

## **SOME SULFATO ADDUCTS AND DERIVATIVE: SYNTHESIS AND SPECTROSCOPIC STUDY**

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**Abstract:** Three new adducts and derivative have been synthesized and studied by infrared and NMR spectroscopies. The suggested structures are discrete with a sulfate behaving as a monochelating, bichelating or monodentate ligand, the environments around the tin centre being octahedral or pentagonal bipyramidal. In all the studied compounds, proposed supramolecular architectures may be obtained when intermolecular hydrogen bonds are considered.

**Keywords:** *bichelating, discrete structures, hydrogen bonds, monochelating or monodentate sulphate, octahedral or pentagonal bipyramidal environments, supramolecular architectures*

## INTRODUCTION

The oxyanions are known for their coordinating ability which is one of the main directions of our research work with several papers yet published in this topic [1-7]. For widening the data on coordinating ability of oxyanions summarized by Hathaway [8], we have, in this work, mixed a MeOH/PrOH solution of Me<sub>4</sub>NOH or diethylenetriamine (DETA) or cyclohexylamine (CyNH<sub>2</sub>) with sulfuric acid and SnBu<sub>2</sub>Cl<sub>2</sub> in specific ratio. This has yielded three new adducts and derivative, infrared and NMR studies of which have been carried out then structures suggested on the basis of spectroscopic data.

## MATERIALS AND METHODS

The compounds **1** and **2** were obtained by mixing a MeOH/PrOH solution of Me<sub>4</sub>NOH with sulfuric acid and SnBu<sub>2</sub>Cl<sub>2</sub> in the ratio 2/1/2 (**1**) or diethylenetriamine with sulfuric acid and SnBu<sub>2</sub>Cl<sub>2</sub> in the ratio 2/4/1 (**2**), while **3** is obtained by allowing an ethanolic solution of (CyNH<sub>3</sub>)<sub>2</sub>SO<sub>4</sub> obtained as a powder on mixing CyNH<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> in water and evaporating the solvent in the oven at 60°C - to react in 1/1 ratio with an ethanolic solution of SnBu<sub>2</sub>Cl<sub>2</sub>. All the mixtures were stirred around two hours then filtered before being submitted to a slow solvent evaporation. The analytical data reported below, have allowed to suggest the following formulae (Table 1).

**Table 1.** Suggested formulae of synthesized compounds and the elemental analyses

Compound	Chemical formulae	Elemental analyses (%)					
		C		H		N	
		calc.	found	calc.	found	calc.	found
<b>1</b>	SnBu <sub>2</sub> OH(SO <sub>4</sub> H) 1/4EtOH	29.5	29.1	5.90	5.66	-	-
<b>2</b>	(DETAH <sub>3</sub> )(HSO <sub>4</sub> ) <sub>3</sub> ·SnBu <sub>2</sub> Cl <sub>2</sub>	19.55	19.87	5.61	6.15	5.70	5.65
<b>3</b>	CyNH <sub>3</sub> HSO <sub>4</sub> ·2SnBu <sub>2</sub> Cl <sub>2</sub>	32.83	31.3	6.34	6.12	1.74	1.87

The elemental analyses have been obtained from the “Laboratoire de Mesures Physiques” Montpellier II University, France. The IR spectra were performed at the “Laboratorio de Espectroscopía” of the “Instituto de Química”, UNAM (Mexico) and at the University of Saint Boniface, Winnipeg, Canada. The <sup>119</sup>Sn NMR spectra were performed at the “Laboratoire de Mesures Physiques” at Montpellier II University, France. NMR spectra were recorded as saturated CDCl<sub>3</sub> at room temperature, using a Bruker 300 MHz spectrometer. <sup>119</sup>Sn NMR spectrum was measured at 111.92 MHz, respectively, δ(<sup>119</sup>Sn) NMR is given in ppm and are referred to SnMe<sub>4</sub> at 0.00 ppm.

## RESULTS AND DISCUSSION

Let us consider the IR and <sup>119</sup>Sn NMR data of the adducts (two) and derivative (one).

**IR (cm<sup>-1</sup>):** **1:** (ν<sub>as</sub> + ν<sub>s</sub>) SO<sub>3</sub> = 1152 (s), 1078 (s); δ SO<sub>3</sub> = 592 (m), ν S-OH = 874(s); ν<sub>as</sub> SnBu<sub>2</sub> = 683(s); ν<sub>s</sub> SnBu<sub>2</sub> = 592 (w);

**2:** ( $\nu_{\text{as}} + \nu_{\text{s}}$ )  $\text{SO}_3 = 1059$  (vs), 1008 (vs), 956 (vs);  $\delta \text{SO}_3 = 502$  (s),  $\nu \text{S-OH} = 875$  (s);  $\nu_{\text{as}} \text{SnBu}_2 = 682$  (m);

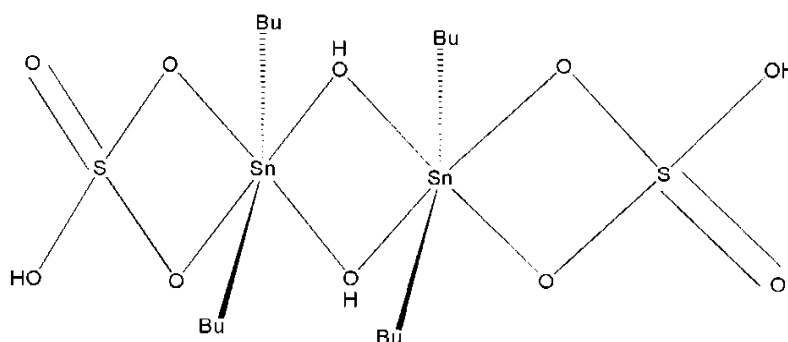
**3:** ( $\nu_{\text{as}} + \delta_{\text{as}}$ )  $\text{SO}_3 = 1164$  (s), 1117 (vs), 1076 (vs), 1011 (vs), ( $\delta_{\text{as}} + \delta_{\text{s}}$ )  $\text{SO}_3 = 682$  (s), 611 (s), 541 (s),  $\nu \text{S-OH} = 875$  (s);  $\nu_{\text{as}} \text{SnBu}_2 = 685$  (s);

$^{119}\text{Sn NMR}$  ( $\text{CDCl}_3$ , ppm): **1:**  $\delta = +128.59$  (s).

From these spectroscopic data, we suggest:

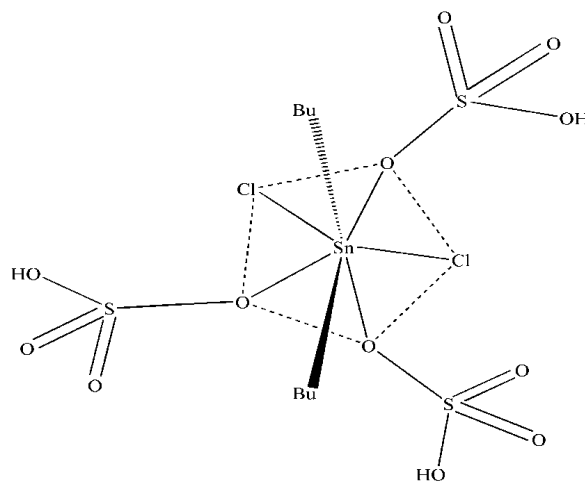
For **1** while considering the complex-cation  $[\text{SnBu}_2\text{SO}_4\text{H}]^+$ , the suggested structure is dimeric with bridging OH groups and a monochelating hydrogenosulfate, the environment around the tin centre being octahedral (Figure 1).

The NMR data ( $^{119}\text{Sn NMR}$  ( $\text{CDCl}_3$ , ppm):  $\delta = +128.59$  (s) closed to the value of  $^{119}\text{Sn NMR}$  ( $\text{CDCl}_3$ )  $\delta = +134$  ppm for  $\text{SnBu}_2\text{Cl}_2$  [9] indicate the presence of the monomer  $\text{SnBu}_2(\text{OH})(\text{HSO}_4)$  in solution allowing to claim the cleavage of  $\text{SnOHSn}$  bridges in  $\text{CDCl}_3$ .



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

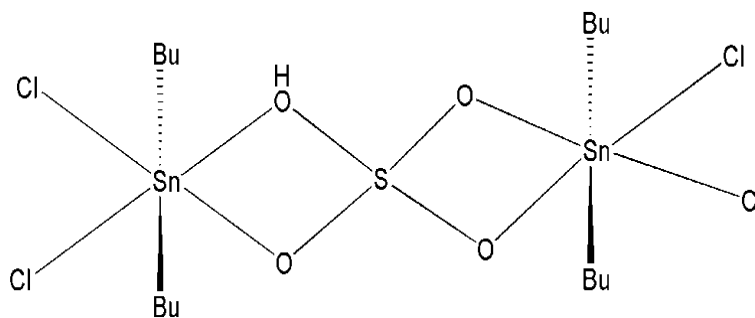
For **2** while considering the complex-anion  $[\text{SnBu}_2\text{Cl}_2(\text{HSO}_4)_3]^{3-}$  a monomeric structure reported on Figure 2 with a tin centre in a pentagonal bipyramidal environment is suggested, the  $\text{HSO}_4^-$  behaving as a monodentate ligand. The coordination number of seven has yet been reported in [10]. When the cation is involved through  $\text{NH}\dots\text{O}$  or  $\text{NH}\dots\text{Cl}$  hydrogen bonds a supramolecular architecture may be obtained.



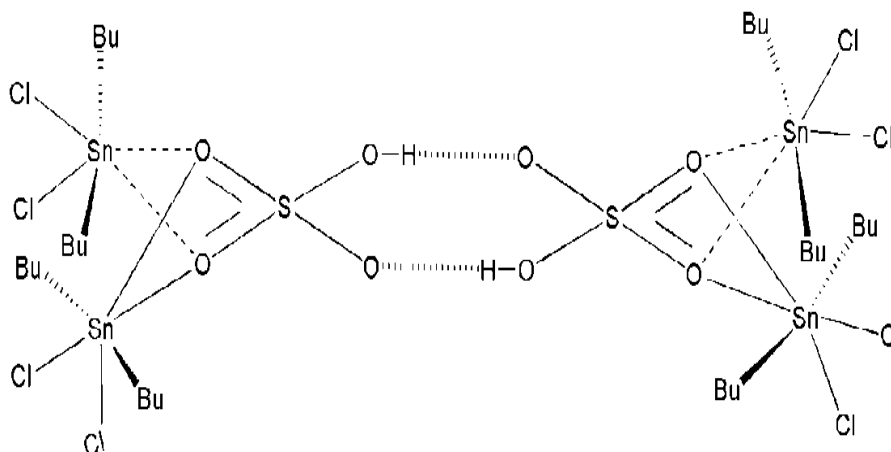
**Figure 2.** Proposed structure for the compound **2**

For **3** the suggested structures are discrete:

- a monomeric structure with a bichelating sulfate (Figure 3a);
- a dimeric structure with bichelating sulfates (Figure 3b), the dimerization being ensured by OH.....O hydrogen bonds of acetic acid type, the environment around the tin centre being octahedral. Our group has yet published the X-ray structure of  $\text{Bu}_4\text{NHSO}_4\text{SnMe}_3\text{Cl}$  which contains  $\text{HSO}_4^-$  involved in an acetic acid hydrogen bonded type dimers [11].



**Figure 3a.** Proposed structure for the compound **3**



**Figure 3b.** Proposed structure for the compound **3**

For compounds **2** and **3** the cations may interact via hydrogen bonds leading to a supramolecular architecture. For the compound **1**, OH groups may also be involved in intermolecular hydrogen bonds leading to a supramolecular architecture.

## CONCLUSIONS

For the studied adducts and derivative a discrete structure has been proposed- monomeric or dimeric- the hydrogenosulfate behaving as a monodentate, the sulfate acting as a monochelating or bichelating ligand, the environment around the tin centre being octahedral or pentagonal bipyramidal. When extra intermolecular hydrogen bonds are considered supramolecular architectures may be obtained.

## ACKNOWLEDGEMENTS

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## LIST OF NOTATIONS AND SYMBOLS

DETAH<sub>3</sub> = diethylenetriammonium

IR abbreviations: vs (very strong); s (strong); m (medium), w (weak)

<sup>119</sup>Sn NMR abbreviations: m (multiplet), t (triplet), s (singlet)

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