

SYNTHESIS AND INFRARED STUDY OF SOME NEW SnC₂O₄Cl₂ ADDUCTS AND COMPLEXES

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Abstract: Eight new SnC₂O₄Cl₂ adducts and derivatives have been synthesized and studied by infrared. Ionic discrete structures have been suggested on the basis of infrared data, the environment around the tin (IV) centre being tetrahedral or octahedral.

Keywords: *infrared, discrete structure, SnC₂O₄Cl₂ adducts, supramolecular architecture, tetrahedral or octahedral environment*

INTRODUCTION

The applications found in organotin (IV) compounds [1] have brought many research groups in attempting to obtain new organotin (IV) compounds for widening this field [2 - 7]. In this dynamic our group has yet published several papers including some heteropolynuclear compounds [8 - 10] and initiates here the study of the interactions between $\text{SnC}_2\text{O}_4\text{Cl}_2$ and MX_2 , R_4NX ($\text{X} = \text{Cl}, \text{BF}_4$) or $(\text{Me}_4\text{N})\text{WO}_4$ which have yielded eight new adducts infrared study of which have been carried out and structures suggested on the basis of infrared data.

EXPERIMENTAL

A mixture of:

- 0.3630 g (1.3030 mmol) of $\text{SnC}_2\text{O}_4\text{Cl}_2$ and 0.5503 g of CuBr_2 (4.0191 mmol) in ethanol, gives green powder of $\text{SnC}_2\text{O}_4\text{Cl}_2 \cdot \text{CuBr}_2 \cdot 1/4\text{EtOH}$: % C: 5.85 (5.63); % H: 0.29 (0.24); % Br: 31.18 (30.93);
- 0.4121 g of $\text{SnC}_2\text{O}_4\text{Cl}_2$ (1.4792 mmol) and 0.3759 g of CuCl_2 (2.794 mmol) in ethanol gives a green powder of $\text{SnC}_2\text{O}_4\text{Cl}_2 \cdot \text{CuCl}_2 \cdot \text{H}_2\text{O}$: % C: 4.96 (4.90); % H: 0.41 (0.38); % Cl: 29.38 (29.02);
- 0.4414 g (1.5844 mmol) of $\text{SnC}_2\text{O}_4\text{Cl}_2$ and 0.6553 g of CoBr_2 (2.996 mmol) in ethanol gives a rose power of $\text{SnC}_2\text{O}_4\text{Cl}_2 \cdot \text{CoBr}_2 \cdot 1/8\text{EtOH}$: % C: 5.37 (5.22); % H: 0.15 (0.13); % Br: 31.82 (31.60);
- 0.4362 g (1.5657 mmol) of $\text{SnC}_2\text{O}_4\text{Cl}_2$ and 0.6811 g Et_4NBF_4 (3.3584 mmol) gives a white precipitate of $(\text{Et}_4\text{N})_2\text{C}_2\text{O}_4 \cdot \text{SnCl}_2\text{F}_2 \cdot 2\text{H}_2\text{O}$: % C: 35.31 (35.02); % H: 7.19 (6.90); % F: 6.21 (6.60);
- 0.5437 g (1.951 mmol) of $\text{SnC}_2\text{O}_4\text{Cl}_2$ and 0.8708 g (3.6898 mmol) of $\text{C}_2\text{O}_4(\text{Me}_4\text{N})_2 \cdot 2\text{H}_2\text{O}$ gives a white precipitate of $(\text{Me}_4\text{N})_2\text{Sn}(\text{C}_2\text{O}_4)\text{Cl}_2$: % C: 28.03 (27.83); % H: 4.67 (4.55); % N: 5.45 (5.55); % Cl: 13.82 (14.09);
- 0.8039 g (2.885 mmol) of $\text{SnC}_2\text{O}_4\text{Cl}_2$ and 0.9041 g (5.4645 mmol) of Et_4NCl in ethanol, gives a white precipitate of $(\text{Et}_4\text{N})_2\text{Sn}(\text{C}_2\text{O}_4)\text{Cl}_2 \cdot (\text{Et}_4\text{N})_2\text{C}_2\text{O}_4 \cdot (\text{SnCl}_4)_2 \cdot \text{EtOH}$ is obtained: % C: 31.13 (31.55); % H: 5.58 (5.95); % N: 3.63 (4.03); % Cl: 23.02 (23.27);
- 0.5120 g (1.8378 mmol) of $\text{SnC}_2\text{O}_4\text{Cl}_2$ and 1.4596 g of $\text{WO}_4(\text{Me}_4\text{N})_2$ (3.6868 mmol) in ethanol solvent, gives white precipitate of $[(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4\text{SnCl}_4]_2 \cdot [(\text{Me}_4\text{N})_2\text{Sn}(\text{C}_2\text{O}_4)_2\text{Cl}_2]_2 \cdot \text{Sn}(\text{WO}_4)_2$: % C: 15.55 (14.86); % H: 3.30 (3.24); % N: 3.30 (3.78);
- 0.8812 g (3.3699 mmol) of SnCl_4 in benzene, 0.4981 g (1.7879 mmol) of $\text{SnC}_2\text{O}_4\text{Cl}_2$ and 0.2674 g (3.9910 mmol) of $\text{C}_5\text{H}_5\text{N}$ both in ethanol, gives $\text{Sn}(\text{C}_2\text{O}_4)_2 \cdot 2[\text{SnCl}_4 \cdot (\text{Pyridine})_2]$: % C: 27.60 (27.01); % H: 2.30 (2.92); % N: 4.95 (5.51); % Cl: 25.12 (24.75);
- 0.4239 g of $\text{SnC}_2\text{O}_4\text{Cl}_2$ and 0.4541 g of Et_4NCN in ethanol gives a white precipitate of $(\text{Et}_4\text{N})_2\text{SnCl}_6 \cdot (\text{Et}_4\text{N})_2\text{C}_2\text{O}_4 \cdot 2\text{SnC}_2\text{O}_4 \cdot (\text{OH})_2$: % C: 32.09 (31.67); % H: 5.91 (5.85); % N: 3.94 (3.86).

The powders were obtained after a slow solvent evaporation while the precipitates were stirred around two hours.

The elemental analyses were performed by either the CNRS - *Service Central d'Analyses* Vernaison (France), the Laboratory of Microanalyses – University of Padova (Italy) or the Microanalyses Centre – University of Bath (UK).

The infrared spectra were recorded 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. Infrared data are given in cm^{-1} and the abbreviations are: (vs) very strong (s) strong, (m) medium, (w) weak, (vw) very weak.

All the chemicals were purchased from Aldrich and Merck Companies and used as such.

RESULTS AND DISCUSSION

$\text{SnC}_2\text{O}_4\text{Cl}_2 \cdot \text{MX}_2$ ($\text{M} = \text{Cu}, \text{Co}; \text{X} = \text{Cl}, \text{Br}$) (A)

These bi-heteronuclear adducts can be considered as non symmetrical molecules with a bichelating oxalate (Figure 1a) or while considering a dimerization process with rearrangement leading to a symmetrical structure (Figure 1b).

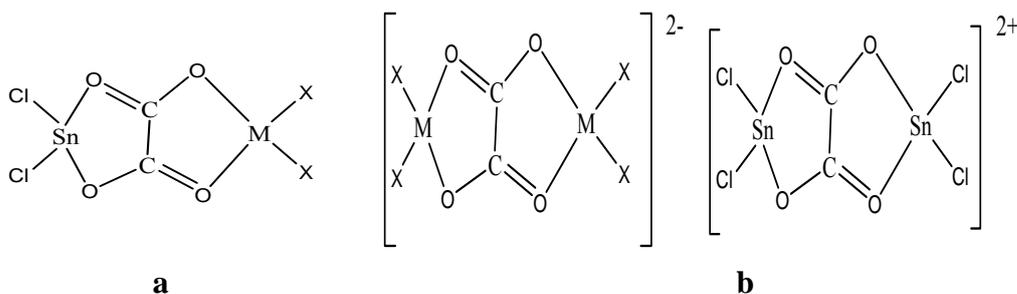


Figure 1 a-b. Proposed structure for the compound A:
a) non symmetrical structure; b) symmetrical structure

$(\text{Et}_4\text{N})_2\text{C}_2\text{O}_4 \cdot \text{SnCl}_2\text{F}_2$ (B)

This compound is an adduct of SnCl_2F_2 as $(\text{Pr}_2\text{NH}_2)_2\text{C}_2\text{O}_4 \cdot \text{SnCl}_4$ which contains $[\text{SnCl}_4 \cdot \text{C}_2\text{O}_4]^{2-}$ with a monochelating oxalate. The structure is reported on (Figure 2).

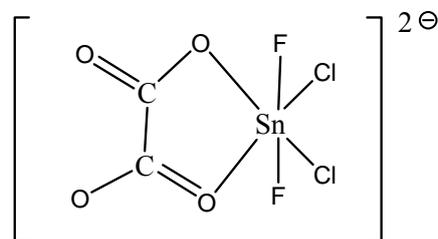


Figure 2. Proposed structure for the compound B

$(\text{Me}_4\text{N})_2\text{Sn}(\text{C}_2\text{O}_4)\text{Cl}_2$, $(\text{Et}_4\text{N})_2\text{Sn}(\text{C}_2\text{O}_4)\text{Cl}_2 \cdot (\text{Et}_4\text{N})_2\text{C}_2\text{O}_4(\text{SnCl}_4)_2$ (C)

$(\text{Me}_4\text{N})_2(\text{C}_2\text{O}_4)\text{Cl}_2$ can be considered as $(\text{Me}_4\text{N})_2\text{SnCl}_6$ in which four chloride ions have been substituted by two oxalate anions leading to the structure on Figure 3a and 3b (the SnCl_2 group can be linear or bent).

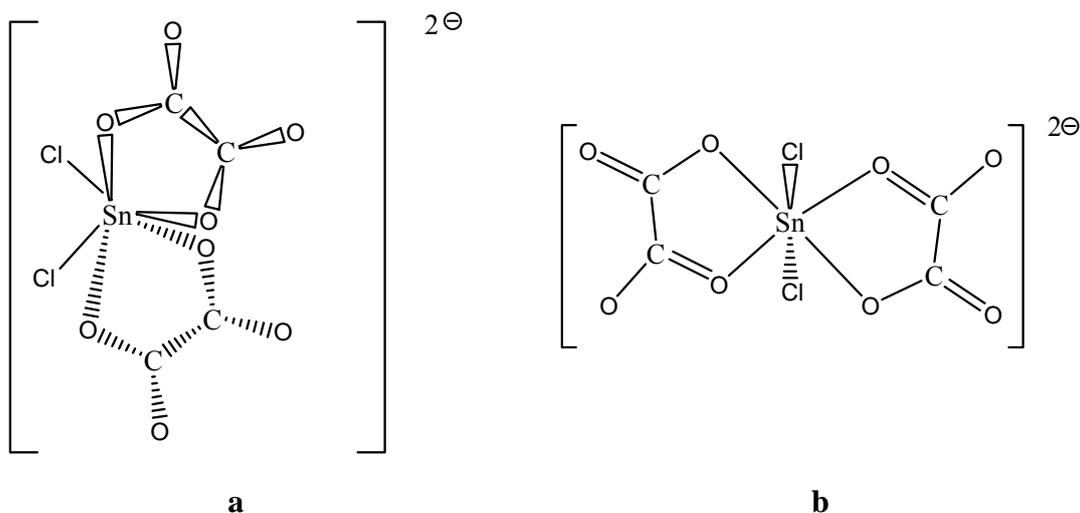


Figure 3 a-b. Proposed structure for the compound **C**: a) bent; b) linear

(Et₄N)₂Sn(C₂O₄)Cl₂·(Et₄N)₂C₂O₄(SnCl₄)₂ (D**)**

The X ray structure of (Et₄N)₂C₂O₄(SnCl₄)₂ contains a bichelating oxalate [11].

This studied compound containing the same cation can be considered as an insertion adduct between (Me₄N)₂Sn(C₂O₄)Cl₂ similar to (Et₄N)₂Sn(C₂O₄)Cl₂ and (Et₄N)₂C₂O₄(SnCl₄)₂ leading to the structure reported on Figure 4. The SnCl₂ group can be considered as bent (Figure 4a) or linear (Figure 4b).

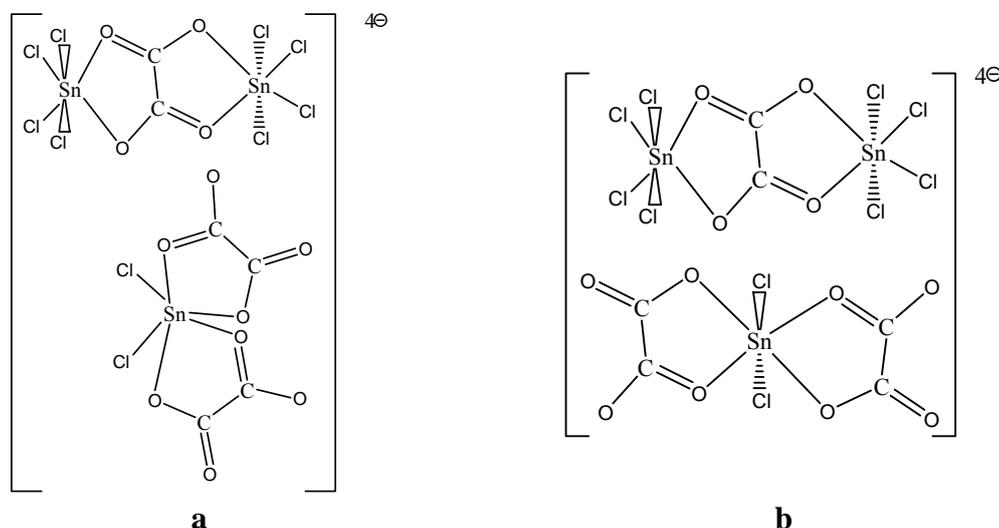


Figure 4 a-b. Proposed structure for the compound **D**: a) bent; b) linear

(Et₄N)₂SnCl₆·(Et₄N)₂C₂O₄·2SnC₂O₄(OH)₂ (E**)**

The anions [SnCl₆]²⁻ and [C₂O₄·2SnC₂O₄(OH)₂]²⁻ with octahedral tin centres can interact through OH...Cl hydrogen bonds, leading to the infinite chain structure reported on Figure 5a or a dimer reported on Figure 5b.

In the two cases, the remaining OH groups of each binuclear complex anion can interact with the neighbours through OH...Cl hydrogen bonds leading to a supramolecular structure.

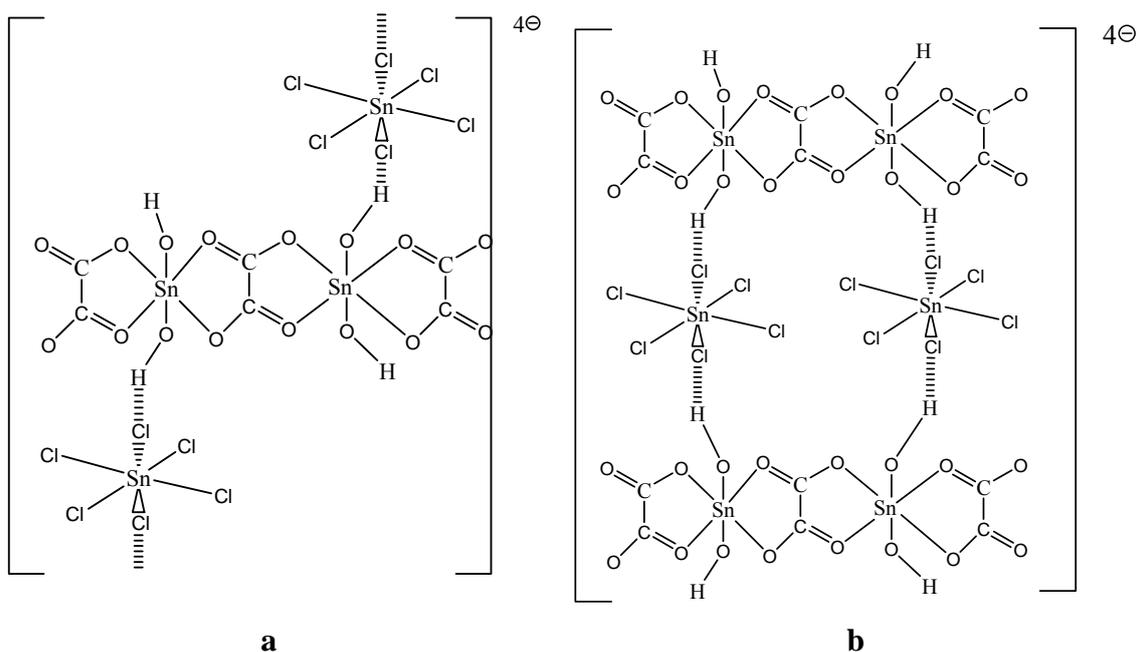


Figure 5 a-b. Proposed structure for the compound **E**: a) infinite chain; b) dimer

$[(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4\text{SnCl}_4]_2[(\text{Me}_4\text{N})_2\text{Sn}(\text{C}_2\text{O}_4)_2\text{Cl}_2]_2\cdot\text{Sn}(\text{WO}_4)_2$ (F**)**

Two oxalate stannic anions are present here $[\text{C}_2\text{O}_4\text{SnCl}_4]^{2-}$ and $[\text{Sn}(\text{C}_2\text{O}_4)_2\text{Cl}_2]^{2-}$; the third stannic component of the structure is $\text{Sn}(\text{WO}_4)_2$ which is tetrahedral because of deriving from SnCl_4 by substitution of the four chloride ions by WO_4^{2-} . The proposed structure is reported on Figure 6.

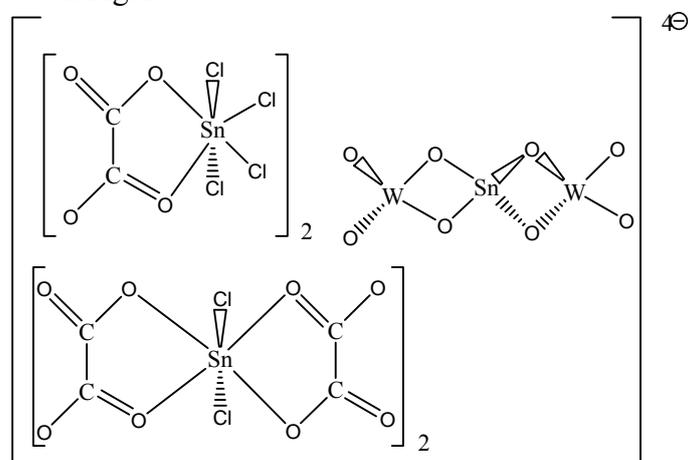


Figure 6. Proposed structure for the compound **F**

In all these adducts the cation, which has not been drawn for reasons of clarity, is in electrostatic interactions with the anions.

$\text{Sn}(\text{C}_2\text{O}_4)_2 \cdot 2[\text{SnCl}_4 \cdot (\text{Pyridine})_2]$ (G**)**

This can be considered as a 1/2 adduct between $\text{Sn}(\text{C}_2\text{O}_4)_2$ and $\text{SnCl}_4 \cdot (\text{Pyridine})_2$ or a 1/2 adduct between $\text{Sn}(\text{C}_2\text{O}_4)_2 \cdot 2\text{Pyridine}$ and $\text{SnCl}_4 \cdot \text{Pyridine}$.

In a first structure the interactions can be considered are weak leading to the structure reported on Figure 7a, a second structure is reported on Figure 7b.

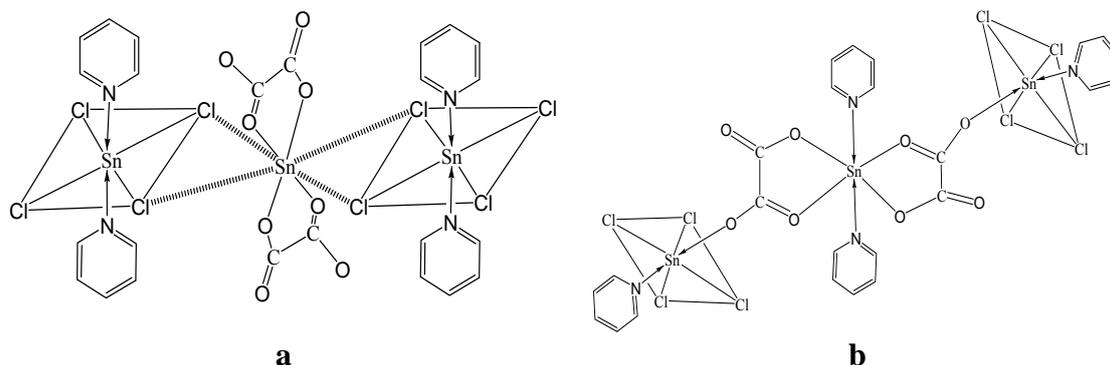


Figure 7a-b. Proposed structures for the compound **G**

CONCLUSIONS

In these studied adducts, the structures are discrete mainly, only one structure is polymeric. The oxalate anion behaves as a mono-, or a bi- chelating anion. Supramolecular architecture is found in one compound.

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