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Interaction of pentaphenylantimony with carboranedicarboxylic acid☆

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ABSTRACT

The reaction of equimolar amounts of pentaphenylantimony with carboranedicarboxylic acid in toluene lead to tetraphenylantimony carborane carboxylate (**1**) in high yield. When using 2:1 M ratio of initial reagents, bis(tetraphenylantimony) carborane bis(carboxylate) (**2**) was obtained in 94% yield. Sb atoms in **1** and **2** form the distorted trigonal-bipyramidal coordination with carboxylate and phenyl ligands in axial positions ($C_{axial}SbO$ are 174.06(12)° and 175.74(13)°, 176.77(13)° respectively). The Sb–O и Sb–C bond distances are 2.469(3) Å and 2.095(4)–2.136(4) Å in **1** and 2.275(3), 2.364(3) and 2.112(4)–2.173(4) Å in **2**. There are no intramolecular contacts in **1** between Sb and O atom of CO group. In **2** the bond distances Sb···O(=C) (3.203(4) и 3.213(4) Å) are much less than a sum of van der Vaals radii of Sb and O atoms. Crystal structures of **1** and **2** are characterized by weak intermolecular hydrogen bonds H···O (2.25–2.53 and 2.54 Å, respectively).

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1. Introduction

The purpose of this work is synthesis and characterization of new carborane carboxylates of organoantimony compounds. The reason of interest to such type of compounds is based on the last results on biological activity of both antimony compounds and carborane derivatives. Different antimony compounds were investigated for antitumor and antileishmanial activity [1–3]. From another site carborane derivatives exhibit a wide spectrum of biological activity [4–8]. Carborane carboxylates of organotin derivatives showed moderate *in vitro* antitumor activity [9].

The reaction of pentaaryl antimony with dicarboxylic acids is known to lead to two types of compounds: tetraarylantimony carboxylates or bis(tetraarylantimony) carboxylates, namely only one or both carboxylate groups react [10–16].

Coordination of Sb atoms in these two type molecules differs essentially according to X-ray investigation. In the first case trigonal-bipyramidal configuration of Sb atom is distorted strongly to tetrahedral configuration due to essential increase of Sb–O distance [10–12]. In the second case these distances are far short, and Sb atoms coordinated by oxygen atom of carboxylate ligand have less distorted trigonal-bipyramidal configuration [11,13–15]. In six bis(tetraarylantimony) carboxylates the carboxylate ligands reveal anizobidentate type of coordination [11,13–15], only oxalate ligand coordinates to Sb atom practically symmetrically, as a result coordination of Sb atom transferred to octahedral one [16].

Carrying on the investigation of organoantimony dicarboxylic acids we studied reactions of pentaphenylantimony with carboranedicarboxylic acid in different molar ratio (1:1 and 2:1). The structures of reaction products were determined by X-ray method.

2. Results and discussion

The reaction of pentaphenylantimony with carboranedicarboxylic acid (molar ration 1:1) in toluene at room temperature proceeds with substitution of hydrogen atom in one carboxylic group to give tetraphenylantimony carborane carboxylate (**1**) in high yield with CO_2 elimination.

It should be mentioned that CO_2 elimination was observed in

☆ This paper is dedicated to Professor Russell Grimes on the occasion of his 80th birthday in recognition of his outstanding contributions to the Boron Chemistry.

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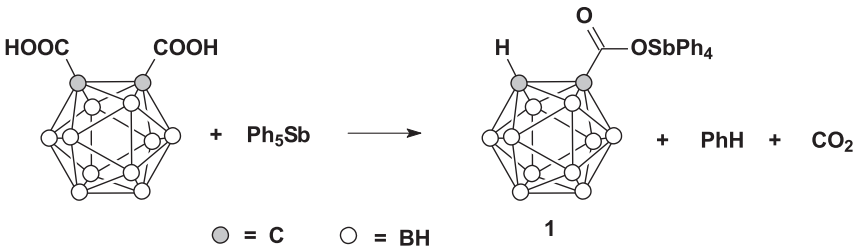
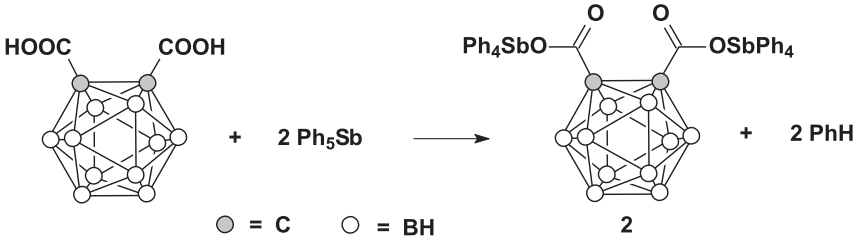


similar reaction of pentaphenylantimony with acetylenedicarboxylic acid giving tetraphenylantimony propionate as a single antimony compound [20].

However the reaction of pentaphenylantimony with carboranedicarboxylic acid at molar ration 2:1 leads to the substitution of both acidic hydrogen atoms in both carboxylic groups to give bis(tetraphenylantimony) carborane bis(carboxylate) (**2**) in 94% yield.

to 352.38(14)° (**1**) and 357.16(16)°, 355.25(16)° (**2**). Antimony atoms go out equatorial planes to axial carbon atom up to 0.34(1) Å (**1**) and 0.21(1), 0.26(1) Å (**2**). Valent angles $OSbC_{equ}$ are less than 90° (76.71(12)°–86.89(13)° (**1**), (81.49(13)°–87.63(12)° (**2**)), but angles $C_{ax}SbC_{equ}$ more than 90° (97.58(15)°–101.19(14)° (**1**), 93.58(16)°–98.42(16)° (**2**)). The Sb–C_{equ} distances are change in interval 2.095(4)–2.116(3) Å (**1**), 2.115(4)–2.122(4), 2.112(4)–2.118(4) (**2**). The distances Sb–C_{ax} (2.136(4) Å (**1**), 2.173(4), 2.165(4) Å (**2**)) are



According to X-ray data antimony atoms in compounds 1 and 2 form the distorted trigonal-bipyramidal coordination with carboxylate and phenyl ligands in axial positions (Figs. 1 and 2).

Axial angles $OSbC_{ax}$ are equal to 174.06(12)° (**1**) и 175.74(13), 176.77(13)° (**2**), sum of angles $C_{equ}SbC_{equ}$ in equatorial planes equal

longer than Sb–C_{equ}. The distances Sb–O (2.469(3) Å (**1**), 2.275(3), 2.364(3) Å (**2**)) exceed the sum of covalent radii of Sb and O (2.07 Å [21]). As expected the distances C–O (1.252(5) Å (**1**), 1.267(5), 1.269(5) Å (**2**)) are longer than distances C = O (1.228(4) Å (**1**), 1.204(5), 1.235(5) Å (**2**)). Contrary to the most of tetraarylantimony

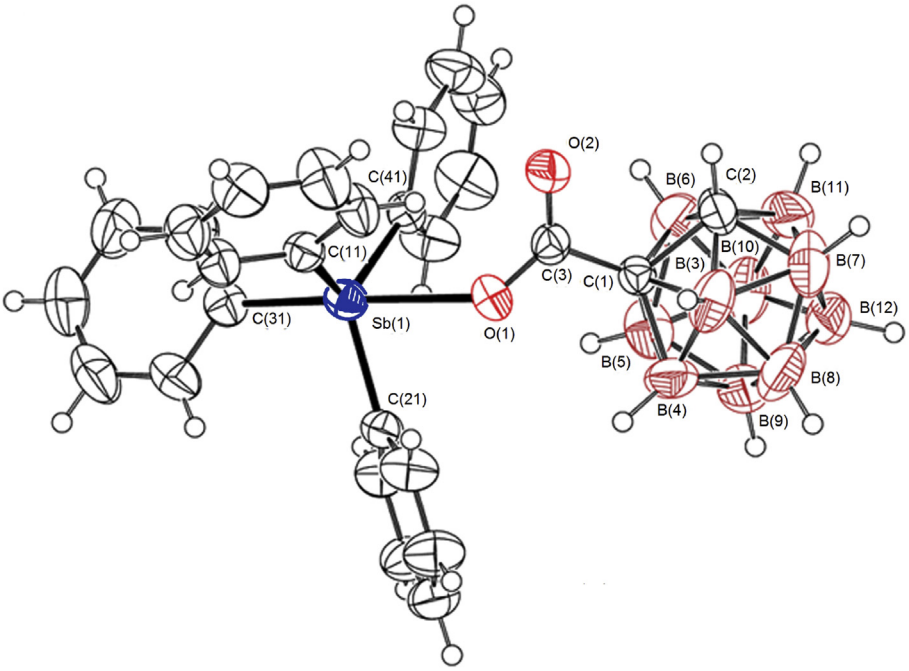


Fig. 1. Molecular structure of tetraphenylantimony carborane carboxylate (**1**).

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