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Synthesis, characterization and biological activity of diorganotin complexes with *ONO* terdentate Schiff base

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ABSTRACT

Diorganotin(IV) complexes with general formula **R_2SnL** [**H_2L** = (*E*)-N′-[1-(5-bromo-2-hydroxyphenyl) ethylidene]-3-hydroxy-2-naphthohydrazide (**H_2L_1**) and (*E*)-N′-[1-(5-chloro-2-hydroxyphenyl)ethylidene]-3-hydroxy-2-naphthohydrazide (**H_2L_2**); R = Me, Bu, Ph, Cy, Bz, o-ClBz and p-ClBz (**1**–**14**)] have been synthesized and characterized by IR, ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopic techniques and single crystal X-ray diffractometry. The structure of the complexes, {[1-(5-bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), **1**, {[1-(5-chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), **8** and {[1-(5-chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dicyclohexyltin(IV), **11** reveals a five-coordinated, trigonal–bipyramidal geometry, whereby the trigonal plane of the complexes consists of the imine nitrogen atom and alkyl groups from the diorganotin moieties. The complexes are stabilized by a strong intramolecular hydrogen bonding between N(2) and O(3)–H(3). 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 MCF7 (hormone-dependent breast carcinoma cell line), for their cytotoxic activities. The dimethyltin derivatives and dibutyltin derivatives of the Schiff base ligands display good cytotoxic activities against the tested cell lines.

1. Introduction

The studies of organotin(IV) compounds have gained interest due to their various industrial and biocidal applications [1–5]. The organotin(IV) compounds have been actively studied because of its versatile chemistry and its potential as biological active compounds. Among these compounds, the chemistry of organotin(IV) complexes of Schiff bases has been extensively studied due to its structural diversity, thermal stability, and the compounds have been proposed to possess mild-to-good antitumor [6–9], antimicrobial [10,11], antifungal [12–14], antibacterial [12–14], antioxidant [15] or anti-inflammatory properties [15,16]. However, the mode of biological activities of the organotin(IV) compounds is not completely known. The structure of the organotin(IV) complexes, its coordination number, the extent of alkylation and the nature of the organic groups attached to the tin atom are the main factors deciding the biological activities of the tin complexes [10,17,18].

In the current article, we report the synthesis and structural studies of diorganotin(IV) complexes with terdentate *ONO* Schiff bases prepared from the condensation reaction of 3-hydroxy-2-naphthoylhydrazide with substituted 2-hydroxyacetophenone. From literature, Schiff bases derived from 3-hydroxy-2-naphthoylhydrazide are reported to have good antimicrobial activities [19]. The *in vitro* cytotoxicity of the Schiff bases and their diorganotin(IV) complexes against three human carcinoma cell lines (HT29, SKOV-3 and MCF7) is evaluated and discussed.

2. Experimental

2.1. Materials and methods

The reagents used are commercially available (Aldrich, Acros or Merck) and used as supplied. Dibenzyltin dichloride, di(*o*-chlorobenzyl)tin dichloride and di(*p*-chlorobenzyl)tin dichloride were prepared according to the literature method [20]. All solvents used in the reaction were procured commercially and used without purification. The melting points of the ligands and complexes were determined using an Electrothermal digital melting point apparatus and were uncorrected. Infrared spectra for the compounds were recorded in 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-400 MHz

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spectrometer and were referenced against Me_4Sn. The chemical shifts were recorded in ppm with reference to Me_4Si for ^1H NMR and ^{13}C NMR. Elemental analyses were carried out on a Perkin_Elmer EA2400 CHNS Elemental Analyzer. Thermal analysis of the complexes was carried out by heating in nitrogen gas at 10 °C per minute on a Perkin–Elmer TGA-4000 thermobalance.

2.1.1. Preparation of the ligands

*(E)-N′-[1-(5-Bromo-2-hydroxyphenyl)ethylidene]-3-hydroxy-2-naphthohydrazide [**H_2L1**]:* 2.03 g (0.01 mol) of 3-hydroxy-2-naphthoic hydrazide in 100 ml methanol was added to a 50 ml hot stirring methanolic solution of 2.15 g (0.01 mol) of 5-bromo-2-hydroxyacetophenone. The solution mixture was refluxed for 2 h. A yellow solid was obtained upon cooling to room temperature and was used without further purification.

Yield: 2.89 g, 72%; m.p. 214–216 °C. *Anal.* Calc. for $C_{19}H_{15}N_2O_3$Br: C, 57.16; H, 3.79; N, 7.02. Found: C, 56.96; H, 3.75; N, 6.98%. IR (cm^{-1}): 3286 *ν*(O–H, N–H), 1656 *ν*(C=O), 1649 *ν*(–C=N), 1176 *ν*(C–O).

^1H NMR *δ* (ppm): 2.43 (s, 3H, H-19), 6.80 (d, 1H, *J* = 8.2 Hz, H-3), 7.25–7.40 (m, 4H, H-4, H-11, H-14, H-15), 7.65–7.80 (m, 3H, H-6, H-13, H-16), 8.39 (s, 1H, H-18), 11.35 (s, 2H, O<u>H</u>), 12.92 (s, 1H, N<u>H</u>) [s = singlet, d = doublet, m = multiplet].

^{13}C NMR *δ* (ppm): 22.6 (C-19), 110.6 (C-5), 119.0 (C-11), 120.1 (C-1), 121.4 (C-9), 123.3 (C-14), 125.8 (C-13), 126.4 (C-3), 127.9 (C-15), 128.3 (C-4), 128.9 (C-16), 130.5 (C-17), 131.6 (C-18), 132.6 (C-6), 134.3 (C-12), 155.0 (C-10), 161.0 (C-2), 166.5 (C-7), 170.5 (C-8).

*(E)-N′-[1-(5-Chloro-2-hydroxyphenyl)ethylidene]-3-hydroxy-2-naphthohydrazide [**H_2L2**]:* 2.03 g (0.01 mol) of 3-hydroxy-2-naphthoic hydrazide in 100 ml methanol was added to a 50 ml hot stirring methanolic solution of 1.71 g (0.01 mol) of 5-chloro-2-hydroxyacetophenone. The solution mixture was refluxed for 2 h. A light yellow solid formed upon cooling to room temperature and was used without further purification.

Yield: 2.62 g, 75%; m.p. 298–300 °C. *Anal.* Calc for $C_{19}H_{15}N_2O_3Cl$: C, 64.32; H, 4.26; N, 7.90. Found: C, 64.02; H, 4.10; N, 7.70% IR (cm^{-1}): 3279 *ν*(O–H, N–H), 1655 *ν*(C=O), 1648 *ν*(–C=N), 1181 *ν*(C–O).

^1H NMR *δ* (ppm): 2.44 (s, 3H, H-19), 6.80 (d, 1H, *J* = 8.2 Hz, H-3), 7.25–7.44 (m, 4H, H-4, H-11, H-14, H-15), 7.70–7.90 (m, 3H, H-6, H-13, H-16), 8.34 (s, 1H, H-18), 11.50 (s, 2H, O<u>H</u>), 12.30 (s, 1H, N<u>H</u>) [s = singlet, d = doublet, m = multiplet],

^{13}C NMR *δ* (ppm): 25.2 (C-19), 110.9 (C-5), 118.6 (C-11), 120.6 (C-1), 121.2 (C-9), 124.0 (C-14), 126.0 (C-13), 126.9 (C-3), 128.5 (C-15), 129.0 (C-4), 129.5 (C-16), 130.6 (C-17), 131.1 (C-18), 132.5 (C-6), 134.4 (C-12), 154.9 (C-10), 162.2 (C-2), 164.1 (C-7), 170.9 (C-8).

*2.2. Preparation of the diorganotin complexes, **1**–**14***

The preparation method used for compound **1** was repeated for compounds **3**, **4**, **8**, **10** and **11** with the appropriate diorganotin oxides and Schiff base ligands. The preparation method used for compound **5** was repeated for compounds **6**, **7**, **12**, **13** and **14** with the appropriate diorganotin chlorides and Schiff base ligands. The preparation method for structurally known compounds **2** and **9** was in accordance to literature method [21,22].

*{[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), Me_2SnL1, **1**:* 0.40 g (1.0 mmol) of *(E)-N′*-[1-(5-bromo-2-hydroxyphenyl)ethylidene]-3-hydroxy-2-naphthohydrazide, **H_2L1** in 20 ml dry toluene was added to a suspension of 0.17 g (1.0 mmol) of dimethyltin(IV) oxide in 40 ml of dry toluene. The mixture was refluxed 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 chloroform. Yellow crystals suitable for X-ray crystallographic studies were obtained from the slow evaporation of the filtrate. Yield: 0.44 g, 81%; m.p. 195–196°C. *Anal.* Calc. for $C_{21}H_{19}N_2O_3$BrSn: C, 46.19; H, 3.51; N, 5.13. Found: C, 46.51; H, 3.48; N, 5.30%. IR (cm^{-1}): 3431 *ν*(OH), 1638 *ν*(C=N), 1578 *ν*(–N=C–C=N), 1171 *ν*(C–O).

*{[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibutyltin(IV), Bu_2SnL1, **2**:* Yield: 0.50 g, 79%; m.p. 138–139 °C. *Anal.* Calc. for $C_{27}H_{31}N_2O_3$BrSn: C, 51.38; H, 5.11; N, 4.44. Found: C, 51.46; H, 4.99; N, 4.63%. IR (cm^{-1}): 3400 *ν*(OH), 1639 *ν*(C=N), 1577 *ν*(–N=C–C=N), 1171 *ν*(C–O).

*{[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diphenyltin(IV), Ph_2SnL1, **3**:* Yield: 0.49 g, 73%; m.p. 149–150 °C. *Anal.* Calc. for $C_{31}H_{23}N_2O_3$BrSn: C, 55.56; H, 3.46; N, 4.18. Found: C, 55.84; H, 3.23; N, 3.98%. IR (cm^{-1}): 3386 *ν*(OH), 1639 *ν*(C=N), 1581 *ν*(–N=C–C=N), 1172 *ν*(C–O).

*{[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dicyclohexyltin(IV), Cy_2SnL1, **4**:* Yield: 0.53 g, 77%; m.p. 158–160°C. *Anal.* Calc. for $C_{31}H_{35}N_2O_3$BrSn: C, 54.58; H, 5.17; N, 4.11. Found: C, 54.48; H, 5.34; N, 4.07%. IR (cm^{-1}): 3386 *ν*(OH), 1639 *ν*(C=N), 1581 *ν*(–N=C–C=N), 1172 *ν*(C–O).

*{[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibenzyltin(IV), Bz_2SnL1, **5**:* 0.40 g (1.0 mmol) of *(E)-N′*-[1-(5-bromo-2-hydroxyphenyl)ethylidene]-3-hydroxy-2-naphthohydrazide, H_2L1 and 0.32 ml of triethylamine (1.0 mmol) were added to 50 ml of absolute ethanol and the mixture was refluxed for 2 h. 0.37 g (1.0 mmol) of dibenzyltin dichloride in 30 ml of absolute ethanol was added and the mixture was further refluxed for 5 h and filtered. The filtrate was evaporated until precipitation was obtained. The precipitation was recrystallized from toluene and the by-product, triethylammonium chloride, was removed through filtration. The solid was recrystallized from a 1:1 mixture of chloroform and hexane.

Yield: 0.50 g, 72%; m.p. 144–145 °C. *Anal.* Calc. for $C_{33}H_{28}N_2O_3$BrSn: C, 56.69; H, 4.04; N, 4.01. Found: C, 56.30; H, 3.91; N, 3.74%. IR (cm^{-1}): 3400 *ν*(OH), 1638 *ν*(C=N), 1580 *ν*(–N=C–C=N), 1171 *ν*(C–O).

*{[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}di(o-chlorobenzyl)tin(IV), (o-ClBz)$_2$SnL1, **6**:* Yield: 0.57 g, 74%; m.p. 187–189 °C. *Anal.* Calc. for $C_{33}H_{26}N_2O_3BrCl_2Sn$: C, 51.60; H, 3.41; N, 3.65. Found: C, 51.96; H, 3.29; N, 3.53%. IR (cm^{-1}): 3402 *ν*(OH), 1638 *ν*(C=N), 1578 *ν*(–N=C–C=N), 1171 *ν*(C–O).

*{[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}di(p-chlorobenzyl)tin(IV), (p-ClBz)$_2$SnL1, **7**:* Yield: 0.56 g, 73%; m.p. 188–190°C. *Anal.* Calc for $C_{33}H_{26}N_2O_3BrCl_2Sn$: C, 51.60; H, 3.41; N, 3.65. Found: C, 51.32; H, 3.32; N, 3.81%. IR (cm^{-1}): 3424 *ν*(OH), 1639 *ν*(C=N), 1578 *ν*(–N=C–C=N), 1172 *ν*(C–O)

*{[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), Me_2SnL2, **8**:* Yield: 0.41 g, 81%; m.p. 234–235 °C. *Anal.* Calc. for $C_{21}H_{19}N_2O_3$ClSn: C, 50.29; H, 3.82; N, 5.59. Found: C, 50.19; H, 3.85; N, 5.80%. IR (cm^{-1}): 3400 *ν*(OH), 1638 *ν*(C=N), 1597 *ν*(–N=C–C=N), 1172 *ν*(C–O).

*{[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibutyltin(IV), Bu_2SnL2, **9**:* Yield: 0.49 g, 83%; m.p. 135–136 °C. *Anal.* Calc for $C_{27}H_{31}N_2O_3$ClSn: C, 55.37; H, 5.34; N, 4.78. Found: C, 55.51; H, 5.40; N, 4.59%. IR (cm^{-1}): 3400 *ν*(OH), 1639 *ν*(C=N), 1596 *ν*(–N=C–C=N), 1172 *ν*(C–O).

*{[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}diphenyltin(IV), Ph_2SnL2, **10**:* Yield: 0.49 g, 79%; m.p. 169–170 °C. *Anal.* Calc. for $C_{31}H_{23}N_2O_3$ClSn: C, 59.51; H, 3.71; N, 4.48. Found: C, 59.80; H, 3.66; N, 4.32%. IR (cm^{-1}): 3405 *ν*(OH), 1638 *ν*(C=N), 1598 *ν*(–N=C–C=N), 1172 *ν*(C–O).

*{[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dicyclohexyltin(IV), Cy_2SnL2, **11**:* Yield: 0.50 g, 78%; m.p. 159–160 °C. *Anal.* Calc. for $C_{31}H_{35}N_2O_3$ClSn: C, 58.38; H, 5.53; N,

4.39. Found: C, 58.70; H, 5.81; N, 4.11%. IR (cm^{-1}): 3424 ν(OH), 1639 ν(C=N), 1598 ν(–N=C–C=N), 1170 ν(C–O).

{[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibenzyltin(IV), Bz_2SnL2, ***12****:* Yield: 0.49 g, 75%; m.p. 140–141 °C. *Anal.* Calc. for $C_{33}H_{27}N_2O_3ClSn$: C, 60.63; H, 4.16; N, 4.29. Found: C, 60.38; H, 3.91; N, 4.58%. IR (cm^{-1}): 3387 ν(OH), 1639 ν(C=N), 1593 ν(–N=C–C=N), 1172 ν(C–O).

{[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}di(o-chlorobenzyl)tin(IV), $(o\text{-}ClBz)_2SnL2$, ***13****:* Yield: 0.55 g, 76%; m.p. 159–160 °C. *Anal.* Calc. for $C_{33}H_{25}N_2O_3Cl_3Sn$: C, 54.85; H, 3.49; N, 3.88. Found: C, 55.08; H, 3.26; N, 3.74%. IR (cm^{-1}): 3387 ν(OH), 1637 ν(C=O), 1594 ν(–N=C–C=N), 1170 ν(C–O).

{[1-(5-Chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}di(p-chlorobenzyl)tin(IV), $(p\text{-}ClBz)_2SnL2$, ***14****:* Yield: 0.56 g, 78%; m.p. 190–191 °C. *Anal.* Calc. for $C_{33}H_{25}N_2O_3Cl_3Sn$: C, 54.85; H, 3.49; N, 3.88. Found: C, 55.09; H, 3.24; N, 3.54%. IR (cm^{-1}): 3400 ν(OH), 1639 ν(C=O), 1596 ν(N=C–C=N), 1172 ν(C–O).

2.3. X-ray structural studies

All measurements were performed on a Bruker SMART APEX2 CCD diffractometer at 100 K with graphite-monochromated Mo Kα (λ = 0.71073 Å). The structures were solved using direct method and refined by full-matrix least-squares procedure based on F^2 using the SHELXL-97 programme [23]. Non-hydrogen atoms were refined with anisotropic displacement parameters. The positions of hydrogen atoms were calculated, and were included in the structure factor calculations.

2.4. Neutral Red cytotoxicity assay

HT29 (human colon carcinoma cell line), SKOV-3 (human ovarian cancer cell line) and MCF7 (hormone-dependent breast carcinoma cell line) were purchased from American Type Culture Collection (ATCC, USA). The HT29 and MCF7 cells were maintained in RPMI 1640 medium (Sigma) while 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 in a 5% CO_2 incubator (Shel Lab water-jacketed) at 37 °C in humidified atmosphere.

The cytotoxicity of the ligands and diorganotin complexes were determined by the Neutral Red cytotoxicity assay [24]. Firstly, the cultured cells were seeded in 96-well micro titer plate (Nunc) and allowed to adhere for 24 h before addition of the test samples. The cells were then treated with test samples at six different concentrations (0.1–100 μg/ml) and incubated for 72 h in a 5% CO_2 incubator at 37 °C. After incubation, the media was replaced with medium containing 50 μg/ml of Neutral Red and further incubated for three hours to allow for uptake of the vital dye into lysosomes of viable cells. The media was then removed and cells were washed with Neutral Red washing solution. The dye was eluted from the cells by adding 200 μg/ml of Neutral Red resorb solution and incubated for another 30 min with rapid agitation on a micro titer plate shaker (LT BioMax 500) at room temperature. The optical density (OD) was measured at 540 nm using a micro titer plate reader (Emax, Molecular Devices) at room temperature.

The assay was conducted in triplicate for all test samples. *Cis*-platin was used as positive control while wells without addition of any test sample were regarded as negative control. Cytotoxicity of each test sample is expressed as IC_{50}, which is the concentration of test sample that caused 50% inhibition or cell death averaged from three experiments. The IC_{50} values were obtained by non-linear regression using GraphPad Prism statistical software. The data are presented as mean ± SEM.

3. Results and discussion

3.1. Synthesis

The Schiff base ligands were prepared from stoichiometric reactions of 3-hydroxy-2-napthoic hydrazide with substituted 2-hydroxyacetophenone. The Schiff base ligands provided three acidic protons which enabled it to readily react with diorganotin oxides and diorganotin dichlorides as shown in Fig. 1. The diorganotin complexes were obtained in good yield and stable towards air and moisture.

3.2. IR Spectra

The IR data for the ligands and diorganotin complexes are presented in the Experimental section. Two sharp bands around 1600–1660 cm^{-1} region are attributed to ν(C=O) and ν(C=N), and are comparable to values reported for Schiff base ligands. In the complexes, the involvement of the azomethine nitrogen in coordination with tin atom weakens the C=N bond and leads to the lowering of the ν(C=N) to be in the region of 1590–1640 cm^{-1} [25–29]. The absence of the ν(C=O) band suggests the deprotonation of the enolic oxygens. In the spectra of ligands $\mathbf{H_2L1}$ and $\mathbf{H_2L2}$, a strong broad peak is observed at 3286 and 3279 cm^{-1} which can be attributed to the overlapping of ν(NH) and ν(OH). While, for the complexes, a smaller band around 3300–3450 cm^{-1} is observed, suggesting the presence of a hydroxyl functional group in its molecular structure.

3.3. NMR spectra

In the ^{1}H NMR spectral, the signals at 6.60–8.00 and 8.20–8.60 ppm are assigned to the aromatic protons of the ligands and diorganotin complexes. For the Schiff base ligands, a singlet signal around 12.30–12.90 ppm is assigned to the –NH– group and the disappearance of the signal in the spectral of the complexes indicates the engagement of the imine nitrogen atoms in complexation. Meanwhile, the strong sharp singlet at 11.35–11.50 ppm is assigned to the hydroxy protons [30,31]. The presence of a small signal in the region 11.40–12.10 ppm in the diorganotin complexes suggests that the phenoxy proton on the naphthalene ring does not participate in the coordination to the tin atom. The ^{1}H NMR chemical shifts of the methyl substituents on the azomethine carbon are found in around 2.44 ppm, while for the complexes, the chemical shifts are slightly downfield in the 2.50–2.90 ppm region.

The ^{13}C NMR spectra for the complexes show a significant downfield shift for the carbon resonances in comparison to the free Schiff base ligands. The signals of the azomethine carbons for the Schiff base ligands and the diorganotin complexes appear in the 160–170 ppm region [32–34] while the chemical shift for the methyl carbon appears in the 18–20 ppm region. The aromatic carbon resonances are assigned by two-dimensional proton-detected heteronuclear single bond chemical shift correlation (HSBC) using values corresponding to $^2J_{(C,H)}$ or $^3J_{(C,H)}$ between the carbons and protons, and DEPT (distortionless enhancement by polarization transfer) spectra.

The satellite signals due to the hydrogen-tin coupling and carbon-tin coupling are observed in most of the complexes except in diphenyltin, dibenzyltin, di(*o*-chlorobenzyl)tin and di(*p*-chlorobenzyl)tin derivatives. The calculated C–Sn–C angles of the diorganotin complexes are based on the Lockhart and Manders equation: θ(C–Sn–C) = 0.0161$|^2J(^{119}Sn–^1H)|^2$ −1.32 $|^2J(^{119}Sn–^1H)|$ + 133.4 [35,36], whereby the $^2J(^{119}Sn–^1H)$ value is obtained from the ^{1}H NMR spectra. Alternatively, the $^1J(^{119}Sn–^{13}C)$ coupling constants from the ^{13}C NMR spectra can be used to estimate the C–Sn–C an-

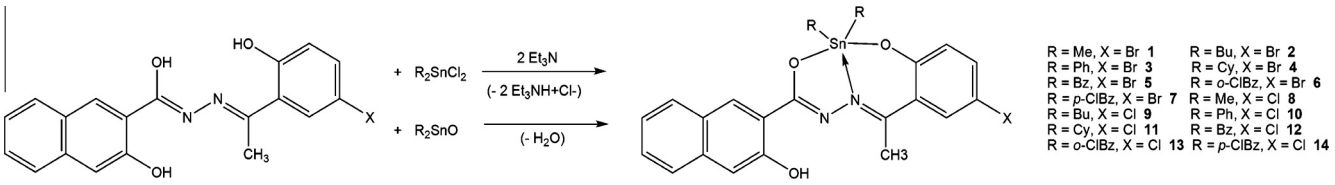

Fig. 1. Reaction scheme for the synthesis of Schiff base ligands with diorganotin dichlorides and diorganotin oxides.

gles of the complexes using the Lockhart's equation; θ(C-Sn-C) = [|^1J(^{119}Sn–^{13}C)| + 875]/11.4 [36]. Overall, the estimated C-Sn-C angles show slight deviation from the values obtained by X-ray crystallographic diffraction [21,22] but they correspond to the values reported for five-coordinate diorganotin complexes .

The presence of a single signal in the ^{119}Sn NMR spectral of the complexes confirms the formation of a single species [37,38]. The ^{119}Sn NMR chemical shifts of the dimethyltin complexes **1** and **8** are found around −176 ppm, dibutyltin complexes **2** and **9** at −216 ppm, and dicyclohexyltin complexes **4** and **11** at −283 ppm. The ^{119}Sn NMR chemical shifts for the dibenzyltin and substituted dibenzyltin complexes are found between −230 and −300 ppm while the ^{119}Sn NMR chemical shifts for the diphenyltin complexes **3** and **10** are found between −344 and −355 ppm. The ^{119}Sn NMR chemical shifts for dibenzyltin and substituted dibenzyltin complexes are found in the range of −230 to −297 ppm. The ^{119}Sn NMR chemical shifts ^1J(^{119}Sn–^{1}H) and ^1J(^{119}Sn–^{13}C) coupling values are in accordance with five-coordination tin center [39–41].

3.4. X-ray crystallography

{[1-(5-Bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), Me_2SnL1, **1**, {[1-(5-chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}-dimethyltin(IV), Me_2SnL2, **8** and {[1-(5-chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dicyclohexyltin(IV), Cy_2SnL2, **11**.

The crystallographic data and refinement details of compounds **1**, **8** and **11** are shown in Table 1 while the selected bond lengths and bond angles are given in Table 2. The molecular structures of **1**, **8** and **11** with the corresponding atomic numbering schemes are given in Figs. 2, 3 and 4.

The molecular structures show that both ligands, *(E)-N′*-[1-(5-bromo-2-hydroxyphenyl)-ethylidene]-3-hydroxy-2-naphthohydrazide (**H_2L1**) and *(E)-N′*-[1-(5-chloro-2-hydroxyphenyl)-ethylidene]-3-hydroxy-2-naphthohydrazide (**H_2L2**), are tridentate dibasic coordinating agent *via* its phenolic oxygen, imino nitrogen and enolic oxygens. The ligand is non-planar due to the steric requirements of the five and six-membered rings. The indices of the trigonality of the plane can be determined from the τ-value which is defined as $\tau = (\beta-\alpha)/60$, whereby α and β are the two largest donor-metal-donor angles in the five-coordinated environment. The τ-value for complexes **1** and **8** is 0.44, whereby the coordination should be nearly half-way between a trigonal–bipyramidal and square-pyramidal geometry. For complex **11**, the τ-value (0.26) indicates a distorted square-pyramidal geometry, whereby the equatorial position consists of two enolic oxygens and two cyclohexyl carbons with the azomethine nitrogen in the apical position [42–44]. The distortion from the ideal trigonal–bipyramidal or square pyramidal geometry of the complexes can also be observed from the deviation of the O(1)–Sn–O(2) angles (154.86°, 154.29° and 153.64°) from 180°.

The chelating planes O(2)–Sn(1)–N(1)–N(2)–C(8) and O(1)–Sn(1)–N(1)–C(7)–C(1)–C(2) in compound **11** are not planar and have an RMS deviation from planarity of 0.15 and 0.20 Å, respectively. The two rings form a dihedral angle of 17.9°. On the other hand, the O(2)–Sn(1)–N(1)–N(2)–C(8) and O(1)–Sn(1)–N(1)–C(7)–C(1)–C(2) planes in compounds **1** and **8** are rather planar, with a smaller dihedral angle of 4.0° and 4.2°, respectively.

The C_i–Sn(1)–C_i' angle increases along with the increase in size of the alkyl groups of the diorganotin moieties. For **1** and **8**,

Table 1
Crystallographic data of {[1-(5-bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), **1**, {[1-(5-chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), **8** and {[1-(5-chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dicyclohexyltin(IV), **11**.

Compound	**1**	**8**	**11**
Empirical formula	$C_{21}H_{19}BrN_2O_3Sn$	$C_{21}H_{19}ClN_2O_3Sn$	$C_{31}H_{35}ClN_2O_3Sn$
Formula weight	545.98	501.52	637.75
Crystal system	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	7.6760(1)	7.6725(1)	8.0138(1)
b (Å)	10.8469(1)	10.7337(2)	11.6732(1)
c (Å)	12.0039(1)	12.0195(2)	29.5049(3)
α (°)	85.419(1)	85.095(1)	90
β (°)	78.538(1)	78.769(1)	91.393(1)
γ (°)	79.196(1)	78.944(1)	90
V (Å^3)	961.216(17)	951.69(3)	2759.27(5)
Z	2	2	4
Calculated density (mg m^{-3})	1.886	1.750	1.535
μ (mm^{-1})	3.433	1.508	1.059
F(000)	536	500	1304
θ (°)	1.73–27.50	1.73–27.50	1.38–27.50
Reflections collected/unique (R_{int})	9184/4388 (0.015)	8957/4340 (0.020)	26129/6348 (0.033)
Maximum and minimum transmission	0.795 and 0.481	0.927 and 0.886	0.949 and 0.770
Data/restraints/parameters	4388/1/255	4340/0/257	6348/1/345
Goodness-of-fit on F	1.06	1.09	1.03
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.018, wR_2 = 0.047	R_1 = 0.025, wR_2 = 0.058	R_1 = 0.024, wR_2 = 0.052
R indices (all data)	R_1 = 0.020, wR_2 = 0.048	R_1 = 0.030, wR_2 = 0.060	R_1 = 0.030, wR_2 = 0.054
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.52 and −0.42	0.62 and −0.58	0.43 and −0.33

Table 2
Selected bond lengths (Å) and angles (°) for {[1-(5-bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), **1**, {[1-(5-chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), **8** and {[1-(5-chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dicyclohexyltin(IV), **11**.

	1	**8**	**11**
Bond lengths			
Sn(1)–O(1)	2.054(1)	2.059(3)	2.088(1)
Sn(1)–O(2)	2.132(1)	2.138(3)	2.200(1)
Sn(1)–N(1)	2.204(2)	2.201(4)	2.183(2)
Sn(1)–C_i	2.111(2)	2.122(4)	2.144(2)
Sn(1)–C_i'	2.111(2)	2.114(4)	2.156(2)
C(2)–O(1)	1.322(2)	1.320(6)	1.331(2)
C(8)–O(2)	1.291(2)	1.288(6)	1.289(2)
C(7)–N(1)	1.311(2)	1.326(6)	1.302(2)
C(8)–N(2)	1.320(2)	1.338(6)	1.326(2)
N(2)–O(3)	2.586(2)	2.560(7)	2.563(2)
Bond angles			
O(1)–Sn(1)–O(2)	154.86(6)	154.29(13)	153.64(5)
C_i–Sn(1)–C_i'	128.67(8)	127.66(19)	137.94(7)
N(1)–Sn(1)–C_i	122.94(7)	108.18(17)	107.95(6)
N(1)–Sn(1)–C_i'	108.07(7)	123.82(16)	113.23(7)

C_i refers to C_{ipso}.
C_i and C_i' for compounds **1** and **8** is C20 and C21 while C_i and C_i' for compound **11** is C20 and C26.

the C_i–Sn(1)–C_i' angles are 128.67(19)° and 127.66(19)° while for **11**, it is 137.94(7)°. The C–Sn–C angle of each complex shows a small degree of deviation from the values estimated using the coupling constants obtained from the NMR spectra.

The Sn(1)–O(1) and Sn(1)–O(2) bond lengths are in the range of 2.05–2.20 Å, which are lower than the sum of the van der Waals radii (3.69 Å). Whereas, the Sn(1)–N(1) bond length (2.204, 2.201 and 2.183 Å) is lower than the sum of the van der Waals radii (3.75 Å) indicating the presence of stable coordinative Sn–N bonds in the complexes. The Sn–C, Sn–O and Sn–N bond distances for the complexes are comparable to the values reported for similar five-coordinated diorganotin complexes. The complexes are stabilized by a strong intramolecular hydrogen bonding interactions between O(3)–H(3) and N(2) [**1**: O–H···N 2.586(2) Å, **8**: O–H···N 2.560(7) Å, and **11**: O–H···N 2.563(2) Å] and the values are comparable to those reported in literature [45–49].

3.5. Thermal properties

The thermogravimetric analysis of the complexes was carried out in the temperature range of 50–900 °C with a heating rate of 10 °C min^{-1}. All the diorganotin complexes are stable until after 120 °C. At temperatures above 120 °C, the TG curves show three steps of weight loss. The first decomposition in the temperature range of 120–250 °C involves the removal of the alkyl or aryl groups of the diorganotin moieties. Next, there is a rapid weight loss in the temperature range of 250–350 °C, followed by a gradual weight loss in the temperature range of 350–800 °C. The total decomposition of both the second and third weight losses may be due to the dissociation of the Schiff base ligands from the tin metal core [50,51]. Thermal decomposition continues until the final residue, SnO_2, is left.

3.6. Cytotoxic activity

The efficiency of the diorganotin compounds as anticancer drug has been tested *in vitro* on three human carcinoma cell lines, which were HT29, SKOV-3 and MCF7. The results of IC_{50} values of the Schiff base ligands and the diorganotin complexes are summarized in Table 3.

Generally, Schiff base ligands were found to display good cytotoxic activities towards all the cell lines, with IC_{50} below 8 μg/ml. The dimethyltin derivative of **H_2L1**, **1** possesses the highest cytotoxic activity among the tested diorganotins, with IC_{50} values ranging from 0.6 to 1.0 μg/ml against all the tested cell lines. The IC_{50} values obtained by the dimethyltin derivative, **1** are even better than the cytotoxicity of *cis*-platin, which is the positive reference standard in this study. The trend of the cytotoxic activities decreases in the following order: dibutyltin > dicyclohexyltin > dibenzyltin > di(*p*-chlorobenzyl)tin > di(*o*-chlorobenzyl)tin > diphenyltin derivatives. The diphenyltin, di(*o*-chlorobenzyl)tin and di(*p*-chlorobenzyl)tin derivatives show mild cytotoxic activities against HT29 cells. The diphenyltin derivative, **3** displays selectivity against SKOV-3 cells while the di(*o*-chlorobenzyl)tin and di(*p*-chlorobenzyl)tin derivatives, **6** and **7** show selectivity against MCF7 and SKOV-3 cells.

Among the **H_2L2** complexes, the dicyclohexyltin derivative **11** has very good cytotoxic activities in all the tested cell lines, with IC_{50} values below 1 μg ml^{-1}. Similarly, the dibutyltin derivative **9** shows good cytotoxic activities too, with IC_{50} values lower than the Schiff base ligands. The IC_{50} values of the two complexes are even better than the cytotoxicity of *cis*-platin, which is the positive reference standard in this study. However, the di(*o*-chlorobenzyl)tin derivative **13** hardly killed any cells in all the tested cell lines while the diphenyltin derivative **10** displays moderate activities only against the HT29 cell line. The di(*p*-chlorobenzyl)tin

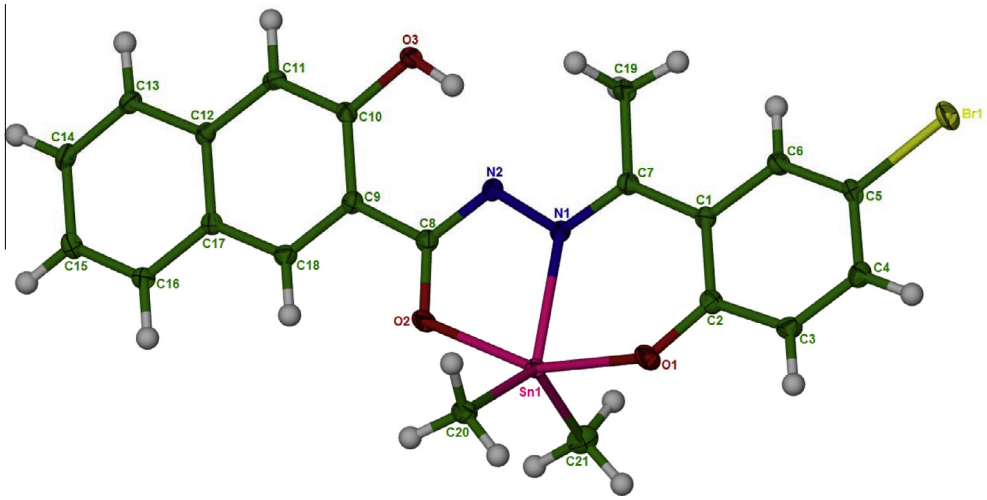

Fig. 2. Molecular structure and crystallographic numbering scheme for {[1-(5-bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), **1**.

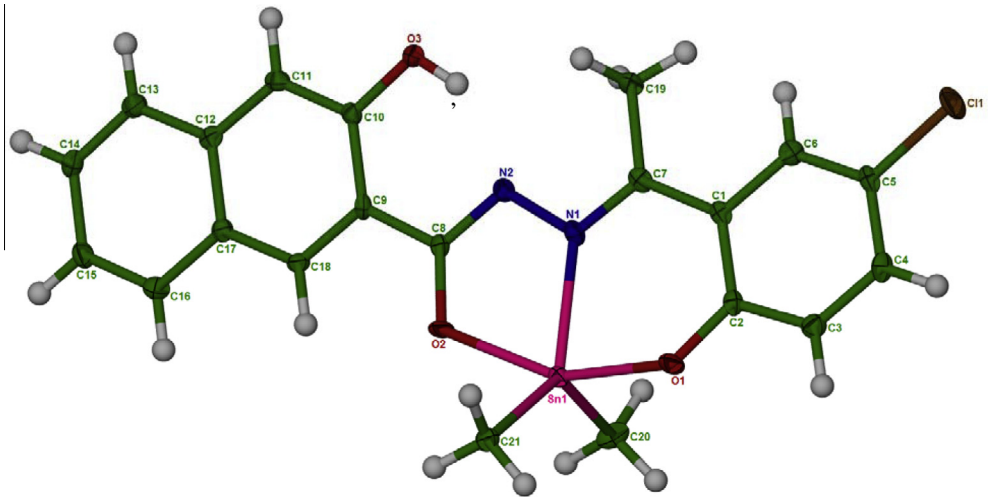

Fig. 3. Molecular structure and crystallographic numbering scheme for {[1-(5-chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), **8**.

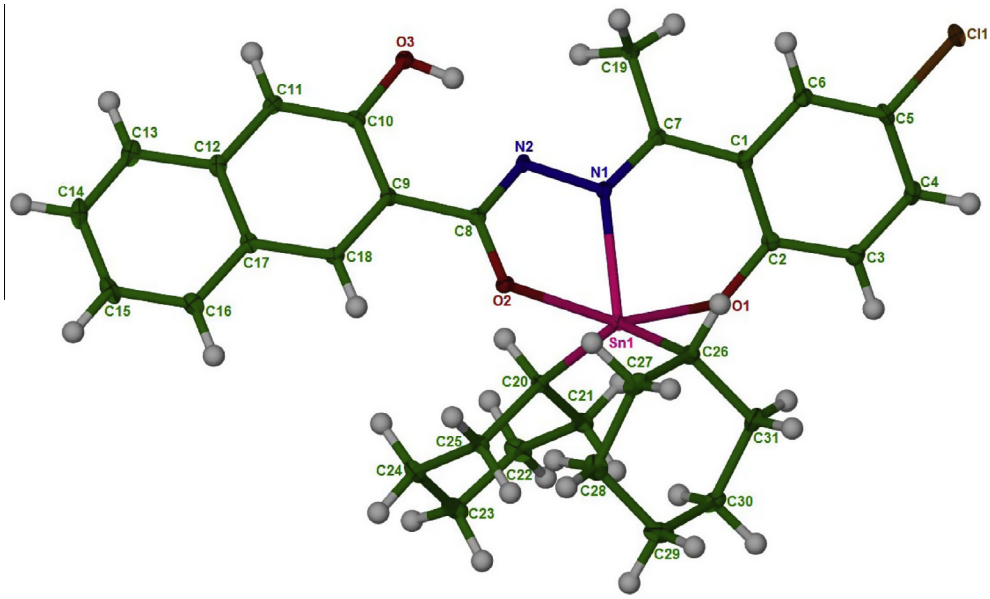

Fig. 4. Molecular structure and crystallographic numbering scheme for {[1-(5-chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dicyclohexyltin(IV), **11**.

derivative, **14** displays selectivity against MCF7 cells. The dimethyltin and dibenzyltin derivatives, **8** and **12** exhibit moderate activities against all the tested cell-lines.

Overall, the dimethyltin, dibutyltin and dicyclohexyltin derivatives show remarkable cytotoxic activities with IC_{50} values that are lower than those of the Schiff base ligands.

4. Conclusion

Several diorganotin complexes have been synthesized and characterized by various spectroscopic techniques. The diorganotin complexes are five-coordinated, as shown by the spectroscopic data and X-ray crystallographic diffraction. The results of the cytotoxic activities of the complexes are promising, whereby, {[1-(5-bromo-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dimethyltin(IV), **1** is most active among the diorganotin complexes of **H_2L1** ligand. For the diorganotin complexes of **H_2L2** ligand, {[1-(5-chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dibutyltin(IV), **9** and {[1-(5-chloro-2-oxidophenyl)ethylidene]-3-hydroxy-2-naphthohydrazidato}dicyclohexyltin(IV), **11** show good cytotoxic activities against all the tested cell lines. Thus, the above complexes can be considered as agents with potential anticancer activities, and can therefore be investigated for further stages of *in vitro* or *in vivo* anticancer studies.

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Appendix A. Supplementary material

CCDC 838875, CCDC 838874 and CCDC 838873 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2013.04.036.

Table 3
Cytotoxic activity (IC_{50} values) of Schiff base ligands and its diorganotin complexes against HT29, MCF7 and SKOV-3 cells.

Compounds	Cytotoxicity (IC_{50}) in μg/ml		
	HT29	MCF7	SKOV-3
H_2L1	5.5 ± 0	1.0 ± 0	8.0 ± 0.3
1	0.9 ± 0.1	0.6 ± 0	1.0 ± 0
2	6.0 ± 0	4.3 ± 0.3	0.5 ± 0
3	28.5 ± 0.5	29.3 ± 1.2	4.7 ± 0.6
4	4.3 ± 0.3	5.3 ± 0.6	3.3 ± 0
5	5.8 ± 0.3	8.8 ± 0.3	3.3 ± 0
6	41.7 ± 1.5	6.4 ± 0.1	8.8 ± 0.3
7	27.7 ± 3.1	5.0 ± 0	5.0 ± 0
H_2L2	7.3 ± 1.5	3.2 ± 0.1	6.4 ± 1.2
8	5.8 ± 0.3	8.0 ± 0	6.0 ± 0
9	3.0 ± 0	0.5 ± 0	0.6 ± 0.1
10	19.0 ± 0	5.7 ± 0.4	1.8 ± 0.3
11	0.7 ± 0	0.7 ± 0	0.3 ± 0
12	6.0 ± 0	6.7 ± 0.2	13.0 ± 0
13	100.0 ± 0	82.0 ± 1.7	>100
14	6.0 ± 0	0.5 ± 0	4.3 ± 0.3
Cis-platin[a]	5.0 ± 0	2.4 ± 0.6	1.4 ± 0

[a] *Cis*-platin was used as positive control.

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