

SHORT COMMUNICATION

**INTERACTIONS BETWEEN  $(\text{Me}_4\text{N})_2(\text{C}_2\text{O}_4)_2\text{SnPh}_2\cdot\text{H}_2\text{O}$   
AND  $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$ :  $(\text{Me}_4\text{N})_2(\text{C}_2\text{O}_4)_2\text{SnPh}_2\cdot 2\text{SnCl}_4$  OR  
 $(\text{Me}_4\text{N})_2(\text{C}_2\text{O}_4)_2\text{SnCl}_2\cdot 2\text{SnPhCl}_3$  ?  
THE MÖSSBAUER EFFECT SOLUTION**

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**Abstract:** The study of the interactions between  $(\text{Me}_4\text{N})_2(\text{C}_2\text{O}_4)_2\text{SnPh}_2\cdot\text{H}_2\text{O}$  and  $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$  in EtOH has yielded a trinuclear adduct which Mössbauer study has allowed to choose  $(\text{Me}_4\text{N})_2(\text{C}_2\text{O}_4)_2\text{SnCl}_2\cdot 2\text{SnPhCl}_3$  rather than  $(\text{Me}_4\text{N})_2(\text{C}_2\text{O}_4)_2\text{SnPh}_2\cdot 2\text{SnCl}_4$  for formula, the oxalate anion behaving as a bichelating ligand, the environment around the tin (IV) centre being octahedral.

**Keywords:** *bichelating oxalate anion, IR and Mössbauer, appearance of  $\text{SnPhCl}_3$  in situ*

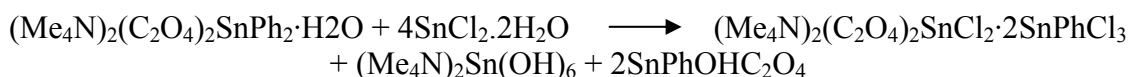
## INTRODUCTION

Many molecules belonging to organotin (IV) family have shown possibilities of applications in various fields (agriculture, medicine, wood preservatives etc.) [1 – 6]. Many research groups have been focusing in attempting to obtain new organotin (IV) molecules for widening that field, in the hope of applications [7, 8]. Our group has yet published many papers dealing with organotin (IV) chemistry [9 – 19]. For obtaining new organotin (IV) molecules, we have initiated here, the study of the interactions between  $(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4\text{SnPh}_2\cdot\text{H}_2\text{O}$  and  $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$  which have yielded one very interesting adduct -  $(\text{Me}_4\text{N})_2(\text{C}_2\text{O}_4)_2\text{SnPh}_2\cdot 2\text{SnCl}_4$  or  $(\text{Me}_4\text{N})_2(\text{C}_2\text{O}_4)_2\text{SnCl}_2\cdot 2\text{SnPhCl}_3$ . Infrared and Mössbauer studies that have been carried out allowed us to propose a structure between the two possible, structure suggested on the basis of spectroscopic data.

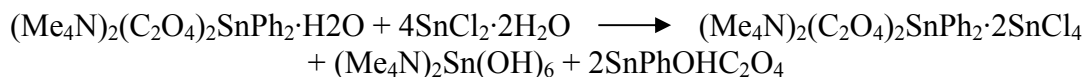
## EXPERIMENTAL

$(\text{Me}_4\text{N})_2(\text{C}_2\text{O}_4)\text{SnPh}_2\cdot\text{H}_2\text{O}$  (**L**) has been obtained as reported in [19]. When (**L**) is mixed with  $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$ , both as ethanolic solutions in 1/4 ratio, a precipitate is obtained, stirred no less than two hours, filtered and washed with hot ethanol. The analytical data C = 25.78 (25.63); H = 3.06 (3.05); N = 2.51 (2.55); Cl = 25.36 (25.23); Sn = 31.85 (32.20) have allowed to suggest  $(\text{Me}_4\text{N})_2(\text{C}_2\text{O}_4)_2\text{SnPh}_2\cdot 2\text{SnCl}_4$  or  $(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4\cdot\text{SnCl}_2\cdot 2\text{SnPhCl}_3$  as formula.

The reaction equation is:



or



The elemental analyses were performed by the CNRS “Service Central d’Analyses” Vernaison, France, the IR spectrum at the University of Padova, Italy, using a PE 580 and a Bruker FTIR spectrometers, the sample being as a Nujol mull, using CsI or polyethylene as optical windows. The Mössbauer spectrum has been obtained at the University of Bath, UK as reported in [21]. The infrared data are given in  $\text{cm}^{-1}$  and the Mossbauer ones in  $\text{mm}\cdot\text{s}^{-1}$ . Infrared abbreviations: very strong (vs), strong (s), medium (m), weak (w), shoulder (sh). Mössbauer abbreviations: IS = isomer shift; QS = quadrupole splitting;  $\Gamma$  = width at half height; A = Area.

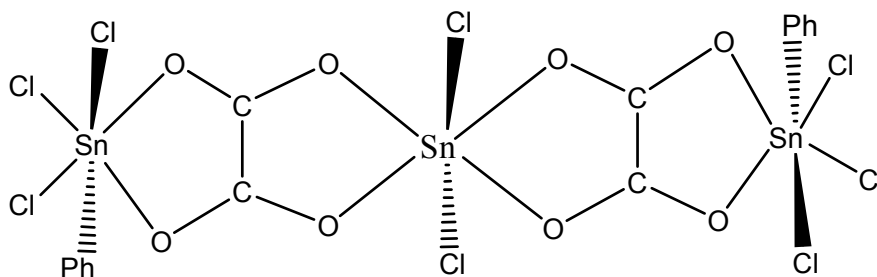
## RESULTS AND DISCUSSION

Let us consider the IR:  $\nu_{\text{asCOO}^-} = 1651$  (vs),  $1572$  (sh);  $\nu_{\text{sCOO}^-} = 1348$  (m),  $1300$  (w);  $\delta_{\text{COO}^-} = 812$  (m);  $\rho_{\text{COO}^-} = 468$  (m);  $\nu_{\text{asSnC}_3} = 298$  (vs);  $\nu_{\text{SnO}} = 218$  (s);  $\nu_{\text{SnCl}} = 298$  (vs) and Mössbauer data of the studied adduct:  $\delta_1 = 0.80 \text{ mm}\cdot\text{s}^{-1}$ ,  $\text{QS}_1 = 1.48 \text{ mm}\cdot\text{s}^{-1}$ ,  $\Gamma_1 = 0.96$ ,  $A_1 = 66$ ,  $\delta_2 = 0.01 \text{ mm}\cdot\text{s}^{-1}$ ;  $\text{QS}_2 = 0.69 \text{ mm}\cdot\text{s}^{-1}$ ,  $\Gamma_2 = 0.85$ ,  $A_2 = 34$ .

The value of the isomer shift of Sn (1) cannot be correlated with the presence of a  $\text{SnPh}_2$  residue but only a halo-coordinated tin (IV) centre what allows to consider the adduct as a central  $\text{SnCl}_2$  residue bichelated by two oxalate anions which are then connected through chelation to the two external  $\text{SnPhCl}_3$  molecules leading to the structure reported below with two bichelating oxalate anions (Figure 1).

So the Mössbauer data have been determinant for choosing between the two possible structures.

The value of the quadrupole splitting of the external tin centre is similar to data reported for  $\text{SnPhCl}_3$  adducts [22].



**Figure 1.** Proposed structure for  $(\text{Me}_4\text{N})_2(\text{C}_2\text{O}_4)_2\text{SnCl}_2 \cdot 2\text{SnPhCl}_3$

## CONCLUSION

The spectroscopic studies of the adduct has allowed to choose  $(\text{Me}_4\text{N})_2(\text{C}_2\text{O}_4)_2\text{SnCl}_2 \cdot 2\text{SnPhCl}_3$  as formula rather than  $(\text{Me}_4\text{N})_2(\text{C}_2\text{O}_4)_2\text{SnPh}_2 \cdot 2\text{SnCl}_4$ . The environment around the tin (IV) centers is octahedral, the oxalate behaving as a bichelating ligand.

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