SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF SOME NEW HYDROGENOXALATO ORGANOTIN (IV) COMPLEXES

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Abstract: The synthesis and spectroscopic studies (infrared and Mössbauer) of new hydrogenoxalato derivatives and adducts containing SnRₙ (R=Me, Ph; n=2, 3) residues are reported. Based on their spectroscopic data dimeric and polymeric structures containing hexacoordinated or pentacoordinated Sn are suggested, the hydrogenoxolate anion behaving as a monocoordinating or a monochelating ligand. In two studied adducts, supramolecular architectures may be obtained when extra hydrogen bonds involving the free NH groups are considered.

Keywords: dimeric and polymeric structures, hydrogenoxalate, monochelating, monocoordinating, octahedral or trigonal bipyramidal environments, spectroscopy, supramolecular architectures.

1. INTRODUCTION

Several papers on oxalato and hydrogenoxalato complexes have been reported [1-6], while only few hydrogenoxalato tin ones are known [7]. In this work we have synthesized four new hydrogenoxalato derivatives and adducts containing SnRₙ (R = Me, Ph and n = 2, 3) residues using the H₂N(CH₂)₂NH₃(HC₂O₄)₂·H₂O salt while the adduct C₄N₂H₁₂(HC₂O₄)₂·2SnP₂Cl₂ is obtained by reacting in situ piperazine [NH(C₄H₈)NH] with H₂C₂O₄ and SnP₂Cl₂. These compounds have been studied by infrared and Mössbauer spectroscopies and structures proposed based on spectroscopic data.

2. EXPERIMENTAL SETUP

2.1. Salt synthesis

H₂N(CH₂)₂NH₃(HC₂O₄)₂·H₂O (L) was obtained as white powder by partial neutralization of the H₂C₂O₄ acid by H₂N(CH₂)₂NH₂ (98%) in 1:1 ratio as reported by Barnes et al. [8] and Vaidhyanathan et al. [9].

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2.2. Compounds synthesis
The studied compounds (A, B, C, D) were obtained as white precipitates.
–(A): by mixing L (1.32 mmol) in water with SnMe2Cl2 (1.32 mmol) in ethanol in 1:1 ratio. m.p. > 260 °C.
–(B): by mixing L (1.85 mmol) in water with SnPh2Cl2 (1.85 mmol) in ethanol in 1:1 ratio. m.p. > 260 °C.
–(C): by mixing L (2.00 mmol) in water with SnMe3Cl (2.00 mmol) in dichloromethane in 1:1 ratio. m.p. = 236 °C.
– (D): by mixing piperazine [NH(CH2)3NH] (1.14 mmol) in water with H2C2O4 (2.48 mmol) in water and SnPh2Cl2 (1.14 mmol) in ethanol in 1:2:1 ratio. m.p. > 260 °C.

All the precipitates were stirred around two hours before being filtered.

The analytical data reported in Table 1, have allowed to suggest the following formulae:
A: SnMe2(HC2O4)2
B: SnPh2(HC2O4)2
C: [H3N(CH2)2NH2(HC2O4)]2SnMe3Cl
D: C2N2H12(HC2O4)2·2SnPh2Cl2

| Compound | Chemical composition [% mass] |
|----------|-------------------------------|
|          | C     | H     | N     |          |          |
|          | Calc. | Found | Calc. | Found   | Calc. | Found |
| L        | 28.36 | 28.59 | 4.72  | 4.43    | 11.02 | 11.20 |
| A        | 22.05 | 21.99 | 2.46  | 2.43    | –     | –     |
| B        | 40.98 | 41.02 | 3.01  | 3.04    | –     | –     |
| C        | 22.57 | 22.60 | 4.73  | 4.66    | 4.39  | 4.36  |
| D        | 40.29 | 40.35 | 3.59  | 3.65    | 2.94  | 2.98  |

Elemental analyses have been obtained at the ICMCB-Bordeaux University (France) with a CHNS: Flash EA 1112 Thermofisher. Infrared spectra have been recorded at the CRPP-Bordeaux University (France) using a Nicolet 6700 FT-IR spectrophotometer on diamond. Mössbauer spectra were recorded at the ICMCB-Bordeaux (France) on a liquid helium cryostat with a HALDER spectrometer.

Infrared abbreviations: br (broad); sh (shoulder) vs (very strong); s (strong); m (medium); w (weak). Mössbauer abbreviations: Δ (quadrupole splitting); δ(isomer shift); Γ(full width at half-height). The chemicals were purchased from Aldrich Company-Germany without any further purification.

3. RESULTS AND DISCUSSION
Spectroscopic study
Let us consider the main IR data (in cm⁻¹) of the compounds A–D:
A: νCO2: 1699(s), 1628(s), 1350(s), vasSnMe2 585(m), vSnO 239(s);
B: νCO2: 1620(sh), 1607(vs), 1352(m), vasSnPh2 284(m), vSnO 206(m);
C: νOH + νNH2 3386(br), νCO2 1635(vs), 1283(vs), 1224(s), vsSnMe3 523(w), vasSnMe2 561(w), vSnO 240(vs);
D: νOH + νNH2 3277(br), νCO2 1569(sh), 1481(m), 1351(m), vPh 729(vs), 690(vs).

and their Mössbauer data (mm s⁻¹) of A and B:
A: Δ=4.46; δ=1.52; Γ=1.08;
B: Δ=4.52; δ=1.33; Γ=0.92.

For A and B, the absence of a band assigned to vsSnC2 on the infrared spectra of these two derivatives allows to conclude to linear SnMe2 and SnPh2 groups. The vasSnC2 vibration is located respectively at 585 cm⁻¹ and at 284 cm⁻¹ on the infrared spectra. The broad absorptions around 3300 cm⁻¹ on the infrared spectra of these two compounds attributed to νOH indicate the existence of hydrogen bonds.
The value of the quadrupole splitting of (A) ($\Delta=4.52 \text{ mm s}^{-1}$) is greater than that of SnMe$_2$Cl$_2$ ($\Delta=3.56 \text{ mm s}^{-1}$) [10] in which the SnMe$_2$ group is disssymmetrically transcoordinated with an octahedral environment around tin atom (in Me$_2$Sn(O$_2$PPh$_2$)$_2$ which contains a tin center in a trans octahedrally coordinated environment ($\Delta=4.45 \text{ mm s}^{-1}$)) [11].

The value of the quadrupole splitting of (B) ($\Delta=4.45 \text{ mm s}^{-1}$) greater than the one of SnPh$_2$Cl$_2$ ($\Delta=2.89 \text{ mm s}^{-1}$) [12] is in agreement with a transcoordinated SnPh$_2$ group and a trans octahedral environment around tin atom [13]. The structure resulting from these spectroscopic data is an infinite chain structure with a transcoordination of the SnR$_2$ group, an octahedral environment around tin center and a chelating hydrogenoxalate anion (Figure 1).

![Fig. 1. Proposed structure for compounds A and B (R = Me, Ph).](image1)

For C, the vibration vsSnMe$_3$ appears at 523 cm$^{-1}$ and indicates a non-planar SnMe$_3$ group. The vasSnMe$_3$ vibration is localized at 550 cm$^{-1}$. The band at 240 cm$^{-1}$ attributed to vSnO indicates the metal-ligand bond.

Based on the spectroscopic data we propose for this compound a dimeric structure with a unidentate anion and a trigonal bipyramidal environment around the tin atom. The monomer of this dimer can be considered as two anions [HC$_2$O$_2$SnMe$_3$Cl]$^{-}$ linked by NH...O type hydrogen bonds via the ethylenediammonium ion [H$_3$N(CH$_2$)$_2$NH$_3^+$] (Figure 2).

![Fig. 2. Proposed structure for the compound (C).](image2)

For D, the broad absorption at 3277 cm$^{-1}$ on the infrared spectrum attributed to vOH of the hydroxyl group of the oxyanion indicates the existence of hydrogen bonds.
Based on the spectroscopic data we propose for this compound a dimeric structure containing octahedral tin centres with a monochelating anion and transcoordinated SnPh\textsubscript{2} residues. By analogy with the complex (C), this complex can be considered as two anions [HC\textsubscript{2}O\textsubscript{4}SnPh\textsubscript{2}Cl\textsubscript{2}]\textsuperscript{−} connected by NH...O hydrogen bonds via [\textit{H}_2N(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}NH\textsubscript{2}] and a dimerization through acetic acid hydrogen bonds types (Figure 3).

![Proposed structure for the compound (D).](image)

In (C) and (D) the free NH groups may be considered involved in extra hydrogen bonds leading to supramolecular architectures.

4. CONCLUSIONS

The studied compounds have dimeric and infinite chain structures, the environment around the tin atoms being octahedral or trigonal bipyramidal, the hydrogenoxalate anion behaving as a monocoordinating or monochelating ligand. The use of diamines has allowed us to isolate two adducts containing dications \textit{H}_3N(CH\textsubscript{2})\textsubscript{2}NH\textsubscript{3}(HC\textsubscript{2}O\textsubscript{4})\textsubscript{2}SnMe\textsubscript{3}Cl and C\textsubscript{4}N\textsubscript{2}H\textsubscript{12}(HC\textsubscript{2}O\textsubscript{4})\textsubscript{2}SnPh\textsubscript{2}Cl\textsubscript{2} whose proposed structures contain hydrogen bonds between the cations and the oxyanions (in these two last adducts, considering extra hydrogen bonds involving the free NH groups may lead to supramolecular architectures).

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