

NEW HALO- AND ORGANOTIN (IV) PHENYLARSENIATO ADDUCTS AND DERIVATIVES

Bocar Traore, Libasse Diop*, Mamadou Sidibe

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

*Corresponding author: dlibasse@gmail.com

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Abstract: Four new phenylarseniato adducts and organotin derivatives have been synthesized and studied by infrared. The suggested structures are polymeric, $(\text{SnX}_4; \text{X} = \text{Cl}, \text{Br})$ and SnPh_3Cl while being discrete for $\text{SnPh}_2\text{Cl}(\text{PhAsO}_3\text{H})_2\text{isoBu}_2\text{NH}_2$. When OH- - - Cl, NH - - - O or NH- - -Cl hydrogen bonds are involved, supramolecular architectures are obtained.

Keywords: *hydrogenphenylarseniato, phenylarseniato, tin centre, polymeric and discrete structures, supramolecular architectures*

INTRODUCTION

Organotin (IV) compounds are known for various applications (industry, medicine, agriculture) [1] and explain the focus of several research groups in this field [2-9]. Our group have yet published several papers dealing with [10-17] and initiate her the study of the interactions between $\text{Cy}_2\text{NH}_2\text{PhAsO}_3\text{H}$ and SnX_4 ($\text{X} = \text{Cl}, \text{Br}$), SnPh_3Cl or SnR_2Cl_2 which have yielded four new phenylarseniato and hydrogen phenylarseniato adducts, infrared study of which have been carried out then structures suggested on the basis of infrared data.

MATERIALS AND METHODS

$\text{Cy}_2\text{NH}_2\text{PhAsO}_3\text{H} \cdot 3/2\text{H}_2\text{O}$ has been obtained as a powder on mixing PhAsO_3H_2 with Cy_2NH in water in 1/1 ratio and allowing water to evaporate at 60°C . When ethanolic solutions of $\text{Cy}_2\text{NH}_2\text{PhAsO}_3\text{H} \cdot 3/2\text{H}_2\text{O}$ are mixed with benzene solutions of SnCl_4 or SnBr_4 , or ethanolic solutions of SnPh_3Cl or SnPh_2Cl_2 (in specific ratios) precipitation occurs. The precipitates were stirred around two hours and filtered. The analytical data % calculated and % found has allowed suggesting the following formulae (Table 1).

Table 1. Results of the elemental analyses

Compound	Chemical formula	Elemental analysis (%)					
		C		H		N	
		calc.	found	calc.	found	calc.	found
A	$2[(\text{Cy}_2\text{NH}_2)_2\text{PhAsO}_3] \cdot \text{SnCl}_4 \cdot \text{H}_2\text{O}_{(1/2)}$	51.18	50.29	7.67	6.69	3.98	3.39
B	$2[(\text{Cy}_2\text{NH}_2)_2\text{PhAsO}_3] \cdot \text{SnBr}_4 \cdot \text{H}_2\text{O}_{(1/2)}$	45.98	44.92	6.76	7.02	3.57	3.52
C	$\text{PhAsO}_3\text{HSnPh}_3 \cdot \text{SnPh}_3\text{Cl} \cdot (\text{Cy}_2\text{NH}_2\text{Cl})_{1/4} \cdot 3\text{H}_2\text{O}_{(1/3)}$	51.76	51.34	4.50	5.36	0.33	0.22
D	$[\text{SnPh}_2\text{Cl}(\text{PhAsO}_3\text{H})_2] \cdot \text{isoBu}_2\text{NH}_{2(1/1)}$	44.83	43.03	4.90	4.85	1.63	1.14

The elemental analyses have been performed by the Laboratory of Microanalyses-University of Montpellier II-France. The infrared spectra have been recorded at the University of Padova, Italy, by means of a Perkin Elmer 180 spectrometer using CsI , the sample being as Nujol mulls. Infrared data are given in cm^{-1} (IR abbreviations: (vs) very strong, (s) strong, (m) medium, (w) weak, (vw) very weak, (br) broad). All the chemicals were purchased from Aldrich-Germany and used as such.

RESULTS AND DISCUSSION

Let us consider the IR data of the studied adducts and derivatives:

- (A): $\nu_s \text{OH}_2 = 3400$ (s); $\nu_s \text{NH}_2 = 2400$ (s); $\nu_{\text{as}} \text{NH}_2 = 2380$ (m); $\nu_s \text{AsO}_3 = 850$ (vs); $\nu_s \text{AsO}_3 = 690$ (s); $\nu_{\text{as}} \text{SnCl}_4 = 300$ (vs)
- (B): $\nu \text{OH}_2 = 3400$ (s); $\nu_s \text{NH}_2 = 2395$ (m); $\nu_{\text{as}} \text{NH}_2 = 2385$ (m); $\nu_{\text{as}} \text{AsO}_3 = 900$ (vs), 850 (vs); $\nu_s \text{AsO}_3 = 750$ (m); $\nu_{\text{as}} \text{SnBr}_4 = 208$ (vs)
- (C): $\nu \text{OH}_2 = 3300$ (s); $\nu_s \text{NH}_2 = 2800$ (br); $\nu_{\text{as}} \text{NH}_2 = 2180$ (br); $\delta \text{NH}_2 = 1610$ (vs); $\nu_{\text{as}} \text{AsO}_3 = 890$ (vs); $\nu_s \text{AsO}_3 = 750$ (vs); $\nu_{\text{as}} \text{SnC}_3 = 270$ (vs)
- (D): $\nu_s \text{NH}_2 = 2800$ (br); $\nu_{\text{as}} \text{NH}_2 = 2300$ (m); $\nu_{\text{as}} \text{AsO}_3 = 895$ (vs); $\nu_s \text{AsO}_3 = 760$ (vs); $\nu_{\text{as}} \text{SnC}_2 = 270$ (vs)

The antisymmetric vibrations $\nu_{\text{as}} \text{SnCl}_4$ and $\nu_{\text{as}} \text{SnBr}_4$ appear as a very strong and symmetrical band consistent with a D_{4h} symmetry according to Group Theory and allow to consider a trans coordinated SnX_4 molecule. The IR data allow to suggest an infinite chain structure for $[\text{PhAsO}_3.\text{SnX}_4]^{2-}$, the anion behaving as a bidentate ligand, the environment of the tin centre being octahedral (Figure 1). When the cations are involved through NH- -O or NH- -X hydrogen bonds, supramolecular architectures are obtained.

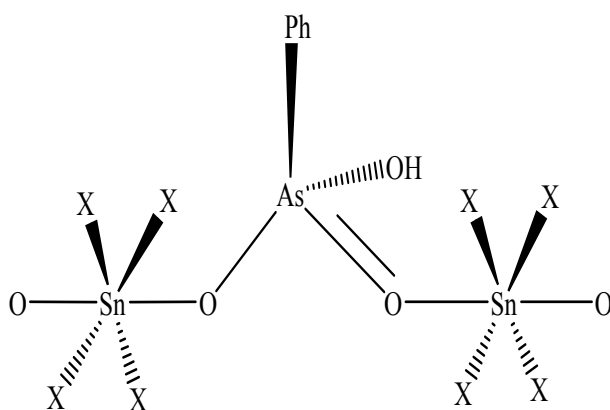


Figure 1. Proposed structure for $[\text{PhAsO}_3.\text{SnX}_4]^{2-}$

For $\text{PhAsO}_3\text{HSnPh}_3.\text{SnPh}_3\text{Cl}(\text{Cy}_2\text{NH}_2\text{Cl})_{1/4}.3\text{H}_2\text{O}$ the suggested structure is an infinite chain of $\text{HOAsO}_2\text{PhSnPh}_3$ to which SnPh_3Cl molecules coordinate through the OH group (the environments of the tin centres are trigonal bipyramidal) (Figure 2). While considering $[\text{SnPh}_2\text{Cl}(\text{PhAsO}_3\text{H})_2]^-$ a discrete structure is suggested, the environment around the tin centre being trigonal bipyramidal, the anion behaving as a monodentate ligand (because of steric effects, PhAsO_3H are on equatorial positions, the phenyl being on apical ones) (Figure 3).

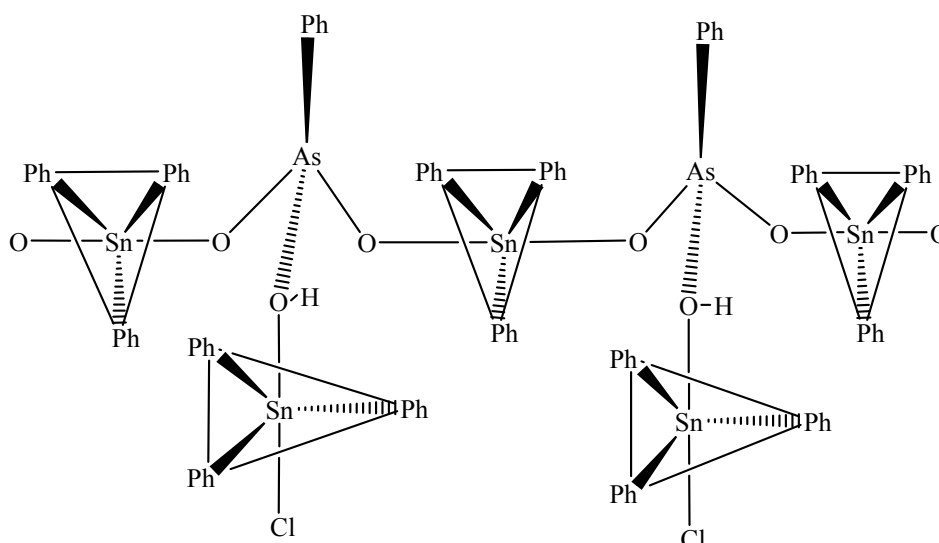


Figure 2. Proposed structure for $\text{PhAsO}_3\text{HSnPh}_3'\text{SnPh}_3\text{Cl}(\text{Cy}_2\text{NH}_2\text{Cl})_{1/4}3\text{H}_2\text{O}$

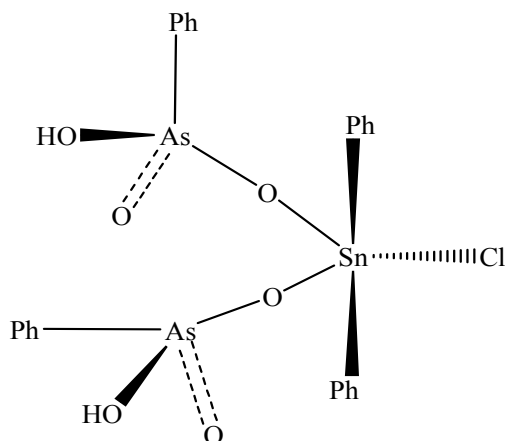


Figure 3. Proposed structure for $[\text{SnPh}_2\text{Cl}(\text{PhAsO}_3\text{H})_2]^-$

When hydroxyl group and cations are involved in hydrogen bond, supramolecular architectures are obtained.

CONCLUSIONS

Infinite chain structures are obtained (three), a discrete one the anion behaving as a bidentate ligand or a monodentate one. When hydrogen bonds are involved supramolecular architectures are obtained.

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