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THERMAL ANALYSIS OF NEW DIMETHYLTIN COMPOUNDS WITH GLYCINE AND DL-VALINE

R. S. Barbiéri[1,2*], *A. K. C. Dias*[2], *S. F. da Silva*[1,2], *V. R. Terra*[3] *and E. P. de Lima*[2]

[1]Faculdade de Minas - FAMINAS, 36880-000 Muriaé, MG, Brazil
[2]Universidade Vale do Rio Verde - UNINCOR, 37410-000 Três Corações, MG, Brazil
[3]Centro Federal de Formação Tecnológica - CEFET, 38045-000 Uberaba, MG, Brazil

The new compounds $[(CH_3)_2SnAACl]_2$ (*AA*=glycinate, $CH_2(NH_2)COO^-$; DL-valinate, $(CH_3)_2CHCH(NH_2)COO^-$) were prepared and characterized by elemental analysis of carbon, hydrogen, nitrogen, chlorine and tin, through their infrared spectra, and by Mössbauer and ^{119m}Sn-NMR spectroscopic studies, and they were examined using TG (DTG) method. The thermal decomposition mechanisms were similar for both compounds and occurred in one step. TG curves suggested the formation of tin metal, in agreement with the stoichiometry of the related compounds.

Keywords: *organotin compounds, thermal decomposition, tin DL-valinate, tin glycinate*

Introduction

Amino acids are potentially polydentate ligands, which can link to metals, enabling the synthesis of compounds with various structures, for which geometry and the coordination numbers are governed by the size of the replacing group and by the degree of branches of the ligand [1]. It is verified from the literature that a relatively high number of diorganotin compounds with N-protected amino acids are known. However, the studies on compounds having the same nature derived from essential and simpler α-amino acids are scant, containing only an amino group and a carboxyl group, except by diglycinatotin(II) [2], trimethyltin(II) glycinate and alaninate [1] and dimethyltin(IV) glycinate and β-alaninate compounds [2]. The present investigation relates to the preparation and characterization of two new complexes $[(CH_3)_2SnAACl]_2$, where *AA*=glycinate, $CH_2(NH_2)COO^-$ and DL-valinate, $(CH_3)_2CHCH(NH_2)COO^-$ and the application of TG and DSC techniques in dynamic helium atmosphere.

Experiment

The TG curves were recorded using Shimadzu TGA-50 model in the range of 25–700°C at a heating rate of 20 K min^{-1} and in a dynamic helium atmosphere with flow rate of 20 mL min^{-1}. The initial sample masses were 7–9 mg.

Shimadzu DSC-50 equipment 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 rate of 50 mL min^{-1}. The initial sample masses were 6–8 mg.

The melting points were determined on a FP-2 Mettler system.

The infrared spectra of complexes were recorded between 5000–275 cm^{-1}, using a Perkin Elmer Paragon 1000 spectrophotometer, in CsI pellets.

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

The elemental analysis for carbon, hydrogen and nitrogen were carried out using Perkin Elmer 2400CHN Elemental Analyzer.

Chlorine determination was done by neutron activation analysis. The samples were irradiated in the central tube of a Triga-3 reactor and the measurement was performed applying a Low Lewel α/β Counting System Model 2200 Canberra proportional detector, on the Nuclear Development Technology Center, of Nuclebrás, in Belo Horizonte-MG, Brazil.

The tin determination has been performed by atomic absorption by means of a Hitachi Z-8200 spectrometer.

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

The ^{119m}Sn-NMR spectrum was obtained with a Bruker DRX 400 MHz Avance spectrophotometer, using D_2O.

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[*] Author for correspondence: barbieri@faminas.edu.br

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

The complex $[(CH_3)_2SnGlyCl]_2$ (compound **I**) was synthesized reacting glycine, $CH_2(NH_2)COOH$, and dimethyltin dichloride with 1:1 molar ratio. The α-amino acid was added to stirred acetonitrile solutions for 2 h. After adding the tin compound, the system was further stirred and refluxed over night. The mixture was then filtered at room temperature and the obtained solid was washed with dichloromethane and dried under vacuum.

The complex $[(CH_3)_2SnValCl]_2$ (compound **II**) was synthesized from DL-valine, $(CH_3)_2CHCH(NH_2)COOH$, using similar procedures which were written for compound **I**. The obtained solid was washed with *n*-heptane and with dichloromethane and dried under vacuum.

Complexes **I** and **II** were characterized by their IR spectra, by elementary analysis of carbon, hydrogen and tin and by Mössbauer and ^{119m}Sn-NMR spectroscopic studies.

Results and discussion

The new complexes $[(CH_3)_2SnGlyCl]_2$ (compound **I**) and $[(CH_3)_2SnValCl]_2$ (compound **II**), were both observed using optical microscope. They exhibited microcrystalline constitution. However, it was not possible to obtain suitable single crystals to determine their structures by X-ray crystallography. During several attempts to recrystallize them, the complexes underwent decomposition, even under inert atmosphere, producing crystals of dimethyltin oxide, $(CH_3)_2SnO$.

The melting points and the results of elementary analysis of carbon, hydrogen, nitrogen, chlorine and tin for **I** and **II** are shown in Table 1.

The most representative stretching vibrations taken from the infrared spectra of **I** and **II** are presented in Table 2. The evaluation of the infrared spectra of glycine and DL-valine allowed to assign the $\nu_{COO_{ass}}$ values which were in a good agreement with the literature data [1]. In the infrared spectra of **I** and **II** relatively small shifts for the $\nu_{COO_{ass}}$ values were verified for the highest region in the spectrum of the complexes, in relation to the free α-amino acids. The observed alterations are from 1600 to 1610 cm^{-1} for glycine in **I** and from 1595 to 1640 cm^{-1} for DL-valine in **II**, indicating the participation of the carboxyl of the α-amino acids in the coordination to the tin [1]. Similar results were obtained for the other compounds $[(CH_3)_2Sn(AA)_2]$ (*AA*=glycine, alanine). In the infrared spectra of both complexes the $\nu_{COO_{ass}}$ values were shifted to 1605 cm^{-1} for free amino acids and to 1629 cm^{-1} for the derivatives [2, 3].

The stretching of N–H may also help to explain the coordination form of amino acid. Free NH_2 groups were found in the amino acid salts, like in sodium glycinate, where ν_{NH} appeared at 3380 cm^{-1}. Compared to the free glycine, where the band of the zwitterion form $H_3N^+–CH_2–COO^-$; appears at ν_{NH}=3170 cm^{-1} [4]. Glycine, in the $H_2N–CH_2–COOH$ isolated form of glycine, the experimental value of the N–H stretching is 3411 cm^{-1} [4]. Thus, for the complexes with amino acids which present ν_{NH} appear at about 3400 cm^{-1}, the amino group must be free. If the band is located between 3100–3300 cm^{-1}, the amino group must be coordinated to the metal [2–8]. For the studied complexes an alteration in $\nu_{COO_{ass}}$ from 3170 to 3250 cm^{-1} for glycine in **I** was verified. In case of DL-valine in **II** a shift from 3140 to 3120 cm^{-1} was observed suggesting also the participation of the NH_2 group in the coordination of the amino acids to the tin [2–8].

Table 1 Melting points and elementary analysis data of the dimethyltin complexes

Compound	Molecular mass/ g mol^{-1}	*m.p.*[1]/ °C	T_{ons}[2]/ °C	C/%	H/%	N/%	Cl/%	Sn/%	
				found (calc.)	found (calc.)	found (calc.)	found (calc.)	found[3] (calc.)	found[4] (calc.)
I	516.58	100–103	96.4	19.17 (18.60)	3.40 (3.90)	5.77 (5.42)	12±2 (13.72)	46.10 (45.95)	45.58 (45.95)
II	598.73	138–141	135.8	28.05 (28.08)	5.87 (5.05)	4.72 (4.68)	11±3 (11.84)	40.99 (39.65)	39.54 (39.65)

[1] Determined on a FP-2 Mettler system; [2] Data taken from DSC curves; [3] by atom absorption; [4] by TG analysis

Table 2 Representative IR stretching data (cm^{-1}) for the dimethyltin complexes

Compound	Free ligand		Complexes						
	ν_{NH}	$\nu_{COO_{ass}}$	$\nu_{COO_{ass}}$	ν_{NH}	ν_{CH}	ν_{SnO}	ν_{SnC}	ν_{SnN}	ν_{SnCl}
I	3170	1600	1610	3250	2930 2970	520	540 560	485	300
II	3140	1595	1640	3120	2935 2955	450	535 550	425	295

In the ^{119}Sn Mössbauer spectroscopy, a single quadrupole splitting doublets was indicated, for the studied compounds, making evidently that **I** and **II** present only one site around the tin atoms, where the Δ and of δ isomer shift values, in mm s^{-1} (**I**: Δ=3.87, δ=1.55; **II**: Δ=3.79, δ=1.49), are consistent with the slightly distorted *trans*-octahedral tin species [9–11]. The Mössbauer spectra of compound **I** is shown in Fig. 1.

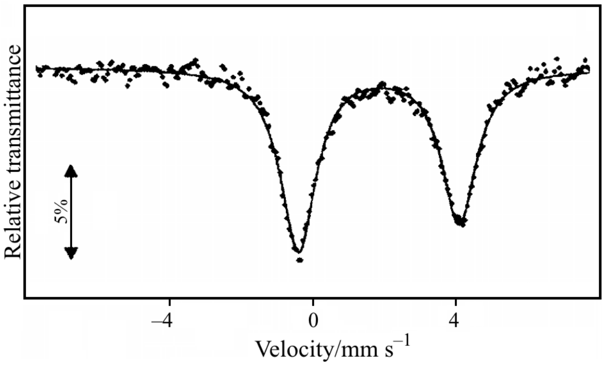

Fig. 1 Mössbauer spectra of compound **I** – $[(CH_3)_2SnGlyCl]_2$ (obtained at T=85 K, using a $CaSnO_3$ source at room temperature)

The presented data allowed the settlement of the proposed formulations and the structures as they are shown in Fig. 2.

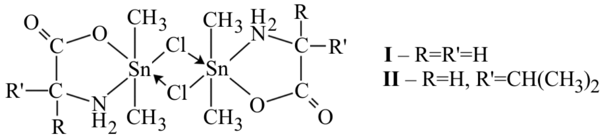

Fig. 2 Proposed structures for dimethyltin complexes **I** – $[(CH_3)_2SnGlyCl]_2$, **II** – $[(CH_3)_2SnValCl]_2$

For compound **I** it was possible to obtain the ^{119m}Sn-NMR spectrum, in D_2O is shown in Fig. 3. The absorption signal $\delta(^{119m}Sn)$ at –121.5 ppm indicates that in solution the compound is present in dissociated form, assuming pentacoordinated geometry [5, 7, 12, 13].

Due to its insolubility for compound **II**, it was not possible to record the NMR spectra. The insolubility of **II**, may be attributed to certain polymerization, as observed for diorganotin compounds with α-hydroxycarboxylic acid [12, 14].

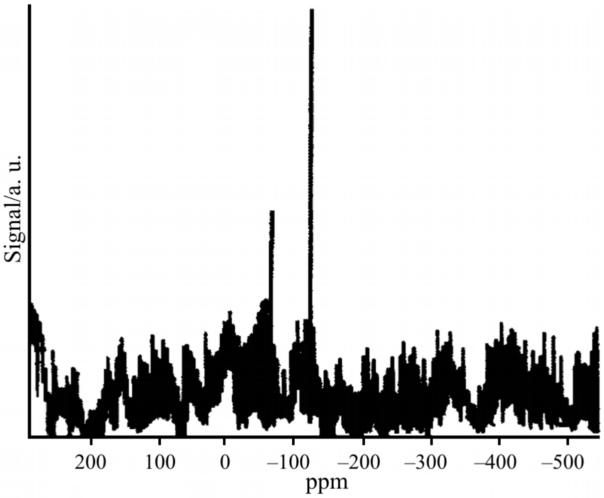

Fig. 3 ^{119m}Sn NMR spectrum of the dimethyltin glycinate compound **I** – $[(CH_3)_2SnGlyCl]_2$ (400 MHz, D_2O)

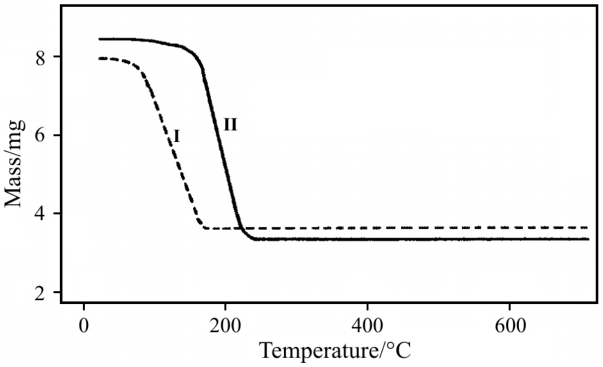

Fig. 4 TG curves of dimethyltin complexes. **I** – $[(CH_3)_2SnGlyCl]_2$, **II** – $[(CH_3)_2SnValCl]_2$

TG curves of the compounds obtained in dynamic helium atmosphere, are presented in Fig. 4. One can notice that the relative thermal stability of the compounds is significantly different. While the thermal degradation of the glycinate derivative starts at 110°C, the DL-valinate starts to decompose at 158°C. These results indicate that even the higher hindrance effect in the case of the DL-valinate derivative, this effect does not cause a decrease in its thermal stability, as it can be observed for diorganotin DL-mandelate complexes containing methyl and butyl groups [12]. In both cases, the thermal decomposition processes occur in one step, with final decomposition temperatures at 155 and 217°C for compounds **I** and **II**, respectively, producing tin metal as final product proved by X-ray fluorescence.

The higher slope of the TG curve of **II** suggests that its decomposition rate is higher than **I** has indicating that the thermal stability of the compound **II** is higher compared to compound **I**.

The DSC curves of the compounds are presented in Fig. 5.

Considering the heat of fusion values (ΔH_{fusion}= –8.45 kJ mol^{-1} for **I** and (ΔH_{fusion}=–22.23 kJ mol^{-1} for **II**) it can be concluded that the compounds exist in dimer forms in solid-state.

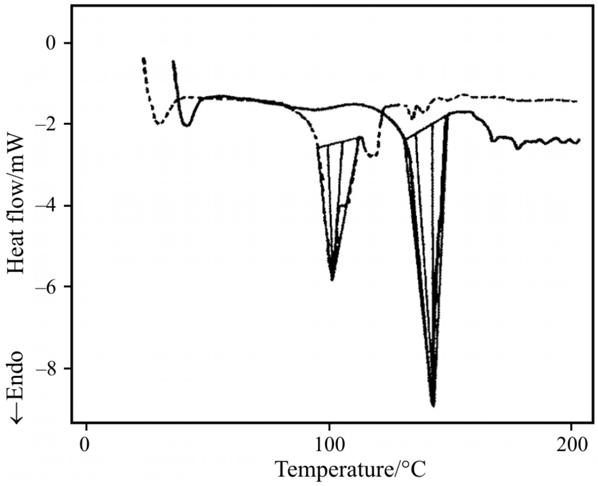

Fig. 5 DSC curves of dimethyltin complexes. **I** – $[(CH_3)_2SnGlyCl]_2$, **II** – $[(CH_3)_2SnValCl]_2$

Conclusions

The studied **I** and **II** compounds exist as slightly distorted *trans*-octahedral tin species with chlorine atom bridging in solid-state. These results are distinct from the ones described for diglycinatotin(II) [2], trimethyltin(II) glycinate and alaninate [1] and dimethyltin(IV) glycinate and β-alaninate compounds [2] which show polymeric species with bridging α-amino acids, should link the carboxylic oxygen to the tin and the amino group to the other tin atom [1, 2].

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