



## Solvothermal synthesis and characterizations of monophenyltin complexes in drum conformations

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### ABSTRACT

A series of drum structures of organotin complexes with various carboxylic acids have been solvothermally synthesized and characterized by elemental analysis, FT-IR, NMR (<sup>1</sup>H, <sup>13</sup>C and <sup>119</sup>Sn) spectra and X-ray crystallography. The molecular structure analyses reveal that all of the complexes have endo drum structures. Furthermore, each of the drum structures has a hole, in which atoms of a given radius could be held.

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### 1. Introduction

In recent years, organotin (IV) carboxylates have been one of the most extensively studied class of anticancer compounds, not only for their significant reduction in the growth rates of tumours [1,2], but also for their interesting and various architectures and topologies [3,4]. The latter has been actively investigated by a large number of researchers, and a multitude of structural types, including monomers, dimers, tetramers, oligomeric ladders, hexameric drums, etc., have been discovered [5,6]. Most of them were synthesized by conventional synthetic techniques. Recently, solvothermal synthesis has become an effective method for preparing various novel coordination complexes using simple inorganic or organometallic compounds and organic ligands as starting materials. It is also a superb technique for crystallizing these products that have hardly arisen from other synthetic methods [7,8]. In our previous work we have obtained 12- and 16-membered cyclic organotin complexes using the solvothermal technique [9,10], and intrigued by this method we chose triphenyltin chloride to react with seven carboxylic acids, in the hope of obtaining novel structures. Herein, we report the syntheses and characterizations of the seven structures, each with a drum configuration, resulting from solvothermal synthesis. These complexes form hexameric organostannoxane drums, which consist of a prismatic Sn<sub>6</sub>O<sub>6</sub> core. All the complexes were characterized by elemental, IR, FT-IR, NMR (<sup>1</sup>H, <sup>13</sup>C and <sup>119</sup>Sn)

and X-ray crystallography spectroscopy. All these complexes were synthesized under the same conditions.

### 2. Results and discussion

#### 2.1. Syntheses

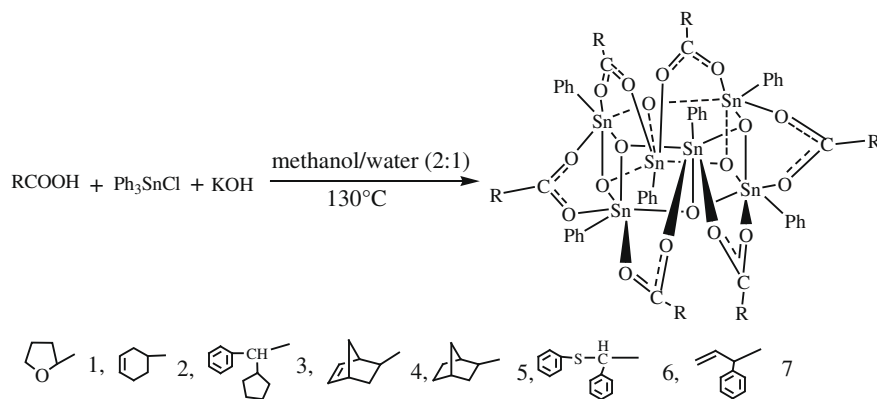
The following general procedure was used for the synthesis of complexes **1–7**. A mixture of the carboxylic acids, triphenyltin (IV) chloride and KOH in a mixture of CH<sub>3</sub>OH and H<sub>2</sub>O (V/V = 2:1) was heated under solvothermal conditions (130 °C). They were heated in a sealed Teflon-lined stainless steel autoclave for 3 days. After cooling down to room temperature, colorless crystals were collected and washed with methanol. The synthetic experiments of complexes **1–7** are shown in Scheme 1.

#### 2.2. IR spectra

In the infrared spectra, strong absorptions in the region of 433–453 cm<sup>-1</sup>, which are absent in the spectra of the free carboxylic acids, are assigned to the Sn–O stretching mode. Strong bands in the region of 621–637 cm<sup>-1</sup> for the complexes are assigned to ν(Sn–O–Sn), indicating the forming of a Sn–O–Sn bridged structure. All these values are consistent with those detected in a number of organotin (IV)-oxygen derivatives [11]. As reported for other organotin complexes, IR spectroscopy can provide useful information relating to the bond formation through the carboxylate moieties in the organotin carboxylate complexes. It is possible to distinguish the coordination mode of the –CO<sub>2</sub> group. For the complexes in this article, the Δν (Δν = ν<sub>as</sub>(COO)–ν<sub>s</sub>(COO)) values of

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Scheme 1.

complexes **1–7** ( $239.4\text{--}304.9\text{ cm}^{-1}$ ) reveal that the carboxylate groups have bidentate coordination modes [12]. The conclusions drawn from the IR data are consistent with the X-ray crystallography spectroscopy data.

### 2.3. NMR spectra

The  $^1\text{H}$  NMR spectra show the expected integration and peak multiplicities. In the spectra of the free ligands, resonances are observed at about 10.12 ppm, and these are absent in the spectra of the complexes, indicating the formation of Sn–O bonds in all the complexes. In complexes **1–7**, the chemical shifts of the signal for the phenyl groups ( $\delta = 7.12\text{--}7.90$  ppm) appear almost in the same positions. The structural changes occurring in the ligands upon deprotonation and coordination to the Sn atoms should be reflected by the changes in the  $^{13}\text{C}$  NMR spectra of complexes **1–7**. If the ligands chelate Sn through the O atom from C–O, the IR bands of the COO group should be shifted to a lower frequency in the spectra of the complexes compared with the spectra of the free ligands.  $^{119}\text{Sn}$  NMR chemical shift values may be used to give tentative indications of the environment around the tin atoms. Holeček et al. [13] have suggested  $\delta$  values from +200 to  $-60$  for four-coordinated,  $-90$  to  $-190$  for five-coordinated and  $-210$  to  $-400$  ppm for six-coordinated tin atoms in solution. The  $^{119}\text{Sn}$  NMR spectra of the complexes show single resonances indicating the presences of only one type of tin atom, which is consistent with other similar complexes [14].

### 2.4. Description of crystal structures

The molecular structure of complex **1** is shown in Fig. 1 (the similar structures of complexes **2–7** are not displayed) and selected bond lengths and angles for **1** are summarized in Table 2. The most ubiquitous cages are the hexanuclear complexes, also known as drums. The centrosymmetric structures are built around a  $\text{Sn}_6\text{O}_6$  central stannoxane core which contains two puckered six-membered  $[\text{Sn}_3(\mu_3\text{-O})_3]$  rings as its top and bottom face (Fig. 1) [15]. The two  $[\text{Sn}_3(\mu_3\text{-O})_3]$  rings are connected further by six Sn–O bonds provided by tri-coordinated O atoms, thus the side faces of the drum are characterized by six puckered four-membered  $[\text{Sn}_2(\mu_3\text{-O})_2]$  rings. Alternate tin atoms are held together by the coordination action of bidentate carboxylate groups to form a symmetrical bridge between two carboxylate ligands. This represents the signature structural feature of stannoxane clusters. The structure features of various ‘drum’ complexes are similar. In general, the Sn–O bond lengths inside the core range between 2.08 and 2.14 Å, and these distances are comparatively shorter than the Sn–O bonds to the bridging carboxylate ligands (2.16(3)–

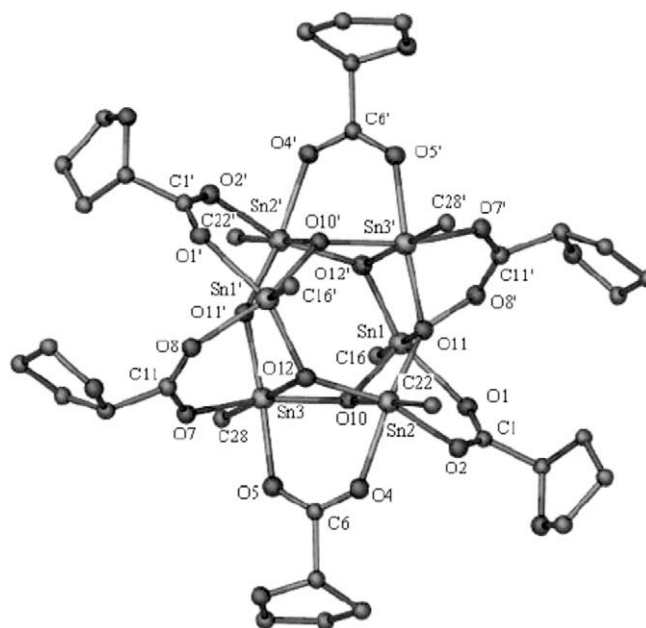


Fig. 1. Molecular structure of complex **1** [The  $\alpha$ -carbon of the phenyl ring (Sn–Ph) is drawn, but the other atoms are omitted for clarity].

2.21(6) Å] [16]. The Sn–O–Sn bond angles in the six-membered rings, in the range  $98.5(4)\text{--}135.0(6)^\circ$ , are wider than those found in the four-membered rings. It can be seen from the structures in Fig. 2, the four-membered  $[\text{Sn}_2(\mu_3\text{-O})_2]$  rings are not planar, the oxygen atoms are tilted toward the cavity of the drum. Thus the interior of the drum can be considered as a crown made of six oxygen atoms in a trigonal antiprismatic arrangement.

The  $^{119}\text{Sn}$  NMR of complexes **1–7** show a single peak characteristic of this class of complexes, indicating that all the tin atoms of the drum complexes are chemically equivalent. A single chemical shift is seen in their  $^{119}\text{Sn}$  NMR spectra [17–19], where the tin atoms are hexa-coordinated (50, 1C) [20,21], with three of the coordination sites being occupied by bridging tri-coordinated oxygen atoms. While the oxygen atoms from the bridging carboxylate ligands occupy two of the coordination sites, the sixth coordination site is occupied by a C atom from the phenyl group. The  $\text{O}_5\text{C}$  donor set defines a distorted octahedron, which is approved by the angles in Table 2. In all the complexes, the distance between the planes defined by the six tin atoms is about 2.32 Å. The corresponding distance between the planes defined by the oxygen atoms is about 1.84 Å. As seen in Fig. 2a and b, we can imagine a center residing in the interior of the cavity, the center being defined by the crown

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