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Synthesis, characterization and crystal structures of the organotin(IV) compounds with the Schiff base ligands of pyruvic acid thiophene-2-carboxylic hydrazone and salicylaldehyde thiophene-2-carboxylic hydrazone

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Abstract

A series of organotin (IV) compounds of the type $[R_3SnL]_2$, R is Me (**1**), Bu (**2**), $[R_2SnL]_2$, R is Ph (**3**), Me (**4**), Bu (**5**), L is pyruvic acid thiophene-2-carboxylic hydrazone, and R_2SnL, R is Me (**6**), Bu (**7**), Ph (**8**), L is salicylaldehyde thiophene-2-carboxylic hydrazone have been synthesized in 1:1 molar ratio. All compounds were characterized by elemental analysis, IR, ^1H NMR, ^{13}C NMR and ^{119}Sn NMR spectra. The crystal structure of compounds **1**, **3**, **4**, **8** have been determined by X-ray single crystal diffraction analyses, study found that the compounds **1** and **3** are rendered one-dimensional chain structure and the tin atoms are five-coordinated in a distorted trigonal-bipyramidal geometry. The compound **4** has a dimeric structure and the central tin atom is rendered seven-coordinate in a distorted pentagonal-bipyramid configuration. While the compound **8** is a monomer in which the tin atom adopts five-coordinated in distorted trigonal-bipyramidal geometry.

Keywords: Organotin(IV); Schiff base; Synthesis; Crystal structure

1. Introduction

Recently the investigation of novel metal-organic compounds have attracted considerable interest and importance, not only due to their intriguing structure motifs, but also their potential applications in catalysis, medicine, host–guest and so on [1–5]. In the various metal-organic frameworks, the one-dimension chain structure has been widely researched. In general the important factor for the formation of interpenetrating structure is that the networks contain large pores or cavities. In the past, compounds based on polycarboxylate have been widely used [6]. However, compounds based on monocarboxylate have rarely reported, especially in the respect of organotin Schiff base with monocarboxylate. Organotin(IV) compounds with Schiff base have been the focus all the while owing to their special anti-tumour activities [7–15]. In addition to their anti-tumor activities, organotin(IV) compounds with Schiff bases present an interesting variety of structural possibilities, we now synthesized a series of organotin(IV) compounds and four of them have been studies by the X-ray single crystal diffraction analysis and reveal that there exist four different types of coordinated tin atoms. X-ray single crystal diffraction study found that the compounds **1** and **3** are all one-dimensional chain structure connected by Sn–O bonds, the difference is in the compound **1** the O atoms from the carbonyl and carboxylate coordinated to the tin atom as a unidentate, while in the compound **3** the Schiff base ligand coordinate to the tin atom as tridentate.

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2. Experimental

2.1. Materials and methods

Tri-*n*-butyltin chloride, trimethyltin chloride, di-*n*-butyltin oxide, pyruvic acid and thiophene-2-carboxylic hydrazide were commercially available and used without future purification. All the solvents used in the reaction were of AR grade and dried using standard literature procedures. The melting points were obtained with Kolfer micro melting point apparatus and were uncorrected. IR spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. ^{1}H NMR, ^{13}C NMR and ^{119}Sn NMR spectra were recorded on a Mercury Plus-400 NMR spectrometer; chemical shifts were given in ppm relative to Me_4Si (^{1}H NMR,^{13}C NMR) and Me_4Sn (^{119}Sn NMR) in $CDCl_3$ solvent, respectively. Elemental analyses were performed in a PE-2400 II elemental analyzer.

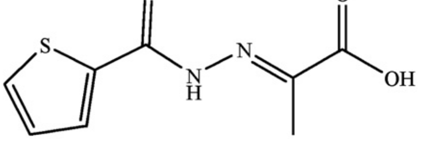
2.2. Synthesis of Schiff base ligand

2.2.1. Pyruvic acid thiophene-2-carboxylic hydrazone

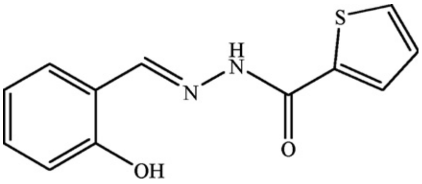
The Schiff base of pyruvic acid thiophene-2-carboxylic hydrazone was prepared from the pyruvic acid and thiophene-2-carboxylic hydrazide in ethanol solution. A mount of yellow powder was obtained. Yield 79%, M.p. 511–512 K. *Anal.* Calc. for $C_8H_8N_2O_3S$: C, 45.27; H, 3.80, N, 13.20. Found: C, 45.42; H, 3.71, N, 13.15% (Scheme 1).

2.2.2. Salicylaldehyde thiophene-2-carboxylic hydrazone

The Schiff base of salicylaldehyde thiophene-2-carboxylic hydrazone was prepared using the same procedure as described in Section 2.2.1. Yield 86%, M.p. 518–519 K. *Anal.* Calc. for $C_{12}H_{10}N_2O_2S$: C, 58.52; H, 4.09, N, 11.37. Found: C, 58.41; H, 3.9, N, 11.25% (Scheme 2).



Scheme 1.



Scheme 2.

2.3. Preparations of the compounds

Synthesis of compound **1**: the reaction was carried out under nitrogen atmosphere with use of Schlenk isolation method. The Schiff base (0.2122 g, 1.0 mmol) was added in the mixture of ethanol and benzene (V/V: 1/3) (30 ml) with sodium ethoxide (0.0685 g, 1.0 mmol), the mixture was stirred for 0.5 h, $(CH_3)_3SnCl$ (0.1193 g, 1.0 mmol) was added, stirring for 10 h under refluxing. After cooling down to room temperature, filtered it and evaporated to dryness, the solid was then recrystallized from dichloromethane-hexane and yellow single crystal was formed by slow evaporation at r.t. Compounds **2** were prepared using the same procedure as described for compound **1.**

Compound **3** was prepared using the procedure as follow described. The reaction mixture of diphenyltin oxide (0.3438 g, 1.0 mmol) and pyruvic acid thiophene-2-carboxylic hydrazone, (0.2122 g, 1.0 mmol) were added to a solution of absolute ethanol (30 ml) and stirred under reflux for 7 h and then filtrated. The clear solution thus obtained and was evaporated under vacuum to leave an orange solid, which was recrystallized from ethanol to give orange crystals.

Compounds **4**–**8** were prepared using the same procedure as described for compound **4**. The reaction was carried out under nitrogen atmosphere with use of stranded Schlenk technique. The Schiff base (0.2122 g, 1.0 mmol) was added in the mixture of ethanol (30 ml) with triethylamine (1.2 mmol), the mixture was stirred for 0.5 h, $(CH_3)_2SnCl_2$ (0.2197, 1.0 mmol) was added, stirring for 10 h under refluxing. After cooling down to room temperature, filtered it and evaporated to dryness, the solid was then recrystallized from dichloromethane-hexane and yellow single crystal was formed by slow evaporation at r.t.

2.3.1. $[(CH_3)_3Sn(C_8H_7N_2O_3S)]_2$ (**1**)

Yield: 65%. *Anal.* Calc. for $C_{22}H_{32}N_4O_6S_2Sn_2$: C, 35.22; H, 4.30, N 7.47. Found: C, 35.15; H, 4.22; N, 7.39%. ^{1}H NMR ($CDCl_3$, 400 MHz): 1.23 (18H, s, $J_{Sn-H} = 80$ Hz, Sn–CH_3), 2.47 (6H, s, –CH_3), 7.83 (2H, s, C–NH), 7.15–7.32 (6H, m, –C_4H_3S). ^{13}C NMR ($CDCl_3$, 400 MHz): 173.36 (COO), 142.78 (CH=N), 163.89 (CO–N), 55.37 (–CH_3), 138.32, 137.65, 129.25, 121.68 (thiophene carbons), 16.79, 9.35, 4.36 (Sn–CH_3, $^{1}J_{Sn-C} = 490$ Hz) ppm. IR (KBr, cm^{-1}): 1608, 1369 (m, CO_2), 3336 (s, NH), 1635 (s, C=N), 570 (m, Sn–O), 537 (w, Sn–C). ^{119}Sn NMR ($CDCl_3$): -170.6 ppm.

2.3.2. $[(n\text{-}C_4H_9)_3Sn(C_8H_7N_2O_3S)]_2$ (**2**)

Yield: 73%. *Anal.* Calc. for $C_{40}H_{68}N_4O_6S_2Sn_2$: C, 47.92; H, 6.83; N, 5.58. Found: C, 47.80; H, 6.74; N, 5.43%. ^{1}H NMR ($CDCl_3$, 400 MHz): 0.85 (18H, t, –CH_3), 1.36–1.68 (36H, m, $SnCH_2CH_2CH_2$), 2.49 (6H, s, –CH_3), 7.86 (2H, s, C–NH), 7.21–7.36 (6H, m, –C_4H_3S). ^{13}C NMR ($CDCl_3$, 400 MHz): 173.85 (COO), 148.65 (CH=N), 167.93 (CO–N), 56.35 (–CH_3), 137.94, 131.55, 129.53, 123.27 (thiophene