

# 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 (<sup>1</sup>H, <sup>13</sup>C, <sup>119</sup>Sn) 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 C<sub>2</sub>-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 Sn<sub>2</sub>O<sub>2</sub> 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 [Ph<sub>2</sub>Sn(Cl)OH]<sub>2</sub> (**3**) or [Ph<sub>4</sub>Sn<sub>2</sub>O(OMe)Cl]<sub>2</sub> (**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]<sup>+</sup>.

In the IR spectra of complexes **2a–2g**, the broad bands observed at approximately 3400 cm<sup>-1</sup> 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<sup>-1</sup>, which are considerably shifted towards lower frequencies with respect to the free ligands (1625–1631 cm<sup>-1</sup>), suggesting the coordination of the azomethine nitrogen to the tin atom [21].

The <sup>1</sup>H and <sup>13</sup>C NMR data suggest that the complexes have a *mirror plane* or a C<sub>2</sub> 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<sub>SnL–LSn</sub> = 0°) having mirror symmetry and the *trans* (θ<sub>SnL–LSn</sub> = 180°) derivative having C<sub>2</sub>-symmetry. In the <sup>1</sup>H 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)

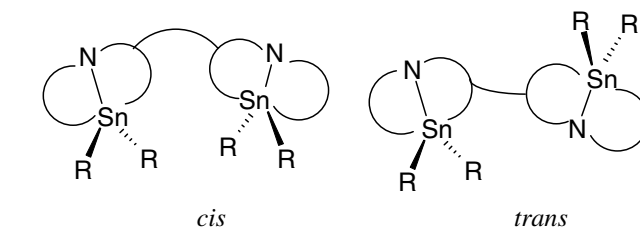
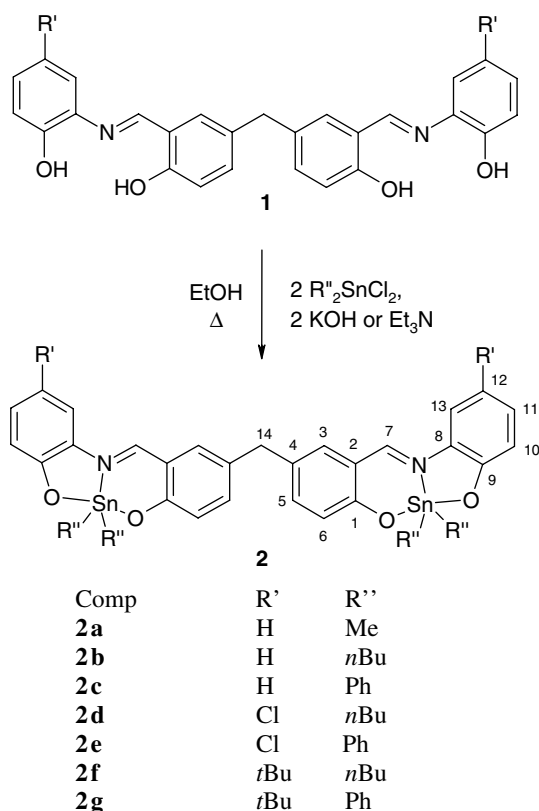


Chart 1. Schematic representation of the two possible conformations for the dinuclear tin compounds. In the *cis* conformation the two diorganotin moieties are oriented in the same direction (θ<sub>SnL–LSn</sub> = 0°), while they have opposite orientation in the *trans* conformation (θ<sub>SnL–LSn</sub>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

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

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