Two Novel Antimony Chalcogenide Compounds and their Mössbauer Investigation

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Antimony in both oxidation states (+3 and +5) has been shown to form a great variety of inorganic chalcogenide compounds. Simple sulphides and oxides [1], mixed oxide–sulphides [1, 2] and oxide–hydroxides [3, 4] are formed. Besides the monomeric species, the existence of oligomeric compounds containing oxide [5, 6] or sulphide [7–9] bridges has been reported in the literature. Carboxyl bridging may also promote dimerization in these systems [10, 11]. Schmidt *et al.* have shown the simultaneous presence of oxide, hydroxide and carboxylate bridges in a given dimeric antimony compound [12, 13].

The chemistry of chalcogenide compounds containing antimony in both oxidation states in the same molecule has led to some contradictions in the literature. Since antimony(V) can readily be reduced by sulphide, Sb_2S_5 samples were considered to be mixtures of Sb_2S_3 and elemental sulphur [14, 15].

New preparation modes were recently elaborated [16, 17], which led to antimony sulphide containing antimony in both oxidation states.

Our aim was to prepare novel dimeric or oligomeric mixed valency antimony compounds containing oxide, sulphide and hydroxide as ligands. Since Mössbauer spectroscopy has proved to give valuable information on the electronic structure and oxidation state of antimony in its compounds [18–20], primarily this method was used to characterize the new species. For comparison, a series of known analogous compounds was also prepared and studied by Mössbauer spectroscopy.

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Experimental

Preparation Modes

$Sb_2S_2O(OH)_2 \cdot 2H_2O$ **(I)**: a solution of 3.3 g of potassium antimonyl tartrate $[K(SbO)C_4H_4O_6 \cdot 0.5H_2O]$ dissolved in 70 cm^3 of water was added gradually under constant stirring to a solution of 4.8 g of sodium thioantimonate $[Na_3(SbS_4) \cdot 9H_2O]$ in 25 cm^3 of 0.2 M NaOH. The deep orange–red precipitate was collected on a glass filter after 2 h, washed alkali metal ion-free with distilled water, and dried at 105 °C.

$Sb_4S_4O(C_4H_4O_6) \cdot 2H_2O$ **(II)**: a solution of 33 g of potassium antimonyl tartrate in 150 cm^3 of hot distilled water was added under constant stirring to a solution of 25 g of $Na_2S_2O_3 \cdot 5H_2O$ in 50 cm^3 of hot water. A deep-red precipitate was formed, which was collected on a glass filter after 12 h, washed alkali metal ion-free with hot distilled water, and dried at 105 °C.

$Na_3(SbS_4) \cdot 9H_2O$ **(III)** was prepared according to ref. 21, by the interaction of Sb_2S_3 and elemental sulphur in alkaline medium.

$K[Sb(OH)_6] \cdot 2.5H_2O$ **(IV)** was a Riedel–de Häen p.a. product.

Sb_2S_4 **(V)** was prepared according to ref. 18.

Sb_2S_3 **(VI)** was a BDH p.a. product.

Sb_2O_3 **(VII)** was a Riedel–de Häen p.a. product.

$K(SbO)C_4H_4O_6 \cdot 0.5H_2O$ **(VIII)**, potassium antimonyl tartrate, was a Merck p.a. product.

Analytical Control Methods

The antimony content of each sample was determined by bromatometric titration after dissolution of the sample in hydrochloric acid and expulsion of the hydrogen sulphide formed in this reaction with a stream of carbon dioxide. Any antimony(V) content was reduced with hydrazine sulphate. The excess of the latter was decomposed by boiling the solution for 30–40 min.

The sulphide content was determined by gravimetry in the form of $BaSO_4$ precipitate, after oxidation of the sulphide with bromine in alkaline medium.

The thermoanalytical (TG, DTG and DTA) study of the samples, performed with a MOM-Q Derivatograph, led primarily to their water content. The thermal decompositions of most samples (**I, II, V** and **VII**) resulted in Sb_2O_4 as the end-product. The formal molecular weight per antimony atom could be calculated from the total weight losses derived from the thermogravimetric curves. The presence of coordinated hydroxide ligand and the organic ligand (tartrate) content are reflected in the corresponding thermoanalytical curves.

The results of the analytical measurements, together with the calculated values (the latter based

TABLE I. Composition, Molecular Weight and Analysis Data on Investigated Compounds

Compound	Composition	Molecular weight		Antimony (%)		Sulphur (%)		Water (%)		Other components (%)	
		calc.	exp.[a]	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.[a]
										H_2O from OH	
I	$Sb_2S_2O(OH)_2 \cdot 2H_2O$	393.6	398.6	61.86	62.0	16.29	15.8	9.15	9.30	4.57	4.5
										$C_4H_4O_6$	
II	$Sb_4S_4O(C_4H_4O_6) \cdot 2H_2O$	815.4	813.0	59.73	56.7	15.73	15.9	4.40	4.30	18.15	17.6
III	$Na_3(SbS_4) \cdot 9H_2O$	481.0		25.31	25.3	26.66	26.35	33.68	33.0		
IV	$K[Sb(OH)_6] \cdot 2.5H_2O$	307.86		39.55	40.3						
V	Sb_2S_4	371.78	370.8	65.50	65.1	34.50	34.8				
VI	Sb_2S_3	339.7	341.3	71.66	71.3	28.34	28.26				
VII	Sb_2O_3	291.5		83.54	83.8						
VIII	$K[SbO(C_4H_4O_6)] \cdot 0.5H_2O$	333.9		36.35	36.4						

[a]From thermoanalytical measurements.

TABLE II. Mössbauer Parameters of Investigated Compounds

Compound	Composition	Antimony(III)		Antimony(V)		Sb(III):Sb(V) ratio
		isomer shift (mm s^{-1})	line width (mm s^{-1})	isomer shift (mm s^{-1})	line width (mm s^{-1})	
I	$Sb_2S_2O(OH)_2 \cdot 2H_2O$	−13.2	3.5	−0.3	7	0.5:0.5
II	$Sb_4S_4O(C_4H_4O_6) \cdot 2H_2O$ [a]	−13.0	7.0			1:0
III	$Na_3(SbS_4) \cdot 9H_2O$			−5.4	3.0	0:1
IV	$K[Sb(OH)_6] \cdot 2.5H_2O$			−0.3	6.5	0:1
V	Sb_2S_4	−12.8	9.2	0.0	11.8	0.5:0.5
VI	Sb_2S_3	−13.6	7.2			1:0
VII	Sb_2O_3	−11.3	4.0			1:0
VIII	$K[SbO(C_4H_4O_6)] \cdot 0.5H_2O$ [a]	−12.2	6.0			1:0

[a]$C_4H_4O_6$ = tartrate. The error in the Mössbauer measurements is less than ± 0.1 mm s^{-1}.

on the assumed chemical compositions), are presented in Table I.

The Mössbauer spectra were recorded using a $Ca^{121}SnO_3$ source. Both source and absorber were thermostated at liquid nitrogen temperature. The isomer shift values are referred to the source. The results are presented in Table II. Three typical Mössbauer spectra are shown in Fig. 1.

The IR spectrum of I, dried at 180 °C, was recorded with a Specord IR-75 apparatus, in emulsions in hexachlorobutadiene or paraffin oil. The spectra reflected the presence of coordinated OH⁻ ligands in the compound. The OH stretching vibration appeared at 3300 cm^{-1} as a broad band, the in-plane deformation vibration at 1115 cm^{-1}, and the out-of-plane vibration at 620 cm^{-1}.

Results and Discussion

In a series of experiments, we checked the different methods recommended in the literature for the preparation of mixed antimony chalcogenides containing sulphide and oxide in the same compound [1]. A critical examination of these procedures and
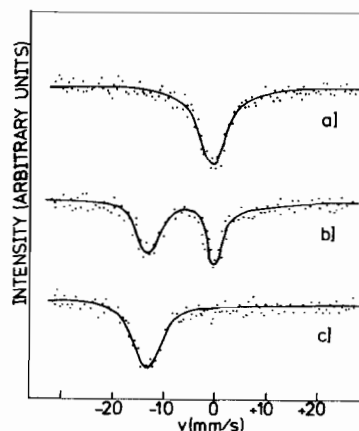

Fig. 1. Mössbauer spectra, recorded at liquid nitrogen temperature, of (a) $K[Sb(OH)_6] \cdot 2.5H_2O$, (b) $Sb_2S_2O(OH)_2 \cdot 2H_2O$, (c) $Sb_4S_4O(C_4H_4O_6) \cdot 2H_2O$.

the analytical control of the products led us to two novel compounds: $Sb_2S_2O(OH)_2 \cdot 2H_2O$ (I) and $Sb_4S_4O(C_4H_4O_6) \cdot 2H_2O$ (II), where $C_4H_4O_6$ is tartrate ion. The compositions of the compounds were established from their antimony, sulphide, water and tartrate contents (Table I), taking into consideration charge and mass balance equations. They were checked through stoichiometric calculations based on the thermal decomposition curves. The results of the analytical measurements are presented in Table I, together with the corresponding calculated values computed on the basis of the suggested molecular compositions. The good agreement between calculated and experimental values confirms the suggested compositions.

Mössbauer spectroscopy was used to study the oxidation states of antimony in the new compounds. It was found (Fig. 1) that compound I contains one antimony(III) and one antimony(V) central atom, whereas II is an antimony(III) compound.

For comparison, Mössbauer studies were performed on a series of antimony compounds containing the moieties of the two novel compounds (Table II). Only two of the compounds ($Na_3[SbS_4] \cdot 9H_2O$ and $K[Sb(OH)_6] \cdot 2.5H_2O$) are stoichiometric antimony(V) species. Both contain antimony(V) in complex anionic form. The entire preparation procedure of the former compound, similarly to that of I, could be performed in alkaline medium. This is why sulphide did not reduce antimony(V) during the preparation processes. The preparation of antimony(V) compounds containing only oxygen donor atoms did not cause difficulties.

Apart from $Sb_2S_2O(OH)_2 \cdot 2H_2O$, only Sb_2S_4 contained antimony in both oxidation states. In both cases, the antimony(III) isomer shifts (*IS*) indicated a lower electron density on the antimony nucleus in the mixed valence compounds than in Sb_2S_3, but a higher one than in Sb_2O_3. This seems to indicate some Sb(III)—Sb(V) interaction in these species. The lack of a suitable reference substance made a similar comparison impossible for the antimony(V) *IS* values. Stoichiometric antimony(V) sulphide has not been prepared so far. The antimony(V) *IS* values in Table II indicate a significantly higher electron density on the antimony(V) nucleus in Na_3SbS_4 than in the other investigated compounds, which display *IS* values near to that for Sb_2O_5 (0.0 mm s^{-1}). A comparison of the antimony(III) *IS* values for Sb_2S_3, Sb_2O_3 and $K[SbO(C_4H_4O_6)] \cdot 0.5H_2O$ reveals that antimony(III) compounds containing oxygen donor atoms exhibit lower electron densities on the antimony(III) nucleus than those of the corresponding sulphur compounds. This is due to the higher antimony—donor atom interaction in the Sb—O than in the Sb—S bonds, resulting in a higher electron density in the shielding orbitals of antimony(III) in the oxides than in the corresponding

sulphides. The presence of tartrate ligand increases the electron density on the antimony(III) nucleus compared to that in Sb_2O_3. This seems to indicate a weaker Sb—O interaction with tartrate oxygens than with oxide ones.

The antimony(III) *IS* value for our novel compound $Sb_4S_4O(C_4H_4O_6) \cdot 2H_2O$ (II) lies between those for Sb_2S_3 and $K[SbO(C_4H_4O_6)] \cdot 0.5H_2O$, indicating that antimony is bound to all three donors, sulphide, oxide and tartrate, in this compound.

The relatively high line widths (e.g. in Sb_2S_4) indicate unresolved large quadrupole splittings due to the non-symmetrical charge distribution around the atomic core of the antimony, underlining the Sb(V)—Sb(III) interaction in V; the corresponding interaction was much less pronounced in I.

Acknowledgement

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