Synthesis, characterization and crystal structure of a new supramolecular system containing triorganotin(IV) and 1,3,5- Benzenetricarboxylic acid

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Abstract

Herein, triorganotin(IV) complex $C_{53}H_{57}NO_8Sn_2$ was prepared by the reaction of triphenyltin(IV) chloride, triethylamine and 1,3,5- benzenetricarboxylic acid in 1:3:3 molar ratio in MeOH. The complex is characterized by FT-IR spectroscopy, (^{1}H, ^{13}C, ^{119}Sn) NMR and X-ray single crystal diffraction. This compound crystallizes in the monoclinic system, space group $P2_1/c$ with $Z= 4$. The unit cell dimensions for complex are: a =15.157(3)Å, b = 20.802(4)Å and c = 15.719(3)Å, β= 105.12(3)°.

Keywords: Organotin(IV), Crystal structure, 1,3,5- Benzenetricarboxylic acid, Spectroscopy.

1. Introduction

Organotin(IV) carboxylates have attracted much attention, owing to the enormous variety of interesting structural topologies and their ecological and biological chemistry activities.

The ecological and biological chemistry of organotin(IV) carboxylates have been the subjects of interest for some time due to their increasingly extensive use in industry and agriculture. The biochemical activity of organotin carboxylates is influenced significantly by the structure of the molecule and the coordination number of the tin atoms. In this work, we selected 1,3,5-benzenetricarboxylic acid (H_3TMA) as ligand because of having three carboxylic acid groups.

Herein, we report the synthesis of triorganotin(IV) complex, $C_{53}H_{57}NO_8Sn_2$, by the reaction of triphenyltin(IV) chloride, triethylamine and 1,3,5- benzenetricarboxylic acid in 1:3:3 molar ratio in MeOH. The complex is characterized by FT-IR spectroscopy, (^{1}H, ^{13}C, ^{119}Sn) NMR and X-ray single crystal diffraction. This compound crystallizes in the monoclinic system, space group $P2_1/c$ with Z= 4. The unit cell dimensions for complex are: a =15.157(3)Å, b = 20.802(4)Å and c = 15.719(3)Å, β= 105.12(3)°.

2. Experimental

All the chemicals were purchased from Merck Co. and were used as received.

2.1. Synthesis of $[(SnPh_3)_2[(TMA)(Et_3N)]].(CH_3OH)_2$

This complex was prepared by the branch tube method. Triphenyltin(IV) chloride (1.5 mmol), triethylamine (420 μL) and H_3TMA (0.5 mmol) was placed in one arm of the branched tube. Methanol was carefully added to fill both branches of tube. After that, the tube wrapped and the arm containing materials immersed in a bath at 60°C while the other was at ambient temperature. After 5 days, white crystals (m.p. = 230 °C) had appeared in the cooler arms of branch tube.

IR (KBr, cm^{-1}): 3296(s), 3064(s), 2678(s), 1622(s), 1429(s), 449(m)

^{1}H-NMR (DMSO-d_6, *ppm*) δH: 1.06(t, 9H, CH_3, J= 7), 2.82(q, 6H, CH_2, J=7), 3.17 (s, 3H, CH_3), 7.34-7.87 (m, 30H, C_6H_5), 8.39(s, 3H)

^{13}C-NMR (DMSO-d_6, *ppm*) δC: 9.4, 45.3, 48.6, 127.6, 128.1, 128.5, 132.4, 135.8, 136.2, 136.5, 143.9, 168.4

^{119}Sn-NMR (DMSO-d_6, *ppm*) δSn: 257.47

3. Results and discussion

In the FT-IR spectrum, the appeared strong absorption at 449 cm^{-1}, which is absent in the spectrum of the free ligand, is assigned to the Sn–O stretching vibration. Two observed absorption bands in the ranges of 1623–1637 cm^{-1} and 1307–1326 cm^{-1} can be assigned to the asymmetric and the symmetric vibrations of COO group, respectively.

In the ^{1}H-NMR spectrum, the observed resonances at δ = 1.06 and δ = 2.82 ppm are related to the protons of methyl and methylene of triethylamine, respectively. The appeared resonance observed at δ = 3.17 ppm is attributed to the proton of methanol. The observed resonances at δ = 7.34-8.87 ppm can be assigned to the protons of phenyl groups with the same positions as in the ligand. The appeared resonance at δ = 8.39 ppm, related to the protons of benzene carboxylic acid. In the ^{13}C NMR spectrum, the singlet resonance at 168.4 is owing to the COO groups in the complex. The observed resonances at 9.4, 45.3, 48.6 and 127.6-143.9 ppm are related to CH_3 and CH_2 of Et_3N, CH_3 of methanol and aromatic rings in the complex, respectively. There is only one resonance at 258.4 ppm in the ^{119}Sn NMR spectrum.

This complex crystallizes in the monoclinic system, space group $P2_1/c$ with Z= 4. The unit cell dimensions for complex are: a =15.157(3)Å, b = 20.802(4)Å and c = 15.719(3)Å, β= 105.12(3)°. The molecular structure of the title compound is shown in Fig. 1. The crystallographic data is listed in Table 1. Selected bond distances and angles are given in Table 2.

Table 1. Crystallographic and structure refinements data for title compound**.**

Empirical formula	C_{53} H_{57} N O_8 Sn_2
Formula weight	1073.42
Temperature (K)	120(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
	a = 15.157(3) Å
	b = 20.802(4) Å
	c = 15.719(3) Å
	β = 105.12(3) °
Volume (Å^3)	4784.6(16)
Z	4
Calculated density (Mg/m^3)	1.490
Absorption coefficient(mm^{-1})	1.099
F(000)	2184
Theta range for data collection (°)	2.38 to 25.00
Reflections collected / unique	22054 / 8377 [R(int) = 0.1525]
Max. and min. transmission	0.9270 and 0.7941
Refinement method	Full-matrix least-squares on F^2
Final R indices [I>2sigma(I)]	R_1 = 0.0779, wR_2 = 0.1273
R indices (all data)	R_1 = 0.1463, wR_2 = 0.1426

Bond lengths and angles within the aromatic rings are in good agreement with those expected for sp^2 hybridization of aromatic carbon atoms. The Sn−O (carboxylate oxygen atom) bond lengths are 2.163(5)–2.267(7) Å and relative Sn–C bond lengths are 2.094(11) –2.157(10) Å. These bond lengths and angles are similar to those of the complexes reported [11]. The distances of Sn–O (solvent (methanol) oxygen atom) bond is 2.487(6) Å.

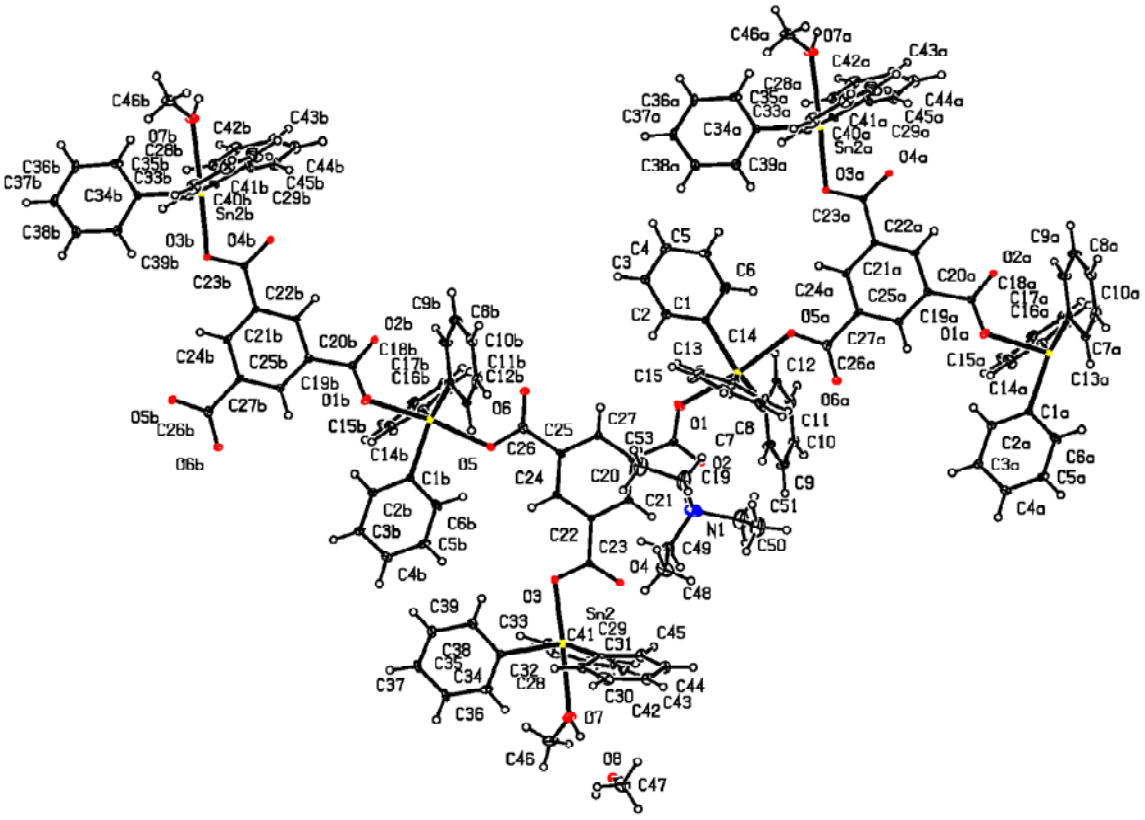

Fig. 1 The molecular structure of the title compound.

Table 2. Selected bond distances (Å) and bond angles (◦) for title compound.

Sn(1)-C(7)	2.118(10)
Sn(1)-C(13)	2.132(10)
Sn(1)-C(1)	2.143(9)
Sn(1)-O(5)#1	2.231(7)
Sn(1)-O(1)	2.267(7)
Sn(2)-C(28)	2.094(11)
Sn(2)-C(40)	2.137(10)
Sn(2)-C(34)	2.157(10)
Sn(2)-O(3)	2.163(5)
Sn(2)-O(7)	2.487(6)
O(5)#1-Sn(1)-O(1)	172.2(2)
C(13)-Sn(1)-O(1)	90.0(3)
C(1)-Sn(1)-O(1)	86.2(3)
C(7)-Sn(1)-O(1)	91.9(3)
C(7)-Sn(1)-O(5)#1	91.0(3)
C(13)-Sn(1)-O(5)#1	93.3(3)
C(1)-Sn(1)-O(5)#1	86.0(3)

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