

NEW PHOSPHINATO ORGANO- AND HALOTIN(IV) DERIVATIVES, ADDUCTS AND COMPLEXES: SYNTHESIS AND SPECTROSCOPIC STUDY

SEYDOU BASSENE¹, MOUHAMADOU SEMBENE BOYE^{*2}, MAMADOU SIDIBE¹, LIBASSE DIOP¹

¹*Department of Chemistry, Faculty of Science and Technology, Laboratory of Mineral and Analytical Chemistry, University Cheikh Anta DIOP, Dakar, Senegal*

²*Department of Physics Chemistry, Faculty of Sciences and Technology of Education and Training, University Cheikh Anta Diop, Boulevard Habib Bourguiba BP 5036 Fann-Dakar, Senegal*

Abstract: Five new phosphinato derivatives, adducts and complexes have been synthesized and characterized by infrared and Mössbauer spectroscopies. Based on their spectroscopic data discrete or infinite chain structures are proposed, the phosphinate ion behaving as a bicoordinating bridging or a monocoordinating ligand, the environments around the tin (IV) centers being octahedral or trigonal bipyramidal. In $\text{Me}_4\text{N}(\text{SnPh}_2)_2(\text{H}_2\text{PO}_2)_2\text{Cl}_3$ and $\text{Cl}_2\text{Sn}(\text{H}_2\text{PO}_2)_2\text{NMe}_4\text{H}_2\text{PO}_2$, the cation is involved in electrostatic interactions with the anions.

Keywords: bridging anion, discrete or two metallic components structures, electrostatic interactions, octahedral or trigonal bipyramidal environments

1. INTRODUCTION

Many research groups have been involved in the search of new molecules belonging to organo- and halotin (IV) families because of the various applications found for several molecules of these families [1–6]. In the continuation of our work in this field since many years, we have synthesized new phosphinato compounds from $\text{Me}_4\text{NH}_2\text{PO}_2\cdot\text{H}_2\text{O}$ and SnR_nCl_2 ($\text{R}=\text{Ph}$, Me ; $n=0, 2$) or SnPh_3Cl ; these complexes were characterized by Infrared and Mössbauer spectroscopies and structures proposed from spectroscopic data.

2. EXPERIMENTAL SETUP

2.1. Salt synthesis

$\text{Me}_4\text{NO}_2\text{PH}_2\cdot\text{H}_2\text{O}$ (L) has been obtained as a powder on neutralizing phosphinic acid $\text{H}_2\text{PO}_2\text{H}$ with Me_4NOH (10 % water solution) in 1:1 ratio and allowing the water to evaporate at 60 °C.

2.2. Complexes synthesis

Compounds **A**, **B**, **C**, **D** and **E** were obtained as white precipitates, on allowing L to react in ethanol with, SnPh_2Cl_2 in 1:1 ratio (**A**), SnCl_2 in 1:1 ratio (**B**), SnPh_3Cl in 2:1 ratio (**C**), SnMe_2Cl_2 in 1:1 ratio (**D**) and SnPh_2Cl_2 in 1:1 ratio (**E**). All mixtures except the one leading to **E** were stirred around two hours and filtered.

*Corresponding author, email: mouhasboye@hotmail.com

N.B.: By reacting in ethanol L and SnPh_2Cl_2 in 1:1 ratio, two different compounds A and E are obtained. This formulae difference comes from the fact that the mixture leading to compound A was stirred while the one giving E wasn't stirred.

The analytical data have allowed to suggest the following formulae (Table 1).

Table 1. The analytical data of the ligand L and compounds A-E.

Compound	Chemical formula	Chemical composition [% mass]					
		C		H		N	
		Calc.	Found	Calc.	Found	Calc.	Found
L	$\text{Me}_4\text{NO}_2\text{PH}_2\text{H}_2\text{O}$	30.57	30.51	10.19	10.26	8.92	8.90
A	$\text{Me}_4\text{N}(\text{SnPh}_2)_2(\text{H}_2\text{PO}_2)_2\text{Cl}_3$	39.25	39.51	4.20	4.36	1.63	1.71
B	$\text{Cl}_2\text{Sn}(\text{H}_2\text{PO}_2)_2\text{NMe}_4\text{H}_2\text{PO}_2$	10.46	10.59	3.92	3.81	3.05	3.01
C	$\text{Me}_4\text{NH}_2\text{PO}_2 \cdot 2\text{SnPh}_3\text{Cl}$	52.75	52.47	4.83	4.96	1.54	1.53
D	$\text{Me}_2\text{Sn}(\text{H}_2\text{PO}_2)_2$	8.62	8.67	3.62	3.55	–	–
E	$\text{Ph}_2\text{Sn}(\text{H}_2\text{PO}_2)_2$	35.77	35.56	3.50	3.67	–	–

Elemental analyses were obtained in the Laboratory of microanalyses from University of Padua–Italy or in the Service Central d'Analyses du CNRS, Vernaison–France. The infrared spectra were recorded at the University of Padua–Italy using a Perkin-Elmer 580 spectrophotometer, as a Nujol mull using CsI optical windows, while the Mössbauer spectrum was recorded at the Université Catholique de Louvain La Neuve–Belgique at 80K. Infrared abbreviations: vs=very strong; s=strong; w=weak; m=medium; sh=shoulder; v=stretching vibration; ν =antisymmetric stretching vibration; δ =deformation vibration. Mössbauer abbreviations: QS=quadrupole splitting; IS=isomer shift; Γ =full width at half-height.

3. RESULTS AND DISCUSSION

In Table 2, the main infrared data of the five compounds are reported.

Table 2. Main infrared bands in cm^{-1} of compounds A-E.

Compound	νPH_2	νPO_2	νPO_2	δPH_2	ν_{asSnC_n} $n=2, 3$	νSnCl
A	2395 (m)	1155 (sh) 1145 (vs) 1060 (s)	495 (m)	950 (m)	290 (m)	260 (m)
B	2390 (m)	1120 (vs) 1070 (vs)	460 (w)	952 (m)	–	285 (w)
C	2392 (m)	1150 (vs) 1065 (s),	460 (s) 450 (sh)	951 (m)	275 (s)	255 (m)
D	2387 (m)	1150 (s) 1135 (sh) 1065 (sh) 1050 (s)	450 (m)	952 (m)	585 (m)	–
E	2390 (m)	1150 (vs) 1085 (s) 1060 (sh)	490 (sh)	950 (m)	300 (m)	–

Mössbauer data ($\text{mm}\cdot\text{s}^{-1}$) of compound A:

$\text{QS}_1=3.99$; $\text{IS}_1=1.16$; $\Gamma=0.86$; 50% and $\text{QS}_2=3.00$; $\text{IS}_2=1.27$; $\Gamma=0.86$; 50%.

For A, the Mössbauer parameters indicate the presence of two tin (IV) centers in octahedral and trigonal bipyramidal environments in 1:1 ratio. This allows to suggest the presence of an infinite chain of $\text{SnPh}_2(\text{H}_2\text{PO}_2)_2$ and discrete ionic $\text{Me}_4\text{NSnPh}_2\text{Cl}_3$. The proposed structure is an infinite chain of $\text{SnPh}_2(\text{H}_2\text{PO}_2)_2$ in which are inserted $\text{Me}_4\text{NSnPh}_2\text{Cl}_3$ and is reported on Figure 1.

The structure of $\text{SnPh}_2(\text{Ph}_2\text{PO}_2)_2$ have already been determined by Shihada and Weller [7] and consists of an infinite chain. In the chain the $[\text{Ph}_2\text{PO}_2]^-$ anion is bridging and the environment around the tin atom is an octahedron (the structures of $\text{SnPh}_2(\text{Ph}_2\text{PO}_2)_2$ and $\text{SnPh}_2(\text{H}_2\text{PO}_2)_2$ are very close). So, the studied compound can be considered as a 1:1 adduct between $\text{SnPh}_2(\text{H}_2\text{PO}_2)_2$ and $\text{Me}_4\text{NSnPh}_2\text{Cl}_3$. In the structure, the tetramethylammonium cation is involved in electrostatic interactions with $[\text{SnPh}_2\text{Cl}_3]^-$.

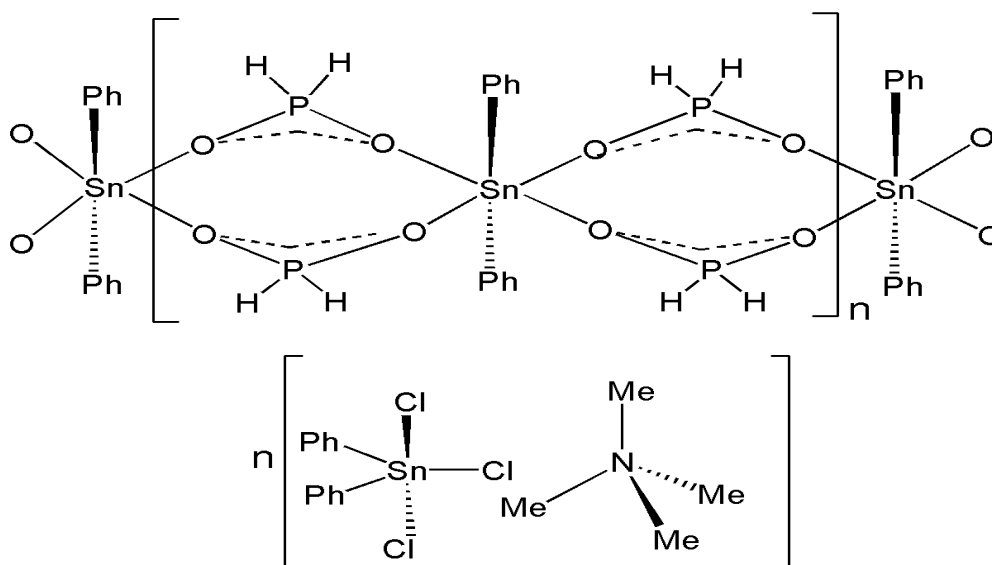


Fig. 1. Proposed structure for **A**.

For **B**: it seems worthy to outline the fact that the Sn (II) has oxidized into Sn (IV). The proposed structure is a discrete one with a trigonal bipyramidal environment around the tin (IV) center, the chloro atoms being in apical positions. Between the cation and the complex-anion the interactions are of electrostatic types (Figure 2).

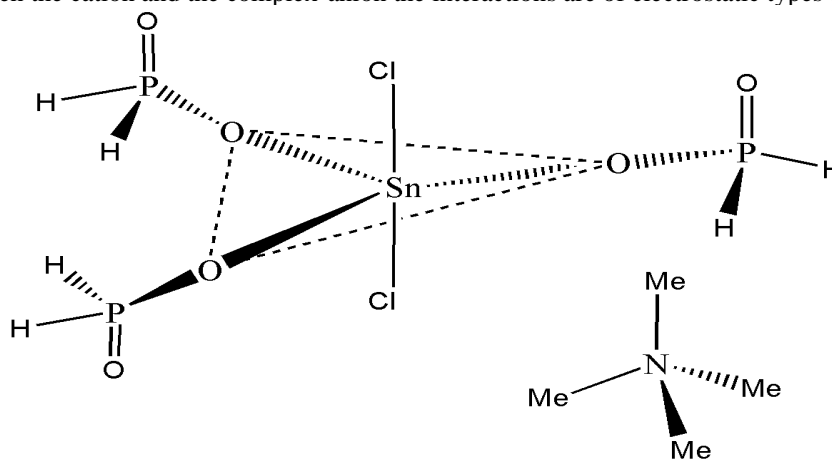
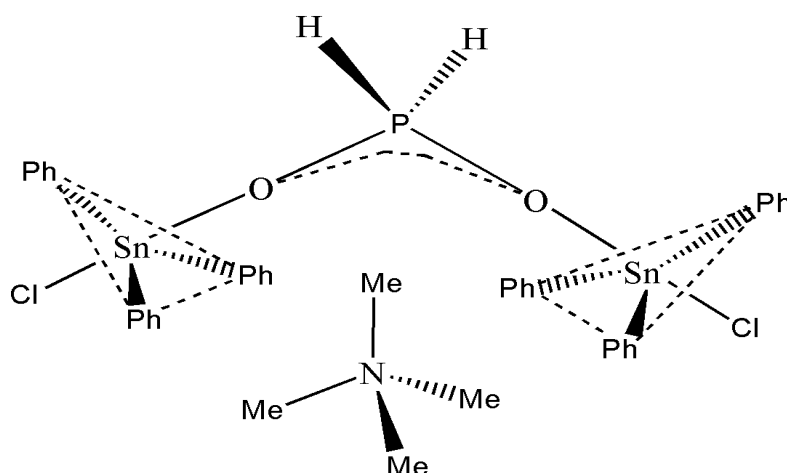
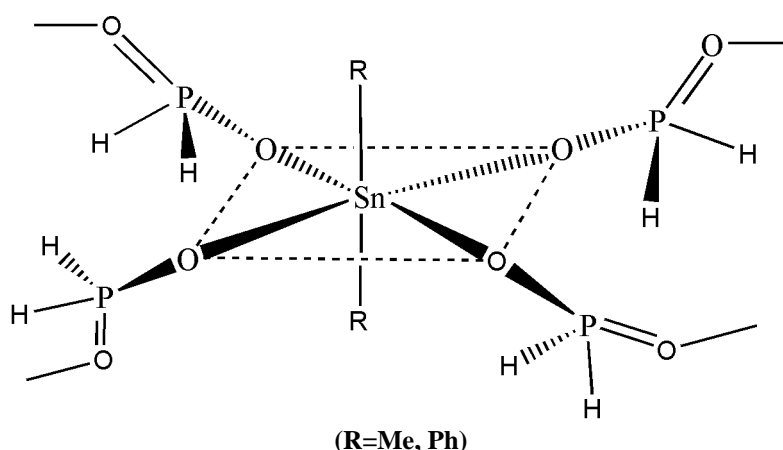


Fig. 2. Proposed structure for **B**.

For **C**: this type of adducts involving a monocoordinated SnPh_3Cl has already been reported for $(\text{R}_4\text{N})_2\text{AO}_4[\text{SnPh}_3\text{X}]_m$ by Diop et al. [8], the proposed structures being discrete, the environment at tin atom being trigonal bipyramidal (Figure 3), the anion behaving as a bridging bidentate ligand. In the structure the tetramethylammonium cation is involved in electrostatic interactions with the anion.

Fig. 3. Proposed structure for **C**.

For **D** and **E**, The structures are similar to the one reported by Shihada and Weller for $\text{SnPh}_2(\text{Ph}_2\text{PO}_2)_2$ [7] and consist of an infinite chain with double bridging $[\text{Ph}_2\text{PO}_2]^-$ and an octahedral environment around the tin atom (Figure 4).

Fig. 4. Proposed structure for **D** and **E**.

4. CONCLUSIONS

The studied compounds have a two metallic components, discrete or infinite chain structures, the phosphinate anion behaving as a bicoordinating bridging or a monocoordinating ligand, the environment around the tin (IV) centers being trigonal bipyramidal or octahedral. The first compound can be considered as an adduct of the last compound and $\text{Me}_4\text{NSnPh}_2\text{Cl}_3$.

ACKNOWLEDGEMENTS

We thank Professor M. Vidali (University of Padua, Italy) and Professor B. Mahieu (University Catholique de Louvain, Belgique) for equipment support.

REFERENCES

[1] Jastrzebski, J.T.H., van Koten, G., Knaap, C.T., Schreurs, A.M.M., Kroon, J., Spek, A.L., Organotin (IV) compounds derived from 2- $\text{Me}_2\text{NC}_6\text{H}_4\text{CH}_2\text{Li}$ and its chiral $\alpha\text{-Me}_3\text{Si}$ derivative. X-ray structure of

- pentacoordinate $[[2-(\text{dimethylamino})\text{phenyl}](\text{trimethylsilyl})\text{methyl-C,N}]\text{methylphenyltin bromide}$ having a chiral Sn center, *Organometallics*, vol. 5, no. 8, 1986, p. 1551-1558.
- [2] Boye, M.S., Diasse-Sarr, A., Grosjean, A., Guionneau, P., Poly[diaqua(μ_4 -carboxylatomethylphosphonato)(μ_4 -carboxymethylphosphonato)pentadecamethylpentatin (IV)], *Acta Crystallographica, Section E: Crystallographic Communications*, vol. 69, no. 2, 2013, p. m110–m111.
- [3] Sougoule, A.S., Xiao, X., Balde, C.A., Sakho, A.M., Zhu, D., An organotin (IV) carboxylate based on amide carboxylic acid: synthesis, crystal structure, and characterizations, *heteroatom chemistry*, vol. 26, no. 4, 2015, p. 270-276.
- [4] Shankar, R., Singla, N., Mendiratta, S., Kociok-Köhn, G., Molloy, K.C., Shestakova, P., Synthesis, characterization, and hydrolytic behavior of diorganotin (IV) coordination polymers with layered structural motifs, *European Journal of Inorganic Chemistry*, no. 30, 2015, p. 5118-5123.
- [5] Sarr, M., Diasse-Sarr, A., Diop, L., New tetranuclear and mononuclear oxalato organotin (IV) complexes with monocyclohexylammonium as adverse cation: Synthesis and infrared study, *Journal of Engineering Studies and Research*, vol. 23, no. 4, 2017, p. 25-31.
- [6] Yusof, E.N.M., Latif, M.A.M., Tahir, M.I.M., Sakoff, J.A., Simone, M.I., Page, A.J., Veerakumarasivam, A., Tiekink, E.R.T., Ravoo, T.B.S.A., o-Vanillin derived schiff bases and their organotin (IV) compounds: synthesis, structural characterisation, in-silico studies and cytotoxicity, *International Journal of Molecular Sciences*, vol. 20, no. 4, 2019, p. 854-892.
- [7] Shihada, A.F., Weller, F., Crystal structures of $[\text{Bu}_2\text{Sn}(\text{O}_2\text{PPh}_2)_2]$, $[\text{Ph}_2\text{Sn}(\text{O}_2\text{PPh}_2)_2]$, and $[\text{PhClSn}(\text{O}_2\text{PPh}_2)\text{OMe}]_2$. Raman spectra of $[\text{Ph}_2\text{Sn}(\text{O}_2\text{PPh}_2)_2]$ and $[\text{PhClSn}(\text{O}_2\text{PPh}_2)\text{OMe}]_2$, *Journal of Inorganic and General Chemistry*, vol. 632, no. 14, 2006, p. 2238-2243.
- [8] Diop, C.A.K., Qamar, H., Cisse, I., Diop, L., Russo, U., $(\text{R}_4\text{N})_2\text{AO}_4[\text{SnPh}_3\text{X}]_m$ (R = Me, Et; A = Mo, S, Cr, C₂; m=2, 3; X=Cl, Br), Synthesis and spectroscopic studies, *Main Group Metal Chemistry*, vol. 22, no. 1, 1999, p. 41-44.