研究简报

有机锡配合物{[(n-C_8H_{17})$_2$Sn($O_2CCH_2CS_2NC_4H_8O$)]$_2$O}$_2$的合成,表征及晶体结构

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Synthesis and Crystal Structure of the Dimeric Organotin Complex {[(n-C_8H_{17})$_2$Sn($O_2CCH_2CS_2NC_4H_8O$)]$_2$O}$_2$

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Abstract: The title complex {[(n-C_8H_{17})$_2$Sn($O_2CCH_2CS_2NC_4H_8O$)]$_2$O}$_2$ has been synthesized by the reaction of (morpholinylthiocarbamoylthio)acetic acid with the di-n-octyltin oxide in 1:1 molar ratio. The complex was characterized by elemental analysis, IR and ^{1}H NMR. The crystal and molecular structure of complex was determined by X-ray single crystal diffraction. The crystal belongs to triclinic system with space group $P\bar{1}$ and unit cell dimensions: a=1.201 5(9) nm, b=1.481 8(11) nm, c=1.894 1(14) nm, α=72.485(10)°, β=88.586(10)°, γ=66.893(9)°, and Z=1, μ=1.034 mm^{-1}, V=2.941(4) nm^3, D_c=1.295 g·cm^{-3}, F(000)=1 196, R_1=0.058 8, wR_2=0.155 8. The complex is a centrosymmetric structure with a four-membered central endo-cyclic Sn_2O_2 unit in which two bridged oxygen atoms both connect with an exo-cyclic tin atom. The endo-cyclic tin atoms and the exo-cyclic tin atom are all five-coordinate and have coordination geometry of distorted trigonal bipyramid with an additional weak coordination carboxylate oxygen. Four carboxylate ligands are divided into two types. And two of them are monodentate and connecting to each of exo-cyclic tin atoms by using one oxygen atom, whereas the others bridge to each pair of exo-and endo-cyclic tin atoms utilizing one oxygen atom. CCDC: 277048.

Key words: organotin complex; (morpholinylthiocarbamoylthio)acetic acid; systhesis; crystal structure

0 Introduction

Organotin derivatives of carboxylic acid have been extensively studied due to their biological activities[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[5~10]. In particular, diorganotin (Ⅳ) derivatives of carboxylic acid attract considerable interest in structural studies because of many possible bonding modes between carboxyl group

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and tin atom. Studies on diorganotin(Ⅳ) derivatives of carboxylic acid containing carboxylate ligands with additional donor atom, such as nitrogen and sulfur have revealed new structural types which may lead to complexes with different activity. As an extension of our studies of organotin(Ⅳ) derivatives of carboxylic acid[11~17], we now report the synthesis of a new complex $\{[(n\text{-}C_8H_{17})_2Sn(O_2CCH_2CS_2NC_4H_8O)]_2O\}_2$. The elemental analysis, IR and ^1H NMR spectroscopic characterization and crystal structure of the new complex have been carried out. 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 employing. Infrared spectra were recorded on a Nicolet-460 spectrophotometer using KBr as discs. ^1H 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.

1.2 Preparation of the title complex

The solution of (morpholinylthiocarbamoylthio) acetic acid (2.0 mmol) in benzene was added to a suspension of $(n\text{-}C_8H_{17})_2SnO$ (2.0 mmol) in benzene. Then the mixture was refluxed for 5 h with water formed during the reaction being removed azeotropically with a Dean and Stark apparatus. The clear solution obtained after filtration was evaporated in vacuum to give a white solid. The products were recrystallized from benzene-ether to give a colorless crystal 0.826 g, yield 72%, m.p. 112~113 ℃, IR (KBr) ν: 2 956, 2 926, 2 849, 1 664, 1 616, 1 370, 1 326, 782, 681, 620, 574, 521, 483, 443 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ: 0.87(t, 12H, J=13 Hz, CH_3), 0.93(t, 12H, J=7 Hz, CH_3), 1.25~1.72 (m, 112H, $SnCH_2CH_2CH_2CH_2CH_2CH_2CH_2$), 3.50 (s, 16H, NCH_2), 3.79 (m, 16H, OCH_2), 4.18 (s, 8H, SCH_2CO); Anal. Calcd. for $C_{92}H_{176}N_4O_{14}S_8Sn_4$ (%): C 48.18, H 7.73, N 2.44, S 11.18; Found (%): C 48.24, H 7.78, N 2.41, S 11.22.

1.3 Crystallographic measurement

A single crystal having approximate dimensions 0.53 mm × 0.48 mm × 0.38 mm was selected for the experiment. All measurements were made on a Bruker Smart-1000 CCD diffractometer with graphite monochromatized Mo $K\alpha$ radiation (0.071 073 nm). A total of 15 151 reflections were collected in the range of $1.85°<\theta<25.03°$ and 10 054 reflections were independent (R_{int}=0.038 4). The crystal belongs to a triclinic system with space group $P\bar{1}$ and unit cell dimensions: a=1.201 5(9) nm, b=1.481 8(11) nm, c=1.894 1(14) nm, α=72.485(10)°, β=88.586(10)°, γ=66.893(9)°, and Z=1, μ=1.034 mm^{-1}, V=2.941(4) nm^3, D_c=1.295 $g\cdot cm^{-3}$, F(000)=1 196, R_1=0.058 8, wR_2=0.155 8. The structure was solved by 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. The weighting scheme was $w=1/[\sigma^2(F_o^2)+(0.117\,7P)^2+3.635\,4P]$ where $P=(F_o^2+2F_c^2)/3$. The refinement was converged to the final R=0.058 8, wR=0.155 8, $(\Delta/\sigma)_{max}$=0.000 and S=1.000. The largest difference peak and hole were 1 512 $e\cdot nm^{-3}$ and −1 174 $e\cdot nm^{-3}$, respectively.

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2 Results and discussion

2.1 IR spectrum

In the complex, a strong band in the 620 cm^{-1} is attributed to ν(Sn-O-Sn) indicating a Sn-O-Sn link for the complex[18], a band in 483 cm^{-1} is assigned to the stretching mode of the Sn-O linkage. The difference $\Delta\nu$ of $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ had been used to determine the type of bonding between metal and carboxyl group[19]. In the complex, the presence of two values for each of $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ indicates that there are two types of carboxylate groups. The two bands which occur at 1 664 cm^{-1} and 1 616 cm^{-1} were assigned to $\nu_{as}(CO_2)$, whereas the bands at 1 370 cm^{-1} and 1 326 cm^{-1} were assigned to $\nu_s(CO_2)$. The magnitudes of $\Delta\nu_1$ [$\nu_{as,1}(CO_2)-\nu_{s,1}(CO_2)$] is 294 cm^{-1} and $\Delta\nu_2$ [$\nu_{as,2}(CO_2)-\nu_{s,2}(CO_2)$] is 290 cm^{-1}. The $\Delta\nu_1$ values and $\Delta\nu_2$ values are much

larger than the $\Delta\nu$ reported for bidentate carboxylates, indicating the monodentate chelating of two different types of bonding of the carboxylate ligands.

2.2 Crystal structure analysis

The molecular structure of the title complex is shown in Fig.1. Fig.2 shows the packing of the molecules in the unit cell as seen in a projection on to its face. The selected bond lengths and angles are listed in Table 1.

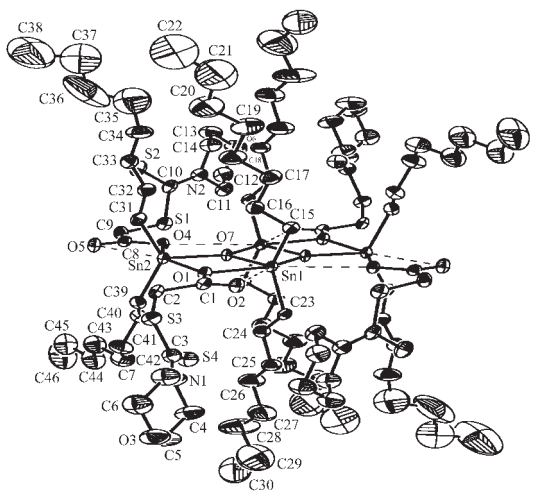

Fig.1　Molecular structure of the title complex

As can be seen from Fig.1, the title complex is a tortuous ladder structure with five-coordinate tin atoms. It can be viewed as a centrosymmetric dimer, where one half of the molecule comprises the crystallographic asymmetric unit and another half is generated by an inversion center located at the center of the oxo-bridging quadrilateral $(SnO)_2$ ring. The centrosymmetric (n-$C_8H_{17})_4Sn_2O_2$ core are attached to two (n-$C_8H_{17})_2$Sn units, making the O(7) and O(7)#1 atoms three-coordinate. The four carboxylate ligands are divided into two different types according to their coordinating fashion. Two of them are monodentate and connect with each of exo-cyclic tin atoms by using one oxygen atom. Whereas the others are bridging to each pair of exo- and endo-cyclic tin atoms by utilizing one oxygen atom. The bond distances of Sn(2)-O(4) is 0.211 7(5) nm, Sn(1)-O(1) and Sn(2)-O(1) are 0.223 9(5) nm and 0.246 7(5) nm, respectively.

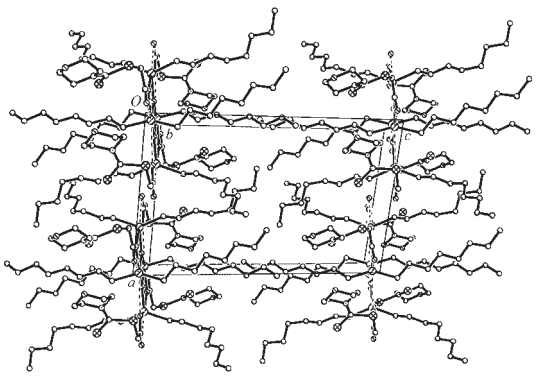

Fig.2　Projection of the unit cell of the title complex

The geometry around the endo-cyclic tin atom Sn (1) is five-coordinate distorted trigonal bipyramid, with atoms C(15), C(23) and O(7) occupying equatorial positions as indicated by the sum of the bond angles

Table 1　Selected bond distances (nm) and angles (°) for the title complex

Sn(1)-O(7)	0.205 2(5)	Sn(1)-O(2)	0.312 3(6)	Sn(2)-C(31)	0.213 2(9)
Sn(1)-C(23)	0.210 9(8)	Sn(1)-O(4)#1	0.316 0(5)	Sn(2)-O(1)	0.246 7(5)
Sn(1)-C(15)	0.210 9(9)	Sn(2)-O(7)	0.200 7(5)	Sn(2)-O(5)	0.289 8(5)
Sn(1)-O(7)#1	0.215 2(2)	Sn(2)-O(4)	0.211 7(5)		
Sn(1)-O(1)	0.223 9(5)	Sn(2)-C(39)	0.210 6(9)		
O(7)-Sn(1)-O(7)#1	72.9(2)	C(15)-Sn(1)-O(2)	77.6(3)	O(4)-Sn(2)-O(1)	149.98(19)
C(23)-Sn(1)-O(7)#1	97.7(3)	C(7)#1-Sn(1)-O(2)	169.23(16)	O(1)-Sn(2)-O(2)	44.81(17)
C(15)-Sn(1)-O(7)#1	98.5(3)	O(7)-Sn(1)-C(23)	113.0(3)	O(7)-Sn(2)-O(4)	81.00(19)
O(7)-Sn(1)-O(1)	73.16(18)	O(7)-Sn(1)-C(15)	112.3(3)	O(7)-Sn(2)-C(39)	115.2(3)
C(15)-Sn(1)-O(1)	96.8(3)	C(23)-Sn(1)-O(1)	92.8(3)	C(39)-Sn(2)-O(4)	102.3(3)
O(7)#1-Sn(1)-O(1)	145.94(18)	C(31)-Sn(2)-O(1)	88.4(3)	O(7)-Sn(2)-C(31)	111.3(3)
O(7)-Sn(1)-O(2)	117.86(18)	O(7)-Sn(2)-O(1)	68.99(18)	O(4)-Sn(2)-C(31)	103.8(3)
C(23)-Sn(1)-C(15)	134.5(3)	C(39)-Sn(2)-O(1)	90.1(3)	C(39)-Sn(2)-C(31)	129.3(4)

Symmetry transformation codes: #1: $-x+2$, $-y+1$, $-z+2$.

(359.8°) around the tin atom involving these atoms, which show that the Sn(1), C(15), C(23), O(7) atoms are in the same plane. The axial positions are occupied by the bridging oxygen atom O(7)#1 and the O(1) atom from the bidentate carboxlate ground. The axial bond angle, O(1)-Sn(1)-O(7)#1, of 145.94(18)° deviates significantly from linearity owing to the tendency of O(1) to bridge the Sn(2) atom. In addition, Sn(1) atom makes a close contact of 0.312 3(6) nm with the O(2) atom. The contact is considerably less than 0.368 nm, the sum of the van der Waals radii for Sn and O atoms[20,21]. Therefore the Sn(1) atom best described as monocapped trigonal bipyramid geometry.

The exo-cyclic tin atom, Sn(2) is also five-coordinate distorted trigonal bipyramid. with atoms C(31), C(39) and O(7) occupying equatorial positions. The sum of the equatorial angles (355.8°) at the tin atom by the two coordinated carbon atoms and one oxygen atom [O(7)-Sn(2)-C(39) 115.2°, O(7)-Sn(2)-C(31) 111.3°, C(39)-Sn(2)-C(31) 129.3°] deviates by 4.2° from 360°. The axial positions are occupied by the bridging oxygen atom O(4) and the O(1) atom from the bidentate carboxlate ground. The axial bond angle, O(4)-Sn(2)-O(1), of 149.98(19)° deviates significantly from linearity owing to the tendency of O(1) to bridge the Sn(1) atom. In addition, Sn(2) atom makes a close contact of 0.289 8 nm with the O(5) atom. The contact is significantly less than 0.368 nm, the sum of the van der Waals radii for Sn and O atoms[20,21], so the Sn(2) atom best described as monocapped trigonal bipyramid geometry.

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