

ATONISHING $[\text{CO}_2\text{SO}_3\text{H}]^-$: CARBONATO AND SULFITO NEW ADDUCTS DERIVING FROM THE INTERACTIONS BETWEEN $\text{R}_4\text{NCO}_2\text{SO}_3\text{H}$ ($\text{R}=\text{Et}, \text{Me}$) AND HgX_2 , SnX_4 ($\text{X}=\text{Cl}, \text{Br}$), SbCl_5

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Abstract: In ethanol, a C-S cleavage occurs in final products on allowing $\text{R}_4\text{NCO}_2\text{SO}_3\text{H}$ – $\text{R} = \text{Me}, \text{Et}$ - to react with HgX_2 , SnX_4 ($\text{M} = \text{Hg}$, $\text{X} = \text{Cl}, \text{Br}$), 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 $(\text{Me}_4\text{N})\text{CO}_2\text{SO}_3\text{H}$ is allowed to react with SbCl_5 , HgX_2 ($\text{X} = \text{Cl}, \text{Br}$), 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 $[4000-200 \text{ cm}^{-1}]$ 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 pentahalo adducts and complexes (**B**, **C**) we can reasonably suggest the discrete structure reported on Figures 1 - 2.

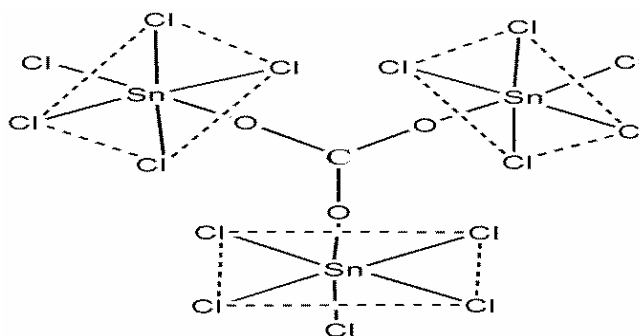


Figure 1. $\text{Et}_4\text{N}_2\text{CO}_3 \cdot 3\text{SnCl}_5\text{Et}_4\text{N}$

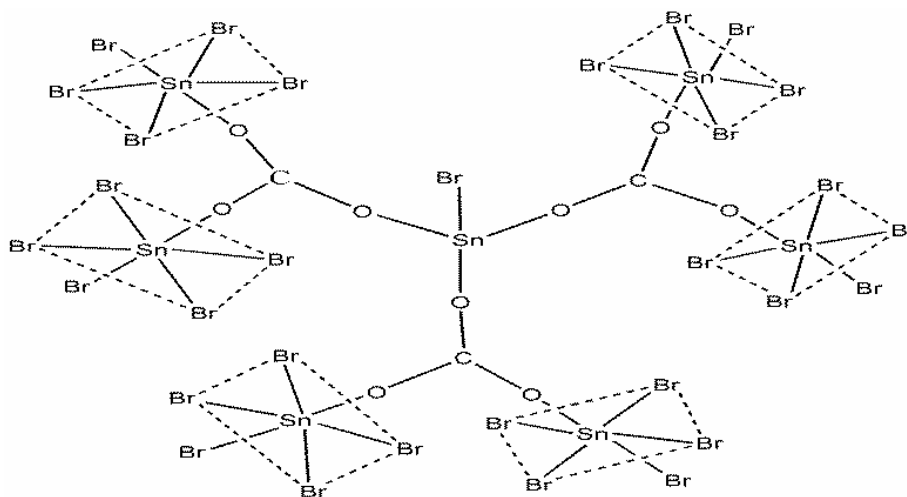


Figure 2. Structure of $\text{Et}_4\text{N} \cdot \text{Sn}(\text{CO}_3)_2\text{Br} \cdot \text{Et}_4\text{N}_2\text{CO}_3 \cdot 6\text{SnBr}_5\text{Et}_4\text{N}$

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

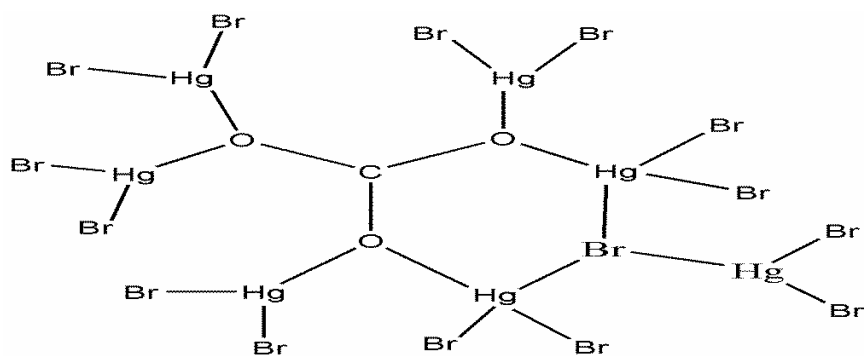


Figure 3. Structure of $\text{Et}_4\text{N}_2\text{CO}_3 \cdot 7\text{HgBr}_2 \cdot 2\text{Et}_4\text{NBr}$

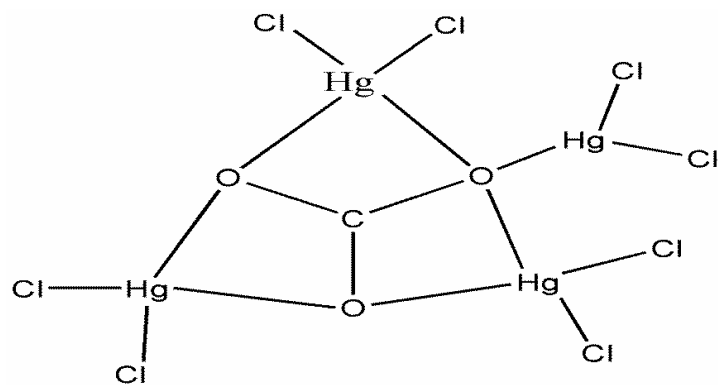


Figure 4. Structure of $\text{Et}_4\text{N}_2\text{CO}_3 \cdot 4\text{HgCl}_2$

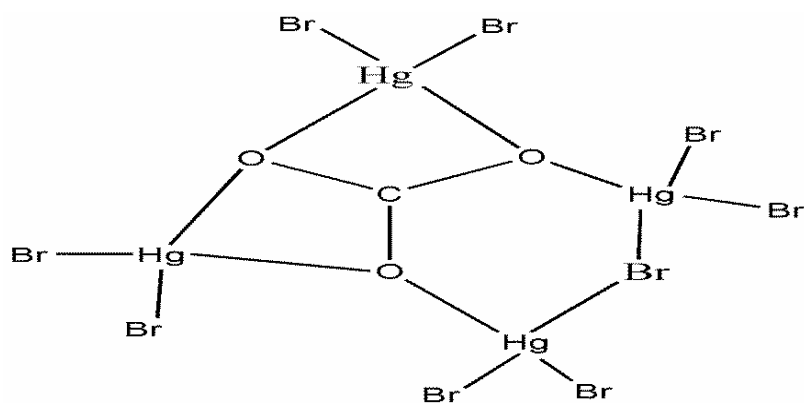


Figure 5. Structure of $\text{Et}_4\text{N}_2\text{CO}_3 \cdot 4\text{HgBr}_2 \cdot \text{Et}_4\text{NBr}$

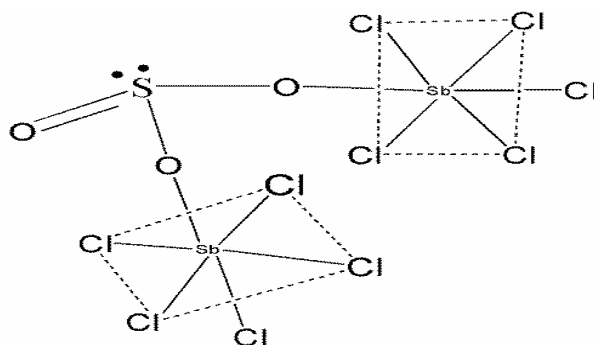


Figure 6. $\text{Me}_4\text{N}_2\text{SO}_3 \cdot 2\text{SbCl}_5 \cdot \text{EtOH}$

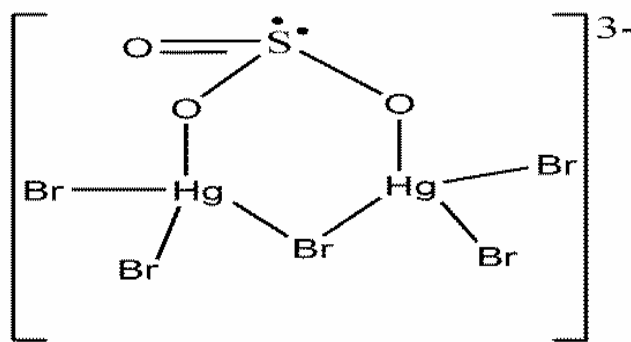


Figure 7. $(\text{Me}_4\text{N})_2\text{SO}_3 \cdot 2\text{HgBr}_2 \cdot \text{Me}_4\text{NBr}$

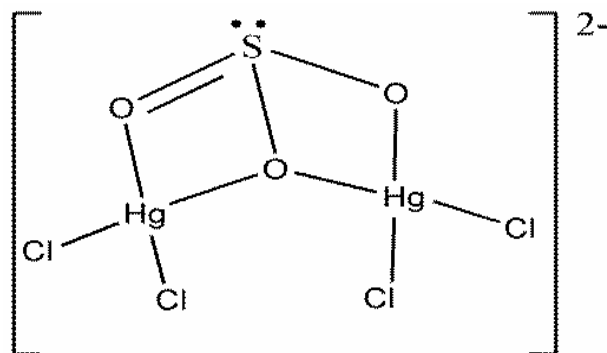


Figure 8. $(\text{Me}_4\text{N})_2\text{SO}_3 \cdot 2\text{HgCl}_2$

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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