

## PHENYLPHOSPHONATO DERIVATIVES AND ADDUCT: SYNTHESIS AND SPECTROSCOPIC STUDIES

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**Abstract:** Nine phenylphosphato derivatives and adduct have been synthesized and studied by infrared and Mössbauer techniques. The structures are polymeric, the oxoanion behaving as a bichelating, a tridentate, or a tetradentate ligand. The environment around the tin (IV) centre is octahedral or a trigonal bipyramidal.

**Keywords:** *phenylphosphato derivatives and adduct, infrared and Mössbauer techniques, polymeric structures.*

## INTRODUCTION

$\text{SnR}_3$  ( $\text{R} = \text{Bu}, \text{Ph}$ ) residues containing compounds are known for being subject of applications in agriculture, medicine, antifouling paints, wood preservatives [1 – 6]. In this field our group has yet reported several papers [7 – 15]. In the framework of our work in the coordination ability of oxyanions and seeking for new organotin (IV) compounds, we carry out here the study the interactions between  $\text{Me}_4\text{NPhPO}_3\text{H}\cdot 2\text{H}_2\text{O}$  or  $\text{Cy}_2\text{NH}_2\text{PhPO}_3\text{H}$  and  $\text{SnMe}_2\text{Cl}_2$ ,  $\text{SnBu}_2\text{Cl}_2$ ,  $\text{SnPh}_2\text{Cl}_2$ ,  $\text{SnMe}_3\text{Cl}$ ,  $\text{SnPh}_3\text{OH}$  or  $\text{SnPh}_3\text{Cl}$  which has yielded nine new derivatives and adduct, infrared and Mössbauer studies of which have been carried out and structures suggested on the basis of spectroscopic data.

## EXPERIMENTAL

$\text{Me}_4\text{NPO}_3\text{H}\cdot 2\text{H}_2\text{O}$  (**L**<sub>1</sub>) and  $\text{Cy}_2\text{NH}_2\text{PhPO}_3\text{H}$  (**L**<sub>2</sub>) have been obtained on mixing  $\text{PhPO}_3\text{H}$  with a water solution of  $\text{Me}_4\text{NOH}$  (20%) or  $\text{Cy}_2\text{NH}$ .

Table 1 presents the elemental analyses of (**L**<sub>1</sub>) and (**L**<sub>2</sub>) compounds.

*Table 1. Elemental analyses of (**L**<sub>1</sub>) and (**L**<sub>2</sub>)*

Symbol	Chemical formula	Elemental analysis (%)					
		C		H		N	
		calc.	found	calc.	found	calc.	found
( <b>L</b> <sub>1</sub> )	$\text{Me}_4\text{NPO}_3\text{H}\cdot 2\text{H}_2\text{O}$	66.79	66.79	9.2	9.33	4.32	4.59
( <b>L</b> <sub>2</sub> )	$\text{Cy}_2\text{NH}_2\text{PhPO}_3\text{H}$	44.62	44.89	8.55	9.02	5.21	5.55

When (**L**<sub>1</sub>) and (**L**<sub>2</sub>) are allowed to react with  $\text{SnMe}_2\text{Cl}_2$ ,  $\text{SnBu}_2\text{Cl}_2$ ,  $\text{SnPh}_2\text{Cl}_2$ ,  $\text{SnMe}_3\text{Cl}$ ,  $\text{SnBu}_3\text{Cl}$ ,  $\text{SnPh}_3\text{OH}$  or  $\text{SnPh}_3\text{Cl}$  as ethanolic solutions in specific ratios, a precipitation occurs or a solution obtained. The precipitates were stirred no less than two hours while the solutions were submitted to a slow solvent evaporation.

The elemental analyses were performed by the CNRS “Service Central d’Analyses” Vernaison, France, or the laboratory of Microanalyses, University of Padova, – Italy. All the chemicals were from Aldrich or Merck Companies and used without any further purification. The infrared spectra were recorded by a PE 580 (4000 – 200  $\text{cm}^{-1}$ ) or a FTIR-Nicolet (600 – 50  $\text{cm}^{-1}$ ) spectrometer at the University of Padova (Italy), the sample being as Nujol mulls, using CsI or polyethylene windows. Mössbauer spectra were obtained as described previously [16]. Infrared data are given in  $\text{cm}^{-1}$  [abbreviations: (vs) very strong, (s) strong, (m) medium, (sh) shoulder, (w) weak, (vw) very weak]. Mössbauer parameters are given in  $\text{mm}\cdot\text{s}^{-1}$  (abbreviations: Q.S = quadrupole splitting, I.S = isomer shift,  $\Gamma$  = full width at half-height).

The chemical composition, according to elemental analyses, of the nine phenylphosphonato derivatives (**A** – **I**) obtained is presented in Table 2.

**Table 2.** Formulae of phenylphosphonatoderivatives, based on the elemental analyses

Compound	Organotin (IV): L ratio	Chemical formula	Elemental analysis (%)							
			C		H		N		Cl	
			a*	b**	a*	b**	a*	b**	a*	b**
<b>A</b>	1 : 2L <sub>1</sub>	SnMe <sub>2</sub> PhPO <sub>3</sub>	31.51	31.37	3.61	3.51				
<b>B</b>	1 : 1L <sub>1</sub>	SnBu <sub>2</sub> PhPO <sub>3</sub>	43.20	42.04	5.90	5.89				
<b>C</b>	1 : 1L <sub>2</sub>	SnPh <sub>2</sub> PhPO <sub>3</sub>	49.08	48.78	3.74	4.61				
<b>D</b>	1 : 1L <sub>1</sub>	SnPh <sub>3</sub> PhPO <sub>3</sub> H	56.84	56.79	4.14	4.05				
<b>E</b>	1 : 1L <sub>1</sub>	SnBu <sub>3</sub> PhPO <sub>3</sub> H	48.35	48.28	7.38	7.50				
<b>F</b>	1 : 1L <sub>1</sub>	SnPh <sub>2</sub> (PhPO <sub>3</sub> H) <sub>2</sub>	49.08	48.68	3.74	3.62				
<b>G</b>	1 : 1L <sub>1</sub>	(SnMe <sub>3</sub> ) <sub>2</sub> PhPO <sub>3</sub>	29.65	29.33	4.32	4.45				
<b>H</b>	3 : 1L <sub>1</sub>	(SnPh <sub>3</sub> ) <sub>2</sub> PhPO <sub>3</sub>	58.88	58.69	4.10	4.20				
<b>I</b>	1 : 3L <sub>1</sub>	(Me <sub>4</sub> N) <sub>2</sub> PhPO <sub>3</sub> .3SnPh <sub>3</sub> Cl	55.40	55.21	4.73	4.74	1.41	1.48	7.24	7.49

\* - calculated;

\*\* - found.

## RESULTS AND DISCUSSION

Let us consider the IR and Mössbauer data of the following compounds **A – I**:

**(A):**  $\nu$  PO<sub>3</sub> = 1140 (m); 1110 (vs); 1080 (w);  $\delta$  PO<sub>3</sub> = 580 (s); 570 (s);  $\rho$  PO = 370 (m);  $\nu$  PC = 760 (s); vs SnC<sub>2</sub> = 514 (w);  $\nu$  SnO = 240 (w);

**(B):**  $\nu$  PO<sub>3</sub> = 1140 (m); 1110 (vs); 1080 (m);  $\delta$  PO<sub>3</sub> = 600 (m); 560 (m);  $\rho$  PO = 385 (m);  $\nu$  PC = 750 (m); vs SnC<sub>2</sub> = 615 (w);  $\nu$  SnO = 227 (vw);

**(C):**  $\nu$  PO<sub>3</sub> = 1140 (m); 1120 (m); 1090 (vs);  $\delta$  PO<sub>3</sub> = 610 (m); 570 (m);  $\rho$  PO = 358 (w); (vas, vs) SnC<sub>2</sub> = 280 (m); 223 (m);  $\nu$  SnO = 210 (w);

**(D):**  $\nu$  PO<sub>3</sub> = 1130 (vs); 1060 (s); 975 (s);  $\delta$  PO<sub>3</sub> = 560 (s);  $\rho$  PO = 390 (m);  $\nu$  PC = 750 (s); (vas, vs) SnC<sub>3</sub> = 275 (s); 230(m);  $\nu$  SnO = 201(vw)

**(E):**  $\nu$  PO<sub>3</sub> = 1140 (m); 1125 (vs); 960 (s);  $\delta$  PO<sub>3</sub> = 560 (s);  $\rho$  PO = 370 (m);  $\nu$  PC = 740 (s); vs SnC<sub>3</sub> = 610 (w);  $\nu$  SnO = 225 (vw)

**(F):**  $\nu$  PO<sub>3</sub> = 1140 (s); 1120 (vs); 1080 (vs); 1050 (s);  $\delta$  PO<sub>3</sub> = 610 (m); 560 (m); 460 (m);  $\rho$  PO = 340 (m);  $\nu$  PC = 570 (m); (vas, vs) SnC<sub>2</sub> = 275 (m) 222 (m);  $\nu$  SnO = 208 (vw)

**(G):**  $\nu$  PO<sub>3</sub> = 1135 (vs); 1060 (vs);  $\delta$  PO<sub>3</sub> = 560 (s);  $\nu$ PC = 755 (s); vs SnC<sub>3</sub> = 515 (vw);

**(H):**  $\nu$  PO<sub>3</sub> = 1140 (m); 1120 (vs); 1090 (vs);  $\delta$  PO<sub>3</sub> = 560 (m);  $\nu$  PC = 755 (s); (vas, vs) SnC<sub>3</sub> = 275 (m); 220 (m);  $\nu$  SnO = 207 (w);

**(I):**  $\nu$  PO<sub>3</sub> = 1140 (m); 1125 (vs); 1060 (s); 970 (s);  $\delta$  PO<sub>3</sub> = 560 (s);  $\rho$  PO = 370 (w);  $\nu$  PC = 760 (s); vsSnC<sub>3</sub> = 215 (m);  $\nu$  SnO = 200 (w);

**(A):**  $\Delta E$  = 3.56;  $\delta$  = 1.15;  $\Gamma$  = 1.03;

**(B):**  $\Delta E$  = 3.32;  $\delta$  = 1.19;  $\Gamma$  = 0.95;

**(C):**  $\Delta E$  = 2.91;  $\delta$  = 1.00;  $\Gamma$  = 0.89;

**(D):**  $\Delta E$  = 3.96;  $\delta$  = 1.07;  $\Gamma$  = 0.99;

**(F):**  $\Delta E$  = 2.88;  $\delta$  = 1.02;  $\Gamma$  = 1.15;

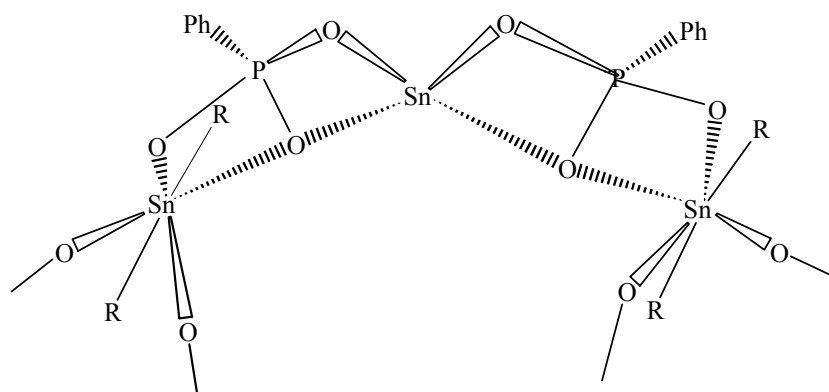
**(H):**  $\Delta E_1$  = 3.34;  $\delta_1$  = 1.20;  $\Gamma_1$  = 0.97;  $\Delta E_2$  = 2.45;  $\delta_2$  = 1.16;  $\Gamma_2$  = 0.97;

**(I):**  $\Delta E$  = 3.06;  $\delta$  = 1.30;  $\Gamma$  = 1.00.

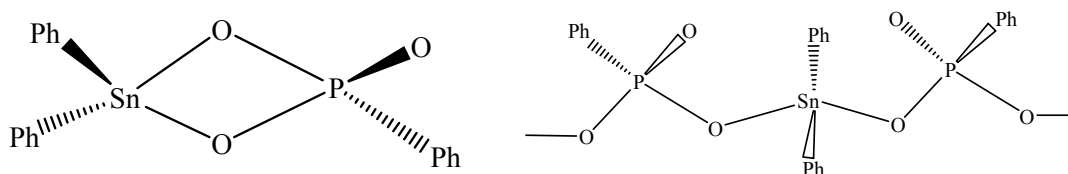
**SnR<sub>2</sub>PhPO<sub>3</sub> (R = Me, Bu, Ph) (A), (B), (C)**

The values of the quadrupole splitting of **(A)** (3.56 mm·s<sup>-1</sup>), **(B)** (3.32 mm·s<sup>-1</sup>) and **(C)** (2.91 mm·s<sup>-1</sup>) are very similar to those reported for SnMe<sub>2</sub>Cl<sub>2</sub> (3.56 mm·s<sup>-1</sup>) SnBu<sub>2</sub>Cl<sub>2</sub> (3.38 mm·s<sup>-1</sup>) and SnPh<sub>2</sub>Cl<sub>2</sub> (2.88 mm·s<sup>-1</sup>) by Platt *et al* [17, 18], and allow suggesting similar structures, i.e.:

- an infinite chain with a distorted *trans*octahedral environment for **(A)** and **(B)** (Figure 1),
- a discrete one or an infinite chain with a tetrahedral environment around the tin centre for **(C)** (Figure 2).



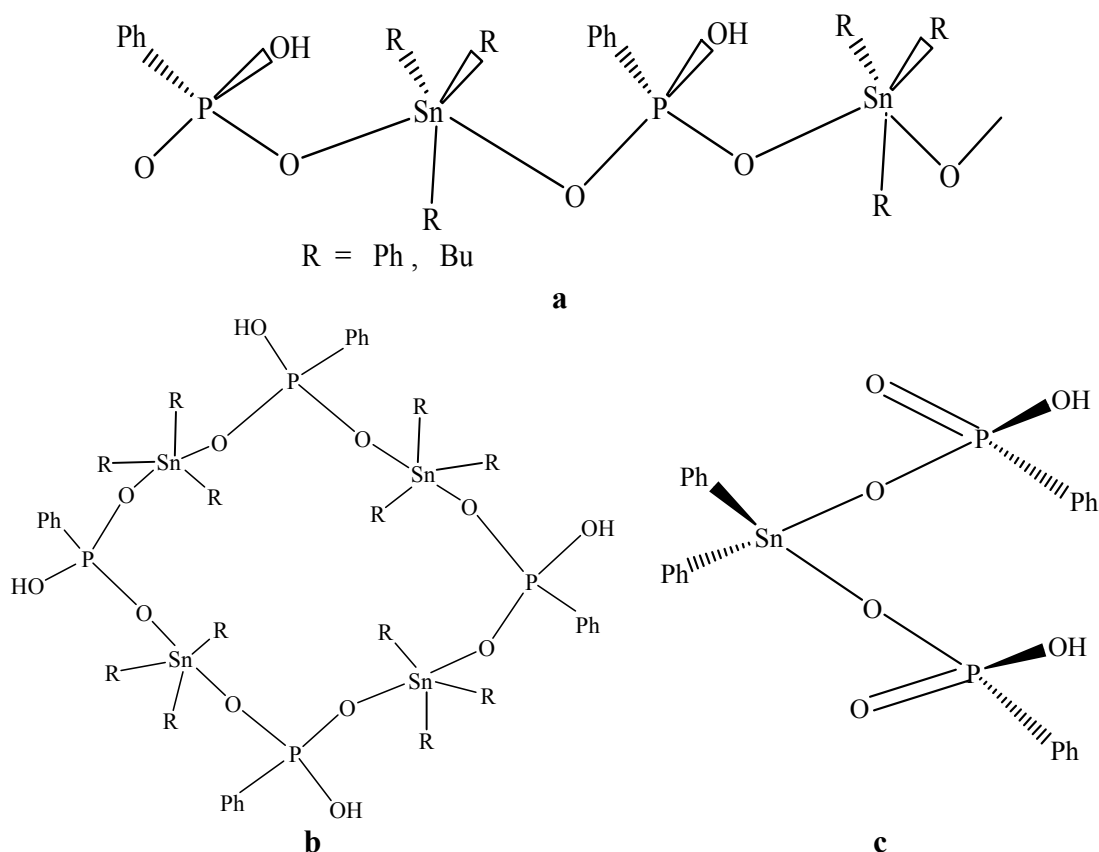
**Figure 1.** Structure of derivatives **(A)** and **(B)** - SnR<sub>2</sub>PhPO<sub>3</sub> (R = Me, Bu),



**Figure 2.** Structures of the derivative **(C)** - SnPh<sub>2</sub>PhPO<sub>3</sub> -

**SnR<sub>3</sub>PhPO<sub>3</sub>H (R = Ph, Bu) (D), (E); SnPh<sub>2</sub>(PhPO<sub>3</sub>H)<sub>2</sub> (F)**

The values of the quadrupole splitting of **(D)** allow to conclude to the presence of a *trans* coordinated SnPh<sub>3</sub> residue **(D)**; the presence of vs SnC<sub>3</sub> on the IR spectrum of **(E)** as a weak band is an indication of D<sub>3h</sub> symmetry for the SnC<sub>3</sub> residue and allow, even in the absence of Mössbauer data for this derivative to conclude to the absence of monocoordinated SnBu<sub>3</sub> residue and the presence of *trans* coordinated SnBu<sub>3</sub> residue. This allows suggesting an infinite chain structure or an oligomer as in [19 – 24] for **(D)**, **(E)** (Figure 3 a, b). We arbitrary draw the infinite chain and the tetramer. Only an X ray study can definitively precise the nucleation (our attempts to get monocrystals were unsuccessful). The value of the quadrupole splitting of **(F)** indicates a tetrahedral environment and allows suggesting a discrete structure with monocoordinating PhPO<sub>3</sub>H<sup>-</sup> (Figure 3 c).

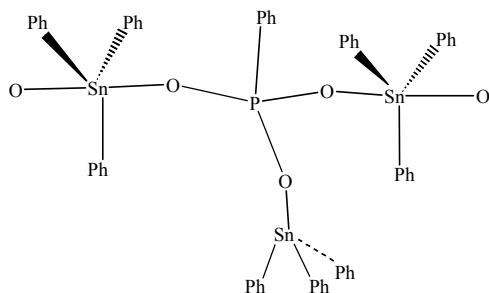


**Figure 3 a-c.** Structures of derivatives (**D**), (**E**) and (**F**): *a*) infinite chain; *b*) tetramer; *c*) structure of the derivative (**F**)

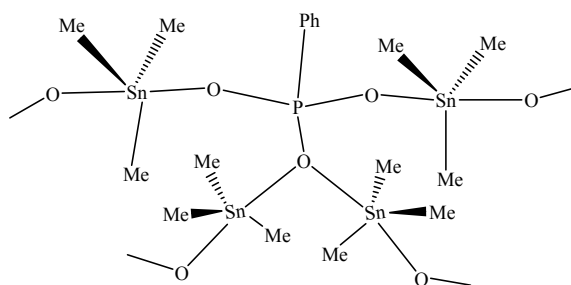
**(SnPh<sub>3</sub>)<sub>2</sub>PhPO<sub>3</sub> (**H**), (SnMe<sub>3</sub>)<sub>2</sub>PhPO<sub>3</sub> (**G**)**

The Mössbauer data of (**H**) have revealed the presence of two different tin centers, one with a tetrahedral environment ( $Q_S = 2.45 \text{ mm.s}^{-1}$ ) and another one *trans* coordinated ( $Q_S = 3.34 \text{ mm.s}^{-1}$ ). The structure consistent with these data is an infinite chain with bridging phenylphosphate anions connected to a pendant monocoordinated SnPh<sub>3</sub> residue (Figure 4).

For the compound (**G**), the absence of vs SnMe<sub>3</sub> is an indication of the presence of only planar SnMe<sub>3</sub> residues allowing suggesting a layered structure with a tetradentate phenylphosphate anion (Figure 5).



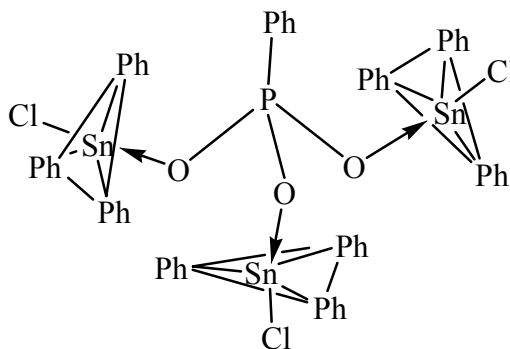
**Figure 4.** Structure of derivative (**H**)



**Figure 5.** Structure of derivative (**G**)

**(Me<sub>4</sub>N)<sub>2</sub>PhPO<sub>3</sub>·3SnPh<sub>3</sub>Cl (I)**

The trinuclear adduct contains monocoordinated SnPh<sub>3</sub>Cl molecules because the enhancement of Q<sub>S</sub> (3.06 mm·s<sup>-1</sup>) compared to its value in free SnPh<sub>3</sub>Cl (2.55 mm·s<sup>-1</sup>) [17, 18], is an indication of coordination. The suggested structure is reported on Figure 6, the anion behaving as a tridentate ligand.



**Figure 6.** Structure of the adduct (Me<sub>4</sub>N)<sub>2</sub>PhPO<sub>3</sub>·3SnPh<sub>3</sub>Cl (I)

**CONCLUSION**

The methyl and butyl derivatives of SnR<sub>2</sub>PhPO<sub>3</sub> have an infinite chain structure while SnPh<sub>2</sub>PhPO<sub>3</sub> has a discrete structure. SnPh<sub>2</sub>(PhPO<sub>3</sub>H) as a discrete structure while (SnR<sub>3</sub>)<sub>2</sub>PhPO<sub>3</sub> have a layered (methyl) or an infinite chain (phenyl) structure. The adduct has a discrete structure. The anion behaves as a bichelating, monochelating, tetradentate, and tridentate ligand.

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