



Structure and conformational motion of seven-coordinate diorganotin(IV) complexes derived from salen and salan type ligands

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ABSTRACT

Reaction of R_2SnCl_2 ($R = Me, nBu, Ph$) and the potassium salts of salen N_3H_3 (N,N' -bis(salicylidene)diethylenetriamine) and salan N_3H_3 (N,N' -bis(*o*-hydroxybenzyl)diethylenetriamine) provided diorganotin(IV) complexes of the composition $[Me_2Sn(salenN_3H)] \cdot solvate$ (solvate = 2.5H₂O, MeOH or DMSO), $[nBu_2Sn(salenN_3H)] \cdot H_2O$, $[Ph_2Sn(salenN_3H)] \cdot 2EtOH$ and $[Me_2Sn(salanN_3H_3)] \cdot 2.5H_2O$. In all compounds the tin atoms are seven-coordinate and have pentagonal–bipyramidal coordination environments, in which the organic substituents attached to the tin atoms occupy the axial positions. This occurs both in solution and the solid state; however, in solution the molecules are involved in conformational equilibria that require the presence of intermediates, in which the $N \rightarrow Sn$ bonds are dissociated. Although the $[salanN_3H_3]^{2-}$ ligand is more flexible and basic, a very similar complexing behavior to that of $[salenN_3H]^{2-}$ has been found, and there is evidence that it is even a weaker ligand. Both ligands show the tendency to adopt a curved conformation within the complex, thus indicating that the dynamic process resembles the flapping of butterfly wings. However, the folding is reduced with increasing steric bulk of the organic substituents attached to the tin atoms. The six-membered heterocyclic rings in the $[R_2Sn(salenN_3H)]$ derivatives have envelope conformation, while those in $[Me_2Sn(salanN_3H_3)]$ have distorted boat-conformation. Thus, small changes in the hybridization and basicity of the nitrogen atoms cause significant differences of the stability and the dynamic behavior of the resulting molecules.

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1. Introduction

In former research work diorganotin(IV) moieties have been brought to reaction with a series of ligands having ONO [1,2] and ONNO [3] donor systems. Generally, the resulting complexes are monomeric or dimeric with coordination geometries close to trigonal–bipyramidal, square–pyramidal, octahedral and pentagonal–bipyramidal polyhedra. Some of them have received special interest in view of possible applications as biocides [4], anti-tumor agents [5], materials with non-linear optical properties [6], fluorescence probes for DNA traces [7] and catalysts [8]. More recently, also di- and trinuclear diorganotin(IV) complexes with macrocyclic structures have been reported [3i,9].

So far, only few diorganotin complexes with ONNNO ligands are known [11,10], which is somewhat surprising, since such multidentate ligands can give compounds having configurations and nuclearities different from those known for complexes with lower coordination numbers. This has been shown for molecules bearing

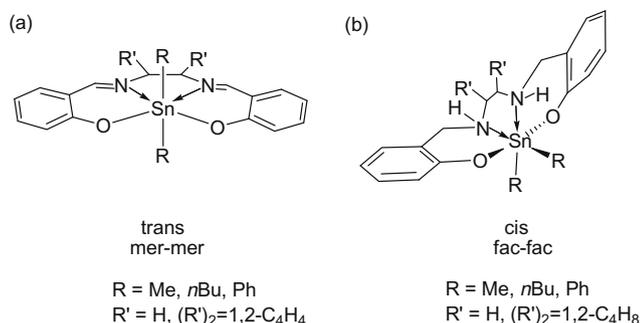
tetradentate ONNO ligands, e.g. with the salen ligands [11] shown in Scheme 1a, compounds having a *mer–mer* configuration are formed. By contrast, with the reduced and also more flexible salan ligands given in Scheme 1b, compounds having a *fac–fac* configuration are obtained [3k]. Furthermore, as outlined in Scheme 2, either mononuclear [3] or dinuclear diorganotin derivatives may be prepared [3m,12].

The combination of salicylaldehyde and diethylenetriamine (DETA) gives a pentadentate ligand that is ideal for complexation studies with diorganotin(IV). So far, this ligand is almost unexplored [13] and a search of the Cambridge Structural Database (CSD) [14] yielded mainly structures of metal complexes derived from the tripodal tris((salicylidene)amino)ethylamine analogue. When salen ligands are reduced at the imine functions, the structurally related, but more flexible and basic salan derivatives are obtained [15].

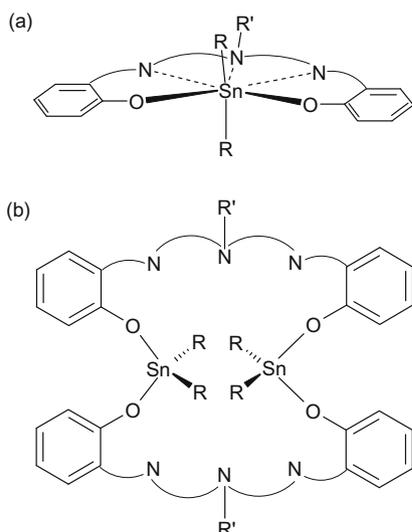
With the latter statements in mind, in this contribution we report on the preparation, structural characterization and conformational motion of four diorganotin(IV) complexes (1–4), which have been obtained from the ONNNO-type salen and salan ligands shown in Scheme 3. All compounds crystallized in form of solvates,

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Scheme 1. For six-coordinate diorganotin complexes containing salen and salan type ligands two different coordination modes have been observed: (a) *mer-mer* and (b) *fac-fac* [3k].



Scheme 2. Pentadentate ONNNO-type ligands can give either (a) mononuclear or (b) dinuclear tin complexes [3m,12].

and in the case of compound **1** solvates of three different compositions could be obtained: [Me₂Sn(salenN₃H)]·solvate with solvate = 2.5H₂O (**1**·2.5H₂O), MeOH (**1**·MeOH) and DMSO (**1**·DMSO), [nBu₂Sn(salenN₃H)]·H₂O (**2**·H₂O), [Ph₂Sn(salenN₃H)]·2EtOH (**3**·2EtOH) and [Me₂Sn(saleanN₃H₃)]·2.5H₂O (**4**·2.5H₂O). The main objectives of this study were (i) to determine, if mononuclear or dinuclear compounds are obtained, (ii) to study the role of the central amino group in the hypercoordination of the tin atom to reach seven-coordinated geometries, and (iii) to compare the coordination patterns of the more rigid salen and the more flexible salan ligands [3]. The crystal structures of **1**·2.5H₂O and **4**·2.5H₂O contain infinite chains of spirocyclic water hexamers. Apparently, the hydrogen-bond forming functions in these tin complexes (NH, O) have the proper spatial distribution to stabilize extended water clusters, which might be reminiscent of the solvation sphere in solution. These features have been reported in a preliminary communication [16].

2. Experimental

2.1. Instrumental

NMR studies were carried out on Varian Gemini 200 and Varian Inova 400 instruments. Standards were TMS (internal, $\delta^1\text{H} = 0.00$,

$\delta^{13}\text{C} = 0.0$ ppm) and SnMe₄ (external, $\delta^{119}\text{Sn} = 0.0$ ppm). COSY and HETCOR experiments have been carried out in order to completely assign the ¹H and ¹³C spectra. IR spectra have been recorded on a Bruker Vector 22 FT spectrophotometer. Mass spectra were obtained on HP 5989A (EI) and Jeol JMS 700 (FAB⁺) equipments. Elemental analyses have been carried out on an Elementar Vario ELIII instrument. For these analyses samples of compounds **3**·2EtOH and **4**·2.5H₂O have been treated previously in an Abderhalden equipment.

2.2. Preparative part

Diethylenetriamine (DETA), 2-hydroxybenzaldehyde (salicylaldehyde), sodium borohydride, dimethyltin dichloride, di-*n*-butyltin dichloride and diphenyltin dichloride were commercial starting materials and have been used without further purification. *N,N*-bis(salicylidene)diethylenetriamine (salenN₃H₃) and *N,N*-bis(*o*-hydroxybenzyl)diethylenetriamine (saleanN₃H₅) have been prepared as described in the literature [13,15].

2.3. Preparation of the diorganotin complexes

2.3.1. [Me₂Sn(salenN₃H)] (**1**)

For the preparation of compound **1**, salenN₃H₃ (0.277 g, 0.89 mmol) and two equivalents of potassium hydroxide (0.100 g, 1.78 mmol) were dissolved in 15 mL of a 2:1 solvent mixture of ethanol and water, whereupon dimethyltin dichloride (0.212 g, 0.96 mmol) previously dissolved in water (5 mL) was added. A pale yellow solid precipitated that was filtered and washed with small amounts of ethanol. Crystals suitable for X-ray crystallography could be grown from ethanol–water, methanol and DMSO solutions to give three different solvates of the composition **1**·2.5H₂O, **1**·MeOH and **1**·DMSO. Yield: 0.314 g (77%). Mp: 246–248 °C (for **1**·2.5H₂O).

IR (KBr): $\tilde{\nu} = 3200$ $\nu(\text{N-H})$ (m), 1639 $\nu(\text{C=N})$ (s) cm⁻¹.

¹H NMR (400 MHz, MeOH-d₄, 20 °C, TMS): δ 8.18 (s, 2H, H7), 7.24 (dd, 2H, H5), 7.16 (d, 2H, H3), 6.88 (d, 2H, H6), 6.63 (dd, 2H, H4), 3.96 (dd, 2H, H8a), 3.52 (d, 2H, H8b), 3.19 (d, 2H, H9b), 2.66 (dd, 2H, H9a), 0.86 (s, 3H, ²J_{Sn-H} = 115 Hz, Sn–Me), 0.15 (s, 3H, ²J_{Sn-H} = 104 Hz, Sn–Me').

¹³C NMR (50 MHz, MeOH-d₄, 20 °C, TMS): δ 167.3 (C1, C7), 134.5 (C5), 133.8 (C3), 123.5 (C4), 122.2 (C2), 115.9 (C6), 59.9 (C8), 50.9 (C9) ppm.

¹¹⁹Sn NMR (74.5 MHz, MeOH-d₄, 20 °C, SnMe₄): δ –505 (s) ppm.

MS (EI): *m/z* (%) 459 (M, 2), 444 (M–CH₃, 28), 325 (M–CH₃–C₇H₅NO, 100), 295 (C₁₀H₁₁N₂O₂Sn, 50), 253 (C₈H₇NOSn, 16), 225 (C₇H₅O₂Sn, 21), 134 (CH₂Sn, 22).

Anal. Calc. for C₂₀H₂₅N₃O₂Sn·2.5H₂O (503.16 g/mol): C, 47.74; H, 6.01; N, 8.35. Found: C, 47.62; H, 6.28; N, 8.26%.

2.3.2. [nBu₂Sn(salenN₃H)] (**2**)

For the preparation of compound **2**, salenN₃H₃ (0.088 g, 0.28 mmol) and two equivalents of potassium hydroxide (0.031 g, 0.56 mmol) were dissolved in ethanol (18 mL), whereupon di-*n*-butyltin dichloride (0.094 g, 0.31 mmol) previously dissolved in ethanol (2 mL) was added. A pale yellow solid precipitated that was filtered and washed with small amounts of ethanol. Crystals of the composition **2**·H₂O, which were suitable for X-ray crystallography, could be grown from ethanol. Yield: 0.130 g (85%). Mp: 191–193 °C.

IR (KBr): $\tilde{\nu} = 3259$ $\nu(\text{N-H})$ (w), 1634 $\nu(\text{C=N})$ (s) cm⁻¹.

¹H NMR (400 MHz, MeOH-d₄, 20 °C, TMS): δ 8.23 (s, 2H, H7), 7.21 (dd, 2H, H5), 7.12 (d, 2H, H3), 6.87 (d, 2H, H6), 6.58 (dd, 2H, H4), 3.73 (br, s, 4H, H8), 2.96 (br, s, 4H, H9), 1.78 (m, 2H, Sn–H α), 1.55 (m, 2H, Sn–H α'), 1.42 (m, 4H, Sn–H β , Sn–H β'), 1.10 (m, 2H, Sn–H γ), 1.31 (m, 2H, Sn–H γ'), 0.98 (t, 3H, Sn–H δ), 0.65 (t, 3H, Sn–H δ').

^{13}C NMR (100 MHz, MeOH- d_4 , 20 °C, TMS): δ 169.5 (C7), 168.7 (C1), 135.7 (C3), 134.8 (C5), 123.6 (C4), 122.1 (C2), 116.2 (C6), 60.5 (C8), 50.7 (C9), 29.5 (Sn-C α), 28.7 and 28.4 (Sn-C γ , Sn-C γ'), 27.6 (Sn-C β), 14.1 (Sn-C δ).

^{119}Sn NMR (74.5 MHz, MeOH- d_4 , 20 °C, SnMe $_4$): δ -503 (s) ppm.

MS (EI): m/z (%) 543 (M, 1), 486 (M- n Bu, 89), 428 (M- n BuH- n Bu, 30), 295 (C $_{10}$ H $_{11}$ N $_2$ Osn, 100), 253 (C $_8$ H $_7$ NOSn, 41), 225 (C $_7$ H $_5$ Osn, 43), 134 (CH $_2$ Sn, 31).

Anal. Calc. for C $_{26}$ H $_{37}$ N $_3$ O $_2$ Sn·H $_2$ O (560.32 g/mol): C, 55.73; H, 7.02; N, 7.50. Found: C, 55.43; H, 6.95; N, 7.48%.

2.3.3. [Ph $_2$ Sn(salenN $_3$ H)] (3)

For the preparation of compound **3**, salenN $_3$ H $_3$ (0.307 g, 0.98 mmol) and two equivalents of triethylamine (0.200 g, 1.97 mmol) were dissolved in ethanol (15 mL), whereupon diphenyltin dichloride (0.340 g, 0.98 mmol) previously dissolved in ethanol (15 mL) was added. A pale yellow crystalline solid precipitated that was filtered and washed with small amounts of ethanol. Crystals of the composition **3**·2EtOH suitable for X-ray crystallography could be grown from ethanol. Yield: 0.540 g (94%). Mp: 209–211 °C.

IR (KBr): $\tilde{\nu}$ = 3244 ν (N–H) (w), 1630 ν (C=N) (s) cm^{-1} .

^1H NMR (400 MHz, DMSO- d_6 , 20 °C, TMS): δ 8.53 (s, 2H, H7), 7.48 (m, 2H, Sn-H $_{ortho}$), 7.13 (m, 9H, H3, H5, Sn-H $_{meta}$, Sn-H $_{para}$), 6.44 (m, 4H, m, H4, H6), 4.37 (dd, 2H, H8a), 3.61 (d, 2H, 8b), 2.75 (d, 2H, H9b), 2.26 (dd, 2H, H9a) ppm.

^{13}C NMR (50 MHz, DMSO- d_6 , 20 °C, TMS): δ 169.1 (C7), 167.7 (C1), 149.6 (Sn-C $_{ipso}$), 133.2 (Sn-C $_{ortho}$), 134.3 (C3), 133.0 (C5), 127.0 (Sn-C $_{meta}$), 127.5 (Sn-C $_{para}$), 122.3 (C4), 119.2 (C2), 112.9 (C6), 57.0 (C8), 46.7 (C9) ppm.

^{119}Sn NMR (74.5 MHz, DMSO- d_6 , 20 °C, SnMe $_4$): δ -640 (s) ppm.

MS (FAB $^+$): m/z (%) 584 (M+H, 64), 505 (M-Ph, 8), 449 (M-C $_8$ H $_8$ NO, 27).

Anal. Calc. for C $_{30}$ H $_{29}$ N $_3$ O $_2$ Sn (582.28 g/mol): C, 61.88; H, 5.02; N, 7.21. Found: C, 61.85; H, 5.12; N, 7.23.

2.3.4. [Me $_2$ Sn(saleanN $_3$ H $_3$)] (4)

For the preparation of compound **4**, saleanN $_3$ H $_5$ (0.100 g, 0.32 mmol) and two equivalents of potassium hydroxide (0.036 g, 0.64 mmol) were dissolved in 15 mL of a 2:1 solvent mixture of ethanol and water, whereupon dimethyltin dichloride (0.075 g, 0.34 mmol) previously dissolved in water (5 mL) was added. Upon cooling to -20 °C a pale yellow crystalline solid precipitated that was filtered and washed with small amounts of ethanol. These crystals were suitable for X-ray crystallography. Yield: 0.050 g (34%). Mp: 207–209 °C.

IR (KBr): $\tilde{\nu}$ = 3286 ν (N–H) (m), 3222 ν (N–H) (m) cm^{-1} .

^1H NMR (200 MHz, DMSO- d_6 , 20 °C, TMS): δ 6.99 (m, 2H, H3), 6.94 (m, 2H, H5), 6.56 (d, 2H, H6), 6.38 (dd, 2H, H4), 3.42 (s, 2H, H7), 2.51 (br, s, 4H, H8, H9), 0.35 (s, 6H, $^2J_{\text{Sn-H}} = 106$ Hz, Sn-H α , Sn-H α').

^{119}Sn NMR (74.5 MHz, DMSO- d_6 , 20 °C, SnMe $_4$): δ -450 (s) ppm.

MS (FAB $^+$): m/z (%) 925 (2 M+H, 3), 464 (M+H, 100), 448 (M-CH $_3$, 43), 327 (M+H-CH $_3$ -C $_7$ H $_8$ NO, 46).

Anal. Calc. for C $_{20}$ H $_{29}$ N $_3$ O $_2$ Sn (462.17 g/mol): C, 51.97; H, 6.32; N, 9.09. Found: C, 52.44; H, 6.24; N, 9.31%.

2.4. X-ray crystallography

X-ray diffraction studies were carried out on a BRUKER-AXS APEX diffractometer with a CCD area detector ($\lambda_{\text{MoK}\alpha} = 0.71073$ Å, monochromator: graphite). Frames were collected at $T = 100$ K (1·2.5H $_2$ O, 1·MeOH, 2·H $_2$ O, 3·2EtOH) and 293 K (1·DMSO, 4·2.5H $_2$ O) via ω - and θ -rotation ($\Delta\omega = 0.3^\circ$) at 10 s per frame [17a]. The measured intensities were reduced to P^2 and corrected for absorption with SADABS [17b]. Structure solution, refinement and data output were carried out with the SHELXTL-NT program pack-

age [17c–d]. Non hydrogen atoms were refined anisotropically, while C–H hydrogen atoms were placed in geometrically calculated positions using a riding model. O–H and N–H hydrogen atoms have been localized by difference Fourier maps and refined fixing the bond lengths to 0.84 and 0.86 Å, respectively; the isotropic temperature factors have been constrained to a value 1.5 times that of the corresponding oxygen/nitrogen atoms. Solvent molecules were present in the crystal lattices of all compounds, of which the EtOH molecules in **3**·2EtOH were disordered over two positions. The complex molecules in **1**·DMSO are localized on crystallographic mirror planes within the crystal lattice. In compound **2**·H $_2$ O one of the n -butyl groups attached to the tin atoms is disordered over two positions (occ = 0.62 and 0.38), while compound **3**·2EtOH presents twofold disorder of the NCH $_2$ CH $_2$ NCH $_2$ CH $_2$ N fragment (occ = 0.34 and 0.66). DFIX, SAME, SIMU and DELU instructions have been used for a proper refinement of the disordered moieties.

3. Results and discussion

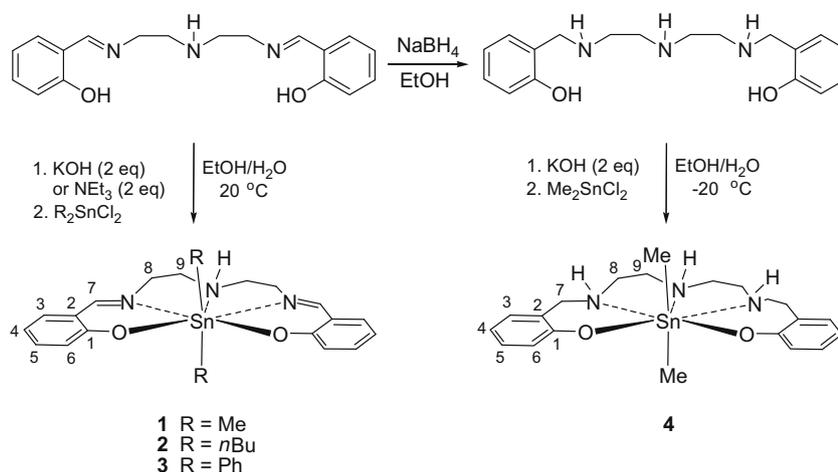
3.1. Preparation and structural characterization of compounds 1–3

The salenN $_3$ H $_3$ ligand shown in Scheme 3 has been prepared as described in the literature [13]. Reaction with dimethyl-, di- n -butyl- and diphenyltin dichloride in the presence of two equivalents of base (KOH or NEt $_3$) gave products in yields of 77%, 85% and 94%, which were characterized by elemental analysis, mass spectrometry, spectroscopic methods (FTIR, ^1H , ^{13}C and ^{119}Sn NMR) and X-ray crystallography.

The successful formation of the tin compounds (**1**–**3**) was indicated by the mass spectra, which gave peaks characteristic for monomeric species at $m/z = 459$ for **1**, 542 for **2** and 584 for **3**.

In the FTIR spectra of **1**–**3**, the bands for the imine and N–H stretching vibrations are well-separated from the remaining bands and their shifts in comparison to the starting ligand permit to establish that all three nitrogen atoms of the ligand are involved in N \rightarrow Sn coordinative bonds. The spectral changes for the imine functions of the tin compounds are small but significant ($\Delta\tilde{\nu} = +7, +2$ and -2 cm^{-1} for **1**, **2** and **3**, respectively), thus indicating a weak coordination [3g–h]. Furthermore, while the FTIR spectrum of the ligand shows only a very broad band for the N–H stretching vibration at 3301 cm^{-1} , this band is well-defined for complexes **1**–**3**, having wavenumbers of 3200 for **1**, 3259 for **2** and 3244 cm^{-1} for **3** [3k, 13b].

The ^1H NMR data for compounds **1**–**3** indicate that the coordinative bond with the central nitrogen atom of the ligand is relatively weak, since signal broadening is observed for the hydrogen atoms belonging to the two NCH $_2$ CH $_2$ N groups. While for compounds **1** and **3** an ABCD pattern typical for ethylene groups embedded in a rigid chelate ring can be identified, for the di- n -butyltin derivative **2** only two broad signals are detected in the aliphatic region. In order to examine the dynamic process occurring in solution, a variable temperature NMR study has been performed for this complex in the temperature range of -80 to +50 °C in CD $_3$ OD. At -80 °C four coupled signals for the expected ABCD pattern are observed, which converge to two signals at -10 °C. According to the Eyring equation [18], the free activation enthalpy for this process is 12.3 kcal mol $^{-1}$. In agreement with these results and according to previously described reaction sequences for five-coordinate diorganotin complexes with ONO ligands [19], the dynamic process must involve at least three steps: (i) rupture of the N(H) \rightarrow Sn coordinative bond, (ii) inversion of the central nitrogen atom, and (iii) recoordination of the NH group to the tin atom (Scheme 4). Dreiding models show that in the present case the rupture of all three N \rightarrow Sn bonds is required to allow for a strain-reduced inversion of the central nitrogen atom.

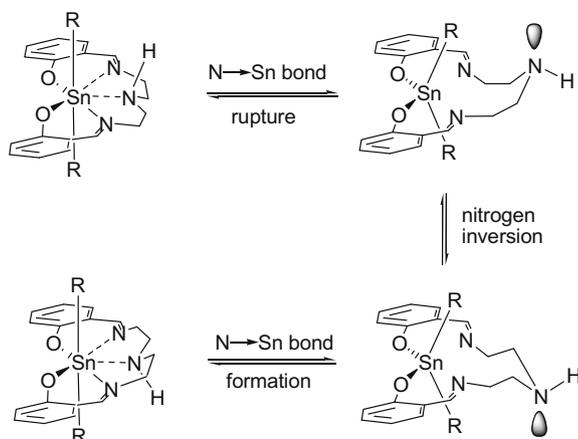


Scheme 3. Reaction sequence for the preparation of compounds **1–4** and atom numbering for the assignment of the NMR spectra.

That a significant population of the molecules dissolved in CD₃OD is seven-coordinate can be seen from both the ¹³C and ¹¹⁹Sn NMR spectra. In comparison to the ligand the chemical shifts of the signals for the imine and NCH₂ carbon atoms are significantly different after complex formation: $\delta_{C=N} = 160.9$ ppm and $\delta_{NCH_2} = 49.9$ and 59.8 ppm for salenN₃H₃ vs. $\delta_{C=N} = 167.3$ ppm and $\delta_{NCH_2} = 50.9$ and 59.9 ppm for **1**, $\delta_{C=N} = 169.5$ ppm and $\delta_{NCH_2} = 50.7$ and 60.5 ppm for **2**, and $\delta_{C=N} = 169.1$ ppm and $\delta_{NCH_2} = 46.7$ and 57.0 ppm for **3**. The chemical shift displacements observed in the ¹¹⁹Sn NMR spectra, $\delta = -505$ for **1**, $\delta = -503$ for **2** and $\delta = -640$ ppm for **3**, are typical for seven-coordinate tin complexes [10,20].

The ¹H and ¹³C NMR spectra reveal also that the organic groups attached to the tin atoms in compounds **1** and **2** have different chemical environments, since two different sets of signals are observed. This excludes the presence of horizontal mirror planes within the molecules and allows the proposal of a curved butterfly conformation generating a concave environment opposite to the N–H hydrogen. For compound **1** the unresolved ²J(¹H–^{117/119}Sn) coupling constants could be measured (115 and 104 Hz), which allowed to estimate the C–Sn–C bond angle in solution. According to Lockhart's equation [21] a bond angle of 182° was calculated [22], which is somewhat larger than the values extracted from the solid-state structures (vide infra): 172.1(2)–174.1(2)°.

In order to determine whether compounds **1–3** have *cis*- or *trans*-configuration regarding the organic substituents attached



Scheme 4. Proposed dynamic conformational equilibrium for compounds **1–3** in solution.

to the tin atoms, X-ray diffraction analyses have been carried out (Table 1). For **1** crystals suitable for X-ray diffraction could be grown from three different solvents: (i) a solvent mixture of ethanol and water, (ii) methanol and (iii) DMSO, giving solid-state structures having the composition **1**·2.5H₂O, **1**·MeOH and **1**·DMSO. Despite the variation of the crystal structures for these solvates, the molecular structures are similar (Table 2, vide infra). For compounds **2** and **3** crystals were obtained from water and ethanol, respectively, to give solid-state structures having the composition **2**·H₂O and **3**·2EtOH. The crystal lattice of **1**·2.5H₂O contains an interesting water cluster, which has been described already in a preliminary communication [16]. Selected geometric parameters for compounds **1–3** are listed in Table 2 and the molecular structures are shown in Fig. 1.

As already shown by NMR spectroscopy, the tin atoms are seven-coordinate in all three complexes and adopt distorted pentagonal-bipyramidal coordination geometries, in which the pentadentate ONNNO ligands occupy equatorial and the organic substituents axial sites. The Sn–C bond lengths vary from 2.108(4)–2.142(4) Å and are in the range expected for seven-coordinate diorganotin(IV) species [10]. The Sn–O bond lengths range from 2.145(2) to 2.194(3) Å and are within the range observed for a series of R₂Sn(salen) and R₂Sn(salan) complexes, 2.073(3)–2.237(2) Å [3k]. In contrast, the Sn–N bond lengths are significantly longer, 2.445(3)–2.649(7) Å vs. 2.266(2)–2.431(4) Å. Since the nitrogen atoms in compounds **1–2** have different hybridizations, the N → Sn bond lengths can vary due to this change [23]. Indeed, for compounds **1** and **2** the Sn–N_{imine} bonds are shorter than the Sn–N_{amine} bonds (Table 2). However, compound **3** shows a different behavior: in this case the Sn–N_{amine} bond is intermediate, 2.461(4) Å, between the Sn–N_{imine} bond lengths, 2.450(4) and 2.543(4) Å, which can be explained with the enhanced steric strain of the organic substituents attached to the tin atoms. Fig. 1 shows that the variation in the steric bulk of the organic substituents attached to the tin atoms has an important influence on the conformation of the molecular structures. In compounds **1** and **2**, which have aliphatic substituents, the ligand adopts a butterfly conformation, while in compound **3** with the more voluminous phenyl groups the ligand has an almost planar arrangement. The difference in the geometric organization of the ligand molecules influences both the bond and torsion angles within the ligand and around the tin atom. In the case of the bond angles, major differences occur for the C–Sn–C bond angles, 172.1(2)–174.1(2)° for **1** and 172.0(2)° for **2** vs. 175.5(2)° for **3**, the O–Sn–O bond angles, 76.2(1)–80.3(1)° for **1** and 77.1(1)° for **2** vs. 74.4(1)° for **3**, and

Table 1
Crystallographic data for compounds **1**·2.5H₂O, **1**·MeOH, **1**·DMSO, **2**·H₂O, **3**·2EtOH and **4**·2.5H₂O.

Crystal data ^a	1 ·2.5H ₂ O ^f	1 ·MeOH ^f	1 ·DMSO ^f	2 ·H ₂ O	3 ·2EtOH	4 ·2.5H ₂ O ^f
Formula	C ₂₀ H ₂₅ N ₃ O ₂ Sn·2.5H ₂ O	C ₂₀ H ₂₅ N ₃ O ₂ Sn·MeOH	C ₂₀ H ₂₅ N ₃ O ₂ Sn·DMSO	C ₂₆ H ₃₇ N ₃ O ₂ Sn·H ₂ O	C ₃₀ H ₂₉ N ₃ O ₂ Sn·2EtOH	C ₂₀ H ₂₉ N ₃ O ₂ Sn·2.5H ₂ O
MW (g mol ⁻¹)	503.16	490.16	536.25	560.29	674.39	507.19
Space group	<i>P</i> 4 ₂ <i>bc</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>Pnma</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 4 ₂ <i>bc</i>
<i>T</i> (K)	100	100	293	100	100	293
<i>a</i> (Å)	20.3573(11)	12.1196(8)	20.362(2)	9.2724(2)	11.8667(9)	20.8481(12)
<i>b</i> (Å)	20.3573(11)	12.5833(8)	15.581(2)	18.687(2)	14.5986(12)	20.8481(12)
<i>c</i> (Å)	10.4631(9)	13.8292(9)	7.5321(9)	15.064(2)	17.7800(14)	10.4021(9)
α (°)	90	90	90	90	90	90
β (°)	90	90	90	90.939(2)	107.584(1)	90
γ (°)	90	90	90	90	90	90
<i>V</i> (Å ³)	4336.1(5)	2109.0(2)	2389.6(5)	2609.9(6)	2936.2(4)	4521.2(5)
<i>Z</i>	8	4	4	4	4	8
μ (mm ⁻¹)	1.21	1.24	1.18	1.01	0.92	1.16
ρ_{calcd} (g cm ⁻³)	1.542	1.544	1.491	1.426	1.526	1.490
<i>R</i> ^{b,c}	0.033	0.029	0.032	0.031	0.048	0.043
<i>R</i> _w ^{d,e}	0.083	0.064	0.079	0.082	0.120	0.091

^a $\lambda_{\text{Mo K}\alpha} = 0.71073$ Å.^b $F_o > 4\sigma(F_o)$.^c $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.^d All data.^e $R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$.^f See also Ref. [16].**Table 2**
Selected bond lengths [Å], bond angles [°], torsion angles [°] and centroid...centroid distances for compounds **1**·2.5H₂O, **1**·MeOH, **1**·DMSO, **2**·H₂O, **3**·2EtOH and **4**·2.5H₂O.

	1 ·2.5H ₂ O ^a	1 ·MeOH ^a	1 ·DMSO ^{a,b}	2 ·H ₂ O ^c	3 ·2EtOH ^c	4 ·2.5H ₂ O ^a
<i>Bond lengths</i>						
Sn–O1	2.194(3)	2.160(2)	2.150(2)	2.169(2)	2.156(3)	2.156(4)
Sn–O2	2.176(3)	2.171(2)	2.150(2)	2.145(2)	2.156(3)	2.150(4)
Sn–N1	2.448(4)	2.445(3)	2.509(3)	2.535(2)	2.450(4)	2.524(5)
Sn–N2	2.488(4)	2.558(3)	2.552(4)	2.602(2)	2.461(4)	2.591(6)
Sn–N3	2.463(4)	2.509(3)	2.509(3)	2.496(2)	2.543(4)	2.649(7)
Sn–C19	2.125(4)	2.120(4)	2.121(4)	2.139(6)	2.142(4)	2.124(5)
Sn–C20/23/25	2.108(4)	2.119(3)	2.106(5)	2.130(2)	2.142(4)	2.116(6)
<i>Bond angles</i>						
O1–Sn–O2/O1'	76.2(1)	76.7(9)	80.3(1)	77.1(1)	74.4(1)	81.6(2)
O1–Sn–N1	75.5(1)	74.8(1)	73.3(1)	74.7(1)	76.3(1)	77.9(2)
O1–Sn–C19	91.0(2)	95.9(1)	95.4(1)	96.0(3)	91.1(2)	93.4(3)
O1–Sn–C20/C23/C25	90.8(1)	90.4(1)	90.7(1)	89.8(1)	93.4(2)	90.2(2)
O2–Sn–N3	71.9(1)	74.4(1)	73.3(1)	75.1(1)	74.0(1)	73.2(2)
O2–Sn–C19	96.6(1)	93.7(1)	95.4(1)	95.7(3)	91.7(1)	98.4(2)
O2–Sn–C20/23/25	89.3(1)	89.1(1)	90.7(1)	90.1(1)	90.1(1)	88.3(2)
N1–Sn–N2	69.4(1)	67.9(1)	67.0(1)	66.4(1)	68.3(3)	67.6(2)
N2–Sn–N3	68.0(1)	66.9(1)	67.0(1)	67.1(1)	67.1(3)	64.8(2)
N2–Sn–C19	89.7(2)	90.0(1)	88.9(2)	87.6(3)	86.8(3)	92.7(3)
N2–Sn–C20/23/25	85.6(1)	84.2(1)	83.2(2)	85.0(1)	89.3(3)	80.7(2)
C19–Sn–C20/23/25	174.1(2)	173.6(2)	172.1(2)	172.0(2)	175.5(2)	172.8(3)
Sn–O1–C1	132.9(3)	130.4(2)	126.8(2)	135.2(2)	137.6(3)	129.4(4)
Sn–O2–C14	120.1(3)	132.0(2)	126.8(2)	132.5(2)	142.0(3)	118.8(4)
<i>Torsion angles</i>						
N1–C8–C9–N2	–58.0(5)	–54.9(4)	–56.8(4)	–56.6(3)	56(3)/–54(2)	60.9(8)
N2–C10–C11–N3	55.0(5)	56.5(4)	56.8(4)	58.0(3)	–58(2)/58(1)	–58.5(8)
Sn–O1–C1–C2	–39.2(7)	–36.4(5)	–50.0(4)	–36.2(4)	23.0(7)	56.0(8)
Sn–O2–C14–C13	59.4(5)	42.5(5)	50.0(4)	41.4(4)	11.0(7)	–76.0(6)
<i>Others</i>						
Centroid...centroid ^d	6.67	7.19	6.76	7.43	7.83	6.60

^a See also Ref. [16].^b Molecule has crystallographic mirror symmetry.^c Molecule presents disorder (see Section 2); where possible, average values are given.^d Centroid 1 corresponds to phenyl ring C1–C6 and centroid 2 corresponds to phenyl ring C13–C18 (C1'–C6' in the case of **1**·DMSO).

the range of the C–Sn–X (X = O, N) bond angles, 83.2(2)–96.6(1)° for **1** and 85.0(1)–96.0(3)° for **2** vs. 86.8(3)–93.4(2)° for **3**. This structural comparison indicates that the tin atoms in compound **3** deviate less from the ideal pentagonal–bipyramidal coordination geometry.

The six-membered {C₃NOSn} heterocyclic rings in compounds **1** and **2** have envelope conformations, in which the tin atoms occupy the vertex. The five-membered {C₂N₂Sn} rings have also approximate envelope conformations, but in this case the N(H)–CH₂ methylene moieties occupy the vertex. The degree of ligand folding in

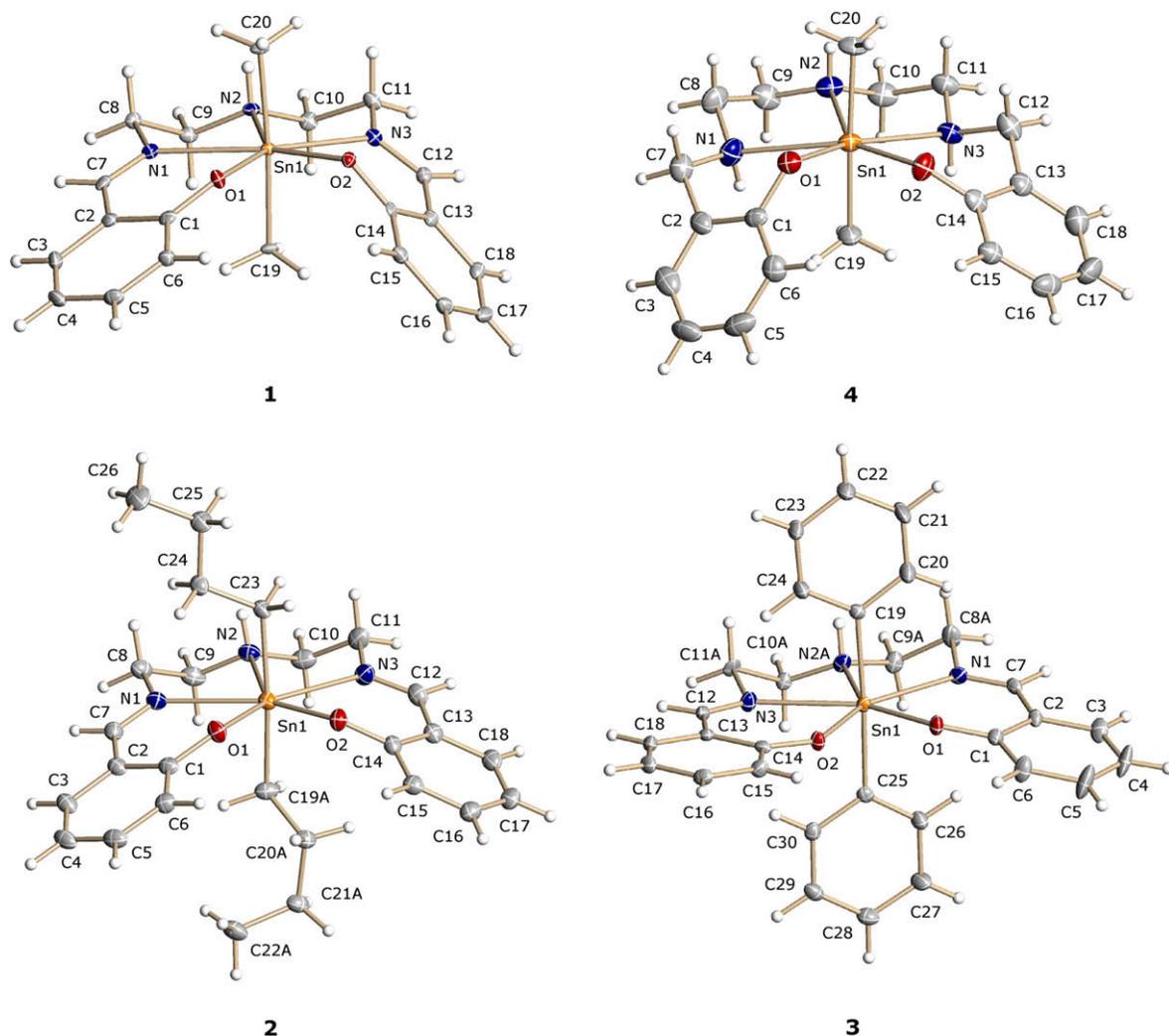


Fig. 1. Perspective views of the molecular structures of compounds 1–4. Ellipsoids are shown at the 30% probability level.

compounds 1–3 can be evaluated threefold: first, comparing the SnOCC torsion angles ($-41.9(7)/50.6(5)^\circ$ for 1, $-36.2(4)/41.4(4)^\circ$ for 2 and $23.0(7)/11.0(7)^\circ$ for 3) [24], second, comparing the centroid–centroid distances between the aromatic rings of the salicylidene moieties (6.67–7.19 Å for 1, 7.43 Å for 2 and 7.83 Å for 3), and third, comparing the angle formed between the tin atom and the centroids of the aromatic rings of the salicylidene moieties (97.8 – 105.9° for 1, 110.0° for 2 and 115.9° for 3). All three parameters show clearly that the ligand is folded to a higher degree in complex 1 (R = Me), followed by compounds 2 and 3, in agreement with the increase of the steric bulk of the organic groups attached to the tin atoms. However, it should be noticed that the molecular conformations present some flexibility, since the above-described geometric parameters vary significantly between the three solvate structures 1·2.5H₂O, 1·MeOH and 1·DMSO. A comparison of the NCCN torsion angles for the five-membered heterocycles shows that the variations are relatively small in this case (Table 2).

There are two further interesting details regarding the overall molecular conformations of 1–3. The ligand distortion from planarity is asymmetric in all three cases, as it can be seen from the differences in the absolute values of the SnOCC torsion angles outlined above: $\Delta = 8.8(7)^\circ$ for 1, $5.2(4)^\circ$ for 2 and $12.0(7)^\circ$ for 3. This may be a consequence of intermolecular interactions within the crystal lattice. Furthermore, it should be noticed that the folding of the salicylidene groups occurs in the same directions for

compounds 1 and 2, but in alternate directions for compound 3 (Fig. 1).

3.2. Preparation and structural characterization of compound 4

As already mentioned, the strength of the N → Sn coordinative bonds and the configuration of the tin complexes can be modified using the reduced form of the salen ligands. In order to evaluate these parameters, the potassium salt of saleanN₃H₅, which has been prepared from salenN₃H₃ by reduction with NaBH₄ [15], was reacted with dimethyltin, di-*n*-butyltin and diphenyltin dichloride. However, only in the first case a monomeric product could be separated and characterized, while for the reactions with *n*Bu₂Sn and Ph₂Sn insoluble product mixtures involving probably oligo- and polymeric compounds were obtained. Complex 4 was isolated as hydrate of the composition 4·2.5H₂O and characterized by elemental analysis, mass spectrometry, spectroscopic methods (FTIR, ¹H, and ¹¹⁹Sn NMR) and X-ray crystallography.

The FAB⁺ mass spectrum showed a peak characteristic for a monomeric species at $m/z = 464$, but interestingly there was also a peak, albeit of low intensity, corresponding to a dimeric species ($m/z = 925$). In the FTIR spectrum there are two bands for N–H stretching vibrations with wavenumbers of 3286 and 3222 cm⁻¹, which correspond to the benzylamino and the central amino group [3k,13b]. The ¹H NMR spectrum of compound 4 showed

significantly broadened signals for the NCH₂ groups at $\delta = 2.51$ and 3.51 ppm, and for the methyl substituents attached to the tin atoms at $\delta = 0.35$ ppm. The ¹¹⁹Sn NMR signal, $\delta = -450$ ppm, is low-field shifted when compared to **1**, $\delta = -505$ ppm, thus probably indicating a weaker N → Sn coordination. The unresolved ²J(¹H–^{117/119}Sn) coupling constant of 106 Hz gave a calculated C–Sn–C bond angle of 174° in solution [21], which is in agreement with the bond angle extracted from the solid-state structure (vide infra): 172.8(3)°.

Due to the higher flexibility of the reduced five-coordinate ligand one might expect that the configuration of the complex is *cis* instead of *trans*, as it occurred in the case of the diorganotin(salan) complexes reported earlier (Scheme 1b) [3k]. Apparently, in the present case the *trans*-configuration is more favorable as it is demonstrated by the X-ray crystallographic study. The crystallographic data for compound **4**·2.5H₂O and selected geometric parameters have been summarized in Tables 1 and 2. The molecular structure of this complex is shown in Fig. 1.

Albeit saleanN₃H₃²⁻ is more flexible than salenN₃H₂⁻, the overall conformation of compound **4** is very similar to its salen analogue **1**. A comparison of the Sn–C, Sn–O and Sn–N bond lengths for **1** and **4** shows that there are significant differences only for the Sn–N bonds. This is not unexpected due to the sp² → sp³ hybridization change for two of the three nitrogen atoms (2.467(4) vs. 2.524(5) Å for Sn–N1, 2.494(4) vs. 2.649(7) Å for Sn–N3), but interestingly, the central N → Sn coordinative bond increases also, from 2.532(4) to 2.591(6) Å. The increase of the N3 → Sn bond length is larger than it might be expected from the sp² → sp³ hybridization change (approximately 0.1 Å) [23], so that additional intra- or intermolecular strain might occur in this part of the molecule. These results show that the reduced salen ligand does not necessarily coordinate stronger to the tin atom than the unreduced species, although sp³-hybridized nitrogen atoms use to be stronger Lewis bases than those with sp²-hybridization. Including, a comparison of the bond angles around the tin atom shows that the deviations from the values for a regular pentagonal bipyramid are larger in compound **4**. Some representative values for the X–Sn–X bond angles are 81.6(2)° for O–Sn–O, 72.3(2) and 77.9(2)° for O–Sn–N, and 64.8(2) and 67.6(2)° for N–Sn–N. The C–Sn–C angle is 172.8(3)° and the C–Sn–X (X = O, N) bond angles range from 77.6(3) to 98.4(2)°. In part, the variations in comparison to compound **1** (Table 2) can be attributed to the conformational differences of the {C₃NOSn} heterocyclic rings, which have now distorted boat-conformations. The SnOCC torsion angles are larger for compound **4**, –76.0(6)/56.0(8) vs. –41.9(7)/50.6(5)° for **1**, and, accordingly, the centroid...centroid distances between the aromatic rings of the salicylidene moieties are smaller, 6.60 vs. 6.67–7.19 Å. This indicates that the folding capacity of the saleanN₃H₃²⁻ ligand is significantly larger than that of salenN₃H₂⁻. The conformations of the five-membered {C₂N₂Sn} heterocyclic rings are similar for **1** and **4**, as indicated by the NCCN torsion angles (Table 2).

4. Conclusions

This study has shown that pentadentate ONNNO analogues of the unsubstituted salen and salan ligands coordinate to diorganotin(IV) groups in the equatorial plane of a pentagonal bipyramid. The conformation of the ligand is folded, if the steric bulk of the diorganotin moiety is small (R = Me, *n*Bu), and approximately coplanar with sterically more demanding substituents such as R = Ph. Although it might be expected that the saleanN₃H₃²⁻ ligand is more flexible and basic than salanN₃H₂⁻, a very similar coordination environment has been found, this behavior being different from the corresponding tetradentate ONNO ligands. It seems to indicate that it is even a weaker coordinating ligand.

The NMR spectroscopic studies have shown that the complexes are involved in conformational equilibria in solution, which requires the dissociation of all three N → Sn bonds. For those diorganotin compounds, for which curved conformations have been observed in the solid state, the dynamic process resembles the flapping of butterfly wings.

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Appendix A. Supplementary material

CCDC 273788, 273789, 273790, 273791, 736978 and 736979 contain the supplementary crystallographic data for compounds **1**·2.5H₂O, **1**·MeOH, **1**·DMSO, **4**·2.5H₂O, **2**·H₂O and **3**·2EtOH. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.08.016](https://doi.org/10.1016/j.jorganchem.2009.08.016).

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