Journal of Organometallic Chemistry 694 (2009) 2402–2408

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

# Synthesis, crystal structure and biological activities of four novel tetranuclear di-organotin(IV) carboxylates ☆

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ARTICLE INFO

*Article history:*
Received 5 January 2009
Received in revised form 9 March 2009
Accepted 16 March 2009
Available online 21 March 2009

*Keywords:*
Organotin(IV) compound
Synthesis
Crystal structure
Trigonal bipyramidal geometry
Biological activities

ABSTRACT

Four complexes: $[Bu_2(L_1)SnOSn(L_1)Bu_2]_2$ (**1**), $[Bu_2(L_2)SnOSn(L_2)Bu_2]_2$ (**2**), $[Bu_2(L_3)SnOSn(L_3)Bu_2]_2$ (**3**), and $[Bu_2(L_4)SnOSn(L_4)Bu_2]_2$ (**4**), (**$HL_1$** = 2-(4-methylbenzoyl)benzoic acid, **$HL_2$** = 2-(2,4-diethylbenzoyl)benzoic acid, **$HL_3$** = 2-(4-chlorobenzoyl)benzoic acid, **$HL_4$** = 2-(4-isopropylbenzoyl)benzoic acid) have been prepared and structurally characterized by means of elemental analysis and vibrational, $^1$H NMR and FT-IR spectroscopies. The crystal structures of all complexes have been determined by X-ray crystallography. Three distannoxane rings are present to the dimeric tetraorganodistannoxane of planar ladder arrangement. Each structure is centro-symmetric and features a central rhombus $Sn_2O_2$ unit with two additional tin atoms linked at the O atoms. Complex **1** exhibited good antibacterial and antitumor activities and have a potential to be used as drugs.



## 1. Introduction

The interest in organotin compounds in general and organotin carboxylates in particular continues to grow because of their biological activity and potential antineoplastic and antituberculosis agents [1–11]. Among those compounds dibutyltin derivatives have displayed both higher activity and lower toxicity [12]. So the antitumor activity of many compounds of the type $[(RCOO-Bu_2Sn)_2O]_2$ and $(RCOO)_2Bu_2Sn$ has been studied [13,14]. This may yield new leads for the development of antitumor drugs that may possess lower toxicity than platinum compounds [2]. Diorganotin carboxylates derived from carboxylic acids are among the most extensively studied class of compounds owing to their rich structural chemistry. The diverse structural motifs known in this family of compounds are attributed to the ambidentate character of the carboxylate ligands [15]. Steric and electronic attributes of organic substituents on tin and/or the carboxylate moiety impart significant influence on the structural characteristics in tin carboxylates. Therefore, synthesis of new organotin carboxylates with different structural features will be beneficial in the development of pharmaceutical organotin and in other properties and application.

Keeping in view the structural and biological diversity of organotin carboxylates and in connection with our interest in coordination chemistry of organotin compounds with different carboxylic acids, herein we report the synthesis, characterization and biological studies of tin(IV) derivatives with some substituted benzoic acids to widen their scope in biological applications. Complexes **1**–**4** have been prepared by azeotropic removal of $H_2O$ from the reaction (in benzene) of the di-*n*-butyltin oxide with **$HL_1$**–**$HL_4$** in a molar ratio of 1:1, respectively (where, **$HL_1$** = 2-(4-methylbenzoyl)benzoic acid, **$HL_2$** = 2-(2,4-diethylbenzoyl)benzoic acid, **$HL_3$** = 2-(4-chlorobenzoyl)benzoic acid, **$HL_4$** = 2-(4-isopropylbenzoyl)benzoic acid). All complexes have been structurally characterized by means of elemental analysis and vibrational, $^1$H NMR and FT-IR spectroscopies. Single-crystal X-ray diffraction studies revealed that all these complexes contain a centrosymmetric $Sn_2O_2$ core which is connected to two *exo*-cyclic tin atoms via $\mu_3$-oxo O-atoms to give a $R_8Sn_4O_2$ central unit. The antibacterial and antitumor activities of complex **1** have also been preliminary tested in vitro. These are the first reported complexes and crystal structures of a novel class of substituted benzoato-tetraalkyl-distannoxanes.

## 2. Experimental

### 2.1. General and instrumental

#### 2.1.1. General

The reagents were used as supplied while the solvents were purified according to standard procedures [16]. Melting points were determined in open capillaries and were not corrected. Ele-

☆ Foundation item: Project (20873181) supported by the NSFC and Project (2007AA06Z214) supported by the high-tech Research and Development Programm of China; Project (ts20070704) supported by Taishan Scholars Construction Engineering.

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doi:10.1016/j.jorganchem.2009.03.025

mental analyses were carried out on a Perkin–Elmer PE 2400 CHN instrument and gravimetric analysis for Sn. $^1$H NMR spectra were recorded in $CDCl_3$ on a Varian Mercury 300 MHz spectrometer. Infrared spectra (KBr pellets) were recorded on an Alpha Centauri FI/IR spectrometer (400–4000 $cm^{-1}$ range). The ligands **$HL_1$**, **$HL_2$**, **$HL_3$** and **$HL_4$** were prepared by a modified literature method [17].

### 2.2. X-ray crystallography

Crystals of **1**, **2**, **3** and **4** were grown by slow evaporation of ethanol solution at room temperature. The colorless crystals were mounted on a sealed tube and used for data collection. Single-crystal X-ray diffraction data for these complexes were recorded on a Bruker CCD Area Detector diffractometer by using the $\varphi/\omega$ scan technique with Mo k$\alpha$ radiation ($\lambda$ = 0.71073 Å). Absorption corrections were applied by using multiscan techniques [18]. The structures were solved by direct methods with SHELXS-97 [19] and refined by full-matrix least-squares with SHELXL-97 [20] within WINGX [21]. All nonhydrogen atoms were refined with anisotropic temperature parameters, hydrogen atoms were refined as rigid groups. A summary of the crystal data, experimental details and refinement results are listed in Table 1.

### 2.3. Biological studies

#### 2.3.1. Antibacterial tests

The antibacterial activities were determined by using the agar well-diffusion method [22]. Broth culture medium was prepared by mixing 10 g of albumin, 3 g of beef cream, 5 g of sodium chloride and 1000 mL distilled water at 37 °C. Five milliliters of broth culture medium was poured into the Petri-dishes and allowed to solidify. 0.2 mL of broth culture medium containing approximately $10 \times 10^6$ CFU/mL of Colon or Hay bacillus was uniformly plated on the surface of the Petri-dishes prepared before. Then three holes of 3 mm diameter were made carefully and these were completely filled with the test solutions (concentration is 200 μg/mL in ethanol), other holes containing ethanol and the reference antibacterial drug served as negative and positive controls, respectively. After the bacterium was incubated for 24 h at ca. 37 °C, the diameter of the inhibiting area around each hole was estimated, which is described as the inhibiting effect against bacteria [23]. The average of three diameters was calculated for each sample.

#### 2.3.2. MTT assay

Hela cell lines were grown in vitro in culture media containing 10% NCS, 1% HEPES and 1% RPMI1640 in a 5% $CO_2$ incubator at 37 °C. The effects of di-*n*-butyltin oxide and complex **1** on cell growth were evaluated using the MTT assay [24]. A total of $2 \times 10^3$ cells were seeded in the wells of 96-well plate and cultured for 24 h. Thereafter, the cells were treated with various concentrations of di-*n*-butyltin oxide and complex **1** for 24 h. After exposure to the drug, the MTT assay was carried out with Tetra Color One. All experiments were performed at least three times and the mean percentage of proliferation was calculated.

### 2.4. Synthesis

#### 2.4.1. Synthesis of 2-(4-methylbenzoyl)benzoic acid (**$HL_1$**)

**$HL_1$** was synthesized according to the modified literature method [17]. Benzene-1,2-dicarboxylic anhydride (5.92 g, 0.04 mol), anhydrous aluminum chloride (10.67 g, 0.08 mol) and dry toluene (22.11 g, 0.24 mol) were added into a three-neck flask. The reaction mixture was stirred for 4 h at 50 °C, then poured into a beaker. After hydrolization with cooled aqueous HCl (20%), a brownish solid was precipitated, which collected by filtration. Then the solid was dissolved by aqueous NaOH (20%), and the surplus toluene was removed by hydrodistillation. The distilled fluid was acidified by 20% HCl, and the crud product was precipitated, then collected

**Table 1**
Crystal data and details of structure refinement parameters for complex **1**, **2**, **3**, **4**.

| Complex | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| Empirical formula | $C_{92}H_{116}O_{14}Sn_4$ | $C_{104}H_{140}O_{14}Sn_4$ | $C_{88}H_{104}Cl_4O_{14}Sn_4$ | $C_{100}H_{132}O_{14}Sn_4$ |
| Formula weight | 1920.69 | 2089.00 | 2002.35 | 2032.90 |
| $T$ (K) | 293(2) | 293(2) | 293(2) | 293(2) |
| Crystal size (mm) | 0.346 × 0.317 × 0.249 | 0.351 × 0.302 × 0.261 | 0.357 × 0.277 × 0.094 | 0.363 × 0.312 × 0.275 |
| Wavelength (Å) | Mo Kα 0.71073 | Mo Kα 0.71073 | Mo Kα 0.71073 | Mo Kα 0.71073 |
| Crystal system | Triclinic | Monoclinic | Triclinic | Triclinic |
| space group | $P\bar{1}$ | $P2(1)/n$ | $P\bar{1}$ | $P\bar{1}$ |
| Unit cell dimensions | | | | |
| $a$ (Å) | 11.586(3) | 14.5876(9) | 11.4222(6) | 12.9345(8) |
| $b$ (Å) | 14.718(4) | 13.8977(9) | 14.8195(8) | 14.3545(9) |
| $c$ (Å) | 14.892(4) | 25.1798(15) | 14.8379(8) | 14.6789(9) |
| α (°) | 68.274(4) | 90.00 | 68.1170(10) | 71.4700(10) |
| $\beta$ (°) | 71.677(4) | 95.9190(10) | 72.9600(10) | 77.9400(10) |
| $\gamma$ (°) | 76.938(4) | 90.00 | 77.9620(10) | 69.2730(10) |
| $V$ (Å$^3$) | 2222.1(10) | 5077.6(5) | 2214.3(2) | 2402.5(3) |
| $Z$ | 1 | 2 | 1 | 1 |
| $D_{calc.}$ (mg m$^{-3}$) | 1.435 | 1.366 | 1.502 | 1.405 |
| Absorption coefficient, $\mu$ (mm$^{-1}$) | 1.171 | 1.031 | 1.295 | 1.088 |
| $F$(000) | 980 | 2152 | 1012 | 1044 |
| Scan mode | $\omega$ | $\omega$ | $\omega$ | $\omega$ |
| $\theta$ Range for data collection (°) | 1.50, 26.08 | 1.55, 26.05 | 1.49, 26.02 | 1.47, 26.03 |
| Reflections collected/unique [$R_{(int)}$] | 12954/8581 [0.0771] | 28061/9994 [0.0583] | 12432/8504 [0.0725] | 13527/9219 [0.0182] |
| Data/parameters | 8581/0/504 | 9994/0/550 | 8504/0/496 | 9219/3/532 |
| Ranges of $h$, $k$, $l$ | $-14 \leqslant h \leqslant 12$, $-13 \leqslant k \leqslant 18$, $-18 \leqslant l \leqslant 18$ | $-17 \leqslant h \leqslant 18$, $-17 \leqslant k \leqslant 17$, $-29 \leqslant l \leqslant 31$ | $-14 \leqslant h \leqslant 12$, $-18 \leqslant k \leqslant 16$, $-18 \leqslant l \leqslant 14$ | $-15 \leqslant h \leqslant 15$, $-17 \leqslant k \leqslant 16$, $-13 \leqslant l \leqslant 18$ |
| Final $R$ induces [$I > 2\sigma(I)$] | $R_1$ = 0.0535, $wR_2$ = 0.0808 | $R_1$ = 0.0405, $wR_2$ = 0.0775 | $R_1$ = 0.0344, $wR_2$ = 0.0908 | $R_1$ = 0.0487, $wR_2$ = 0.1202 |
| $R$ indices (all data) | $R_1$ = 0.1153, $wR_2$ = 0.0976 | $R_1$ = 0.0674, $wR_2$ = 0.0853 | $R_1$ = 0.0384, $wR_2$ = 0.0937 | $R_1$ = 0.0653, $wR_2$ = 0.1324 |
| Goodness-of-fit (GOF) on $F^2$ | 0.784 | 0.907 | 1.027 | 1.021 |
| Largest difference in peak/hole (e Å$^{-3}$) | 0.755 and −0.958 | 0.787 and −0.626 | 1.347 and −1.570 | 1.375 and −0.624 |

by filtration and washed with water. The pure product was obtained by recrystallization from ethanol as a white powder, yield: 67%, m.p. 145–146 °C. IR (KBr, $cm^{-1}$): $\nu$(O–H···O) 3443; $\nu_{as}$(COO) 1710, 1680; $\nu_{sym}$(COO) 1458, 1410; $^1$H NMR($CDCl_3$, $\delta$): 2.39 (s, 3H, –$CH_3$), 7.19–7.64 (m, 8H, Ar–H), 11.65 (s, 1H, –COOH). Anal. Calc. for $C_{15}H_{12}O_3$ (240.254 g $mol^{-1}$): C, 74.99; H, 5.03. Found: C, 74.47; H, 5.09%.

*2.4.2. Synthesis of 2-(2,4-diethylbenzoyl)benzoic acid (**$HL_2$**)*

**$HL_2$** was synthesized by the same procedure as **$HL_1$** with benzene-1,2-dicarboxylic anhydride (5.92 g, 0.04 mol) and anhydrous aluminum chloride (10.67 g, 0.08 mol) and dry 1,3-diethylbenzene (32.21 g, 0.24 mol). The product was white powder, yield: 56%, m.p. 100–102 °C. IR (KBr, $cm^{-1}$): $\nu$(O–H···O) 3436; $\nu_{as}$(COO) 1667, 1606; $\nu_{sym}$ (COO) 1588, 1564; $^1$H NMR($CDCl_3$, $\delta$): 1.27(t, 6H, –$CH_3$), 2.63–2.71 (m, 4H, –$CH_2$–), 7.07–7.43 (m, 7H, –ArH), 11.65 (s, –COOH). Anal. Calc. for $C_{18}H_{18}O_3$ (282.334 g $mol^{-1}$): C, 76.57; H, 6.43. Found: C, 76.61; H, 6.21%.

*2.4.3. Synthesis of 2-(4-chlorobenzoyl)benzoic acid (**$HL_3$**)*

**$HL_3$** was synthesized by the same procedure as **$HL_1$** with benzene-1,2-dicarboxylic anhydride (5.92 g, 0.04 mol) and anhydrous aluminum chloride (10.67 g, 0.08 mol) and dry 1-chlorobenzene (29.41 g, 0.24 mol). The product was white powder, yield: 54%, m.p. 118–120 °C. IR (KBr, $cm^{-1}$): $\nu$(O–H···O) 3443 $cm^{-1}$; $\nu_{as}$(COO) 1678, 1586; $\nu_{sym}$(COO) 1485, 1426; $\nu$(C–Cl)845; $^1$H NMR($CDCl_3$, $\delta$): 7.6–8.2 (m, 8H, Ar–H), 113.3 (s, 1H, –COOH). Anal. Calc. for $C_{14}H_9O_3Cl$ (260.672 g $mol^{-1}$): C, 64.51; H, 3.48. Found: C, 64.23; H, 3.51%.

*2.4.4. Synthesis of 2-(4-isopropylbenzoyl)benzoic acid (**$HL_4$**)*

**$HL_4$** was synthesized by the same procedure as **$HL_1$** with benzene-1,2-dicarboxylic anhydride (5.92 g, 0.04 mol) and anhydrous aluminum chloride (10.67 g, 0.08 mol) and dry cumene (28.85 g, 0.24 mol). The product was white powder, yield: 63%, m.p. 118–120 °C. IR (KBr, $cm^{-1}$): $\nu$(O–H···O) 3440 $cm^{-1}$; $\nu_{as}$(COO) 1700, 1680; $\nu_{sym}$(COO) 1450, 1410; $^1$H NMR ($CDCl_3$, $\delta$): 1.281 (*d*, *J* = 6.9, 6H, –$CH_3$), 2.91–3.02 (m, 1H, Ar–$CHMe_2$), 7.1–7.7 (m, 8H, Ar–H), 11.65 (s, 1H, –COOH). Anal. Calc. for $C_{17}H_{16}O_3$ (268.307 g $mol^{-1}$): C, 76.10; H, 6.01. Found: C, 75.97; H, 5.81%.

*2.4.5. Synthesis of $[Bu_2(L_1)SnOSn(L_1)Bu_2]_2$ (**1**)*

To a suspension of di-*n*-butyltin oxide (0.249 g, 1 mmol) in dry benzene (30 ml) was added **$HL_1$** (0.240 g, 1 mmol). The mixture was heated under reflux for 10 h in a Dean-Stark apparatus for azeotropic removal of the water formed in the reaction. After cooling down to room temperature, the solution was filtered and the solvent of the filtrate was gradually removed by evaporation under vacuum until solid product was obtained. The solid was then recrystallized from ethanol to give colorless crystals of complex **1**. Yield: 61.4%, m.p. 186–187 °C. Anal. Calc. for $C_{92}H_{116}O_{14}Sn_4$ (1920.737 g $mol^{-1}$): C, 57.53; H, 6.09; Sn, 24.72. Found: C, 57.46; H, 6.02; Sn, 24.69%. IR (KBr, $cm^{-1}$): $\nu$(C–H) 2956, 2927, 2869; $\nu_{as}$(-COO) 1666, 1525; $\nu_{sym}$(COO) 1400, 1350; $\nu$(Sn–O–Sn) 487, 425; $\nu$(Sn–C) 544 $cm^{-1}$. $^1$H NMR ($CDCl_3$, ppm): 0.74 (t, 24H, *J* = 6.9, –$CH_3$), 1.07–1.30 (m, 48H, $SnCH_2CH_2CH_2$–), 2.37 (S, 12H, Ar–$CH_3$), 7.2–7.7 (m, 32H, Ar–H).

*2.4.6. Synthesis of $[Bu_2(L_2)SnOSn(L_2)Bu_2]_2$ (**2**)*

Complex **2** was synthesized by the same procedures as **1** with di-*n*-butyltin oxide (0.249 g, 1 mmol) and **$HL_2$** (0.282 g, 1 mmol). The product was colorless crystals, yield: 53.2%, m.p. 106–108 °C. Anal. Calc. for $C_{104}H_{140}O_{14}Sn_4$ (2089.056 g $mol^{-1}$): C, 59.79; H, 6.75; Sn, 22.73. Found: C, 59.48; H, 6.87; Sn, 22.69%. IR (KBr, $cm^{-1}$): $\nu$(C–H), 2958, 2927, 2869; $\nu_{as}$(COO) 1675, 1515; $\nu_{sym}$(COO) 1400, 1354; $\nu$(Sn–O–Sn) 475, 423; $\nu$(Sn–C) 562 $cm^{-1}$. $^1$H NMR ($CDCl_3$, ppm): 0.75–0.82 (t, 24H, *J* = 6.8, –$CH_2CH_2CH_2$–$CH_3$), 1.07–1.30 (m, 48H, $SnCH_2CH_2CH_2$–), 2.61–2.68 (m, 16H, Ar–$CH_2$–), 1.13–1.18 (m, 24H, Ar–$CH_2$–$CH_3$), 7.1–7.8 (m, 28H, Ar–H).

*2.4.7. Synthesis of $[Bu_2(L_3)SnOSn(L_3)Bu_2]_2$ (**3**)*

Complex **3** was synthesized by the same procedures as **1** with di-*n*-butyltin oxide (0.249 g, 1 mmol) and **$HL_3$** (0.261 g, 1 mmol). The product was colorless crystals, yield: 51%, m.p. 158–159 °C. Anal. Calc. for $C_{88}H_{104}Cl_4O_{14}Sn_4$ (2002.410 g $mol^{-1}$): C, 52.78; H, 5.24; Sn, 23.71. Found: C, 52.46; H, 5.29; Sn, 23.69%. IR (KBr, $cm^{-1}$): $\nu$(C–H) 2956, 2868; $\nu_{as}$(COO) 1675, 1520; $\nu_{sym}$(COO) 1450, 1395; $\nu$(Sn–O–Sn) 470, 420; $\nu$(Sn–C) 541 $cm^{-1}$; $\nu$(C–Cl) 845 $cm^{-1}$. $^1$H NMR ($CDCl_3$, ppm): 0.83 (t, 24H, *J* = 6.7, –$CH_3$), 1.31–1.51 (m, 48H, $SnCH_2CH_2CH_2$–), 7.5–7.9 (m, 32H, Ar–H).

*2.4.8. Synthesis of $[Bu_2(L_4)SnOSn(L_4)Bu_2]_2$ (**4**)*

Complex **4** was synthesized by the same procedures as **1** with di-*n*-butyltin oxide (0.249 g, 1 mmol) and **$HL_4$** (0.268 g, 1 mmol). The product was colorless crystals, yield: 56%, m.p. 175–177 °C. Anal. Calc. for $C_{100}H_{132}O_{14}Sn_4$ (2032.950 g $mol^{-1}$): C, 59.08; H, 6.54; Sn, 23.36. Found: C, 59.03; H, 6.87; Sn, 23.28%. IR (KBr, $cm^{-1}$): $\nu$(C–H) 2958, 2926, 2869; $\nu_{as}$(COO) 1616, 1586; $\nu_{sym}$(COO) 1475, 1452; $\nu$(Sn–O–Sn) 490, 430; $\nu$(Sn–C), 570 $cm^{-1}$. $^1$H NMR ($CDCl_3$, ppm): 0.67–0.87 (t, 24H, *J* = 6.8, –$CH_3$), 1.23–1.38 (m, 48H, $SnCH_2CH_2CH_2$–), 2.90–2.94 (m, 4H, Ar–CH–$Me_2$), 7.2–7.7 (m, 32H, Ar–H).

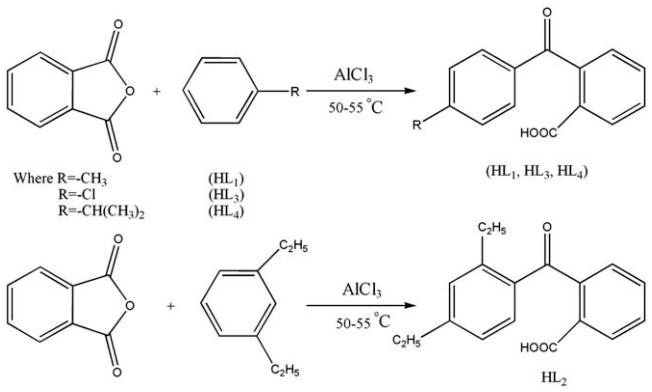
## 3. Result and discussion

### 3.1. Synthetic aspects

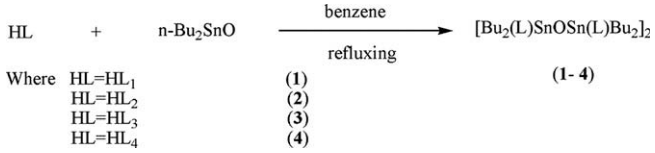
Ligands **$HL_1$**–**$HL_4$** were synthesized according to Friedel–Crafts acylation from benzene-1,2-dicarboxylic anhydride and the substituted aromatic compounds in the presence of anhydrous aluminum chloride, Scheme 1. Complexes **1**–**4** were obtained by azeotropic removal of $H_2O$ from the reaction (in benzene) between the di-*n*-butyltin oxide and **$HL_1$**–**$HL_4$** in a molar ratio of 1:1, respectively, Scheme 2.

### 3.2. IR spectra

Comparing the IR spectra of the free ligands **$HL_1$**–**$HL_4$** with complexes **1**–**4**, the bands at 3100–3550 $cm^{-1}$ which appear in the spectra of the free ligands as the $\nu$(O–H) vibration, are absent in those of complexes **1**–**4**, thus indicating metal-ligand bond formation through these sites. The $\nu_{as}$(COO) and $\nu_{sym}$(COO) bands appear at 1675–1515 $cm^{-1}$ and 1475–1350 $cm^{-1}$, respectively. The differ-




**Scheme 1.** The reaction scheme for synthesis of **$HL_1$**, **$HL_2$**, **$HL_3$** and **$HL_4$**.




**Scheme 2.** The reaction scheme for synthesis of **1**, **2**, **3** and **4**.

ences, $\Delta[\nu_{as}(COO)-\nu_{sym}(COO)]$ between these frequencies are close to that found for monodentate (266 $cm^{-1}$ for **1**, 275 $cm^{-1}$ for **2** and 225 $cm^{-1}$ for **3**) and bridging bidentate carboxylto groups (175 $cm^{-1}$ for **1**, 161 $cm^{-1}$ for **2** and 125 $cm^{-1}$ for **3**). The differences between these two bands for **4**, i.e. 141 and 134 $cm^{-1}$ is close to that found for bridging bidentate carboxylato groups [25,26]. This is totally consistent with the X-ray structures. Two bands at 490–470 and 430–420 $cm^{-1}$, are assigned to $\nu_{as,sym}(SnO)_2$, indicating nonlinear O–Sn–O moieties, while the bands at 543–562 $cm^{-1}$ are attribute to $\nu$(Sn–C) stretching modes [26,27].

### 3.3. $^1$H NMR spectra

The $^1$H NMR spectra of the complexes **1–4** are given in Section 2. In the $^1$H NMR spectra of ligands, the COOH group resonance appear at 11–12 ppm. Whereas this resonance disappear when the carboxyl group participated in coordination to the Sn atoms in complexes. The *n*-butyl protons in the complexes show a multiple resonance due to $-CH_2-CH_2-CH_2-$ skeleton in the range of 1.07–1.51 ppm and clear triple due to the terminal methyl groups at 0.67–0.87 ppm, respectively. It is shown that the chemical shifts of the protons on the phenyl groups of complexes **1**–**4** exhibit signals at about 7.1–7.9 ppm as multiplets.

### 3.4. Crystal structures

#### 3.4.1. Crystal structures of $\{[n\text{-}Bu_2Sn(L_1)_2]_2O\}_2$ (**1**), $\{[n\text{-}Bu_2Sn(L_2)_2]_2O\}_2$ (**2**) and $\{[n\text{-}Bu_2Sn(L_3)_2]_2O\}_2$ (**3**)

The molecular structures of **1**, **2** and **3** are shown in Figs. 1–3, and selected bond distances and angles are listed in Tables 2–4, respectively. Each of the three structures is centrosymmetric about a $Bu_4Sn_2O_2$ core. Attached to each bridging oxygen atom is an *exo*-cyclic $Bu_2Sn$ unit leading to a three-coordinate O atom. Further connections between the tin atoms arise as a result of bridging carboxylate ligands which form experimentally equivalent Sn–O bonds distances to the *endo*- and *exo*-cyclic tin atoms, i.e. Sn(1)–O(2) 2.275(4) Å and Sn(2)–O(1) 2.284(4) Å for **1**, Sn(2A)–O(4A) 2.280(3) Å and Sn(1)–O(5A) 2.277(3) Å for **2** and Sn(1)–O(1) 2.2871(19) Å and Sn(2A)–O(2) 2.288(2) Å for **3**. The remaining independent carboxylate ligand coordinates in the monodentate mode to the *exo*-cyclic tin atom exclusively with Sn(2)–O(5) 2.174(4) Å for **1**, Sn(1)–O(1) 2.183(2) Å for **2** and Sn(2)–O(4) 2.170(2) Å for **3**, respectively. This configuration leads to five-coordinate tin centers, each existing in a distorted trigonal bipyramidal geometry [axial angles: O(2)–Sn(1)–O(7A) 162.45(15)° and O(1)–Sn(2)–O(5) 168.30(17)° for **1**; O(4)–Sn(2)–O(7) 164.13(9)° and O(1)–Sn(1)–O(5A) 166.62(10)° for **2**; O(1)–Sn(1)–O(7) 163.11(7)° and O(4)–Sn(2)–O(2A) 168.33(7)° for **3**].

Distortions from the ideal geometries may be traced, in part, to the presence of close intramolecular Sn···O interactions. Thus, the centrosymmetrically related O(5A) atom forms a contact of 2.916 Å with the Sn(1) atom, which opens up the C(51)–Sn(1)–C(61) angle to 142.2(3)° from the ideal angle of 120°, and an interaction of 2.847 Å between Sn(2) and O(4) atoms results in the expansion of the C(81)–Sn(2)–C(71) angle to 141.7(3)° in complex **1**. Similarly, the same Sn···O interactions were observed to exist in both **2** and **3**. Whereas the intramolecular Sn···O contacts mentioned above are well within the van der Waals distances for these atoms,

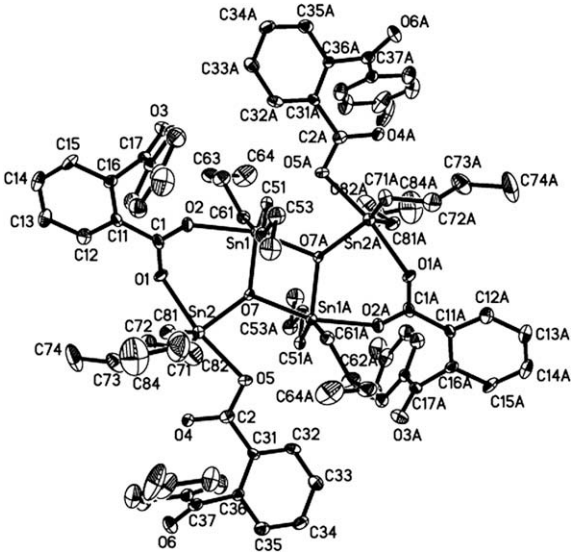



**Fig. 1.** Perspective view of **1** showing the atomic numbering scheme.

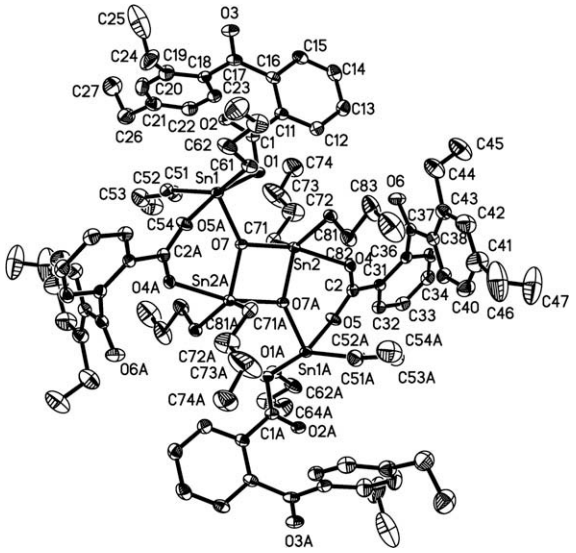



**Fig. 2.** Perspective view of **2** showing the atomic numbering scheme.

the relatively large separations and the minor perturbations from the ideal trigonal bipyramidal geometries indicate that these interactions must be considered as weak [28]. The molecular structures of **1**, **2** and **3** conform to the common structural motif found for compounds with the general formula $\{[R_2Sn(O_2CR')_2]_2O\}_2$ [29].

#### 3.4.2. Crystal structures of $\{[n\text{-}Bu_2Sn(L_4)_2]_2O\}_2$ (**4**)

The molecular structure of **4** is shown in Fig. 4, selected bond distances and angles are listed in Table 5. Complex **4** is also a centro-symmetric dimer built up around the planar cyclic $Sn_2O_2$ unit. The two oxygen atoms O(7) and O(7A) are triply bridging, each linking one *exo*-cyclic (Sn(1) or Sn(1A)) and two *endo*-cyclic (Sn(2) and Sn(2A)) atoms. Additional links between the *exo*- and *endo*-cyclic tin centers Sn(1) and Sn(2), respectively, are provided by four bidentate bridging carboxylate ligands. The Sn–O bond distances involving the bridging carboxylate ligands differ by 0.174 and 0.112 Å indicating asymmetrical bridges; the variations in the C–O bond distances are much less and suggest charge delocalization over the carboxylato group COO. The coordination number around each tin is five for Sn(1) and six for Sn(2), respectively. The

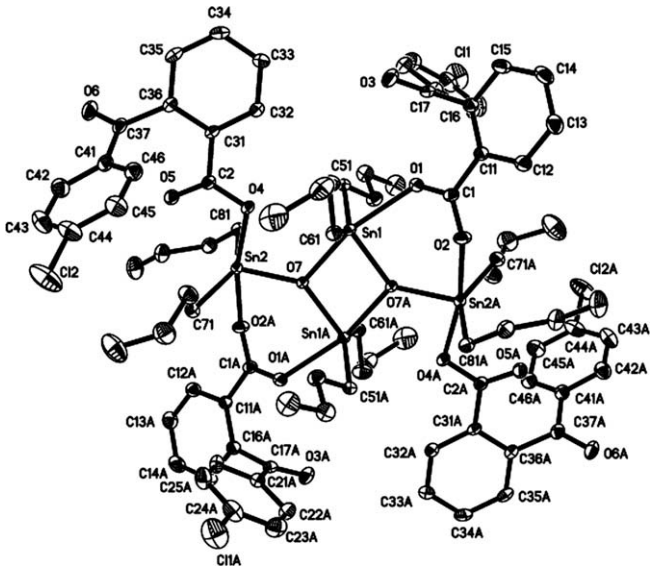



**Fig. 3.** Perspective view of **3** showing the atomic numbering scheme.

**Table 2**
Selected bond lengths (Å) and bond angles (°) for complex **1**.

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Sn(1)–O(7) | 2.029(4) | Sn(2)–O(1) | 2.284(4) |
| Sn(1)–C(51) | 2.106(6) | O(1)–C(1) | 1.265(8) |
| Sn(1)–C(61) | 2.107(6) | O(2)–C(1) | 1.247(8) |
| Sn(1)–O(7)#1 | 2.170(4) | O(3)–C(17) | 1.211(7) |
| Sn(1)–O(2) | 2.275(4) | O(4)–C(2) | 1.251(8) |
| Sn(2)–O(7) | 2.035(4) | O(5)–C(2) | 1.290(7) |
| Sn(2)–C(81) | 2.112(7) | O(6)–C(37) | 1.220(8) |
| Sn(2)–C(71) | 2.147(8) | O(7)–Sn(1)#1 | 2.170(4) |
| Sn(2)–O(5) | 2.174(4) | | |
| *Bond angles* | | | |
| O(7)–Sn(1)–C(51) | 112.6(2) | O(7)–Sn(2)–O(1) | 88.70(16) |
| O(7)–Sn(1)–C(61) | 104.6(2) | C(81)–Sn(2)–O(1) | 88.6(2) |
| C(51)–Sn(1)–C(61) | 142.2(3) | C(71)–Sn(2)–O(1) | 83.4(3) |
| O(7)–Sn(1)–O(7)#1 | 74.86(18) | O(5)–Sn(2)–O(1) | 168.30(17) |
| C(51)–Sn(1)–O(7)#1 | 97.0(2) | C(1)–O(1)–Sn(2) | 125.1(4) |
| C(61)–Sn(1)–O(7)#1 | 99.1(2) | C(1)–O(2)–Sn(1) | 125.2(5) |
| O(7)–Sn(1)–O(2) | 88.83(16) | C(2)–O(5)–Sn(2) | 108.7(4) |
| C(51)–Sn(1)–O(2) | 83.1(2) | Sn(1)–O(7)–Sn(2) | 132.7(2) |
| C(61)–Sn(1)–O(2) | 91.1(2) | Sn(1)–O(7)–Sn(1)#1 | 105.14(18) |
| O(7)#1–Sn(1)–O(2) | 162.45(15) | Sn(2)–O(7)–Sn(1)#1 | 120.75(18) |
| O(7)–Sn(2)–C(81) | 105.7(2) | O(2)–C(1)–O(1) | 125.3(7) |
| O(7)–Sn(2)–C(71) | 111.4(3) | O(2)–C(1)–C(11) | 118.0(7) |
| C(81)–Sn(2)–C(71) | 141.7(3) | O(1)–C(1)–C(11) | 116.7(7) |
| O(7)–Sn(2)–O(5) | 81.45(16) | O(4)–C(2)–O(5) | 122.0(6) |
| C(81)–Sn(2)–O(5) | 100.1(2) | O(4)–C(2)–C(31) | 120.1(6) |
| C(71)–Sn(2)–O(5) | 94.3(3) | O(5)–C(2)–C(31) | 117.7(6) |

**Table 3**
Selected bond lengths (Å) and bond angles (°) for complex **2**.

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Sn(1)–O(7) | 2.037(2) | Sn(2)–O(4) | 2.280(3) |
| Sn(1)–C(61) | 2.112(4) | O(1)–C(1) | 1.293(4) |
| Sn(1)–C(51) | 2.116(4) | O(2)–C(1) | 1.233(4) |
| Sn(1)–O(1) | 2.183(2) | O(3)–C(17) | 1.215(5) |
| Sn(1)–O(5)#1 | 2.277(3) | O(4)–C(2) | 1.261(4) |
| Sn(2)–O(7)#1 | 2.038(2) | O(5)–C(2) | 1.260(4) |
| Sn(2)–C(71) | 2.110(4) | O(5)–Sn(1)#1 | 2.277(2) |
| Sn(2)–C(81) | 2.118(4) | O(6)–C(37) | 1.216(5) |
| Sn(2)–O(7) | 2.159(2) | O(7)–Sn(2)#1 | 2.038(2) |
| *Bond angles* | | | |
| O(7)–Sn(1)–C(61) | 110.13(14) | O(7)#1–Sn(2)–O(4) | 89.99(9) |
| O(7)–Sn(1)–C(51) | 104.25(14) | C(71)–Sn(2)–O(4) | 89.54(14) |
| C(61)–Sn(1)–C(51) | 145.01(17) | C(81)–Sn(2)–O(4) | 83.04(13) |
| O(7)–Sn(1)–O(1) | 81.01(9) | O(7)–Sn(2)–O(4) | 164.13(9) |
| C(61)–Sn(1)–O(1) | 92.16(13) | C(1)–O(1)–Sn(1) | 105.0(2) |
| C(51)–Sn(1)–O(1) | 99.49(14) | C(2)–O(4)–Sn(2) | 124.4(2) |
| O(7)–Sn(1)–O(5)#1 | 89.25(10) | C(2)–O(5)–Sn(1)#1 | 128.2(3) |
| C(61)–Sn(1)–O(5)#1 | 82.54(13) | Sn(1)–O(7)–Sn(2)#1 | 131.72(12) |
| C(51)–Sn(1)–O(5)#1 | 91.77(14) | Sn(1)–O(7)–Sn(2) | 122.61(11) |
| O(1)–Sn(1)–O(5)#1 | 166.62(10) | Sn(2)#1–O(7)–Sn(2) | 104.76(10) |
| O(7)#1–Sn(2)–C(71) | 106.76(14) | O(2)–C(1)–O(1) | 122.3(4) |
| O(7)#1–Sn(2)–C(81) | 115.68(13) | O(2)–C(1)–C(11) | 120.2(4) |
| C(71)–Sn(2)–C(81) | 136.82(16) | O(1)–C(1)–C(11) | 117.3(4) |
| O(7)#1–Sn(2)–O(7) | 75.24(10) | O(5)–C(2)–O(4) | 124.1(4) |
| C(71)–Sn(2)–O(7) | 100.13(14) | O(5)–C(2)–C(31) | 117.3(4) |
| C(81)–Sn(2)–O(7) | 97.98(13) | O(4)–C(2)–C(31) | 118.6(4) |

**Table 4**
Selected bond lengths (Å) and bond angles (°) for complex **3**.

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Sn(1)–O(7)#1 | 2.0433(18) | Cl(1)–C(24) | 1.742(4) |
| Sn(1)–C(61) | 2.124(3) | Cl(2)–C(44) | 1.749(4) |
| Sn(1)–C(51) | 2.124(3) | O(1)–C(1) | 1.266(3) |
| Sn(1)–O(7) | 2.1641(19) | O(2)–C(1) | 1.260(3) |
| Sn(1)–O(1) | 2.2871(19) | O(2)–Sn(2)#1 | 2.288(2) |
| Sn(2)–O(7) | 2.0275(18) | O(3)–C(17) | 1.211(4) |
| Sn(2)–C(71) | 2.122(3) | O(4)–C(2) | 1.307(3) |
| Sn(2)–C(81) | 2.133(3) | O(5)–C(2) | 1.233(4) |
| Sn(2)–O(4) | 2.170(2) | O(6)–C(37) | 1.216(4) |
| Sn(2)–O(2)#1 | 2.288(2) | O(7)–Sn(1)#1 | 2.0433(18) |
| *Bond angles* | | | |
| O(7)#1–Sn(1)–C(61) | 105.31(9) | O(7)–Sn(2)–O(2)#1 | 89.47(7) |
| O(7)#1–Sn(1)–C(51) | 112.99(9) | C(71)–Sn(2)–O(2)#1 | 88.16(10) |
| C(61)–Sn(1)–C(51) | 140.94(11) | C(81)–Sn(2)–O(2)#1 | 83.58(10) |
| O(7)#1–Sn(1)–O(7) | 75.18(8) | O(4)–Sn(2)–O(2)#1 | 168.33(7) |
| C(61)–Sn(1)–O(7) | 100.13(9) | C(1)–O(1)–Sn(1) | 125.79(18) |
| C(51)–Sn(1)–O(7) | 96.76(9) | C(1)–O(2)–Sn(2)#1 | 125.40(19) |
| O(7)#1–Sn(1)–O(1) | 89.52(7) | C(2)–O(4)–Sn(2) | 108.47(17) |
| C(61)–Sn(1)–O(1) | 90.66(10) | Sn(2)–O(7)–Sn(1)#1 | 131.34(10) |
| C(51)–Sn(1)–O(1) | 82.48(9) | Sn(2)–O(7)–Sn(1) | 122.65(9) |
| O(7)–Sn(1)–O(1) | 163.11(7) | Sn(1)#1–O(7)–Sn(1) | 104.82(8) |
| O(7)–Sn(2)–C(71) | 104.77(10) | O(2)–C(1)–O(1) | 123.5(3) |
| O(7)–Sn(2)–C(81) | 110.31(10) | O(2)–C(1)–C(11) | 118.6(3) |
| C(71)–Sn(2)–C(81) | 143.80(12) | O(1)–C(1)–C(11) | 117.9(2) |
| O(7)–Sn(2)–O(4) | 81.07(7) | O(5)–C(2)–O(4) | 122.8(3) |
| C(71)–Sn(2)–O(4) | 100.81(10) | O(5)–C(2)–C(31) | 120.9(2) |
| C(81)–Sn(2)–O(4) | 93.25(10) | O(4)–C(2)–C(31) | 116.2(2) |

metal coordination geometry is therefore described as distorted trigonal bipyramidal with O(1) and O(5) atoms occupying the axial positions and O(7), C(51) and C(61), the equatorial positions for Sn(1), and a distorted octahedral for Sn(2) center. Different to the complexes **1**, **2**, and **3** mentioned above, complex **4** adopted another structural type, this fact indicates that there is subtle energy difference among these types and that the structure ultimately adopted in the solid state may depend largely on the crystallization conditions employed.

## 4. Biological studies

### 4.1. Antibacterial screening

Antibacterial activity was performed against one Gram positive (*Bacillus subtilis*) and another Gram negative (*Escherichia coli*) bacteria and the results are summarized in Table 6. In order to compare the results obtained, the Imipinem is used as standard drug [30]. Complex **1** shows higher activity than *n*-$Bu_2SnO$ and the ligand $\mathbf{HL_1}$, but lower than the standard drug. The results also showed that the activity of complex **1** against *E. coli* is better than against *B. subtilis*. It is noteworthy that **1** has a better antibacterial activity against the two bacteria than the corresponding ligand $\mathbf{HL_1}$, which have shown that the complex **1** is potential bactericide than it's corresponding ligand compound.

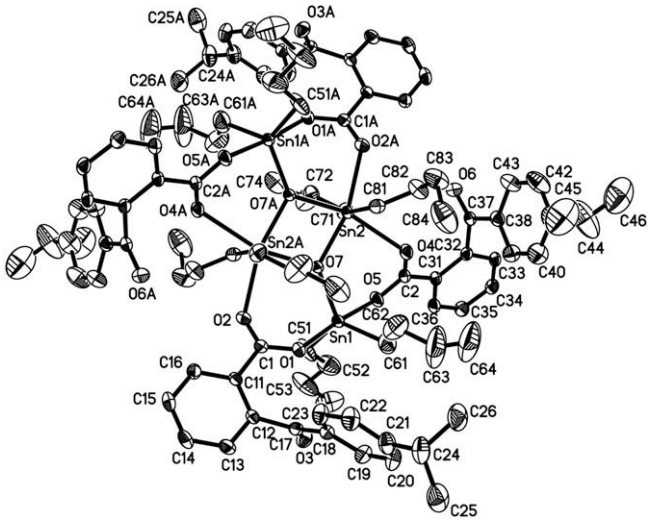



**Fig. 4.** Perspective view of **4** showing the atomic numbering scheme.

**Table 5**
Selected bond lengths (Å) and bond angles (°) for complex **4**.

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Sn(1)–O(7) | 2.001(3) | Sn(2)–O(4) | 2.481(4) |
| Sn(1)–C(61) | 2.105(9) | O(1)–C(1) | 1.260(6) |
| Sn(1)–C(51) | 2.121(7) | O(2)–C(1) | 1.245(6) |
| Sn(1)–O(5) | 2.207(4) | O(2)–Sn(2)#1 | 2.350(4) |
| Sn(1)–O(1) | 2.228(4) | O(3)–C(17) | 1.222(6) |
| Sn(2)–O(7)#1 | 2.115(3) | O(4)–C(2) | 1.233(6) |
| Sn(2)–C(71) | 2.120(6) | O(5)–C(2) | 1.280(6) |
| Sn(2)–C(81) | 2.126(6) | O(6)–C(37) | 1.210(6) |
| Sn(2)–O(7) | 2.139(3) | O(7)–Sn(2)#1 | 2.115(3) |
| Sn(2)–O(2)#1 | 2.350(4) | | |
| *Bond angles* | | | |
| O(7)–Sn(1)–C(61) | 119.4(3) | O(7)–Sn(2)–O(2)#1 | 162.86(13) |
| O(7)–Sn(1)–C(51) | 113.4(3) | O(7)#1–Sn(2)–O(4) | 162.92(12) |
| C(61)–Sn(1)–C(51) | 127.1(4) | C(71)–Sn(2)–O(4) | 81.29(18) |
| O(7)–Sn(1)–O(5) | 91.86(13) | C(81)–Sn(2)–O(4) | 81.57(18) |
| C(61)–Sn(1)–O(5) | 91.0(3) | O(7)–Sn(2)–O(4) | 86.68(11) |
| C(51)–Sn(1)–O(5) | 88.1(2) | O(2)#1–Sn(2)–O(4) | 110.33(13) |
| O(7)–Sn(1)–O(1) | 92.98(13) | C(1)–O(1)–Sn(1) | 121.9(3) |
| C(61)–Sn(1)–O(1) | 86.7(3) | C(1)–O(2)–Sn(2)#1 | 128.8(4) |
| C(51)–Sn(1)–O(1) | 89.9(2) | C(2)–O(4)–Sn(2) | 120.5(3) |
| O(5)–Sn(1)–O(1) | 175.16(14) | C(2)–O(5)–Sn(1) | 123.7(4) |
| O(7)#1–Sn(2)–C(71) | 102.43(19) | Sn(1)–O(7)–Sn(2)#1 | 128.07(15) |
| O(7)#1–Sn(2)–C(81) | 99.69(18) | Sn(1)–O(7)–Sn(2) | 128.02(15) |
| C(71)–Sn(2)–C(81) | 154.0(2) | Sn(2)#1–O(7)–Sn(2) | 103.73(13) |
| O(7)#1–Sn(2)–O(7) | 76.27(13) | O(2)–C(1)–O(1) | 124.2(5) |
| C(71)–Sn(2)–O(7) | 99.6(2) | O(2)–C(1)–C(11) | 118.5(5) |
| C(81)–Sn(2)–O(7) | 98.75(17) | O(1)–C(1)–C(11) | 117.3(5) |
| O(7)#1–Sn(2)–O(2)#1 | 86.67(12) | O(4)–C(2)–O(5) | 123.9(5) |

**Table 6**
Antibacterial screening results of complex **1**.

| Compound | ($\mu g/mL^{-1}$) | Antimicrobial circle diameter (mm) | |
|---|---|---|---|
| | | $G^-$ | $G^+$ |
| $CH_3CH_2OH$ | 20 | 2.0 | 1.5 |
| *n*-$Bu_2SnO$ | 20 | 4.6 | 0 |
| $HL_1$ | 20 | 6.1 | 3.0 |
| 1 | 20 | 15.6 | 8.2 |
| Imipinem [30] | 20 | 30 | 31 |

Concentration used: 1000 μg/mL in ethanol.

### 4.2. Antitumor activity

The results of cytostatic activity are summarized in Table 7. $IC_{50}$ values of the compounds are expressed in μM, together with that of cisplatin for comparison. The low concentrations of complex **1** showed higher activities than of *n*-$Bu_2SnO$ in vitro antitumor activity in Hela cell lines, whereas the high concentrations of it displayed a lower activities than of *n*-$Bu_2SnO$. At concentrations of 10 μg/L, the results showed that complex **1** provides 88% growth inhibition, and the $IC_{50}$ in vitro values is 2.3 μg/mL. Complex **1** presents lower $IC_{50}$ values than those of cisplatin ($IC_{50}$ = 3.50) [31], which indicates their high activity against the tumoral cell lines evaluated. As these results are preliminary, further study on the antitumor effects of these compounds is highly recommended.

**Table 7**
The in vitro antitumor activities of complex **1** against Hela cell.

| Compound | Dose (μg/mL) | Anticancer activity (%) | $IC_{50}$ (μg/mL) |
|---|---|---|---|
| *n*-$Bu_2SnO$ | 0.1 | −5.5 ± 9.0 | |
| | 0.3 | 18.7 ± 3.0 | |
| | 1 | 30.8 ± 3.2 | |
| | 3 | 67.0 ± 1.6 | |
| | 10 | 88.7 ± 0.1 | 1.6 |
| Complex **1** | 0.1 | 0.0 ± 2.8 | |
| | 0.3 | 8.5 ± 4.4 | |
| | 1 | 21.8 ± 2.1 | |
| | 3 | 58.4 ± 0.6 | |
| | 10 | 88.0 ± 0.2 | 2.3 |

## Acknowledgement

We acknowledged the Project (20873181) supported by the NSFC and the Project (2007AA06Z214) supported by the high-tech Research and Development Programm of China; Project is (ts20070704) supported by Taishan Scholars Construction Engineering.

## Appendix A. Supplementary material

CCDC 706617, 706619, 706618 and 706620 contains the supplementary crystallographic data for **1**, **2**, **3** and **4**. 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 doi:10.1016/j.jorganchem.2009.03.025.

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