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Highly symmetrical 24-membered macrocyclic organoantimony(V) complexes constructed from Schiff base ligands possessing two terminal carboxyl groups

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ABSTRACT

Two novel organoantimony(V) complexes $[Ph_3SbL^a]_2$ (**1**) and $[Ph_3SbL^b]_2$ (**2**) (H_2L^a = 5-{[(2-carboxyphenyl) methylene]amino}-4-chlorobenzoic acid, and H_2L^b = 5-{[(2-carboxyphenyl)methylene]amino}-2-chlorobenzoic acid) have been synthesized by the reaction of triphenylantimony dichloride and Schiff base ligands with the ratio of 1:1, and characterized by elemental analysis, IR, ^1H and ^{13}C NMR spectroscopy. X-ray single-crystal diffraction analyses reveal that two highly symmetrical 24-membered macrocyclic organoantimony derivatives were found unprecedentedly, in which two antimony atoms are bridged by four terminal carboxyl groups of the Schiff base ligands, and antimony atoms exhibit typical five-coordinated trigonal-bipyramid geometry with two carboxyl oxygen atoms occupying the axial positions. In complexes **1** and **2**, there exist several types of secondary interactions (C–H…π, C–Cl…π and C-H…Cl), which contribute to the formation of a 1D infinite chain in **1** and a 2D supramolecular network structure in **2** in their crystal structures, respectively.

Over the past several decades, organoantimony(V) complexes have received much attention not only for their fascinating structural diversity from discrete monomeric molecular species to associated structures and supramolecular [1–5], but also for their antibacterial, antitumour and antitubercular activities [6–8]. Moreover, this class of complexes has potential applications in organic synthesis either as reagents or as catalysts [9–11]. Therefore, syntheses of new organoantimony complexes and studies of their properties are of interest and important. Our interest in organoantimony chemistry has been associated with synthesizing new organoantimoy complexes and exploring whether these complexes also possess antitumor properties. In our previous work, we have reported one novel organoantimony(V) complex derived from internally functionalized acetylferroceneoxime, which exhibit well inhibition for human hepatocellular carcinoma (Bel-7402) and human gastric carcinoma (BGC-823) [12].

In addition, Schiff base complexes containing an imine group are well known for their biological activities [13], as well as their prospective applications in catalysis, magnetic properties, molecular architectures and materials chemistry by coordination chemists at all times [14]. Although considerable advance has been reached in the development of this branch of organometallic compounds with Schiff base [15–19], there are still some fields that have received little attention thus far by the scientific community working in this area. To the best of our knowledge, crystal structures of organoantimony complexes with Schiff base ligands have never been reported.

As part of our studies of Schiff base organoantimony(V) complexes, we intend to modify the composition of the Schiff base ligands, as well as adjust the placement of the substituent groups for obtaining some novel structures and exploring their structure-activity relationship in antitumor activity in the future. Here, we have synthesized two Schiff base ligands containing two terminal carboxyl groups for obtaining cyclic structures by coordinating with metal atoms, H_2L^a and H_2L^b (Scheme 1) [20], and in these two ligands the chlorine atom occupies the *ortho*- or *para*- position of one carboxyl group differently. Making use of the two new Schiff base ligands, two triphenylantimony(V) complexes $[Ph_3SbL^a]_2$ (**1**) and $[Ph_3SbL^b]_2$ (**2**) have been synthesized [21] (Scheme 2), which have been characterized by elemental analysis, IR, ^1H, ^{13}C NMR spectroscopy and single-crystal X-ray diffraction [22]. Structural analyses reveal that, due to the existing of two terminal carboxyl groups in the ligands, two highly symmetrical 24-membered macrocycles were observed in organoantimony derivatives for the first time. Furthermore, there exist several types of secondary interactions in the crystal structures of **1** and **2**, leading to the formation of 1D infinite chain in **1** and 2D supramolecular network in **2**. Each of the two novel organoantimony complexes possesses four active centers, that is, two triphenylantimony(V) moieties and two –C=N– groups belonged to Schiff bases. We hope our work will be helpful for the further studies on biological activities.

The IR and ^1H NMR spectra of complexes provide useful information about the coordination mode of the functional groups.

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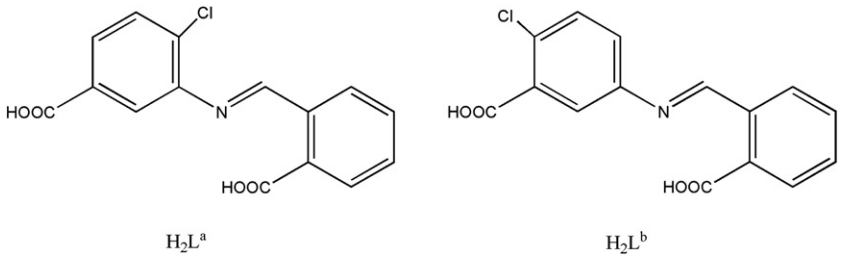
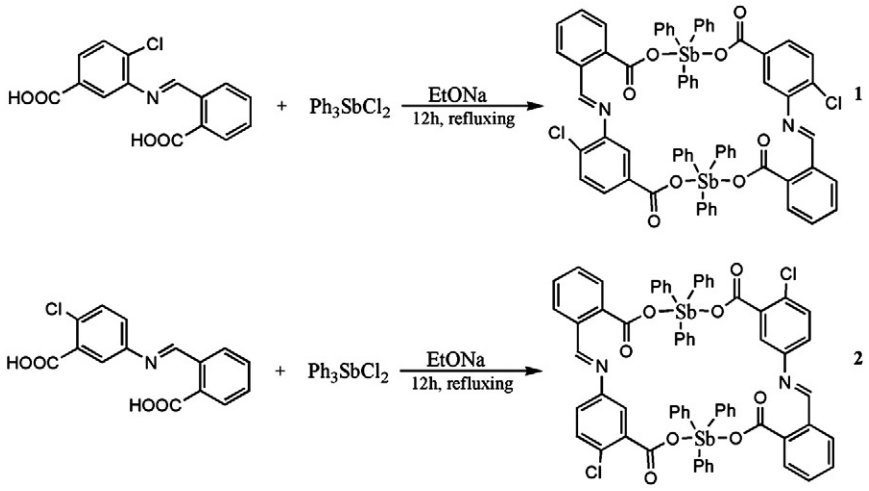


H_2L^a H_2L^b

Scheme 1. Structures of the Schiff base ligands H_2L^a and H_2L^b.



Scheme 2. Synthesis routes for the complexes **1** and **2**. Both **1** and **2** exhibit 24-membered macrocyclic consisting of two Schiff base ligands and two triphenylantimony(V) moieties.

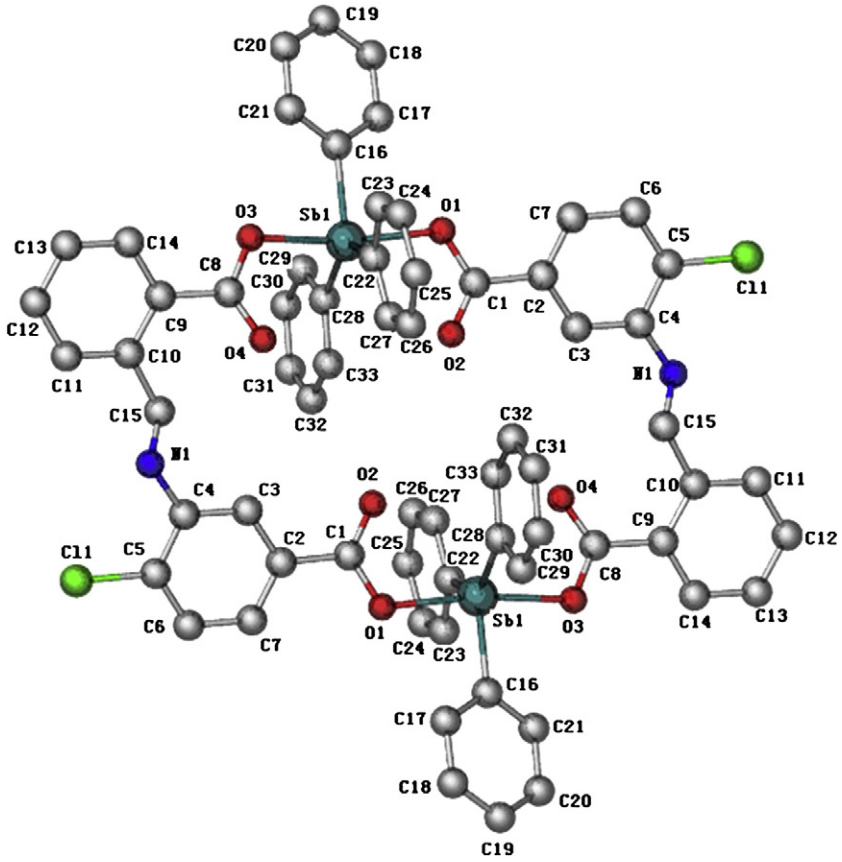


Fig. 1. Molecular structure of complex **1**. All H atoms and dichloromethane solvent molecules are omitted for clarity. Selected bond distances (Å): Sb(1)–C(28) = 2.104(4), Sb(1)–C(22) = 2.110(5), Sb(1)–C(16) = 2.120(5), Sb(1)–O(3) = 2.120(3), Sb(1)–O(1) = 2.124(3). Selected bond angles (°): C(28)–Sb(1)–C(22) = 134.3(2), C(28)–Sb(1)–C(16) = 110.91(18), C(22)–Sb(1)–C(16) = 114.80(19), O(3)–Sb(1)–O(1) = 171.76(12).