



# Self-assembled pentagonal bipyramidal and skew trapezoidal organotin(IV) complexes of substituted benzoic acids: Their antibacterial, antifungal, cytotoxic, insecticidal and urease inhibition activities

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## ABSTRACT

Fourteen di- and triorganotin(IV) derivatives with pentagonal bipyramidal and skew trapezoidal geometries have been synthesized and characterized. Dimethylstannyl bis[3-amino-4-chlorophenylcarboxylate] (**1**), bis[3-amino-4-chlorophenylcarboxylate] tetraethyldistannoxane (**2**) and bis[3,5-dinitro-4-chlorophenylcarboxylate] tetra-*n*-butyldistannoxane (**10**) are dinuclear and tetranuclear complexes of bidentate ligands. The crystal structure of (**1**) is dimeric in which each Sn atom is seven coordinated. Study of weak intramolecular Sn···O interactions is very important to decide geometry around tin. Furthermore, it has been investigated that these compounds exhibit fairly good antibacterial, antifungal, cytotoxic, insecticidal and antiurease activities.

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## 1. Introduction

Organotin(IV) carboxylates have been extensively studied due to their structural chemistry and biological applications. The diversity in structure of these compounds is due to the ability of carboxylate ligand to bind with Sn centre in monodentate, bidentate and bridging manner. These anionic ligands are highly effective for metals due to the reason that steric and electronic factors of organic substituents on tin make the complexes more stable. Dimeric tetraorganodicarboxylato stannoxanes are important class of organotin compounds having variety in coordination around tin both in solid and solution states as well. The Lewis acid properties of such type of compounds are helpful for catalysis of various carbonyl transformations under virtually inert conditions [1].

Furthermore, the biological and industrial applications of organotin(IV) complexes are well documented also. The presence of longer molecular interactions in these complexes affects their biological properties. The broad spectrum of applications wrap their usage as antifouling paints [2–4], homogeneous catalysts in esterification, *trans* esterification reactions [5], and ion carriers in electrochemical membranes design [6]. These complexes exhibit

promising antifungal, antibacterial and antitumor activities [7–12]. Their activity depends upon the nature of carboxylate ligands and alkyl/aryl groups bonded to Sn atom. Normally, triorganotin(IV) compounds display a higher biological activity than their di- and mono-organotin(IV) analogues due to their ability to bind with proteins [13–16].

Our research group has made efforts to know the competitive coordination modes of different S, N and O donor ligands around tin atom and to find a rationale, related to the stability and structural motifs of this class of compounds [17–20]. As an extension of this work, we report herein the synthesis, spectroscopic analysis, X-crystallography and biological properties of fourteen organotin(IV) derivatives of substituted benzoic acids.

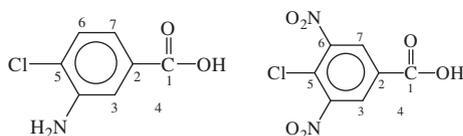
## 2. Experimental

### 2.1. Materials and methods

Reagents, di-, triorganotin(IV) chlorides and ligands were purchased from commercial sources (Aldrich, USA) and were used without further purification. Solvents were dried before use by the literature procedure [21]. Elemental analyses (C, H and N) were carried out by Leco CHNS-932 analyzer USA while multi EA<sup>®</sup> 5000 series analyzer Germany was used for chlorine analysis. Infrared

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**Scheme 1.** Numbering scheme of ligands atoms in complexes (1–14).

(IR) measurements were taken as KBr pellets on a Bio-Rad Excalibur FT-IR, model FTS 4800 MX spectrophotometer (USA) in the frequency range of 4000–200  $\text{cm}^{-1}$ .  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR spectra in solution were undertaken using Bruker ARX 300, 400 and 500 MHz-FT-NMR spectrometers, respectively. The chemical shifts are reported in ppm relative to the external references, tetramethylsilane (TMS) for  $^1\text{H}$ ,  $^{13}\text{C}$  and tetramethyltin for  $^{119}\text{Sn}$  shifts. Crystallographic studies were carried out on a Nonius Kappa CCD diffractometer with graphite monochromated Mo  $\text{K}\alpha$  radiation.

## 2.2. General procedure for synthesis of complexes

All compounds (1–14) were prepared by reaction of organotin(IV) oxides/hydroxides/chlorides with carboxylic acids/Na-salts as already discussed [17,18]. Synthesis of all compounds is given in Scheme 1. Dimeric stannoxanes were also prepared by partial hydrolysis of diorganotin(IV) derivatives. The spectral data of all compounds is arranged as numbered in Scheme 2.

### 2.2.1. Dimethylstannyl bis[3-amino-4-chlorophenylcarboxylate] (1)

$\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4\text{Cl}_2\text{Sn}$ , M.P. 130–132  $^\circ\text{C}$ , Yield 83%, *Anal.* Calc.: C, 39.2; H, 3.3; N, 5.7; Cl, 14.5. Found: C, 38.4; H, 3.9; N, 4.9; Cl, 14.4%. Recrystallization: chloroform and *n*-hexane in 4:1. IR (KBr): 1638  $\nu(\text{COO})_{\text{asym}}$ , 1498  $\nu(\text{COO})_{\text{sym}}$ , 140  $\Delta\nu(\nu\text{COO}_{\text{asym}} - \nu\text{COO}_{\text{sym}})$

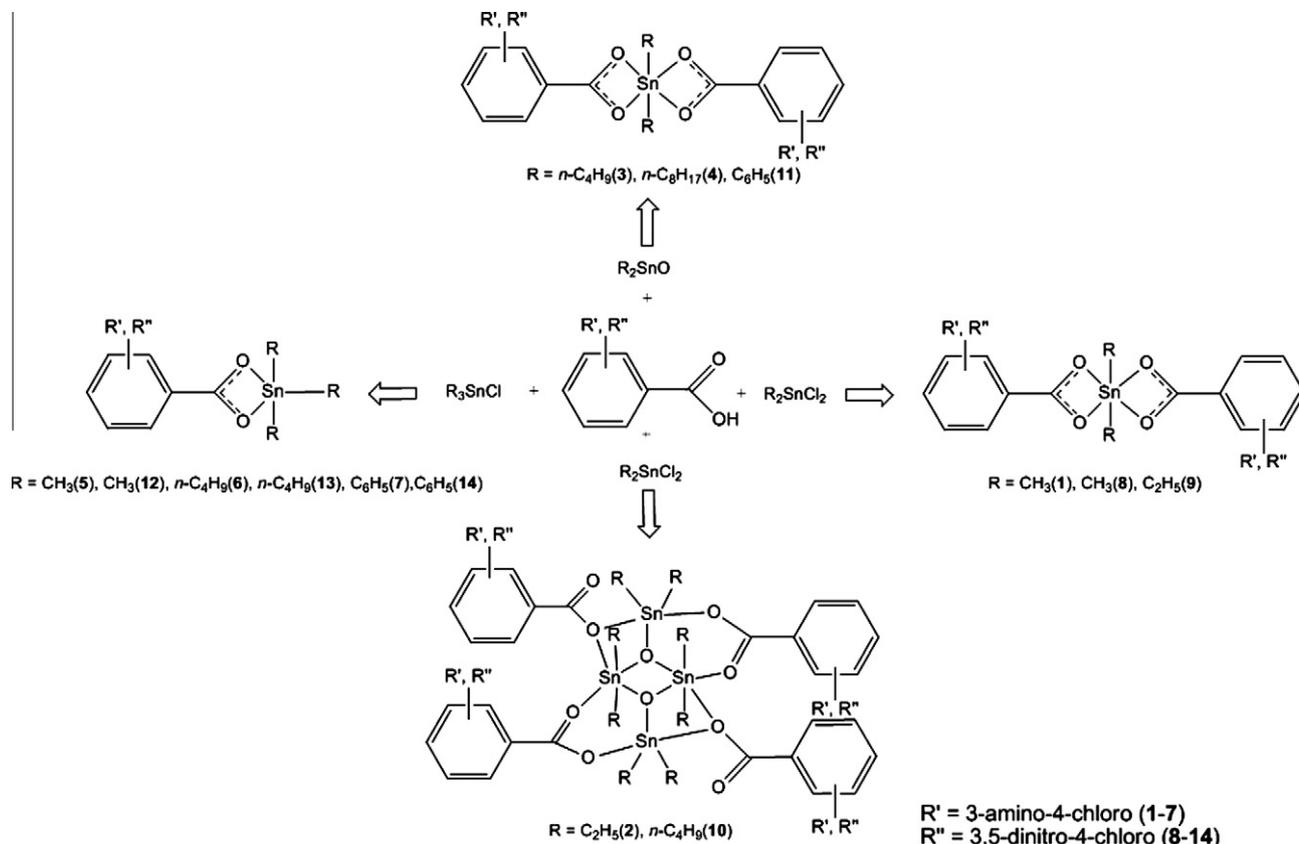
$\text{COO}_{\text{sym}}$ , 497  $\nu(\text{Sn}-\text{C})$ , 423  $\nu(\text{Sn}-\text{O})$ , 3371  $\nu(\text{NH})$ .  $^1\text{H}$  NMR  $\delta$  (ppm)  $^nJ(^{119}\text{Sn}, ^1\text{H})$  Hz: 1.06[76] (s, 6H,  $\text{H}_\alpha$ ), 6.89 (s, 2H,  $\text{H}_3$ ), 7.72 (d, 2H,  $\text{H}_6$ )  $^3J$ [7.1], 7.86 (d, 2H,  $\text{H}_7$ )  $^3J$ [7.1], 5.71 (s, 4H, NH).  $^{13}\text{C}$  NMR  $\delta$  (ppm)  $^nJ(^{119}\text{Sn}, ^{13}\text{C})$ Hz: -1.7[645]  $\text{C}_\alpha$ , 173.3  $\text{C}_1$ , 128.7  $\text{C}_2$ , 119.6  $\text{C}_3$ , 138.4  $\text{C}_4$ , 126.3  $\text{C}_5$ , 129.4  $\text{C}_6$ , 121.2  $\text{C}_7$ .  $^{119}\text{Sn}$  NMR  $\delta$  (ppm): -136.9.

### 2.2.2. Bis[3-amino-4-chlorophenylcarboxylate] tetraethylstannoxane (2)

$\text{C}_{44}\text{H}_{60}\text{Cl}_4\text{N}_4\text{O}_{10}\text{Sn}_4$ , M.P. 190–192  $^\circ\text{C}$ , Yield 76%, *Anal.* Calc.: C, 37.2; H, 4.2; N, 3.9; Cl, 10.0. Found: C, 38.1; H, 3.8; N, 4.5; Cl, 9.9%. Recrystallization: chloroform and *n*-hexane in 4:1. IR (KBr): 1693  $\nu(\text{COO})_{\text{asym}}$ , 1438  $\nu(\text{COO})_{\text{sym}}$ ,  $\Delta\nu(\nu\text{COO}_{\text{asym}} - \nu\text{COO}_{\text{sym}})$  255, 1563  $\nu(\text{COO})_{\text{asym}}$ , 1430  $\nu(\text{COO})_{\text{sym}}$ , 133  $\Delta\nu(\nu\text{COO}_{\text{asym}} - \nu\text{COO}_{\text{sym}})$ , 559, 502  $\nu(\text{Sn}-\text{C})$ , 483, 440  $\nu(\text{Sn}-\text{O})_2$ , 286, 252 (Sn-O).  $^1\text{H}$  NMR  $\delta$  (ppm)  $^nJ(^{119}\text{Sn}, ^1\text{H})$  Hz: 1.40–1.27 (m, 20H,  $\text{H}_\alpha$ ,  $\text{H}_\beta$ ), 7.20 (s, 2H,  $\text{H}_3$ ), 7.55 (d, 2H,  $\text{H}_6$ )  $^3J$ [7.2], 7.62 (d, 2H,  $\text{H}_7$ )  $^3J$ [7.2], 4.19 (s, 4H, NH).  $^{13}\text{C}$  NMR  $\delta$  (ppm)  $^nJ(^{119}\text{Sn}, ^{13}\text{C})$ Hz: 17.8[604], 16.4[584]  $\text{C}_\alpha$ , 9.7[58], 8.4[49]  $\text{C}_\beta$ , 172.3  $\text{C}_1$ , 129.0  $\text{C}_2$ , 117.0  $\text{C}_3$ , 143.0  $\text{C}_4$ , 132.2  $\text{C}_5$ , 129.4  $\text{C}_6$ , 120.8  $\text{C}_7$ .  $^{119}\text{Sn}$  NMR  $\delta$  (ppm): -211.8, -163.3.

### 2.2.3. Di-*n*-butylstannyl bis[3-amino-4-chlorophenylcarboxylate] (3)

$\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_4\text{Cl}_2\text{Sn}$ , M.P. 105–107  $^\circ\text{C}$ , Yield 84%, *Anal.* Calc.: C, 46.0; H, 4.9; N, 4.9; Cl, 12.3. Found: C, 45.4; H, 4.5; N, 4.2; Cl, 12.2%. Recrystallization: chloroform and *n*-hexane in 4:1. IR (KBr): 1636  $\nu(\text{COO})_{\text{asym}}$ , 1489  $\nu(\text{COO})_{\text{sym}}$ , 147  $\Delta\nu(\nu\text{COO}_{\text{asym}} - \nu\text{COO}_{\text{sym}})$ , 582  $\nu(\text{Sn}-\text{C})$ , 474  $\nu(\text{Sn}-\text{O})$ , 3351  $\nu(\text{NH})$ .  $^1\text{H}$  NMR  $\delta$  (ppm)  $^nJ(^{119}\text{Sn}, ^1\text{H})$  Hz: 1.36[77] (t, 4H,  $\text{H}_\alpha$ ),  $^3J$ [7.5], 1.36–1.41 (m, 8H,  $\text{H}_\beta$ ,  $\text{H}_\gamma$ ), 0.91 (t, 6H,  $\text{H}_\delta$ )  $^3J$ [7.5], 7.23 (s, 2H,  $\text{H}_3$ ), 7.58 (d, 2H,  $\text{H}_6$ )  $^3J$ [7.1], 7.62 (d, 2H,  $\text{H}_7$ )  $^3J$ [7.2], 4.2 (s, 4H, NH).  $^{13}\text{C}$  NMR  $\delta$  (ppm)  $^nJ(^{119}\text{Sn}, ^{13}\text{C})$ Hz: 25.5[569]  $\text{C}_\alpha$ , 29.4[34]  $\text{C}_\beta$ , 26.6[93]  $\text{C}_\gamma$ , 13.5  $\text{C}_\delta$ ,



**Scheme 2.** Schematic diagram for synthesis of compounds (1–14).

175.5 C<sub>1</sub>, 129.3 C<sub>2</sub>, 117.4 C<sub>3</sub>, 142.8 C<sub>4</sub>, 124.1 C<sub>5</sub>, 129.4 C<sub>6</sub>, 120.8 C<sub>7</sub>. <sup>119</sup>Sn NMR δ (ppm): –150.3.

#### 2.2.4. Di-*n*-octylstannyl bis[3-amino-4-chlorophenylcarboxylate] (4)

C<sub>30</sub>H<sub>44</sub>N<sub>2</sub>O<sub>4</sub>Cl<sub>2</sub>Sn, M.P. 286–288 °C, Yield 83%, *Anal. Calc.*: C, 52.5; H, 6.5; N, 4.0; Cl, 10.3. Found: C, 51.7; H, 6.1; N, 3.7; Cl, 10.2%. Recrystallization: chloroform and *n*-hexane in 4:1. IR (KBr): 1674 ν(COO)<sub>asym</sub>, 1489 ν(COO)<sub>sym</sub>, 185 Δν(vCOO<sub>asym</sub> – νCOO<sub>sym</sub>), 541 ν(Sn–C), 483 ν(Sn–O), 3316 ν(NH). <sup>1</sup>H NMR δ (ppm) <sup>η</sup>J[<sup>119</sup>Sn, <sup>1</sup>H] Hz: {1.08–1.70 m, 0.53–0.70 m, 0.76 t(7.2 Hz)}, 34H, H<sub>α</sub>, H<sub>β</sub>, H<sub>γ</sub>, H<sub>δ</sub>, H<sub>α'</sub>, H<sub>β'</sub>, H<sub>γ'</sub>, H<sub>δ'</sub>, 7.24 (s, 2H, H<sub>3</sub>), 7.51 (d, 2H, H<sub>6</sub>) <sup>3</sup>J[6.9], 7.59 (d, 2H, H<sub>7</sub>) <sup>3</sup>J[7.1], 5.14 (s, 4H, NH). <sup>13</sup>C NMR δ (ppm) <sup>η</sup>J[<sup>119</sup>Sn, <sup>13</sup>C]Hz: 25.2[554] C<sub>α</sub>, 24.6[34] C<sub>β</sub>, 32.4[94] C<sub>γ</sub>, {13.8, 23.9, 29.1, 29.3, 32.6, C<sub>δ</sub>, C<sub>α'</sub>, C<sub>β'</sub>, C<sub>γ'</sub>, C<sub>δ'</sub>}, 171.8 C<sub>1</sub>, 130.1 C<sub>2</sub>, 119.4 C<sub>3</sub>, 142.6 C<sub>4</sub>, 133.2 C<sub>5</sub>, 128.1 C<sub>6</sub>, 121.4 C<sub>7</sub>. <sup>119</sup>Sn NMR δ (ppm): –163.7.

#### 2.2.5. Trimethylstannyl [3-amino-4-chlorophenylcarboxylate] (5)

C<sub>10</sub>H<sub>14</sub>NO<sub>2</sub>ClSn, M.P. 130–133 °C, Yield 83%, *Anal. Calc.*: C, 35.9; H, 4.2; N, 4.2; Cl, 10.6. Found: C, 35.2; H, 3.9; N, 3.6; Cl, 10.5%. Recrystallization: chloroform and *n*-hexane in 4:1. IR (KBr): 1630s ν(COO)<sub>asym</sub>, 1489 m ν(COO)<sub>sym</sub>, 141 Δν(vCOO<sub>asym</sub> – νCOO<sub>sym</sub>), 581 m ν(Sn–C), 437w ν(Sn–O), 3368 ν(NH). <sup>1</sup>H NMR δ (ppm) <sup>η</sup>J[<sup>117/119</sup>Sn, <sup>1</sup>H] Hz: 0.88[55, 58] (s, 9H, H<sub>α</sub>), 7.1 (s, 1H, H<sub>3</sub>), 7.3 (d, 1H, H<sub>6</sub>) <sup>3</sup>J[7.3], 7.48 (d, 1H, H<sub>7</sub>) <sup>3</sup>J[7.3], 4.01 (s, 1H, NH). <sup>13</sup>C NMR δ (ppm) <sup>η</sup>J[<sup>117/119</sup>Sn, <sup>13</sup>C]Hz: –2.2[376, 394] C<sub>α</sub>, 171.2 C<sub>1</sub>, 129.0 C<sub>2</sub>, 117.3 C<sub>3</sub>, 142.6 C<sub>4</sub>, 131.2 C<sub>5</sub>, 129.1 C<sub>6</sub>, 120.6 C<sub>7</sub>. <sup>119</sup>Sn NMR δ (ppm): 141.7.

#### 2.2.6. Tri-*n*-butylstannyl [3-amino-4-chlorophenylcarboxylate] (6)

C<sub>19</sub>H<sub>32</sub>NO<sub>2</sub>ClSn, M.P. 285–287 °C, Yield 83%, *Anal. Calc.*: C, 49.5; H, 7.0; N, 3.0; Cl, 7.7. Found: C, 48.6; H, 6.7; N, 2.7; Cl, 7.6%. Recrystallization: chloroform and *n*-hexane in 4:1. IR (KBr): 1643 ν(COO)<sub>asym</sub>, 1458 ν(COO)<sub>sym</sub>, 174 Δν(vCOO<sub>asym</sub> – νCOO<sub>sym</sub>), 580 ν(Sn–C), 469w ν(Sn–O), 3309 ν(NH). <sup>1</sup>H NMR δ (ppm) <sup>η</sup>J[<sup>119</sup>Sn, <sup>1</sup>H] Hz: 1.33–1.69 (m, 18H, H<sub>α</sub>, H<sub>β</sub>, H<sub>γ</sub>), H<sub>δ</sub> 0.86 (t, 9H, <sup>3</sup>J[7.3]), 7.28 (s, 1H, H<sub>3</sub>), 7.43 (d, 1H, H<sub>6</sub>) <sup>3</sup>J[7.2], 7.58 (d, 1H, H<sub>7</sub>) <sup>3</sup>J[7.2] 7.2 Hz, 4.21 (s, 2H, NH). <sup>13</sup>C NMR δ (ppm) <sup>η</sup>J[<sup>117/119</sup>Sn, <sup>13</sup>C]Hz: 16.4[344, 351] C<sub>α</sub>, 27.1[34] C<sub>β</sub>, 29.4[92] C<sub>γ</sub>, 13.7 C<sub>δ</sub>, 171.8 C<sub>1</sub>, 128.9 C<sub>2</sub>, 118.5 C<sub>3</sub>, 140.0 C<sub>4</sub>, 125.6 C<sub>5</sub>, 130.2 C<sub>6</sub>, 119.8 C<sub>7</sub>. <sup>119</sup>Sn NMR δ (ppm): 117.3.

#### 2.2.7. Triphenylstannyl [3-amino-4-chlorophenylcarboxylate] (7)

C<sub>25</sub>H<sub>20</sub>NO<sub>2</sub>ClSn, M.P. 152–155 °C, Yield 81%, *Anal. Calc.*: C, 57.7; H, 3.9; N, 2.7; Cl, 6.8. Found: C, 57.3; H, 3.4; N, 2.3; Cl, 6.7%. Recrystallization: chloroform and *n*-hexane in 4:1. IR (KBr): 1615 ν(COO)<sub>asym</sub>, 1430s ν(COO)<sub>sym</sub>, 185 Δν(vCOO<sub>asym</sub> – νCOO<sub>sym</sub>), 263 ν(Sn–C), 440 ν(Sn–O), 3374 ν(NH). <sup>1</sup>H NMR δ (ppm) <sup>η</sup>J[<sup>119</sup>Sn, <sup>1</sup>H] Hz: 7.49–7.81 (m, 15H, H<sub>β</sub>, H<sub>γ</sub>, H<sub>δ</sub>), 7.28–7.46 (m, 3H, H<sub>3</sub>, H<sub>6</sub>, H<sub>7</sub>), 4.12 (s, 2H, NH). <sup>13</sup>C NMR δ (ppm) <sup>η</sup>J[<sup>117/119</sup>Sn, <sup>13</sup>C] Hz: 137.2[645, 663] C<sub>α</sub>, 136.6[46] C<sub>β</sub>, 128.3[61] C<sub>γ</sub>, 128.9 C<sub>δ</sub>, 172.2 C<sub>1</sub>, 130.3 C<sub>2</sub>, 142.7 C<sub>3</sub>, 142.3 C<sub>4</sub>, 129.4 C<sub>5</sub>, 121.1 C<sub>6</sub>, 129.8 C<sub>7</sub>. <sup>119</sup>Sn NMR δ (ppm): 148.4.

#### 2.2.8. Dimethylstannyl bis[3,5-dinitro-4-chlorophenylcarboxylate] (8)

C<sub>16</sub>H<sub>10</sub>N<sub>4</sub>O<sub>12</sub>Cl<sub>2</sub>Sn, M.P. 133–135 °C, Yield 95%, *Anal. Calc.*: C, 30.0; H, 1.6; N, 8.8; Cl, 11.1. Found: C, 29.1; H, 1.0; N, 8.3; Cl, 11.0%. Recrystallization: chloroform and *n*-hexane in 4:1. IR (KBr): 1654 ν(COO)<sub>asym</sub>, 1478 ν(COO)<sub>sym</sub>, 176 Δν(vCOO<sub>asym</sub> – νCOO<sub>sym</sub>), 291 ν(Sn–C), 430 ν(Sn–O). <sup>1</sup>H NMR δ (ppm) <sup>η</sup>J[<sup>119</sup>Sn, <sup>1</sup>H] Hz: 1.12[76] (s, 6H, H<sub>α</sub>), 8.42 (s, 4H, H<sub>3,7</sub>). <sup>13</sup>C NMR δ (ppm) <sup>η</sup>J[<sup>119</sup>Sn, <sup>13</sup>C]Hz: 1.0[652] C<sub>α</sub>, 170.3 C<sub>1</sub>, 130.5 C<sub>2</sub>, 125.1 C<sub>3,7</sub>, 149.7 C<sub>4,6</sub>, 128.8 C<sub>5</sub>. <sup>119</sup>Sn NMR δ (ppm): –128.4.

#### 2.2.9. Diethylstannyl bis[3,5-dinitro-4-chlorophenylcarboxylate] (9)

C<sub>18</sub>H<sub>14</sub>N<sub>4</sub>O<sub>12</sub>Cl<sub>2</sub>Sn, M.P. 222–225 °C, Yield 89%, *Anal. Calc.*: C, 32.4; H, 2.1; N, 8.4; Cl, 10.6. Found: C, 31.8; H, 1.9; N, 8.1; Cl, 10.5%. Recrystallization: chloroform and *n*-hexane in 4:1. IR (KBr): 1645 ν(COO)<sub>asym</sub>, 1496 ν(COO)<sub>sym</sub>, 149 Δν(vCOO<sub>asym</sub> – νCOO<sub>sym</sub>), 552 ν(Sn–C), 484 ν(Sn–O). <sup>1</sup>H NMR δ (ppm) <sup>η</sup>J[<sup>119</sup>Sn, <sup>1</sup>H] Hz: 1.48[79] (q, 4H, H<sub>α</sub>), <sup>3</sup>J[7.3], 1.18 (t, 6H, H<sub>β</sub>), <sup>3</sup>J[7.3], 8.52 (s, 4H, H<sub>3,7</sub>). <sup>13</sup>C NMR δ (ppm) <sup>η</sup>J[<sup>119</sup>Sn, <sup>13</sup>C]Hz: 18.4[551] C<sub>α</sub>, 8.4[45] C<sub>β</sub>, 169.5 C<sub>1</sub>, 130.1 C<sub>2</sub>, 134.7 C<sub>3,7</sub>, 148.9 C<sub>4,6</sub>, 127.4 C<sub>5</sub>. <sup>119</sup>Sn NMR δ (ppm): –156.5.

#### 2.2.10. Bis[3,5-dinitro-4-chlorophenylcarboxylate] tetra-*n*-butyl-distannoxane (10)

C<sub>60</sub>H<sub>80</sub>N<sub>8</sub>O<sub>26</sub>Cl<sub>4</sub>Sn<sub>4</sub>, M.P. 240–243 °C, Yield 93%, *Anal. Calc.*: C, 37.0; H, 4.1; N, 5.8; Cl, 7.3. Found: C, 37.6; H, 3.0; N, 7.2; Cl, 7.2%. Recrystallization: chloroform and *n*-hexane in 4:1. IR (KBr): 1674, 1576 ν(COO)<sub>asym</sub>, 1439, 1430 ν(COO)<sub>sym</sub>, 235, 146 Δν(vCOO<sub>asym</sub> – νCOO<sub>sym</sub>), 531, 513 ν(Sn–C), 484, 431 ν(Sn–O)<sub>2</sub>, 274, 233 (Sn–O). <sup>1</sup>H NMR δ (ppm) <sup>η</sup>J[<sup>119</sup>Sn, <sup>1</sup>H] Hz: 0.91 (t, 24H, H<sub>δ(endo)</sub>, H<sub>δ(exo)</sub>) <sup>3</sup>J[7.2] Hz, 1.32–1.44 (m, 48H, H<sub>α(endo)</sub>, H<sub>β(endo)</sub>, H<sub>γ(endo)</sub>, H<sub>α(exo)</sub>, H<sub>β(exo)</sub>, H<sub>γ(exo)</sub>), 8.52 (s, 8H, H<sub>3,7</sub>). <sup>13</sup>C NMR δ (ppm) <sup>η</sup>J[<sup>119</sup>Sn, <sup>13</sup>C] Hz: 25.4[648], 25.9[584] C<sub>α</sub>, 27.6[36], 27.1[30] C<sub>β</sub>, 26.8[94], 26.4[79] C<sub>γ</sub>, 13.2, 13.7 C<sub>δ</sub>, 171.5 C<sub>1</sub>, 130.1 C<sub>2</sub>, 134.4 C<sub>3,7</sub>, 148.6 C<sub>4,6</sub>, 127.1 C<sub>5</sub>. <sup>119</sup>Sn NMR δ (ppm): –196.5, –200.1.

#### 2.2.11. Di-*n*-octylstannyl bis[3,5-dinitro-4-chlorophenylcarboxylate] (11)

C<sub>30</sub>H<sub>38</sub>N<sub>4</sub>O<sub>12</sub>Cl<sub>2</sub>Sn, M.P. 151–154 °C, Yield 90%, *Anal. Calc.*: C, 43.1; H, 4.6; N, 6.7; Cl, 8.5. Found: C, 42.3; H, 3.9; N, 6.5; Cl, 8.4%. Recrystallization: chloroform and *n*-hexane in 4:1. IR (KBr): 1637 ν(COO)<sub>asym</sub>, 1479 ν(COO)<sub>sym</sub>, 158 Δν(vCOO<sub>asym</sub> – νCOO<sub>sym</sub>), 557 ν(Sn–C), 460 ν(Sn–O). <sup>1</sup>H NMR δ (ppm) <sup>η</sup>J[<sup>119</sup>Sn, <sup>1</sup>H] Hz: {1.56–1.73 m, 1.53–1.73 m, 0.94 t(7.2 Hz)}, 34H, H<sub>α</sub>, H<sub>β</sub>, H<sub>γ</sub>, H<sub>δ</sub>, H<sub>α'</sub>, H<sub>β'</sub>, H<sub>γ'</sub>, H<sub>δ'</sub>, 8.30 (s, 4H, H<sub>3,7</sub>). <sup>13</sup>C NMR δ (ppm) <sup>η</sup>J[<sup>119</sup>Sn, <sup>13</sup>C]Hz: 25.2[476] C<sub>α</sub>, 24.6[36] C<sub>β</sub>, 32.4[97] C<sub>γ</sub>, {33.5, 33.0, 32.6, 29.3, 29.2, 29.1, 22.7, 14.0, C<sub>δ</sub>, C<sub>α'</sub>, C<sub>β'</sub>, C<sub>γ'</sub>, C<sub>δ'</sub>}, 170.3 C<sub>1</sub>, 128.3 C<sub>2</sub>, 130.6 C<sub>3,7</sub>, 149.3 C<sub>4,6</sub>, 128.1 C<sub>5</sub>. <sup>119</sup>Sn NMR δ (ppm): –163.7.

#### 2.2.12. Trimethylstannyl [3,5-dinitro-4-chlorophenylcarboxylate] (12)

C<sub>10</sub>H<sub>11</sub>N<sub>2</sub>O<sub>6</sub>ClSn, M.P. 212–215 °C, Yield 91%, *Anal. Calc.*: C, 29.3; H, 2.7; N, 6.8; Cl, 8.7. Found: C, 28.4; H, 2.4; N, 7.1; Cl, 8.6%. Recrystallization: chloroform and *n*-hexane in 4:1. IR (KBr): 1634 ν(COO)<sub>asym</sub>, 1465 ν(COO)<sub>sym</sub>, 169 Δν(vCOO<sub>asym</sub> – νCOO<sub>sym</sub>), 544 ν(Sn–C), 433 ν(Sn–O). <sup>1</sup>H NMR δ (ppm) <sup>η</sup>J[<sup>117/119</sup>Sn, <sup>1</sup>H] Hz: 0.88[55, 57] (s, 9H, H<sub>α</sub>), 8.72 (s, 2H, H<sub>3,7</sub>). <sup>13</sup>C NMR δ (ppm) <sup>η</sup>J[<sup>117/119</sup>Sn, <sup>13</sup>C]Hz: 1.03[374, 396] C<sub>α</sub>, 166.5 C<sub>1</sub>, 129.1 C<sub>2</sub>, 124.3 C<sub>3,7</sub>, 149.4 C<sub>4,6</sub>, 128.7 C<sub>5</sub>. <sup>119</sup>Sn NMR δ (ppm): 141.7.

#### 2.2.13. Tri-*n*-butylstannyl [3,5-dinitro-4-chlorophenylcarboxylate] (13)

C<sub>19</sub>H<sub>29</sub>N<sub>2</sub>O<sub>6</sub>ClSn, M.P. 230–232 °C, Yield 85%, *Anal. Calc.*: C, 42.6; H, 5.5; N, 5.2; Cl, 6.6. Found: C, 41.8; H, 5.1; N, 4.8; Cl, 6.5%. Recrystallization: chloroform and *n*-hexane in 4:1. IR (KBr): 1640 ν(COO)<sub>asym</sub>, 1464 ν(COO)<sub>sym</sub>, 176 Δν(vCOO<sub>asym</sub> – νCOO<sub>sym</sub>), 509 ν(Sn–C), 464 ν(Sn–O). <sup>1</sup>H NMR δ (ppm) <sup>η</sup>J[<sup>119</sup>Sn, <sup>1</sup>H] Hz: {1.61(bs), 1.36–1.41(m), 18H, H<sub>α</sub>, H<sub>β</sub>, H<sub>γ</sub>), 0.86 (t, 9H, H<sub>δ</sub>) <sup>3</sup>J[<sup>1</sup>H, <sup>1</sup>H] 7.3 Hz 7.97 (s, 2H, H<sub>3,7</sub>). <sup>13</sup>C NMR δ (ppm) <sup>η</sup>J[<sup>117/119</sup>Sn, <sup>13</sup>C]Hz: 16.2[372, 386] C<sub>α</sub>, 27.2[29] C<sub>β</sub>, 26.5[97] C<sub>γ</sub>, 14.0 C<sub>δ</sub>, 172.8 C<sub>1</sub>, 130.3 C<sub>2</sub>, 123.7 C<sub>3,7</sub>, 147.6 C<sub>4,6</sub>, 128.7 C<sub>5</sub>. <sup>119</sup>Sn NMR δ (ppm): 143.9.

#### 2.2.14. Triphenylstannyl [3,5-dinitro-4-chlorophenylcarboxylate] (14)

C<sub>25</sub>H<sub>17</sub>N<sub>2</sub>O<sub>6</sub>ClSn, M.P. 141–144 °C, Yield 65%, *Anal. Calc.*: C, 50.4; H, 2.9; N, 4.7; Cl, 6.0. Found: C, 49.6; H, 2.5; N, 4.3; Cl, 5.9%. Recrystallization: chloroform and *n*-hexane in 4:1. IR (KBr): 1648 ν(COO)<sub>asym</sub>, 1467 ν(COO)<sub>sym</sub>, 181 Δν(vCOO<sub>asym</sub> – νCOO<sub>sym</sub>), 291

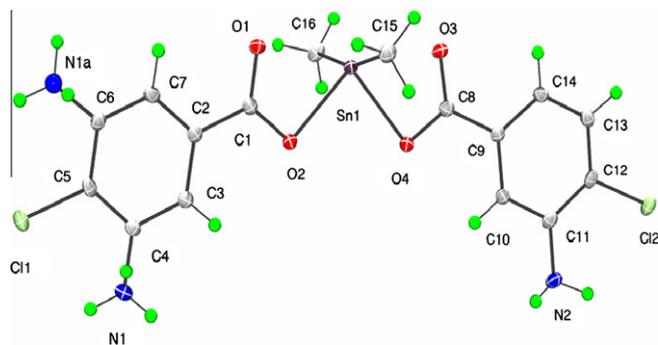


Fig. 1. Asymmetric unit of compound with numbering without interactions (1).

$\nu(\text{Sn}-\text{C})$ , 443  $\nu(\text{Sn}-\text{O})$ .  $^1\text{H NMR } \delta$  (ppm)  $^nJ[^{119}\text{Sn}, ^1\text{H}]$  Hz: {7.28–7.63, 7.71–7.9 m, 15H,  $\text{H}_\beta$ ,  $\text{H}_\gamma$ ,  $\text{H}_\delta$ }, 8.66 (s, 2H,  $\text{H}_{3,7}$ ).  $^{13}\text{C NMR } \delta$  (ppm)  $^nJ[^{117/119}\text{Sn}, ^{13}\text{C}]$ Hz: 138.4[649, 664]  $\text{C}_\alpha$  136.9[42]  $\text{C}_\beta$ , 128.9[70]  $\text{C}_\gamma$ , 129.3  $\text{C}_\delta$ , 167.1  $\text{C}_1$ , 130.5  $\text{C}_2$ , 123.5  $\text{C}_{3,7}$ , 149.4  $\text{C}_{4,6}$ , 128.3  $\text{C}_5$ .  $^{119}\text{Sn NMR } \delta$  (ppm):  $-109.3$ .

### 3. Results and discussion

#### 3.1. Vibrational spectroscopy

The vibrational frequencies of OCO, Sn–C, Sn–O and Sn–O–Sn moieties are taken into consideration. These frequencies provide useful information to identify the coordination around tin [22,23]. The characteristic absorption signals of carboxylate group for compounds **1**, **3–9** and **11–14** are assigned in the range 1615–1674  $\text{cm}^{-1}$  for asymmetric stretching and 1430–1498  $\text{cm}^{-1}$  for symmetric stretching frequencies. A set of two sharp peaks for asymmetric (1674–1693 and 1576–1563  $\text{cm}^{-1}$ ) and symmetric frequencies (1438–1439 and 1430  $\text{cm}^{-1}$ ) is observed for compounds **2** and **10**, respectively.  $\Delta\nu$  values (133–185  $\text{cm}^{-1}$ ) for all compounds point towards bridging bidentate mode of ligand around Sn atom. In case of dimeric distannoxanes **2** and **10**, the carboxylate ligand exhibits anisobidentate mode of coordination. These values suggest that skew trapezoidal geometry exists in diorganotin(IV) complexes while triorganotin(IV) complexes retain trigonal bipyramidal geometry in solid state. The vibration signals for Sn–C, Sn–O and O–Sn–O moieties are observed in their expected region [24,25].

Table 1

Crystal data and structure refinement parameters for complexes (1) and (2).

Empirical formula	$\text{C}_{16}\text{H}_{16}\text{Cl}_2\text{N}_2\text{O}_4\text{Sn}$ ( <b>1</b> )	$\text{C}_{44}\text{H}_{60}\text{Cl}_4\text{N}_4\text{O}_{10}\text{Sn}_4$ ( <b>2</b> )	$\text{C}_{60}\text{H}_{80}\text{Cl}_4\text{N}_8\text{O}_{26}\text{Sn}_4$ ( <b>10</b> )
Formula weight	489.90	1421.52	1945.88
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$C2/c$	$P\bar{1}$
$a$ (Å)	9.0688(9)	17.810(2)	12.178(11)
$b$ (Å)	10.7486(11)	13.8787(17) Å	12.514(12)
$c$ (Å)	11.0411(12)	22.693(3) Å	13.568 (12)
$\alpha$ (°)	113.9310(10)	90	104.59(10)
$\beta$ (°)	110.283(2)	103.7	110.77(10)
$\gamma$ (°)	93.623(2)	90	95.96(10)
$V$ (Å <sup>3</sup> )	896.28(16)	5449.1(12)	1827.9(3)
$Z$	2	4	1
$D_{\text{calc}}$ (mg/m <sup>3</sup> )	1.815	1.733	1.768
Crystal size (mm <sup>3</sup> )	$0.50 \times 0.40 \times 0.30$	$0.50 \times 0.40 \times 0.40$	$0.40 \times 0.20 \times 0.20$
$F(0\ 0\ 0)$	484	2800	972
Total reflections	3593	15 315	14 580
Independent reflections		5514	7352
$R$ indices (all data)	$R_1 = 0.0246$ , $wR_2 = 0.602$	$R_1 = 0.0563$ , $wR_2 = 0.1270$	$R_1 = 0.0374$ , $wR_2 = 0.0864$
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0233$ , $wR_2 = 0.0595$	$R_1 = 0.0448$ , $wR_2 = 0.1162$	$R_1 = 0.0324$ , $wR_2 = 0.0835$
Goodness-of-fit (GOF)	1.073	1.043	1.030
Theta range for data collection (°)	2.27–26.37	1.85–26.40	1.69–26.46°

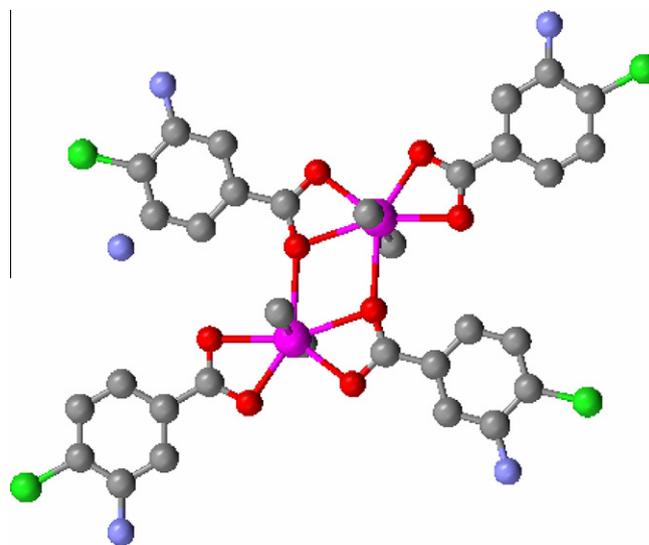


Fig. 2. Dimeric structure of compound (1) showing intermolecular interactions.

#### 3.2. NMR spectroscopy

$^1\text{H NMR}$  data is given in experimental section and resonances for compounds (**1–14**) have been assigned. In compounds (**1–7**), downfield shift (5.71–4.01 ppm) of amino group indicates that this site remains protonated showing no coordination while disappearance of acidic protons in all compounds recognize that coordination occurs through this site. The aromatic protons were also assigned with well resolved coupling due to neighbouring protons. The most interesting feature is  $^nJ[^{119}\text{Sn}, ^1\text{H}]$  coupling values which are used to assess the coordination number around Sn.  $^2J$  values calculated for dimethyltin (**1**, **8**)  $^2J$  [76 Hz], diethyltin (**9**)  $^2J$  [79 Hz], di-*n*-butyltin (**3**)  $^2J$  [77 Hz] and trimethyltin (**5**, **12**)  $^2J$  [55/58, 55/57 Hz] appear in the range normally five coordinated to diorganotin and four for triorganotin(IV) compounds [18,26]. In compounds (**2**) and (**10**), exo- and endocyclic protons of ethyl and butyl groups appear at different  $\delta$  values but signals are intermixed due to overlapping. However, the presence of these resonances is in agreement with pair wise heterotopic non-equivalence of the exocyclic and endocyclic  $\text{Et}_2\text{Sn}$  and  $\text{Bu}_2\text{Sn}$  moieties. Similarly, a complex pattern is observed for butyl protons of compounds **3**, **6** and **13** due to

**Table 2**

Selected bond lengths and bond angles of compounds (1), (2) and (10).

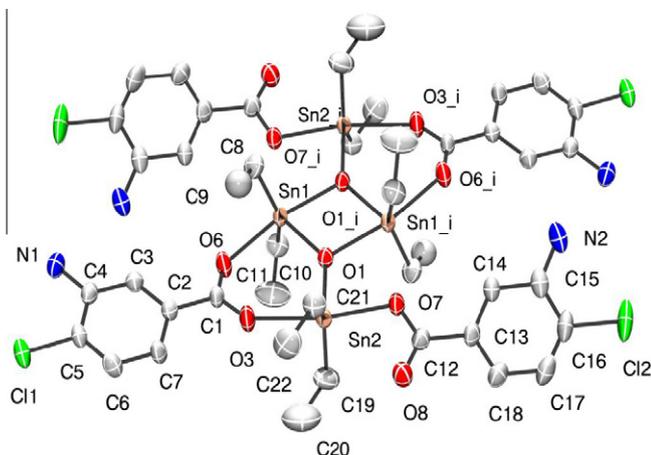
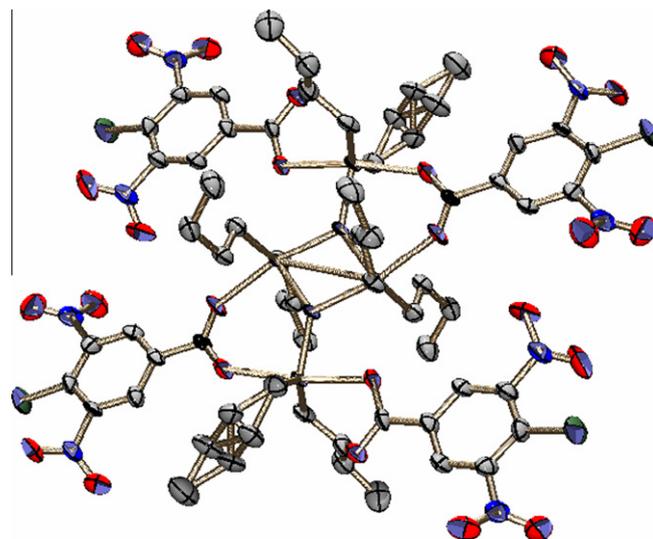
Compound (1)		Compound (2)		Compound (10)	
Sn(1)–C(15)	2.099(2)	Sn(1)–O(1)	2.049(3)	Sn(1)–O(13)	2.0394(19)
Sn(1)–C(16)	2.103(2)	Sn(1)–C(8)	2.213(6)	Sn(1)–C(19)	2.125(3)
Sn(1)–O(2)	2.2038(16)	Sn(1)–C(10)	2.130(5)	Sn(1)–C(15)	2.135(3)
Sn(1)–O(4)	2.2113(16)	Sn(1)–C(1)#1	2.169(3)	Sn(1)–O(1)	2.187(2)
Sn(1)–O(3)	2.3461(17)	Sn(1)–O(6)	2.224(3)	Sn(1)–O(7)	2.286(2)
Sn(1)–O(1)	2.4382(16)	Sn(2)–O(1)	2.002(3)	Sn(2)–O(13)#1	2.037(2)
Sn(1)–C(8)	2.648(2)	Sn(2)–C(21)	2.122	Sn(2)–C(23)	2.119(3)
C(11)–C(5)	1.742(2)	Sn(2)–C(19)	2.145(7)	Sn(2)–O(13)	2.1708(19)
O(1)–C(1)	1.265(3)	Sn(2)–O(7)	2.183(3)	Sn(2)–Sn(2)#1	3.2907(5)
O(1)–Sn(1)–C(8)	106.5(2)	O(1)–Sn(1)#1	2.169(3)	Sn(2)–O(8)	2.276(2)
C(15)–Sn(1)–C(16)	162.98(10)	O(3)–C(8)	1.258(3)	O(13)–Sn(1)–C(15)	108.70(10)
C(15)–Sn(1)–O(2)	97.01(9)	O(1)–Sn(1)–C(10)	105.5(2)	C(19)–Sn(1)–C(15)	144.28(12)
C(16)–Sn(1)–O(2)	95.33(8)	O(1)–Sn(1)–O(1)#1	76.66(12)	O(13)–Sn(1)–O(1)	83.09(8)
C(15)–Sn(1)–O(4)	95.52(8)	C(8)–Sn(1)–O(1)#1	96.87(19)	C(19)–Sn(1)–O(1)	99.15(10)
C(16)–Sn(1)–O(4)	97.10(8)	C(10)–Sn(1)–O(1)1	93.9(2)	C(15)–Sn(1)–O(1)	93.15(10)
O(2)–Sn(1)–O(3)	142.88(6)	O(1)–Sn(1)–O(6)	91.86(13)	O(13)–Sn(1)–O(7)	89.89(8)
O(4)–Sn(1)–O(3)	57.44(6)	C(8)–Sn(1)–O(6)	88.0(2)	C(19)–Sn(1)–O(7)	86.79(10)
C(15)–Sn(1)–O(1)	88.71(8)	C(10)–Sn(1)–O(6)	87.4(2)	C(15)–Sn(1)–O(7)	85.11(11)
C(16)–Sn(1)–O(1)	88.50(8)	O(1)–Sn(1)–O(6)	91.86(13)	O(1)–Sn(1)–O(7)	171.82(8)
O(2)–Sn(1)–O(1)	56.08(6)	O(1)#1–Sn(1)–O(6)	168.38(13)	C(23)–Sn(2)–O(13)	97.17(10)
O(4)–Sn(1)–O(1)	141.50(6)	O(1)–Sn(2)–C(21)	112.79(19)	O(13)–Sn(2)–O(8)	168.57(8)
O(3)–Sn(1)–O(1)	161.02(6)	C(1)–Sn(2)–C(19)	109.5(3)	C(1)–O(1)–Sn(1)	108.57(18)
C(15)–Sn(1)–C(8)	91.02(8)	C(21)–Sn(2)–C(19)	137.5(3)	C(8)–O(7)–Sn(1)	135.0(2)
C(16)–Sn(1)–C(8)	94.47(8)	O(1)–Sn(2)–O(7)	80.53(11)	Sn(1)–O(13)–Sn(2)	120.81(9)

CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>– skeleton in the normal reported range (1.36–1.41 ppm), (1.33–1.69 ppm) and terminal methyl protons demonstrate triplets at 0.86 and 0.91 ppm, respectively. The aromatic protons of triphenyltin(IV) **7** and **14** were also marked as multiplets.

In <sup>13</sup>C NMR of complexes (**1**–**14**), carboxylate moiety appears at downfield shift due to coordination with metal atom. The compounds **2** and **10** exhibit pair wise signals of Et–Sn and Bu–Sn moieties with upfield shift for exocyclic and downfield shift for endocyclic alkyl groups [27–29]. A single signal for carboxylate moiety is obviously due to fluxional behaviour of this group [30]. There may be a fast exchange in coordination behaviour of carboxylate moiety around endo- and exocyclic tin atoms. The coupling satellites in <sup>13</sup>C NMR are also important indicators for structural evaluation of organotin carboxylates. <sup>η</sup>J[<sup>119</sup>Sn, <sup>13</sup>C] values measured for trimethyltin(IV) (**5**) <sup>1</sup>J[376/394 Hz], (**12**) <sup>1</sup>J[374/396 Hz], tri-*n*-butyltin(IV) (**6**) <sup>1</sup>J[344/351 Hz], <sup>2</sup>J[34], <sup>3</sup>J[92], (**13**) <sup>1</sup>J[372/386 Hz], <sup>2</sup>J[29], <sup>3</sup>J[97] and triphenyltin(IV) (**7**) <sup>1</sup>J[645/663], <sup>2</sup>J[46], <sup>3</sup>J[61], (**14**) <sup>1</sup>J[649/664], <sup>2</sup>J[42], <sup>3</sup>J[70] were characteristic of four coordination [31]. <sup>η</sup>J[<sup>119</sup>Sn, <sup>13</sup>C] values measured for compounds **1** <sup>1</sup>J[645 Hz], **2** <sup>1</sup>J[607 Hz, 584], <sup>2</sup>J[58, 49 Hz], **3** <sup>1</sup>J[569 Hz],

<sup>2</sup>J[34 Hz], <sup>3</sup>J[93 Hz], **4** <sup>1</sup>J[554 Hz], <sup>2</sup>J[34 Hz], <sup>3</sup>J[94 Hz], **8** <sup>1</sup>J[652 Hz], **9** <sup>1</sup>J[551 Hz], <sup>2</sup>J[45 Hz], **10** <sup>1</sup>J[648 Hz, 584 Hz], <sup>2</sup>J[36 Hz, 30 Hz], <sup>3</sup>J[94 Hz, 79 Hz] and **11** <sup>1</sup>J[476 Hz], <sup>2</sup>J[36 Hz], <sup>3</sup>J[97 Hz] suggested skew trapezoidal geometries [32,33]. These coupling constant values and bond angles show that weaker interactions among the atoms appeared in crystalline state are broken down in solution state.

<sup>119</sup>Sn NMR spectra of all compounds were recorded and given in experimental section. However, δ(<sup>119</sup>Sn) is influenced by several factors yet it may be used with confidence to infer the coordination number around tin atom [34]. The compounds **1**, **3**, **4**, **8**, **9** and **11** exhibit single resonances at –136.9, –150.3, –163.7, –128.4, –156.5 and –163.7 ppm, respectively, characteristic of penta-coordinated tin atom as earlier reports manifested [34–38]. Trimethyltin (**5**, **12**), tri-*n*-butyltin (**6**, **13**) and triphenyltin (**7**, **14**) compounds have single peaks in the region for tetrahedral compounds [39–40]. For compounds (**2**) and (**10**), two isotropic <sup>119</sup>Sn resonances were observed (–211.8, –163.3 ppm) and (–196.5,

**Fig. 3.** Ortep diagram of compound (2) with numbering scheme.**Fig. 4.** Ortep diagram of compound (10) excluding hydrogen atoms.

**Table 3**  
Antibacterial activity<sup>a,b</sup> of organotin(IV) derivatives (1–14) of ligand acids.

Name of bacterium	Zone of inhibition (mm)														Ref. drug
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	
<i>Escherichia coli</i>	10	18	16	14	12	9	16	14	16	14	10		13	12	35
<i>Bacillus subtilis</i>		15	11	7	11	13	15	19	11	8	13		10	18	38
<i>Shigella flexneri</i>	7		8	8	10	7	14		10	14	12	15	14	15	32
<i>Pseudomonas aeruginosa</i>	11			8	7	9	10	14	8	10	11	14	11		38
<i>Staphylococcus aureus</i>	6	12	8			8	11				18	9		18	29
<i>Salmonella typhi</i>	5		11	10	9	8	8	12	10	12	9	15	16		28

<sup>a</sup> In vitro, agar well diffusion method, concentration 3 mg/mL of DMSO.

<sup>b</sup> Reference drug = Imipenem.

**Table 4**  
Antifungal activity<sup>a,b,c,d</sup> data of organotin(IV) derivatives (1–14) of ligand acids.

Fungus	Zone of inhibition (mm)														Standard drug	MIC (µg/mL)
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)		
<i>T. longifusus</i>	17	22	35	35	90	97	94		30			79	90	65	Miconazole	70
<i>C. albicans</i>	32	41		24	81	92	82	45	30	48	45	45	100	50	Miconazole	110.8
<i>A. flavus</i>	52	38	43	32	100	81	90	62	25	22		94	92	90	Amphotericin-B	20
<i>M. canis</i>	67	38	27	18	85	74	85		34	40	30	100	92		Miconazole	98.4
<i>F. solane</i>	28	45	40	35	34	90	80	42	41	46		74	60	40	Miconazole	73.25
<i>C. glabrata</i>	26	32	35		27	65	67	31		15	46	80	40		Miconazole	110.8

<sup>a</sup> Concentration: 100 µg/mL of DMSO.

<sup>b</sup> MIC: minimum inhibitory concentration.

<sup>c</sup> Percent inhibition (standard drug) = 100.

<sup>d</sup> % Inhibition = 100.

–200.1 ppm), respectively. The broadness of endo <sup>119</sup>Sn peaks and shift of frequency in compound (2) is indicative of a dynamic behaviour of endocyclic tin atom. The difference of exo- and endocyclic  $\delta$  values (49 ppm) is very small. However, it points toward trapezoidal geometry around endocyclic tin while exocyclic tin atom gives trigonal bipyramidal geometry. The resonances of Bu<sub>2</sub>Sn are in the range for penta coordination around endo- and exocyclic tin atoms. These values are in agreement with the literature values reports for similar distannoxanes [30,41].

### 3.3. X-ray crystallographic studies

The molecular structure of compound (1) with intermolecular interactions is given in Figs. 1 and 2 while selected geometric parameters, bond lengths and bond angles are summarized in Tables 1 and 2. The compound is dimeric and geometry around Sn appears as distorted pentagonal bipyramidal with methyl

groups at axial and four oxygen atoms of carboxylate moiety at plan positions. Seventh position is occupied by bridging oxygen atom of adjacent molecule connected by weaker Sn...O interactions. The C–Sn–C angle is 163.0° showing that enough space is available around tin for further coordination [42,43]. Two ligands are coordinated to Sn atom in bidentate fashion with tin-oxygen bonds [(Sn(1)–O(1) = 2.438, Sn(1)–O(2) = 2.204 Å) and (Sn(1)–O(3) = 2.346, Sn(1)–O(4) = 2.211 Å)]. Two molecular units are interconnected with each other by bridging of oxygen atoms with Sn moiety of neighbouring molecule having Sn...O distance (2.657 Å). Although these interactions are weaker than sum of covalent radii (2.13 Å) and not considered in many cases but these are stronger than Van der Waal's radii (3.68 Å) and can be reported confidently [17].

The solid state structure of 2 is depicted in Fig. 3 and interatomic parameters are given in Tables 1 and 2. It is tetranuclear centro symmetric dimer of oxidotin unit having central four mem-

**Table 5**  
Brine shrimp lethality bioassay of organotin(IV) derivatives (1–14) of ligand acids.

Compound no.	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)
LD <sub>50</sub> (µg/mL)		35.4	10.8			6.3	5.9	25.8	68.4	12.6	7.9	3.62	5.85	

Against brine-shrimps (*in vitro*).

Standard drug etoposide LD<sub>50</sub> 7.46 µg/mL.

**Table 6**  
Insecticidal bioassay of organotin(IV) (1–14) derivatives of ligand acid.

Insecticides	% Mortality													
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)
<i>Tribolium castaneum</i>	2	3	4		4	10	8	43	14			45	17	11
<i>Sitophilus oryzae</i>	2	2	3		4	3	6	10	10	16	9	8	11	
<i>Rhyzopertha dominica</i>	4	6	5		6	4	4		22		7			7
<i>Callosbruchus analis</i>	6	8	8		2	7	8	16	10	8		22	10	16

+ve control = 100%, –ve control = 0%, reference drug = Permethrin.

**Table 7**  
Antifungal activity of organotin(IV) derivatives (**1–14**) of ligand acids<sup>a</sup>.

Compound no.	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)
% Inhibition	84.3 ± 0.24	77.1 ± 0.33	39.5 ± 0.13	14.2 ± 0.16	74.2 ± 0.24	51.0 ± 0.43	83.2 ± 0.14	63.2 ± 0.21	68.2 ± 0.34	34.3 ± 0.36	19.3 ± 0.24	71.2 ± 0.21	47.0 ± 0.45	82.3 ± 0.36

<sup>a</sup>Standard error of mean, standard drug thiourea, % inhibition 100.

bered ring composed of Sn(1)–O(1)–Sn(1A)–O(1A). The geometry around endo- and exocyclic tin atoms varies between six and five coordination which is probably due to intra-molecular interactions between the atoms. In this compound, central Sn<sub>2</sub>O<sub>2</sub> core is fused with two four-membered and two six membered rings. The four membered rings [Sn<sub>2</sub>O<sub>2</sub>, i.e., O(1)–Sn(2)–O(7)–Sn(1A) and O(1A)–Sn(2A)–O(7A)–Sn(1)] are due to the bridging of monodentate ligand through oxygen atoms O(7)–Sn(1A) and O(7A)–Sn(1), respectively. Although, the Sn···O distance for these interactions is quite longer (2.76 Å) than sum of covalent radii of tin-oxygen atoms (2.13 Å) yet significantly shorter than sum of Van der Waal's radii of these atoms (3.68 Å) [33]. If these weaker interactions are taken into consideration, the geometry around endocyclic tin atoms looks like skew trapezoidal with three Sn–O bonds and two Sn–C covalent interactions. Sixth position is occupied by weaker Sn–O interaction. The axial C–Sn–C angle [C(25)–Sn(2)–C(29) = 147.5(4)°] deviates from ideal value (180°) and it shows that adequate space is available for equatorial ligands to coordinate with metal atom [44]. Two six membered rings [Sn<sub>2</sub>O<sub>3</sub>C, i.e., Sn(1)–O(6)–C(1)–O(3)–Sn(2)–O(1), Sn(1A)–O(6A)–C(1A)–O(3A)–Sn(2A)–O(1A)] also overlap central Sn<sub>2</sub>O<sub>2</sub>. The exocyclic tin atoms show trigonal bipyramidal environment arranged by two carbon atoms and three oxygen atoms. In crystal structure of di-*n*-butyltin (**10**) (Fig. 4), One of the carboxylate ligand is attached to both endocyclic [(Sn(2)–O(8) = 2.276 Å] and exocyclic tin atoms [(Sn(2)–O(8) = 2.276 Å] have equal Sn–O interactions while second shows unidentate behaviour. The C–Sn–C angles around endocyclic [C(23)–Sn(2)–C(27) = 136.7(4)°] and exocyclic tin [C(15)–Sn(1)–C(19) = 144.3(4)°] atoms show that distortion around endocyclic tin atoms is relatively higher than exocyclic tin atoms. The weak Sn···O interaction [Sn(1)···O(9) = 2.913 Å], is however, close to that calculated for compound (**2**) but relatively weaker than previous one. In this view, the geometry around endocyclic tin atom can be suggested as trigonal bipyramidal with high distortion. Crystal structure of compound (**7**) has been reported [45] earlier by our group.

## 4. Biological studies

### 4.1. Antibacterial activity

The synthesized compounds (**1–14**) were tested for their antibacterial activity against six bacterial strains, *Escherichia coli*, *Bacillus subtilis*, *Shigella flexenari*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Salmonella typhi*, using agar well diffusion method [46] and data are listed in Table 3. It is observed that all compounds have shown activity against all strains with few exceptions. According to earlier reports [35,36], triorganotin(IV) are more active than the corresponding diorganotin(IV) compounds but a mixed behaviour is observed during this study and sequence varies from strain to strain. However, phenyl derivatives in triorganotin(IV) compounds are found more active than their analogues and butyltin(IV) compounds in diorganotin(IV) stood before methyl and ethyltin(IV) derivatives. This may be due to high lipophilic character of these moieties. The high activity of methyltin(IV) derivatives in some cases can be explained on the basis of ease of diffusion of these compounds through cell membrane due to their smaller size.

### 4.2. Antifungal activity

The reported compounds (**1–14**) were tested for their antifungal activity against six strains, *Trichophyton longifusus*, *Candida albicans*, *Aspergillus flavus*, *Microsporum canis*, *Fusarium solane*, *Candida glaberata* using the agar well protocol [46] and data are listed

in Table 4. All derivatives, in general, showed markedly higher antifungal activity than the ligand with few exceptions. Triorganotin(IV) derivatives were found more active than the diorganotin derivatives, a behaviour quite consistent with the earlier report [47].

#### 4.3. Cytotoxicity

Compounds were also screened for cytotoxic data, using Brine-shrimp (*Artemia salina*) bioassay lethality method [46,48] and results are shown in Table 5. The data illustrate that compounds (1), (4), (5) and (14) show no cytotoxicity. However, the LD<sub>50</sub> value for Bu<sub>3</sub>Sn and Ph<sub>3</sub>Sn (7), derivatives is comparable with standard drug whereas compounds 2, 3, 8, 9 and 10 were found more cytotoxic than the standard drug.

#### 4.4. Insecticidal activity

Four insecticides *Tribolium castaneum*, *Callosobruchus analis*, *Sitophilus oryzae* and *Rhyzopartha dominica* were used for insecticidal activity. The activities were determined by direct contact application using filter paper [49]. The reference drug used was Permethrin (235.71 µg/cm<sup>2</sup>) (Table 6). All compounds were found active but the mortality rate is less than reference insecticidal drug.

#### 4.5. Urease inhibition activity

Antiurease inhibition activity was tested by reported protocol [50] using thiourea as a standard inhibitor and results are given in Table 7. All tested compounds demonstrated fairly good inhibition even at micromolar level. Among these, the most promising activity was noted for alkyltin(IV) derivatives (1 and 2) and phenyltin(IV) derivative (7 and 14). This can be attributed to the ability of these compounds to establish secondary interactions with the active site of enzyme, i.e., nickel. The relatively less activity in case of di-*n*-butyltin (3, 10), di-*n*-octyltin (4, 11) and tri-*n*-butyltin (6, 13) derivatives is presumably due to bulky alkyl group that hinder such kind of interaction of the ligand moiety with enzyme.

### 5. Conclusions

New mononuclear, dinuclear and tetranuclear organotin(IV) derivatives of substituted carboxylate ligands have been synthesized and structurally characterized by various spectroscopic techniques and X-ray crystallography. The later technique authenticated the dinuclear and tetranuclear nature of compounds 1, 2 and 10, respectively. The compound 1 is of particular interest because each Sn atom has pentagonal bipyramidal geometry with one bidentate ligand attached is acting as a bridging one as well. All compounds have been seen biologically active. However, it is observed during biological testing that major role is attributed to the alkyl/aryl groups attached to tin atom while ligands play secondary role.

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#### Appendix A. Supplementary material

CCDC 760097, 760094 and 760095 contain the supplementary crystallographic data for complexes 1, 2 and 10, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://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.ica.2011.01.007.

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