

**ATONISHING [CO₂SO₃H]: CARBONATO AND SULFITO
NEW ADDUCTS DERIVING FROM THE INTERACTIONS
BETWEEN R₄NCO₂SO₃H (R=Et, Me) AND
HgX₂, SnX₄ (X=Cl, Br), SbCl₅**

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Abstract: In ethanol, a C-S cleavage occurs in final products on allowing R₄NCO₂SO₃H – R = Me, Et - to react with HgX₂, SnX₄ (M = Hg, X= Cl, Br), leading to carbonate and sulfite adducts and complexes, infrared study of which have been carried out, then structures suggested on the basis of spectroscopic data. When (Me₄N)CO₂SO₃H is allowed to react with SbCl₅, HgX₂ (X = Cl, Br), sulfite adducts were obtained, studied by infrared. The suggested structures are discrete, the sulfite anion behaving as a bidentate ligand.

Keywords: *C-S bond cleavage, carbonate and sulfite ligand in situ
infrared, discrete structures*

INTRODUCTION

The coordination of oxyanion has been reviewed by Hathaway [1]. Our group had yet published several papers dealing with the coordinating behavior of the anions [2-4]. We had initiated, for obtaining carbonato new adducts the study of the interactions of Et_4HCO_3 with very many organotin and MX_2 without any result [5]. In the dynamic of getting $[\text{O}_2\text{CSO}_3\text{H}]^-$ containing compounds, we have initiated here, the study of the interactions between $\text{R}_4\text{NCO}_2\text{SO}_3\text{H}\cdot n\text{H}_2\text{O}$ – $\text{R} = \text{Et}, \text{Me}$ - with SnCl_4 , SnBr_4 , HgBr_2 and HgCl_2 which have yielded eight carbonato and sulfito new adducts and complexes. Infrared study of which have been carried out, then the structures was suggested on the basis of infrared data.

EXPERIMENTAL

The analytical data reported below, allow suggesting the following formulae: % Calculated (% Found).

Table 1. Results of the elemental analyses

| Compound | Chemical formula | Elemental analysis (%) | | | | | |
|----------|--|------------------------|-------|-------|-------|-------|-------|
| | | C | | H | | N | |
| | | calc. | found | calc. | found | calc. | found |
| A | $\text{Et}_4\text{NHSO}_3\text{CO}_2\cdot 2\text{H}_2\text{O}$ | 35.16 | 33.92 | 8.25 | 8.28 | 4.81 | 4.71 |
| B | $\text{Et}_4\text{N}_2\text{CO}_3\cdot 3\text{SnCl}_5\text{Et}_4\text{N}$ | 30.79 | 31.22 | 6.25 | 6.60 | 4.38 | 4.83 |
| C | $\text{Et}_4\text{N}\cdot \text{Sn}(\text{CO}_3)_2\text{BrEt}_4\text{N}_2\text{CO}_3\cdot 6\text{SnBr}_5\text{Et}_4\text{N}$ | 19.32 | 19.25 | 3.86 | 3.94 | 2.70 | 2.56 |
| D | $\text{Et}_4\text{N}_2\text{CO}_3\cdot 7\text{HgBr}_2\cdot 2\text{Et}_4\text{NBr}$ | 12.14 | 11.29 | 2.45 | 2.11 | 1.71 | 1.60 |
| E | $\text{Et}_4\text{N}_2\text{CO}_3\cdot 4\text{HgCl}_2$ | 14.51 | 14.64 | 2.84 | 2.78 | 1.99 | 2.18 |
| F | $\text{Et}_4\text{N}_2\text{CO}_3\cdot 4\text{HgBr}_2\text{Et}_4\text{NBr}$ | 15.21 | 14.59 | 3.04 | 2.48 | 2.13 | 1.73 |
| G | $\text{Me}_4\text{NHSO}_3\text{CO}_2\cdot 2\text{H}_2\text{O}$ | 25.75 | 26.70 | 6.86 | 9.33 | 12.01 | 12.33 |
| H | $(\text{Me}_4\text{N})_2\text{SO}_3\cdot 2\text{SbCl}_5\cdot \text{EtOH}1/4\text{Me}_4\text{NCl}$ | 14.19 | 14.26 | 3.54 | 3.41 | 3.55 | 3.38 |
| I | $(\text{Me}_4\text{N})_2\text{SO}_3\cdot 2\text{HgCl}_2$ | 12.45 | 11.67 | 3.11 | 2.88 | 3.63 | 3.64 |
| J | $(\text{Me}_4\text{N})_2\text{SO}_3\cdot 2\text{HgBr}_2\cdot \text{Me}_4\text{NBr}$ | 13.06 | 12.97 | 3.26 | 3.04 | 3.87 | 4.08 |

The elemental analyses have been performed by the CNRS << Service Central d'Analyses >> Vernaison-France, the infrared spectra at the University of Padova-Italy using a PE 580 spectrometer [$4000\text{-}200\text{ cm}^{-1}$] and CsI windows, the samples being as Nujol mulls. Infrared data are given in cm^{-1} (abbreviations: (vs) very strong, (s) strong, (m) medium, (sh) shoulder, (w) weak). The chemicals were purchased from Aldrich and used as such.

RESULTS AND DISCUSSION

Let us consider the infrared data of the studied compounds:

A: $\nu_{\text{as}} \text{COO} = 1630.5\text{s}$; $\nu_{\text{s}} \text{COO} = 1310\text{s}$; $\nu_{\text{SnCl}} = 290\text{w}$; $\nu_{\text{SnO}} = 200\text{w}$

B: $\nu_{\text{as}} \text{COO} = 1590.9\text{s}$; $\nu_{\text{s}} \text{COO} = 1310\text{s}$; $\nu_{\text{SnBr}} = 260.5\text{w}$; $\nu_{\text{SnO}} = 210\text{w}$

C: $\nu_{\text{as}} \text{COO} = 1585.5\text{s}$; $\nu_{\text{s}} \text{COO} = 1290.5\text{s}$; $\nu_{\text{HgO}} = 265\text{w}$

D: $\nu_{\text{as}} \text{COO} = 1598.7\text{s}$; $\nu_{\text{s}} \text{COO} = 1290.9\text{s}$; $\nu_{\text{HgO}} = 260\text{w}$

E: $\nu_{\text{as}} \text{COO} = 1590.8\text{s}$; $\nu_{\text{s}} \text{COO} = 1300\text{w}$

For the pentahalogeno adducts and complexes (**B**, **C**) we can reasonably suggest the discrete structure reported on Figures 1 - 2.

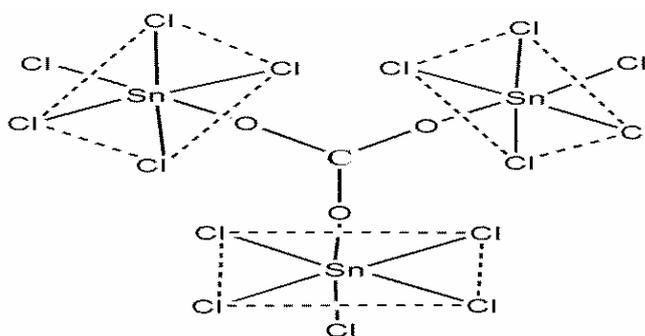


Figure 1. $\text{Et}_4\text{N}_2\text{CO}_3 \cdot 3\text{SnCl}_5\text{Et}_4\text{N}$

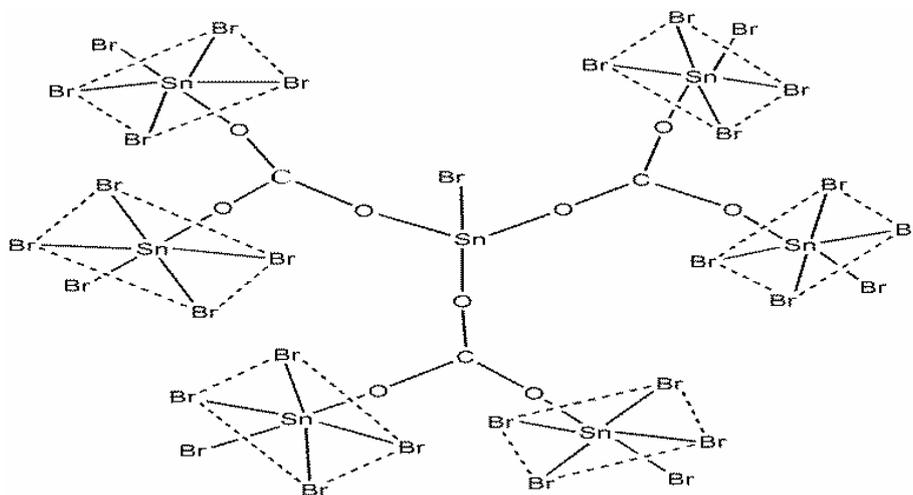


Figure 2. Structure of $\text{Et}_4\text{N} \cdot \text{Sn}(\text{CO}_3)_2\text{BrEt}_4\text{N}_2\text{CO}_3 \cdot 6\text{SnBr}_5\text{Et}_4\text{N}$

The structures proposed for the compounds **D**, **E**, **F**, **H**, **I** and **J** are presented in the Figures 3-8.

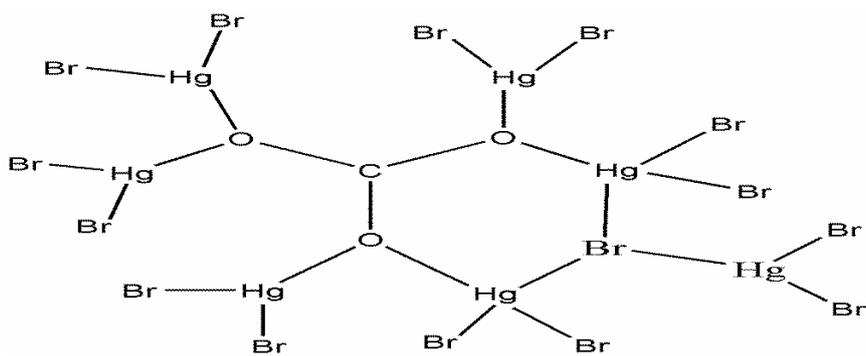


Figure 3. Structure of $Et_4N_2CO_3 \cdot 7HgBr_2 \cdot 2Et_4NBr$

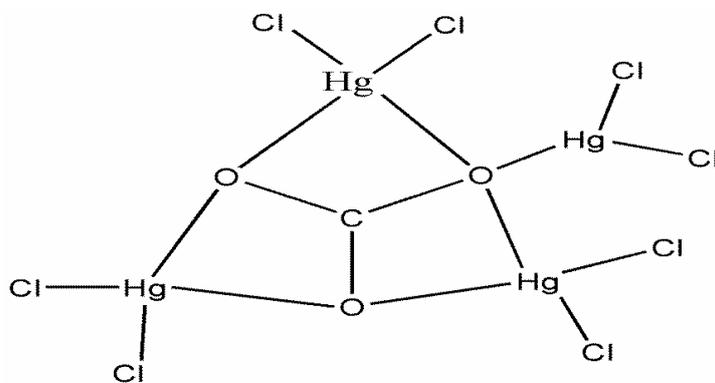


Figure 4. Structure of $Et_4N_2CO_3 \cdot 4HgCl_2$

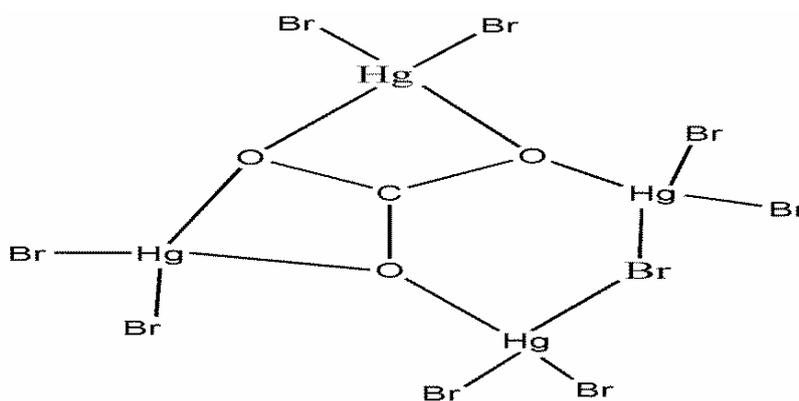


Figure 5. Structure of $Et_4N_2CO_3 \cdot 4HgBr_2 \cdot Et_4NBr$

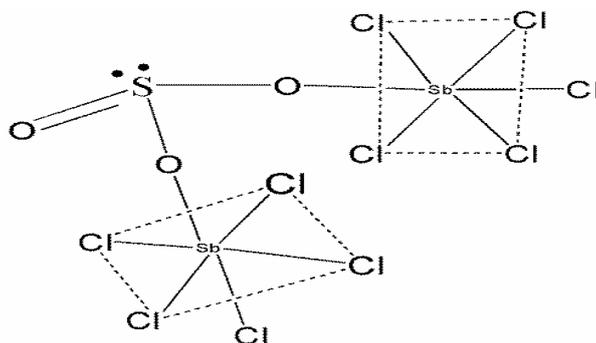


Figure 6. $\text{Me}_4\text{N}_2\text{SO}_3 \cdot 2\text{SbCl}_5 \cdot \text{EtOH}$

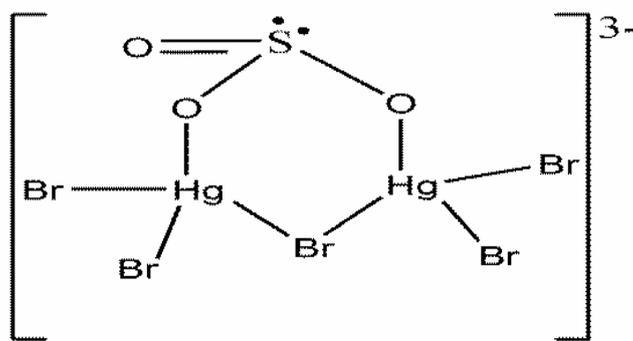


Figure 7. $(\text{Me}_4\text{N})_2\text{SO}_3 \cdot 2\text{HgBr}_2 \cdot \text{Me}_4\text{NBr}$

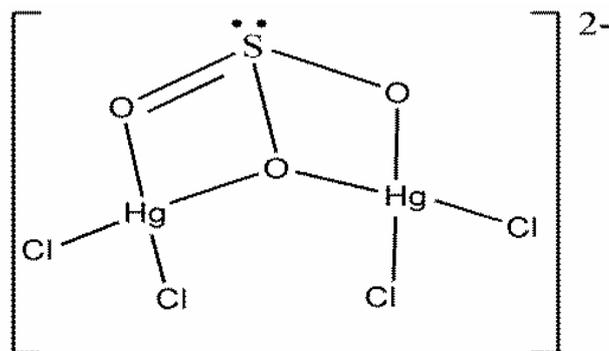


Figure 8. $(\text{Me}_4\text{N})_2\text{SO}_3 \cdot 2\text{HgCl}_2$

CONCLUSION

A C-S bond cleavage occurs when the adverse cation is tetraethylammonium leading to carbonate adducts while with the tetramethylammonium homologue C-S bond cleavage leads to sulfite adducts. The carbonate behaves as a trichelating, a hexadentate or a monochelating and bidentate ligand while the sulfite anion behaves as a bidentate, a bichelating and a monochelating ligand, the environment around the Sn and Sb being octahedral, the Hg centre having a tetrahedral environment.

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