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"Cage-like" Carboxyl Bridged Octaphenyltetraantimony Compounds $(SbPh_2)_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(\mu\text{-}O_2CR)_2$: Synthesis and Structural Characterization

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Keywords: Biphenyl; Antimony; Tetranuclear; Cage; Crystal structure

Abstract. The metal-directed self-assembly of biphenylantimony trichloride and homocarboxylic acids LH [L = 2-CHO-$C_6H_4COO^-$ (**1**), 2,3-2F-$C_6H_4COO^-$ (**2**), 4-CF_3–$C_6H_4COO^-$ (**3**)] provided three novel tetranuclear organoantimony(V) complexes, which were characterized by elemental analysis, FT-IR, ^1H, and ^{13}C NMR spectroscopy as well as melting point, and X-ray single crystal analysis. In the molecular structure, four hexacoordinate antimony atoms are linked into a $[Sb_2(\mu\text{-}O)_2]_2(\mu\text{-}O)_2$ "cage" architecture by oxo-bridges which are terminally bridged by two carboxyl groups.

Introduction

Organoantimony compounds are playing essential roles in many aspects of neoteric chemistry, because of their diverse structural chemistry, which arises partly from the various local coordination spheres, and their potential applications. Traditional research on organoantimony compounds mostly focuses on the structural diversity and a large number of organoantimony derivatives derived from carboxylates, oximates, halides, alkoxyls, and sulfonates have been synthesized.[1] A growing number of chemists have turned attention exploring their applications. For example, an organoantimony complex has been used as a catalyst for direct diastereoselective Mannich reaction in water.[2] Antimony was also incorporated into thermoelectric materials such as Sb_2Te_3 and $Ag_{1-x}Pb_{18}SbTe_{20}$ to modify the physical properties.[3] One of the most promising fields is the exploration of their bioactivity and several articles related to this subject have been reported.[4] Because coordination number, types of ligand, and molecular structures exert influence on the performance of bioactivity, a substantial number of organoantimony derivatives need to be synthesized in order to investigate the mechanism and to explore the structure-activity relationship. The structural characterization of such organoantimony compounds will, in turn, help chemists to further optimize the reaction conditions and to construct more organoantimony complexes with novel topologies or higher bioactivity.

It is well-known that organoantimony salts used to construct organoantimony complexes are mostly surrounded by tri- or tetra-organo groups, and owing to bulk and steric hindrance, the obtained organoantimony(V) compounds are mononuclear.[1] In contrast, only a few dinuclear and multinuclear organoantimony complexes have been reported so far.[5] In order to generate more information on this subject and to relieve the steric effect especially, diphenylantimony trichloride was synthesized and utilized to construct organoantimony complexes.[6] Among the most common ligands used for the construction of organoantimony(V) compounds with mono- or multinuclear structures are carboxylic acids, which are able to coordinate to central metal atoms in many ways, such as unidentate, chelating-bidentate, and bridging-bidentate. Considering their various coordination modes and potential bioactivity, we choose three structurally similar carboxylic acids LH [L = 2-CHO-$C_6H_4COO^-$ (**1**), 2,3-2F-$C_6H_4COO^-$ (**2**), and 4-CF_3–$C_6H_4COO^-$ (**3**)], which are bound to electron withdrawing groups for higher bioactivity performance[7] as supporting ligands to construct organoantimony derivatives. As expected, three tetranuclear organoantimony compounds with molecular structures similar to compounds reported previously were prepared, which could be able to play an important role in exploring the relationship between the number of nuclei and bioactivity performance.[8] Herein, the syntheses and the crystal structures of these compounds are reported, the bioactivity screening experiment is ongoing in our group and the results will be reported later.

Results and Discussion

Synthesis

According to the documented method, biphenylantimony trichloride was synthesized and reacted with carboxylic acids in an atmosphere of dry nitrogen using standard Schlenk techniques. Three organoantimony derivatives from carboxylic acids were obtained and crystals suitable for X-ray crystallographic investigations were obtained by recrystallizing from

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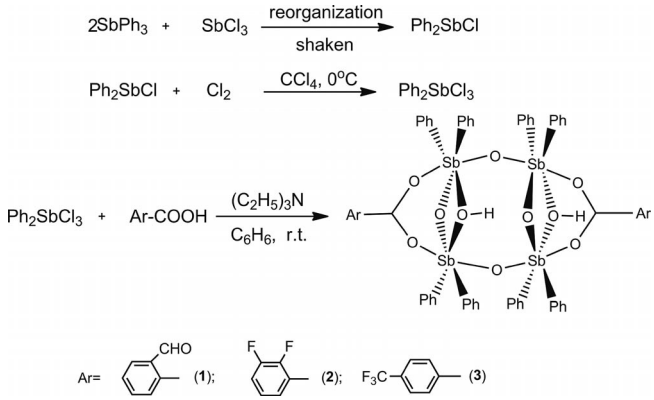
different organic solvents (Scheme 1, for the details see Experimental Section).



Scheme 1. Synthesis procedures for the title compounds.

IR Spectroscopy

In the FT-IR spectra, bands at 1535 to 1555 and 1425 to 1440 cm^{-1} are assigned to $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ respectively and $\Delta\nu$ = 95–130 cm^{-1}, thus carboxyl groups coordinate to the metal atom in a bidentate mode, which are also supported by the C–O bond lengths (Table 1). A strong band at 789–795 cm^{-1} shows the presence of Sb–O–Sb stretching, whereas Sb–O absorption can be found at 450–480 cm^{-1}, which are in accordance with the crystal structure. All the bands observed are consistent with the data in the earlier literature.[8]

NMR Spectroscopy

In the ^{1}H NMR spectra of compounds **1**, **2**, and **3**, no signal resonance of COOH is observed, which suggests that the carboxyl group is deprotonated and coordinates to the central antimony atom. The NMR spectra of the compounds show that the chemical shifts of the protons on the aryl group were assigned reasonably. In the ^{13}C NMR spectra of the title compounds, the signal derived from the carboxylate group is observed in the range from 168 to 193 ppm. Besides, co-crystallized solvent molecules can also be assigned reasonably and the NMR spectroscopic data are in good agreement with the crystal structure.

Structure Description

The three title compounds have similar molecular structures, which are shown in Figure 1, Figure 2, and Figure 3. Selected bonds lengths and angles are listed in Table 1 whereas the most relevant crystallographic data are listed in Table 2. Herein we just take compound **1** as an example, whereas for antimony atoms we take Sb(1) as example, because of the analogue coordination environment of every antimony atom in compounds **1**–**3**. According to Figure 1, it is obvious that every antimony atom is hexacoordinate and the arrangement is best described as distorted octahedral, with two oxygen atoms in the axial position and two carbon atoms from phenyl groups together with two oxygen atoms occupying the equatorial plane. The *trans* angle between two axial oxygen atoms is in the range between 171–178°, just slightly deviating from the linear angle 180°.

Table 1. Selected bond lengths /Å and angles /° for complexes **1**–**3**.

1			
Sb(1)–O(7)	1.919(10)	Sb(1)–O(9)	2.010(10)
Sb(1)–O(10)	2.084(10)	Sb(1)–C(17)	2.089(17)
Sb(1)–C(23)	2.106(17)	Sb(1)–O(1)	2.200(10)
Sb(1)–Sb(2)	3.2128(14)	O(1)–C(1)	1.238(18)
O(2)–C(1)	1.253(18)	O(9)–Sb(1)–O(10)	74.6(4)
O(9)–Sb(1)–C(17)	94.8(6)	O(10)–Sb(1)–C(23)	89.6(5)
C(17)–Sb(1)–C(23)	99.2(7)	O(7)–Sb(1)–O(1)	175.0(4)
Sb(1)–O(7)–Sb(3)	141.5(6)	Sb(1)–O(10)–Sb(2)	100.5(4)
2			
Sb(1)–O(9)	1.936(6)	Sb(1)–O(5)	2.019(6)
Sb(1)–O(6)	2.079(6)	Sb(1)–C(15)	2.136(9)
Sb(1)–C(21)	2.142(10)	Sb(1)–O(1)	2.291(6)
Sb(1)–Sb(2)	3.2508(9)	O(1)–C(1)	1.247(11)
O(2)–C(1)	1.269(11)	O(5)–Sb(1)–O(6)	75.9(2)
O(6)–Sb(1)–C(15)	91.1(3)	O(5)–Sb(1)–C(21)	93.6(3)
C(15)–Sb(1)–C(21)	97.4(4)	O(9)–Sb(1)–O(1)	175.0(2)
Sb(1)–O(5)–Sb(2)	106.4(3)	Sb(1)–O(9)–Sb(4)	141.0(3)
3			
Sb(1)–O(10)	1.929(6)	Sb(1)–O(5)	2.030(5)
Sb(1)–O(6)	2.068(6)	Sb(1)–C(23)	2.121(10)
Sb(1)–C(17)	2.132(8)	Sb(1)–O(1)	2.207(6)
Sb(1)–Sb(2)	3.2403(8)	O(1)–C(1)	1.250(10)
O(2)–C(1)	1.268(9)	O(5)–Sb(1)–O(6)	75.5(2)
O(5)–Sb(1)–C(23)	91.7(3)	O(6)–Sb(1)–C(17)	89.1(3)
C(23)–Sb(1)–C(17)	102.4(4)	O(10)–Sb(1)–O(1)	176.8(2)
Sb(1)–O(5)–Sb(2)	104.9(2)	Sb(4)–O(10)–Sb(1)	148.6(3)

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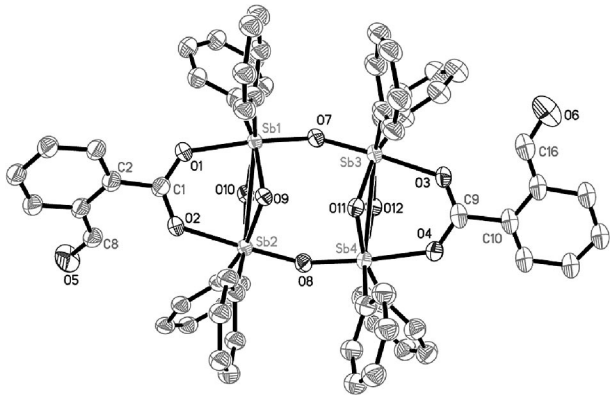

Figure 1. Molecular structure of complex **1** (the uncoordinated solvent molecules and hydrogen atoms are omitted for clarity).

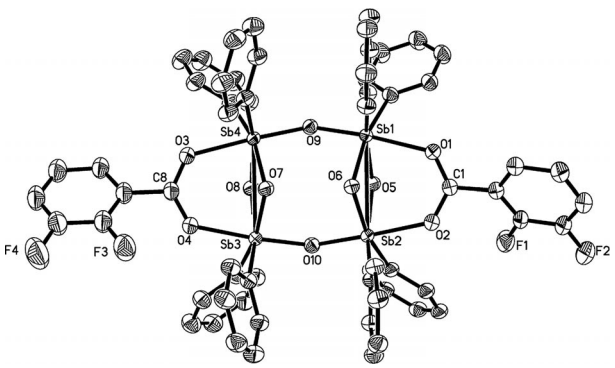

Figure 2. Molecular structure of complex **2** (the uncoordinated solvent molecule and hydrogen atoms are omitted for clarity).

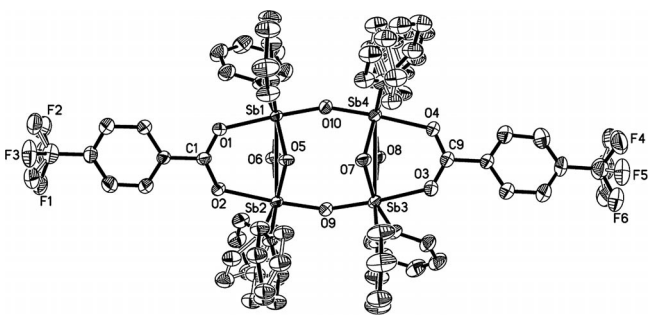

Figure 3. Molecular structure of complex **3** (the uncoordinated solvent molecule and hydrogen atoms are omitted for clarity).

A pair of antimony atoms is bridged by a carboxyl group, an oxygen atom and a hydroxyl oxygen atom to form a Sb_2O_2 four-membered ring. Due to the bulk and steric effect of the phenyl group, the angle of O(9)–Sb(1)–O(10) is only 74.6(4)°, and the angle of C(17)–Sb(1)–C(23) is 99.2(7)° (Figure 1). Two oxygen atoms interlink two four-membered rings on both sides, forming a Sb_4O_6 cage-like conformation. It should be noted that the angles involving the single oxo bridges [i.e. Sb(1)–O(7)–Sb(3)] are between 140–145° whereas the angles in the Sb_2O_2 ring [i.e. Sb(1)–O(10)–Sb(2)] are in the range 104–106°.

The Sb–O bonds in the molecule are in the range between 1.91 and 2.20 Å, whereas the Sb–O bond lengths reported in literature are larger than 2.00 Å.[1b,4b,9] The shortest are those associated with monodentately bridging oxygen atoms [i.e. O(7)], which are in agreement with the above angle data. The longest are those bonded to the oxygen atoms of carboxyl groups, but every two Sb–O bonds in the same carboxyl group are nearly equal, which indicates almost complete delocalization of the π electrons. The distance between Sb(1) and Sb(2) is 3.2128(14) Å, which is longer than the sum of the covalent radii but much shorter than the sum of the van der Waals radii, and there exists strong interaction between the two antimony atoms.[10] Instead of a tetra-bridged structure, the products exhibit a $(SbPh_2)_4(\mu\text{-}O)_4(\mu\text{-}OH)_2$ "cage" structure, which is preferred to the tetra-bridged product, $(SbPh_2)_2(\mu\text{-}O)_2(\mu\text{-}O_2CR)_2$, and can be rationalized: such tetra-bridged compounds would be strained from the short "bite" of the carboxyl group, but when only one carboxyl-bridge is present, the strain will be relieved and the axial angles are close to linearity.

The three title compounds co-crystallize with different solvent molecules, one water molecule and a quarter of a diethyl ether molecule for **1**, one water molecule and two diethyl ether molecules for **2** and one ethanol molecule for **3**, but they exhibit similar molecular structures. This implies that the nature of the solvent molecule does not exert great influence on the overall structural topology.[11]

Conclusions

According to the documented method, biphenylantimony trichloride was synthesized. As expected, through reduction of the number of organo-group, the bulk and the steric hindrance were relieved and tetranuclear organoantimony complexes with Sb_4O_6 "cage" structure derived from carboxylic acids were obtained. Although different carboxylic acids were chosen, a similar structure was obtained in all three cases, which indicates the extensive applicability of the synthesis method and the stability of the "cage" structure. Together with other mono- and dinuclear organoantimony compounds, the title complexes will play an important role in exploring the relationship between the number of nuclei and bioactivity performance. Herein, the synthesis method and the crystal structure are reported, the bioactivity screening experiment is ongoing in our group and the results will be reported later.

Experimental Section

Synthesis of $(SbPh_2)_4(\mu\text{-}O)_4(\mu\text{-}OH)_2[\mu\text{-}O_2C\text{-}(2\text{-}CHO\text{-}C_6H_3)]_2$ (1): The reaction was carried out in an atmosphere of nitrogen by using standard Schlenk techniques. 2-Aldehyde benzoic acid (60 mg, 0.4 mmol) and triethylamine (40.5 mg, 0.4 mmol) were solved in benzene (40 mL) solution and stirred for 0.5 h. Afterwards, biphenylantimony trichloride (169.6 mg, 0.4 mmol) was added to the mixture, and the reaction was allowed to continue for 8 h at room temperature. After filtration, the solvents were evaporated in vacuo. The obtained solid was recrystallized from diethyl ether/petroleum ether (1:1).Yield 75 %, m.p. 192–194 °C. Anal. $C_{260}H_{226}O_{53}Sb_{16}$ (6146.41): calcd. C 50.8; H 3.71 %; found C 51.15; H 3.82 %. **IR** (KBr): $\tilde{\nu}$ = 1538 $\nu_{as}(CO_2)$, 1429

Table 2. Crystal data and structure refinement parameters for complexes **1**–**3**.

	1	**2**	**3**
Empirical formula	$C_{260}H_{226}O_{53}\ Sb_{16}$	$C_{70}H_{70}F_4O_{13}\ Sb_4$	$C_{136}H_{122}F_{12}O_{23}Sb_8$
Formula weight	6146.41	1682.26	3326.34
Wavelength /Å	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a /Å	19.835(2)	19.619(2)	12.0161(13)
b /Å	16.8628(18)	16.3154(19)	15.2652(16)
c /Å	21.298(2)	16.3154(19)	19.314(2)
α /°	90	90	83.108(2)
β /°	90.386(2)	90.112(2)	76.7670(10)
γ /°	90	90	80.664(2)
V /Å^3	7123.4(14)	6997.3(13)	3390.3(6)
Z	1	4	1
D_{calc} /Mg·m^{-3}	1.433	1.597	1.629
μ /mm^{-1}	1.555	1.598	1.651
F(000)	3026	3336	1638
Crystal size /mm	$0.21 \times 0.19 \times 0.18$	$0.49 \times 0.40 \times 0.22$	$0.44 \times 0.24 \times 0.15$
Reflections collected	36087	35480	17498
Unique reflections [R_{int}]	12554 [$R_{(int)}$ = 0.1680]	12260 [$R_{(int)}$ = 0.0404]	11613 [$R_{(int)}$ = 0.0200]
Data / restraints / parameters	12554 / 1422 / 775	12260 / 2423 / 839	11613 / 0 / 1078
Goodness-of-fit on F^2	0.893	1.164	1.133
Final R indices [$I>2\sigma$ (I)]	R_1 = 0.1040, wR_2 = 0.2471	R_1 = 0.0507, wR_2 = 0.0953	R_1 = 0.0456, wR_2 = 0.0936
R indices (all data)	R_1 = 0.1852, wR_2 = 0.2901	R_1 = 0.1073, wR_2 = 0.1313	R_1 = 0.0997, wR_2 = 0.1302

$\nu_s(CO_2)$, 790 (Sb–O–Sb), 465 (Sb–C), 481 (Sb–O) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C): δ = 10.23 (s, 2 H, CHO), 7.06–7.81 (m, 48 H, Ph-H), 3.12 (m, 1 H, OCH_2–), 1.31 (1.5 H, t, OCH_2CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C): δ = 192.96, 170.43, 127.80, 128.84, 129.11, 129.94, 130.02, 130.58, 131.64, 131.92, 132.97, 133.84, 134.07, 135.55, 136.47, 137.05, 137.55, 77.57, 77.25, 46.94, 45.85, 8.79 ppm.

Synthesis of $(SbPh_2)_4(\mu\text{-}O)_4(\mu\text{-}OH)_2[\mu\text{-}O_2C\text{-}(2,3\text{-}F_2\text{-}C_6H_3)]_2$ (2): The synthesis procedure was the same as applied for **1** with the exception that 2,3-difluorobenzoic acid was used instead of 2-aldehyde benzoic acid. The colorless solid was recrystallized from petroleum ether/ethyl ether (1:1). Yield 74%, m.p. 184–186 °C. Anal. $C_{70}H_{70}F_4O_{13}Sb_4$ (1682.26): calcd. C 49.98; H 4.19%; found C 50.02; H 4.12%. **IR** (KBr): $\tilde{\nu}$ = 1533 $\nu_{as}(CO_2)$, 1425 $\nu_s(CO_2)$, 794 (Sb–O–Sb), 455 (Sb–C), 484 (Sb–O) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C): δ = 7.15–7.35 (m, 40 H, Sb-PhH), 6.99–7.01 (m, 6 H, Ph-H), 3.14 (m, 8 H, OCH_2–) 1.42 (t, 12 H, OCH_2CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C): δ = 168.6, 137.00, 134.21, 133.86, 133.56, 131.71, 129.82, 128.21, 127.28, 77.56, 77.24, 76.93, 46.11, 8.80 ppm.

Synthesis of $(SbPh_2)_4(\mu\text{-}O)_4(\mu\text{-}OH)_2[\mu\text{-}O_2C\text{-}(4\text{-}CF_3\text{–}C_6H_3)]_2$ (3): The synthesis procedure was the same as applied for **1** with the exception that 4-trifluoromethylbenzoic acid was used instead of 2-aldehyde benzoic acid. The colorless solid was recrystallized from ethanol/ethyl ether (1:1). Yield 78%, m.p. 188–189 °C. Anal. $C_{136}H_{122}F_{12}O_{23}Sb_8$ (3326.34): calcd. C 49.11; H 3.70%; found C 49.22; H 3.56%. **IR** (KBr): $\tilde{\nu}$ = 1549 ν_{as}(CO2), 1432 ν_s(CO2), 793 (Sb-O-Sb), 451 (Sb-C), 477 (Sb-O) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C) : δ = 6.83–6.95 (m, 8 H, Ph–H), 7.19–7.35 (m, 40 H, Sb–PhH), 3.71 (t, 2 H, –CH_2–Me), 3.18 (m, 2 H, OCH_2–), 9.10 (s, 1 H, EtOH), 1.23 (t, 3 H, CH_3), 1.45 (t, 3 H, OCH_2CH_3). **^{13}C NMR** (100 MHz, CDCl3, 25 °C): δ = 168.9, 137.39, 136.19, 133.9, 133.46, 131.76, 130.68, 130.43, 129.88, 129.54, 128.27, 125.32, 125.29, 77.57, 77.25, 76.93, 66.11 ppm.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-841760 (**1**), CCDC-841761 (**2**), and CCDC-841762 (**3**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

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