

氯化三有机基锡和氯化三有机基铅与三苯基氧膦 配合物的合成和晶体结构研究

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描述了一水合三苯基氧膦 $\text{Ph}_3\text{AsO} \cdot \text{H}_2\text{O}$ (1) 及其与氯化三苯基锡, 氯化三对氯苯基锡及氯化三苯基铅配合物 $[\text{Ph}_3\text{SnCl}(\text{OAsPh}_3)]$ (2), $[(\text{ClPh})_3\text{SnCl}(\text{OAsPh}_3)]$ (3) 和 $[\text{Ph}_3\text{PbCl}(\text{OAsPh}_3)]$ (4) 的合成和晶体结构, 晶体数据分别为 (1) 单斜晶系, 空间群 $P2_1/n$, $a = 9.4604(7)$, $b = 16.6347(7)$, $c = 11.1544(11) \text{ \AA}$, $\beta = 113.233(6)^\circ$, $V = 1613.0(2) \text{ \AA}^3$, $Z = 4$, $D_{\text{calcd}} = 1.401 \text{ g} \cdot \text{cm}^{-3}$, $R = 0.0576$, $R_w = 0.0683$; (2) 单斜晶系, 空间群 $P2_1/n$, $a = 18.235(4)$, $b = 18.203(4)$, $c = 18.917(4) \text{ \AA}$, $\beta = 94.07(3)^\circ$, $V = 6263(2) \text{ \AA}^3$, $Z = 8$, $D_{\text{calcd}} = 1.501 \text{ g} \cdot \text{cm}^{-3}$, $R = 0.0510$, $R_w = 0.0648$; (3) 三斜晶系, 空间群 $P\bar{1}$, $a = 12.9787(11)$, $b = 13.873(2)$, $c = 20.183(3) \text{ \AA}$, $\alpha = 98.051(10)^\circ$, $\beta = 99.176(9)^\circ$, $\gamma = 91.212(8)^\circ$, $V = 3548(7) \text{ \AA}^3$, $Z = 4$, $D_{\text{calcd}} = 1.518 \text{ g} \cdot \text{cm}^{-3}$, $R = 0.074$, $R_w = 0.1248$; (4) 单斜晶系, 空间群 $P2_1/n$, $a = 18.336(2)$, $b = 18.316(2)$, $c = 18.810(2) \text{ \AA}$, $\beta = 94.250(10)^\circ$, $V = 6299.8(11) \text{ \AA}^3$, $Z = 8$, $D_{\text{calcd}} = 1.679 \text{ g} \cdot \text{cm}^{-3}$, $R = 0.0808$, $R_w = 0.1829$. 三苯基砷同一个水分子共结晶, 该水分子通过氢键与两个三苯基氧膦的氧原子结合。该配体可与氯化三有机锡和氯化三有机铅形成同构配合物。这些化合物的晶体结构中每个不对称单元有两个 $[\text{Ph}_3\text{MCl}(\text{OAsPh}_3)]$ 分子。锡和铅原子的几何构型近似于三角双锥, 三个芳基环占据赤道位置, 氯和氧原子占据轴向位置。砷原子的构型基本为四面体。

关键词: 有机锡 有机铅 配合物 晶体结构
分类号: O614.43 O621.25*8

Synthesis and Structures of Coordination Compounds of Triphenylarsine with Triorganotin and Triorganolead Chlorides

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Report here are the synthesis and X-ray crystal structures of triphenylarsine oxide monohydrate $\text{Ph}_3\text{AsO} \cdot \text{H}_2\text{O}$ (1) and its coordination compounds with triphenyltin chloride, tri(p-chlorophenyl)tin chloride and triphenyllead chloride $[\text{Ph}_3\text{SnCl}(\text{OAsPh}_3)]$ (2), $[(\text{ClPh})_3\text{SnCl}(\text{OAsPh}_3)]$ (3) and $[\text{Ph}_3\text{PbCl}(\text{OAsPh}_3)]$ (4). Crystal data (1) monoclinic, $P2_1/n$, $a = 9.4604(7)$, $b = 16.6347(7)$, $c = 11.1544(11) \text{ \AA}$, $\beta = 113.233(6)^\circ$, $V = 1613.0(2) \text{ \AA}^3$, $Z = 4$, $D_{\text{calcd}} = 1.401 \text{ g} \cdot \text{cm}^{-3}$, $R =$

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Keyword: organotin organolead coordination compound crystal structure

0 Introduction

It is well known that oxygen donor ligands containing the $\text{C}=\text{O}$, $\text{S}=\text{O}$, $\text{N}=\text{O}$, $\text{P}=\text{O}$ or $\text{As}=\text{O}$ groups are potential Lewis bases which are able to coordinate to metal atoms or ions^[1,2]. Hence, the ligand Ph_3AsO forms stable coordination compounds with triorganotin chloride in which the lone pair electron on the oxygen donor atom interacts with the vacant d orbital of the tin atom forming a stable coordination bond. This Sn-O interaction causes an increase in the coordination number of tin from four to five and the structure usually adopt the trigonal bipyramidal geometry^[3].

This paper reports the syntheses and structures of triphenylarsine oxide monohydrate and its coordination compounds with triphenyltin chloride, tri(*p*-chlorophenyl)tin chloride and triphenyllead chloride with emphasis on the variation of the M-O and As-O bonds.

1 Experimental section

1.1 Synthesis and characterization

Triphenylarsine oxide (Ph_3AsO), triphenyltin chloride and triphenyllead chloride were obtained commercially and used without further purification. Tri(*p*-chlorophenyl)tin chloride was prepared by published method^[4].

Recrystallization of triphenylarsine oxide (compound 1) from toluene yielded colourless crystals which are suitable for X-ray diffraction study.

Preparation of coordination compound of triphenyltin (IV) chloride with triphenylarsine oxide (compound 2).

A mixture of triphenyltin (IV) chloride (0.1g, 0.3mmol) and triphenylarsine oxide (0.1g, 0.31mmol) were dissolved in chloroform. The mixture was heated for about 5 minutes and was filtered while hot. The filtrate was left undisturbed and a white solid was obtained. The product was recrystallized from toluene to yield 0.14g(81%) of fine colorless crystals; m. p. 164 ~ 166°C. Anal.

Found: C, 62.77; H, 4.11%. $C_{40}H_{30}ClOAsSn$ Calcd.: C, 63.14; H, 4.82%. ^{119}Sn NMR ($CDCl_3$, rel. to Me_4Sn): -73.4ppm.

The following compounds were similarly prepared: tri(*p*-chlorophenyl) tin (IV) chloride. triphenylarsine oxide (compound 3), m. p. 169 ~ 172°C. Anal. Found: C, 53.08; H, 2.98%. $C_{36}H_{27}Cl_4OAsSn$ Calcd.: C, 53.31; H, 3.36%. ^{119}Sn NMR($CDCl_3$, rel to Me_4Sn): -120.9 ppm.

Triphenyllead (IV) chloride. triphenylarsine oxide (compound 4), m. p. 204 ~ 207°C. Anal. Found: C, 53.11; H, 3.62%. $C_{36}H_{30}ClOAsPb$ Calcd.: C, 54.31; H, 3.80%.

1.2 Physical measurements

Elemental analysis was carried out using a Perkin-Elmer 2400 Series II CHN Analyser. The infrared spectra of the compounds were recorded as Nujol mulls between KBr cells using a Perkin-Elmer 1600 spectrometer, and were calibrated with polystyrene. The ^{119}Sn NMR spectra for compound 3 and 6 were recorded on a JEOL JNM GX270 spectrometer operating at 100.6MHz. Nuclear Overhauser suppressed conditions were used to obtain the ^{119}Sn spectra; the chemical shift are relative to Me_4Sn and are accurate to ± 0.1 ppm.

1.3 X-ray analysis and crystal data

X-ray crystallographic data collection was carried out on an automated Enraf-Nonius CAD4 diffractometer with graphite-monochromated $MoK\alpha$ ($=0.71703\text{\AA}$) radiation and determination of crystal class, orientation matrix and accurate cell parameters were performed by standard procedures. Intensities were recorded at the room temperature of 27°C up to a $2\theta_{max}$ of 50°. Unit cell constants for the structure lattices were derived from the angular settings of 25 strong random reflections. Crystal decay was monitored by using 3 standard reflections. The structures were solved by the direct method and refined by full-matrix least squares with anisotropic temperature factors for all non-H atoms. The H- atoms were either obtained from the Difference Fourier Map or placed in calculated positions, with riding mode on their parent atoms and included in structure-factor calculations. Structure solution and refinement were performed with SHELXS-86^[5] and SHELXL-93^[6] programs on a Pentium 150MHz personal computer. Crystallographic data: (1) $C_{18}H_{17}O_2As$, FW = 340.24, monoclinic, $P2_1/n$, $a = 9.4604(7)$, $b = 16.6347(7)$, $c = 11.1544(11)\text{\AA}$, $\beta = 113.233(6)^\circ$, $V = 1613.0(2)\text{\AA}^3$, $Z = 4$, $D_{calcd} = 1.401\text{g} \cdot \text{cm}^{-3}$, $R = 0.0576$, $R_w = 0.0683$ for 2921 observed reflections, $w^{-1} = \sigma^2(F) + 0.005F^2$, $(\Delta/\sigma)_{max} = 0.083$, $\Delta\rho_{max} = 0.72\text{e} \cdot \text{\AA}^{-3}$, $\Delta\rho_{min} = -0.48\text{e} \cdot \text{\AA}^{-3}$, $S = 1.77$; (2) $C_{36}H_{30}ClOAsSn$, FW = 707.66, monoclinic, $P2_1/n$, $a = 18.253(4)$, $b = 18.203(4)$, $c = 18.917(4)\text{\AA}$, $\beta = 94.07(3)^\circ$, $V = 6263(2)\text{\AA}^3$, $Z = 8$, $D_{calcd} = 1.501\text{g} \cdot \text{cm}^{-3}$, $R = 0.0510$, $R_w = 0.0648$ for 4061 observed reflections, $w^{-1} = \sigma^2(F) + 0.0015F^2$, $(\Delta/\sigma)_{max} = 0.016$, $\Delta\rho_{max} = 0.46\text{e} \cdot \text{\AA}^{-3}$, $\Delta\rho_{min} = -0.31\text{e} \cdot \text{\AA}^{-3}$, $S = 1.81$; (3) $C_{36}H_{27}Cl_4OAsSn$, FW = 810.99, triclinic, $P\bar{1}$, $a = 12.9787(11)$, $b = 13.873(2)$, $c = 20.183(3)\text{\AA}$, $\alpha = 98.051(10)$, $\beta = 99.176(9)$, $\gamma = 91.212(8)^\circ$, $V = 3548(7)\text{\AA}^3$, $Z = 4$, $D_{calcd} = 1.518\text{g} \cdot \text{cm}^{-3}$, $R = 0.074$, $R_w = 0.1248$ for 3986 observed reflections, $w^{-1} = \sigma^2(F) + 0.006F^2$, $(\Delta/\sigma)_{max} = 0.032$, $\Delta\rho_{max} = 0.83\text{e} \cdot \text{\AA}^{-3}$, $\Delta\rho_{min} = -0.76\text{e} \cdot \text{\AA}^{-3}$, $S = 1.12$; (4) $C_{36}H_{30}ClOAsPb$, FW = 796.16, monoclinic, $P2_1/n$, $a = 18.336(2)$, $b = 18.316(2)$, $c = 18.810(2)\text{\AA}$, $\beta = 94.250(10)^\circ$, $V = 6299.8(11)\text{\AA}^3$, $Z = 8$,

$D_{\text{calc}} = 1.679 \text{ g} \cdot \text{cm}^{-3}$, $R = 0.0808$, $R_w = 0.1532$ for 3886 observed reflections, $w^{-1} = \sigma^2(F) + 0.006 F^2$, $(\Delta/\sigma)_{\text{max}} = 0.078$, $\Delta\rho_{\text{max}} = 1.083 \text{ e} \cdot \text{\AA}^{-3}$, $\Delta\rho_{\text{min}} = -0.98 \text{ e} \cdot \text{\AA}^{-3}$, $S = 1.07$, respectively. The structures with their numbering scheme are given in Figures 1, 2, 3 and 4. Final refinement details are included in the experimental section while the selected bond distances and bond angles are given in Tables 2. Lists of fractional atomic coordinates hydrogen coordinates, anisotropic temperature parameters can be obtained from the author on request.

2 Results and Discussion

The reaction of triphenyltin, tri(*p*-chlorophenyl) tin and triphenyllead chlorides with triphenylarsine oxide resulted in the formation of pentacoordinated complexes in which the coordination bond was formed as a result of the M-O interaction. This interaction was evidenced from the shift to lower frequencies of the As-O infrared stretching band. Hence the $\nu(\text{As-O})$ vibration, which appeared at 1084 cm^{-1} for the uncomplexed triphenylarsine oxide molecule, shifts to lower frequencies at 1066, 1064 and 1065 cm^{-1} when the molecule is involved in coordination to the metal atom of triphenyltin, tri(*p*-chlorophenyl)tin and triphenyllead chlorides, respectively [Table 1]. Further evidence on the formation of 5-coordinate structures must come from the X-structural studies of these complexes.

Table 1 As-O Vibration Frequencies for the Free Ligand and its Organotin and Organolead Complexes

compound	$\nu(\text{As-O})/\text{cm}^{-1}$
Ph_3AsO (compound 1)	1084
$\text{Ph}_3\text{SnCl}(\text{OAsPh}_3)$ (compound 2)	1066
$(p\text{-ClPh})_3\text{SnCl}(\text{OAsPh}_3)$ (compound 3)	1064
$\text{Ph}_3\text{PbCl}(\text{OAsPh}_3)$ (compound 4)	1065

The X-ray crystal structures of the free ligand, triphenylarsine oxide monohydrate (compound 1), was shown in Fig. 1 while its coordination compound with triphenyltin chloride (compound 2), tri(*p*-chlorophenyl) tin chloride (compound 3) and triphenyllead chloride (compound 4) are given in figures 2, 3 and 4, respectively. The structure of compound 1 revealed a distorted tetrahedral geometry at the arsenic atom, in which the three phenyl rings are not coplanar but make interplanar angles of 108.6° [for C13-As-C7], 108.8° [for

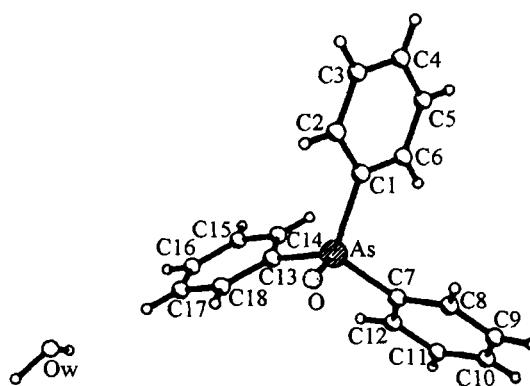


Fig. 1 Molecular structure of triphenylarsine oxide monohydrate

C13-As-C1] and 106.4° [for C1-As-C7] to avoid steric interaction. Unit cell packing diagram projecting down *a*-axis shows intermolecular H-bonding between the hydrogen from the H_2O molecule and oxygen atoms of two triphenylarsine oxide molecules (symmetry code for $\text{O}_w\text{-H2a}\cdots\text{O}'$: $-1 + x, y, z$ and for $\text{O}_w\text{-H2b}\cdots\text{O}''$: $-1 + x, 2 - y, 1 - z$) at a value of $2.813 \text{\AA}$ and $2.805 \text{\AA}$, respectively (Fig. 1a).

The crystal of triphenylarsine oxide coordination compound with triphenyltin chloride

(compound 2) is made up of two molecules of $[\text{Ph}_3\text{SnCl}(\text{OAsPh}_3)]$. The triphenyltin chloride moiety is close to a regular trigonal bipyramid with the 3 phenyl rings in the equatorial positions while the Cl and O in axial positions. The triphenylarsine oxide is covalently bonded to tin through its oxygen atom, with a consequent small lengthening of the O-As bond [1.663(4) Å for molecule A and 1.672(4) Å for molecule B] compared to that in the free ligand of 1.653(3) Å. The geometry at arsenic atom is essentially tetrahedral, with the average O-As-C angle of 109.8° and the average C-As-C angle of 109° . However, the C_{3v} trigonal symmetry is not present in the triphenylarsine oxide molecule because of the different inclination of the three aromatic rings with respect to the planes defined by oxygen, arsenic and carbon atoms bonded to As. The value of the Sn-O-As angle is 139.4° indicates that bent coordination by triphenylarsine oxide occurs for compound 2.

The reaction of tri(*p*-chlorophenyl) tin chloride with triphenylarsine oxide yielded crystals (compound 3) which is isostructure as compound 2. There is, however, a shortening of Sn-Cl [2.516(3) Å] bond compared to that for compound 2 [2.613(2) Å]. This may be due to the electron withdrawing effect of the chlorine atom on the chlorophenyl ligand. On the other hand, the electron withdrawing effect of the chlorophenyl ligand did not produce any significant changes to the Sn-O interaction [Sn-O 2.249(6) Å compared to 2.260(4) Å for compound 2].

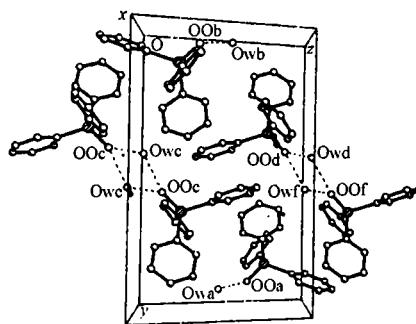


Fig. 1a Unit cell packing diagram for triphenylarsine oxide monohydrate projected down a-axis showing hydrogen bonding in the molecule

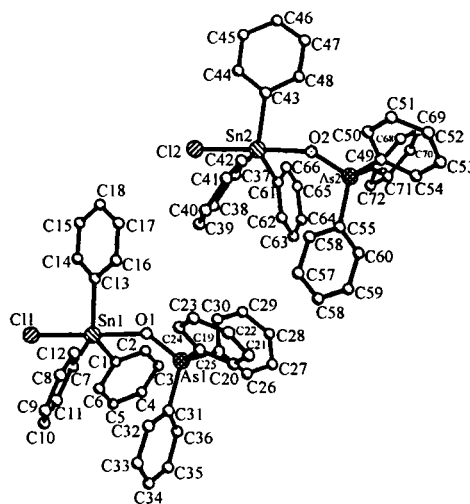


Fig. 2 Molecular plot of compound 2

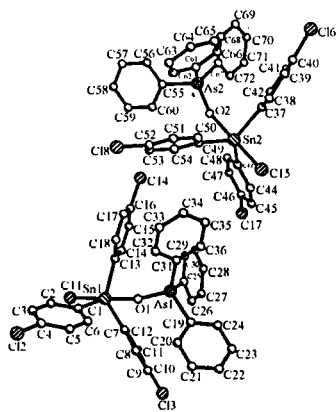


Fig. 3 Molecular plot of compound 3

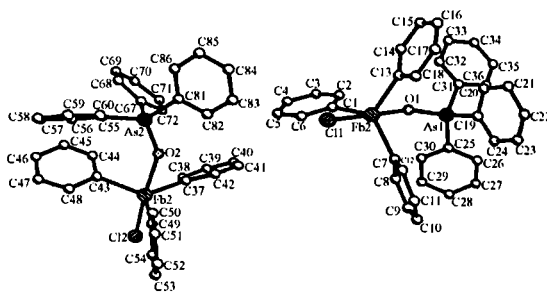


Fig. 4 Molecular structure of compound 4

There is no steric effect due to the presence of chlorine atom on the phenyl ring on the formation of the coordination compound as was indicated by the As-O-Sn angles and the three C-Sn-O angles which are not significantly enlarged (Table 2). Compound **4** was obtained from the reaction of triphenyllead chloride with triphenylarsine oxide. As anticipated, the structure of compound **4** is isostructural with those of compounds **2** and **3**. The small lengthening of the covalently bonded Pb-O bond [2.429(9) Å] compared to Sn-O [2.260(4) Å for compound **2**] probably due to the electron density on the metal atom.

Table 2 Selected Bond Distances (Å) and Angles (°)

	compound 1	compound 2	compound 3	compound 4*
Sn-C(1)	—	2.143(6)	2.144(10)	2.196(13)
		2.132(6)	2.132(11)	2.21(2)
Sn-C(7)	—	2.141(6)	2.125(11)	2.172(13)
		2.123(6)	2.124(10)	2.184(14)
Sn-C(13)	—	2.150(6)	2.131(10)	2.191(13)
		2.139(6)	2.151(10)	2.206(14)
Sn-O	—	2.260(4)	2.249(6)	2.429(9)
		2.283(4)	2.267(7)	2.462(9)
Sn-Cl	—	2.613(2)	2.516(3)	2.660(4)
		2.634(2)	2.522(3)	2.658(4)
As-O	1.653(3)	1.663(4)	1.661(7)	1.651(9)
		1.672(4)	1.652(6)	1.661(9)
C(1)-Sn-C(7)	—	118.5(2)	117.6(4)	118.3(6)
		120.0(2)	119.0(2)	119.3(3)
C(7)-Sn-C(13)	—	121.7(2)	122.2(4)	118.3(6)
		117.2(2)	118.4(4)	120.8(5)
C(1)-Sn-C(13)	—	119.3(2)	119.4(4)	123.9(5)
		122.5(2)	121.7(4)	119.2(6)
C(1)-Sn-O	—	90.4(2)	85.5(3)	86.5(4)
		91.6(2)	85.6(3)	84.9(4)
C(7)-Sn-O	—	87.4(2)	88.0(4)	88.5(4)
		85.6(2)	88.9(3)	90.1(5)
C(13)-Sn-O	—	84.5(2)	87.5(3)	85.0(4)
		87.1(2)	86.0(3)	86.7(5)
As-O-Sn	—	139.4(2)	135.9(4)	140.3(6)
		139.3(2)	134.7(4)	139.2(6)

* The bond distances and angles in Compound 4 referred to those involving the lead atom.

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