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THERMOANALYTICAL STUDIES OF COMPOUNDS OF GENERAL FORMULA $Cs_3[Sb_xBi_{2-x}Cl_9]$

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ABSTRACT

Thermoanalytical studies have been carried out on crystalline complex salts of the general formula $Cs_3[Sb_xBi_{2-x}Cl_9]$ formed between antimony(III) chloride, bismuth(III) chloride and caesium chloride in hydrochloric acid solutions. Some conclusions concerning the thermal stability of these compounds have been drawn. From chemical and X-ray analyses of their solid decomposition products schematic representations of the thermal decomposition reactions were established.

INTRODUCTION

Foreign atoms introduced into the crystal lattice exert a considerable influence on a number of physical and chemical properties of the crystals. This influence is relatively simple when the foreign atoms have the same valence as the mother lattice atoms or when they form chemical compounds with the same composition and structure as the host crystals. Most of the chemical and physical properties change monotonically as the composition changes. It is interesting to study if and how the thermal stability and the course of the thermal decomposition reaction changes when one of its atoms is replaced by another having the same valency, the stoichiometric composition remaining the same.

The crystalline compounds $Cs_3[Sb_2Cl_9]$ and $Cs_3[Bi_2Cl_9]$ as well as a number of mixed compounds of the general formula $Cs_3[Sb_xBi_{2-x}Cl_9]$ were chosen for investigation. Caesium nonachlorodiantimonate and caesium nonachlorodibismuthate are isostructural [1,2]. Thermal analysis of these complex salts was carried out and thermal stability and schemes of the thermal decomposition were established [3,4].

EXPERIMENTAL

Apparatus

Thermal analyses of the compounds under study were carried out in air using a MOM derivatograph (Budapest) type OD-102, over the temperature range 20–1000 °C at a heating rate of 10 °C min^{-1}. The sensitivity of the galvanometers for the DTA and DTG was 1/5; the TG sensitivity was 100 mg. The mass of sample taken was 100 mg and α-Al_2O_3 was used as a reference material. Thermal decomposition of the compounds was effected in a temperature-programmed silite furnace, VEB Electro-Industrieofenbau Römbild (G.D.R.) type KO 14.

The X-ray diffraction patterns of the parent compounds and mixed crystals were obtained using a DRON-1 diffractometer with nickel-filtered Cu K_α radiation. Diffracted rays were recorded over the range 2θ, angles 2–60 °.

Preparation and chemical analysis

The compounds of the general formula $Cs_3[Sb_xBi_{2-x}Cl_9]$ were prepared by dissolving the appropriate quantity of Sb_2O_3 and $(BiO)_2CO_3$ in an excess of hot 2 M hydrochloric acid, adding a stoichiometric quantity of CsCl in 2 M HCl and slowly evaporating the solution at room temperature. After several minutes a fine crystalline precipitate separated from the solution. This was filtered off, rinsed with diethyl ether and dried in air. The crystals were stored in polyethylene vials.

For successive crystallisations such quantities of Sb_2O_3 and $(BiO)_2CO_3$ were taken so that the molar proportions Sb : Bi were 2 : 0, 1.75 : 0.25, 1.5 : 0.5, 1 : 1, 0.5 : 1.5, 0.25 : 1.75 and 0 : 2. The compounds obtained were analysed by standard analytical methods. The molar proportions of antimony to bismuth in the resulting compounds were slightly different from those calculated from the quantity of Sb_2O_3 and $(BiO)_2CO_3$ used for the crystallisation. The theoretical formulae of the compounds calculated from the quantities of Sb and Bi taken for the crystallisation and those obtained from the chemical analysis as well as the colours of the compounds under study are presented in Table 1.

The compounds $Cs_3[Sb_xBi_{2-x}Cl_9]$ were also prepared by the method of slow diffusion through a semipermeable membrane of caesium chloride into the solutions Sb_2O_3 and $(BiO)_2CO_3$ in 2 M hydrochloric acid [5]. The well-formed crystals, coloured as indicated in Table 1, were analysed for their antimony and bismuth contents. The results of the analyses indicate that the real formulae of the compounds are then slightly closer to the theoretical ones than were the formulae of the compounds prepared by the method described previously. For further investigations the compounds obtained by slow evaporation of the appropriate solutions were used.

Some of the crystalline compounds of the general formula $Cs_3[M_2X_9]$ (where M = Sb, Bi; X = Cl, Br, I) have found application for the determination of caesium [6–9], e.g., the sparingly soluble in concentrated CH_3COOH complex $Cs_3[SbCl_6]$ is widely applied for the detection and determination of caesium in the presence of potassium and rubidium [10]. In the present work

TABLE 1

Theoretical and real formulae of compounds

Theoretical formula	Real formula	Colour of compound
$Cs_3[Sb_2Cl_9]$	$Cs_3[Sb_2Cl_9]$	colourless
$Cs_3[Sb_{1.75}Bi_{0.25}Cl_9]$	$Cs_3[Sb_{1.66}Bi_{0.34}Cl_9]$	intense yellow
$Cs_3[Sb_{1.5}Bi_{0.5}Cl_9]$	$Cs_3[Sb_{1.34}Bi_{0.66}Cl_9]$	intense yellow
$Cs_3[Sb_{1.0}Bi_{1.0}Cl_9]$	$Cs_3[Sb_{0.89}Bi_{1.11}Cl_9]$	yellow
$Cs_3[Sb_{0.5}Bi_{1.5}Cl_9]$	$Cs_3[Sb_{0.56}Bi_{1.44}Cl_9]$	yellow
$Cs_3[Sb_{0.25}Bi_{1.75}Cl_9]$	$Cs_3[Sb_{0.38}Bi_{1.62}Cl_9]$	pale yellow
$Cs_3[Bi_2Cl_9]$	$Cs_3[Bi_2Cl_9]$	colourless

the solubility in acetic acid (80%) of some of the complexes under study was determined. The average results are presented in Table 2.

Caesium nonachlorodibismuthate is more sparingly soluble than nonachlorodiantimonate. The substitution of some of the Bi atoms by Sb atoms diminishes the solubility slightly. A more detailed study concerning solubility and analytical application of the compounds under study is soon to be undertaken.

X-ray diffraction studies

$Cs_3[Sb_2Cl_9]$ and $Cs_3[Bi_2Cl_9]$ are isostructural [1,2]. The X-ray diffraction patterns of all the compounds under study (the X-ray diffraction pattern of $Cs_3[Sb_{1.81}Bi_{0.19}Cl_9]$ was also obtained) are almost identical. The results of X-ray analysis indicate that the identity period slightly decreases when a small quantity of bismuth atoms is introduced into $Cs_3[Sb_2Cl_9]$ and then gradually increases as the molar ratio Bi:Sb increases. As an example, the values of the angles at 2θ, d/n and the intensities of the three highest peaks chosen for the average 2θ angles are presented in Table 3. When in $Cs_3[Sb_2Cl_9]$ antimony atoms are successively replaced by bismuth atoms, the distinct broadening of peaks is not observed. These results, as well as the

TABLE 2

Solubility of some compounds under study in CH_3COOH (80%)

Compound	Solubility (g l^{-1})
$Cs_3[Bi_2Cl_9]$	0.055
$Cs_3[Sb_{0.89}Bi_{1.11}Cl_9]$	0.051
$Cs_3[Sb_{1.34}Bi_{0.66}Cl_9]$	0.099
$Cs_3[Sb_2Cl_9]$	0.234

TABLE 3

X-ray diffraction data

Formula of compound	Peak A			Peak B			Peak C		
	2θ	d/n	I	2θ	d/n	I	2θ	d/n	I
$Cs_3[Sb_2Cl_9]$	33.78	2.653	120	41.38	2.180	47	59.81	1.545	136
$Cs_3[Sb_{1.81}Bi_{0.19}Cl_9]$	33.88	2.646	132	41.60	2.189	48	60.00	1.541	61
$Cs_3[Sb_{1.66}Bi_{0.34}Cl_9]$	33.80	2.652	135	41.55	2.172	55	59.90	1.543	61
$Cs_3[Sb_{1.34}Bi_{0.66}Cl_9]$	33.65	2.664	196	41.50	2.174	56	–	–	–
$Cs_3[Sb_{0.89}Bi_{1.11}Cl_9]$	33.59	2.669	137	41.37	2.181	72	59.80	1.545	103
$Cs_3[Sb_{0.38}Bi_{1.62}Cl_9]$	33.37	2.686	123	41.18	2.190	119	59.66	1.549	109
$Cs_3[Bi_2Cl_9]$	33.35	2.687	140	41.15	2.192	185	59.55	1.552	130

observation that during the crystallisation processes homogeneous, well-formed crystals are obtained, indicates that in $Cs_3[Sb_2Cl_9]$, antimony(III) atoms can be replaced by bismuth(III) atoms in any proportions without a crystal structure change and without observable deformation of the crystal lattice.

TABLE 4

Thermal decomposition data

	Formula of compound	Temp. range of decomposition (°C)	DTA peak temp. [a] (°C)	DTG peak temp. (°C)	Mass loss from TG (%)
I	$Cs_3[Sb_2Cl_9]$ I step	320–445	447	445	20,5
	$Cs_3[Sb_2Cl_9]$ II step	445–535	527 642	520	20,5
II	$Cs_3[Sb_{1.66}Bi_{0.34}Cl_9]$ I step	310–435	420	410	20,0
	$Cs_3[Sb_{1.66}Bi_{0.34}Cl_9]$ II step	435–560	560	542	13,0
III	$Cs_3[Sb_{1.34}Bi_{0.66}Cl_9]$ I step	320–480	470	460	19,5
	$Cs_3[Sb_{1.34}Bi_{0.66}Cl_9]$ II step	480–585	575 670	570	3,5
IV	$Cs_3[Sb_{0.89}Bi_{1.11}Cl_9]$	385–535	520 670	505	19,0
V	$Cs_3[Sb_{0.56}Bi_{1.44}Cl_9]$	410–595	590 685	585	16,0
VI	$Cs_3[Sb_{0.38}Bi_{1.62}Cl_9]$	420–615	600 683	593	16,0
VII	$Cs_3[Bi_2Cl_9]$	460–620	612 695	607	13,0

[a] All DTA peaks are endothermic.

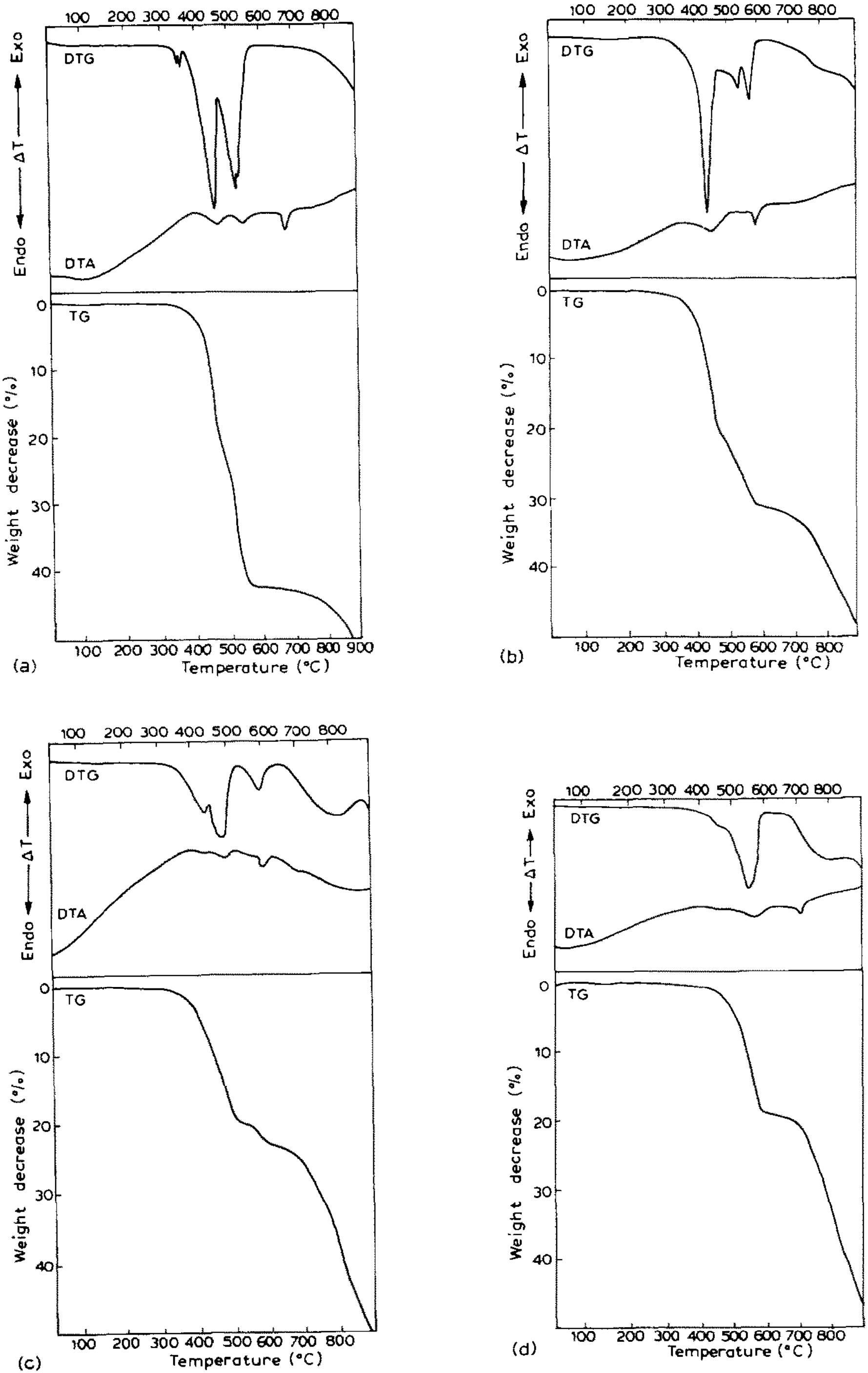

Fig. 1. Thermal analysis curves of (a) $Cs_3[Sb_2Cl_9]$, (b) $Cs_3[Sb_{1.66}Bi_{0.34}Cl_9]$, (c) $Cs_3[Sb_{1.34}Bi_{0.66}Cl_9]$ and (d) $Cs_3[Sb_{0.89}Bi_{1.11}Cl_9]$.

Thermoanalytical studies

Thermoanalytical curves of compounds I–IV are shown in Fig. 1. The curves of the other compounds under study are similar to that of $Cs_3[Sb_{0.89}Bi_{1.11}Cl_9]$ (IV). The characteristic peak temperatures as well as mass losses at particular stages of the thermal decomposition are collected in Table 4.

TG curves of compounds I–III show a two-stage decomposition reaction. The decomposition begins at similar temperatures. The mass loss of the first step of the decomposition diminishes slightly and the second stage of the reaction diminishes in the following order: $Cs_3[Sb_2Cl_9] > Cs_3[Sb_{1.66}Bi_{0.34}Cl_9] > Cs_3[Sb_{1.34}Bi_{0.66}Cl_9]$. The thermoanalytical curves of the other compounds are similar to that of $Cs_3[Bi_2Cl_9]$. Only one stage of their decomposition process is visible. The temperatures at which the decomposition begins are distinctly higher than those of the former compounds. The mass loss diminishes in the order $Cs_3[Sb_{0.89}Bi_{1.11}Cl_9] > Cs_3[Sb_{0.56}Bi_{1.44}Cl_9] = Cs_3[Sb_{0.38}Bi_{1.62}Cl_9] > Cs_3[Bi_2Cl_9]$. The endothermic peak connected with the melting of CsCl (642 ° C) is visible only on the DTA curve of $Cs_3[Sb_2Cl_9]$. The peak on the DTA curve of $Cs_3[Bi_2Cl_9]$ at the temperature 595 ° C is connected with incongruent melting of $Cs_3[Bi_2Cl_9]$ and the peak at 675 ° C indicates the presence of $Cs_3[BiCl_6]$ [11].

The effect of mass of the sample of $Cs_3[Sb_2Cl_9]$ on characteristic peak temperatures was also studied. The thermoanalytical curves were made using 20, 100 and 300 mg of sample and experimental conditions as described above. The DTA sensitivity for 300 mg sample was 1/10. Peaks on the DTA curve of the 20 mg sample were slight and indistinct and therefore characteristic peak temperatures could only be defined approximately. The results are collected in Table 5. It is seen from Table 4 that with increasing mass of sample, characteristic DTA and DTG peak temperatures are distinctly higher.

Investigation of the products of thermal decomposition reactions

In order to follow the course of thermal decomposition reactions of the compounds under study, the samples of ca. 100 mg were heated in a silite

TABLE 5

Characteristic DTA and DTG peak temperatures of $Cs_3[Sb_2Cl_9]$

Sample mass (mg)	DTA peak temp. (° C)	DTG peak temp. (° C)
20	400, 440, 640 [a]	380, 440
100	440, 517, 642 [a]	430, 497
300	470, 533, 637 [a]	462, 525

[a] Melting temperature of CsCl.

TABLE 6

Results of analyses of thermal decomposition products (a, from analysis; b, calculated from equation)

Compound	Sb		Bi		Cs		Cl	
	a	b	a	b	a	b	a	b
I	0.6	–	–	–	77.2	78.9	19.8	21.1
II	1.7	1.9	11.1	12.2	63.2	62.8	22.5	24.0
III	2.2	3.0	17.9	18.2	52.2	52.6	24.4	26.0
IV	0.7	–	25.6	27.1	45.6	46.6	24.9	26.1
V	0.6	4.3	26.5	28.2	44.4	43.3	21.3	22.8
VI	–	–	26.5	29.9	44.0	43.2	20.8	26.9
VII	–	–	31.6	32.6	46.8	40.1	22.4 23.0	27.2

furnace at a rate of 10 °C min^{-1} up to appropriate temperature determined from the thermal analysis curves. For further investigations, the products of decomposition which showed mass losses identical to or similar to those evaluated from the TG-curves were used. The products of thermal decomposition were dissolved in hydrochloric or nitric acid and, when necessary, the solution was heated. The antimony, bismuth and chlorine were determined by standard chemical methods and caesium by means of flame photometry. The results of the chemical analyses are presented in Table 6.

According to the thermal and chemical analyses, the decomposition reactions of the compounds under study heated up to the temperatures at which the appropriate decomposition step appears to be complete and can be supposed to be in agreement with the following schemes

$$\mathrm{Cs_3[Sb_2Cl_9] = 3CsCl + SbCl_3} \tag{1}$$

$$\mathrm{Cs_3[Sb_{1.66}Bi_{0.34}Cl_9] = Cs_3[Sb_{0.1}Bi_{0.34}Cl_{4.32}] + 1.56SbCl_3} \tag{2}$$

$$\mathrm{Cs_3[Sb_{1.34}Bi_{0.66}Cl_9] = Cs_3[Sb_{0.19}Bi_{0.66}Cl_{5.55}] + 1.15SbCl_3} \tag{3}$$

$$\mathrm{Cs_3[Sb_{0.89}Bi_{1.11}Cl_9] = Cs_3[Bi_{1.11}Cl_{6.33}] + 0.89SbCl_3} \tag{4}$$

$$\mathrm{Cs_3[Sb_{0.56}Bi_{1.44}Cl_9] = Cs_3[Bi_{1.24}Cl_{6.72}] + 0.56SbCl_3 + 0.2BiCl_3} \tag{5}$$

$$\mathrm{Cs_3[Sb_{0.38}Bi_{1.62}Cl_9] = Cs_3[Bi_{1.32}Cl_{6.96}] + 0.38SbCl_3 + 0.3BiCl_3} \tag{6}$$

$$\mathrm{Cs_3[Bi_2Cl_9] = Cs_3[Bi_{1.55}Cl_{7.65}] + 0.45BiCl_3} \tag{7}$$

The loss of mass above these temperatures is probably caused by a further gradual decomposition connected with the sublimation of the decomposition products.

CONCLUSIONS

The sparingly soluble compounds of the general formula $\mathrm{Cs_3[Sb_xBi_{2-x}Cl_9]}$ can be easily prepared by crystallisation at room temperature from the solution Sb_2O_3, $(BiO)_2CO_3$ and Cs_2CO_3 in hot 2 M HCl, or by the method of slow diffusion through a semipermeable membrane of caesium chloride to the acid solution containing $SbCl_3$ and $BiCl_3$. The molar ratios of antimony to bismuth in the obtained complex salts are slightly different from those used for the crystallisation (Table 1). The atom with the smaller molar content appears in the prepared compounds in larger molar quantity than that used for the crystallisation. Bismuth atoms are more easily bound into the crystal lattice of the compounds under study than antimony atoms. The solubility of some compounds in acetic acid (80%) was determined. Those with a large bismuth content have smaller solubility than the other compounds (Table 2).

$Cs_3[Sb_2Cl_9]$ and $Cs_3[Bi_2Cl_9]$ are isostructural. According to the results of X-ray analyses, antimony atoms in caesium nonachlorodiantimonate can be replaced by any quantity of bismuth atoms without changing the structure. After introducing a small quantity of bismuth atoms to $Cs_3[Sb_2Cl_9]$, the identity period diminishes significantly and subsequently increases with increasing molar proportions of Bi:Sb.

In the thermal decomposition of $Cs_3[Sb_xBi_{2-x}Cl_9]$, gaseous $SbCl_3$ and $BiCl_3$ are liberated. The intermediate and final solid products of the decomposition reactions constitute a crystalline phase. All thermal effects on the DTA curves are endothermic. The peak corresponding to the melting of CsCl is only present on the DTA of $Cs_3[Sb_2Cl_9]$. Concise thermoanalytical data of the compounds under study are presented in Table 4. Compounds with large molar proportions of $SbCl_3$:$BiCl_3$ (I–III) decompose in two steps, whilst during the decomposition of the other compounds, a one-stage process is observed. The complex salts IV–VII are distinctly more thermally stable than the compounds I–III whose thermal stabilities differ slightly. The thermal stability defined by the temperature of the first endothermic peak on the DTA curve corresponding to the first decomposition step decreases in the order: $VII > VI > V \gg IV \gg III > I > II$. The results of the thermal and chemical analyses of the reaction products (Table 6) are compatible with the decomposition reaction schemes (1)–(7).

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