

## 有机锡 2-(3-吡啶甲基硫代)苯甲酸酯与 2-吡啶硫代乙酸酯的合成、结构与抗真菌活性

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**摘要:** 通过二乙基氧化锡、二丁基氧化锡以及三苯基氧化锡与 2-(3-吡啶甲基硫代)苯甲酸和 2-吡啶硫代乙酸的反应, 3 个四核有机锡羧酸酯以及 2 个单核三苯基锡羧酸酯被合成。它们的结构通过 X-射线单晶衍射结构分析得到确证。生物活性测试表明, 四核二丁基锡 2-吡啶硫代乙酸酯以及单核三苯基锡 2-(3-吡啶甲基硫代)苯甲酸酯对西瓜炭疽病菌、花生褐斑以及苹果轮纹菌等具有高的抑制活性。

**关键词:** 有机锡羧酸酯; 吡啶基; 晶体结构; 抗真菌活性

中图分类号: O614.43<sup>2</sup> 文献标识码: A 文章编号: 1001-4861(2008)09-1504-06

## Synthesis, Structure and Fungicidal Activity of Organotin 2-(3-Pyridylmethylthio)benzoate and (2-Pyridylthio)acetate

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**Abstract:** Three dimeric complexes  $\{[2-(3\text{-PyCH}_2\text{S})\text{C}_6\text{H}_4\text{CO}_2\text{SnR}_2]_2\text{O}\}_2$  and  $\{[(2\text{-PySCH}_2\text{CO}_2)\text{SnR}_2]_2\text{O}\}_2$  (Py=pyridyl) as well as two monomeric complexes  $(2\text{-PySCH}_2\text{CO}_2)\text{SnPh}_3$  and  $[2-(3\text{-PyCH}_2\text{S})\text{C}_6\text{H}_4\text{CO}_2]\text{SnPh}_3$  have been synthesized by the reaction of 2-(3-pyridylmethylthio)benzoic acid or (2-pyridylthio)acetic acid with  $\text{R}_2\text{SnO}$  (R=Et or <sup>n</sup>Bu) and  $(\text{Ph}_3\text{Sn})_2\text{O}$ . Their structures have also been confirmed by X-ray single crystal diffraction. Preliminary *in vitro* tests for fungicidal activity show that complexes  $\{[(2\text{-PySCH}_2\text{CO}_2)\text{SnBu}^n]_2\text{O}\}_2$  and  $[2-(3\text{-PyCH}_2\text{S})\text{C}_6\text{H}_4\text{CO}_2]\text{SnPh}_3$  display high activity to *Colletotrichum lagenarium*, *Cercospora arachidicola* and *Physalospora piricola* in a low concentration. CCDC: 685778, 2; 685777, 4.

**Key words:** organotin carboxylate; pyridyl; crystal structure; fungicidal activity

Organotin carboxylates have been the subject of extensive investigations due to their wide applications in many fields, for example as pesticidal, bactericidal and antitumor agents<sup>[1-3]</sup>. The coordination geometries of the tin atoms in these complexes can be easily adjusted by changing the steric and electronic factors of

carboxylic acid ligands and substituents linked to the tin atoms<sup>[3]</sup>. In recent years, more and more investigations have focused on the synthesis of organotin carboxylates of functionalized carboxylic acids with additional O, S or N donor groups<sup>[4-10]</sup>. Due to the presence of additional coordinating atoms, the tin atoms in these

收稿日期: 2008-05-05。收修改稿日期: 2008-06-09。

教育部“新世纪优秀人才”计划(No.NCET-04-0227), 宜宾学院科研基金资助项目。

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organotin carboxylates show considerable structural diversity<sup>[23]</sup>. Many investigations have suggested that the bioactivity of the organotin carboxylates significantly depends on the nature and the number of the organic groups bonded to the tin atoms<sup>[11]</sup>. Recently, we have reported the synthesis and the bioactivity of some organotin carboxylates of functionalized carboxylic acids with additional S or N donor groups<sup>[12,13]</sup>. As an extension of our investigations on biologically active organotin complexes, we herein report the synthesis and the fungicidal activity *in vitro* of organotin derivatives with 2-(3-pyridylmethylthio)benzoic acid and (2-pyridylthio)acetic acid.

## 1 Experimental

Multinuclear NMR spectra were obtained with a Bruker AV300 spectrometer using CDCl<sub>3</sub> as solvent unless otherwise noted, and the chemical shifts were reported in ppm with respect to reference standards (internal SiMe<sub>4</sub> for <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra, external SnMe<sub>4</sub> for <sup>119</sup>Sn NMR). IR spectra were obtained from a Bio-Rad FTS 6000 spectrometer using KBr discs. Elemental analyses were carried out on an Elementar Vairo EL analyzer. Melting points were measured with an X-4 digital micro melting-point apparatus and were uncorrected.

### 1.1 Preparation of 2-(3-pyridylmethylthio)benzoic acid

This acid was prepared from the method in the literature<sup>[14]</sup> with a slight modification. Thiosalicylic acid (50 mmol) and 3-chloromethylpyridine-HCl (50.1 mmol) were added to a solution of KOH (160 mol) in 50 mL of EtOH and 10 mL of water. The reaction mixture was stirred at room temperature for 2 h, and then water (100 mL) was added. The water solution was extracted with diethyl ether (3×50 mL), and the organic phase was discarded to remove unreacted starting materials. The water phase was acidified to a pH value of 4 with dilute HCl to give yellow precipitation, which was filtered off, washed with water, and dried in air. This acid can be recrystallized with large amount of alcohol. Yield: 60%, m.p. 206~208 °C. <sup>1</sup>H NMR (DMSO) δ: 8.66, 8.48 (s, s, 1H, 1H, C<sub>5</sub>H<sub>4</sub>N), 7.89 (m, 2H, C<sub>6</sub>H<sub>4</sub>),

7.53~7.24 (m, 4H, C<sub>5</sub>H<sub>4</sub>N and C<sub>6</sub>H<sub>4</sub>), 4.26 (s, 2H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (DMSO) δ: 167.3 (CO<sub>2</sub>H), 150.0, 148.2, 140.2, 136.6, 132.8, 132.3, 130.9, 128.1, 126.0, 124.3, 123.5 (C<sub>5</sub>H<sub>5</sub>N and C<sub>6</sub>H<sub>4</sub>), 32.8 (CH<sub>2</sub>) ppm. IR ν(C=O): 1 696.6 cm<sup>-1</sup>.

### 1.2 Preparation of {[2-(3-PyCH<sub>2</sub>S)C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>SnEt<sub>2</sub>]<sub>2</sub>O]<sub>2</sub> (1)

The mixture of 2-(3-pyridylmethylthio)benzoic acid (1 mmol) and Et<sub>2</sub>SnO (1 mmol) in anhydrous benzene (40 mL) was stirred and heated at reflux for 8 h to yield a clear solution. After removing benzene *in vacuo*, the crude product was recrystallized from benzene/hexane to afford white crystals of **1**. Yield: 40%, m.p. 146~148 °C. <sup>1</sup>H NMR δ: 8.56, 8.41 (s, d, *J*=4.5 Hz, 1H, 1H, C<sub>5</sub>H<sub>4</sub>N), 7.81, 7.66 (d, d, *J*=7.2 Hz, 7.8 Hz, 1H, 1H, C<sub>5</sub>H<sub>4</sub>N and C<sub>6</sub>H<sub>4</sub>), 7.25, 7.19~7.05 (d, *J*=7.2 Hz, m, 1H, 3H, C<sub>5</sub>H<sub>4</sub>N and C<sub>6</sub>H<sub>4</sub>), 4.05 (s, 2H, CH<sub>2</sub>), 1.62~1.51 (m, 4H, SnCH<sub>2</sub>CH<sub>3</sub>), 1.31, 1.25 (t, t, *J*=8.1 Hz, 3H, 3H, SnCH<sub>2</sub>CH<sub>3</sub>) ppm. <sup>13</sup>C NMR δ: 172.9 (COO), 150.2, 148.6, 139.6, 136.4, 132.7, 131.5, 131.2, 128.3, 126.3, 124.5, 123.4 (C<sub>5</sub>H<sub>4</sub>N and C<sub>6</sub>H<sub>4</sub>), 34.7 (CH<sub>2</sub>), 22.9, 21.0 (SnCH<sub>2</sub>CH<sub>3</sub>), 10.0, 9.8 (SnCH<sub>2</sub>CH<sub>3</sub>) ppm. <sup>119</sup>Sn NMR δ: -192.5, -193.3 ppm. IR ν<sub>as</sub>(COO): 1 607, 1 591 cm<sup>-1</sup>, ν<sub>s</sub>(COO): 1 397, 1 340 cm<sup>-1</sup>. Anal. Calcd. for C<sub>34</sub>H<sub>40</sub>N<sub>2</sub>O<sub>5</sub>S<sub>2</sub>Sn<sub>2</sub> (%): C 47.58, H 4.70, N 3.26; found (%): C 47.38, H 4.24, N 3.36.

### 1.3 Preparation of {[2-(PySCH<sub>2</sub>CO<sub>2</sub>)SnEt<sub>2</sub>]<sub>2</sub>O]<sub>2</sub> (2)

The mixture of (2-pyridylthio)acetic acid (1 mmol) and Et<sub>2</sub>SnO (1 mmol) in anhydrous benzene (40 mL) was stirred and heated at reflux for 6 h. After removing benzene *in vacuo*, the crude product was recrystallized from benzene/hexane to afford white crystals of **2**. Yield: 58%, m.p. 122~124 °C. <sup>1</sup>H NMR δ: 8.36 (d, *J*=4.2 Hz, 1H), 7.46 (m, 1H), 7.20 (d, *J*=8.1 Hz, 1H), 6.94 (m, 1H), 3.86 (s, 2H, CH<sub>2</sub>), 1.46~1.36 (m, 4H, SnCH<sub>2</sub>CH<sub>3</sub>), 1.24, 1.22 (t, t, *J*=7.8 Hz, 3H, 3H, SnCH<sub>2</sub>CH<sub>3</sub>) ppm. <sup>13</sup>C NMR δ: 174.5 (COO), 158.1, 149.1, 135.9, 122.3, 119.5 (C<sub>5</sub>H<sub>4</sub>N), 34.3 (CH<sub>2</sub>), 21.9, 19.6 (SnCH<sub>2</sub>CH<sub>3</sub>), 9.8, 9.4 (SnCH<sub>2</sub>CH<sub>3</sub>) ppm. <sup>119</sup>Sn NMR δ: -188.9, -195.9 ppm. IR ν<sub>as</sub>(COO): 1 645, 1 598 cm<sup>-1</sup>, ν<sub>s</sub>(COO): 1 398, 1 332 cm<sup>-1</sup>. Anal. Calcd. for C<sub>22</sub>H<sub>32</sub>N<sub>2</sub>O<sub>5</sub>S<sub>2</sub>Sn<sub>2</sub> (%): C 37.42, H 4.57, N 3.97; found (%): C 37.59, H 4.81, N 3.68.

#### 1.4 Preparation of $\{[(2\text{-PySCH}_2\text{CO}_2)\text{Sn}^n\text{Bu}_2]_2\text{O}\}_2$ (**3**)

The mixture of (2-pyridylthio)acetic acid (1 mmol) and  $^n\text{Bu}_2\text{SnO}$  (1 mmol) in anhydrous benzene (40 mL) was stirred and heated at reflux for 6 h. After removing benzene *in vacuo*, the crude product was recrystallized from hexane to afford white crystals of **3**. Yield: 82%, m.p. 78~80 °C.  $^1\text{H}$  NMR  $\delta$ : 8.35 (d,  $J=4.5$  Hz, 1H), 7.45 (m, 1H), 7.23 (d,  $J=7.8$  Hz, 1H), 6.95 (m, 1H), 3.85 (s, 2H,  $\text{CH}_2$ ), 1.62~1.52, 1.44~1.36, 1.31~1.21 (m, m, m, 4H, 4H, 4H,  $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 0.85, 0.82 (t, t,  $J=7.5$  Hz, 3H, 3H,  $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR  $\delta$ : 174.5 (COO), 158.1, 149.2, 135.8, 122.0, 119.4 ( $\text{C}_5\text{H}_4\text{N}$ ), 34.2 ( $\text{CH}_2$ ), 29.3, 27.6, 27.3, 27.1, 26.9, 26.7, 13.6, 13.5 ( $\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ) ppm.  $^{119}\text{Sn}$  NMR  $\delta$ : -188.0, -196.7 ppm. IR  $\nu_{\text{as}}$  (COO): 1 651, 1 575  $\text{cm}^{-1}$ ,  $\nu_{\text{s}}$  (COO): 1 375, 1 333  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{30}\text{H}_{48}\text{N}_2\text{O}_5\text{S}_2\text{Sn}_2$  (%): C 44.03, H 5.91, N 3.42; found (%): C 43.80, H 5.38, N 3.52.

#### 1.5 Preparation of $[2\text{-(3-PyCH}_2\text{S)}\text{C}_6\text{H}_4\text{CO}_2]\text{SnPh}_3$ (**4**)

The mixture of 2-(3-pyridylmethylthio)benzoic acid (2 mmol) and  $(\text{Ph}_3\text{Sn})_2\text{O}$  (1 mmol) in anhydrous benzene (60 mL) was stirred and heated at reflux for 6 h. After removing benzene *in vacuo*, the crude product was recrystallized from benzene/hexane to afford white crystals of **4**. Yield: 80%, m.p. 148~150 °C.  $^1\text{H}$  NMR  $\delta$ : 8.59, 8.50 (s, d,  $J=4.5$  Hz, 1H, 1H,  $\text{C}_5\text{H}_4\text{N}$ ), 8.12, 7.95~7.70, 7.47~7.16 (d,  $J=7.8$  Hz, m, m, 1H, 8H, 12H,  $\text{C}_5\text{H}_4\text{N}$ ,  $\text{C}_6\text{H}_4$  and  $\text{SnC}_6\text{H}_5$ ), 4.10 (s, 2H,  $\text{CH}_2$ ) ppm.  $^{13}\text{C}$  NMR  $\delta$ : 172.4 (COO), 150.2, 148.6, 140.3, 138.4, 137.3, 137.0, 136.7, 136.6, 132.6, 132.1, 130.2, 128.9, 126.3, 124.6, 123.5 ( $\text{C}_6\text{H}_5$ ,  $\text{C}_5\text{H}_4\text{N}$  and  $\text{C}_6\text{H}_4$ ), 34.7 ( $\text{CH}_2$ ) ppm.  $^{119}\text{Sn}$  NMR

$\delta$ : -108.7 ppm. IR  $\nu_{\text{as}}$  (COO): 1 607  $\text{cm}^{-1}$ ,  $\nu_{\text{s}}$  (COO): 1 340  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{31}\text{H}_{25}\text{NO}_2\text{SSn}$  (%): C 62.65, H 4.24, N 2.36; found (%): C 62.45, H 4.37, N 2.52.

#### 1.6 Preparation of $2\text{-PySCH}_2\text{CO}_2\text{SnPh}_3$ (**5**)

The mixture of (2-pyridylthio)acetic acid (2 mmol) and  $(\text{Ph}_3\text{Sn})_2\text{O}$  (1 mmol) in anhydrous benzene (60 mL) was stirred and heated at reflux for 6 h. After removing benzene *in vacuo*, the crude product was recrystallized from benzene/hexane to afford white powders of **5**. Yield: 81%, m.p. 106~108 °C.  $^1\text{H}$  NMR  $\delta$ : 8.11 (d,  $J=5.1$  Hz, 1H,  $\text{C}_5\text{H}_4\text{N}$ ), 7.77~7.59, 7.42~7.37 (m, m, 6H, 10H,  $\text{C}_5\text{H}_4\text{N}$  and  $\text{SnC}_6\text{H}_5$ ), 7.18 (d,  $J=8.1$  Hz, 1H,  $\text{C}_5\text{H}_4\text{N}$ ), 6.89~6.85 (m, 1H,  $\text{C}_5\text{H}_4\text{N}$ ), 4.03 (s, 2H,  $\text{CH}_2$ ) ppm.  $^{13}\text{C}$  NMR  $\delta$ : 175.6 (COO), 157.5, 149.2, 138.0, 136.9, 135.8, 130.2, 128.9, 121.9, 119.4 ( $\text{C}_5\text{H}_4\text{N}$  and  $\text{C}_6\text{H}_5$ ), 32.8 ( $\text{CH}_2$ ) ppm.  $^{119}\text{Sn}$  NMR  $\delta$ : -102.0 ppm. IR  $\nu_{\text{as}}$  (COO): 1 635  $\text{cm}^{-1}$ ,  $\nu_{\text{s}}$  (COO): 1 334  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{25}\text{H}_{21}\text{NO}_2\text{SSn}$  (%): C 57.94, H 4.08, N 2.70; found (%): C 57.56, H 4.35, N 2.89.

#### 1.7 Crystal structure determinations

Crystals of **2** and **4** suitable for X-ray analyses were obtained by slowly cooling their hot benzene/hexane solutions. The diffraction data were collected with a Bruker SMART APEX CCD diffractometer, using graphite monochromatized Mo  $K\alpha$  radiation ( $\lambda=0.071$  073 nm). The structures were resolved by the direct method using SHELXS-97 program. All non-hydrogen atoms were refined on  $F^2$  anisotropically by full-matrix least-squares method. Hydrogen atoms were located from the difference Fourier map and added to the structure calculations. A summary of the fundamental crystal data for these two complexes is listed in Table 1.

CCDC: 685778, **2**; 685777, **4**.

Table 1 Crystallographic data and refinement parameters for complexes **2** and **4**

Complex	<b>2</b>	<b>4</b>
Formula	$\text{C}_{44}\text{H}_{64}\text{N}_4\text{O}_{10}\text{S}_4\text{Sn}_4$	$\text{C}_{31}\text{H}_{25}\text{NO}_2\text{SSn}$
Formula weight	1411.99	594.27
Crystal size / mm	0.20×0.14×0.12	0.26×0.20×0.14
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
$a$ / nm	0.897 7(1)	1.026 8(1)
$b$ / nm	1.339 7(2)	1.215 1(2)
$c$ / nm	1.345 9(2)	1.218 7(2)

Continued Table 1

$\alpha / (^{\circ})$	63.724(2)	98.805(3)
$\beta / (^{\circ})$	77.357(2)	98.287(3)
$\gamma / (^{\circ})$	70.660(2)	112.504(3)
$V / \text{nm}^3$	1.364 5(4)	1.353 5(4)
$Z$	1	2
$T / \text{K}$	294(2)	293(2)
$D_{\text{calc}} / (\text{g} \cdot \text{cm}^{-3})$	1.718	1.458
$2\theta \text{ range} / (^{\circ})$	3.38~50.04	3.46~52.80
$F(000)$	700	600
$\mu / \text{mm}^{-1}$	2.017	1.049
Number of reflections measured	7 108	7 666
Number of reflections unique ( $R_{\text{int}}$ )	4 773 (0.022 6)	54 38 (0.021 2)
Number of reflections observed [ $I \geq 2\sigma(I)$ ]	3 646	4 233
Number of parameters	302	325
Residuals $R$ , $wR$ [ $I \geq 2\sigma(I)$ ]	0.031, 0.066	0.037, 0.082
Goodness-of-fit	1.018	1.021

## 2 Results and discussion

### 2.1 Synthesis and characterization

Reaction of 2-(3-pyridylmethylthio)benzoic acid or (2-pyridylthio)acetic acid with  $\text{R}_2\text{SnO}$  ( $\text{R}=\text{Et}$  or  $^n\text{Bu}$ ) in a 1:1 molar ratio in anhydrous benzene yields dimeric complexes  $\{[2-(3-\text{PyCH}_2\text{S})\text{C}_6\text{H}_4\text{CO}_2\text{SnEt}_2]_2\text{O}\}_2$  (**1**) and  $\{[(2-\text{PySCH}_2\text{CO}_2)\text{SnR}_2]_2\text{O}\}_2$  ( $\text{R}=\text{Et}$  (**2**) and  $^n\text{Bu}$  (**3**);  $\text{Py}=\text{pyridyl}$ ), which have been characterized by IR and NMR spectra as well as elemental analyses. The NMR spectra of these three complexes support the suggested structures as dimeric distannoxanes. For example, their  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra exhibit two sets of ethyl signals for **1** and **2** as well as butyl signals for **3**, respectively. Furthermore, their  $^{119}\text{Sn}$  spectra also show the presence of endo- and exo-cyclic tin atoms. A pair of resonances of equal intensities is observed at 192.5 and 193.3 ppm for **1**, -188.9 and -195.9 ppm for **2** as well as -188.0 and -196.7 ppm for **3**, respectively, which are comparable with the reported values for other dimeric distannoxanes<sup>[12,13,15]</sup>.

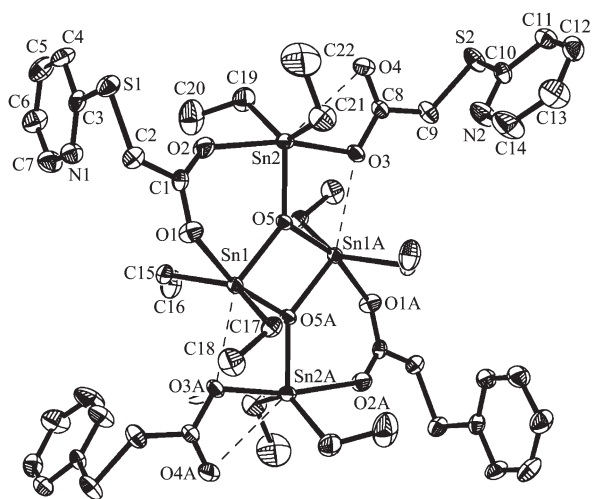
Upon treatment of 2-(3-pyridylmethylthio)benzoic acid or (2-pyridylthio)acetic acid with  $(\text{Ph}_3\text{Sn})_2\text{O}$  in a 2:1 molar ratio, complexes  $[2-(3-\text{PyCH}_2\text{S})\text{C}_6\text{H}_4\text{CO}_2]\text{SnPh}_3$  (**4**) and  $2-\text{PySCH}_2\text{CO}_2\text{SnPh}_3$  (**5**) are obtained. Their IR and NMR spectra are also consistent with the suggested structures. For instance, the  $^{119}\text{Sn}$  NMR spectra of these

two complexes display only one resonance at -108.7 ppm for **4** and -102.0 ppm for **5**, respectively, which are very close to these values reported in the corresponding four-coordinated triphenyltin carboxylates, such as -103.44 ppm in  $2-(2-\text{PyCH}_2\text{S})\text{C}_6\text{H}_4\text{CO}_2\text{SnPh}_3$ <sup>[13]</sup> and -105.97 ppm in  $\text{Ph}_3\text{SnO}_2\text{CCH}_2\text{CH}_2\text{COC}_6\text{H}_4\text{C}_6\text{H}_5$ <sup>[16]</sup>.

### 2.2 Crystal structures of **2** and **4**

To verify the role of these heteroatoms in the carboxylate ligands, the structures of **2** and **4** have also been confirmed further by X-ray crystal structure determination. The molecular structure of **2** is presented in Fig.1, to a first approximation, the fundamental molecular skeleton of **2** is similar with that of  $\{[(4-\text{PyCH}_2\text{S})\text{C}_6\text{H}_4\text{CO}_2\text{SnEt}_2]_2\text{O}\}_2$ <sup>[13]</sup>. For instance, they both have tetranuclear distannoxane structures, and the pyridyl nitrogen atoms do not coordinate to the tin atoms in these two complexes. On the other hand, some noticeable differences exist between these two complexes. Two tin atoms in **2** have the same coordination mode, a five-coordinate distorted trigonal bipyramidal geometry. While in  $\{[(4-\text{PyCH}_2\text{S})\text{C}_6\text{H}_4\text{CO}_2\text{SnEt}_2]_2\text{O}\}_2$ , one tin atom adopts a five-coordinate distorted trigonal bipyramidal geometry, and the other is in a six-coordinate distorted octahedral geometry. The coordination modes of the crystallographically unique carboxylic ligands are also different in these two compounds. In

**2**, one carboxylic ligand acts as a mono-dentate ligand by the carboxylate oxygen, while the other is a bridging bidentate ligand by two oxygen atoms of the carboxyl group. In  $\{[(4\text{-PyCH}_2\text{S})\text{C}_6\text{H}_4\text{CO}_2\text{SnEt}_2]_2\text{O}\}_2$ , one carboxylic ligand acts as a bidentate bridging ligand, while the other is a bidentate chelating ligand. In addition, some weak intramolecular  $\text{Sn}\cdots\text{O}$  interactions are also observed in **2**. The  $\text{Sn}\cdots\text{O}$  distances ( $\text{Sn}(1)\cdots\text{O}(3\text{A})$  0.272 0(2) nm,  $\text{Sn}(2)\cdots\text{O}(4)$  0.286 2(2) nm) are significantly shorter than the sum of the van der Waals radii for the Sn and O atom of 0.357 nm<sup>[17]</sup>. These values are also comparable to the corresponding  $\text{Sn}\cdots\text{O}$  distances in  $\{[(4\text{-PyCH}_2\text{S})\text{C}_6\text{H}_4\text{CO}_2\text{SnEt}_2]_2\text{O}\}_2$ <sup>[13]</sup>.



Hydrogen atoms are omitted for clarity

Selected bond distances (nm) and angles (°):

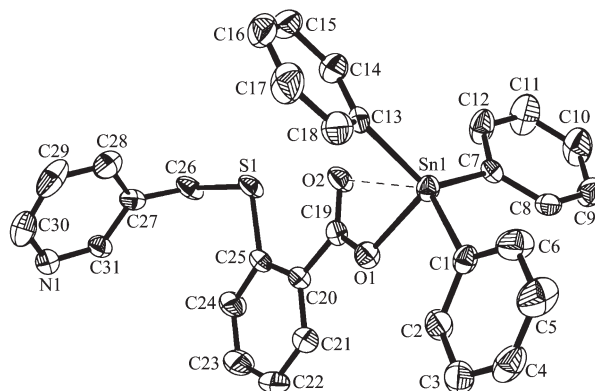
$\text{Sn}(1)\cdots\text{O}(1)$ 0.232 6(3),	$\text{Sn}(1)\cdots\text{O}(5)$ 0.204 8(3),
$\text{Sn}(1)\cdots\text{O}(5\text{A})$ 0.215 2(3),	$\text{Sn}(2)\cdots\text{O}(2)$ 0.223 4(3),
$\text{Sn}(2)\cdots\text{O}(3)$ 0.218 0(3),	$\text{Sn}(2)\cdots\text{O}(5)$ 0.202 0(3),
$\text{C}(1)\cdots\text{O}(1)$ 0.125 1(5),	$\text{C}(1)\cdots\text{O}(2)$ 0.124 3(5),
$\text{C}(8)\cdots\text{O}(3)$ 0.128 3(5),	$\text{C}(8)\cdots\text{O}(4)$ 0.122 5(5),
$\text{Sn}(1\text{A})\cdots\text{O}(5)$ 0.215 2(3),	$\text{Sn}(1)\cdots\text{O}(3\text{A})$ 0.272 0(2),
$\text{Sn}(2)\cdots\text{O}(4)$ 0.286 2(2)	
$\text{O}(1)\cdots\text{C}(1)\cdots\text{O}(2)$ 124.1(4),	$\text{O}(3)\cdots\text{C}(8)\cdots\text{O}(4)$ 122.5(5),
$\text{O}(1)\cdots\text{Sn}(1)\cdots\text{O}(5)$ 91.3(1),	$\text{O}(1)\cdots\text{Sn}(1)\cdots\text{O}(5\text{A})$ 165.9(1),
$\text{O}(5)\cdots\text{Sn}(1)\cdots\text{O}(5\text{A})$ 75.5(1),	$\text{O}(2)\cdots\text{Sn}(2)\cdots\text{O}(3)$ 167.1(1),
$\text{O}(3)\cdots\text{Sn}(2)\cdots\text{O}(5)$ 78.8(1),	$\text{C}(1)\cdots\text{O}(1)\cdots\text{Sn}(1)$ 128.5(3),
$\text{C}(1)\cdots\text{O}(2)\cdots\text{Sn}(2)$ 136.9(3),	$\text{C}(8)\cdots\text{O}(3)\cdots\text{Sn}(2)$ 109.6(3),
$\text{Sn}(1)\cdots\text{O}(5)\cdots\text{Sn}(1\text{A})$ 104.5(1),	$\text{Sn}(2)\cdots\text{O}(5)\cdots\text{Sn}(1)$ 135.0(1),
$\text{Sn}(2)\cdots\text{O}(5)\cdots\text{Sn}(1\text{A})$ 120.0(1)	

Symmetry code: A:  $-x, -y, 1-z$

Fig.1 Molecular structure of **2** with the thermal ellipsoids at the 30% probability level

The molecular structure of **4** is presented in Fig.2.

Like that in **2** and  $2\text{-PyCH}_2\text{SC}_6\text{H}_4\text{CO}_2\text{SnPh}_3$ , the pyridyl nitrogen atom does not coordinate to the tin atom. The tin atom is in a distorted tetrahedral geometry, and the carboxylate group acts as unidentate ligand. However, complex **4** forms a linkage coordination polymer through the intermolecular  $\text{Sn}\cdots\text{N}$  and  $\text{S}\cdots\text{S}$  interactions as shown in Fig.3. The  $\text{Sn}\cdots\text{N}$  distance is 0.295 5(1) nm, markedly longer than those in  $2\text{-PyCH}_2\text{SC}_6\text{H}_4\text{CO}_2\text{SnPh}_3$



Hydrogen atoms are omitted for clarity

Selected bond distances (nm) and angles (°):

$\text{Sn}(1)\cdots\text{O}(1)$ 0.208 9(2),	$\text{Sn}(1)\cdots\text{O}(2)$ 0.297 4(5),
$\text{C}(19)\cdots\text{O}(1)$ 0.129 9(4),	$\text{C}(19)\cdots\text{O}(2)$ 0.122 8(4),
$\text{S}(1)\cdots\text{C}(25)$ 0.177 2(4),	$\text{S}(1)\cdots\text{C}(26)$ 0.182 9(4),
$\text{O}(1)\cdots\text{Sn}(1)\cdots\text{C}(1)$ 93.24(12),	$\text{C}(7)\cdots\text{Sn}(1)\cdots\text{C}(1)$ 113.70(13),
$\text{C}(13)\cdots\text{Sn}(1)\cdots\text{C}(1)$ 111.18(14),	$\text{C}(25)\cdots\text{S}(1)\cdots\text{C}(26)$ 104.08(17),
$\text{C}(19)\cdots\text{O}(1)\cdots\text{Sn}(1)$ 115.1(2),	$\text{O}(1)\cdots\text{C}(19)\cdots\text{O}(2)$ 122.6(3)

Fig.2 Molecular structure of **4** with the thermal ellipsoids at the 30% probability level

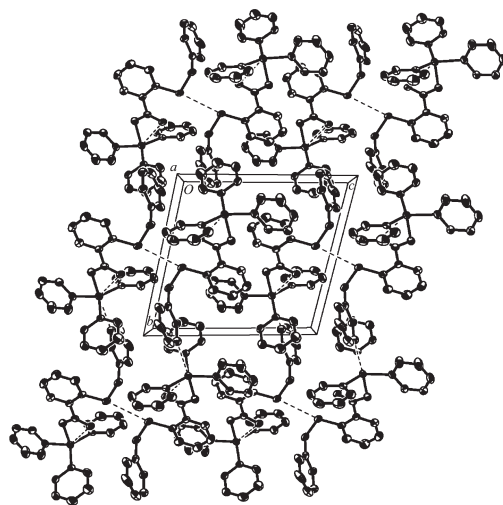


Fig.3 Crystal packing diagram of complex **4** emphasizing the intermolecular  $\text{Sn}\cdots\text{N}$  and  $\text{S}\cdots\text{S}$  interactions ( $\text{Sn}\cdots\text{N}^{\text{i}}=0.295\ 5(1)$  nm and  $\text{S}\cdots\text{S}^{\text{ii}}=0.330\ 3(1)$  nm; symmetry code: <sup>i</sup>  $x, -1+y, z$ ; <sup>ii</sup>  $-x, 1-y, -z$ ) and the one-dimensional chain



(0.252 4(2) nm)<sup>[13]</sup> and other related polymeric triphenyltin derivatives containing pyridyl carboxylate ligands, such as 4-PyCO<sub>2</sub>SnPh<sub>3</sub> (0.251 2(6) nm)<sup>[18,19]</sup>, indicating that this interaction is very weak. In fact, the <sup>119</sup>Sn NMR chemical shift of **4** is very close to these values reported in the corresponding four-coordinated triphenyltin carboxylates, suggesting that this interaction does not exist in solution. Similar results have been extensively observed in other polymeric or oligomeric organotin derivatives<sup>[20]</sup>.

### 2.3 Fungicidal activity

Preliminary *in vitro* tests for fungicidal activity of complexes **1**~**5** have been carried out by the fungi

growth inhibition method<sup>[13]</sup>. The data are summarized in Table 2, showing that complexes **3** and **4** display high activity to *Colletotrichum lagenarium*, *Cercospora arachidicola* and *Physalospora piricola* in a low concentration. The inhibition percentage of **3** *in vitro* for *Colletotrichum lagenarium*, *Cercospora arachidicola* and *Physalospora piricola* is 90.5%, 88.2% and 97.1%, respectively, while in **4** the corresponding value is 95.2%, 94.1% and 97.1%, respectively. Moreover, these two complexes are more active than the corresponding organotin carboxylates of 2-(2-pyridylmethylthio)benzoic and 2-(4-pyridylmethylthio)benzoic acids<sup>[13]</sup>.

Table 2 Fungicidal activities of complexes 1~5

Complex	Inhibition ratio (%) (50 μg·mL <sup>-1</sup> ) in DMF				
	1	2	3	4	5
<i>Fusarium oxysporum</i>	4.2	0.0	62.5	62.5	33.3
<i>Alternaria solani</i>	7.0	7.0	72.1	72.1	7.0
<i>Colletotrichum lagenarium</i>	19.1	42.9	90.5	95.2	23.8
<i>Cercospora arachidicola</i>	41.2	23.5	88.2	94.1	23.5
<i>Physalospora piricola</i>	58.8	29.4	97.1	97.1	20.6

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