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氧化-4-吡啶甲酸桥联的一维链状三丁基锡配合物的合成与晶体结构

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摘要:利用双三丁基氧化锡与氧化-4-吡啶甲酸($HOCOC_5H_4NO$)以物质的量比 1:2 反应,合成了有机锡配合物$[Bu_3Sn(OCOC_5H_4NO)]_n$。通过元素分析、红外光谱和核磁共振氢谱对其结构进行了表征,用 X 射线单晶衍射测定了它的晶体结构。结果表明,该配合物晶体属单斜晶系,空间群为 $C2/c$, 晶胞参数 a=2.002 8(9) nm,b=1.224 7(6) nm,c=1.913 6(12) nm,β=119.145(6)°,Z=8,V=4.166(4) nm^3,D_c=1.365 g·cm^{-3},μ=1.239 mm^{-1},F(000)=1 760,R=0.052 9,wR=0.192 1,GOF=1.013。在配合物中锡原子由氧化-4-吡啶甲酸桥联为五配位的畸变的三角双锥构型。氧化-4-吡啶甲酸配体中 N-O 基团中的氧原子和另一配体中的羧基氧原子与中心锡原子配位,形成无限一维链状有机锡配合物。该配合物具有良好的热稳定性和较高的抗肿瘤活性。

关键词:有机锡配合物;氧化-4-吡啶甲酸;合成;晶体结构
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Synthesis and Crystal Structure of the One-Dimensional Chain Tributyltin Compound Bridged by Pyridine-4-carboxylic Acid *N*-Oxide

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Abstract: An organotin compound $[Bu_3Sn(OCOC_5H_4NO)]_n$ has been synthesized by the reaction of bistributyltin oxide with pyridine-4-carboxylic acid *N*-oxide ($HOCOC_5H_4NO$) in molar ratio of 1:2 and characterized by elemental analysis, IR and ^{1}H NMR. The crystal structure has been determined by X-ray single crystal diffraction. The crystal belongs to monoclinic space group $C2/c$, with a=2.002 8(9) nm, b=1.224 7(6) nm, c=1.913 6(12) nm, β=119.145(6)°, Z=8, V=4.166(4) nm^3, D_c=1.365 g·cm^{-3}, μ=1.239 mm^{-1}, F(000)=1 760, R=0.052 9, wR=0.192 1, GOF =1.013. In the compound, tin atoms are five-coordinated distorted trigonal bipyramid configuration with bridging pyridine-4-carboxylic acid *N*-oxide. A one-dimensional linear polymer is formed through an interaction between the central tin atom and two O atoms. One O atom is from N-O and the other is from carboxyl group of another ligand. The compound exhibits good thermal stability and high antitumor activity. CCDC: 821908.

Key words: organotin compound; pyridine-4-carboxylic acid *N*-oxide; synthesis; crystal structure

Organotin carboxylates are widely used as biocides, fungicides and in industry as homogeneous catalysts [1-4]. Organotin carboxylates have been extensively studied during the last decade due to their biological activities including their use as anticancer agents. In the solid state, the structures of most compounds of general formula R_3SnO_2CR' approximate an infinite chain polymer, in which oxygen atoms

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occupy apical positions in a more or less distorted trigonal bipyramid. In different compounds there is a continual graduation of the SnO and CO bond lengths[5]. Studies on organotin compounds containing carboxylate ligands with additional donor atoms (e. g. N, O or S) available for coordinaton to tin atom, have revealed that new structural types may lead to different activities[6-8]. In order to explore whether or not the hetero-atoms (N, O or S) of the carboxylic acid have an effect on the coordination mode and extension of triaryltin (Ⅳ) compounds with heteroatom carboxylate ligands. We have synthesized and structurally chara-cterized an organotin compound $[Bu_3Sn(OCOC_5H_4NO)]_n$, where $HOCOC_5H_4NO$ is pyridine-4-carboxylic acid *N*-oxide, and the results of this study are reported herein.

1 Experimental

1.1 General procedure

All reactants were of analytical grade. The solvents used in this work were dried before use. Infrared spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs. ^{1}H NMR spectra were obtained on a Mercury Plus-400 NMR spectrometer, chemical shifts were given in parts per million relative to Me_4Si in $CDCl_3$ solvent. Elemental analyses were performed with a PE-2400 Ⅱ elemental apparatus. Thermal analyses were performed in nitrogen with a heating rate of 10 ℃·min^{-1} on a Perkin-Elmer Pyris-1 instrument.

1.2 Preparation of the title complex

A mixture of $(Bu_3Sn)_2O$ (0.595 g, 1.0 mmol) and pyridine-4-carboxylic acid *N*-oxide (0.278 g, 2.0 mmol) was heated under reflux in acetonitrile for 5 h. The water liberated was removed azeotropically by use of a Dean-Stark apparatus. The clear solution obtained by filtration was evaporated in vacuum to give a white solid. The product was recrystallized from dichloro-methane-hexane, obtaining colorless crystals: 0.679 g, yield 79.3%. m.p.: 142 ~143 ℃. Anal. Calcd. for $C_{18}H_{31}NO_3Sn$ (M_r=428.13)(%): C, 50.50; H, 7.30; N, 3.27. Found (%): C, 50.45; H, 7.34; N, 3.23. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.81 (2H, d, J=9.4 Hz, 2,6-pyridine-H), 7.97 (2H, d, J=5.6 Hz, 3,5-pyridine-H), 1.83(6H, m, $SnCH_2$),1.35(12H, m, CH_2CH_2), 0.87(9H, t, J=6.7 Hz, CH_3). IR (KBr) ν: 2 962, 2 933 (m, C-H), 1 646, 1 354(s, CO_2), 946(w, N-O), 575(m, Sn-C), 458 (m, Sn-O) cm^{-1}.

1.3 Determination of the crystal structure

A single crystal having approximate dimensions of 0.23 mm×0.16 mm×0.12 mm was mounted in a glass capillary. All measurements were made on a Bruker Smart 1000 CCD diffractometer equipped with a graphite -monochromated Mo $K\alpha$ (λ=0.071 073 nm) radiation at 298 (2) K by using φ-ω scan technique. A total of 10 374 reflections were collected in the range of 2.01°<θ<25.05°, of which 3 667 were independent with R_{int} = 0.023 5. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 with SHELXL program[9]. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were located on the calculated positions and refined isotropically. The final cycle of refinement converged to R=0.052 9, wR=0.192 1 (w=1/[$\sigma^2(F_o^2)$+(0.189 4P)^2+1.896 9P], where P=(F_o^2+2F_c^2)/3), S=1.013, $(\Delta\rho)_{max}$=984 and $(\Delta\rho)_{min}$=−1.460 e·nm^{-3}. Crystallographic data are listed in Table 1. The selected bond lengths and angles for compound **1** are given in Table 2.

CCDC: 821908.

Table 1　Crystallographic data for 1

Empirical formula	$C_{18}H_{31}NO_3Sn$	V / nm^3	4.166(4)
Formula weight	428.13	Z	8
Crystal system	Monoclinic	D_c / (g·cm^{-3})	1.365
Space group	$C2/c$	F(000)	1 760
a / nm	2.002 8(9)	Goodness of fit on F^2	1.013
b / nm	1.247 7(6)	R_1, wR_2 (I>2σ(I))	0.052 9, 0.192 1
c / nm	1.913 6(12)	R_1, wR_2 (All data)	0.064 6, 0.226 4
β / (°)	119.145(6)	$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ / (e·nm^{-3})	984, −1 460

Table 2 Selected bond lengths (nm) and angles (°)

Sn(1)-C(7)	0.215 0(9)	Sn(1)-C(15)	0.209 0(10)	Sn(1)-O(3)	0.244 3(4)
Sn(1)-C(11)	0.211 3(8)	Sn(1)-O(1)^{i}	0.216 2(4)	O(3)-N(1)	0.131 8(7)
C(15)-Sn(1)-C(11)	116.2(3)	C(11)-Sn(1)-O(1)^{i}	96.5(3)	C(7)-Sn(1)-O(3)	87.3(3)
C(15)-Sn(1)-C(7)	116.7(4)	C(7)-Sn(1)-O(1)^{i}	96.1(3)	O(1)^{i}-Sn(1)-O(3)	176.41(19)
C(11)-Sn(1)-C(7)	125.3(4)	C(15)-Sn(1)-O(3)	89.3(4)		
C(15)-Sn(1)-O(1)^{i}	90.2(4)	C(11)-Sn(1)-O(3)	80.6(3)		

Symmetry codes: ^{i} $x+1/2, -y+1/2, z+1/2$; ^{ii} $x-1/2, -y+1/2, z-1/2$.

2 Results and discussion

2.1 IR spectrum

The assignment of IR bands of the title compound has been determined by comparison with the other two compounds: pyridine-4-carboxylic acid *N*-oxide and bistributyltin oxide. It is worth noting that $\Delta\nu$ value between ν_{as}(COO) and ν_{s}(COO) is important because these frequencies can be used to determine the bonding type between metal and carboxyl[10]. Asymmetric stretching vibration peak of carboxyl (ν_{as}(COO)) is located at 1 646 cm^{-1} and the corresponding symmetric one (ν_{s}(COO)) at 1 354 cm^{-1}. The magnitude of $\Delta\nu$(ν_{as}(COO)–ν_{s} (COO)) is above 292 cm^{-1}, thus indicating that the carboxylate ligand functions as a monodentate ligand under the conditions employed[11-13]. The bands in the region of 458 cm^{-1} are assigned to ν(Sn-O). The N-O absorption at 946 cm^{-1} in the complex shifted towards higher frequencies with respect to the corresponding free ligand, which shows that O atom of N-O coordinates to tin atom[14], indicating that the macrocycle is formed through an interaction between the O atoms of N-O and tin atoms of an adjacent molecule.

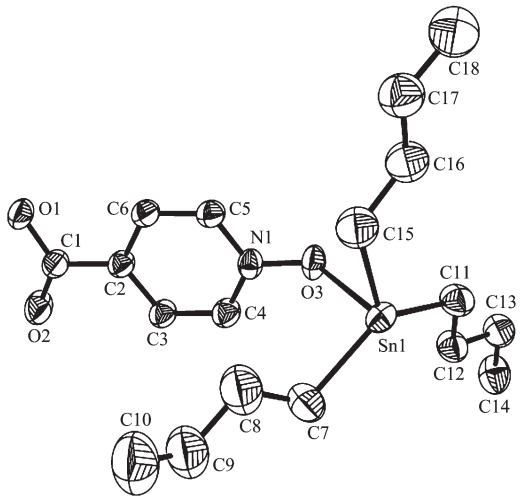
2.2 ^{1}H NMR spectrum

The ^{1}H NMR spectra of the title compound show that the chemical shifts of the protons on the butyl groups exhibit three signals about 1.83 ppm as multiplet, 1.35 ppm as multiplet, and 0.87 ppm as a triplet caused by the tin (^{119}Sn)-hydrogen coupling. The spin-spin coupling constant J_{Sn-H} is equal to 6.7 Hz.

The chemical shift of the protons of pyridine ring exhibits signals at 7.97 or 8.81 ppm as doublet, which are considerably shifted towards higher frequencies with respect to that corresponding free pyridine-4-carboxylic acid *N*-oxide.

2.3 Crystal structure

Unsymmetrical ellipsoid structure and one-dimensional chain structure are illustrated in Fig.1 and 2, respectively.



Probability of ellipsoid is 30%, hydrogen atoms have been omitted for clarity

Fig.1 Unsymmetrical ellipsoid structural unit of the compound

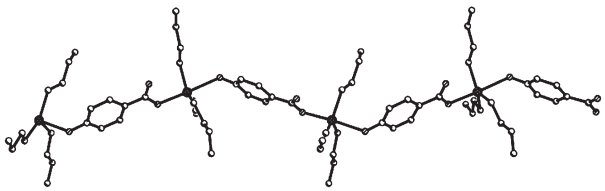


Fig.2 One-dimensional chain structure of the compound

This compound possesses unequivocally polymeric structures, different from compounds [$(PhCH_2)_3Sn(O_2CCH_3)$][15] and [$Ph_3Sn(OCOC_5H_4NO)]_4\cdot 3(CH_2Cl_2)$][16]. Each tin atom is five-coordinated by coordinating to the oxygen atom of carboxyl group from another ligand molecule. The central tin atom is in a distorted trigonal

bipyramidal structure, surrounded axially by one carboxylic oxygen atom as well as one intermolecular oxygen atom of pyridinyl *N*-oxide and equatorial by the α-carbon atoms of the butyl groups.

In the title compound, the Sn(1)-O(1)^{i} bond length is 0.216 2(4) nm, longer than that in $\{[^{n}Bu_2Sn(2\text{-pic})]_2O\}_2$ (0.205 4 nm and 0.211 0 nm)[17] and $[(o\text{-Cl-PhCH}_2)_3SnOCOC_{10}H_8N]\cdot 0.5C_6H_6$ (0.204 3 nm)[18], but shorter than that in $\{[(n\text{-}C_8H_{17})_2Sn(O_2CCH_2CS_2NC_4H_8O)]_2O\}_2$ (0.223 9 nm)[19], similar to that in $[Ph_3Sn(OCOC_5H_4NO)]_n$ (0.217 4 nm)[20]. The Sn(1)-O(2)^{i} distance of 0.304 1 nm is much longer than the sum of the Van der waals′ radii for Sn and O of 0.280 nm. It is shown that the O(2)^{i} atom does not have any significant contact with the Sn(1) atom in this compound. The Sn(1)-O(3) distance of 0.244 3(4) nm is longer than the sum of the covalent radius of Sn and O (0.207 nm), but considerably shorter than the sum of the Van der waals′ radii (0.280 nm), so it should be considered as a bonding interaction. It can be seen from the above data that the two Sn-O bonds fromed by each tin atom and two oxygen atoms are different.

The distortions from ideal trigonal bipyramidal symmetry for the title compound are reflected by the bond angles around the tin atom: C(15)-Sn(1)-O(1)^{i}, C(11)-Sn(1)-O(1)^{i}, C(7)-Sn(1)-O(1)^{i}, C(7)-Sn(1)-O(3), C(15)-Sn(1)-O(3) and C(11)-Sn(1)-O(3) of 90.2(4)°, 96.5(3)°, 96.1(3)°, 87.3(3)°, 89.3(4)° and 80.6(3)°, respectively. The bond angle O(1)^{i}-Sn(1)-O(3) is 176.41(19)° which is deviating from the linear angle by 3.59°, indicating the structure deviates from the true trigonal bipyramidal structure. The sum of the C(7)-Sn(1)-C(15) (116.7(4)°), C(11)-Sn(1)-C(7) (125.3(4)°) and C(15)-Sn(1)-C(11) (116.2(3)°) bond angles is 358.2°, which shows that the atoms of Sn(1), C(7), C(15) and C(11) are almost in the same plane. Therefore the tin atom forms a distorted trigonal bipyramidal structure.

2.3 Thermal stability

To study the stability of the compound, thermogravimetric analysis (TGA) was performed in the temperature range of 30~500 ℃ under N_2 atmosphere. The TGA curve of the compound (Fig.3) exhibits two continuous mass loss stages in the ranges of 180~288 and 288~480 ℃, corresponding to the concomitant release of $3CH_2CH_2CH_3$ and C_5H_4N (obs. 48.30%, calcd. 48.43%), and $3CH_2$ and CO (obs. 16.81%, calcd. 16.35%), respectively. The residual compound is SnO_2 (obs. 34.45%, cald. 35.20%). In general, the compound exhibits good thermal stability.

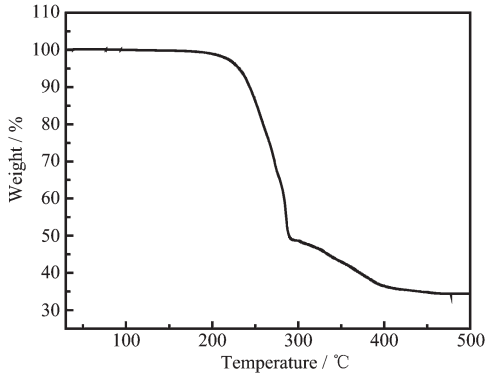


Fig.3　TGA curve of the compound

2.4 Antitumor activity

The antitumor activity was assayed by the SRB methods[21]. The compound was test *in vitro* against to human hepatocellular carcinoma (SMMC-7721) and muose pmh adenomaly (P388), which displayed quite high activity with inhibition value IC_{50} being 18, 31 ng·mL^{-1}, respectively. Compared with the organotin compounds $[(p\text{-}C_8H_8NO_3\text{-}C_6H_4\text{-}COOBu_2Sn)_2O]_2$ and $(p\text{-}C_8H_8NO_3\text{-}C_6H_4\text{-}COO)_2SnBu_2$, the compound possess higher cytotoxicity to tumor cell of P388[22]. *In vitro* biological assays suggest that the compound is still rather active against selected tumor cell lines, and the compound exhibits cytotoxic effects against the two cell lines varying in the order SMMC-7721>P388.

In summary, a one-dimensional linear polymer has been obtained by the reaction of bistributyltin oxide with pyridine-4-carboxylic acid N-oxide. The compound exhibits good thermal stability and high antitumor activity. The successful synthesis of the compound confirms that it is crucial to choose an appropriate ligand for the formation of one-dimensional linear polymers.

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