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## Synthesis, IR, Mössbauer and solid-state NMR studies of 1,1-dimethylguanidinium triphenyltin sulphate

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### Abstract

1,1-Dimethylguanidinium triphenyltin sulphate has been synthesised and characterized by infrared, Mössbauer and solid-state NMR spectroscopies. An infinite chain structure with a bidentate sulphate is suggested, the sulphate appearing in a *Td* symmetry, since the two remaining oxygen atoms are involved in strong H-bonds with the 1,1-dimethylguanidinium, indicating the important influence of the counteranion nature on the structure. **To cite this article:** M. Sembène Boye et al., *C. R. Chimie* 10 (2007).

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### Résumé

Le triphénylétain sulfate de 1,1-diméthylguanidinium a été synthétisé et étudié par spectroscopies infrarouge, Mössbauer et RMN <sup>13</sup>C et <sup>117</sup>Sn à l'état solide. La structure découlant de ces données spectroscopiques est une chaîne infinie, contenant des sulfates bidentates, la symétrie du sulfate étant tétraédrique du fait que les deux atomes oxygènes non liés à l'étain sont engagés dans des liaisons hydrogène avec l'ion diméthylguanidinium. Ceci montre que la nature du cation joue un rôle important sur la symétrie de l'anion dans de tels composés. **Pour citer cet article :** M. Sembène Boye et al., *C. R. Chimie* 10 (2007).

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**Keywords:** Infrared; Mössbauer; Solid-state <sup>13</sup>C and <sup>117</sup>Sn NMR; Triphenyltin derivative; 1,1-Dimethylguanidinium; H-bonds

**Mots-clés :** Infrarouge ; Mössbauer ; RMN <sup>13</sup>C et <sup>117</sup>Sn à l'état solide ; Dérivé du triphénylétain ; 1,1-Diméthylguanidinium ; Liaisons hydrogène

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## 1. Introduction

Some  $\text{SnPh}_3$ -containing derivatives involving inorganic oxyacids are reported [1–3]. The important role of the cation on the structure of oxalate  $\text{SnPh}_3$ -containing derivatives has been reported and a *cis* chelating oxalate has been reported in  $(\text{Cy}_2\text{NH}_2)(\text{C}_2\text{O}_4)(\text{SnPh}_3)$  [4] and a polymeric structure in  $(\text{Me}_4\text{N})(\text{C}_2\text{O}_4)(\text{SnPh}_3)$  [3]: this shows the key role of the cation in the  $[\text{C}_2\text{O}_4\text{SnPh}_3]^-$  arrangement. Recently derivatives of general formula  $(\text{R}_4\text{N})(\text{XO}_4)(\text{SnPh}_3)$  ( $\text{R} = \text{Cy}, \text{H}, \text{Bu}, \text{Me}; \text{X} = \text{S}, \text{Se}$ ) have been reported, in which the role of the counter cation size on the structure has been specified [5]; the structure, in solution, of  $(\text{Bu}_4\text{N})(\text{SO}_4)(\text{SnPh}_3)$  is monomeric, while, in  $(\text{Me}_4\text{N})(\text{SO}_4)(\text{SnPh}_3)$ ,  $\text{SnPh}_3$  residues are still *trans*-coordinated by oxygens, conferring bipyramidal trigonal environment to the tin atoms.

In the framework of our research work on oxy-anions acting as ligands [6–10], we describe in this paper the synthesis and spectroscopic studies of the 1,1-dimethylguanidinium triphenyltin sulphate.

## 2. Experimental

$[\text{Me}_2\text{NC}(=\text{NH})\text{NH}_2]_2\text{H}_2\text{SO}_4$  and  $\text{SnPh}_3\text{Cl}$  are Aldrich chemicals, used without further purification. The title derivative is obtained by mixing in a 1:1 ratio  $[\text{Me}_2\text{NC}(=\text{NH})\text{NH}_2]_2\text{H}_2\text{SO}_4$  dissolved in a minimum of water and  $\text{SnPh}_3\text{Cl}$  dissolved in ethanol (20 ml). The white precipitate obtained is washed with ethanol.

The elemental analyses were performed in the Microanalyses Laboratory of the Inorganic Metallorganic and Analytical Chemistry Department (University of Padua, Italy), the Mössbauer spectrum is obtained as described in [11], while the solid-state  $^{13}\text{C}$  and  $^{117}\text{Sn}$  NMR spectra were recorded using a Bruker Avance 250 NMR spectrometer, equipped with a broadband MAS probe, operating at 62.90 and 89.15 MHz for  $^{13}\text{C}$  and  $^{117}\text{Sn}$  nuclei, respectively. Rotors of 4 mm were used, and spinning rates of 7000 and 9000 Hz for  $^{117}\text{Sn}$  acquisition and 4000 Hz for  $^{13}\text{C}$  acquisition. Adamantane and tetracyclohexyltin were used as external standards for  $^{13}\text{C}$  and  $^{117}\text{Sn}$ , respectively.

Microanalytical data: % calculated (% found)

% C: 46.00(46.45) % H: 4.79(4.67) % N: 8.05(8.76);  
m.p. > 260 °C; yield: 85%

Infrared data ( $\text{cm}^{-1}$ )

3371s, 3169s, 3049br  $\nu\text{NH}_3^+$ ; 1652s, 1640s  $\delta\text{NH}_3^+$ ;  
1545m  $\nu\text{C}=\text{N}$ ; 1108vs  $\nu_{\text{as}}\text{SO}_4^{2-}$ ; 616s  $\delta_{\text{as}}\text{SO}_4^{2-}$ ;  
393w  $\delta_{\text{s}}\text{SO}_4^{2-}$ ; 222m  $\nu\text{SnO}$

Mössbauer data ( $\text{mm s}^{-1}$ )

Q.S. = 3.73; I.S. = 1.47;  $T = 0.94$ ;  $A\% = 1.05$

NMR data [ $\delta$  (ppm)]

$^{13}\text{C}$ : 156,  $\text{C}=\text{N}$ ; 138, Ph: C (*i*) and C (*o*); 130 Ph: C (*m*) and C (*p*); 38,  $\text{N}-\text{CH}_3$

$^{117}\text{Sn}$ : -227

## 3. Discussion

The absence of  $\nu_{\text{s}}\text{SO}_4^{2-}$  indicates a *Td* symmetry for the sulphate [12]. The Q.S. value of  $3.73\text{ mm s}^{-1}$ , higher than  $3.00\text{ mm s}^{-1}$ , is indicative of a *trans*- $\text{O}_2\text{SnPh}_3$  stereochemistry about the tin centres [13]. The isotropic  $^{117}\text{Sn}$  chemical shift of -227 ppm is consistent with the presence of *trans*-coordinated  $\text{Ph}_3\text{Sn}$  residues [14].

On the basis of these spectroscopic data, the proposed structure is a polymeric chain, in which  $\text{Ph}_3\text{Sn}$  residues are *trans* coordinated, the sulphate behaving as a bidentate ligand, the two other oxygen atoms being involved in  $\text{NH}\cdots\text{O}$  hydrogen bonds with the 1,1-dimethylguanidinium (the characteristic absorptions are localized at 3371 and  $3169\text{ cm}^{-1}$  on the infrared spectrum), conferring a *Td* symmetry to the sulphate. In  $\text{SO}_4(\text{SnPh}_3)$  ( $\text{H}_2\text{O}\cdot\text{SnPh}_3$ ) [15], the sulphate appears as belonging to the *Td* symmetry group (in this compound, there is *no free oxygen atom*, three being bonded to the tin center and the fourth one involved in the hydrogen bond linking the two adjacent chains, allowing the anion to appear as belonging to the *Td* point group). In  $(\text{R}_4\text{N})(\text{SnPh}_3)(\text{SO}_4)$  ( $\text{R} = \text{Bu}, \text{Me}$ ) [5], the sulphate group has a  $\text{C}_{2v}$  symmetry [5]. The number of the protons linked to N allows us to consider all the non-coordinating oxygen atoms to be involved in H-bonds. While considering the polymeric chains, the cations can be involved in  $\text{NH}\cdots\text{O}$  hydrogen bonds in two ways:

- (1) the cations link to oxygen atoms of the same sulphate, allowing the formation of an  $\text{SO}_2\text{N}_2$  cycle (Fig. 1);

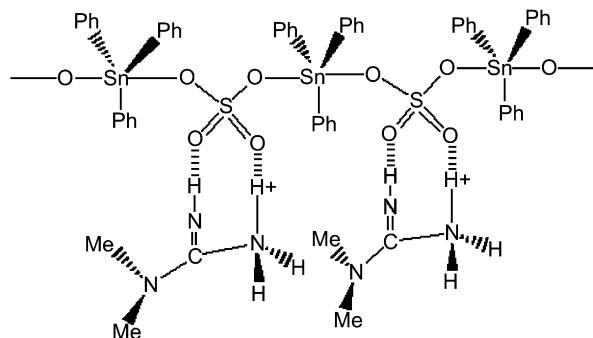


Fig. 1.

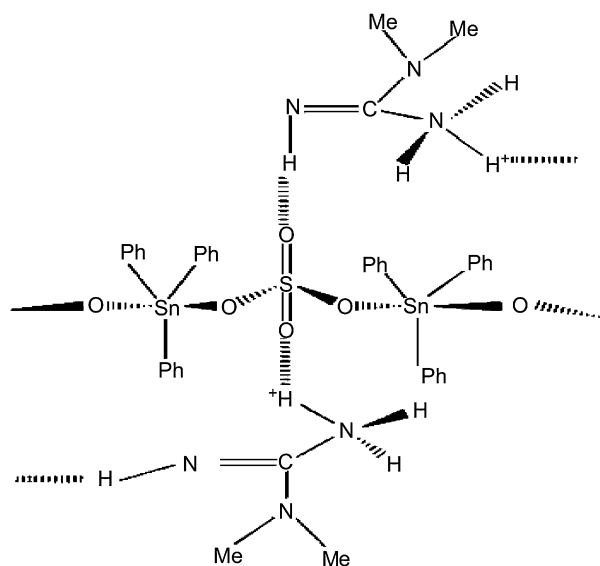


Fig. 2.

(2) the cations link two adjacent polymeric chains, the resulting structure being a three-dimensional network (Fig. 2).

#### 4. Conclusion

In the title compound, the sulphate behaves as a bridging bidentate ligand involving a polymeric chain;

H-bonds involving the two other oxygen atoms of the sulphate and the counter cation are noteworthy.

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