

线性聚合物 3-吲哚乙酸基三丁基锡的合成 及晶体结构研究

尹汉东 马春林* 张如芬 张立云
(聊城师范学院化学系, 聊城 252059)

用三丁基氯化锡与 3-吲哚乙酸钠反应, 合成 3-吲哚乙酸基三丁基锡, 经元素分析、IR、¹H NMR 和 X-晶体衍射测定了其晶体结构, 属于单斜晶系, $P2_1/n$ 空间群, $a = 13.1361(4)$, $b = 10.266(2)$, $c = 17.299(5)$ Å, $\beta = 98.48(3)^\circ$, 中心锡原子具有五配位三角双锥结构。

关键词: 晶体结构 三丁基锡 3-吲哚乙酸根 线性结构
分类号: O614.37

Synthesis and X-Ray Crystal Structure of a Linear Polymeric Tri-*n*-Butyltin 3-Indolylacetate

YIN Han-Dong MA Chun-Lin* ZHANG Ru-Fen ZHANG Li-Yun
(Department of Chemistry, Liaocheng Teachers University, Liaocheng 252059)

The complex $(n-C_4H_9)_3SnO_2CCH_2R$ ($R = 3\text{-indolyl}$) was prepared by reaction of $(n-C_4H_9)_3SnCl$ with sodium 3-indolylacetate in benzene. It has been determined by IR, ¹H NMR, elemental analyses and X-ray structural analyses. The crystals are monoclinic, space group $P2_1/n$, with $a = 13.1361(4)$, $b = 10.266(2)$, $c = 17.299(5)$ Å and $\beta = 98.48(3)^\circ$. In the crystal the tin atoms are rendered five-coordinate in a trigonal bipyramidal structure by coordinating with 3-indolylacetate groups. The resulting structure is a linear polymer containing two different Sn-O bond lengths of 2.194(3) and 2.522(3) Å.

Keywords: crystal structure tri-*n*-butyltin 3-indolylacetate linear structure

0 Introduction

The study of organotin (IV) carboxylates is of current interest owing to their wide range of application such as biocides and homogenous catalysts in industry^[1-4]. More recently, pharmaceutical properties of organotin (IV) carboxylates have been investigated for their antitumour activity^[5-6]. Crystallographic studies have revealed that organotin carboxylates adopt structures which are

收稿日期: 1999 06 14, 收修改日期: 1999 08 05.

晶体材料国家重点实验室(山东大学)及山东省自然科学基金(Q 98B01117)资助课题。

* 通讯联系人。

第一作者: 尹汉东, 43岁; 研究方向: 金属有机化学。

dependent on both the nature of the allyl (or aryl) substituent bound to the tin atom and on the type of carboxylate ligand^[7-8]. Several crystal structural data of triorganotin carboxylates (R_3SnO_2R') are available^[9-12], in these complexes the tin atom was confirmed four or five coordinate due to the influence of R or R' group^[10-13]. We report here the synthesis, spectroscopic and crystal structure characterization of tri-*n*-butyltin 3-indolylacetate, $(n-C_4H_9)_3SnO_2CCH_2R$ (R= 3-indolyl) as it is of interest to determine whether the presence of the nitrogen atom which is an additional potential donor atom on the R group and a large bulky 3-indolyl acetate ligand have any influence on the geometry of tin.

1 Experimental

1.1 General procedures

All reaction was carried out under nitrogen atmosphere with use of standard Schlenk techniques. The solvents were distilled under nitrogen from sodium and benzophenone immediately before use. IR spectra were recorded with a Nicolet 5DX spectrophotometer, samples were prepared as KBr discs. ¹H NMR spectra were recorded on Jeol 90Q NMR spectrometer, chemical shifts are given in ppm relative to Me₄Si in CDCl₃ solvent. Elemental analyses were performed with a Yanaca MT-3 apparatus. Tin was estimated as SnO₂.

1.2 Synthesis of tri-*n*-butyltin (IV) 3-indolylacetate

Tri-*n*-butyltin chloride (0.43g, 1mmol), sodium 3-indolylacetate (0.22g, 1.1mmol), and 10 mL benzene were stirred for 15h at 30 °C. The sodium was filtered while it was still hot. Solvent was gradually removed by vaporation under vacuum until solid product was obtained. The solid was then recrystallized from acetone-hexane. Colourless needle-shaped crystals were formed. Yield 0.44g (94%), M. P. 53~54 °C. Anal. Found: C, 57.05; H, 7.72; N, 3.06; Sn, 25.63. Calc. For C₂₂H₃₅NO₂Sn: C, 56.92; H, 7.60; N, 3.02; Sn, 25.57. IR (KBr): $\nu(COO_{asym})$ 1576; $\nu(COO_{sym})$ 1398; $\nu(Sn-O)$ 457; $\nu(Sn-C)$ 543 cm⁻¹. ¹H NMR (CDCl₃): δ 0.80~1.6 (m, 27H, C₄H₉); 3.76 (s, 2H, Ar-CH₂-); 7.04~7.66 (m, 5H, Ar-H); 8.10 (s, ¹H, N-H). (Ar= 3-indolyl).

1.3 Crystal structure determination

Intensity data for a crystal with dimension 0.2 × 0.3 × 0.4 mm³ were measured at 299K on a Enraf-Nonius CAD4F diffractometer fitted with graphite monochromator MoK α radiation, $\lambda = 0.71073 \text{ \AA}$. The $\omega/2\theta$ scan technique was employed to measure a total of 3620 reflection up to a maximum Bragg angle of 23°. Correction were applied for Lorentz and polarization effects but not for absorption, The 2559 out of the 3336 independent reflection ($R_{int} = 0.018$) satisfying the $I \geq 3\sigma(I)$ criterion of observability were used for the solution and refinement. The structure was solved by using direct methods and refined by a full-matrix least squares procedure based on F^2 using the TEXSAN program system. All non-H atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in the model at their calculated positions. The weighted residual is defined as $R_w = \sum (|F_o| - |F_c|)^2$. Final residuals R and R_w were 0.037 and 0.045 respectively. The final difference map had peaks between -0.61 and 0.57 e · Å⁻³ only.

Table 1 Crystal Data and Refinement Details for $(n\text{-C}_4\text{H}_9)_3\text{SnO}_2\text{CC}_6\text{H}_5\text{N}$

formula	$\text{C}_{22}\text{H}_{35}\text{NO}_2\text{Sn}$	formula weight	464.22
crystal system	monoclinic	space group	$P2_1/n$
$a/\text{\AA}$	13.361(4)	$b/\text{\AA}$	10.361(4)
$c/\text{\AA}$	17.299(5)	$\beta/^\circ$	98.48(3)
$V/\text{\AA}^3$	2347(2)	Z	4
$D_x(\text{mg} \cdot \text{m}^{-3})$	1.314	U/mm^{-1}	1.1046
$F(000)$	960	R_w	0.045
R	0.037	reflections collected	3620
ω	$e_w(1 F_o - F_c)^2$	No. of parameters refined	232
observed reflections 2559 ($I \geq 3\delta(I)$)			
largest diff. peak and hole ($e \cdot \text{\AA}^{-3}$) 0.57 and -0.61			
independent reflections 3336 ($R_{int} = 0.018$)			

Table 2 Atomic Coordination and Isotropic Equivalent Displacement Parameters

atom	x	y	z	$Beq(\text{\AA}^2)$	atom	x	y	z	$Beq(\text{\AA}^2)$
Sn(1)	0.28113(3)	0.20088(5)	0.21338(3)	3.8846(9)	O(1)	0.3393(3)	0.0445(4)	0.1459(3)	4.4(1)
O(2)	0.2844(4)	-0.1015(5)	0.2234(3)	5.4(1)	N(1)	0.5469(5)	-0.1445(6)	-0.0137(4)	5.5(1)
C(1)	0.1253(5)	0.1417(9)	0.1886(5)	6.0(2)	C(2)	0.062	0.193	0.122	7.6(1)
C(3)	-0.049	0.134	0.121	5.9(2)	C(4)	-0.128	0.190	0.066	10.2(1)
C(5)	0.3695(6)	0.1684(9)	0.3253(5)	5.8(2)	C(6)	0.4747(6)	0.115(1)	0.3263(5)	6.8(2)
C(7)	0.5324(7)	0.107(1)	0.4094(6)	9.6(2)	C(8)	0.6344(9)	0.048(1)	0.4102(8)	11.4(4)
C(9)	0.3341(6)	0.3435(7)	0.1381(4)	4.8(2)	C(10)	0.4516(5)	0.3687(7)	0.1630(4)	4.8(2)
C(11)	0.4876(6)	0.4668(8)	0.1060(5)	6.3(2)	C(12)	0.6030(7)	0.489(1)	0.1264(6)	8.0(3)
C(21)	0.3210(5)	-0.0738(7)	0.1634(4)	4.4(2)	C(22)	0.3419(5)	-0.1821(7)	0.1077(4)	5.2(2)
C(23)	0.4406(5)	-0.1638(6)	0.0743(4)	4.4(2)	C(24)	0.4444(6)	-0.1566(7)	-0.0052(4)	5.4(2)
C(25)	0.5395(5)	-0.1551(7)	0.1160(4)	5.0(2)	C(26)	0.6058(6)	-0.1411(8)	0.0592(5)	5.4(2)
C(27)	0.7088(6)	-0.130(1)	0.0784(6)	7.2(2)	C(28)	0.7463(7)	-0.133(1)	0.1566(7)	9.5(2)
C(29)	0.6845(8)	-0.148(1)	0.2162(7)	9.9(2)	C(30)	0.5794(7)	-0.157(1)	0.1946(5)	7.0(2)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as: $Beq = (4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table 3 Selected Bond Distances and Angles for $(n\text{-C}_4\text{H}_9)_3\text{SnO}_2\text{CC}_6\text{H}_5\text{N}$

bond	distance/ \AA	bond	distance/ \AA	bond	distance/ \AA
Sn(1)-O(1)	2.194(4)	Sn(1)-O(2a)	2.522(3)	Sn(1)-C(1)	2.150(6)
Sn(1)-C(5)	2.141(5)	Sn(1)-C(9)	2.147(5)	O(1)-C(21)	1.28(1)
O(2)-C(21)	1.24(1)	N(1)-C(24)	1.406(7)	N(1)-C(26)	1.384(9)
C(1)-C(2)	1.42(7)	C(9)-C(10)	1.588(7)	C(21)-C(22)	1.52(2)
C(22)-C(23)	1.526(7)	C(23)-C(24)	1.386(7)	C(23)-C(25)	1.412(9)
C(5)-C(6)	1.51(7)				
angle	($^\circ$)	angle	($^\circ$)	angle	($^\circ$)
O(1)-Sn(1)-O(2a)	172.9(1)	O(1)-Sn(1)-C(1)	95.5(2)	O(1)-Sn(1)-C(5)	100.1(2)
O(1)-Sn(1)-C(9)	90.2(1)	O(2a)-Sn(1)-C(1)	85.8(2)	O(2a)-Sn(1)-C(5)	85.0(2)
O(2a)-Sn(1)-C(9)	83.2(2)	C(1)-Sn(1)-C(5)	121.7(2)	C(5)-Sn(1)-C(9)	117.9(2)
C(1)-Sn(1)-C(9)	117.9(2)	Sn(1)-O(1)-C(21)	118.2(4)	Sn(1d)-O(2)-C(21)	138.6(5)
Sn(1)-C(1)-C(2)	119.2(3)	C(1)-C(2)-C(3)	108.0(2)	Sn(1)-C(5)-C(6)	117.2(4)
Sn(1)-C(9)-C(10)	110.4(3)	O(1)-C(21)-O(2)	121.7(7)	O(1)-C(21)-C(22)	118.8(7)
O(2)-C(21)-C(22)	119.5(7)	C(21)-C(22)-C(23)	113.5(5)	C(22)-C(23)-C(24)	122.8(5)
N(1)-C(24)-C(23)	106.8(5)	N(1)-C(26)-C(25)	107.3(6)	N(1)-C(26)-C(27)	129.6(5)

The crystal data and refinement details are given in Table 1. Bond lengths and angles in Table 2 and fractional atomic coordinates and their isotropic equivalent displacement parameters are listed in Table 3.

2 Result and discussion

The labeling of the atoms is shown in Fig. 1, which displays the molecule as it appears in projection down the *c* axis. Fig. 2 shows the packing of the molecules in the unit cell as seen in projection on the *bc* plane.

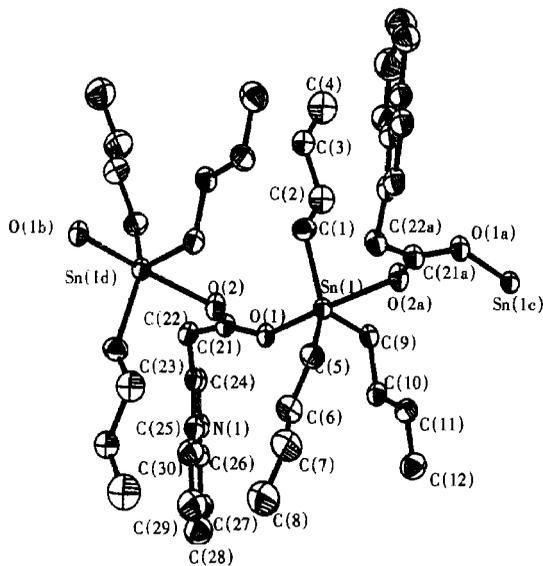


Fig. 1 Molecular structure of tris-*n*-butyltin 3-indolyacetate, showing atomic numbering

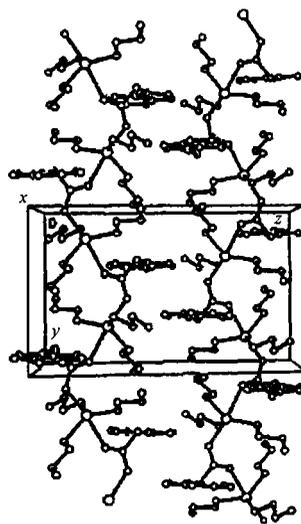


Fig. 2 Projection of the unit cell on the *bc* plane

Tri-*n*-butyltin 3-indolyacetate possesses an unequivocally polymeric structure. Each tin atom is rendered five-coordinate by coordination of the “free” oxygen of 3-indolyacetate group from an adjacent molecule. The coordination at the tin atom is trigonal bipyramidal, surrounded axially by two oxygen atoms and equatorial by the α -carbon atoms of the *n*-butyl groups. The tin axis swings through 60° with every 3-indolyacetate bridge. This effect is clearly seen in Fig. 2. Thus, the structure is similar to the compound $(C_6H_5CH_2)_3SnO_2CCH_3$ ^[9].

The mean Sn-C distance of 2.146 \AA is shorter than the average bond distance (2.17 \AA) found in tribenzyltin acetate^[9], and the sum of the covalent radii (2.17 \AA)^[4]. The intramolecular Sn(1) – O(1) bond length of 2.194 \AA is longer than that in $(C_6H_5CH_2)_3SnO_2CCH_3$ (2.14 \AA)^[9], $(C_6H_{11})_3SnO_2CCH_3$ (2.142 \AA)^[10], and in agreement with value of 2.185 \AA found for $Me_3SnO_2CC_5H_4N \cdot H_2O$ ^[11]. The intermolecular Sn(1) – O(2a) distance of 2.522 \AA is shorter than that in $(C_6H_5CH_2)_3SnO_2CCH_3$ (2.65 \AA), but is longer than that in $Me_3SnO_2CC_5H_4N \cdot H_2O$ (2.43 \AA). The C-O bond length for the strongly coordinating oxygen atoms O(1), O(2) of 1.24 \AA , 1.28 \AA is also in good agreement with the value of 1.24 \AA , 1.31 \AA found for $(C_6H_5CH_2)_3SnO_2CCH_3$.

The distortions from true trigonal bipyramidal symmetry are reflected in the interatomic angles. The angles of O(1) - Sn(1) - C(1) (95.5°), O(1) - Sn(1) - C(5) (100.1°), O(1) - Sn(1) - C(9) (90.2°) are greater than 90° ; In contrast, all angles of O(2a) - Sn(1) - C(1) (85.8°), O(2a) - Sn(1) - C(5) (85.0°), O(2a) - Sn(1) - C(9) (83.2°) are less than 90° ; So on the side of the intramolecular Sn-O bond{ Sn-O(1)} the *n*-butyl group is moved away from the bulk of the acetate group; Particularly from the sterically large indolyl group. The angle of O(1) - Sn(1) - O(2a) (172.9°) is larger than that of (168°) in complex $(C_6H_5CH_2)_3SnO_2CCH_3$, but is less than the mean value of 174.6° in compound $Me_3SnO_2CC_5H_4N \cdot H_2O$ ^[9], this shows that the atoms O(1), Sn(1) and O(2a) are nearly linear. The angles of O(1) - C(21) - O(2) (121.7°), C(1) - Sn(1) - C(5) (121.7°), C(1) - Sn(1) - C(9) (117.9°) and C(5) - Sn(1) - C(9) (117.9°) consistent with that of in the literature of the $Me_3SnO_2CC_5H_4N \cdot H_2O$.

The most interesting aspect of the structure concerns the non-coordination of the nitrogen atom of indolylacetate ligand. As can be seen from Fig. 1, the nitrogen atom is directed away from the tin atom. Furthermore, the nitrogen atom does not coordinate to tin atom in the crystal lattice. This is different from the compound $[(n-Bu)_2Sn(O_2CC_5H_4N)]_2O$ in which the nitrogen atom in pyridyl group can coordinate to Sn atom^[15].

The assignment of IR bands of this complex has been made by comparison with the IR spectrum of sodium 3-indolylacetate, IR spectral data of the title compound also imply the presence of bidentate in carboxylate groups, with $\Delta\nu[\nu(COO)_{asym} - \nu(COO)_{sym}]$ of 187 cm^{-1} , this is 47 cm^{-1} lower than that of sodium salt of the ligand ($\Delta\nu$ 234 cm^{-1}). So in the complex the two oxygen atoms do not chelate the same Sn atom^[16].

The 1H NMR spectrum shows the expected integration and peak multiplicities. The tri-*n*-butyltin compound exhibits resonance in the 0.8~1.6 ppm region. Signals for the other groups, such as indolyl H appear at the same positions as in the ligand.

3 Supplementary material

Tables of atomic positional and thermal parameters, full list of bond distances and angles, and lists of observed and calculated structure factors are available from the authors on request.

Acknowledgements: We acknowledge the Financial support of the Shandong Province Natural Science Foundation, P. R. China.

References

- [1] Molloy K. C., Purcell T. G., Hahn E. et al *Organometallics*, **1986**, **5**, 85.
- [2] Evans C. J., Karpel S. *Organotin Compounds in Modern Technology*, Elsevier Amsterdam, **1985**.
- [3] Gross D. C. *Inorg. Chem.*, **1989**, **28**, 2355.
- [4] Yokoo M., Ogura J., Kanzawa T. *J. Polym. Sci. Polym. Lett. Ed.*, **1967**, **5**, 57.
- [5] Tienink E. R. T. *Appl. Organomet. Chem.*, **1991**, **5**, 1.
- [6] Haidue I., Silvestru C. *Coord. Chem. Rev.*, **1990**, **99**, 253.

- [7] Vasta C., Jain V. K., Das T. K., Tiekink E. R. T. J. *Organomet. Chem.*, **1991**, **421**, 21.
- [8] Ng S. W., Kumar Das V. G., Skelton B. W. et al *J. Organomet. Chem.*, **1989**, **377**, 211.
- [9] Alcock N. W., Timms R. E. *J. Chem. Soc. A*, **1968**, 1873.
- [10] Alcock N. W., Timms R. E. *J. Chem. Soc. A*, **1968**, 1876.
- [11] Harrison P. G., Philips R. C. *J. Organomet. Chem.*, **1979**, **182**, 37.
- [12] Calogero S., Ganis P. J. *Organomet. Chem.*, **1981**, **191**, 381.
- [13] Wang R. J., Wang H. G., Yao X. K. *Acta Chimica Sinica*, **1989**, **47**, 209.
- [14] Wells A. F. *Structure Inorganic Chemistry*, Oxford University Press: London, **1962**, p54.
- [15] Parulekar C. S., Jain V. K., Das T. K., Gupta A. R. *J. Organomet. Chem.*, **1989**, **372**, 193.
- [16] Xie J. L., Li X. Z., Zhang S. H., Zhang D. K. *Acta Chimica Sinica*, **1991**, **49**, 723.