



Dedicated to Professor Ionel Haiduc  
on the occasion of his 75<sup>th</sup> anniversary

## STRUCTURAL CHARACTERIZATION OF SOME NEW TRIS(2,6-DIMETHYLPHENYL)TIN(IV) DERIVATIVES

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The triaryltin(IV) bromide (2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>SnBr (**1**) was prepared by treating SnCl<sub>4</sub> with (2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)MgBr. Exchange reactions between the bromide and KF or KOH afforded (2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>SnF (**2**) and (2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>SnOH (**3**). The solution behavior of compounds **1** – **3** was investigated by multinuclear (<sup>1</sup>H, <sup>13</sup>C and <sup>119</sup>Sn) NMR spectroscopy. Single-crystal X-ray diffraction analyses for compounds **1**, **3** and **3**·THF revealed that the coordination geometry around the metal atom is distorted tetrahedral.

### INTRODUCTION

Most of the triaryltin(IV) chlorides,<sup>1-10</sup> bromides<sup>11,12</sup> and iodides<sup>13-16</sup> for which the molecular structures were reported are monomeric in solid state, with a tetrahedral C<sub>3</sub>SnX core of different distortion degree. Typical examples are Ph<sub>3</sub>SnX (X = Cl,<sup>7</sup> I<sup>13</sup> Br,<sup>11</sup> I<sup>14-16</sup>), (2-MeOC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>SnX (X = Cl,<sup>7</sup> I<sup>13</sup>) or Mes<sub>3</sub>SnX (X = Cl,<sup>8</sup> Br,<sup>12</sup> I<sup>14</sup>). Molecular species are also formed when the aryl groups attached to tin have at least one substituent able to provide intramolecular coordination through a donor atom,<sup>17-27</sup> thus resulting in distorted trigonal bipyramidal geometry at the tin, e.g. [2-(PhN=N)C<sub>6</sub>H<sub>4</sub>]Ph<sub>2</sub>SnCl,<sup>17</sup> [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]Ph<sub>2</sub>SnX (X = Cl,<sup>18,20</sup> Br,<sup>24</sup> I<sup>20</sup>), [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>PhSnCl,<sup>19</sup> [2,6-(ROCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]Ph<sub>2</sub>SnCl (R = Me,<sup>21,22</sup> Et<sup>22</sup>), [2,6-(ROCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]Ph<sub>2</sub>SnI (R = Me,<sup>26</sup> Bu<sup>i</sup>,<sup>27</sup>) or (2-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>)Ph<sub>2</sub>SnCl, (2-Pr<sup>i</sup>PC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>PhSnCl.<sup>23</sup> By contrast, the structures of triaryltin(IV) fluorides and hydroxides are dependent on the steric requirements of the organic groups attached to the tin atom. Thus, Ph<sub>3</sub>SnF<sup>28</sup> and Ph<sub>3</sub>SnOH<sup>29,30</sup> exhibit chain polymeric structures in solid state, with fluorine or

hydroxy bridges between metal atoms and consequently trigonal bipyramidal coordination environments around tin. When steric protection or potential intramolecular coordination is provided by the aryl groups, then molecular species can be obtained as described so far in the literature for few compounds, i.e. Mes<sub>3</sub>SnX (X = F, OH),<sup>31</sup> (2-MeOC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>SnF,<sup>7</sup> [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]Ph<sub>2</sub>SnF.<sup>20,32</sup> On the other hand the triaryltin(IV) hydroxides are generally rare due to the tendency for condensation to bis(triaryltin) oxides.<sup>7</sup>

We report here on the synthesis, the solution behavior of three new molecular triaryltin(IV) derivatives, (2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>SnX [X = Br (**1**), F (**2**), OH (**3**)] as well as the solid state structure for **1**, **3** and the adduct **3**·THF.

### RESULTS

The triaryltin(IV) bromide (2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>SnBr (**1**) was isolated from the reaction mixture obtained by treatment of SnCl<sub>4</sub> with (2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)MgBr as result of a halogen exchange reaction. The bromide **1** was used to obtain the corresponding fluorine

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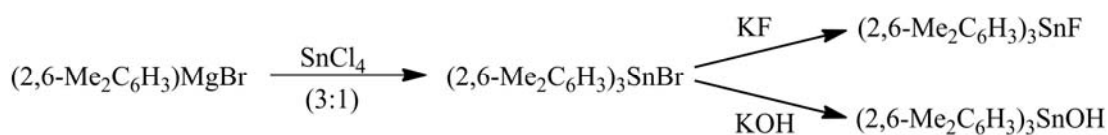
and hydroxy derivatives  $(2,6\text{-Me}_2\text{C}_6\text{H}_3)_3\text{SnF}$  (**2**) and  $(2,6\text{-Me}_2\text{C}_6\text{H}_3)_3\text{SnOH}$  (**3**), respectively, by exchange of the halogen following treatment with KF or by treatment with potassium hydroxide in a two-layer solvent system ( $\text{H}_2\text{O}/\text{MeOH}/\text{CH}_2\text{Cl}_2$ ) (Scheme 1).

The triaryltin(IV) hydroxide **3** was also obtained after the reduction of **1** with potassium in THF, due to the presence of moisture in the reaction mixture. Details of the preparations are given in the Experimental section. All compounds were isolated as air-stable, colorless, crystalline products. They are soluble in common organic solvents.

All compounds were investigated by multinuclear ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{119}\text{Sn}$ ) NMR spectroscopy in solution at room temperature. The assignment of the  $^1\text{H}$  and  $^{13}\text{C}$  resonances was based on the comparison with the starting material and tin-carbon coupling constants. The solution NMR spectra of the isolated products, recorded in  $\text{CDCl}_3$ , are consistent with the formation of the title

compounds. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra showed the expected resonances in the alkyl as well as in the aryl regions for the organic groups attached to tin atom. Most  $^{13}\text{C}$  resonances are surrounded by the satellites corresponding to tin-carbon couplings.

Single crystals of **1** and **3** were grown from a  $\text{CH}_2\text{Cl}_2/\text{n-hexane}$  mixture using the slow diffusion technique. Crystals of **3**·THF were obtained at low temperature from the clear filtrate of the reaction mixture (See Experimental section). The crystal and molecular structures of **1**, **3** and **3**·THF were established by X-ray diffraction studies. The crystals of both compounds contain discrete monomers, with no unusual intermolecular distances shorter than the sum of the van der Waals radii between heavy atoms. Selected bond distances and angles are listed in Table 1. Fig. 1 shows the ORTEP-like view of the molecular structure of **1**, **3** and adduct **3**·THF, respectively, with the atom numbering scheme.



Scheme 1

Table 1

Selected interatomic distances (Å) and angles (deg) in  $(2,6\text{-Me}_2\text{C}_6\text{H}_3)_3\text{SnX}$ 

	<b>1</b> (X = Br)	<b>3</b> (X = OH)	<b>3</b> ·THF (X = OH)
Sn(1)–C(1)	2.162(4)	2.149(6)	2.144(9)
Sn(1)–C(9)	2.159(4)	2.156(5)	2.149(9)
Sn(1)–C(17)	2.151(4)	2.154(6)	2.174(11)
Sn(1)–X(1)	2.5443(6)	2.001(4)	2.058(7)
O(1)–H(1)		0.79(2)	0.8200
C(1)–Sn(1)–C(9)	115.44(16)	117.1(2)	115.9(4)
C(1)–Sn(1)–C(17)	113.88(16)	114.6(2)	116.8(4)
C(9)–Sn(1)–C(17)	117.61(15)	111.1(2)	111.7(4)
X(1)–Sn(1)–C(1)	103.16(12)	101.5(2)	103.6(3)
X(1)–Sn(1)–C(9)	101.51(11)	106.3(2)	101.4(4)
X(1)–Sn(1)–C(17)	102.01(11)	104.6(2)	105.0(3)
C(2)–C(1)–Sn(1)	120.6(3)	122.6(5)	117.7(7)
C(6)–C(1)–Sn(1)	119.5(3)	117.2(5)	120.3(9)
C(10)–C(9)–Sn(1)	119.9(3)	120.8(4)	122.4(7)
C(14)–C(9)–Sn(1)	120.3(3)	119.7(4)	121.2(8)
C(18)–C(17)–Sn(1)	120.0(3)	118.6(4)	119.7(9)
C(22)–C(17)–Sn(1)	120.9(3)	122.8(4)	121.7(8)
Sn(1)–O(1)–H(1)		102(6)	109.5

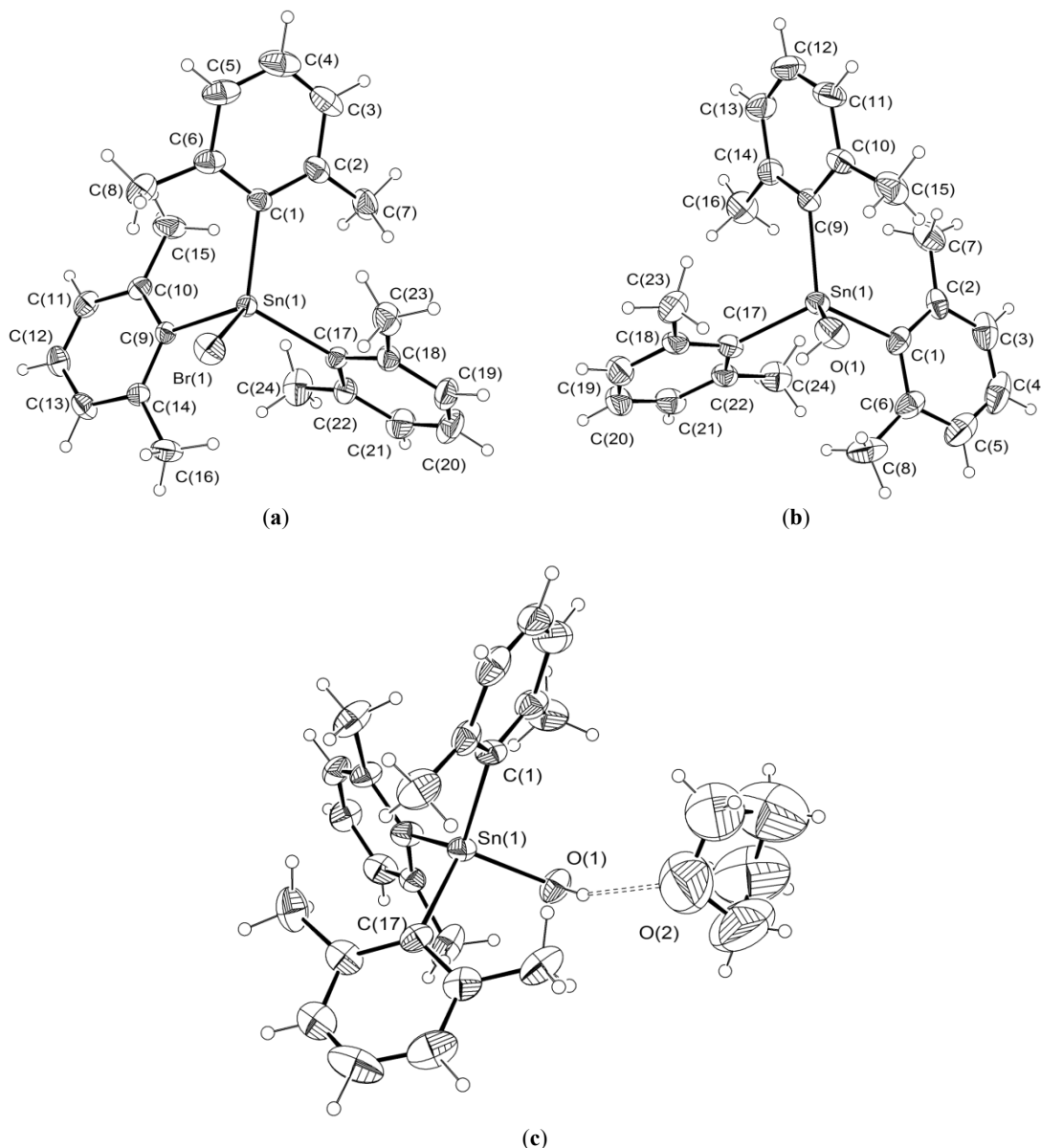


Fig. 1 – ORTEP representation at 30% probability and atom numbering scheme for (a) (2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>SnBr (**1**), (b) (2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>SnOH (**3**) and (c) (2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>SnOH·THF (**3**)·THF.

## DISCUSSION

### Solution behavior

The NMR (<sup>1</sup>H, <sup>13</sup>C) spectra of compounds **1**, **2** and **3**·THF are very similar with respect to the 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> groups attached to tin. The presence of only one set of resonances for the three organic groups in the (2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>Sn moiety suggests that they are equivalent in solution. Moreover, only one resonance was observed for the methyl groups in position 2 and 6 of the aromatic ring thus indicating that a fast rotation around to Sn–C bond is allowed to bring the methyl protons in similar

environment on NMR time scale. In addition to the resonances for the aromatic groups attached to tin, the <sup>1</sup>H NMR spectrum of **3**·THF also shows the resonances for the OH group and for the tetrahydrofuran solvent molecule. The <sup>13</sup>C spectra of these compounds also contain only one set of four resonances in the aromatic region. Each signal was surrounded by tin satellites, the magnitude of the carbon-tin coupling constants being used for assignment of the aromatic <sup>13</sup>C resonances. For compound **2** a fluorine-carbon coupling was observed not only for the resonance corresponding to the *ipso* carbon from the aromatic ring (<sup>2</sup>J<sub>FC</sub> 9.8 Hz), but also for the resonance of the methyl carbons which appears as a doublet (<sup>4</sup>J<sub>FC</sub> 2.9 Hz).

The  $^{119}\text{Sn}$  NMR spectra of compounds **1**, **2** and **3**·THF exhibit only one sharp resonance, a behavior consistent with the presence of only one tin-containing species in solution. A doublet pattern was observed for the  $^{119}\text{Sn}$  resonance of **2** due to the tin-fluorine coupling ( $^1J_{\text{SnF}}$  2295 Hz; cf.  $^1J_{\text{SnF}}$  -2285.5 ppm in  $\text{CDCl}_3$  for  $\text{Mes}_3\text{SnF}^{31}$ ). The magnitude of room temperature  $^{119}\text{Sn}$  chemical shifts for compounds **1**, **2** and **3**·THF ( $\delta$  -130.5, -76.7 and -109.7 ppm for **1**, **2** and **3**·THF, respectively, in  $\text{CDCl}_3$ ) is consistent with tetracoordinate tin(IV) species [cf.  $\delta$  -59.8 ppm in  $\text{CDCl}_3$  for  $\text{Ph}_3\text{SnBr}$ ;<sup>33</sup>  $\delta$  -120.98 ppm in  $\text{CDCl}_3$  for  $\text{Mes}_3\text{SnBr}$ ;<sup>6</sup>  $\delta$  -66.51 ppm in  $\text{CDCl}_3$  for  $\text{Mes}_3\text{SnF}$ ;<sup>31</sup>  $\delta$  -86 ppm in saturated  $\text{CH}_2\text{Cl}_2$  for  $\text{Ph}_3\text{SnOH}$ <sup>34</sup>].

### Solid state structure

The molecules of compounds **1**, **3** and **3**·THF feature a tetracoordinated metal atom with distorted tetrahedral coordination geometry (Fig. 1). The nature of the inorganic substituent on the metal center has little effect on the coordination geometry and the angles around the tin atom [range for the angles around the metal center: 101.51(11)° - 117.61(15)° for **1**, 101.5(2)° - 117.1(2)° for **3** and 101.4(4)° - 116.8(4)° for **3**·THF] (see Table 1). The molecular structures of compounds investigated in this work are similar with those reported for other triaryltin(IV) halides as are the magnitudes of the geometric parameters (Table 2; see also reference 7).

The length of the Sn–Br bond in the molecule of **1** [Sn(1)–Br(1) 2.5443(6) Å] is similar to that observed in the related  $\text{Mes}_3\text{SnBr}$  [2.546(1) / 2.544(1) Å for the two independent molecules in the unit cell],<sup>12</sup> but slightly longer than found in  $\text{Ph}_3\text{SnBr}$  [2.490(2) / 2.500(2) Å for the two independent molecules in the unit cell].<sup>11</sup> The Sn–O bond in the molecule of **3** [Sn(1)–O(1) 2.001(4) Å] has the same magnitude as in the monomeric hydroxide  $\text{Mes}_3\text{SnOH}$  [1.999(6) Å],<sup>31</sup> while in **3**·THF the corresponding Sn–O bond [Sn(1)–O(1) 2.058(7) Å] is slightly elongated due to the hydrogen bonding established between the hydroxyl group and the oxygen atom of the solvent molecule (see subsequent discussion).

A closer check of the crystal structures revealed that intermolecular hydrogen bonding interactions shorter than the sum of the corresponding van der Waals radii [ $\Sigma_{\text{vdW}}(\text{Br},\text{H}) = 3.15$  Å,  $\Sigma_{\text{vdW}}(\text{O},\text{H}) = 2.55$  Å]<sup>35</sup> are present in the crystals of **1** and **3**·THF. Thus, compound **1** forms dimeric units in solid state which are further linked in a three-dimensional supramolecular architecture (Fig. 2) through weak H···Br interactions [H(4)···Br(1) = 3.073(1) Å, C(4)–H(4)···Br(1) = 155.4(4)° and H(20)···Br(1) = 3.128(2) Å, C(20)–H(20)···Br(1) = 134.9(4)°].

In compound **3**·THF a strong hydrogen bond is formed between the OH bonded to tin and the oxygen atom of the solvent molecule [H(1)···O(2) = 2.104(2) Å, O(1)–H(1)···O(2) = 150(7)°] (Fig. 1c).

### EXPERIMENTAL

Most of the syntheses were carried out in argon atmosphere using Schlenk techniques. Solvents were dried and freshly distilled prior to use. The NMR spectra were recorded at room temperature on Bruker Avance 300 instrument using solutions in  $\text{CDCl}_3$ . The chemical shifts are reported in  $\delta$  units (ppm) relative to the residual peak of the deuterated solvent (ref.  $\text{CHCl}_3$ :  $^1\text{H}$  7.26,  $^{13}\text{C}$  77.0 ppm) for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, respectively. The  $^{119}\text{Sn}$  chemical shifts are referred to neat  $\text{SnMe}_4$ . 2-Bromo-1,3-dimethylbenzene, magnesium, tin tetrachloride and potassium hydroxide were commercially available.

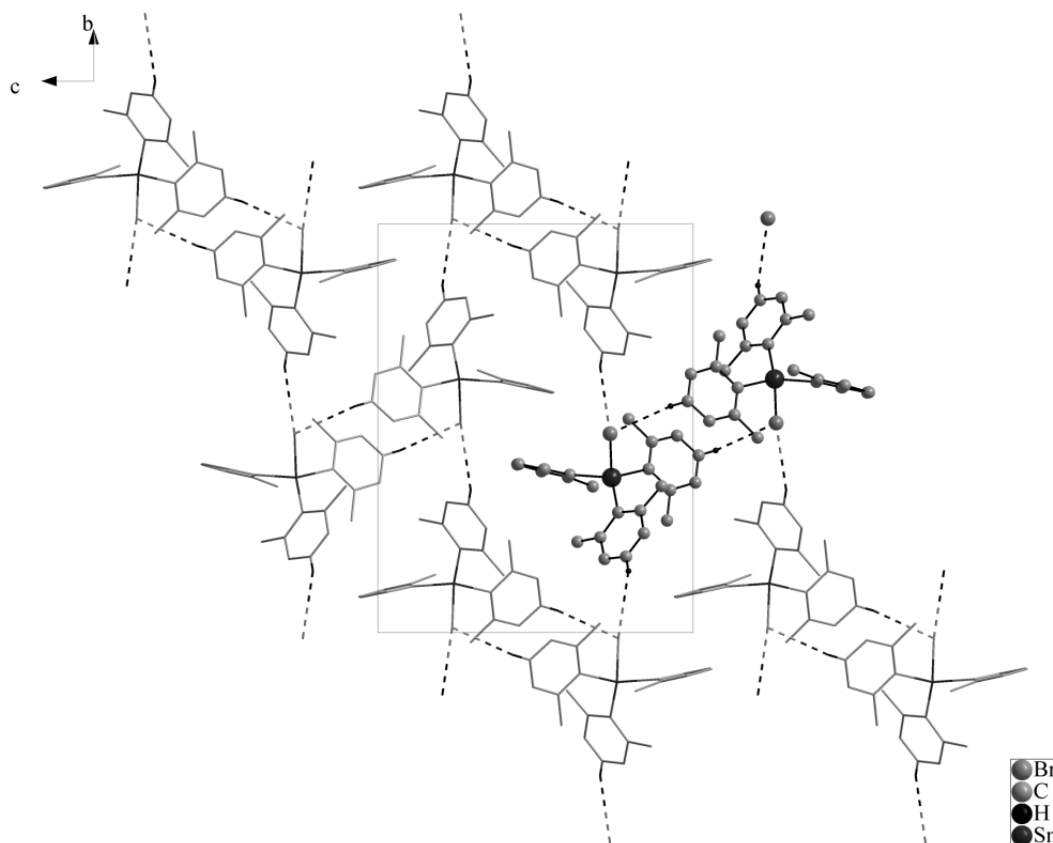
#### *Synthesis of tris(2,6-dimethylphenyl)tin(IV) bromide, (2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>SnBr (**1**)*

A Grignard reagent solution prepared from 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Br (7.2 mL, 10 g, 54 mmol) and Mg (1.3 g, 53.5 mmol) in diethyl ether was added dropwise, under argon, to a solution of  $\text{SnCl}_4$  (1.6 mL, 3.56 g, 13.66 mmol) in diethyl ether. The reaction mixture was stirred for two and a half days, then filtered and the precipitate was washed with  $\text{Et}_2\text{O}$ . The solvent was removed in vacuum from the clear filtrate and the residue was recrystallized from EtOH to give the title compound as a white crystalline solid. Yield: 5.8 g (83%). M.p. = 177–178 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 20 °C): 2.48s (18H,  $\text{C}_6\text{H}_3\text{-CH}_3$ ,  $^4J_{\text{SnH}}$  6.6 Hz), 7.09d (6H,  $\text{C}_6\text{H}_3\text{-meta}$ ,  $^3J_{\text{HH}}$  7.6 Hz,  $^4J_{\text{SnH}}$  25 Hz), 7.24m (3H,  $\text{C}_6\text{H}_3\text{-para}$ ).  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ , 20 °C): 25.83s ( $\text{C}_6\text{H}_3\text{-CH}_3$ ,  $^3J_{\text{SnC}}$  41.6 Hz), 128.13s ( $\text{C}_6\text{H}_3\text{-meta}$ ,  $^3J_{\text{SnC}}$  50.1 / 52.6 Hz), 129.72s ( $\text{C}_6\text{H}_3\text{-para}$ ,  $^4J_{\text{SnC}}$  11.3 Hz), 144.13s ( $\text{C}_6\text{H}_3\text{-ortho}$ ,  $^2J_{\text{SnC}}$  42.5 / 43.8 Hz), 144.48s ( $\text{C}_6\text{H}_3\text{-ipso}$ ,  $^1J_{\text{SnC}}$  545.2 / 570.6 Hz).  $^{119}\text{Sn}$  NMR (111.9 MHz,  $\text{CDCl}_3$ , 20 °C): -130.5s ( $^1J_{\text{SnC}}$  570.3 Hz,  $^2J_{\text{SnC}}$  43.5 Hz,  $^3J_{\text{SnC}}$  52.6 Hz).

Table 2

Geometric parameters for (2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>SnX.<sup>a</sup>

Compound	$\Sigma\theta_{ax}$	$\Sigma\theta_{eq}$	$\Sigma\theta_{ax} - \Sigma\theta_{eq}$
<b>1</b>	306	347	41
<b>3</b>	312	343	31
<b>3</b> ·THF	310	341	31

<sup>a</sup>  $\Sigma\theta_{ax} = \Sigma\text{angle}_{\text{CSnX}} (^{\circ})$ ,  $\Sigma\theta_{eq} = \Sigma\text{angle}_{\text{CSnC}} (^{\circ})$ .Fig. 2 – View along the *a* axis of the supramolecular architecture in the crystal of **1** based on intermolecular Br···H, showing the dimeric units and inter-dimer interactions.*Synthesis of tris(2,6-dimethylphenyl)tin(IV) fluoride, (2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>SnF (**2**)*

Methylene dichloride was added to a suspension of **1** (0.3 g, 0.58 mmol) in 10 mL of MeOH until the solid compound dissolved. An aqueous solution of KF (0.2 g, 3.44 mmol) was then added and the mixture was stirred for 3 h at room temperature. The organic layer was separated and the water solution was washed twice with 5 mL of CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then filtered. The solvent was removed in vacuum from the clear filtrate and the obtained white solid residue was recrystallized from a CH<sub>2</sub>Cl<sub>2</sub>/n-hexane mixture to give the title compound. Yield: 0.23 g (87%). M.p. = 208-210 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 20 °C): 2.41s (18H, C<sub>6</sub>H<sub>3</sub>-CH<sub>3</sub>), 7.08d (6H, C<sub>6</sub>H<sub>3</sub>-meta, <sup>3</sup>J<sub>HH</sub> 7.5 Hz, <sup>4</sup>J<sub>SnH</sub> 24.5 Hz), 7.24m (3H, C<sub>6</sub>H<sub>3</sub>-para). <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>, 20 °C): 24.45d (C<sub>6</sub>H<sub>3</sub>-CH<sub>3</sub>, <sup>3</sup>J<sub>SnC</sub> 39.6 Hz, <sup>4</sup>J<sub>FC</sub> 2.9 Hz), 127.75s (C<sub>6</sub>H<sub>3</sub>-meta, <sup>3</sup>J<sub>SnC</sub> 53.3 Hz), 129.96s (C<sub>6</sub>H<sub>3</sub>-para, <sup>4</sup>J<sub>SnC</sub> 10.7 Hz), 144.15s (C<sub>6</sub>H<sub>3</sub>-ortho, <sup>2</sup>J<sub>SnC</sub> 43.3 Hz), 144.22d (C<sub>6</sub>H<sub>3</sub>-ipso, <sup>2</sup>J<sub>FC</sub> 9.8 Hz). <sup>119</sup>Sn NMR (111.9 MHz, CDCl<sub>3</sub>, 20 °C): -76.7d (<sup>1</sup>J<sub>SnF</sub> 2295 Hz).

*Synthesis of tris(2,6-dimethylphenyl)tin(IV) hydroxide, (2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>SnOH (**3**)*

(a) Compound **3** was prepared as above from a solution of **1** (0.3 g, 0.58 mmol) in MeOH/CH<sub>2</sub>Cl<sub>2</sub> and an aqueous solution of KOH (0.17 g, 3 mmol), at room temperature. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane mixture gave the title compound as colorless crystals. Yield: 0.20 g (76%). M.p. = 141-143 °C.

(b) A solution of **1** (0.3 g, 0.58 mmol) in 10 mL of THF was added to potassium (0.0625 g, 1.6 mmol) in THF (10 mL). The reaction mixture was stirred for 2 hours, then it was filtered with a cannula under inert atmosphere and the resulted solution was stored at low temperature for several weeks to give **3**·THF (0.2 g, 66%) as colorless crystals. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 20 °C): 0.51s (1H, -OH), 1.85m (4H, -CH<sub>2</sub>-CH<sub>2</sub>, THF), 2.40s (18H, C<sub>6</sub>H<sub>3</sub>-CH<sub>3</sub>, <sup>4</sup>J<sub>SnH</sub> 7.0 Hz), 3.75m (4H, -O-CH<sub>2</sub>-, THF), 7.04d (6H, C<sub>6</sub>H<sub>3</sub>-meta, <sup>3</sup>J<sub>HH</sub> 7.5 Hz, <sup>4</sup>J<sub>SnH</sub> 22.6 Hz), 7.20m (3H, C<sub>6</sub>H<sub>3</sub>-para). <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>, 20 °C): 24.90s (C<sub>6</sub>H<sub>3</sub>-CH<sub>3</sub>, <sup>3</sup>J<sub>SnC</sub> 38.0 Hz), 25.59s (-CH<sub>2</sub>-CH<sub>2</sub>-, THF), 67.95s (-O-CH<sub>2</sub>-, THF), 127.71s (C<sub>6</sub>H<sub>3</sub>-

*meta*,  $^3J_{\text{SnC}}$  49.8 / 51.4 Hz), 129.45s ( $\text{C}_6\text{H}_3$ -*para*,  $^4J_{\text{SnC}}$  10.7 Hz), 144.16s ( $\text{C}_6\text{H}_3$ -*ortho*,  $^2J_{\text{SnC}}$  39.7 / 40.9 Hz), 145.08s ( $\text{C}_6\text{H}_3$ -*ipso*,  $^1J_{\text{SnC}}$  579.5 / 606.2 Hz).  $^{119}\text{Sn}$  NMR (111.9 MHz,  $\text{CDCl}_3$ , 20 °C): -109.7s.

#### Crystal structure determination

Crystallographic data for the structural analysis of compounds **1**, **3** and **3**·THF have been collected on a Bruker SMART APEX system (Babes-Bolyai University, Cluj-Napoca) using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Cell constants are given in Table 3, along with other experimental parameters and relevant information pertaining to structure solution and refinement.

The structures were refined with anisotropic thermal parameters. All C-bound H atoms were placed in calculated positions (C–H = 0.93–0.97 Å) and treated using a riding model with  $U_{\text{iso}} = 1.5U_{\text{eq}}(\text{C})$  for methyl H atoms and  $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$  for the rest. The methyl group was allowed to

rotate, but not to tip, to best fit the electron density. The hydrogen atom from the OH in compound **2** was found in the difference map and refined with a restrained distance of 0.79(2) Å. For structure solving and refinement the software package SHELX-97 was used.<sup>37</sup> The drawings were created with the ORTEP-3<sup>38</sup> and Diamond programs.<sup>39</sup>

#### Supplementary material

CCDC-865940 (**1**), -865942 (**3**), and -865941 (**3**·THF) contain the supplementary crystallographic data for this paper. These data have been deposited with the Cambridge Crystallographic Data Centre. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Table 3

Crystallographic data for (2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>SnX

Compound	<b>1</b> (X = Br)	<b>3</b> (X = OH)	<b>3</b> ·THF (X = OH)
Molecular formula	C <sub>24</sub> H <sub>27</sub> SnBr	C <sub>24</sub> H <sub>28</sub> OSn	C <sub>28</sub> H <sub>36</sub> O <sub>2</sub> Sn
<i>M</i>	514.06	451.15	523.26
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> -1	<i>C</i> <i>c</i>
Temperature (K)	297(2)	297(2)	297(2)
<i>a</i> /Å	8.0258(6)	9.5433(15)	15.858(5)
<i>b</i> /Å	18.8799(15)	10.1264(15)	15.928(5)
<i>c</i> /Å	14.5968(12)	12.1334(19)	10.552(3)
$\alpha^\circ$	90	99.176(2)	90
$\beta^\circ$	95.5010(10)	101.092(2)	103.735(6)
$\gamma^\circ$	90	110.039(2)	90
<i>V</i> /Å <sup>3</sup>	2201.6(3)	1048.2(3)	2589.1
<i>Z</i>	4	2	4
<i>D</i> <sub>calc</sub> /gcm <sup>-3</sup>	1.551	1.429	1.342
<i>F</i> (000)	1024	460	1080
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	2.980	1.228	1.007
Crystal size (mm <sup>3</sup> )	0.25 x 0.24 x 0.22	0.25 x 0.20 x 0.13	0.32 x 0.28 x 0.25
$\theta$ range for data collection (°)	1.77 to 26.37	2.21 to 25.00	1.84 to 25.00
Reflections collected	17500	10174	9233
Independent reflections	4485 [ <i>R</i> <sub>int</sub> = 0.0356]	3689 [ <i>R</i> <sub>int</sub> = 0.0476]	4470 [ <i>R</i> <sub>int</sub> = 0.0495]
Absorption correction	Multi-Scan <sup>36</sup>	Multi-Scan <sup>36</sup>	Multi-Scan <sup>36</sup>
Maximum and minimum transmissions	0.5601 and 0.5229	0.8567 and 0.7488	0.7868 and 0.7388
Data / restraints / parameters	4485 / 0 / 241	3689 / 1 / 245	4470 / 71 / 286
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.211	1.173	1.071
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>a</sup>	<i>R</i> <sub>1</sub> = 0.0460 <i>wR</i> <sub>2</sub> = 0.0935	<i>R</i> <sub>1</sub> = 0.0552 <i>wR</i> <sub>2</sub> = 0.1051	<i>R</i> <sub>1</sub> = 0.0671 <i>wR</i> <sub>2</sub> = 0.1420
<i>R</i> indices (all data) <sup>a</sup>	<i>R</i> <sub>1</sub> = 0.0513 <i>wR</i> <sub>2</sub> = 0.0958	<i>R</i> <sub>1</sub> = 0.0667 <i>wR</i> <sub>2</sub> = 0.1089	<i>R</i> <sub>1</sub> = 0.0822 <i>wR</i> <sub>2</sub> = 0.1497
Largest difference peak and hole (e Å <sup>-3</sup> )	0.971 and -0.782	0.666 and -1.313	1.192 and -0.518

<sup>a</sup> Definition of the *R* values:  $R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o|$ ;  $wR_2 = \{[\sum w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$  with  $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ .

## CONCLUSION

The triorganotin(IV) derivatives presented in this work exhibit a tetrahedral structure as expected for derivatives containing aryl groups with substituted *ortho* positions. Their monomeric

nature was confirmed in solution by the magnitude of the  $^{119}\text{Sn}$  chemical shifts, while in solid state the tetracoordination of the metal center was established for **1**, **3** and **3**·THF by single-crystal X-ray diffraction. Weak intermolecular interactions

resulted in the formation of a three-dimensional supramolecular architecture in the case of **1**.

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