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# Synthesis, crystal structure and theoretical calculation of triphenyltin (IV) polymer based on 2,4-dichlorophenylacrylic acid

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#### ABSTRACT

Reaction between 2,4-dichlorophenylacrylic acid (HL) and triphenyltin (IV) hydroxide to yield the complex  $[(Ph_3Sn)L]_n$  (1). The complex has been characterized by elemental analysis, infrared spectrum and single crystal X-ray diffraction. The structural analysis shows that complex 1 possesses 1 D chain structure in which every tin atom is five coordinated. The 1 D chains linked by C(66)-H(66)-Cl(2) hydrogen bonds to aggregate in 2 D framework. Additionally, the PXRD, TG, and luminescent property were also investigated. The quantum chemistry calculations was performed with the Gaussian09 program.

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#### KEYWORDS

2,4-dichlorophenylacrylic acid; triphenyltin (IV) polymer; crystal structure; theoretical calculations

### Introduction

Coordination polymers<sup>[1]</sup> and metal-organic frameworks,<sup>[2-4]</sup> colloquially known as MOFs, have attracted increasing attention, due to their potential broad applications in catalysis,<sup>[5,6]</sup> batteries,<sup>[7]</sup> gas storage/separation,<sup>[8]</sup> sensor,<sup>[9]</sup> and drug delivery.<sup>[10]</sup> Organotin chemistry is an important part of organometallic chemistry. The environmental and biological chemisty of Organotin complexes have been the subjects of interest for some time due to their increasingly widespread use.[11,12] Organotin complexes are widely used in industry, agriculture and medicine,<sup>[13,14]</sup> for example as homogeneous catalysts (function as supports for anchoring electroactive, photoactive, coordination platforms),<sup>[15,16]</sup> special anti-tumour materials,<sup>[17,19]</sup> wood preservatives and fungicides for plant protection.<sup>[20]</sup> From all the studied organotin compounds, the tin coordination polymers<sup>[21]</sup> are no doubt the most intensively investigated.<sup>[22]</sup> The tin complexes have a rich variety of coordination modes so that it makes the property diversified,<sup>[23]</sup> among these coordination modes the carboxylate ligands have monodentate and bidentate coordination forms. Through changing the types of carboxylate ligands and the hydrocarbon groups in organotin compounds, a large number of organotin carboxylates compounds with novel and diverse structures can be obtained. Mazhar et al. summarized the synthetic methods, physical properties and chemical properties of more than 300 organotin carboxylates.<sup>[24]</sup>

In order to further exploring the structural types of organotin carboxylates and the coordination mode of central tin atoms, an organotin carboxylate was designed and synthesized from the reaction of 2,4-dichlorophenylacrylic acid (HL) with triphenyltin hydroxide.

#### Experimental

## Synthesis of 2,4-dichlorophenyl acrylic acid

 $\beta$ -substituted phenylacrylic acid has many physiological functions and it can be prepared by Knoevenagel-Doebner synthesis method.<sup>[25]</sup> 2,4-dichlorophenylacrylic acid (HL) was synthesized from 2,4-dichlorobenzaldehyde and malonic acid with pyridine as basic solvent and toluene as dispersant under the condition of aniline as the catalyst (Route 1). The detail steps are as follows:

In a round-bottom flask, 7.5 g malonic acid (0.07 mol) and 8 mL pyridine were added to dissolve malonic acid. After the malonic acid dissolved, toluene 15 mL, 2,4-Dichlorobenzaldehyde 11.37 g (0.065 mol) and with catalytic amount 0.7 mL aniline were added. A reflux equipment was assembled and heated for 2 hours under electromagnetic stirring. After the reaction, the mixture cooled to room temperature, K<sub>2</sub>CO<sub>3</sub> solution added to the reaction solution, stirred for 10 minutes (if the solid precipitated, then heated dissolved completely in water bath), separated the solution while hot, the water layer is adjusted to pH 2-3 using concentrated HCl. The precipitated solids are filtered, washed and dried. Colorless crystals were obtained by recrystallizing in anhydrous ethanolwater. Productivity: 63.2%, melting point: 158.7-159.4°C. Elemental analysis: calcd. (%) for C<sub>9</sub>H<sub>6</sub>O<sub>2</sub>Cl<sub>2</sub>: C, 49.80; H, 2.79; found (%): C, 47.54; H, 2.62. IR (cm<sup>-1</sup>): 2823~2567  $\nu$ (COOH), 1690  $\nu$ (C = O), 1619  $\nu$ (C = C).

#### Synthesis of [(Ph<sub>3</sub>Sn)L]n (1)

HL (0.43 g, 2.0 mmol) and triphenyltin hydroxide (0.77 g, 2.0 mmol) were added to 40 mL anhydrous toluene solution, heated and refluxed under stirring for 8 hours, cooled to

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room temperature, filtered, and the filtrate was evaporated to obtain white solid (Route 2). The solid was dissolved in ethanol and stayed at room temperature. The colorless transparent crystal was obtained by slowly volatilizing the solvent. Productivity: 52.6%, melting point: 261.1-262.7 °C. Elemental analysis: calcd.(%) for C<sub>54</sub>H<sub>40</sub>C<sub>14</sub>O<sub>4</sub>Sn<sub>2</sub>: C, 57.29; H,3.56; found (%): C, 57.44; H, 3.36. IR data (cm<sup>-1</sup>): 1638 vas(COO),  $1582\nu$ (-C = C-),  $1469\nu$ s(COO), 1514, 1428,  $1398\nu$ (C-C of benzene ring),  $569\nu$ (Sn-C),  $453\nu$ (Sn-O).

# X-ray crystallography

Crystal structure measurement was performed on a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromatic Mo K $\alpha$  ( $\lambda = 0.071073$  nm) radiation by using the  $2\theta$  and  $\omega$  scan mode at 296(2) K.<sup>[26,27]</sup> The structure was determined by direct method and refined by full-matrix least-squares procedure using the SHELXL-2013.<sup>[28]</sup> A total of 27332 independent diffraction intensity data were collected in the range of  $3.42^{\circ} \leq 2\theta \leq 52.18^{\circ}$ , of which 9938 were observed reflections  $[I > 2\sigma (I)]$ . The final deviation factor is  $R_1$ =0.0233,  $wR_2$ =0.0522. Crystallographic parameters and the data collection statistics are given in Table 1. Selected bond lengths and bond angles are listed in Table 2. The Crystallographic data have been deposited with the Cambridge Crystallographic Data Center: deposition numbers CCDC 1922167. These data may be obtained free of charge from the Cambridge Crystallographic Data Center through http://www.ccdc.cam.ac.uk/data request/cif.

#### **Results and discussion**

#### Description of crystal structure

The structure of complex **1** is shown in Figures 1 and 2. The carboxylate as bridging ligand connects two adjacent



Route 1.

triphenyltin groups and forms a one-dimensional chain structure. Each tin atom is five coordinated, forming a twisted trigonal bipyramidal configuration.<sup>[29]</sup> The positions on the equatorial plane are occupied by carbon atoms from three benzene rings, and oxygen atoms from two different carboxyl groups occupy the axial positions. In Table 2, Sn(1)-O(1) = 2.2704(1) Å, Sn(1)-O(3) = 2.2101(2) Å, Sn(2)-O(2) = 2.1944(2) Å, Sn(2)-O(4) = 2.2941(2) Å, these distances are in accordance with the simillar complex in literature.<sup>[30]</sup> The sum of angles between carbon atoms and Sn (1) atoms on the equatorial plane is 359.8 degrees, and that between Sn (2) atoms is 360 degrees, indicating that Sn (1), C (31), C (41) and C (51) are almost coplanar, Sn (2), C (61), C (71) and C (81) are on the same plane.

At the same time, there are interesting intermolecular interactions in complex 1 which help in the construction of the supramolecule. As shown in Figure 3, every pair of chain structure of the molecule is linked by intermolecular

 Table 1. Crystallographic data and structure refinement parameters for the complex 1.

complex 1.		
Empirical formula	$C_{54}H_{40}CI_4O_4Sn_2$	
Formula weight	1132.04	
Temperature	296(2) K	
Wavelength (Å)	0.71073	
Crystal system	Monoclinic	
Space group	P21/n	
a (Å)	10.0635(13)	
b (Å)	23.887(3)	
c (Å)	21.551(3)	
α (°)	90	
β (°)	102.636(2)	
γ (°)	90	
Volume (Å <sup>3</sup> )	5055.0(11)	
Ζ	4	
Density (Mg/m <sup>3</sup> ) calculated	1.487	
Absorption coefficient (mm <sup>-1</sup> )	1.243	
F(000)	2256	
Crystal size (mm <sup>3</sup> )	0.28 imes 0.26 imes 0.22	
Theta range (°)	1.71–26.09	
Limiting indices	$-12 \le h \le 12, -29 \le k \le 17,$	
	$-26 \le l \le 26$	
Reflections collected/unique	27332/9938 [R <sub>int</sub> = 0.0168]	
Refinement method	Full-matrix least-squares on $F^2$	
Data/restraints/parameters	9938/0/577	
Goodness-of-fit on $F^2$	1.027	
Final R indices $[l > 2\sigma (l)]$	$R_1 = 0.0233, wR_2 = 0.0522$	
R indices (all data)	$R_1 = 0.0312, wR_2 = 0.0562$	
Largest diff. peak and hole (e $Å^{-3}$ )	0.436 and -0.454	



Table 2. Selected bond length and angles for complex 1.

O(1)-Sn(1)	2.2704(1)	O(2)-Sn(2)	2.1944(2)
O(3)-Sn(1)	2.2101(2)	O(4)-Sn(2)	2.2941(2)
C(1)-O(1)	1.249(2)	C(1)-O(2)	1.264(2)
C(10)-O(3)	1.255(2)	C(10)-O(4)#1	1.260(3)
C(31)-Sn(1)	2.130(2)	C(41)-Sn(1)	2.129(2)
C(51)-Sn(1)	2.121(2)	C(61)-Sn(2)	2.118(2)
C(71)-Sn(2)	2.125(2)	C(81)-Sn(2)	2.128(2)
C(51)-Sn(1)-C(41)	120.09(9)	C(51)-Sn(1)-C(3)	118.44(9)
C(41)-Sn(1)-C(31)	121.27(9)	C(51)-Sn(1)-O(3)	88.77(8)
C(41)-Sn(1)-O(3)	96.88(8)	C(31)-Sn(1)-O(3)	88.76(7)
C(51)-Sn(1)-O(1)	90.72(8)	C(41)-Sn(1)-O(1)	89.38(7)
C(31)-Sn(1)-O(1)	85.38(7)	O(3)-Sn(1)-O(1)	173.04(6)
C(61)-Sn(2)-C(71)	123.51(9)	C(61)-Sn(2)-C(8)	120.42(9)
C(71)-Sn(2)-C(81)	116.07(9)	C(61)-Sn(2)-O(2)	92.57(7)
C(71)-Sn(2)-O(2)	83.92(7)	C(81)-Sn(2)-O(2)	93.11(7)
C(61)-Sn(2)-O(4)	92.63(7)	C(71)-Sn(2)-O(4)	90.21(7)
C(81)-Sn(2)-O(4)	87.36(7)	O(2)-Sn(2)-O(4)	173.68(6)

Symmetry transformations used to generate equivalent atoms: #1 x + 1/2, -y + 1/2, z + 1/2.



Figure 1. Molecular Structure of Complex 1. (The Symmetry Code A: 0.5 + x, 0.5 - y, 0.5 + z, Ellipsoid Probability 30%).

C(66)-H(66)····Cl(2) hydrogen bonding [H(66)····Cl(2)] = 2.941 Å, C(66)····Cl(2)] = 3.446 Å, and the angle of the C(66)-H(66)····Cl(2) = 115.56°]. The complex is further interconnected and assembled into two-dimensional network structure.

#### IR spectra

The infrared spectra of complex 1 is consistent with those of organotin carboxylates with similar structures.<sup>[31,32]</sup> The bands at 2823-2567 cm<sup>-1</sup> which appear in the free ligand as the  $\nu(OH)$  stretching vibrations, are not observed in complex 1, thus indicating metale-ligand bond formation. The difference between the asymmetric  $[\nu as(COO)]$ and symmetric [ $\nu$ s(COO)] stretching vibrations frequencies of carboxyl groups is a reflection of coordination mode between carboxyl oxygen atoms and Sn atoms.<sup>[33,34]</sup> The asymmetric stretching vibration  $[\nu as (COO)]$  and the symmetric stretching vibration  $[\nu s$ (COO)] of the carboxyl groups of the complex 1 appear at  $1638 \text{ cm}^{-1}$  and  $1469 \text{ cm}^{-1}$ , respectively, the  $\Delta \nu$  [ $\nu$ as (COO)  $-\nu s$ (COO)] is 169 cm<sup>-1</sup>, which indicates that the carboxyl group in complex 1 coordinated with tin atoms in the bidentate form. In addition, the absorption peaks at 569 and  $453 \, \text{cm}^{-1}$  indicate that Sn-C and Sn-O bonds are present in the product.<sup>[35]</sup>

# Luminescent spectra

The luminescent properties of complex 1 and ligand HL have been tested with a 150 W xenon lamp as the excitation source at room temperature and the fluorescence emission spectra of them are illustrated in Figure 4. The emission peak of the ligand HL is located at 410 nm (excitation at 287 nm) and the maximum emission wavelength of the complex 1 shows at 428 nm (excitation at 325 nm). The results indicate that optical transitions of complex is centered on the 2,4-dichlorophenylacrylic acid ligand and the emission peaks are attributed to intra-ligand  $\pi^* \rightarrow \pi$  transitions. Compared to the ligand HL, complex1 exhibits a significant red shift and lower intensity, which can be assigned to the formation of the complex.



Figure 2. One-dimensional Chain Molecular Structure of Complex 1.



Figure 3. 2D network structure assembled by intermolecular hydrogen bonds.



Figure 4. Solid-state emission spectra of HL and complex 1.

**PXRD** and thermal analyses



Figure 5. PXRD patterns of complex 1.

PXRD analyses of complex **1** was carried out at room temperature in order to confirm the phase purity (Figure 5). The experimental PXRD pattern is closely matched with those in the simulated pattern from single-crystal structure, revealing the good phase purity of the bulk crystalline material.

To study the thermal stability of complex 1, the thermogravimetric analyses were performed in the temperature range 30-800 °C (Figure 6). Complex 1 was stable up to 214 °C. The obvious weight loss process occurred in the range of 214-603 °C, which indicated the decomposition of the whole structure. The final residue was  $SnO_2$  (found 22.4%, calc. 13.31%). In general, complex 1 exhibited good thermal stability.<sup>[36–38]</sup>

#### Theoretical calculation

The quantum chemistry calculation of complex 1 was performed with the Gaussian09  $\text{program}^{[39]}$  at the B3LYP/ GenECP level (the 6–31 + G(d) basis set for C, H, O, Cl and

LANL2DZ basis set for Sn). The initial structure of the title complex 1 was obtained from the X-ray refinement data (cif). On the base of the crystal fragments, the single point energy calculations were performed. For keeping the charge balance in the model, we used a neutral 2,4-dichlorophenyl acrylic acid (containing a proton) and used two deprotonated 2,4-dichlorophenyl acrylic anion in complex 1 for simplifying the polymeric complexes 1 to a 'monomer'. The calculation covered 123 atoms, 1482 basis functions, 2752 primitive gaussians, 291  $\alpha$  electrons and 291  $\beta$ electrons for the model of complex 1. The total molecular energy is -5646.718 a.u., the energies of HOMO and LUMO are -0.211 and -0.129 a.u., respectively, with the  $\Delta E$ (ELUMO -EHOMO) value to be -0.082 a.u., which shows the complex is stable in the ground state. The HOMO and LUMO are presented in Figure 7, from which we can see the HOMO electron cloud is mainly located at the



Figure 6. TG curves of complex 1.

deprotonated 2,4-dichlorophenyl acrylic acid (left L in Figure 7) and the LUMO electron cloud at the 2,4-dichlorophenyl acrylic acid which contains proton (right HL in Figure 7). The electron cloud of the LUMO + 2 is mainly located at the benzene ring of HL. The LUMO + 1 and HOMO-1 is mainly located at deprotonated L (middle L in Figure 7 for LUMO + 1 and the left L in Figure 7 for HOMO-1). While the electron cloud of HOMO-2 is mainly sited at phenyl (the benzene ring which bonds the Sn2A in the left in Figure 7). Selected atom net charges and electronic configuration of the title complex at the B3LYP/ (6-31+G(d) (for C, H, O and Cl) and LANL2DZ (for Sn) levels are listed in Table 3. The calculation results show that electronic configurations of the central Sn atoms are  $5 s^{0.80 \sim 0.82} 5 p^{0.94}$ , and those of O and Cl atoms are  $2 s^{1.61 \sim 1.72} 2 p^{4.94 \sim 5.16} 3 p^{0.01} 3 d^{0.01}$  and  $2 s^{0.76} 2 p^{2.42} 3 d^{0.01} 4 p^{0.03}$ . The net charge of Sn is above 2. It indicated the Sn partially obtains electrons from the 2, 4-dichlorophenyl acrylic acid and the benzene ring.

Table 3. Selected atom net charges and electronic configuration of complex 1 at the B3LYP/(6-31 +G(d) (for C, H, Cl and O) and Lanl2dz (for Sn) levels.

at the $BSLTP/(0-ST + G(d))$ (for C, H, CI and O) and Language (for ST) levels.		
Atom	Charge	Electron configuration
Sn1	2.22818	[core]5s(0.82)5p(0.94)
Sn2A	2.25424	[core]5s(0.80)5p(0.94)
01	-0.68892	[core]2s(1.68)2p(4.99)3p(0.01)
02A	-0.85803	[core]2s(1.68)2p(5.16)3p(0.01)
02	-0.71275	[core]2s(1.61)2p(5.08)3p(0.01)3d(0.01)
01A	-0.67983	[core]2s(1.72)2p(4.94)3d(0.01)
03	-0.80622	[core]2s(1.66)2p(5.12)3p(0.01)
O4A	-0.77941	[core]2s(1.68)2p(5.08)3p(0.01)
C1	0.77461	[core]2s(0.76)2p(2.42)3d(0.01)4p(0.03)
C10	0.84063	[core]2s(0.75)2p(2.36)4S(0.01)3d(0.01)4p(0.02)
C31	-0.54139	[core]2s(1.04)2p(3.47)4p(0.02)
C41	-0.55369	[core]2s(1.04)2p(3.49)4p(0.02)
C51	-0.55549	[core]2s(1.05)2p(3.48)4p(0.02)
C61	-0.53603	[core]2s(1.05)2p(3.46)4p(0.02)
C71	-0.54846	[core]2s(1.05)2p(3.46)4p(0.02)
C81	-0.53818	[core]2s(1.05)2p(3.45)4p(0.02)



Figure 7. The molecular orbitals of the complex 1.

#### Conclusion

This contribution has shown that the combination of triphenyltin (IV) moiety with the 2,4-dichlorophenyl acrylic acid result in the formation of a chain polymer. The intermolecular hydrogen bonds of C-H…Cl play an important role in the 2D network structure. The calculation results show reasonable electronic configurations of the central Sn atoms. In addition, complex1 has good thermal stability and exhibit the red shifts in solid state. These properties are expected to have further applications in the future.

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