SYNTHESIS AND CHARACTERIZATION OF A TETRAHEDRAL AND MONOMERIC MONOBUTYLTIN COMPOUND WITH Α-HYDROXYISOBUTYRIC ACID

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ABSTRACT

The monobutyltin compound [BuSnLCl$_2$], L = Me$_2$C(OH)COO$^-$, was prepared and characterized by elemental analysis of carbon, hydrogen, chlorine and tin, and infrared, ^{119m}Sn-Mössbauer and ^{119m}Sn-NMR spectroscopies. In the compound, a tetrahedral tin species, L is coordinated monodentatedly by the oxygen of the deprotonated hydroxyl of the carboxylic group. The compound was studied by the application of TG and DSC in dynamic atmosphere of helium. The thermal decomposition mechanism for the compound and TG curve suggests the formation of tin in accordance with their stoichiometry. The Mössbauer parameters of complexes are in agreement with a monomeric structure for the complex in the solid state.

Keywords: organotin compound, tin isobutyric acid compound, thermal decomposition.

INTRODUCTION

The α-hydroxycarboxylic acids are ligands potentially polydentated, that can bond to metals, enabling the synthesis of compounds with varied structures, for which the geometry and the coordination number are governed by the size and for the ramification degree of the ligand.[1] In the years 1995-2005, we have developed systematic works about the synthesis and characterization of organotin compounds derived from α-hydroxycarboxylic acids[2-5], which have shown efficient microcide activity on fungi and pathogenic bacteria in agriculture and in humans.[6-8] The present investigation relates to the preparation and characterization of a new complex [BuSnLCl$_2$], L = Me$_2$C(OH) COO, characterized by elemental analysis of carbon, hydrogen, chlorine and tin, by infrared, ^{119m}Sn-Mössbauer and ^{119m}Sn-RMN spectroscopies, and the applications of TG and DSC techniques in dynamic helium atmosphere.

EXPERIMENTAL

The TG curve was recorded using Shimadzu TGA-50 model thermogravimetric analyzer in the range of 25–700 °C at heating rate of 20 K min^{-1} and in a dynamic atmosphere of helium with a flow rate of 20 mL min^{-1}. The initial sample masses used were 3–4 mg.

A Shimadzu DSC-50 differential scanning calorimetry analyzer was used to record the DSC curves. The experimental conditions were: 25–200 °C temperature range, β = 10 K min^{-1} heating rate, helium purging with a flow of 50.0 mL min^{-1}. The initial sample masses were 5–6 mg.

The melting point was determined on a FP-2 Mettler system.

The infrared spectrum of the complex was recorded between 5000–200 cm^{-1}, using a Perkin Elmer Paragon 1000 spectrophotometer, in CsI pellets.

The X-ray fluorescence characterization of the TG analysis was performed by means of a Rigaku-Geigerflex spectrophotometer.

The elemental analysis of carbon and hydrogen was carried out using Perkin Elmer 2400CHN Elemental Analyzer.

Chlorine determination was done by neutron activation analysis. The sample was irradiated in the central tube of the Triga-3 reactor and the measurement was performed applying a Low Lewel α/β Counting System Model 2200 Canberra proportional detector, at the Nuclear Development Technology Centre, of CNEN (National Nuclear Energy Commission), in Belo Horizonte-MG, Brazil.

The tin determination was performed by atomic absorption using a Hitachi Z-8200 spectrometer.

The ^{119m}Sn-Mössbauer spectra were provided by a constant acceleration spectrometer equipped with a BaSnO$_3$ source, at 85 K.

The ^{119m}Sn-NMR spectrum was obtained with a Bruker DRX 400 MHz Avance spectrophotometer, using C$_5$D$_5$N.

The complex [BuSnLCl$_2$] was synthesized reacting α-hydroxyisobutyric acid, (CH$_3$)$_2$C(OH)COOH, and monobutyltin trichloride, BuSnCl$_3$, in 1:1 molar ratio. The carboxylic acid was added to stirred acetonitrile solution and after adding the tin compound, the system was further stirred and refluxed for 24 hours. After complete solvent evaporation an oily compound was obtained, which was washed with 1:1 hexane-chloroform mixture (3 x 2 mL) and dried at 100 °C in an Abderhalden pistol for 1 h, with all manipulations performed in air, allowing the attainment of a white solid.

The complex [BuSnLCl$_2$] was characterized by the IR spectrum, by elemental analysis of carbon, hydrogen, chlorine and tin, by ^{119m}Sn-Mössbauer and ^{119m}Sn-NMR spectroscopic studies and by TG and DSC techniques.

RESULTS AND DISCUSSION

The complex [BuSnLCl$_2$] was observed using optical microscope and a microcrystalline constitution was exhibited by the complex. As it was observed for other organotin derivatives previously prepared by us[2-5], it was not possible to obtain suitable single crystals to determine their structure by X-ray crystallography too.

The melting point observed for the [BuSnLCl$_2$] was 151-152 °C; the results of elemental analysis were C = 27.2%, H = 4.3%, Cl = 19.0% and Sn = 33.5% in agreement with the calculated values C = 27.5%, H = 4.6%, Cl = 20.3%, and Sn = 33.9%.

The most representative stretching vibrations from the infrared spectrum of the α-hydroxyisobutyric acid, in cm^{-1}, were $\nu_{COOasym}$ = 1740; ν_{COOsym} = 1280; ν_{OH} = 3430; and from the infrared spectrum of the [BuSnLCl$_2$], in cm^{-1}, were $\nu_{COOasym}$ = 1655, 1563; ν_{COOsym} = 1310; ν_{OH} = 3200; ν_{CH} = 2950, 2900, 2850; ν_{SnO} = 480; ν_{SnCl} = 270, 280.

The observed alteration of the ν_{COOsym} value from 1740 cm^{-1} in the α-hydroxycarboxylic acid[9,10], to 1655 and to 1620 cm^{-1} in the complex, indicates the participation of the carboxyl of the α-hydroxyisobutyric acid in the coordination to the tin.[11] Similar results were obtained for the other compounds [(LR$_2$Sn)$_2$O] {R = Me, Bu; L = PhCH(OH)COO}[3,4] and for the compounds [R$_2$SnL$_2$] {R = Bu, Ph; L = MeOC$_6$H$_4$CH(OH)COO, PhCH(OH) COO}[7] studied by us. In a complementary form, the dislocation of the ν_{OH} from 3430 cm^{-1} in the α-hydroxyisobutyric acid to 3200 cm^{-1} in the complex, suggests the existence of strong intramolecular hydrogen bonding, indicating an absence of the alcoholic hydroxyl group in the coordination of the tin atom.[12-14]

In the ^{119m}Sn Mössbauer spectroscopy, a single quadrupole splitting doublet was observed, making evident that [BuSnLCl$_2$] was present at only one site around the tin atom. The values for the quadrupole splitting doublet, Δ = 1.92 mm s^{-1}, and isomer shift, δ = 1.02 mm s^{-1}, are consistent with the tin atoms located in site with coordination number equal to four, which is highlighted by the relationship around the value ρ = Δ/δ = 1.93.[15-18] The Mössbauer spectrum for the compound is presented in Figure 1.

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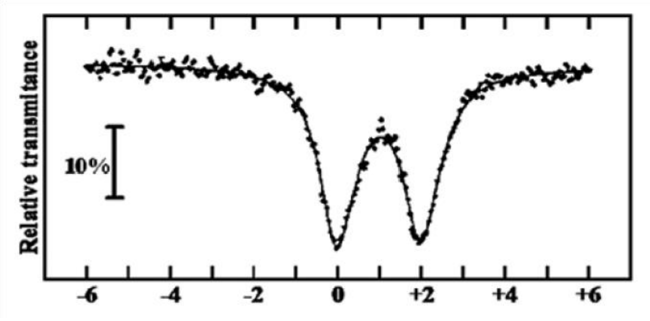

Figure 1: Mössbauer spectrum of [$BuSnLCl_2$], L = $(CH_3)_2C(OH)COO$, obtained at T = 85 K, using a $CaSnO_3$ source at room temperature.

The presented data allowed the design of the proposed formulation and the structure of [$BuSnLCl_2$], a tetrahedral tin species, as it is shown in Figure 2.[19-20]

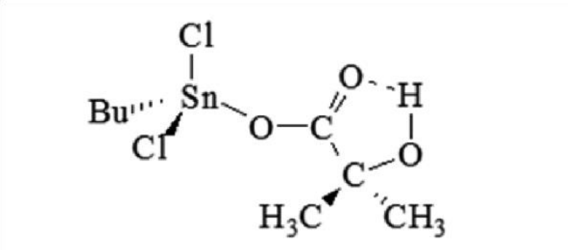

Figure 2: Proposed structure for [$BuSnLCl_2$], L = $(CH_3)_2C(OH)COO$.

For the compound [$BuSnLCl_2$] it was possible to obtain the ^{119m}SnNMR spectrum only in C_5D_5N, presented in Figure 3. In this spectrum one unexpected absorption signal δ(^{119m}Sn) at -421.88 ppm was observed, indicating a coordination number higher than four for the tin atom. As the spectrum was obtained in the environment of deuterated pyridine, it is possible to obtain coordination of the solvent to the tin, justifying the dislocation of the sign for a higher field. This is justifiable by the increase in the coordination numbers from 4 to 5, or even to 6, corresponding to a large screening of the tin nucleus.[19,20]

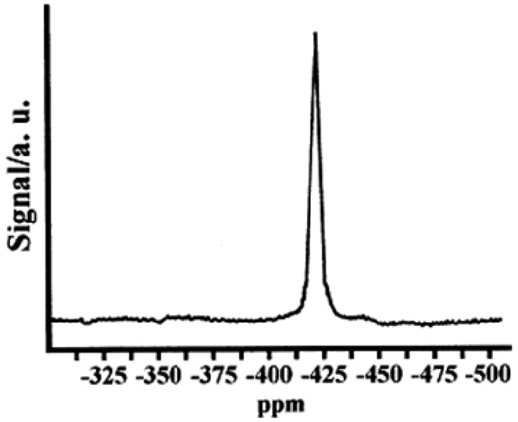

Figure 3: ^{119m}Sn-NMR spectrum of the [$BuSnLCl_2$], L = $(CH_3)_2C(OH)$ COO (400 MHz, C_5D_5N).

TG curve of the [$BuSnLCl_2$] obtained in dynamic helium atmosphere is presented in Figure 4. The initial and final temperatures of thermal decomposition process are 106 and 369 °C, respectively. From 3.699 mg of the complex we obtained 1.255 mg (33.9%) of a final residue, in accordance with the theoretical tin content (33.9%) of the compound. The formation of tin metal as the final product is proved by X-ray fluorescence.

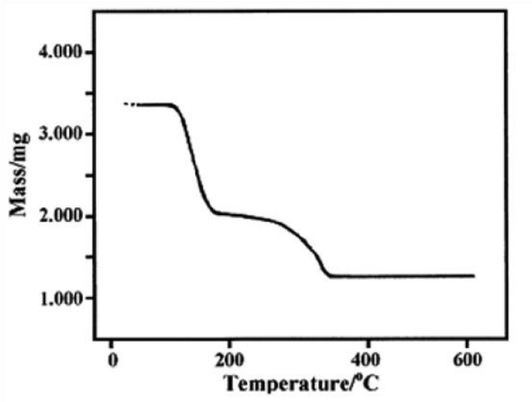

Figure 4: TG curve of [$BuSnLCl_2$], L = $(CH_3)_2C(OH)COO$.

For the compound [BuSnLCl2], the TG curve suggests that the thermal decomposition proceeds in two steps consecutively. In the first step there is a loss of mass of 45.2% in the range 106–177 °C, and in the second step, a loss of mass of 20.3% with final temperature of 350 °C, in agreement with the loss of butyl and α-hydroyisobutyrate ligands in the first step and by loss of the two chlorides in the second step. Based on these observations it is possible to establish a tentative mechanism of their thermal decomposition, as indicated.

$$[BuSnLCl_2] \xrightarrow{106–177\ ^{o}C} SnCl_2 \xrightarrow{192–350\ ^{o}C} Sn$$

The DSC curve of the [$BuSnLCl_2$] is presented in Figure 5. The temperature value observed at the peak (T_{onset}) is 147.2 °C, according to the corresponding melting point of the compound, 151–152 °C, and its calculated heat fusion is ΔH_{fusion} = -13,4 kJ mol^{-1}.

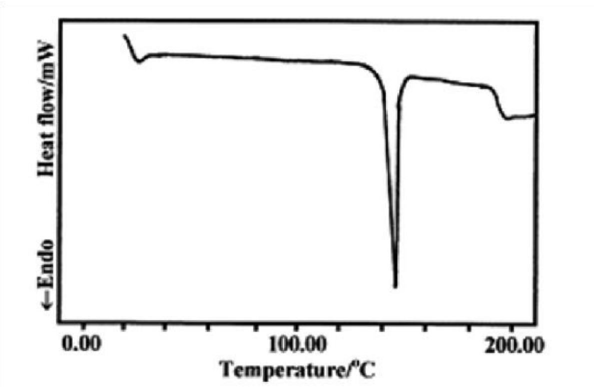

Figure 5: DSC curve of [$BuSnLCl_2$], L = $(CH_3)_2C(OH)COO$.

CONCLUSION

The studied compound [$BuSnLCl_2$], L = $(CH_3)_2C(OH)COO$, exists as tetrahedral tin species in solid-state, with the ligand α-hydroxyisobutyrate monocoordinated to the tin atom only by deprotonated oxygen atom of the hydroxyl acid group, while the hydrogen atom of the alcoholic hydroxyl group forms a strong intramolecular hydrogen bond. The ^{119m}Sn-NMR spectrum in C_5D_5N suggests the existence of a penta- or hexacoordinated tin species in solution, which can be explained by an eventual coordination of solvent molecules with the tin atom.

ACKNOWLEDGEMENTS

The authors are grateful to Dr. Carlos Alberto L. Filgueiras, of the Universidade Federal do Rio de Janeiro, and Dr. Anuar Abras, of the Universidade Federal de Minas Gerais, for experimental support; and to FAPEMIG (Fundação de Amparo à Pesquisa do Estado de Minas Gerais, Brazil) for financial support.

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