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Syntheses and characterization of triorganotin complexes: X-ray crystallographic study of triorganotin pyridinedicarboxylates with trinuclear, 1D polymeric chain and 2D network structures

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Abstract

A series of new triorganotin(IV) pyridinedicarboxylates $[(C_2H_5)_3NH][(Me_3Sn)_3(2,6\text{-pdc})_2(H_2O)_2]$ (**1**), $[(C_2H_5)_3NH][(Ph_3Sn)_3(2,6\text{-pdc})_2(H_2O)_2]$ (**2**), $[(C_2H_5)_3NH]\{[(PhCH_2)_3Sn]_3(2,6\text{-pdc})_2(H_2O)_2\}$ (**3**), $[Me_3Sn(3,5\text{-pdc})]_n$ (**4**), $[Ph_3Sn(3,5\text{-pdc})]_n$ (**5**), $[(PhCH_2)_3Sn(3,5\text{-pdc})]_n$ (**6**), $[(Me_3Sn)_2(2,5\text{-pdc})]_n$ (**7**), $[(Ph_3Sn)_2(2,5\text{-pdc})]_n$ (**8**) and $\{[(PhCH_2)_3Sn]_2(2,5\text{-pdc})\}_n$ (**9**) were synthesized by the reaction of trimethyltin(IV), triphenyltin(IV) or tribenzyltin(IV) chloride with 2,6(3,5 or 2,5)-H_2pdc (pdc = pyridinedicarboxylate) when triethylamine was added. Complexes **1**–**9** have been characterized by elemental, IR, ^1H, ^{13}C and ^{119}Sn NMR analyses. Among them complexes **1**, **5** and **7** have also been characterized by X-ray crystallographic diffraction analyses. Complex **1** has a trinuclear structure and forms a 2D supramolecular structure due to the coordinated water molecules via hydrogen bonds to the pendant O atoms of the carboxyl groups and the N atoms derived of the pyridine ring. Complex **5** forms a 1D polymeric chain by the intermolecular Sn···N (N atom derived of pyridine ring) interactions. Complex **7** has a network structure where 2,5-pyridinedicarboxylate acts as a tetradentate ligand coordinated to trimethyltin(IV) ions.

Keywords: Pyridinedicarboxylic acid; Triorganotin; Hydrogen bond; X-ray crystallography; Supramolecular structure

1. Introduction

Organotin(IV) carboxylates have attracted much attention owing to their potential biocidal activities [1–4] and cytotoxicities [5] as well as their industrial and agricultural applications [6–11]. Among them, the study of the structural chemistry of triorganotin carboxylates has received considerable attention owing to the various structural types that may be adopted in the solid state [12–19]. Although a large number of structural studies have been carried out on the triorganostannyl esters of monofunctional carboxylic acids [20], relatively little work has so far been undertaken on the triorganotin esters of dicarboxylic acids [21–24]. The organotin(IV) dicarboxylates have been studied in considerable detail, and in general the reported organotin(IV) dicarboxylates exist as dinuclear [25] one-dimensional zigzag chain [26] and cyclic structures [27]. Recently, our interest has focused on triorganotin(IV) complexes containing dicarboxylate ligands which have an additional hetero-donor atom (e.g., N, O, S) residing on the R′ group that is, potentially pentadentate ligands, in order to examine what effect the presence of the heteroatom has on the structure adopted by these complexes [28]. As a part of our continuing program in this area, we have synthesized and structurally characterized triorganotin(IV) pyridinedicarboxylates of 2,6(3,5 or 2,5)-pyridinedicarboxylic acid and the results of this study are reported herein.

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2. Results and discussion

2.1. Syntheses

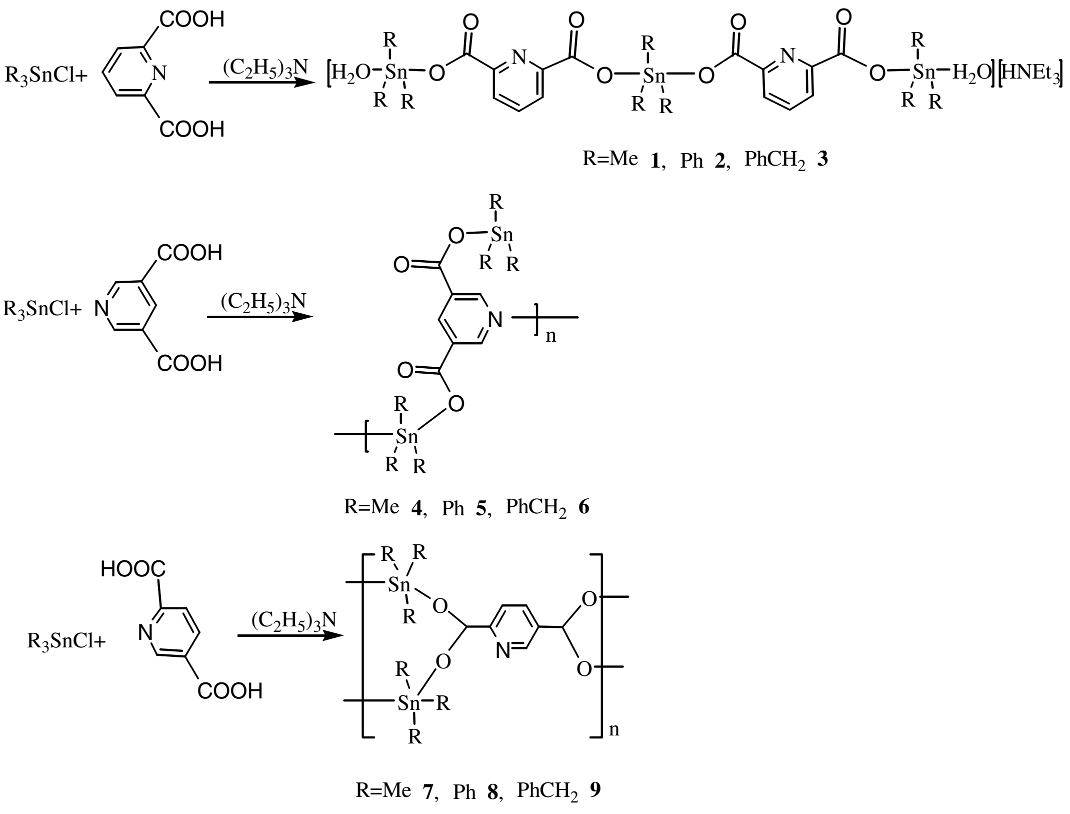
The triorganotin(IV) pyridinedicarboxylates $[(C_2H_5)_3NH][(Me_3Sn)_3(2,6\text{-pdc})_2(H_2O)_2]$ (**1**), $[(C_2H_5)_3NH][(Ph_3Sn)_3(2,6\text{-pdc})_2(H_2O)_2]$ (**2**), $[(C_2H_5)_3NH]\{[(PhCH_2)_3Sn]_3(2,6\text{-pdc})_2(H_2O)_2\}$ (**3**), $[Me_3Sn(3,5\text{-pdc})]_n$ (**4**), $[Ph_3Sn(3,5\text{-pdc})]_n$ (**5**), $[(PhCH_2)_3Sn(3,5\text{-pdc})]_n$ (**6**), $[(Me_3Sn)_2(2,5\text{-pdc})]_n$ (**7**), $[(Ph_3Sn)_2(2,5\text{-pdc})]_n$ (**8**) and $\{[(PhCH_2)_3Sn]_2(2,5\text{-pdc})\}_n$ (**9**) were synthesized by the reaction of trimethyltin(IV), triphenyltin(IV) or tribenzyltin(IV) chloride with 2,6(3,5 or 2,5)-pyridinedicarboxylic acid with the mole ratio of 1:2 when triethylamine was added. The syntheses procedure is shown in Scheme 1.

2.2. IR spectra

The infrared spectrum of the three free ligands show $\nu(C{=}O)$ of COOH at 1667, 1681 and 1678 cm^{-1}, respectively, as a strong band, which indicate that there are intermolecular hydrogen bonds of the type $C{=}O\cdots H\text{–}O$ in the uncoordinated 2,6-pyridinedicarboxylic acid, 3,5-pyridinedicarboxylic acid and 2,5-pyridinedicarboxylic acid molecules. This is commonly observed in the case of carboxylic acids [29]. After deprotonation and coordinated to tin atoms, these bands disappear and are replaced by strong bands in the 1617–1623 and 1305–1433 cm^{-1} regions, which correspond to the asymmetric and symmetric vibrations, respectively, of the COO moiety. Also strong absorption appear at 478–489 cm^{-1} in the respective spectra of the complexes **1**–**9**, which is absent in the spectra of the free ligand, and is assigned to the Sn–O stretching mode of vibration. All these values are consistent with that detected in a number of organotin(IV) derivatives [30–32]. The peak at about 3325 cm^{-1} in the infrared spectrum indicates the existence of the coordinated water molecules in complexes **1**–**3**. Besides, as reported in the literature [33,34], the IR spectra can provide useful information concerning the mode of coordination of the carboxylate in organotin complexes (coordination mode see Scheme 2). The $\Delta\nu[\nu_{as}(COO^-) - \nu_{sym}(COO^-)]$ values for complexes **1**–**6** (301–320 cm^{-1}) and **7**–**9** (184–186 cm^{-1}) reveal that the coordination mode of the carboxylate groups in **1**–**6** and **7**–**9** are mode I and III type, respectively.

2.3. NMR spectra

The ^1H NMR spectra show the expected integration and peak multiplicities. The single resonance of –OH in the spectra of the free ligands are absent in the spectra of all the complexes **1**–**9** indicating the replacement of the carboxylic acid protons by a triorganotin moiety on complex formation. In addition, the resonances appear at 8.95–8.98 ppm for **1**–**3** are attributed to the protons of coordinated water molecules in the structures. The resonances



Scheme 1.