

三邻氯苄基锡-2-吲哚甲酸酯的合成、谱学性质和晶体结构

尹汉东* 王其宝 薛绳才
(聊城大学化学化工学院, 聊城 252059)

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Synthesis, Spectroscopic Properties and Structural Characterization of Tri(*o*-chlorobenzyl)tin Ester of 2-indolylcarboxylic Acid

YIN Han-Dong* WANG Qi-Bao XUE Sheng-Cai
(Department of Chemistry, Liaocheng University, Liaocheng 252059)

The tri (*o*-chlorobenzyl)tin ester of 2-indolylcarboxylic acid has been synthesized and characterized by elemental analysis, IR and ¹H NMR. The crystal structure has been determined by X-ray single crystal diffraction. The crystal belongs to triclinic with space group $P\bar{1}$, $a=1.020\ 0(16)$ nm, $b=1.125\ 9(18)$ nm, $c=1.321(2)$ nm, $\alpha=83.10(2)^\circ$, $\beta=67.597(18)^\circ$, $\gamma=84.83(2)^\circ$, $Z=2$, $V=1.391(4)$ nm³, $D_x=1.565$ Mg·m⁻³, $\mu=1.235$ mm⁻¹, $F(000)=656$, $R=0.049\ 2$, $wR=0.131\ 4$. In this compound, the central tin atom is rendered four-coordinated in a tetrahedral structure. The resulting structure is a monomer containing Sn-O bond length of 0.205 4(4) nm. CCDC: 236286.

Keywords: tri(2-chlorobenzyl)tin 2-indolylcarboxylic acid synthesis crystal structure

0 Introduction

Organotin esters of carboxylic acid are widely used as biocides, fungicides and in industry as homogeneous catalysts^[1-4]. In recent years, several reports of the synthesis, antitumour activities, biocidal activities, antibioic activities and structural elucidation of various organotin derivatives of carboxylic acid have appeared, revealing new structural possibilities^[5,6]. In general, the biocidal activity of organotin compounds is greatly influenced by the structure of the molecule and the coordination number of the tin atoms^[7,8]. Studies on organotin compounds containing carboxylate

ligands with additional donor atom (e. g. N, O or S) that are available for coordinating to tin atom, have revealed that new structural types may lead to different activities^[9,10]. In order to continue exploring of relationships between the biological activity and structure, we report the novel compound tri(*o*-chlorobenzyl)tin ester of 2-indolylcarboxylic acid. The elemental analysis, IR and ¹H NMR spectroscopic characterization and crystal structure of the new compound have been carried out. And the results of this study are reported herein.

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* 通讯联系人。E-mail:handongyin@lctu.edu.cn

第一作者:尹汉东,男,47岁,教授;研究方向:金属有机化学。

1 Experimental

1.1 General Comments

All reactants were reagent grade. IR spectra were recorded on a Nicolet-460 spectrophotometer, by using KBr as discs. ^1H NMR spectra were obtained with Mercury Plus-400 NMR spectrometer and the chemical shifts are given in ppm relative to Me_4Si in CDCl_3 . Elemental analyses were performed on PE-2400-II elemental analyzer. Tin was estimated as SnO_2 . X-ray measurements were made on a Bruker Smart-1000 CCD diffractometer with graphite monochromated $\text{MoK}\alpha$ (0.071 073 nm) radiation.

1.2 Synthesis

A mixture of bis[tri(*o*-chlorobenzyl)tin] oxide (1.0 mmol) and 2-indolylcarboxylic acid (2.0 mmol) was heated under reflux with stirring for 7 h in dry benzene. The water liberated was removed azeotropically by use of a Dean-Stark apparatus. The clear solution obtained after filtration was evaporated in vacuum to give a white solid. The products were recrystallized from dichloromethane-hexane to give a colorless crystals 1.07 g, yield 82%, 106~108 $^\circ\text{C}$, IR (KBr) ν : 3 445, 1 613, 1 385, 476, 434 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ : 8.58(1H, s, N-H), 7.68~7.18(5H, m, indole-H), 7.16(12H, m, Ar-H), 2.84(6H, t, $J_{\text{Sn-H}}=70.86$, ArCH_2Sn). Anal. Calcd for $\text{C}_{30}\text{H}_{24}\text{Cl}_3\text{NO}_2\text{Sn}$ (%): C 54.96, H 3.69, N 2.14, Sn 18.10; Found: C 54.82, H 3.66, N 2.12, Sn 18.35.

1.3 Crystallographic Measurements

An colorless crystal having approximate dimensions of $0.49 \times 0.37 \times 0.22 \text{ mm}^3$ was selected for the experiment in a glass capillary. X-ray diffraction were performed on a Bruker Smart-1000 CCD diffractometer with graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda=0.071\ 073 \text{ nm}$) at 298(2) K and the ϕ - ω scan technique. A total of 7 020 reflections were collected in

the range of $1.67^\circ < \theta < 25.03^\circ$ and 4 810 reflections were independent ($R_{\text{int}}=0.046\ 7$), of which 4 223 reflections were observed ($I>2\sigma(I)$). The crystal belongs to triclinic with space group $P\bar{1}$, $a=1.020\ 0(16) \text{ nm}$, $b=1.125\ 9(18) \text{ nm}$, $c=1.321\ (2) \text{ nm}$, $\alpha=83.10(2)^\circ$, $\beta=67.597(18)^\circ$, $\gamma=84.83(2)^\circ$, $Z=2$, $V=1.391(4) \text{ nm}^3$, $D_x=1.565 \text{ Mg}\cdot\text{m}^{-3}$, $\mu=1.235 \text{ mm}^{-1}$, $F(000)=656$. The structure was solved by direct method and difference Fourier syntheses by using SHELXL-97 program, and refined by full-matrix least-squares on F^2 . All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added according to theoretical models. The weighting scheme was $w=1/[S^2(F_o^2)+(0.102\ 2P)^2+0.187\ 9P]$ where $P=(F_o^2+2F_c^2)/3$. The refinement was converged to the final $R=0.049\ 2$, $wR=0.131\ 4$ ($I\geq 2\sigma(I)$), $(\Delta/\sigma)_{\text{max}}=0.000$ and $S=1.037$. The largest difference peak and hole were $1.148 \times 10^3 \text{ e}\cdot\text{nm}^{-3}$ and $-1.485 \times 10^2 \text{ e}\cdot\text{nm}^{-3}$, respectively.

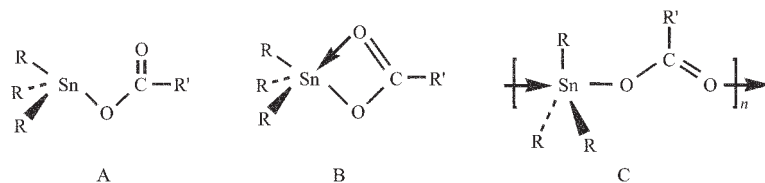
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2 Results and Discussion

2.1 IR Spectra

The assignment of IR bands of this compound has been determined by comparison with the IR spectra of related organotin compounds, 2-indolylcarboxylic acid and bis[tri(*o*-chlorobenzyl)tin] oxide. It is to note that the difference $\Delta\nu$ between $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ is important because these frequencies can be used to determine the type of bonding between metal and carboxyl^[1,12]. Generally triorganotin esters of carboxylic acid adopt three types of structures in the solid state (A, B and C) (as shown in Scheme 1).

The magnitude of $\Delta\nu$ [$\nu_{\text{as}}(\text{COO})-\nu_{\text{s}}(\text{COO})$] of 228 cm^{-1} for the compound is much greater than that of the corresponding sodium of carboxylic acid. This information indicates the presence of monodentate carboxylate groups^[1-4,13,14]. The appearance of the signal at



Scheme 1

3 432~3 445 cm^{-1} as N-H vibration shows that the indole nitrogen have no significant interaction with the tin atom.

2.2 ^1H NMR Spectra

The chemical shifts of the protons on the *o*-chlorobenzyl groups of the compound exhibit two suit signals about 7.01~7.16 ppm as multiplet and about 2.84 ppm as a triplet which are caused by the tin (^{119}Sn)-hydrogen coupling, the spin-spin coupling constant $J_{\text{Sn-H}}$ is equal 70.86 Hz.

The chemical shift of the protons of indolyl group of compound exhibit signals at 7.18~8.58 ppm as multiplet. This is similar to that of the free 2-indolyl-carboxylic acid. This finding may be consistent with previous conclusion, which suggest that only pyridine type N atoms, present in the carboxylate R' group, coordinate to Sn, but there is no evidence of intra- or inter-molecular coordination to Sn by the S, O or N atoms of the thiophenyl, furanyl and indolyl groups^[10]. In addition, the presence of the N-H proton signal in this compound strongly supports the indolyl group N atom in no coordination to Sn.

2.3 Crystal and Molecule Structure

The selected bond distances and angles are collected in Table 1. The crystal structure and crystal packing of are shown in Fig.1 and 2 respectively.

The molecular structure of compound for tri(*o*-chlorobenzyl)tin ester of 2-indolylcarboxylic acid is shown in Fig.1. Fig.2 shows the packing of the molecules in the unit cell as seen in projection on the plane. Selected bond distances and angles are listed in Table 1.

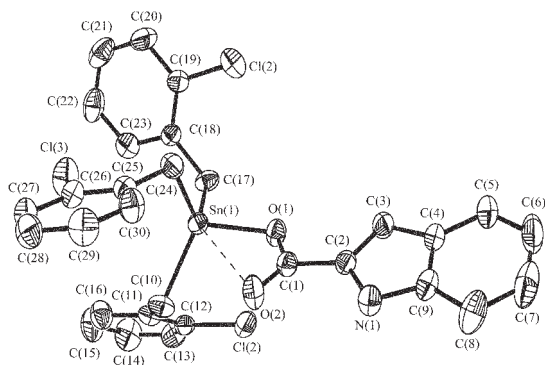


Fig.1 Molecular structure of compound

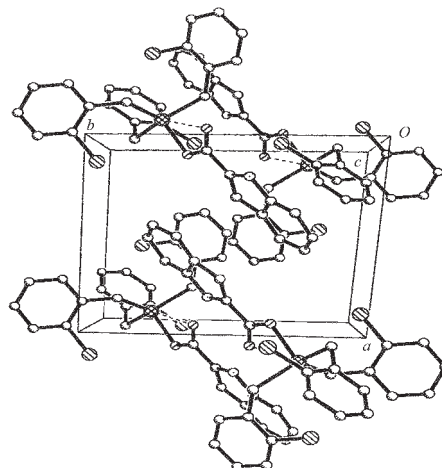


Fig.2 Projection of the unit cell of compound

Table 1 Selected Bond Distances (nm) and Angles ($^{\circ}$) for Compound

Sn(1)-O(1)	0.205 4(4)	Sn(1)-O(2)	0.295 6(5)
Sn(1)-C(24)	0.213 0(5)	O(1)-C(1)	0.129 9(6)
Sn(1)-C(10)	0.214 4(5)	O(2)-C(1)	0.120 9(6)
Sn(1)-C(17)	0.215 1(5)	C(1)-C(2)	0.147 6(7)
O(1)-Sn(1)-C(24)	99.8(2)	C(24)-Sn(1)-O(2)	82.8(2)
O(1)-Sn(1)-C(10)	111.8(2)	C(10)-Sn(1)-O(2)	81.4(2)
C(24)-Sn(1)-C(10)	118.5(2)	C(17)-Sn(1)-O(2)	146.29(17)
O(1)-Sn(1)-C(17)	98.5(2)	C(1)-O(1)-Sn(1)	114.5(3)
C(24)-Sn(1)-C(17)	114.0(2)	C(1)-O(2)-Sn(1)	73.1(3)
C(10)-Sn(1)-C(17)	111.6(2)	O(2)-C(1)-O(1)	123.7(4)
O(1)-Sn(1)-O(2)	48.40(13)		

Compound adopts monomeric structures with the tin atom four-coordinated in a tetrahedral structure. One oxygen atom and three carbon atoms respectively take up the four apical positions. The nitrogen atom of the indolyl group has no coordination to the tin atom, which was confirmed by the IR and ^1H NMR analyses showing above. The structure is similar to the compound $\text{Ph}_3\text{SnO}_2\text{CC}_4\text{H}_3\text{S}^{[15]}$ and $\text{Ph}_3\text{SnO}_2\text{CC}_3\text{HSN}^{[16]}$, but is different from compounds tri(*o*-fluorobenzyl)tin esters of 4-pyridinecarboxylic acid, 3-pyridinecarboxylic acid^[14] and tributyltin ester of 3-indolmethylcarboxylic acid^[17].

The basic structure of this compound, results from a distortion from tetrahedral geometry induced by the approach of an oxygen atom, O(2), of the carboxylate group at a tetrahedral face opposite one of the tin *o*-chlorobenzyl groups. The distortion is toward a trigo-

nal bipyramid that contains O(2) and the latter *o*-chlorobenzyl group at axial sites. The axial Sn(1)···O(2) (0.295 6(5) nm) length is considerably longer than the equatorial Sn(1)-O(1) (0.205 4(4) nm) bond length. On the basis of such interaction, the C(24)-Sn(1)-O(1) (99.8(2)°) angle significantly deviates from the ideal tetrahedral angle. However, other angles around the central Sn atom are comparable to tetrahedral angle.

In addition, a hydrogen bond was formed between the N(1) and the intermolecular O(2) atoms of the carboxylate group. The distance of the hydrogen bond is 0.299 5 nm, the angle of N(1)-H(1)···O(2i) is 158.8° and the symmetry transformation used to generate the O(2i) atom is: $2-x, 1-y, -z$.

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