5.1 INTRODUCTION

Thioesters represent an important class of chemical compounds containing the functional group -C-S-CO-C. They have found applications in many fields especially in biochemistry as thioesters are intermediates in numerous biosynthetic reactions such as malonyl Co-A and acetyl Co-A, which includes the degradation of free fatty acids in muscle cells [Nelson and Cox, 2000].

Generally, thioesters are prepared from the reactions between thiol compounds and carboxylic acids. Thioesters could also be prepared from the carbonylation of alkynes and alkenes in the presence of thiol compounds [Bertleff *et al.*, 2007].

In this research, a thioester which was first prepared by other research group was further converted to include a hydrazone group. The reaction of this hydrazone with salicylaldehyde and substituted salicylaldeyhde groups yielded Schiff base ligands reported here.

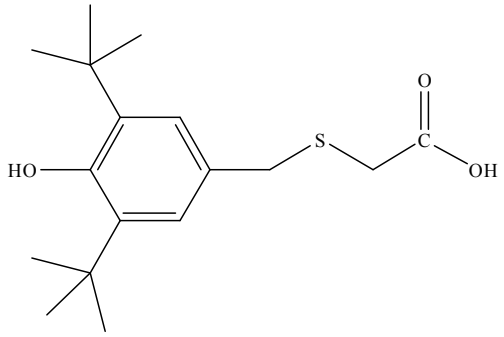
5.2 SYNTHESIS

The following commercial chemicals of reagent grade were used in the synthesis: 3,5-di-*tert*-butyl-4-hydroxybenzyl alcohol, thioglycolic acid, hydrazine hydrate, anhydrous calcium chloride, sodium hydrogen carbonate, dimethyltin dichloride, dibutyltin dichloride, diphenyltin dichloride, triphenyltin hydroxide, tricyclohexyltin hydroxide, salicylaldehyde, 5-bromosalicylaldehyde, 5-chlorosalicylaldehyde and triethylamine. The organotin starting materials were dicyclohexyltin dichloride, dibenzyltin dichloride, di(*o*-chlorobenzyl)tin dichloride,

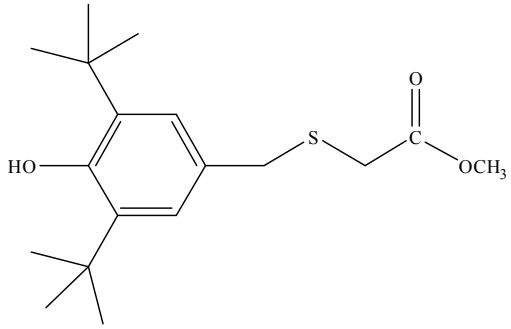
di(*p*-chlorobenzyl)tin dichloride and cyclopentyldiphenyltin hydroxide. The solvents used in the preparation of the Schiff base ligands and compounds were toluene, absolute ethanol, methanol, chloroform and hexane.

Figure 5.1.1
Structural formula for the ligands

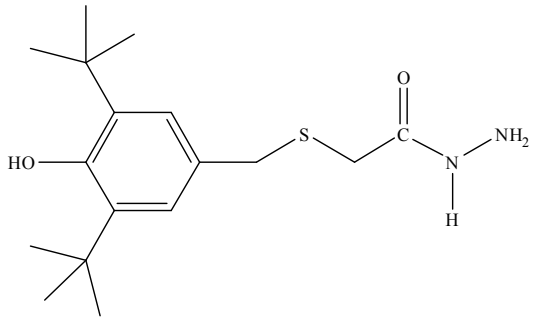
[2-(3,5-di-tert-butyl-4-hydroxybenzyl)sulfanyl]acetic acid, **A1**



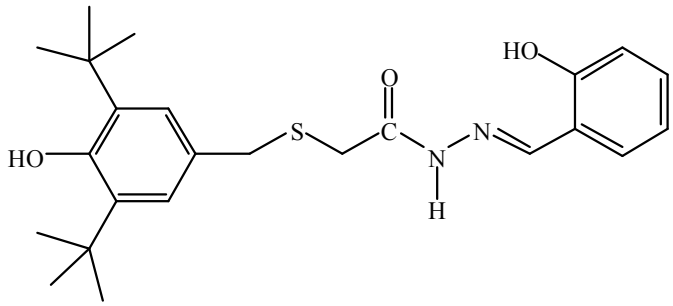
[2-(3,5-di-tert-butyl-4-hydroxybenzyl)sulfanyl]acetate, **A2**



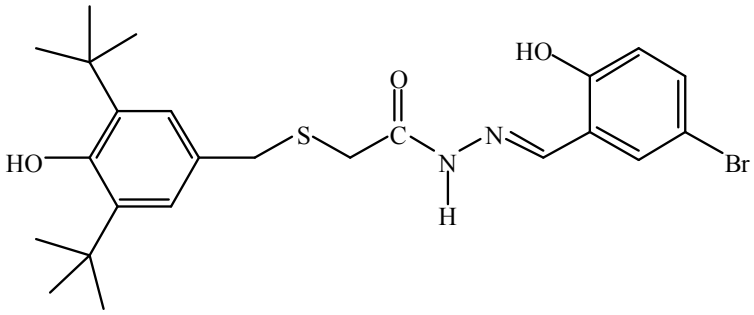
[2-(3,5-di-tert-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazine, **A3**



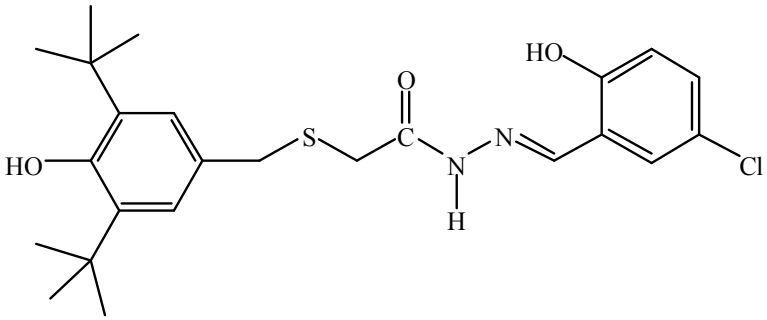
N'-(2-oxidobenzylidene)[2-(3,5-di-tert-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazide, **DA**



N'-(5-bromo-2-oxidobenzylidene)[2-(3,5-di-tert-butyl-(4-hydroxy-benzyl)sulfanyl]-acetatohydrazide, **DB**



N'-(5-chloro-2-oxidobenzylidene)[2-(3,5-di-tert-butyl-4-hydroxy-benzyl)sulfanyl]-acetatohydrazide, **DC**



5.2.1 Preparation of Ligands

Preparation of [2-(3,5-di-tert-butyl-4-hydroxybenzyl)sulfanyl]acetic acid, **A1**

3,5-di-*tert*-butyl-4-hydroxybenzyl alcohol (2.37 g, 0.01 mol) was dissolved in minimal amount of toluene and excess thioglycolic acid (2.1 ml, 0.03 mol) was added to the solution. The mixture was refluxed using a Dean and Stack apparatus for 8 hours. The mixture was washed with water for several times and the organic layer was dried with anhydrous calcium chloride. The solution was filtered and evaporated until a sticky oil was obtained. Hexane was added to the oily fraction to obtain a white solid. Yield: 2.43 g (78.3 %) ; m.p. 115-116^{o}C.

Anal. Calc for $C_{17}H_{26}O_3S$: C, 65.77: H, 8.38: S, 4.51%. Found: C, 66.17: H, 8.68: S, 4.28% **IR** (cm^{-1}): 3424 *v*(O-H), 1700 *v*(C=N), 1165 *v*(C-O), **^{1}H NMR (ppm)**: 1.44-1.58 (m, 18H), 3.29 (s, 2H), 3.94 (s, 2H), 5.34 (m, 2H from 2 OH), 7.26-7.41 (m, 2H) [s=singlet, m=multiplet], **^{13}C NMR (ppm)**: 29.5, 30.2, 32.4, 34.2, 36.9, 66.3, 125.9, 127.1, 129.4, 130.2, 132.3, 153.0, 176.2 *δ*(C=O)

Preparation of [2-(3,5-di-tert-butyl-4-hydroxybenzyl)sulfanyl]acetate, **A2**

[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetic acid, **A1** (3.10 g, 0.01 mol) was dissolved in 100 ml of methanol. The solution was stirred for 48 hours and was then extracted with 10% sodium hydrogen carbonate. The organic layer was washed with hexane to obtain a white solid.

Yield: 2.21 g (68.2 %) ; m.p. 80-81^{o}C. Anal. Calc for $C_{18}H_{28}O_3S$: C, 66.67: H, 8.63: S, 4.32%. Found: C, 66.37: H, 8.68: S, 4.08% **IR** (cm^{-1}): 3422 *v*(O-H), 1638 *v*(C=N), 1168 *v*(C-O), **^{1}H NMR (ppm)**: 1.44-1.56 (m, 18H), 3.30 (s, 2H), 3.92 (s, 2H), 4.15 (s, 3H), 5.35 (m, 2H from 2 OH), 7.26-7.40 (m, 2H) [s=singlet, m=multiplet], **^{13}C NMR**

(ppm): 29.4, 30.2, 32.5, 34.4, 36.9, 56.9, 65.9, 69.9, 125.8, 127.3, 129.5, 130.4, 132.0, 153.0, 176.5 δ(C=O)

Preparation of [2-(3,5-di-tert-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazine, **A3**

[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetate (3.25 g, 0.01 mol) was dissolved in hexane and excess hydrazine hydrate (6.0 ml, 0.12 mol) was added to the solution. The mixture was stirred for 24 hours until white solid formed. The white solid was recrystallized in methanol. Yield: 1.90 g (58.5 %) ; m.p. 75-77^{o}C.

Anal. Calc for $C_{17}H_{28}N_2O_2S$: C, 62.95: H, 8.63: S, 4.32%. Found: C, 63.17: H, 8.68: S, 4.08% **IR** (cm^{-1}): 3424 ν(O-H), 1700 ν(C=N), 1165 ν(C-O), **^{1}H NMR (ppm)**: 1.44-1.58 (m, 18H), 3.29 (s, 2H), 3.94b (s, 2H), 5.34 (m, 2H from 2 OH), 7.26-7.41 (m, 2H), 12.10 (s, 1H), 13.05 (s, 2H) [s=singlet, m=multiplet], **^{13}C NMR (ppm)**: 29.4, 30.2, 32.5, 34.0, 36.8, 66.0, 125.9, 127.3, 129.4, 130.7, 132.7, 153.3, 176.9 δ(C=O)

Preparation of N'-(2-oxidobenzylidene)[2-(3,5-di-tert-butyl-4-hydroxybenzyl)-sulfanyl]acetatohydrazide, **DA**

[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazine, **A3** (3.25 g, 0.01 mol) was dissolved in methanol and salicylaldehyde (1.1 mL, 1 mmol) was slowly added to the solution. The mixture was refluxed for 4 hours and the resulting light yellow solution was filtered. The filtrate was left at room temperature during which a light yellow solid formed. The solid was recrystallized from ethanol. Yield: 2.71 g (63.4 %) ; m.p. 80-82^{o}C.

Preparation of N'-(5-bromo-2-oxidobenzylidene)[2-(3,5-di-tert-butyl-(4-hydroxy-benzyl)sulfanyl]acetatohydrazide, **DB**

[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazine, **A3** (3.25 g, 0.01 mol) and 5-bromosalicylaldehyde (2.01 g, 0.01 mmol) were dissolved in 200 mL of methanol. The mixture was refluxed for 4 hours and the resulting light yellow solution was filtered. The filtrate was left at room temperature during which a light yellow solid formed. The solid was recrystallized from ethanol. Yield: 3.16 g (62.3 %) ; m.p. 94-96^{o}C.

Preparation of N'-(5-chloro-2-oxidobenzylidene)[2-(3,5-di-tert-butyl-4-hydroxy-benzyl)sulfanyl]acetatohydrazide, **DC**

[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazine, **A3** (2.77 g, 0.01 mol) and 5-chlorosalicylaldehyde (1.57 g, 0.01 mol) were dissolved separately in methanol and mixed together. The solution was refluxed for 4 hours and the resulting beige-coloured solution was filtered. A light yellow solid formed after the filtrate was evaporated slowly. The solid was recrystallized from ethanol. Yield: 2.69 g (58.1 %) ; m.p. 89-90^{o}C.

5.2.2 Preparation of Organotin Compounds

Preparation of catena-poly{bis[triphenyltin(IV)[2-(3,5-di-tert-butyl-4-hydroxybenzyl)-sulfanyl]acetate]}, **AC1**

Triphenyltin hydroxide (0.37 g, 1.0 mmol) and [2-(3,5-*di-tert*-butyl-4-hydroxybenzyl)sulfanyl]acetic acid, **A1** (0.31 g, 1.0 mmol), was dissolved in absolute ethanol and refluxed for 4 hours. The colourless solution was allowed to stand at room

temperature during which a pale white solid formed. It was recrystallized from ethanol to obtain colourless crystals. Yield: 0.52 g (78.9 %) ; m.p. 101-102^{o}C.

Anal. Calc for $C_{70}H_{80}O_3SSn$: C, 63.75: H, 6.07: S, 2.12%. Found: C, 63.32: H, 6.24: S, 2.16% **IR** (cm^{-1}): 3632 *v*(O-H), 1720 *v*(C=N), 1156 *v*(C-O), **^{1}H NMR (ppm)**: 1.28-1.43 (m, 18H), 3.22 (s, 2H), 3.94 (s, 2H), 5.17 (m, 2H from 2 OH), 7.10-7.76 (m, 2H) [s=singlet, m = multiplet], **^{13}C NMR (ppm)**: 29.5, 30.3, 34.2, 34.4, 36.8, 125.9, 127.7, 128.4, 128.7, 129.1, 129.4, 130.4, 136.0, 136.8, 137.3, 138.0, 153.0, 176.5 *δ*(C=O)

Preparation of tricyclohexyltin(IV)[2-(3,5-di-tert-butyl-4-hydroxybenzyl)-sulfanyl]acetate, **AC2**

An ethanolic solution of tricyclohexyltin hydroxide (0.38 g, 1.0 mmol) was added to [2-(3,5-*di-tert*-butyl-4-hydroxybenzyl)sulfanyl]acetic acid, **A1** (0.31 g, 1.0 mmol) and refluxed for 4 hours. The colourless solution was allowed to stand at room temperature during which a pale white solid formed and was recrystallized from ethanol. Colourless crystals were obtained after several days. Yield: 0.44 g (64.8 %) ; m.p. 115-117^{o}C.

Anal. Calc for $C_{35}H_{58}O_3SSn$: C, 62.04: H, 8.56: S, 2.07 %. Found: C, 61.91: H, 8.09: S, 2.33 % **IR** (cm^{-1}): 3623 *v*(O-H), 1700 *v*(C=N), 1164 *v*(C-O), **^{1}H NMR (ppm)**: 1.32-1.92 (m, 51H), 3.14 (s, 2H), 3.77 (s, 2H), 5.14 (m, 2H from 2 OH), 7.10-7.26 (m, 2H) [s=singlet, m = multiplet], **^{13}C NMR (ppm)**: 26.8, 28.9 [^{3}J(^{119}Sn-^{13}C) = 68 Hz], 30.3 [^{2}J(^{119}Sn-^{13}C) = 22 Hz], 30.9, 31.1, 31.2, 33.7, 33.9, 34.3, 36.9 [^{1}J(^{119}Sn-^{13}C) = 444 Hz], 125.8, 135.8, 127.1, 152.9, 175.6 *δ*(C=O)

Preparation of cyclopentyldiphenyltin(IV)[2-(3,5-di-tert-butyl-4-hydroxybenzyl)-sulfanyl]acetate, **AC3**

An ethanolic solution of cyclopentyldiphenyltin hydroxide (0.36 g, 1.0 mmol) was added to [2-(3,5-*di-tert*-butyl-4-hydroxybenzyl)sulfanyl]acetic acid, **A1** (0.31 g, 1.0 mmol) and refluxed for 4 hours. The solution was allowed to stand at room temperature during which a pale white solid formed and was recrystallized from ethanol. Yield: 0.39 g (60.2 %) ; m.p. 101-102^{o}C. Anal. Calc for $C_{34}H_{42}O_3SSn$: C, 62.91: H, 6.47: S, 2.16 %. Found: C, 63.96: H, 6.57: S, 2.08% **IR** (cm^{-1}): 3633 *v*(O-H), 1730 *v*(C=N), 1153 *v*(C-O), **^{1}H NMR (ppm)**: 1.44-1.58 (m, 27H), 3.29 (s, 2H), 3.94b (s, 2H), 5.10 (m, 2H from 2 OH), 7.06-7.65 (m, 12H) [s=singlet, m = multiplet], **^{13}C NMR (ppm)**: 17.8, 25.7, 26.0, 29.5, 30.2, 30.4, 31.0, 32.4, 34.3, 36.9, 44.5, 125.7, 125.9, 127.1, 128.4, 128.7, 128.8, 136.7, 137.3, 137.4, 137.6, 139.2, 153.0, 176.2 *δ*(C=O)

Preparation of {N'-(2-oxidobenzylidene)[2-(3,5-di-tert-butyl-4-hydroxybenzyl)-sulfanyl]acetatohydrazidato}dimethyltin(IV), **DA1**

The ligand, *N'*-(2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-sulfanyl]acetatohydrazide (0.42 g, 1.0 mmol) and triethylamine (0.14 mL, 1.0 mmol) were added to 100 mL of absolute ethanol and the mixture was heated under reflux for 2 hours. Dimethyltin dichloride (0.22 g, 1.0 mmol) was then added and the mixture was further refluxed for 5 hours and filtered. The filtrate was evaporated until precipitation was obtained. The precipitation was recrystallised from toluene and the by-products, triethylammonium chloride, was removed through filtration. A yellow crystalline solid was obtained upon slow evaporation of the solution. Yield: 0.30 g (52.2 %) ; m.p. 134-135^{o}C.

Preparation of {N'-(2-oxidobenzylidene)[2-(3,5-di-tert-butyl-4-hydroxybenzyl)-sulfanyl]acetatohydrazidato}dibutyltin(IV), **DA2**

An excess amount of triethylamine (0.14 mL, 1.0 mmol) was added to a ethanolic solution containing ligand *N'*-(2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazide (0.42 g, 1.0 mmol) and refluxed for 2 hours. Then, an ethanolic solution containing (0.31 g, 1.0 mmol) dibutyltin dichloride was added to the mixture. The mixture was further refluxed for another 6 hours and filtered. The filtrate was evaporated until precipitation was obtained. The precipitation was recrystallised from toluene and the by-products, triethylammonium chloride, was removed through filtration. A yellow crystalline solid was obtained upon slow evaporation of the solution. Yield: 0.36 g (54.2 %) ; m.p. 214-215^{o}C

Preparation of {N'-(2-oxidobenzylidene)[2-(3,5-di-tert-butyl-4-hydroxybenzyl)-sulfanyl]acetatohydrazidato}diphenyltin(IV), **DA3**

An ethanolic solution containing (0.31 g, 1.0 mmol) ligand *N'*-(2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazide (0.42 g, 1.0 mmol) was refluxed with triethylamine (0.14 mL, 1.0 mmol) for 2 hours. Then, an ethanolic solution containing (0.34 g, 1.0 mmol) diphenyltin dichloride was added to the mixture. The mixture was refluxed for another 6 hours and filtered. The filtrate was evaporated until precipitation was obtained. The precipitation was recrystallised from toluene and the by-products, triethylammonium chloride, was removed through filtration. A yellow crystalline solid was obtained upon slow evaporation of the solution. Yield: 0.41 g (59.3 %) ; m.p. > 350^{o}C (dec.)

Preparation of {N'-(2-oxidobenzylidene)[2-(3,5-di-tert-butyl-4-hydroxybenzyl)-sulfanyl]acetatohydrazidato}dicyclohexyltin(IV), **DA4**

The ligand, *N'*-(2-oxidobenzylidene){2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-sulfanyl]acetatohydrazide} (0.42 g, 1.0 mmol) and triethylamine (0.14 mL, 1.0 mmol) were added to 100 mL of absolute ethanol and the mixture was heated under reflux for 2 hours. Dicyclohexyltin dichloride (0.36 g, 1.0 mmol) was then added and the mixture was further refluxed for 5 hours and filtered. The filtrate was evaporated until precipitation was obtained. The precipitation was recrystallised from toluene and the by-products, triethylammonium chloride, was removed through filtration. A yellow crystalline solid was obtained upon slow evaporation of the solution. Yield: 0.35 g (49.2 %) ; m.p. 134-136^{o}C

Preparation of {N'-(2-oxidobenzylidene)[2-(3,5-di-tert-butyl-4-hydroxybenzyl)-sulfanyl]acetatohydrazidato}dibenzyltin(IV), **DA5**

An excess amount of triethylamine (0.14 mL, 1.0 mmol) was added to a ethanolic solution containing the ligand *N'*-(2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazide (0.42 g, 1.0 mmol) and refluxed for 2 hours. Then, an ethanolic solution containing dibenzyltin dichloride (0.37 g, 1.0 mmol) was added to the mixture. The mixture was further refluxed for another 6 hours and filtered. The filtrate was evaporated until precipitation was obtained. The precipitation was recrystallised from toluene and the by-products, triethylammonium chloride, was removed through filtration. A yellow crystalline solid was obtained upon slow evaporation of the solution. Yield: 0.43 g (59.8 %) ; m.p. 96-97^{o}C.

Preparation of {N'-(2-oxidobenzylidene)[2-(3,5-di-tert-butyl-4-hydroxybenzyl)-sulfanyl]acetatohydrazidato}di(o-chlorobenzyl)tin(IV), **DA6**

An ethanolic solution containing (0.31 g, 1.0 mmol) of the ligand *N'*-(2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazide (0.42 g, 1.0 mmol) was refluxed with triethylamine (0.14 mL, 1.0 mmol) for 2 hours. Then, an ethanolic solution containing (0.44 g, 1.0 mmol) di(*o*-chlorobenzyl)tin dichloride was added to the mixture. The mixture was refluxed for another 6 hours and filtered. The filtrate was evaporated until precipitation was obtained. The precipitation was recrystallised from toluene and the by-products, triethylammonium chloride, was removed through filtration. A yellow crystalline solid was obtained upon slow evaporation of the solution. Yield: 0.46 g (58.0 %) ; m.p. 118-120^{o}C

Preparation of {N'-(2-oxidobenzylidene)[2-(3,5-di-tert-butyl-4-hydroxybenzyl)-sulfanyl]acetatohydrazidato}di(p-chlorobenzyl)tin(IV), **DA7**

The ligand, *N'*-(2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-sulfanyl]acetatohydrazide (0.42 g, 1.0 mmol) and triethylamine (0.14 mL, 1.0 mmol) were added to 100 mL of absolute ethanol and the mixture was heated under reflux for 2 hours. Di(*p*-chlorobenzyl)tin dichloride (0.44 g, 1.0 mmol) was then added and the mixture was further refluxed for 5 hours and filtered. The filtrate was evaporated until precipitation was obtained. The precipitation was recrystallised from toluene and the by-products, triethylammonium chloride, was removed through filtration. A yellow crystalline solid was obtained upon slow evaporation of the solution. Yield: 0.44 g (55.8 %) ; m.p. 92-94^{o}C.

5.2.3 Physical measurement of the Schiff base ligands and organotin complexes

The melting points of the compounds were determined on a 'Electrothermal' digital melting point apparatus and were uncorrected. Elemental analyses of the complexes were carried out on a Perkin Elmer EA2400 CHNS Elemental Analyzer in the University of Malaya.

The infrared spectra for the compounds were recorded in the region 400-4000 cm^{-1} with a Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer and a Perkin-Elmer Spectrum RX1 FT-IR spectrophotometer. The samples were prepared as nujol mull or KBr pellet. The UV spectra for the ligands and organotin complexes were recorded using a Shimadzu UV-PC1601 UV-visible spectrophotometer in the wavelength range of 190 to 600 nm.

The ^{1}H and ^{13}C NMR spectra for the ligands were recorded in $CDCl_3$ or deuterated DMSO at ambient temperature on a JEOL JNM-GSX270 FT NMR SYSTEM spectrometer operating at 270.05 MHz for ^{1}H NMR and 67.80 MHz for ^{13}C NMR. The ^{119}Sn NMR spectra were recorded on a JEOL ECA-400MHz. The chemical shifts were recorded in ppm with reference to Me_4Si for ^{1}H NMR, $CDCl_3$ and DMSO for ^{13}C NMR and Me_4Sn for ^{119}Sn NMR. The ^{1}H and ^{13}C NMR spectra of some of the complexes in DMSO gave poor spectra and hence assignment of peaks was not satisfactory.

The X-ray crystallographic intensity data were measured using Mo-K_α radiation graphite-crystal monochromator (λ= 0.71073Å) radiation on a Bruker SMART APEX2 CCD diffractometer in University of Malaya. The structure of the compounds were solved by direct methods and refined by the full-matrix least-squares procedure based

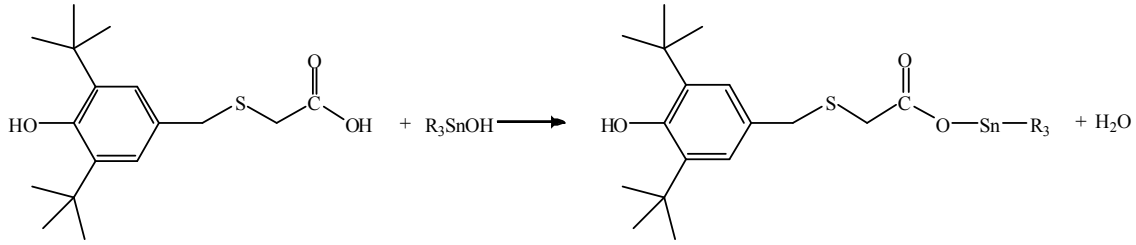
on F^2 using the SHELXL programme. Supplementary data including observed and calculated structure factors for the complexes are available from the author on request.

5.3 RESULTS AND DISCUSSION

5.3.1 Analytical Data

The triorganotin compounds were prepared from reactions between a carboxylic acid with triorganotin hydroxides. The triorganotin compounds were white solids and a general reaction scheme of the preparation of the compounds is shown in scheme 5.3.1.

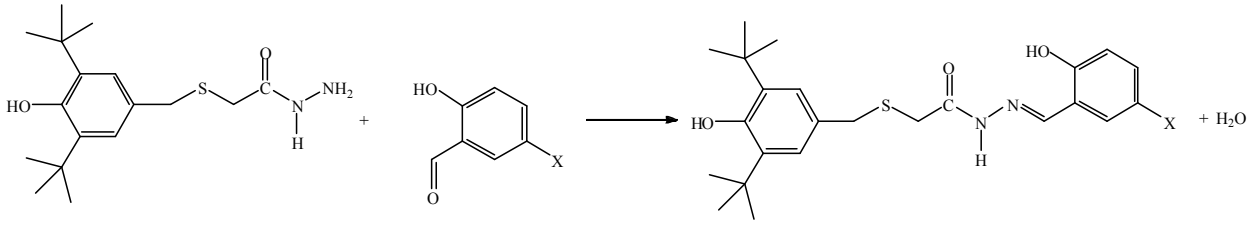
Scheme 5.3.1 General reaction scheme for the preparation of the triorganotin compounds



R_3 = triphenyl (Ph_3), tricyclohexyl (Cy_3) or cyclopentyldiphenyl ($CypPh_2$)

Several hydrazone Schiff base ligands were prepared from the reactions of 1:1 mole ratio of the [2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazine with salicylaldehyde and substituted salicylaldehyde. A general reaction scheme of the preparation of the Schiff base ligands is shown in scheme 5.3.2.

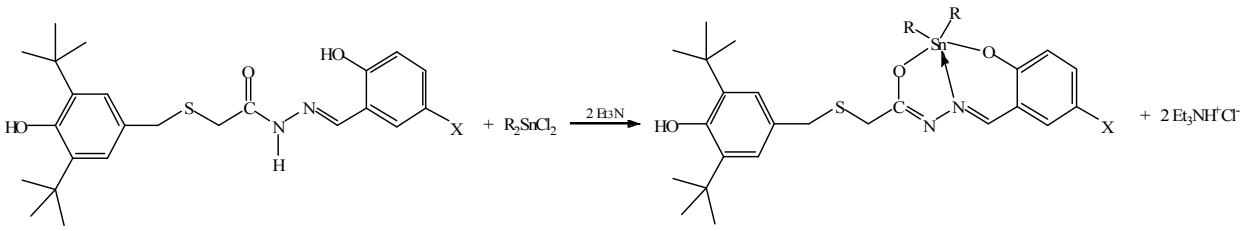
Scheme 5.3.2 General reaction scheme for the preparation of the Schiff base ligands



X = Br, Cl or H

The Schiff base ligands were yellow in colour and their melting points were in the range of 80-100^{o}C. The prepared ligands could possibly exist in the keto-enol form as discussed in chapter 3 and 4. The enolised form of the Schiff base ligands contained several potential sites such as the azomethine nitrogen, one hydroxyl group on the salicylaldehyde ring and the hydroxyl group attached to the C=N- moiety could be used for coordination with the tin atom. The presence of acidic hydroxyl groups enabled it to readily react with diorganotin halides in the presence of a weak base. In addition, the donation of the lone pair of electrons on the azomethine nitrogen to the tin atom to form a coordination bond, N ⟶ Sn tended to stabilize the overall structure. A general reaction scheme for the preparation of the complexes is shown in scheme 5.3.3.

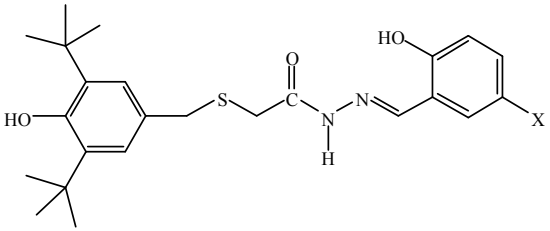
Scheme 5.3.3 General reaction scheme for the preparation of the diorganotin Schiff base complexes



X = Br, Cl or H
R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 5.3.1
Analytical data for substituted [2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazide ligands

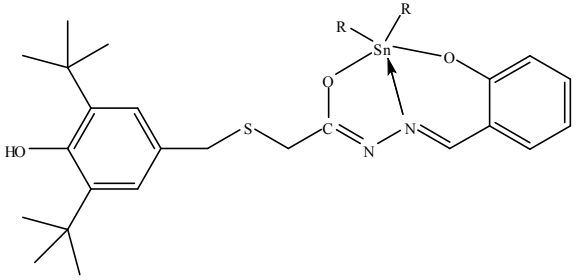
	Colour	Percentage Yield (%)	Melting-Point (^{o}C)	Elemental Analysis Found (Calculated) (%)			
				C	H	N	S
N'-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]-acetatohydrazide, **DA**	Yellow	63.4	80-82	67.06 (67.27)	7.20 (7.47)	6.87 (6.53)	3.01 (3.27)
N'-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-(4-hydroxybenzyl)sulfanyl]-acetatohydrazide, **DB**	Yellow	62.3	94-96	56.53 (56.81)	5.97 (6.11)	5.62 (5.52)	2.58 (2.76)
N'-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]-acetatohydrazide, **DC**	Yellow	58.1	89-90	62.50 (62.27)	6.99 (6.70)	6.14 (6.05)	2.77 (3.02)



DA: X = H
DB: X = Br
DC: X = Cl

Table 5.3.2a
Analytical data for {*N'*-(2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}diorganotin complexes

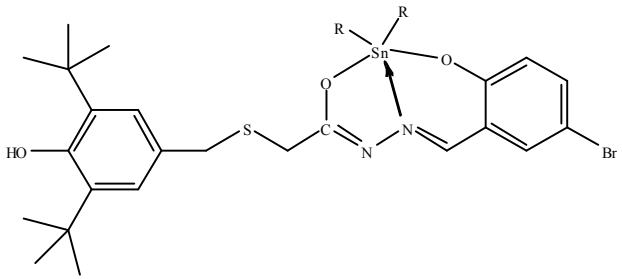
Complex	Colour	Percentage Yield (%)	Melting-Point (^{o}C)	Elemental Analysis Found (Calculated) (%)			
				C	H	N	S
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-dimethyltin(IV), **DA1**	Yellow	52.2	134-135	53.83 (54.10)	5.95 (6.24)	4.70 (4.85)	2.30 (2.43)
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-dibutyltin(IV), **DA2**	Yellow	54.2	214-215	58.05 (58.30)	6.88 (7.28)	8.72 (8.49)	2.01 (2.12)
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-diphenyltin(IV), **DA3**	Yellow	59.3	> 350 (dec.)	61.45 (61.83)	5.45 (5.72)	4.33 (4.00)	2.26 (2.00)
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-dicyclohexyltin(IV), **DA4**	Yellow	49.2	134-136	60.33 (60.78)	6.99 (7.31)	4.15 (3.94)	1.77 (1.97)
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-dibenzyltin(IV), **DA5**	Yellow	59.8	95-96	63.03 (62.75)	6.27 (6.05)	4.05 (3.85)	2.16 (1.92)
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-di(*o*-chlorobenzyl)tin(IV), **DA6**	Yellow	58.0	128-130	57.17 (57.33)	5.52 (5.28)	3.44 (3.52)	1.92 (1.76)
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-di(*p*-chlorobenzyl)tin(IV), **DA7**	Yellow	55.8	> 350 (dec.)	57.62 (57.33)	5.48 (5.28)	3.82 (3.52)	1.53 (1.76)



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 5.3.2b
Analytical data for {*N'*-(5-bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}diorganotin complexes

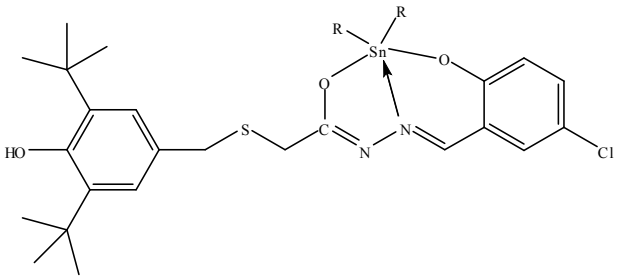
Complex	Colour	Percentage Yield (%)	Melting-Point (^{o}C)	Elemental Analysis Found (Calculated) (%)			
				C	H	N	S
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dimethyltin(IV), **DB1**	Yellow	56.3	179-180	47.47 (47.74)	5.01 (5.35)	4.52 (4.28)	2.57 (2.14)
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dibutyltin(IV), **DB2**	Yellow	50.2	70-71	52.40 (52.07)	6.52 (6.37)	3.81 (3.79)	1.81 (1.90)
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}diphenyltin(IV), **DB3**	Yellow	53.2	> 350 (dec.)	55.97 (55.56)	4.80 (5.01)	3.61 (3.60)	1.58 (1.80)
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dicyclohexyltin(IV), **DB4**	Yellow	57.2	109-110	54.32 (54.73)	6.12 (6.46)	3.89 (3.54)	1.99 (1.77)
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dibenzyltin(IV), **DB5**	Yellow	55.3	133-134	56.42 (56.61)	5.57 (5.33)	3.19 (3.47)	1.88 (1.74)
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}di(*o*-chlorobenzyl)tin(IV), **DB6**	Yellow	58.1	226-227	51.87 (52.15)	4.84 (4.68)	2.98 (3.20)	1.74 (1.60)
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}di(*p*-chlorobenzyl)tin(IV), **DB7**	Yellow	50.5	200-202	52.45 (52.15)	4.32 (4.68)	2.98 (3.20)	1.50 (1.60)



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 5.3.2c
Analytical data for {*N'*-(5-chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}diorganotin complexes

Complex	Colour	Percentage Yield (%)	Melting-Point (^{o}C)	Elemental Analysis Found (Calculated) (%)			
				C	H	N	S
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dimethyltin(IV), **DC1**	Yellow	59.5	206-207	50.90 (51.22)	6.03 (5.74)	4.86 (4.59)	2.06 (2.30)
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dibutyltin(IV), **DC2**	Yellow	50.2	80-81	55.14 (55.41)	6.50 (6.78)	4.43 (4.04)	2.07 (2.02)
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}diphenyltin(IV), **DC3**	Yellow	55.6	> 350 (dec.)	58.55 (58.93)	5.01 (5.32)	4.05 (3.82)	2.06 (1.91)
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dicyclohexyltin(IV), **DC4**	Yellow	50.9	90-91	57.49 (57.97)	6.70 (6.84)	4.05 (3.75)	2.00 (1.88)
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dibenzyltin(IV), **DC5**	Yellow	54.2	129-130	60.28 (59.91)	5.98 (5.64)	3.45 (3.68)	1.97 (1.84)
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}di(*o*-chlorobenzyl)tin(IV), **DC6**	Yellow	57.8	205-207	55.24 (54.94)	5.21 (4.94)	3.12 (3.37)	1.50 (1.69)
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}di(*p*-chlorobenzyl)tin(IV), **DC7**	Yellow	49.2	220-221	54.77 (54.94)	4.66 (4.94)	3.56 (3.37)	1.47 (1.69)



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

5.3.2 IR Spectral data

Table 5.3.3 summarizes the characteristic infrared stretching frequencies for the diorganotin complexes of the Schiff bases. In the Schiff base ligands, the secondary amine and hydroxyl stretching frequencies of the free ligands were found in the expected region of 3100-3400 cm^{-1}. These absorption bands were not well resolved as they overlapped in the same region. In the organotin complexes, a band due to the hydroxyl stretching frequency was observed, indicating the presence of the hydroxyl group on the *para*-position in the phenyl ring.

Both the carboxylic acid and the triorganotin compounds displayed a strong C=O stretching frequency around 1700 cm^{-1}. All the Schiff base ligands exhibited the C=N and -O=C-N- stretching frequencies in the region of 1620-1660 cm^{-1} as derived from the two azomethine groups. This was within the range reported for the similar group of Schiff base ligands as in chapter 3 and 4. This observation for the organotin complexes showed the involvement of the azomethine nitrogen in coordination with the tin atom which weakened the C=N bond and led to the lowering of the C=N stretching frequencies. Therefore, the band of *v*(-N=C-C=N-) was found in the region between 1500-15900 cm^{-1} and was due to decrease in the electron densities in the azomethine nitrogen and carbonyl moieties. The phenolic C-O stretching frequency for the ligands and organotin complexes was recorded in the 1000-1200 cm^{-1} region.

Several new bands were observed in the region of 400-800 cm^{-1} in the spectra of the organotin complexes. The medium absorption in the region of 670-710 cm^{-1} had been assigned to the Sn-O stretching vibration while the weak absorption in the region

of 450-470 cm^{-1} had been assigned to the Sn-N stretching vibration. All these values were within the range reported for a number of organotin complexes.

5.3.3 NMR Spectral Data

The ^{1}H and ^{13}C NMR spectra for the free ligands and complexes were recorded in deuterated DMSO. The ^{1}H NMR chemical shifts for the Schiff base ligands are listed in table 5.3.5 while the ^{13}C NMR chemical shifts for the Schiff base ligands are listed in table 5.3.7. The ^{1}H NMR chemical shifts for the complexes are listed in table 5.3.6, the ^{13}C NMR chemical shifts for the complexes are listed in table 5.3.8 and the ^{119}Sn NMR chemical shifts for the complexes are listed in table 5.3.9.

^{1}H NMR Spectra

The amine protons could be observed as sharp resonance signals in the range of 11.00-12.00 ppm for the Schiff base ligands. This peak was not observed in the spectra of the complexes. The azomethine proton, -N=C(H)- occured as a single peak in the region between 8.00-9.00 ppm for Schiff base ligands and diorganotin complexes. The chemical shifts for the phenyl groups in ligands and complexes exhibited a group of multiplets in the range of 6.40-7.90 ppm while the protons from the *tert*-butyl protons were observed in the region of 1.00-2.00 ppm. Also, both the methylene protons attached to the sulfur group were found in the range between 3.00-4.60 ppm.

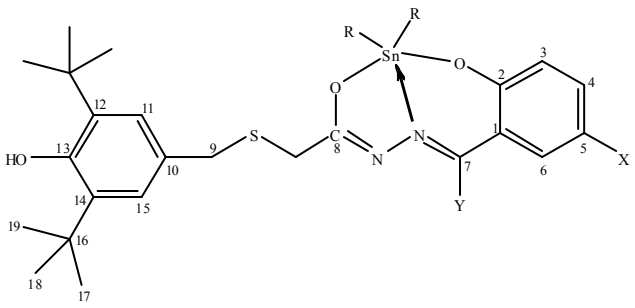
The OH proton signal for the ligands and organotin complexes was observed in the 5.00-5.40 ppm region. The absence of a NH proton signal in the ^{1}H NMR spectra of the organotin complexes suggested that the Schiff base ligand adopted the enolised form

when it reacted with the diorganotin dichlorides through the displacement of the proton in the azomethine group.

The chemical shift values of the aromatic and aliphatic protons of the complexes were located in the expected region of the spectra and were in good agreement with those of the predicted structures of the complexes.

^{13}C NMR spectra

The chemical shifts of the azomethine carbon in the ligands occured in the range of 160-175 ppm. The carbonyl carbon, C(8) was more deshielded than C(7) and its chemical shift was higher and found in the region between 162-168 ppm. The chemical shift of C(5) was the highest in ligands **DB** and **DC**, and was between 170-175 ppm. This was due to the presence of the electron-withdrawing substituents, which were bromine and chlorine on the phenyl ring.



In the ^{13}C NMR spectra of the diorganotin complexes, rigorous assignments of the carbon peaks could not be done especially on the *J*-coupling of the organotin fragments due to the poor solubility of the complexes in deuterated solvents, including deuterated DMSO.

The chemical shifts of the carbonyl carbons, C(7) and C(8) of the organotin complexes were in the range of 160-170 ppm. Compared to chemical shift values of the ligands, C(7) and C(8) were found to be shifted to lower values. The chemical shift of C(5) was also found in the similar region as the Schiff base ligands.

The ^{13}C NMR spectra for the complexes showed several shifts in the chemical shift value for the carbon resonances when compared to the free ligands. This is a consequence of the electron density transfer from the ligand to the acceptor. The aromatic carbons of the ligand as well as the diorganotin complexes appeared within the expected range and were in close agreement with the reported literature values.

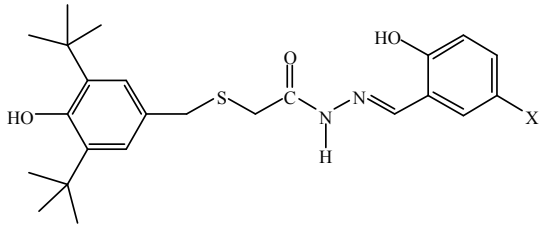
^{119}Sn NMR Spectra

The ^{119}Sn NMR chemical shifts values were only obtained for selected organotin complexes due to the insolubility of most of the complexes in deuterated solvents. In general, the ^{119}Sn NMR chemical shifts of the alkyltins were formed in the upfield region, followed by the cycloalkyltin and aryltin which have the largest downfield shift. However, the ^{119}Sn NMR chemical shift values for the dibenzyltin, di(*o*-chlorobenzyl)tin and di(*p*-chlorobenzyl)tin were found over a wider range, from -200 to -400 ppm. One of the reasons could be due to the existence of six or seven-coordination for these complexes in the presence of the donor solvent such as dimethyl sulfoxide (DMSO).

Table 5.3.3
Infrared spectral data for substituted [2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazide ligands

Ligand	*v*(O-H, N-H)	*v*(C=O)	*v*(C=N)	*v*(C-O)
N'-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazide, **DA**	3400b	1666s	1619m	1153m
N'-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-(4-hydroxybenzyl)sulfanyl]acetatohydrazide, **DB**	3404b	1670s	1615m	1166m
N'-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazide, **DC**	3390b	1677s	1617m	1166m

[a] s = strong, m = medium, w = weak, sh = shoulder, b = broad

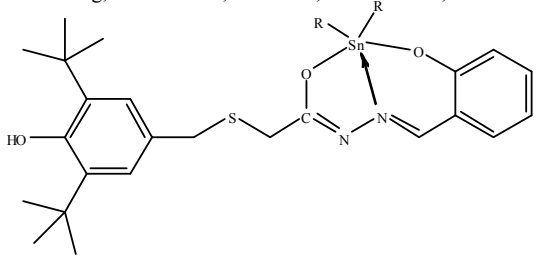


DA: X = H
DB: X = Br
DC: X = Cl

Table 5.3.4a
Infrared spectral data for {*N'*-(2-oxidobenzylidene) [2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}diorganotin complexes

Complex	*v*(O-H)	*v*(C=N)	*v*(-N=C-C=N-)	*v*(C-O)	*v*(Sn-O)	*v*(Sn-N)
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-dimethyltin(IV), **DA1**	3404b	1625s	1572m	1151m	680w	459w
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-dibutyltin(IV), **DA2**	3429b	1625s	1579m	1158m	683w	460w
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-diphenyltin(IV), **DA3**	3402b	1620s	1579m	1153m	697w	460w
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-dicyclohexyltin(IV), **DA4**	3431b	1625s	1579m	1155m	683w	461w
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-dibenzyltin(IV), **DA5**	3388b	1625s	1570m	1150m	684w	459w
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-di(*o*-chlorobenzyl)tin(IV), **DA6**	3410b	1618s	1566m	1148m	670w	459w
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-di(*p*-chlorobenzyl)tin(IV), **DA7**	3402b	1624s	1576m	1153m	670w	459w

[a] s = strong, m = medium, w = weak, sh = shoulder, b = broad

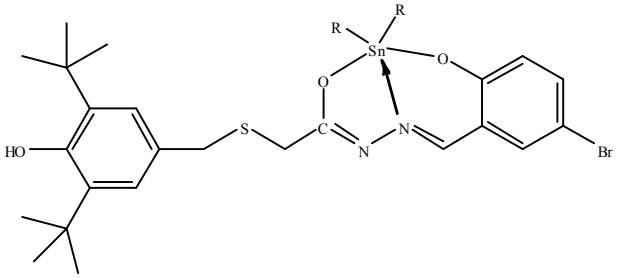


R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 5.3.4b
Infrared spectral data for {*N'*-(5-bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}diorganotin complexes

Complex	*v*(O-H)	*v*(C=N)	*v*(-N=C-C=N-)	*v*(C-O)	*v*(Sn-O)	*v*(Sn-N)
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-dimethyltin(IV), **DB1**	3367b	1606m	1550m	1176m	682w	467w
{*N'*-(5-Bromo-2-oxidobenzylidene) [2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}dibutyltin(IV), **DB2**	3425b	1608m	1562m	1177m	674w	462w
{*N'*-(5-Bromo-2-oxidobenzylidene) [2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-diphenyltin(IV), **DB3**	3407b	1610m	1563m	1179m	697w	460w
{*N'*-(5-Bromo-2-oxidobenzylidene) [2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-dicyclohexyltin(IV), **DB4**	3430b	1610m	1562m	1170m	671w	460w
{*N'*-(5-Bromo-2-oxidobenzylidene) [2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-dibenzyltin(IV), **DB5**	3425b	1604m	1562m	1174m	694w	459w
{*N'*-(5-Bromo-2-oxidobenzylidene) [2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-di(*o*-chlorobenzyl)tin(IV), **DB6**	3396b	1609m	1562m	1170m	700w	455w
{*N'*-(5-Bromo-2-oxidobenzylidene) [2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-di(*p*-chlorobenzyl)tin(IV), **DB7**	3426b	1610m	1562m	1172m	690w	472w

[a] s = strong, m = medium, w = weak, sh = shoulder, b = broad

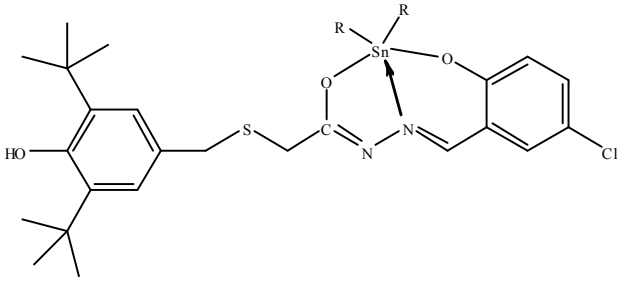


R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 5.3.4c
Infrared spectral data for {*N'*-(5-chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}diorganotin complexes

Complex	*v*(O-H)	*v*(C=N)	(-N=C-C=N-)	*v*(C-O)	*v*(Sn-O)	*v*(Sn-N)
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-dimethyltin(IV), **DC1**	3423b	1611m	1564m	1182m	710w	460w
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}dibutyltin(IV), **DC2**	3425b	1611m	1543m	1181m	700w	459w
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-diphenyltin(IV), **DC3**	3428b	1612m	1563m	1182m	698w	462w
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-dicyclohexyltin(IV), **DC4**	3429b	1611m	1563m	1179m	699w	454w
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-dibenzyltin(IV), **DC5**	3423b	1614m	1561m	1182m	696w	462w
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-di(*o*-chlorobenzyl)tin(IV), **DC6**	3424b	1611m	1526m	1178m	697w	459w
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-di(*p*-chlorobenzyl)tin(IV), **DC7**	3399b	1610m	1532m	1182m	696w	453w

[a] s = strong, m = medium, w = weak, sh = shoulder, b = broad

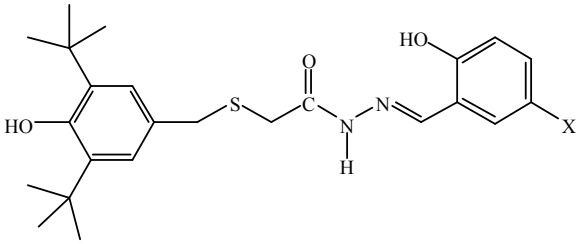


R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 5.3.5
^{1}H NMR chemical shifts for substituted [2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazide ligands

Ligand	Assignments[a] [δ(^{1}H)/ppm]				
	Aryl	-N=C(H)	-OH	-CH_2-	-C(CH_3)$_3$
N'-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]-acetatohydrazide, **DA**	6.66-7.04 (m, 4H), 7.32-7.74 (m, 2H)	8.43 (s, 1H)	5.38 (s, 2H)	3.42-3.67 (m, 2H), 4.11-4.26 (m, 2H)	1.20-1.45 (m, 18H)
N'-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-(4-hydroxybenzyl)sulfanyl]-acetatohydrazide, **DB**	6.68-7.09 (m, 3H), 7.33-7.74 (m, 2H)	8.33 (s, 1H)	5.30 (s, 2H)	3.68-3.73 (m, 2H), 4.30-4.35 (m, 2H)	1.29-1.57 (m, 18H)
N'-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]-acetatohydrazide, **DC**	6.63-7.05 (m, 3H), 7.38-7.71 (m, 2H)	8.30 (s, 1H)	5.26 (s, 2H)	3.77-3.79 (m, 2H), 4.30-4.35 (m, 2H)	1.25-1.49 (m, 18H)

[a] s = singlet, d = doublet, t = triplet, m = multiplet

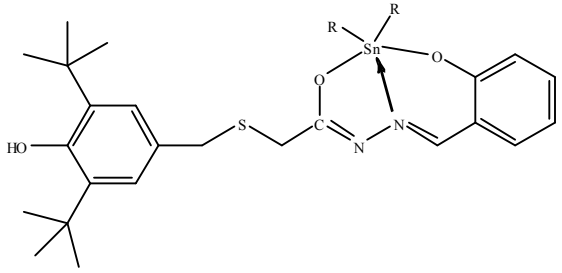


DA: X = H
DB: X = Br
DC: X = Cl

Table 5.3.6a
^{1}H NMR chemical shifts for {*N'*-(2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}diorganotin complexes

Complex	Assignments[a] [δ(^{1}H)/ppm]					
	Aryl	-N=C(H)	-OH	-CH_2-	-$C(CH_3)_3$	R groups
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-dimethyltin(IV), **DA1**	6.74-7.13 (m, 4H), 7.36-7.46 (m, 2H)	8.72 (s, 1H)	5.16 (s, 1H)	3.77-3.79 (m, 2H), 4.30-4.35 (m, 2H)	1.25-1.49 (m, 18H)	0.81 (s, 6H)
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-dibutyltin(IV), **DA2**	6.83-7.32 (m, 6H)	8.61 (s, 1H)	5.20 (s, 1H)	3.77-3.79 (m, 2H), 4.33-4.36 (m, 2H)	1.25-1-56 (m, 18H)	0.78-1.67 (m, 18H)
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-diphenyltin(IV), **DA3**	6.85-7.64 (m, 6H)	8.64 (s, 1H)	5.05 (s, 1H)	3.48-3.60 (m, 2H), 4.23-4.30 (m, 2H)	1.22-1.40 (m, 18H)	6.85-7.64 (m, 10H)
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-dicyclohexyltin(IV), **DA4**	6.93-7.65 (m, 6H)	8.94 (s, 1H)	5.00 (s, 1H)	3.42-3.53 (m, 2H), 4.23-4.29 (m, 2H)	1.12-1.31 (m, 18H)	1.09-1.82 (m, 22H)
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-dibenzyltin(IV), **DA5**	6.69-7.65 (m, 6H)	8.95 (s, 1H)	5.10 (s, 1H)	3.35-3.45 (m, 2H), 4.27-4.45 (m, 2H)	1.12-1.35 (m, 18H)	1.00-1.10 (m, 2H), 6.69-7.65 (m, 10H)
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-di(*o*-chlorobenzyl)tin(IV), **DA6**	6.74-7.68 (m, 6H)	8.90 (s, 1H)	5.50 (s, 1H)	3.42-3.62 (m, 2H), 4.30-4.33 (m, 2H)	1.30-1.40 (m, 18H)	1.17-1.20 (m, 2H), 6.74-7.68 (m, 8H)
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-di(*p*-chlorobenzyl)tin(IV), **DA7**	6.82-7.40 (m, 6H)	8.72 (s, 1H)	5.16 (s, 1H)	3.33-3.40 (m, 2H), 4.34-3.39 (m, 2H)	1.31-1.48 (m, 18H)	0.93-1.00 (m, 2H), 6.82-7.40 (m, 8H)

[a] s = singlet, d = doublet, t = triplet, m = multiplet

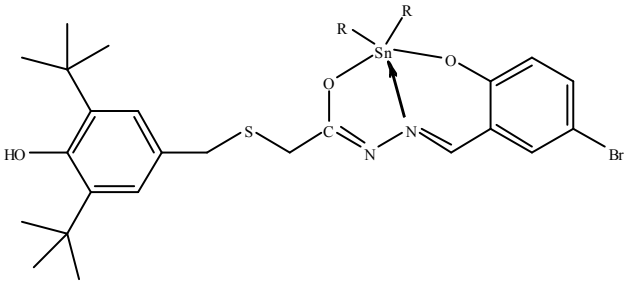


R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 5.3.6b
^{1}H NMR chemical shifts for {*N'*-(5-bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}diorganotin complexes

Complex	Assignments[a] [δ(^{1}H)/ppm]					
	Aryl	-N=C(H)	-OH	-CH_2-	-C(CH_3)$_3$	R groups
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dimethyltin(IV), **DB1**	6.55-7.65 (m, 5H)	8.56 (s, 1H)	5.30 (s, 1H)	3.40-3.58 (m, 2H), 4.35-4.40 (m, 2H)	1.11-1.35 (m, 18H)	0.60 (s, 6H)
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dibutyltin(IV), **DB2**	6.55-7.50 (m, 5H)	8.64 (s, 1H)	5.20 (s, 1H)	3.09-3.11 (m, 2H), 3.70-3.82 (m, 2H)	1.12-1.87 (m, 18H)	0.70-1.87 (m, 18H)
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}diphenyltin(IV), **DB3**	6.83-7.87 (m, 5H)	8.53 (s, 1H)	5.18 (s, 1H)	3.32-3.35 (m, 2H), 4.37-4.40 (m, 2H)	1.21-1.78 (m, 18H)	6.83-7.87 (m, 10H)
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dicyclohexyltin(IV), **DB4**	6.84-7.70 (m, 5H)	8.65 (s, 1H)	5.22 (s, 1H)	3.40-3.74 (m, 2H), 4.26-4.49 (m, 2H)	1.12-1.93 (m, 22H)	1.12-1.93 (m, 22H)
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dibenzyltin(IV), **DB5**	6.83-7.58 (m, 5H)	8.63 (s, 1H)	5.34 (s, 1H)	3.71-3.75 (m, 2H), 4.36-4.40 (m, 2H)	1.22-1.48 (m, 18H)	1.04-1.14 (m, 2H), 6.83-7.58 (m, 10H)
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}di(*o*-chlorobenzyl)tin(IV), **DB6**	7.00-7.30 (m, 5H)	8.20 (s, 1H)	5.30 (s, 1H)	3.35-3.39 (m, 2H), 4.50-4.52 (m, 2H).	1.20-1.38 (m, 18H)	1.04-1.10 (m, 2H), 7.01-7.30 (m, 8H)
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}di(*p*-chlorobenzyl)tin(IV), **DB7**	7.00-7.30 (m, 5H)	8.29 (s, 1H)	5.35 (s, 1H)	3.35-3.42 (m, 2H), 4.40-4.50 (m, 2H).	1.20-1.38 (m, 18H)	1.01-1.10 (m, 2H), 7.10-7.34 (m, 8H)

[a] s = singlet, d = doublet, t = triplet, m = multiplet

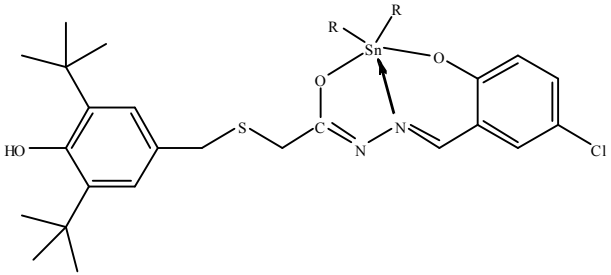


R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 5.3.6c
^{1}H NMR chemical shifts for {*N'*-(5-chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}diorganotin complexes

Complex	Assignments[a] [δ(^{1}H)/ppm]					
	Aryl	-N=C(H)	-OH	-CH_2-	-C(CH_3)$_3$	R groups
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dimethyltin(IV), **DC1**	6.85-7.73 (m, 5H)	8.90 (s, 1H)	5.20 (s, 1H)	3.38-3.42 (m, 2H), 4.14-4.32 (m, 2H)	0.61-1.37 (m, 18H)	0.59 (s, 6H)
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dibutyltin(IV), **DC2**	6.92-7.75 (m, 5H)	8.18 (s, 1H)	5.32 (s, 1H)	3.38-3.47 (m, 2H), 4.24-4.39 (m, 2H)	0.60-1.42 (m, 18H)	0.70-2.09 (m, 18H)
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}diphenyltin(IV), **DC3**	6.90-7.77 (m, 5H)	8.43 (s, 1H)	5.22 (s, 1H)	3.32-3.35 (m, 2H), 4.37-4.40 (m, 2H)	0.90-1.62 (m, 18H)	6.85-7.87 (m, 10H)
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dicyclohexyltin(IV), **DC4**	6.66-7.44 (m, 5H)	8.30 (s, 1H)	5.30 (s, 1H)	3.05-3.08 (m, 2H), 3.90-3.94 (m, 2H)	0.70-1.70 (m, 18H)	1.01-1.70 (m, 22H)
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dibenzyltin(IV), **DC5**	6.60-7.20 (m, 5H)	8.26 (s, 1H)	5.20 (s, 1H)	3.03-3.14 (m, 2H), 3.76-3.80 (m, 2H)	0.93-1.40 (m, 18H)	1.13-1.20 (m, 2H), 6.60-7.40 (m,10H)
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}di(*o*-chlorobenzyl)tin(IV), **DC6**	6.45-7.27 (m, 5H)	8.20 (s, 1H)	5.18 (s, 1H)	3.01-3.10 (m, 2H), 3.50-3.59 (m, 2H)	0.90-1.43 (m, 18H)	1.12-1.21 (m, 2H), 6.45-7.27 (m, 8H)
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}di(*p*-chlorobenzyl)tin(IV), **DC7**	6.41-7.23 (m, 5H)	8.15 (s, 1H)	5.16 (s, 1H)	3.00-3.16 (m, 2H), 3.58-3.70 (m, 2H)	0.99-1.31 (m, 18H)	1.10-1.20 (m, 2H), 6.41-7.23 (m, 8H)

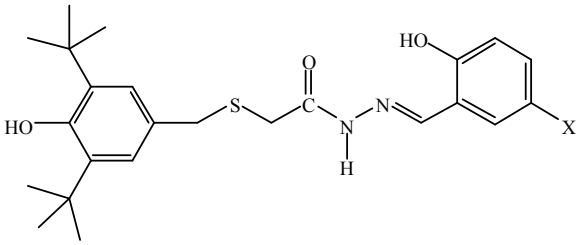
[a] s = singlet, d = doublet, t = triplet, m = multiplet



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 5.3.7
^{13}C NMR chemical shifts for substituted [2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazide ligands

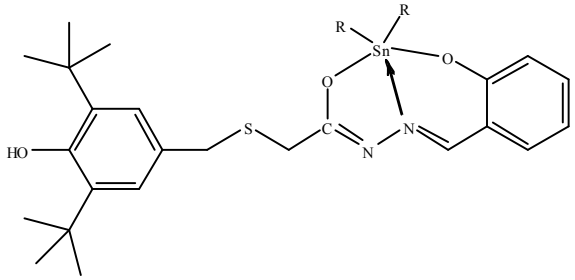
Ligand	^{13}C NMR chemical shifts [$\delta(^{13}C)$/ppm]
N'-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazide, **DA**	29.3, 30.0, 34.2, 34.5, 37.2, 55.8, 116.3, 118.8, 119.9, 121.7, 124.6, 127.4, 128.4, 132.5, 135.9, 137.0, 153.0, 159.7, 164.0, 166.8
N'-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-(4-hydroxybenzyl)sulfanyl]acetatohydrazide, **DB**	29.5, 30.8, 34.0, 34.7, 36.8, 54.5, 111.0, 116.5, 124.0, 125.8, 127.8, 129.3, 131.1, 135.5, 136.1, 139.7, 155.3, 160.0, 165.2, 173.4
N'-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazide, **DC**	29.2, 30.3, 33.0, 34.4, 37.0, 57.7, 115.1, 118.0, 123.1, 125.0, 126.7, 127.8, 128.4, 131.8, 133.2, 139.6, 153.3, 161.4, 167.5, 172.0



DA: X = H
DB: X = Br
DC: X = Cl

Table 5.3.8a
^{13}C NMR chemical shifts for the {*N'*-(2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}diorganotin complexes

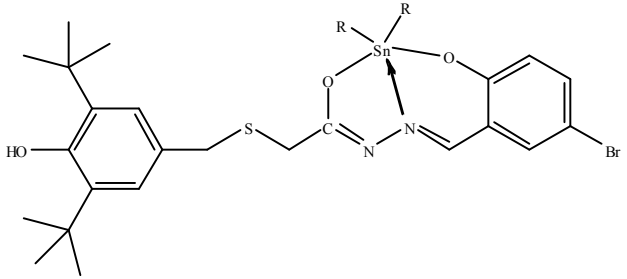
Complex	^{13}C NMR chemical shifts [δ(^{13}C)/ppm]
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-dimethyltin(IV), **DA1**	1.5, 29.3, 29.5, 30.0, 30.3, 34.2, 58.2, 116.3, 118.8, 119.9, 121.7, 124.6, 127.4, 128.4, 132.5, 135.9, 137.0, 153.0, 159.7, 164.7, 166.3
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-dibutyltin(IV), **DA2**	13.6, 21.4, 22.6, 27.3, 29.7, 30.1, 30.3, 32.2, 34.3, 56.8, 117.0, 117.9, 119.7, 124.6, 128.8, 132.1, 132.5, 133.0, 133.4, 136.0, 153.1, 159.7, 164.7, 166.0
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-diphenyltin(IV), **DA3**	29.5, 29.8, 30.2, 31.8, 33.9, 57.6, 116.3, 117.0, 119.5, 120.2, 125.0, 128.5, 128.8, 129.4, 130.0, 130.5, 131.4, 132.7, 135.4, 136.8, 139.7, 153.4, 156.5, 159.1, 163.2, 166.8
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-dicyclohexyltin(IV), **DA4**	26.5, 28.8, 29.9, 30.2, 30.5, 30.9, 32.9, 34.4, 40.6, 60.7, 116.4, 118.0, 119.5, 126.8, 127.0, 129.0, 131.0, 132.2, 133.0, 136.0, 139.6, 152.9, 160.4, 166.0
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-dibenzyltin(IV), **DA5**	8.7, 29.4, 29.6, 30.0, 30.4, 34.3, 57.3, 115.9, 116.7, 118.2, 120.3, 124.0, 124.7, 126.0, 126.6, 127.9, 128.2, 128.5, 129.2, 129.6, 131.0, 133.4, 135.5, 139.3, 153.1, 158.8, 163.0
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-di(*o*-chlorobenzyl)tin(IV), **DA6**	9.1, 29.8, 30.1, 30.9, 32.4, 35.0, 57.7, 116.3, 117.0, 119.5, 120.2, 125.1, 126.7, 126.9, 127.2, 127.8, 128.5, 128.7, 129.1, 131.4, 133.8, 135.9, 139.7, 153.5, 156.5, 159.2, 163.3
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-di(*p*-chlorobenzyl)tin(IV), **DA7**	13.9, 29.5, 29.7, 30.3, 30.3, 34.3, 58.2, 117.2, 119.7, 119.9, 124.6, 127.5, 128.3, 128.6, 128.8, 130.0, 131.2, 132.6, 133.4, 134.2, 136.1, 137.2, 140.1, 153.1, 157.1, 159.8, 164.7



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 5.3.8b
^{13}C NMR chemical shifts for the {*N'*-(5-bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}diorganotin complexes

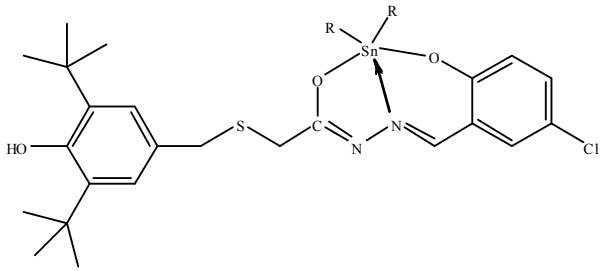
Complex	^{13}C NMR chemical shifts [δ(^{13}C)/ppm]
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dimethyltin(IV), **DB1**	6.4, 29.8, 30.8, 32.2, 34.3, 36.5, 58.0, 106.8, 111.0, 116.5, 124.2, 125.8, 127.2, 128.0, 131.3, 135.7, 136.0, 139.7, 155.3, 160.0, 165.2, 173.0
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dibutyltin(IV), **DB2**	14.0, 24.5, 26.2, 28.8, 29.7, 30.8, 32.3, 34.4, 37.0, 53.2, 106.6, 119.3, 123.8, 125.8, 129.1, 131.3, 132.4, 134.9, 136.3, 139.7, 153.3, 159.5, 166.0, 173.2
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}diphenyltin(IV), **DB3**	29.5, 30.2, 32.0, 34.5, 37.1, 56.6, 108.5, 117.9, 119.8, 124.0, 125.8, 128.0, 129.0, 130.1, 130.7, 132.2, 135.9, 136.1, 138.0, 138.4, 139.6, 140.0, 152.9, 160.4, 166.0, 173.7
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dicyclohexyltin(IV), **DB4**	26.5, 28.8, 29.9, 30.5, 30.8, 33.0, 34.2, 37.0, 40.2, 57.2, 110.2, 118.7, 123.3, 125.8, 128.9, 130.7, 132.0, 134.2, 135.5, 139.8, 157.5, 161.5, 166.2, 173.8
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dibenzyltin(IV), **DB5**	12.6, 29.4, 30.2, 33.3, 34.6, 38.1, 58.0, 107.9, 118.6, 121.7, 123.3, 124.8, 125.1, 125.9, 127.0, 127.8, 128.8, 129.9, 132.2, 134.5, 135.6, 136.7, 139.7, 152.9, 160.4, 166.0, 173.2
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}di(*o*-chlorobenzyl)tin(IV), **DB6**	11.3, 29.6, 30.8, 32.1, 34.3, 37.3, 60.7, 110.5, 116.7, 122.0, 126.4, 126.8, 127.1, 127.6, 128.6, 129.1, 130.9, 131.2, 132.2, 134.4, 135.6, 138.3, 154.6, 157.8, 160.9, 165.5, 173.4
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}di(*p*-chlorobenzyl)tin(IV), **DB7**	11.1, 29.4, 30.5, 32.3, 34.4, 37.1, 57.7, 110.2, 116.6, 120.1, 124.4, 125.9, 127.0, 127.8, 128.8, 129.9, 130.9, 131.7, 132.4, 134.6, 135.7, 138.6, 154.6, 157.8, 160.9, 166.0, 173.5



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

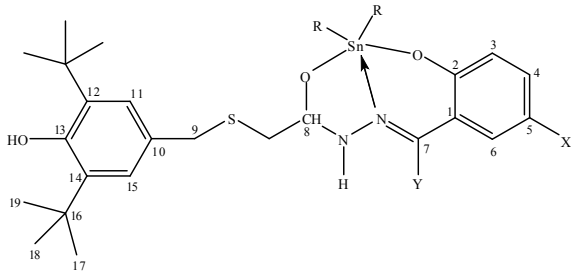
Table 5.3.8c
^{13}C NMR chemical shifts for the {*N'*-(5-chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}diorganotin complexes

Complex	^{13}C NMR chemical shifts [δ(^{13}C)/ppm]
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dimethyltin(IV), **DC1**	6.2, 29.7, 30.3, 30.8, 32.5, 34.3, 57.7, 118.0, 119.9, 125.0, 126.7, 127.5, 127.9, 128.5, 131.8, 133.2, 139.6, 157.2, 160.7, 167.5, 172.3
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dibutyltin(IV), **DC2**	14.2, 21.8, 22.6, 27.2, 29.9, 30.4, 32.2, 34.0, 36.9, 58.2, 116.6, 119.3, 123.0, 126.7, 127.8, 129.1, 131.0, 132.3, 133.0, 139.7, 158.1, 161.4, 168.4, 172.0
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}diphenyltin(IV), **DC3**	29.6, 30.1, 30.9, 33.9, 37.4, 56.3, 116.0, 119.2, 124.1, 125.8, 126.6, 128.0, 129.0, 129.2, 129.5, 133.3, 133.5, 134.4, 134.7, 135.2, 139.8, 146.9, 153.3, 165.2, 168.6, 172.4
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dicyclohexyltin(IV), **DC4**	26.5, 28.8, 29.8, 30.1, 30.4, 30.9, 33.2, 34.5, 37.0, 40.5, 56.9, 116.7, 119.5, 123.3, 125.1, 126.7, 127.8, 128.3, 131.0, 133.4, 139.8, 157.5, 161.5, 166.2, 172.8
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dibenzyltin(IV), **DC5**	11.7, 29.5, 30.5, 33.1, 34.4, 37.2, 55.9, 116.0, 118.4, 122.4, 123.8, 124.4, 125.5, 127.6, 128.3, 128.7, 129.0, 129.2, 129.4, 132.3, 133.2, 139.4, 140.0, 157.2, 160.2, 165.8, 172.4
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}di(*o*-chlorobenzyl)tin(IV), **DC6**	12.7, 29.4, 30.4, 32.1, 33.9, 37.0, 55.8, 116.6, 119.0, 124.4, 125.1, 125.9, 127.8, 128.8, 129.9, 130.9, 131.3, 132.5, 133.4, 134.5, 135.7, 138.3, 139.7, 156.4, 160.1, 166.1, 172.1
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}di(*p*-chlorobenzyl)tin(IV), **DC7**	13.7, 29.3, 30.6, 32.3, 34.2, 37.3, 58.8, 116.2, 118.4, 123.6, 123.9, 125.6, 125.9, 127.6, 128.5, 128.8, 130.6, 131.1, 132.5, 133.4, 134.5, 138.5, 139.4, 153.0, 160.1, 165.5, 172.0



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 5.3.9
^{119}Sn NMR chemical shifts of substituted [2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}diorganotin complexes

	^{119}Sn NMR chemical shifts [δ(^{119}Sn)/ppm]						
	R = Me	R = Bu	R = Ph	R = Cy	R = Bz	R = *o*-ClBz	R = *p*-ClBz
DA : X = H, Y = H, Z = H	-152.1	-139.5	-327.6	-267.9	-302.3	-267.5	-229.7
DB : X = Br, Y = H, Z = H	-198.2	-285.3	-382.6	-	-	-272.8	-292.2
DC : X = Cl, Y = H, Z = H	-231.0	-285.8	-388.2	-261.0	-360.5	-274.5	-

5.3.4 Electronic Spectra

The electronic spectral data of the Schiff base ligands and diorganotin complexes in acetonitrile (CH_3CN) were recorded in the 190-600 nm regions. Selected spectral data for the free tridentate Schiff base ligands and the diorganotin complexes are given in tables 5.3.10 and 5.3.11.

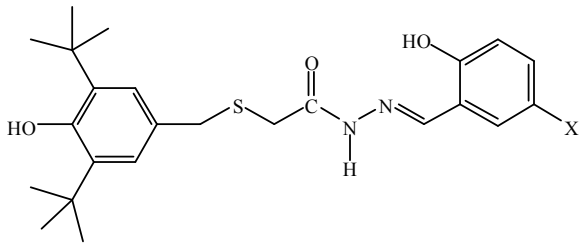
In general, the absorption bands of the Schiff base ligands could be classified into two absorption regions of 200-299 nm and 300-420 nm regions. An intense band in the 390-420 nm could be attributed to the $n \longrightarrow \pi^*$ transitions which was associated with azomethine chromophore [Bella *et al.*, 1997]. In the diorganotin complexes, this band showed a small bathochromic shift, probably because only one of the azomethine nitrogen was coordinated to the metal centre in the complexes. The presence of a weak peak between 320-340 nm could be attributed to the $n \longrightarrow \pi^*$ transitions of the phenyl rings.

The strong band between 200-299 nm was assigned as $\pi \longrightarrow \pi^*$ electronic transition which occurred for all the free tridentate Schiff bases ligands and the organotin complexes. This $\pi \longrightarrow \pi^*$ electronic transition involved the molecular orbitals of the C=N chromophore and both the phenyl rings.

As no other strong bands were observed in the electronic spectra for both ligands and complexes, it could be concluded that electronic spectra are of little help in assigning and confirming an accurate structure for the ligands and complexes.

Table 5.3.10
Electronic spectral data for substituted [2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidate ligands

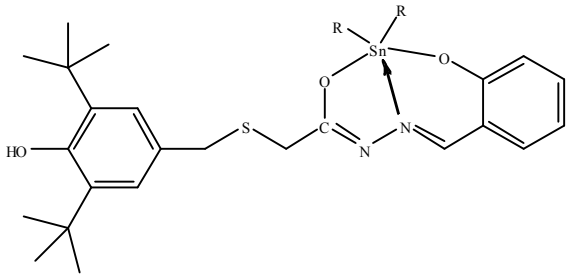
Ligand	Intraligand transfer transition	
	π-π*	n-π*
N'-(2-Oxidobenzylidene){2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazide, **DA**	206, 289	354
N'-(5-Bromo-2-oxidobenzylidene){2-(3,5-di-*tert*-butyl-(4-hydroxybenzyl)sulfanyl]acetatohydrazide, **DB**	205, 280	327
N'-(5-Chloro-2-oxidobenzylidene){2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazide, **DC**	206, 280	329



DA: X = H
DB: X = Br
DC: X = Cl

Table 5.3.11a
Electronic spectral data for {*N'*-(2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}diorganotin complexes

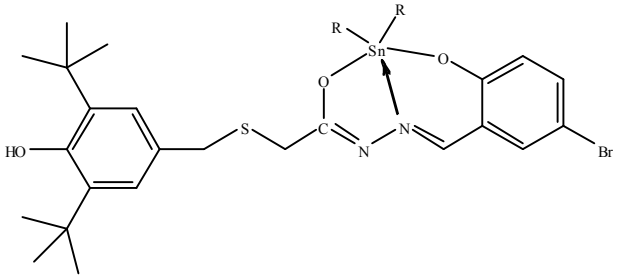
Complex	Intraligand transfer transition	
	π-π^*	n-π^*
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-dimethyltin(IV), **DA1**	291	351, 401
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-dibutyltin(IV), **DA2**	292	353, 402
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-diphenyltin(IV), **DA3**	290	318, 399
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-dicyclohexyltin(IV), **DA4**	291	332, 395
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-dibenzyltin(IV), **DA5**	281	401
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-di(*o*-chlorobenzyl)tin(IV), **DA6**	290	317, 390
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-di(*p*-chlorobenzyl)tin(IV), **DA7**	287	398



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 5.3.11b
Electronic spectral data for {*N'*-(5-bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}diorganotin complexes

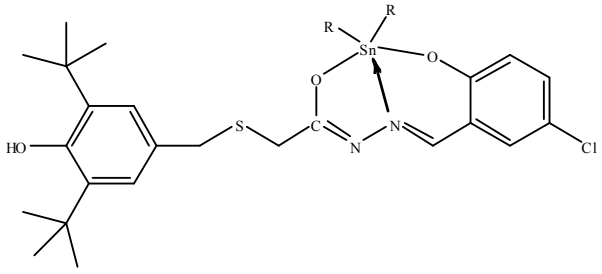
Complex	Intraligand transfer transition	
	π-π*	n-π*
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dimethyltin(IV), **DB1**	281	402
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dibutyltin(IV), **DB2**	290	409
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}diphenyltin(IV), **DB3**	292	410
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dicyclohexyltin(IV), **DB4**	280	395
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dibenzyltin(IV), **DB5**	284	390
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}di(*o*-chlorobenzyl)tin(IV), **DB6**	286	402
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}di(*p*-chlorobenzyl)tin(IV), **DB7**	290	390



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

Table 5.3.11c
Electronic spectral data for {*N'*-(5-chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}diorganotin complexes

Complex	Intraligand transfer transition	
	π-π^*	n-π^*
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dimethyltin(IV), **DC1**	290	400
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dibutyltin(IV), **DC2**	281	402
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}diphenyltin(IV), **DC3**	294	402
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dicyclohexyltin(IV), **DC4**	298	395
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dibenzyltin(IV), **DC5**	293	398
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}di(*o*-chlorobenzyl)tin(IV), **DC6**	290	400
{*N'*-(5-Chloro-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}di(*p*-chlorobenzyl)tin(IV), **DC7**	288	396



R = CH_3, C_4H_9, phenyl (Ph), cyclohexyl (Cy), benzyl (Bz), *o*-chlorobenzyl (*o*-ClBz), *p*-chlorobenzyl (*p*-ClBz)

5.3.5 X-Ray Structures

Catena-poly[_bis_{triphenyltin(IV)[2-(3,5-di-_tert_-butyl-4-hydroxybenzyl)-sulfanyl]acetate}], AC1 and tricyclohexyltin(IV)[2-(3,5-di-_tert_-butyl-4-hydroxybenzyl)sulfanyl]acetate, AC2

Two of the triorganotin carboxylates derived from the [2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetic acid, namely *catena*-poly[*bis*{triphenyltin(IV)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetate}], **AC1** and tricyclohexyltin(IV)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetate, **AC2** were analyzed by X-ray crystallography. Details of the crystallographic parameters are given in table 5.3.12 and 5.3.14, while the selected bond lengths and angles are tabulated in table 5.3.13 and 5.3.15. The molecular structure of the compounds **AC1** and **AC2** are shown in figure 5.3.1a and 5.3.1b respectively.

In general, triorganotin carboxylates were either monomeric or polymeric, depending on the steric bulk of the organic substituents. Triphenyltin carboxylates generally adopted a five-coordinated tin geometry with carboxylate bridges linking adjacent molecules into a polymeric chain, whereas tricyclohexyltin carboxylates had discrete four-coordinated tin structures [Tiekink 1991].

The molecular structure of the carboxylate, **AC1** was found to contain two symmetry-independent five-coordinated triphenyltin molecules which were linked by carboxylate bridges forming a polymeric chain. The tin atom was in a distorted *trans*-C_3SnO_2 trigonal-bipyramidal geometry in which the axial positions were occupied by the carboxylate-*O* atoms of the adjacent [2-(3,5-di-*tert*-4-hydroxybenzyl)sulfanyl]acetic acid ligands. The Sn-O bond distances of 2.186 (2) Å, 2.452 (2) Å, 2.151 (2) Å and

2.384 (2) Å were in good agreement with values reported for many polymeric triorganotin carboxylates [Tiekink 1991]. The presence of two bulky *tert*-butyl groups on the benzene ring prevented any hydrogen-bonding interactions involving the hydroxyl substituent.

AC2 is an example of a four-coordinated tricyclohexyltin carboxylate, in which the tin atom adopts a distorted tetrahedral geometry. The close proximity of the carboxylate O3 towards the Sn atom [Sn1···O3 = 2.897 (3) Å] contributed to the distortion of the geometry [Alcock and Timms 1968a, Alcock and Timms 1968b].

Figure 5.3.1a Molecular plot of *catena*-poly{*bis*[triphenyltin(IV)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetate]}, **AC1**

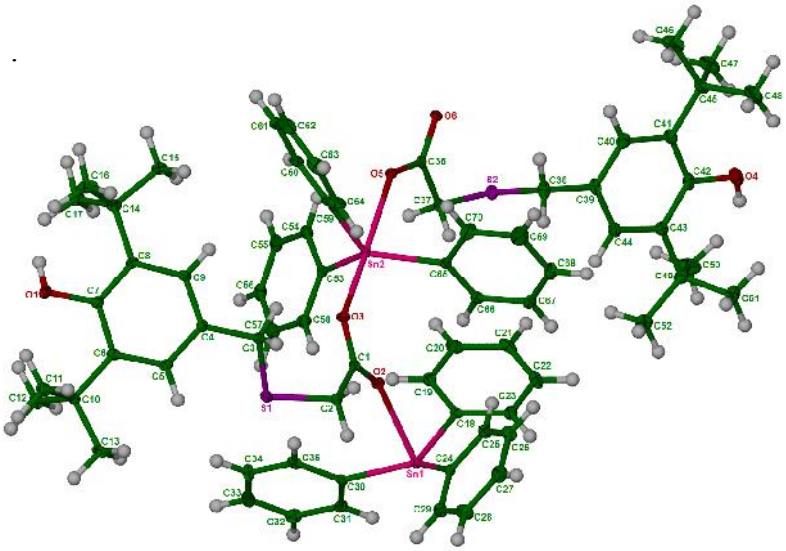


Figure 5.3.1b Molecular plot of tricyclohexyltin(IV)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetate, **AC2**

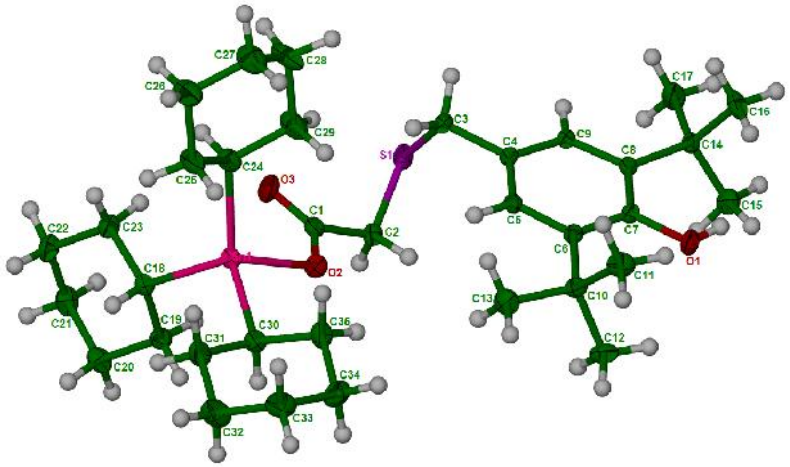


Table 5.3.12
Crystal data and structure refinement for *catena*-poly{*bis*[triphenyltin(IV)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetate]}, **AC1**

Empirical formula	$(C_{35}H_{40}O_3SSn)_2$
Formula weight	1318.84
Crystal system	Monoclinic
Space group	$P2_1/n$
	a (Å) = 23.1141(3) b (Å) = 10.69330(10) c (Å) = 26.4904(3) α (°) = 90 β (°) = 105.3180(10) γ (°) = 90
Volume (Å^3)	6314.92(12)
Z	4
Calculated density D_{calc} (Mgm^{-3})	1.387
Absorption coefficient, μ (mm^{-1})	0.908
F(000)	2720
Crystal size (mm)	0.33 x 0.12 x 0.05
Limiting indices	$-30 \leq h \leq 30$, $-13 \leq k \leq 13$, $-34 \leq l \leq 34$
Reflections collected / unique	46753 / 14430 [$R_{(int)}$ = 0.0583]
Max. and min. transmission	0.9603 and 0.7538
Data / restraints / parameters	14430 / 0 / 735
Goodness-of-fit on F^2	1.012
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0412, wR_2 = 0.0779
R indices (all data)	R_1 = 0.0784, wR_2 = 0.0942
Largest diff. peak and hole (eÅ^{-3})	0.912 and -0.596

Table 5.3.13
Bond lengths (Å) and angles (°) with estimated standard deviation for *catena*-poly{*bis*[triphenyltin(IV)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetate]}, **AC1**

Sn(1)-O(2)	2.452(2)	O(1)-C(4)-C(3)	117.0(3)
Sn(1)-O(5)#1	2.186(2)	O(1)-C(4)-C(5)	120.4(3)
Sn(1)-C(35)	2.120(4)	O(2)-C(17)-O(3)	123.7(3)
Sn(1)-C(41)	2.124(3)	O(2)-C(17)-C(16)	121.6(3)
Sn(1)-C(47)	2.122(4)	O(3)-C(17)-C(16)	114.6(3)
Sn(2)-O(3)	2.151(2)	O(3)-Sn(2)-O(4)	170.70(9)
Sn(2)-O(4)	2.384(2)	O(4)-C(18)-O(5)	123.2(3)
Sn(2)-C(53)	2.130(4)	O(4)-C(18)-C(19)	117.8(3)
Sn(2)-C(59)	2.125(4)	O(5)-C(18)-C(19)	118.9(3)
Sn(2)-C(65)	2.129(4)	O(5)#1-Sn(1)-O(2)	174.26(8)
O(1)-C(4)	1.384(4)	O(6)-C(24)-C(23)	116.2(4)
O(2)-C(17)	1.254(4)	O(6)-C(24)-C(25)	120.5(4)
O(3)-C(17)	1.279(4)	C(1)-C(6)-C(5)	122.0(3)
O(4)-C(18)	1.254(4)	C(1)-C(15)-S(1)	110.8(2)
O(5)-C(18)	1.264(4)	C(2)-C(1)-C(15)	121.6(3)
O(5)-Sn(1)#2	2.186(2)	C(2)-C(3)-C(4)	117.3(3)
O(6)-C(24)	1.387(4)	C(2)-C(3)-C(11)	121.4(3)
S(1)-C(16)	1.822(4)	C(3)-C(2)-C(1)	122.1(3)
S(1)-C(15)	1.824(4)	C(4)-C(3)-C(11)	121.2(3)
S(2)-C(19)	1.792(3)	C(4)-C(5)-C(6)	117.4(3)
S(2)-C(20)	1.803(4)	C(4)-C(5)-C(7)	121.4(3)
C(1)-C(2)	1.397(5)	C(5)-C(4)-C(3)	122.6(3)
C(1)-C(6)	1.388(5)	C(6)-C(1)-C(2)	118.6(3)
C(1)-C(15)	1.511(5)	C(6)-C(1)-C(15)	119.8(3)
C(2)-C(3)	1.391(5)	C(6)-C(5)-C(7)	121.2(3)
C(3)-C(4)	1.405(5)	C(8)-C(7)-C(5)	110.6(3)
C(3)-C(11)	1.541(5)	C(9)-C(7)-C(5)	111.1(3)
C(4)-C(5)	1.399(5)	C(9)-C(7)-C(8)	107.1(3)
C(5)-C(6)	1.399(5)	C(9)-C(7)-C(10)	106.9(4)
C(5)-C(7)	1.555(5)	C(10)-C(7)-C(5)	111.3(3)
C(7)-C(8)	1.548(6)	C(10)-C(7)-C(8)	109.7(4)
C(7)-C(9)	1.519(6)	C(12)-C(11)-C(3)	109.3(3)
C(7)-C(10)	1.546(5)	C(12)-C(11)-C(13)	110.7(3)
C(11)-C(12)	1.531(5)	C(12)-C(11)-C(14)	107.6(3)
C(11)-C(14)	1.533(5)	C(13)-C(11)-C(3)	110.8(3)
C(11)-C(13)	1.537(5)	C(14)-C(11)-C(3)	111.5(3)
C(16)-C(17)	1.513(5)	C(14)-C(11)-C(13)	106.8(3)
C(18)-C(19)	1.524(5)	C(16)-S(1)-C(15)	101.51(17)
C(20)-C(21)	1.509(5)	C(17)-C(16)-S(1)	111.6(3)
C(21)-C(22)	1.385(6)	C(17)-O(2)-Sn(1)	143.5(2)
C(21)-C(26)	1.390(5)	C(17)-O(3)-Sn(2)	129.3(2)
C(22)-C(23)	1.395(5)	C(18)-O(4)-Sn(2)	134.3(2)
C(23)-C(24)	1.407(6)	C(18)-O(5)-Sn(1)#2	121.0(2)
C(23)-C(31)	1.538(5)	C(18)-C(19)-S(2)	118.4(3)
C(24)-C(25)	1.408(6)	C(19)-S(2)-C(20)	99.24(18)
C(25)-C(26)	1.395(5)	C(21)-C(20)-S(2)	110.3(3)
C(25)-C(27)	1.542(6)	C(21)-C(22)-C(23)	121.9(4)
C(27)-C(28)	1.547(6)	C(21)-C(26)-C(25)	122.6(4)
C(27)-C(29)	1.531(6)	C(22)-C(21)-C(20)	120.7(4)
C(27)-C(30)	1.538(6)	C(22)-C(21)-C(26)	119.0(4)
C(31)-C(32)	1.526(6)	C(22)-C(23)-C(24)	117.0(4)
C(31)-C(33)	1.532(6)	C(22)-C(23)-C(31)	120.8(4)

C(31)-C(34)	1.526(6)
C(35)-C(36)	1.382(5)
C(35)-C(40)	1.396(5)
C(36)-C(37)	1.393(5)
C(37)-C(38)	1.372(6)
C(38)-C(39)	1.376(6)
C(39)-C(40)	1.387(6)
C(41)-C(42)	1.394(5)
C(41)-C(46)	1.396(5)
C(42)-C(43)	1.382(5)
C(43)-C(44)	1.383(6)
C(44)-C(45)	1.375(6)
C(45)-C(46)	1.389(5)
C(47)-C(48)	1.398(5)
C(47)-C(52)	1.399(5)
C(48)-C(49)	1.391(5)
C(49)-C(50)	1.369(5)
C(50)-C(51)	1.372(5)
C(51)-C(52)	1.380(5)
C(53)-C(54)	1.400(5)
C(53)-C(58)	1.394(5)
C(54)-C(55)	1.394(5)
C(55)-C(56)	1.369(6)
C(56)-C(57)	1.368(6)
C(57)-C(58)	1.401(5)
C(59)-C(60)	1.391(5)
C(59)-C(64)	1.385(5)
C(60)-C(61)	1.379(5)
C(61)-C(62)	1.381(7)
C(62)-C(63)	1.372(7)
C(63)-C(64)	1.396(6)
C(65)-C(66)	1.379(5)
C(65)-C(70)	1.391(5)
C(66)-C(67)	1.392(6)
C(67)-C(68)	1.359(6)
C(68)-C(69)	1.380(6)
C(69)-C(70)	1.374(6)

C(24)-C(23)-C(31)	122.2(4)
C(24)-C(25)-C(27)	122.8(3)
C(25)-C(24)-C(23)	123.3(4)
C(25)-C(27)-C(28)	111.1(4)
C(26)-C(21)-C(20)	120.3(4)
C(26)-C(25)-C(24)	116.2(4)
C(26)-C(25)-C(27)	121.0(4)
C(29)-C(27)-C(25)	110.6(4)
C(29)-C(27)-C(28)	111.3(4)
C(29)-C(27)-C(30)	105.9(4)
C(30)-C(27)-C(25)	112.4(3)
C(30)-C(27)-C(28)	105.4(4)
C(32)-C(31)-C(23)	109.5(4)
C(32)-C(31)-C(33)	110.3(4)
C(32)-C(31)-C(34)	107.0(4)
C(33)-C(31)-C(23)	111.2(4)
C(34)-C(31)-C(23)	111.6(4)
C(34)-C(31)-C(33)	107.2(4)
C(35)-Sn(1)-C(41)	114.26(14)
C(35)-Sn(1)-C(47)	134.63(13)
C(35)-Sn(1)-O(5)#1	97.85(12)
C(35)-C(36)-C(37)	120.6(4)
C(35)-Sn(1)-O(2)	84.09(11)
C(36)-C(35)-C(40)	118.4(3)
C(36)-C(35)-Sn(1)	124.6(3)
C(37)-C(38)-C(39)	119.6(4)
C(38)-C(37)-C(36)	120.5(4)
C(38)-C(39)-C(40)	120.4(4)
C(39)-C(40)-C(35)	120.5(4)
C(40)-C(35)-Sn(1)	117.0(3)
C(41)-Sn(1)-O(2)	85.69(11)
C(41)-Sn(1)-O(5)#1	88.59(12)
C(42)-C(41)-C(46)	118.5(3)
C(42)-C(41)-Sn(1)	119.8(3)
C(43)-C(42)-C(41)	121.0(4)
C(44)-C(43)-C(42)	119.9(4)
C(44)-C(45)-C(46)	120.6(4)
C(45)-C(44)-C(43)	119.9(4)
C(45)-C(46)-C(41)	120.1(4)
C(46)-C(41)-Sn(1)	121.7(3)
C(47)-Sn(1)-C(41)	109.53(14)
C(47)-Sn(1)-O(2)	87.90(11)
C(47)-Sn(1)-O(5)#1	94.48(12)
C(48)-C(47)-Sn(1)	117.0(3)
C(48)-C(47)-C(52)	117.7(3)
C(49)-C(48)-C(47)	120.6(4)
C(49)-C(50)-C(51)	120.1(4)
C(50)-C(49)-C(48)	120.3(4)
C(50)-C(51)-C(52)	120.4(4)
C(51)-C(52)-C(47)	120.9(3)
C(52)-C(47)-Sn(1)	125.0(3)
C(53)-C(58)-C(57)	119.7(4)
C(53)-Sn(2)-O(3)	98.22(12)
C(53)-Sn(2)-O(4)	89.67(11)
C(54)-C(53)-Sn(2)	119.8(3)
C(55)-C(54)-C(53)	121.0(4)

C(55)-C(56)-C(57)	120.7(4)
C(56)-C(55)-C(54)	119.5(4)
C(56)-C(57)-C(58)	120.6(4)
C(58)-C(53)-C(54)	118.4(3)
C(58)-C(53)-Sn(2)	121.6(3)
C(59)-Sn(2)-C(65)	113.54(14)
C(59)-Sn(2)-C(53)	114.45(14)
C(59)-Sn(2)-O(3)	90.04(11)
C(59)-C(64)-C(63)	121.1(4)
C(59)-Sn(2)-O(4)	82.19(11)
C(60)-C(59)-Sn(2)	120.4(3)
C(61)-C(60)-C(59)	120.9(4)
C(62)-C(61)-C(60)	119.9(5)
C(62)-C(63)-C(64)	119.2(4)
C(63)-C(62)-C(61)	120.6(4)
C(64)-C(59)-C(60)	118.3(4)
C(64)-C(59)-Sn(2)	121.0(3)
C(65)-C(66)-C(67)	121.1(4)
C(65)-Sn(2)-C(53)	130.52(13)
C(65)-Sn(2)-O(3)	93.07(12)
C(65)-Sn(2)-O(4)	85.43(11)
C(66)-C(65)-C(70)	117.6(4)
C(66)-C(65)-Sn(2)	124.5(3)
C(67)-C(68)-C(69)	120.0(4)
C(68)-C(67)-C(66)	120.1(4)
C(69)-C(70)-C(65)	121.5(4)
C(70)-C(65)-Sn(2)	117.9(3)
C(70)-C(69)-C(68)	119.8(4)

Symmetry transformations used to generate equivalent atoms:
#1 x,y+1,z #2 x,y-1,z

Table 5.3.14
Crystal data and structure refinement for tricyclohexyltin(IV)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetate, **AC2**

Empirical formula	$C_{35}H_{58}O_3SSn$
Formula weight	677.56
Crystal system	Monoclinic
Space group	$P2_1/c$
	a (Å) = 15.5048(3) b (Å) = 11.4261(3) c (Å) = 19.9794(4) α (°) = 90 β (°) = 94.603(2) γ (°) = 90
Volume (Å^3)	3528.12(14)
Z	4
Calculated density D_{calc} (Mgm^{-3})	1.276
Absorption coefficient, μ (mm^{-1})	0.814
F(000)	1432
Crystal size (mm)	0.23 x 0.16 x 0.12
Limiting indices	$-20 \leq h \leq 20$, $-14 \leq k \leq 14$, $-25 \leq l \leq 25$
Reflections collected / unique	32619 / 8086 [$R_{(int)}$ = 0.0676]
Max. and min. transmission	0.9087 and 0.8349
Data / restraints / parameters	8086 / 0 / 368
Goodness-of-fit on F^2	0.999
Final R indices[$I>2\sigma(I)$]	R_1 = 0.0500, wR_2 = 0.0968
R indices (all data)	R_1 = 0.1052, wR_2 = 0.1173
Largest diff. peak and hole (eÅ^{-3})	0.645 and -0.370

Table 5.3.15
Bond lengths (Å) and angles (°) with estimated standard deviation for tricyclohexyltin(IV)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetate, **AC2**

Sn(1)-O(2)	2.081(3)	O(1)-C(7)-C(6)	115.6(3)
Sn(1)-C(18)	2.148(4)	O(1)-C(7)-C(8)	121.4(3)
Sn(1)-C(24)	2.157(5)	O(2)-C(1)-C(2)	114.4(4)
Sn(1)-C(30)	2.166(4)	O(2)-Sn(1)-C(24)	108.65(15)
O(1)-C(7)	1.383(4)	O(2)-Sn(1)-C(30)	95.82(14)
O(2)-C(1)	1.294(5)	O(3)-C(1)-C(2)	122.8(4)
S(1)-C(2)	1.792(4)	O(3)-C(1)-O(2)	122.7(4)
S(1)-C(3)	1.806(5)	C(1)-O(2)-Sn(1)	112.7(3)
C(1)-O(3)	1.211(5)	C(1)-C(2)-S(1)	113.8(3)
C(1)-C(2)	1.515(6)	C(2)-S(1)-C(3)	100.3(2)
C(3)-C(4)	1.514(5)	C(4)-C(3)-S(1)	114.4(3)
C(4)-C(5)	1.373(5)	C(4)-C(5)-C(6)	122.4(4)
C(4)-C(9)	1.380(5)	C(4)-C(9)-C(8)	122.6(4)
C(6)-C(5)	1.400(5)	C(5)-C(4)-C(3)	121.0(4)
C(6)-C(10)	1.538(5)	C(5)-C(4)-C(9)	119.0(4)
C(7)-C(6)	1.405(5)	C(5)-C(6)-C(7)	116.4(3)
C(8)-C(7)	1.401(5)	C(5)-C(6)-C(10)	120.9(4)
C(8)-C(14)	1.542(5)	C(6)-C(10)-C(11)	110.6(3)
C(9)-C(8)	1.390(5)	C(6)-C(10)-C(12)	110.0(4)
C(10)-C(11)	1.540(6)	C(7)-C(6)-C(10)	122.6(3)
C(10)-C(12)	1.538(6)	C(7)-C(8)-C(14)	122.9(3)
C(10)-C(13)	1.529(6)	C(8)-C(7)-C(6)	123.0(3)
C(14)-C(15)	1.533(6)	C(9)-C(4)-C(3)	120.1(4)
C(14)-C(16)	1.521(6)	C(9)-C(8)-C(7)	116.6(3)
C(14)-C(17)	1.524(6)	C(9)-C(8)-C(14)	120.5(3)
C(18)-C(19)	1.520(6)	C(12)-C(10)-C(11)	108.7(4)
C(18)-C(23)	1.513(6)	C(13)-C(10)-C(6)	111.8(4)
C(20)-C(19)	1.526(6)	C(13)-C(10)-C(11)	107.4(4)
C(21)-C(20)	1.497(7)	C(13)-C(10)-C(12)	108.2(4)
C(22)-C(21)	1.509(6)	C(15)-C(14)-C(8)	111.9(3)
C(23)-C(22)	1.521(6)	C(16)-C(14)-C(8)	110.2(4)
C(24)-C(25)	1.481(6)	C(16)-C(14)-C(15)	109.7(4)
C(24)-C(29)	1.471(7)	C(16)-C(14)-C(17)	107.5(4)
C(25)-C(26)	1.517(7)	C(17)-C(14)-C(8)	111.9(3)
C(27)-C(26)	1.449(7)	C(17)-C(14)-C(15)	105.5(4)
C(28)-C(27)	1.461(8)	C(18)-Sn(1)-C(24)	115.72(18)
C(29)-C(28)	1.533(8)	C(18)-Sn(1)-C(30)	108.43(16)
C(30)-C(31)	1.520(6)	C(18)-C(19)-C(20)	111.9(4)
C(30)-C(35)	1.493(6)	C(18)-C(23)-C(22)	112.2(4)
C(31)-C(32)	1.529(6)	C(19)-C(18)-Sn(1)	111.3(3)
C(32)-C(33)	1.478(7)	C(20)-C(21)-C(22)	111.5(4)
C(33)-C(34)	1.513(7)	C(21)-C(20)-C(19)	110.8(4)
C(35)-C(34)	1.530(7)	C(21)-C(22)-C(23)	111.7(4)

C(23)-C(18)-Sn(1)	114.5(3)
C(23)-C(18)-C(19)	111.4(3)
C(24)-Sn(1)-C(30)	116.65(18)
C(24)-C(25)-C(26)	113.5(5)
C(24)-C(29)-C(28)	112.1(5)
C(25)-C(24)-Sn(1)	110.8(3)
C(26)-C(27)-C(28)	113.0(5)
C(27)-C(26)-C(25)	112.8(5)
C(27)-C(28)-C(29)	113.4(5)
C(29)-C(24)-C(25)	112.7(4)
C(29)-C(24)-Sn(1)	116.1(4)
C(30)-C(31)-C(32)	111.2(4)
C(30)-C(35)-C(34)	112.5(4)
C(31)-C(30)-Sn(1)	110.9(3)
C(32)-C(33)-C(34)	110.9(5)
C(33)-C(32)-C(31)	112.1(5)
C(33)-C(34)-C(35)	111.5(4)
C(35)-C(30)-C(31)	111.3(4)
C(35)-C(30)-Sn(1)	113.9(3)

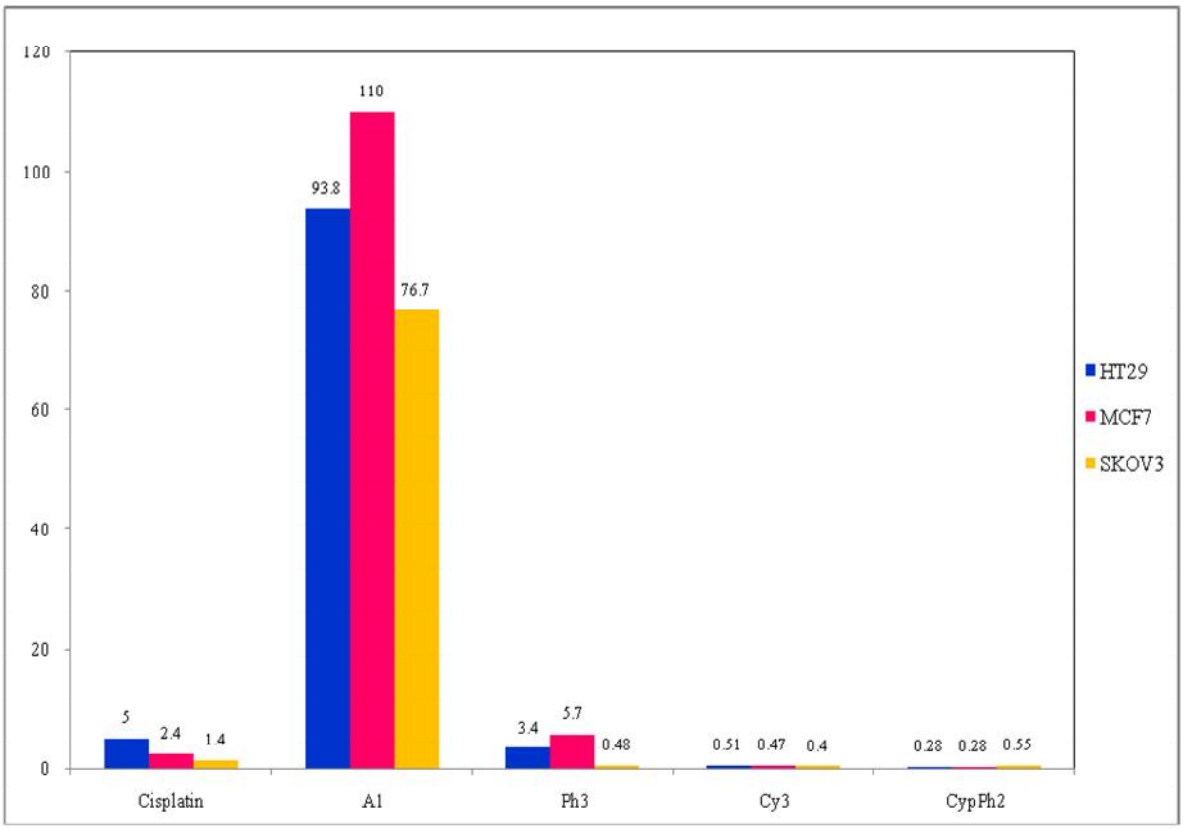
5.4 Cytotoxic Activity

The *in vitro* cytotoxic activity of the ligands and organotin complexes had been evaluated against three human carcinoma cell lines, namely HT-29 (human colon carcinoma cell line), SKOV-3 (human ovarian cancer cell line) and MCF-7 (hormone-dependent breast carcinoma cell line). In the anticancer screening, the ligands and their organotin complexes were dissolved in DMSO and the amount of DMSO used did not reveal any cytotoxic activity.

Cisplatin was used as positive control while the well containing untreated cells was used as the negative control. The cytotoxicity of each sample was expressed as IC_{50} value which was the concentration of test compounds that caused 50 % inhibition or cell death as averaged from the three experiments. The IC_{50} value was obtained by plotting the graph of percentage inhibition (%) versus concentration of test compounds (μg mL^{-1}). As the yield obtained for the complexes was low, only selected complexes were tested for their anticancer screening and the IC_{50} values of the selected ligands and the organotin complexes are listed in table 5.4.1.

In the present study, *cisplatin* was found to exhibit remarkable growth inhibitory activities with IC_{50} values ranging from 1.4-5.0 μg mL^{-1} on the studied cancer cell lines. The triorganotin compounds generally displayed pronounced cytotoxicity against all the tested human cell lines as compared to the ligand. The ligand, [2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetic acid, **A1**, was essentially not active in all the tested cell lines. However, the triorganotin carboxylates obtained from the ligand **Al** showed prominent cytotoxic activities against the three cell lines with IC_{50} values below 6 μg ml^{-1}.

Graph 5.4.1
Bar chart showing the comparison of the IC_{50} value of [2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetic acid and its triorganotin derivatives against *cisplatin*



The Schiff base ligands displayed moderate cytotoxic activity against all the three cell-lines, HT-29, MCF-7 and SKOV-3 cell-lines (for **DA** ligand, IC_{50} = 47 μg ml^{-1}, 66.3 μg ml^{-1} and 77.3 μg ml^{-1}; for **DB** ligand, IC_{50} = 27 μg ml^{-1}, 34 μg ml^{-1} and 35.7 μg ml^{-1}). The diphenyltin and dibenzyltin of this Schiff base showed moderate anticancer activities as compared to the other tested diorganotins in all the cell lines. The dimethyltin, dibutyltin and di(*p*-chlorobenzyl)tin derivatives showed no cytotoxic activities in all the cell lines except for **DA2** in MCF-7 (50 μg ml^{-1}).

Graph 5.4.2
Bar chart showing IC_{50} value of the Schiff base ligands and its diorganotin complexes

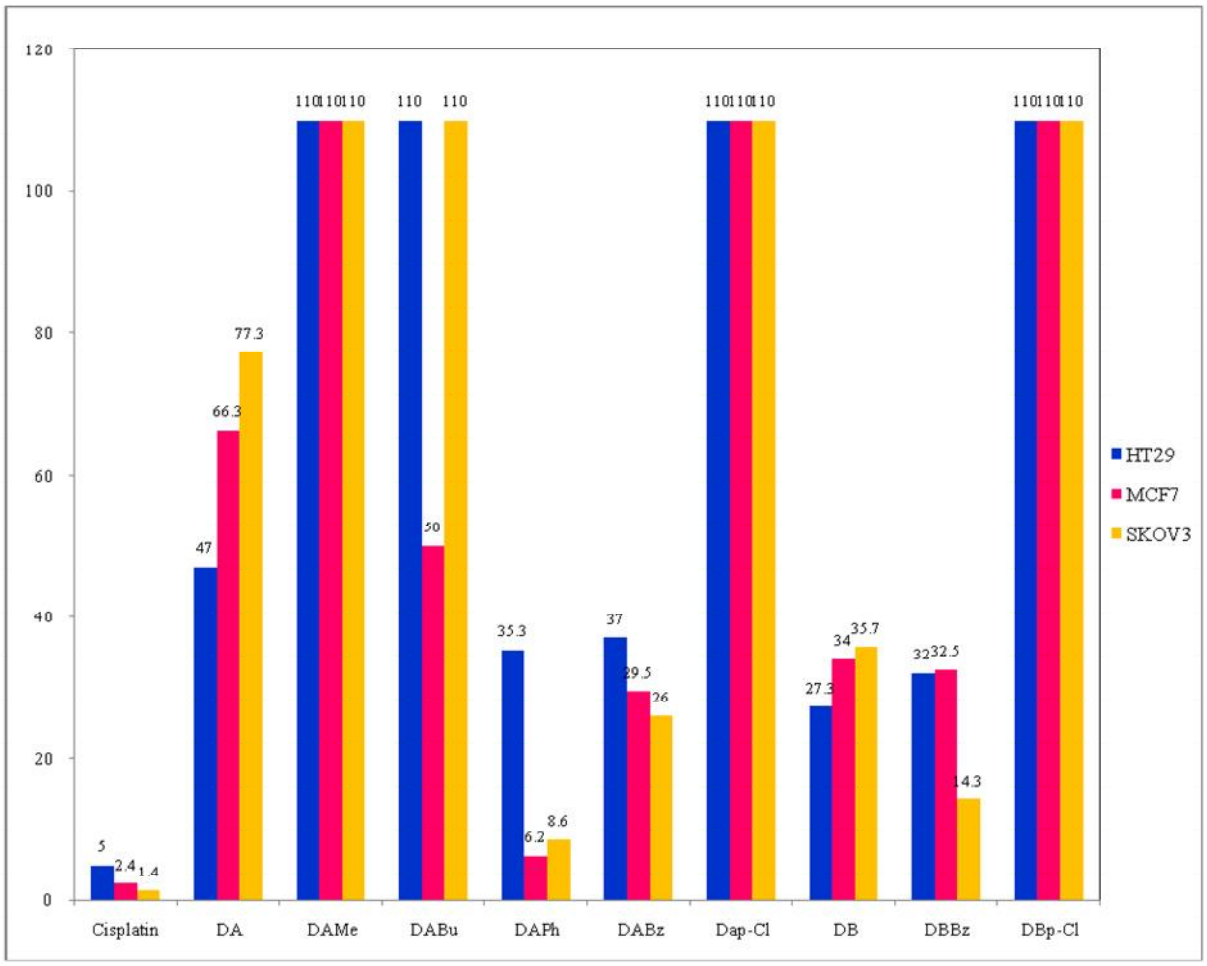


Table 5.4.1
Cytotoxic activity of the ligands and its organotin compounds

Compound	Cell lines (IC_{50} μg ml^{-1})[a]		
	HT29	**MCF7**	**SKOV3**
cisplatin	5± 0	2.4 ± 0.6	1.4 ± 0
[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]-acetic acid, **A1**	93.8 ± 0.3	> 100	76.7 ± 0.6
catena-poly{*bis*[triphenyltin(IV)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetate]}, **AC1**	3.4 ± 0.1	5.7 ± 0.6	0.48 ± 0.01
Tricyclohexyltin(IV)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetate, **AC2**	0.51 ± 0.02	0.47 ± 0.01	0.4 ± 0.02
Cyclopentyldiphenyltin(IV)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetate, **AC3**	0.28 ± 0.04	0.28 ± 0.01	0.55 ± 0.01
[*N'*-(2-Oxidobenzylidene){2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazide}], **DA**	47 ± 1	66.3 ± 0.6	77.3 ± 2.3
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-dimethyltin(IV), **DA1**	> 100	> 100	> 100
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-dibutyltin(IV), **DA2**	> 100	50 ± 0	> 100
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-diphenyltin(IV), **DA3**	35.3 ± 0.6	6.2 ± 0.1	8.6 ± 0.1
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-dibenzyltin(IV), **DA5**	37 ± 0	29.5 ± 0.5	26 ± 0
{*N'*-(2-Oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetatohydrazidato}-di(*p*-chlorobenzyl)tin(IV), **DA7**	> 100	> 100	> 100
[*N'*-(5-Bromo-2-oxidobenzylidene){2-(3,5-di-*tert*-butyl-(4-hydroxybenzyl)sulfanyl]acetato-hydrazide}], **DB**	27.3 ± 0.6	34 ± 0	35.7 ± 1.2
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}dibenzyltin(IV), **DB5**	32 ± 1	32.5 ± 0	14.3 ± 1.2
{*N'*-(5-Bromo-2-oxidobenzylidene)[2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-hydrazidato}di(*p*-chlorobenzyl)tin(IV), **DB7**	> 100	> 100	> 100

[a] IC_{50} values (μg ml^{-1}) = inhibition concentration at 50% *i.e.*, the concentration to reduce growth of cancer cells by 50%