

## SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF SOME NEW $PO_4^{3-}$ , $HPO_4^{2-}$ AND $HPO_3^{2-}$ CONTAINING ORGANOTIN (IV) DERIVATIVES

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**Abstract:** Four new organotin (IV) derivatives containing coordinating phosphate, hydrogenophosphate and hydrophosphonate anions have been synthesized and studied by infrared and Mössbauer spectroscopies. Discrete, infinite chain or oligomeric structures have been suggested, the anion behaving as a bi- or a tridentate ligand, the environment around the tin (IV) center being in all cases *trans* trigonal bipyramidal. The starting  $HPO_3H_2$  in three cases has turned into phosphate when reacting with  $SnPh_3OH$  while in the presence of  $SnMe_3OH$  this oxidation does not occur. Some of the derivatives are hydrated ones while the others are not, the water molecules deriving from the condensation reaction being kept or not in the lattice. The presence of ethylenediamine in a monoprotonated and diprotonated forms and involved in hydrogen bonding in some of the compounds seems noteworthy and may explain the presence of water molecules or not. Supramolecular architectures are obtained when secondary interactions are considered.

**Keywords:** *discrete, infinite chain, oligomeric structures, organotin (IV) derivatives, polydentate  $PO_4^{3-}$ ,  $HPO_4^{2-}$ ,  $HPO_3^{2-}$ , supramolecular architectures*

## INTRODUCTION

Many groups are involved in the seek of new organotin (IV) compounds because of applications found for some tin (IV) molecules in the fields of medicine, agriculture, and industry [1 – 7]. In this dynamic, our group has yet published some papers dealing with the interactions between inorganic acids and  $\text{SnR}_3\text{OH}$ , ( $\text{R} = \text{Me}, \text{Ph}$ ) [8 – 10]. The  $\text{PO}_4(\text{SnPh}_3)_3$  derivative has a discrete structure and contains two monocoordinated residues and a *trans* coordinated one [11]. In this paper we have initiated the study of the interactions between ethylenediamine,  $\text{HPO}_3\text{H}_2$  and  $\text{SnPh}_3\text{OH}$  or  $\text{HPO}_3\text{H}_2$ ,  $\text{SnR}_3\text{OH}$  ( $\text{R} = \text{Ph}, \text{Me}$ ) and  $\text{Et}_4\text{NCN}$  which have yielded four derivatives, infrared and Mössbauer studies of which have been carried out, then structures suggested on the basis of spectroscopic data.

## MATERIALS AND METHODS

On mixing aqueous solutions of ethylenediamine (en) and  $\text{HPO}_3\text{H}_2$  with a solution of  $\text{SnPh}_3\text{OH}$  in acetone in 1:1:2 ratio or with an ethanolic solution of  $\text{SnPh}_3\text{OH}$  in 1:1:1 ratio, compounds **A** and **B** respectively are obtained as white precipitates.

When  $\text{HPO}_3\text{H}_2$  is allowed to react with  $\text{SnPh}_3\text{OH}$  and  $\text{Et}_4\text{NCN}$  in hot ethanol in a 1:2:2 ratio, a white precipitate (**C**) is obtained.

A mixture of  $\text{HPO}_3\text{H}_2$ ,  $\text{SnMe}_3\text{OH}$  and  $\text{Et}_4\text{NCN}$  in a 1:2:2 ratio gives a clear solution and a white powder (**D**) collected after a slow solvent evaporation.

All the precipitates were stirred around two hours then filtered and washed with hot ethanol.

The analytical data reported below (Table 1) have allowed to suggest the following formulae for the four new compounds:

*Table 1. Suggested formulae of the synthesized compounds*

Comp	Suggested formulae	Chemical composition [% mass]					
		C		H		N	
		Calc.	Found	Calc.	Found	Calc.	Found
<b>A</b>	$\text{H}_2\text{enPO}_4\text{SnPh}_3$	47.37	47.47	4.97	4.90	5.52	5.47
<b>B</b>	$\text{HenPO}_4(\text{SnPh}_3)_2 \cdot 2\text{H}_2\text{O}$	51.16	50.80	4.86	4.82	3.14	3.12
<b>C</b>	$\text{Et}_4\text{NHPO}_4\text{SnPh}_3$	54.19	54.36	6.30	6.37	2.43	2.39
<b>D</b>	$\text{HPO}_3(\text{SnMe}_3)_2 \cdot \text{H}_2\text{O}$	16.89	17.00	5.20	5.15	-	-

The elemental analyses were performed by the Department of Chemistry, University of Bath (UK). The infrared spectra were recorded by a FTIR-Nicolet (4000 – 400  $\text{cm}^{-1}$ ) spectrometer at the Cheikh Anta Diop University of Dakar (Senegal), the sample being as Nujol mulls, using CsI windows. Infrared data are given in  $\text{cm}^{-1}$  [IR abbreviations: (br) broad, (vs) very strong, (s) strong, (m) medium, (sh) shoulder, (w) weak, (vw) very weak].  $^{119}\text{Sn}$  Mössbauer spectra were collected at 80 K as reported in [12].

All the chemicals were purchased from Aldrich or Merck Chemicals Companies and were used without any further purification.

## RESULTS AND DISCUSSION

### General considerations on the process of obtention of the studied derivatives

One molecule of  $\text{PO}_4\text{H}_3$  obtained in situ by the oxidation of  $\text{HPO}_3\text{H}_2$  reacts with two molecules of  $\text{SnPh}_3\text{OH}$  by condensation leading to  $\text{HPO}_4(\text{SnPh}_3)_2$ ; this derivative reacting with one molecule of ethylenediamine leads to  $[\text{enH}^+][\text{PO}_4(\text{SnPh}_3)(\text{H}_2\text{O})]$ : this derivative contains  $\text{enH}^+$  obtained by a protonation of ethylenediamine by the single remaining proton.

The second molecule of  $\text{PO}_4\text{H}_3$  obtained as above reacts with one molecule of  $\text{SnPh}_3\text{OH}$  by condensation leading to  $\text{enH}_2\text{PO}_4[\text{SnPh}_3(\text{H}_2\text{O})]$ ; this derivative contains  $\text{enH}_2^+$  obtained by a double protonation of ethylenediamine by the two remaining protons of the starting  $\text{PO}_4\text{H}_3$ .

The derivatives **A** and **C** are similar while considering the reaction involved because of containing only one  $\text{SnPh}_3$  residue. In the case of  $\text{Et}_4\text{NOH}$  only one of the two remaining protons reacts with  $\text{EtNOH}$ ; this explains the presence of  $[\text{PO}_4\text{H}]^{2-}$  rather than  $[\text{PO}_4]^{3-}$ .

### Spectroscopic study

Let us consider the infrared data in  $\text{cm}^{-1}$  of the studied derivatives:

**A:**  $\nu(\text{NH}_3^+) = 3450\text{-}2600$  br;  $\delta(\text{NH}_3^+) = 1650$  s,  $1580$  s;  $\nu(\text{PO}_4) = 1090$  vs,  $1020$  vs,  $970$  vs;

**B:**  $\nu(\text{NH}_2) + \nu(\text{NH}_3^+) + \nu(\text{OH}_2) = 3428\text{-}2282$  br;  $\delta(\text{NH}_2) + \delta(\text{NH}_3^+) + \delta(\text{OH}_2) = 1634$  s,  $1580$  s;  $\nu(\text{PO}_4) = 1127$  vs,  $1054$  vs;

**C:**  $\nu(\text{OH}_2) = 3375$  s;  $\delta(\text{H}_2\text{O}) = 1650$  m;  $\nu(\text{PO}_4) = 1075$  vs,  $1025$  s,  $1000$  m;

**D:**  $\nu(\text{OH}_2) = 3419$  vs;  $\nu(\text{PH}) = 2350$  m;  $\delta(\text{OH}_2) = 1630$  s;  $\nu(\text{PO}_3) = 1126$  vs,  $1055$  vs,  $987$  s;  $\nu_{\text{as}}(\text{SnC}_3) = 552$  s.

and their Mössbauer parameters in  $\text{mm}\cdot\text{s}^{-1}$ :

**A:**  $\delta = 1.27$ ,  $\text{QS} = 3.99$ ,  $\Gamma = 0.96$ ;

**B:**  $\delta = 1.19$ ,  $\text{QS} = 2.96$ ,  $\Gamma = 0.98$ ;

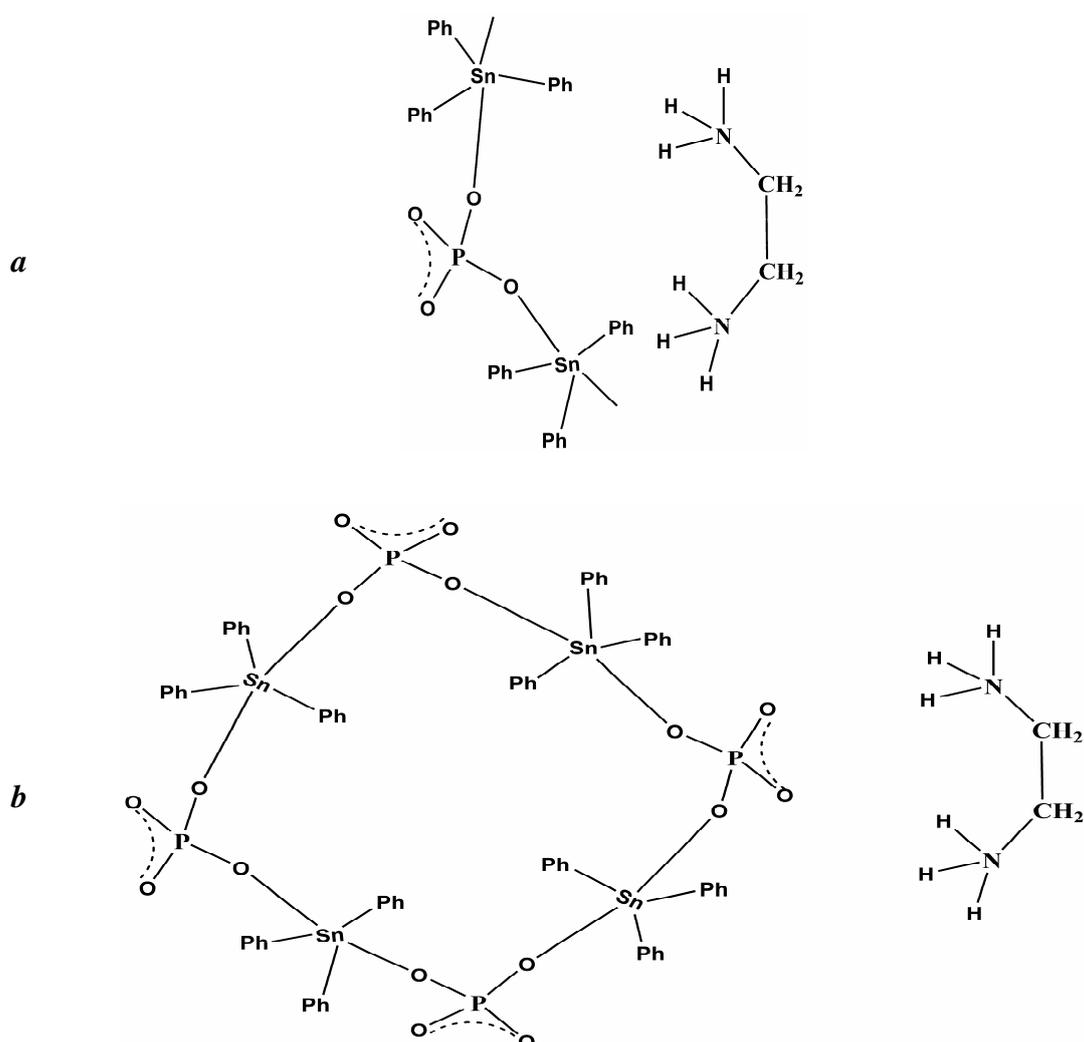
**C:**  $\delta = 1.23$ ,  $\text{QS} = 2.93$ ,  $\Gamma = 0.92$ ;

**D:**  $\delta = 1.30$ ,  $\text{QS} = 3.73$ ,  $\Gamma = 0.84$ .

### $\text{H}_2\text{enPO}_4\text{SnPh}_3$ (A)

The value of the quadrupole splitting of this compound ( $\text{QS} = 3.99 \text{ mm}\cdot\text{s}^{-1}$ ) indicates the presence of a *trans* coordinated residue according to Bancroft *et al.* [13] and Parish *et al.* [14]. While considering  $[\text{PO}_4(\text{SnPh}_3)]^{2-}$  complex-anion, an infinite chain (Figure 1a) or an oligomer (Figure 1b) as in [15] is suggested. The anion behaves as a bidentate ligand, the environment around the tin center being *trans* trigonal bipyramidal. We have arbitrarily reported the tetramer, but any oligomeric structure is a possible structure.

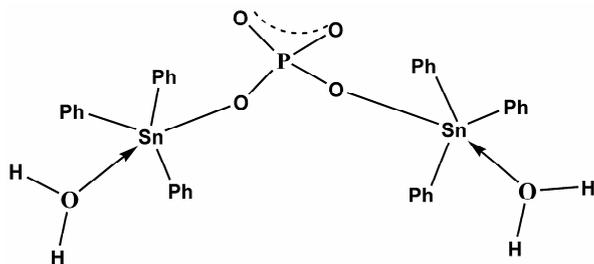
The cation  $\text{enH}_2^{2+}$ , when involved in  $\text{NH}\cdots\text{O}$  hydrogen bonds, as indicated by the strong and wide absorption centered at  $2800 \text{ cm}^{-1}$ , may lead to a supramolecular architecture.



**Figure 1.** Proposed structures for  $H_2enPO_4SnPh_3$  (**A**)  
*a* – as infinite chain structure; *b* – as oligomeric structure

### ***HenPO<sub>4</sub>(SnPh<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (B)***

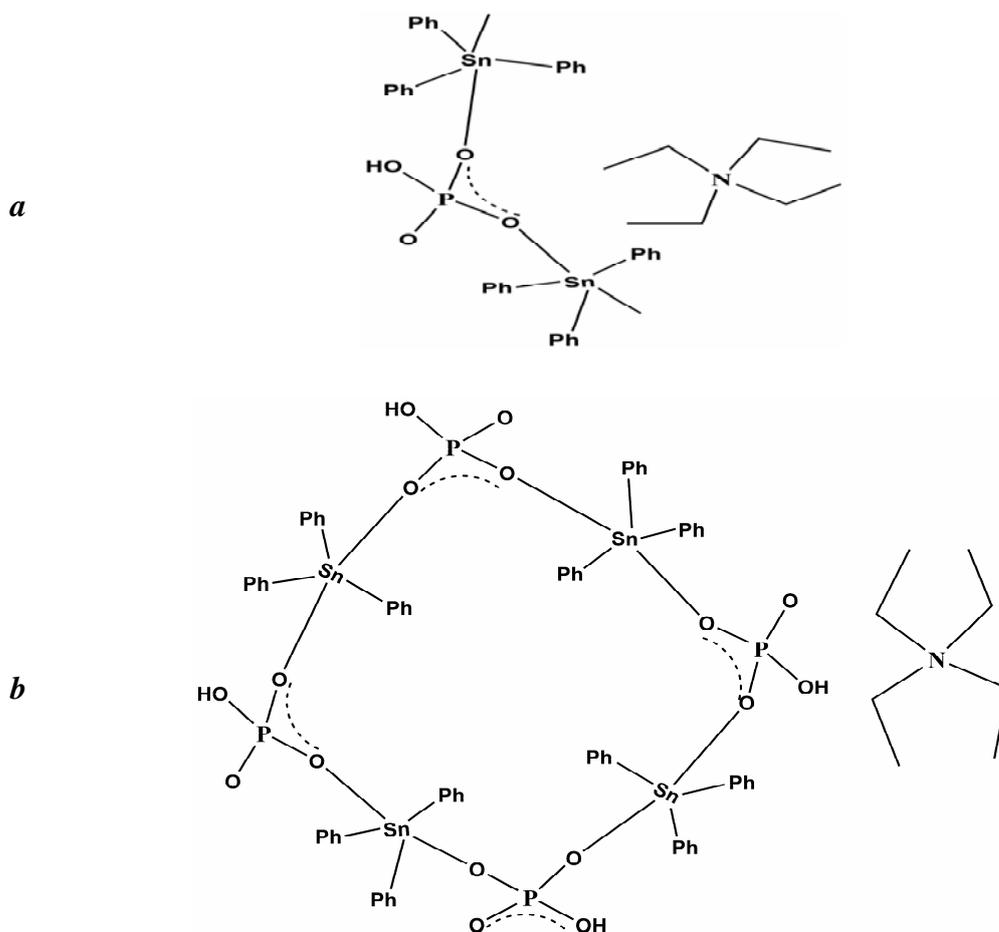
The  $SnPh_3 \cdot H_2O$  moieties have been already reported in  $SeO_4(SnPh_3 \cdot H_2O)SnPh_3 \cdot 0.5 H_2O$  [11]. In this derivative, the cation is monoprotonated. The value of the quadrupole splitting ( $QS = 2.96 \text{ mm} \cdot \text{s}^{-1}$ ) shows the presence of *trans* coordinated  $SnPh_3$  residues in this derivative [13, 14] with a  $SnC_3O_2$  framework in a *trans* trigonal bipyramidal arrangement; the water molecules are coordinated leading to two  $O-SnPh_3-H_2O$  frameworks. While considering the complex-anion  $[PO_4(SnPh_3 \cdot H_2O)_2]^-$ , the suggested structure reported on Figure 2 is discrete with the anion behaving as a bidentate ligand. The  $OH \cdots O$  and  $NH \cdots O$  hydrogen bonds are responsible of the wide absorption on the IR spectrum at  $2800 \text{ cm}^{-1}$ , when there are considered a supramolecular architecture may be obtained.



**Figure 2.** Proposed structure for  $\text{HenPO}_4(\text{SnPh}_3)_2 \cdot 2\text{H}_2\text{O}$  (**B**)

**$\text{Et}_4\text{NHPO}_4\text{SnPh}_3$  (**C**)**

The value of the quadrupole splitting ( $\text{QS} = 2.93 \text{ mm} \cdot \text{s}^{-1}$ ) shows the presence of a planar  $\text{SnPh}_3$  residue according to Bancroft *et al.* [13] and Parish *et al.* [14], and allows to suggest, while considering  $[\text{HPO}_4\text{SnPh}_3]^-$  complex-anion, an infinite chain (Figure 3a) or an oligomer (Figure 3b) as structures, the environment around the tin center being *trans* trigonal bipyramidal.

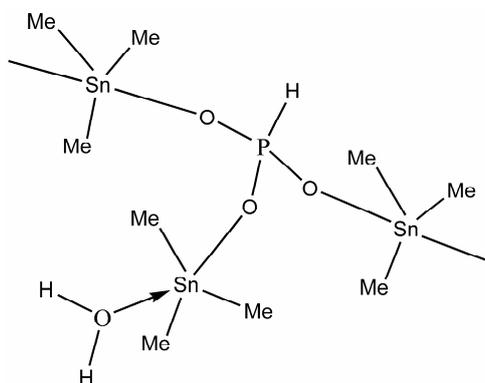


**Figure 3.** Proposed structures for  $\text{Et}_4\text{NHPO}_4\text{SnPh}_3$  (**C**)  
**a** – as infinite chain structure; **b** – as oligomeric structure

A supramolecular structure may be obtained when OH...O hydrogen bonds responsible of by the strong and wide absorption centered at  $2800\text{ cm}^{-1}$  on the IR spectrum are considered.

#### *HPO<sub>3</sub>(SnMe<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O (D)*

The presence of a medium band at  $2350\text{ cm}^{-1}$  in **(D)** is an indication of the presence of a PH group showing the non-oxidation of the hydrophosphonate ion into phosphate. The value of its quadruple splitting ( $QS = 3.73\text{ mm}\cdot\text{s}^{-1}$ ) and the absence of  $\nu_s(\text{SnC}_3)$  ( $A'_1$  vibration type) expected around  $515\text{ cm}^{-1}$  are clear indications of the presence of *trans* coordinated SnMe<sub>3</sub> residues [8, 16]. The suggested structure is an infinite chain with a tridentate HPO<sub>3</sub> anion and a pendant SnMe<sub>3</sub>·H<sub>2</sub>O moiety as in SeO<sub>3</sub>(SnMe<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O [17], the environment around the tin center being *trans* trigonal bipyramidal (Figure 4).



**Figure 4.** Proposed structure for *HPO<sub>3</sub>(SnMe<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O (D)*

## CONCLUSIONS

The studied phosphate, hydrogenophosphate and hydrophosphonate, hydrated and anhydrous derivatives have discrete, infinite chain or oligomeric structures, the anion behaving as a bi- or a tridentate ligand. Supramolecular architectures may be obtained when secondary interactions are considered. Ethylenediamine is present as mono-, or diprotonated. The oxidation of HPO<sub>3</sub>H<sub>2</sub> into PO<sub>4</sub>H, in most cases, is noteworthy.

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