

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

MOUHAMADOU SEMBENE BOYE^{1*}, AMINATA DIASSE-SARR², LIBASSE DIOP²

¹University Cheikh Anta Diop, Faculty of Sciences and Technologies of Education and Training, Department of Physics Chemistry, Boulevard Habib Bourguiba, 5036 Fann-Dakar, Senegal

²Senegal Cheikh Anta Diop University, Faculty of Science and Technology, Department of Chemistry, Laboratory of Mineral and Analytical Chemistry, Dakar, Senegal.

Abstract: The synthesis and spectroscopic studies (infrared and Mössbauer) of new hydrogenoxalato derivatives and adducts containing SnR_n (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 hydrogenoxalate 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 SnR_n (R = Me, Ph and n = 2, 3) residues using the H₃N(CH₂)₂NH₃(HC₂O₄)₂·H₂O salt while the adduct C₄N₂H₁₂(HC₂O₄)₂·2SnPh₂Cl₂ is obtained by reacting in situ piperazine [NH(C₄H₈)NH] with H₂C₂O₄ and SnPh₂Cl₂. These compounds have been studied by infrared and Mössbauer spectroscopies and structures proposed based on spectroscopic data.

2. EXPERIMENTAL SETUP

2.1. Salt synthesis

H₃N(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].

*Corresponding author, email: mouhasboye@hotmail.com

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 SnMe_2Cl_2 (1.32 mmol) in ethanol in 1:1 ratio. m.p. > 260 °C.
- (**B**): by mixing **L** (1.85 mmol) in water with SnPh_2Cl_2 (1.85 mmol) in ethanol in 1:1 ratio. m.p. > 260 °C.
- (**C**): by mixing **L** (2.00 mmol) in water with SnMe_3Cl (2.00 mmol) in dichloromethane in 1:1 ratio. m.p. = 236 °C.
- (**D**): by mixing piperazine $[\text{NH}(\text{C}_4\text{H}_8)\text{NH}]$ (1.14 mmol) in water with $\text{H}_2\text{C}_2\text{O}_4$ (2.48 mmol) in water and SnPh_2Cl_2 (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: $\text{SnMe}_2(\text{HC}_2\text{O}_4)_2$

B: $\text{SnPh}_2(\text{HC}_2\text{O}_4)_2$

C: $[\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_3(\text{HC}_2\text{O}_4)_2] \cdot 2\text{SnMe}_3\text{Cl}$

D: $\text{C}_4\text{N}_2\text{H}_{12}(\text{HC}_2\text{O}_4)_2 \cdot 2\text{SnPh}_2\text{Cl}_2$

Table 1. Analytical data of compounds **A–D**.

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: νCO_2^- 1699(s), 1628(s), 1350(s), νasSnMe_2 585(m), νSnO 239(s);

B: νCO_2^- 1620(sh), 1607(vs), 1352(m), νasSnPh_2 284(m), νSnO 206(m);

C: $\nu\text{OH} + \nu\text{NH}_3^+$ 3386(br), νCO_2^- 1635(vs), 1283(vs), 1224(s), νasSnMe_3 523(w), νasSnMe_3 561(w), νSnO 240(vs);

D: $\nu\text{OH} + \nu\text{NH}_3^+$ 3277(br), νCO_2^- 1569(sh), 1481(m), 1351(m), νPh 729(vs), 690(vs).

and their Mössbauer data ($\text{mm}\cdot\text{s}^{-1}$) of **A** and **B**:

A: $\Delta=4.46$; $\delta=1.52$; $\Gamma=1.08$;

B: $\Delta=4.52$; $\delta=1.33$; $\Gamma=0.92$.

For **A** and **B**, the absence of a band assigned to νSnC_2 on the infrared spectra of these two derivatives allows to conclude to linear SnMe_2 and SnPh_2 groups. The νasSnC_2 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)** ($\Delta=4.52 \text{ mm}\cdot\text{s}^{-1}$) is greater than that of SnMe_2Cl_2 ($\Delta=3.56 \text{ mm}\cdot\text{s}^{-1}$) [10] in which the SnMe_2 group is dissymmetrically transcoordinated with an octahedral environment around tin atom (in $\text{Me}_2\text{Sn}(\text{O}_2\text{PPh}_2)_2$ which contains a tin center in a trans octahedrally coordinated environment ($\Delta=4.45 \text{ mm}\cdot\text{s}^{-1}$)) [11].

The value of the quadrupole splitting of **(B)** ($\Delta=4.45 \text{ mm}\cdot\text{s}^{-1}$) greater than the one of SnPh_2Cl_2 ($\Delta=2.89 \text{ mm}\cdot\text{s}^{-1}$) [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).

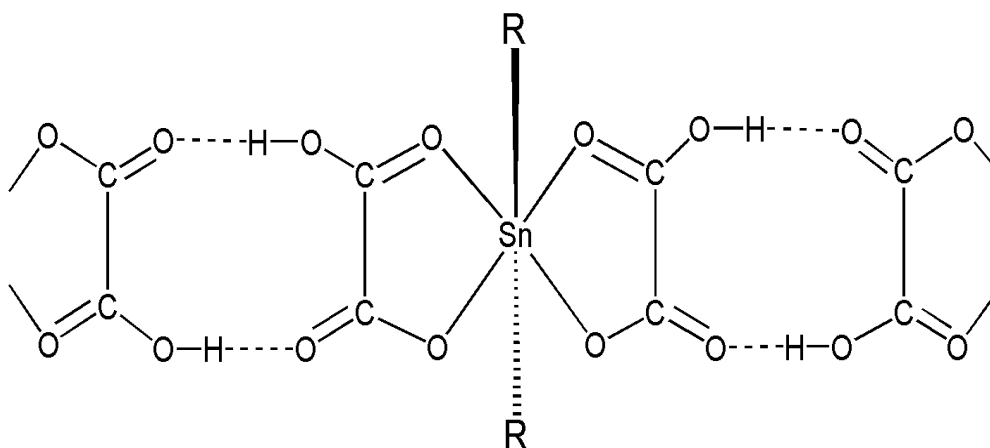


Fig. 1. Proposed structure for compounds **A** and **B** ($\text{R} = \text{Me}, \text{Ph}$).

For **C**, the vibration νSnMe_3 appears at 523 cm^{-1} and indicates a non-planar SnMe_3 group. The νSnMe_3 vibration is localized at 550 cm^{-1} . The band at 240 cm^{-1} attributed to νSnO 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 $[\text{HC}_2\text{O}_4\text{SnMe}_3\text{Cl}]^-$ linked by $\text{NH}\cdots\text{O}$ type hydrogen bonds via the ethylenediammonium ion $[\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_3]^+$ (Figure 2).

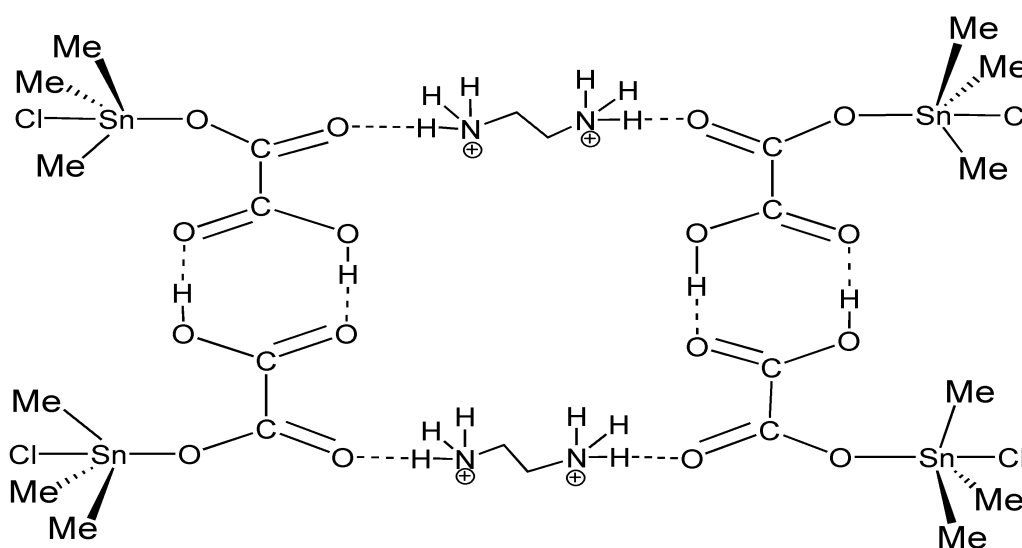


Fig. 2. Proposed structure for the compound **(C)**.

For **D**, the broad absorption at 3277 cm^{-1} on the infrared spectrum attributed to νOH 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_2 residues. By analogy with the complex (C), this complex can be considered as two anions $[\text{HC}_2\text{O}_4\text{SnPh}_2\text{Cl}_2]^-$ connected by $\text{NH}\cdots\text{O}$ hydrogen bonds via $[\text{H}_2\text{N}(\text{C}_4\text{H}_8)\text{NH}_2]^+$ and a dimerization through acetic acid hydrogen bonds types (Figure 3).

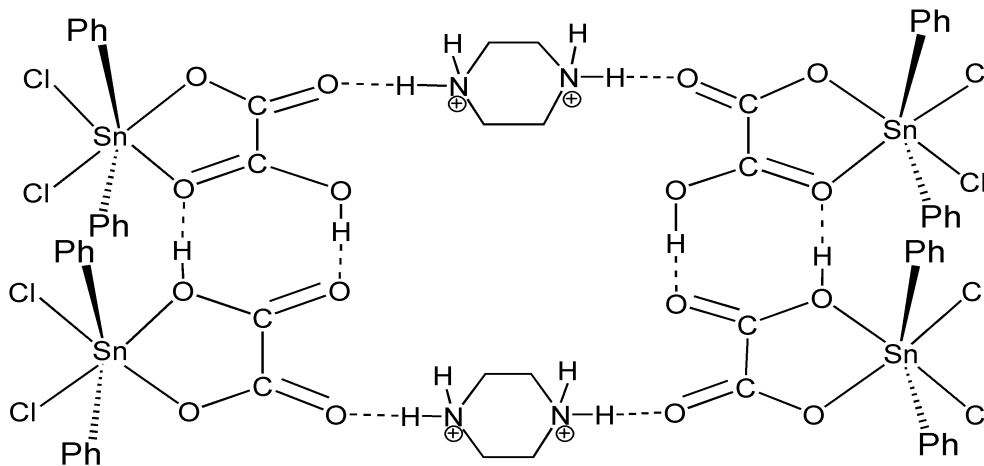


Fig. 3. Proposed structure for the compound (D).

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 dication $\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_3(\text{HC}_2\text{O}_4)_2 \cdot 2\text{SnMe}_3\text{Cl}$ and $\text{C}_4\text{N}_2\text{H}_{12}(\text{HC}_2\text{O}_4)_2 \cdot 2\text{SnPh}_2\text{Cl}_2$ whose proposed structures contain hydrogen bonds between the cations and the oxanions (in these two last adducts, considering extra hydrogen bonds involving the free NH groups may lead to supramolecular architectures).

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