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ORIGINAL RESEARCH PAPER

NEW THIO S^{2-} ADDUCTS WITH ANTIMONY (III AND V) HALIDE: SYNTHESIS AND INFRARED STUDY

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Abstract: Five new S^{2-} adducts with Sb^{III} and Sb^{V} halides have been synthesized and studied by infrared. Discrete structures have been suggested, the environment around the antimony being tetrahedral, trigonal bipyramidal or octahedral.

Keywords: *S^{2} - polynuclear adducts, Sb^{III}, Sb^{V}, discrete structures, S^{2-} bridges, sulfuration*

INTRODUCTION

The Lewis acidity of SbX_3 (X = F, Cl, Br, I) have been studied by some authors obtaining adducts such as $SbCl_3 \cdot L$ and $SbCl_3 \cdot 2L$ (L = Me_3PO, Me_2CO, $OPCl_3$) and binuclear adducts such as $2SbCl_3 \cdot C_6H_6$ and $2SbCl_3 \cdot C_{10}H_8$ [1-4]. Adducts with dinuclear complex-anions such as $[Sb_2F_7]$, $[Sb_2F_{11}]^-$ and $[Sb_3F_{16}]^-$ or complexes such as $(C_5H_5NH)(Sb_2Br_9)Br_2$ have been reported [5-8]. Our group had yet reported papers dealing with antimony compounds and initiate here, for understanding the coordinating behaviour of S^{2-}, the study of the interactions between $(Me_4N)_2S$ and SbX_3 (X = Cl, Br, I) which have yielded five new adducts, infrared study of which have been carried out then structures suggested from the data obtained.

MATERIALS AND METHODS

An ethanolic solution of $(Me_4N)_2S$ have been obtained on mixing ethanolic solutions of Na_2S and Me_4NCl. In the refrigerator after two months, all NaCl precipitates leading to a supposed solution of $(Me_4N)_2S$. The weight of NaCl allows to deduce the concentration of $(Me_4N)_2S$.

On mixing:

- 0.3600 g of SbI_3 in hot methanol and 0.2579 g (mmol) of $(Me_4N)_2S$ as ethanolic solution a yellow precipitate is obtained (**A**);
- 0.6053 g of $SbCl_3$ in methanol and 0.2386 g of $(Me_4N)_2S$ in ethanol, an orange precipitate is obtained (**B**);
- 0.6410 g of SbI_3 in hot methanol and 0.1148 g $(Me_4N)_2S$ in ethanol a yellow precipitate is obtained (**C**);
- 0.5370g of SbI_3 in hot methanol and 0.1923g $(Me_4N)_2S$ in ethanol a yellow precipitate is obtained (**D**);
- 0.6720g of $SbBr_3$ in methanol and 0.3346g of $(Me_4N)_2S$ in ethanol, a yellow precipitate is obtained (**E**).

The elemental analyses were performed by either the CNRS "Service Central d'Analyses" Vernaison-France, the laboratory of Microanalyses – University of Padova – Italy or the Microanalyses Centre – University of Bath- UK. The analytical data with the ratio-derivative/Lewis base or halide- and the yields, reported in Table 1, have allowed to suggest the formulae below.

Table 1. *Suggested formulae of synthesized compounds and the elemental analyses*

Compound	Chemical formula	Elemental analysis (%)							
		C		H		N		X[a]	
		calc.	found	calc.	found	calc.	found	calc.	found
A	$(SbI_3S)_{1.5}(Me_4N)_2S \cdot 2H_2O$	16.70	16.77	4.52	4.42	4.87	4.79	49.67	49.40
B	$(SbCl_5)_2(Me_4N)_2S$	15.74	15.94	3.93	4.02	4.32	4.23	32.87	33.59
C	$(SbI_3S)_2(Me_4N)_2S$	8.09	8.14	2.02	1.99	2.22	2.22	60.41	59.97
D	$(SbI_3S)_{1.5}(Me_4N)_2S \cdot 1/4EtOH$	10.27	10.38	2.56	2.66	2.82	2.89	57.49	57.63
E	$(SbBr_3S)_{1.5}(Me_4N)_2S \cdot 1/8EtOH$	12.76	13.04	3.19	3.18	3.60	3.80	46.34	46.73

[a] I for compounds **A**, **C** and **D**; Cl for compound **B**; Br for compound **E**.

The infrared spectra were recorded at the University of Padova (Italy) using a PE 580 or a Bruker FTIR spectrometer, the sample being as Nujol mulls, the windows being CsI or polyethylene. Infrared data are given in cm^{-1} with abbreviations: (vs) very strong (s) strong, (m) medium, (w) weak, (vw) very weak.
All the chemicals were purchased from Aldrich or Merck and used as such.

RESULTS AND DISCUSSION

Let us consider the IR data (in cm^{-1}) of these adducts:
(A): ν SbI_3 = 175-147; δ SbI_3 = 71; ν Sb-S = 264; **(B)**: ν $SbCl_3$ = 350-260; ν $SbCl_3$ = 174-149-70; ν Sb-S = 260; **(D)**: ν SbI_3 = 150-140; δ SbI_3 = 94; ν Sb-S = 496;
(E): ν $SbBr_3$ = 184; δ $SbBr_3$ = 124-128; ν Sb-S = 269.

$[(Me_4N)_2S]_2 \cdot (SbI_3)_3 \cdot 4H_2O$
The compound is the only SbI_3 adduct obtained. The suggested structures are reported on Figure 1 (the water molecules can be considered as lattice ones or coordinated).

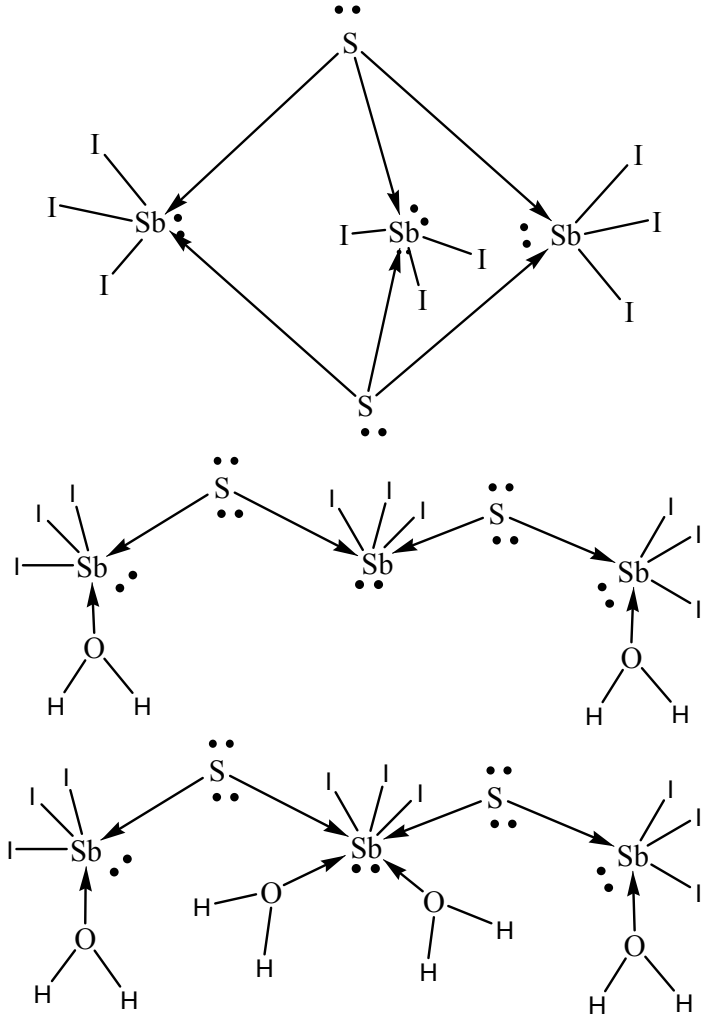

Figure 1. *Suggested structures for $[(Me_4N)_2S]_2 \cdot (SbI_3)_3 \cdot 4H_2O$*

$(SbI_3S)_{1.5}(Me_4N)_2S$; $(SbBr_3S)_{1.5}(Me_4N)_2S$ adducts

In these adduct the trihalide has caught in situ an atom of sulfur leading to SbX_3S. The suggested structures for these adducts are reported on Figure 2 and 3. The adduct $[(Me_4N)_2S]_2\cdot[SbX_3S]_3$ derives from $[(Me_4N)_2S]_2\cdot(SbI_3)_3$ by sulfuration of SbX_3.

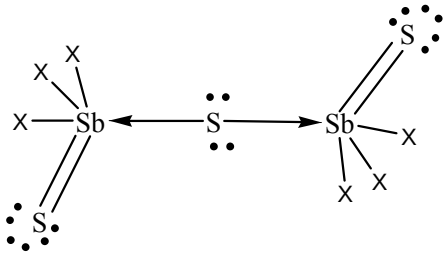

Figure 2. *Suggested structure for $(SbI_3S)_{1.5}(Me_4N)_2S$*

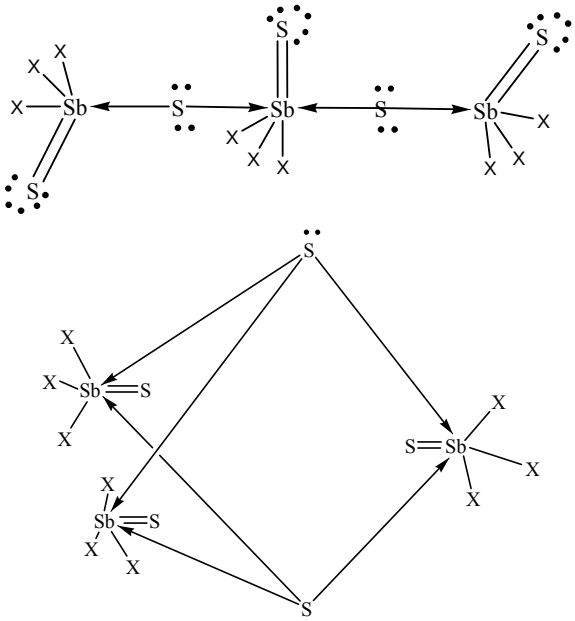

Figure 3. *Suggested structure for $(SbBr_3S)_{1.5}(Me_4N)_2S$*

$(Me_4N)_2S\cdot 2SbCl_5$

While SbI_3 and $SbBr_3$ catch a sulfur atom, $SbCl_3$ oxidizes leading to $SbCl_5$ in the ethanolic media. The suggested structure is reported on Figure 4.

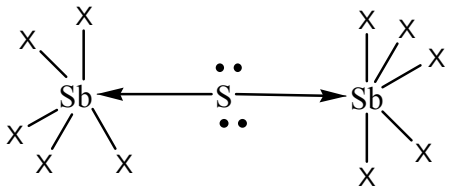

Figure 4. *Proposed structure for $(Me_4N)_2S\cdot 2SbCl_5$*

CONCLUSIONS

In the studied adducts S^{2-} behaves as a bidentate bridging donor or a tridentate one. SbI_3, $SbBr_3$ turn into SbX_3S while $SbCl_3$ gives $SbCl_5$.

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