

Note

Synthesis, Properties and Crystal Structure of Seven-coordinated Organotin Complex [$^n\text{Bu}_2\text{Sn}(\text{OCC}_5\text{H}_4\text{N-2})_2(\text{H}_2\text{O})$]

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A novel seven-coordinated organotin complex [$^n\text{Bu}_2\text{Sn}(\text{OCC}_5\text{H}_4\text{N-2})_2(\text{H}_2\text{O})$] was unexpectedly synthesized by reaction of $^n\text{Bu}_3\text{SnCl}$ with 2-pyridinecarboxylic acid in 1:1 molar ratio in the presence of organic base Et_3N . The crystal structure was determined by single crystal X-ray diffraction analysis. The crystal belongs to rhombohedral with space group $R\bar{3}c$, $a = 1.5807(3)$ nm, $b = 1.5807(3)$ nm, $c = 1.5807(3)$ nm, $\alpha = 105.717(2)^\circ$, $\beta = 105.717(2)^\circ$, $\gamma = 105.717(2)^\circ$, $Z = 6$, $V = 3.397(8)$ nm³, $D_c = 1.452$ g/cm³, $\mu = 1.158$ mm⁻¹, $F(000) = 1512$, $R_1 = 0.0447$, $wR_2 = 0.1038$. In crystal, the tin atoms rendered seven-coordinate in a distorted pentagonal bipyramidal geometry. The two-dimensional network structure was formed by H-bonding interaction between the free oxygen atoms of carboxyl groups and the coordinated water molecules.

Keywords organotin complex, 2-pyridinecarboxylic acid, synthesis, crystal structure

Introduction

Organotin(IV) derivatives of carboxylic acid were extensively studied due to their biological activities.¹⁻⁵ In recent years more and more reports on the synthesis, anti-tumour activities, biocidal activities, antibiotic activities and structural elucidation of various organotin(IV) derivatives of carboxylic acid have appeared.⁶⁻⁹ In particular, people take considerable interest in structural studies of diorganotin(IV) complexes of carboxylic acid, because there are many possible bonding modes between the oxygen atom of carboxyl group and tin atom. Studies on organotin(IV) complexes of carboxylic acid having car-

boxylate ligands with additional donor atom, such as nitrogen, available for coordination to tin atom, have revealed new structural types which may lead to complexes with different activities. We have studied a series of diorganotin(IV) and triorganotin(IV) complexes of carboxylic acids with additional donor atoms.¹⁰⁻¹⁵ In this paper, we report the synthesis resulting from a new debutylation, spectroscopic characterization, antitumor activity and crystal structure of an unexpected complex [$^n\text{Bu}_2\text{Sn}(\text{OCC}_5\text{H}_4\text{N-2})_2(\text{H}_2\text{O})$], which were ascertained whether the N hetero-atoms coordinate to tin atom, and the relationships between their biological activities and structure.

Experimental

Starting materials and instruments

The tributyltin chloride and 2-pyridinecarboxylic acid were of analytical grade. Melting points were determined with a Kofler micro melting point apparatus and the thermometer was uncorrected. IR spectra were recorded on an Nicolet-460 spectrophotometer in KBr. ¹H NMR spectra were measured with a JEOL-FX-90Q spectrometer using TMS as the internal standard and CDCl₃ as the solvent. Elemental analysis was performed on a PE-2400 II elemental analyzer.

Synthesis of complex

A 50-mL flask was charged with 2.0 mmol of 2-

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Received March 18 2002; revised June 3, 2002; accepted July 25, 2002.

Project supported by the Natural Science Foundation of Shandong Province (No. Z2001B02).

pyridinecarboxylic acid, 2.5 mmol of Et_3N , 2.0 mmol of ${}^n\text{Bu}_3\text{SnCl}$ and 25 mL of benzene. The mixture was refluxed for about 2 h. The solvent was evaporated under vacuum to get a white solid. The product was recrystallized from methanol to get colorless crystals. M. p. 123—125 $^\circ\text{C}$; ${}^1\text{H}$ NMR (CDCl_3 , 90 MHz) δ : 8.76 (br, 2H), 8.10 (br, 2H), 7.83 (br, 2H), 7.31 (br, 2H), 1.09—1.50 (m, 12H), 0.70 (t, $J = 7.24$ Hz, 6H); IR (KBr) ν : 3440, 3060, 3024, 2925, 1670, 1386, 562, 490, 445 cm^{-1} . Anal. calcd for $\text{C}_{20}\text{H}_{28}\text{N}_2\text{O}_5\text{Sn}$ ($M_r = 495.13$): C 48.52, H 5.70, N 5.66, Sn 23.97; found C 48.38, H 5.57, N 5.72, Sn 23.77.

Determination of crystal structure

A single crystal having approximate dimensions of 0.30 mm \times 0.25 mm \times 0.15 mm was mounted on a fiber. All measurements were made on a Bruker smart-1000 CCD diffractometer with graphite monochromated Mo K α ($\lambda = 0.071073$ nm) radiation. The data were collected at temperature of 293(2) K to maximum θ value of 25.03 $^\circ$. The crystal belongs to rhombohedral with space group $R\bar{3}c$, $a = 1.5807(3)$ nm, $b = 1.5807(3)$ nm, $c = 1.5807(3)$ nm, $\alpha = 105.717(2)^\circ$, $\beta = 105.717(2)^\circ$, $\gamma = 105.717(2)^\circ$, $Z = 6$, $V = 3.397(8)$ nm 3 , $D_c = 1.452$ g/cm 3 , $\mu = 1.158$ mm $^{-1}$, $F(000) = 1512$. The structure was solved by direct method and expanded using Fourier techniques. The non-hydrogen atoms were refined by full-matrix least-squares calculation to $R_1 = 0.0447$, $wR_2 = 0.1038$ for 1646 independent reflections with $I \geq 2(I)$, $R_{\text{int}} = 0.0618$. In the final difference map, the residuals are 786 and -517 e/nm 3 , respectively.

Results and discussion

Synthesis, IR and ${}^1\text{H}$ NMR spectra

It was expected that ${}^n\text{Bu}_3\text{Sn}(\text{OCC}_5\text{H}_4\text{N}-2)$ was synthesized by reaction of ${}^n\text{Bu}_3\text{SnCl}$ with 2-pyridine carboxylic acid in 1:1 molar ratio in the presence of organic base Et_3N , but an unexpected complex $[{}^n\text{Bu}_2\text{Sn}(\text{OCC}_5\text{H}_4\text{N}-2)_2(\text{H}_2\text{O})]$ was obtained.

The $\nu_{\text{as}}(\text{CO}_2)$ and $\nu_{\text{s}}(\text{CO}_2)$ bands were assigned to the regions of 1670 cm^{-1} and 1386 cm^{-1} , respectively. The magnitude of $\nu[\nu_{\text{as}}(\text{CO}_2) - \nu_{\text{s}}(\text{CO}_2)]$, 274 cm^{-1} , indicated that the carboxylate groups function as mon-

odentate ligands,^{3,4,7} in agreement with the former crystal structure.

In the ${}^1\text{H}$ NMR spectra of the complex, the butyl group appeared a triplet peak (δ 0.70) and a broad multiplet peak (δ 1.09—1.50) owing to the terminal CH_3 of the long alkyl chain and the $(-\text{CH}_2-)_3$ chain respectively.

The values of the chemical shift, δ 7.31—8.76 for the protons of 2-pyridine ring are obviously greater than those of the corresponding free 2-pyridinecarboxylic acid. This finding might be consistent with previous reports^{4,11,14} which suggested that the pyridine N atom, presenting in the carboxylate R group, is coordinated to the Sn atom.

Crystal structure

The molecular structure of $[{}^n\text{Bu}_2\text{Sn}(\text{OCC}_5\text{H}_4\text{N}-2)_2(\text{H}_2\text{O})]$ is shown in Fig. 1 and the selected bond lengths and angles are listed in Table 2. The molecule possesses a monomeric structure, but this structure differs from those of $\text{Me}_2\text{Sn}(2\text{-Pic})_2$ and $\text{Et}_2\text{Sn}(\text{O}_2\text{CC}_4\text{H}_3\text{S})_2$.^{16,17} The tin atom is seven-coordinated in a pentagonal bipyramidal structure. The central tin atom is surrounded equatorially by three oxygen atoms from the two carboxyl groups and the water molecule, two nitrogen atoms from pyridinyl groups and axially by two carbon atoms of the butyl groups. The atoms Sn(1), O(3), O(1), O(1A), N(1) and N(1A) are co-planar (± 0.00177 nm).

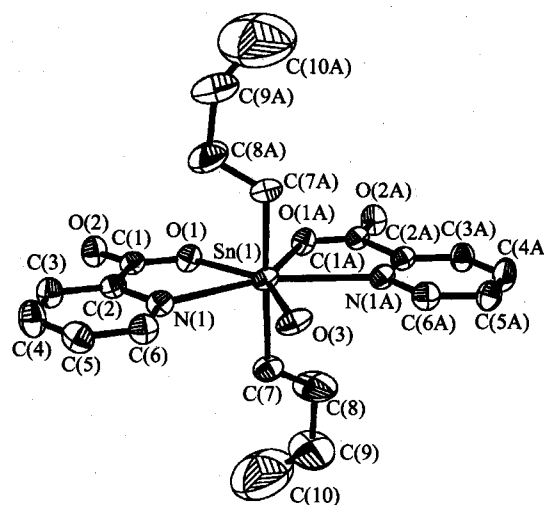


Fig. 1 Molecular structure of $[{}^n\text{Bu}_2\text{Sn}(\text{OCC}_5\text{H}_4\text{N}-2)_2(\text{H}_2\text{O})]$.

Table 1 Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^5$ nm²)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Sn(1)	5700(1)	2714(1)	2286(1)	62(1)	Sn(1)	5700(1)	2714(1)	2286(1)	62(1)
N(1)	8350(4)	4397(4)	3460(4)	66(2)	N(1)	8350(4)	4397(4)	3460(4)	66(2)
O(1)	7993(4)	2791(4)	3778(4)	75(2)	O(1)	7993(4)	2791(4)	3778(4)	75(2)
O(2)	8660(5)	3570(4)	5324(4)	92(2)	O(2)	8660(5)	3570(4)	5324(4)	92(2)
O(3)	7500(1)	3657(3)	1343(3)	84(3)	O(3)	7500(1)	3657(3)	1343(3)	84(3)
C(1)	8405(6)	3550(6)	4513(6)	65(2)	C(1)	8405(6)	3550(6)	4513(6)	65(2)
C(2)	8592(5)	4464(5)	4356(6)	65(2)	C(2)	8592(5)	4464(5)	4356(6)	65(2)
C(3)	9014(7)	5318(6)	5103(7)	83(3)	C(3)	9014(7)	5318(6)	5103(7)	83(3)
C(4)	9190(9)	6107(8)	4904(10)	105(4)	C(4)	9190(9)	6107(8)	4904(10)	105(4)
C(5)	8950(7)	6079(7)	4021(9)	90(3)	C(5)	8950(7)	6079(7)	4021(9)	90(3)
C(6)	8532(7)	5213(7)	3303(8)	80(3)	C(6)	8532(7)	5213(7)	3303(8)	80(3)
C(7)	8819(6)	2740(6)	2182(6)	87(3)	C(7)	8819(6)	2740(6)	2182(6)	87(3)
C(8)	8900(9)	1911(9)	1615(12)	197(7)	C(8)	8900(9)	1911(9)	1615(12)	197(7)
C(9)	9906(11)	2048(15)	1585(17)	238(11)	C(9)	9906(11)	2048(15)	1585(17)	238(11)
C(10)	10750(20)	2410(30)	2400(20)	500(30)	C(10)	10750(20)	2410(30)	2400(20)	500(30)

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

Sn(1)—O(1)	0.2232(5)	Sn(1)—O(1A)	0.2232(5)	Sn(1)—C(7)	0.2126(8)
Sn(1)—C(7A)	0.2126(8)	Sn(1)—O(3)	0.2377(8)	Sn(1)—N(1)	0.2522(6)
Sn(1)—N(1B)	0.2522(6)	N(1)—C(2)	0.1330(9)	N(1)—C(6)	0.1350(10)
O(2)—C(1)	0.1223(9)	O(1)—C(1)	0.1274(9)	C(1)—C(2)	0.1496(10)
O(1A)-Sn(1)-C(7)	95.2(3)	O(1)-Sn(1)-C(7)	91.8(3)	O(1A)-Sn(1)-C(7A)	91.8(3)
C(7)-Sn(1)-C(7A)	171.2(5)	O(1)-Sn(1)-C(7A)	95.2(3)	C(7)-Sn(1)-O(3)	85.6(2)
O(3)-Sn(1)-C(7A)	85.6(2)	O(1A)-Sn(1)-O(3)	143.02(14)	O(1)-Sn(1)-O(3)	143.02(14)
C(7)-Sn(1)-N(1A)	89.9(3)	C(7A)-Sn(1)-N(1A)	87.9(3)	O(1)-Sn(1)-N(1A)	141.7(2)
O(1A)-Sn(1)-N(1A)	67.78(19)	O(3)-Sn(1)-N(1A)	75.26(14)	C(7A)-Sn(1)-N(1)	89.9(3)
O(1A)-Sn(1)-N(1)	141.7(2)	C(7)-Sn(1)-N(1)	87.9(3)	O(1)-Sn(1)-N(1)	67.78(19)
N(1A)-Sn(1)-N(1)	150.5(3)	C(2)-N(1)-Sn(1)	113.3(5)	O(3)-Sn(1)-N(1)	75.26(14)
C(8)-C(7)-Sn(1)	120.9(7)	C(1)-O(1)-Sn(1)	125.5(5)	C(6)-N(1)-Sn(1)	129.4(6)
O(1)-Sn(1)-O(1A)	74.0(3)				

In this complex, the two Sn—O bond lengths of 0.2232(5) nm are longer than those in $\{[{}^n\text{Bu}_2\text{Sn}(2\text{-pic})]_2\text{O}\}_2$ (0.20544 nm and 0.2110 nm)¹⁸ and $[(\text{PhCH}_2)_3\text{Sn}(\text{O}_2\text{CC}_3\text{H}_4\text{N}) \cdot (\text{H}_2\text{O})]_n$ (0.2188(4) nm).¹⁹ The Sn—N distance, 0.2522(6) nm, is longer than the sum of the covalent radii of Sn and N (0.215 nm), but considerably shorter than the sum of the van der Waals radii (0.375 nm) therefore which should be considered as a bonding interaction.⁷ In this connection it is relevant to note the Sn—N bond distances found in three other crystal structures of organotin compounds containing the 2-pyridine carboxylate ligand. In polymeric $[\text{Me}_2\text{SnCl}(2\text{-pic})]_n$ the two unique Sn—N bond distances are 0.250(3) nm and 0.247(2) nm, respectively.²⁰ In polymeric

$[\text{Me}_2\text{Sn}(2\text{-pic})_2]_n$ the two Sn—N bond distances are 0.2507(4) and 0.2477(4) nm respectively,¹⁶ and in $\{[{}^n\text{Bu}_2\text{Sn}(2\text{-pic})]_2\text{O}\}_2$ the two Sn—N bond distances are 0.2550(5) nm and 0.3150(5) nm, respectively.¹⁸

In this complex, because of the 2-pyridine carboxylate ligand bond with tin atom in bidentate fashion by one oxygen atom of carboxyl group and one nitrogen atom of pyridinyl group, the angle, forming by oxygen atom and nitrogen atom of 2-pyridine carboxylate ligand occupying equatorial place, deviates from the standard pentagonal bipyramidal angle. For example, the angles of three oxygen atoms and two nitrogen atoms around Sn(1) atom are O(1)-Sn(1)-N(1) 67.78(19)°, O(3)-Sn(1)-N(1) 75.26(14)°, O(3)-Sn(1)-N(1A) 75.26(14)°,

O(1A)-Sn(1)-N(1A) $67.78(19)^\circ$ and O(1)-Sn(1)-O(1A) $74.0(3)^\circ$. All angles deviate from 72° , but the sum of these angles is 360.08° , which shows that these atoms are co-planar. Furthermore, the angle C(7)-Sn(1)-C(7A) being axial plane is $171.2(5)^\circ$, which deviates from linear angle 180° . These data indicate that the tin atom of this complex is distorted pentagonal bipyramidal configuration.

Moreover, in the crystal the H-bonding exists between the coordinated water molecule and free oxygen atom of carboxyl group of adjacent complex as verified by the O(3)—O(2A) distance of 0.2633 nm, so that the complex molecules form the two-dimensional network through the intermolecular H-bond (Fig. 2).

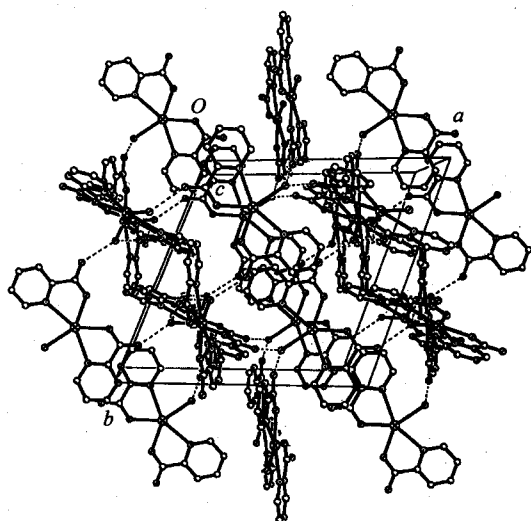


Fig. 2 Projection of the unit cell (butyl groups have been omitted for clarity).

In vitro antitumour activity

According to the known method,²¹ this complex was tested *in vitro* against two human tumour cell lines, MCF-7 a mammary tumour, and WiDr, a colon carcinoma, and displayed higher activity *in vitro*. Whose inhibition doses ID_{50} (ng/mL) values were 60 and 205, respectively. The activities were slightly better than (2-methylthio-3-pyridinecarboxylato)dibutyltin(IV),²¹ but much better than *cis*-platin.²¹ This might be the reason why this complex was of better solubility in water.

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