Structural Chemistry of Organotin(IV) Complexes

S. Shahzadi and S. Ali*

Department of Chemistry, Quaid-i-Azam University, Islamabad- 45320, Pakistan

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The amazing structural diversity in organotin compounds is discussed in the systems containing -O and -S donor ligands. It is demonstrated that there exist a fascinating range of structural diversity for organotin(IV) complexes, including differences in coordination number and molecular geometry. The difference in structure is correlated with the nature of tin and ligand bonded R groups. Despite the large number of different structures found in organotin(IV) carboxylates, there is limited range of coordination geometries about the Sn atom. The four coordinated Sn atom in triorganotin(IV) complexes is invariably distorted tetrahedral and five coordinated Sn is distorted trigonal bipyramidal. A large range has been observed for diorganotin carboxylate structures, where five, six and seven coordinate geometries have been reported. The Sn atom in mono-organotin has only been demonstrated to exist in distorted octahedral geometries (the single exception being a pentagonal bipyramidal geometry). In the case of organotin(IV) complexes of S donor ligands, it has been shown that there exists a rich diversity in Sn atom geometries and coordination modes of the sulfur donor ligands themselves. As in related carboxylate systems, the assignment of coordination numbers to the Sn centers in some compounds is controversial. As a general trend, it has been shown that, the overall coordination number at the Sn atom decreases with the increasing number of organic substituents at the Sn atom. This phenomenon is usually achieved by increased asymmetry in the mode of coordination of the sulfur donor ligands.

Keywords: Organotin(IV) complexes, O-donor ligands, S-donor ligands, Structural chemistry

INTRODUCTION

The increasing interest in organotin(IV) carboxylates of substituted benzoic acids in recent years has, to a large extent, been prompted by their new structural diversity [1] and broad therapeutic activity [2]. Information on the structure of organotin(IV) carboxylates continues and at the same time some new applications of such a high importance are being discovered which are relevant to ecological medicinal applications. The increasing interest in the chemistry of organotin(IV) compounds has led to the extended studies on their reactions with different biomolecules including carbohydrates [3-5], nucleic acid derivatives [6-8], amino acids [9-11] and peptides [12-14].

The aim of this review is to summarize each category of organotin carboxylates in order to illustrate the diverse modes of coordination/association of the carboxylate ligand/dithiocarbamate ligand, as determined by crystallographic methods. We will discuss the structural chemistry of organotin(IV) complexes under the two categories: oxygen donor ligands and sulfur donor ligands.

OXYGEN DONOR LIGANDS

Oxygen donor ligands coordinate to the organotin moiety in monodentate or bidentate fashion in different stochiometries giving the diversity of structures. We will discuss this section
as four-, five- and six-coordinated complexes and distannoxanes.

**Four Coordinated Complexes**

When the oxygen donor ligands act as monodentate, the geometry around the tin atom will be distorted tetrahedral, as reported in the literature [15-18]. Representative structure of this class is given in Fig. 1, which shows that the Sn atom exists in a distorted tetrahedral geometry defined by three ipso-C atoms of the phenyl groups and O1 atom [Sn1-O1 = 2.0557(14) Å] of the (E)-3-(3-fluorophenyl)-2-(4-chlorophenyl)-2-propenoate. The major distortion from the ideal tetrahedral geometry is found in the O1-Sn1-C1 angle of 96.54(7)°. The relatively close interaction between O2 and Sn1 [Sn1…O2 = 2.8309(5) Å] does not disrupt the O1-Sn1-C7 and O1-Sn1-C13 angles significantly, which are 108.91(7)° and 110.10(7)°, respectively. However it is noteworthy that C7-Sn1-C13 angle of 119.06(8)° is the next major distortion from the ideal geometry. The monodentate mode of coordination of (E)-3-(3-fluorophenyl)-2-(4-chlorophenyl)-2-propenoate is reflected in the disparate O1-C19 and O2-C19 bond distances of 1.313(2) and 1.229(2) Å, respectively, with the longer separation being associated with the stronger Sn1-O1 interaction [15]. Another example of this class is given in Fig. 2 in which also the distorted tetrahedral geometry is observed [16,18].

**Five Coordinated Complexes**

Among the organotin(IV) complexes, trimethyltin derivatives form a polymeric structure with trigonal bipyramidal geometry [19-22]. The representative structure of this class is given in Fig. 3. Here the geometry around the tin atom is distorted trigonal bipyramidal. Three methyl groups are bonded to the Sn atom at equatorial positions with essentially identical bond distances [mean Sn-C = 2.119(6) Å]. The Sn atom lies 0.065(2) Å out of the equatorial plane formed by three methyl C atoms, towards the more strongly bonded atom O1. The O-Sn-O angle is approximately linear [171.21(9)°] and the C-Sn-C and O-Sn-C angles are within the expected range of values [C-Sn-C = 119.24(15)°-120.62(15)° and O-Sn-C = 84.47(12)-97.24(12)°] [21].

Earlier reports [23-26] have shown that the coordination of different alkyl groups with O-donor ligands does not change the coordination geometry of triorganotin complexes and they show a polymeric structure with the trigonal bipyramidal geometry. Examples are given in Figs. 4 [23], 5 and 6 [24].

The tetrameric structure shown in Fig. 7 is also reported in the literature [27] which is formed with tributyltin moiety. The