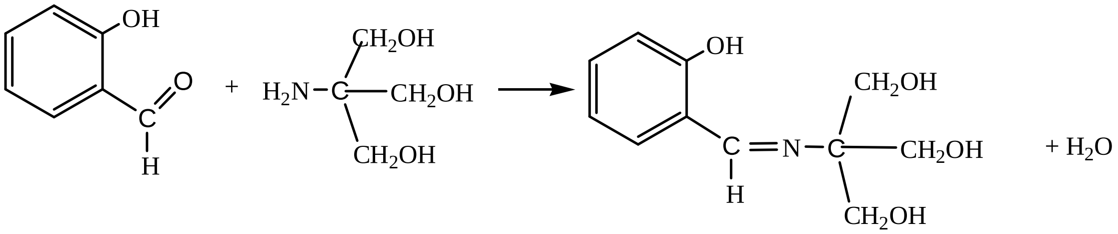
	x	*y*	*z*	U_{iso}*/U_{eq}
Sn1	0.474718 (13)	0.580180 (13)	0.753402 (10)	0.01404(5)
Sn2	0.456706 (13)	0.604166 (12)	0.476911 (10)	0.01191 (5)
O1	0.41023 (18)	0.72441 (17)	0.74041 (13)	0.0253 (4)
O2	0.40862 (16)	0.75903 (15)	0.58632 (12)	0.0191 (3)
O3	0.37161 (16)	0.95576 (15)	0.57647 (12)	0.0214 (3)
O4	0.54344 (15)	0.43088 (14)	0.72857 (11)	0.0163 (3)
O5	0.51748 (16)	0.45675 (15)	0.89385 (12)	0.0201 (3)
O6	0.55126 (18)	0.31818 (17)	0.99204 (13)	0.0265 (4)
O7	0.48810(14)	0.54280 (13)	0.59784 (11)	0.0140 (3)
C1	0.2821 (2)	0.4578 (2)	0.76932 (18)	0.0209 (4)
C2	0.1914 (2)	0.5184 (2)	0.80106 (18)	0.0214 (4)
C3	0.0665 (2)	0.4265 (2)	0.8274 (2)	0.0274 (5)
C4	-0.0249 (3)	0.4862 (3)	0.8588 (2)	0.0366 (6)
C5	0.6564 (2)	0.7396 (2)	0.84066 (17)	0.0197 (4)
C6	0.7543 (2)	0.7138 (2)	0.89931 (18)	0.0228 (4)
C7	0.8873 (2)	0.8329 (2)	0.94411 (18)	0.0239 (5)
C8	0.9803 (3)	0.8134 (3)	1.0124 (2)	0.0369 (6)
C9	0.2521 (2)	0.4950 (2)	0.41335 (16)	0.0172 (4)
C10	0.1726 (2)	0.4388 (2)	0.49052 (17)	0.0183 (4)
C11	0.0273 (2)	0.3510 (2)	0.44359 (19)	0.0252 (5)
C12	-0.0483(2)	0.2992 (3)	0.5246 (2)	0.0330 (6)
C13	0.6307 (2)	0.76707 (19)	0.47831 (16)	0.0160 (4)
C14	0.7264 (2)	0.8419 (2)	0.58388 (16)	0.0171 (4)

Table 5.12: Selected bond distances (Å) and bond angles(^{o}) for bis[1,1,3,3- tetrabutyl-1,3-bis[2-hydroxybenzoato)1,3-distannoxane]

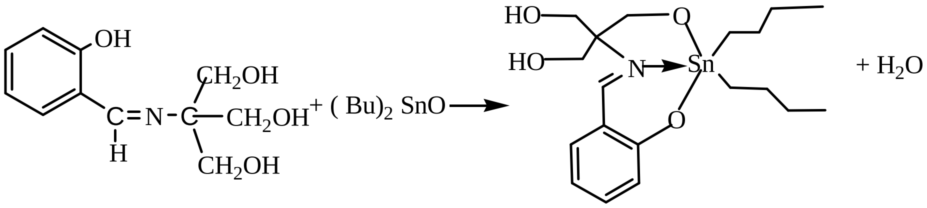
Sn(1)-O(7)	2.0459(10)
Sn(1)-C(27)	2.1235(16)
Sn(1)-C(23)	2.1261(16)
Sn(1)-O(7)	2.1476(11)
Sn(1)O(5)	2.3253(11)
Sn(1)Sn(2)	3.27976(19)
Sn(2)-O(7)	2.0398(10)
Sn(2)-C(8)	2.1302(17)
Sn(2)-C(12)	2.1344(17)
Sn(2)-O(4)	2.2174(12)
Sn(2)-O(2)	2.2208(11)
O(1)-C(7)	1.2509(19)
O(2)-C(7)	1.2912(18)
O(3)-C(2)	1.350(2)
O(4)-C(16)	1.2535(19)
O(5)-C(16)	1.2748(19)
O(6)-C(18)	1.3542(19)
O(7)-Sn(2)	2.0398(10)
O(7)-Sn(1)	2.0459(10)
O(7)-Sn-C(27)	109.36(5)
O(7)-Sn(1)-C(23)	105.65(5)
C(27)- Sn(1)-C(23)	144.08(6)
O(7)-Sn(1)-O(7)	77.12(4)
C(23)- Sn(1)-O(7)	97.06(5)
O(7)- Sn(1)-O(5)	92.57(4)
C(27)- Sn(1)-O(5)	83.41(5)
C(23)-Sn(1)-O(5)	87.29(5)
O(7)- Sn(1)-O(5)	169.54(4)
O(7)- Sn(1)Sn(1)	39.67(3)
C(27)-Sn(1)-Sn(1)	107.50(4)
C(23)-Sn(1)-Sn(1)	104.40(4)
O(7)- Sn(1)- Sn(1)	37.45(3)
O(5)- Sn(1)-Sn(1)	132.21(3)
O(7)- Sn(2)-C(8)	106.95(6)
O(7)- Sn(2)-C(12)	110.00(6)
C(8)- Sn(2)-C(12)	142.80(6)
O(7)-Sn(2)-O(4)	88.26(4)
C(8)- Sn(2)-O(4)	86.54(6)
C(12)-Sn(2)-O(4)	90.34(6)
O(7)- Sn(2)-O(2)	78.69(4)
C(8)- Sn(2)-O(2)	96.62(5)
C(12)-Sn(2)-O(2)	94.66(5)

5.4 Dibutyltin complexes of Schiff base ligands

In this part of the project, a series of potentially tridentate ligands namely 2-salicylideniminato-2-(hydroxymethyl)-1, 3-dihydroxypropane (saltris), 5-chloro-2-salicylideniminato-2-(hydroxymethyl)-1, 3-dihydroxypropane (5-Clsaltris), 5- bromo-2-salicylideniminato-2-(hydroxymethyl)-1, 3-dihydroxypropane (5-Btsaltris) and 5- nitro-2-salicylideniminato-2-(hydroxymethyl)-1, 3-dihydroxypropane ($5\text{-}NO_2$saltris) were synthesized by the condensation reactions between tris(hydroxymethyl)aminomethane with salicylaldehyde, 5-chloro salicylaldehyde , 5-bromo salicylaldehyde and 5-nitro salicylaldehyde , respectively. An example of the synthesis is shown below for dibutyltin saltris.



The saltris and substituted saltris ligands were then reacted with dibutyltin oxide to afford the dibutyltin saltris or substituted saltris complexes as shown below:



The dibutyltin saltris complexes were all yellow crystalline solids which melt in the range between 120 to 160°C. The melting points of the saltris ligands and their dibutyltin saltris complexes are given in Table 5.13. The CHN elemental analysis for the dibutyltin complexes of the Schiff ligands are all in agreement with the proposed molecular formula of the complexes.

Table 5.13: Melting Point and elemental data of schiff base ligands and their dibutyltin(IV) complexes

Compound	m.p.	%C (calcd)	%H (calcd)	%N (calcd)
Saltris	140 -142 °C	-	-	-
5-ClSaltris	148-150 °C	-	-	-
5-BrSaltris	145-147 °C	-	-	-
5-NO_2Saltris	244-246 °C	-	-	-
Dibutyltin of Saltris	122-124 °C	49.5 (50.0)	6.22(6.57)	3.28(3.07)
Dibutyltin of 5-ClSaltris	134-136 °C	48.1(46.6)	5.44(5.91)	2.24(2.85)
Dibutyltin of 5-BrSaltris	126-128 °C	41.5(42.6)	4.95(5.42)	2.60(2.62)
Dibutyltin of 5-NO_2Saltris	150-152 °C	45.3(44.9)	6.11(5.79)	5.10(5.59)

5.5 IR Spectral data for Schiff base ligands and their dibutyltin complexes

The full IR spectral data and the assigned stretching frequencies of selected functional groups are tabulated in Table 5.14 and 5.15, respectively. The useful stretching frequencies for the discussion of the dibutyltin saltris complexes are the imine C=N vibration which occurs at between 1700 to 1600 cm^{-1} and the –OH stretching vibration which occur at around 3300 cm^{-1}. Other stretching vibration recorded are that of Sn-O and Sn-N which are usually found in the region 400 to 600 cm^{-1}.

It can be seen in Table 5.15 that upon forming the dibutyltin Schiff base complexes, the stretching frequency of C=N had shifted to lower frequency, while the frequencies around 421-434 cm^{-1} and 512-528 cm^{-1} which belong to Sn-N and Sn-O stretching vibration and was absent in the ligands (Kovacic, 1967; Saraswat and Mehrotera, 1979). On the other hand, the presence of OH stretching frequencies before and after the complex formation indicates that two of the methanoic hydroxyl group are retained after the formation of the diorganotin complex.

Table 5.14: IR spectral data for schiff base ligands and their dibutyltin(IV) complexes

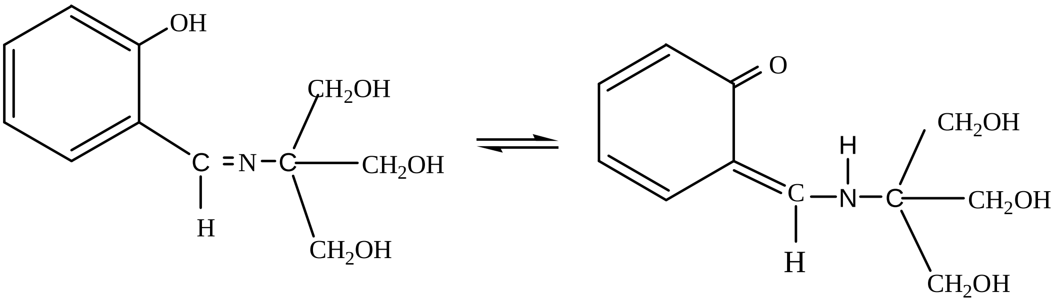
Compounds	IR stretching frequencies (cm^{-1})
Saltris	3321br, 1994w, 1658s, 1533w, 1487w, 1395w,1340s,1305s, 1224w,1153s,1100s 1059w, 981s, 943w, 918s, 892s,870w 799s, 767s,736s,648w, 628w, 568s, 545s 490w, 476s, 441s, 400s
Dibutyltin Saltris complex	3337.7br, 3062w, 2920w, 2851w, 2361w, 1949w, 1830w, 1793w, 1735w, 1609vs, 1538vs, 1466s, 1441s, 1411s, 1377s, 1320s,1248w, 1207w, 1183 w, 1148s, 1095s, 1075s, 1037s, 1010w, 994w, 923s, 895w, 854w, 818s, 760s, 696w, 659s, 595s, 547w, 528vs, 436s, 421s
5Br saltris ligand	3350br, 2931vw, 1637vs, 1522s, 1491vw, 1328vw, 1232w, 1175w, 1115w, 1053s, 908w, 860w, 821w, 626w, 532w
Dibutyltin 5-Br saltris complex	3368br, 3072br, 2954w, 2924w, 2818w, 2723w, 1611vs, 1528s, 1458s, 1424w, 1368w, 1310s, 1180s, 1094w, 1070s, 1039s, 990s, 925w, 872s, 826s, 796s, 684w, 660w, 637w, 527vs, 418vs
5-NO$_2$ saltris ligand	3448w, 3115br, 2808vw, 1651vs, 1545s, 1513s, 1491s, 1449s, 1401w, 1307s,1234w, 1194w, 1154s, 1132s, 1102w, 1051s, 980w, 946sw, 902s, 836s, 757w, 729w, 679w, 629w, 564w, 510w, 482w, 460w, 428w, 385w
Dibutyltin 5-NO$_2$ saltris complex	3493s, 3247br, 2955 w, 2931w, 2856w, 1631s, 1603s, 1550s, 1491w, 1460w, 1405w, 1308s, 1245s, 1195 w, 1130 w, 1100 s, 1067s, 954 w, 931w, 846s, 795s 735w, 679w, 628w, 559s, 512s, 472w, 454s, 437s
5-Cl saltris ligand	3388br, 1639s, 1523s, 1232m, 1175m, 1053s, 915m, 858m, 822m, 783m, 626 w 537s, 485w, 455w, 428w
Dibutyltin 5-Cl saltris complex	3326br, 2955br, 1613vs, 1532vs, 1459s, 1425s, 1392m, 1314s, 1233w, 1170m 1142w, 1060s, 1037s, 990m, 929w, 869m, 836m, 800s, 609m, 660s, 526vs, 414vs

Table 5.15 : Selected stretching frequencies of schiff base ligands and their dibutyltin(IV) complexes

Compounds	ν C=N- (cm^{-1})	ν Sn-N (cm^{-1})	ν Sn-O (cm^{-1})
Saltris ligand **Saltris dibutyltin complex**	1638 1609	- 421	- 528
5-Cl saltris ligand **5-Cl saltris dibutyltin complex**	1639 1613	- 414	- 526
5-Br saltris ligand **5-Br saltris dibutyltin complex**	1637 1611	- 418	- 527
5-NO_2 saltris ligand **5-NO_2 saltris dibutyltin complex**	1651 1631	- 434	- 512

5.6 NMR data of Schiff base ligands and their dibutyltin complexes

The ^{1}H NMR and ^{13}C NMR chemical shifts of schiff base ligands and their respective dibutyltin complexes were recorded and their data are given in Tables 5.16 and 5.17, while the ^{119}Sn NMR chemical shifts of the dibutltin saltris complexes are listed in Table 5.18. Salicylimines in solution can occur in the keto and enole tautomeric forms.



Enole form Keto form

The ^{1}H NMR peak for the phenolic proton which is usually found at 10.8 ppm was not observed in the saltris ligands, indicating the ligands in solution exist in the keto form rather than the enolic form. The phenolic proton is transferred to the imine nitrogen. This tautomeric form had been reported (Yu.M.Chumakov et al. 2003; Mishtu Dey et al. 2003). However, the appearance IR peak at 1638-1651 cm^{-1} that belongs to C=N showed that the ligands exist in the enolic form in the solid state. The methanoic protons are found at the region between 4.75 to 4.82 ppm. The other aliphatic and aromatic protons are located in expected regions.

In addition, the appearance a ^{13}C NMR peak at 164 ppm attributed to C=O is another evidence for the existence of keto form in solution. The peak of azomethine proton has shifted downfield (deshielding) after complexation, due to the donation of N lone pair to the tin atom. In the dibutyltin(IV) complexes, the peaks at the region between 0.8 to 1.6 ppm are belongs to the butyl group.

Table 5.16 : ^{1}H NMR data of Schiff base ligands and their dibutyltin(IV) complexes

Compound	^{1}H NMR chemical shift (ppm)
Saltris ligand	3.44-3.61(CH_2), 4.75 (OH), 6.7-7.4 (phenyl), 8.54 (imine)
Dibutyltin Saltris complex	0.83-1.61 (butyl), 3.6-3.7 (CH_2), 6.6-7.31(phenyl), 8.96(imine)
5 -Cl saltris ligand	3.27-3.59 (CH_2), 4.82 (OH), 6.71-7.49 (phenyl), 8.45-8.51 (azomethine)
Dibutyltin 5-Cl saltris complex	0.84-2.03 (butyl), 3.66-3.78 (CH_2), 5.27 (OH), 6.64-7.25(phenyl), 8.91 (azomethine)
5-Br saltris ligand	3.41-3.77 (CH_2), 4.82 (OH), 6.68-7.69(phenyl)
Dibutyltin 5-Br saltris complex	0.84-1.59 CH_3 (butyl), 3.66-3.76 (CH_2) , 6.58-7.26 (phenyl), 8.91 imine

Table 5.17. ^{13}C NMR of[1-hydroxy-2-hydroxymethyl-2-(2-oxidobenzylideneamino)-3-oxidomethylpropane]dibutyltin(IV) (saltris) ligands and their dibutyltin(IV) complexes

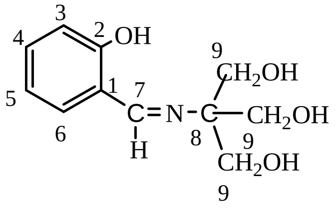
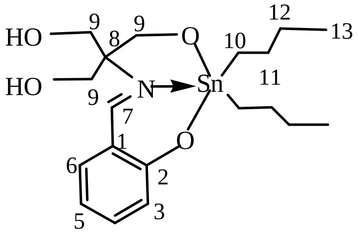
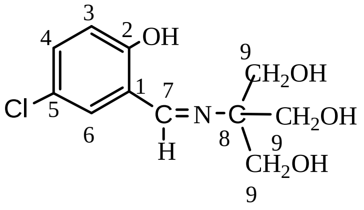
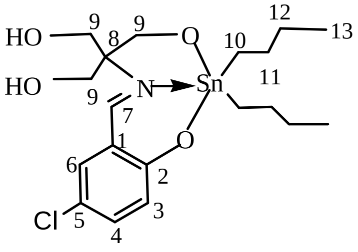
Compound	^{13}C Chemical shift (ppm)	
	C1	118.5
	C2	163.5
	C3	117.5
	C4	117.1
	C5	132.2
	C6	132.4
	C7	164.5
	C8	61.4
	C9	67.1
	C1	122.5
	C2	170
	C3	117.9
	C4	116.3
	C5	136.1
	C6	136.9
	C7	174
	C8	64.1
	C9	67.1
	C10	21.4
	C11	27.6
	C12	27.4
	C13	13.9
	C1	120.8
	C2	164.2
	C3	120
	C4	119.2
	C5	131.6
	C6	133
	C7	164.6
	C8	61.6
	C9	67.6
	C1	124.1
	C2	168.3
	C3	120.3
	C4	118.9
	C5	134.1
	C6	136.6
	C7	173
	C8	63.8
	C9	67.3
	C10	21.4
	C11	27.4
	C12	26.9
	C13	13.7

Table 5.17. Continued:

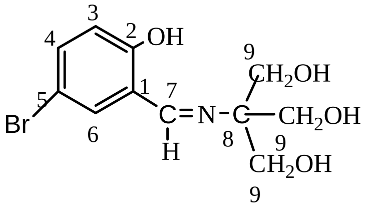
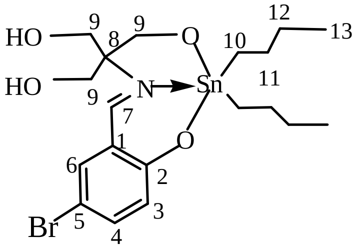
Compound	^{13}C chemical shift (ppm)	
	C1	121.4
	C2	164.1
	C3	119.8
	C4	107
	C5	134.7
	C6	135.8
	C7	165.3
	C8	61.5
	C9	67.5
	C1	124.4
	C2	168.7
	C3	118.9
	C4	106.8
	C5	137.3
	C6	139.2
	C7	172.9
	C8	63.7
	C9	67.4
	C10	21.4
	C11	27.4
	C12	26.9
	C13	13.7

Table 5.18 : ^{119}Sn NMR Chemical shifts of dibutyltin(IV) saltris complexes

Compound	^{119}Sn NMR chemical shifts
Dibutytin saltris complex	-187.1
Dibutytin 5-Clsaltris complex	-184.3
Dibutytin 5-Brsaltris complex	-184.3

Upon complexation, the three equivalent CH_2 carbon because non equivalent, giving rise to two types ^{13}C chemical shifts for CH_2. The ^{13}C NMR peaks at 163-164 ppm for saltris ligands was found to have shifted to 169-173 ppm after complex formation. This peak belongs to azomethine that shifted after complexation. The ^{119}Sn NMR Chemical shift of the dibutyltin complexes showed that the complexes has coordination number of five as similar range of ^{119}Sn chemical shift for diorganotin complexes has been reported (Otera, 1981).

5.7 X-ray crystallographic study of dibutyltin 5 –chlorosaltris complex

The single crystal data for the dibutyltin 5-chlorosaltris complex were collected and the structural solved.

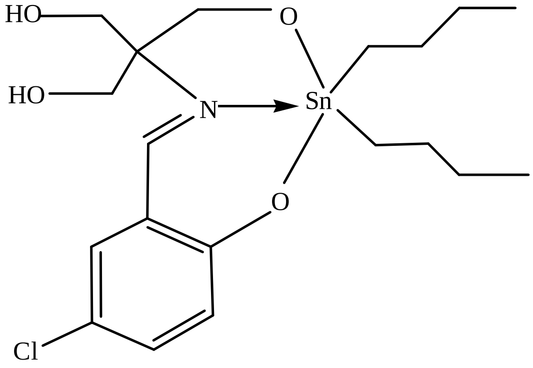


Figure 5.5 Structural formula of [1-hydroxy-2-hydroxymethyl-2-(5-chloro- 2-oxidobenzylideneamino)-3-oxidomethylpropane]dibutyltin(IV)

In the title compound, [1-hydroxy-2-hydroxymethyl-2-(5-chloro- oxidobenzylideneamino)-3-oxidomethylpropane]dibutyltin(IV) , the ligand, tris{(hydroxymethyl)aminomethane 5-chlorosalicylideniminate acts as a tridentate ligand and coordinated to the tin atom via the phenoxyl oxygen, one methoxyl oxygen and the imino nitrogen, forming a bicyclic ring. The complex crystallizes in the monoclinic *C2/c* space group with cell dimension and other crystallographic details given in Table 5.19. The bond distances and bond angles is given in Table 5.20. The atomic coordinates and equivalent isotropic displacement parameters is given in Table 5.21. The molecular structure as depicted in Fig. 5.6 showed that the tin adopts a distorted trigonal bipyramidal geometry with the imino nitrogen and the two butyl group forming the equatorial plane (sum of angles subtended at tin is 359.93^o). The axial position occupied by the phenoxyl and methoxyl oxygens atoms and the apical O1-Sn1-O2 angle is 156.01(6)°. The Sn-O1 and Sn-O2 bond distances are 2.119(2) and 2.107(2) Å, respectively while the Sn-N bond distance is 2.215(2) Å. These bond distances are within the range of bond distances reported in the literature for Sn-O and Sn-N coordination.

It was also noted that there is an intramolecular C-H---O hydrogen bond [C-H….O 2.164(2) Å] between one of the free methoxyl oxygen and imino hydrogen, producing an 6-membered ring motif. In the crystal structure, neighboring molecules are linked together by intermolecular O-H⋯O hydrogen bonds [O-H⋯O 2.611(2) and 2.739(2) Å] to form 3-D infinite network structure.

Table 5.19: Crystal data and structure refinement for [1-hydroxy-2-hydroxymethyl-2-(5-chloro- 2-oxidobenzylideneamino)-3-oxidomethylpropane]dibutyltin(IV)

Empirical formula	C_{19} H_{30}Cl N O_4 Sn
Formula weight	490.58
Temperature	123 K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic C2/c
Unit cell dimensions	
	a =18.6212 (2) Å b = 13.4657(2) Å c = 16.6949(10) Å
	alpha = 90.00 ^{o} beta = 91.8450 (10) ^{o} gamma = 90.00 ^{o}
Volume	4184.03 (8) $Å^3$
Z, calculated density	8, 1.558 Mg/m^3
Absorption coefficient	1.372 mm^{-1}
F(000)	2000
Crystal size	0.43 x 0. 30x 0.25 mm
Theta range for data collection	1.87 to 27.50 deg.
Limiting indices	-24<=h<=24, -15<=k<=17, -21<=l<=21
Reflections collected / unique	2531/4807
Completeness to theta	1.8 -27.50 ^{o}
Max. and min. transmission	0.7255/0.5900 [R(int) = 0.025]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	23531, 0 ,4807
Goodness-of-fit on F^2	1.291
Final R indices [I>2sigma(I)]	R1= 0.0201,WR^2= 0.0872
R indices (all data)	
Largest diff. peak and hole	0.89 and -0.65($eÅ^{-3}$)

Table 5.20: Selected bond distances (Å) and bond angles (^{o}) for [1-hydroxy-2-hydroxymethyl-2-(5-chloro- 2-oxidobenzylideneamino)-3- oxidomethylpropane]dibutyltin(IV)

Sn(1)- O(2)	2.136(2)
Sn(1)- O(1)	2.2149(18)
Sn(1)- C(5)	2.137(3)
Sn(1)- C(1)	2.136(2)
Sn(1)- N(1)	2.2149(18)
C(l1)- C(12)	1.748(2)
N(1)- C(15)	1.292(3)
N(1)- C(16)	1.486(3)
O(1)- C(9)	1.314(3)
O(2)- C(17)	1.409(3)
O(3)- C(18)	1.422(3)
O(4)- C(19)	1.421(3)
C(1)- C(2)	1.527(4)
C(2)- C(3)	1.523(4)
C(3)- C(4)	1.506(5)
C(5)- C(6)	1.521(4)
C(6)- C(7)	1.504(4)
C(7)- C(8)	1.512(4)
C(9)- C(1)	4 1.414(3)
C(9)- C(10)	1.413(3)
C(10)- C(11)	1.377(3)
C(11)- C(12)	1.392(3)
C(12)- C(13)	1.370(3)
C(13)- C(14)	1.414(3)
C(14)- C(15)	1.445(3)
C(16)- C(19)	1.533(3)
C(16)- C(18)	1.534(3)
C(16)- C(17)	1.542(3)
O(2)- Sn(1)-O(1)	156.01(6)
O(2)- Sn(1)- C(5)	98.14(9)
O()-1 Sn(1)- C(5)	97.76(9)
O(2)- Sn(1)- C(1)	91.32(8)
O(1)- Sn(1)- C(1)	91.99(9)
C(5)- Sn(1)- C(1)	130.29(11)
O(2)- Sn(1)- N(1)	76.31(6)
O(1)- Sn(1)- N(1)	81.66(6)
C(5)- Sn(1)- N(1)	108.56(9)
C(1)- Sn(1)- N(1)	121.07(9)
C(15)- N(1)- C(16)	120.95(18)
C(15)- N(1)- Sn(1)	124.97(15)
C(16)- N(1)- Sn(1)	113.77(13).
C(9)- O(1)- Sn(1)	126.37(15)
C(17)-O(2)- Sn(1)	115.26(12)
C(2)- C(1)- Sn(1)	117.51(17)
C(6)- C(5)- Sn(1)	117.25(19)
C(13)- C(14)- C(15)	116.2(2)
N(1)- C(15)- C(14)	126.5(2)
N(1)- C(16)- C(19)	115.46(17)

Table 5.21. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å x 10^3) for [1-hydroxy-2-hydroxymethyl-2-(5-chloro- 2-oxidobenzylideneamino)-3-oxidomethylpropane]dibutyltin(IV)

	x	*y*	*z*	U_{iso}*/U_{eq}
Sn1	0.32418(1)	0.37407(1)	0.25405(1)	0.0178(1)
Cl1	0.05353(4)	0.31245(5)	-0.07289(4)	0.0378(2)
O1	0.26798(9)	0.26134(13)	0.18941(10)	0.0246(5)
O2	0.39663(9)	0.49315(12)	0.27014(9)	0.0209(4)
O3	0.51910(8)	0.51559(13)	0.10310(10)	0.0204(5)
O4	0.37040(9)	0.56257(13)	-0.01897(10)	0.0228(5)
N1	0.33157(9)	0.43790(14)	0.13232(11)	0.0165(5)
C1	0.40250(13)	0.27082(19)	0.29943(16)	0.0276(7)
C2	0.38068(15)	0.1616(2)	0.30331(17)	0.0313(8)
C3	0.31879(17)	0.1403(2)	0.35822(19)	0.0363(9)
C4	0.3351(2)	0.1658(4)	0.4448(2)	0.0625(13)
C5	0.23404(14)	0.4389(2)	0.31042(17)	0.0294(7)
C6	0.16717(16)	0.3750(2)	0.3172(2)	0.0398(10)
C7	0.10270(16)	0.4284(2)	0.3479(2)	0.0416(10)
C8	0.03790(19)	0.3636(3)	0.3610(3)	0.0552(13)
C9	0.22118(12)	0.27460(17)	0.12975(13)	0.0189(6)
C10	0.16249(13)	0.20871(18)	0.11998(14)	0.0232(7)
C11	0.11135(13)	0.22159(19)	0.05949(14)	0.0241(7)
C12	0.11875(12)	0.29761(18)	0.00383(14)	0.0226(7)
C13	0.17670(13)	0.36027(17)	0.00833(15)	0.0225(7)
C14	0.22780(12)	0.35104(17)	0.07240(13)	0.0182(6)
C15	0.28647(11)	0.42127(17)	0.07340(13)	0.0177(6)
C16	0.38985(11)	0.51239(16)	0.12515(13)	0.0155(6)
C17	0.39586(12)	0.56360(17)	0.20770(13)	0.0187(6)
C18	0.45806(11)	0.45281(16)	0.10877(13)	0.01

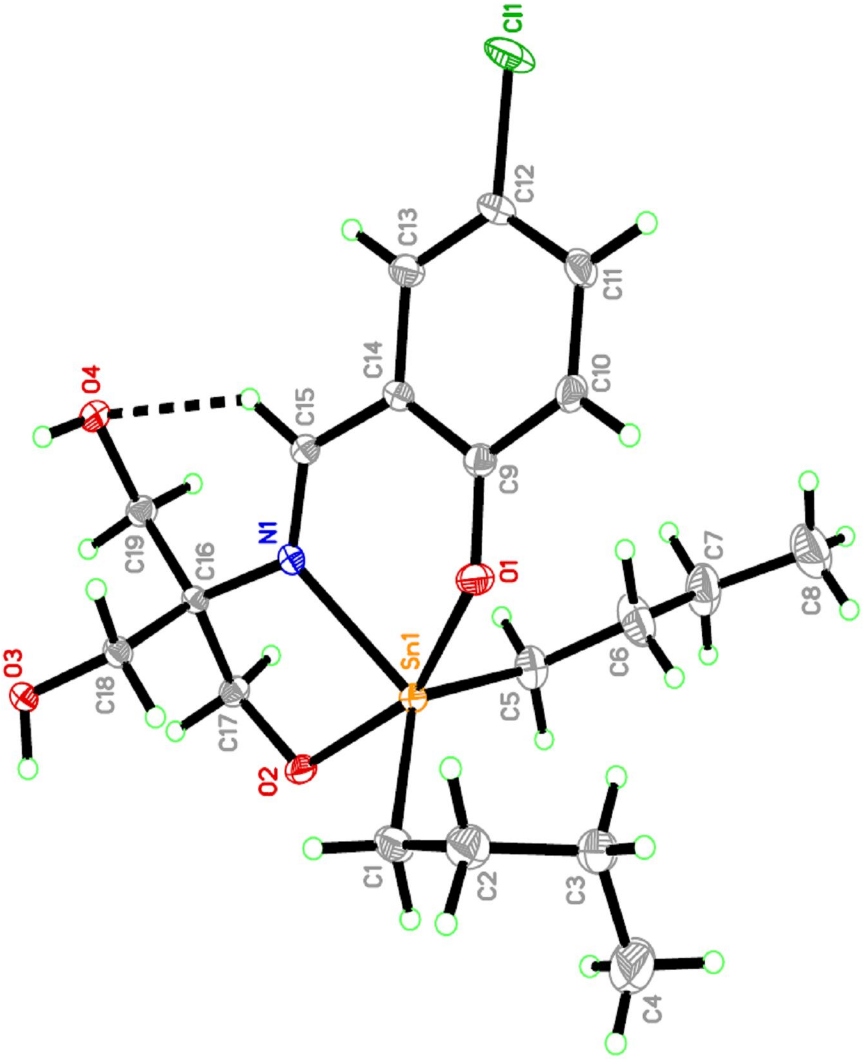


Figure 5.6 Molecular structure of [1-hydroxy-2-hydroxymethyl-2-(5-chloro- 2-oxidobenzylideneamino)-3-oxidomethylpropane]dibutyltin(IV)