Note

One-dimensional Infinite Chain Organotin Compounds: Synthesis and Structural Characterization of Triphenyltin Thiazole-2-carboxylate and Triphenyltin 3-Pyridinylcarboxylate

YIN, Han-Dong*(尹汉东) WANG, Chuan-Hua(王传华) MA, Chun-Lin(马春林)
WANG, Yong(王勇)
Department of Chemistry, Liaocheng University, Liaocheng, Shandong 252059, China

Triphenyltin thiazole-2-carboxylate (1) and triphenyltin 3-pyridinylcarboxylate (2) were synthesized by the reaction of sodium thiazole-2-carboxylate or sodium 3-pyridinylcarboxylate with the triphenyltin chloride and their crystal structures were determined by single crystal X-ray diffraction analysis. In the structure of 1, the tin atom is five-coordinated in a distorted trigonal bipyramidal structure. Due to the presence of a close intermolecular Sn···S interaction distance of 0.3666 nm, the structure can be described as a weakly-bridged one-dimensional chain compound. In the structure of 2, the tin atom is five-coordinated with bridging 3-pyridinylcarboxylate ligands N atom and resulting structure is one-dimensional chain compound.

Keywords triphenyltin, thiazole-2-carboxylate, 3-pyridinylcarboxylate, one-dimensional chain compound, crystal structure

Introduction

Organotin carboxylates are widely used as biocides, fungicide and as homogeneous catalysts in industry.[1-6] In order to explore the relationships between biological activity and structure, a number of such molecules have been synthesized and studied in recent years.[7-15] Studies on organotin compounds having carboxylate ligands with additional donor atoms, such as a nitrogen (available for coordination to tin atom) have revealed some new structural types. For example, dimethyltin di-(2-pyridinylcar-boxylate)[9] has a seven-coordinated tin atom, owing to the multidentate nature of the bridging 2-pyridinylcarboxylate ligand. However, the dimethyl di-(2-furanylcarboxylate) and diethyl di-(2-thiophenylcarboxylate) contain six-coordinated tin centers.[10] As an extension of our studies of organotin carboxylate with additional donor atoms residing on the carboxylate ligand,[11-13] we now report the syntheses and structures of triphenyltin thiazole-2-carboxylate (1) and triphenyltin 3-pyridinylcarboxylate (2), in order to ascertain whether the S or N hetero atom coordinates to the tin atom or not.

Experimental

General procedure

All reactions were carried out under nitrogen atmosphere with use of standard Schlenk technique. Benzene was distilled under nitrogen in the presence of sodium and benzophenone before use. IR spectra were recorded with a Nicolet-460 spectrophotometer as KBr discs. Elemental analyses were performed in a Perkin-Elmer II elemental analyzer. Tin was estimated as SnO_2.

Syntheses of triphenyltin thiazole-2-carboxylate (1) *and triphenyltin 3-pyridinylcarboxylate* (2)

Anhydrous sodium thiazole-2-carboxylate or sodium 3-pyridinecarboxylate (1.2 mmol) was added to a ben-

* E-mail: handongyin@163.com
Received February 6, 2002; revised June 3, 2002; accepted June 4, 2002.
Project supported by the Natural Science Foundation of Shandong Province (No. Z2001B02) and the Foundation of State Key Laboratory of Crystal Materials, Shandong University.

zene (10 mL) solution of Ph_3SnCl (1.0 mmol) and stirred for 15 h at 40 ℃. The precipitated salts were removed by filtration. The clear solution thus obtained was evaporated under vacuum to leave a white solid. The white solid was dissolved in 5 mL of dichloromethane. Hexane (10 mL) was added to the solution. The mixture was allowed to stand for 3—5 days, and then the crystals were formed.

1 Yield 0.36 g, 75%, m.p. 78—80 ℃; IR (KBr) ν: 3061, 3025 (ArH), 1620, 1426 (CO_2), 542 (Sn—C), 448 (Sn—O) cm^{-1}. Anal. calcd for $C_{22}H_{17}NO_2SSn$: C 55.27, H 3.58, N 2.93, S 6.71, Sn 24.82; found C 55.48, H 3.64, N 3.09, S 6.54, Sn 24.99.

2 Yield 0.37 g, 78%, m.p. 189—190℃; IR (KBr) ν: 3052, 3046 (ArH), 1653, 1351 (CO_2), 575 (Sn—C), 492 (Sn—N), 451 (Sn—O) cm^{-1}. Anal. calcd for $C_{24}H_{19}NO_2Sn$: C 61.06, H 4.06, N 2.97, Sn 25.14; found C 61.31, H 4.18, N 2.90, Sn 25.21.

Crystal structure determination

The X-ray diffration experiments for triphenyltin(IV) thiazole-2-carboxylate (**1**) and triphenyltin(IV) 3-pyridinylcarboxylate (**2**) were made on a Bruker Smart 1000 CCD diffractometer with graphite monochromated Mo Kα ($\lambda = 0.071073$ nm) radiation. The structure was solved by the direct methods and expanded using Fourier techuiques with Shelxl-97 program. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations. Crystallographic data for **1** and **2** are listed in Table 1.

Results and discussion

The crystal structures and stereograms of the compounds packing in a crystal unit cell are shown in Figs. 1—4. Selected bond distances and angles are listed in Tables 2 and 3.

Table 1 Crystallographic data for **1** and **2**

Crystal data	**1**	**2**
Molecular formula	$C_{22}H_{17}NO_2SSn$	$C_{24}H_{19}NO_2Sn$
Formular weight	478.12	472.09
Crystal system	Monoclinic	Tetragonal
Space group	$P2_1/n$	$P4_3$
Unit cell dimensions		
a (nm)	1.3433(4)	1.20649(16)
b (nm)	1.2773(4)	1.20649(16)
c (nm)	1.4241(4)	1.4566(3)
α (°)	90	90
β (°)	106.498(4)	90
γ (°)	90	90
V (nm^3)	2.3428(8)	2.1202(6)
Z	4	4
D_{cal} (g/cm^3)	1.356	1.479
μ (mm^{-1})	1.387	1.223
$F(000)$	954	944
Crystal size (mm)	0.60×0.50×0.40	0.60×0.50×0.40
Theta range (°)	$1.73 \leqslant \theta \leqslant 26.46$	$1.69 \leqslant \theta \leqslant 25.03$
T (K)	301(2)	293(2)
Observed reflections/cut-off	$4096/2\sigma(I)$	$3727/2\sigma(I)$
R_{int}	0.0233	0.0299
R_1/wR_2	0.0265/0.0634	0.0382/0.0908
Largest difference Fouzies	5.10/−5.03	7.07/−3.92
Peak hole ($e \times 10^2 \cdot nm^{-3}$)		

Table 2 Selected bond distances (nm) and angles (°) for **1**

Sn(1)—O(1)	0.2082(2)	Sn(1)—O(2)	0.2771(2)	Sn(1)—C(17)	0.2139(3)
Sn(1)—C(11)	0.2118(3)	Sn(1)—C(5)	0.2123(3)	Sn(1)···S(1)#	0.3666
S(1)—C(4)	0.1675(4)	S(1)—C(2)	0.1702(3)	O(1)—C(1)	0.1307(3)
N(1)—C(2)	0.1429(4)	N(1)—C(3)	0.1445(5)	O(2)—C(1)	0.1221(4)
O(1)-Sn(1)-C(11)	108.15(10)	O(1)-Sn(1)-C(5)	109.23(10)	O(1)-Sn(1)-C(17)	94.32(9)
C(11)-Sn(1)-C(5)	118.08(11)	C(11)-Sn(1)-C(17)	113.61(11)	C(5)-Sn(1)-C(17)	110.70(10)
O(2)-Sn(1)-C(11)	85.2(2)	O(2)-Sn(1)-C(5)	81.2(3)	O(2)-Sn(1)-C(17)	145.8(5)
O(2)-Sn(1)-O(1)	51.8(5)	C(10)-C(5)-Sn(1)	120.5(2)	C(6)-C(5)-Sn(1)	121.5(2)
C(1)-O(1)-Sn(1)	108.29(18)	C(16)-C(11)-Sn(1)	119.5(2)	C(12)-C(11)-Sn(1)	121.7(2)
C(18)-C(17)-Sn(1)	120.5(2)	C(22)-C(17)-Sn(1)	121.3(2)	N(1)-C(2)-S(1)	112.5(2)

Symmetry operations.

Table 3 Selected bond distances (nm) and angles (°) for **2**

Sn(1)—O(1)	0.2138(5)	Sn(1)···O(2)	0.3259	Sn(1)—C(13)	0.2120(7)
Sn(1)—C(19)	0.2132(7)	Sn(1)—C(7)	0.2139(8)	Sn(1)—N(1)	0.2529(7)
N(1)—C(6)	0.1331(11)	N(1)—C(2)	0.1335(9)	O(1)—C(1A)	0.1254(8)
O(1)-Sn(1)-C(13)	90.1(2)	O(1)-Sn(1)-C(19)	96.0(2)	O(1)-Sn(1)-C(7)	97.9(2)
C(13)-Sn(1)-C(19)	117.7(3)	C(13)-Sn(1)-C(7)	117.8(3)	C(19)-Sn(1)-C(7)	123.6(3)
O(1)-Sn(1)-N(1)	172.49(19)	C(19)-Sn(1)-N(1)	88.1(2)	C(7)-Sn(1)-N(1)	84.9(2)
C(13)-Sn(1)-N(1)	87.4(2)	C(1A)-O(1)-Sn(1)	124.1(5)	C(2)-N(1)-Sn(1)	117.0(4)
C(6)-N(1)-Sn(1)	126.8(6)	C(8)-C(7)-Sn(1)	121.3(7)	C(12)-C(7)-Sn(1)	118.9(6)
C(14)-C(13)-Sn(1)	11.9(6)	C(18)-C(13)-Sn(1)	123.1(7)	C(24)-C(19)-Sn(1)	117.6(5)
C(20)-C(19)-Sn(1)	122.3(7)				

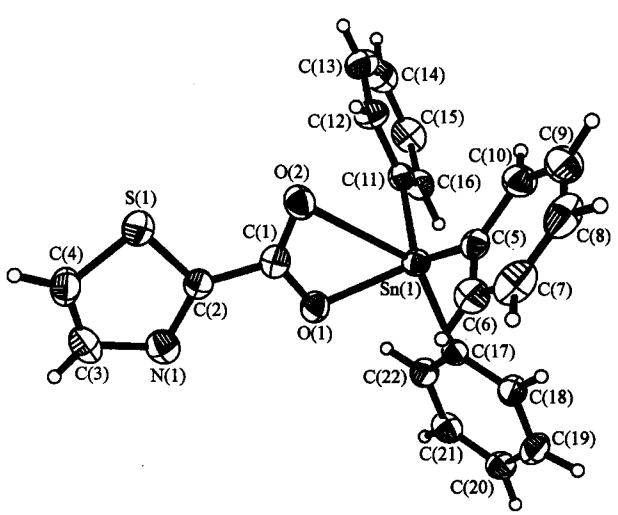

Fig. 1 Crystal structure of **1**.

The molecular structure of **1** is depicted in Fig. 1. The tin atom is five-coordinated with a distorted trigonal bipyramid [Sn(1)—O(1) 0.2082(2) nm, Sn(1)—O(2) 0.2771(2) nm, Sn(1)—C(5) 0.2123(3) nm, Sn(1)—C(11) 0.2118(3) nm, Sn(1)—C(17) 0.2139(3) nm]. An additional feature was noticed that a close intermolecular Sn···S interaction distance of 0.3666 nm (the sum of the Van Der Waals radii for Sn and S of 0.40 nm) was found. The structure was thus described as a one-dimensional chain catena-polymer through a weakly interaction between the sulfur atom and tin atom of adjacent molecule. This phenomenon was not observed in the compounds $Et_2Sn(O_2CC_4H_3S)_2$[11] and $\{[^nBu_2Sn(O_2CC_4H_3S)]_2O\}_2$.[13]

The tin atom in **1** is essentially at the center of a distorted trigonal bipyramid geometry with the two carbon atoms, C(5) and C(11) of the phenyl groups and the oxygen atom O(1) occupying the equatorial position. The third carbon atom C(17) of the phenyl group clearly occupies one axial position, while the second oxygen atom O(2) of the thiazole-2-carboxylate ligand occupies the second axial site but at a distance much large than expected for a normal covalent Sn—O bond, forming an angle of 145.8(5)° rather than 180° with the Sn(1)—C(17)

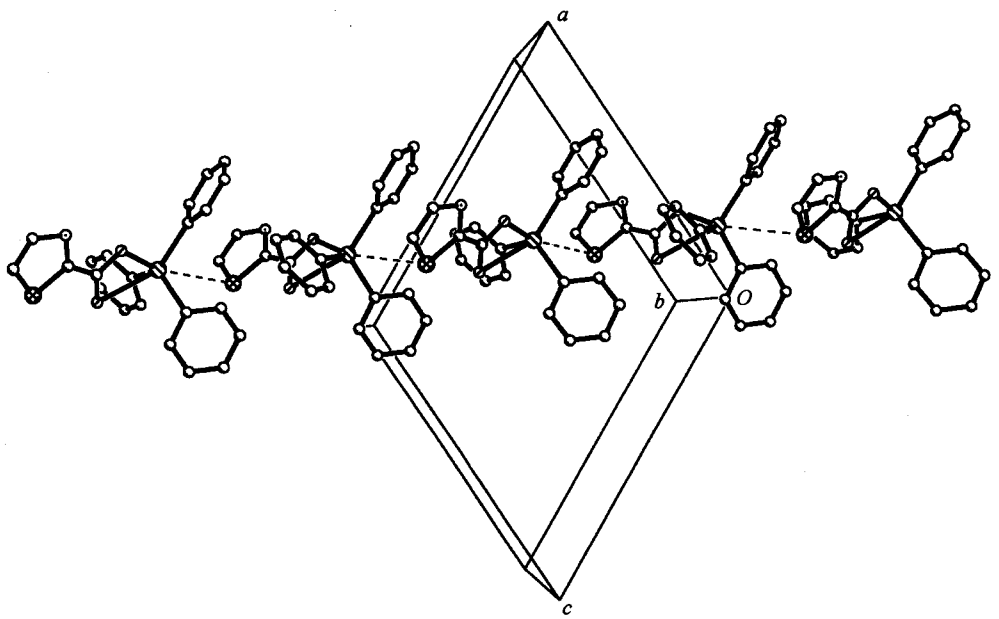

Fig. 2 Perspective view showing the Sn···S weakly-bridged one-dimensional chain network of **1**.

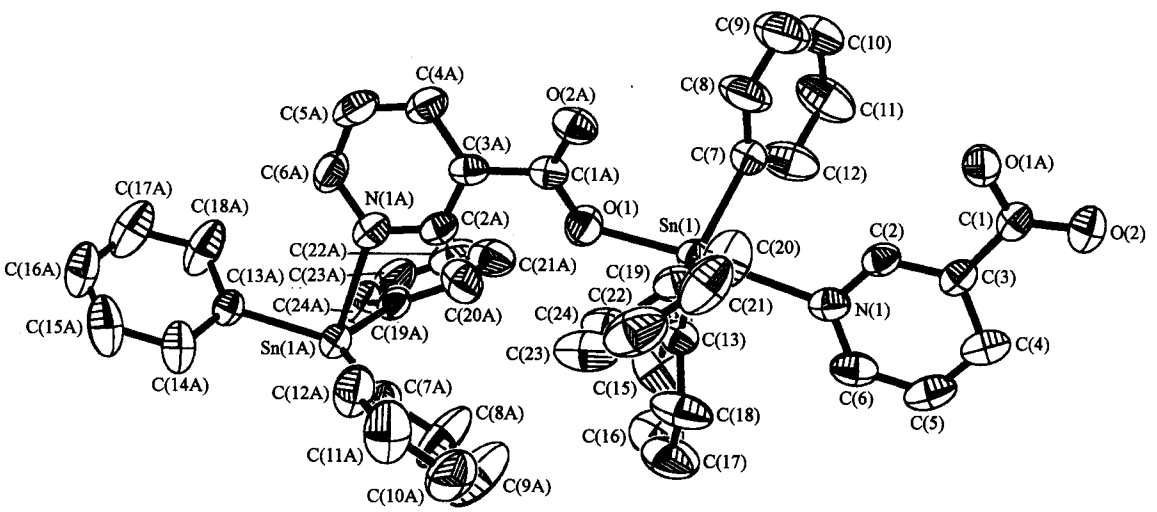

Fig. 3 Crystal structure of **2**.

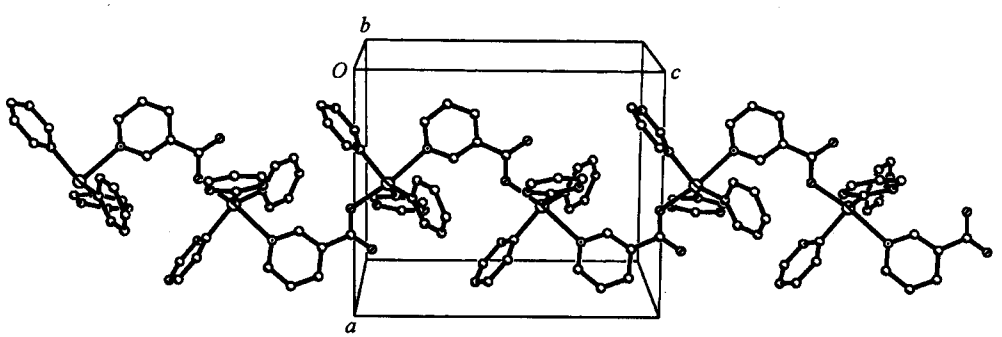

Fig. 4 Perspective view showing the Sn—N bridged one-dimensional chain network of **2**.

bond. As an indication the sum of the equatorial angles (335.46°) deviates by 24.54° from the 360°, sothe atoms C(11), O(1), C(5) and Sn(1) are not in the same plane.

Triphenyltin 3-pyridinecarboxylate (**2**) possesses an unequivocally polymeric structure, which differs from those of tributyltin 2-(5-*tert*-butyl)furanylcarboxylate[9] and tribenzyltin 2-(5-*tert*-butyl)furanylcarboxylate.[9] Each tin atom is five-coordinated in a trigonal bipyramidal structure by coordination of the nitrogen atom of an adjacent 3-pyridinylcarboxylate molecule. The central tin atoms are surrounded axially by one oxygen, one nitrogen atoms and equatorially by the three carbon atoms of the phenyl groups. The intramolecular Sn(1)—O(1) bond distance of 0.2138 (5) nm is longer than those in $\{[^nBu_2Sn(2\text{-pic})]_2O\}_2$(0.20544 nm and 0.2110 nm),[7] but is shorter than those in $Me_3SnO_2CC_5H_4N\cdot H_2O$ (0.218 nm and 2.21 nm).[16] The Sn(1)—O(2) distance of 0.3259 nm is much larger than the sum of the covalent radii for Sn and O of 0.207 nm, showing that the O(2) does not contact with the Sn atom closely. The Sn(1)—N(1) bond distance of 0.2529(7) nm is larger than the sum of the covalent radii of Sn and N (0.215 nm), but is considerably less than the sum of the Van der Waals radii (0.375 nm) which indicates that there are interaction between them.

In compound **2**, the angles of O(1)-Sn(1)-C(13) [90.1(2)°], O(1)-Sn(1)-C(7) [97.9(2)°], O(1)-Sn(1)-C(19) [96.0(2)°], the later two are greater than 90°. In contrast, the angles of C(13)-Sn(1)-N(1) [87.4(2)°], C(7)-Sn(1)-N(1) [84.9(2)°], C(19)-Sn(1)-N(1) [88.1(2)°] are all less than 90°, and all much moved away from 90°. The angle of O(1)-Sn(1)-N(1) [172.49 (19)°] shows that the atoms O(1), Sn(1) and N(1) are nearly linear.

The IR bands of **1** and **2** have been assigned by comparison with those of related sodium thiazole-2-carboxylate, sodium 3-pyridinylcarboxylate and Ph_3SnCl. The difference $\Delta\nu$ between $\nu_{as}(COO)$ and $\nu_s(COO)$ is used to determine the interaction between metal and carboxyl.[17-19] The $\Delta\nu$ [$\nu_{as}(COO) - \nu_s(COO)$] value of 194 cm^{-1} for **1** strongly indicates the bidentate chelating of the carboxylate group.[20] The $\Delta\nu$ [$\nu_{as}(COO) - \nu_s(COO)$] value of 302 cm^{-1} for **2** indicates the monodentate coordinating of the carboxylate group.[20] The bands in the region of 448 and 451 cm^{-1} were assigned to ν(Sn—O). The IR spectrum of **2** at 492 cm^{-1} is assigned to $\nu_{Sn\text{-}N}$[21] which shows that the N hetero atom in the pyridine group coordinates to tin atom.

References

1 Xie, Q.-L.; Li, S.-H.; Zhang, D.-K.; Zhang, Z.-G.; Hu, J.-M. *Acta Chim. Sinica* **1991**, *49*, 723 (in Chinese).

2 Luo, N.; Sun, L.-J.; Liu, Z.-Z.; Xie, Q.-L.; Mu, Z.-D. *J. Appl. Chem.* **2000**, *17*, 155 (in Chinese).

3 Yin, H.-D.; Zhang, R.-F. Ma, C.-L. *Fine Chem.* **1999**, *16*, 14 (in Chinese).

4 Yin, H.-D.; Ma, C.-L.; Zhang, R.-F. *Spec. Petro. Chem.* **1999**, *93*, 14 (in Chinese).

5 Lu, W.-G.; Tao, J.-X..; Li, X.-Y.; Wang, Y.-Z. *J. Appl. Chem.* **2000**, *17*, 12 (in Chinese).

6 Gielen, M.; Khloufi, A. M.; Biesmans, M.; Kayser, R. *Appl. Organomet. Chem.* **1993**, *7*, 201.

7 Parulekar, C. S.; Jain, V. K.; Das, T. K.; Gupta, A. R.; Hoskins, B. F.; Tiekink, E. R. T. *J. Organoment. Chem.* **1989**, *372*, 193.

8 Parulekar, C. S.; Jain, V. K.; Das, T. K.; Tiekink, E. R. T. *J. Organoment. Chem.* **1990**, *387*, 163.

9 Xie, Q.-L.; Xu, X.-H.; Wang, H.-G.; Yao, X.-K.; Wang, R.-J.; Zhang, Z.-G.; Hu, J.-M. *Acta Chim. Sinica* **1991**, *49*, 1085 (in Chinese).

10 Lockhart, T. P.; Davidson, F. *Organometallics* **1987**, *6*, 2471.

11 Vatsa, C.; Jain, V. K.; Kesavadas, T.; Tiekink, E. R. T. J. *Organomet. Chem.* **1991**, *410*, 135.

12 Yin, H.-D.; Zhang, R.-F.; Ma, C.-L. *J. Inorg. Chem.* **1998**, *14*, 101 (in Chinese).

13 Vatsa, C.; Jain, V. K.; Das, T. K.; Tiekink, E. R. T. *J. Organomet. Chem.* **1990**, *396*, 9.

14 Vatsa, C.; Jain, V. K.; Das, T. K.; Tiekink, E. R. T. *J. Organomet. Chem.* **1991**, *418*, 329.

15 Vatsa, C.; Jain, V. K.; Das, T. K.; Tiekink, E. R. T. *J. Organomet. Chem.* **1991**, *421*, 21.

16 Harrison, P. G.; Philips, R. C. *J. Organomet. Chem.* **1979**, *182*, 37.

17 Yin, H.-D.; Wang, C.-H.; Wang, Y.; Zhang, R.-F.; M, C.-L.; Tao, X.-Q. *Chin. J. Chem.* **2001**, *19*, 783.

18 Yin, H. D.; Wang, C. H.; Wang, Y.; Ma, C. L. *Indian J. Chem.* **2001**, *40A*, 1089.

19 Fang, X. N.; Song, X. W.; Xie, Q. L. *J. Organomet. Chem.* **2001**, *619*, 43.

20 Yin, H.-D.; Ma, C.-L.; Zhang, R.-F.; Zhang, L.-Y. *J. Inorg. Chem.* **2000**, *16*, 97 (in Chinese).

21 Dey, D. K.; Saha, M. K.; Das, M. K.; Bhartiya, N.; Bansal, R. K.; Rosair, G.; Mitra, S. *Polyhedron* **1999**, *18*, 2687.

(E0202064 SONG, J. P.; DONG, L. J.)