

## NEW ORGANOTIN (IV) OXALATO ADDUCTS: SYNTHESIS AND SPECTROSCOPIC STUDIES

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**Abstract:** Seven new oxalato organotin (IV) adducts have been synthesized, their infrared and Mössbauer studies carried out. Their structures are discrete, the oxalate behaving as a chelating or bridging ligand. The key role of the cation is noteworthy.

**Keywords:** *discrete structures, halo- adducts, ionic, IR, macromolecules, Mössbauer, organotin (IV) adducts, oxalato*

## INTRODUCTION

Many research teams are involved in organotin (IV) chemistry because of structural interest and applications [1-4]. The X-ray structure of  $(Et_4N)_2C_2O_4(SnX_4)_2$  ( $X = Cl, Br$ ) has been reported by Spaski *et al.* [5]. In frame work of our research on organotin chemistry and the coordinating behaviour of oxyanions, we have yet reported various papers [6 – 11]. In this work we report the study of the interactions between  $(Cy_2NH_2)_2C_2O_4 \cdot 2H_2O$  or tetramethylenediammonium oxalate and  $SnPh_2Cl_2$ ,  $SnBu_2Cl_2$  or  $SnCl_4$  which has yielded seven new adducts, IR, Raman and Mössbauer studies of which have been carried out then structures suggested on the basis of the spectroscopic data.

## EXPERIMENTAL

The mixture of  $(Cy_2NH_2)_2C_2O_4 \cdot 2H_2O$  (in hot  $CHCl_3$ ) with  $SnPh_2Cl_2$  or  $SnBu_2Cl_2$  (in MeOH), gives a white powder after a slow solvent evaporation. The mixture of  $(Cy_2NH_2)_2C_2O_4$  (in MeOH or EtOH) with  $SnCl_4$  (in MeOH or EtOH) gives also a white powder after a slow solvent evaporation.  $Me_4EnH_2C_2O_4$  is obtained by mixing  $H_2C_2O_4 \cdot 2H_2O$  in EtOH with tetramethylethylenediamine ( $Me_4En$ ) in EtOH too in the 1/1 ratio. The obtained precipitate, stirred no less than two hours, has been filtered and dried under  $P_2O_5$ . On mixing  $Me_4EnH_2C_2O_4$  in water and  $SnCl_4$  in MeOH, a white powder is obtained after a slow solvent evaporation. The analytical data reported below, allow suggesting the following formulae (Table 1).

*Table 1. Suggested formulae of synthesized compounds*

Comp	Suggested formulae	Chemical composition (% mass)					
		C		H		N	
		Calc.	Found	Calc.	Found	Calc.	Found
<b>A</b>	$(Cy_2NH_2)_2C_2O_4 \cdot 2SnPh_2Cl_2$	52.66	51.82	6.01	5.96	2.46	2.50
<b>B</b>	$2(Cy_2NH_2)_2C_2O_4 \cdot 3SnBu_2Cl_2$	50.24	49.66	8.32	8.47	3.08	3.19
<b>C</b>	$2(Cy_2NH_2)_2C_2O_4 \cdot SnCl_4 \cdot 3H_2O$	51.20	50.70	8.43	7.65	4.59	4.49
<b>D</b>	$(Cy_2NH_2)_2C_2O_4 \cdot 3SnCl_4 \cdot H_2O$	24.24	23.00	4.22	4.02	2.17	2.01
<b>E</b>	$(Cy_2NH_2)_2C_2O_4 \cdot SnCl_4 \cdot Cy_2NH_2Cl$	48.09	48.04	7.86	7.46	4.43	4.22
<b>F</b>	$Me_4En \cdot H_2C_2O_4 \cdot SnCl_4 \cdot H_2O$	19.83	19.82	4.08	4.16	5.60	5.78
<b>G</b>	$(Cy_2NH_2)_2C_2O_4 \cdot 2SnCl_4 \cdot Cy_2NH_2Cl$	38.31	37.89	6.09	6.11	3.53	3.27

The infrared data are given in  $cm^{-1}$  and the Mössbauer ones in  $mm.s^{-1}$ ; infrared abbreviations (m: medium; s: strong; vs: very strong). Mössbauer abbreviations (IS = isomer shift, QS = quadrupole splitting,  $\Gamma$  = width at half height, A = area). The infrared spectra were recorded at the University of Cheikh Anta Diop Dakar by means of a Bruker FT-IR type, the sample being as Nujol mulls using CsI windows. The  $^{119}Sn$  Mössbauer spectra were measured at the University of Munich, Germany, with a source of  $^{119m}Sn$  in a matrix of  $CaSnO_3$ . Both the source and the absorber were kept at 4.2 K in a liquid helium bath cryostat. The Mössbauer spectrometer was operated with a sinusoidal velocity waveform, a scintillation detector being used for gamma-ray detection. The isomer shifts are referred to the  $CaSnO_3$  source. The elemental analyses were performed at the Microanalyses Centre of the Faculty of Pharmacy, University of

Geneva, Switzerland. All the chemicals were from Aldrich or Merck Companies and used without any further purification.

## RESULTS AND DISCUSSION

Let us consider the infrared data in  $\text{cm}^{-1}$ :

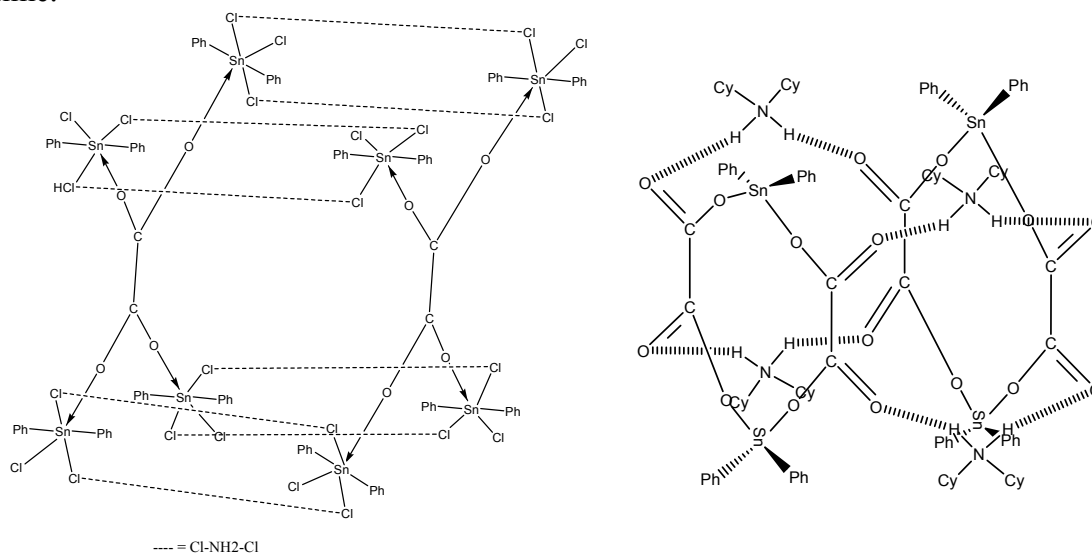
- A:**  $\nu\text{asCO}_2$ : 1700s, 1640s, 1580s;  $\nu\text{sCO}_2$ : 1440s, 1400s;  $\delta\text{CO}_2$ : 780m;  
**B:**  $\nu\text{asCO}_2$ : 1640vs, 1560s;  $\nu\text{sCO}_2$ : 1280s;  $\delta\text{CO}_2$ : 800s, 700s;  $\nu\text{Sn-C}_2$ : 690s, 595m;  
**C:**  $\nu\text{asCO}_2$ : 1687vs, 1580s;  $\nu\text{sCO}_2$ : 1364vs, 1249s;  $\delta\text{CO}_2$ : 798s;  
**D:**  $\nu\text{asCO}_2$ : 1657vs, 1560m;  $\nu\text{sCO}_2$ : 1413s, 1347s;  $\delta\text{CO}_2$ : 817m;  
**E:**  $\nu\text{asCO}_2$ : 1706vs, 1676vs;  $\nu\text{sCO}_2$ : 1350s;  $\delta\text{CO}_2$ : 894m, 799vs;  
**F:**  $\nu\text{asCO}_2$ : 1720vs, 1600vs;  $\nu\text{sCO}_2$ : 1400s, 1280s;  $\delta\text{CO}_2$ : 800s;  
**G:**  $\nu\text{asCO}_2$ : 1701vs, 1685vs;  $\nu\text{sCO}_2$ : 1250m;  $\delta\text{CO}_2$ : 894m, 797s;

and the Mössbauer data in  $\text{mm.s}^{-1}$ :

- A:**  $\text{QS}_1 = 3.99$ ,  $\text{QS}_2 = 2.71$ ;  $\text{IS}_1 = 1.29$ ,  $\text{IS}_2 = 1.35$ ;  $\Gamma_1 = 0.90$ ,  $\Gamma_2 = 1.09$ ;  $A_1/A_2 = 2$ ;  
**B:**  $\text{QS} = 3.75$ ;  $\text{IS} = 1.54$ ;  $\Gamma = 0.90$ ;  $A = 100\%$ ;  
**C:**  $\text{QS} = 0.36$ ;  $\text{IS} = 0.20$ ;  $\Gamma = 0.86$ ;  $A = 100\%$ ;  
**D:**  $\text{QS} = 0.41$ ;  $\text{IS} = 0.34$ ;  $\Gamma = 0.99$ ;  $A = 100\%$ ;  
**E:**  $\text{QS} = 0.25$ ;  $\text{IS} = 0.33$ ;  $\Gamma = 0.96$ ;  $A = 100\%$ .

The value of the QS of the complex **A** is consistent with the presence of a *trans* octahedrally coordinated  $\text{SnPh}_2$  residue –  $3.99 \text{ mm.s}^{-1}$  - while the second tin centre has a tetrahedral environment according to Platt *et al.* [12, 13]. This allows to suggest, while considering a hexamerization of the molecule followed by a rearrangement, the presence of eight O coordinated  $[\text{SnPh}_2\text{Cl}_3]^-$  complex-anions and dimers of  $\text{SnPh}_2\text{C}_2\text{O}_4$  molecules, leading to the structure reported in Figure 1, with a dimeric form of  $\text{SnPh}_2\text{C}_2\text{O}_4$ .

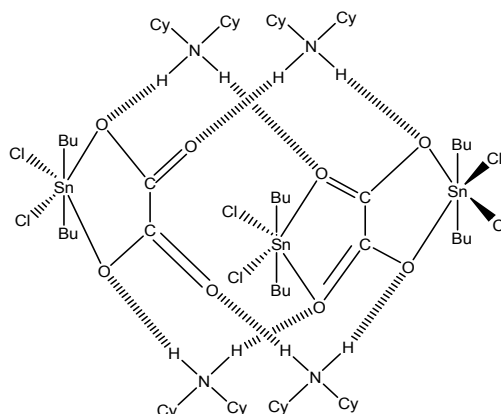
To the best of our knowledge, a dimeric form of  $\text{SnPh}_2\text{C}_2\text{O}_4$  is obtained for the first time.



**Figure 1.** Suggested structures for compound **A**

No X-ray determination of the structure of  $\text{SnPh}_2\text{C}_2\text{O}_4$  is reported but a polymeric structure with a bichelating oxalate, the  $\text{SnPh}_2$  residue being octahedrally *trans* coordinated has been suggested on the basis of Mössbauer data [14].

For the complex **B**, the presence of more than two stretching oxalate bands allow to suggest a non centrosymmetrical anion. The IR and Raman spectra show a medium band and line at  $595\text{ cm}^{-1}$  assigned to  $\nu_s\text{SnBu}_2$  and allows concluding to the presence of a non linear  $\text{SuBu}_2$  residue. The Mössbauer spectra show one type of tin (IV) with the value of the quadrupole splitting ( $QS = 3.75\text{ mm.s}^{-1}$ ) consistent to a *trans* dissymmetrically  $\text{SnBu}_2$  residue according to Platt *et al.* [12, 13]. This allows to suggest two complex anions  $[\text{C}_2\text{O}_4\cdot\text{SnBu}_2\text{Cl}_2]^{2-}$  and  $[\text{C}_2\text{O}_4\cdot(\text{SnBu}_2\text{Cl}_2)_2]^{2-}$  connected by  $\text{Cy}_2\text{NH}_2^+$  through  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds (Figure 2).



**Figure 2.** Suggested structure for compound **B**

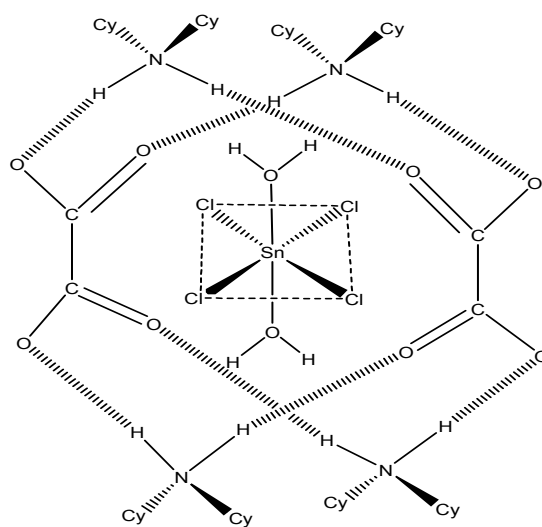
The Mössbauer data of **C**, above all the isomer shift, is consistent with the presence of  $\text{O}_2\text{SnCl}_4$  framework as claimed by Tudela *et al.* [15]. The oxalate anion is well known to chelate  $\text{SnX}_4$  ( $\text{X} = \text{Cl}, \text{Br}$ ) [5] but  $\text{SnX}_4\cdot 2\text{L}$  ( $\text{L} = \text{Lewis base}$ ) are known too [16]. So we can consider two possibilities:

- Coordinating  $\text{SnCl}_4$  by the water molecules;
- Coordinating  $\text{SnCl}_4$  by the oxalate anion.

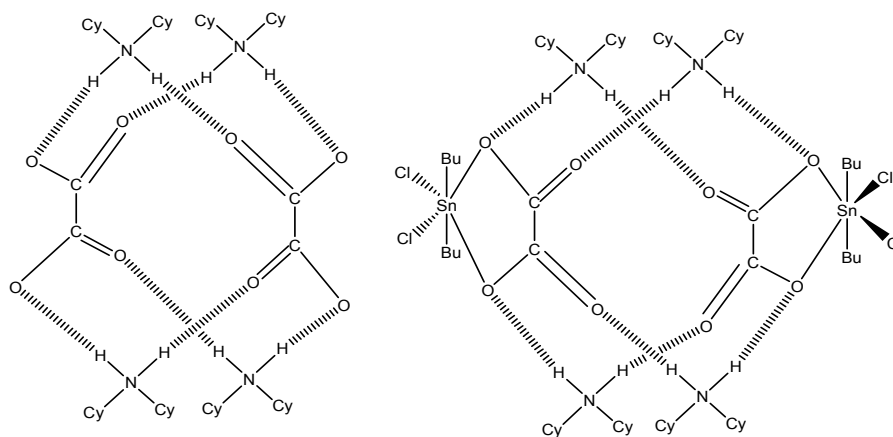
This allows in the first hypothesis to consider the adduct *cis* or *trans*  $\text{SnCl}_4(\text{H}_2\text{O})_2$  yet reported by [17 – 21] at the centre of the cage built from two oxalate anion connected by cations; the suggested structures are presented in Figure 3.

The IR spectrum of the complex **D** shows three stretching oxalate bands allowing suggesting a non centrosymmetrical oxalate. The Raman spectrum shows only one strong line at  $351\text{ cm}^{-1}$  assigned to  $\nu\text{SnCl}$  and allows suggesting a *cis* coordinated  $\text{SnCl}_4$  molecule according to Group Theory [16]. We consider therefore the complex **D** as built of  $[\text{C}_2\text{O}_4\cdot 2\text{SnCl}_4]^{2-}$  and  $\text{SnCl}_4\cdot 2\text{H}_2\text{O}$  linked by the water molecules through hydrogen bonds. A dimeric or oligomeric structure can be built with this basic structure, cations ensuring the connections (Figure 4).

The Mössbauer data of **E** and **F**, above all the isomer shift, is consistent with the presence of  $\text{O}_2\text{SnCl}_4$  frame work as claimed by Tudela *et al.* [15]. While considering a chelating oxalate, we suggest the following structures containing a cage built with two monochelating oxalate anions connected by two cation-Cl-cation bridges and two  $\text{Cy}_2\text{NH}_2^+$  (Figure 5) or  $\text{Me}_4\text{EnH}_2^{2+}$  through  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds and (Figure 6).

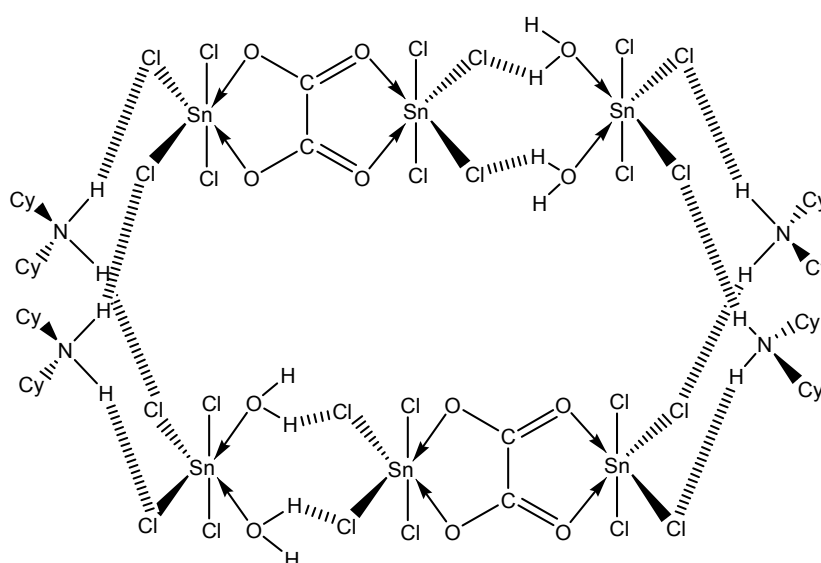


*a - Coordinating  $\text{SnCl}_4$  by the water molecules*

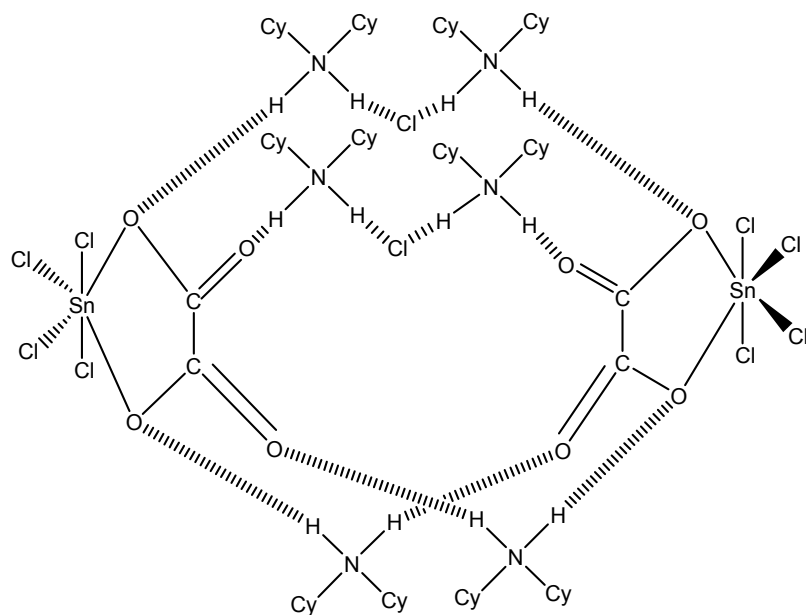


*b - Coordinating  $\text{SnCl}_4$  by the oxalate anion*

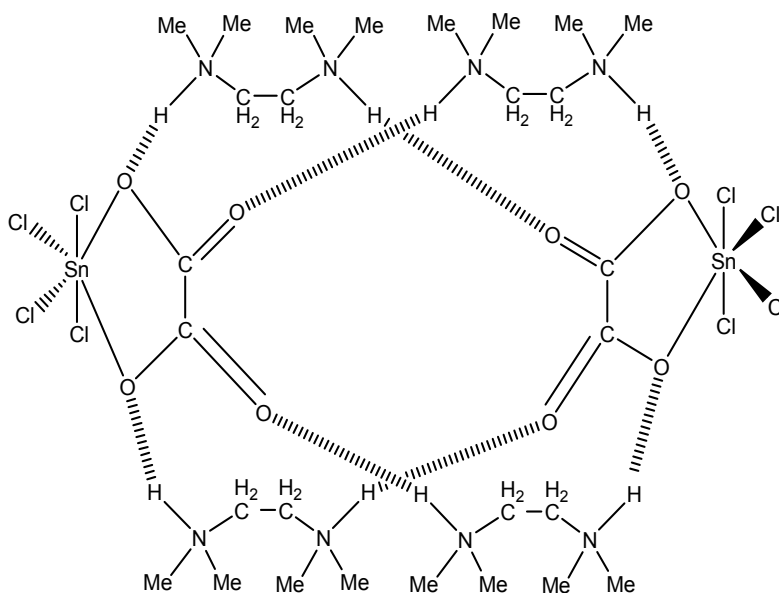
**Figure 3.** Suggested structures for compound **C**



**Figure 4.** Suggested structure for compound **D**



**Figure 5.** Suggested structure for compound **E**



**Figure 6.** Suggested structure for compound **F**

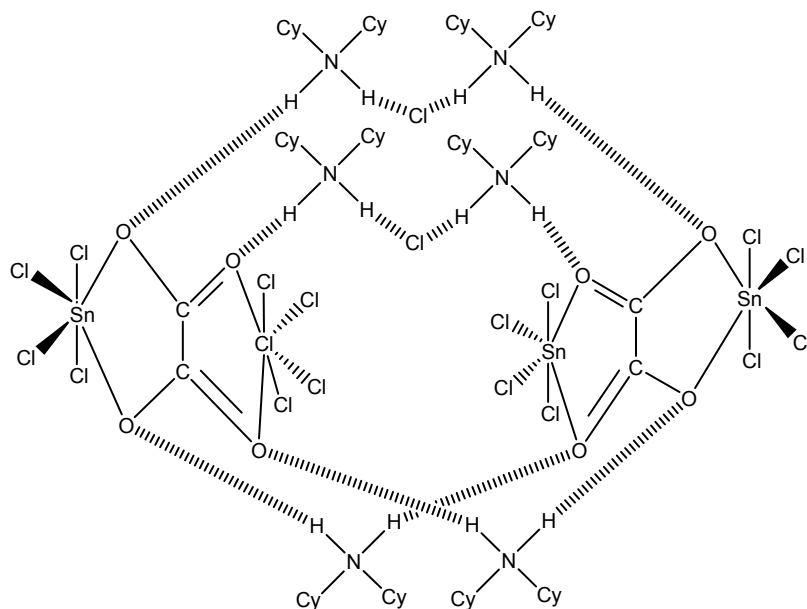
The suggested structure of **G** derives from the one of **E** by addition of two molecules of  $\text{SnCl}_4$  by chelation (Figure 7).

The wide adsorption around  $3400\text{ cm}^{-1}$  in all the IR spectra is related to the presence of hydrogen bonds.

## CONCLUSION

All the adducts studied here, have a discrete structure in which the cation plays a key role. Hydrogen bonded cage of oxalate are present in many structures. The anion

behaves as a mono - or bichelating ligand. The dimeric structure of  $\text{SnPh}_2\text{C}_2\text{O}_4$  reported for the first time in this work is noteworthy. In  $(\text{Et}_4\text{N})_2\text{C}_2\text{O}_4(\text{SnCl}_4)_2$ , the anion  $[\text{C}_2\text{O}_4(\text{SnCl}_4)_2]^{2-}$  is in electrostatic interactions with the cation while in these studied adducts the  $[\text{C}_2\text{O}_4(\text{SnCl}_4)_2]^{2-}$  anion or its  $\text{SnBu}_2\text{Cl}_2$  homologue are involved in hydrogen bonds.



**Figure 7.** Suggested structure for compound **G**

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