



Communication

Synthesis and crystal structure of dinuclear tetraphenylantimony carboxylate derivatives based on different coordination modes

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ABSTRACT

Two novel dinuclear tetraorganoantimony carboxylate derivatives were synthesized based on two different coordination modes, in which the environment of one of the two Sb atoms is described as trigonal bipyramid and the other is ascribed to distorted octahedron carrying four phenyl and one benzoate substituent. Structures of compound **1** and **2** were determined by single-crystal X-ray analysis, IR and NMR. Of the two compounds, a novel double-chain structure was shown in compound **1** through C–H... π weak interaction, while compound **2** exhibited a 1D chain by C–H... π weak interaction identically.

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1. Introduction

While metal-based drugs have been increasingly researched due to their certain advantages over purely organic compounds in drug therapy [1], numerous main-group metal derivatives have been screened for potential anticancer activity [2]. Up to now in this area organotin carboxylates have been most extensively investigated, whereas organoantimony compounds have received much less attention [3–8] even most of the studies have been focused on the inorganic antimony and organoantimony(III) compounds [9,10]. As is known that the vacant 5d orbital of the antimony atom can accept lone electron pairs of ligands to process five-coordinate trigonal bipyramidal geometry, but six- [11,12] or seven- [7,13] coordination are often obtained. Whereas in the title compounds, the centers of antimony atoms are mainly considered as three center four electron bond using p-orbital of antimony rather than d-orbital contributing to describe the structure. To our interest, carboxylate group can coordinate to metal center in many ways, including as the unidentate ligand, the chelating ligand, the bridging bidentate ligand, and so on [14]. For many organoantimony carboxylates, there are interactions between the carbonyl oxygen atoms and the antimony atoms [7,11,12,14,15]. Therefore, the interests in studying the Sb coordination sphere of antimony-compounds with axial carboxylic ester ligands as the primary Sb–O bonding were augmented by weak secondary Sb...O=C interactions [16]. There are many references about mono-nuclear organoantimony carboxylate compounds, while few dinuclear or multi-

nuclear ones are reported. In our article, compounds **1** and **2** are unique di-nuclear organoantimony carboxylates synthesized with four phenyls in reactants. To our surprise, carbonyl oxygen atoms could coordinate to antimony atoms under so large space resistance. However, compounds **1** and **2** were synthesized under facile condition, and the general reaction scheme is shown in Scheme 1. The result indicates that the reaction system can absorb CO₂ from atmosphere to give compound **1** [17] that has been synthesized by other methods [18,19].

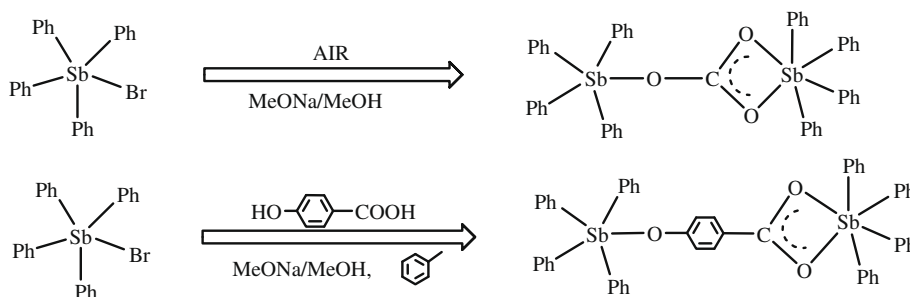
2. Results and discussion

2.1. IR

The IR spectroscopic data provide further support for the molecular constitution of the title compounds. The IR stretching vibration frequencies of carbonyl groups of organoantimony carboxylates are very important for determining their structures. When there are interactions between the antimony atom and the carbonyl oxygen atoms of the carboxylate groups, the differences [$\Delta\nu(\text{CO}_2)$] decrease [2,20,21]. In their IR spectra, $\nu(\text{C}=\text{O})$ of the compounds (1606–1618 cm⁻¹) have experienced a low wave number shift from the position in the respective ligands (1662–1702 cm⁻¹), which indicates that the oxygen atoms of the carbonyl groups are involved in coordination to the antimony like Sb...O=C (seen from the crystal structure of **1** and **2**) [22,23]. The band at 1455 cm⁻¹ can be assigned to the CO₃²⁻ stretching vibration [24]. In the IR spectrum absorption bands at 570–650 cm⁻¹ correspond to the stretching vibration of Sb–O bonds. In addition, the frequencies of Sb–C deformations appear at 495–568 cm⁻¹ [25].

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Scheme 1.

These spectral characteristics are consistent with the X-ray structure analysis.

2.2. ^1H NMR

In the ^1H NMR data of the title compounds, the protons of the phenyl groups appear between 7.94 and 7.21 ppm. The protons of the methyl groups appear at 2.31 ppm in compound **2** assigned to solvent molecules. All the protons in the compounds have been identified and the total number of protons calculated from the integration curve tallies with what is expected from the molecular formula.

2.3. Crystal structure of compounds **1** and **2**

Molecular and supramolecular structures of compounds **1** and **2** are shown in Figs. 1–4 and given the atoms numbering scheme; and the selected bond lengths and angles for compounds **1** and **2** are given in Table 1. Mono-antimony compound of carboxylic acid is well known, its antimony center was often shown as the penta-coordinated state by X-ray crystallographic analysis [26]. When the carboxyl coordinates to antimony with monodentate coordination mode, the coordination polyhedron of Sb (trigonal pyramid) corresponds to d^2sp^2 hybridization and the coordination number of antimony center is five. When it exhibits bidentate coordination mode, three center four electron bond is formed for the octahedron geometry using p -orbital of antimony and the coordination number of antimony center is six [26]. The coordination environments of central antimony atoms in the two dinuclear compounds are

shown in Figs. 1 and 3. For each compound there exists two central antimony atoms with different coordination modes, one is five-coordination under the coordination of hydroxyl group and the other is six-coordinated with the carboxyl group. The distances of Sb(1)–O(1) and Sb(2)–O(3) [2.185(4), 2.253(4) Å in compound **1** and 2.277(4), 2.186(4) Å in compound **2**] are significantly different from the corresponding distances in $\text{Ph}_3\text{Sb}(\text{O}_2\text{C}-2-\text{C}_4\text{H}_3\text{S})_2$ [2.145(4), 2.095(4) Å] [13] and in $\text{Me}_3\text{Sb}(\text{O}_2\text{C}-2-\text{C}_4\text{H}_3\text{S})_2$ [2.136(6), 2.124(6) Å] [15]. Firstly, weak interactions between antimony and carbonyl oxygen atoms are considered, because the distances of Sb–O are much longer than the covalent radii (2.15 Å) [1.41 and 0.74 Å, respectively] [27], and considerable much shorter than the sum of the van der Waals radii (3.6 Å) [2.2 and 1.4 Å, respectively] [27]. But the distances of Sb(1)–O(2) [2.314(4) in **1**; 2.574(4) in **2**], which have been considered as the distances of weak $\text{Sb} \cdots \text{O}$ (from $\text{O}=\text{C}$) are different from the corresponding distances in $\text{Ph}_3\text{Sb}(\text{O}_2\text{C}-2-\text{C}_4\text{H}_3\text{S})_2$ [2.744(4), 2.949(4) Å] [13]. At last, all the interactions between antimony and oxygen atoms must be considered as bonding, though the interactions are assumed to be weak. The average distances of Sb–C under six-coordinated environment in compounds **1** and **2** (2.176 Å for **1**, 2.150 Å for **2**) are slightly larger than the average value of Sb–C under five-coordinated environment (2.135 Å for **1**, 2.134 Å for **2**). Which for the five-coordination, the axial Sb–C [2.173(6) Å] in compound **1** is almost equal to that [2.179(6) Å] in compound **2**. As shown in Figs. 2a and b, the molecules of compound **1** form a double-chain structure via inversion center through $\text{C}-\text{H} \cdots \pi$ weak interaction. In the crystal structure of compound **1**, a pair of enantiomorph (A and B) forms two chains, one is formed by A and the other is

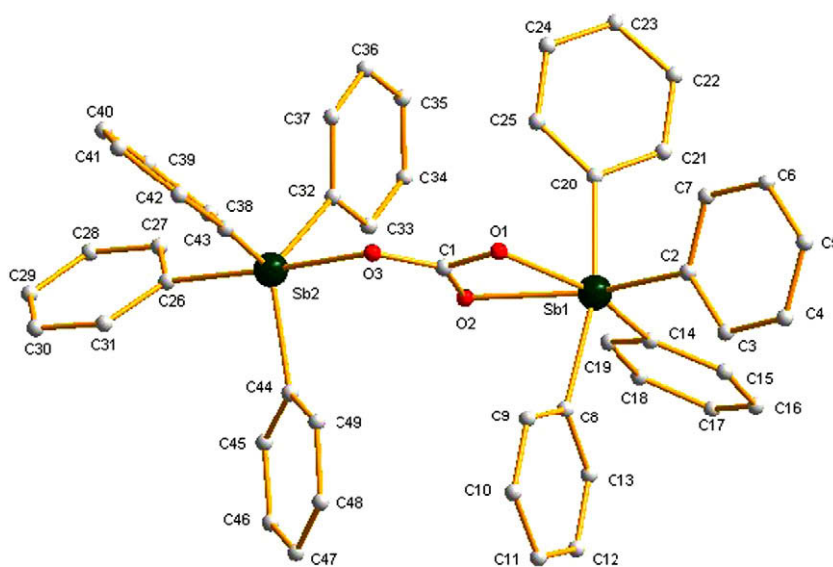


Fig. 1. Molecule structure of compound **1**. All H atoms are omitted for clarity.

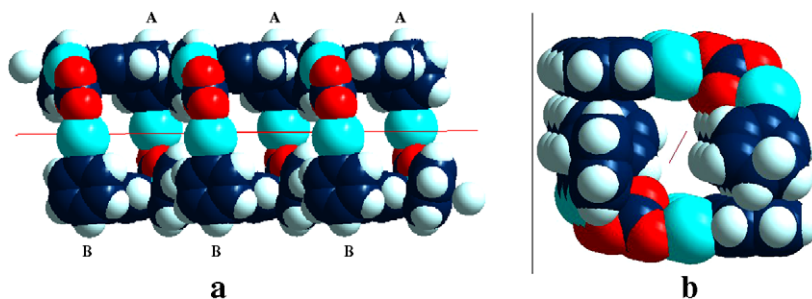


Fig. 2. (a) Transverse double-chain structure of **1**. (b) Lengthways double-chain structure of **1** through weak C–H $\cdots\pi$ bonds, for clarity only atoms on squares were retained.

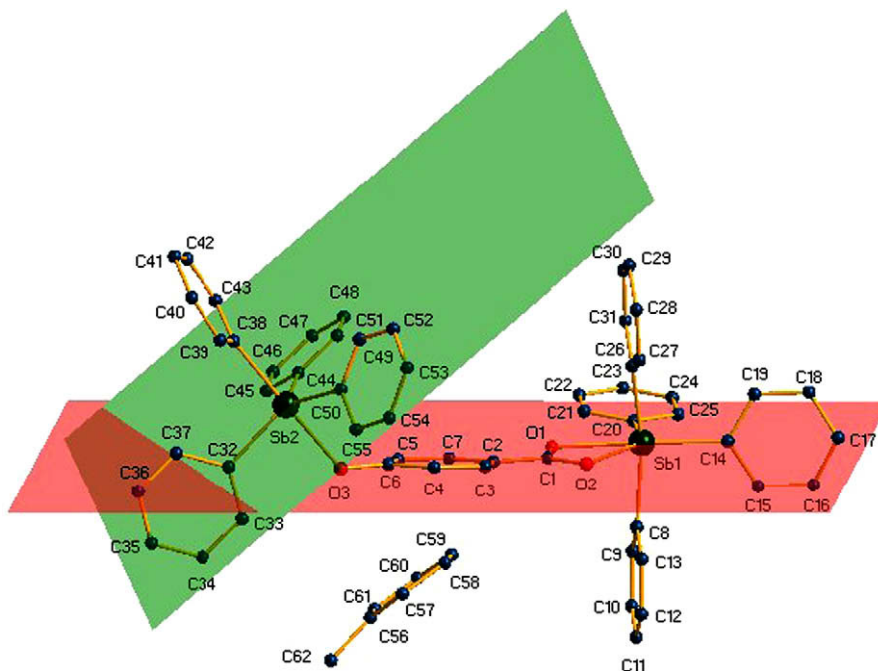


Fig. 3. Molecule structure of compound **2** with two planes. The dihedral angle between the two planes, which are composed of Sb(2), C(44), C(32), C(50) atoms and Sb(1), O(1), O(2), C(1), C(2), C(3), C(4), C(5), C(6), C(7), O(3) atoms, respectively, is 41.18 (4)°. All H atoms are omitted for clarity.

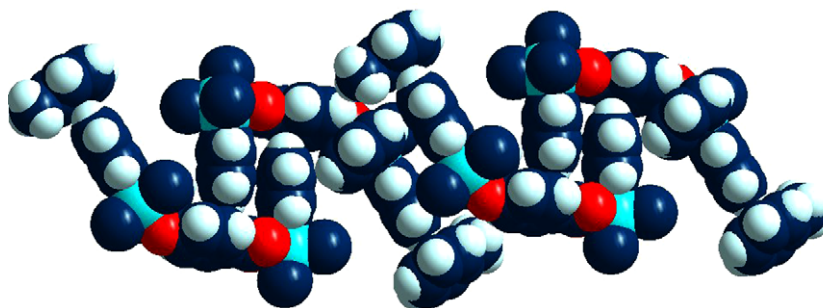


Fig. 4. A 1D chain of compound **2** through weak C–H $\cdots\pi$ bonds, for clarity only atoms on chains were retained.

formed by B through C(11)–H(11) $\cdots\pi$ [C(14)–C(19)] interaction, which are linked together by C(12)–H(12) $\cdots\pi$ [C(26)–C(31)] interaction. In the crystal structure of compound **2**, a 1D chain is exhibited (Fig. 4) by C–H $\cdots\pi$ weak interaction identically. As shown in Fig. 3, the dihedral angle placed on two planes for compound **2** is 41.18 (4)°. One is determined by Sb(2), C(44), C(32), C(50) atoms with no atoms out of the plane, and the other is determined by Sb(1), O(1), O(2), C(1), C(2), C(3), C(4), C(5), C(6), C(7), O(3) atoms with the average distance 0.0588 Å out of the plane.

3. Experimental

3.1. General

Tetraphenylantimony bromide and 4-hydroxybenzoic acid were purchased from Aldrich. Analytical grade solvents were not dried before use. The melting points were obtained with Kofler micromelting point apparatus and uncorrected. Infrared-spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs

Table 1
Selected bond lengths (Å) and angles (°) for **1** and **2**.

Bond	Distances	Bond	Angles
1			
Sb(1)–C(14)	2.175(6)	C(14)–Sb(1)–C(2)	105.2(2)
Sb(1)–C(2)	2.176(6)	C(14)–Sb(1)–C(20)	91.8(3)
Sb(1)–C(20)	2.169(7)	C(2)–Sb(1)–C(20)	96.0(3)
Sb(1)–C(8)	2.182(6)	C(14)–Sb(1)–C(8)	92.7(2)
Sb(1)–O(1)	2.185(4)	C(2)–Sb(1)–C(8)	95.1(2)
Sb(1)–O(2)	2.314(4)	C(20)–Sb(1)–C(8)	166.5(3)
Sb(2)–C(32)	2.109(6)	C(14)–Sb(1)–O(1)	157.8(2)
Sb(2)–C(38)	2.125(6)	C(2)–Sb(1)–O(2)	155.01(19)
Sb(2)–C(44)	2.131(7)	C(32)–Sb(2)–C(38)	116.9(2)
Sb(2)–C(26)	2.173(6)	C(32)–Sb(2)–C(44)	125.3(2)
Sb(2)–O(3)	2.253(4)	C(38)–Sb(2)–C(44)	115.3(3)
O(1)–C(1)	293(7)	O(3)–C(1)–O(2)	123.6(5)
O(2)–C(1)	1.280(7)	O(3)–C(1)–O(1)	119.6(5)
O(3)–C(1)	1.274(7)	O(2)–C(1)–O(1)	116.8(5)
2			
Sb(1)–C(20)	2.119(5)	C(20)–Sb(1)–C(8)	102.8(2)
Sb(1)–C(8)	2.150(5)	C(20)–Sb(1)–C(26)	100.5(2)
Sb(1)–C(26)	2.159(6)	C(8)–Sb(1)–C(26)	153.8(2)
Sb(1)–C(14)	2.173(5)	C(14)–Sb(1)–O(1)	169.89(17)
Sb(1)–O(1)	2.277(4)	C(20)–Sb(1)–O(2)	142.37(17)
Sb(1)–O(2)	2.574(4)	C(14)–Sb(1)–O(2)	116.18(16)
Sb(2)–C(44)	2.111(6)	O(1)–Sb(1)–O(2)	53.72(12)
Sb(2)–C(50)	2.121(6)	C(44)–Sb(2)–C(50)	120.7(2)
Sb(2)–C(32)	2.123(5)	C(44)–Sb(2)–C(32)	115.4(2)
Sb(2)–C(38)	2.179(6)	C(50)–Sb(2)–C(32)	122.1(2)
Sb(2)–O(3)	2.186(4)	C(38)–Sb(2)–O(3)	176.93(19)
O(1)–C(1)	1.274(6)	C(5)–O(3)–Sb(2)	128.3(3)
O(2)–C(1)	1.261(6)	O(2)–C(1)–O(1)	121.2(5)
O(3)–C(5)	1.292(6)		

Table 2
Crystal data and structure refinement details of **1** and **2**.

Compound	1	2
Empirical formula	C ₄₉ H ₄₀ O ₃ Sb ₂	C _{58.50} H ₄₈ O ₃ Sb ₂
Formula weight	920.31	1042.47
Temperature (K)	298(2)	298(2)
Crystal system	Triclinic	Triclinic
Space group	P1	P1
<i>a</i> (Å)	10.123(3)	10.324(2)
<i>b</i> (Å)	13.988(4)	13.807(3)
<i>c</i> (Å)	15.653(4)	19.155(4)
α (°)	74.031(3)	72.698(2)
β (°)	79.938(3)	78.218(2)
γ (°)	74.272(3)	85.289(2)
<i>V</i> (Å ³)	2039.0(9)	2551.4(8)
<i>Z</i>	2	2
<i>F</i> (0 0 0)	920	1050
<i>D</i> _{calc} (g cm ⁻³)	1.499	1.357
Dimensions (mm)	0.53 × 0.52 × 0.30	0.47 × 0.40 × 0.20
θ Range (°)	1.36–25.01	1.55–25.01
Reflections collected	10 463	13 309
Independent Reflections	6986	8859
<i>R</i> _{int}	0.0349	0.0185
Max. and min. transmission	0.6847 and 0.5313	0.8099 and 0.6258
Data/restraints/parameters	6986/96/487	8859/133/605
Goodness-of-fit (GOF) on <i>F</i> ²	1.037	1.079
Final <i>R</i> indices	<i>R</i> ₁ = 0.0475	<i>R</i> ₁ = 0.0392
<i> I</i> > 2 σ (<i>I</i>)	<i>wR</i> ₂ = 0.1223	<i>wR</i> ₂ = 0.1172
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0682	<i>R</i> ₁ = 0.0580
	<i>wR</i> ₂ = 0.1478	<i>wR</i> ₂ = 0.1338
Largest differences in peak/hole [e Å ⁻³]	1.346 and –1.522	1.064 and –0.468

and sodium chloride optics. ¹H NMR spectra was recorded on a Varian Mercury Plus 400 spectrometer operating at 400 MHz. The chemical shifts were given in ppm in CDCl₃ solvent.

3.2. Synthesis of compound **1**

Synthesis of compound **1** is according to Ref. [17]. Sodium methoxide (0.0108 g, 0.2 mmol) and Ph₄SbBr (0.102 g, 0.2 mmol) were added into 25 mL methanol in a flask. After stirring for 72 h, the resulting suspension was filtered. The solvent was slowly evaporated from the filtrate in air to give the product as colorless crystals. Anal. Calc. for C₄₉H₄₀O₃Sb₂: C, 63.95; H, 4.38; O, 5.22. Found: C, 63.76; H, 4.51; O, 5.03%. ¹H NMR (CDCl₃): 7.21 (m, *p*-protons Ph, 8H); 7.41 (m, *m*-protons Ph, 16H); 7.94 (m, *o*-protons Ph, 16H). IR (KBr, cm⁻¹): 1455 (CO₃).

3.3. Synthesis of compound **2**

The 4-hydroxybenzoic acid (0.138 g, 0.1 mmol) was added to the solution of methanol (15 mL) together with sodium methoxide (0.0108 g, 0.2 mmol), and the mixture was stirred for 30 min at room temperature and then tetraphenylantimony bromide (0.102 g, 0.2 mmol) in toluene (25 mL) was added. After totally stirring for 24 h, the solution was filtered. The solvent was gradually removed from the filtrate by evaporation under vacuum until solid product obtained and then crystallized from dichloromethane / petroleum ether. Colorless crystals were obtained. Anal. Calc. for C_{58.50}H₄₈O₃Sb₂: C, 67.40; H, 4.64; O, 4.60. Found: C, 67.21; H, 4.86; O, 4.82. ¹H NMR (CDCl₃): 2.31 (s, CH₃-Ph, 3H); 7.35–7.85 (m, *m*- and *p*-protons Ph, 27H); 7.58–7.87 (m, *o*-protons Ph, 22H).

3.4. X-ray crystallography

Single crystals suitable for X-ray analysis are mounted in a fiber. All measurements are made on a Bruker Smart-1000 CCD diffrac-

tometer with graphite monochromated Mo K α (λ = 0.71073 Å) radiation at 298(2) K using the multi-scan technique. The structure is solved by direct method and different Fourier syntheses using SHELXL-97 program, and refined by full-matrix least-squares on *F*². All non-hydrogen atoms are refined anisotropically. The H atoms bonded to carbon atoms were refined as rigid groups. The hydroxy H atoms were located in a difference Fourier map and refined isotropically with *U*_{iso}(H) = 1.2*U*_{eq} for phenyl group and *U*_{iso}(H) = 1.5*U*_{eq} for the methyl group. Crystallographic data and experimental details of the structure determinations are listed in Table 2.

4. Supplementary material

CCDC 707789 and 707790 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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