

**(Cation)₂C₂O₄·nSnPh₂C₂O₄(n=1, 2; cation=Pr₂NH₂, MeNH₃)
AND SOME OF THEIR ADDUCTS:
SYNTHESIS, INFRARED AND MOSSBAUER STUDIES**

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Abstract: Three $[\text{SnPh}_2(\text{C}_2\text{O}_4)_2]^{2-}$ containing new adducts have been synthesized and characterized by elemental analyses, infrared and Mossbauer spectroscopy, the suggested structures being discrete, the SnPh_2 residues octahedral *cis* or *trans* coordinated. A *trans* $[\text{SnPh}_2(\text{C}_2\text{O}_4)_2]^{2-}$ complex- anion has been evidenced by spectroscopic methods for the first time in this work. The new complex-anion $[\text{SnPh}_2\text{Cl}(\text{C}_2\text{O}_4)_2]^{3-}$ with a seven coordinated tin centre has been reported in this paper and a two metallic components structure containing a tetranuclear and a mononuclear components with octahedral environments around the tin centers interacting with cations and involving OH groups leading to a supramolecular architecture has also been reported. The anion behaves as a mono- or a bichelating ligand.

Keywords: *a two metallic components structure, cis and trans octahedral coordinated SnPh₂ residues, H bonds, mono and bichelating oxalates, supramolecular architecture*

INTRODUCTION

The focus of many research groups including ours in organotin(IV) chemistry is mainly due to the several applications found within this family [1 - 8]. The X-ray structure of $(i\text{-Pr}_2\text{NH}_2)_2\text{C}_2\text{O}_4\text{SnPh}_2\text{C}_2\text{O}_4$ has been reported Tao and al [9]: it consists of a *cis* octahedral coordinated SnPh_2 residue, the oxalate anion behaving as a monochelating ligand. In the framework of our search of new SnPh_2 residue containing compounds for widening this family, we have initiated here the synthesis of three new compounds containing the complex-anion $[(\text{C}_2\text{O}_4)_2\text{SnPh}_2]^{2-}$ stabilized by the Pr_2NH_2^+ and MeNH_3^+ cations; from their infrared study, structures are suggested on the basis of spectroscopic data.

MATERIALS AND METHODS

$\text{C}_2\text{NH}_2\text{C}_2\text{O}_4\text{SnPh}_3$ and $(\text{Me}_4\text{N})_2(\text{C}_2\text{O}_4)_2\text{SnPh}_2\cdot\text{H}_2\text{O}$ have been synthesized according to Ng and Rae [10] and by Qamar-Kane et al [11] respectively.

$(\text{Pr}_2\text{NH}_2)_2\text{C}_2\text{O}_4$: the completed neutralization of oxalic acid by Pr_2NH in water mixture in 1/2 ratio gives a white precipitate. Analytical data: % calculated (% found):

%C = 57.50(57.09), %H = 11.03(10.89), %N = 9.59 (9.55).

The mixture of $(\text{Pr}_2\text{NH}_2)_2\text{C}_2\text{O}_4$ with SnPh_3OH (A) or $(\text{Me}_4\text{N})_2(\text{C}_2\text{O}_4)_2\text{SnPh}_2\cdot\text{H}_2\text{O}$ (C) as ethanolic solutions in 1:1 ratio gives a white precipitate, in both cases, which is stirred around two hours. When $\text{C}_2\text{NH}_2\text{C}_2\text{O}_4\text{SnPh}_3$ is mixed with MeNH_3Cl in 1/1 ratio (both in pure ethanol), a white powder (B) is obtained after a slow solvent evaporation.

The analytical data reported below, allow suggesting the following formulate presented in Table 1.

Table 1. Results of the elemental analyses of compounds A, B and C

Compound	Chemical formula	Elemental analysis (%)					
		C		H		N	
		calc.	found	calc.	found	calc.	found
A	$[\text{Pr}_2\text{NH}_2]_2[\text{C}_2\text{O}_4\cdot 2\text{SnPh}_2\text{C}_2\text{O}_4\cdot 2\text{SnPh}_2(\text{OH})_2]\cdot \text{Sn}(\text{C}_2\text{O}_4)_2\cdot 3\text{H}_2\text{O}$	45.31	45.35	5.70	5.65	3.00	2.94
B	$(\text{MeNH}_3)_2\text{C}_2\text{O}_4\cdot \text{SnPh}_2\text{C}_2\text{O}_4\cdot \text{MeNH}_3\text{Cl}$	39.30	39.81	4.86	5.05	7.24	7.18
C	$(\text{Pr}_2\text{NH}_2)_2\text{C}_2\text{O}_4\cdot \text{SnPh}_2\text{C}_2\text{O}_4$	48.69	49.01	6.67	6.58	4.05	4.09

The infrared spectra were recorded at the *Instituto de Química - U.N.A.M.*, Mexico, by means of a BX FT-IR type spectrometer. Elemental analyses have been performed at the *Instituto de Química - U.N.A.M.*, Mexico. The Mössbauer spectra were obtained as described previously [12].

Infrared data are given in cm^{-1} (IR abbreviations: (vs) very strong, (s) strong, (m) medium, (w) weak, (vw) very weak).

Mossbauer parameters are given in mm^{-1} (Mossbauer abbreviations: Q.S = quadrupole splitting, I.S = isomer shift, Γ = full width at half-height, A = area). All the chemicals were purchased from Aldrich Company Germany, and used as such.

RESULTS AND DISCUSSION

Let us consider the infrared and Mossbauer data for synthesized compounds are:

(Pr₂NH₂)₂C₂O₄·SnPh₂C₂O₄ (**A**): vasCOO⁻: 1663 (s), 1650 (vs); vsCOO⁻: 1245 (vs), 1230 (s); δCOO: 795 (s); Q.S₁ = 3.83 mm/s, IS₁ = 1.16 mm/s, Γ₁ = 0.95 mm/s, A₁(%) = 08, Q.S₂ = 2.04 mm/s, IS₂ = 1.05 mm/s, Γ₂ = 0.95 mm/s, A₂(%) = 92;

(MeNH₃)₂C₂O₄·SnPh₂C₂O₄·MeNH₃Cl (**B**): vasCOO⁻: 1678 (vs), 1646 (vs); vsCOO⁻: 1330 (s), 1270 (s); δCOO: 796 (s);

[Pr₂NH₂]₂[C₂O₄·2SnPh₂C₂O₄·2SnPh₂(OH)₂]·Sn(C₂O₄)₂·3H₂O (**C**): vasCOO⁻: 1700 (m), 1673 (s), 1641 (s); vsCOO⁻: 1292 (vs), 1268 (s); δCOO: 782 (s); Q.S₁ = 4.37 mm/s, IS₁ = 1.37 mm/s, Γ₁ = 0.90 mm/s, A₁(%) = 80, Q.S₂ = 2.11 mm/s, IS₂ = 0.52 mm/s, Γ₂ = 0.88 mm/s, A₂(%) = 20.

The Mossbauer data of (Pr₂NH₂)₂C₂O₄SnPh₂C₂O₄ are consistent with the simultaneous presence of *cis* octahedral coordinated SnPh₂ residue (92 %) - main isomer and *trans* octahedral coordinated SnPh₂ residue (8 %) - minor isomer, according to Platt and al [13]. We suggest a similar structure to the one reported for (Pr₂NH₂)₂C₂O₄SnPh₂C₂O₄ the *i*-Pr being replaced by Pr (Figure 1) for the main isomer (92 %) and a *trans* octahedral coordinated [SnPh₂(C₂O₄)₂]²⁻ complex anion containing structure for the minor isomer (8 %).

A *trans* octahedral coordinated [SnPh₂(C₂O₄)₂]²⁻ complex anion has been reported for the first time in this work.

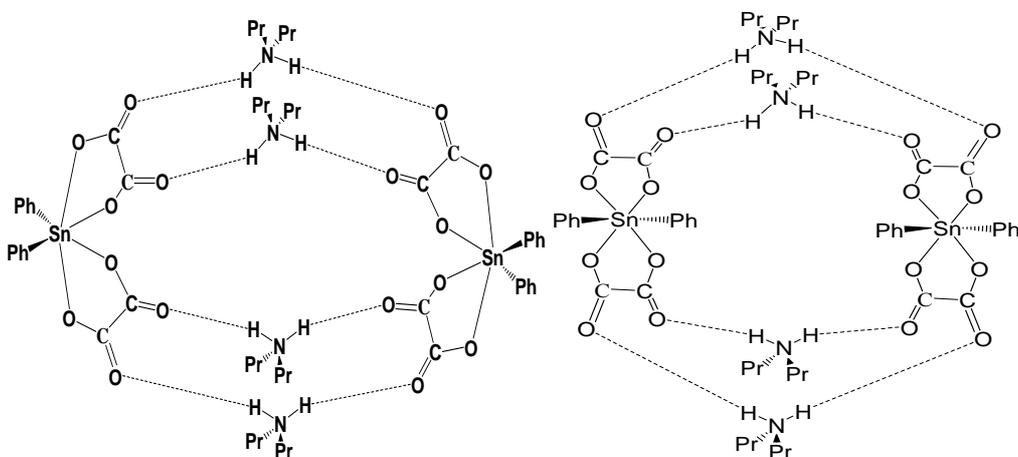


Figure 1. Proposed structure for (Pr₂NH₂)₂C₂O₄SnPh₂C₂O₄ - main and minor isomers

(MeNH₃)₃SnPh₂(C₂O₄)₂]Cl can be considered as an adduct between MeNH₃Cl and (MeNH₃)₂SnPh₂(C₂O₄)₂ allowing to suggest a structure similar to the one of (Cy₂NH₂)₂SnMe₂(C₂O₄)₂·H₂O·EtOH [14] which contains a seven coordinated Sn centre, the oxalate being monocoordinating ligands -EtOH is lattice. When cations are involved the structure reported on Figure 2 is obtained.

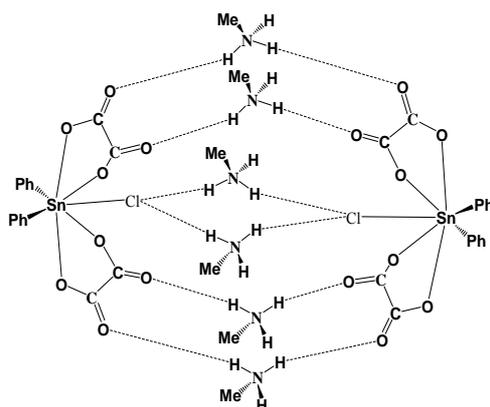


Figure 2. Suggested structure for compound **B**

For the pentanuclear adduct two metallic components are present according to the Mossbauer data, the tin(IV) centres being in the ratio 4/1. So the tetranuclear complex anion $[\text{C}_2\text{O}_4 \cdot 2\text{SnPh}_2 \cdot \text{C}_2\text{O}_4 \cdot 2\text{SnPh}_2(\text{OH})_2]^{2-}$ is one component, the second component being $\text{Sn}(\text{C}_2\text{O}_4)_2 \cdot 3\text{H}_2\text{O}$, the water molecules being all coordinated (this type of coordination is similar to the one in $[\text{SnMe}_2(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}]^{2-}$), the environment around the four tin(IV) centres being octahedral while the fifth one is heptacoordinated (the hydrated derivative $\text{Sn}(\text{C}_2\text{O}_4)_2 \cdot 3\text{H}_2\text{O}$ has been reported for the first time in this work). The obtained structure is reported on Figure 3. When free OH groups or cation interact with free O atoms a supramolecular architecture is obtained.

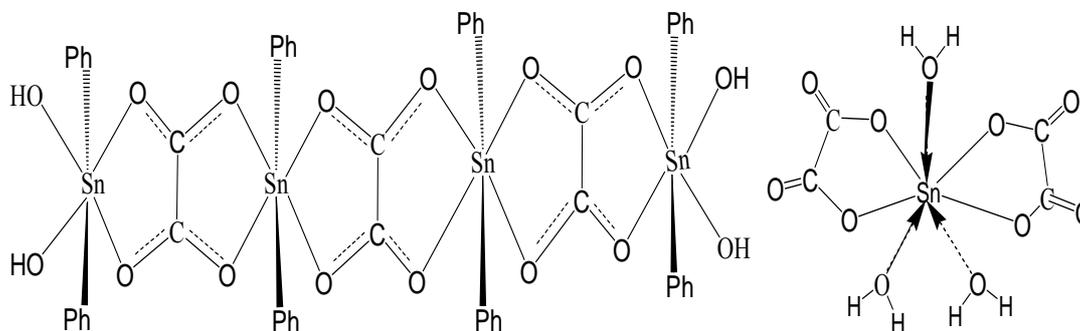


Figure 3. Suggested structure for compound **C**

CONCLUSION

The three oxalato adducts and derivatives studied here, have discrete structures, the oxalato ion behaving as a mono- or a bichelating ligand.

A *trans* octahedrally coordinated $[\text{SnPh}_2(\text{C}_2\text{O}_4)_2]^{2-}$ complex anion and the hydrated derivative $\text{Sn}(\text{C}_2\text{O}_4)_2 \cdot 3\text{H}_2\text{O}$ have been reported for the first time in this work. When the cation and free OH groups are involved in H bonding a supramolecular architecture is obtained for $[\text{Pr}_2\text{NH}_2]_2[\text{C}_2\text{O}_4 \cdot 2\text{SnPh}_2 \cdot \text{C}_2\text{O}_4 \cdot 2\text{SnPh}_2(\text{OH})_2] \cdot \text{Sn}(\text{C}_2\text{O}_4)_2 \cdot 3\text{H}_2\text{O}$.

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