

(Cy₂NH₂O₂CPh)₃(SnCl₄)₂ AND (SnBu₂)₄(O₂CPh)₁₆Cl₆(OH)₂(Cy₂NH₂)₁₆: SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION

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Abstract: The two title compounds have been synthesized, their IR and Mössbauer studies carried out. The structures are discrete and contain mono- and bidentate PhCO₂⁻, the environment around the tin (IV) centre being octahedral (in SnCl₄ adduct), trapezoidal bipyramidal (in the SnBu₂ residue containing derivative). A tetranuclear monomeric or an oligomeric structure is suggested in the tetranuclear SnBu₂ residue containing derivative.

Keywords: *benzoate, IR, Mössbauer, monomer or oligomeric structures, SnCl₄, SnBu₂ residue*

INTRODUCTION

Many organotin (IV) compounds display applications (in agriculture, as wood preservatives, antifouling paints) [1, 2]. The dibutyltin perfluoro alkane carboxylate has been reported to be more active than 5-fluorouracil and etoposide towards some kinds of cancer [3]. For widening this family of compounds, we initiate in this work, the study of the interactions between $\text{Cy}_2\text{NH}_2\text{O}_2\text{CPh}$ and SnCl_4 or SnBu_2Cl_2 which has yielded two new compounds, IR and Mössbauer studies of which have been carried out and structures suggested on the basis of spectroscopic data.

EXPERIMENTAL

The neutralization of benzoic acid by Cy_2NH in water gives a white precipitate which has been stirred no less than two hours, recrystallized from CHCl_3 and washed by ether. Its analytical data % calculated (% found): C = 75.25 (75.17); H = 9.57 (9.38); N = 4.62 (4.55) indicate $\text{Cy}_2\text{NH}_2\text{O}_2\text{CPh}$ (**L**) as formula. The studied adducts have been obtained by mixing (**L**) dissolved in CHCl_3 with SnCl_4 in benzene – 1 : 1 **L** or SnBu_2Cl_2 in EtOH – 1 : 4 **L**. A white precipitate was obtained with SnCl_4 and a solution with SnBu_2Cl_2 ; in this last case a slow solvent evaporation gives a white powder. The analytical data reported below have allowed suggesting the following formulae:

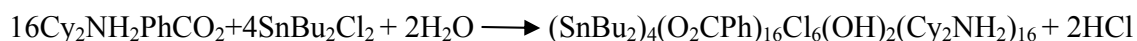
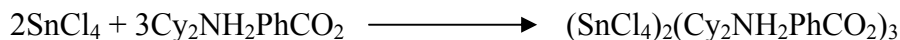
(A) $(\text{SnCl}_4)_2(\text{Cy}_2\text{NH}_2\text{PhCO}_2)_3$:

C = 47.83 (47.36); H = 6.13 (6.26); N = 2.94 (2.86); Cl = 19.81 (19.74);

(B) $(\text{SnBu}_2)_4(\text{O}_2\text{CPh})_{16}\text{Cl}_6(\text{OH})_2(\text{Cy}_2\text{NH}_2)_{16}$:

C = 66.21 (66.09); H = 8.72 (8.89); N = 3.86 (4.45); Cl = 3.66 (3.60).

The reaction equations are:



All the chemicals were purchased from Aldrich Company and used without any further purification. The infrared spectra were recorded by a PE 580 ($4000 - 200 \text{ cm}^{-1}$) or a FTIR-Nicolet ($600 - 50 \text{ cm}^{-1}$) spectrometer at the University of Padova (Italy), the sample being as Nujol mulls while CsI or polyethylene windows were used. Mössbauer spectra were obtained as described previously [4]. Infrared data are given in cm^{-1} ; abbreviations: (vs) very strong, (s) strong, (m) medium, (sh) shoulder. Mössbauer parameters are given in mms^{-1} ; abbreviations: Q.S. = quadrupole splitting, I.S. = isomer shift, Γ = full width at half-height.

RESULTS AND DISCUSSION

Let us consider the main IR data of:

(A) $(\text{SnCl}_4)_2(\text{Cy}_2\text{NH}_2\text{PhCO}_2)_3$:

$\nu\text{CO}_2 = 1690$ (vs), 1530 (s), 1315 (s); $\delta\text{CO}_2 = 650$ (s); $\rho\text{CO}_2 = 550$ (m); $\omega\text{CO}_2 = 470$ (s); $\nu\text{SnCl} = 358$ (m), 333 (w), 315 (m); $\nu\text{SnO} = 203$ (m);

(B) (SnBu₂)₄(O₂CPh)₁₆Cl₆(OH)₂(Cy₂NH₂)₁₆:

$\nu\text{CO}_2 = 1625$ (vs), 1540 (vs), 1380 (vs); $\delta\text{CO}_2 = 675$ (s); $\rho\text{CO}_2 = 550$ (s); $\omega\text{CO}_2 = 435$ (m); $\nu\text{SnC}_2 = 617$ (sh); $\nu\text{SnO} = 208$ (m);

and their Mössbauer data:

(A) (SnCl₄)₂(Cy₂NH₂PhCO₂)₃:

$\delta = 0.30$ mms⁻¹, Q.S. = 0.46 mms⁻¹, $\Gamma = 0.97$ mms⁻¹

(B) (SnBu₂)₄(O₂CPh)₁₆Cl₆(OH)₂(Cy₂NH₂)₁₆:

$\delta_1 = 1.49$ mms⁻¹, Q.S.₁ = 3.87 mms⁻¹, $\Gamma_1 = 0.91$ mms⁻¹, $\delta_2 = 1.33$ mms⁻¹, Q.S.₂ = 3.09 mms⁻¹, $\Gamma_2 = 0.91$ mms⁻¹

(A) (SnCl₄)₂(Cy₂NH₂PhCO₂)₃

The appearance of four IR bands due to ν_{as} SnCl₄ is consistent with the presence of *cis* coordinated SnCl₄ molecules according to Group Theory. The value of the isomer shift is consistent with the predictions of Tudela *et al.* for O₂SnCl₄ framework containing adducts [5]. This allows to consider the complex - anion [(SnCl₄)₂(PhCO₂)₃]³⁻ consisting of a central bidentate benzoate linked to two SnCl₄ molecules; two external benzoate anions are then connected to these SnCl₄ molecules conferring an octahedral environment to the tin(IV) centres. The suggested structure for **A** is a dimer, the two dinuclear monomers being connected through NH---O (linking external PhCO₂⁻) and NH---Cl (linking *trans* Cl) hydrogen bonds (Figure 1) – the wide and strong absorption on the IR spectrum around 2900 cm⁻¹ is due to NH---O and NH---Cl hydrogen bonds.

(B) (SnBu₂)₄(O₂CPh)₁₆Cl₆(OH)₂(Cy₂NH₂)₁₆

On the IR spectrum of this compound, the presence of a very weak bond at 617 cm⁻¹ allows to conclude to the presence of linear SnBu₂ moieties. The Mössbauer spectrum indicates two types of tin(IV) centers in 1/1 ratio: one tin centre (Q.S. = 3.87 mms⁻¹) has a *trans* trapezoidal bipyramidal environment while the other one (Q.S. = 3.09 mms⁻¹) has a trigonal bipyramidal environment according to Platt *et al.* [6, 7]. The structure, while considering [(SnBu₂)₄(PhCO₂)₁₆]⁸⁻ consists of two SnBu₂ central residues in a *trans* trapezoidal bipyramidal environment and two external SnBu₂ residues in a trigonal bipyramidal environment, these four moieties being linked by the cations through NH....O hydrogen bonds. In the monomeric structure the remaining cations, the OH group and the chloride ions ensure the connection of the external PhCO₂⁻ leading to the structure reported in Figure 2 it is also possible to connect two or more pentanuclear architectures (in Figure 3 we arbitrary reported the dimer while any oligomer form works).

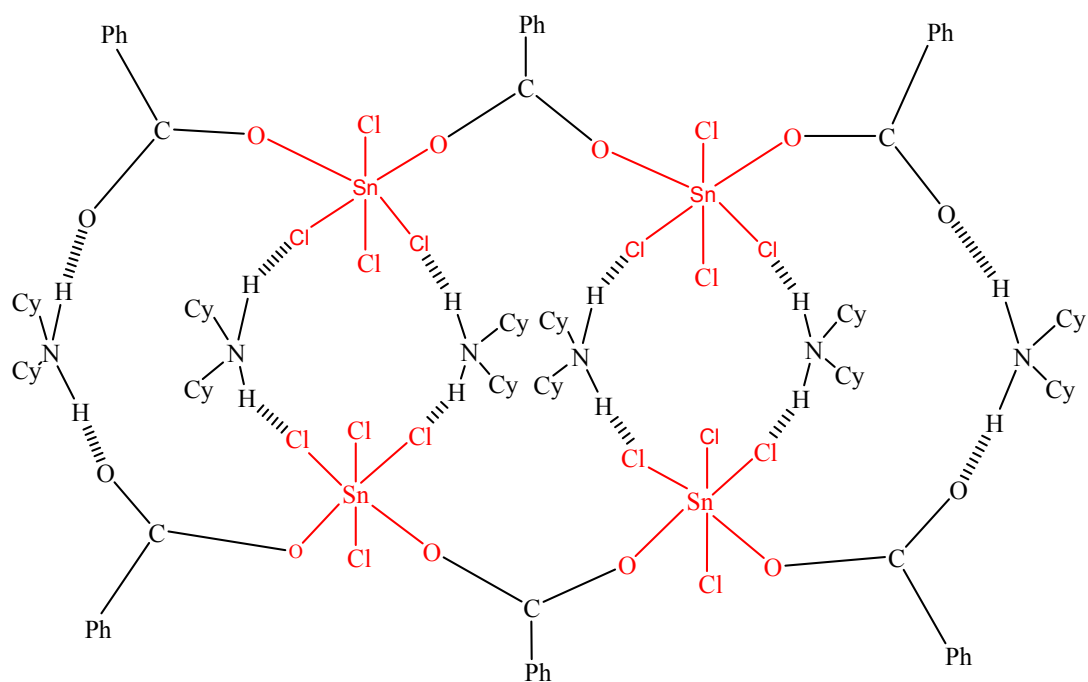


Figure 1. Suggested structure for (A): $(\text{SnCl}_4)_2(\text{Cy}_2\text{NH}_2\text{PhCO}_2)_3$

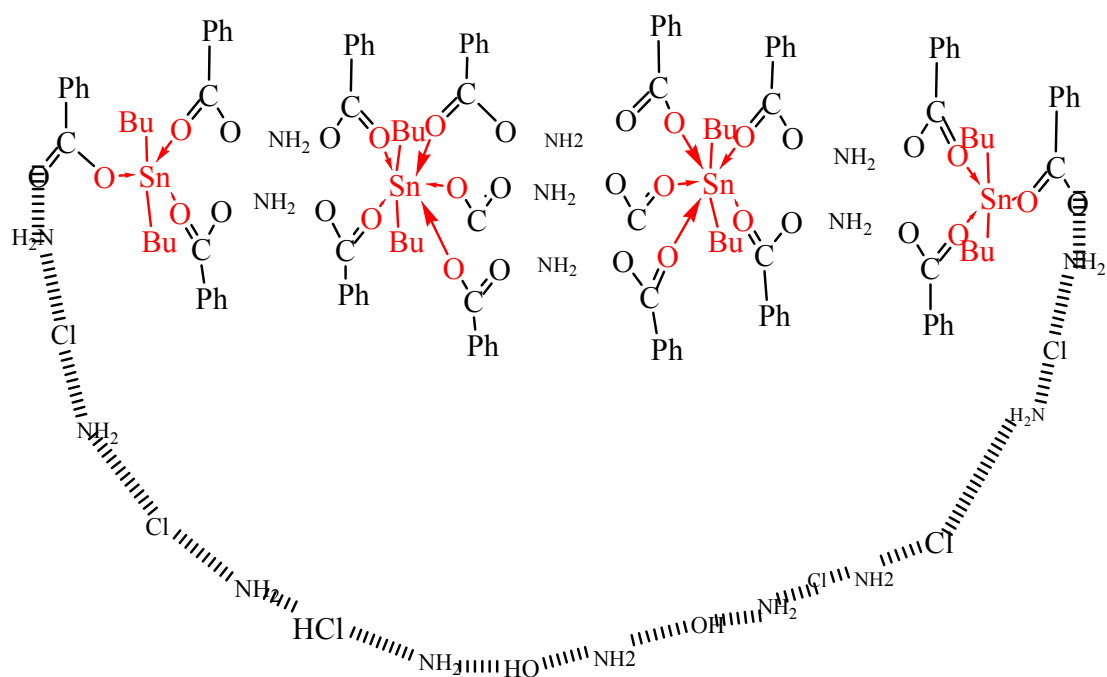


Figure 2. Suggested structure for (B): $(\text{SnBu}_2)_4(\text{O}_2\text{CPh})_{16}\text{Cl}_6(\text{OH})_2(\text{Cy}_2\text{NH}_2)_{16}$

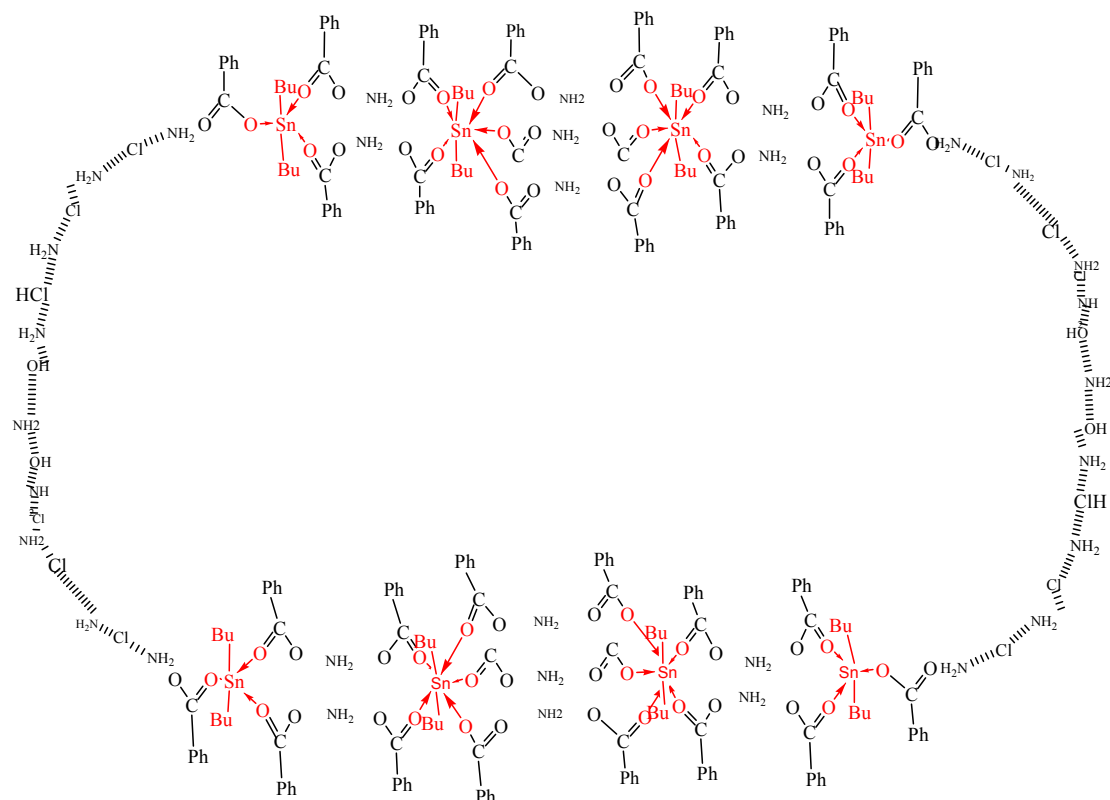


Figure 3. Suggested structure for dimer (**B**)

CONCLUSION

In the two studied compounds the benzoate anion behaves as a monodentate or a bidentate ligand. The key role of the cation is noteworthy. A monomeric or an oligomeric structure is obtained in the SnBu₂ residue containing compound when the cations are involved.

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