

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

Waly Diallo, Libasse Diop*

*Université Cheikh Anta Diop, Faculté des Sciences et Techniques,
Département de Chimie, Laboratoire de Chimie Minérale et Analytique,
Dakar, Sénégal*

*Corresponding author: dlibasse@gmail.com

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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 SnR_3OH , ($\text{R} = \text{Me}, \text{Ph}$) [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, HPO_3H_2 and SnPh_3OH or HPO_3H_2 , SnR_3OH ($\text{R} = \text{Ph}, \text{Me}$) and Et_4NCN 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 HPO_3H_2 with a solution of SnPh_3OH in acetone in 1:1:2 ratio or with an ethanolic solution of SnPh_3OH in 1:1:1 ratio, compounds **A** and **B** respectively are obtained as white precipitates.

When HPO_3H_2 is allowed to react with SnPh_3OH and Et_4NCN in hot ethanol in a 1:2:2 ratio, a white precipitate (**C**) is obtained.

A mixture of HPO_3H_2 , SnMe_3OH and Et_4NCN 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
A	$\text{H}_2\text{enPO}_4\text{SnPh}_3$	47.37	47.47	4.97	4.90	5.52	5.47
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
C	$\text{Et}_4\text{NHPO}_4\text{SnPh}_3$	54.19	54.36	6.30	6.37	2.43	2.39
D	$\text{HPO}_3(\text{SnMe}_3)_2 \cdot \text{H}_2\text{O}$	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 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 cm^{-1} [IR abbreviations: (br) broad, (vs) very strong, (s) strong, (m) medium, (sh) shoulder, (w) weak, (vw) very weak]. ^{119}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 PO_4H_3 obtained in situ by the oxidation of HPO_3H_2 reacts with two molecules of SnPh_3OH 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 enH^+ obtained by a protonation of ethylenediamine by the single remaining proton.

The second molecule of PO_4H_3 obtained as above reacts with one molecule of SnPh_3OH by condensation leading to $\text{enH}_2\text{PO}_4[\text{SnPh}_3(\text{H}_2\text{O})]$; this derivative contains enH_2^+ obtained by a double protonation of ethylenediamine by the two remaining protons of the starting PO_4H_3 .

The derivatives **A** and **C** are similar while considering the reaction involved because of containing only one SnPh_3 residue. In the case of Et_4NOH only one of the two remaining protons reacts with 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 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 enH_2^{2+} , when involved in $\text{NH}\cdots\text{O}$ hydrogen bonds, as indicated by the strong and wide absorption centered at 2800 cm^{-1} , may lead to a supramolecular architecture.

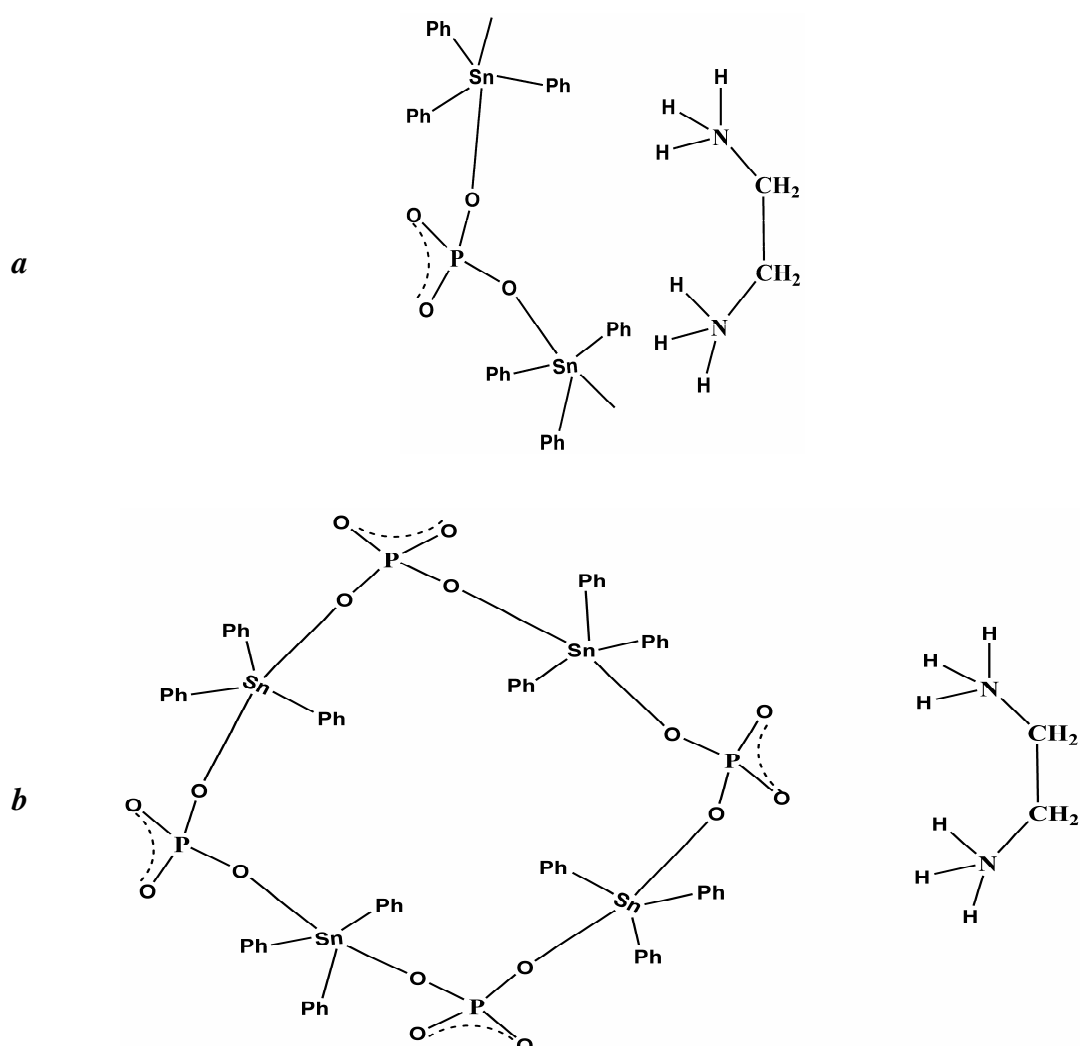


Figure 1. Proposed structures for $H_2enPO_4SnPh_3$ (A)
a – as infinite chain structure; **b** – as oligomeric structure

$HenPO_4(SnPh_3)_2 \cdot 2H_2O$ (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 cm^{-1} , when there are considered a supramolecular architecture may be obtained.

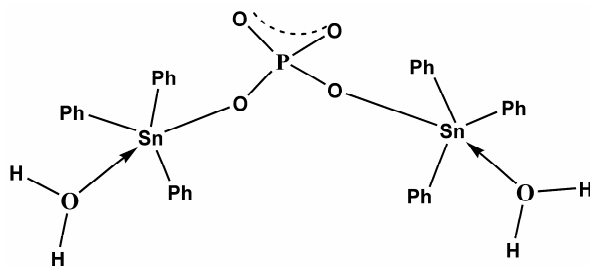


Figure 2. Proposed structure for $\text{HenPO}_4(\text{SnPh}_3)_2 \cdot 2\text{H}_2\text{O}$ (**B**)

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

The value of the quadrupole splitting ($\text{QS} = 2.93 \text{ mm} \cdot \text{s}^{-1}$) shows the presence of a planar 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.

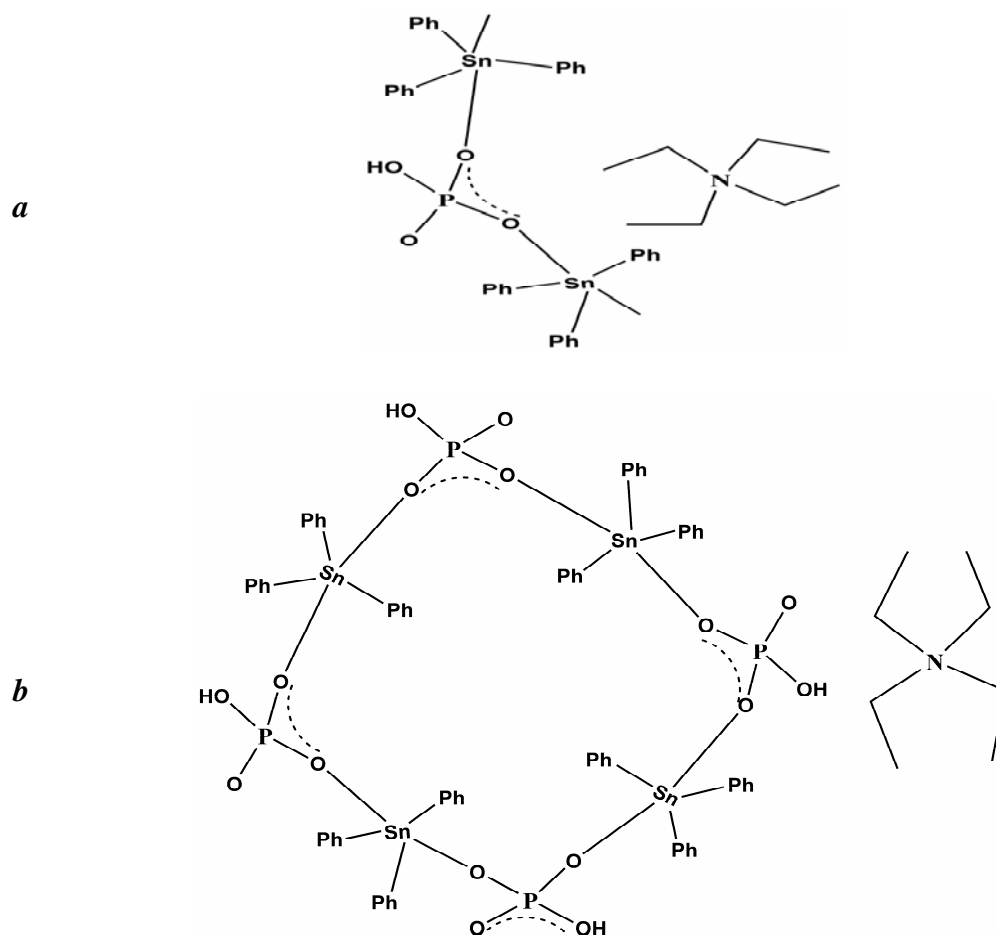


Figure 3. Proposed structures for $\text{Et}_4\text{NHPO}_4\text{SnPh}_3$ (**C**)
a – as infinite chain structure; **b** – as oligomeric structure

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

HPO₃(SnMe₃)₂·H₂O (D)

The presence of a medium band at 2350 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 cm^{-1} are clear indications of the presence of *trans* coordinated SnMe₃ residues [8, 16]. The suggested structure is an infinite chain with a tridentate HPO₃ anion and a pendant SnMe₃·H₂O moiety as in SeO₃(SnMe₃)₂·H₂O [17], the environment around the tin center being *trans* trigonal bipyramidal (Figure 4).

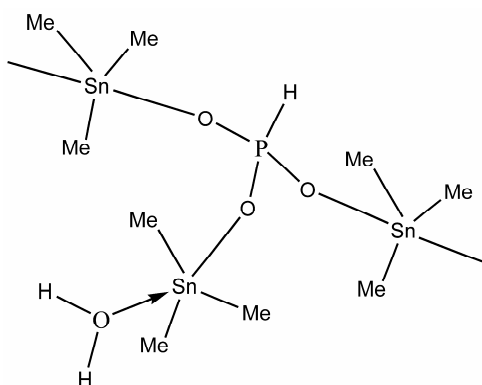


Figure 4. Proposed structure for *HPO₃(SnMe₃)₂·H₂O (D)*

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 HPO₃H₂ into PO₄H, in most cases, is noteworthy.

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