



Original Paper

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Synthesis, infrared and mossbauer studies of two new oxalato SnPh₂Cl₂ and SnPh₂Cl(OH) adducts

Yaya SOW^{1*}, Libasse DIOP¹ and Jose Domingos ARDISSON²

¹ *Laboratoire de Chimie Minérale et Analytique (LACHIMIA), Département de Chimie, Faculté des Sciences et Techniques, Université Cheikh Anta Diop, Dakar, Sénégal.*

² *Laboratorio de Fosica Aplicada, CDTN/CNEN, Belo Horizonte-M.G., 31270-901, Brazil.*

*Corresponding author; E-mail: yayasow81@yahoo.fr

ABSTRACT

Two new oxalato chloridodiorganostannic adducts have been synthesized, their elemental analyses performed, infrared and Mossbauer studies carried out. Discrete cages or a double discrete cages structures have been suggested, the oxalate behaving as a monocoordinating or a monochelating donor. The key role of R₂NH₂⁺ cations, involved in NH...O hydrogen bonds is noteworthy.

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INTRODUCTION

Several SnPh₂Cl₂ adducts (Cashin et al., 2002; Cunningham et al., 2004; Estudiante-Negrete et al., 2004; Kapoor et al., 2005; Muller et al., 2008; Papadaki et al., 2008) and SnPh₂ residue containing derivatives (Cruz-Huerta et al., 2008; Gonzalez et al., 2009; Linden et al., 2005; Peveling et al., 2004) have been reported. The relatively high antitumor activity of R₂SnX₂ derivatives and complexes emphasized by several authors including recent reviews (Amini et al., 2002; Evans and Karpel, 1985; Farina et al., 2001; Gielen et al., 1991; Khoo and Ng, 2001) explains all the interest of research workers for organostannic compounds. In the framework of our search of new SnPh₂ residue containing compounds

such as the R₄N₂C₂O₄.2SnR'₂Cl₂ (R=Et, Me et R'=Me, Ph) compounds reported by (Qamar et al., 2009), we have initiated here the study of the interactions between (Pr₂NH₂)₂C₂O₄ and SnPh₃Cl, isoBu₂NH₂C₂O₄SnPh₃ and SnMe₃Cl which have yielded two new oxalato adducts infrared and Mossbauer studies of which have been carried out, then structures suggested on the basis of spectroscopic data.

MATERIALS AND METHODS

(Pr₂NH₂)₂C₂O₄: the complete neutralization of oxalic acid by Pr₂NH in water gives a white precipitate. Analytical data: % calculated (%found)-C=57.50(57.39), H=11.03(10.95), N=9.59(9.55), i-Bu₂NH₂C₂O₄SnPh₃ has been synthesized according to (Fall et al., 2010). The mixture of

$(\text{Pr}_2\text{NH}_2)_2\text{C}_2\text{O}_4$ with SnPh_3Cl as ethanolic solutions in 1:2 ratio gives a white precipitate [A] which is stirred around two hours. On mixing $i\text{-Bu}_2\text{NH}_2)_2\text{C}_2\text{O}_4\text{SnPh}_3$ (Fall et al., 2010) with SnMe_3Cl in 1:1 ratio, both as ethanolic solutions, a white powder is obtained after a slow solvent evaporation [B]. The analytical data reported below, allow to suggest the following formulae: $2(\text{Pr}_2\text{NH}_2)_2\text{C}_2\text{O}_4\cdot\text{SnPh}_2\text{Cl}_2$ [A] -%C=51.74 (51.61), %H=7.97 (8.00), %N=6.03(6.04)-; $(i\text{-Bu}_2\text{NH}_2)_2\text{C}_2\text{O}_4\cdot\text{SnPh}_2(\text{OH})\text{Cl}$ [B] -%C=46.97 (47.12), %H=6.05 (6.00), %N=2.49 (2.46)- . The infrared spectra were recorded at the "Instituto de Quimica", -(U.N.A.M), Mexico-, by means of a BX FT-IR spectrometer type. Elemental analyses have been performed at the "Instituto de Quimica, -(U.N.A.M), Mexico" - while Mössbauer spectra were obtained as described previously (DE Sousa et al., 2006). The infrared spectra were obtained with FTIR spectrometer, the samples being as KBr pellets. Infrared data are given in cm^{-1} . IR abbreviations: (vs) very strong, (s) strong, (m)

medium, (w) weak, (vw) very weak). Mössbauer parameters are given in mm/s (Mössbauer abbreviations: Q.S= quadrupole splitting, I.S= isomer shift, Γ =full width at half-height, A=area). All the chemicals were purchased from Aldrich-Germany- and used as such.

RESULTS

Let us consider the infrared and Mössbauer data of $2(\text{Pr}_2\text{NH}_2)_2\text{C}_2\text{O}_4\cdot\text{SnPh}_2\text{Cl}_2$ [A]:

$V_{\text{as}}(\text{CO}_2)$: 1678vs, 1592s; $V_{\text{s}}(\text{CO}_2)$: 1273vs; δCO_2 : 790s; Q.S = 3.03, IS = 1.19, Γ = 0.97, A(%) = 100 and $(i\text{-Bu}_2\text{NH}_2)_2\text{C}_2\text{O}_4\cdot\text{SnPh}_2(\text{OH})\text{Cl}$ [B] $V_{\text{as}}(\text{CO}_2)$: 1681s, 1637vs; $V_{\text{s}}(\text{CO}_2)$: 1286s, 1250m; δCO_2 : 784s; Q.S = 3.48, IS = 1.32, Γ = 0.99, A(%) = 100. (V_{as} and V_{s} are respectively the asymmetric and the symmetric stretching vibrations while δ is the bending vibration).

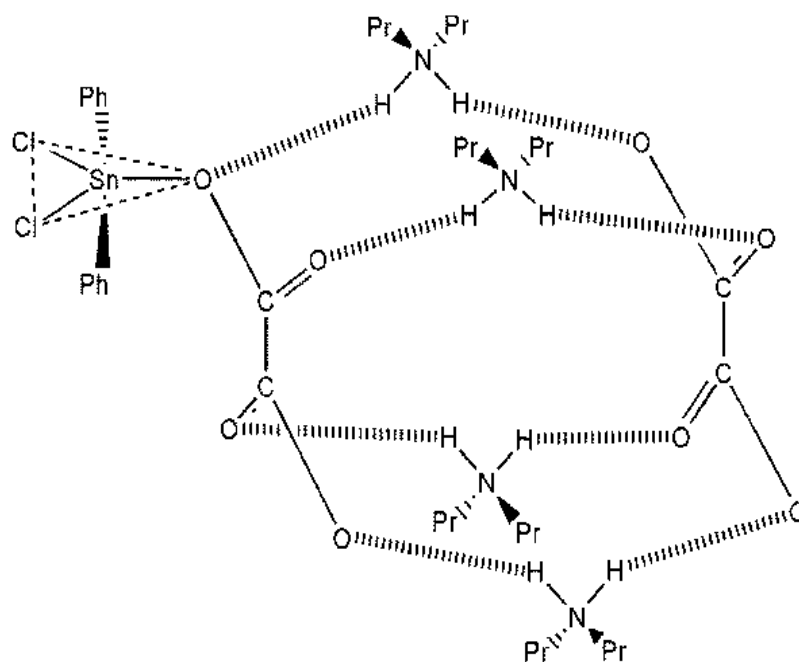


Figure 1a: Suggested structure for (A).

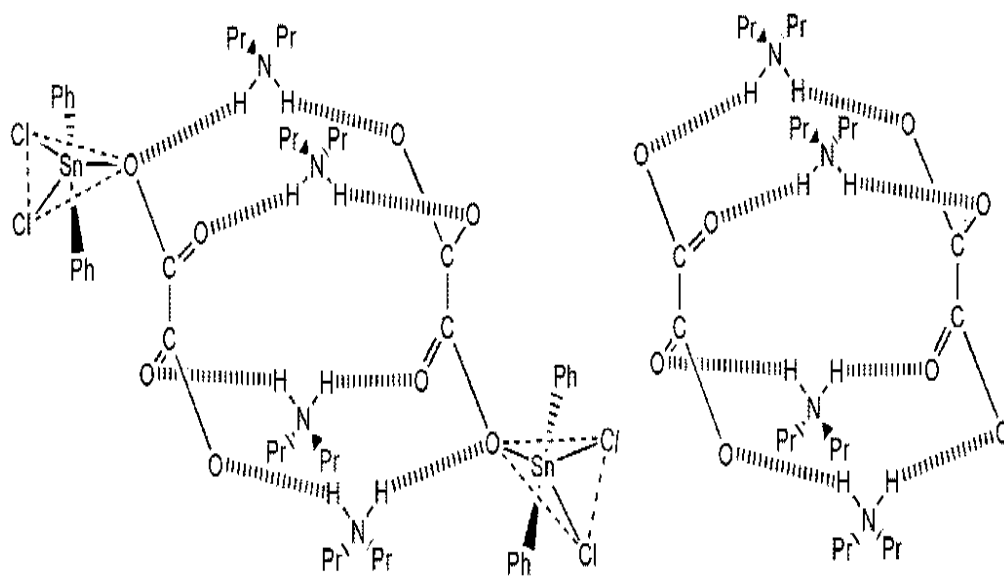


Figure 1b: Suggested structure for (A).
(Pr = Propyl; Ph = phenyl)

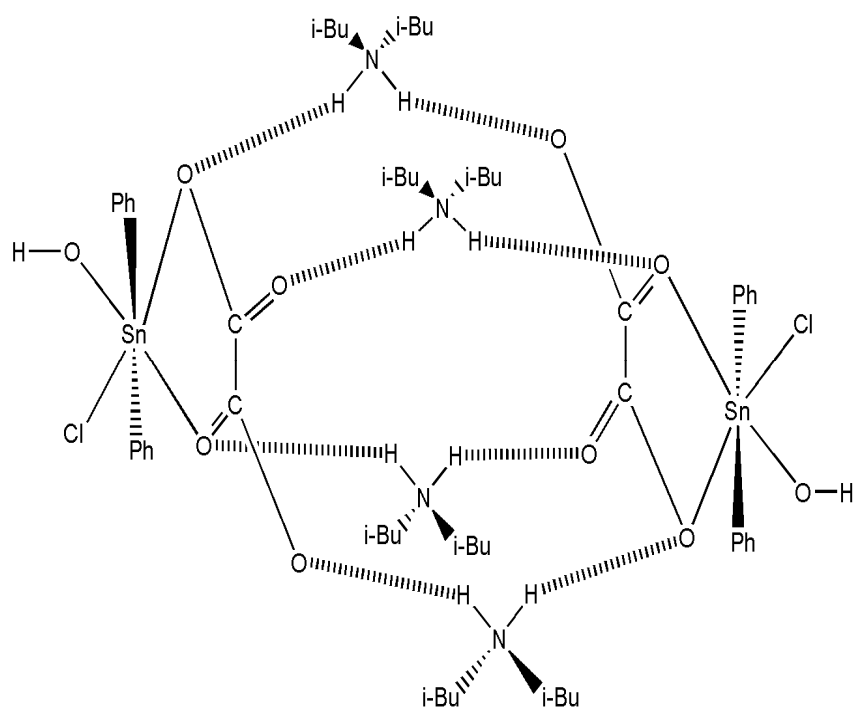


Figure 2: Suggested structure for (B).
(i-Bu = isobutyl; Ph = phenyl)

DISCUSSION

The x-ray structure of SnPh_2ClOH has been determined by (Anaconda et al., 2003). The infrared spectra of these two complexes (**A**, **B**) exhibit the presence of a non-centrosymmetrical oxalate because of the presence of more than two bands in the stretching vibrations region. On the infrared spectra of the two compounds, the wide absorption centered at 2900 cm^{-1} indicates the presence of hydrogen bonds.

The value of $Q.S = 3.03\text{ mm/s}$ for the adduct (**A**) is consistent with the presence of trigonal bipyramidal environment around the tin centre indicating a monocoordinating SnPh_2Cl_2 according to (Bancroft and Platt, 1972). The $Q.S$ value of free SnPh_2Cl_2 is 2.88 mms^{-1} (Bancroft and Platt, 1972) - the enhancement of the quadrupole splitting is an indication of coordination. These spectroscopic data make possible to suggest two structures:

- two parallel oxalate connected by the cations through $\text{NH}\dots\text{O}$ hydrogen bonds - giving a cage- to which a molecule of SnPh_2Cl_2 is monocoordinated (Figure 1a);

- a double cage with one coordinated to two SnPh_2Cl_2 molecules the second one being free of coordination as reported in (Figure 1b). Our group had yet published a paper including cage structures for compounds of general formulae $(\text{R}_2\text{NH}_2)\text{C}_2\text{O}_4.n\text{SnPh}_3\text{Cl}$ - $n=1,2,3$ - (Fall et al., 2010).

The value of the quadrupole splitting in (**B**) is in a good agreement with a trans octahedral environment around the tin centre according to (Bancroft and Platt, 1972).

These spectroscopic data make possible to suggest the cage structure reported on Figure 2 with two $[(\text{C}_2\text{O}_4)_2[\text{SnPh}_2\text{Cl}(\text{OH})]_2]_2$ -complex-anions -containing a monochelating oxalate- connected as cages by diisobutylammonium cations -; when OH groups and Cl atoms are involved in hydrogen

bonds a supramolecular architecture is obtained.

Conclusion

The suggested structures for the two studied adducts are discrete, the oxalate anion behaving as a monocoordinating or a monochelating ligand, the environment around the tin(IV) centre being trigonal bipyramidal or octahedral. One or two hydrogen bonded oxalato cages are present in the structures reported here for the two adducts studied here. The key role of the non symmetrical cations involved in cage building, is noteworthy. When secondary interactions are considered in the second structure, a supramolecular architecture is obtained.

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