

二聚体有机锡配合物 $\{[n\text{-Bu}_2\text{Sn}(\text{O}_2\text{CCH}_2\text{CS}_2\text{NC}_4\text{H}_8)]_2\text{O}\}_2$ 的合成, 表征及晶体结构

尹汉东* 薛绳才 王其宝

(聊城大学化学化工学院, 聊城 252059)

关键词: 有机锡配合物 吡咯烷氨羧基乙酸 合成 晶体结构
分类号: O614.12

Synthesis, Characterization and Crystal Structure of the Dimeric Organotin Compound: $\{[n\text{-Bu}_2\text{Sn}(\text{O}_2\text{CCH}_2\text{CS}_2\text{NC}_4\text{H}_8)]_2\text{O}\}_2$

YIN Han-Dong* XUE Sheng-Cai WANG Qi-Bao

(Department of Chemistry, Liaocheng University, Liaocheng 252059)

The title compound, $\{[n\text{-Bu}_2\text{Sn}(\text{O}_2\text{CCH}_2\text{CS}_2\text{NC}_4\text{H}_8)]_2\text{O}\}_2$, has been synthesized by the reaction of (tetrahydropyrroldithiolocarbamoylthio)acetic acid with the di-*n*-butyltin oxide in 1:1 molar ratio. The complex has been characterized by elemental analysis, IR and NMR. The crystal structure of it has been determined by X-ray single crystal diffraction. And the results showed that the crystal belongs to triclinic system with space group $P\bar{1}$ and some crystal parameters: $a=1.220\,2(9)$ nm, $b=1.315\,8(10)$ nm, $c=1.380\,4(10)$ nm, $\alpha=111.215(9)^\circ$, $\beta=99.357(9)^\circ$, $\gamma=96.075(10)^\circ$, $V=2.006(2)$ nm³, $Z=1$, $F(000)=908$, $\mu=1.489$ mm⁻¹, $D_c=1.474$ g·cm⁻³, $R_1=0.037\,5$, $wR_2=0.083\,9$. The complex has a centrosymmetric dimer structure mode with a four-membered central endo-cyclic Sn₂O₂ unit in which two bridged oxygen atoms both connect with an exo-cyclic tin atom which has a distorted octahedron. Each of the endo-cyclic tin atoms exhibits a distorted trigonal bipyramid coordination geometry with an additional weak coordination carboxylate oxygen. Four carboxylate ligands are divided into two types. And two of them are bidentate and connecting to each of exo-cyclic tin atoms by using both oxygen atoms, whereas the others bridge to each pair of exo-and endo-cyclic tin atoms utilizing one oxygen atom only. CCDC: 220513.

Keywords: organotin complex (tetrahydropyrroldithiolocarbamoylthio)acetic acid synthesis
crystal structure

0 Introduction

Organotin derivatives of carboxylic acid were extensively studied due to their biological activities^[1-4].

In recent years, several reports of the synthesis, anti-tumour activities, biocidal activities, antibioic activities and structural elucidation of various organotin derivatives of carboxylic acid have appeared, reveal-

收稿日期:2003-08-07. 收修改稿日期:2004-02-12.

国家自然科学基金(No.20271025),教育部骨干教师基金(No.)和山东省自然科学基金(No.L2003B01)资助项目。

* 通讯联系人。E-mail:handongyin@lctu.edu.cn

第一作者:尹汉东,男,45岁,教授;研究方向:金属有机化学。

ing 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 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. For example, [di-*n*-butyl(2-pyridinecarboxylato)tin(IV)] oxide^[11] and dimethyltin(IV)2-pyridinecarboxylate^[12] have special structure, owing to the multidentate nature of the bridging 2-pyridinecarboxylate ligands which utilize both the carboxylate O and the pyridinyl N atoms to coordinate to tin atom. As an extension of our studies of organotin(IV) derivatives of carboxylic acid, we have synthesized a new complex $\{[n\text{-Bu}_2\text{Sn}(\text{O}_2\text{CCH}_2\text{CS}_2\text{NC}_4\text{H}_8)]_2\text{O}\}_2$. The elemental analysis, IR and 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. NMR spectra were obtained on a Mercury Plus-400 NMR spectrometer, chemical shifts were given in relative to Me_4Si and Me_4Sn in CDCl_3 solvent. Elemental analyses were performed with a PE-2400 II elemental apparatus, and tin was gravimetrically estimated as SnO_2 . The di-*n*-butyltin oxide was prepared according to the known method^[13]. And (tetrahydropyrro-dithiolocarbamoylthio)acetic acid was synthesized by way of the literature^[14].

1.2 Preparation of the Title Complex

The solution of (tetrahydropyrro-dithiolocarbamoylthio)acetic acid (2.1 mmol) in benzene was added to a suspension of *n*- Bu_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 0.694 g, yield 78%, m.p. 178~179°C, IR (KBr) ν : 2 954, 2 925, 2 869, 1 664, 1 606, 1 509, 1 346, 681, 617, 559, 485, 457 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ : 0.90 (t, 12H, $J=7.0$ Hz, CH_3), 0.93 (t, 12H, $J=7.0$ Hz, CH_3), 1.36 (m, 16H, SnCCCH_2), 1.66 (m, 16H, SnCCH_2), 1.53 (m, 16H, SnCH_2), 1.98 (m, 8H, NCCH_2), 2.09 (m, 8H, NCCH_2), 3.71 (t, 8H, $J=6.8$ Hz, NCH_2), 3.91 (t, 8H, $J=7.2$ Hz, NCH_2), 4.05 (s, 8H, SCH_2CO_2); ^{13}C NMR (CDCl_3 , 400 MHz) δ : 191.71 (CSS), 173.33 (COO), 55.35, 50.77 (C-N), 40.61 (C-S), 26.39, 24.56 (C-C), 29.12, 27.89, 27.49, 27.23, 27.05, 14.00, 13.96 (BuSn); ^{119}Sn NMR (CDCl_3 , 400 MHz) δ (Me_4Sn): -207, -223; Anal. Calcd for $\text{C}_{60}\text{H}_{112}\text{N}_4\text{O}_{10}\text{S}_8\text{Sn}_4$ (%): C 40.41, H 6.36, N 3.16, S 14.36, Sn 26.60; Found: C 40.26, H 6.24, N 3.15, S 14.40, Sn 26.86.

1.3 Crystal Structure Determination

A single crystal having approximate dimensions 0.43 mm \times 0.35 mm \times 0.28 mm was mounted on a glass fiber. All measurements were made on a Bruker Smart-1000 CCD diffractometer with graphite monochromated $\text{MoK}\alpha$ radiation (0.071 073 nm). A total of 10 246 reflections were collected in the range of $2.48^\circ < \theta < 25.03^\circ$ and 6 842 reflections were independent ($R_{\text{int}}=0.028\,01$). The crystal belongs to a triclinic system with space group $P\bar{1}$ and unit cell parameters: $a=1.220\,2(9)$ nm, $b=1.315\,8(10)$ nm, $c=1.380\,4(10)$ nm, $\alpha=111.215(9)^\circ$, $\beta=99.357(9)^\circ$, $\gamma=96.075(10)^\circ$, and $Z=1$, $V=2.006(2)$ nm³, $F(000)=908$, $D_c=1.474$ g $\cdot\text{cm}^{-3}$, $\mu=1.489$ mm⁻¹. The structure was solved by direct methods using SHELXTL-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 $w=1/[\sigma^2(F_o^2)+(0.0437P)^2+1.9207P]$ where $P=(F_o^2+2F_c^2)/3$. The refinement was converged to the final $R_1=0.037\,5$, $wR_2=0.083\,9$, $(\Delta/\sigma)_{\text{max}}=0.001$ and $S=1.021$. The largest difference peak and hole were 982 e $\cdot\text{nm}^{-3}$ and -513

$\text{e} \cdot \text{nm}^{-3}$, respectively.

CCDC: 220513.

2 Results and Discussion

2.1 IR and NMR Spectra Analysis

The assignment of IR bands of the title complex has been made in comparison with the IR spectra related organotin complex (carboxylate and $n\text{-Bu}_2\text{SnO}$). The free acid shows a broad O-H absorption at $3\,000\sim 2\,500\text{ cm}^{-1}$ which is absent from the spectra of the title complex, showing the deprotonation of the COOH groups during the reactions. The Sn-C absorption band at 559 cm^{-1} and 457 cm^{-1} reveals the possibility of a trans arrangement of the Bu_2Sn moiety. A band in the 485 cm^{-1} region is assigned to the stretching mode of the Sn-O linkage. A strong band in the 617 cm^{-1} is attributed to $\nu(\text{Sn-O-Sn})$ indicating a Sn-O-Sn link for the complex^[3,15]. The difference $\Delta\nu$ of $\nu_{\text{as}}(\text{CO}_2)$ and $\nu_{\text{s}}(\text{CO}_2)$ had been used to determine the type of bonding between metal and carboxyl group^[16]. In the complex, the presence of two values for each of $\nu_{\text{as}}(\text{CO}_2)$ and $\nu_{\text{s}}(\text{CO}_2)$ indicates that there are two types of carboxylate groups. The two bands which occur at $1\,664\text{ cm}^{-1}$ and $1\,606\text{ cm}^{-1}$ were assigned to $\nu_{\text{as}}(\text{CO}_2)$, whereas the bands at $1\,509\text{ cm}^{-1}$ and $1\,346\text{ cm}^{-1}$ were assigned to $\nu_{\text{s}}(\text{CO}_2)$. The magnitudes of $\Delta\nu_1 [\nu_{\text{as},1}(\text{CO}_2) - \nu_{\text{s},1}(\text{CO}_2)]$ is 155 cm^{-1} and $\Delta\nu_2 [\nu_{\text{as},2}(\text{CO}_2) - \nu_{\text{s},2}(\text{CO}_2)]$ is 260 cm^{-1} . The $\Delta\nu_1$ values are approximately in the range observed for some bidentate carboxylates^[17], indicating the presence of bidentate carboxylate groups in the complex. $\Delta\nu_2$ is much larger than the $\Delta\nu$ reported for bidentate carboxylates, indicating different type of bonding of the carboxylate ligands.

The ^{13}C NMR of complex exhibited two sets of Sn-Bu resonances. Ligand carbons show a significant downfield shift of all carbon resonances compared with the free ligand. The shift is a consequence of an electron density transfer from the ligand to the acceptor, which is consistent with that reported in the literature^[18].

The ^{119}Sn NMR of complex showed two well separated resonances, characteristic of the tetraorganodis-

tannoxane structure^[19]. The low- and high-field resonances observed for this complex is attributed to the exo-cyclic and endo-cyclic tin atoms, respectively^[20]. Single resonances at -207 ppm and -223 ppm in the ^{119}Sn NMR spectra of complex suggest that the tin atoms exhibit penta- and hexa-coordination^[19].

2.2 Crystal Structure

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.

Table 1 Selected Bond Distances (nm) and Angles ($^\circ$) for the Title Complex

Sn(1)-O(5)	0.201 5(3)	Sn(2)-O(5)	0.200 4(3)
Sn(1)-C(15)	0.212 1(6)	Sn(2)-O(3)	0.211 6(4)
Sn(1)-C(19)	0.212 5(6)	Sn(2)-C(23)	0.212 0(6)
Sn(1)-O(5)#1	0.217 8(3)	Sn(2)-C(27)	0.212 2(7)
Sn(1)-O(1)	0.223 9(4)	Sn(2)-O(1)	0.258 7(4)
Sn(1)-O(2)	0.304 3(4)	Sn(2)-O(4)	0.277 1(4)
O(5)-Sn(1)-C(15)	111.5(2)	C(23)-Sn(2)-C(27)	130.3(3)
O(5)-Sn(1)-C(19)	113.6(2)	O(5)-Sn(2)-O(1)	67.82(12)
C(15)-Sn(1)-C(19)	134.8(3)	O(3)-Sn(2)-O(1)	151.44(12)
O(5)-Sn(1)-O(5)#1	73.87(13)	C(23)-Sn(2)-O(1)	86.02(18)
C(15)-Sn(1)-O(5)#1	95.1(2)	C(27)-Sn(2)-O(1)	87.9(2)
C(19)-Sn(1)-O(5)#1	96.8(2)	O(5)-Sn(2)-O(4)	134.54(12)
O(5)-Sn(1)-O(1)	74.69(12)	O(3)-Sn(2)-O(4)	50.94(13)
C(15)-Sn(1)-O(1)	97.3(2)	C(23)-Sn(2)-O(4)	85.33(12)
C(19)-Sn(1)-O(1)	94.7(2)	C(27)-Sn(2)-O(4)	82.1(2)
O(5)#1-Sn(1)-O(1)	148.5(13)	O(1)-Sn(2)-O(4)	157.59(11)
O(5)-Sn(1)-O(2)	120.92(12)	O(5)-Sn(2)-O(3)	83.85(13)
C(15)-Sn(1)-O(2)	77.12(19)	O(5)-Sn(2)-C(23)	112.4(2)
C(19)-Sn(1)-O(2)	80.4(2)	O(3)-Sn(2)-C(23)	102.25(19)
C(5)#1-Sn(1)-O(2)	164.90(11)	O(5)-Sn(2)-C(27)	110.5(2)
O(1)-Sn(1)-O(2)	46.42(12)	O(3)-Sn(2)-C(27)	106.1(2)

As can be seen from Fig.1, the title complex is dimeric with tortuous ladder structure with five- and six-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 $(\text{SnO})_2$ ring. The centrosymmetric $n\text{-Bu}_4\text{Sn}_2\text{O}_2$ core are

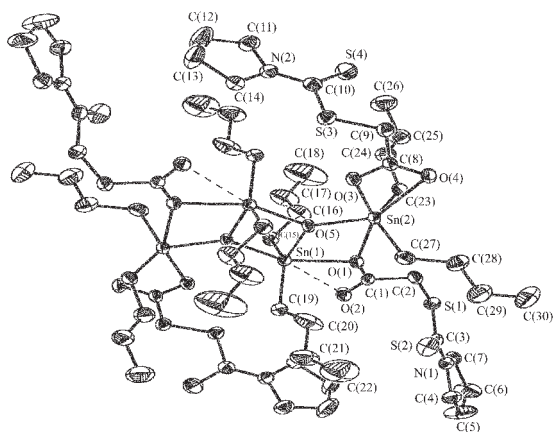


Fig.1 Molecular structure of the complex

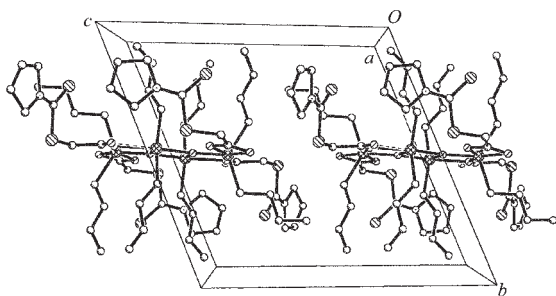


Fig.2 Projection of the unit cell of the complex

attached to two $n\text{-Bu}_2\text{Sn}$ units, making the O(5) and O(5)#1 atoms three-coordinate. The four carboxylate ligands are divided into two different types according to their coordinating fashion. Two of them are bidentate and connect with each of *exo*-cyclic tin atoms by using both oxygen atoms. Whereas the others are bridging to each pair of *exo*- and *endo*-cyclic tin atoms by utilizing one oxygen atom only. The bond distances of Sn(2)-O(3) and Sn(2)-O(4) are 0.2116(4) nm and 0.277 1(4) nm, respectively. Sn(1)-O(1) equal 0.223 9(4) nm and Sn(2)-O(1) equal 0.258 7(4) nm.

The geometry around the *endo*-cyclic tin atom Sn(1) is five-coordinate distorted trigonal bipyramid, with atoms C(15), C(19) and O(1) occupying equatorial positions as indicated by the sum of the bond angles (326.8°) around the tin atom involving these atoms. The axial positions are occupied by the bridging oxygen atom O(5)#1 and the O(1) atom from the bidentate carboxylate ground. The axial bond angle, O(1)-Sn(1)-O(5)#1, of $148.55(13)^\circ$ 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 0.304 3(4) nm with the O(2) atom. The contact is significantly less than 0.368 nm, the sum of the van der Waals radii for Sn and O atoms^[21, 22]. Therefore the Sn(1) atom best described as monocapped trigonal bipyramid geometry. The *exo*-cyclic tin atom, Sn(2), forms six Sn-O bonds, Sn(2)-O(1) 0.223 9(4) nm, Sn(2)-O(3) 0.211 6(4) nm, Sn(2)-O(4) 0.277 1(4) nm, Sn(2)-C(23) 0.212 0(6) nm, Sn(2)-C(27) 0.212 2(7) and bond Sn(2)-O(5) 0.200 4(3) nm. The geometry is distorted octahedral, with atoms C(23), C(27), O(5) and O(3) occupying equatorial positions. The axial positions are occupied by the oxygen atom O(1) and the O(4) atom from two different bidentate, bridging carboxylate ligand which subtend an angle of $157.59(11)^\circ$ at the *exo*-cyclic tin atom Sn(2). The structure reported here for $\{[n\text{-Bu}_2\text{Sn}(\text{O}_2\text{CCH}_2\text{CS}_2\text{NC}_4\text{H}_8)_2\text{O}]\}_2$ represents a kind structural type for dicarboxyl tetraorganostannoxanes in that two carboxylate groups function as bridging ligands via one oxygen atom only and the other two carboxylate groups connect with *exo*-cyclic tin atoms via both the oxygen atoms. The structure is similar to those of the complexes^[24, 25]. To our surprised, each ester sulphur atom in the carboxylate groups interacts with corresponding sulphur atom from another molecule by weak interaction $\text{S} \cdots \text{S}$ between molecules forming a one-dimensional infinite chain because $\text{S} \cdots \text{S}$ distance is 0.354 0 nm which is shorter than the sum of the Van der Waals radii for S and S of 0.370^[23].

References

- [1] XIE Qing-Lan(谢庆兰), LI Shu-Zheng(李树正), ZHANG Su-Hua(张素华), ZHANG Dian-Kun(张殿坤), ZHANG Zhao-Gui(张招贵), HU Jin-Min(胡锦民) *Huaxue Xuebao(Acta Chim. Sinica)*, **1991**, *49*, 723.
- [2] YIN Han-Dong(尹汉东), WANG Chuan-Hua(王传华), WANG Yong(王勇), MA Chun-Lin(马春林), SAO Jian-Xin(邵建新) *Huaxue Xuebao(Acta Chim. Sinica)*, **2002**, *60*, 143.
- [3] Yin H. D., Wang C. H., Wang Y., Ma C. L. *Indian J. Chem.*, **2003**, *42A*, 1656.
- [4] Yin H. D., Ma C. L., Wang Y., Zhang R. F. *Indian J. Chem.*, **2003**, *42B*, 889.

- [5] YIN Han-Dong(尹汉东), WANG Chuan-Hua(王传华), WANG Yong(王 勇), ZHANG Ru-Fen(张如芬), MA Chun-Lin(马春林) *Wuji Huaxue Xuebao(Chin. J. Inorg. Chem.)*, **2002**,**18**,201.
- [6] YIN Han-Dong(尹汉东), WANG Chuan-Hua(王传华), WANG Yong(王 勇), MA Chun-Lin(马春林) *Wuji Huaxue Xuebao(Chin. J. Inorg. Chem.)*, **2001**,**17**,806.
- [7] YIN Han-Dong(尹汉东), WANG Chuan-Hua(王传华), MA Chun-Lin(马春林), WANG Yong(王 勇), ZHANG Ru-Fen(张如芬) *Wuji Huaxue Xuebao(Chin. J. Inorg. Chem.)*, **2002**, **18**,347.
- [8] YIN Han-Dong(尹汉东), MA Chun-Lin(马春林), ZHANG Ru-Fen(张如芬) *Wuji Huaxue Xuebao(Chin. J. Inorg. Chem.)*, **2000**,**16**,619.
- [9] Tao J., Xiao W. J. *J. Organomet. Chem.*, **1996**,**526**,21.
- [10] YIN Han-Dong(尹汉东), WANG Chuan-Hua(王传华), MA Chun-Lin(马春林), ZHU De-Zhong(朱德中) *Wuji Huaxue Xuebao(Chin. J. Inorg. Chem.)*, **2002**,**18**,819.
- [11] Rulekar C. S., Jain X. K., Das T. K., Gupta A. R., Hoskins B. F., Tiekink E. R. T. *J. Organomet. Chem.*, **1989**,**372**, 1993.
- [12] Lockhart T. P., Davidson F. *Organometallics*, **1987**,**6**,2471.
- [13] LI Quan(李 全), LI Hong-You(李洪友), LIN Jun(林 军), LIU Fu-Chu(刘复初), WANG Hui-Chang(王惠昌) *Yunnan Huagong(Yunnan Chem.)*, **2002**,**29**,47.
- [14] Tiwari S. S., Pandey V. G. *J. Indian. Chem. Soc.*, **1974**,**51**, 440.
- [15] Vatsa C., Jian V. K., Das T. K., Tiekink E. R. T. *J. Organomet. Chem.*, **1990**,**396**,9.
- [16] Fang X. N., Song X. Q., Xie Q. L. *J. Organomet. Chem.*, **2001**,**619**,43.
- [17] Ho B. Y. K., Zuckerman J. J. *Inorg. Chem.*, **1973**,**12**,1 552.
- [18] YU Zheng-Kun(余正坤), WANG Shi-Hua(王世华), YANG Zhen-Yun(杨振云), HAN Xiu-Wen(韩秀文) *Bopuxue Zazhi(Chin. J. Magn. Reson.)*, **1999**,**11**,36.
- [19] Hadjikakou S. K., Demeertzis M. A., Kubicecki M., Kovalas Demertzi D. *Appl. Organomet. Chem.*, **2000**,**14**,727.
- [20] Ribot F., Sanchez C., Meddour A., Gielen M., Tiekink E. R. T., Biesemans M., Willem R. *J. Organomet. Chem.*, **1998**, **552**,177.
- [21] Eoh S. G., Ang S. H., Declercq J. P. D. *Polyhedron*, **1997**, **16**,3729.
- [22] Tiekink E. R. T., Gielen M., Bouhdid A., Biesemans M., Willem R. *J. Organomet. Chem.*, **1995**,**494**,247.
- [23] Jie D., Megumu M., Wu L. P., Takayoshi K.S., Yusaku S. *Inorg. Chim. Acta*, **1997**,**258**,65.
- [24] Tao J. X., Xiao W. J., Yang Q. C. *J. Organomet. Chem.*, **1997**,**531**,223.
- [25] LU Wen-Guan(卢文贯), TAO Jia-Xun(陶家洵), LI Xu-Yu(李旭宇), WANG Yu-Zhen(王玉珍) *Wuli Huaxue Xuebao(Acta Phys. Chim. Sin.)*, **2001**,**17**,836.