

Structural and conformational analysis of neutral dinuclear diorganotin(IV) complexes derived from hexadentate Schiff base ligands

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Abstract

The synthesis of three hexadentate Schiff base ligands has been carried out, which contain two sets of ONO donor atoms. These were reacted with diorganotin(IV) dichloride derivatives (R = Me, *n*Bu, Ph) to prepare seven dinuclear diorganotin(IV) complexes in moderate yields. Aside from IR and NMR (¹H, ¹³C, ¹¹⁹Sn) spectroscopic studies, mass spectrometry and elemental analysis, four tin complexes were characterized by X-ray diffraction analysis. The spectroscopic analyses showed that in solution the tin atoms have five-coordinate environments with a *distorted trigonal bipyramidal* geometry. Each tin atom is coordinated to the nitrogen atom and forms covalent bonds with two oxygen atoms and two carbon atoms. Due to the presence of a methylene group as bridge between the two ONO chelates, the overall molecular structures can have *cis* or *trans* conformation, having either mirror or C₂-symmetry. While in solution a fast equilibrium can be supposed, in the solid state different intermediate conformations have been detected. Furthermore, for the dialkyltin derivatives Sn···O intermolecular interactions were found allowing for a dimeric or crinkled polymeric organization, whereas for the diphenyltin derivatives no such interactions were observed.

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1. Introduction

The chemistry of diorganotin(IV) compounds derived from ligands containing nitrogen and oxygen donor atoms has attracted much attention in the last few years, a fact that underlies the increasing number of publications dealing with this class of compounds [1–5]. In particular, diorganotin(IV) complexes using Schiff bases as ligands are being widely studied (e.g. [6–8]). The easy accessibility and structural features made them the target of numerous biological [9–11] and catalytic [12–14] studies.

Most of the diorganotin(IV) complexes resulting from tridentate Schiff base ligands have been synthesized from salicylaldehyde derivatives in combination with aliphatic aminoalcohols [15], aminoacids [16–19] and aminophenols [20–23]. The importance of diorganotin(IV) complexes derived from tridentate Schiff base ligands is in part due to their biocide and toxicological activities [15], as well as their use as initiators for lactide polymerization [24]. Usually, tin atoms in complexes derived from ONO tridentate ligands are penta-coordinate with a *trigonal bipyramidal* (TBP) geometry [15–23]. Generally, in this class of compounds the oxygen atoms occupy the axial positions, while the nitrogen atom and the two additional organic substituents are in equatorial positions. In tin derivatives with TBP geometry, the metal center can act as Lewis acid, which allows to increase its coordination number by addition of

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molecules having electron donating atoms (e.g. solvent molecules) [16–21], changing the geometry to *distorted octahedral*. For that reason, five-coordinate tin complexes frequently form Sn···O intermolecular bonds in the solid state, thus giving dimeric aggregates through the formation of a Sn₂O₂ four-membered ring [22,23].

As part of our investigation dealing with the study of diorganotin(IV) species derived from Schiff base ligands, we report herein the synthesis and structural analysis of seven new derivatives containing hexadentate Schiff base ligands. The ligands are derived from 5,5'-methylenebis(salicylaldehyde) and three different 2-aminophenols, and contain a double set of ONO donor atoms, thus allowing for the preparation of dinuclear metal complexes.

2. Results and discussion

2.1. Synthesis of the diorganotin(IV) complexes

The hexadentate ligands **1a–1c** were obtained in moderate yields from the reaction of 5,5'-methylenebis(salicylaldehyde) [25] with 2-aminophenol (**1a**), 2-amino-4-chlorophenol (**1b**) and 2-amino-4-*t*-butylphenol (**1c**). The dinuclear tin compounds **2a–2g** were prepared by reaction of one equivalent of the ligands **1a–1c** with two equivalents of the corresponding diorganotin(IV) dichloride derivative (R = Me, *n*Bu, Ph). Potassium hydroxide was used as base for the deprotonation of the ligand as described in the pre-

parative part (Scheme 1) for the organometallic tin derivatives containing aliphatic groups (**2a**, **2b**, **2d** and **2f**), while triethyl amine was used in the case of the phenyl tin derivatives (**2c**, **2e** and **2g**). Using KOH for the reaction of the diphenyltin derivative, the formation of either [Ph₂Sn(Cl)OH]₂ (**3**) or [Ph₄Sn₂O(OMe)Cl]₂ (**4**) was observed, inhibiting the formation of the desired tin complexes. Compounds **2a–2g** are solids with intense colors (from orange to dark red), which are soluble in polar organic solvents and are stable under atmospheric conditions. The title compounds were purified by slow precipitation of saturate solutions from methanol allowing the isolation of pure products in moderate yields (59–91%). In all seven cases the melting points of the products are higher than those of the ligands, whereby the highest melting points correspond to the diphenyltin(IV) derivatives.

2.2. Spectroscopic analysis

The mass spectrometric data of **2a–2g** indicate the formation of dinuclear bis-diorganotin(IV) complexes. For all seven compounds, the molecular ion was detected and the base peaks correspond to the ion resulting from a fragmentation involving one of the organic groups directly attached to the tin atoms [M–R]⁺.

In the IR spectra of complexes **2a–2g**, the broad bands observed at approximately 3400 cm⁻¹ for the stretching vibrations of the O–H groups in the free ligands are absent. For each of these compounds, bands typical for ν(C=N) vibrations were detected in the range of 1615–1617 cm⁻¹, which are considerably shifted towards lower frequencies with respect to the free ligands (1625–1631 cm⁻¹), suggesting the coordination of the azomethine nitrogen to the tin atom [21].

The ¹H and ¹³C NMR data suggest that the complexes have a *mirror plane* or a *C₂ axis* as symmetry element in solution, since there are only signals for a half of the molecular entity. As shown in Chart 1 two isomers are possible indeed, the *cis*-derivative (θ_{SnL–LSn} = 0°) having mirror symmetry and the *trans* (θ_{SnL–LSn} = 180°) derivative having *C₂*-symmetry. In the ¹H NMR spectra the chemical shifts for the hydrogen atoms of the ligands vary only slightly after complexation with the diorganotin(IV) fragment. The hydrogen atoms of the azomethine group (HC=N)

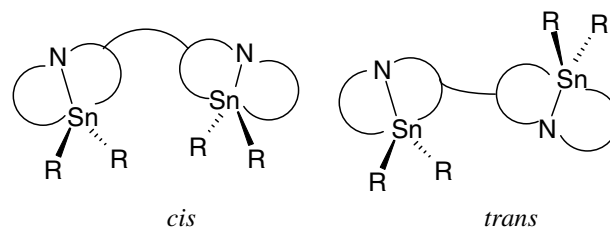
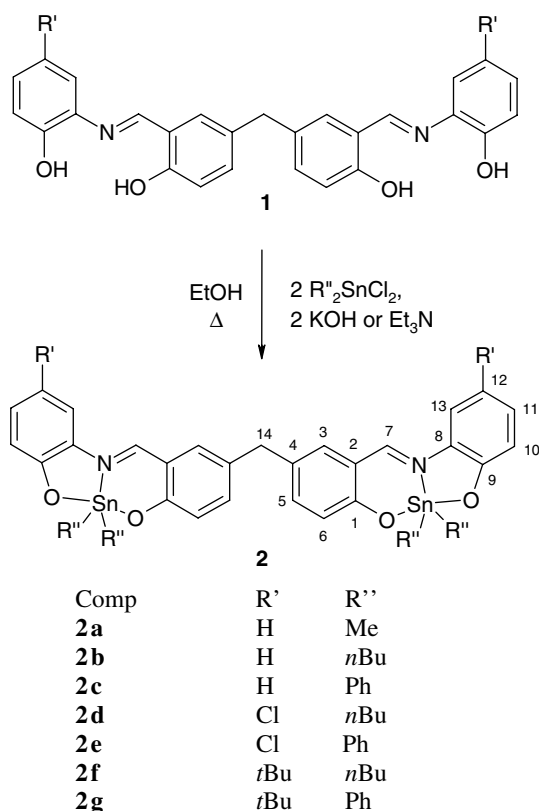


Chart 1. Schematic representation of the two possible conformations for the dinuclear tin compounds. In the *cis* conformation the two diorganotin moieties are oriented in the same direction (θ_{SnL–LSn} = 0°), while they have opposite orientation in the *trans* conformation (θ_{SnL–LSn} = 180°).

Scheme 1. Synthesis of the dinuclear diorganotin(IV) complexes **2a–2g**.

exhibit single signals in the $\delta = 8.51$ – 8.60 ppm range for compounds **2a**–**2g**, which are similar for other diorganotin(IV) compounds derived from ligands containing the ONO set of donor atoms [20–23]. Interestingly, in all cases it was possible to observe signals resulting from the coupling between the azomethine proton and the tin atoms ($^3J_{\text{Sn-H}} = 54$ – 56 Hz, Table 1), indicating that the Sn–N coordination bond is present in solution. When comparing the ^{13}C NMR spectra of the free ligands and the tin complexes, the most important changes occurred for the C_{Ph} –O carbon atoms numbered C1 and C9 (Scheme 1), whereby a downfield chemical shift was observed in agreement with the formation of covalent Sn–O bonds ($\Delta\delta \sim 10$ ppm).

The existence of five-coordinate tin(IV) cores could be demonstrated by ^{119}Sn NMR spectroscopy, whereby single signals were observed at $\delta = -152$ ppm for the dimethyltin derivative **2a**, at $\delta = -192$, -178 and -188 ppm for the di-*n*-butyltin derivatives **2b**, **2d** and **2f**, and at $\delta = -333$, -329 and -331 ppm for the diphenyltin complexes **2c**, **2e** and **2g**, respectively. These shifts are in the range of reported values for related five-coordinate diorganotin(IV) complexes [20–23], the highfield chemical shifts for the phenyltin derivatives being a consequence of anisotropic shielding effects in addition with the *pi* interactions.

The $^1J(^{119}\text{Sn}-^{13}\text{C})$ coupling constants of the diorganotin(IV) compounds are consistent with those generally observed for five-coordinate tin species (Table 1). The C_α –Sn– C_α' angles were estimated with the equations reported by Lockhart (R = Me) [26], Holeček (R = *n*Bu) [27] and Beltrán (R = Ph) [16] giving values of 131° for the methyltin derivative **2a** [26], 133 – 139° for **2b**, **2d** and **2f** (R = *n*Bu), and 124 – 128° for **2c**, **2e** and **2f** (R = Ph). They agree well with the proposed coordination geometry. As observed in previous reports, an increase of the bond angles from 120 – 125° to more than 130° , as it occurs in the cases of **2a**, **2b**, **2d** and **2f**, indicates the possibility to have an increment in the coordination sphere of the tin atoms, a characteristic that has been denoted by the X-ray diffraction study for complexes **2a** and **2b**.

2.3. Solid state structure analysis

From the NMR spectroscopic analyses carried out in solution it was not clear, whether the dinuclear tin com-

plexes belong to the C_s or C_2 point group. Fortunately, compounds **2a**, **2b**, **2c** and **2e** could be crystallized by slow evaporation of concentrate ethanol/methylene chloride solutions (1:1 ratio), and their structures determined by single crystal X-ray diffraction analyses (Fig. 1). The most relevant crystallographic data are summarized in Table 2. For compound **2c** crystals could be also grown from a concentrate solution in benzene, so that it was possible to analyze two isomorphs, one solventless (**2c**) and the other containing two benzene molecules in the unit cell (**2c'**). Both systems crystallized in the monoclinic space group $P2_1/c$ and only small differences in their molecular structures were observed (Table 3). In the case of compounds **2a** and **2e**, coordinating solvent molecules were included in the unit cell (EtOH for **2a** and H_2O for **2e**), which, however, did not form part of the tin atom coordination sphere.

In all structures analyzed, each of the two tin atoms has a coordination number of five, resulting from the bonding to one nitrogen and two oxygen atoms from the ligand, and two carbon atoms from the organic tin substituents. The distortion from the perfect *trigonal bipyramidal* geometry is mainly due to the rigidity of the chelate rings and the large covalent radius of tin(IV) atoms. As observed in similar compounds, the oxygen atoms are in axial position; the nitrogen atom forms a coordination bond with the tin atom and it is found in equatorial position, as well as the two organic substituents.

Interestingly, most of the molecules do not possess ideal or approximate mirror or C_2 symmetry, as it might have been expected from the spectroscopic data. Only in the case of compound **2e** the molecule is located at a crystallographic mirror plane. Apparently, the flexibility present in the $-\text{CH}_2$ -moiety of the systems allows the complexes to adopt different orientations when relating the two diorganotin moieties. As a consequence, the angles between the planes of the two salicylidene rings attached to the bridging methylene group have values ranging from 34.8° to 174.5° (Fig. 2). Compounds **2b** and **2e** with torsion angles of 34.8° and 76.4° show a disposition closer to the *cis* conformation (*mirror*-symmetry), whereas for compounds **2a**, **2c** and **2c'** a disposition closer to the *trans* conformation (C_2 -symmetry) was observed (154.9° , 174.5° and 143.2° , respectively) (Fig. 2). These different conformations are attributed to packing effects in the crystalline structure and it may be

Table 1
Selected ^1H , ^{13}C and ^{119}Sn NMR spectroscopic data and comparison between calculated and experimental C–Sn–C bond angles for compounds **2a**–**2g**

Entry	^1H (H-7) (ppm)	^{13}C (C-7) (ppm)	^{119}Sn (ppm)	$^3J(^{119}\text{Sn}-^1\text{H}7)$ (Hz)	$^1J(^{119}\text{Sn}-^{13}\text{C}_\alpha)$ (Hz)	θ C–Sn–C ($^\circ$) _{Calcd} ^a	θ C–Sn–C ($^\circ$) _{Found} ^b
2a	8.54	161.7	–152	50	625	131.12	130.6(6)/129.3(7)
2b	8.58	161.9	–192	44	650	139.74	143.1(5)/118.0(7)
2c	8.60	161.2	–333	58	1020	126.93	121.0(3)/128.7(3) ^c
2d	8.56	162.1	–178	44	588	133.53	
2e	8.51	161.8	–329	52	1070	128.87	119.5(4)
2f	8.59	160.8	–188	48	610	135.73	
2g	8.60	160.6	–331	56	955	124.54	

^a Calculated using the equations reported in Ref. [26] (**2a**), [27] (**2b**, **2d** and **2f**) and [16] (**2c**, **2e** and **2g**).

^b From X-ray data.

^c Values taken from the data collection of **2c**.

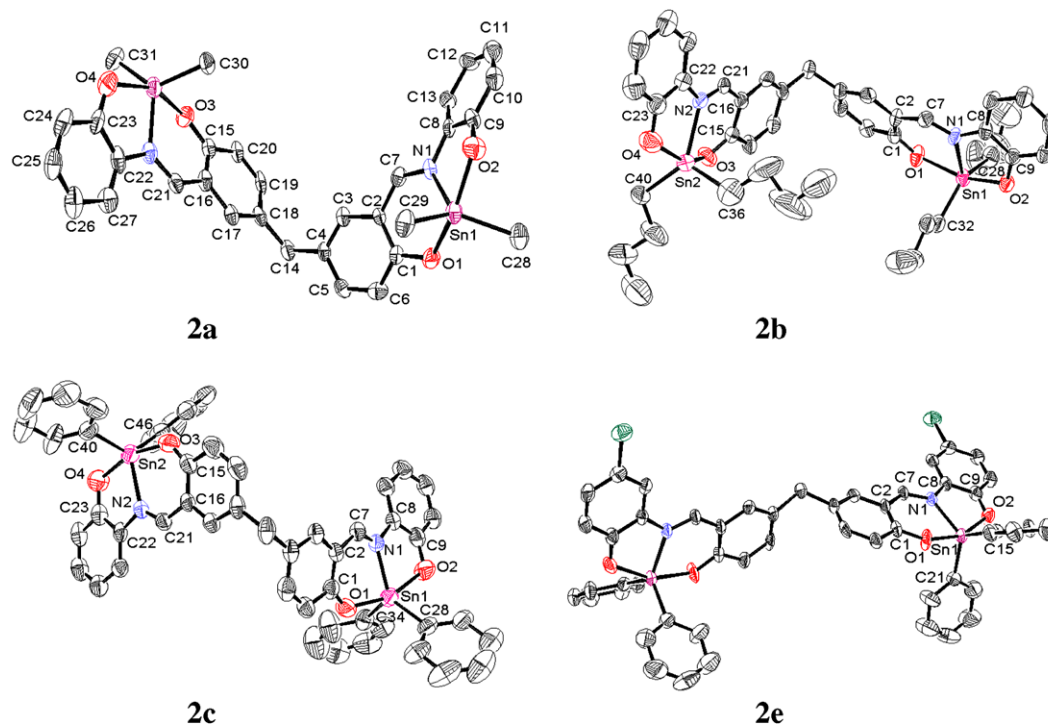
Fig. 1. Molecular structures for complexes **2a**, **2b**, **2c** and **2e**.

Table 2

Crystallographic data for compounds **2a–2c** and **2e**

Identification code	2a	2b	2c	2c'	2e
Empirical formula	C ₃₁ H ₃₀ N ₂ O ₄ Sn ₂ · C ₂ H ₅ OH	C ₄₃ H ₅₄ N ₂ O ₄ Sn ₂	C ₅₁ H ₃₈ N ₂ O ₄ Sn ₂	C ₅₁ H ₃₈ N ₂ O ₄ Sn ₂ · 2C ₆ H ₆	C ₅₁ H ₃₆ Cl ₂ N ₂ O ₄ Sn ₂ · 4H ₂ O
Formula weight (g mol ⁻¹)	778.02	900.26	980.21	1136.43	1121.16
Crystal size (mm ³)	0.20 × 0.14 × 0.10	0.20 × 0.12 × 0.10	0.20 × 0.20 × 0.16	0.30 × 0.20 × 0.16	0.22 × 0.18 × 0.12
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P2 ₁ /n	P1̄	P2 ₁ /c	P2 ₁ /c	P2/c
<i>Unit cell dimensions</i>					
<i>a</i> (Å)	12.696(3)	10.8083(12)	17.066(3)	19.860(4)	8.9824(10)
<i>b</i> (Å)	15.595(3)	14.791(2)	26.523(5)	13.853(3)	13.0474(15)
<i>c</i> (Å)	17.125(3)	15.4376(18)	9.6710(19)	19.915(4)	21.631(3)
α (°)	90	64.342(3)	90	90	90
β (°)	108.435(4)	74.681(2)	96.83(3)	109.394(3)	91.874(2)
γ (°)	90	68.857(2)	90	90	90
Volume (Å ³)	3216.5(11)	2057.6(4)	4346.4(15)	5168.2(17)	2533.7(5)
<i>Z</i>	4	2	4	4	2
<i>D</i> _{calc} (g/cm ³)	1.607	1.453	1.498	1.461	1.470
μ (mm ⁻¹)	1.595	1.256	1.196	1.017	1.144
Collected refl.	24 608	9052	17 526	48 879	20 291
Independent refl. (<i>R</i> _{int})	4210 (0.1120)	5605 (0.0458)	5898 (0.0414)	9089 (0.0416)	3539 (0.0602)
Parameters	370	465	533	641	294
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0837	0.0738	0.0571	0.0361	0.0715
<i>wR</i> ₂ (all data)	0.1991	0.1837	0.1496	0.0903	0.1998
GOF	1.093	1.012	1.063	1.025	1.175

supposed that in solution there is a fast dynamic equilibrium between them.

Selected bond distances and angles are summarized in Table 3. Considerable variations could be only found for some bond angles that are affected by the different organic substituents attached to the tin atoms. For example, the

axial oxygen substituents have O–Sn–O bond angles ranging from 154.5(5)° for the dimethyltin derivative **2a** to 161.6(3)° for the diphenyltin derivative **2c**. Interesting variations are also observed for the C–Sn–C angles: if phenyl groups are attached to the tin atom, then the angle is close to 120°, whereas with aliphatic moieties the angles tend to

Table 3
Selected bond distances (Å) and angles (°) for compounds **2a**, **2b**, **2c**, **2c'** and **2e**

	2a (R = Me)	2b (R = nBu)	2c (R = Ph)	2c' (R = Ph)	2e^a (R = Ph)
<i>Bond distances (Å)^b</i>					
Sn1–N1/Sn2–N2	2.166(11)/2.192(12)	2.212(8)/2.236(9)	2.188(5)/2.178(5)	2.189(2)/2.175(2)	2.191(7)
Sn1–O1/Sn2–O3	2.110(9)/2.125(10)	2.164(7)/2.074(9)	2.085(5)/2.077(5)	2.067(2)/2.083(2)	2.079(6)
Sn1–O2/Sn2–O4	2.136(11)/2.100(11)	2.132(7)/2.080(9)	2.065(5)/2.084(6)	2.076(2)/2.088(2)	2.094(6)
Sn1–C α /Sn2–C α''	2.105(15)/2.092(14)	2.125(11)/2.06(2)	2.113(8)/2.102(8)	2.104(4)/2.110(3)	2.094(10)
Sn1–C α' /Sn2–C α'''	2.115(14)/2.130(15)	2.113(12)/2.149(12)	2.128(7)/2.108(8)	2.113(3)/2.113(3)	2.114(10)
N1–C7/N2–C21	1.287(15)/1.325(17)	1.295(12)/1.292(13)	1.295(7)/1.277(7)	1.306(4)/1.301(4)	2.293(10)
<i>Bond angles (°)</i>					
O1–Sn1–N1/O3–Sn2–N2	81.8(4)/81.6(4)	81.3(3)/82.0(3)	82.61(19)/84.65(18)	83.51(9)/82.96(8)	83.2(3)
O1–Sn1–O2/O3–Sn2–O4	156.0(4)/154.5(5)	156.7(3)/149.8(4)	159.7(2)/161.6(3)	160.25(9)/159.79(9)	158.6(3)
O1–Sn1–C α /O3–Sn2–C α''	97.4(6)/96.9(5)	93.2(4)/99.7(8)	91.6(3)/92.3(3)	95.45(14)/93.17(11)	96.8(4)
O1–Sn1–C α' /O3–Sn2–C α'''	91.7(5)/89.8(5)	90.6(4)/89.1(5)	96.3(3)/93.1(3)	91.99(12)/92.94(11)	90.5(3)
O2–Sn1–N1/O4–Sn2–N2	75.1(4)/76.4(5)	75.4(3)/75.9(4)	77.2(2)/77.1(2)	77.29(9)/76.86(9)	76.8(3)
O2–Sn1–C α /O4–Sn2–C α''	96.6(6)/100.8(6)	94.6(4)/106.1(8)	96.4(3)/96.3(3)	96.72(14)/95.86(11)	98.4(4)
O2–Sn1–C α' /O4–Sn2–C α'''	93.9(5)/93.1(6)	96.2(4)/92.3(4)	95.5(3)/96.7(3)	94.45(12)/95.82(11)	95.0(3)
N1–Sn1–C α /N2–Sn2–C α''	110.5(6)/104.0(6)	108.2(4)/106.6(6)	118.3(2)/116.5(2)	114.70(11)/113.60(10)	114.9(3)
N1–Sn1–C α' /N2–Sn2–C α'''	118.9(5)/126.7(5)	108.6(5)/135.4(4)	120.7(2)/114.9(2)	122.62(10)/118.93(10)	125.6(3)
C α –Sn1–C α' /C α'' –Sn2–C α'''	130.6(6)/129.3(7)	143.1(5)/118.0(7)	121.0(3)/128.7(3)	122.67(12)/127.47(11)	119.5(4)

^a Only one value is described due to the mirror symmetry of the molecule.

^b α and α' = carbon atoms located at the *endo* position; α'' and α''' = carbon atoms located at the *exo* position.

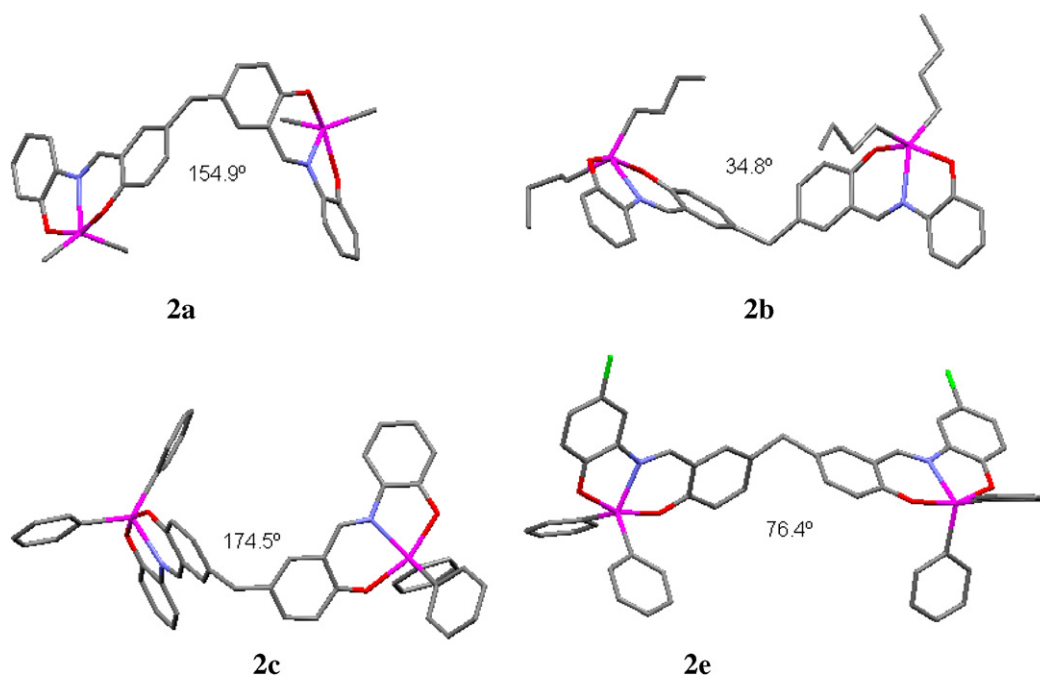


Fig. 2. Overall conformation of the molecular structures of **2a**, **2b**, **2c** and **2e**, showing the angles between the planes of the two salicylidene moieties ($\theta_{\text{SnL-L}_{\text{Sn}}} = 34.8\text{--}174.5^\circ$) attached to the bridging methylene group.

be larger. In the case of the dimethyltin derivative (compound **2a**), the C–Sn–C bond angles have values of $129.3(7)^\circ$ and $130.6(6)^\circ$, allowing for the interaction with neighboring molecules through Sn \cdots O intermolecular interactions to form a 1D crinkled polymeric chain (Fig. 3). The four-membered Sn₂O₂ rings within the coordination polymer are not symmetric, since one Sn \cdots O interaction is formed with the oxygen atom of the five-membered chelate ring (3.36 Å), whereas the other is

formed to the oxygen corresponding to the six-membered heterocycle (3.81 Å). As it can be noticed, the latter interaction is significantly weaker and slightly longer than the sum of the van der Waals radii (3.69 Å). Due to the Sn \cdots O intermolecular interactions the tin atoms adopt a *distorted octahedral* geometry in the solid state, which is not observed in solution. It is important to remark that in all Schiff base–tin complexes reported so far, the Sn \cdots O interactions occur between the oxygen atoms forming part of

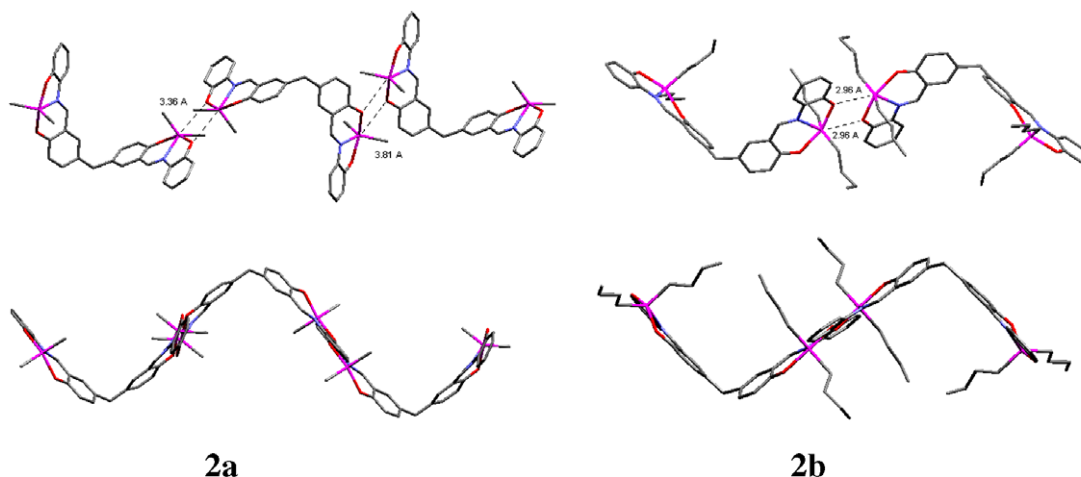


Fig. 3. Sn...O interactions give rise to a crinkled 1D polymeric structure for **2a**, and a dimeric compound in the case of **2b**.

the five-membered heterocycles, so that this is the first case, in which Sn...O interactions occur with the oxygen atoms involved in a six-membered heterocycle. In the case of compound **2b**, the C–Sn–C bond angles have values of 143.1(5)° and 118.0(7)° for the two chelate rings present in the complex. The larger angle allows for the formation of a Sn...O intermolecular interaction (2.96 Å), giving place to a dimeric organization (Fig. 3). The smaller angle at the opposite side of the molecule (118.0(7)°) inhibits such an interaction, so that the polymeric organization observed in the case of **2a** is avoided. In the case of the diphenyltin derivatives **2c** and **2e**, Sn...O intermolecular interactions were not observed.

As mentioned above, compounds [Ph₂Sn(Cl)OH]₂ (**3**) and [Ph₄Sn₂O(OMe)Cl]₂ (**4**) resulted from the hydrolysis of Ph₂SnCl₂ when the reactions were carried out in the presence of KOH. Suitable crystals for the X-ray analysis were isolated after leaving the reaction mixture over night

at room temperature. The central part of the molecular structure of compound **3** [28] consists of a four-membered heterocycle with the composition (Sn(OH))₂ (Fig. 4), in which the hydroxyl groups bridge the two tin atoms. The Sn–O distance of 2.170(16)° is analogous to that found in a related compound containing quinoline in the unit cell [29]. In the molecular structure of compound **4** [30] three four-membered Sn₂O₂ rings are present, of which the central ring is formed by bridging oxygen atoms, while the lateral rings involved also bridging methoxy groups (Fig. 4). The bond distances and angles are in accordance with those previously reported for an analogous compound, which contains OH instead of OMe fragments [31].

3. Conclusions

Schiff base ligands having a two-fold ONO donor system can give rise to dinuclear tin complexes, in which the diorganotin chelates are connected by a methylene group. In solution, the tin atoms have a five-coordinate coordination geometry, which is retained in the solid state for the diphenyltin derivatives, while the dimethyl and dibutyl derivatives can change their geometry to *distorted octahedral* owing to the presence of Sn...O intermolecular interactions. Two molecular conformations are possible, which involve either a *cis*- or a *trans*-orientation of the diorganotin groups. Since in the solid state different intermedium states have been observed that approximate to one or the other isomer, it can be supposed that in solution a fast dynamic equilibrium is present.

4. Experimental

4.1. Materials and methods

All reagents and solvents used were obtained from commercial suppliers and used without further purification. The ¹H, ¹³C and ¹¹⁹Sn NMR spectra were recorded at room temperature using a Varian Gemini 200 spectropho-

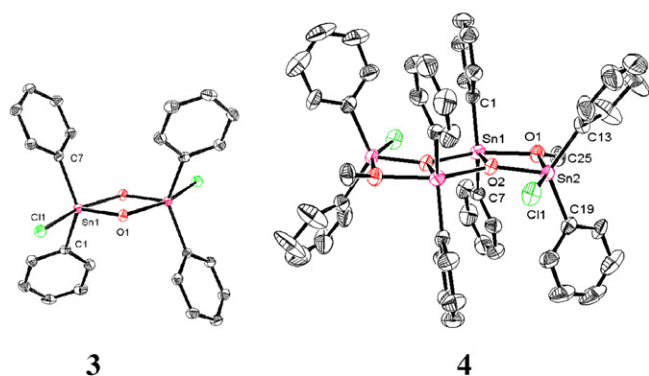


Fig. 4. Molecular structures for compounds [Ph₂Sn(Cl)OH]₂ (**3**) and [Ph₄Sn₂O(OMe)Cl]₂ (**4**). Selected bond distances (Å) and angles (°) for **3**: Sn1–O1 2.0170(16), Sn1–Cl1 2.4748(6), Sn1–C1 2.114(2), Sn1–C7 2.120(2), O1–Sn1–Cl1 115.32(8), C1–Sn1–C7 129.27(9), O1–Sn2–O1' 70.62(7). **4**: Sn1–O1 2.175(5), Sn1–O2 2.031(4), Sn2–O1 2.196(5), Sn2–O2 2.014(4), Sn2–Cl1 2.466(2), Sn1–O1–Sn2 101.62(19), Sn1–O2–Sn2 113.8(2), C13–Sn2–C19 124.6(3), O2–Sn2–Cl1 85.50(13), O1–Sn1–O2 72.26(17), O1–Sn2–O2 72.13(17).

tometer. As standard references TMS (internal, ^1H , $\delta = 0.00$ ppm, ^{13}C , $\delta = 0.00$ ppm) and SnMe_4 (external, ^{119}Sn , $\delta = 0.0$ ppm) were used as standard references. 2D COSY and HMQC experiments have been carried out for the unambiguous assignment of the ^1H and ^{13}C NMR spectra. Infrared spectra have been recorded on a Bruker Vector 22 FT-IR spectrophotometer. Mass spectra were obtained on a Jeol JMS 700 equipment. Elemental analyses were carried out on a Perkin Elmer Series II 2400 instrument. Melting points were determined with a Büchi B-540 digital apparatus.

4.2. X-ray crystallography

X-ray diffraction studies were performed on a Bruker-APEX diffractometer equipped with a CCD area detector, $\text{MoK}\alpha$ -radiation ($\lambda = 0.71073 \text{ \AA}$), and a graphite monochromator. Frames were collected at $T = 293 \text{ K}$. The measured intensities were reduced to F^2 and corrected for absorption with SADABS (SAINT-NT) [32]. Corrections were made for Lorentz and polarization effects. Structure solution, refinement and data output were carried out with the SHELXTL-NT program package [33]. All non-hydrogen atoms were refined anisotropically except for **2a**, wherein the ethanol solvent molecule was refined only isotropically. Hydrogen atoms were placed in geometrically calculated positions using a riding model. High R values are observed in some cases due to solvent molecule disorder.

4.3. Syntheses

4.3.1. General procedure for the preparation of the hexadentate ligands **1a–1c**

A mixture of one equivalent of 5,5'-methylenebis(salicylaldehyde) and two equivalents of the corresponding *o*-aminophenol was dissolved in ethanol. The solution was refluxed for 60 min using a Dean-Stark trap to remove the water formed during the reaction and part of the solvent. The solution was evaporated to dryness to give compounds **1a–1c** as orange solids, which were used for the subsequent reaction without further purification.

4.3.1.1. Ligand 1a. Ligand **1a** was prepared from 1.00 g (3.9 mmol) of 5,5'-methylenebis(salicylaldehyde) and 0.852 g (7.8 mmol) of 2-aminophenol. An orange solid was obtained in a yield of 83% (1.42 g). M.p. = 227–230 °C. IR (KBr) ν : 3405, 3048, 2896, 2557, 1631 (C=N), 1590, 1526, 1492, 1458, 1369, 1304, 1273, 1244, 1138, 823, 797, 746 cm^{-1} . ^1H NMR (200 MHz, CDCl_3) δ : 9.73 (2H, s, OH), 8.92 (2H, s, H-7), 7.46 (2H, s, H-3), 7.34 (2H, d, $J = 7.8 \text{ Hz}$, H-5), 7.26 (2H, d, $J = 7.8 \text{ Hz}$, H-6), 7.11 (2H, t, $J = 8.0 \text{ Hz}$, H-12), 6.95 (2H, d, $J = 8.0 \text{ Hz}$, H-13), 6.90 (2H, d, $J = 8.0 \text{ Hz}$, H-10), 6.86 (2H, t, $J = 8.0 \text{ Hz}$, H-11), 3.90 (2H, s, H-14) ppm. ^{13}C NMR (50 MHz, CDCl_3) δ : 161.0 (C-7), 158.6 (C-1), 150.7 (C-9), 132.9 (C-5), 131.5 (C-3), 131.2 (C-4,8), 127.6 (C-11), 119.3 (C-2), 119.0 (C-6, 12), 116.5 (C-10), 116.1 (C-13),

39.7 (C-14) ppm. Anal. Calc. for $\text{C}_{27}\text{H}_{22}\text{N}_2\text{O}_4$: C, 73.95; H, 5.05; N, 6.38. Found: C, 73.76; H, 4.98; N, 6.23%.

4.3.1.2. Ligand 1b. Ligand **1b** was prepared from 1.00 g (3.9 mmol) of 5,5'-methylenebis(salicylaldehyde) and 1.121 g (7.8 mmol) of 2-amino-4-chlorophenol. An orange solid was obtained in a yield of 71 % (1.41 g). M.p. = 242–245 °C. IR (KBr) ν : 3429, 2370, 1625 (C=N), 1579, 1491, 1360, 1276, 1229, 1149, 920, 816 cm^{-1} . ^1H NMR (200 MHz, DMSO-d_6) δ : 10.12 (2H, s, OH), 8.91 (2H, s, H-7), 7.46 (2H, d, $J = 2.4 \text{ Hz}$, H-3), 7.29 (2H, dd, $J = 8.2, 2.4 \text{ Hz}$, H-5), 7.26 (2H, d, $J = 2.2 \text{ Hz}$, H-13), 7.15 (2H, dd, $J = 8.2, 2.2 \text{ Hz}$, H-11), 6.95 (2H, d, $J = 8.2 \text{ Hz}$, H-6), 6.91 (2H, d, $J = 8.2 \text{ Hz}$, H-10), 3.95 (2H, s, H-14) ppm. ^{13}C NMR (50 MHz, DMSO-d_6) δ : 162.6 (C-7), 158.8 (C-1), 149.9 (C-9), 136.2 (C-8), 133.6 (C-5), 131.9 (C-3), 131.6 (C-4), 127.1 (C-11), 122.9 (C-12), 119.1 (C-2), 117.6 (C-6), 117.3 (C-13), 116.4 (C-10), 39.9 (C-14) ppm. Anal. Calc. for $\text{C}_{27}\text{H}_{20}\text{N}_2\text{O}_4\text{Cl}_2$: C, 63.91; H, 3.97; N, 5.52. Found: C, 63.57; H, 3.82; N, 5.32%.

4.3.1.3. Ligand 1c. Ligand **1c** was prepared from 1.00 g (3.9 mmol) of 5,5'-methylenebis(salicylaldehyde) and 1.29 g (7.8 mmol) of 2-amino-4-*t*-butylphenol. An orange solid was obtained in a yield of 74% (1.6 g). M.p. = 248–251 °C. IR (KBr) ν : 3448, 2959, 2373, 1627 (C=N), 1516, 1494, 1363, 1278, 1243, 1148, 817 cm^{-1} . ^1H NMR (200 MHz, DMSO-d_6) δ : 9.54 (2H, s, OH), 8.93 (2H, s, H-7), 7.48 (2H, d, $J = 2.0 \text{ Hz}$, H-3), 7.33 (2H, d, $J = 2.2 \text{ Hz}$, H-13), 7.27 (2H, dd, $J = 8.4, 2.0 \text{ Hz}$, H-5), 7.12 (2H, dd, $J = 8.0, 2.2 \text{ Hz}$, H-11), 6.88 (2H, d, $J = 8.4 \text{ Hz}$, H-6), 6.86 (2H, d, $J = 8.0 \text{ Hz}$, H-10), 3.86 (2H, s, H-14) ppm. ^{13}C NMR (50 MHz, DMSO-d_6) δ : 161.8 (C-7), 159.6 (C-1), 149.2 (C-9), 142.6 (C-12), 134.7 (C-8), 133.7 (C-5), 132.5 (C-3), 132.1 (C-4), 125.9 (C-11), 119.9 (C-2), 117.3 (C-6), 117.0 (C-10), 116.5 (C-13), 39.6 (C-14) ppm. Anal. Calc. for $\text{C}_{35}\text{H}_{38}\text{N}_2\text{O}_4$: C, 76.33; H, 6.95; N, 5.08. Found: C, 76.17; H, 6.85; N, 4.97%.

4.3.2. General procedure for the preparation of the diorganotin(IV) complexes **2a–2g**

To a solution of one equivalent of the ligand (**1a–1c**) in 20 ml of methanol, two equivalents of the base were added (KOH in case of compounds **2a**, **2b**, **2d** and **2f**, and NEt_3 for **2c**, **2e** and **2g**). After 15 min of stirring, two equivalents of the dialkyltin dichloride (**2a**, **2b**, **2d** and **2f**) or diphenyltin dichloride (**2c**, **2e** and **2g**) were added. The reaction mixture was refluxed for 6 h using a Dean-Stark trap to remove the water formed during the reaction and/or part of the solvent. The solution was evaporated to dryness to give compounds **2a–2g** as orange-red dark solids. The title compounds were purified by slow precipitation of saturate solutions from methanol allowing the isolation of pure products in moderate to good yields (59–91%).

4.3.2.1. Complex 2a. Compound **2a** was obtained from 0.30 g (0.68 mmol) of ligand **1a** and 0.30 g (1.36 mmol) of

dichlorodimethyltin. A red dark solid was obtained in a yield of 78% (0.39 g). M.p. = 238–241 °C. IR (KBr) ν : 2919, 1616 (C=N), 1590, 1534, 1473, 1381, 1305, 1214, 1157, 743 cm^{-1} . EI MS, m/z (%): 734 ([M+1], 64), 732 (M^+ , 65), 717 ([M-Me] $^+$, 100), 702 ([M-2Me] $^+$, 43). ^1H NMR (200 MHz, CDCl_3) δ : 8.54 (2H, s, $^3J_{\text{Sn-H}} = 25$ Hz, H-7), 7.25 (2H, d, $J = 8.2$ Hz, H-5), 7.16 (2H, d, $J = 7.8$ Hz, H-13), 7.09 (2H, t, $J = 7.8$ Hz, H-12), 6.74 (2H, d, $J = 8.2$ Hz, H-6), 6.67 (2H, d, $J = 7.8$ Hz, H-10), 6.61 (2H, t, $J = 7.8$ Hz, H-11), 6.95 (2H, s, H-3), 3.75 (2H, s, H-14), 0.89 (2H, s, Me) ppm. ^{13}C NMR (50 MHz, CDCl_3) δ : 168.0 (C-1), 161.8 (C-7), 159.0 (C-9), 138.0 (C-5), 137.8 (C-3), 134.4 (C-8), 130.4 (C-4, 11), 122.9 (C-12), 118.7 (C-6), 118.0 (C-2), 116.8 (C-10), 114.9 (C-13), 39.0 (C-14), 22.3 (Me) ppm. ^{119}Sn NMR (75 MHz, CDCl_3) δ : -152 ppm. Anal. Calc. for $\text{C}_{31}\text{H}_{30}\text{N}_2\text{O}_4\text{Sn}_2$: C, 50.86; H, 4.13; N, 3.82. Found: C, 50.76; H, 3.98; N, 3.70%.

4.3.2.2. Complex 2b. Compound **2b** was obtained from 0.26 g (0.60 mmol) of ligand **1a** and 0.36 g (1.20 mmol) of dichlorodibutyltin. A red dark solid was obtained in a yield of 59 % (0.32 g). M.p. = 242–245 °C. IR (KBr) ν : 2954, 2920, 2853, 1616 (C=N), 1588, 1532, 1473, 1380, 1306, 1212, 1155, 833, 741 cm^{-1} . EI MS, m/z (%): 902 ([M+1], 82), 900 (M^+ , 84), 843 ([M-Bu] $^+$, 100), 786 ([M-2Bu] $^+$, 35). ^1H NMR (200 MHz, CDCl_3) δ : 8.58 (2H, t, $^3J_{\text{Sn-H}} = 22$ Hz, H-7), 7.29 (2H, d, $J = 8.1$ Hz, H-5), 7.20 (2H, d, $J = 8.0$ Hz, H-13), 7.15 (2H, t, $J = 8.0$ Hz, H-12), 7.01 (2H, d, $J = 2.2$ Hz, H-3), 6.82 (2H, d, $J = 8.1$ Hz, H-6), 6.74 (2H, d, $J = 8.0$ Hz, H-10), 6.65 (2H, t, $J = 8.0$ Hz, H-11), 3.81 (2H, s, H-14), 1.56–1.64 (8H, m, CH_2 - β), 1.40–1.50 (8H, m, CH_2 - α), 1.31 (8H, sex, $J = 7.3$ Hz, CH_2 - γ), 0.83 (12H, t, $J = 7.3$ Hz, CH_2 - δ) ppm. ^{13}C NMR (50 MHz, CDCl_3) δ : 168.2 (C-1), 161.4 (C-7), 159.5 (C-9), 137.8 (C-3, 5), 134.3 (C-8), 130.4 (C-4, C-11), 122.8 (C-12), 118.6 (C-6), 117.6 (C-2), 116.4 (C-10), 114.8 (C-13), 39.7 (C-14), 27.4 (C- β), 27.0 (C- γ), 22.4 (C- α), 14.0 (C- δ) ppm. ^{119}Sn NMR (75 MHz, CDCl_3) δ : -192 ppm. Anal. Calc. for $\text{C}_{43}\text{H}_{54}\text{N}_2\text{O}_4\text{Sn}_2$: C, 57.36; H, 6.04; N, 3.11. Found: C, 56.96; H, 5.88; N, 3.20%.

4.3.2.3. Complex 2c. Compound **2c** was obtained from 0.19 g (0.436 mmol) of ligand **1a** and 0.30 g (0.87 mmol) of dichlorodiphenyltin. An orange solid was obtained in a yield of 91% (0.39 g). M.p. = 285–287 °C. IR (KBr) ν : 3050, 1615 (C=N), 1590, 1535, 1473, 1379, 1305, 1157, 835, 735 cm^{-1} . FAB MS, m/z (%): 982 ([M+2], 70), 980 (M^+ , 75), 903 ([M-Ph] $^+$, 100). ^1H NMR (200 MHz, CDCl_3) δ : 8.60 (2H, s, $^3J_{\text{Sn-H}} = 29$ Hz, H-7), 7.84 (8H, dd, $J = 7.3, 1.8$ Hz, H- o), 6.90–7.20 (18H, m, H-3, 5, 6, 10, 12, 13, m , p), 6.66 (2H, td, $J = 8.4, 2.2$ Hz, H-11), 3.82 (2H, s, H-14) ppm. ^{13}C NMR (50 MHz, CDCl_3) δ : 168.2 (C-1), 161.2 (C-7), 156.5 (C-9), 139.7 (C-5, C- i), 138.1 (C-3), 136.5 (C- o), 134.5 (C-8), 130.3 (C-11, C- p), 128.7 (C- m), 128.1 (C-4), 123.1 (C-12), 119.0 (C-6), 117.3 (C-2), 116.9 (C-10), 114.7 (C-13), 39.7 (C-14) ppm. ^{119}Sn NMR (75 MHz, CDCl_3) δ : -333 ppm. Anal. Calc for

$\text{C}_{51}\text{H}_{38}\text{N}_2\text{O}_4\text{Sn}_2$: C, 62.48; H, 3.90; N, 2.85. Found: C, 61.85; H, 3.93; N, 2.72%.

4.3.2.4. Complex 2d. Compound **2d** was obtained from 0.10 g (0.20 mmol) of ligand **1b** and 0.12 g (0.40 mmol) of dichlorodibutyltin. A red dark solid was obtained in a yield of 68% (0.13 g). M.p. = 257–260 °C. IR (KBr) ν : 2954, 2921, 1617 (C=N), 1585, 1531, 1472, 1414, 1378, 1299, 819 cm^{-1} . EI MS, m/z (%): 970 ([M+1], 61), 968 (M^+ , 65), 912 ([M-Bu] $^+$, 100). ^1H NMR (200 MHz, CDCl_3) δ : 8.56 (2H, s, $^3J_{\text{Sn-H}} = 22$ Hz, H-7), 7.29 (2H, dd, $J = 7.4, 2.2$ Hz, H-5), 7.26 (2H, d, $J = 2.0$ Hz, H-13), 7.12 (2H, td, $J = 8.7$ Hz, 2.0 Hz, H-11), 7.04 (2H, d, $J = 2.2$ Hz, H-3), 6.78 (2H, d, $J = 7.4$ Hz, H-6), 6.77 (2H, d, $J = 8.7$ Hz, H-10), 3.84 (2H, s, H-14), 1.58–1.65 (8H, m, H- β), 1.45–1.52 (8H, m , H- α), 1.30 (8H, sex, $J = 7.2$ Hz, H- γ), 0.86 (12H, t, $J = 7.2$ Hz, H- δ) ppm. ^{13}C NMR (50 MHz, CDCl_3) δ : 168.9 (C-1), 162.2 (C-7), 158.2 (C-9), 138.6 (C-3, 5), 132.4 (C-8), 129.9 (C-11), 129.5 (C-4), 121.0 (C-12), 119.6 (C-10), 117.5 (C-2, 6), 115.1 (C-13), 39.5 (C-14), 27.4 (C- β), 26.9 (C- γ), 22.4 (C- α), 13.8 (C- δ) ppm. ^{119}Sn NMR (75 MHz, CDCl_3) δ : -178 ppm. Anal. Calc. for $\text{C}_{43}\text{H}_{52}\text{N}_2\text{O}_4\text{Cl}_2\text{Sn}_2$: C, 53.28; H, 5.40; N, 2.89. Found: C, 53.62; H, 5.14; N, 2.98%.

4.3.2.5. Complex 2e. Compound **2e** was obtained from 0.10 g (0.20 mmol) of ligand **1b** and 0.14 g (0.40 mmol) of dichlorodiphenyltin. An orange solid was obtained with yield of 48% (0.10 g). M.p. = 295–298 °C. IR (KBr) ν : 2946, 1617 (C=N), 1590, 1534, 1473, 1377, 1296, 825, 732 cm^{-1} . FAB MS, m/z (%): 1050 ([M+1], 54), 1048 (M^+ , 60), 974 ([M-Ph] $^+$, 100). ^1H NMR (200 MHz, CDCl_3) δ : 8.51 (2H, s, $^3J_{\text{Sn-H}} = 27$ Hz, H-7), 7.82–7.92 (8H, m , H- o), 7.32–7.42 (12H, m, H- m , p), 6.96–7.30 (12H, m, H-3, 5, 6, 10, 11, 13), 3.81 (2H, s, H-14) ppm. ^{13}C NMR (50 MHz, CDCl_3) δ : 168.4 (C-1), 161.8 (C-7), 157.4 (C-9), 139.4 (C-5), 138.6 (C-3, C- i), 136.5 (C- o), 131.7 (C-8), 130.5 (C-11), 129.9 (C- p), 129.8 (C-4), 128.7 (C- m), 121.5 (C-12), 119.9 (C-10), 117.5 (C-2, 6), 114.9 (C-13), 39.6 (C-14) ppm. ^{119}Sn NMR (75 MHz, CDCl_3) δ : -329 ppm. Anal. Calc. for $\text{C}_{51}\text{H}_{36}\text{N}_2\text{O}_4\text{Cl}_2\text{Sn}_2$: C, 58.38; H, 3.45; N, 2.67. Found: C, 57.99; H, 3.43; N, 2.73%.

4.3.2.6. Complex 2f. Compound **2f** was obtained from 0.10 g (0.18 mmol) of ligand **1c** and 0.11 g (0.36 mmol) of dichlorodibutyltin. A red dark solid was obtained in a yield of 80 % (0.16 g). Mp = 288–291 °C. IR (KBr) ν : 2923, 2861, 1616 (C=N), 1589, 1532, 1492, 1465, 1375, 1279, 1168, 827 cm^{-1} . FAB MS, m/z (%): 1014 ([M+1], 92), 1012 (M^+ , 98), 956 ([M-Bu] $^+$, 100). ^1H NMR (200 MHz, CDCl_3) δ : 8.59 (2H, s, $^3J_{\text{Sn-H}} = 24$ Hz, H-7), 7.15–7.25 (6H, m, H-5, H-11, H-13), 7.08 (2H, s, H-3), 6.78 (2H, d, $J = 8.4$ Hz, H-6), 6.74 (2H, d, $J = 8.4$ Hz, H-10), 3.83 (2H, s, H-14), 1.60–1.70 (8H, m, H- β), 1.40–1.50 (8H, m, H- α), 1.32 (18H, m, t -Bu), 1.27 (8H, sex, $J = 7.4$ Hz, H- γ), 0.83 (12H, t, $J = 7.4$ Hz, H- δ) ppm. ^{13}C NMR (50 MHz, CDCl_3) δ : 167.9 (C-1), 160.8 (C-7), 157.1 (C-9), 139.7 (C-

5), 137.6 (C-3), 134.2 (C-12), 130.6 (C-8), 129.2 (C-4), 127.5 (C-11), 122.7 (C-10), 117.9 (C-6), 117.7 (C-2), 111.2 (C-13), 39.8 (C-14), 34.7 (C(Me)₃), 32.0 (C(Me)₃), 27.4 (C-β), 27.0 (C-γ), 22.4 (C-α), 14.0 (C-δ) ppm. ¹¹⁹Sn NMR (75 MHz, CDCl₃) δ: −188 ppm. Anal. Calc. for C₅₁H₇₀N₂O₄Sn₂: C, 60.49; H, 6.96; N, 2.76. Found: C, 60.72; H, 5.74; N, 2.42%.

4.3.2.7. Complex 2g. Compound **2g** was obtained from 0.10 g (0.18 mmol) of ligand **1c** and 0.12 g (0.36 mmol) of dichlorodiphenyltin. An orange solid was obtained in a yield of 63% (0.14 g). M.p. = 293–296 °C. IR (KBr) ν: 2957, 2372, 1616 (C=N), 1536, 1494, 1468, 1374, 1289, 1164, 829, 730 cm^{−1}. FAB MS, *m/z* (%): 1094 ([M+1], 14), 1092 (M⁺, 15), 1016 ([M-Ph]⁺, 100). ¹H (200 MHz, CDCl₃) δ: 8.60 (2H, s, ³J_{Sn-H} = 28 Hz, H-7), 7.90–7.92 (8H, *m*, H-*o*), 7.22–7.38 (16H, *m*, H-5, 13, *m*, *p*), 7.02 (2H, *d*, *J* = 9.0, H-6), 6.98–7.10 (6H, *m*, H-3, 10, 11), 3.83 (2H, *s*, H-14), 1.30 (18H, *s*, *t*-Bu) ppm. ¹³C NMR (50 MHz, CDCl₃) δ: 167.8 (C-1), 160.6 (C-7), 156.5 (C-9), 139.8 (C-*i*), 139.7 (C-5), 137.8 (C-3), 136.6 (C-*o*), 134.5 (C-12), 130.2 (C-*p*), 130.0 (C-8), 129.6 (C-4), 128.6 (C-*m*), 127.8 (C-11), 123.1 (C-10), 118.4 (C-6), 117.7 (C-2), 111.1 (C-13), 39.8 (C-14), 34.7 (C-15), 31.9 (C-16) ppm. ¹¹⁹Sn NMR (75 MHz, CDCl₃) δ: −331 ppm. Anal. Calc. for C₅₉H₅₄N₂O₄Sn₂: C, 64.86; H, 4.98; N, 2.56. Found: C, 65.19; H, 5.01; N, 2.57%.

Acknowledgements

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Appendix A. Supplementary material

CCDC 607131, 607132, 607133, 607134, 607135, 616312 and 616313 contain the supplementary crystallographic data for **2a**, **2b**, **2c**, **2c'**, **2e**, **3** and **4**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.09.064.

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