

NEW TRANS-1,2- CYCLOHEXYLDIAMINO-NN,N'N' (CH₂CO₂)(CH₂CO₂H)₃ ANION CONTAINING ADDUCTS AND DERIVATIVES: SYNTHESIS AND INFRARED STUDY

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Abstract: Five Cyclohexyldiamino-NN, N'N'(CH₂CO₂)(CH₂CO₂H)₃ anion containing adducts and derivatives with tin, antimony and mercury halides have been synthesized and characterized by infrared spectroscopy. The suggested structures are discrete, the anion behaving as a monodentate or a monochelating ligand: the environments around the metallic centres are trigonal bipyramidal or octahedral. The carboxylic groups and the cation, when involved in extra OH---O, OH---Cl or NH---Cl or O hydrogen bonds may lead to supramolecular architectures.

Keywords: monodentate or monochelating ligand, supramolecular architectures, trigonal bipyramidal or octahedral environments

1. INTRODUCTION

Since decades our group has been focusing in studying the interactions between carboxylic and non carboxylic alkylammonium salts with transition and non transition metals halides to obtain some more data on the coordination ability of the oxyanions [1–3]. In this paper we have initiated the study of the interactions between Et₃NH. Cyclohexyldiamino-NN, N'N'(CH₂CO₂)(CH₂CO₂H)₃ and SnPh₃Cl, SnBu₂Cl₂, HgCl₂ or SbF₃ which have yielded the studied adducts and derivatives, infrared study of which have been carried, then structures suggested on the basis of infrared data.

2. MATERIALS AND METHODS

Et₃NH.Cyclohexyldiamino-NN, N'N'(CH₂CO₂)(CH₂CO₂H) (**L**) has been obtained as a white powder on partially neutralizing in water the corresponding tetracetic acid with Et₃N (ratio 1/1). The resulting solution when submitted to water evaporation in the oven at 60 °C gives a powder. Its analytical data [% calculated (% found) - % **C** = 53.68 (53.69), % **H** = 8.33 (8.25), % **N** = 9.39 (9.41)-] have allowed to suggest C₁₄H₂₁O₈N₂.HNEt₃ as formula.

When (**L**) is allowed to react with SnPh₃Cl, SnBu₂Cl₂, HgCl₂ or SbCl₅ in the ratio 1/1 as ethanolic solutions, a precipitate is obtained (for **A**, **C**, **D** and **E**) or a powder (for **B**) collected after a slow solvent evaporation. The elemental analyses [calculated (found)] are summarized on Table 1 have allowed to suggest the following formula:

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Table 1. Analytical data.

Complexes	% C	% H	% N
A	49.27(49.43)	6.35(6.39)	6.05(6.12)
B	39.34(39.21)	6.86(6.66)	5.29(5.27)
C	54.79(54.64)	6.29(6.13)	5.04(4.99)
D	31.84(31.49)	6.28(6.14)	5.57(5.58)
E	31.47(31.32)	5.38(5.41)	5.65(5.61)

A: Et₃NH(C₁₄H₂₁O₈N₂)₂.SnPh₂Cl.2H₂O.1/4C₆H₆;

B: Et₃NHC₁₄H₂₁O₈N₂.SnBuCl₃.EtOH.H₂O;

C: Et₃NHC₁₄H₂₁O₈N₂.SnPh₃Cl;

D: Et₃NHC₁₄H₂₁O₈N₂.SbF₅.5H₂O;

E: Et₃NHC₁₄H₂₁O₈N₂.3/2H_gCl₂.Et₃NHCl.

The elemental analyses have been obtained from the Microanalyses Laboratory (University of Burgundy, Dijon – France). The infrared spectra have been obtained from the University of Caen-France using a Bruker FT-IR spectrometer.

IR abbreviations: br = broad, vs = very strong, s = strong, m = medium.

The chemicals were obtained from ALDRICH Company-Germany and used as such.

3. RESULTS AND DISCUSSION

Let us consider the infrared data of the studied compounds:

- **L:** ν OH + ν NH 2930(br), ν CO₂ 1539(m), 1450(s), 1225(s);
- **A:** ν OH + ν NH 2975(br), ν CO₂ 1645(vs), 1620(vs), 1386(s), 1308(s), phenyl bands: 728(vs), 695 (vs);
- **B:** ν OH + ν NH 2950(br), ν CO₂ 1728(vs), 1620(vs), 1582(s), 1399(s), 1216(s);
- **C:** ν OH + ν NH 2859(br), ν CO₂ 1542(vs), 1479(s), 1249(m), phenyl bands: 730(vs), 695(vs);
- **D:** ν OH + ν NH 2967(br), ν CO₂ 1585(s), 1455(s), 1394(s), 1218(s);
- **E:** ν OH + ν NH 2969(br), ν CO₂ 1634(s), 1455(s), 1344(s), 1278(s).

It seems worthy to outline the dearylation of SnPh₃Cl into SnPh₂Cl in **A**.

A: Et₃NH(C₁₄H₂₁O₈N₂)₂.SnPh₂Cl.2H₂O.1/4C₆H₆

This type of compound has yet been reported by Ma and al in Aqua-dimethyl-bis (2-pyrazinecarboxylato-N,O)-tin(IV) trihydrate [4] (its structure contains a seven coordinated tin centre with two monochelating ligands).

From these considerations and infrared data we suggest two structures:

- A first discrete one with a SnPh₂Cl residue transcoordinated by two monocoordinating anions (Figure 1a). The environment around the tin centre is trigonal bipyramidal;
- A second discrete structure with monochelating ligands with a seven coordinated tin as the one reported in [4] (Figure 1b).

B: Et₃NHC₁₄H₂₁O₈N₂.SnBuCl₃.EtOH.H₂O

A dinuclear adduct of O, O-monochelated SnBuCl₃ has been reported by Cunningham *et al* [5]. This allows to suggest for **B**, a discrete structure with the anion monochelating SnBuCl₃ the environment around the tin centre being octahedral (Figure 2).

C: Et₃NHC₁₄H₂₁O₈N₂.SnPh₃Cl

O-coordinated SnPh₃Cl carboxylato adducts have yet been reported by several authors Gabe *et al*, Khoo *et al* [6 – 7]. While considering in **C** the SnPh₃Cl molecule O-coordinated, we suggest for **C**, a discrete structure with a monocoordinating anion, the environment around the tin centre being trigonal bipyramidal (Figure 3).

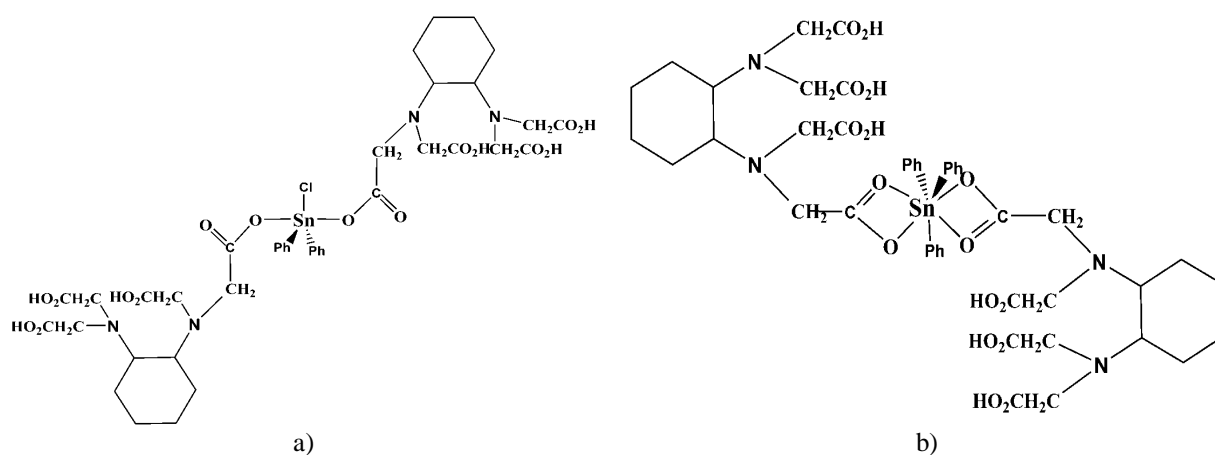


Fig. 1. Proposed structure for A.

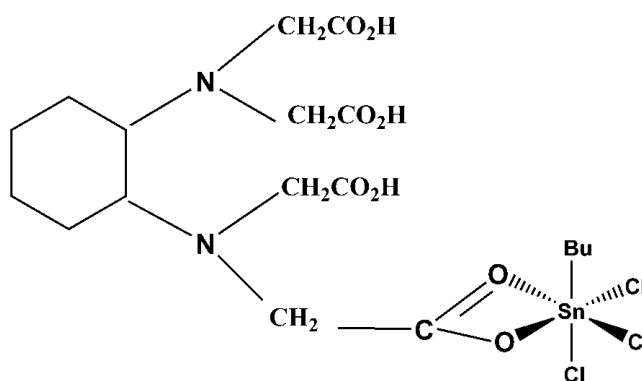


Fig. 2. Proposed structure for B.

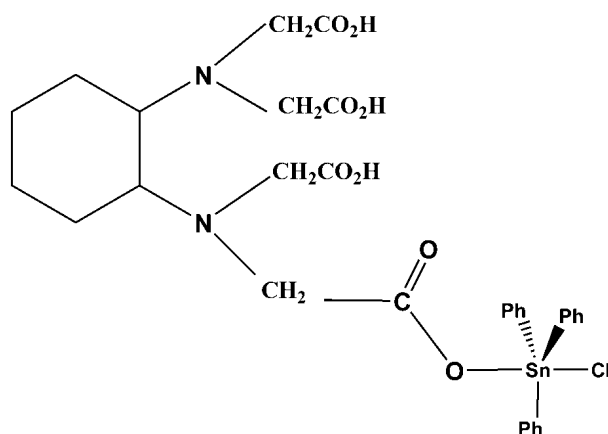
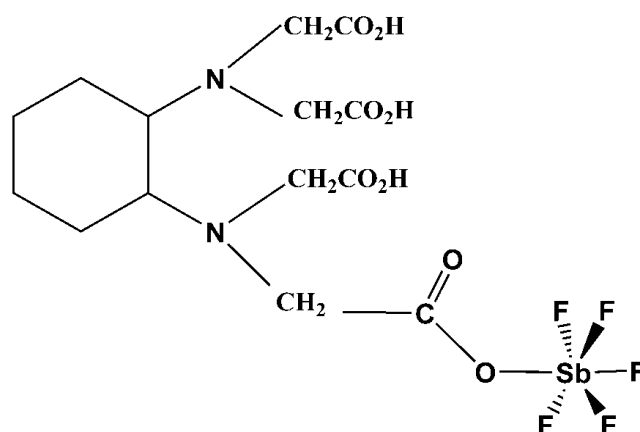


Fig. 3. Proposed structure for C.

D: $\text{Et}_3\text{NHC}_{14}\text{H}_{21}\text{O}_8\text{N}_2 \cdot \text{SbF}_5 \cdot 5\text{H}_2\text{O}$

Notice in this compound the oxidation of SbF_3 into SbF_5

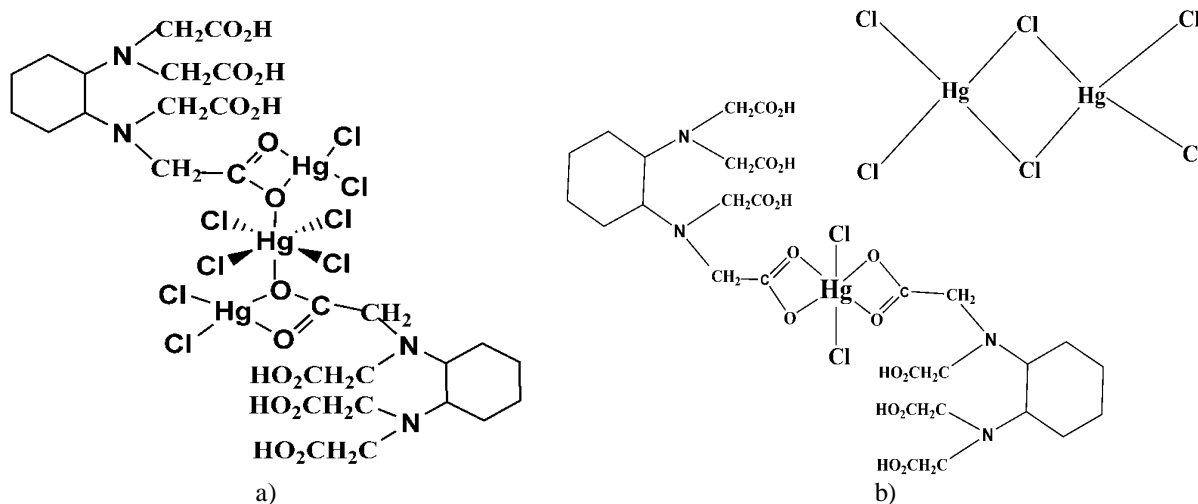
For **D**, a discrete structure with a monocoordinating anion, the environment around the antimony centre being trigonal bipyramidal (Figure 4).

Fig. 4. Proposed structure for **D**.

E: $\text{Et}_3\text{NHC}_{14}\text{H}_{21}\text{O}_8\text{N}_2 \cdot 3/2\text{HgCl}_2 \cdot \text{Et}_3\text{NHCl}$

For **E**, we suggest two types of structure:

- a first discrete one with a central $[\text{HgCl}_4]^{2-}$ monocoordinated by two anions, two other HgCl_2 molecules being monochelated, the environment around the mercury being tetrahedral and octahedral (Figure 5a);
- a second two metallic components one: a binuclear component with two bridging chloro atoms - the environment around the Hg centres being tetrahedral- while the mononuclear component has an octahedral environment around the Hg (Figure 5b) - $[\text{Hg}_2\text{Cl}_6]^{2-}$ has yet been reported by Liu *et al* [8].

Fig. 5. Proposed structure for **E**.

For all these structures while considering the involvement of the cation through $\text{NH} \cdots \text{Cl}$ or $\text{OH} \cdots \text{Cl}$ bonds or extra hydrogen bonds involving the CO_2H groups, a supramolecular architecture may be obtained.

4. CONCLUSION

The five adducts and derivatives studied have a discrete structure, the anion behaving as a monodentate or a monochelating ligand. The environments around the metallic centres are trigonal bipyramidal, tetrahedral or octahedral. When extra intermolecular hydrogen bonds involving the cation or CO_2H groups, a supramolecular architecture may be obtained.

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