

## CARBOXYLATO ADDUCTS AND DERIVATIVES CONTAINING $\text{SnR}_3$ (R = Ph, Me) AND $\text{SnMe}_2$ RESIDUES: SYNTHESIS, INFRARED AND MÖSSBAUER STUDIES

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**Abstract:** Twelve new carboxylato adducts and derivatives containing  $\text{SnR}_3$  (R = Ph, Me) and  $\text{SnMe}_2$  residues have been synthesized and characterized by elemental analyses, infrared and <sup>119</sup>Sn-Mössbauer spectroscopies. The proposed structures are discrete or of infinite chain type, the carboxylate anion behaving as a bridging bidentate, a monodentate, a tetradentate or a monochelating ligand.

**Keywords:** carboxylate, discrete or infinite chain structures,  $\text{SnR}_3$  (Ph, Me) and  $\text{SnMe}_2$  residues, trigonal bipyramidal environment around tin (IV), supramolecular architectures

### 1. INTRODUCTION

Because of the applications found within the family of organotin (IV) (industry, medicine, agriculture) many research groups have been searching new compounds belonging to this family [1-5]; our group which is one of those has already reported many papers [6-8]. In this dynamic, we have synthesized in this work twelve new carboxylato adducts and derivatives, obtained by reacting:

- $\text{SnPh}_3\text{OH}$  with dinitrobenzoic acid;
- $\text{SnPh}_3\text{Cl}$ ,  $\text{SnMe}_3\text{Cl}$  or  $\text{SnMe}_2\text{Cl}$  with some salts;
- $\text{HOC}_6\text{H}_4\text{CO}_2\text{SnPh}_3$  derivative with some salts;
- $\text{SnMe}_3\text{OH}$  with some acids after its obtention from  $\text{SnMe}_3\text{Cl}$  by KCl precipitation.

These compounds have been characterized *via* infrared and <sup>119</sup>Sn-Mössbauer studies.

### 2. EXPERIMENTAL SETUP

#### 2.1. Salts synthesis

$\text{Me}_4\text{NHXC}_6\text{H}_4\text{CO}_2\cdot\text{H}_2\text{O}$  (**L**<sub>1</sub>, **L**<sub>2</sub>; X = O, S),  $(\text{Me}_4\text{N})_2(\text{CH}_2)_4(\text{CO}_2)_2(\text{SnPh}_3)_2\cdot 2\text{H}_2\text{O}$  (**L**<sub>3</sub>),  $\text{Me}_4\text{NPhCH}=\text{CHCO}_2\cdot 2\text{H}_2\text{O}$  (**L**<sub>4</sub>),  $\text{Me}_4\text{N}(\text{NO}_2)_2\text{C}_6\text{H}_3\text{CO}_2\cdot\text{H}_2\text{O}$  (**L**<sub>5</sub>) have been obtained by reacting in water salicylic, thiosalicylic, adipic, cinnamic and dinitrobenzoic acids (Merck products) with a 25% water solution of tetramethylammonium hydroxide (Merck products) in 1:1 or 1:2 ratio while  $(\text{Cy}_2\text{NH}_2)_2(\text{CH}_2\text{CH}_2\text{CO}_2)_2\cdot\text{H}_2\text{O}$  (**L**<sub>6</sub>)

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has been obtained by reacting in water adipic acid with dicyclohexylamine in 1:1 ratio. The solutions have been evaporated in an oven (60 °C) giving powders or crystals which are recrystallized from ethanol, washed with ether and then maintained under P<sub>2</sub>O<sub>5</sub> in a desiccator.

## 2.2. Complexes synthesis

The compounds **A-L** have been obtained by mixing:

- (**A**): L<sub>3</sub> (1.360 mmol) in ethanol with SnPh<sub>3</sub>Cl (2.720 mmol) in ethanol in 1:2 ratio;
- (**B**): dinitrobenzoic acid (1.360 mmol) in ethanol with SnPh<sub>3</sub>OH (1.360 mmol) in ethanol in 1:1 ratio;
- (**C**) and (**J**): respectively (L<sub>1</sub>) (0.820 mmol) in ethanol with HOC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>SnPh<sub>3</sub> (0.820 mmol) in 1:1 ratio or SnMe<sub>2</sub>Cl<sub>2</sub> in ethanol in 1:1. [HOC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>SnPh<sub>3</sub> is prepared by mixing in ethanol HOC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H and SnPh<sub>3</sub>OH in 1-1 ratio];
- (**D**): Me<sub>4</sub>NSCN (2.080 mmol) in ethanol with HOC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>SnPh<sub>3</sub> (2.080 mmol) in ethanol in 1:1 ratio;
- (**E**): (L<sub>2</sub>) (1.820 mmol) in ethanol with SnPh<sub>3</sub>Cl (1.820 mmol) in dichloromethane in 1:1 ratio;
- (**F**): in EtOH adipic acid (6.070 mmol), SnMe<sub>3</sub>Cl (12.140 mmol) and KOH (12.140 mmol) in 1:2:2 ratio;
- (**G**): in MeOH cinnamic acid (5.320 mmol), SnMe<sub>3</sub>Cl (5.320 mmol) and KOH (5.320 mmol) in 1:1:1 ratio;
- (**H**): in MeOH thiosalicylic acid (2.560 mmol), SnMe<sub>3</sub>Cl (2.560 mmol) and KOH (2.560 mmol) in 1:1:1 ratio;
- (**I**): (L<sub>6</sub>) (6.720 mmol) in methanol with SnMe<sub>3</sub>Cl (13.440 mmol) in dichloromethane in 1:2 ratio;
- (**J**): (L<sub>1</sub>) (2.270 mmol) in ethanol with SnMe<sub>2</sub>Cl<sub>2</sub> (2.270 mmol) in ethanol in 1:1 ratio;
- (**K**): in EtOH (L<sub>4</sub>) (2.560 mmol) with SnMe<sub>2</sub>Cl<sub>2</sub> (2.560 mmol) 1:1 ratio;
- (**L**): (L<sub>5</sub>) (2.270 mmol) in ethanol with SnMe<sub>2</sub>Cl<sub>2</sub> (2.270 mmol) in dichloromethane in 1:1 ratio.

The various complexes were obtained as crystals or white precipitates stirred for around two hours, filtered and washed with hot ethanol.

The analytical data reported in Table 1, have allowed to suggest the following formulae.

Table 1. Results of elemental analyses of synthesized salts and complexes.

Compound	Suggested formulae	Chemical composition [% mass]					
		C		H		N	
		Calc.	Found	Calc.	Found	Calc.	Found
L <sub>1</sub>	Me <sub>4</sub> NHOC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> ·H <sub>2</sub> O	57.64	57.54	8.29	8.31	6.11	6.22
L <sub>2</sub>	Me <sub>4</sub> NHSC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> ·H <sub>2</sub> O	53.87	53.65	7.75	7.62	5.71	5.77
L <sub>3</sub>	(Me <sub>4</sub> N) <sub>2</sub> (CH <sub>2</sub> ) <sub>4</sub> (CO <sub>2</sub> ) <sub>2</sub> (SnPh <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	51.22	51.42	10.97	10.91	8.54	8.65
L <sub>4</sub>	Me <sub>4</sub> NPhCH=CHCO <sub>2</sub> ·2H <sub>2</sub> O	60.70	60.59	8.95	8.87	5.45	5.52
L <sub>5</sub>	Me <sub>4</sub> N(NO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CO <sub>2</sub> ·H <sub>2</sub> O	43.56	43.58	5.61	5.59	13.86	13.80
L <sub>6</sub>	(C <sub>7</sub> NH <sub>2</sub> ) <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> ) <sub>2</sub> ·H <sub>2</sub> O	68.44	68.58	11.03	11.11	5.32	5.42
A	(CH <sub>2</sub> ) <sub>4</sub> (CO <sub>2</sub> ) <sub>2</sub> (SnPh <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O)	59.75	59.51	4.50	4.53	–	–
B	(NO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CO <sub>2</sub> SnPh <sub>3</sub> ·H <sub>2</sub> O	51.85	51.72	3.48	3.30	4.84	4.83
C	Me <sub>4</sub> N(HOC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> ) <sub>2</sub> SnPh <sub>3</sub>	61.91	61.72	5.29	5.32	2.00	1.98
D	Me <sub>4</sub> NHOC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> SnPh <sub>3</sub> SCN	58.08	57.92	5.36	5.23	4.52	4.40
E	Me <sub>4</sub> NHSC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> ·SnPh <sub>3</sub> Cl	56.84	56.68	5.22	5.24	2.28	2.32
F	(CH <sub>2</sub> ) <sub>4</sub> (CO <sub>2</sub> ) <sub>2</sub> (SnMe <sub>3</sub> ) <sub>2</sub>	30.54	30.64	5.51	5.62	–	–
G	PhCH=CHCO <sub>2</sub> SnMe <sub>3</sub>	46.35	46.52	5.19	5.24	–	–
H	HSC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> SnMe <sub>3</sub>	37.89	37.67	4.42	4.58	–	–
I	(C <sub>7</sub> NH <sub>2</sub> ) <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> ) <sub>2</sub> ·2SnMe <sub>3</sub> Cl	45.48	45.51	7.16	7.28	3.31	3.26
J	HOC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> SnMe <sub>2</sub> Cl	33.62	33.54	3.10	3.14	–	–
K	PhCH=CHCO <sub>2</sub> ·SnMe <sub>2</sub> Cl	39.85	39.82	3.93	3.94	–	–
L	Me <sub>4</sub> N(NO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CO <sub>2</sub> ·SnMe <sub>2</sub> Cl <sub>2</sub>	30.91	30.88	4.10	4.07	8.32	8.42

Elemental analyses have been obtained at the Service Central d'Analyse (SCA-CNRS) (Vernaison, France) or in the Laboratory of microanalyses from University of Padova (Italy). The infrared spectra have been obtained at the University of Padova (Italy) using a PE580 spectrophotometer, as Nujol mulls using CsI optical windows while the Mössbauer spectra were recorded at the Louvain La Neuve University (Belgium) at 80 K as reported in [9]. Infrared abbreviations: vs = very strong; s = strong; vvw = very very weak; w = weak; m = medium; sh = shoulder; ν = stretching vibration; ν<sub>s</sub> = symmetric stretching vibration; ν<sub>as</sub> = antisymmetric stretching vibration;

$\delta$  = deformation vibration. Mössbauer abbreviations:  $\Delta E$  = quadrupole splitting;  $\delta$  = isomer shift;  $\Gamma$  = full width at half-height.

### 3. RESULTS AND DISCUSSION

In Tables 2 and 3, the main infrared and Mössbauer data of the twelve compounds are reported.

Table 2. Frequencies in  $\text{cm}^{-1}$  of the main IR bands of the compounds A-L.

Compound	Attributions $\nu\text{CO}_2$	$\delta\text{CO}_2$	$\nu_{\text{as}}\text{SnC}_n$ $n = 2, 3$	$\nu_{\text{s}}\text{SnC}_n$ $n = 2, 3$	$\nu\text{SnCl}$	$\nu\text{SnO}$
A	1572 (m) 1523 (vs) 1304 (m) 1237 (w)	785 (m)	276 (m)	217 (vvw)	–	202 (m)
B	1633 (vs) 1539 (vs)	787 (m)	274 (vs)	216 (m)	–	202 (m)
C	1576 (s) 1304 (s)	760 (s) 666 (s)	277 (vs)	–	–	202 (m)
D	1575 (m) 1302 (m)	761 (m) 667 (m)	277 (s)	–	–	202 (m)
E	1633 (s) 1607 (s)	749 (s) 655 (m)	276 (vs)	217 (w)	276(vs)	201 (s)
F	1552 (vs) 1377 (m)	771 (vs)	555 (s)	513 (vvw)	–	235 (m)
G	1640 (s) 1577 (m) 1378 (vs) 1255 (m)	774 (vs)	554 (sh)	515 (w)	–	219 (s)
H	1620 (sh) 1580 (vs) 1555 (s) 1377 (vs)	783 (s) 654 (m)	568 (m)	518 (w)	–	229 (s)
I	1557 (vs) 1377 (vs) 1280 (w)	771 (vs) 649 (s)	553 (m)	515 (vvw)	253(sh)	227 (m)
J	1655 (s) 1611 (vs) 1578 (vs) 1377 (vs) 1295 (s)	784 (m) 659 (m)	567 (m)	–	264(s)	210 (m)
K	1639 (vs) 1580 (m) 1548 (s) 1376 (vs)	770 (vs)	562 (s)	514 (s)	296(vs)	257 (s)
L	1622 (vs) 1550 (vs) 1537 (vs) 1346 (vs)	791 (s) 644 (w)	570 (m)	519 (s)	243(s)	212 (s)

Table 3. Mössbauer parameters for compounds A-L.

Compound	$\Delta E$ ( $\text{mm}^{-1}$ )	$\delta$ ( $\text{mm}^{-1}$ )	$\Gamma$ ( $\text{mm}^{-1}$ )
A	3.19	1.20	0.92
B	3.36	1.29	0.88
C	3.10	1.38	0.90
D	3.21	1.21	1.00
E	3.44	1.27	0.81
F	3.64	1.30	0.94
G	3.50	1.23	0.89
H	3.53	1.27	0.96
I	3.80	1.29	0.89
J	3.58	1.34	0.94
K	3.43	1.20	0.98
L	3.70	1.40	0.87

– For the derivatives **A** and **B**, the values of the quadrupole splitting greater than  $3 \text{ mm s}^{-1}$  are consistent with *trans* coordinated  $\text{SnPh}_3$  residues according to Brancoft and Platt [10] allowing to propose a discrete structure with a bidentate carboxylate and coordinating water molecules (Figure 1) and an infinite chain with a bridging carboxylate anion for **A** and **B** respectively (Figure 2), the environment around the tin (IV) atom being in both cases trigonal bipyramidal.

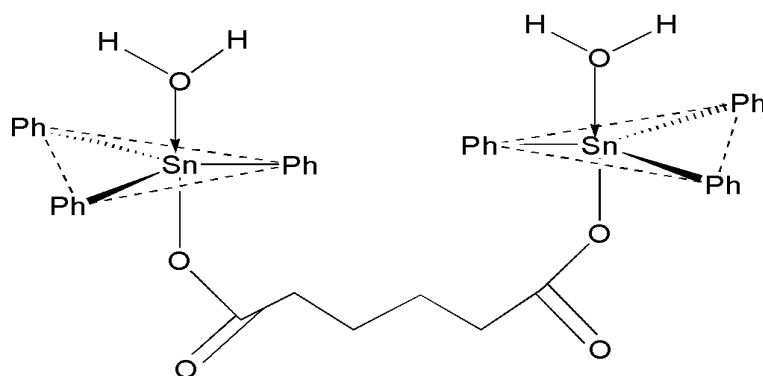


Fig. 1. Proposed structure for A.

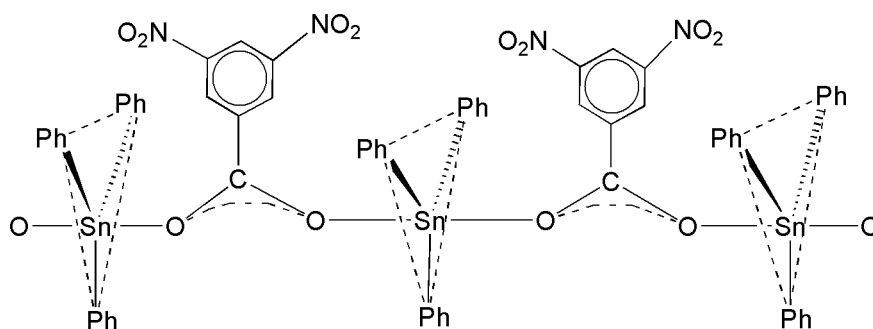


Fig. 2. Proposed structure for B.

– For the adducts **C**, **D** and **E**, the values of the quadrupole splitting (over  $3 \text{ mm s}^{-1}$ ) indicate the presence of *trans* coordinated  $\text{SnPh}_3$  residues (case of **C**) or monocoordinated  $\text{SnPh}_3\text{X}$  ( $\text{X} = \text{SCN}, \text{Cl}$ ) molecules (**D**, **E**) allowing to propose the discrete structures (Figures 3, 4 and 5), the carboxylate anions behaving as a monodentate ligand.

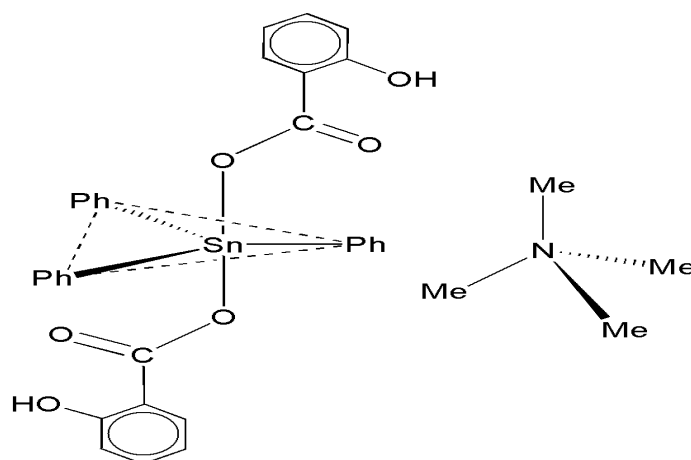


Fig. 3. Proposed structure for C.

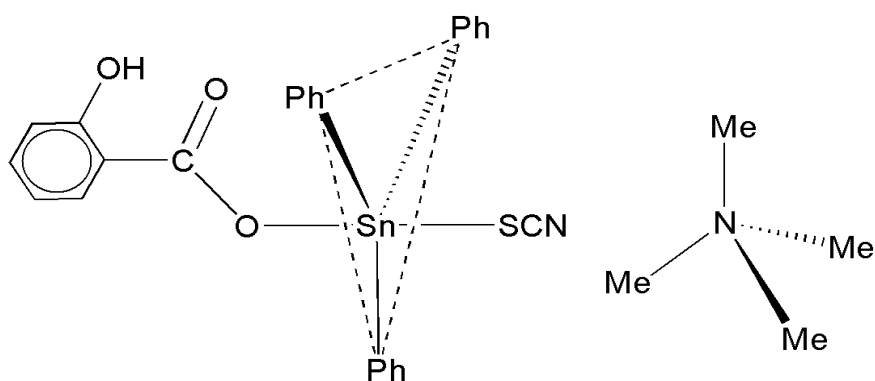


Fig. 4. Proposed structure for D.

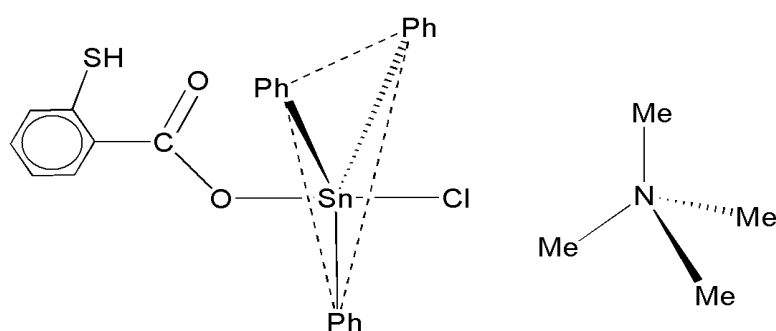


Fig. 5. Proposed structure for E.

N.B.: The quality of the infrared spectra of compounds **C** and **D** did not allow to locate  $\nu\text{OH}$  and  $\nu\text{SH}$

– For **F**, **G** and **H**, the Mössbauer data are consistent with transcoordinated  $\text{SnMe}_3$  residues ( $\text{SnC}_3\text{O}_2$  *trans* trigonal bipyramidal environment), allowing to propose a 3D structure for **F** and infinite chain structures for **G** and **H** (Figures 6, 7 and 8), the carboxylate anions behaving as a tetradentate or bridging bidentate ligand.

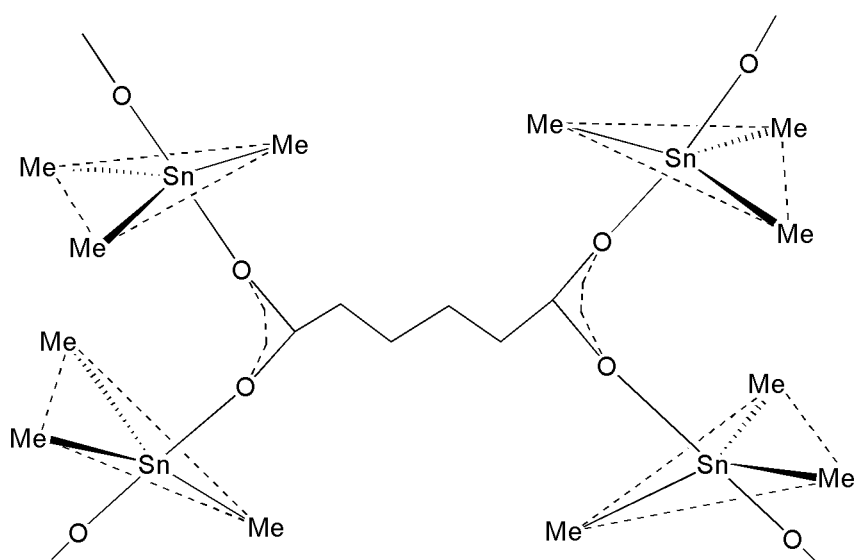


Fig. 6. Proposed structure for F.

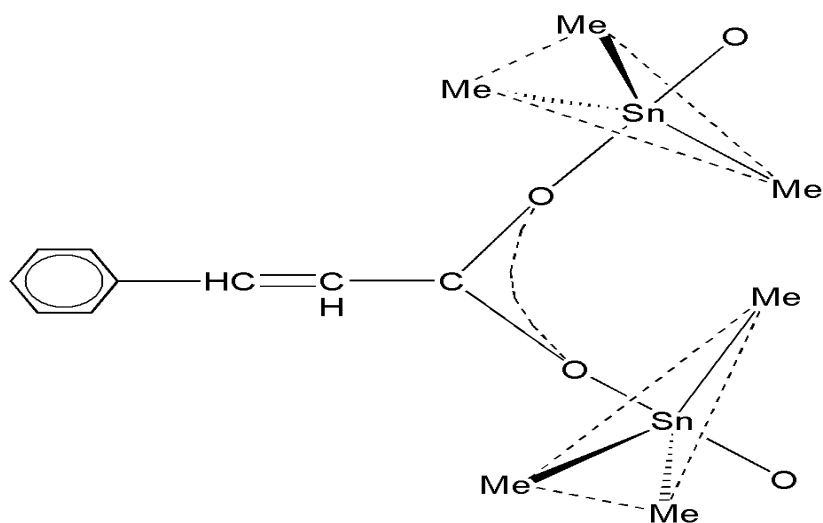


Fig. 7. Proposed structure for G.

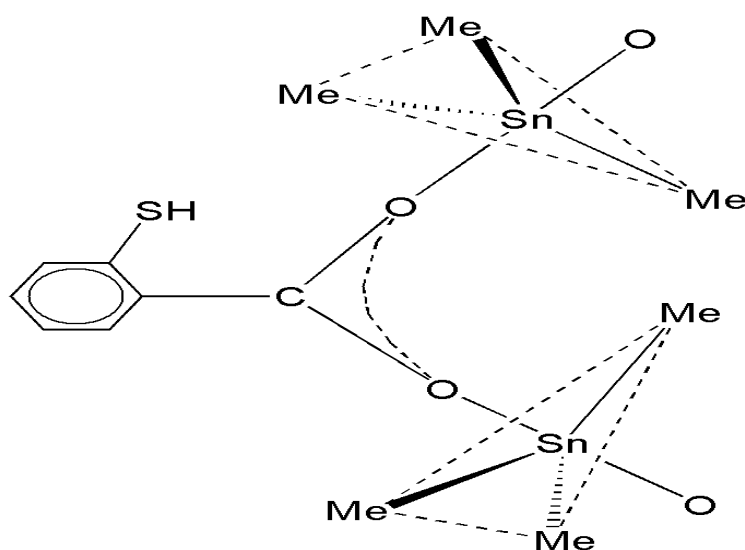


Fig. 8. Proposed structure for H.

– For **I**, the value of the quadrupole splitting ( $\Delta E = 3.80 \text{ mm}\cdot\text{s}^{-1}$ ) is in agreement with a transcoordinated  $\text{SnMe}_3$  residue, monocoordinated  $\text{SnMe}_3\text{Cl}$  ( $\text{SnC}_3\text{OCl}$  *trans* trigonal bipyramidal environment). A discrete structure has been proposed with a bidentate carboxylate anion (Figure 9). In this compound when cations are considered interacting through  $\text{N}\cdots\text{H}\cdots\text{O}$  hydrogen bonds, a supramolecular architecture may be obtained.

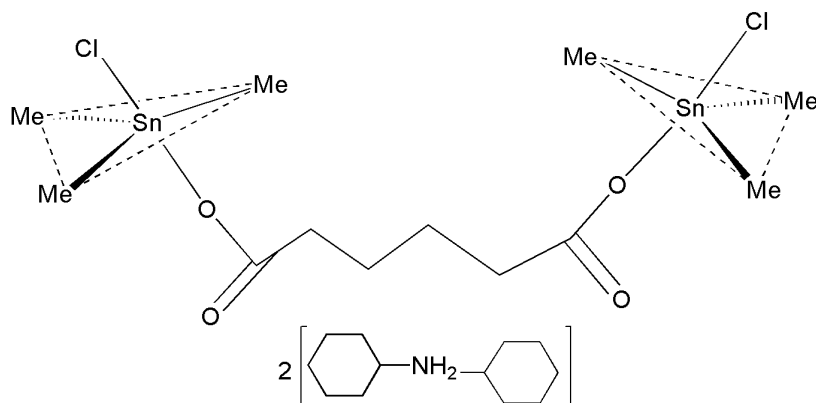


Fig. 9. Proposed structure for I.

– For **J** and **K**, the Mössbauer parameters for the two compounds respectively ( $\Delta E = 3.58 \text{ mm s}^{-1}$ ;  $\delta = 1.34 \text{ mm s}^{-1}$ ;  $\Gamma = 0.94 \text{ mm s}^{-1}$ ) and ( $\Delta E = 3.43 \text{ mm s}^{-1}$ ;  $\delta = 1.20 \text{ mm s}^{-1}$ ;  $\Gamma = 0.98 \text{ mm s}^{-1}$ ) are similar. The proposed structure is an infinite chain, the environment around tin atom being trigonal bipyramidal (Figure 10), the anion behaving as a bridging bidentate ligand:

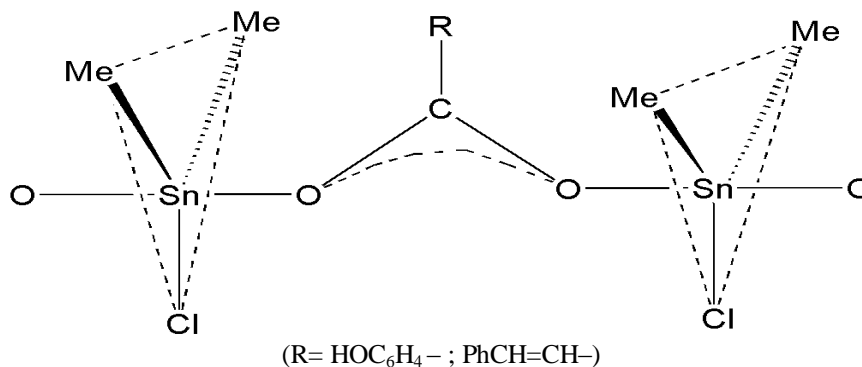


Fig. 10. Proposed structure for J and K.

– For **L**,  $\nu_8 \text{SnC}_2$  is localized at  $519 \text{ cm}^{-1}$  showing the presence of a bent  $\text{SnC}_2$  group. The value of the quadrupole splitting ( $\Delta E = 3.70 \text{ mm s}^{-1}$ ) indicates a *trans* octahedral environment around the tin atom allowing to proposed the discrete structure reported on Figure 11, the carboxylate anion behaving as a monochelating ligand.

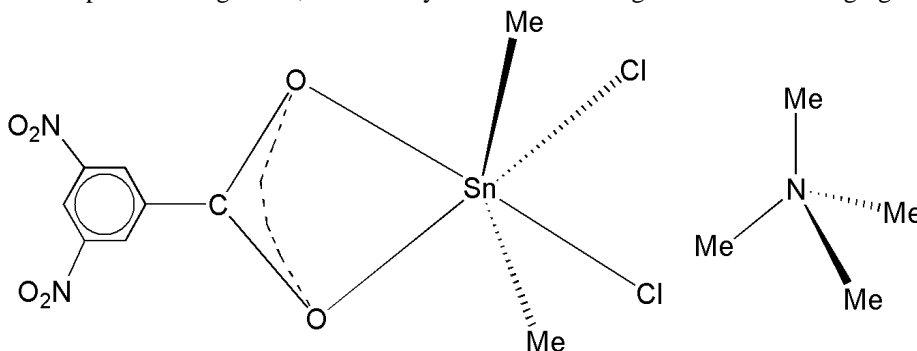


Fig. 11. Proposed structure for L.

#### 4. CONCLUSIONS

The carboxylato adducts and derivatives reported in this paper have discrete, 3D or infinite chain type structures, the anion behaving as a mono-, bi-, or tetracoordinating ligand or a monochelating one, the environment around the tin (IV) atom is in most cases trigonal bipyramidal or octahedral in the last compound. When the cation is involved through hydrogen bonds a supramolecular architecture may be obtained.

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