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Syntheses and crystal structures of diorganotin (IV) moieties with 3-hydroxy-2-pyridinecarboxylic acid

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Abstract

A series of new organotin (IV) complexes with 3-hydroxy-2-pyridinecarboxylic acid (3-OH-2-picH) of two types: $R_2SnCl(3\text{-OH-}2\text{-pic})$ (**I**) (R = Me **1**, *n*-Bu **2**, Ph **3**, $PhCH_2$ **4**) and R_2 $Sn(3\text{-OH-}2\text{-pic})_2$ (**II**) (R = Me **5**, *n*-Bu **6**, Ph **7**, $PhCH_2$ **8**) have been synthesized by reactions of diorganotin (IV) dichloride with 3-hydroxy-2-pyridinecarboxylic acid in the presence of sodium ethoxide. All complexes are characterized by elemental analyses, IR spectra and NMR spectra analyses. Among them, complexes **1**, **5**, **6** and **7** are also characterized by X-ray crystallography diffraction analyses. Complex **1** is a 1D polymeric chain with six-coordinate tin atoms and the packing of complex **1** is stabilized by the C–H···Cl intermolecular weak interactions, thus a 2D network of **1** is formed. Complex **5** is also a 1D polymeric chain with seven-coordinate tin atoms. Complex **6** is a zigzag polymeric chain linked by Sn···O intermolecular weak interactions. Complex **7** is a monomeric complex with distorted octahedral geometry.

Keywords: 3-Hydroxy-2-pyridinecarboxylic acid; Organotin (IV); Weak interactions

1. Introduction

Metal-directed self-assembly of organic ligands and metal ions or organometallic substances with various intriguing topologies have been extensively studied [1,2]. An important objective is the synthesis of new higher soluble metal complexes useful for testing the distinctive reactivity patterns of the multimetallic systems. In recent years, organotin (IV) carboxylates have been the subjects of interest for some time because of their biochemical and commercial applications [3]. In general, the biochemical activity of organotin (IV) carboxylates is greatly influenced by the structure of the molecule and the coordination number of the tin atoms [4–6]. Therefore, recognition of the importance between the biological properties and the structure of organotin (IV) carboxylates [7], have together spurred on the study of carboxylate of tin. Crystallographic studies reveal that organotin (IV) carboxylates adopt structure which are dependent on both the nature of the alkyl (or aryl) subsistent bound to the tin atom and the type of carboxylate ligand [8–10]. Studies on organotin (IV) complexes having carboxylate ligands with additional donor atoms, such as a nitrogen, available for coordination to Sn, have revealed new structural types which may lead to complexes with different activity, such as pyridine-2, 6-dicarboxylic acid and pyridinecarboxylic acid.

In our previous work, we have reported several novel molecular structures of organotin (IV) complexes with 2-pyrazinecarboxylic acid [11]. As an extension of this research program and in connection with our current interest in the coordination chemistry of organotin (IV) complexes with heterocyclic ligands, we choose

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another fascinating ligand: 3-hydroxy-2-pyridinecarboxylic acid (3-OH-2-picH). This ligand is interesting because of its hydroxyl in the pyridine ring. With the introduction of hydroxyl, the solubility of the complexes may be increased. Although its analogical ligand, such as pyridinedicarboxylic acid have been extensively studied before [12], to our knowledge, no organotin (IV) derivatives of 3-hydroxy-2-pyridinecarboxylic acid have been reported so far. Therefore, one of the aims of this work is to investigate and characterize the structures of new organotin (IV) derivatives of 3-hydroxy-2-pyridinecarboxylic acid, and to investigate whether or not the existence of hydroxyl will influence the coordination modes.

The above considerations stirred our interest in some detailed syntheses, structure patterns for diorganotin (IV) derivatives of the ligand. Finally, we obtained a series of diorganotin (IV) complexes by reaction of diorganotin (IV) dichloride with 3-hydroxy-2-pyridinecarboxylic acid in the presence of sodium ethoxide. When using 1:1:1 molar ratio of R_2SnCl_2:(3-OH-2-picH):EtONa, we obtained polymeric complexes **1**–**4** of the type R_2SnCl(3-OH-2-pic) (R = Me **1**, *n*-Bu **2**, Ph **3**, $PhCH_2$ **4**) and with 1:2:2 molar ratio, another four monomeric or polymeric complexes were obtained and the general formula is R_2Sn(3-OH-2-pic)$_2$ (R = Me **5**, *n*-Bu **6**, Ph **7**, $PhCH_2$ **8**). Determinations by elemental analyses, IR and NMR spectra analyses of all the complexes are given. Among them, complexes **1**, **5**, **6** and **7** are also characterized by X-ray crystallography diffraction analyses.

2. Experimental

2.1. Materials and measurements

Diphenyltin dichloride, di-*n*-butyltin dichloride, dimethyltin dichloride and 3-hydroxy-2-pyridinecarboxylic acid were commercially available, and they were used without further purification. Dibenzyltin dichloride was prepared by a standard method reported in the literature [13]. The melting points were obtained with Kofler micro melting point apparatus and were uncorrected. Infrared-spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. ^{1}H, ^{13}C and ^{119}Sn NMRspectra were recorded on Varian Mercury Plus 400 spectrometer operating at 400, 100.6 and 149.2 MHz, respectively. The spectra were acquired at room temperature (298K) unless otherwise specified; ^{13}C spectra are broadband proton decoupled. The chemical shifts were reported in ppm with respect to the references and were stated relative to external tetramethylsilane (TMS) for ^{1}H and ^{13}C NMR, and to neat tetramethyltin for ^{119}Sn NMR. Elemental analyses (C, H, N) were performed with a PE-2400II apparatus.

2.2. Syntheses

The general route of synthesis is shown in the following. The reaction was carried out under nitrogen atmosphere with use of standard Schlenk technique. The 3-hydroxy-2-pyridinecarboxylic acid and sodium ethoxide were added to the solution of benzene, the mixture was stirred for 30 min, and then added organotin (IV) chlorides to the mixture, continuing the reaction about 12 h at 40 °C. After cooling down to room temperature, filtered it. The solvent of the filtrate was gradually removed by evaporation under vacuum until solid product was obtained. The details of synthetic experiments of complexes **1**–**8** were shown in Scheme 1.

2.2.1. Me_2SnCl(3-OH-2-pic) (**1**)

Recrystallized from dichloromethane–hexane. M.p. 212–215 °C. Yield, 74%. Anal. Calc. for $C_8H_{10}ClNO_3Sn$: C, 29.81; H, 3.13; N, 4.35. Found: C, 29.65; H, 3.10; N, 4.27%. IR (KBr, cm^{-1}): 1628 (ν_{as}COO), 1452 (ν_sCOO), 1591 (C=N), 583 (Sn–C), 476 (Sn–O), 457 (Sn–N), 270 (Sn–Cl), 3427 (O–H). ^{1}H NMR (CDCl$_3$, ppm): δ 1.43(s, 6H, $^2J_{SnH}$ = 94.6Hz, Me), 7.29–8.70 (br, 3H, ligand). ^{13}C NMR (CDCl$_3$, ppm): δ 10.2 (^1J(^{119}Sn–^{13}C), 893 Hz, Me), 149.6 (C2, ligand), 121.2 (C3), 137.5 (C4), 124.6 (C5), 147.1 (C6), 166.7 (COO). ^{119}Sn NMR (CDCl$_3$, ppm): −223.2.

2.2.2. Bu_2SnCl(3-OH-2-pic) (**2**)

Recrystallized from dichloromethane–hexane. M.p. 52–54 °C. Yield, 78%. Anal. Calc. for $C_{14}H_{22}ClNO_3Sn$: C, 41.37; H, 5.46; N, 3.45. Found: C, 41.27; H, 5.51; N, 3.37%. IR (KBr, cm^{-1}): 1622 (ν_{as}COO), 1448 (ν_sCOO), 1595 (C=N), 558 (Sn–C), 475 (Sn–O), 458 (Sn–N), 263 (Sn–Cl), 3429 (O–H). ^{1}H NMR (CDCl$_3$, ppm): δ 0.91–2.11(m, 18H, ^{n}Bu), 7.28–8.65 (br, 3H, ligand). ^{13}C NMR (CDCl$_3$, ppm): δ 28.0, 27.5, 26.1, 13.4 (^{n}Bu), 149.5 (C2, ligand), 121.1 (C3), 137.4 (C4), 124.3 (C5), 146.8 (C6), 167.0 (COO). ^{119}Sn NMR (CDCl$_3$, ppm): −341.6.

2.2.3. Ph_2SnCl(3-OH-2-pic) (**3**)

Recrystallized from dichloromethane–hexane. M.p. 80–82 °C. Yield, 71%. Anal. Calc. for $C_{18}H_{14}ClNO_3Sn$: C, 48.42; H, 3.16; N, 3.14. Found: C, 48.21; H, 3.07; N, 3.15. IR (KBr, cm^{-1}): 1634 (ν_{as}COO), 1445 (ν_sCOO), 1597 (C=N), 558 (Sn–C), 481 (Sn–O), 457 (Sn–N), 267 (Sn–Cl), 3425 (O–H). ^{1}H NMR (CDCl$_3$, ppm): δ 7.47–7.80 (m, 10H, Ph), 7.29–8.65 (br, 3H, ligand). ^{13}C NMR (CDCl$_3$, ppm): δ 136.9 (*o*-C), 124.7 (*m*-C), 129.6 (*p*-C), 146.5 (*i*-C), 149.0 (C2, ligand), 121.3 (C3), 137.5 (C4), 124.5 (C5), 147.0 (C6), 167.1 (COO). ^{119}Sn NMR (CDCl$_3$, ppm): −371.5.

2.2.4. $PhCH_2)_2SnCl$(3-OH-2-pic) (**4**)

Recrystallized from dichloromethane–hexane. M.p. 114–116 °C. Yield, 81%. Anal. Calc. for $C_{20}H_{18}ClNO_3$-