

# $[(i\text{-Bu}_2\text{NH}_2)_2\text{C}_2\text{O}_4]_4\cdot\text{SnPh}_2\text{C}_2\text{O}_4\cdot\text{C}_2\text{O}_4(\text{SnPh}_3)_2$ and $[(i\text{-Bu}_2\text{NH}_2)_2\text{C}_2\text{O}_4]_3\cdot\text{SnBu}_2\text{C}_2\text{O}_4$ : SYNTHESIS, INFRARED AND MOSSBAUER STUDIES

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**Abstract:**  $[(i\text{-Bu}_2\text{NH}_2)_2\text{C}_2\text{O}_4]_4\cdot\text{SnPh}_2\text{C}_2\text{O}_4\cdot\text{C}_2\text{O}_4(\text{SnPh}_3)_2$  and  $[(i\text{-Bu}_2\text{NH}_2)_2\text{C}_2\text{O}_4]_3\cdot\text{SnBu}_2\text{C}_2\text{O}_4$  have been synthesized and characterized by infrared and Mossbauer spectroscopies. The suggested structure are discrete (one being a two metallic components), the environments around the tin(IV) centres being octahedral and pentagonal bipyramidal, the oxalate anions being monodentate, the cations linking through N-H...O hydrogen bonds the free oxygen atoms of the oxalate. The second metallic component of one of the structures is *cis* coordinated  $\text{C}_2\text{O}_4(\text{SnPh}_3)_2$ .

**Keywords:** *cis coordinated  $\text{C}_2\text{O}_4(\text{SnPh}_3)_2$ , discrete structures, monodentate oxalate, N-H...O hydrogen bonds, two metallic components structures*

## INTRODUCTION

The interest of research workers for organostannic compounds is related to their very exiting structural aspects and the various applications found for some of this family of compounds [1 - 8]. Within this family the compounds  $(\text{SnBu}_2)_2(\text{C}_2\text{O}_4)_3(\text{Cy}_2\text{NH}_2)_2$  has been reported containing *trans* octahedral coordinated  $\text{SnR}_2$  residue [9]. In a recent paper our group has published the X ray structure of  $\text{C}_2\text{O}_4(\text{SnPh}_3)_2$  which contains monocoordinated  $\text{SnPh}_3$  residues and a bridging oxalate, the environment around the tin centre being tetrahedral [10]. Our group has yet published several papers in the field of organotin chemistry [11 - 13] including  $\text{SnPh}_2$  residue containing compounds. In this paper we have initiated the synthesis of two new compounds containing the complex-anion  $[(\text{C}_2\text{O}_4)_4\text{SnBu}_2]^{6-}$  and  $[(\text{C}_2\text{O}_4)_5\text{SnPh}_2]^{8-}$  stabilized by the  $i\text{-Bu}_2\text{NH}_2^+$  cation and the neutral compound  $\text{C}_2\text{O}_4(\text{SnPh}_3)_2$ , in of them, their infrared and Mossbauer studies have been carried out, then structures suggested on the basis of spectroscopic data.

## MATERIALS AND METHODS

The oxalic acid salts have been obtained as a white precipitate on mixing aqueous solutions of  $i\text{-Bu}_2\text{NH}$  with  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  in 2/1 or 1/1 ratio respectively. Analytical data of oxalic salts are presented in Table 1.

**Table 1.** Results of the elemental analyses of oxalic salts

Compound	Chemical formula	Elemental analysis (%)					
		C		H		N	
		calc.	found	calc.	found	calc.	found
<b>L<sub>1</sub></b>	$(i\text{-Bu}_2\text{NH}_2)_2\text{C}_2\text{O}_4$	62.03	62.00	11.57	11.49	8.04	8.06
<b>L<sub>2</sub></b>	$i\text{-Bu}_2\text{NH}_2\text{HC}_2\text{O}_4$	54.77	55.00	9.55	9.49	6.39	6.45

$[(i\text{-Bu}_2\text{NH}_2)_2\text{C}_2\text{O}_4]_4 \cdot \text{SnPh}_2\text{C}_2\text{O}_4 \cdot \text{C}_2\text{O}_4(\text{SnPh}_3)_2$  (**A**) and  $[(i\text{-Bu}_2\text{NH}_2)_2\text{C}_2\text{O}_4]_3 \cdot \text{SnBu}_2\text{C}_2\text{O}_4$  (**B**) have been prepared by allowing  $i\text{-Bu}_2\text{NH}_2\text{HC}_2\text{O}_4$  or  $(i\text{-Bu}_2\text{NH}_2)_2\text{C}_2\text{O}_4$  to react with  $\text{SnPh}_3\text{OH}$  or  $\text{SnBu}_3\text{Cl}$  in ethanol in the 1/1 and 2/1 ratio respectively; a white precipitate was obtained in both cases and stirred around two hours.

**Table 2.** Results of the elemental analyses of compounds **A** and **B**

Compound	Chemical formula	Elemental analysis (%)					
		C		H		N	
		calc.	found	calc.	found	calc.	found
<b>A</b>	$[(i\text{-Bu}_2\text{NH}_2)_2\text{C}_2\text{O}_4]_4 \cdot \text{SnPh}_2\text{C}_2\text{O}_4 \cdot \text{C}_2\text{O}_4(\text{SnPh}_3)_2$	58.56	58.20	7.93	7.77	4.41	4.25
<b>B</b>	$[(i\text{-Bu}_2\text{NH}_2)_2\text{C}_2\text{O}_4]_3 \cdot \text{SnBu}_2\text{C}_2\text{O}_4$	56.25	56.35	10.18	9.97	6.15	6.18

The infrared spectra were recorded at the *Instituto de Química - U.N.A.M., Mexico*, by means of a BX FT-IR type spectrometer. Elemental analyses have been performed at the

Instituto de Química - U.N.A.M, Mexico. Mössbauer spectra were obtained as described previously [14].

Infrared data are given in cm<sup>-1</sup> (IR abbreviations: (vs) very strong, (s) strong, (m) medium, (w) weak, (vw) very weak). Mossbauer parameters are given in mm·s<sup>-1</sup> (Mossbauer abbreviations: Q.S = quadrupole splitting, I.S = isomer Shift, Γ = full width at half-height, A = area). All the chemicals were purchased from Aldrich Company Germany and used as such.

## RESULTS AND DISCUSSION

Let us consider the infrared and Mossbauer data of the studied compounds:

**A:** ν<sub>as</sub>COO<sup>-</sup>: 1682 (vs), 1662 (s), 1634 (s); ν<sub>s</sub>COO<sup>-</sup>: 1288 (s), 1262 (s); δCOO<sup>-</sup>: 789 (s); I.S<sub>1</sub> = 0.74; Q.S<sub>1</sub> = 2.01; Γ<sub>1</sub> = 0.87; A<sub>1</sub> = 66; I.S<sub>2</sub> = 1.11; Q.S<sub>2</sub> = 3.79; Γ<sub>2</sub> = 0.87; A<sub>2</sub> = 33;

**B:** ν<sub>as</sub>COO<sup>-</sup>: 1700 (s), 1620 (vs); ν<sub>s</sub>COO<sup>-</sup>: 1250 (vs); δCOO<sup>-</sup>: 780 (s); I.S = 1.45; Q.S = 3.63; Γ = 0.88; A = 100.

The infrared spectra of these two complexes (**A**, **B**) exhibit the presence of a non-centrosymmetrical oxalate because of the presence of more than two bands in the stretching vibrations region. On the infrared spectra of the two compounds, the wide absorption band centered in 2900 cm<sup>-1</sup> indicates the presence of hydrogen bonds.

(SnBu<sub>2</sub>)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>(Cy<sub>2</sub>NH<sub>2</sub>)<sub>2</sub> has been reported to contain almost linear SnBu<sub>2</sub> groups in a *trans* octahedral environment with mono- and bichelating oxalates [9]. According to Bancroft and Platt [15] the values of the quadrupole splitting, (3.79 and 3.63 mm·s<sup>-1</sup>), the SnBu<sub>2</sub> and SnPh<sub>2</sub> residue are linear leading to an octahedral environment and a pentagonal bipyramidal environment around the tin(IV) centres, while the Q.S of 2.01 mm·s<sup>-1</sup> related to C<sub>2</sub>O<sub>4</sub>(SnPh<sub>3</sub>)<sub>2</sub> is consistent with the presence of *cis* coordinated SnPh<sub>3</sub> residues. In the proposed discrete structures the oxalate anions are monodentate when linked to a SnR<sub>2</sub> residue, the cations linking through N-H...O hydrogen bonds the free oxygen atoms of the oxalate. In the case of the adduct the structure is a two metallic components one the second metallic component being the *cis* coordinated C<sub>2</sub>O<sub>4</sub>(SnPh<sub>3</sub>)<sub>2</sub> (Figures 1 and 2).

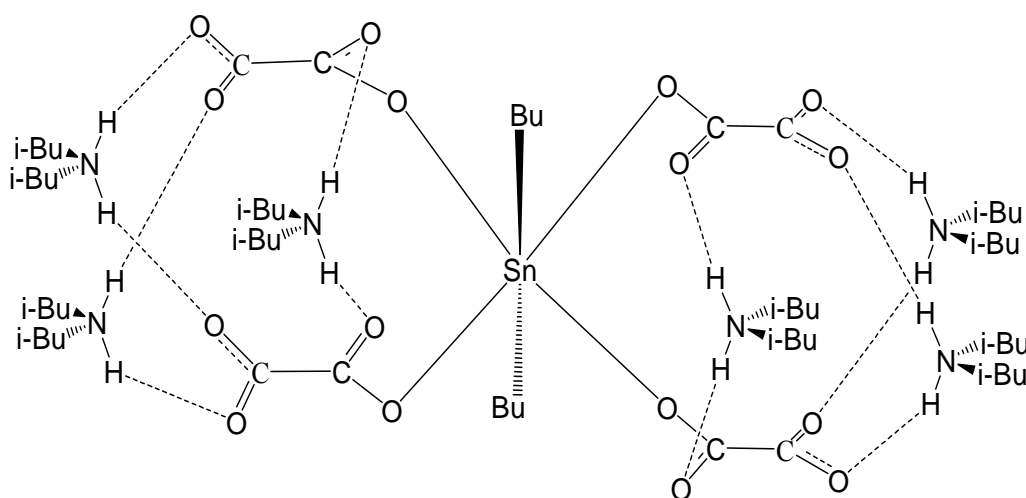
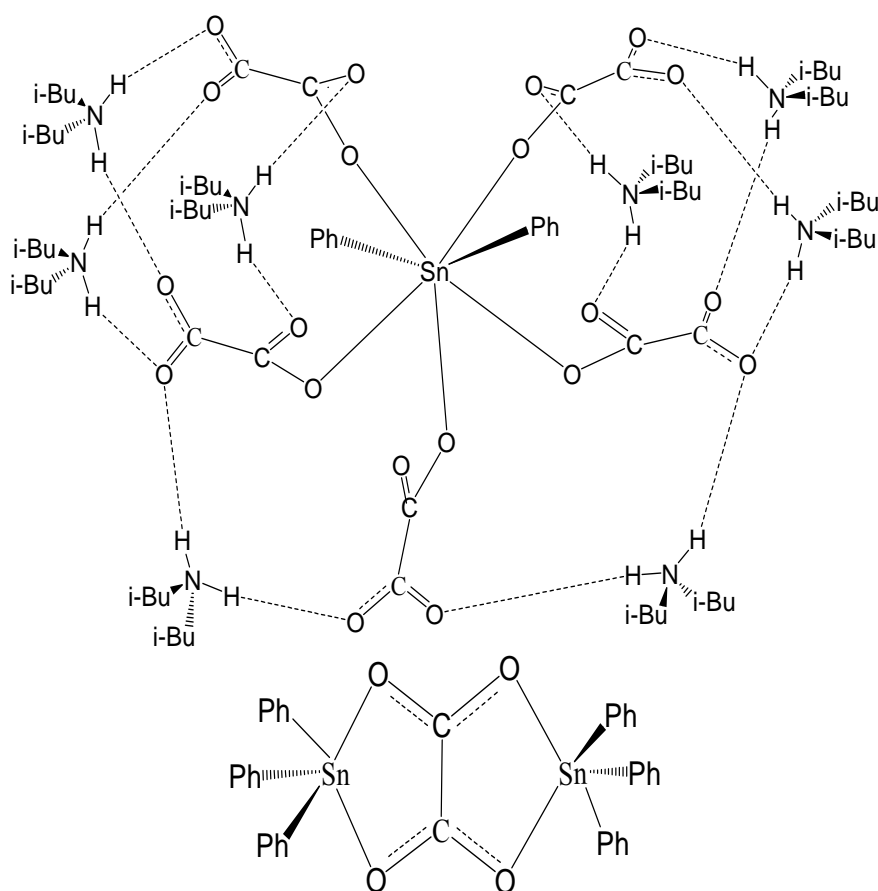


Figure 1. Suggested structure for [(*i*-Bu<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>]<sub>3</sub>.SnBu<sub>2</sub>C<sub>2</sub>O<sub>4</sub>



**Figure 2.** Suggested structure for  $[(i\text{-Bu}_2\text{NH}_2)_2\text{C}_2\text{O}_4]_4.\text{SnPh}_2\text{C}_2\text{O}_4.\text{C}_2\text{O}_4(\text{SnPh}_3)_2$

## CONCLUSION

The complex-anion  $[(\text{C}_2\text{O}_4)_4\text{SnBu}_2]^{6-}$  and  $[(\text{C}_2\text{O}_4)_5\text{SnPh}_2]^{8-}$  stabilized by the  $i\text{-Bu}_2\text{NH}_2^+$  cation have been characterized in the work. The suggested structures are discrete with octahedral and pentagonal bipyramidal environments around the tin(IV) centre and a monodentate oxalate ion. The second metallic component of one of the structures is the *cis* coordinated  $\text{C}_2\text{O}_4(\text{SnPh}_3)_2$ . The key role of non-symmetrical cations involved in N-H...O hydrogen bonds is noteworthy.

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