

**[Cy₂NH₂SO₄(SnPh₃)₂X]₂ (X = F, Cl):
SYNTHESIS AND SPECTROSCOPIC STUDIES**

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Abstract: Two new tetranuclear (sulphato)(halo)triphenyltin(IV) complexes (halo = F, Cl) have been synthesized and studied by infrared and Mossbauer spectroscopies. The suggested structures are discrete, the anion acting as a bichelating, a monochelating and monocoordinating or a bidentate ligand. The key role of the cation, which appears to link the two components of the structures *via* hydrogen bonds, is noteworthy.

Keywords: *sulphato, triphenyltin(IV), fluoro, chloro, hydrogen bonds*

INTRODUCTION

Much research work has been and is still being published nowadays on SnPh₃ residue containing compounds because of their structural interest, antitumor activity and industrial applications [1-6]. In the framework of our research work on the coordinating

ability of oxyanions in organotin compounds we have yet published several papers [7-9] and have initiated here the study of the interactions between $\text{Cy}_2\text{NH}_2\text{SO}_4\text{SnPh}_3 \cdot \text{H}_2\text{O}$ and Et_4NF or Et_4NCl . Two new adducts have been obtained and spectroscopically characterized. Structures have been suggested on the basis of spectroscopic data.

EXPERIMENTAL

Chemicals were obtained from Aldrich and were used without further purification. $\text{Cy}_2\text{NH}_2\text{SO}_4\text{SnPh}_3 \cdot 1/2\text{H}_2\text{O}$ was prepared by allowing $\text{Cy}_2\text{NH}_2\text{HSO}_4 \cdot \text{H}_2\text{O}$ (obtained on mixing Cy_2NH_2 and H_2SO_4 in water-1/1 ratio-) to react with SnPh_3OH ; $\text{Et}_4\text{NF} \cdot 2\text{H}_2\text{O}$ was obtained by allowing Et_4NOH as 20% water solution to react with HF in water; commercial $\text{Et}_4\text{NF} \cdot x\text{H}_2\text{O}$ and $\text{Et}_4\text{NCl} \cdot x\text{H}_2\text{O}$ are dried by pumping.

$\text{Cy}_2\text{NH}_2\text{SO}_4\text{SnPh}_3 \cdot 1/2\text{H}_2\text{O}$: - % calculated (% found) C = 56.53 (56.32); H = 6.33 (6.15) N = 2.20 (2.25)

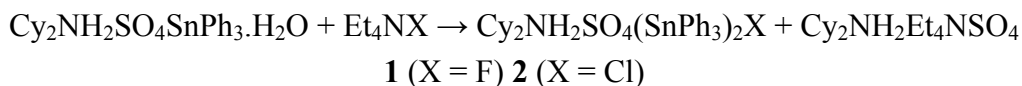
On allowing $\text{Cy}_2\text{NH}_2\text{SO}_4\text{SnPh}_3 \cdot 1/2\text{H}_2\text{O}$, in methanol, to react with either Et_4NF or Et_4NCl , both as ethanolic solutions, a white powder was obtained after slow solvent evaporation.

Analytical data of $\text{Cy}_2\text{NH}_2\text{SO}_4\text{SnPh}_3\text{SnPh}_3\text{F}$ **1**: % calculated (% found) for $\text{C}_{48}\text{H}_{54}\text{NO}_4\text{SFSn}_2$: C = 57.75 (57.66); H = 5.41 (5.36); N = 1.40 (1.43); Sn = 23.80 (23.71); F = 1.90 (1.95).

Analytical data of $\text{Cy}_2\text{NH}_2\text{SO}_4\text{SnPh}_3\text{SnPh}_3\text{Cl}$ **2**: % calculated (% found) for $\text{C}_{48}\text{H}_{54}\text{NO}_4\text{SClSn}_2$: C = 56.86 (57.22); H = 5.37 (5.18); N = 1.38 (1.31); Cl = 3.50 (3.61); Sn = 23.42 (23.37).

The elemental analyses were performed by the «Service Central d'Analyses» CNRS, Vernaison, France and the Faculty of Chemistry, University of Konstanz, Germany. The IR spectra were obtained as Nujol mulls with a PE 580 spectrometer ($4000 - 200 \text{ cm}^{-1}$) and a FTIR Nicolet ($600 - 50 \text{ cm}^{-1}$) using CsI or polyethylene windows. Mossbauer spectra were obtained as described previously [10]. Infrared data are given in cm^{-1} (abbreviations: (br) broad, (s) strong, (m) medium, (sh) shoulder, (w) weak). Mössbauer parameters are given in mm.s^{-1} (abbreviations: Q.S = quadrupole splitting, I.S = isomer shift, Γ = full width at half-height).

For adducts **1** and **2** we propose the following chemical reaction:



RESULTS AND DISCUSSION

Let us consider the most significant IR data, of **1** (X = F): 974sh, 1124vs, 1066vs- $\nu_1+\nu_3\text{SO}_4$; 590m - $\nu_4\text{SO}_4$; 356vs- $\nu_2\text{SO}_4$; 314s- νSnF ; 210s -vs SnC_3 ; 206s - νSnO ; and **2** (X = Cl) : 1124vs, 1068vs, 970s- $\nu_1+\nu_3\text{SO}_4$; 662w - $\nu_4\text{SO}_4$; 358vs- $\nu_2\text{SO}_4$; 205m -vs SnC_3 + νSnO -. In both IR spectra vs SnC_3 appears as a very strong band around 270 cm^{-1} .

The Mossbauer data for **1** and **2** both consist of two doublets of equal area (**1**: I.S_{1a} = 1.26 mm.s^{-1} , Q.S_{1a} = 3.41 mm.s^{-1} ; I.S_{1b} = 1.37 mm.s^{-1} , Q.S_{1b} = 2.04 mm.s^{-1} ,

$\Gamma_1 = 0.94 \text{ mm.s}^{-1}$; **2**: $I.S_{2a} = 1.30 \text{ mm.s}^{-1}$, $Q.S_{2a} = 2.81 \text{ mm.s}^{-1}$, $I.S_{2b} = 1.20 \text{ mm.s}^{-1}$, $Q.S_{2b} = 2.58 \text{ mm.s}^{-1}$; $\Gamma_2 = 1.04 \text{ mm.s}^{-1}$.

The Mossbauer data of **1** are consistent with the simultaneous presence of *cis*-coordinated SnPh_3 ($QS = 2.08 \text{ mm.s}^{-1}$) and *trans*-coordinated SnPh_3 residues ($QS = 3.41 \text{ mm.s}^{-1}$), the tin centres being in a trigonal bipyramidal environment according to Bancroft and Platt [11]. The structure suggested for the fluoro complex is a dimer containing $(\text{SnPh}_3)_2\text{SO}_4$ with a bichelating sulphate and $[(\text{SnPh}_3\text{F})_2\text{SO}_4]^{2-}$ with a bidentate sulphate (figure 1a) or two $[\text{SO}_4(\text{SnPh}_3)\text{SnPh}_3\text{F}]^-$ moieties with a monochelating and monocoordinating sulphate (figure 1b); the two components of the two structures are connected through cations by means of $\text{NH}\cdots\text{O}$ hydrogen bonds, characterized by the broad absorption around 2900 cm^{-1} in the infrared spectrum (the structures are consistent with IR data-splitting of ν_3 , appearance of ν_2 and $\nu_s\text{SnC}_3^-$).

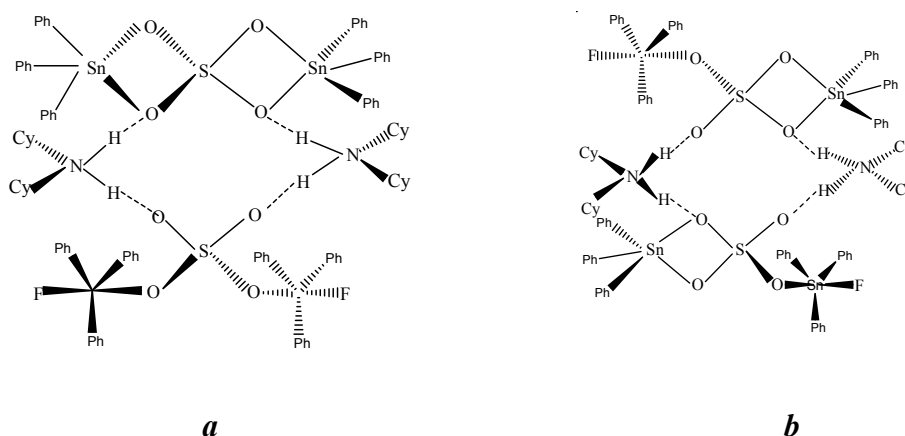


Figure 1. $\text{Cy}_2\text{NH}_2\text{SO}_4(\text{SnPh}_3)_2\text{F}$

The Mossbauer data of **2** are consistent with the presence of both tetrahedral (2.58 mm.s^{-1}) and *trans*-coordinated (2.81 mm.s^{-1}) SnPh_3 residues, according to Bancroft and Platt [11].

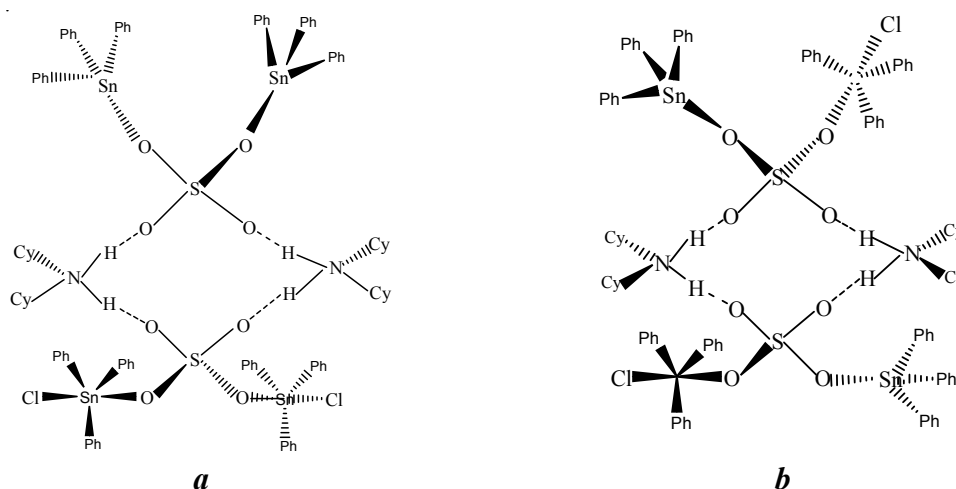


Figure 2. $\text{Cy}_2\text{NH}_2\text{SO}_4(\text{SnPh}_3)_2\text{Cl}$

This allows to suggest a structure containing $(\text{SnPh}_3)_2\text{SO}_4$ with a bidentate sulphate and $[(\text{SnPh}_3\text{Cl})_2\text{SO}_4]^{2-}$ also with a bidentate sulphate or two $[\text{SO}_4(\text{SnPh}_3)\text{SnPh}_3\text{Cl}]^-$ moieties with a bidentate sulphate too. In these two structures, the two components are linked by cations through N-H... O hydrogen bonds in a similar manner than in **1** (Figures 2a, b) (the structures are consistent with the IR data-splitting of ν_3 , appearance of ν_2 and ν_{SnC_3}). The appearance of ν_{SnC_3} is indicative of the presence of non planar SnC_3 groups. The structures **1b** and **2b** are centrosymmetrical.

CONCLUSION

The adducts $\text{Cy}_2\text{NH}_2\text{SO}_4(\text{SnPh}_3)_2\text{X}$ have discrete structures with two different types of SnPh_3 residue. The two components of the structures are connected by dicyclohexylammonium cations *via* NH---O hydrogen bonds. The key role of the cation is noteworthy.

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