

NEW OXALATO AND BENZOATO ADDUCTS CONTAINING A SnR_3 or SnR_2 RESIDUE ($\text{R}=\text{Me}$, Bu , Ph): SYNTHESIS, INFRARED AND MOSSBAUER STUDIES

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Abstract: The reactions between $(i\text{-Bu}_2\text{NH}_2)_2\text{C}_2\text{O}_4$, $(\text{Cy}_2\text{NH}_2)_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $(\text{Pr}_2\text{NH}_2)_2\text{C}_2\text{O}_4$, $\text{Pr}_2\text{NH}_2\text{HC}_2\text{O}_4$, $(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ or $\text{Cy}_2\text{NH}_2\text{O}_2\text{CPh}$ and SnPh_3Cl , SnBu_3Cl or SnMe_3Cl have yielded seven adducts that have been investigated by infrared and Mössbauer techniques. The suggested structures are discrete, the oxalate behaving as a non coordinating entity, only involved in hydrogen bonding while the benzoate is a mono-, bichelating or a monocoordinating ligand, the environments around the tin centres being *trans* or *cis* trigonal bipyramidal. When extra hydrogen bonds are considered involving free OH groups, a supramolecular architecture may be obtained. Noteworthy, is the key role of the cation and water molecules in the obtained structures.

Keywords: *N-H...O and O-HO hydrogen bonds, non bonding oxalate, supramolecular architectures, trigonal bipyramidal environments*

INTRODUCTION

Applications found in some molecules of tin (IV) family in various fields [1-4] and structural varieties are the reasons of the focusing of several groups in the attempt to get new tin (IV) molecules [5-12]. We report here the study of the interactions between (*i*-Bu₂NH₂)₂C₂O₄, (Cy₂NH₂)₂C₂O₄·2H₂O, (Pr₂NH₂)₂C₂O₄, Pr₂NH₂HC₂O₄, (Me₄N)₂C₂O₄·2H₂O or Cy₂NH₂O₂CPh and SnPh₃Cl, SnBu₃Cl or SnMe₃Cl that gave the seven studied adducts. The data obtained from the infrared and Mossbauer spectra of these compounds have allowed suggesting structures.

MATERIALS AND METHODS

(*i*-Bu₂NH₂)₂C₂O₄ (**L**₁) (Cy₂NH₂)₂C₂O₄·2H₂O (**L**₂) and (Pr₂NH₂)₂C₂O₄ (**L**₃) Pr₂NH₂HC₂O₄ (**L**₄) (Me₄N)₂C₂O₄·2H₂O (**L**₅) have been obtained as white precipitates on mixing aqueous solutions of *i*-Bu₂NH, Cy₂NH, Pr₂NH or Me₄NOH with H₂C₂O₄·2H₂O in 2/1 or 1/1 ratio. Analytical data - % calculated (% found) – C = 62.03 (62.00), H = 11.57 (11.49), N = 8.04 (8.06) for (**L**₁) and C = 68.99 (69.02), H = 10.69 (10.59), N = 6.19 (6.20) for (**L**₂) – C = 57.50 (57.09), H = 11.03 (10.89), N = 9.59 (9.55) for (**L**₃). C = 43.78 (44.02), H=11.02 (10.50), N=10.21 (10.15) (**L**₅). Cy₂NH₂O₂CPh has been obtained as a powder on mixing benzoic acid with the amine in 1/1 ratio and allowing the water to evaporate at 60 °C. Analytical data: % calculated (% found) - C = 75.21 (75.39), H = 9.63 (10.05), N = 4.62 (4.65).

(Cy₂NH₂)₂C₂O₄·2SnBu₃Cl·2H₂O (**A**); 2(*i*-Bu₂NH₂)₂C₂O₄·SnBu₃Cl·H₂O (**B**); (Pr₂NH₂)₂C₂O₄·SnPh₃Cl·2H₂O·1/8Pr₂NH₂Cl (**C**); 3(Pr₂NH₂)₂C₂O₄·3SnPh₂Cl₂·SnCl₄ (**D**); (*i*-Bu₂NH₂)₂C₂O₄·(Me₄N)₂C₂O₄·3SnBu₂Cl₂ (**E**); Cy₂NH₂PhCO₂·SnPh₃Cl·Cy₂NH₂Cl (**F**) and Cy₂NH₂Cl·3PhCO₂SnMe₃·H₂O (**G**) have been prepared by allowing (Cy₂NH₂)₂C₂O₄·2H₂O or (*i*-Bu₂NH₂)₂C₂O₄ to react with SnBu₃Cl, (Pr₂NH₂)₂C₂O₄ to react with SnPh₃Cl, Pr₂NH₂HC₂O₄ with SnPh₃OH, (*i*-Bu₂NH₂)₂C₂O₄, (Me₄N)₂C₂O₄ and SnBu₂Cl₂ and Cy₂NH₂O₂CPh to react with SnPh₃Cl or SnMe₃Cl in ethanol in 1/2, 2/1, 1/1, 2/1, 1/1/2, 1/2 and 1/2 or ratio respectively; a white precipitate was obtained in all cases and stirred around two hours. Analytical data % calculated (% found) – C = 52.69 (52.58), H = 9.37 (9.28), N = 2.46 (2.39) for (**A**) and C = 55.40 (55.35), H = 10.56 (10.57), N = 5.38 (5.47) for (**B**); C = 53.36 (53.33), H = 6.63(6.80) N = 4.00 (4.09) for (**C**) - % C = 43.19 (43.72), % H = 5.85 (5.83), % N = 3.87 (3.90) for' (**D**) -% C = 41.74 (41.61), % H = 7.95 (7.89), % N = 3.74 (3.64) for (**E**). C = 64.91 (64.80), H = 7.56 (7.67), N = 3.09 (3.08) for (**F**) and C = 46.26 (46.33), H = 6.28 (6.31), N = 1.28 (1.25) for (**G**).

The infrared spectra were recorded at the “Instituto de Química, U.N.A.M, Mexico”, using a BX FT-IR spectrophotometer. Elemental analyses have been performed at the “Instituto de Química, UNAM, Mexico”. Mössbauer spectra were obtained as described previously [13]. 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.

RESULTS AND DISCUSSION

Let us consider the infrared and Mossbauer data of $(\text{Cy}_2\text{NH}_2)_2\text{C}_2\text{O}_4 \cdot 2\text{SnBu}_3\text{Cl} \cdot 2\text{H}_2\text{O}$ (**A**): $\nu_{\text{as}}\text{COO}^-$ (1640 vs, 1625 s); $\nu_{\text{s}}\text{COO}^-$ (1283 vs, 1269 vs); δCOO^- (784 s), $\nu_{\text{as}}\text{SnBu}_3$ (690 s), $\nu_{\text{s}}\text{SnBu}_3$ (601 vw); I.S = 1.46 $\text{mm}\cdot\text{s}^{-1}$; Q.S = 3.79 $\text{mm}\cdot\text{s}^{-1}$; Γ = 0.86; % A = 100; $2(i\text{-Bu}_2\text{NH}_2)_2\text{C}_2\text{O}_4 \cdot \text{SnBu}_3\text{Cl} \cdot \text{H}_2\text{O}$ (**B**): $\nu_{\text{as}}\text{COO}^-$ (1610 vs); $\nu_{\text{s}}\text{COO}^-$ (1313 vs, 1280 s); δCOO^- (788 s), $\nu_{\text{as}}\text{SnBu}_3$ (686 s), $\nu_{\text{s}}\text{SnBu}_3$ (600 vw); $(\text{Pr}_2\text{NH}_2)_2\text{C}_2\text{O}_4 \cdot \text{SnPh}_3\text{Cl} \cdot 2\text{H}_2\text{O} \cdot 1/8\text{Pr}_2\text{NH}_2\text{Cl}$ (**C**): $\nu_{\text{as}}\text{COO}^-$ (1679 vs, 1677 vs); $\nu_{\text{s}}\text{COO}^-$ (1271 s); δCOO^- (790 s); Q.S = 2.78 $\text{mm}\cdot\text{s}^{-1}$, I.S = 1.25 $\text{mm}\cdot\text{s}^{-1}$, Γ = 0.97 $\text{mm}\cdot\text{s}^{-1}$, A (%) = 100; $3(\text{Pr}_2\text{NH}_2)_2\text{C}_2\text{O}_4 \cdot 3\text{SnPh}_2\text{Cl}_2 \cdot \text{SnCl}_4$ (**D**); $(i\text{-Bu}_2\text{NH}_2)_2\text{C}_2\text{O}_4 \cdot (\text{Me}_4\text{N})_2\text{C}_2\text{O}_4 \cdot 3\text{SnBu}_2\text{Cl}_2$ (**E**); $\nu_{\text{as}}\text{COO}^-$ (1647 s, 1612 vs); $\nu_{\text{s}}\text{COO}^-$ (1261 vs); δCOO^- (798 s) for (**F**); $\nu_{\text{as}}\text{COO}^-$ (1637 vs); $\nu_{\text{s}}\text{COO}^-$ (1234 s, 1299 vs); δCOO^- (790 s), $\nu_{\text{as}}\text{SnBu}_2$ (686 vs), $\nu_{\text{s}}\text{SnBu}_2$ (601 vw) for (**G**).

The infrared spectra of these complexes exhibit the presence of a non-centrosymmetric oxalate because of the presence of more than two bands in the stretching vibrations region. On the infrared spectra of these compounds, the wide absorption band centered in 2900 cm^{-1} indicates the presence of hydrogen bonds. On the infrared spectra of the compounds (**A**, **B**), the appearance of $\nu_{\text{s}}\text{SnR}_3$ (R = Bu, Me) as a very weak band at 601 and 520 cm^{-1} , reveals the presence of the planar SnR_3 residues.

The value of the quadrupole splitting of $(\text{Cy}_2\text{NH}_2)_2\text{C}_2\text{O}_4 \cdot 2\text{SnBu}_3\text{Cl} \cdot 2\text{H}_2\text{O}$ is consistent with a monocoordinated SnBu_3Cl according to Bancroft and Platt [14] allowing to suggest the discrete structure reported on Figure 1 with dimeric hydrogen bonded oxalates linked to four $\text{H}_2\text{O} \cdot \text{SnBu}_3\text{Cl}$ through $\text{OH} \dots \text{O}$ hydrogen bonds.

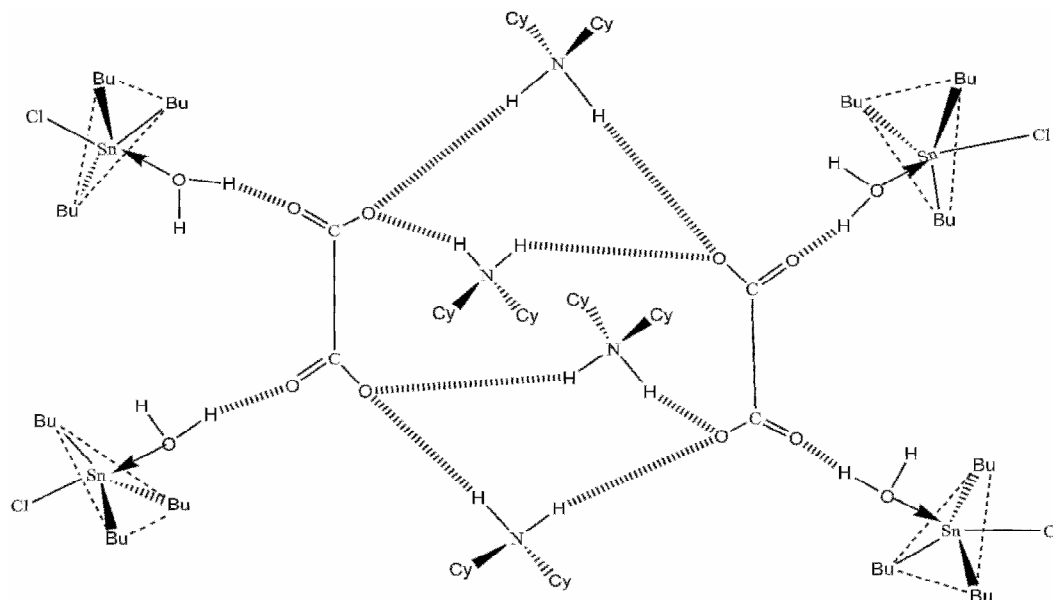


Figure 1. Proposed structure for A

For $2(i\text{-Bu}_2\text{NH}_2)_2\text{C}_2\text{O}_4 \cdot \text{SnBu}_3\text{Cl} \cdot \text{H}_2\text{O}$ only one $\text{SnBu}_3\text{Cl} \cdot \text{H}_2\text{O}$ can be considered connected to the dimeric hydrogen bonded oxalates (Figure 2a) ($\nu_{\text{s}}\text{SnBu}_3$ is a weak band) or as central and hydrogen bonded to four oxygen atoms through bifurcated hydrogen bonds (Figure 2b).

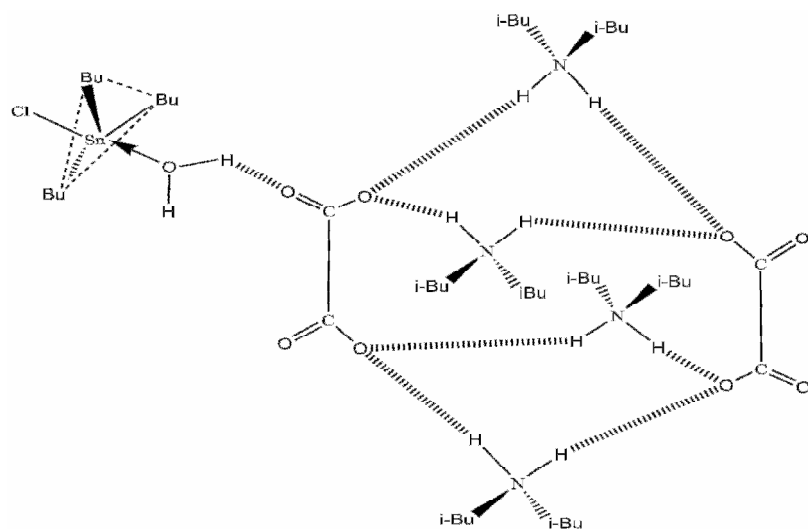


Figure 2a. Proposed structure for B

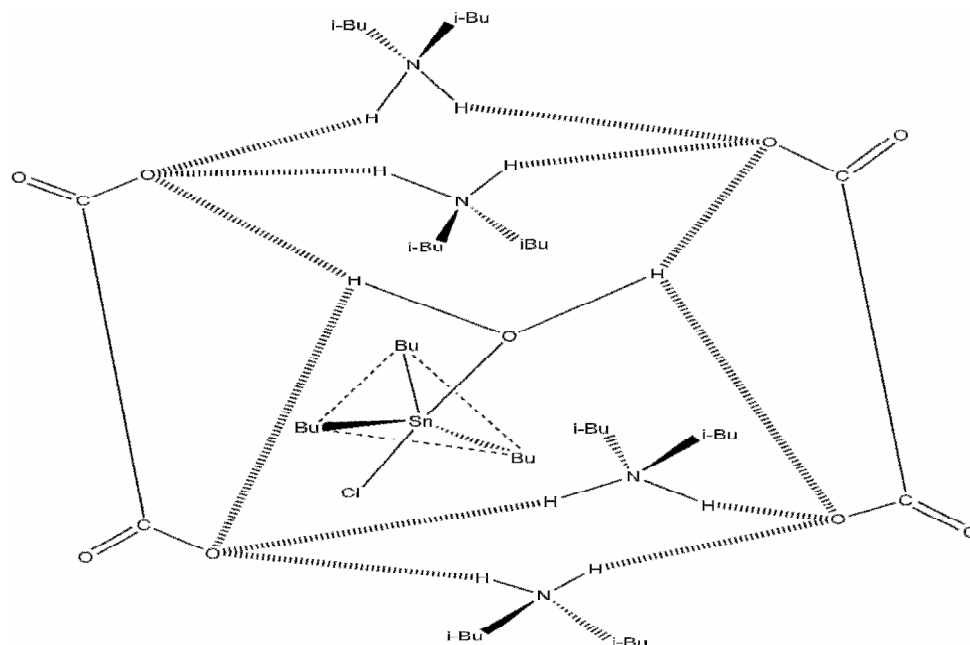


Figure 2b. Proposed structure for B

For $(\text{Pr}_2\text{NH}_2)_2\text{C}_2\text{O}_4 \cdot \text{SnPh}_3\text{Cl} \cdot 2\text{H}_2\text{O} \cdot 1/8 \text{ Pr}_2\text{NH}_2\text{Cl}$ the Mossbauer data are consistent with the presence of monocoordinated SnPh_3 residue - in $\text{C}_2\text{O}_4(\text{SnPh}_3)_2$ the Q.S value is $2.82 \text{ mm} \cdot \text{s}^{-1}$, the SnPh_3 residues monocoordinated [14] - allowing to suggest the structure reported on Figure 3 with two $[\text{C}_2\text{O}_4\text{SnPh}_3]^-$ complex-anion containing a monocoordinated oxalate, linked by cation $\cdots \text{Cl} \cdots$ cation, the water being lattice or involved extra-intermolecular hydrogen bonds leading to a supramolecular architecture.

The infrared spectra of these two complexes (**D**, **E**) exhibit the presence of a non-centrosymmetric 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 band centered in 2900 cm^{-1} indicates the presence of hydrogen bonds.

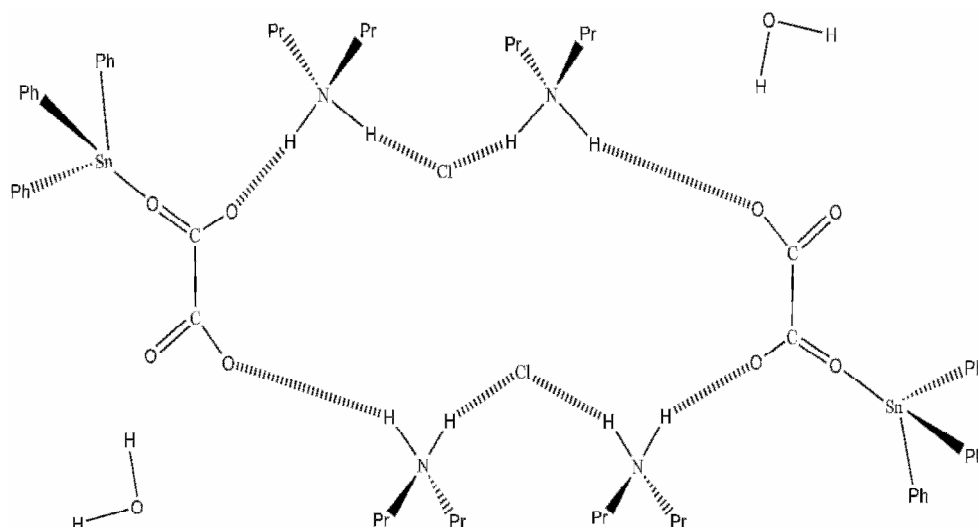


Figure 3. Proposed structure for compound C

In the case of (E), the band at 950 cm^{-1} confirms the presence of the tetramethylammonium ion. The adduct $(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4 \cdot 2\text{SnPh}_2\text{Cl}_2$ has been reported by Gueye and al [15]. The anions $[\text{C}_2\text{O}_4\text{SnR}_2\text{Cl}_2]^{2-}$ (R = Ph, Bu) have not been reported to the best knowledge but both $[\text{C}_2\text{O}_4\text{SnCl}_4]^{2-}$ and $[\text{C}_2\text{O}_4 \cdot 2\text{SnCl}_4]^{2-}$ have been reported [9, 16]. From the existence of some of these complex-oxyanions we can suggest for our studied adducts the presence of $[\text{C}_2\text{O}_4\text{SnR}_2\text{Cl}_2]^{2-}$ and $[\text{C}_2\text{O}_4 \cdot 2\text{SnR}_2\text{Cl}_2]^{2-}$ (R = Ph, Bu) allowing to suggest the discrete structure reported on Figures 4 and 5, the environments being octahedral, the oxalate behaving as a mono- and bichelating ligand. The key role of the cation is noteworthy. The tetramethylammonium ions interact electrostatically with the metallic component of the structure.

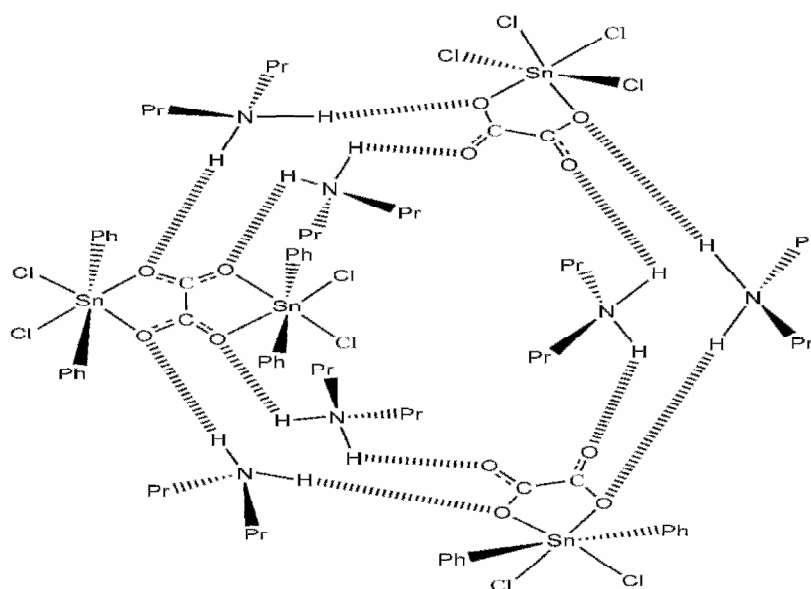


Figure 4. Proposed structure for compound D

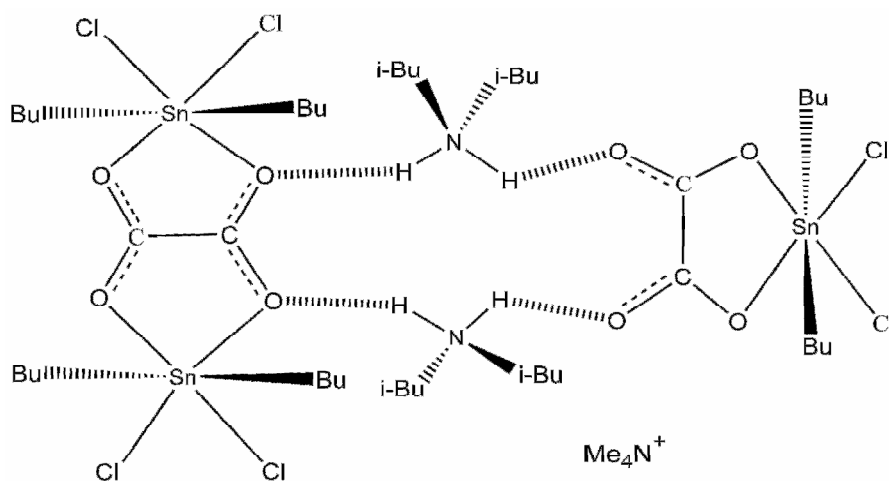


Figure 5. Proposed structure for compound *E*

Let us consider the IR and Mossbauer data of the benzoato adducts: $\text{Cy}_2\text{NH}_2\text{PhCO}_2\text{SnPh}_3\text{Cl} \cdot \text{Cy}_2\text{NH}_2\text{Cl}$ (**F**): ν_{asCOO^-} (1622 m, 1601 vs, 1542 m); ν_{sCOO^-} (1378 vs); δCOO^- (727 s); $\text{I.S}_1 = 1.22 \text{ mm s}^{-1}$; $\text{Q.S}_1 = 3.01 \text{ mm s}^{-1}$; $\Gamma_1 = 0.86$; % $A_1 = 67$; $\text{I.S}_2 = 0.55 \text{ mm s}^{-1}$; $\text{Q.S}_2 = 2.19 \text{ mm s}^{-1}$; $\Gamma_2 = 0.86$; % $A_2 = 33$ and $\text{Cy}_2\text{NH}_2\text{Cl} \cdot 3\text{PhCO}_2\text{SnMe}_3 \cdot \text{H}_2\text{O}$ (**G**): ν_{asCOO^-} (1610 vs, 1600 s); ν_{sCOO^-} (1219 vs, 1209 s); δCOO^- (788 s), ν_{asSnMe_3} (556 s), ν_{sSnMe_3} (520 vw). For $\text{Cy}_2\text{NH}_2\text{O}_2\text{CPhSnPh}_3\text{Cl} \cdot \text{Cy}_2\text{NH}_2\text{Cl}$ the Mossbauer data are consistent with the presence of two types of tin centres in the ratio $\frac{1}{2}$, the structure consisting of $\text{O}_2\text{CPhSnPh}_3$ with a *cis* coordinated SnPh_3 residue (2.19 mm s^{-1}) and a cyclic hydrogen bonded metallic component with monocoordinated SnPh_3Cl (3.01 mm s^{-1}) (Figure 6).

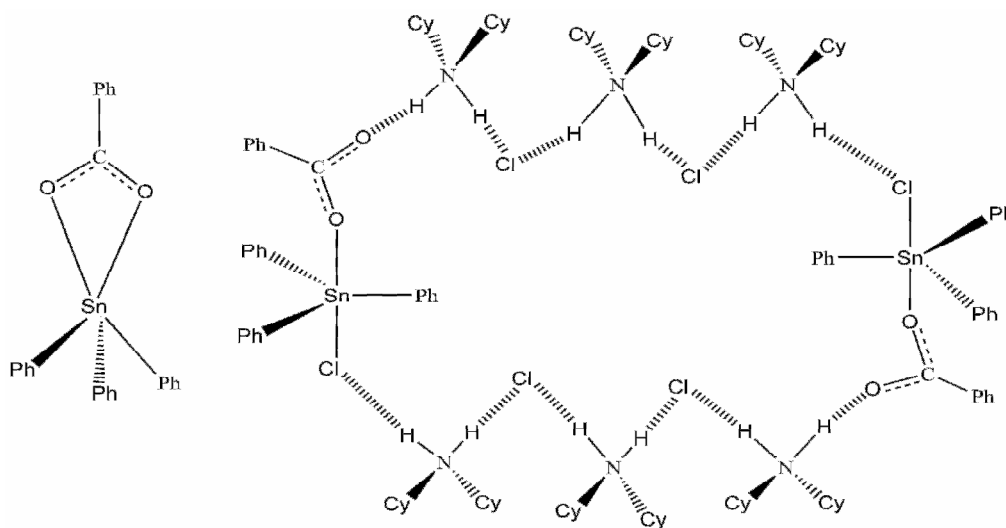


Figure 6. Proposed structure for *F*

For $\text{Cy}_2\text{NH}_2\text{Cl} \cdot 3\text{O}_2\text{CPhSnMe}_3 \cdot \text{H}_2\text{O}$ the absence of ν_{sSnMe_3} indicates a planar residue allowing to suggest while considering the complex-anion $[\text{Cl} \cdot 3\text{O}_2\text{CPhSnMe}_3]^-$ a structure with a central chloride linked to three $\text{O}_2\text{CPhSnMe}_3$ which dimerizes through the cation leading to the structure reported on Figure 7 the water molecule is lattice or involved in hydrogen bonding leading to a supramolecular architecture.

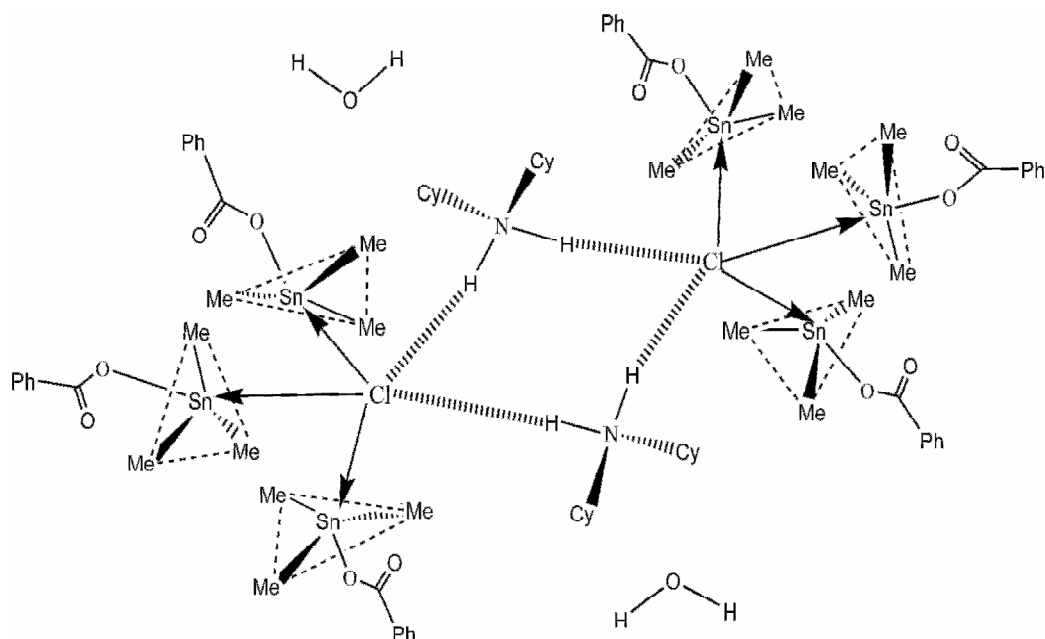


Figure 7. Proposed structure for *G*

CONCLUSION

The characterized complexes have discrete structures with *trans* or *cis* coordinated SnR_3 residues, the oxalate behaving as a non coordinating entity, only involved in hydrogen bonding, monocoordinating, mono- and bichelating ligand while the benzoate is a monochelating or a monocoordinating ligand. When extra hydrogen bonds are considered involving free OH groups, a supramolecular architecture may be obtained.

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