



Dedicated to Professor Cristian Silvestru  
on the occasion of his 65th anniversary

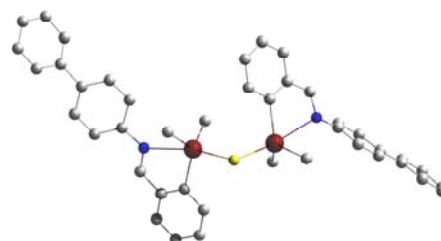
## SYNTHESIS AND CHARACTERIZATION OF NOVEL HOMOBIMETALLIC ORGANOTIN(IV) COMPOUNDS

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The (imino)aryltin(IV) chloride [2-(1,1'-C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>4</sub>-4-N=CH)C<sub>6</sub>H<sub>4</sub>]SnMe<sub>2</sub>Cl (**1**) was prepared by mixing [2-(O=CH)C<sub>6</sub>H<sub>4</sub>]SnMe<sub>2</sub>Cl with (1,1'-biphenyl)-4-amine in the absence of a solvent or catalyst. Reaction of **1** with sodium sulfide gave [{2-(1,1'-C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>4</sub>-4-N=CH)C<sub>6</sub>H<sub>4</sub>}SnMe<sub>2</sub>]<sub>2</sub>S (**2**). Treatment of **2** with ZnCl<sub>2</sub> or ZnSO<sub>4</sub> led to the isolation of the corresponding chloride (**1**) or sulfate [{2-(1,1'-C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>4</sub>-4-N=CH)C<sub>6</sub>H<sub>4</sub>}SnMe<sub>2</sub>]<sub>2</sub>SO<sub>4</sub> (**3**), respectively. All compounds were characterized in solution by multinuclear (<sup>1</sup>H, <sup>13</sup>C and <sup>119</sup>Sn) NMR spectroscopy and mass spectrometry. In solid state, for all derivatives, IR spectroscopy confirms the presence of C=N double bonds, while single-crystal X-ray diffraction analyses revealed the presence of pentacoordinated metal centers with a distorted trigonal bipyramidal geometry.



### INTRODUCTION

Interest in organotin compounds with *C,N*-pendant arm ligands containing a *sp*<sup>2</sup> hybridized nitrogen, part of an imine functional group (*C,N*<sub>imine</sub>), has increased in the last years.<sup>1-5</sup> These type of derivatives have been obtained, until recently, starting from an imine containing ligand either by *ortho*-lithiation of the ligand and subsequent reaction with tin derivatives<sup>6-8</sup> or *ortho*-metalation through rearrangement of benzylideneaminotin(IV) halides.<sup>9,10</sup> Derivatization of a carbonyl group from an organic moiety bonded to tin with different amines gives organotin(IV) compounds that can (i) stabilize unusual species,<sup>1</sup> (ii) coordinate to other metal centers through

additional donor atoms or groups present in the parent amine<sup>2,5</sup> or (iii) result in homobimetallic derivatives by using diamines.<sup>5</sup> On the other hand, homobimetallic organotin(IV) compounds with *C,N*-pendant arm ligands can be obtained by using sulfur to bridge two tin atoms. In most cases these sulfides are a result of reactivity studies performed on the corresponding organotin(IV) derivatives<sup>11-14</sup> and only rarely are used themselves in reactions.<sup>16,17</sup>

We report here on the synthesis, characterization and crystal structure of some new homobimetallic triorganotin(IV) species with *C,N*<sub>imine</sub>-pendant arm ligands, *i.e.* [2-(1,1'-C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>4</sub>-4-N=CH)C<sub>6</sub>H<sub>4</sub>]SnMe<sub>2</sub>Cl (**1**), [{2-(1,1'-C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>4</sub>-4-N=CH)C<sub>6</sub>H<sub>4</sub>}SnMe<sub>2</sub>]<sub>2</sub>S (**2**) and [{2

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(1,1'-C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>4</sub>-4-N=CH)C<sub>6</sub>H<sub>4</sub>}SnMe<sub>2</sub>]<sub>2</sub>SO<sub>4</sub> (**3**), and the reactivity of **2** towards ZnCl<sub>2</sub> and ZnSO<sub>4</sub>.

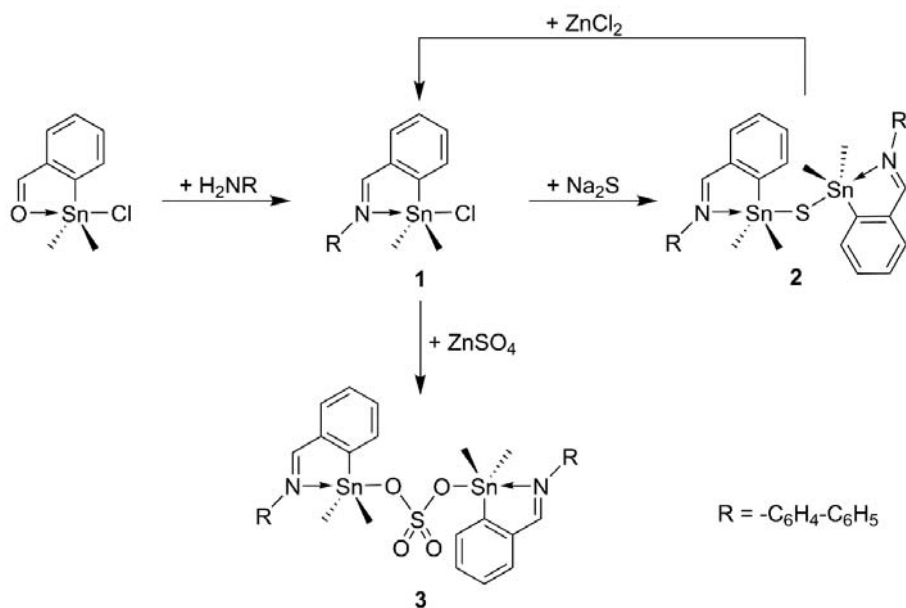
## RESULTS

Condensation reaction to obtain compound [2-(1,1'-C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>4</sub>-4-N=CH)C<sub>6</sub>H<sub>4</sub>}SnMe<sub>2</sub>Cl (**1**) was performed by mixing [2-(O=CH)C<sub>6</sub>H<sub>4</sub>}SnMe<sub>2</sub>Cl<sup>5</sup> with (1,1'-biphenyl)-4-amine in the absence of a solvent or catalyst, as described previously for related organotin(IV) species.<sup>1-5</sup> Total conversion to the desired compound was confirmed by the <sup>1</sup>H NMR spectra of the crude product. Reaction of imine **1** with sodium sulfide gave the homobimetallic derivative **2**. Treating **2** with ZnCl<sub>2</sub> or ZnSO<sub>4</sub> resulted in the corresponding chloride (**1**) or sulfate (**3**), respectively (Scheme 1).

The compounds were isolated as air-stable solids. The monochloride **1** shows good solubility

in chlorinated solvents (CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>), while the imine containing compounds **2** and **3** exhibit a low solubility in common solvents. Compounds **1-3** were characterized by multinuclear NMR spectroscopy and high-resolution mass spectrometry, and satisfactory analytical results were obtained. For all species the base peaks in the APCI+ mass spectra were assigned to [RMe<sub>2</sub>Sn<sup>+</sup>] fragments. The IR stretching vibration of the carbon-nitrogen double bond in derivatives **1-3** appears in the region 1623–1614 cm<sup>-1</sup> as typical for compounds containing Schiff-base ligands.

Single crystals suitable for X-ray diffraction studies were obtained by slow diffusion of *n*-hexane into CH<sub>2</sub>Cl<sub>2</sub> solutions of the title compounds. The solid state molecular structures of these dimethyltin(IV) derivatives are depicted in Figures 1–3. Selected interatomic distances and angles are summarized in Tables 1 and 2.



Scheme 1 – Synthesis of compounds **1-3**.

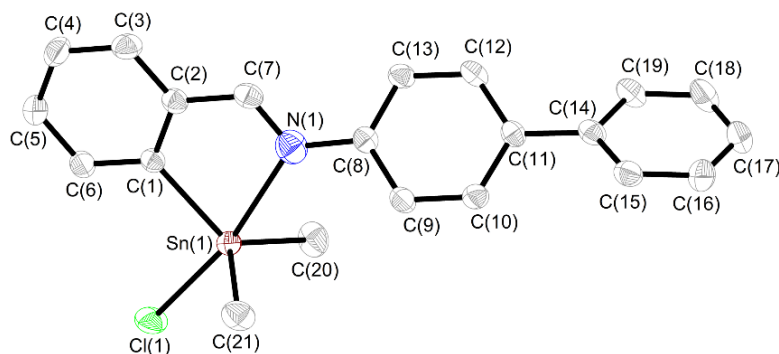


Fig. 1 – ORTEP representation at 30% probability and the atom numbering scheme for compound **1** (hydrogen atoms are removed for clarity).

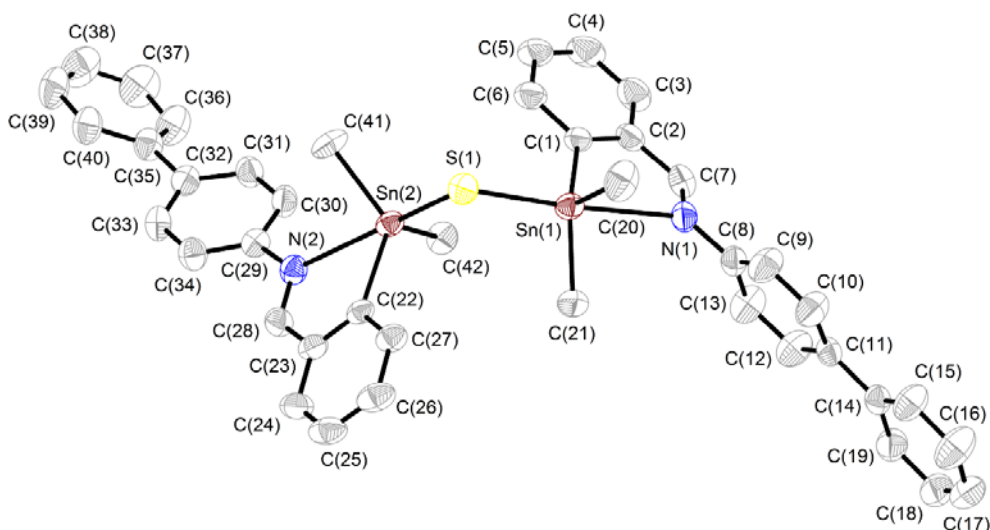


Fig. 2 – ORTEP representation at 30% probability and the atom numbering scheme for compound **2** (hydrogen atoms are removed for clarity).

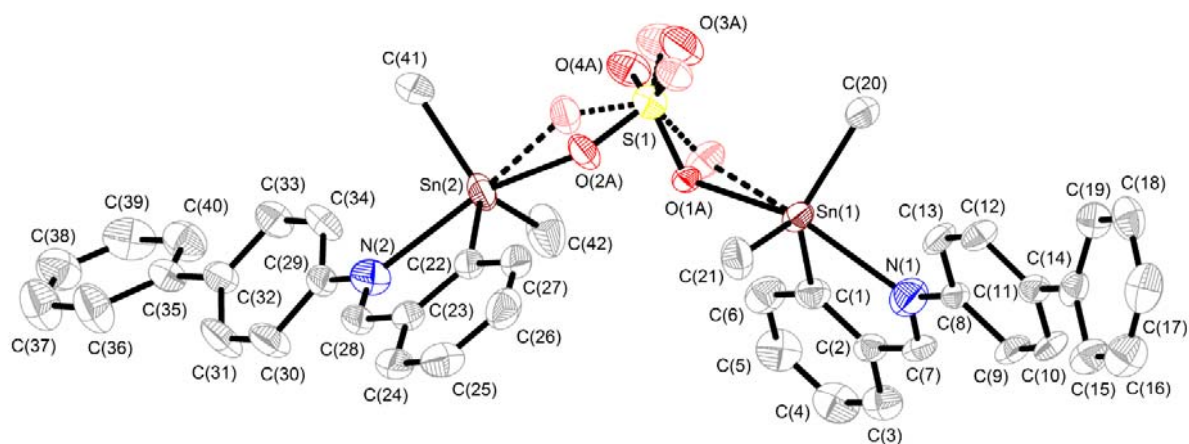


Fig. 3 – ORTEP representation at 30% probability and the atom numbering scheme for compound **3** (hydrogen atoms are removed for clarity).

Table 1

Selected bond distances (Å) and angles (°) for compound **1**

Sn(1)–C(1)	2.133(4)	N(1)–Sn(1)–C(1)	73.87(14)
Sn(1)–C(20)	2.115(5)	N(1)–Sn(1)–C(21)	87.03(16)
Sn(1)–C(21)	2.109(4)	N(1)–Sn(1)–C(21)	93.03(15)
Sn(1)–Cl(1)	2.486(1)	C(1)–Sn(1)–C(20)	124.48(17)
Sn(1)–N(1)	2.484(3)	C(1)–Sn(1)–C(21)	115.19(17)
Cl(1)–Sn(1)–C(1)	95.78(11)	C(20)–Sn(1)–C(21)	117.50(19)
Cl(1)–Sn(1)–C(20)	95.33(14)	Cl(1)–Sn(1)–N(1)	168.64(9)
Cl(1)–Sn(1)–C(21)	95.70(13)		

Table 2

Selected bond distances (Å) and angles (°) for compounds **2** and **3**<sup>a</sup>

	<b>2</b>	<b>3</b>		<b>2</b>	<b>3</b>
Sn(1)–C(1)	2.151(5)	2.118(7)	Sn(2)–C(22)	2.140(5)	2.127(6)
Sn(1)–C(20)	2.128(7)	2.116(7)	Sn(2)–C(41)	2.133(5)	2.129(7)
Sn(1)–C(21)	2.133(6)	2.113(8)	Sn(2)–C(42)	2.127(6)	2.113(9)
Sn(1)–E(1)	2.4258(16)	2.159(13) / 2.214(12)	Sn(2)–E(2)	2.459(2)	2.215(13) / 2.138(10)

Table 2 (continued)

Sn(1)–N(1)	2.728(4)	2.428(5)	Sn(2)–N(2)	2.699(4)	2.470(6)
E(1)–Sn(1)–N(1)	171.78(11)	162.3(3) / 160.8(3)	E(2)–Sn(1)–N(2)	167.20(9)	155.6(4) / 167.2(3)
E(1)–Sn(1)–C(1)	102.72(15)	91.7(4) / 87.2(4)	E(2)–Sn(1)–C(22)	100.40(15)	81.3(4) / 96.3(4)
E(1)–Sn(1)–C(20)	100.4(2)	102.5(3) / 90.8(3)	E(2)–Sn(1)–C(41)	98.37(17)	102.5(4) / 83.2(3)
E(1)–Sn(1)–C(21)	105.03(16)	86.2(4) / 102.4(4)	E(2)–Sn(1)–C(42)	108.20(15)	95.3(4) / 99.3(4)
N(1)–Sn(1)–C(1)	69.40(18)	74.3(2)	N(2)–Sn(1)–C(22)	70.28(17)	74.7(2)
N(1)–Sn(1)–C(21)	85.3(2)	93.8(2)	N(2)–Sn(1)–C(41)	80.2(2)	93.2(2)
N(1)–Sn(1)–C(21)	77.45(18)	90.9(3)	N(2)–Sn(1)–C(42)	83.69(17)	93.3(3)
C(1)–Sn(1)–C(20)	113.4(2)	118.5(3)	C(22)–Sn(1)–C(41)	121.81(19)	120.0(3)
C(1)–Sn(1)–C(21)	117.0(2)	118.1(3)	C(22)–Sn(1)–C(42)	110.3(2)	120.5(3)
C(20)–Sn(1)–C(21)	115.4(2)	122.3(3)	C(41)–Sn(1)–C(42)	115.0(2)	118.7(3)
Sn(1)–S(1)–Sn(2)	108.23(6)				

<sup>a</sup> E(1) = S(1) for **2** and O(1) for **3**; E(2) = S(1) for **2** and O(2) for **3**.

## DISCUSSION

### Solid state structure

All these triorganotin(IV) derivatives contain a distorted trigonal bipyramidal (C,N)SnC<sub>2</sub>X (X = Cl, S, O) cores as result of intramolecular N<sub>imine</sub>→Sn interactions established *trans* to the chlorine or chalcogen atoms. The N→Sn intramolecular interaction distances exceed the sum of the covalent radii [ $\Sigma r_{\text{cov}}(\text{Sn}, \text{N})$  2.1 Å] but are shorter than the sum of the van der Waals radii [ $\Sigma r_{\text{vdw}}(\text{Sn}, \text{N})$  3.74 Å] of the corresponding atoms.<sup>18</sup> For compounds **1** and **3** the tin-nitrogen distances [range 2.428(5) - 2.484(3) Å; see Tables 1 and 2] are similar to the ones found in the related [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]SnMe<sub>2</sub>Cl [N→Sn 2.485(3) / 2.488(3) Å for the two polymorphs, respectively],<sup>19</sup> with no obvious difference due to the hybridization of the donor atom [better donor properties of a N(sp<sup>2</sup>) vs. a N(sp<sup>3</sup>) atom, respectively] as found for the related R<sub>2</sub>SnCl<sub>2</sub> [R = (imino)aryl and 2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>] compounds.<sup>2,19,20</sup> The longer N→Sn intramolecular interaction distances observed in **2** [2.728(4) / 2.699(4) Å] are the result of the lower electronegativity of the axial substituent *trans* to the N(sp<sup>2</sup>) atom from the pendant arm [sulfur *versus* chlorine in **1** and oxygen in **3**, respectively].

No intermolecular interactions between heavy atoms were observed in compounds **1–3**. A closer check of the solid state structures revealed both intra- and intermolecular C–H⋯Cl hydrogen bonds and intermolecular C–H⋯π interactions between hydrogen atoms and the aromatic rings present in the molecule (*i.e.* H⋯Ph<sub>centroid</sub> contacts shorter than 3.1 Å, with an angle γ between the normal to the aromatic ring and the line defined by the H atom and Ph<sub>centroid</sub> smaller than 30°),<sup>21</sup> respectively. In the crystal of **1** dimers are formed through C–H⋯π(Ph<sub>centroid</sub>) interactions [C(15)–H(15)<sub>aryl</sub>⋯Ph<sub>centroid</sub>{C(1a)–C(6a)} 2.94 Å, γ = 5.8° and C(21)–H(21B)<sub>methyl</sub>⋯Ph<sub>centroid</sub>{C(8a)–C(13a)} 2.88 Å, γ = 9.6°, respectively; symmetry-equivalent atoms (2–x, 2–y, 1–z) given by “a”] and are further connected in a layer type structure by C–H⋯Cl intermolecular interactions [Cl(1)⋯H(5b)<sub>aryl</sub> 2.92 Å and Cl(1)⋯H(13c)<sub>aryl</sub> 2.98 Å, respectively; symmetry-equivalent atoms (1–x, 1–y, 2–z) and (–1+x, y, z) given by “b” and “c”] (Figure 4). Tubular polymers along the *a* axis are generated by the molecules in the crystal of **2** via C–H⋯π (Ph<sub>centroid</sub>) intermolecular interactions [C(31)–H(31)<sub>aryl</sub>⋯Ph<sub>centroid</sub>{C(14a)–C(19a)} 2.96 Å, γ = 9.5°; C(18)–H(18)<sub>aryl</sub>⋯Ph<sub>centroid</sub>{C(22b)–C(27b)} 2.98 Å, γ = 14.4° and C(24)–H(24)<sub>aryl</sub>⋯Ph<sub>centroid</sub>{C(35c)–C(40c)} 2.99 Å, γ = 23.9°, respectively; symmetry-equivalent atoms (1–x, 2–y, 1–z), (2–x, 2–y, 1–z) and (1+x, y, z) given by “a”, “b” and “c”] (Figure 5). The treatment of the disordered solvent with SQUEEZE<sup>22</sup> and the disorder of the sulfate core prevent similar considerations on the supramolecular architecture in the crystal of **3**.

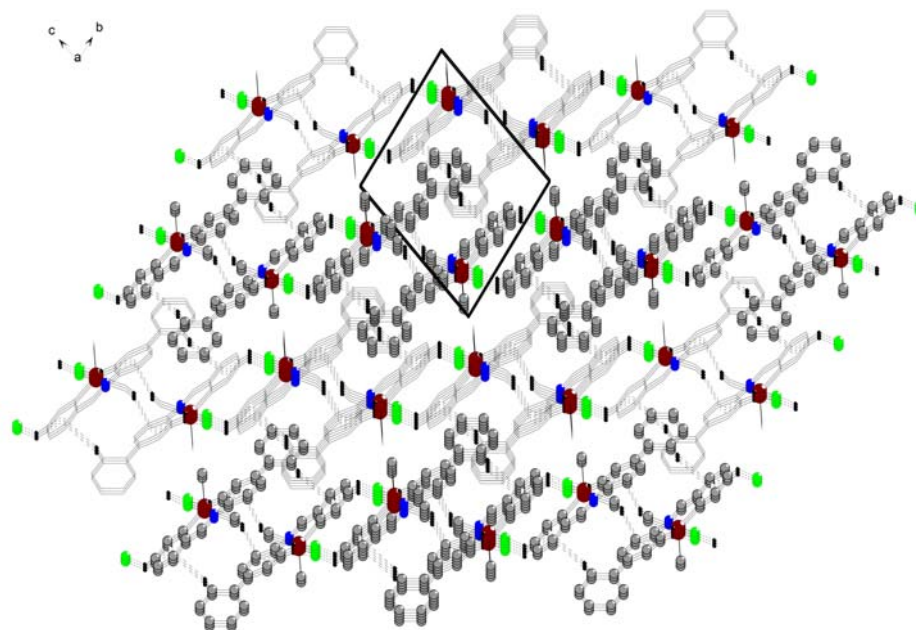


Fig. 4 – Packing of **1** along *a* axis showing the arrangement of the supramolecular layers in crystal (only hydrogen atoms involved in intermolecular contacts are shown).

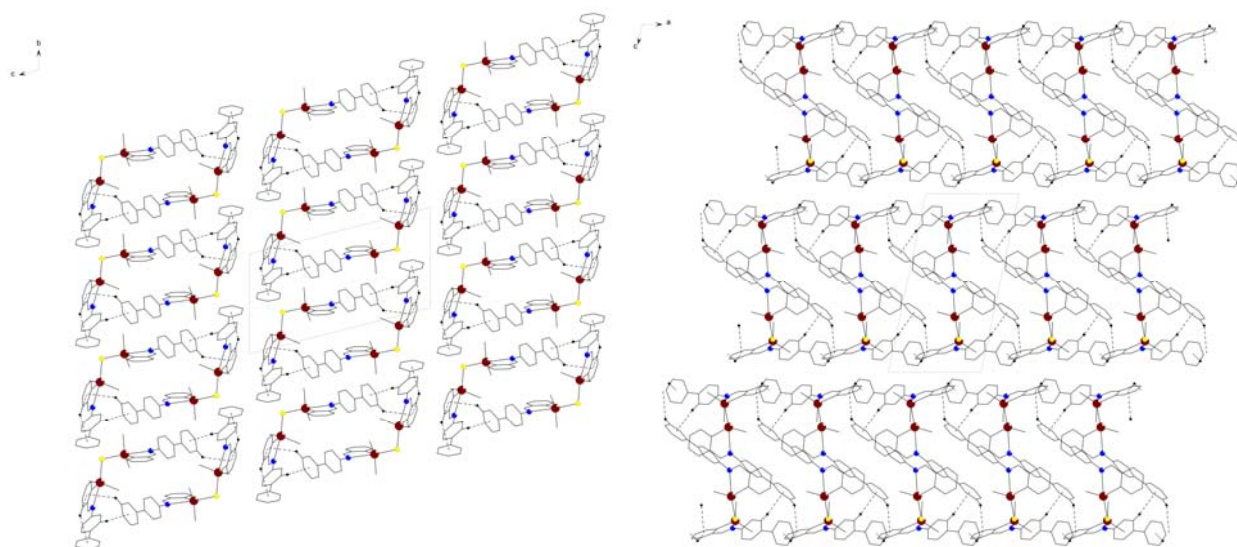


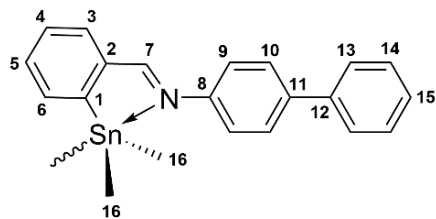
Fig. 5 – Packing along *a* (left) and *b* (right) axis in the crystal of **2** showing the arrangement of the supramolecular *tubular* polymers (only hydrogen atoms involved in intermolecular contacts are shown).

### Solution behavior

The assignment of the resonances in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra was based on 2D NMR (HSQC, HMBC and COSY) correlation spectra and tin-carbon coupling constants according to the numbering shown in Scheme 2.

The room-temperature NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ) spectra for compounds **1–3** show one set of characteristic resonance signals corresponding to the organic groups bonded to tin with the expected patterns. This behavior is consistent with equivalence of the

organic groups attached to tin on the NMR time scale. The coordination geometry around the metal center similar to the one found in solid state, *i.e.* trigonal bipyramidal, is evidenced by the NMR parameters.<sup>23</sup> The values of the calculated C–Sn–C (carbon atoms from the two methyl groups) angles based on the relationships between  $^2J(^{119}\text{Sn}^1\text{H})$  and  $^1J(^{119}\text{Sn}^{13}\text{C})$  coupling constants and the C–Sn–C angle<sup>23,24</sup> (Table 3) show a good correlation between the structure found in solution and the one determined in solid state.



Scheme 2 – Numbering scheme for the NMR assignments.

In solution, at room temperature, the  $^{119}\text{Sn}$  NMR spectra for all dimethyltin(IV) derivatives **1–3** contain one single resonance showing that only one species is present and that analogous fragments of the homobimetallic compounds are equivalent. The  $^{119}\text{Sn}$  chemical shifts ( $\delta$  –60.7 ppm, –36.4 ppm and –75.25 ppm for **1**, **2** and **3**) are typical for five-coordinate triorganotin(IV) species

in solution, thus consistent with the presence of N $\rightarrow$ Sn intramolecular interactions. These values are comparable with the  $^{119}\text{Sn}$  chemical shifts reported for the related [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]SnMe<sub>2</sub>Cl ( $\delta$  –48.7 ppm, in CH<sub>2</sub>Cl<sub>2</sub>/acetone-*d*<sub>6</sub>)<sup>19</sup> and [2-{Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>N(Me)CH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>]SnMe<sub>2</sub>Cl ( $\delta$  –45 ppm, in CDCl<sub>3</sub>).<sup>25</sup>

Reaction of **2** with ZnCl<sub>2</sub> was monitored by  $^1\text{H}$  and  $^{119}\text{Sn}$  NMR showing the total conversion to **1** in about 3.5 hours at room temperature. The obvious shift of the methyl, imine and H-6 proton resonance signals in the  $^1\text{H}$  NMR and of the  $^{119}\text{Sn}$  resonance in the corresponding spectra are very useful in monitoring the reaction (Figure 6).

Table 3

Correlations between  $^1\text{H} - ^{119}\text{Sn}$  and  $^{13}\text{C} - ^{119}\text{Sn}$  coupling constants (Hz) and C–Sn–C angles ( $\theta$ , °) in compounds **1–3**

Compound	$^1\text{H}$		$^{13}\text{C}$	
	$^2J(^{119}\text{Sn}^1\text{H})$	C–Sn–C <sup>a</sup>	$^1J(^{119}\text{Sn}^{13}\text{C})$	C–Sn–C <sup>b</sup>
<b>1</b>	71.5	121.3	548	124.8
<b>2</b>	65.4	115.9	491.5	119.9
<b>3</b>	71.3	121.1	556	125.5

<sup>a</sup>  $\theta = 0.0161|J|^2 - 1.32|J| + 133.4$ ; <sup>b</sup>  $|J| = 11.4\theta - 875$

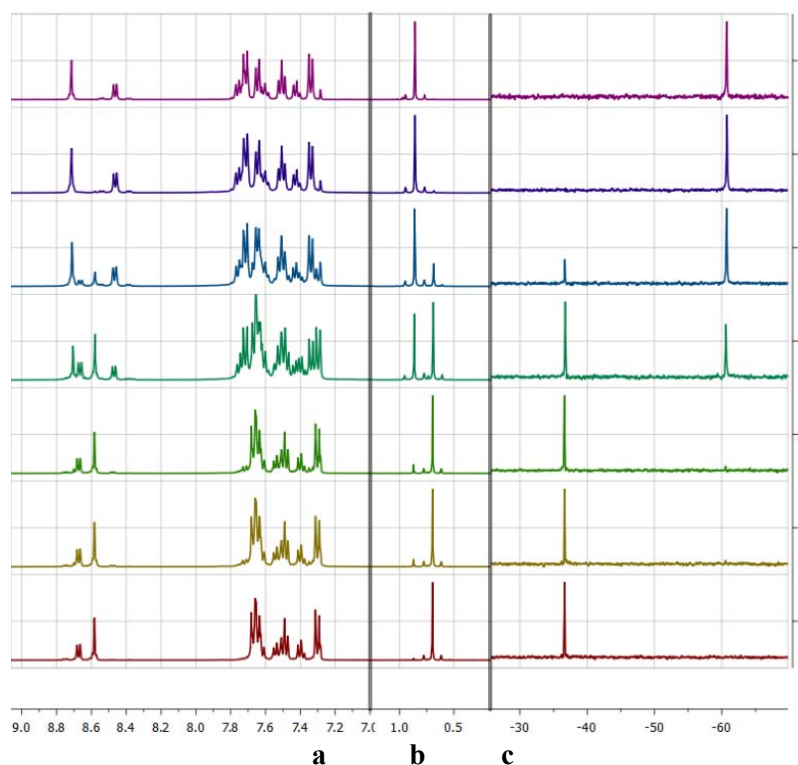


Fig. 6 – (a) Aromatic, (b) aliphatic regions of  $^1\text{H}$  NMR and (c)  $^{119}\text{Sn}$  NMR spectra of **2** (**1**), the reaction of **2** with ZnCl<sub>2</sub> after: 5' (**2**), 20' (**3**), 1h15' (**4**), 2h30' (**5**), 3h45' (**6**) and of **1** (**7**).

## EXPERIMENTAL

### General procedures

Multinuclear NMR spectra ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{119}\text{Sn}$  and 2D) were recorded at room temperature on Bruker Avance III 400 and 600 spectrometers. The  $^1\text{H}$  chemical shifts are reported in  $\delta$  units (ppm) relative to the residual peak of the deuterated solvent (ref.  $\text{CDCl}_3$ :  $^1\text{H}$  7.16 ppm). The  $^{13}\text{C}$  chemical shifts are reported in  $\delta$  units (ppm) relative to the peak of the solvent (ref.  $\text{CDCl}_3$ :  $^{13}\text{C}$  77.0 ppm). For the  $^{119}\text{Sn}$  NMR spectra the chemical shifts are reported in ppm relative to  $\text{SnMe}_4$ .  $^1\text{H}$  and  $^{13}\text{C}$  resonances were assigned using 2D NMR experiments (COSY, HMQC and HMBC). The NMR spectra were processed using the *MestReNova* software.<sup>17</sup> Mass spectra were recorded on a Thermo Scientific LTQ Orbitrap XL mass spectrometer equipped with a standard ESI/APCI source. Infrared spectra were recorded on a JASCO FT/IR-615 instrument. Melting points were measured with an Electrothermal 9200 apparatus and are not corrected. Elemental analyses were carried out on a VarioEl analyser. Solvents were dried and freshly distilled under argon prior to use. Starting materials such as  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ ,  $\text{ZnSO}_4$ ,  $\text{ZnCl}_2$ , (1,1'-biphenyl)-4-amine, were obtained from Aldrich or Merck, and were used as received except the amines which were purified by distillation or recrystallisation prior to use.  $[\text{2}-(\text{O}=\text{CH})\text{C}_6\text{H}_4]\text{SnMe}_2\text{Cl}$  was prepared according to literature methods.<sup>5</sup>

**Synthesis of  $[\text{2}-(\text{1,1}'\text{-C}_6\text{H}_5\text{C}_6\text{H}_4\text{-4-N}=\text{CH})\text{C}_6\text{H}_4]\text{SnMe}_2\text{Cl}$  (1). a)**  $[\text{2}-(\text{O}=\text{CH})\text{C}_6\text{H}_4]\text{SnMe}_2\text{Cl}$  (0.2 g, 0.69 mmol) and 1,1'- $\text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{-4-NH}_2$  (0.12 g, 0.7 mmol) were mixed in absence of a solvent and the reaction mixture was heated until a clear melt was obtained. The temperature was maintained for 5 min and vacuum was applied to remove the resulting water. After cooling, the title compound was obtained as a yellow solid (0.29 g, 95%).

**b)** To a solution of **2** (0.1 g, 0.119 mmol) in 10 mL  $\text{CH}_2\text{Cl}_2$ , an aqueous solution of  $\text{ZnCl}_2$  (0.016 g, 0.119 mmol) was added. The reaction mixture was stirred overnight at room temperature. The organic layer was separated and the water solution was washed with 2x5 mL  $\text{CH}_2\text{Cl}_2$ . The combined organic solutions were dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed *in vacuo* to obtain the compound as a yellow solid (0.1 g, 96 %), mp 227–229 °C.  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  0.83s (6H, H-16,  $^2J_{\text{SnH}} = 68.3/71.5$  Hz), 7.32d (2H, H-9,  $^3J_{\text{HH}} = 8.5$  Hz), 7.40t (1H, H-15,  $^3J_{\text{HH}} = 7.3$  Hz), 7.48t (2H, H-14,  $^3J_{\text{HH}} = 7.6$  Hz), 7.58td (1H, H-4,  $^3J_{\text{HH}} = 7.4$  Hz,  $^4J_{\text{HH}} = 1.3$  Hz), 7.62d (2H, H-13,  $^3J_{\text{HH}} = 7$  Hz), 7.69 two overlapped signals [7.69d (2H, H-10,  $^3J_{\text{HH}} = 7.4$  Hz); 7.69t (1H, H-5,  $^3J_{\text{HH}} = 8.5$  Hz)], 7.74d (1H, H-3,  $^3J_{\text{HH}} = 7.5$  Hz), 8.44d (1H, H-6,  $^3J_{\text{HH}} = 7.2$  Hz,  $^3J_{\text{SnH}} = 62.6$  Hz), 8.69s (1H, H-7,  $^4J_{\text{SnH}} = 9.8$  Hz).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  2.17s (C-16,  $^1J_{\text{SnC}} = 524/548$  Hz), 121.84s (C-9), 127.09s (C-13), 127.95s (C-15), 128.59s (C-10), 129.09s (C-14), 129.97s (C-4,  $^4J_{\text{SnC}} = 12.5$  Hz), 132.40s (C-3,  $^3J_{\text{SnC}} = 49.4$  Hz), 133.46s (C-5,  $^3J_{\text{SnC}} = 62.8$  Hz), 138.04s (C-6,  $^2J_{\text{SnC}} = 37.5$  Hz), 138.75s (C-2,  $^2J_{\text{SnC}} = 31.2$  Hz), 139.87s (C-12), 141.05s (C-11), 143.52s (C-1), 145.76s (C-8), 163.69s (C-7,  $^3J_{\text{SnC}} = 20.0$  Hz).  $^{119}\text{Sn}$  NMR (149.2 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  -60.73s. HR MS (APCI+),  $m/z$  (%): 406.16668 (100)  $[\text{RMe}_2\text{Sn}^+]$ . IR (KBr pellet,  $\text{v}$ ,  $\text{cm}^{-1}$ ): 3441 (br), 3057 (w), 3027 (w), 2924 (w), 2370 (w), 1954 (w), 1887 (w), 1845 (w), 1764 (w), 1661 (w), 1614 (s), 1594 (m), 1556 (s), 1506 (s), 1482 (vs), 1459 (w), 1438 (w), 1407 (w), 1358 (m), 1296 (w), 1257 (m), 1237 (w), 1192 (m), 1159 (w), 1113 (m), 1076 (w), 1049 (w), 1005 (w), 982 (w), 904 (m), 846 (m), 773 (vs), 739 (w), 721 (m), 697 (s),

656 (w), 644 (w), 571 (w), 551 (m), 528 (w), 518 (w), 482 (w), 422 (m).

**Synthesis of  $[\text{2}-(\text{1,1}'\text{-C}_6\text{H}_5\text{C}_6\text{H}_4\text{-4-N}=\text{CH})\text{C}_6\text{H}_4]\text{SnMe}_2\text{S}$  (2).** To a solution of **1** (0.25 g, 0.57 mmol) in 15 mL  $\text{CH}_2\text{Cl}_2$ , an aqueous solution of  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  (0.5 g, 2.08 mmol) was added. The reaction mixture was stirred overnight at room temperature. The organic layer was separated and the water solution was washed with 2x5 mL  $\text{CH}_2\text{Cl}_2$ . The combined organic solutions were dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed *in vacuo* to obtain the compound as a yellow solid (0.23 g, 96 %). Recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexane afforded colourless crystals, m.p. 192–194 °C.  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  0.67s (12H, H-16,  $^2J_{\text{SnH}} = 62.9/65.4$  Hz), 7.28d (4H, H-9,  $^3J_{\text{HH}} = 8.5$  Hz), 7.37t (2H, H-15,  $^3J_{\text{HH}} = 7.3$  Hz), 7.46t (4H, H-14,  $^3J_{\text{HH}} = 7.6$  Hz), 7.51td (2H, H-4,  $^3J_{\text{HH}} = 7.4$  Hz,  $^4J_{\text{HH}} = 1.3$  Hz), 7.57–7.67m (12H, H-3, H-5, H-10, H-13), 8.56s (2H, H-7,  $^4J_{\text{SnH}} = 9.1$  Hz), 8.64d (2H, H-6,  $^3J_{\text{HH}} = 7.1$  Hz,  $^3J_{\text{SnH}} = 60.1$  Hz).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  2.16s (C-16,  $^1J_{\text{SnC}} = 469.6/491.6$  Hz), 121.66s (C-9), 127.08s (C-13), 127.56s (C-15), 128.23s (C-10), 128.99s (C-14), 129.11s (C-4,  $^4J_{\text{SnC}} = 11.1$  Hz), 131.89s (C-5,  $^3J_{\text{SnC}} = 56.8$  Hz), 132.49s (C-3,  $^3J_{\text{SnC}} = 43.8$  Hz), 138.83s (C-6,  $^2J_{\text{SnC}} = 37.0$  Hz), 139.72s (C-11, C-2,  $^3J_{\text{SnC}} = 26.8$  Hz), 140.45s (C-12), 144.07s (C-1), 148.75s (C-8), 162.26s (C-7,  $^3J_{\text{SnC}} = 12.5$  Hz).  $^{119}\text{Sn}$  NMR (149.2 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  -36.43s. HR MS (APCI+),  $m/z$  (%): 406.16668 (100)  $[\text{RMe}_2\text{Sn}^+]$ . IR (KBr pellet,  $\text{v}$ ,  $\text{cm}^{-1}$ ): 3448 (br), 3049 (w), 3029 (w), 2989 (w), 2895 (w), 1948 (w), 1902 (w), 1624 (m), 1597 (m), 1596 (m), 1516 (w), 1484 (s), 1449 (w), 1436 (w), 1407 (w), 1361 (w), 1291 (w), 1258 (w), 1241 (w), 1197 (w), 1184 (w), 1173 (w), 1113 (w), 1077 (w), 1048 (w), 1006 (w), 978 (w), 897 (s), 838 (s), 766 (vs), 735 (m), 722 (m), 697 (s), 652 (w), 565 (w), 534 (m), 514 (w), 425 (w).

**Synthesis of  $[\text{2}-(\text{1,1}'\text{-C}_6\text{H}_5\text{C}_6\text{H}_4\text{-4-N}=\text{CH})\text{C}_6\text{H}_4]\text{SnMe}_2\text{SO}_4$  (3).** To a solution of **1** (0.08 g, 0.095 mmol) in 10 mL  $\text{CH}_2\text{Cl}_2$ , an aqueous solution of  $\text{ZnSO}_4$  (0.015 g, 0.095 mmol) was added. The reaction mixture was stirred overnight at room temperature. The organic layer was separated and the water solution was washed with 2x5 mL  $\text{CH}_2\text{Cl}_2$ . The combined organic solutions were dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed *in vacuo* to obtain the compound as a yellow solid (0.08 g, 93 %). Recrystallization from  $\text{CH}_2\text{Cl}_2$ /hexane afforded colourless crystals, m.p. 184–186 °C.  $^1\text{H}$  NMR (600.1 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  0.92s (12H, H-16,  $^2J_{\text{SnH}} = 71.5$  Hz), 7.33d (4H, H-9,  $^3J_{\text{HH}} = 8.0$  Hz), 7.38t (2H, H-15,  $^3J_{\text{HH}} = 7.5$  Hz), 7.47t (4H, H-14,  $^3J_{\text{HH}} = 7.5$  Hz), 7.52t (2H, H-4,  $^3J_{\text{HH}} = 7.5$  Hz), 7.60d (4H, H-13,  $^3J_{\text{HH}} = 7.8$  Hz), 7.62t (2H, H-5,  $^3J_{\text{HH}} = 7.4$  Hz), 7.66d (4H, H-10,  $^3J_{\text{HH}} = 8.1$  Hz), 7.73d (2H, H-3,  $^3J_{\text{HH}} = 7.7$  Hz), 8.50d (2H, H-6,  $^3J_{\text{HH}} = 7.2$  Hz,  $^3J_{\text{SnH}} = 57.8$  Hz), 8.71s (2H, H-7).  $^{13}\text{C}$  NMR (150.9 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  0.23s (C-16,  $^1J_{\text{SnC}} = 531.1/556$  Hz), 121.88s (C-9), 127.07s (C-13), 127.90s (C-15), 128.54s (C-10), 129.04s (C-14), 129.76s (C-4,  $^4J_{\text{SnC}} = 11.8$  Hz), 132.33s (C-3,  $^3J_{\text{SnC}} = 49.4$  Hz), 133.59s (C-5,  $^3J_{\text{SnC}} = 60.8$  Hz), 138.55s (C-6,  $^2J_{\text{SnC}} = 33.3$  Hz), 138.91s (C-2,  $^2J_{\text{SnC}} = 33.1$  Hz), 139.82s (C-12), 141.08s (C-11), 144.38s (C-1), 145.23s (C-8), 164.02s (C-7,  $^3J_{\text{SnC}} = 21.6$  Hz).  $^{119}\text{Sn}$  NMR (149.2 MHz,  $\text{CDCl}_3$ , 20 °C):  $\delta$  -75.25s. MS (APCI+),  $m/z$  (%): 406.06036 (100)  $[\text{RMe}_2\text{Sn}^+]$ , 258.12718 (97.93)  $[\text{R}+\text{H}^+]$ . IR (KBr pellet,  $\text{v}$ ,  $\text{cm}^{-1}$ ): 3448 (br), 3052 (w), 3030 (w), 2917 (w), 1614 (m), 1600 (m), 1551 (m), 1516 (w), 1486 (m), 1460 (w), 1441 (w), 1410 (w), 1370 (w), 1230 (m), 1198 (m), 1183 (m), 1129 (vs), 1076 (w), 1050 (w), 1004 (vs), 963 (s), 905 (s), 842 (m), 768 (vs), 725 (m), 698 (m), 658 (w), 646 (w), 623 (w), 609 (w), 561 (w), 518 (w), 496 (w), 425 (w).

### Crystal structures

The details of the crystal structure determination and refinement are given in Table 4. The crystals were mounted on cryoloops and data were collected with a Bruker SMART APEX diffractometer by using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at room temperature (297 K). The structures were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the software package SHELX-97 was used.<sup>26</sup> The drawings were created with the Diamond program.<sup>27</sup>

In a final difference Fourier map highly disordered electron density was observed for compound **7**. The residual electron density was difficult to model and therefore, the SQUEEZE routine in PLATON<sup>22</sup> was used to eliminate this contribution of the electron density in the solvent region from the intensity data. The solvent-free model was employed for the final refinement. It was estimated that each cavity contains around 42 electrons which corresponds to a solvent molecule of dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>). Compound **7** also exhibits disorder at the sulfate fragment with 42 : 58 occupancy for the two positions.

### CONCLUSIONS

The synthesis of three new triorganotin(IV) derivatives containing an (imino)aryl pendant arm ligand is reported. Solution and solid state characterization of the compounds show the

presence of distorted trigonal bipyramidal (C,N)SnC<sub>2</sub>X (X = Cl, S, O) cores. Compound **1** was obtained using a solvent and catalyst free method, by condensation of [2-(O=CH)C<sub>6</sub>H<sub>4</sub>]SnMe<sub>2</sub>Cl with (1,1'-biphenyl)-4-amine. The homobimetallic derivatives [2-(1,1'-C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>4</sub>-4-N=CH)C<sub>6</sub>H<sub>4</sub>]SnMe<sub>2</sub>]<sub>2</sub>S (**2**) and [2-(1,1'-C<sub>6</sub>H<sub>5</sub>C<sub>6</sub>H<sub>4</sub>-4-N=CH)C<sub>6</sub>H<sub>4</sub>]SnMe<sub>2</sub>]<sub>2</sub>SO<sub>4</sub> (**3**) were isolated after treatment of **1** with Na<sub>2</sub>S and reaction of **2** with ZnSO<sub>4</sub>, respectively. Sulfide **2** can be converted in the corresponding chloride **1** with ZnCl<sub>2</sub>, reaction monitored by NMR spectroscopy. Intermolecular C–H $\cdots$ Cl and C–H $\cdots$  $\pi$  interactions present in crystal of **1** lead to the formation of a layer type supramolecular structure, while compound **2** forms tubular polymers through C–H $\cdots$  $\pi$  interactions.

### SUPPLEMENTARY DATA

CCDC 1959611, 1959612 and 1959613 contain the supplementary crystallographic data for **1–3**, 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).

Table 4

Crystallographic data for compounds **1–3**

	<b>1</b>	<b>2</b>	<b>3</b>
Empirical formula	C <sub>21</sub> H <sub>20</sub> ClNSn	C <sub>42</sub> H <sub>40</sub> N <sub>2</sub> SSn <sub>2</sub>	C <sub>42</sub> H <sub>40</sub> N <sub>2</sub> O <sub>4</sub> SSn <sub>2</sub>
Formula weight	440.52	842.20	906.20
Temperature (K)	297(2)	297(2)	297(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic
Space Group	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 <sub>1</sub> / <i>c</i>
Unit cell dimensions			
a (Å)	9.8006(9)	9.8307(10)	20.687(3)
b (Å)	9.8269(9)	10.5415(10)	14.4316(19)
c (Å)	10.5105(10)	19.3795(19)	14.862(2)
$\alpha$ (°)	70.447(1)	102.071(2)	90.00
$\beta$ (°)	89.435(2)	98.871(2)	97.295(3)
$\gamma$ (°)	85.399(2)	101.645(2)	90.00
Volume (Å <sup>3</sup> )	950.66(15)	1882.6(3)	4401.1(10)
Z	2	2	4
D <sub>c</sub> (mg/cm <sup>3</sup> )	1.539	1.486	1.368
Absorption coefficient (mm <sup>-1</sup> )	1.486	1.413	1.221
F(000)	440	844	1816
$\theta$ range for data collection (°)	2.06 to 25.00	2.06 to 25.00	2.29 to 25.00
Reflections collected	8974	18024	41330
Independent reflections	3307 (R <sub>int</sub> = 0.0379)	6607 (R <sub>int</sub> = 0.0421)	7745 (R <sub>int</sub> = 0.0736)
Data / restraints / parameters	3307 / 0 / 219	6607 / 0 / 428	7745 / 0 / 500
Goodness-of-fit on F <sup>2</sup>	1.068	1.053	1.065
Final R indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	R <sub>1</sub> = 0.0358 wR <sub>2</sub> = 0.0748	R <sub>1</sub> = 0.0479 wR <sub>2</sub> = 0.1025	R <sub>1</sub> = 0.0625 wR <sub>2</sub> = 0.1387
R indices (all data)	R <sub>1</sub> = 0.0425 wR <sub>2</sub> = 0.0784	R <sub>1</sub> = 0.0674 wR <sub>2</sub> = 0.1113	R <sub>1</sub> = 0.0907 wR <sub>2</sub> = 0.1508



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