

## SYNTHESIS, INFRARED AND NMR STUDIES OF SOME SULFATO DIORGANOSTANNIC DERIVATIVES

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**Abstract:** EthylenediammoniumSO<sub>4</sub>·SnBu<sub>2</sub>Cl<sub>2</sub>·1/4ethylenediammoniumCl<sub>2</sub> (A), 2ethylenediammoniumSO<sub>4</sub>·SnBu<sub>2</sub>Cl<sub>2</sub> (B) and Cy<sub>2</sub>NH<sub>2</sub>SO<sub>4</sub>H·Cy<sub>2</sub>NH<sub>2</sub>SnBu<sub>2</sub>Cl<sub>3</sub> (C) complexes have been obtained on allowing ethylenediammoniumSO<sub>4</sub> and Cy<sub>2</sub>NH<sub>2</sub>HSO<sub>4</sub> to react respectively with SnBu<sub>2</sub>Cl<sub>2</sub> in specific ratios. The molecular structures of these compounds have been determined on the basis of infrared and NMR data. The suggested structures are dimeric and tetrameric, the tin atom being hexacoordinated, the sulphate anions behaving as a monochelating ligand or non-coordinating and only involved in hydrogen bonds. The hydrogenosulfate is a non-sigma coordinating anion but only involved in hydrogen bonds of acetic acid type or NH...O bonds. The presence of dimeric [(SnBu<sub>2</sub>Cl<sub>3</sub>)<sub>2</sub>]<sup>2-</sup> in one of the structures is noteworthy. The key role of the cations involved in hydrogen bonds is outlined.

**Keywords:** *cation, chloro bridges, dinuclear dimer, hydrogen bonds, monochelating and non-sigma involved sulphate anion, non-sigma involved HSO<sub>4</sub><sup>-</sup>, Td symmetry*

## INTRODUCTION

Organotin (IV) complexes have been extensively studied due to their applications in the area of medicine and agriculture. Numerous studies on organotin (IV) complexes have been carried out in order to determine their biological properties against bacteria, fungi and cancer cell lines [1-4]. Our group has been involved in seeking new organotin (IV) molecules and has previously reported the structures of the compounds  $[\text{SO}_4(\text{Ph}_3\text{Sn})(\text{SnPh}_3\text{OH}_2)]_n$  [5],  $\text{C}_2\text{O}_4(\text{SnPh}_3)_2$  [6],  $\text{SeO}_3(\text{SnPh}_3)_2$  [7],  $(\text{SnMe}_3)\text{SeO}_3[\text{SnMe}_3(\text{H}_2\text{O})]$  [8] and  $\text{Et}_2\text{NH}_2\text{SO}_4\text{SnMe}_2\text{Cl}\cdot 2\text{H}_2\text{O}$ ,  $(\text{Cy}_2\text{NH}_2)_2\text{SO}_4\cdot\text{SnBu}_2\text{Cl}_2\cdot 2\text{H}_2\text{O}$  [9]. In the continuation of these works, we have initiated here the study of the interactions between  $\text{enH}_2\text{SO}_4$  or  $\text{Cy}_2\text{NH}_2\text{SO}_4\text{H}$  and  $\text{SnBu}_2\text{Cl}_2$  that have yielded the three studied compounds which have been characterized by NMR ( $^1\text{H}$  and  $^{119}\text{Sn}$ ) and infrared then structures suggested on the basis of spectroscopic data.

## MATERIALS AND METHODS

### Synthesis of $\text{enH}_2\text{SO}_4\cdot\text{SnBu}_2\text{Cl}_2\cdot 1/4 \text{enH}_2\text{Cl}_2$ (A)

$\text{enH}_2\text{SO}_4$  was obtained on neutralizing  $\text{H}_2\text{SO}_4$  (98 %) with ethylenediamine; yellow crystals were collected after a water evaporation at 60 °C.

When an ethanolic solution of  $\text{enH}_2\text{SO}_4$  (0.06 g, 0.40 mmol) was mixed with an ethanolic solution of  $\text{SnBu}_2\text{Cl}_2$  0.12 g (0.40 mmol), a clear solution was obtained and stirred for around two hours. When submitted to a slow solvent evaporation, this solution yields a white powder.

### Synthesis of $2\text{enH}_2\text{SO}_4\cdot\text{SnBu}_2\text{Cl}_2$ (B)

When an ethanolic solution of ethylenediammonium $\text{SO}_4$  (0.11 g, 0.70 mmol) was mixed with an ethanolic solution of  $\text{SnBu}_2\text{Cl}_2$  (0.11 g, 0.35 mmol), a clear solution was obtained and stirred for around two hours. When submitted to a slow solvent evaporation, this solution yields a white powder.

### Synthesis of $\text{Cy}_2\text{NH}_2\text{SO}_4\text{H}\cdot\text{Cy}_2\text{NH}_2\text{SnBu}_2\text{Cl}_3$ (C)

$\text{Cy}_2\text{NH}_2\text{SO}_4\text{H}$  was obtained on semi neutralizing  $\text{H}_2\text{SO}_4$  (98 %) with  $\text{Cy}_2\text{NH}$ ; white crystals were collected after water evaporation at 60 °C.

When an ethanolic solution of  $\text{Cy}_2\text{NH}_2\text{SO}_4\text{H}$  (0.12 g, 0.42 mmol) was mixed with an ethanolic solution of  $\text{SnBu}_2\text{Cl}_2$  (0.13 g, 0.42 mmol), a clear solution was obtained and stirred for around two hours. When submitted to a slow solvent evaporation, this solution yields a white powder.

Elemental analyses: [% calculated (% found)]: % C: 25.46 (25.40); % H: 6.21 (6.19); % N: 7.07 (6.82) for **A**, % C: 22.61 (22.50); % H: 6.19 (6.24); % N: 9.71 (9.69) for **B** and % C: 47.98 (47.40); % H: 8.43 (8.26); % N: 3.50 (3.40) for **C**, have allowed to suggest respectively  $\text{enH}_2\text{SO}_4\cdot\text{SnBu}_2\text{Cl}_2\cdot 1/4\text{enH}_2\text{Cl}_2$  (**A**),  $2\text{enH}_2\text{SO}_4\cdot\text{SnBu}_2\text{Cl}_2$  (**B**) and  $\text{Cy}_2\text{NH}_2\text{SO}_4\text{H}\cdot\text{Cy}_2\text{NH}_2\text{SnBu}_2\text{Cl}_3$  (**C**) as formulae.

The infrared spectra were recorded by a Perkin Elmer (4400-350  $\text{cm}^{-1}$ ) spectrometer (Dakar University), the sample being as Nujol mulls while CsI windows were used. The elemental analyses have been performed at the laboratory of Microanalyses at the University of Bath (UK). Infrared data are given in  $\text{cm}^{-1}$  – IR abbreviations: (br) broad, (vs) very strong, (s) strong, (m) medium, (sh) shoulder, (vw) very weak.

Solution NMR spectra were recorded from a saturated  $\text{CD}_3\text{OD}$  solution, at 250.53 and 89.27 MHz for  $^1\text{H}$  and  $^{119}\text{Sn}$ , respectively.  $^1\text{H}$  and  $^{119}\text{Sn}$  chemical shifts are given in ppm and are referred, respectively, to  $\text{SiMe}_4$  and  $\text{SnMe}_4$ , all set to 0.00 ppm. These NMR data were recorded by means of a Bruker 300 MHz at University of Bath (UK) and University of Montpellier II (France).

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

## RESULTS AND DISCUSSION

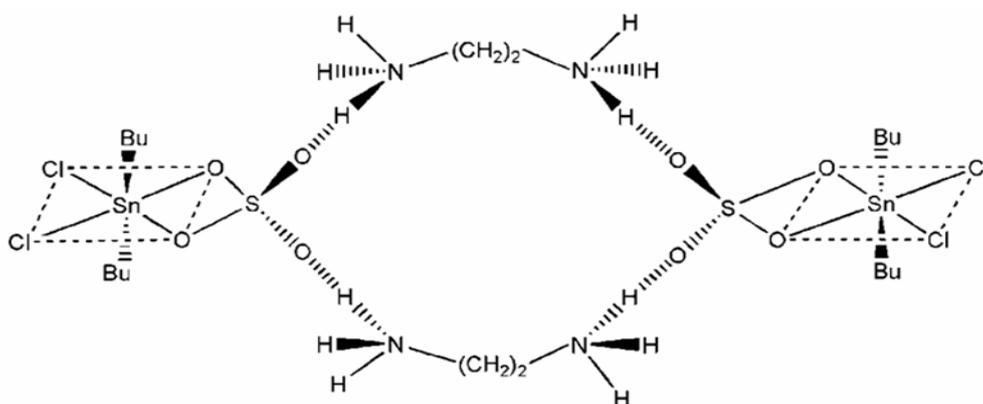
Let us consider infrared data ( $\text{cm}^{-1}$ ) and NMR data (ppm):

- for **(A)**:  $\nu_1(\text{SO}_4)$ : 990 vw;  $\nu_3(\text{SO}_4)$ : 1079 s;  $\nu_4(\text{SO}_4)$ : 607 m;  $\nu_s(\text{SnBu}_2)$ : 605 vw;  $\nu(\text{NH}_2)$ : 2900 br;
- for **(B)**:  $\nu_1(\text{SO}_4)$ : 990 vw;  $\nu_3(\text{SO}_4)$ : 1081 vs;  $\nu_4(\text{SO}_4)$ : 608 vs;  $\nu_s(\text{SnBu}_2)$ : 605 vw;  $\nu(\text{NH}_2)$ : 2900 br;
- for **(C)**:  $\nu(\text{SO}_3)$ : 1108 vs, 1067sh;  $\nu(\text{S-OH})$ : 864 m;  $\nu(\text{SnBu}_2)$ : 605 m;  $\nu(\text{NH}_2)$ : 2900 br;  $^1\text{H}$  NMR (MeOD): 2.06 – 0.92 [m,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Sn}$  (18H) and  $\text{C}_6\text{H}_{11}$  (44H)], 3.19 [s,  $\text{NH}_2$  (4H)];  $^{119}\text{Sn}$  NMR (MeOD): 138 ppm.

### Characterization of $\text{enH}_2\text{SO}_4 \cdot \text{SnBu}_2\text{Cl}_2 \cdot 1/4\text{enH}_2\text{Cl}_2$ (A)

On the infrared spectrum, the presence of  $\nu_1(\text{SO}_4)$  as a very weak band and the absence of  $\nu_2(\text{SO}_4)$  allow to conclude to a  $T_d$  symmetry for sulphate anion in the structure according to Theory Group [10]. The presence of a very weak band at 605  $\text{cm}^{-1}$  due to  $\nu_s(\text{SnBu}_2)$  indicates the presence of a linear  $\text{SnBu}_2$  residue [10]. The broad band centred at 2900  $\text{cm}^{-1}$  indicates the presence of hydrogen bonds.

The suggested structure is a dimer. Each of the tin atoms is hexa-coordinated to two chlorine atoms, two butyl groups and one chelating sulphate anion. Thus, the environment around the tin atom is octahedral and the  $\text{SnBu}_2$  skeleton linear. The two  $[\text{SO}_4\text{SnBu}_2\text{Cl}_2]^{2-}$  anionic components are interconnected by hydrogen bonds involving the non-coordinated oxygen atoms from the sulphate anions and the labile hydrogen atoms of the ethylenediammonium cations (Figure 1). The free NH groups can interact with the chloro or oxygen atoms through N-H...O or N-H...Cl intermolecular hydrogen bonds leading to a supramolecular architecture.

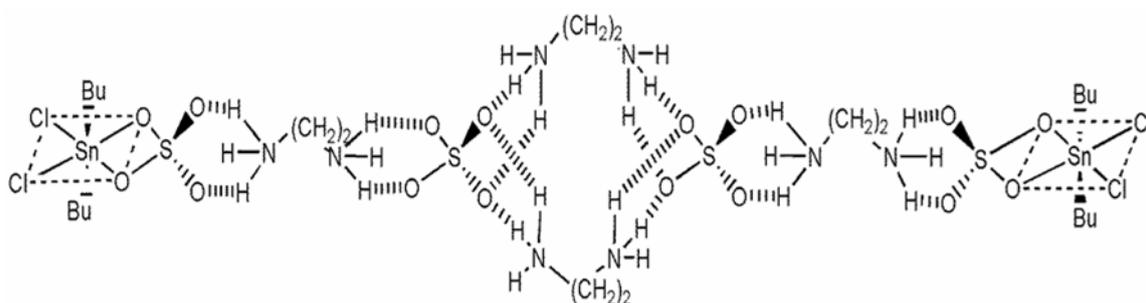


**Figure 1. Compound A**

### Characterization of $2\text{enH}_2\text{SO}_4 \cdot \text{SnBu}_2\text{Cl}_2$ (B)

On the infrared spectrum, the broad band centred at  $2900\text{ cm}^{-1}$  indicates the presence of N-H...O hydrogen bonds. The appearance of very weak bands for  $\nu_1(\text{SO}_4)$  and  $\nu_2(\text{SO}_4)$  allows to conclude to the presence of a sulphate anion of Td symmetry according to Theory Group [10]. The localization of  $\nu_s(\text{SnBu}_2)$  at  $605\text{ cm}^{-1}$  as a very weak band is an indication of the presence of a linear SnBu<sub>2</sub> residue [10].

This compound can be considered as a 1/1 adduct between  $\text{enH}_2\text{SO}_4$  and  $\text{enH}_2\text{SO}_4 \cdot \text{SnBu}_2\text{Cl}_2$ . If we consider the dimerization, the interactions between the second  $\text{enH}_2\text{SO}_4$  don't disturb the coordination around the tin center because of the strength of sigma bonding. So ensuring its insertion by the cleavage of hydrogen bonds seems relevant. Therefore, the bridge between the  $[\text{SO}_4 \cdot \text{SnBu}_2\text{Cl}_2]^{2-}$  complex-anions enhances compared to the first structure, leading to the suggested structure reported on Figure 2. The cations are similarly involved in hydrogen bonding. Extra NH...O and N-H...Cl hydrogen bonds involving the free NH groups of the cations lead to a supramolecular architecture.



**Figure 2. Compound B**

### Characterization of $\text{Cy}_2\text{NH}_2\text{SO}_4\text{H} \cdot \text{Cy}_2\text{NH}_2\text{SnBu}_2\text{Cl}_3$ (C)

On the infrared spectrum, the presence of  $\nu_s(\text{SnBu}_2)$  as a medium band at  $605\text{ cm}^{-1}$  indicates a non-linear SnBu<sub>2</sub> residue [10]. The broad band centred at  $2900\text{ cm}^{-1}$  indicates the presence of hydrogen bonds.

On the  $^{119}\text{Sn}$  NMR (MeOD) spectrum, the value of the signal at -138 ppm reveals the presence of only one type of tin center, the  $\text{SnBu}_2\text{Cl}_2$  molecule being coordinated because the  $^{119}\text{Sn}$  signal for free  $\text{SnBu}_2\text{Cl}_2$  molecule appears at 122 ppm [11].

From these data, we have suggested basically two components – an acetic acid type hydrogen bonded dimer of  $\text{HSO}_4^-$  linked to a dimer of  $[\text{SnBu}_2\text{Cl}_3]^-$  with chloro bridges, these entities being connected by cations through  $\text{NH}\dots\text{Cl}$  and  $\text{NH}\dots\text{O}$  hydrogen bonds. The suggested structure is reported on Figure 3.

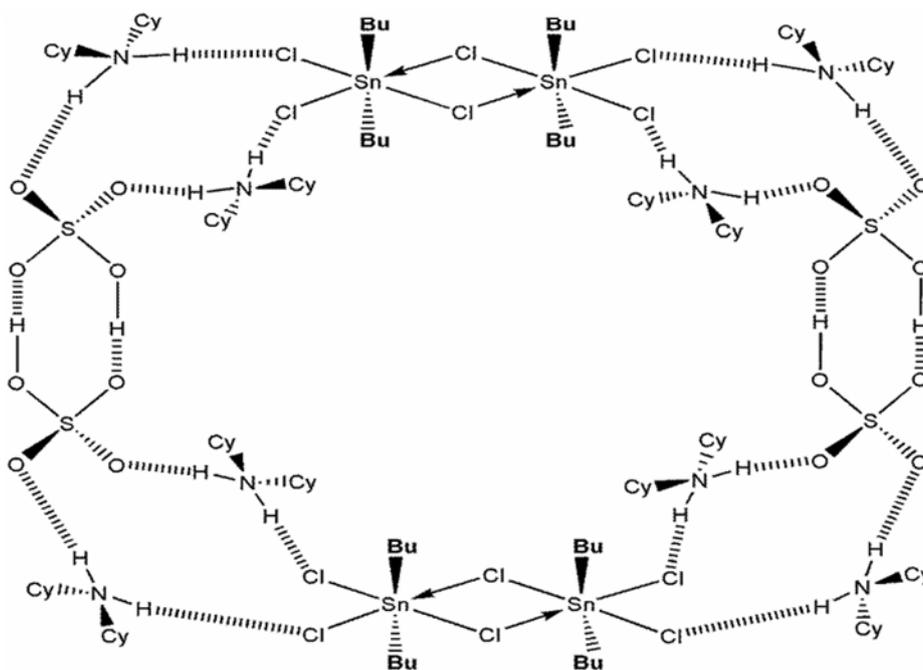


Figure 3. Compound C

## CONCLUSION

The studied compounds have dimeric structures, the tin center being in an octahedral environment, the sulphate behaving as a monochelating ligand while  $\text{HSO}_4^-$  is only involved in hydrogen bonds. Macromolecules have been obtained because of the involvement of cations through hydrogen bonds. Dealing with the macromolecules in the ethylenediammonium cations containing compounds, when extra hydrogen bonds involving the free NH groups a supramolecular architecture is obtained.

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