

## NEW $[\text{SnR}_2(\text{C}_2\text{O}_4)_2]^{2-}$ (R = Ph, Bu) MOIETY CONTAINING ADDUCTS AND COMPLEXES: SYNTHESIS, INFRARED AND MOSSBAUER STUDIES

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Received: March, 02, 2015

Accepted: March, 30, 2015

**Abstract:** New oxalato and hydrogenoxalato organotin (IV) derivatives containing mono- and bichelating oxalates or a monochelating hydrogenoxalate, have been synthesized and characterized by elemental analyses, infrared and Mossbauer spectroscopy. The suggested structures are discrete, the environments around the tin (IV) atoms being *trans* octahedral, seven coordinated or tetrahedral. The cations when present are involved in NH...O bonds. A 1 D supramolecular architecture is suggested for  $\text{SnPh}_2(\text{HC}_2\text{O}_4)_2 \cdot 1/2 \text{C}_6\text{H}_6$ . The  $\text{C}_6\text{H}_6$  molecules obtained *in situ* molecules are lattice.  $\text{SnPh}_3\text{OH}$  is involved in hydrogen bonding.

**Keywords:** *1 D supramolecular architecture, discrete structures, hydrogen bonds, infrared, lattice benzene molecules, Mossbauer, seven coordinated, trans octahedral or tetrahedral environments*

## INTRODUCTION

Organotin (IV) family molecules have been subject of investigation by many research groups because the several applications of some of them in various fields including pesticides, fungicides, but also for their potential antitumor activity [1 – 11]. In the framework of our research work attempting to get new organotin compounds, we report here the synthesis of new compounds containing the complex-anions  $[\text{C}_2\text{O}_4(\text{SnPh}_2\text{C}_2\text{O}_4)_2]^{2-}$  or  $[\text{SnBu}_2(\text{C}_2\text{O}_4)_2]^{2-}$  stabilized by dipropylammonium, diisobutyl ammonium and the neutral derivative  $[(\text{HC}_2\text{O}_4)_2\text{SnPh}_2]$ , their infrared and Mossbauer studies have been carried out, then discrete or polymeric structures suggested on the basis of spectroscopic data.

## MATERIALS AND METHODS

$\text{Pr}_2\text{NH}_2\text{HC}_2\text{O}_4$ ,  $(i\text{-Bu}_2\text{NH}_2)_2\text{C}_2\text{O}_4$ ,  $(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  have been obtained as a powder or a precipitate by totally or semi neutralizing  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  by  $\text{Pr}_2\text{NH}$ ,  $i\text{-Bu}_2\text{NH}$  or  $\text{Me}_4\text{NOH}$  in water and allowing the water to evaporate at the oven at  $60^\circ\text{C}$ . On mixing  $\text{Pr}_2\text{NH}_2\text{HC}_2\text{O}_4$  with  $\text{SnPh}_3\text{OH}$ , in 1:2 ratio,  $(i\text{-Bu}_2\text{NH}_2)_2\text{C}_2\text{O}_4$ ,  $(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{SnBu}_2\text{Cl}_2$  in 1/1/2 ratio, as in ethanol, a white powder [**A** and **C**] is obtained after a slow solvent evaporation. When ethanolic solutions of  $\text{C}_2\text{O}_4(\text{SnPh}_3)_2$  - obtained as reported in [12] and  $\text{SO}_4(\text{SnPh}_3)_2 \cdot 2\text{H}_2\text{O}$  - obtained on mixing sulfuric acid with  $\text{SnPh}_3\text{OH}$  in ethanol - are mixed in 1:2 ratio a white precipitate [**B**] is obtained and stirred around two hours.  $\text{Cy}_2\text{NH}_2\text{C}_2\text{O}_4\text{SnPh}_3$  has been synthesized according to Ng and Rae [13]. A solution is obtained on mixing  $\text{Cy}_2\text{NH}_2\text{C}_2\text{O}_4\text{SnPh}_3$  with  $\text{SnBu}_3\text{Cl}$  in 1:3 ratio, in ethanol and a white powder collected after a slow solvent evaporation [**D**].

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

*Table 1. Analytical data of synthesized compounds*

Comp	Chemical composition [% mass]					
	C		H		N	
	Calc.	Found	Calc.	Found	Calc.	Found
[A]	58.19	58.29	5.28	5.22	1.56	1.60
[B]	44.28	44.17	3.01	3.02	-	-
[C]	41.74	41.61	7.95	7.89	3.74	3.64
[D]	47.75	48.27	5.37	5.60	1.27	1.25

[A]:  $(\text{Pr}_2\text{NH}_2)_2\text{C}_2\text{O}_4 \cdot 2\text{SnPh}_2\text{C}_2\text{O}_4 \cdot 2\text{SnPh}_3\text{OH} \cdot 3\text{C}_6\text{H}_6 \cdot 1/4\text{Pr}_2\text{NH}_2\text{OH}$

[B]:  $\text{SnPh}_2(\text{HC}_2\text{O}_4)_2 \cdot 1/2\text{C}_6\text{H}_6$

[C]:  $(i\text{-Bu}_2\text{NH}_2)_2(\text{C}_2\text{O}_4)_2\text{SnBu}_2 \cdot 2\text{SnBu}_2\text{Cl}_3\text{NMe}_4$

[D]:  $[\text{Cy}_2\text{NH}_2]_2\text{C}_2\text{O}_4 [\text{SnPh}_2(\text{C}_2\text{O}_4)]_3 \cdot 2\text{H}_2\text{O} \cdot [\text{SnBu}_2\text{C}_2\text{O}_4]_2$

The infrared spectra were recorded at the Instituto de Química, Universidad Nacional Autónoma de México (U.N.A.M.) - Mexico, by means of a BX FT-IR type spectrometer. The elemental analyses have been also performed at the Instituto de Química - U.N.A.M., Mexico. The Mössbauer spectra were obtained as described

previously [14].

Infrared data are given in  $\text{cm}^{-1}$  [IR abbreviations: (vs) very strong, (s) strong, (m) medium, (w) weak, (vw) very weak]. Mossbauer parameters are given in  $\text{mm}\cdot\text{s}^{-1}$  [Mossbauer abbreviations: Q.S. = quadrupole splitting, I.S. = isomer shift,  $\Gamma$  = full width at half-height, A = area].

All the chemicals were purchased from Aldrich Company (Germany) and used without any further purification.

## RESULTS AND DISCUSSION

Let us consider the main IR data of the studied adducts and complexes:

[A]:  $\nu_{\text{as}}(\text{CO}_2) = 1685$  vs,  $1601$  s;  $\nu_{\text{s}}(\text{CO}_2) = 1327$  s,  $1292$  s;  $\delta(\text{COO}^-) = 798$  s;

[B]:  $\nu(\text{C}=\text{O}) = 1679$  vs;  $\nu_{\text{as}}(\text{CO}_2) = 1617$  s,  $1572$  m;  $\nu_{\text{s}}(\text{CO}_2) = 1349$  s;  $\nu(\text{COH}) = 1308$  s;  $\delta(\text{COO}^-) = 797$  s;

[C]:  $\nu_{\text{as}}(\text{CO}_2) = 1637$  vs;  $\nu_{\text{s}}(\text{CO}_2) = 1229$  s,  $1292$  s;  $\delta(\text{COO}^-) = 790$  s;  $\nu_{\text{as}}(\text{SnBu}_2) = 686$  vs;  $\nu_{\text{s}}(\text{SnBu}_2) = 600$  vw;

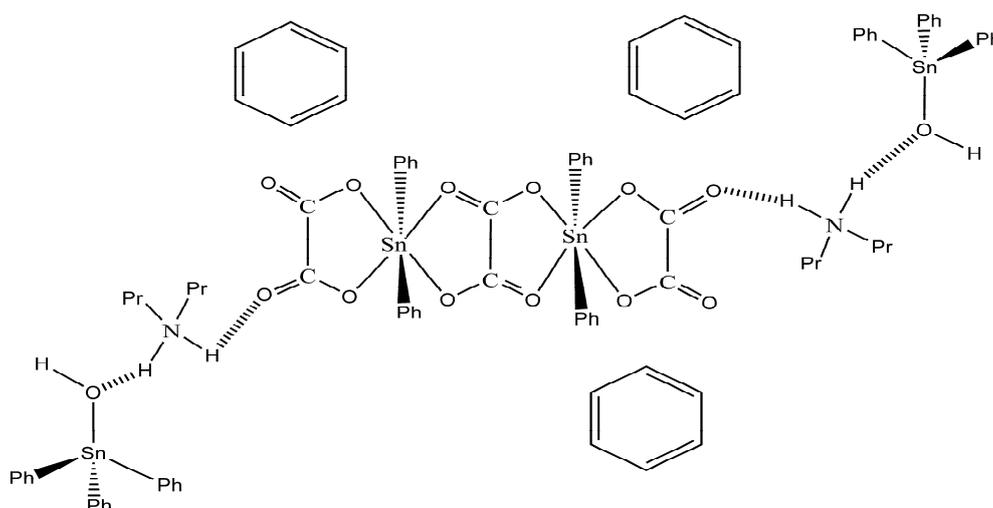
[D]:  $\nu_{\text{as}}(\text{COO}^-) = 1675$  s,  $1627$  vs;  $\nu_{\text{s}}(\text{COO}^-) = 1345$  s,  $1272$  vs;  $\delta(\text{COO}^-) = 785$  s;  $\nu_{\text{as}}(\text{SnBu}_2) = 695$  vs,  $\nu_{\text{s}}(\text{SnBu}_2) = 601$  vw.

and the Mossbauer data of:

[A]: Q.S<sub>1</sub> =  $4.37$   $\text{mm}\cdot\text{s}^{-1}$ , I.S<sub>1</sub> =  $1.40$   $\text{mm}\cdot\text{s}^{-1}$ ,  $\Gamma_1 = 0.91$   $\text{mm}\cdot\text{s}^{-1}$ , A<sub>1</sub> (%) = 50; Q.S<sub>2</sub> =  $2.60$   $\text{mm}\cdot\text{s}^{-1}$ , I.S<sub>2</sub> =  $1.35$   $\text{mm}\cdot\text{s}^{-1}$ ,  $\Gamma_2 = 1.06$   $\text{mm}\cdot\text{s}^{-1}$ , A (%) = 50;

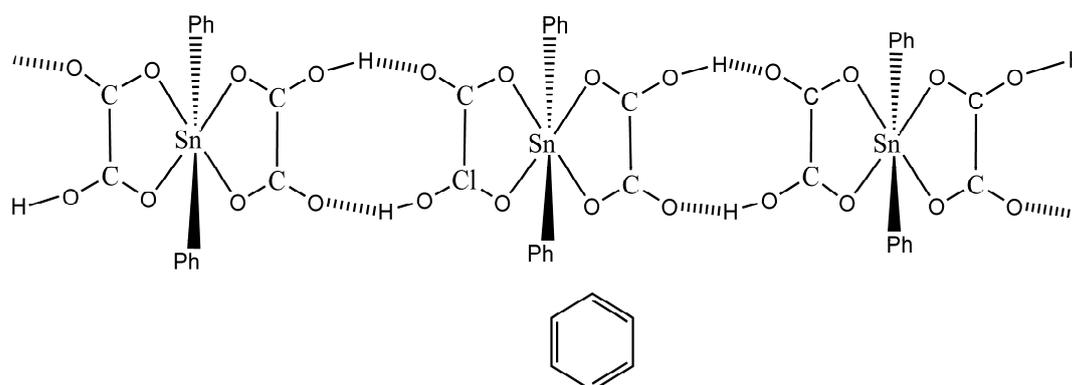
[B]: Q.S. =  $4.22$   $\text{mm}\cdot\text{s}^{-1}$ , I.S. =  $1.24$   $\text{mm}\cdot\text{s}^{-1}$ ,  $\Gamma_2 = 1.00$   $\text{mm}\cdot\text{s}^{-1}$ , A (%) = 100.

The structure of [A] contains the anion  $[\text{C}_2\text{O}_4(\text{SnPh}_2\text{C}_2\text{O}_4)_2]^{2-}$  yet reported by Gueye *et al.* [15] with  $\text{SnPh}_2$  residues *trans* octahedrally coordinated (Q.S. =  $4.37$   $\text{mm}\cdot\text{s}^{-1}$ ). To this complex- anions are linked two  $\text{Pr}_2\text{NH}_2\cdots\cdots\text{OHSnPh}_3$  hydrogen bonded adducts leading to the structure reported on Figure 1, the oxalate behaving as a mono- and bichelating ligand, the environment around the tin centres being octahedral while considering  $\text{SnPh}_2$  residues. The  $\text{SnPh}_3\text{OH}$  molecules are involved in hydrogen bonding with the cation, the environment of the tin centre in  $\text{SnPh}_3\text{OH}$  being tetrahedral (Q.S. =  $2.60$   $\text{mm}\cdot\text{s}^{-1}$ ). The OH groups when involved in extra hydrogen bonds lead to a supramolecular architecture. The benzene molecules are lattice. This number of 3 lattice benzene molecules has yet been reported [16].



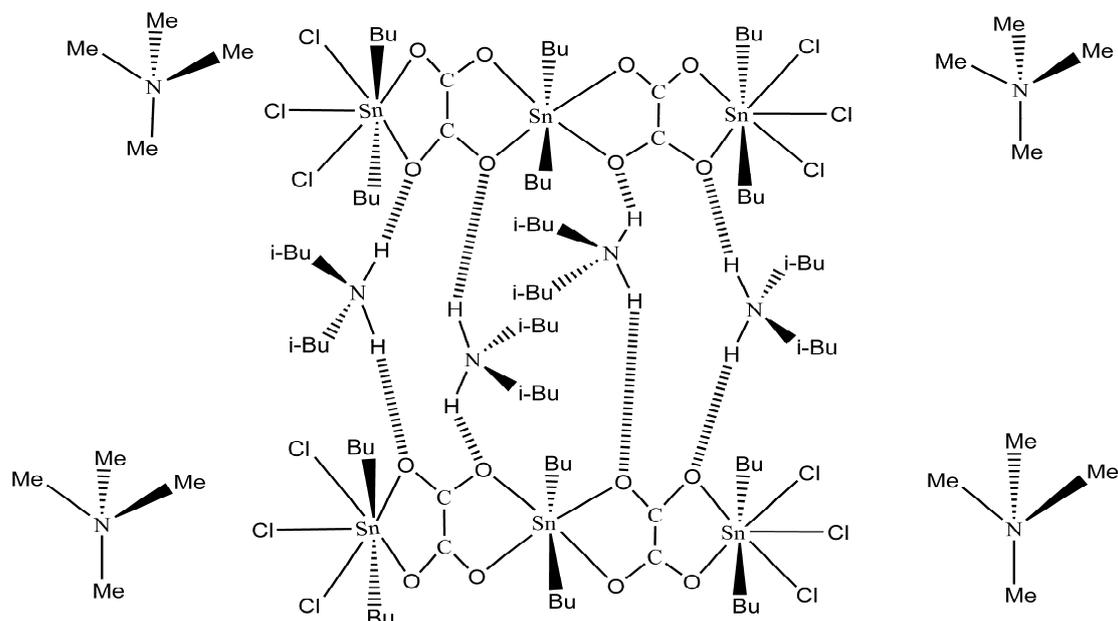
**Figure 1.** Proposed structure for compound **A**

The structure of [**B**] consists of a  $\text{SnPh}_2$  residue *trans* coordinated by  $\text{HC}_2\text{O}_4^-$  in an octahedral environment ( $Q.S. = 4.22 \text{ mm}\cdot\text{s}^{-1}$ ). These complex-anions can interact through acetic acid hydrogen bonding type leading to an infinite supramolecular chain, the benzene molecules being lattice (Figure 2).



**Figure 2.** Proposed structure for compound **B**

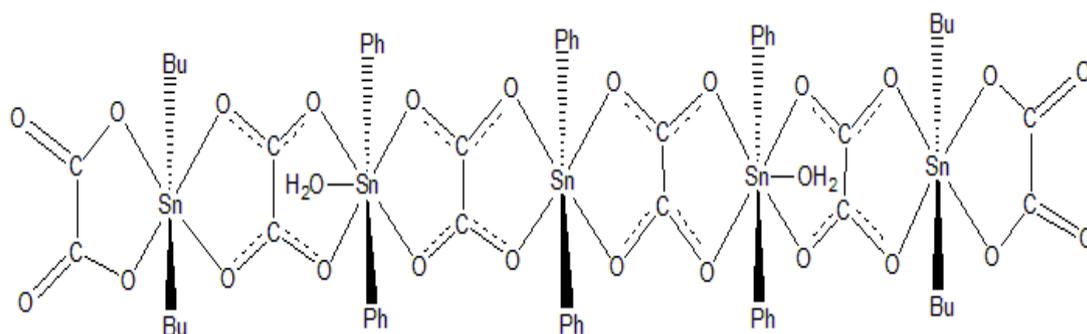
The basic structure of [**C**] consists of a  $[\text{SnBu}_2(\text{C}_2\text{O}_4)_2]^{2-}$  core coordinated to two  $\text{SnBu}_2\text{Cl}_3\text{NMe}_4$  adducts, the anion behaving as a bichelating ligand, the Sn centre being seven coordinated, the tetramethylammonium cation interacting electrostatically with the main component of the structure. The two main trimetallic components of the dimeric structure are parallel and are linked by the four cations through  $\text{O}\cdots\text{HN}$  hydrogen bonds (Figure 3).



**Figure 3.** Proposed structure for compound **C**

The infrared spectrum of the complex [**D**] exhibits the presence of a non-centrosymmetrical oxalate because of the presence of more than two bands in the stretching vibrations region. On the infrared spectrum of the compound, the wide absorption band centered in  $2900\text{ cm}^{-1}$  indicates the presence of hydrogen bonds. The appearance of  $\nu_s(\text{SnBu}_2)$  as a very weak band at  $601\text{ cm}^{-1}$ , reveals the presence of the linear  $\text{SnBu}_2$  groups.

The structure of [**D**] contains the anion  $[\text{C}_2\text{O}_4(\text{SnPh}_2\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}]^{2-}$  has yet been reported by Gueye *et al.* [15]. The suggested structure is discrete and consists of a central bichelating oxalate linked to two  $\text{SnPh}_2\text{C}_2\text{O}_4$  molecules themselves linked to one water and one  $\text{SnBu}_2\text{C}_2\text{O}_4$  molecules, the environments around the tin centres being tetrahedral, octahedral or seven coordinated, the oxalate anions being mono- and bichelating (Figure 4).



**Figure 4.** Proposed structure for compound **D**

## CONCLUSIONS

The characterized complexes have discrete structures with *trans* coordinated SnR<sub>2</sub> residues, the oxalate behaving as a mono- or a bichelating ligand, the hydrogenoxalate as a monochelating ligand. SnPh<sub>3</sub>OH is only involved in hydrogen bonding. When extra hydrogen bonds are considered involving OH, supramolecular architectures are obtained.

## ACKNOWLEDGEMENTS

We thank Professor Jose D. Ardisson – Laboratório de Física Aplicada, Centro de Desenvolvimento de Tecnologia Nuclear, CDTN-CNEN, Belo Horizonte, Minas Gerais (Brazil), for running the Mossbauer spectra and Dr. Raymundo Cea Olivares – Instituto de Química - U.N.A.M. (Mexico) for recording the infrared spectra and performing the elemental analyses.

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