CRYSTAL STRUCTURES OF BIS(TRIPHENYLPHOSPHINE OXIDE)TRIBUTYLTIN AND BIS(TRIPHENYLARSINE OXIDE)TRIBUTYLTIN TETRAPHENYLBORATES

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Abstract

The tin atom in the cationic complexes, bis(triphenyltin oxide)tributyltin tetraphenylborate and bis(triphenylarsine oxide)tributyltin tetraphenylborate, shows *trans*-C₃SnO₂ trigonal bipyramidal coordination. The O-Sn-O skeleton is linear in the two compounds; however, whereas the Sn←O=P entities are approximately linear in the phosphine oxide complex, the Sn←O=As units in the arsine oxide complex are bent.

Introduction

The literature on organotin compounds lists only a small number of cationic complexes compared with the much larger number of anionic complexes, the examples being largely limited to those complexes whose positive charge at tin is balanced by the tetraphenylborate counterion. The mesylimide anion, [(CH₃SO₂)₂N]⁻, is also able to stabilize the organotin cation [1] as is this anion, like the tetraphenylborate anion, has limited Lewis basicity. Additionally, the organotin cation must be stabilized by neutral donor ligands. The water ligand can only stabilize the cation to a small extent by hydrogen bonding; the water molecules in the diaquatributyltin cation are readily replaced by stronger Lewis bases [2]. Among the cationic organotin complexes, the triorganotin system takes advantage of the increased aqueous solubility arising from the separation of charges [3] for possible biocidal applications. Crystallographic evidence on cationic organotin complexes is sparse; in the unit cell of bis(triphenylarsine oxide)(*p*-chlorophenyl)diphenyltin tetraphenylborate [4], the cations and anions were packed such that there are no interactions between the species. The two title compounds constitute additions to the structural literature on such complexes.

Experimental

Bis(triphenylphosphine oxide)tributyltin tetraphenylborate was obtained by reacting tributyltin chloride, triphenylphosphine oxide and sodium tetraphenylborate in a 1:2:1 stoichiometry in ethanol. Sodium chloride was formed when the solutions of the reagents were mixed together. Water was added in drops to dissolve the sodium chloride; the cationic complex was forced out of solution by the addition of more water [3]. The solid material was collected and then thoroughly dried by contact with filter paper. The pure compound (1) was obtained by using ethanol as the solvent for crystallization. The triphenylarsine oxide analog (2) was prepared in an identical manner.

Room-temperature diffraction measurements for the crystals of the compounds were carried out on a Siemens CCD area-detector diffractometer ($\lambda = 0.71073$ Å). The structures were solved by direct methods [5] and were refined on F^2 [6]. Both structures are disordered in the butyl chains, and a number of restraints were used to treat the disorder. In (2), each butyl chain was disordered as two half-occupancy chains sharing a common C _{α} -atom. As the disorder affect the other part of the molecule, phenyl rings were refined as rigid hexagons. The structures of the cations are shown as ORTEP [7] plots. For (1), the absolute structure parameter refined to a value close to zero, which enabled the absolute structure [8] to be assigned. Crystal data and refinement values for both compounds are listed in Table 1.

Figure 1. ORTEP plot of the bis(triphenylphosphine oxide)tributyltin cation of (1) at the 10% probability level. Selected bond distances and angles: Sn1-C1 = 2.11(1), Sn1-C5 = 2.19(1), Sn1-C9 = 2.249(6), Sn1-O2 = 2.278(5), P1-O1 = 1.501(6), P2-O2 = 1.486(5) Å; C1-Sn1-C5 = 116.8(5), C1-Sn1-C9 = 118.4(5), C1-Sn1-O1 = 90.8(4), C1-Sn1-O2 = 92.2(4), C5-Sn1-C9 = 124.4(6), C5-Sn1-O1 = 92.6(5), C5-Sn1-O2 = 86.1(5), C9-Sn1-O1 = 92.8(4), C9-Sn1-O2 = 85.7(4), O1-Sn1-O2 = 177.0(2), P1-O1-Sn1 = 167.4(4), P2-O2-Sn1 = 152.5(4)°.

Figure 2. ORTEP plot of the bis(triphenylarsine oxide)tributyltin cation of (2) at the 30% probability level. Selected bond distances and angles: Sn1-C1 = 2.155(8), Sn1-C5 = 2.151(9), Sn1-C9 = 2.147(8), Sn1-O1 = 2.238(4), Sn1-O2 = 2.254(4), As1-O1 = 1.653(4), As2-O2 = 1.663(3) Å; C1-Sn1-C5 = 116.0(4), C1-Sn1-C9 = 123.3(3), C1-Sn1-O1 = 93.1(3), C1-Sn1-O2 = 86.2(3), C9-Sn1-O1 = 88.1(2), C5-Sn1-C9 = 120.7(4), C5-Sn1-O1 = 86.6(3), C5-Sn1-O2 = 91.2(3), C9-Sn1-O2 = 94.5(2), O1-Sn1-O2 = 177.2(2), As1-O1-Sn1 = 144.0(3), As2-O2-Sn1 = 144.6(2)°.

Table 1. Crystal and refinement data for (1) and (2)

	1	2
Empirical formula	C ₇₂ H ₇₇ BO ₂ P ₂ Sn	C ₇₂ H ₇₇ As ₂ BO ₂ Sn
Formula weight	1165.78	1253.68
Crystal system, space group	Orthorhombic, <i>Pna</i> 2 ₁	Triclinic, <i>P</i> -1
Cell dimensions		
<i>a</i> Å, α°	19.3888(2), 90	11.2273(3), 109.129(1)
<i>b</i> Å, β°	15.1486(3), 90	14.7650(3), 92.571(1)
<i>c</i> Å, γ°	22.171(1), 90	21.4819(5), 99.980(1)
Volume, Å ³	6511.9(2)	3293.7(1)
<i>Z</i>	4	2
Calculated density, g cm ⁻³	1.189	1.264
Absorption coefficient, mm ⁻¹	0.484	1.427
<i>F</i> (000)	2440	1292
Crystal size, mm	0.48 x 0.42 x 0.40	0.46 x 0.40 x 0.28
θ range of data, °	1.63 to 25.00	1.01 to 25.00
Limiting indices, ± <i>h</i> , ± <i>k</i> , ± <i>l</i>	-22 to 23, -15 to 18, -26 to 24	-13 to 10, -16 to 17, -25 to 25
Reflections collected / unique	35029 / 11247 (<i>R</i> _{int} = 0.090)	18855 / 11394 (<i>R</i> _{int} = 0.059)
Completeness to θ = 25°	100.0 %	98.2 %
Max. and min. transmission	0.830 to 0.801	0.691 to 0.560
Restraints / parameters	142 / 584	156 / 610
Goodness-of-fit on <i>F</i> ²	0.935	0.981
Weighting scheme, <i>w</i>	[σ ² + (0.1067 <i>P</i>) ²] ⁻¹	[σ ² + (0.0687 <i>P</i>) ²] ⁻¹
Reflections with <i>I</i> > 2σ(<i>I</i>)	6190	7569
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.063, <i>wR</i> ₂ = 0.159	<i>R</i> ₁ = 0.058, <i>wR</i> ₂ = 0.147
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.116, <i>wR</i> ₂ = 0.191	<i>R</i> ₁ = 0.083, <i>wR</i> ₂ = 0.160
Absolute structure parameter	-0.05(3)	
Extinction coefficient	0.0020(3)	0.0020(3)
Largest diff. peak and hole, eÅ ⁻³	0.47 to -0.46	0.69 to -0.99
CCDC deposition number	162188	168189

Results and Discussion

The bis(triphenylphosphine oxide)tributyltin (Figure 1) and bis(triphenylarsine oxide)tributyltin (Figure 2) cations have their five-coordinate metal atoms in a *trans*-C₃SnO₂ trigonal bipyramidal geometry; this coordination geometry was suggested from tin-119m Mössbauer spectroscopic measurements [2]. In the bis(triphenylphosphine oxide)tributyltin cation, the tin atom is displaced by 0.078(8) Å out of the trigonal plane in the direction of the O1 atom, which forms a marginally shorter bond than the O2 atom, i.e., the phosphine-oxide ligand bearing the O1 atom appears to be more Lewis basic than the ligand bearing the O2 atom as implied by the less bent Sn←O=P skeleton. The unusually large Sn←O=P angle is a typical feature of organotin complexes of phosphine oxides, and there are more than 140 examples in the structural literature that have the C-Sn←O=P fragment [9]. In contrast, the angles at the oxygen atom in carbonyl [10] and amine-oxide [11] donor complexes are much smaller, these being close to the 120° angle expected for *sp*²-hybridized oxygen. In the triphenylarsine oxide complex, the tin atom is displaced out of the trigonal plane by 0.027(5) Å, in the direction of the O2 atom. The bond distances and angles of the two triphenylarsine oxide ligands are similar. The tin-oxygen distances are not significantly different from each other in the two cations, and the greater Lewis basicity of the arsine oxide donor compared with the phosphine oxide donor has only a minor effect on these bond dimensions (Sn←O_P = 2.249(6), 2.278(5) Å; Sn←O_{As} = 2.238(4), 2.254(4) Å). The most significant difference is shown by the angles at the oxygen linkage (Sn←O=P = 152.5(4), 167.4(4)°) in the phosphine oxide adduct whereas that in the arsine analog oxide is bent (Sn←O=As = 144.0(3), 144.6(2)°).

In both compounds, the tetrahedral tetraphenylborate anions do not interact with the cations. Because of the size of the cation and anion, both compounds do not pack well. The triclinic cell has 4 voids totaling 89.8 Å³ and the orthorhombic cell 8 voids totaling 146.2 Å³. However, the voids are not large enough to accommodate water molecules.

Several complexes of triorganotin derivatives with the same phosphine oxide and arsine oxide ligands have been authenticated crystallographically; the 2:1 triphenyltin coumarin-3-carboxylate adducts of triphenylphosphine and triphenylarsine oxides are isomorphous (Sn←O=P = 166.4(2), Sn←O=As = 159.4(2)°) [12], the pair having matching cell dimensions. On the other hand, the triphenyltin nitrate complex of the same donors are not isomorphous, the phosphine oxide complex crystallizing in a centrosymmetric space group (Sn←O=P = 153(1)°) and the arsine oxide

($\text{Sn} \leftarrow \text{O} = \text{As} = 136.0(3)^\circ$) in a non-centric space group [13]. The 2:1 triphenyltin chloride adduct with 1,2-bis(diphenylphosphinyl)ethane ($\text{Sn} \leftarrow \text{O} = \text{P} = 161.8(2)^\circ$) and 1,2-bis(diphenylarsoryl)ethane ($\text{Sn} \leftarrow \text{O} = \text{As} = 134.5(2)^\circ$) differ significantly in the coordination environment of the metal atom [14]. In these comparison structures, the angle is larger in the phosphine oxide complex.

In chloroform solution, both compounds retain their five-coordinate status, as noted from the one-bond coupling constants [δ (coupling constant) = 21.4 ($^1J[\text{Sn}-\text{C}_1] = 461.4$), 27.7 ($^2J[\text{Sn}-\text{C}_2] = 27.8$), 26.6 ($^2J[\text{Sn}-\text{C}_3] = 79.4$ Hz), 13.1 ppm for the triphenylphosphine oxide adduct; δ (coupling constant) = 22.4 ($^1J[\text{Sn}-\text{C}_1] = 478.0$), 27.9 ($^2J[\text{Sn}-\text{C}_2] = 31.2$), 26.7 ($^3J[\text{Sn}-\text{C}_3] = 77.7$ Hz), 13.3 ppm for the triphenylarsine oxide adduct]. The 1J values exceed that for tributyltin chloride (339.5 Hz) in the same solvent, but are comparable with the values for tributyltin chloride dissolved in the donor solvents, dimethylsulfoxide and hexamethylphosphoramide [15]; when dissolved in the solvents, the Lewis acid is assumed to be coordinated by the donor molecules.

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