



## Research paper

## Structural analysis of diorganotin(IV) complexes derived from thio bis-tridentate Schiff base ligands



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## ABSTRACT

Twelve dinuclear diorganotin(IV) complexes based on bis-tridentate Schiff bases and  $R_2SnO$  (IV) oxides ( $R = Me, n-Bu, Ph$ ) were synthesized by multicomponent reactions in moderate yields. The complexes were characterized by common spectroscopic techniques such as FT-IR, mass spectrometry and NMR ( $^1H$ ,  $^{13}C$  and  $^{119}Sn$ ) analysis. X-ray diffraction analysis was done for compounds **1c**, **1d**, **1f**, **1j** and **1l**.  $^{119}Sn$  NMR spectra showed signals at  $\delta = 135$ – $145$ ,  $175$ – $185$  and  $319$ – $323$  ppm for  $Me$ ,  $n-Bu$  and  $Ph$  derivatives respectively, indicating the pentacoordinate geometry for tin atoms. In solid state, for methyl derivatives (**1c**, **1d**) a distorted octahedral geometry for tin atoms was observed owing the presence of  $Sn\cdots O$  intermolecular interactions.

## 1. Introduction

Schiff bases are a well-known class of versatile ligands obtained by facile condensation reactions involving primary amines and carbonyl compounds [1]. The appropriate choice of initial fragments and substituents can tune the physical, chemical and electronic properties of the Schiff bases [2]. The importance of the Schiff base ligands can be noticed from the publication of over 15,000 related papers described at *scifinder*, these compounds can be easily combined with either alkaline, main group or transition metals [3]. Generally, Schiff bases are used in neutral or deprotonated forms to give metal complexes with variable stoichiometry and different coordination modes [4].

By the way, tin complexes derived from Schiff bases have been widely studied showing interesting applications in industrial, agriculture or medicinal fields [5–17]. In fact, mainly diorganotin(IV) Schiff base complexes are reported to have excellent biological properties such as antimicrobial [18–22], antifungal [23–24], antibacterial [25–26], antitumor [27–30], antioxidant [31], anti-insecticidal [32–23], antiviral [34–35], antitubercular [36], antifertility [37–38], and anti-inflammatory [39–40].

Previously, we have described the synthesis of diorganotin(IV) complexes derived from Schiff bases including a double set of ONO donor atoms. Monomeric, dimeric or 1D polymeric structures were observed depending on the coordination tin geometry [41]. In this work, the introduction of a sulfur atom connecting two aromatic aldehyde fragments was done, with the aim to analyze structural and conformation changes on this type of complexes. Therefore, we hope to

contribute to the investigation dealing with the study of diorganotin(IV) species derived from Schiff base ligands [42–44]. Twelve diorganotin(IV) complexes derived from 5,5-thio-bis(salicylaldehyde), four different aminophenols and diorganotin(IV) oxides ( $R = Me, n-Bu, Ph$ ) are described. All compounds were obtained in moderate yields by using multicomponent reactions. Products consist on dinuclear metal complexes in where each metal is bonded to a set of ONO donor atoms together with two carbon atoms from the organic groups.

## 2. Experimental part

## 2.1. Materials and methods

The compound 5,5-thio-bis(salicylaldehyde) was prepared according to the procedure described [45]. All reagents and solvents were obtained from commercial suppliers and used without further purification.

The  $^1H$ ,  $^{13}C$  and  $^{119}Sn$  NMR spectra were recorded at room temperature using a Varian Gemini 500. TMS (internal,  $^1H$ ,  $\delta = 0.00$  ppm,  $^{13}C$ ,  $\delta = 0.00$  ppm) and  $SnMe_4$  (external,  $^{119}Sn$ ,  $\delta = 0.00$  ppm) were used as standard references. Two dimensional COSY and HSQC correlation experiments have been carried out for unambiguous assignment of the  $^1H$  and  $^{13}C$  NMR spectra. Infrared spectra were recorded on a Nicolet 6700 FT-IR Thermo Scientific spectrophotometer. Mass spectra and mass exact were obtained on a Jeol JMS 700 equipment. Melting points were determined with a Büchi B-540 digital apparatus.

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## 2.2. X-ray crystallography

Intensity data for all compounds (**1c**, **1d**, **1f**, **1j** and **1l**) were collected at  $T = 100$  K, with Cu-K $\alpha$  radiation  $\lambda = 1.54184 \text{ \AA}$ , graphite monochromator on an Agilent Technologies SuperNova diffractometer equipped with the EoS2 CCD area detector and an Oxford Instruments Cryogen cooler. The measured intensities were reduced to  $I^2$  and corrected for absorption using spherical harmonics (CryAlisPro) [46]. Intensities were corrected for Lorentz and polarization effects. Structure solution, refinement, and data output were performed with the OLEX2 program package [47] using SHELXL-2014 [48] for the refinement. Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in geometrically calculated positions using the riding model. Intermolecular distances were analyzed with DIAMOND [49].

CCDC numbers 1838244, 1838246–1838249 (for compounds **1c**, **1d**, **1f**, **1j** and **1l** respectively) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

## 2.3. Synthesis

### 2.3.1. General procedure for preparation of diorganotin(IV) complexes 1a–1l

One equivalent of 5,5'-thio-bis(salicylaldehyde) (L), two equivalents of the corresponding *o*-aminophenol and two equivalents of the corresponding diorganotin(IV) oxide ( $R = \text{Me}, n\text{-Bu}, \text{Ph}$ ) were added into a flask using a toluene/methanol (4:1) solvent mixture and refluxed for 12 h (Me), 8 (*n*-Bu), and 24 h (Ph). A Dean-Stark trap was used to remove the water formed during the reaction and part of the solvent, after work-up compounds **1a–1l** were isolated as orange to red dark solids in moderate yields.

Compound **1a** (HL-Sn-Me<sub>2</sub>) was obtained from 0.050 g (0.18 mmol) of 5,5'-thio-bis(salicylaldehyde), 0.039 g (0.36 mmol) of *o*-aminophenol and 0.060 g (0.36 mmol) of dimethyltin oxide. A red dark solid was obtained in 63% (0.087 g) yield. M.p. 164–167 °C. FTIR<sub>max</sub> (ATR): 1600 (C=N), 1518, 1473, 1374, 1283, 1164, 832, 739, 695, 602 cm<sup>-1</sup>. FAB<sup>+</sup> MS,  $m/z$  (%): 751 ([M + 1], 85), 750 (M<sup>+</sup>, 100), 720 ([M – 2Me]<sup>+</sup>, 25), 690 ([M – 4Me]<sup>+</sup>, 15). <sup>1</sup>H NMR (500.13 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.58 (2H, s, <sup>3</sup>J<sub>Sn-H</sub> = 49.5 Hz, H-7), 7.38 (2H, dd,  $J = 8.8, 2.4$  Hz, H-5), 7.33 (2H, d,  $J = 1.1$  Hz, H-3), 7.32 (2H, d,  $J = 2.4$  Hz, H-13), 7.18 (2H, td,  $J = 8.4, 1.4$  Hz, H-12), 6.82 (2H, dd,  $J = 8.4, 1.1$  Hz, H-10), 6.74 (2H, d,  $J = 8.8$  Hz, H-6), 6.69 (2H, td,  $J = 8.4, 1.1$  Hz, H-11), 0.77 (12H, s, Me <sup>3</sup>J(<sup>119/117</sup>Sn-<sup>1</sup>H) = 77.5/75.3 Hz) ppm. <sup>13</sup>C NMR (125.76 MHz, CDCl<sub>3</sub>)  $\delta$ : 168.7 (C-1), 161.3 (C-7), 159.1 (C-9), 140.3 (C-5), 138.1 (C-3), 131.3 (C-12), 130.8 (C-8), 124.1 (C-4), 123.2 (C-6), 118.9 (C-10), 118.4 (C-2), 117.0 (C-11), 115.1 (C-13), 1.51 (Me <sup>1</sup>J(<sup>119/117</sup>Sn-<sup>13</sup>C) = 659/626 Hz) ppm. <sup>119</sup>Sn NMR (186.50 MHz, CDCl<sub>3</sub>)  $\delta$ : -145.2 ppm. HRMS (FAB<sup>+</sup>):  $m/z$  [M + H]<sup>+</sup> Calc. for C<sub>30</sub>H<sub>29</sub>N<sub>2</sub>O<sub>4</sub>SSn<sub>2</sub>: 752.9891; Found: 753.0167.

Compound **1b** (MeL-Sn-Me<sub>2</sub>) was obtained from 0.05 g (0.18 mmol) of 5,5'-thio-bis(salicylaldehyde), 0.044 g (0.36 mmol) of 2-amino-*p*-cresol and 0.060 g (0.36 mmol) of dimethyltin oxide. A red solid was obtained in 62% (0.089 g) yield. M.p. 232–235 °C. FTIR<sub>max</sub> (ATR) 1597 (C = N), 1518, 1489, 1474, 1370, 1268, 1173, 1130, 814, 765, 729, 693, 655, 627 cm<sup>-1</sup>. FAB<sup>+</sup> MS,  $m/z$  (%): 779 ([M + 1], 10), 778 (M<sup>+</sup>, 12), 748 ([M – 2Me]<sup>+</sup>, 4). <sup>1</sup>H NMR (500.13 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.57 (2H, s, <sup>3</sup>J<sub>Sn-H</sub> = 49.5 Hz, H-7), 7.38 (2H, dd,  $J = 8.8, 2.3$  Hz, H-5), 7.33 (2H, d,  $J = 2.3$  Hz, H-3), 7.14 (2H, s, H-13), 7.01 (2H, dd,  $J = 8.2, 1.5$  Hz, H-11), 6.75 (2H, d,  $J = 8.8$  Hz, H-6), 6.73 (2H, d,  $J = 8.2$  Hz, H-10), 2.30 (6H, s, CH<sub>3</sub>), 0.76 (12H, s, Me <sup>3</sup>J(<sup>119/117</sup>Sn-<sup>1</sup>H) = 76.5/75.5 Hz) ppm. <sup>13</sup>C NMR (125.76 MHz, CDCl<sub>3</sub>)  $\delta$ : 168.5 (C-1), 160.8 (C-7), 156.9 (C-9), 140.1 (C-5), 138.0 (C-3), 131.7 (C-11), 130.7 (C-8), 126.3 (C-12), 124.0 (C-4), 123.2 (C-6), 118.5 (C-10, C-2), 115.2 (C-13), 21.0 (CH<sub>3</sub>), 1.42 (Me <sup>1</sup>J(<sup>119/117</sup>Sn-<sup>13</sup>C) = 660/631 Hz) ppm. <sup>119</sup>Sn NMR (186.50 MHz, CDCl<sub>3</sub>)  $\delta$ : -143.9 ppm. HRMS (FAB<sup>+</sup>):  $m/z$  [M + H]<sup>+</sup> Calc. for C<sub>32</sub>H<sub>33</sub>N<sub>2</sub>O<sub>4</sub>SSn<sub>2</sub>: 781.0204; Found: 781.0216.

Compound **1c** (CLL-Sn-Me<sub>2</sub>) was obtained from 0.05 g (0.18 mmol) of 5,5'-thio-bis(salicylaldehyde), 0.052 g (0.36 mmol) of 4-chloro-2-aminophenol and 0.60 g (0.36 mmol) of dimethyltin oxide. A red dark solid was obtained in 60% (0.091 g) yield. M.p. 191–194 °C. FTIR<sub>max</sub> (ATR): 1599 (C=N), 1518, 1489, 1472, 1373, 1275, 1183, 1132, 815, 773, 718, 653, 624 cm<sup>-1</sup>. FAB<sup>+</sup> MS,  $m/z$  (%): 820 ([M + 1], 21), 819 (M<sup>+</sup>, 30), 789 ([M – 2Me]<sup>+</sup>, 8), 759 ([M – 4Me]<sup>+</sup>, 4). <sup>1</sup>H NMR (500.13 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.48 (2H, s, <sup>3</sup>J<sub>Sn-H</sub> = 47.6 Hz, H-7), 7.36 (2H, dd,  $J = 8.8, 2.0$  Hz, H-5), 7.29 (2H, s, H-3), 7.27 (2H, s, H-13), 7.08 (2H, dd,  $J = 8.8, 2.0$  Hz, H-11), 6.71 (4H, d,  $J = 8.8$  Hz, H-6, H-10), 0.75 (12H, s, Me <sup>3</sup>J(<sup>119</sup>Sn-<sup>1</sup>H) = 76 Hz) ppm. <sup>13</sup>C NMR (125.76 MHz, CDCl<sub>3</sub>)  $\delta$ : 169.0 (C-1), 161.8 (C-7), 157.7 (C-9), 140.8 (C-5), 138.3 (C-3), 131.8 (C-11), 130.4 (C-8), 124.2 (C-4), 123.4 (C-6), 121.5 (C-12), 119.8 (C-10), 118.2, (C-2), 115.2 (C-13), 1.64 (Me <sup>1</sup>J(<sup>119</sup>Sn-<sup>13</sup>C) = 656 Hz) ppm. <sup>119</sup>Sn NMR (186.50 MHz, CDCl<sub>3</sub>)  $\delta$ : -139.8 ppm. HRMS (FAB<sup>+</sup>):  $m/z$  [M + H]<sup>+</sup> Calc. for C<sub>30</sub>H<sub>27</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>4</sub>SSn<sub>2</sub>: 820.9112; Found: 820.9130.

Compound **1d** (NO<sub>2</sub>L-Sn-Me<sub>2</sub>) was obtained from 0.05 g (0.18 mmol) of 5,5'-thio-bis(salicylaldehyde), 0.056 g (0.36 mmol) of 4-nitro-2-aminophenol and 0.60 g (0.36 mmol) of dimethyltin oxide. A red dark solid was obtained in 62% (0.096 g) yield. M.p. 214–218 °C. FTIR<sub>max</sub> (ATR): 1601 (C=N), 1520, 1480, 1454, 1378, 1291, 1193, 1157, 1084, 887, 827, 776, 714, 646 cm<sup>-1</sup>. FAB<sup>+</sup> MS,  $m/z$  (%): 841 ([M + 1], 12), 840 (M<sup>+</sup>, 8), 810 ([M – 2Me]<sup>+</sup>, 6). <sup>1</sup>H NMR (500.13 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.93 (2H, s, <sup>3</sup>J<sub>Sn-H</sub> = 47.7 Hz, H-7), 8.48 (2H, s, H-13), 7.98 (2H, d,  $J = 7.8$  Hz, H-5), 7.62 (2H, s, H-3), 7.54 (2H, d,  $J = 7.2$  Hz, H-6), 6.85 (2H, d,  $J = 8.3$  Hz, H-11), 6.79 (2H, d,  $J = 8.3$  Hz, H-10), 0.85 (12H, s, Me <sup>3</sup>J(<sup>119</sup>Sn-<sup>1</sup>H) = 74.8 Hz) ppm. <sup>13</sup>C NMR (125.76 MHz, CDCl<sub>3</sub>)  $\delta$ : 169.5 (C-1), 165.3 (C-7), 164.0 (C-9), 141.5 (C-5), 138.4 (C-3), 137.5 (C-12), 131.1 (C-8), 126.4 (C-11), 124.3 (C-4), 123.7 (C-6), 118.3 (C-10), 118.2, (C-2), 112.2 (C-13), 1.78 (Me <sup>1</sup>J(<sup>119</sup>Sn-<sup>13</sup>C) = 653.7 Hz) ppm. <sup>119</sup>Sn NMR (186.50 MHz, CDCl<sub>3</sub>)  $\delta$ : -135.8 ppm. HRMS (FAB<sup>+</sup>):  $m/z$  [M + H]<sup>+</sup> Calc. for C<sub>30</sub>H<sub>27</sub>N<sub>2</sub>O<sub>4</sub>SSn<sub>2</sub>: 842.9593; Found: 843.0233.

Compound **1e** (HL-Sn-Bu<sub>2</sub>) was obtained from 0.05 g (0.18 mmol) of 5,5'-thio-bis(salicylaldehyde), 0.039 g (0.36 mmol) of *o*-aminophenol and 0.90 g (0.36 mmol) of dibutyltin oxide. A red dark solid was obtained in 58% (0.090 g) yield. M.p. 85–89 °C. FTIR<sub>max</sub> (ATR): 1599 (C=N), 1518, 1473, 1375, 1282, 1164, 834, 794, 740, 696, 602 cm<sup>-1</sup>. FAB<sup>+</sup> MS,  $m/z$  (%): 919 ([M + 1], 94), 918 (M<sup>+</sup>, 100), 864 ([M – Bu]<sup>+</sup>, 18), 804 ([M – Bu]<sup>+</sup>, 38), 690 ([M – 2Bu]<sup>+</sup>, 52). <sup>1</sup>H NMR (500.13 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.58 (2H, s, <sup>3</sup>J<sub>Sn-H</sub> = 44.8 Hz, H-7), 7.38 (2H, dd,  $J = 8.8, 2.2$  Hz, H-5), 7.32 (2H, s, H-13), 7.30 (2H, s, H-3), 7.17 (2H, t,  $J = 7.4$  Hz, H-12), 6.84 (2H, d,  $J = 8.2$ , H-10), 6.76 (2H, d,  $J = 8.8$  Hz, H-6), 6.68 (2H, t,  $J = 7.4$ , H-11), 1.64–1.59 (8H, m, H- $\beta$ ), 1.50–1.47 (8H, m, H- $\alpha$ ), 1.35–1.28 (8H, sex,  $J = 7.3$  Hz, H- $\gamma$ ), 0.84 (12H, t,  $J = 7.3$  Hz, H- $\delta$ ) ppm. <sup>13</sup>C NMR (125.76 MHz, CDCl<sub>3</sub>)  $\delta$ : 169.3 (C-1), 161.0 (C-7), 159.8 (C-9), 140.2 (C-5), 138.0 (C-3), 131.6 (C-12), 130.6 (C-8), 124.0 (C-4), 122.8 (C-6), 118.9 (C-10), 118.5 (C-2), 116.7 (C-13), 115.0 (C-13), 27.2 (C- $\beta$ ), 26.8 (C- $\gamma$ ), 22.4 (C- $\alpha$  <sup>1</sup>J(<sup>119/117</sup>Sn-<sup>13</sup>C) = 615/588 Hz), 13.8 (C- $\delta$ ) ppm. <sup>119</sup>Sn NMR (186.50 MHz, CDCl<sub>3</sub>)  $\delta$ : -184.9 ppm. HRMS (FAB<sup>+</sup>):  $m/z$  [M + H]<sup>+</sup> Calc. for C<sub>42</sub>H<sub>53</sub>N<sub>2</sub>O<sub>4</sub>SSn<sub>2</sub>: 921.1769; Found: 921.1740.

Compound **1f** (MeL-Sn-Bu<sub>2</sub>) was obtained from 0.05 g (0.18 mmol) of 5,5'-thio-bis(salicylaldehyde), 0.044 g (0.36 mmol) of 2-amino-*p*-cresol and 0.90 g (0.36 mmol) of dibutyltin oxide. A red dark solid was obtained in 60% (0.103 g) yield. M.p. 105–109 °C. FTIR<sub>max</sub> (ATR): 1596 (C=N), 1519, 1490, 1455, 1372, 1268, 1174, 1130, 814, 767, 691, 655 cm<sup>-1</sup>. FAB<sup>+</sup> MS,  $m/z$  (%): 947 ([M + 1], 84), 946 (M<sup>+</sup>, 100), 832 ([M – 2Bu]<sup>+</sup>, 36), 718 ([M – 4Bu]<sup>+</sup>, 68). <sup>1</sup>H NMR (500.13 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.49 (2H, s, <sup>3</sup>J<sub>Sn-H</sub> = 45.2 Hz, H-7), 7.31 (2H, dd,  $J = 8.8, 2.4$  Hz, H-5), 7.24 (2H, d,  $J = 2.3$  Hz, H-3), 7.05 (2H, s, H-13), 6.93 (2H, dd,  $J = 8.3, 1.4$  Hz, H-11), 6.68 (2H, dd,  $J = 8.3, 1.4$  Hz, H-6, H-10), 2.22 (6H, s, CH<sub>3</sub>), 1.56–1.51 (8H, m, H- $\beta$ ), 1.42–1.38 (8H, m, H- $\alpha$ ), 1.27–1.20 (8H, sex,  $J = 7.4$  Hz, H- $\gamma$ ), 0.76 (12H, t,  $J = 7.3$  Hz, H- $\delta$ ). <sup>13</sup>C NMR (125.76 MHz, CDCl<sub>3</sub>)  $\delta$ : 169.2 (C-1), 160.6 (C-7), 157.6 (C-9),

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