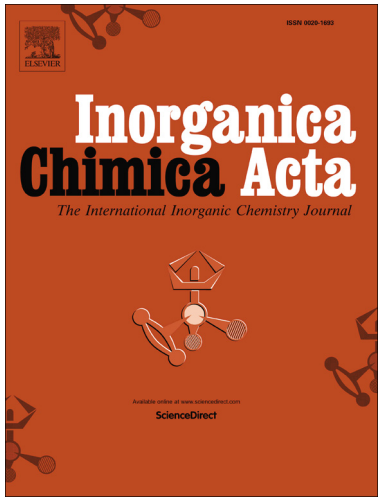

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SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL STUDIES OF DIORGANOTIN(IV) COMPLEXES WITH *TRIS*[(HYDROXYMETHYL)AMINOMETHANE] SCHIFF BASES

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Abstract

Several Schiff base ligands derived from *tris*(hydroxymethyl)aminomethane were synthesized and a series of diorganotin(IV) complexes were obtained from the reaction of diorganotin dichlorides or oxides with Schiff base ligands. The ligands and complexes have been characterized by elemental analysis, IR, ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopies. Single-crystal X-ray diffraction analysis reveals that *bis*[(2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}phenolato)]-dimethyltin(IV), **1** and *bis*[(2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-bromophenolato)]dimethyltin(IV), **7** are dimeric structures, in which the central tin atom is rendered six-coordinate while (2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-bromophenolato)diphenyltin(IV), **9,** (2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-chlorophenolato)dimethyltin(IV), **13**, (2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-chlorophenolato)diphenyltin(IV), **15** and (2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-chlorophenolato)dicyclohexyltin(IV), **16** are monomeric structures, whereby the tin atom is in a distorted trigonal-bipyramidal configuration. The Schiff bases and their corresponding diorganotin(IV) complexes have been evaluated against three human carcinoma cell lines, namely

HT29 (human colon carcinoma cell line), SKOV-3 (human ovarian cancer cell line) and MCF-7 (hormone-dependent breast carcinoma cell line), for its *in vitro* cytotoxic activities. The dibutyltin and dicyclohexyltin derivatives of the Schiff base ligands display good cytotoxic activities against the tested cell lines.

Keywords: organotin, hydrogen-bonding, cytotoxic activity, X-ray structures

1. Introduction

Organotin(IV) compounds have been actively studied due to their medical, industrial and agricultural applications [1-5]. Among these compounds, the chemistry and applications of organotin(IV) complexes with monodentate, bidentate, tridentate and multidentate Schiff bases are extensively studied because of their structural diversity, thermal stability and biological properties such as antimicrobial [6], antifungal [7,8], antibacterial [7,8], antitumour [7,9-11], antioxidant [11], anti-insecticidal [12] and anti-inflammatory [11,13]. The biological activities of the organotin(IV) complexes are largely influenced by the structure of the complexes, coordination number at the tin atom and by the alkyl/aryl groups in the complexes [14,15].

Schiff bases play an important role as chelating ligands in both main group metal and transition metal coordination chemistry. This is due to their stability in a variety of oxidative-reductive condition and their structural versatilities [16]. *Tris*(hydroxymethyl)aminomethane (TRIS) has been widely used in biochemistry, physiology and medicine as an inexpensive buffer in the physiological pH range. From literature, *tris*(hydroxymethyl)aminomethane (TRIS) and its Schiff base derivatives are known to have a broad spectrum of biological activities including anti-tumour, antibiotic, anticancer, antihistamine, antifungal, anti-inflammatory and many others [16-19]. Some metal complexes with TRIS Schiff base have been reported. For example, TRIS Schiff bases with

dioxomolydenum(VI) complexes have been investigated and used as catalysts in epoxidation of alkenes while its dioxovanadium(IV) complexes have been studied as potential biomimetics [20, 21].

The coordination chemistry of diorganotin(IV) complexes with *ONO*, *ONS* and *NNO* terdentate ligands is widely discussed for its biological and pharmacological properties. In the current article, we report the synthesis and structural studies of diorganotin complexes with terdentate *ONO* Schiff bases prepared from the condensation reaction of *tris*(hydroxymethyl)aminomethane with substituted salicylaldehydes. The prepared diorganotin complexes could be a monomeric or dimeric structure with coordination geometries which are close to trigonal-bipyramidal, octahedral and pentagonal-bipyramidal. The *in vitro* cytotoxicity of the Schiff bases and their diorganotin complexes against three human carcinoma cell lines (HT29, SKOV-3 and MCF7) is evaluated and discussed.

2. Experimental

2.1 Materials and physical measurements

The reagents used were of reagent grade quality and used as supplied. Dibenzyltin dichloride and di(*p*-chlorobenzyl)tin dichloride were prepared according to the literature method [22]. The solvents used in the reaction were of AR grade and were dried using standard literature procedures [23]. The melting points of the ligands and complexes were determined using an Electrothermal digital melting point apparatus and were uncorrected. The IR spectra for the compounds were recorded using KBr pellets on a Perkin-Elmer Spectrum RX1 FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM GX-270 FT NMR SYSTEM spectrometer while ^{119}Sn NMR spectra were recorded on a JEOL ECA-400MHz NMR spectrometer and were referenced against Me_4Sn. The chemical shifts were recorded in ppm with reference to Me_4Si for ^{1}H NMR and ^{13}C NMR. Microanalyses were carried out on an Eager 300 CHNS Elemental Analyzer and a Perkin-Elmer EA2400 CHNS Elemental Analyzer.

2.2 Preparation of the ligands

2-{[1,1-Bis(hydroxymethyl)-2-oxidoethyl]iminomethyl}phenol, **H_2L1**

Tris(hydroxymethyl)aminomethane (1.21 g, 0.01 mol) and salicylaldehyde (1.07 mL, 0.01 mol) were added to 100 mL of ethanol. The solution mixture was refluxed for 2 hours. A yellow solid was obtained upon cooling to room temperature, and was used without further purification. Yield: 1.90 g (84.5 %) ; m.p. 139-140^{o}C. Anal. Calc for $C_{11}H_{15}NO_4$: C, 58.66: H, 6.71: N, 6.22. Found: C, 58.11: H, 6.33: N, 6.70 IR (cm^{-1}): 3321 *v*(O-H), 1636 *v*(C=N), 1189 *v*(C-O).

The preparation method used for ligand **H_2L1** was repeated for ligands **H_2L2** and **H_2L3** with the respective substituted salicylaldehydes.

2-{[1,1-Bis(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-bromophenol, **H_2L2**

Yield: 2.13 g (70.1%); m.p. 141-142^{o}C. Anal. Calc for $C_{11}H_{14}NO_4Br$: C, 43.44: H, 4.64: N, 4.61. Found: C, 43.01: H, 4.60: N, 4.49 **IR** (cm^{-1}): 3357 *v*(O-H), 1637 *v*(C=N), 1175 *v*(C-O).

2-{[1,1-Bis(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-chlorophenol, **H_2L3**

Yield: 1.95 g (75.1%); m.p. 137-138^{o}C. Anal. Calc for $C_{11}H_{14}NO_4Cl$: C, 50.88: H, 5.43: N, 5.39. Found: C, 51.18: H, 5.42: N, 5.01 **IR** (cm^{-1}): 3339 *v*(O-H), 1639 *v*(C=N), 1175 *v*(C-O).

2.3 Preparation of the diorganotin complexes, 1-18

The preparation method used for compound **1** was repeated for compounds **3**, **4**, **7**, **9**, **10**, **13**, **15** and **16** with the appropriate diorganotin oxides and Schiff base ligands. The preparation method used for compound **2** was repeated for compounds **5**, **6**, **8**, **11**, **12**, **14, 17** and **18** with the appropriate diorganotin chlorides and Schiff base ligands.

Bis[(2-{[1,1-bis(hydroxymethyl)-2-oxidoethyl]iminomethyl}phenolato)]dimethyltin(IV), **1**

0.23 g (1.0 mmol) of 2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}phenol, **H_2L1** in 20 mL dry toluene was added to a suspension of 0.17 g (1.0 mmol) of dimethyltin oxide in 50 mL of dry toluene. The mixture was heated under azeotropic removal of water using a Dean-Stark trap. The solvent was gradually removed by evaporation under vacuum to give a yellow precipitate. The precipitate was recrystallized from a 1:1 mixture of ethanol:dichloromethane. Yellow crystals suitable for X-ray crystallographic studies were obtained from the slow evaporation of the filtrate.

Yield: 0.58 g (77.8 %) ; m.p. 196-198^{o}C Anal.Calc for $C_{26}H_{38}N_2O_8Sn_2$: C, 41.97; H, 5.15; N, 3.77%. Found: C, 42.02 ; H, 5.02 ; N, 3.98%. **IR** (cm^{-1}): 3495 *v*(O-H), 1614 *v*(C=N), 1191 *v*(C-O), 669 *v*(Sn-O), 419 *v*(Sn-N).

(2-{[1,1-Bis(hydroxymethyl)-2-oxidoethyl]iminomethyl}phenolato)dibutyltin(IV), **2**

0.23 g (1.0 mmol) of 2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}phenol, **H_2L1**, and 0.14 mL (1.0 mmol) of triethylamine were added to 50 mL of absolute ethanol and the mixture was heated under reflux for 2 hours. Dibutyltin dichloride (0.30 g, 1.0 mmol) in 30 mL of absolute ethanol was added and the mixture was further refluxed for 5 hours and filtered. The filtrate was evaporated until precipitation was obtained. The precipitation was recrystallized from toluene and the by-products, triethylammonium chloride, was removed through filtration. The yellow precipitate was recrystallized from a 1:1 mixture of ethanol:dichloromethane.

Yield: 0.36 g (79.2 %) ; m.p. 126-127^{o}C Anal.Calc for $C_{19}H_{31}NO_4Sn$: C, 50.03; H, 6.85; N, 3.07%. Found: C, 49.94; H, 7.12; N, 2.79%. **IR** (cm^{-1}): 3422 *v*(O-H), 1611 *v*(C=N), 1182 *v*(C-O), 678 *v*(Sn-O), 422 *v*(Sn-N).

(2-{[1,1-Bis(hydroxymethyl)-2-oxidoethyl]iminomethyl}phenolato)diphenyltin(IV), **3**

Yield: 0.37 g (74.4 %); m.p. >350^{o}C (dec.) Anal.Calc for $C_{23}H_{23}NO_4Sn$: C, 55.68; H, 4.67; N, 2.82 %. Found: C, 56.00; H, 4.64; N, 2.73 %. **IR** (cm^{-1}): 3281 *v*(O-H), 1611 *v*(C=N), 1173 *v*(C-O), 699 *v*(Sn-O), 436 *v*(Sn-N).

(2-{[1,1-Bis(hydroxymethyl)-2-oxidoethyl]iminomethyl}phenolato)dicyclohexyltin(IV), **4**

Yield: 0.38 g (75.5%) ; m.p. 190-191^{o}C Anal.Calc for $C_{23}H_{35}NO_4Sn$: C, 54.35; H, 6.94; N, 2.76%. Found: C, 53.70; H, 6.87; N, 3.02%. **IR** (cm^{-1}): 3369 *v*(O-H), 1616 *v*(C=N), 1149 *v*(C-O), 669 *v*(Sn-O), 421 *v*(Sn-N).

(2-{[1,1-Bis(hydroxymethyl)-2-oxidoethyl]iminomethyl}phenolato)dibenzyltin(IV), **5**

Yield: 0.34 g (65.2%); m.p. >350^{o}C (dec.) Anal.Calc for $C_{25}H_{27}NO_4Sn$: C, 57.28; H, 5.19; N, 2.67%. Found: C, 56.95; H, 5.57; N, 2.43%. **IR** (cm^{-1}): 3401 *v*(O-H), 1612 *v*(C=N), 1174 *v*(C-O), 698 *v*(Sn-O), 458 *v*(Sn-N).

(2-{[1,1-Bis(hydroxymethyl)-2-oxidoethyl]iminomethyl}phenolato)di(p-chlorobenzyltin)(IV), **6**

Yield: 0.39 g (65.0 %) ; m.p. > 350^{o}C (dec.) Anal.Calc for $C_{25}H_{25}Cl_2NO_4Sn$: C, 50.63; H, 4.25; N, 2.36 %. Found: C, 50.35; H, 3.90; N, 2.20 %. **IR** (cm^{-1}): 3282 *v*(O-H), 1610 *v*(C=N), 1172 *v*(C-O), 688 *v*(Sn-O), 420 *v*(Sn-N).

Bis[(2-{[1,1-bis(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-bromophenolato)]dimethyltin(IV), **7**

Yield: 0.71 g (72.1 %) ; m.p. 208-209^{o}C. Anal.Calc for $C_{26}H_{36}Br_2N_2O_8Sn_2$: C, 34.63; H, 4.02; N, 3.11%. Found: C, 34.72; H, 3.83; N, 3.55%. **IR** (cm^{-1}): 3293 *v*(O-H), 1612 *v*(C=N), 1169 *v*(C-O), 684 *v*(Sn-O), 455 *v*(Sn-N).

(2-{[1,1-Bis(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-bromophenolato)dibutyltin(IV), **8**

Yield: 0.42 g (78.5 %) ; m.p. 110-112^{o}C. Anal.Calc for $C_{19}H_{30}BrNO_4Sn$: C, 42.65; H, 5.65; N, 2.62 %. Found: C, 42.84; H, 5.69; N, 2.42 %. **IR** (cm^{-1}): 3290 *v*(O-H), 1612 *v*(C=N), 1169 *v*(C-O), 661 *v*(Sn-O), 451 *v*(Sn-N).

(2-{[1,1-Bis(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-bromophenolato)diphenyltin(IV), **9**

Yield: 0.40 g (70.5 %) ; m.p. >350^{o}C. Anal.Calc for $C_{23}H_{22}BrNO_4Sn$: C, 48.04 : H, 3.86 : N, 2.44 %. Found: C, 48.07; H, 3.79; N, 2.86 %. **IR** (cm^{-1}): 3380 *v*(O-H), 1608 *v*(C=N), 1177 *v*(C-O), 660 *v*(Sn-O), 448 *v*(Sn-N).

(2-{[1,1-Bis(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-bromophenolato) dicyclohexyltin(IV), **10**

Yield: 0.40 g (70.5 %) ; m.p. 194-195^{o}C. Anal.Calc for $C_{23}H_{34}BrNO_4Sn$: C, 47.05 : H, 5.84 : N, 2.39 %. Found: C, 47.32; H, 5.27; N, 2.78 %. **IR** (cm^{-1}): 3369 *v*(O-H), 1612 *v*(C=N), 1172 *v*(C-O), 658 *v*(Sn-O), 434 *v*(Sn-N).

(2-{[1,1-Bis(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-bromophenolato)dibenzyltin(IV), **11**

Yield: 0.40 g (70.5 %) ; m.p. >350^{o}C. Anal.Calc for $C_{25}H_{26}BrNO_4Sn$: C, 49.79 : H, 4.35 : N, 2.32 %. Found: C, 50.29; H, 4.40; N, 2.55 %. **IR** (cm^{-1}): 3373 *v*(O-H), 1618 *v*(C=N), 1172 *v*(C-O), 657 *v*(Sn-O), 463 *v*(Sn-N).

(2-{[1,1-Bis(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-bromophenolato)di(p-chlorobenzyl)-tin(IV), **12**

Yield: 0.40 g (70.5 %) ; m.p.212-213^{o}C. Anal.Calc for $C_{25}H_{24}BrCl_2NO_4Sn$: C, 44.68 : H, 3.60: N, 2.08 %. Found: C, 45.02; H, 3.90; N, 2.35 %. **IR** (cm^{-1}): 3285 *v*(O-H), 1611 *v*(C=N), 1176 *v*(C-O), 653 *v*(Sn-O), 420 *v*(Sn-N).

(2-{[1,1-Bis(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-chlorophenolato)dimethyltin(IV), **13**

Yield: 0.33 g (80.2%); m.p. 220-221^{o}C. Anal.Calc for $C_{13}H_{18}ClNO_4Sn$: C, 38.42; H, 4.46; N, 3.45%. Found: C, 38.79; H, 4.00; N, 3.80%. **IR** (cm^{-1}): 3376 *v*(O-H), 1618 *v*(C=N), 1180 *v*(C-O), 702 *v*(Sn-O), 430 *v*(Sn-N).

(2-{[1,1-Bis(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-chlorophenolato)dibutyltin(IV), **14**

Yield: 0.39 g (78.5%); m.p. 133-134^{o}C. Anal.Calc for $C_{19}H_{30}ClNO_4Sn$: C, 46.51; H, 6.16; N, 2.85%. Found: C, 46.34; H, 5.99; N, 3.02%. **IR** (cm^{-1}): 3372 *v*(O-H), 1614 *v*(C=N), 1170 *v*(C-O), 690 *v*(Sn-O), 414 *v*(Sn-N).

(2-{[1,1-Bis(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-chlorophenolato)diphenyltin(IV), **15**

Yield: 0.40 g (75.3%); m.p. >350^{o}C. Anal.Calc for $C_{23}H_{22}ClNO_4Sn$: C, 52.06; H, 4.18; N, 2.64%. Found: C, 52.27; H, 3.99; N, 2.65%. **IR** (cm^{-1}): 3380 *v*(O-H), 1611 *v*(C=N), 1178 *v*(C-O), 698 *v*(Sn-O), 431 *v*(Sn-N).

(2-{[1,1-Bis(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-chlorophenolato)dicyclohexyltin(IV), **16**

Yield: 0.38 g (70.5%); m.p. 180-181^{o}C. Anal.Calc for $C_{23}H_{34}ClNO_4Sn$: C, 50.90; H, 6.32; N, 2.58%. Found: C, 50.59; H, 5.89; N, 2.70%. **IR** (cm^{-1}): 3367 *v*(O-H), 1617 *v*(C=N), 1172 *v*(C-O), 702 *v*(Sn-O), 435 *v*(Sn-N).

(2-{[1,1-Bis(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-chlorophenolato)dibenzyltin(IV), **17**

Yield: 0.45 g (81.1%); m.p. >350^{o}C. Anal.Calc for $C_{25}H_{26}ClNO_4Sn$: C, 53.75; H, 4.69; N, 2.51%. Found: C, 53.38; H, 4.30; N, 2.67%. **IR** (cm^{-1}): 3399 *v*(O-H), 1619 *v*(C=N), 1170 *v*(C-O), 699 *v*(Sn-O), 467 *v*(Sn-N).

(2-{[1,1-Bis(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-chlorophenolato)di(p-chlorobenzyl)-tin(IV), **18**

Yield: 0.42 g (66.2 %); m.p. >350^{o}C. Anal.Calc for $C_{25}H_{24}Cl_3NO_4Sn$: C, 47.85; H, 3.86; N, 2.23 %. Found: C, 47.50; H, 3.47; N, 2.03 %. **IR** (cm^{-1}): 3283 *v*(O-H), 1614 *v*(C=N), 1167 *v*(C-O), 700 *v*(Sn-O), 430 *v*(Sn-N).

2.4 X-ray structural studies

The X-ray crystallographic data for compounds **7**, **9**, **13**, and **15** were collected on a Bruker SMART CCD 1000 diffractometer, while compounds **1** and **16** were collected on a Bruker SMART APEX2 CCD diffractometer. The structures were solved by direct method and refined by the full-matrix least-squares procedure based on F^2 using the SHELXL-97 programme [24]. All data were collected at 100K or 123 K using graphite-monochromated Mo-Kα (λ= 0.71073Å) radiation. The positions of hydrogen atoms were calculated, and their contributions in structure factor calculations were included.

2.5 *In vitro* cytotoxicity

HT29 (human colon carcinoma cell line), SKOV-3 (human ovarian cancer cell line) and MCF7 (hormone-dependent breast carcinoma cell line) were purchased from the American Type Culture Collection (ATCC, USA). The HT29 and MCF7 cells were maintained in RPMI 1640 medium (Sigma) while the SKOV-3 cells in Dulbecco's Modified Eagle's Medium (DMEM; Sigma), supplemented with 10% fetal bovine serum (FBS; PAA Lab, Austria), 100 µg ml^{-1} penicillin or streptomycin (PAA Lab, Austria), and 50 µg ml^{-1} of fungizone (PAA Lab, Austria). The cells were maintained at 37°C in an atmosphere humidified with 5% CO_2. The *in vitro* cytotoxicity of the ligands and diorganotin complexes were determined by the Neutral Red cytotoxicity assay with cisplatin as positive control [25]. All the tests were repeated three times.

2.6 Statistical Analysis

Data were presented as mean ± S.E.M. The IC_{50} values were obtained by non-linear regression using GraphPad Prism statistical software.

3. Results and discussion

3.1 Synthesis

The Schiff base ligands were synthesized by the condensation process of salicylaldehyde and substituted salicylaldehydes with *tris*(hydroxymethyl)aminomethane. Each of the Schiff base ligands has four potential donor atoms, namely one nitrogen atom and three oxygens from hydroxyl groups, which enables it to form coordination bonds with metal ions. These ligands are enolized in solution as shown in Figure 1. The enolized form of the Schiff base ligands provides three acidic protons which can react with the diorganotin oxides and diorganotin dichlorides as shown in Figure 2. The coordination of one of the oxygen donor atom to the central tin metal further stabilized the overall structure. The diorganotin complexes are obtained in reasonable yield and they are stable towards moisture and air. They are soluble in dichloromethane, chloroform and moderately soluble in polar solvents. The structural features of the diorganotin complexes are characterized using various spectroscopic techniques.

Figure 1 Enolized form of ligand **H_2L2**

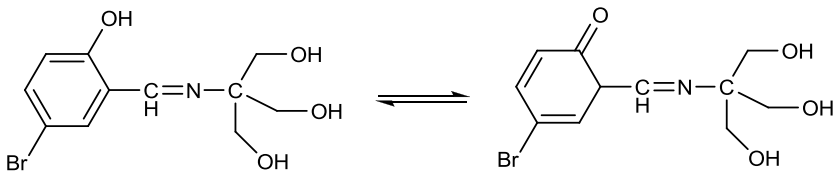
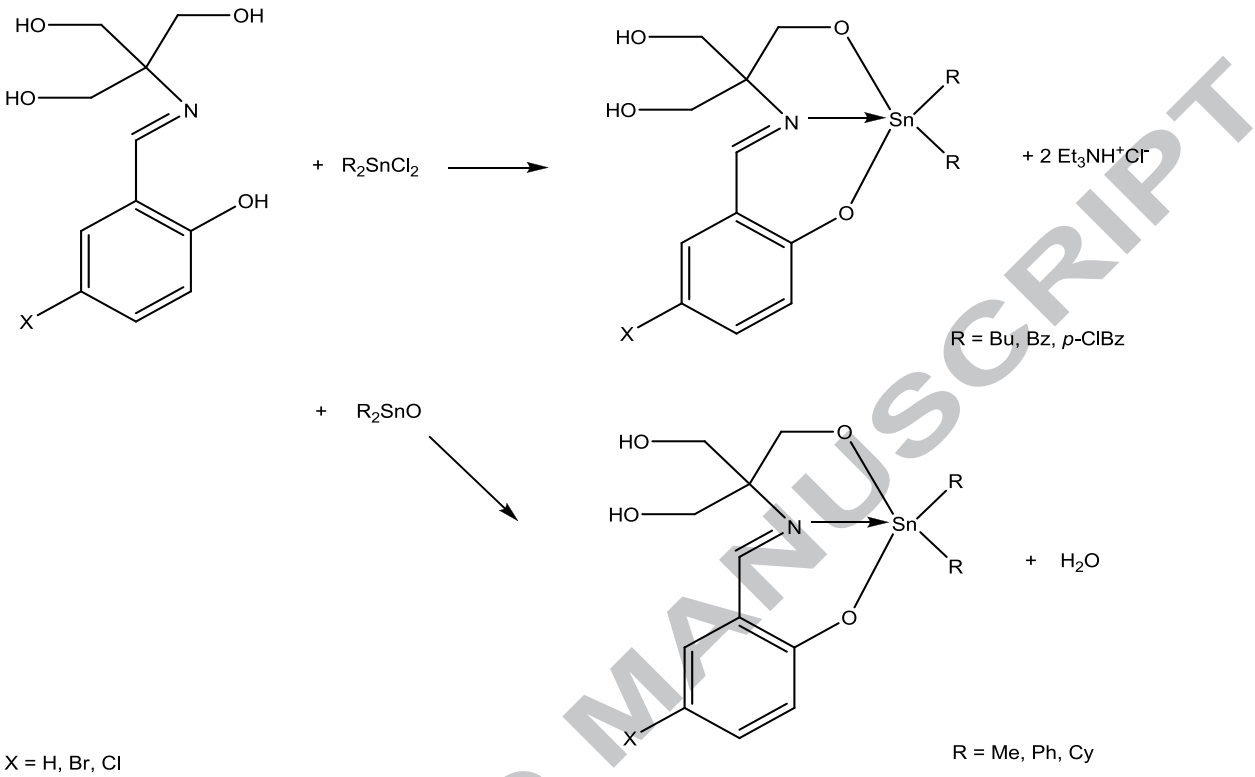


Figure 2. Reaction scheme for the reaction of the ligands with diorganotin dichlorides and diorganotin oxides



3.2 IR Spectral

The infrared spectra data of the ligands and the complexes are given in the Experimental section. From the infrared spectra, the hydroxyl stretching frequencies of the free ligands, **H_2L1**, **H_2L2** and **H_2L3** are located at 3321, 3357 and 3339 cm^{-1}, respectively. However, no visible N-H stretching is observed in the ligands' infrared spectra. This might be due to the overlapping of the N-H stretching frequency with the O-H stretching frequency. In the diorganotin complexes, a characteristic absorption is clearly observed in the 3200-3400 cm^{-1} region [26] suggesting that not all the hydroxy oxygens participated in the coordination to the central metal atom.

The Schiff base ligands exhibit a C=N stretching frequencies in the region of 1630-1640 cm^{-1} for the azomethine group, which is within the range reported for the similar group of Schiff base ligands [27-30]. Meanwhile, the C=N stretching frequencies for the diorganotin complexes are found in the

region between 1610-1620 cm^{-1} which is about 20 cm^{-1} lower than those reported for the ligands. This confirms the involvement of the azomethine nitrogen in the coordination with the central tin atom for the complexes. The C-O stretching frequencies for both ligands and complexes are within the 1150-1200 cm^{-1} region [31].

Two new bands are observed in the 400-750 cm^{-1} region. The medium band in the region of 650-710 cm^{-1} is assigned to the Sn-O stretching frequency while the weak absorption band in the region of 410-470 cm^{-1} to the Sn-N stretching frequency. Both the Sn-O and Sn-N stretching frequencies are in the range reported for diorganotin derivatives [32-34].

3.3 Multinuclear (^{1}H, ^{13}C and ^{119}Sn) NMR Spectra

The ^{1}H, ^{13}C and ^{119}Sn NMR spectral data of the Schiff base ligands and its diorganotin complexes are presented in Tables 1, 2 and 3. Overall, the chemical shifts for the ligands and the complexes are found within the expected range. In the ^{1}H NMR spectral, the signals at 6.60-7.40 are assigned to the aromatic protons of the ligands and diorganotin complexes. The signal for the methylene protons is found as a group of multiplets in the range of 3.39-4.00 ppm. The ^{1}H NMR chemical shifts of the hydroxyl protons in the ligands are found around 4.80 ppm, while for the complexes, the chemical shifts are slightly downfield, in the 5.00-5.45 ppm region. In the diorganotin complexes, the decrease in the integration value of the hydroxy protons signal suggests the bonding of the tin atom to one of the oxygen atom of the Schiff base ligand through the replacement of one of the phenolic protons. Meanwhile, a singlet peak around 8.39-8.60 is assigned to the methine protons of the azomethine carbon [35].

The ^{13}C NMR spectra for the complexes show a significant downfield shift for the carbon resonances in comparison to the free ligands. The signals of the azomethine carbons (C-7) for the Schiff base

ligands and the diorganotin complexes appear in the 164-173 ppm region [28, 30]. Meanwhile, the signals for the quarternary carbon (C-8) are observed between 66-68 ppm. The chemical shift values for the methylene carbons, (C-9), (C-10) and (C-11) can be found in the region of 61-62 ppm for the ligands while for the diorganotin complexes, its chemical shift value range is slightly wider, between 60-70 ppm due to the influence of the interaction between the methylene oxygen and the tin atom.

The heteronuclear coupling constant is used to predict the geometry and the coordinating environment of the tin atom in the complexes. In most of the diorganotin complexes, the satellite signals due to hydrogen-tin coupling and carbon-tin coupling are observed and the coupling constants are reported. However, for the diphenyltin, dibenzyltin and di(*p*-chlorobenzyl)tin, the spin-spin coupling peak between the tin nucleus and its neighbouring carbons is not well resolved. The geometry of the diorganotin complexes is predicted from the C-Sn-C angle which is calculated based on the Lockhart and Manders equation: θ(C-Sn-C) = 0.0161|$^{2}J(^{119}\mathrm{Sn}\text{-}^{1}\mathrm{H})|^{2}$ -1.32 |$^{2}J(^{119}\mathrm{Sn}\text{-}^{1}\mathrm{H})$| + 133.4 [36, 37]. The observed coupling constants $^{2}J(^{119}\mathrm{Sn}\text{-}^{1}\mathrm{H})$ values for the diorganotin complexes are in the range 72-88 Hz, which suggests a five- and six-coordinated geometry. Similarly, the C-Sn-C angle of the diorganotin complexes can also be estimated from $^{1}J(^{119}\mathrm{Sn}\text{-}^{13}\mathrm{C})$ coupling constants obtained from the ^{13}C NMR spectra using the Lockhart's equation; θ(C-Sn-C) = [|$^{1}J(^{119}\mathrm{Sn}\text{-}^{13}\mathrm{C})$| + 875]/11.4. The calculation of the C-Sn-C angle values based on the coupling constant obtained from the NMR spectra show a slight deviation from the C-Sn-C angles obtained by X-ray diffractometry studies. The calculated C-Sn-C angles lies in the range 120-137^{o}, which correspond to five- and six-coordination of the tin atom in the complexes [38].

The presence of a single peak in the ^{119}Sn NMR spectral of the complexes confirms the formation of a single species. The ^{119}Sn NMR chemical shifts of the dimethyltin complexes, **1** and **7** are found around -174 ppm while for compound **13**, it is found at -117 ppm. The ^{119}Sn NMR chemical shifts

of the dibutyltin complexes, **2**, **8** and **14** are found around -187 ppm, while the dicyclohexyltin complexes, **4**, **10** and **16**, are found around -244 ppm. The ^{119}Sn NMR chemical shifts for the dibenzyltin and substituted dibenzyltin complexes are found between -217 to -296 ppm while the ^{119}Sn NMR chemical shifts for the diphenyltin complexes, **3**, **9**, and **15**, are found between -344 to -355 ppm. The ^{119}Sn NMR chemical shifts, $^{1}J(^{119}\text{Sn-}^{1}\text{H})$ and $^{1}J(^{119}\text{Sn-}^{13}\text{C})$ coupling values are in accordance with five-coordination tin centre [39-43]. Also, these ^{119}Sn NMR chemical shift values are found to be in the similar range as those reported for the respective diorganotin complexes [44-46], indicating most of the diorganotin complexes are in a five-coordinated tin geometry except for compounds **1** and **7**.

3.4 X-ray structural studies

The molecular structures of the molecules are depicted in Figure 3, 4, 5, 6, 7 and 8 respectively. The crystallographic data and refinement details for compounds are given in Table 4 while selected bond lengths and angles are given in Table 5.

The molecular structures revealed that the ligands, 2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}phenol, **H_2L1**, 2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-bromophenol, **H_2L2** and 2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-chlorophenol, **H_2L3** act as dianionic ligands and is coordinated to the tin atom *via* the phenoxy oxygen, one methoxy oxygen, and an imino nitrogen forming five- and six-membered chelate rings with the corresponding bite angles of 76.8^{o} and 82.1^{o}, respectively. The six-membered cyclic rings are relatively planar with root mean square (RMS) deviations from planarity in the range of 0.01-0.12 Å. On the other hand, the five-membered ring is slightly pluckered with a RMS deviation of 0.15-0.18 Å from planarity. The dihedral angles between these chelate rings are in the range of 6.7-12.5^{o}, and this clearly indicates the non-planarity of the ligand plane around the tin atom.

Except for compounds **1** and **7**, the tin atom in the other diorganotin complexes (compounds **9, 13, 15** and **16**) adopts a distorted trigonal-bipyramidal geometry in which the trigonal plane consists of the imine nitrogen and two alkyl/aryl groups. The axial positions are occupied by the phenoxy oxygen and ethoxy oxygen. The distortion from the ideal trigonal-bipyramidal geometry are evidenced from their O(1)-Sn-O(2) angles of 159.33^{o}, 159.03^{o}, 156.46^{o} and 158.29^{o} for compounds **9**, **13**, **15** and **16**, respectively. This is also reflected in the indices of the trigonality of the plane which could be determined from the τ-value, defined as $\tau = (\beta-\alpha)/60$, whereby α and β are the two largest donor-metal-donor angles in the five-coordinated environment. For an ideal trigonal-bipyramid, the τ-value will be close to 1, while for an ideal tetragonal-pyramid, the τ-value should be close to zero. In this case, the determined τ-values for compounds **9**, **13, 15** and **16** are in the range of 0.42 - 0.57, indicative of a distorted trigonal-bipyramidal geometry [45].

In contrast, compounds **1** and **7** form dimers *via* the coordination of the methoxy oxygen to the tin atom of an adjacent molecules forming a central planar Sn_2O_2 four-membered ring [Sn(1)-O(2); **1**: 2.079(2), 2.379(2) Å; **7**: 2.075(2), 2.090(3) 2.329(2), 2.348(3) Å]. This has resulted in the formation of a six-coordinate tin species in these two compounds. In addition, the C-Sn-C angles are also found to have opened up to 144.4(1)^{o} for **1** and 147.9(2), 150.9(2)^{o} for compound **7** as compared to those of the five-coordinate compounds [120.8-126.6^{o}]. The crystal structures of compounds **1** and **7** also revealed that the two terminal hydroxyl groups are involved in intermolecular hydrogen-bonding with the terminal hydroxyl group and the coordinated phenoxy oxygen of a neighbouring molecule (Figure 9) [**1**: O-H..O 2.724(3), 2.829(3) Å; **7**: O-H..O 3.117(5), 2.697(4), 2.705(4) and 2.703(4) Å]. On the other hand, the two terminal hydroxyl groups in compounds **9**, **13**, **15** and **16** are intermolecular hydrogen-bonded to the methoxy oxygen and terminal hydroxy oxygen of the neighbouring molecules [**9**: O-H..O 2.623(3) and 2.666(3) Å; **13**: O-H..O 2.620(2) and 2.707(2) Å;

15: O-H..O 2.639(2) and 2.695(3) Å; **16**: O-H..O 2.747(6) and 2.548(6) Å] [47-51] and prevent the formation of dimeric tin structures in compounds **9**, **13**, **15** and **16** (Figure 10).

Apart from the dative Sn(1)-O(2) and Sn(2)-O(6) bond distances in compounds **1** and **7** which are are slightly longer (2.333 – 2.349 Å), the rest of the covalent Sn-O bond distances are shorter and within the values of those reported for five-coordinated diorganotin complexes [**9**: 2.083(2) Å and 2.073(2) Å, **13**: 2.125(2) Å and 2.075(2) Å, **15**: 2.092(2) Å and 2.082(2) Å, **16**: 2.076(5) Å, 2.093(4) Å, 2.131(4) Å and 2.107(4) Å respectively]. The dative Sn(1)-N(1) bond distances [2.19-2.22 Å] for all the complexes are also well within those reported in the literature for similar complexes [30, 45, 47].

3.5 *In vitro* cytotoxicity

The efficiency of the diorganotin compounds as anticancer drug has been tested *in vitro* on three cell lines, HT29 (human colon carcinoma cell line), SKOV3 (human ovarian cancer cell line), and MCF-7 (hormone-dependent breast carcinoma cell line). The results of the IC_{50} values of the Schiff base ligands and the diorganotin complexes are summarized in Table 6.

Cisplatin as the positive control in the present study is found to exhibit remarkable growth inhibitory activities with mean IC_{50} values ranging from 1.4-5.0 μg ml^{-1} on the studied cancer cell lines. Overall, the Schiff base ligands are found to be not cytotoxic against all the tested human cell lines.

The dimethyltin derivative of **H_2L1**, **1** is only active against the MCF-7 cell line. The dibutyltin and dicyclohexyltin derivatives [compounds **2** and **4]** show prominent cytotoxicity activities for all the tested cell lines. However, the dibenzyltin and di(*p*-chlorobenzyl)tin derivatives are found to be inactive in all the tested cell lines.

Among the **H_2L2** complexes, the dicyclohexyltin derivative, **10** displays good cytotoxic activities in all the tested cell lines. The dibutyltin derivative, **8** is found to be active against the MCF-7 and SKOV-3 cell lines while, the diphenyltin derivative, **9** is only active against the SKOV-3 cell lines. Similarly, the dibenzyltin and di(*p*-chlorobenzyl)tin derivatives are found to be inactive in all the tested cell lines.

Among the **H_2L3** complexes, the dibutyltin and dicyclohexyltin derivatives [compounds **14** and **16]** show good cytotoxic activities in all the tested cell lines. While, the diphenyltin derivative, **15** is only active against the MCF7 and SKOV3 cell lines.

In general, the dibutyltin and dicyclohexyltin derivatives show good cytotoxic activities with IC_{50} values ranging between 2-9 μg ml^{-1}. The dimethyltin, diphenyltin, dibenzyltin and di(*p*-chlorobenzyl)tin derivatives are relatively less cytotoxic against most of the tested cell lines.

4. Conclusion

Several diorganotin complexes have been synthesized and characterized by various spectroscopic techniques. The diorganotin complexes are five or six-coordinated, as shown by the spectroscopic data and X-ray crystallographic diffraction. Compound **1** and **7** show a dimeric structure whereas compounds **9**, **13**,**15** and **16** are monomeric structures. The results of the cytotoxic activities of the complexes are promising, whereby compounds **2** and **4** are most active among the diorganotin complexes of **H_2L1** ligand. For the diorganotin complexes of **H_2L2** ligand, compound **10** shows good cytotoxic activities against all the tested cell lines. Meanwhile, for the diorganotin complexes of **H_2L3** ligand, compounds **14** and **16** show good cytotoxic activities against all the tested cell lines. Thus, the above complexes can be considered as agents with potential anticancer activities.

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Appendix

Crystallographic data for the compounds **1**, **7**, **9**, **13, 15** and **16** have been deposited at the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC 1017649, CCDC 1017650, CCDC 1017651, CCDC 1017652, CCDC 1017653, CCDC 1022850. Copies of available material may be obtained on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 1223 336 033; or email: deposit@ccdc.cam.ac.uk).

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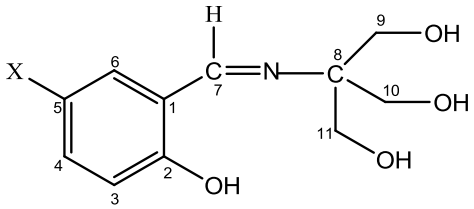
Table 1: ^{1}H NMR chemical shifts (δ, ppm) of the Schiff base ligands and their diorganotin(IV) complexes

Compound No.	H-3, H-4, H-6 (aromatic protons)	-CH=N-	-OH	-CH_2-	Sn-R
H_2L1	6.63, d (1H, *J* = 8.3 Hz), 7.13-7.26, m (4H)	8.47, s (1H)	4.76, s (3H)	3.47-3.59, m (6H)	-
1[a]	6.67, d (1H, *J* = 8.1 Hz), 7.25-7.35, m (4H)	8.39, s (1H)	5.21, s (2H)	3.47-3.60, m (6H)	0.43, s (6H, H_α, $^2J(^{119}Sn\text{-}^1H)$ = 88 Hz)
2[a]	6.62, d (1H, *J* = 8.1 Hz), 7.26-7.37, m (4H)	8.94, s (1H)	5.24, s (2H)	3.55-3.65, m (6H)	1.64, t (4H, H_α, *J* = 6.3 Hz, $^2J(^{119}Sn\text{-}^1H)$ = 75 Hz), 1.59, sbr (4H, H_β, $^3J(^{119}Sn\text{-}^1H)$ = 27 Hz), 1.34, sbr (4H, H_γ, $^4J(^{119}Sn\text{-}^1H)$ = 50 Hz), 0.86, t (6H, H_δ, *J* = 6.9 Hz, $^5J(^{119}Sn\text{-}^1H)$ = 10 Hz)
3[b]	6.67, d (1H, *J* = 8.5 Hz), 7.15-7.26, m (4H)	8.58, s (1H)	5.27, s (2H)	3.48-3.63, m (6H)	7.28-7.38, m (4H), 7.40-7.52, m (6H)
4[a]	6.60, d (1H, *J* = 8.2 Hz), 7.10-7.22, m (4H)	8.39, s (1H)	5.02, s (2H)	3.57-3.70, m (6H)	2.25, t (2H, H_α, *J* = 6.5 Hz, $^2J(^{119}Sn\text{-}^1H)$ = 72 Hz), 1.24-1.76 (m, 20H, H_β, H_γ, H_δ)
5[c]	6.92, d (1H, *J* = 8.3 Hz), 7.10-7.21, m (4H)	8.40, s (1H)	5.04, s (2H)	3.56-3.70, m (6H)	1.60, t (4H, H_α, *J* = 6.6 Hz, $^2J(^{119}Sn\text{-}^1H)$ = 78 Hz), 7.51-7.75, m (10H)
6[c]	6.74, d (1H, *J* = 8.3 Hz), 7.12-7.28, m (4H)	8.56, s (1H)	5.20, s (2H)	3.60-3.77, m (6H)	1.20, t (4H, H_α, *J* = 6.5 Hz, $^2J(^{119}Sn\text{-}^1H)$ = 78 Hz), 7.50-7.66, m (8H)
H_2L2	6.67, d (1H, *J* = 8.4 Hz), 7.34-7.50, m (4H)	8.50, s (1H)	4.85, s (3H)	3.47-3.59, m (6H)	-
7[a]	6.60, d (1H, *J* = 8.1 Hz), 7.23-7.40, m (4H)	8.85, s (1H)	5.30, s (2H)	3.69-3.80, m (6H)	0.63, s (6H, H_α, $^2J(^{119}Sn\text{-}^1H)$ = 88 Hz)
8[a]	6.60, d (1H, *J* = 8.2 Hz), 7.20-7.38, m (4H)	8.94, s (1H)	5.45, s (2H)	3.50-3.75, m (6H)	1.67, t (4H, H_α, *J* = 6.4 Hz, $^2J(^{119}Sn\text{-}^1H)$ = 78 Hz), 1.62, sbr (4H, H_β, $^3J(^{119}Sn\text{-}^1H)$ = 28 Hz), 1.42, sbr (4H, H_γ, $^4J(^{119}Sn\text{-}^1H)$ = 52 Hz), 0.86, t (6H, H_δ, *J* = 6.9 Hz, $^5J(^{119}Sn\text{-}^1H)$ = 10 Hz)
9[b]	6.90, d (1H, *J* = 8.4 Hz), 7.15-7.28, m (4H)	8.52, s (1H)	5.04, s (2H)	3.56-3.82, m (6H)	7.37-7.47, m (4H), 7.50-7.76, m (6H)
10[a]	6.52, d (1H, *J* = 8.3 Hz), 7.10-7.34, m (4H)	8.59, s (1H)	5.10, s (2H)	3.50-3.62, m (6H)	2.25, t (2H, H_α, *J* = 6.6 Hz, $^2J(^{119}Sn\text{-}^1H)$ = 74 Hz), 1.24-1.76, m (20H, H_β, H_γ, H_δ)
11[c]	6.60, d (1H, *J* = 8.2 Hz), 7.12-7.40, m (4H)	8.58, s (1H)	5.21, s (2H)	3.50-3.68, m (6H)	1.30, t (4H, H_α, *J* = 6.6 Hz, $^2J(^{119}Sn\text{-}^1H)$ = 77 Hz), 7.45-7.68, m (10H)

12[c]	6.70, d (1H, *J* = 8.2 Hz), 7.10-7.35, m (4H)	8.60, s (1H)	5.20, s (2H)	3.69-3.80, m (6H)	1.20, t (4H, H_α, *J* = 6.5 Hz, $^2J(^{119}Sn\text{-}^1H)$ = 77 Hz), 7.40-7.65, m (8H)
H_2L3	6.73, d (1H, *J* = 8.4 Hz), 7.13-7.25, m (4H)	8.51, s (1H)	4.83, s (2H)	3.50-3.65, m (6H)	-
13[a]	6.73, d (1H, *J* = 8.1 Hz), 7.13-7.38, m (4H)	8.40, s (1H)	5.02, s (2H)	3.40-3.62, m (6H)	0.42, s (6H, $^2J(^{119}Sn\text{-}^1H)$ =76 Hz)
14[a]	6.64, d (1H, *J* = 8.2 Hz), 7.05-7.34, m (4H)	8.91, s (1H)	5.27, s (2H)	3.50-3.68, m (6H)	1.64, t (4H, H_α, *J* = 6.4 Hz, $^2J(^{119}Sn\text{-}^1H)$ = 78 Hz), 1.60, sbr (4H, H_β, $^3J(^{119}Sn\text{-}^1H)$ = 28 Hz), 1.42, sbr (4H, H_γ, $^4J(^{119}Sn\text{-}^1H)$ = 52 Hz), 0.86, t (6H, H_δ, *J* = 6.9 Hz, $^5J(^{119}Sn\text{-}^1H)$ = 10 Hz)
15[b]	6.86, d (1H, *J* = 8.4 Hz), 7.10-7.25, m (4H)	8.53, s (1H)	5.05, s (2H)	3.66-3.80, m (6H)	7.31-7.42, m (4H), 7.45-7.58, m (6H)
16[a]	6.71, d (1H, *J* = 8.3 Hz), 7.12-7.34, m (4H)	8.56, s (1H)	5.05, s (2H)	3.39-3.73, m (6H)	2.25, t (2H, H_α, *J* = 6.6 Hz, $^2J(^{119}Sn\text{-}^1H)$ = 74 Hz), 1.24-1.76, m (20H, H_β, H_γ, H_δ)
17[c]	6.65, d (1H, *J* = 8.2 Hz), 7.12-7.35, m (4H)	8.55, s (1H)	5.08, s (2H)	3.40-3.73, m (6H)	1.70, t (4H, H_α, *J* = 6.6 Hz, $^2J(^{119}Sn\text{-}^1H)$ = 77 Hz), 7.45-7.70, m (10H)
18[c]	6.65, d (1H, *J* = 8.2 Hz), 7.10-7.35, m (4H)	8.54, s (1H)	5.10, s (1H)	3.40-3.70, m (6H)	2.80, t (4H, H_α, *J* = 6.5 Hz, $^2J(^{119}Sn\text{-}^1H)$ = 77 Hz), 7.40-7.65, m (8H)

[s: singlet; sbr: singlet broad; d: doublet; t: triplet; m: complex pattern]
[a] spectra recorded in $CDCl_3$
[b] spectra recorded in DMSO-d_6
[c] spectra recorded in 1,4-dioxane + 2-3 drops of $CDCl_3$



X = Br, Cl, H

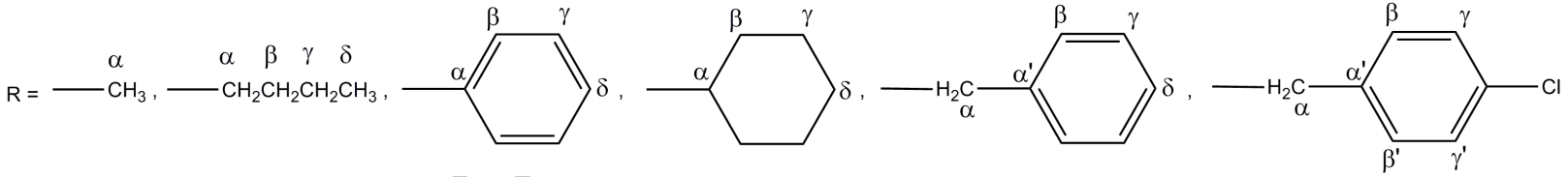
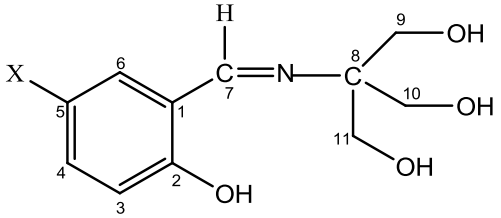


Table 2: ^{13}C NMR chemical shifts (δ, ppm) of the Schiff base ligands and their corresponding diorganotin(IV) complexes

Compound No.	C-1, C-2, C-3, C-4, C-5, C-6	C-8	C-7	C-9, C-10, C-11	Sn-(C_α to C_δ)
H_2L1	118.6, 163.7, 117.7, 132.6, 117.3, 132.4	67.2	164.6	61.2	-
1[a]	121.9, 168.4,18.5, 136.5, 117.8, 133.5	67.3	173.3	61.5, 62.4	1.1 (C_α, $^1J(^{119}Sn\text{-}^{13}C)$ = 710 Hz)
2[b]	122.3, 169.7, 117.6, 135.9, 116.1, 133.9	66.9	173.6	63.7, 64.2	21.2 (C_α, $^1J(^{119}Sn\text{-}^{13}C)$ = 565 Hz), 27.3 (C_β, $^2J(^{119}Sn\text{-}^{13}C)$ = 28 Hz), 26.8 (C_γ, $^3J(^{119}Sn\text{-}^{13}C)$ = 77 Hz), 13.6 (C_δ)
3[b]	122.0, 168.8, 117.7, 136.7, 116.6, 132.9	67.9	173.7	61.5, 60.4	137.5 (C_α, $^1J(^{119}Sn\text{-}^{13}C)$ = 510 Hz), 130.0 (C_β, $^2J(^{119}Sn\text{-}^{13}C)$ = 22 Hz), 127.8 (C_γ, $^3J(^{119}Sn\text{-}^{13}C)$ = 56 Hz), 131.8 (C_δ)
4[a]	122.0, 170.1, 118.0, 136.9, 116.8, 133.0	67.5	173.4	60.4, 61.8	41.0 (C_α, $^1J(^{119}Sn\text{-}^{13}C)$ = 574 Hz), 30.4 (C_β, $^2J(^{119}Sn\text{-}^{13}C)$ = 22 Hz), 28.8 (C_γ, $^3J(^{119}Sn\text{-}^{13}C)$ = 76 Hz), 26.4 (C_δ)
5[c]	122.0, 168.9, 118.2, 136.4, 116.8, 132.6	67.0	172.3	61.4, 63.2	10.8 (C_α, $^1J(^{119}Sn\text{-}^{13}C)$ = 602 Hz), 135.7, 125.3, 124.2, 128.2
6[c]	122.9, 167.9, 118.3, 135.9, 117.3, 133.6	66.3	172.2	61.7, 62.5	8.9 (C_α, $^1J(^{119}Sn\text{-}^{13}C)$ = 596 Hz), 133.3, 127.6, 124.9, 131.0
H_2L2	120.4, 163.8, 119.6, 132.7, 118.8, 131.3	67.2	163.8	61.2	-
7[a]	124.3, 158.8, 114.9, 136.9, 106.6, 132.0	67.3	172.0	63.8, 64.4	12.2 (C_α, $^1J(^{119}Sn\text{-}^{13}C)$ = 690 Hz)
8[a]	124.4, 168.5, 118.8, 139.1, 106.8, 137.2	67.3	172.9	62.4, 63.6	21.3 (C_α, $^1J(^{119}Sn\text{-}^{13}C)$ = 565 Hz), 27.3 (C_β, $^2J(^{119}Sn\text{-}^{13}C)$ = 31 Hz), 26.8 (C_γ, $^3J(^{119}Sn\text{-}^{13}C)$ = 78 Hz), 13.6 (C_δ)
9[b]	124.5, 167.7, 119.3, 138.4, 106.4, 134.4	68.3	172.7	61.1, 64.0	136.3 (C_α, $^1J(^{119}Sn\text{-}^{13}C)$ = 498 Hz), 130.2 (C_β, $^2J(^{119}Sn\text{-}^{13}C)$ = 24 Hz), 129.6 (C_γ, $^3J(^{119}Sn\text{-}^{13}C)$ = 56 Hz),

					135.0 (C_{δ})
10[a]	124.4, 168.6, 119.1, 137.4, 106.5, 135.2	67.0	172.1	61.0, 61.2	43.9 (C_{α}, $^{1}J(^{119}Sn\text{-}^{13}C)$ = 530 Hz), 29.9 (C_{β}, $^{2}J(^{119}Sn\text{-}^{13}C)$ = 22 Hz), 28.1 (C_{γ}, $^{3}J(^{119}Sn\text{-}^{13}C)$ = 78 Hz), 26.4 (C_{δ})
11[c]	124.0, 165.8, 119.7, 137.5, 106.9, 130.5	67.5	171.5	60.8, 61.9	9.3 (C_{α}, $^{1}J(^{119}Sn\text{-}^{13}C)$ = 587 Hz), 135.0, 128.2, 124.5, 129.9
12[c]	124.5, 165.8, 120.0, 137.6, 109.5, 131.1	66.4	169.7	59.3, 61.0	9.4 (C_{α}, $^{1}J(^{119}Sn\text{-}^{13}C)$ = 590 Hz), 138.2, 128.4, 127.3, 129.8
H_2L3	121.1, 163.8, 119.4, 135.5, 106.6, 134.4	67.2	165.1	61.2	-
13[a]	123.8, 167.1, 118.5, 135.6, 118.1, 134.5	68.0	171.9	61.0, 61.2	8.7 (C_{α}, $^{1}J(^{119}Sn\text{-}^{13}C)$ = 590 Hz)
14[a]	124.1, 168.1, 120.3, 136.6, 118.9, 134.1	67.3	172.9	61.1, 63.8	21.4 (C_{α}, $^{1}J(^{119}Sn\text{-}^{13}C)$ = 560 Hz), 27.4 (C_{β}, $^{2}J(^{119}Sn\text{-}^{13}C)$ = 31 Hz), 26.9 (C_{γ}, $^{3}J(^{119}Sn\text{-}^{13}C)$ = 78 Hz), 13.6 (C_{δ})
15[b]	123.9, 167.3, 119.2, 136.4, 118.3, 129.0	68.1	172.6	61.1, 64.3	136.9 (C_{α}, $^{1}J(^{119}Sn\text{-}^{13}C)$ = 498 Hz), 130.2 (C_{β}, $^{2}J(^{119}Sn\text{-}^{13}C)$ = 24 Hz), 128.7 (C_{γ}, $^{3}J(^{119}Sn\text{-}^{13}C)$ = 56 Hz), 131.2 (C_{δ})
16[a]	123.8, 168.6, 119.5, 136.5, 118.5, 134.6.	68.0	171.8	60.7, 61.5	40.4 (C_{α}, $^{1}J(^{119}Sn\text{-}^{13}C)$ = 530 Hz), 30.2 (C_{β}, $^{2}J(^{119}Sn\text{-}^{13}C)$ = 22 Hz), 28.8 (C_{γ}, $^{3}J(^{119}Sn\text{-}^{13}C)$ = 78 Hz), 24.2 (C_{δ})
17[c]	123.8, 167.7, 119.6, 135.6, 118.9, 133.4	67.4	171.7	61.4, 63.4	9.0 (C_{α}, $^{1}J(^{119}Sn\text{-}^{13}C)$ = 587 Hz), 135.0, 128.2, 124.3, 129.1
18[c]	124.0, 168.5, 120.1, 135.2, 118.1, 134.0	67.6	171.7	61.3, 62.2	8.6 (C_{α}, $^{1}J(^{119}Sn\text{-}^{13}C)$ = 590 Hz), 138.2, 128.4, 127.3, 129.8

[a] spectra recorded in $CDCl_3$
[b] spectra recorded in DMSO-d_6
[c] spectra recorded in 1,4-dioxane + 2-3 drops of $CDCl_3$



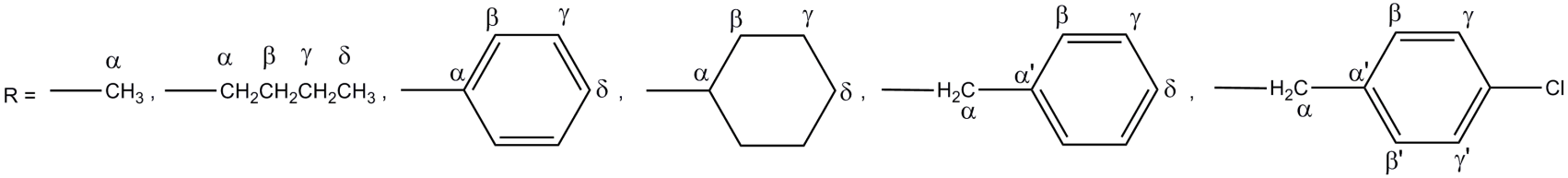


Table 3: ^{119}Sn NMR spectral data of the diorganotin(IV) complexes

Compound No.	δ (ppm)
1[a]	-164.4
2[a]	-189.2
3[b]	-324.7
4[a]	-244.5
5[c]	-174.4
6[c]	-174.9
7[c]	-174.8
8[a]	-186.9

9[a]	-325.5
10[b]	-243.1
11[a]	-174.7
12[c]	-179.1
13[c]	-163.4
14[c]	-186.6
15[a]	-325.3
16[a]	-244.2
17[b]	-190.1
18[a]	-188.9

[a] spectra recorded in $CDCl_3$
[b] spectra recorded in DMSO-d_6
[c] spectra recorded in 1,4-dioxane + 2-3 drops of $CDCl_3$

Table 4
Crystallographic data of *bis*[(2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}phenolato)[dimethyltin(IV), **1**, *bis*[(2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-bromophenolato)]dimethyltin(IV), **7**, (2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-bromophenolato)diphenyltin(IV), **9**, 2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-chlorophenolato)dimethyltin(IV), **13**, (2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-chlorophenolato)diphenyltin(IV), **15** and (2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-chlorophenolato)dicyclohexyltin(IV), **16**

Compound	**1**	**7**	**9**
Empirical formula	$C_{13}H_{19}NO_4Sn$	$C_{26}H_{36}Br_2N_2O_8Sn_2$	$C_{23}H_{22}BrNO_4Sn$
Formula weight	371.98	901.77	575.02
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$	Triclinic, $P\bar{1}$
a (Å)	8.5456(2)	18.9301(4)	8.0138(1)
b (Å)	8.8357(2)	8.8951(2)	11.6732(1)
c (Å)	10.5779(2)	19.8873(4)	29.5049(3)
α (°)	65.470(1)	90	104.680(1)
β (°)	71.212(1)	114.075(1)	94.759(1)
γ (°)	89.592(1)	90	113.230(1)
Volume (Å^3)	680.42(3)	3057.43(11)	1123.57(5)
Z	2	4	2
Calculated density (mg m^{-3})	1.816	1.959	1.700
μ (mm^{-1})	1.887	4.297	2.944
F(000)	372	1760	568
θ range (°) for data collection	2.26 to 27.50	1.25 to 27.49	1.45 to 27.50
Reflections collected / unique	6470 / 3089 [$R_{(int)}$ = 0.020]	21362 / 7016 [$R_{(int)}$ = 0.0279]	8208 / 5038 [$R_{(int)}$ = 0.018]
Max. and min. transmission	0.746and 0.600	0.390 and 0.0.278	0.417 and 0.364
Data / restraints / parameters	3089 / 0 / 176	7016 / 0 / 365	5038 / 0 / 274
Goodness-of-fit on F^2	1.13	1.16	1.16
Final R indices [$I>2\sigma(I)$]	R_1 = 0.024, wR_2 = 0.076	R_1 = 0.029, wR_2 = 0.085	R_1 = 0.024, wR_2 = 0.071
R indices (all data)	R_1 = 0.025, wR_2 = 0.077	R_1 = 0.039, wR_2 = 0.105	R_1 = 0.029, wR_2 = 0.009
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	1.51 and -0.95	1.60 and -1.09	0.75 and -0.79

Table 4 (continued)
Crystallographic data of *bis*[(2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}phenolato)[dimethyltin(IV), **1**, *bis*[(2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-bromophenolato)]dimethyltin(IV), **7**, (2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-bromophenolato)diphenyltin(IV), **9**, 2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-chlorophenolato)dimethyltin(IV), **13**, (2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-chlorophenolato)diphenyltin(IV), **15** and (2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-chlorophenolato)dicyclohexyltin(IV), **16**

Compound	**13**	**15**	**16**
Empirical formula	$C_{13}H_{18}ClNO_4Sn$	$C_{23}H_{22}ClNO_4Sn$	$C_{23}H_{34}ClNO_4Sn$
Formula weight	406.42	530.56	542.65
Crystal system, space group	Monoclinic, *C*2/*c*	Triclinic, *P*$\bar{1}$	Monoclinic, $P2_1/n$
a (Å)	14.8956(6)	8.6518(3)	17.0081(4)
b (Å)	13.8128(5)	9.9622(4)	12.6893(4)
c (Å)	16.7610(6)	15.0439(6)	22.1755(6)
α (^{o})	90	100.951(2)	90
β (^{o})	114.299(2)	102.843(2)	97.778(2)
γ (^{o})	90	113.111(1)	90
Volume (Å^3)	3143.1(2)	1105.8(7)	4764.2(2)
Z	8	2	8
Calculated density (mg m^{-3})	1.718	1.593	1.513
μ (mm^{-1})	1.807	1.305	1.213
F(000)	1616	532	2224
θ range (^{o}) for data collection	2.14 to 31.56	2.13 to 31.55	2.28 to 19.84
Reflections collected / unique	16984 / 3594 [$R_{(int)}$ = 0.027]	9422 / 4953 [$R_{(int)}$ = 0.016]	37000 / 8392 [$R_{(int)}$ = 0.137]
Max. and min. transmission	0.899 and 0.497	0.926 and 0.591	0.942 and 0.839
Data / restraints / parameters	3594 / 2 / 191	4973 / 0 / 273	8392 / 0 / 545
Goodness-of-fit on F^2	1.24	1.34	1.00
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.018, wR_2 = 0.054	R_1 = 0.020, wR_2 = 0.060	R_1 = 0.053, wR_2 = 0.086
R indices (all data)	R_1 = 0.021, wR_2 = 0.068	R_1 = 0.026, wR_2 = 0.097	R_1 = 0.110, wR_2 = 0.105
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.75 and -0.46	0.66 and -1.17	0.68 and -0.68

Table 5
Selected bond lengths (Å) and angles (°) for *bis*[(2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}phenolato)[dimethyltin(IV), **1**, *bis*[(2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-bromophenolato)]dimethyltin(IV), **7**, (2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-bromophenolato)diphenyltin(IV), **9**, 2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-chlorophenolato)dimethyltin(IV), **13**, (2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-chlorophenolato)diphenyltin(IV), **15** and (2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-chlorophenolato)dicyclohexyltin(IV), **16**

	1	**7**	**9**
Bond lengths			
Sn(1)-O(1)	2.296(2)	2.262(3), 2.281(3)	2.083(2)
Sn(1)-O(2)	2.079(2)	2.075(2), 2.090(3)	2.073(2)
Sn(1)-O(2)#	2.379(2)	2.329(2), 2.348(3)	-
Sn(1)-N(1)	2.237(2)	2.269(3), 2.269(3)	2.191(2)
Sn(1)-C_i	2.110(3)	2.113(4), 2.117(4)	2.123(3)
Sn(1)-C_i'	2.114(3)	2.113(4), 2.109(4)	2.125(3)
C(2)-O(1)	1.306(3)	1.291(5), 1.320(5)	1.319(3)
C(9)-O(2)	1.405(3)	1.403(4), 1.405(5)	1.403(4)
C(10)-O(3)	1.423(3)	1.400(4), 1.408(5)	1.411(3)
C(11)-O(4)	1.425(3)	1.419(4), 1.409(5)	1.406(4)
C(7)-N(1)	1.290(4)	1.296(4), 1.285(5)	1.292(4)
C(8)-N(1)	1.490(3)	1.479(4), 1.475(5)	1.485(3)
Bond angles			
O(1)-Sn(1)-O(2)	155.23(7)	155.32(10), 152.04(10)	159.33(8)
C_i-Sn(1)- C_i'	144.39(11)	147.94(18), 150.87(19)	120.80(2)
N(1)-Sn(1)- C_i	101.63(10)	105.06(15), 99.65(15)	112.97(10)
N(1)-Sn(1)- C_i'	107.81(10)	100.46(14), 103.03(16)	121.49(10)

Note:
C_i refers to Ci_{pso}
C_i and C_i' for compounds **1**, **7** and **13** is C12 and C13 while C_i and C_i' for compound **9**, **15** and **16** is C12 and C18.

Table 5 (continued)
Selected bond lengths (Å) and angles (°) for *bis*[(2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}phenolato)[dimethyltin(IV), **1**, *bis*[(2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-bromophenolato)]dimethyltin(IV), **7**, (2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-bromophenolato)diphenyltin(IV), **9**, 2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-chlorophenolato)dimethyltin(IV), **13**, (2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-chlorophenolato)diphenyltin(IV), **15** and (2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-chlorophenolato)dicyclohexyltin(IV), **16**

	13	**15**	**16**
Bond lengths			
Sn(1)-O(1)	2.125(2)	2.092(2)	2.093(4), 2.131(4)
Sn(1)-O(2)	2.075(2)	2.082(2)	2.076(5), 2.107(4)
Sn(1)-N(1)	2.209(2)	2.197(2)	2.215(6), 2.196(5)
Sn(1)-C_i	2.117(2)	2.129(2)	2.143(6), 2.143(6)
Sn(1)-C_i'	2.117(2)	2.130(2)	2.147(7), 2.133(7)
C(2)-O(1)	1.312(3)	1.314(3)	1.315(7), 1.315(7)
C(9)-O(2)	1.413(2)	1.414(3)	1.401(8), 1.401(7)
C(10)-O(3)	1.413(3)	1.416(3)	1.486(8), 1.417(7)
C(11)-O(4)	1.421(3)	1.408(3)	1.415(8), 1.416(7)
C(7)-N(1)	1.300(3)	1.293(3)	1.295(8), 1.301(7)
C(8)-N(1)	1.492(3)	1.490(3)	1.426(7), 1.512(7)
Bond angles			
O(1)-Sn(1)-O(2)	158.37(6)	159.03(7)	156.46(17), 158.29(16)
C_i-Sn(1)- C_i'	125.83(9)	126.60(9)	122.2(3), 132.9(3)
N(1)-Sn(1)- C_i	119.51(8)	121.86(8)	110.4(2), 118.6(2)
N(1)-Sn(1)- C_i'	114.52(8)	111.39(8)	127.3(2), 108.5(2)

Note:
C_i refers to Ci_{pso}
C_i and C_i' for compounds **1**, **7** and **13** is C12 and C13 while C_i and C_i' for compound **9**, **15** and **16** is C12 and C18.

Table 6
Cytotoxic activity of the Schiff base ligands and its diorganotin complexes

Compound	Cell lines (IC_{50} μg ml^{-1})[a]		
	HT-29	MCF-7	SKOV-3
Cisplatin	5.0± 0	2.4 ± 0.6	1.4 ± 0
H_2L1	> 100	> 100	> 100
1	> 100	5.7	> 100
2	6.7 ± 0.1	1.6 ± 0.3	2.2 ± 0.2
3	65.2 ± 1.3	46.7 ± 1.2	36 ± 0.5
4	7.8 ± 0.3	4.0 ± 0.2	6.0 ± 0.2
5	> 100	> 100	> 100
6	> 100	> 100	> 100
H_2L2	> 100	> 100	83.3 ± 0.8
7	> 100	> 100	72.3 ± 0.3
8	35.3 ± 0.6	6.7 ± 0.1	5.7 ± 0.1
9	34.7 ± 0.6	27.7 ± 0.3	5.6 ± 0.1
10	7.1 ± 0.3	3.6 ± 0.2	5.7 ± 0.1
11	> 100	> 100	> 100
12	> 100	> 100	> 100
H_2L3	> 100	> 100	100 ± 0
13	> 100	> 100	> 100
14	8.2 ± 0.2	2.2 ± 1.2	5.6 ± 0.1
15	41 ± 1	7.9 ± 0.1	5.7 ± 0
16	4.6 ± 0.1	8.2 ± 0.2	5.4 ± 0.1
17	> 100	> 100	> 100
18	> 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%

Figure 3
Molecular structure and crystallographic numbering scheme for *bis*(2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]-iminomethyl}phenolato)dimethyltin(IV), **1**

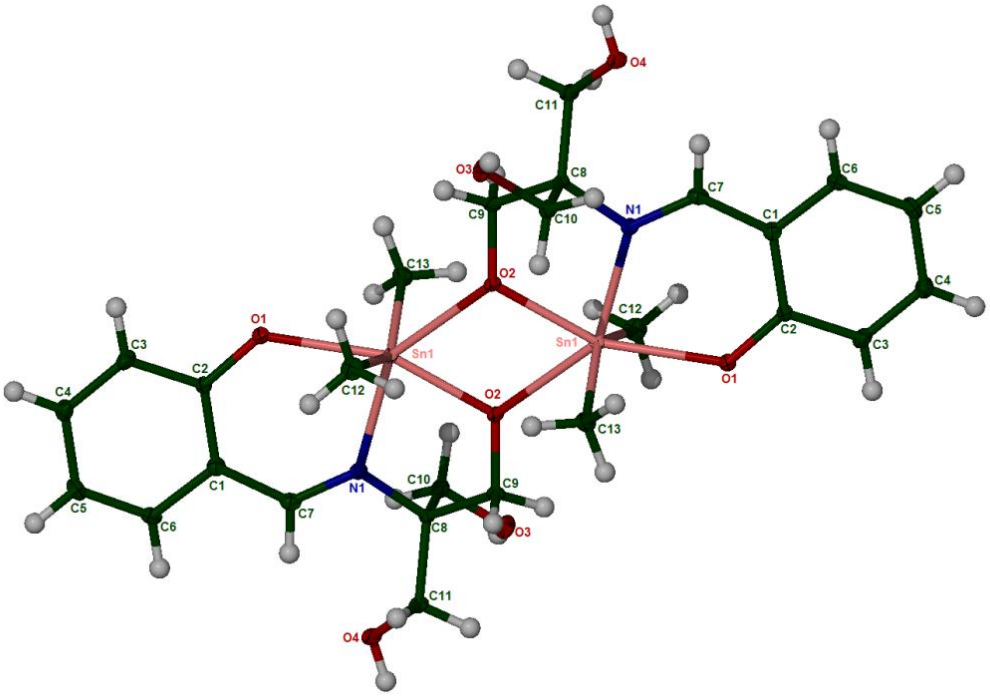


Figure 4
Molecular structure and crystallographic numbering scheme for *bis*[(2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-bromophenolato)]dimethyltin(IV), **7**

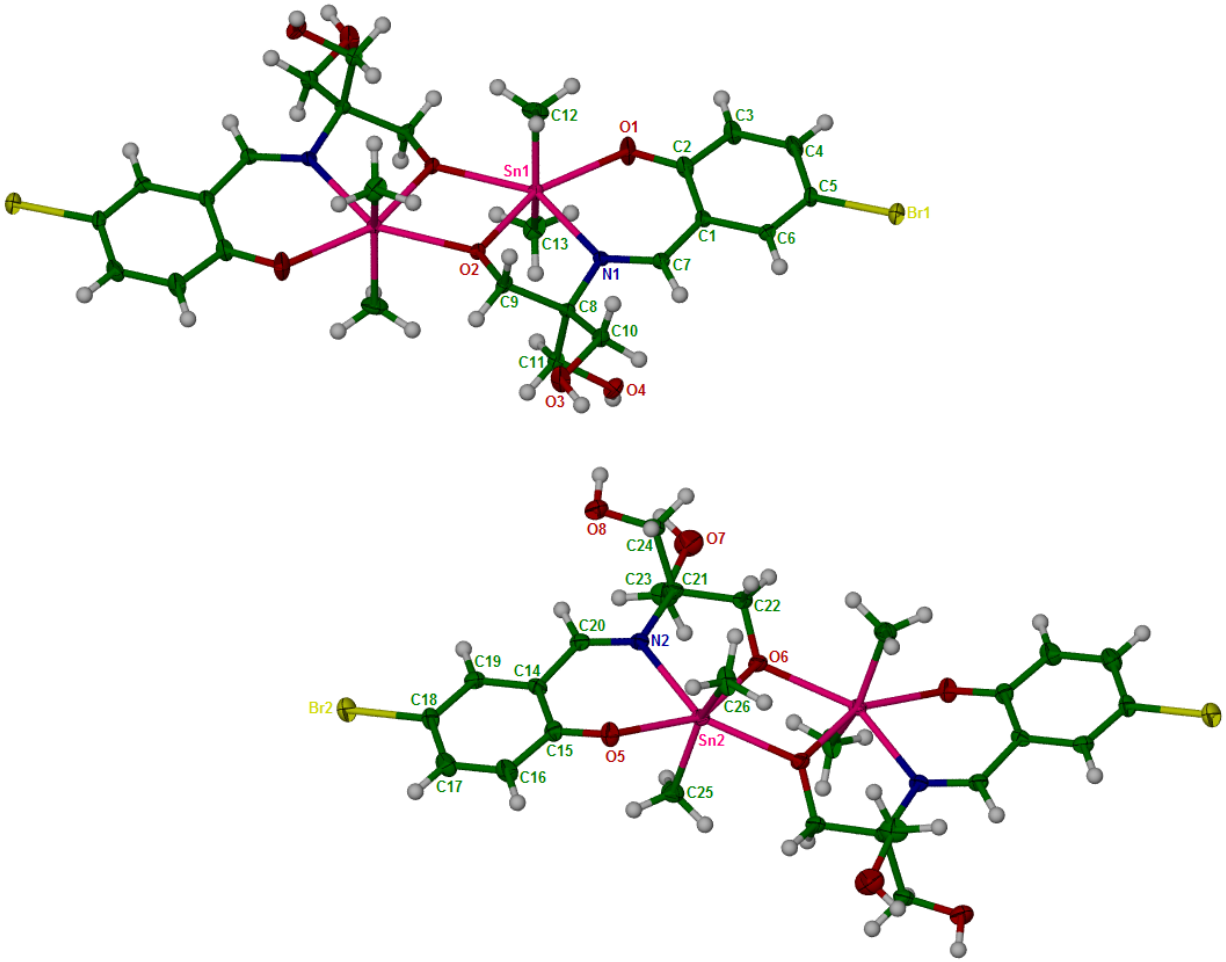


Figure 5
Molecular structure and crystallographic numbering scheme for [(2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-bromophenolato)]diphenyltin(IV), **9**

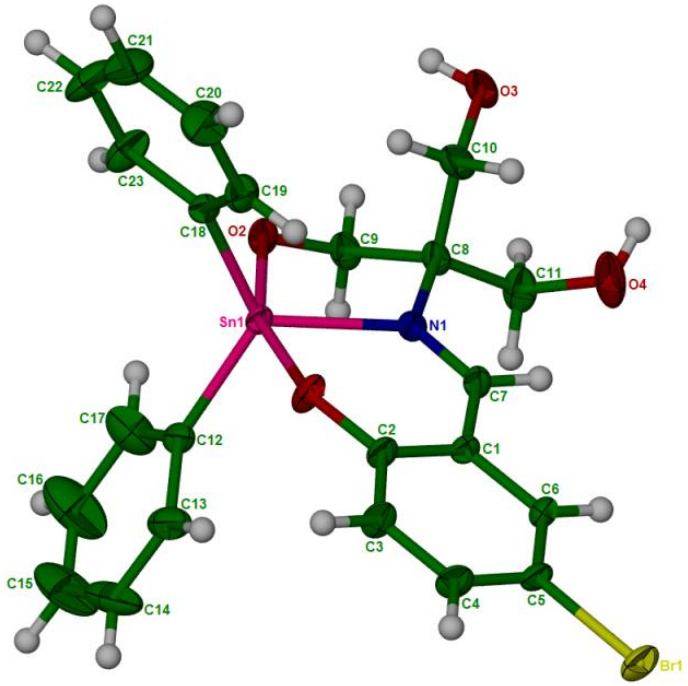


Figure 6
Molecular structure and crystallographic numbering scheme for [(2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-chlorophenolato)]dimethyltin(IV) **13**

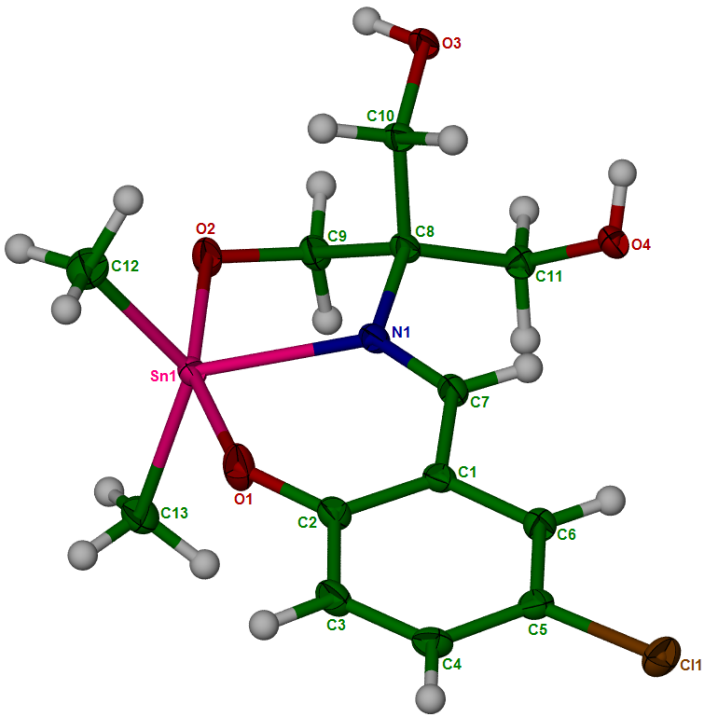


Figure 7
Molecular structure and crystallographic numbering scheme for [(2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-chlorophenolato)]diphenyltin(IV) **15**

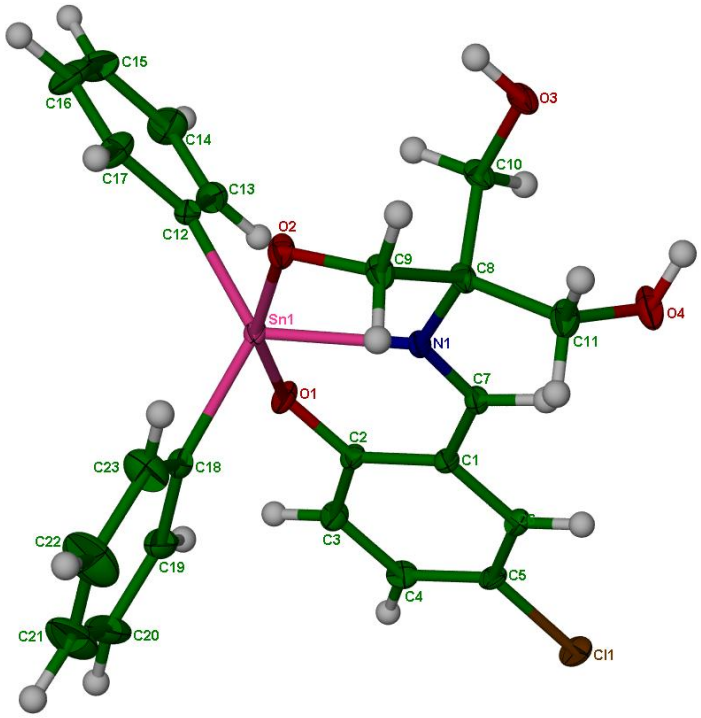


Figure 8
Molecular structure and crystallographic numbering scheme for [(2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-bromophenolato)]dicyclohexyltin(IV), **16**

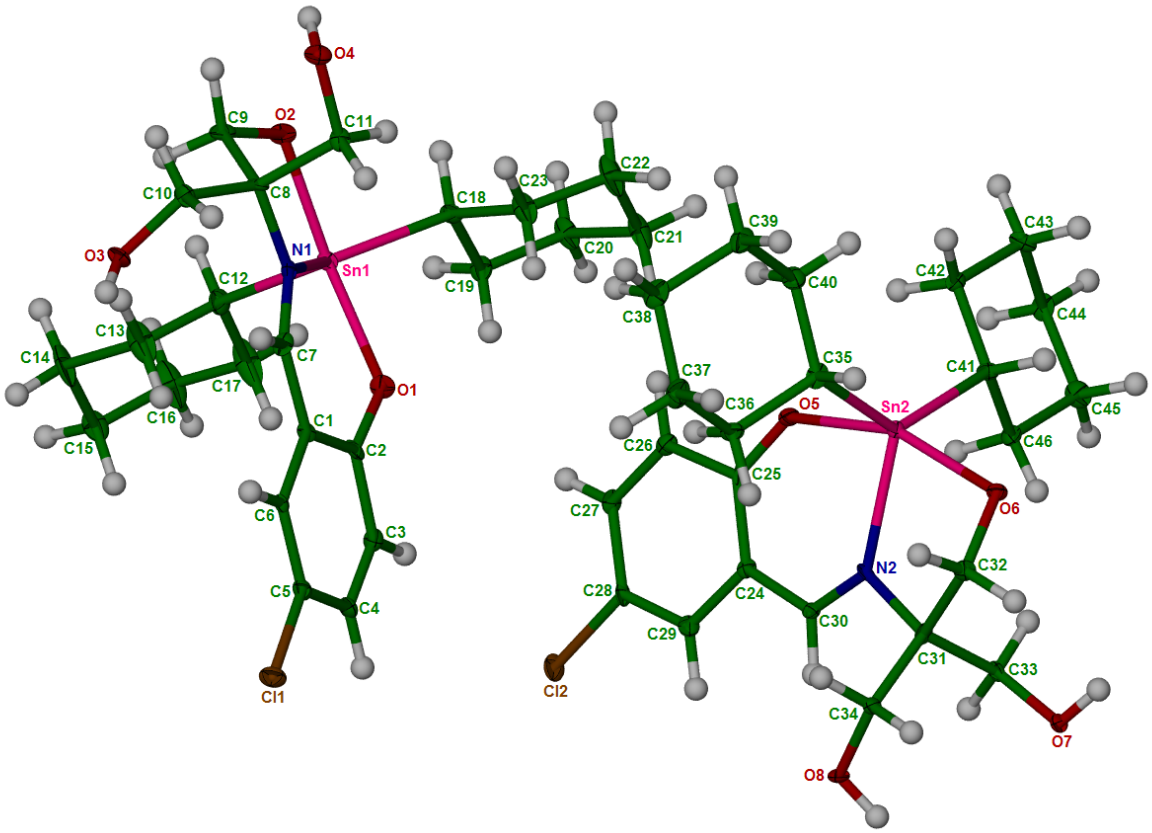


Figure 9
Packing diagram of *bis*[(2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-bromophenolato)]dimethyltin(IV), **7**

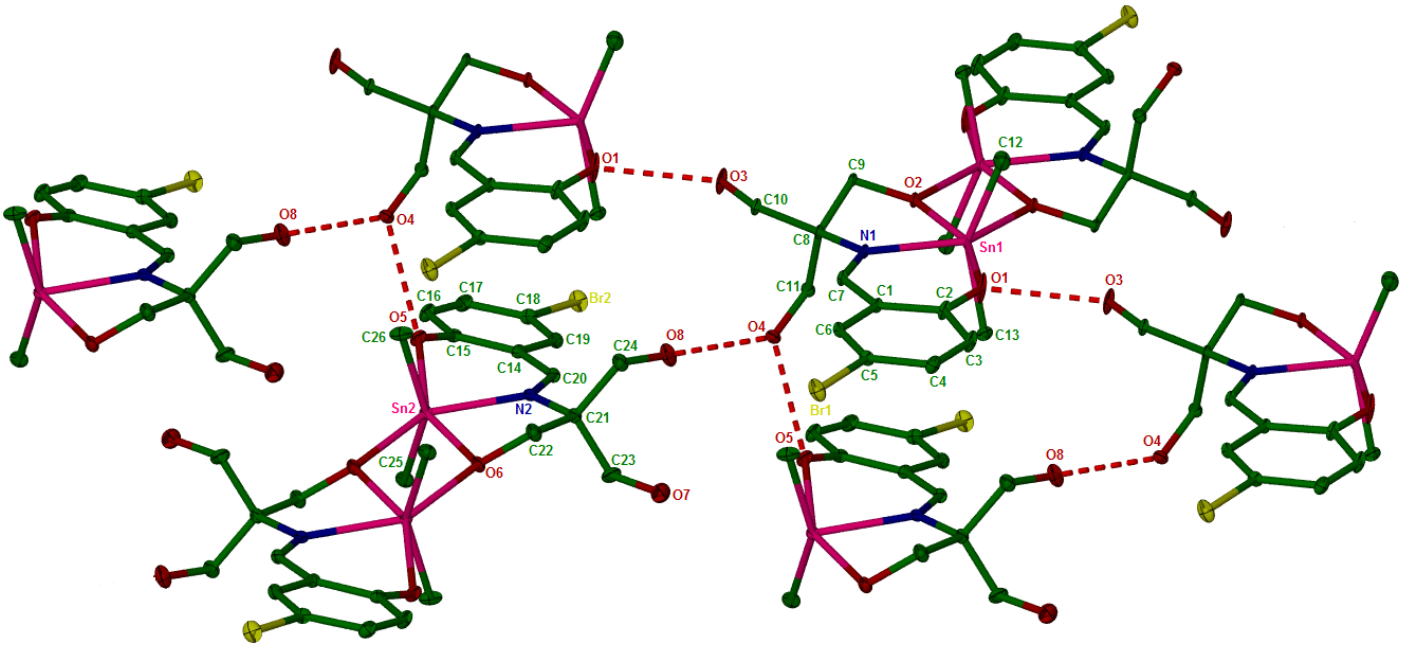
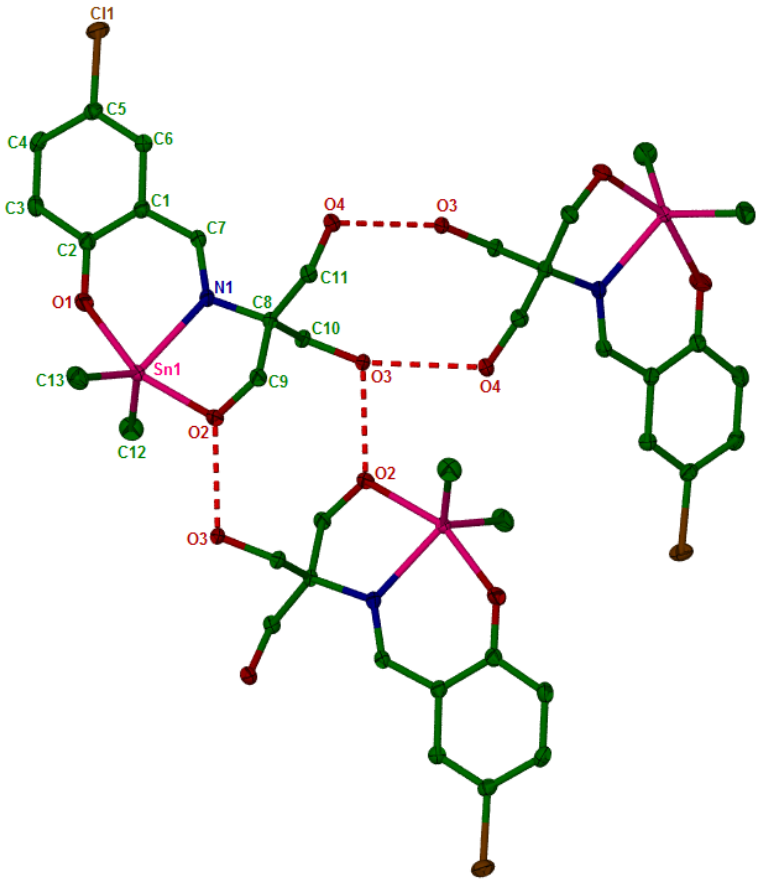


Figure 10
Packing diagram of [(2-{[1,1-*bis*(hydroxymethyl)-2-oxidoethyl]iminomethyl}-4-chlorophenolato)]dimethyltin(IV) **13**



Synthesis, characterization and biological studies of diorganotin(IV) complexes with *tris*[(hydroxymethyl)aminomethane] Schiff base

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Highlights

- Formation of dimers in two complexes.
- Two intermolecular hydrogen-bondings in observed in each of of the complexes.
- Diorganotin(IV) complexes can be considered as agents with potential anticancer activities.

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Diorganotin(IV) complexes with *ONO* donors Schiff base ligands are obtained. X-ray crystallographic analysis of organotin(IV) complexes.