

## DEARYLATION IN THE INTERACTIONS BETWEEN (Et<sub>3</sub>NH)HC<sub>2</sub>O<sub>4</sub> OR (Et<sub>3</sub>NH)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> AND SnPh<sub>3</sub>Cl: INFRARED STUDY

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**Abstract:** Five new oxalato, hydrogenoxalato and hydrogenocarbonato adducts (three) and complexes (two) obtained on allowing (Et<sub>3</sub>NH)HC<sub>2</sub>O<sub>4</sub> or (Et<sub>3</sub>NH)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> to react with SnPh<sub>3</sub>Cl have been studied by infrared spectroscopy, then discrete structures suggested on the basis of spectroscopic data. The anions behave as monochelating ligands, the environments around the metallic centres being octahedral. In two of the compounds, the benzene molecules obtained *in situ* are lattice. In all these structures when considering the cation involved in extra hydrogen bonds, a supramolecular architecture may be obtained.

**Keywords:** discrete structures, hydrogen bonds, IR technic, lattice benzene molecules, monochelating oxoanions, octahedral environments, supramolecular architectures

### 1. INTRODUCTION

During the past few decades, the synthesis of new molecules belonging to organo- and halotin(IV) family have been of great research interest worldwide due to their applications in medicine and industry and also for structural considerations [1-5].

In this dynamic our group has initiated here the study of the interactions between (Et<sub>3</sub>NH) HC<sub>2</sub>O<sub>4</sub> or (Et<sub>3</sub>NH)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and SnPh<sub>3</sub>Cl which has yielded the five studied adducts and complexes. The new compounds obtained have been studied by infrared technic and structures suggested on the basis of infrared data.

### 2. MATERIALS AND METHODS

(Et<sub>3</sub>NH) HC<sub>2</sub>O<sub>4</sub>(L<sub>1</sub>) -[% Calculated (% Found): % C = 50.25(50.19), % H = 8.96(8.67), % N = 7.32(7.42)]- and (Et<sub>3</sub>NH)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (L<sub>2</sub>) -[ % C = 57.50(57.10), % H = 11.03(10.87), % N = 9.58(9.53)]- have been obtained as crystals on semi- or totally neutralizing H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> with Et<sub>3</sub>N in water and allowing the obtained solution to evaporate in the oven at 60°C.

When (L<sub>1</sub>) is allowed to react with SnPh<sub>3</sub>Cl, in ethanol in the ratio 1/1, 2/1 and 1/2 -**A**, **B**, **C**-, white powders are collected after a slow solvent evaporation. When ethanolic solutions of (L<sub>2</sub>) and SnPh<sub>3</sub>Cl are allowed to react in 1/2 and 1/1 ratio -**D** and **E**- white precipitates are obtained, stirred around two hours and filtered. The analytical data [% Calculated (% Found)], summarized on Table 1, have allowed to suggest the following formulae:

The elemental analyses have been obtained from the Microanalyses Laboratory (University of Burgundy, Dijon-France). The infrared spectra have been obtained from the University of Caen-France using a Bruker FT-IR spectrometer. IR abbreviations: broad (br), very strong (vs), strong (s), medium (m), shoulder (sh), weak (w).

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The chemicals were obtained from ALDRICH Company-Germany- and used as such.

Table 1. Analytical data.

Compound	% C	% H	% N
<b>A</b>	45.32 (45.28)	5.44 (5.59)	3.07 (3.13)
<b>B</b>	50.93 (50.78)	5.42 (5.61)	2.28 (2.30)
<b>C</b>	51.28 (51.25)	4.90 (4.88)	1.39 (1.38)
<b>D</b>	43.53 (43.61)	7.26 (7.35)	5.64 (5.61)
<b>E</b>	41.51 (41.66)	6.26 (6.38)	4.61 (4.65)

Note:

**A:** (Et<sub>3</sub>NH)HC<sub>2</sub>O<sub>4</sub>.SnPh<sub>2</sub>Cl<sub>2</sub>.1/4Et<sub>3</sub>NHCl

**B:** (Et<sub>3</sub>NH) HC<sub>2</sub>O<sub>4</sub>. SnPh<sub>2</sub>Cl<sub>2</sub>.C<sub>6</sub>H<sub>6</sub>

**C:** (Et<sub>3</sub>NH) HCO<sub>3</sub>. 2SnPh<sub>2</sub>Cl<sub>2</sub>. 2C<sub>6</sub>H<sub>6</sub>

**D:** (Et<sub>3</sub>NH)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.SnPhCl<sub>3</sub>.Et<sub>3</sub>NHCl.1/6C<sub>6</sub>H<sub>6</sub>

**E:** (Et<sub>3</sub>NH)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.SnPhCl<sub>3</sub>.1/6C<sub>6</sub>H<sub>6</sub>

### 3. RESULTS AND DISCUSSION

#### 3.1. General considerations

It seems worthy to outline the fact that the three first compounds -hydrogenoxalato- were obtained after a slow solvent evaporation while the two last ones -oxalato- were precipitates.

Dearylation of SnPh<sub>3</sub>Cl into SnPh<sub>2</sub>Cl<sub>2</sub> occurs in the obtention of **A**, **B**, **C** and into SnPhCl<sub>3</sub> for **D** and **E** (dearylation and lattice benzene molecules have yet been reported by Alcock and Roe [6]). For the compound **C**, beside the dearylation a cleavage of the C-C bond of the hydrogenoxalate is observed leading to an hydrogenocarbonate.

#### 3.2. Spectroscopic study

Let us consider the main infrared data of the studied compounds:

**L1:** (νOH + νNH) 2948 (br), vas(COO<sup>-</sup>) 1704 (m), 1665 (s), vs(COO<sup>-</sup>) 1321 (m), δ(COO<sup>-</sup>) 792(m);

**L2:** νNH 2987 (br), vas(COO<sup>-</sup>) 1650 (s), vs(COO<sup>-</sup>) 1348 (m), δ(COO<sup>-</sup>) 796 (m);

**A:** (νOH + νNH) 3039, 2735(br), vas(COO<sup>-</sup>) 1704 (m), 1665 (vs), (COO<sup>-</sup>) 1427 (sh), 1371 (m), δ(COO<sup>-</sup>) 788(m), phenyl bands 742 (s), 700 (s);

**B:** (νOH + νNH) 3050 (br), 2720 (br), (νC=O + vasCOO<sup>-</sup>) 1714 (m), 1703 (m), 1682 (s), 1670 (vs), 1615 (vs), vs(COO<sup>-</sup>) 1383 (sh), 1373 (vs), 1360 (sh), δ(COO<sup>-</sup>) 791 (s), phenyl bands 728 (vs), 695 (vs);

**C:** (νOH + νNH) 3150 (br), vas(CO<sub>3</sub><sup>-</sup>) 1714 (w), 1703 (w), 1680 (m), 1668 (m), 1620 (m), vs(CO<sub>3</sub><sup>-</sup>) 1375 (m), 1331 (m), 1303 (m), δ(CO<sub>3</sub><sup>-</sup>) 794 (m), phenyl bands 728 (vs), 694 (vs);

**D:** νNH 2970 (br), vas(COO<sup>-</sup>) 1714 (w), 1709 (w), 1661 (s), 1665 (vs), vs(COO<sup>-</sup>) 1371 (s), δ(COO<sup>-</sup>) 788 (s), phenyl bands 728 (vs), 695 (vs);

**E:** νNH 2971 (br), vas(COO<sup>-</sup>) 1703 (m), 1666 (vs), vs(COO<sup>-</sup>) 1385 (sh), 1372 (s), δ(COO<sup>-</sup>) 796 (s), phenyl bands 729 (vs), 696(vs).

For all these studied compounds we just consider the complex-anion for proposing a structure.

Dealing with hydrogenoxalate, Braga et al [7] and Viadhyathan et al [8] have reported structures containing hydrogen bonded dimers of [HC<sub>2</sub>O<sub>4</sub>]<sup>-</sup> with a ten atoms ring. For our two hydrogenoxalate adducts we will consider the anion in this dimeric form.

For A the infrared data allows to suggest a structure consisting of the above dimeric hydrogen bonded hydrogenoxalates monochelating two  $\text{SnPh}_2\text{Cl}_2$  molecules, the environment around the tin centre being octahedral (Figure 1).

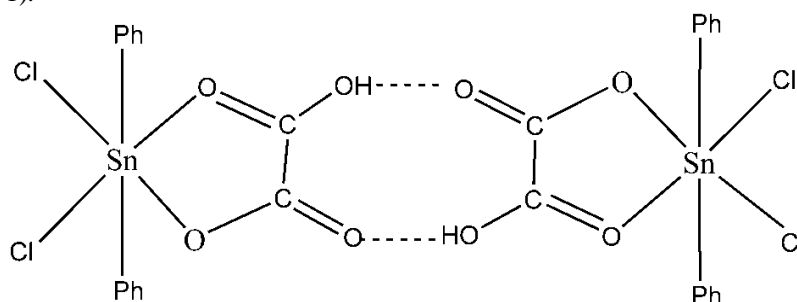


Fig. 1. Proposed structure for A.

The structure of B is deduced from the one of A on adding, two lattice benzene molecules (Figure 2).

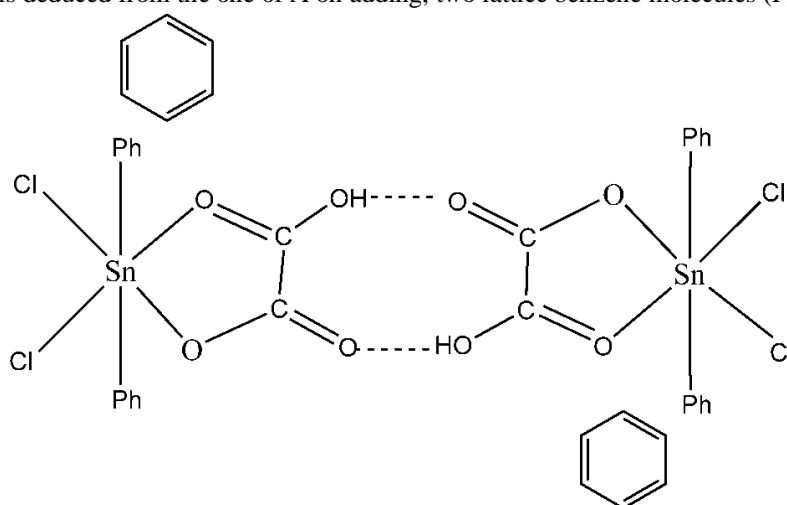


Fig. 2. Proposed structure for B.

The main features of the spectrum of the compound C is the strong reduction of the intensity of the bands of the hydrogenoxalate which has turned into an hydrogenocarbonate.

For C, a basic hydrogen bonded hydrogenocarbonates dimer chelates four  $\text{SnPh}_2\text{Cl}_2$  molecules (Figure 3). The environment around the tin centres is octahedral -four benzene molecules obtained *in situ* are lattice.

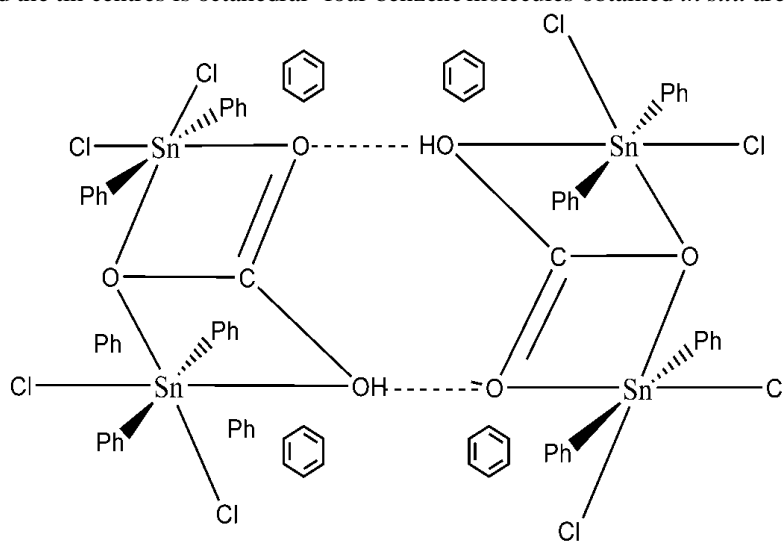


Fig. 3. Proposed structure for C.

The number of stretching bands for D and E -only two with a little splitting due to crystal effects- allows concluding to the presence of a centrosymmetrical oxalate.

A structure containing a seven coordinated tin centre has yet been reported by Ma *et al* for aqua-dimethyl-bis (2-pyrazinecarboxylato-N,O)-tin(IV) trihydrate [9]. We suggest for D a structure consisting of an oxalate monochelating  $[\text{SnPhCl}_4]^-$  leading to an heptacoordinated tin centre (Figure 4).

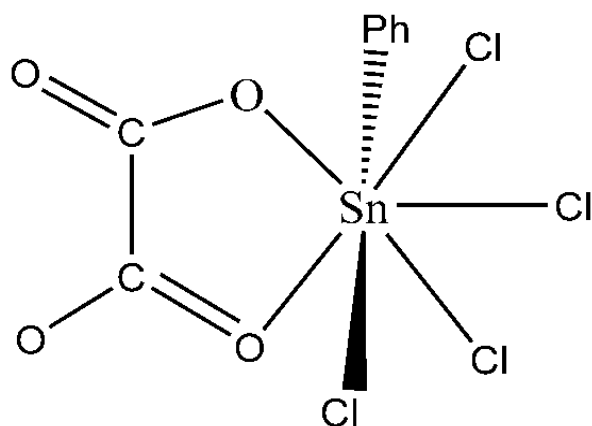


Fig. 4. Proposed structure for D.

The structure of E is deduced from the one of D on withdrawing one chloro atom leading to an octahedral environment (Figure 5).

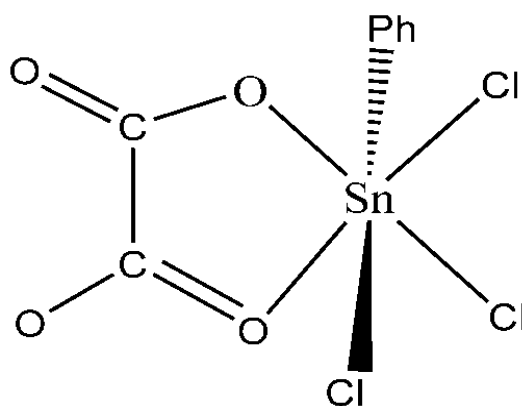


Fig. 5. Proposed structure for E.

In all these structures the cation may be involve through hydrogen bonds leading to supramolecular architectures.

#### 4. CONCLUSION

The five new oxalato, hydrogenoxalato and hydrogencarbonato compounds studied here have discrete structures with mainly a monochelating anion, the environments around tin centres being in most cases octahedral, the tin centre being in an heptacoordinating environment in one case. Mono- or bidearylations of  $\text{SnPh}_3\text{Cl}$  occurs in the studied compounds leading to  $\text{SnPh}_2\text{Cl}_2$  and  $\text{SnPhCl}_3$  adducts, the benzene molecules obtained *in situ* being lattice. When extra hydrogen bonds involving the cation are considered, supramolecular architectures may be obtained.

#### 5. ACKNOWLEDGMENTS

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