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# THERMAL ANALYSES OF DIORGANOTIN *dl*-MANDELATES

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## Abstract

The compounds $[(LR_2Sn)_2O]$ $\{R=CH_3$ (Me), $n$-$C_4H_9$ $(B^n)$; $L=C_6H_5CH(OH)COO^-\}$ were studied by thermogravimetric and differential scanning calorimetry in a dynamic atmosphere of helium. The thermal decomposition mechanisms are similar for both compounds and occur in two consecutive steps. The TG curves of the complexes suggest the liberation of the ligand *L* in the first step, with probable formation of a tin oxide $R_2SnO$ intermediate. At the end of the second step free tin is obtained in accordance with the stoichiometry of the related compounds. An inverse relation between $\Delta H_{\text{fusion}}$ and solubility of the compounds suggests a polymeric structure for the compound with $B^n$ ligand in relation to the compound with M ligand.

**Keywords:** *dl*-mandelate compounds, organotin compounds, thermal decomposition

## Introduction

The organotin carboxylate compounds consist of a vast class of compounds which have been subject of detailed studies. A great number of these compounds, the structures of which are known, are obtained by X-ray diffratometry [1–5]. The pertinent literature also includes extensive study of the organotin carboxylates characteristics, with the involvement of practically all instrumental techniques of analysis [6–10]. Its functional applications are various, and they can be used, for example, as catalysts in industry [11], as biocides in agriculture [9, 12, 13] and as anti-tumorals in medicine [14]. As for diorganotin compounds with α-hydroxycarboxylic acids, besides the compounds described here, the literature is limited to the synthesis and infrared studies of tri- and diorganotin derivatives of the benzilic acid [15]. The present investigations report the use of thermogravimetric analysis (TG) and differential scanning cal-

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orimetry (DSC) in helium atmosphere for study of the complexes $[(LR_2Sn)_2O]$ $\{R{=}CH_3$ (Me), $n$-$C_4H_9$ ($B^n$); $L{=}C_6H_5CH(OH)COO^-\}$.

## Experimental

The TG curve in the range 25–700°C was obtained with the TGA-50 equipment from Shimadzu. 8–10 mg samples were used, with a heating rate of 20°C $min^{-1}$ under a dynamic atmosphere of helium.

The DSC curves, also in the range 25–700°C, from 5–10 mg samples, with a heating rate of 10°C $min^{-1}$, also under a dynamic atmosphere of helium, were plotted with the DSC-50 calorimetry from Shimadzu.

The infrared spectrum of the complexes in the region 5000–275 $cm^{-1}$ were obtained with a Perkin Elmer Paragon 1000 spectrophotometer, using CsI pellets.

The $^{119m}$Sn Mössbauer spectra were provided by a constant acceleration spectrometer equipped a $BaSnO_3$ source, at 85 K.

The complexes $[(LR_2Sn)_2O]$ $\{R{=}CH_3$ (Me), $n$-$C_4H_9$ ($B^n$); $L{=}C_6H_5CH(OH)COO^-\}$ were prepared from *dl*-mandelic acid and $R_2SnO$ by methods previously described in literature [16], and characterized through their IR spectra, by elementary carbon, hydrogen and tin analyses and by Mössbauer and $^{119m}$Sn-NMR spectroscopies.

## Results and discussion

From the reactions under reflux between acid *dl*-mandelic, $C_6H_5CH(OH)COOH$, and dimethyltin oxide, $Me_2SnO$, in ethanol medium or dibutyltin oxide, $B^n_2SnO$, in acetonitrile medium, the compounds $[(LMe_2Sn)_2O]$ (compound **I**) and $[(LB^n_2Sn)_2O]$ (compound **II**, $L{=}C_6H_5CH(OH)COO^-$), respectively, were prepared. The compounds, both white, observed through microscope, presented microcrystalline constitution. However, neither of them provided conditions to obtain single crystals with suitable features to determine the structure by X-ray crystallography. In many attempts to recrystalize, the complexes experienced decomposition, even under inert atmosphere, producing crystals of the respective diorganotin oxides $(R_2SnO)_n$ ($R$=Me, $B^n$).

The melting point of **I** appeared to be significantly higher than **II**, which, in addition with the results of elementary analysis of carbon, hydrogen and tin, are summarized in Table 1.

**Table 1** Analytical results of diorganotin *dl*-mandelate complexes

| Compound | Mass formula | *M. p.*/°C | C/% found (calc.) | H/% found (calc.) | Sn/% found (calc.) |
|---|---|---|---|---|---|
| I | 614.79 | 323–326 | 40.19 (39.07) | 3.61 (4.10) | 39.07 (38.61) |
| II | 783.11 | 177–179 | 49.14 (49.08) | 6.19 (6.31) | 30.41 (30.31) |

In infrared spectrum of the compounds, it was possible to attribute the Sn–C (555–545 cm$^{-1}$), Sn–O (360 cm$^{-1}$), Sn–O–Sn (680 cm$^{-1}$) and alcoholic O–H (3400 cm$^{-1}$) stretching modes, which, together with the data from elementary analysis, permitted the establishment of the proposed formulations and the structures shown in Fig. 1 [17–19].

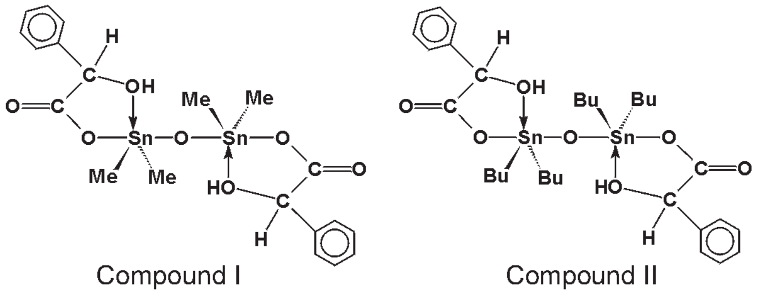

**Fig. 1** Proposed diorganotin *dl*-mandelate structures I – [(LMe$_2$Sn)$_2$O], II – [(LB$_2^n$Sn)$_2$O]

The compounds were studied through $^{119}$Sn Mössbauer spectroscopy, whose spectra of which, presented in Fig. 2, indicate single quadrupole splitting doublets, Δ, making evident that **I** and **II** present only one site around the tin atoms, where the values of Δ and of isomer shift, δ, in mm s$^{-1}$ (**I**: Δ=3.65, δ=1.27; **II**: Δ=3.65, δ=1.37), are consistent with pentacoordinated tin species [20, 21], in accordance to the structures proposed.

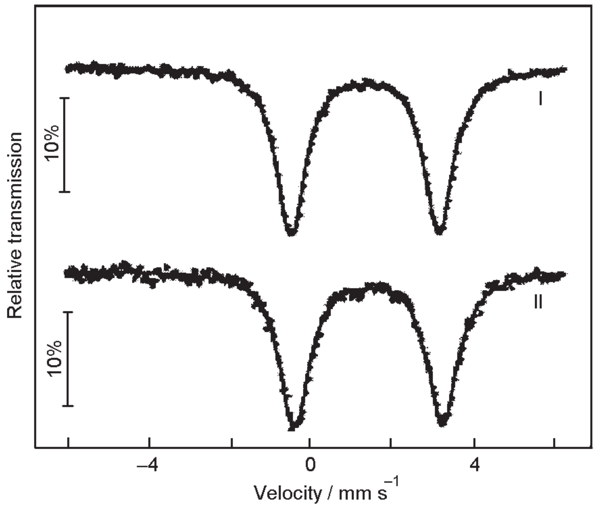

**Fig. 2** Mössbauer spectra for *dl*-mandelates compounds, obtained at *T*=85 K, using a CaSnO$_3$ source at room temperature, I – [(LMe$_2$Sn)$_2$O], II – [(LB$_2^n$Sn)$_2$O]

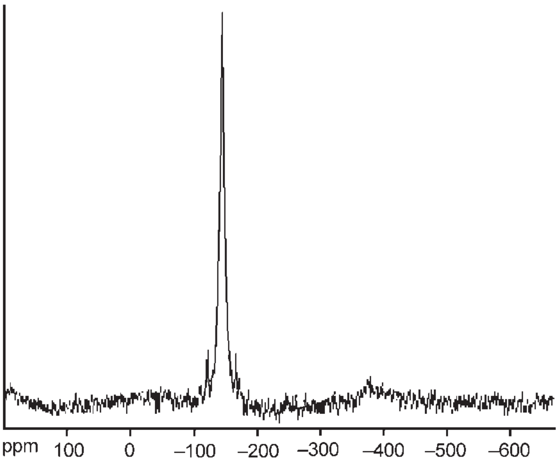

**Fig. 3** RMN-$^{119m}$Sn spectrum (400 MHz, $CDCl_3$) for the *dl*-mandelate compound $[(LB^n_2Sn)_2O]$

For compound **II** it was possible to obtain the $^1$H, $^{13}$C and $^{119m}$Sn NMR spectra, in deuterated chloroform medium. The $^{119m}$Sn-NMR spectrum is shown in Fig. 3, and only one sign of absorption $\delta(^{119m}Sn)$ at –146.90 ppm was observed, which also shows clearly its pentacoordinated geometry, in accordance with the interpretations obtained from the $^1$H, $^{13}$C NMR spectra [22, 23].

For the compound **I**, due to its insolubility, it was not possible to obtain the NMR spectra. This relative insolubility related to **II**, may be a sign of a certain polymerization degree.

The TG curves of the compounds, obtained in dynamic atmosphere of helium, are presented in Fig. 4. One can notice that the relative thermal stability is significantly different for each compound; while the methyl derivative starts its thermal degradation at 271.5°C, that of the butyl derivated starts in 231.7°C. The lower thermal stability of this compound may be explained in terms of a greater hindrance effect of the butyl groups, in relation to the methyl groups of the first complex. The

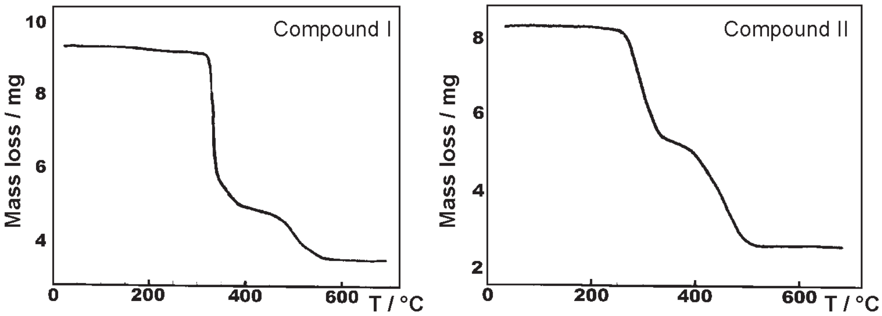

**Fig. 4** TG curves of *dl*-mandelates compound. Heating rate: 20°C min$^{-1}$, I – $[(LMe_2Sn)_2O]$, II – $[(LB^n_2Sn)_2O]$

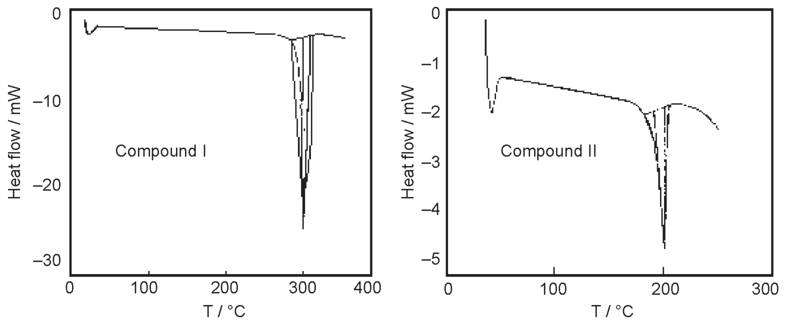

**Fig. 5** DSC curves of *dl*-mandelate compounds. Heating rate: 10°C $\mathrm{min}^{-1}$, I – $[(\mathrm{LMe_2Sn})_2\mathrm{O}]$, II – $[(\mathrm{LB}^{n}_{2}\mathrm{Sn})_2\mathrm{O}]$

thermal decomposition processes, in both cases, occur in two consecutive steps, before 500°C, producing tin as final residue. The analysis of the TG curves of the complexes, according to its respective stoichiometric compositions, suggests that, the liberation of the organic ligands occurs up to the end of the first step of thermal decomposition, whereas by the end of the second step, tin is obtained. Therefore, it is possible to propose the following mechanism for the thermal decomposition process:

$$[(\mathrm{LR_2Sn})_2\mathrm{O}] \rightarrow \mathrm{R_2SnO} \rightarrow \mathrm{Sn}$$

As from the DSC curves, presented in Fig. 5, obtained in a dynamic helium atmosphere, the respective values of $\Delta H_{\mathrm{melting}}$, in kJ $\mathrm{mol}^{-1}$ (**I**= –85.53; **II**= –19.67) have been calculated. The value for the compound **I** was calculated taking into consideration the monomeric unit.

The higher melting point value and $\Delta H_{\mathrm{melting}}$ to **I** in relation to **II**, in an inverse relation with the mass formulas calculated for the monomeric units, together with the differences of solubility observed, confirmed the possibility that **I** is a polymeric compound.

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