

SOME NEW SULFATO AND HYDROGENOSULFATO ADDUCTS: SYNTHESIS, INFRARED AND MÖSSBAUER STUDIES

Waly Diallo¹, Kochikpa Y.A. Okio¹, Libasse Diop^{1*},
Lamine Diop², Umberto Russo³, Alain Wattiaux⁴

¹*Laboratoire de Chimie Minérale et Analytique (LACHIMIA),
Département de Chimie, Faculté des Sciences et Techniques,
Université Cheikh Anta Diop, Dakar, Sénégal*

²*Collège Universitaire de Saint-Boniface, Winnipeg, Canada*

³*Dipartimento di Chimica Inorganica Metallorganica ed Analitica,
Via Loredan 4, Università degli studi di Padova, I-35135 Padova, Italy*

⁴*CNRS, Université de Bordeaux, ICMCB, 87 avenue du Dr A.
Schweitzer, Pessac, F-33608, France*

*Corresponding author: dlibasse@gmail.com

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Abstract: Eight organotin (IV) (mainly sulfato) adducts have been synthesized and studied by spectroscopic methods. While considering the anionic component, the suggested structures are discrete; supramolecular architectures are obtained with secondary interactions through NH---Cl and NH---O hydrogen bonds while considering the cations, the anions behaving as monochelating, bridging or monocoordinating ligands, the environment around the tin (IV) centre being octahedral. Tetrahedral SnMe_2Cl_2 has been characterized spectroscopically.

Keywords: organotin (IV) adducts, infrared, Mossbauer, ionic structures, hydrogen bonds, supramolecular architectures, tetrahedral SnMe_2Cl_2 .

INTRODUCTION

The various applications of organotin (IV) compounds in many fields: agriculture, medicine, antifouling paints, wood preservatives, ...[1 – 3], are mainly the reasons for many research groups to be involved in the synthesis of compounds of this family. Structures of some sulfato derivatives: $(\text{SnMe}_3)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ and $(\text{SnPh}_3)_2\text{SO}_4 \cdot \text{H}_2\text{O}$, and adducts: $\text{Bu}_4\text{NHSO}_4 \cdot \text{SnMe}_3\text{Cl}$, have been reported by Molloy *et al.* [4] and us [5, 6]. Our group has yet reported many papers dealing with the coordinating behavior of oxoanions [7 – 9]. We have initiated here, the study of the interactions between:

- Bu_4NHSO_4 and SnBu_2Cl_2
- $\text{Cy}_2\text{NH}_2\text{HSO}_4$ and SnR_2Cl_2 ($\text{R} = \text{Me}, \text{Bu}$), SnMe_3Cl
- $\text{NH}_2\text{SO}_3\text{H}$, Et_2NH and SnMe_2Cl_2 ,
- isoBu_2NH , H_2SO_4 and SnMe_2Cl_2

which have yielded eight new SnR_2 and SnMe_3 residues containing adducts. Infrared and Mössbauer studies of these adducts have been carried out and structures were suggested on the basis of spectroscopic data.

EXPERIMENTAL

When Bu_4NHSO_4 in ethanol or $\text{Cy}_2\text{NH}_2\text{HSO}_4$ in methanol is mixed with SnBu_2Cl_2 in ethanol in 2 : 1 ratio (**A**), in ether in 1 : 1 ratio (**B**) or SnMe_2Cl_2 in ether in 1 : 1 (**C**) or 1 : 2 (**D**), white powders are obtained after a slow solvent evaporation.

Mixing $\text{H}_2\text{NSO}_3\text{H}$ in water, Et_2NH in water with SnMe_2Cl_2 in ethanol in 1 : 1 : 2 ratio gives a white powder after a slow solvent evaporation (**E**).

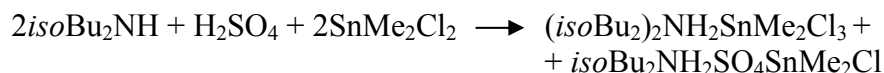
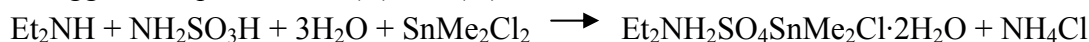
On mixing $(\text{Cy}_2\text{NH}_2)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ (obtained on mixing in water H_2SO_4 and Cy_2NH in 1 : 2 ratio and allowing water evaporation) in MeOH with SnBu_2Cl_2 in MeOH in 1 : 2 ratio, a white powder is obtained after a slow solvent evaporation (**F**).

Mixing $\text{Cy}_2\text{NH}_2\text{HSO}_4 \cdot 2\text{H}_2\text{O}$ (obtained on mixing in water H_2SO_4 and Cy_2NH in 1 : 1 ratio and allowing water evaporation) in MeOH with SnMe_3Cl in MeOH in 1 : 1 ratio, a white powder is obtained after a slow solvent evaporation (**G**).

The mixture of isoBu_2NH in water, H_2SO_4 in water with SnMe_2Cl_2 in ethanol in 1 : 1 : 1 ratio gives a white powder after a slow solvent evaporation (**H**).

The analytical data reported below allows suggesting the following formulae, presented in Table 1.

The suggested equations for (**E**) and (**H**) are:



In the first reaction, the hydrolysis of $\text{NH}_2\text{SO}_3\text{H}$ in basic media has led to the sulphate.

$\text{isoBu}_2\text{NH}_2\text{SO}_4\text{SnMe}_2\text{Cl}$, the homologue of $\text{Et}_2\text{NH}_2\text{SO}_4\text{SnMe}_2\text{Cl} \cdot 2\text{H}_2\text{O}$ in the second reaction has not been isolated but $(\text{isoBu}_2)_2\text{NH}_2\text{SnMe}_2\text{Cl}_3$.

Table 1. Formulae of synthesized adducts, based on the elemental analyses

Adduct	Chemical formula	Elemental analysis (%)									
		C		H		N		Sn		Cl	
		a*	b**	a*	b**	a*	b**	a*	b**	a*	b**
A	$\text{Bu}_4\text{NHSO}_4 \cdot \text{SnBu}_2\text{Cl}_2$	44.80	44.95	8.55	8.65	2.18	2.26	18.46	18.26	11.04	11.22
B	$\text{Cy}_2\text{NH}_2\text{HSO}_4 \cdot \text{SnBu}_2\text{Cl}_2$	41.15	41.32	7.37	7.50	2.40	2.32	20.35	20.40	12.17	12.31
C	$\text{Cy}_2\text{NH}_2\text{HSO}_4 \cdot \text{SnMe}_2\text{Cl}_2$	33.66	33.44	6.21	6.33	2.81	2.77	23.78	23.87	14.23	14.43
D	$3\text{Cy}_2\text{NH}_2\text{HSO}_4 \cdot 2\text{SnMe}_2\text{Cl}_2$	37.57	37.42	6.81	6.64	3.29	3.15	18.58	19.00	11.12	11.34
E	$\text{Et}_2\text{NH}_2\text{SO}_4\text{SnMe}_2\text{C} \cdot 2\text{H}_2\text{O}$	18.45	18.22	5.64	5.54	3.59	3.73				
F	$(\text{Cy}_2\text{NH}_2)_2\text{SO}_4 \cdot \text{SnBu}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	48.02	48.26	8.75	8.64	3.50	3.45				
G	$\text{Cy}_2\text{NH}_2\text{HSO}_4 \cdot \text{SnMe}_3\text{Cl}$	37.56	37.46	7.09	6.93	2.92	3.07				
H	$(\text{isoBu})_2\text{NH}_2\text{SnMe}_2\text{Cl}_3$	29.05	29.24	7.15	7.04	3.46	3.39				

* - calculated;

** - found.

The elemental analyses have been performed by the CNRS “Service Central d’Analyses” Vernaison-France or the Centre of Microanalyses, University of Bath, UK. The IR spectra were recorded at the University of Cheikh Anta Diop (Dakar, Sénégal) and at the University College of Saint-Boniface (Winnipeg, Canada) by means of a Bruker FT-IR spectrometer, at the University of Padova (Italy) using a PE 580 or a Bruker FTIR spectrometer, the sample being as Nujol mulls, the windows being CsI or polyethylene. Mössbauer spectra were obtained as described previously [9, 10]. Infrared data are given in cm^{-1} [abbreviations: (vs) very strong, (s) strong, (m) medium, (w) weak, (sh) shoulder]. Mössbauer parameters are given in $\text{mm} \cdot \text{s}^{-1}$ (abbreviations: Q.S = quadrupole splitting, I.S = isomer shift, Γ = full width at half-height, A = Area). All the chemicals are from Aldrich Company and were used without any further purification.

RESULTS AND DISCUSSION

Let us consider the more relevant IR bands of the studied compounds:

(A): $\nu \text{SnC}_2 = 691 \text{ m}$; $\nu \text{SnC}_2 = 625 \text{ w}$; $\nu \text{SO}_4 = (1060 \text{ vs}, 1150 \text{ sh}, 1224 \text{ vs})$; $\delta \text{SO}_4 = 589 \text{ s}$; $\nu \text{SnCl} = 254 \text{ m}$;

(B): $\nu \text{SnC}_2 = 557 \text{ w}$; $\nu \text{SO}_4 = (979 \text{ m}, 1080 \text{ s}, 1111 \text{ vs})$; $\delta \text{SO}_4 = (427 \text{ vs}, 592 \text{ m}, 619 \text{ m})$; $\nu \text{SnCl} = 302 \text{ s}$; $\nu \text{SnO} = 212 \text{ w}$; $\nu \text{NH}_2 = 3434 \text{ s}$; $\delta \text{NH}_2 = 1646 \text{ s}$;

(C): $\nu \text{SnC}_2 = 549 \text{ m}$; $\nu \text{SnCl} = 253 \text{ m}$; $\nu \text{SnO} = 202 \text{ s}$; $\nu \text{SO}_4 = (964 \text{ w}, 1095 \text{ s}, 1184 \text{ vs})$; $\delta \text{SO}_4 = (445 \text{ w}, 592 \text{ vs})$; $\nu \text{NH}_2 = 3434 \text{ s}$; $\delta \text{NH}_2 = 1646 \text{ s}$;

(D): $\nu \text{SnC}_2 = 520 \text{ w}$; $\nu \text{SnC}_2 = 547 \text{ m}$; $\nu \text{SO}_4 = (964 \text{ m}, 1057 \text{ sh}, 1095 \text{ s}, 1140 \text{ sh})$; $\delta \text{SO}_4 = (445 \text{ w}, 592 \text{ m})$; $\nu \text{SnCl} = 254 \text{ vs}$; $\nu \text{SnO} = 202 \text{ w}$; $\nu \text{NH}_2 = 3434 \text{ s}$; $\delta \text{NH}_2 = 1646 \text{ s}$;

(E): $\nu \text{SnC}_2 = 519 \text{ m}$; $\nu \text{SnCl} = 353 \text{ m}$; $\nu \text{SnO} = 212 \text{ s}$; $\nu \text{SO}_4 = (1050 \text{ vs}, 1195 \text{ vs})$; $\delta \text{SO}_4 = (427 \text{ vs}, 584 \text{ vs})$; $\nu \text{NH}_2 = 3434 \text{ s}$; $\delta \text{NH}_2 = 1646 \text{ s}$;

(F): $\nu \text{SnC}_2 = 546 \text{ s}$; $\nu \text{SnC}_2 = 520 \text{ m}$; $\nu \text{SnCl} = 254 \text{ vs}$; $\nu \text{SnO} = 202 \text{ w}$; $\nu \text{NH}_2 = (3100 \text{ s}, 3530 \text{ s})$; $\delta \text{NH}_2 = (1594 \text{ s}, 1610 \text{ s})$;

(G): $\nu \text{SnC}_2 = 622 \text{ s}$; $\nu \text{SnC}_2 = 595 \text{ m}$; $\nu \text{SO}_4 = (1040 \text{ s}, 1174 \text{ s})$; $\nu \text{NH}_2 = 3430 \text{ s}$; $\delta \text{NH}_2 = 1566 \text{ m}$;

(H): $\nu \text{SnC}_2 = 557 \text{ m}$; $\nu \text{SO}_4 = (871 \text{ vs}, 1035 \text{ vs}, 1120 \text{ vs})$; $\delta \text{SO}_4 = (452 \text{ m}, 480 \text{ m}, 580 \text{ m}, 616)$; $\nu \text{NH}_2 = (2856 \text{ vs}, 2937 \text{ vs}, 3047 \text{ vs})$; $\delta \text{NH}_2 = 1594 \text{ s}$;

and their Mossbauer data:

(A): $\text{IS} = 1.68$, $\text{QS} = 4.18$, $\Gamma = 1.00$;

(B): $\text{IS} = 1.52$, $\text{QS} = 3.72$, $\Gamma = 1.02$;

(C): n/a

(D): $\text{IS} = 1.58$, $\text{QS} = 4.85$, $\Gamma = 1.01$;

(E): $\text{IS}_1 = 1.41$, $\text{QS}_1 = 2.83$, $\Gamma_1 = 0.97$, $A_1 = 50$, $\text{IS}_2 = 0.94$, $\text{QS}_2 = 2.24$, $\Gamma_2 = 0.87$, $A_2 = 50$;

(F): $\text{IS} = 1.05$, $\text{QS} = 2.01$, $\Gamma = 0.98$;

(G): $\text{QS} = 3.67$, $\text{IS}_1 = 1.04$, $\Gamma = 0.98$;

(H): $\text{IS} = 0.80$, $\text{QS} = 3.19$, $\Gamma = 0.90$.

Bu₄NHSO₄·SnBu₂Cl₂ (A), Cy₂NH₂HSO₄·SnBu₂Cl₂ (B), Cy₂NH₂HSO₄·SnMe₂Cl₂ (C)

The values of the quadrupole splitting of **(A)** and **(B)** (4.18 and 3.72 mm·s⁻¹) are consistent with trans coordinated SnBu₂ residue according to Platt *et al.* [12, 13]. The absence of νSnMe_2 on the IR spectrum of **(C)** is an indication of the presence of a *trans* coordinated SnR₂ residue according to Group Theory [14].

The Mössbauer and infrared data allow to suggest while considering the complex-anion [HSO₄·SnR₂Cl₂]⁻ (R = Me, Bu), the structure reported on Figure 1, the hydrogenosulfate behaving as a monochelating ligand. The monomers are linked by OH----O hydrogen bonds leading to a dimeric structure.

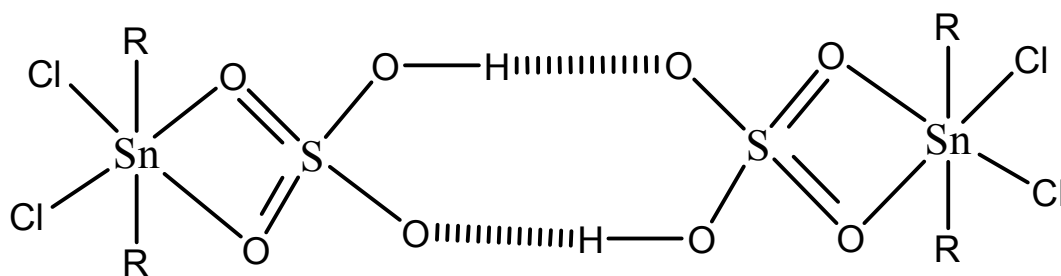


Figure 1. Dimeric structure of the complex-anion [HSO₄·SnR₂Cl₂]⁻ (R = Me, Bu)

In the case of **(B)** and **(C)** when the cations, involved through hydrogen bonds (NH----O or NH----Cl) are considered, supramolecular architecture are obtained.

3C₂NH₂HSO₄·2SnMe₂Cl₂ (D)

While considering the complex-anion $[(H-OSO_3)_3(SnMe_2Cl_2)_2]^{3-}$, the value of the quadrupole splitting ($4.85 \text{ mm}\cdot\text{s}^{-1}$) indicates a SnMe_2 residue in a *trans* octahedral environment according to Platt *et al.* [12, 13] allowing to suggest the dimeric structure reported on Figure 2 (the very high value of the QS indicates planar SnMe_2Cl_2 molecules belonging to D_{2h} point group). When the cations are involved through $\text{NH}\cdots\text{O}$ or $\text{NH}\cdots\text{Cl}$ hydrogen bonds create supramolecular architectures.

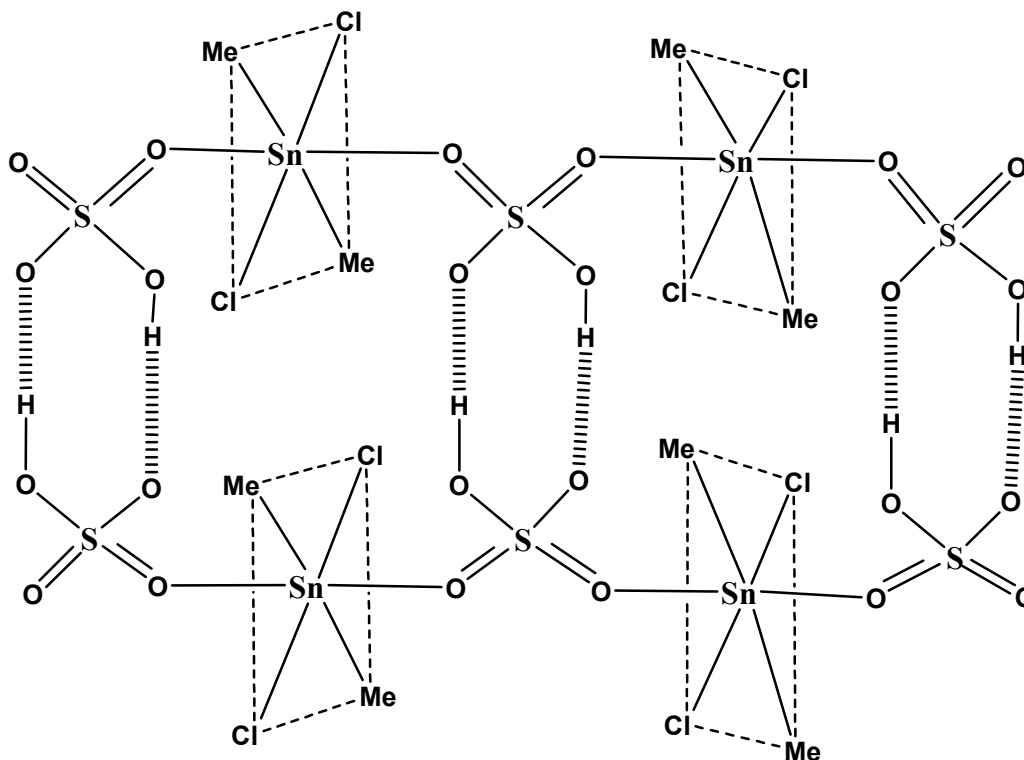


Figure 2. Structure of the the complex-anion $[(H-OSO_3)_3(SnMe_2Cl_2)_2]^{3-}$

Et₂NH₂SO₄SnMe₂Cl·2H₂O (E)

The Mössbauer data show the presence of two types of tin centre in (E) consistent with the presence of the complex-anion $[SnMe_2(SO_4)_2]^{2-}$ (in *cis* conformation ($QS = 2.24 \text{ mm}\cdot\text{s}^{-1}$) with monochelating sulfate anions, the tin centre being octahedral and tetrahedral lattice SnMe_2Cl_2 molecules ($QS = 2.83 \text{ mm}\cdot\text{s}^{-1}$) according to Platt *et al.* [12, 13] – in SnPh_2Cl_2 , $QS = 2.88 \text{ mm}\cdot\text{s}^{-1}$. The complex anions are hold together by cations through hydrogen bonds giving a supramolecular structure, a piece of which is reported in Figure 3 (a structure containing lattice SnMe_2Br_2 molecules has yet been reported from an X ray study) [15]. The anion $[SnMe_2(SO_4)_2]^{2-}$ is structurally similar to $[SnMe_2(C_2O_4)_2]^{2-}$ yet reported [16, 17]. To the best of our knowledge a tetrahedral SnMe_2Cl_2 has never been characterized by Mössbauer spectroscopy. The water molecules can be lattice ones or involved in the hydrogen bonds network of the supramolecular architecture.

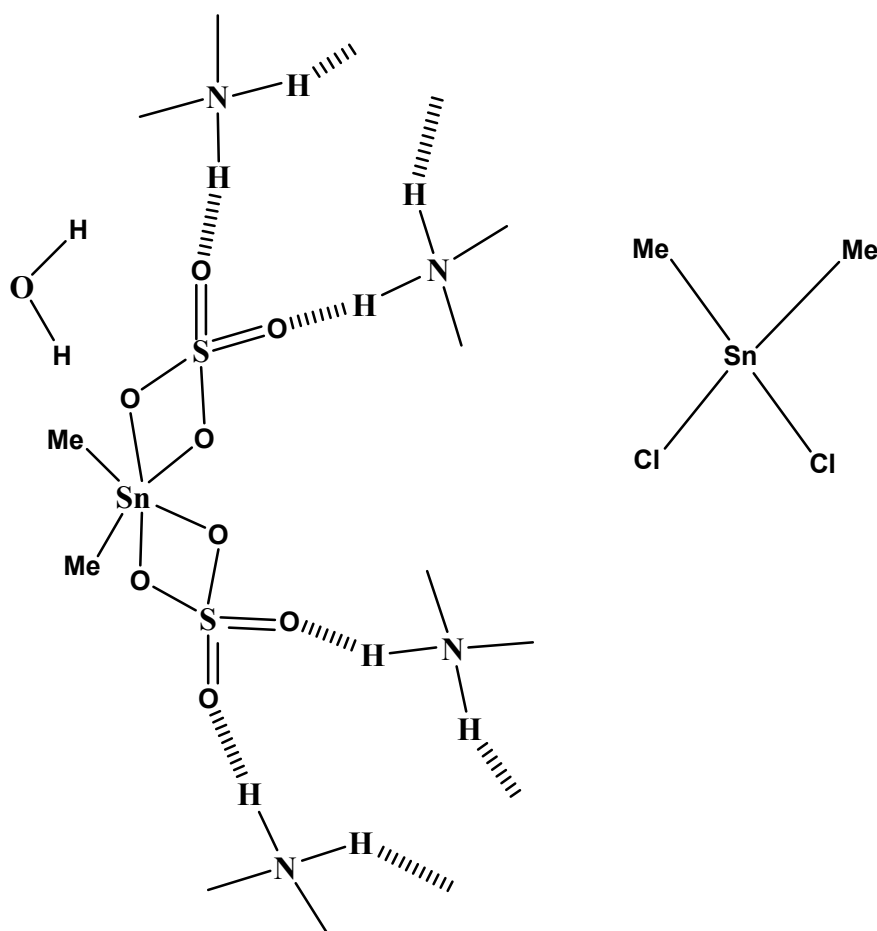


Figure 3. Supramolecular structure of adduct (E)

(Cy₂NH₂)₂SO₄·SnBu₂Cl₂·2H₂O (F)

The value of the quadrupole splitting (QS = 2.01) is consistent with a SnBu₂ residue *cis* octahedrally coordinated according to Platt *et al.* [12, 13] allowing to suggest while considering the complex-anion [SO₄·SnBu₂Cl₂]²⁻ the discrete structure reported on Figure 4). When the cations, through NH---O or NH---Cl hydrogen bonds are involved, supramolecular architecture are obtained (we report arbitrary the dimeric structure involving the cations in Figure 5).

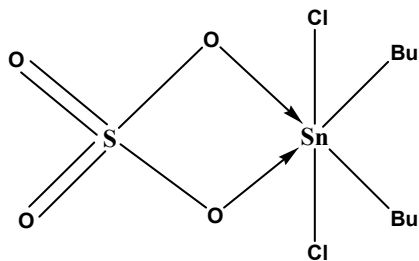


Figure 4. Structure of the complex-anion [SO₄·SnBu₂Cl₂]²⁻

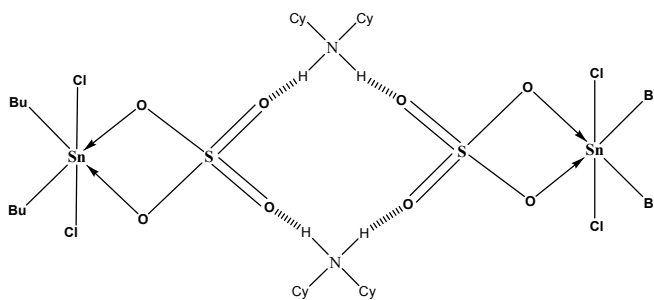


Figure 5. The supramolecular structure due to the NH---O or NH---Cl hydrogen bonds

Cy₂NH₂HSO₄·SnMe₃Cl (G)

In recent papers we have reported the X ray structure of Bu₄NHSO₄·SnMe₃Cl [5, 6]. The value of the quadrupole splitting ($QS = 3.67 \text{ mm}\cdot\text{s}^{-1}$) of this compound is consistent with a trans coordinated SnMe₃ residue [12, 13] allowing to suggest while considering the complex-anion $[\text{HO-SO}_3\cdot\text{SnMe}_3\text{Cl}]^-$ a dimeric structure similar to the one reported for Bu₄NHSO₄·SnMe₃Cl (Figure 6).

When the cation, through NH---O or NH---Cl hydrogen bonds is involved, supramolecular architectures are obtained.

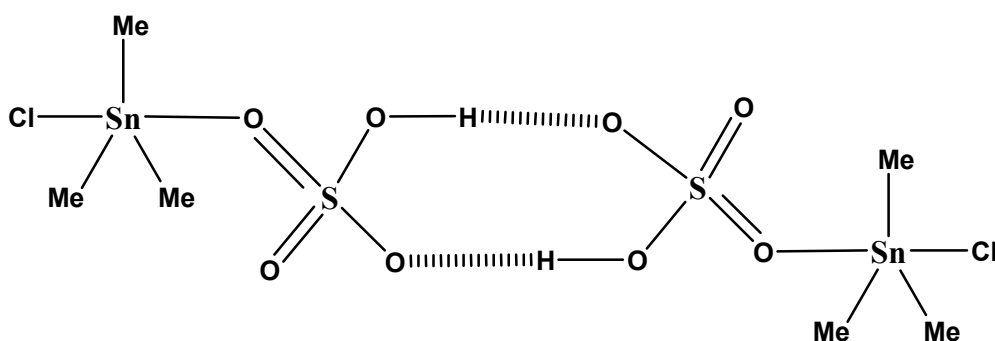


Figure 6. Supramolecular structures obtained from dimeric $[\text{HO-SO}_3\cdot\text{SnMe}_3\text{Cl}]^-$ anions

(isoBu₂)₂NH₂SnMe₂Cl₃ (H)

The quadrupole splitting of **(F)** ($3.19 \text{ mm}\cdot\text{s}^{-1}$) is consistent with a trigonal bipyramidal environment around the tin (IV) centre as yet reported in [18, 19] and allows to suggest a supramolecular architecture, when cations are involved through NH---Cl hydrogen bonds (infinite chains or oligomers). We have arbitrary reported the dimer and the infinite chain (Figures 7 and 8).

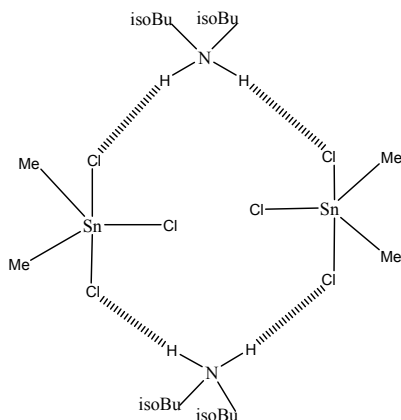


Figure 7. Structure of $(\text{isoBu}_2)_2\text{NH}_2\text{SnMe}_2\text{Cl}_3$ dimer

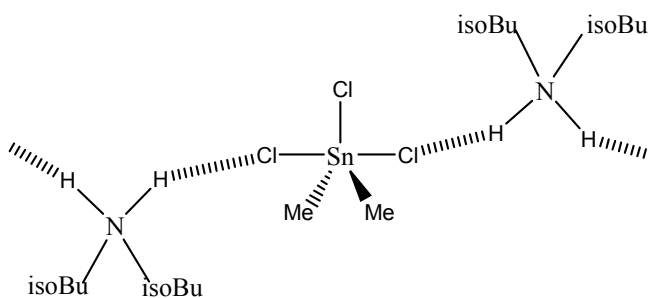


Figure 8. Part of the $(\text{isoBu}_2)_2\text{NH}_2\text{SnMe}_2\text{Cl}_3$ infinite chain

The wide absorption on the infrared spectra of all compounds containing a nonsymmetrical cation around 2900 cm^{-1} is due to hydrogen bonds involving the cation or HSO₄⁻.

CONCLUSION

The structure of the studied adducts are discrete mainly or polymeric while considering the complex-anion. When the cations are involved, supramolecular structures are obtained. The anions are chelating, monocoordinating or bidentate ligands. Tetrahedral SnMe_2Cl_2 has been characterized spectroscopically.

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