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Synthesis and Characterization of Three New di-n-butyl [bis (alkyl-aminopropionic acid)]tin (IV)

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Abstract: The synthesis of novel di-n-butyl [bis (alkyl-aminopropionic acid)]tin (IV) (alkyl = octyl, dodecyl, octadecyl) 2a-2c is reported. The complexes were characterized by 1H, 13C, 119Sn NMR, IR, MS and elemental analyses. For compound 2a the 119Sn NMR showed the presence of five signals suggesting the existence of a mixture of five hexa-coordinated species in equilibrium, two trans (I, II) and three cis (III, IV, V). In contrast, the compounds 2b and 2c present only unique hexa-coordinated specie.

Keywords: Diorganotin; Sn (IV) complex; tin; organotin; spectroscopy.

Introduction

Organotin compounds have been extensively studied in the structural chemistry. For organotin (IV) compounds present frequently the formation of polyhedra with tetrahedral, trigonal-bipyramidal, octahedral and pentagonal-bipyramidal coordination geometries, the final coordination number depends strongly on the number of organic substituents attached to tin atom and the nature of the ligands [1-6].

The organotin (IV) compounds and them derives exhibit antitumor activity [7, 8], biocides [9], material with non-linear optical properties [10], fluorescence probes for DNA traces [11], model systems like nucleotides [12], amino acids [13], peptides [14] and corrosion inhibitors [15].

In particular, diorganotin (IV) compounds derived from ligands containing nitrogen and oxygen donor atoms present increasing number of reports, mainly derivates of aminoacids and analogues have been investigated [16, 17]. Our current interest in the synthesis of organotin compounds and structural analysis [18-22], prompted us to extend our investigation in the synthesis of new organotin (IV) compounds, which could have corrosion inhibitors properties [23].

This paper describes the synthesis of three new di-n-butyl [bis (alkyl-aminopropionic acid)]tin (IV) (alkyl = octyl, dodecyl and octadecyl) 2a-2c, by the reaction of di-n-butyl (IV) oxide and alkyl aminopropionic acid (alkyl = octyl, dodecyl and octadecyl) 1a-1c in a 1:2 molar ratio. All compounds were characterized by 1H, 13C, 119Sn NMR, infrared spectroscopy, mass spectrometry and elemental analyses.

Results and Discussion

Herein we report the reaction of alkyl aminopropionic acids 1a-1c, with di-n-butyltin (IV) oxide in a 2:1 ratio to obtain di-n-butyl [bis (alkyl-aminopropionic acid)]tin (IV) 2a-2c as white solids (Fig. 1). The compounds 1a-1c were obtained through the reaction of alkyl amine (alkyl = octyl, dodecyl and octadecyl) and acrylic acid [24].

The 1H NMR spectra in CDCl3 of all the compounds 2a-2c (1H NMR data are summarized in Table 1) show only one set of signal for each magnetically equivalent H nucleus, thus both (n-Bu)2Sn proton and those of the ligands are in 1:2 ratio, respectively. For 2b and 2c compounds, this indicate the formation of unique species or a fast-exchanging equilibrium on the NMR time scale (Support information). For the compound 2b for example, the H3 and H4 (3.008 and 2.823 ppm) proton appeared as broad signals at higher field (Δδ = 0.05 and 0.083) with respect to the free ligand 1b (Support information). This suggests a shielding of these protons upon coordination giving evidence for the formation of a Sn-O bonded and NH→Sn coordination bond.
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For the compound 2b the \textit{^{13}C} NMR spectrum in CDCl\textsubscript{3}, the carbon C3 and C4 appeared as broad signals (47.623 and 44.748 ppm) at low field (\(\Delta\delta = 0.521\) and \(0.170\)) with respect to the free ligand 1b, the chemical shift of these carbons gave evidence for the formation of NH\text{\rightarrow}Sn coordination bond. Likewise, the chemical shift of the signals of the compound 2b the carbons C1 and C2 appeared as broad signals (177.242 and 33.154 ppm) with respect to the carbons of free ligand 1b (\(\Delta\delta = 0.316\) and \(1.254\)) giving evidence for the formation of Sn-O bonded. The \textit{^{13}C} NMR data are summarized in Table 2.

All compounds (2a-2c) exhibited \(^{1}J(\text{\textit{^{119}Sn}-^{13}C})\) and \(^{2}J(\text{\textit{^{117}Sn}-^{13}C})\) coupling 749/608, 720/690 and 705/633 Hz respectively within the range of trans six-coordinated tin compound [16-19] The \textit{^{119}Sn} NMR spectra of 2b and 2c at room temperature in chloroform show only one signal at -203.96 and -204.20 ppm respectively. This can indicate unique species or a fast exchanging equilibrium, on the NMR time scale. The chemical shifts are within the range of di-\textit{n}-butyl (IV) hexacoordinated compounds [3-6, 18-22]. Nevertheless, for compound 2a, the \textit{^{119}Sn} NMR spectrum show five signals in ca. 0.9:1.0:1.1:1.5:1.0 ratio, \(\delta\) -176.21, -186.10, -194.50, -204.37 and -215.91 ppm associate to the hexa-coordinated species, this result suggested the existence of a mixture of an equilibrium between five different hexacoordinated isomers, two trans (I, II) and three cis (III, IV, V) in solution at room temperature, the isomerism is atributed to different arrangement of the ligands [28, 21] as show in Fig. 2, a possible explanation in formation of hexacoordinate isomers due to the presence of chain short, giving as a result the existence of equilibrium dynamic.

The IR spectra for the compounds 2a-2c exhibit one \(\nu_{(C=O)}\) carbonyl band in 1654 cm\textsuperscript{-1}. Also a broad band one of them assigned to the N-H in 1566 cm\textsuperscript{-1} and other due Sn-O band is observed in 430 cm\textsuperscript{-1}.

The mass spectra in all three cases for 2a-2c, (15 eV IE) displayed the presence of molecular ion confirming of the
formation of the products, the fragmentation process start with the loss of a ligand, followed by loss of \( n \)-butyl groups (yielding the base peak for \( 2a \)), and later loss of Sn atom giving the base peak for compounds \( 2b \) and \( 2c \). The spectra show others fragment ion and a possible fragmentation pattern is given in Fig. 3.

### Experimental section

**Materials**

The reagents were purchased from Aldrich Co. Melting points were determined in open capillaries on Electrothermal melting apparatus (UK) and are uncorrected. IR spectra were recorded on Bruker Tensor-27 FT-IR using KBr pellets. \( ^1H, ^{13}C \) and \( ^{119}Sn \) NMR spectra were recorded on VARIAN Mercury 200-BB spectrometer. The \( ^1H \) and \( ^{13}C \) chemical shifts [ppm] are relative to internal SiMe\(_4\) (TMS) and the \( ^{119}Sn \) chemical shifts [ppm] are relative to internal SnMe\(_4\). Results are presented as, chemical shift in ppm, multiplicity coupling constants in Hz, number of protons, proton’s position. Multiplicities are shown as the abbreviations: s (singlet), d (doublet), t (triplet), and m (multiplet). Mass spectra were obtained in HP 5973 MSD eV = 15.2 (Direct insertion probe). Elemental analyses were performed on CHNS analysis in Perkin Elmer Series II 2400. Solvent were commercially available reagent grade.

**Synthesis of alkyl-aminopropionic acid 1a-3a** (alkyl = octyl, dodecyl and octadecyl)

**Octyl-aminopropionic acid 1a:** 5.0 g (0.038 mol) of octylamine was slowly added 3.35 g (0.046 mol) of acrylic acid; the reaction was placed in flask equipped with a magnetic stirred, thermometer and reflux system. The reaction was carried to 90-95 °C during 2 hours. After being cooled to room temperature the residue was treated with hexane, the solution is filtered and the residue was treated with chloroform, the solution was filtered and the solvent was evaporated under vacuum to yield 7.82 g (95 %) of compound \( 1a \) as white solid. Yield 95%; mp 86-87 °C; IR (KBr, \( \nu_{\text{max}}/\text{cm}^{-1} \)) 3375 (N-H), 1655 (C=O); \( ^1H \) NMR (200MHz, CDCl\(_3\), \( \delta \text{ ppm} \)): 0.856 (t, \( J = 6.6 \text{ Hz} \), 3H, H-11), 1.241 (m, 10H, H-6 to H-10), 1.721 (m, 2H, H-5), 2.506 (t, \( J = 5.5 \text{ Hz} \), 2H, H-2), 2.895 (t, \( J = 7.8 \text{ Hz} \), 2H, H-4), 3.055 (t, \( J = 5.5 \text{ Hz} \), 2H, H-3); \( ^{13}C \) NMR (50MHz, CDCl\(_3\), \( \delta \text{ ppm} \)); 176.920 (C-1), 46.964 (C-3), 44.518 (C-4), 31.792 (C-2), 31.675 (C-5), 29.068 (C-6, C-7), 26.710 (C-8), 26.169 (C-9), 22.566 (C-10), 14.043 (C-11); elemental analysis: C\(_{11}\)H\(_{23}\)NO\(_2\) Calc.: C 65.97, H 12.22, N 6.95; found: C 65.65, H 12.18, N 6.94.

**Dodecyl-aminopropionic acid 1b:** 5.0 g (0.027 mol) of dodecylamine and 2.3 g (0.032 mol) of acrylic acid gave 6.52 g (94%) of compound \( 1b \) as white solid. Yield 94%; mp 89-90 °C; IR (KBr, \( \nu_{\text{max}}/\text{cm}^{-1} \)) 3374 (N-H), 1655 (C=O); \( ^1H \) NMR (200MHz, CDCl\(_3\), \( \delta \text{ ppm} \)): 0.879 (t, \( J = 6.6 \text{ Hz} \), 3H, H-15),

### Table 2. Chemical shift of \( ^{13}C \) NMR for compounds 2a-2c.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( ^{13}C ) NMR</th>
<th>( ^{119}Sn ) NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>177.242</td>
<td>27.399</td>
</tr>
<tr>
<td>C2</td>
<td>33.066</td>
<td>13.560</td>
</tr>
<tr>
<td>C3</td>
<td>47.579</td>
<td>13.604</td>
</tr>
<tr>
<td>C4</td>
<td>44.723</td>
<td>13.574</td>
</tr>
<tr>
<td>C5</td>
<td>31.646</td>
<td>13.574</td>
</tr>
<tr>
<td>C6</td>
<td>29.117</td>
<td>13.574</td>
</tr>
<tr>
<td>C7</td>
<td>29.068</td>
<td>13.574</td>
</tr>
<tr>
<td>C8-C9</td>
<td>26.813</td>
<td>13.574</td>
</tr>
<tr>
<td>C10</td>
<td>22.507</td>
<td>13.574</td>
</tr>
<tr>
<td>C11</td>
<td>13.995</td>
<td>13.574</td>
</tr>
<tr>
<td>C6-C11</td>
<td>29.257-29.537</td>
<td></td>
</tr>
<tr>
<td>C12-C13</td>
<td>26.710-26.888</td>
<td></td>
</tr>
<tr>
<td>C14</td>
<td>22.581</td>
<td></td>
</tr>
<tr>
<td>C15</td>
<td>14.014</td>
<td></td>
</tr>
<tr>
<td>C6-C17</td>
<td>29.156-29.626</td>
<td></td>
</tr>
<tr>
<td>C18</td>
<td>26.696</td>
<td></td>
</tr>
<tr>
<td>C19</td>
<td>26.154</td>
<td></td>
</tr>
<tr>
<td>C20</td>
<td>22.581</td>
<td></td>
</tr>
<tr>
<td>C21</td>
<td>14.014</td>
<td></td>
</tr>
<tr>
<td>Co-</td>
<td>27.399 [749/608]</td>
<td></td>
</tr>
<tr>
<td>CB- Cγ</td>
<td>27.252-27.399</td>
<td></td>
</tr>
<tr>
<td>Cδ</td>
<td>13.560</td>
<td></td>
</tr>
</tbody>
</table>

Chemical shifts in ppm respect to TMS \( ^1J(^{13}C-^{119}Sn) \), \( ^2J(^{13}C-^{117}Sn) \) coupling constant between square brackets.
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1.250 (m, 18H, H-6 to H-14), 1.746 (m, 2H, H-5), 2.522 (t, \( J = 6.0 \) Hz, 2H, H-2), 2.906 (t, \( J = 7.8 \) Hz, 2H, H-4), 3.057 (t, \( J = 6.0 \) Hz, 2H, H-3); 13C NMR (50MHz, CDCl3, ppm): 176.926 (C-1), 47.102 (C-3), 44.612 (C-4), 31.900 (C-2), 31.564 (C-5), 29.103-29.613 (C-6 to C-11), 26.731 (C-12), 26.394 (C-13), 22.689 (C-14), 14.137 (C-15); elemental analysis: C_{15}H_{31}NO_2 Calc.: C 67.42, H 12.45, N 5.26; found: C 67.46, H 12.50, N 5.26.

Octadecyl-aminopropionic acid 1c: 5.0 g (0.018 mol) of octadecylamine and 1.6 g (0.022 mol) of acrylic acid gave 5.52 g
Complex di-n-butyl [bis(alkyl-aminopropionic acid)]tin (IV) 2a-2c (alkyl = octyl, docetyl and octadecyl)

Complex di-n-butyl [bis(alkyl-aminopropionic acid)]tin (IV) 2a: A solution of 0.5 g (0.00248 mol) of 1a in 100.0 ml of ethanol was placed in flask equipped with a magnetic stirred and dean-Stark trap and 0.3 g (0.0012 mol) of di-n-butyltin (IV) oxide were added. The suspension was refluxed during 10 hours. After being cooled to room temperature, the solvent was evaporated under vacuum. The residue was treated with chloroform, the solution was filtered and the solvent was evaporated under vacuum to yield 1.25 g (80 %) of compound 2a as yellow solid. Yield 80%; mp 90-91 ºC; IR (KBr, ν_max/cm⁻¹) 1654 (C=O), 1566 (N-H), 430 (Sn-O); ¹H NMR (200MHz, CDCl₃, δ ppm): 0.877 (t, J = 6.6 Hz, 6H, H-11), 1.262 (m, 10H, H-6 to H-10), 1.662 (2H, H-2), 2.869 (b, 2H, H-4), 3.045 (b, 2H, H-3), 1.214 (m, 4H, Hα-Hβ), 1.180 (2H, Hγ), 0.877 (t, J=6 Hz, 3H, Hδ); ¹³C NMR (50MHz, CDCl₃, δ ppm): 177.242 (C-1), 47.579 (C-3), 44.723 (C-4), 33.066 (C-2), 31.646 (C-5), 29.068 (C-7), 26.813 (C-8), 22.507 (C-10), 13.995 (C-11), 27.399 [Ca, ¹¹¹Sn=13C=749], ¹¹¹Sn=13C=608 Hz], 27.252-27.399 (CB-Cγ), 13.560 (Cδ); ¹¹⁹Sn NMR (200MHz, CDCl₃, δ ppm) -176.21, -186.10, -194.50, -204.37, -215.91 ppm; elemental analysis: C₃₅H₇₂N₂O₧Sn Calc.: C 53.90, H 10.44, N 4.32; found: C 53.79, H 10.52, N 4.27.

Conclusions

Novel di-n-butyl [bis(alkyl-aminopropionic acid)]tin (IV) (alkyl= octyl, docetyl and octadecyl) 2a-2c were obtained. The hexacoordinated complexes were characterized by ¹H, ¹³C, ¹¹⁹Sn NMR, infrared spectroscopy, mass spectrometry and elemental analyses. The compound 2a showed five hexa-coordinated species indicating the existence of a mixture in equilibrium between two trans (I, II) and three cis (III, IV, V) hexacoordinated isomers. Whereas for the compounds 2b and 2c only unique species were observed due to steric hindrance of alkyl substituents.

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References