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Research Paper

Synthesis and characterization of dibutyltin compounds with α-amino acids

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ABSTRACT

This study describes the preparation and description of four new complexes: $Bu_2Sn(AA)Cl$ (AA = glycine, DL = valine and L = leucine) and $Bu_2SnPhen_2$ (Phen = DL-phenylalanine). They were characterized by elemental analyses for carbon, hydrogen, nitrogen, chlorine and tin by infrared, ^{119m}Sn-Mössbauer and ^{119m}Sn-RMN spectroscopies and by the applications of TG and DSC techniques in a dynamic helium atmosphere. For the trigonalbipyramidal tin species $[Bu_2Sn(AA)Cl]$, AA were co-ordinated bidentatedly by carboxylic oxygen and NH_2 group. The $Bu_2SnPhen_2$ compound with tin atoms in trans-octahedral sites had the Phen - coordinated by both carboxylic oxygen atoms.

Key words: Organotin compounds, dibutyltin compounds, tin α-amino acids compounds and thermal decomposition.

INTRODUCTION

Amino acids are potential polidentated ligands that can bond to metals enabling the synthesis of compounds with varied structures and its geometry and co-ordination number are governed by the size and ramification degree of the ligand (Ho and Zuckerman, 1973). The existence of cis-platinum complexes $[Pt(NH_3)_2Cl_2]$ and related bis (amine) complexes in the treatment of cancer motivated the investigation of metallic compounds with the same molecular modeling, among which organotin derivatives with nitrogenated group stand out thereby presenting promising results (Huheey et al., 1993; Galanski et al., 2005; Dasari and Tchounwou, 2014; Johnstone et al., 2014; Trivedi et al., 2015; Stojic et al., 2016; Naqeebullah et al., 2013).

The first reports on diorganotin compounds with antitumoral activities were published in 1980. Ever since, diorganotin compounds were tested for their effects on biological systems and it was verified that the effects are related with the stability of the compounds and length of the Sn-Nbond. It was verified that stable compounds whose length of the Sn-N connection is inferior to 239 nm are inactive, suggesting that its effects on biological systems are related with the dissociation of the nitrogenated ligand, as a part of the mechanism of action (Iqbal et al., 2016; Sainorudin et al., 2015; Arjmand et al., 2014; Pellerito and Nagy, 2002).

A relatively high number of diorganotin compounds with N-protected amino acids, known and studied was verified in the pertinent literature. The first solid state studies on diorganotin compounds of the same nature derived from simple essential □-amino acids, containing one amino and carboxyl group except for a dimethyl diglycinate compound (Hall and Zuckerman, 1977), some dibutyltin (IV) Schiff base complexes derived from phenylalanine, isoleucine and glycine (Singh and Singh, 2014) dimethyltindimeric compounds with glycine or *dl*-valine are also presented in this study (Barbiéri et al., 2004, 2005).

The present investigation relates to the preparation and characterization of four new complexes: $Bu_2Sn(AA)Cl$ (AA = glycine, DL= valine and L= leucine) and $Bu_2SnPhen_2$ (Phen = DL-phenylalanine) characterized by the elemental analyses for carbon, hydrogen, nitrogen, 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.

Table 1: Melting points and elementary analysis data for the dibutyltin complexes.

Compound	Molecular mass (g mol^{-1})	Yield (%)	*m.p.*[1](°C)	C (%)	H (%)	N (%)	Cl (%)	Sn (%)	
				Found (calc.)				found[2](calc.)	found[3](calc.)
I	342.45	65	150-153	34.4(35.1)	5.8(6.5)	4.1(4.1)	12 ± 2(10.4)	33.6(34.6)	34.1(34.7)
II	384.53	70	138 -141	41.0(40.6)	8.4(7.3)	3.7(3.6)	9 ± 1(9.2)	30.2(30.9)	30.1(30.9)
III	398.56	60	107-110	40.9(42.2)	7.7(7.6)	3.3(3.5)	11 ± 3(8.9)	28.9(29.9)	29.2(29.8)
IV	561.31	50	191-194	55.7(55.6)	7.2(6.8)	5.6(5.0)	-	20.8(21.1)	20.8(21.1)

[1]Determined on a FP-2 Mettler system; [2]by atomic absorption; [3]by TG analysis.

MATERIALS AND METHODS

The TG curve was recorded with the use of a Shimadzu TGA-50 model at the range of 25 to 700°C with a heating rate of 20 Kmin^{-1} and a dynamic atmosphere of helium at a flowrate of 20 mlmin^{-1} flow. The initial sample masses used were 8 to 10 mg.

A Shimadzu DSC-50 device was used to record the DSC curves. The experimental conditions were: a temperature range of 25 to 200°C, □ = 10 Kmin^{-1} heating rate and helium purging with a flow of 50.0 mlmin^{-1}. The initial sample masses were 6 to 8 mg and the melting points were determined on a FP-2 Mettler system.

The infrared spectra of the complexes were recorded between 5000 to 275 cm^{-1} with the use of a Perkin Elmer Paragon 1000 spectrophotometer for CsI pellets, the X-ray fluorescence characterization of the TG analyses was performed by means of a Rigaku-Geigerflex spectrophotometer and elemental analyses for carbon, hydrogen and nitrogen carried out using a Perkin Elmer 2400CHN Elemental Analyzer.

Chlorine determination was made by neutron activation analysis; the samples were irradiated in the central tube of the Triga-3 reactor and the measurement was performed by applying a Low Lewel □/□ Counting System Model 2200 Canberra Proportional Detector at the Nuclear Development Technology Center of Nuclebrás, Belo Horizonte-MG, Brazil. The tin determination was performed by atomic absorption by means of a Hitachi Z-8200 spectrometer.

The ^{119m}Sn-Mössbauer spectra was provided by a constant acceleration spectrometer equipped at the $BaSnO_3$ source at 85 K and the ^{119m}Sn-NMR spectrum obtained with a Bruker DRX 400 MHz Avance spectrophotometer using D_2O.

The complex, $Bu_2SnGlyCl$ (compound I) was composed of synthesized reacting glycine [$CH_2(NH_2)COOH$] and dibutyltin dichloride with a molar ratio of 1:1. The □-amino acid was added to methanol solutions and stirred for 2 h. After addition of the tin compound, the system was further stirred and refluxed overnight and the solution maintained at -18°C for 24 to 48 h after a 50% solvent volume reduction. The mixture was then filtered at room temperature; the solid obtained was washed with methanol (3 × 2 ml) and dried at 100°C in an Abderhalden pistol for 1 h with all manipulations performed in air.

The complex $Bu_2SnValCl$ (compound II) was synthesized from DL-valine [$(CH_3)_2CHCH(NH_2)COOH$], $Bu_2SnLeuCl$ (compound III) from L-leucine [$(CH_3)_2CHCH_2CH(NH_2)COOH$] and $Bu_2SnPhen_2$ (compound IV) from DL-phenylalanine [$C_6H_5CH_2CH(NH_2)COOH$] using procedures that are similar to those described for compound I. Complexes I to IV were characterized by their IR spectra, elementary analyses of carbon, hydrogen, nitrogen, chlorine and tin and also by ^{119m}Sn-Mössbauer and ^{119m}Sn-NMR spectroscopic studies.

RESULTS AND DISCUSSION

The new complexes: $Bu_2SnGlyCl$ (compound I), $Bu_2SnValCl$ (compound II), $Bu_2SnLeuCl$ (compound III) and $Bu_2SnPhen_2$ (compound IV) were observed using optical microscopy. They exhibited a microcrystalline constitution as observed for the glycine and DL-valine dimethyltin derivatives previously in this study (Barbiéri et al., 2004, 2005); it was not possible to obtain suitable single crystals inorder to determine their structures by X-ray crystallography. Similarly, during several attempts to recrystallize the complexes which had undergone decomposition, even when under inert atmosphere, they produced crystals of dibutyltin oxide (Bu_2SnO). Table 1 shows the melting points and results of elementary carbon, hydrogen, nitrogen, chlorine and tin analyses for I to IV.

In the experiments for the synthesis of the dibutyltin compounds described in this study, it was verified that the relative reactivity of the □-amino acid ligands was sensibly lower than the one of □-hydroxycarboxylic acids used in the synthesis of the organotin compounds; this was also previously described by Barbiéri et al. (2002), Carlos (1999) Terra (1997) and Terra et al. (1998).

Table 2 shows the most representative stretching vibrations from the infrared spectra of I to IV. The evaluation of the infrared spectra of glycine, DL-valine, L-leucine and DL-phenylalanine allowed the assigning of $□_{COOass}$ values which were in good agreement with the report of Terra et al. (1998). In the infrared spectra of I to

Table 2: Representative stretching data (cm^{-1}) for the dibutyltin complexes.

Compounds	Free ligands		Complexes								
	ν_{NH}	ν_{COOass}	ν_{COOass}	ν_{COOsym}	$\Delta\nu$	ν_{NH}	ν_{CH}	ν_{SnO}	ν_{SnC}	ν_{SnN}	ν_{SnCl}
I	3170	1600	1620	1440	180	3190	2960, 2900, 2850	450	560, 550	410	310
II	3140	1595	1605	1410	195	3120	2940, 3920, 2840	445	570, 555	395	255
III	3100	1580	1590	1405	185	3150	2940, 2900, 2840	455	565, 555	380	325
IV	3100	1620 1585	1640	1410	230	3410	2960, 2900	445	570, 550	-	-

IV, relatively small shifts of the ν_{COOass} values were verified for the highest region in the complexes spectra in relation to the free α-amino acids. The observed alterations are from 1600 to 1620 cm^{-1}, 1595 to 1605 cm^{-1}, 1580 to 1590 cm^{-1} and 1620 to 1585 to 1640 cm^{-1} for glycine in I, DL-valine in II, DL-leucine in III and DL-phenylalanine in IV respectively, thus, indicating the participation of the carboxyl of α-amino acids in co-ordination with tin (Farias et al., 2003; Silverstein et al., 2015; Gokel and George, 2003).

Additionally, similar results were obtained for the other compounds $[(CH_3)_2Sn(AA)_2$; AA = glycine, alanine] (Ho and Zuckerman, 1973; Hall and Zuckerman, 1977) and for the compound $[(CH_3)_2Sn(AA)Cl$; AA = glycine, DL-valine] (Barbiéri et al., 2004, 2005). In the first case, ν_{COOass} values for the infrared spectra of both complexes were shifted to 1605 cm^{-1} for free amino acids and to 1629 cm^{-1} for the derivatives (Ho and Zuckerman, 1973; Arjmand et al., 2014; Terra et al., 1998; Farias et al., 2003; Silverstein et al., 2015; Gokel and George, 2003; Sandhu et al., 1985), whereas in the second case, ν_{COOass} values for the infrared spectra of both complexes were shifted to 1600 and 1595 cm^{-1} for free amino acids and to 1610 and 1640 cm^{-1} for the derivatives respectively (Barbiéri et al., 2005).

The $\Delta\nu = \nu_{COO\,(ass)} - \nu_{COO\,(sym)}$ values were also used as criterion for the evaluation of the forms of co-ordination of amino acids metals, helping in the molecular structure inferences (Ho and Zuckerman, 1973; Sandhu et al., 1985). The magnitude of $\Delta\nu$ can be indicated in carboxylate groups that are linked by one or both atoms of oxygen due to simultaneous co-ordination by both carboxylic and amine groups or with the formation of intermolecular hydrogen bonds as in free liquid carboxylic acids (Sandhu et al., 1985, 1986, 1989, 1991; Sandhu and Kaur, 1990; Sandhu and Hundal, 1992; Barbiéri et al., 1994).

However, conflicting values were mentioned in the literature. The study of Ho and Zuckerman (1973) on trialkyltin amino acids and dipeptides derivatives set up of $\Delta\nu$ = 205 to 264 cm^{-1} indicated co-ordination by the deprotonated alcoholic oxygen of the carboxylate and NH groups. For organotin compounds with EDTA, Sandhu and Hundal (1992) established that $\Delta\nu$ = 400 to 435 cm^{-1} indicates intermolecularly bonded carboxylate groups, while $\Delta\nu$ = 205 to 264 cm^{-1} indicate bidentatedly bonded carboxylates (Barbiéri et al., 1994). In the studied complexes, $\Delta\nu$ = 180 cm^{-1} for glycine in I, $\Delta\nu$ = 195 cm^{-1} for DL-valine in II and $\Delta\nu$ = 185 cm^{-1} for L-leucine in III were verified, suggesting that only the oxygen atoms of the carboxylic group participated in the co-ordination of the amino acids with the tin. In the case of DL-phenylalanine in IV with $\Delta\nu$ = 230 cm^{-1}, conditions were observed and it suggested the participation of both oxygen atoms of the carboxylic group in the co-ordination of the amino acids with the tin (Sandhu et al., 1985, 1986, 1989, 1991; Sandhu and Kaur, 1990; Sandhu and Hundal, 1992; Barbiéri et al., 1994).

More so, the stretching of N-H may also help to explain the co-ordination 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 zwitterions form H_3N^+-CH_2-COO and appears at ν_{NH} = 3170 cm^{-1} (Grenie et al., 1970), glycine in the H_2N-CH_2-COOH isolated form of glycine appears with the experimental value of N-H stretching at 3411 cm^{-1} (Grenie et al., 1970).

Thus, for complexes with amino acids presenting ν_{NH} appearing at about 3400 cm^{-1}, the amino group must be free. If the band is located at 3100 to 3300 cm^{-1}, the amino group must be co-ordinated with the metal (Ho and Zuckerman, 1973; Hall and Zuckerman, 1977; Gokel and George, 2003; Sandhu et al., 1985; Souza et al., 1992; Teles et al., 1994; Chen et al., 2004). For the compounds studied, ν_{COOass} was from 3170 to 3190 cm^{-1} for glycine in I, 3140 to 3120 cm^{-1} for DL-valine in II and 3100 to 3150 cm^{-1} for DL-leucine in III; an alteration was verified suggesting the participation of the NH_2 group in the co-ordination of amino acids with tin (Ho and Zuckerman, 1973; Hall and Zuckerman, 1977; Gokel and George, 2003; Sandhu et al., 1985; Souza et al., 1992; Teles et al., 1994; Chen et al., 2004). For DL-phenylalanine in IV, a shift from 3100 to 3410 cm^{-1} was observed, indicating that the amino group must be free in this complex (Ho and Zuckerman, 1973; Hall and Zuckerman, 1977; Gokel and George, 2003; Sandhu et al., 1985; Souza et al., 1992; Teles et al., 1994; Chen et al., 2004).

In the spectra of the compounds I to IV studied, the presence of two absorption bands was observed in the 550 to 570 cm^{-1} region; this was attributed to the stretching of the Sn-C bonds which indicates a trans non-linear configuration of the skeleton C-Sn-C (Sandhu et al., 1992), as well as, those at 395 to 480 cm^{-1} attributed to the stretching of the Sn-N bonds (Ho and Zuckerman, 1973;

Table 3: Values of the Mössbauer parameters (mm s^{-1}) for the dibutyltin complexes.

Compounds		Mössbauer parameters (mm s^{-1})			
		δ	Δ	Γ[1]	ρ = Δ/δ
I	[$Bu_2SnGlyCl$]	1.44	3.33	0.95	2.31
II	[$Bu_2SnValCl$]	1.40	3.25	0.88	2.32
III	[$Bu_2SnLeuCl$]	1.40	3.26	0.81	2.33
IV	[$Bu_2SnPhen_2$]	1.41	3.29	0.84	2.33

[1]Fullwidth at half maximum.

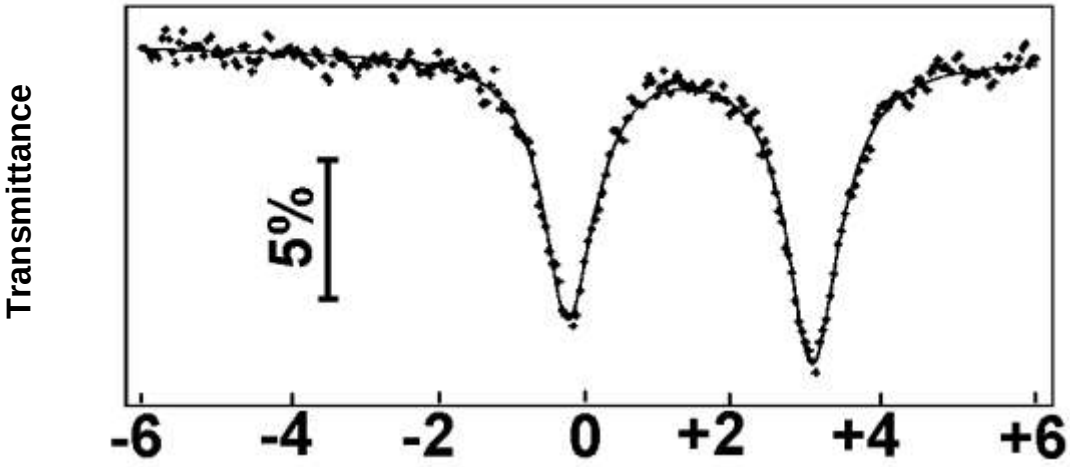

Figure 1: Mössbauer spectra of compound IV - [$Bu_2SnPhen_2$] (obtained at T = 85 K, using a $CaSnO_3$ source at room temperature).

Sandhu et al., 1985; Souza et al., 1992; Teles et al., 1994).

In the ^{119m}Sn Mössbauer spectroscopy, a single quadrupole splitting doublet was indicated, making evident that I to IV was present in only one site around the tin atoms and quadrupole splitting doublets and isomer shift values in mm s^{-1} are consistent with the tin atoms located in sites that have co-ordination numbers higher than four which is highlighted by the relationship among the values ρ = /δ > 2.1 (Sandhu and Kaur, 1990; Sandhu et al., 1989, 1986, 1991; Sandhu and Hundal, 1992; Omae, 2004; Davies, 2004; Zuckerman, 1970; Abras et al., 1994). Table 3 and Figure 1 shows the values of the Mössbauer parameters and spectrum for the compound ($Bu_2SnPhen_2$).

The presented data allowed the settlement of the proposed formulations and structures of I, II and III; a trigonalbipyramidal tin species as shown in Figure 2, whereas Figure 3 shows a slightly distorted trans-octahedral tin specie for structure IV (Sandhu et al., 1985, 1986, 1989, 1991; Sandhu and Kaur, 1990; Sandhu et al., 1986; Sandhu and Hundal, 1992).

For the compounds I and III, it was possible to obtain the ^{119m}Sn-NMR spectra in D_2O and the spectrum of I (Figure 4). The absorption signals δ(^{119m}Sn) (I = -143.6 ppm and III = -146.1 ppm) indicate that in solution, the compounds I and II are present in dissociated forms and assumes a trigonalbipyramidal geometry (Gokel and George, 2003; Sandhu et al., 1985, 1986, 1989, 1991; Souza et al., 1992; Teles et al., 1994; Sandhu and Kaur, 1990; Sandhu and Hundal, 1992; Barbiéri et al., 1994; Grenie et al., 1970). The proximity of the absorption signal δ(^{119m}Sn) values of I and III is an evidence that the structural differences of these compounds are distant from the tin sites and they do not affect the degree of protection or no protection of the tin nucleus. A second signal of lower intensity was also observed in the ^{119m}Sn-NMR spectra of the two compounds (δ = 96.2 ppm for both cases) attributed to the probable products of reactions of the complexes with D_2O.

Due to the insolubility of compounds II and IV, it was not possible to record the NMR spectra. The insolubility of II and IV may be attributed to a certain polymerization degree, as observed for diorganotin compounds with -hydroxycarboxylic acid (Barbiéri et al., 2002; Terra et al., 1998).

Figure 5 shows the TG curves of the compounds obtained in dynamic helium atmosphere. Table 4 shows the initial and final temperatures of the thermal decomposition process and the thermogravimetric data for the dibutyltin complexes. It can be seen that the relative thermal stability of the compound is significantly different, while the thermal degradation of the glycinate derivative (I) starts at 183°C, DL-valinate complex (II) and L-

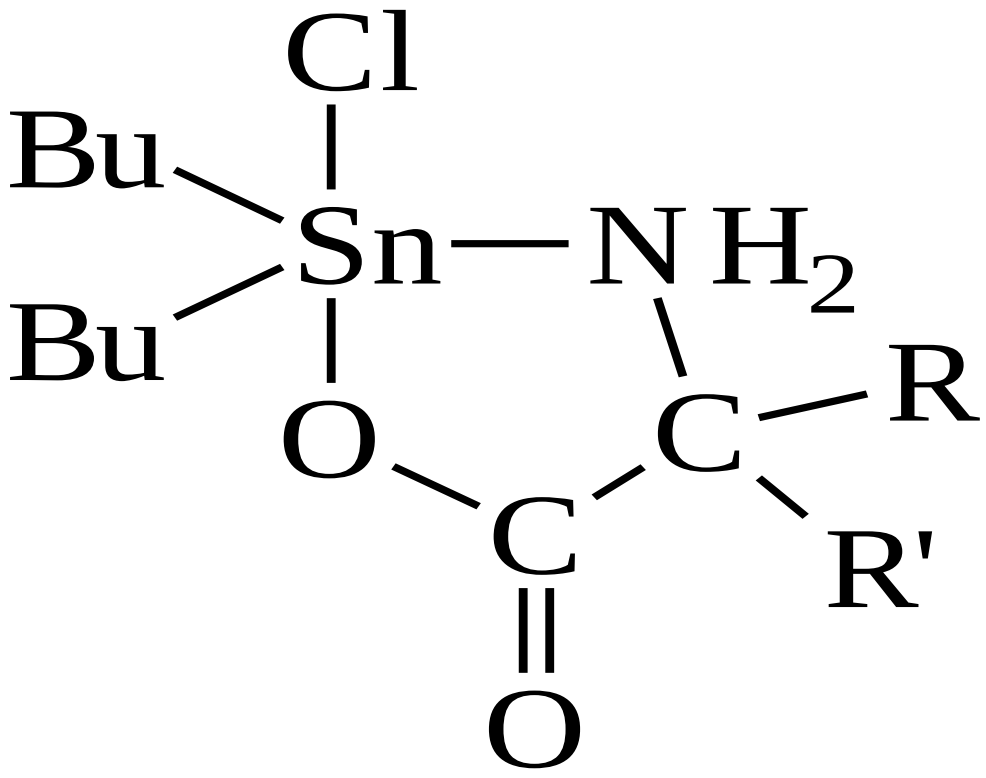

Figure 2: Proposed structures for dibutyltin complexes; I - [$Bu_2SnGlyCl$] (Gly = glycine, R = R' = H), II - [$Bu_2SnValCl$] (Val = DL-valine, R = H, R' = -$CH(CH_3)_2$) and III - [$Bu_2SnLeuCl$] (Leu = L-leucine, R = H, R' = -$CH_2CH(CH_3)_2$).

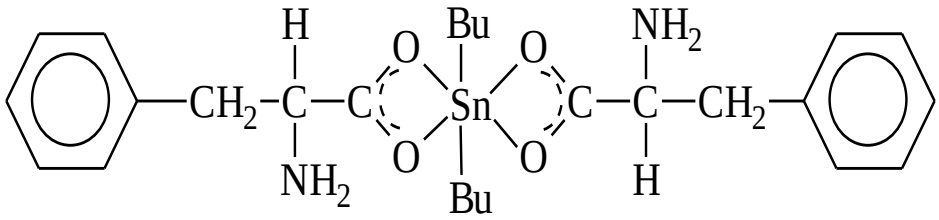

Figure 3: Proposed structure for [$Bu_2SnPhen_2$], IV - Phen = DL-phenylalanine.

leucinatederivative (III) starts to decompose at 130 and 125°C respectively and where all are penta-coordinated species in inverse correlation for the increase of their respective mass weights. For the dimethyltin compounds ([$(CH_3)_2SnAACl]_2$; AA = glycine, DL-valine) that were previously described by the Barbiéri et al. (2004), an increase was related to its thermal stability in agreement with increase in their respective mass weights, indicating that even though there are higher hindrance effects in the case of the dimethyltin DL-valinate derivative, they do not cause the decrease in its thermal stability.

For the DL-phenylalaninate derivative (IV) hexa-coordinated specie, the thermal degradation starts at 165°C. For the compounds I and III, thermal decomposition processes occur in one step with final decomposition temperatures at 375 and 372°C, with a mass loss corresponding to 65.92 and 70.80% respectively. For compound II, the TG curve suggests that the thermal decomposition proceeds in two steps consecutively.

In the first step, there is a mass loss of 30.21% for up to 130 to 162°C and in the second step, a mass loss of 39.67% with a final temperature of 370°C, in agreement with the loss of one DL-valine ligand in the first step and by loss of other ligands in the second step. The TG curve of compound IV suggests that the thermal decomposition proceeds in four consecutive steps ending at 700°C with total loss mass corresponding to 79.20%. In the first step, there is a mass loss of 20.15% in intervals of 162 to 250°C; in the second step, a mass loss of 29.73% in intervals of 263 to 344°C and in the third and fourth steps, a loss of 29.32% with final temperature at 700°C. This is in

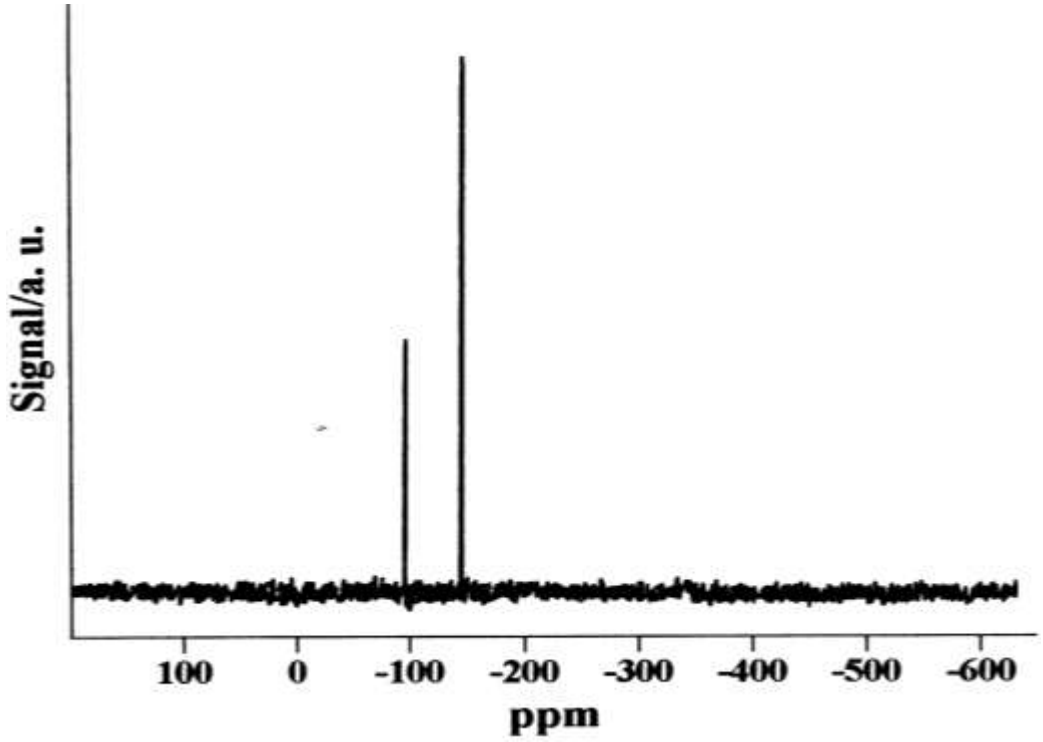

Figure 4: ^{119m}Sn-NMR spectrum of the compound I - [$Bu_2SnGlyCl$] (400 MHz, D_2O).

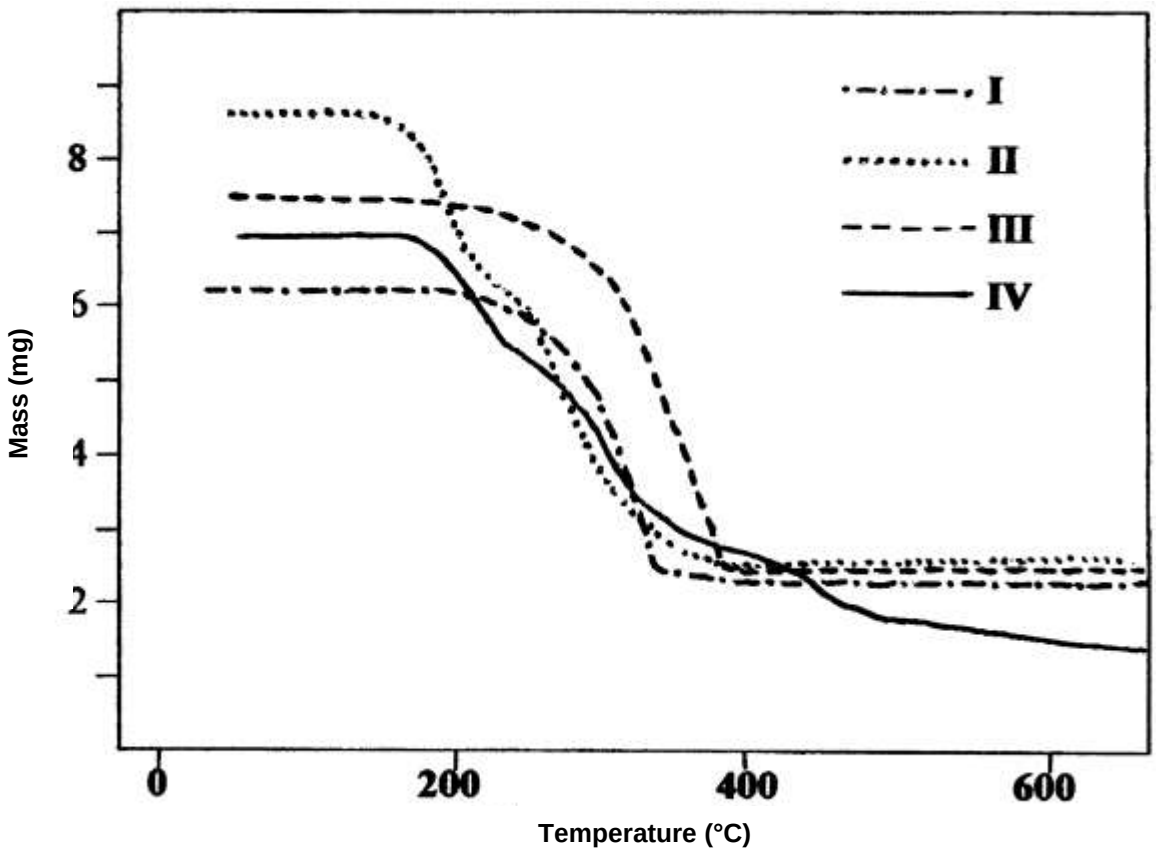

Figure 5: TG curves of dibutyltin complexes, I - [$Bu_2SnGlyCl$], II - [$Bu_2SnValCl$], III - [$Bu_2SnLeuCl$], and IV - [$Bu_2SnPhen_2$].

Table 4. Initial and final temperatures of thermal decomposition and the thermogravimetric data for the dibutyltin complexes

Compounds		Temperature/°C		Thermogravimetric data			
		Initial	Final	$m_{initial}$/mg	m_{final}/mg	Sntheor./ %	Sn found/%
I	[$Bu_2SnGlyCl$]	183	375	6.280	2.140	34.66	34.08
II	[$Bu_2SnValCl$]	130	370	8.640	2.601	30.87	30.12
III	[$Bu_2SnLeuCl$]	125	372	7.490	2.187	29.78	29.20
IV	[$Bu_2SnPhen_2$]	165	700	6.914	1.438	21.15	20.80

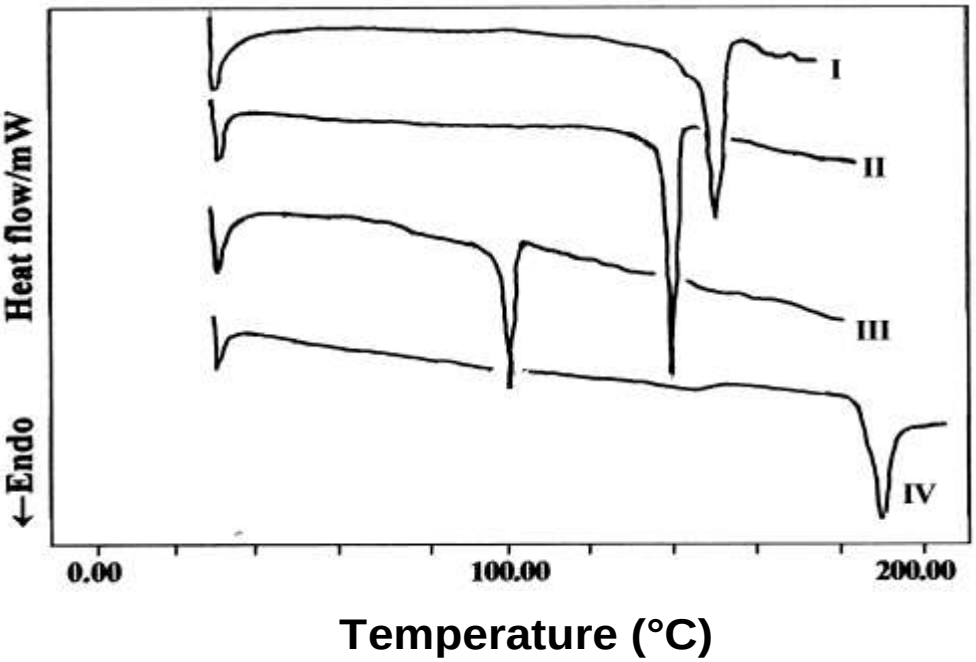

Figure 6: DSC curves of dibutyltin complexes, I - [$Bu_2SnGlyCl$], II - [$Bu_2SnValCl$], III - [$Bu_2SnLeuCl$] and IV - [$Bu_2SnPhen_2$].

agreement with the simultaneous loss of two butyl groups in the first step, loss of a DL-phenylalanine ligand in the second step and a second DL-phenylalanine in the third and fourth consecutive steps. In all the processes, tin metal was produced as a final product which was proven by X-ray fluorescence.

Based on the mass losses observed in the TG curves, it is possible to establish tentative mechanisms for the thermal decompositions of dibutyltin complexes:

I – ($Bu_2SnGlyCl$) $\xrightarrow{183\text{-}375°C}$ Sn

II - ($Bu_2SnValCl$) $\xrightarrow{130\text{-}250°C}$ Bu_2SnlCl $\xrightarrow{263\text{-}370°C}$ Sn

III - ($Bu_2SnLeuCl$) $\xrightarrow{125\text{-}372°C}$ Sn

IV - ($Bu_2SnFalCl$) $\xrightarrow{165\text{-}250°C}$ $SnFal_2$ $\xrightarrow{260\text{-}350°C}$ Sn

Figure 6 shows the DSC curves of the compounds, while Table 5 shows the corresponding melting points, temperature values at the peaks observed and the calculated heat fusion values (kJmol^{-1}) for the dibutyltin compounds.

In these DSC curves, the temperature values at the peaks are in accordance with the determined fusion intervals. Considering the heat fusion values for the compounds I and III (ΔH_{fusion} = -4.24 and -3.27 kJ mol^{-1}, respectively) in comparison with the values for the compounds II and IV (ΔH_{fusion} = -8.30 and -6.93 kJ mol^{-1}, respectively), it can be concluded that compounds I and III can exist as monomeric species in solid-state, while for compounds II and IV, there is a minor solubility it in relation to the solubility of compounds I and III that were described to get their respective ^{119m}Sn-NMR spectra.

Table 5: The melting points (°C), the onset points (°C) and the heat of fusion (kJ mol^{-1}) for the dibutyltin complexes.

Compounds		m.p. (°C)	T_{onset} (°C)	ΔH_{fusion} (kJmol^{-1})
I	[$Bu_2SnGlyCl$]	150-153	149.5	-4.24
II	[$Bu_2SnValCl$]	138-141	239.8	-8.30
III	[$Bu_2SnLeuCl$]	107-110	103.6	-3.27
IV	[$Bu_2SnPhen_2$]	191-194	191.2	-6.93

Conclusions

The studied compounds I, II and III exist as trigonalbipyramidal tin species while compound IV exists as a slightly distorted trans-octahedral tin species in solid-state, probably as monomeric or as a structure with a certain degree of polymerization as observed for diorganotin compounds with □-hydroxycarboxylic acid (Barbiéri et al., 2002; Carlos, 1999; Terra, 1997, 1998) or □-amino acids (Barbiéri et al., 2004). These results are distinct from the ones described for diglycinatotin (II) (Ho and Zuckerman,1973), trimethyltin (IV), glycinate and alaninate (Farias et al., 2003), dimethyltin (IV), glycinate and □-alaninate compounds (Ho and Zuckerman, 1973), which showed polymeric species with bridging □-amino acids that should link the carboxylic oxygen to the tin and amino group to the other tin atoms (Ho and Zuckerman, 1973; Farias et al., 2003). Among these compounds, dibutyltin derivatives displayed both higher anti-tumor activity and relatively low toxicity (Zuo et al., 2001).

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