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A STUDY OF THERMAL DECOMPOSITION OF COMPLEX COMPOUNDS OF $Cs_3[Sb_{2-x}Pb_xCl_{9-x}]$ TYPE

B. PTASZYŃSKI

Institute of General Chemistry, Polytechnical University, 90-924 Łódź (Poland)

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ABSTRACT

Thermoanalytical studies have been carried out on crystalline complex salts of the type $Cs_3[Sb_{2-x}Pb_xCl_{9-x}]$ formed between antimony(III) chloride, lead(II) 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

The introduction of even small amounts of foreign atoms into a chemical compound often causes radical changes in a number of its physical and chemical properties. To date no systematic studies have been carried out to determine the influence of foreign atoms introduced into the crystal lattice of complex compounds on the thermal stability of these compounds. The only work on the subject that has been published [1] refers to thermoanalytical studies of the crystalline complex salts $Cs_3[Sb_2Cl_9]$ and $Cs_3[Bi_2Cl_9]$ and a number of mixed complexes of the general formula $Cs_3[Sb_xBi_{2-x}Cl_9]$ which are formed by replacing some Sb(III) atoms in $Cs_3[Sb_2Cl_9]$ by different amounts of bismuth(III). Caesium nonachlorodiantimonate(III) and nonachlorodibismuthate(III) are isostructural [1,2]. It has been shown that any number of Sb(III) atoms in $Cs_3[Sb_2Cl_9]$ can be replaced by Bi(III) atoms without any resulting change in the crystalline structure of the compound. However, the identity period grows slightly as the molar ratio Bi : Sb increases. The thermal decomposition of compounds with a high antimony content takes a course similar to that of $Cs_3[Sb_2Cl_9]$ the decomposition of which involves two stages while in other compounds only one stage is visible and able to be characterized. Complex salts of high Bi : Sb molar ratio are much more thermally stable than are those with low bismuth content and their stability, with only one exception, increases as more Sb atoms in $Cs_3[Sb_2Cl_9]$ are replaced by Bi.

In the present study we investigated a number of complex compounds which were obtained by introducing different amounts of lead(II) into the crystalline structure of $Cs_3[Sb_2Cl_9]$. It was expected that the replacement of some of the central Sb atoms in the lattice by atoms of an element with a different ionic radius and different oxidation state would cause more distinct changes in the thermal stability and the thermal decomposition reaction than when antimony atoms in $Cs_3[Sb_2Cl_9]$ were replaced by bismuth atoms with the same oxidation state.

The study of the thermal stability of $Cs_3[Sb_2Cl_9]$ and the determination of its thermal decomposition mechanism has been reported previously [3–5]. Halogen complexes of antimony(III) and bismuth(III) are compounds of considerable significance in the analytical chemistry of caesium; they are used for its determination and separation.

EXPERIMENTAL

Apparatus

Thermal investigation of the compounds under study was carried out in air using a type OD-102 MOM Derivatograph (Budapest) over the temperature range 20–1000 °C at a heating rate 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 the samples taken was 100 mg. α-Al_2O_3 was used as a reference material.

In order to follow the course of the thermal decomposition, the samples of ca. 100 mg were heated in a VEB Electro-Industrieofenbau Römbild (G.D.R.) type KO 14 furnace at a rate of 10 °C min^{-1} to the appropriate temperature determined from the thermal analysis curves.

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

Preparation and chemical analysis of the compounds

Compounds of the general formula $Cs_3[Sb_{2-x}Pb_xCl_{9-x}]$ were prepared by dissolving the appropriate quantity of Sb_2O_3 and $PbCO_3$ in an excess of hot hydrochloric acid (2 M) and slowly adding a stoichiometric quantity of CsCl in HCl (2 M). The fine precipitates were dissolved immediately in a hot mother liquor and recrystallized by slowly cooling the solution. The well-formed crystals were filtered off and dried in air at ambient temperature. To prevent the possible precipitation of caesium chloroplumbate(II), a little less caesium carbonate was used in the syntheses than is necessary for a stoichiometric composition. In successive crystallizations of the examined

TABLE 1

Results of the analyses and the theoretical and real formulae of the compounds under study

No.	Theoretical formula	Results of analyses (%)			Real formula	Colour
		Sb	Pb	Cl		
I	$Cs_3[Sb_2Cl_9]$	25.0	–	33.2	$Cs_3[Sb_2Cl_9]$	Colourless
II	$Cs_3[Sb_{1.78}Pb_{0.22}Cl_{8.78}]$	23.0	4.3	31.0	$Cs_3[Sb_{1.80}Pb_{0.25}Cl_{8.90}]$	Pale yellow
III	$Cs_3[Sb_{1.60}Pb_{0.40}Cl_{8.60}]$	20.2	10.2	31.05	$Cs_3[Sb_{1.72}Pb_{0.51}Cl_{9.06}]$	Pale yellow
IV	$Cs_3[Sb_{1.0}Pb_{1.0}Cl_{8.0}]$	12.65	23.3	27.65	$Cs_3[Sb_{1.12}Pb_{1.21}Cl_{8.42}]$	Yellow
V	$Cs_3[Sb_{0.40}Pb_{1.60}Cl_{7.40}]$	3.0	52.5	24.45	$Cs_3[Sb_{0.53}Pb_{5.31}Cl_{15.06}]$	Colourless

series of complexes the amounts of Sb_2O_3 and $PbCO_3$ correspond to the following Sb : Pb molar ratios: 8 : 1, 4 : 1, 1 : 1 and 1 : 4. These proportions correspond to the formulae presented in the first column of Table 1.

The real chemical composition of the complex salts obtained were determined by dissolving the complex in concentrated H_2SO_4 at high temperature, following the procedure used for bearing alloy analysis [6]. Antimony was determined bromometrically with methyl orange as indicator. Lead was precipitated in the form of $PbSO_4$, the precipitate was dissolved in ammonium acetate and precipitated again as $PbCrO_4$. Chloride was determined using Volhard's method. Caesium content was calculated from the difference of the percentages obtained for other constituents. The results of the analyses, the real formulae thereby determined and the colours of the compounds are presented in Table 1.

Considering the available structural data [1,2] and the chemical examinations and X-ray studies presented below, the formulae of the complexes were written in the form: $Cs_3[Sb_xPb_yCl_z]$.

The chloride content of the compounds was slightly different from stoichiometric in relation to the other elements (Table 1). This may be due to analytical error and/or to the non-stoichiometric composition of complex salts of this type.

X-ray diffraction studies

The crystalline structure of $Cs_3[Sb_2Cl_9]$ is known [1,2]. Within this structure the $Sb_2Cl_9^{3-}$ ion comprises a separate structural unit. The *d/n* values and intensities (*I*) of the chloroantimonates(III) under study are presented in Table 2. These compounds (with the exception of $Cs_3[Sb_{0.53}Pb_{5.31}Cl_{15.06}]$) have similar diffraction patterns, which allows the supposition that the crystalline structure of $Cs_3[Sb_2Cl_9]$ within them is retained. Slight differences in the diffraction pattern may be caused by deformations of the $Cs_3[Sb_2Cl_9]$ mother compound lattice which result from

TABLE 2

X-ray diffraction data

$Cs_3[Sb_2Cl_9]$			$Cs_3[Sb_{1.80}Pb_{0.25}Cl_{8.90}$			$Cs_3[Sb_{1.72}Pb_{0.51}Cl_{9.06}$			$Cs_3[Sb_{1.12}Pb_{1.21}Cl_{8.42}$			$Cs_3[Sb_{0.53}Pb_{5.31}Cl_{15.0}$		
2θ	d/n	I	2θ	d/n	I	2θ	d/n	I	2θ	d/n	I	2θ	d/n	I
9.5	9.30	Weak	9.4	9.40	25	9.4	9.90	19	9.3	9.5	Weak	10.7	8.26	17
11.7	7.40	Weak	11.9	7.43	16	11.9	7.43	50	–			12.0	7.37	100
												13.7	6.46	4
19.1	4.64	20	19.0	4.66	27	18.9	4.69	35	19.0	4.66	Weak	19.5	4.55	3
19.7	4.50	27	–			–			–			21.8	4.07	18
									22.3	3.98	100			
23.5	3.78	58	23.3	3.81	100	23.3	3.81	23	23.3	3.81	53	24.2	3.67	100
						24.0		52				25.0	3.56	9
28.8	3.10	100	28.7	3.11	84	28.7	3.11	100	28.7	3.11	26	28.8	3.10	2
												30.5	2.93	10
30.9	2.89	28	–						32.0	2.79	29	32.8	2.73	3
33.5	2.67	48	33.3	2.69	41	33.2	2.69	10	33.3	2.60	26	36.6	2.45	100
36.6	2.45	10	–			36.4	2.46	14	–			39.3	2.29	5
									39.4	2.25	32			
41.3	2.18	15	41.1	2.19	34	41.1	2.19	9	41.1	2.19	24	42.9	2.11	4
												44.3	2.04	6
43.9	2.06	10	–			–			45.9	1.92	21			
48.2	1.89	13	47.7	1.90	9	47.8	1.90	7	47.8	1.90	18	49.5	1.84	100

the introduction of lead(II) ions. The disordering, however, is slight as no distinct broadening of the peaks is observed in the diffraction patterns. When $Cs_3[Sb_2Cl_9]$ is transformed into $Cs_3[Sb_{1.80}Pb_{0.25}Cl_{8.90}]$ a slight decrease in identity period is observed which remains virtually unchanged for further compounds in the series. The last compound in the series, $Cs_3[Sb_{0.53}Pb_{5.31}Cl_{15.06}]$, has an entirely different diffraction pattern, which suggests that introducing a sufficient number of lead(II) atoms into the $Cs_3[Sb_2Cl_9]$ lattice causes a change in the crystalline structure.

Thermoanalytical studies

Thermal analysis curves of the chloroantimonates(III) under study with the admixture of lead(II) are similar to those of $Cs_3[Sb_2Cl_9]$ [3]. The last compound in the series, $Cs_3[Sb_{0.53}Pb_{5.31}Cl_{15.06}]$, is an exception. The characteristic temperatures of the DTA and DTG peaks, the temperature ranges of individual thermal decomposition reaction stages, and the corresponding mass losses are presented in Table 3. The decomposition of compounds **I**–**IV** (see Tables for numbering) takes a two-stage course and the total mass loss decreases gradually as the content of lead in the complexes increases. The thermal curves of compound **V** show only the first stage of decomposition. The mass loss corresponding to the second stage of decomposition coincides with sublimation or evaporation of the decomposition products. The peak in the DTA curve which corresponds to the melting of CsCl (melting point 642° C) is visible only in the curve for $Cs_3[Sb_2Cl_9]$.

The thermal stability of the investigated fluoroantimonates(III) with the lead(II) admixture, measured as the temperature at which the decomposition of the compounds begins, increases slightly in the order **I** < **II** < **III** and then decreases distinctly for complex **IV** which is a little more stable than compound **V**. The order of stability for the compounds is similar when measured as the temperature of the peak on the DTA curve which corresponds to the first stage of the thermal decomposition reaction. The second stage of the decomposition follows the first immediately; it is even probable that both stages partly overlap. Therefore, the temperature corresponding to the inflexion point on the TG curve was taken as the temperature at which the first stage of decomposition ends and the second begins. At a temperature several dozen degrees higher than that at which the second stage of decomposition ends, a further rapid decline of the TG curve occurs; this is related to the sublimation or evaporation of the products of further thermal decomposition of the substance. These processes have not been examined in detail.

The total loss mass related to the first and second stages of the decomposition reaction diminishes in the order **I** > **II** > **III** > **IV**. In the case of compound **V** the mass loss examined corresponded only to the first stage of the reaction.

TABLE 3

Thermal decomposition data

No.	Formula	Reaction step	Temp. range of decomposition (° C)	DTA peak temp. (° C)	DTG peak temp. (° C)	Mass loss from TG (%)	Mass loss of steps 1 + 2 (%)
I	$Cs_3[Sb_2Cl_9]$	1	320–446	441	435	19.0	37.0
		2	446–600	529	520	18.0	
				634			
II	$Cs_3[Sb_{1.80}Pb_{0.25}Cl_{8.90}]$	1	330–455	447	440	20.0	35.0
		2	455–600	488	493	15.0	
III	$Cs_3[Sb_{1.72}Pb_{0.51}Cl_{9.06}]$	1	335–450	450	440	18.0	33.0
		2	450–585	474	472	15.0	
IV	$Cs_3[Sb_{1.12}Pb_{1.21}Cl_{8.42}]$	1	275–435	430	424	10.0	19.5
		2	435–540	460	450	9.5	
V	$Cs_3[Sb_{0.53}Pb_{5.31}Cl_{15.06}]$		270–490	270	Difficult to locate	4.0	
				430			
				600			

TABLE 4

Results of the analyses of the thermal decomposition products (%)

Compound	Temperature (°C)	Sb	Pb	Cl
I	600	3.70	0.0	22.70
II	600	4.60	8.20	23.50
III	585	5.05	15.05	24.50
IV	540	1.85	30.40	23.30
V	490	2.25	53.30	24.90

Investigation of the products of thermal decomposition reactions

The course of the thermal decomposition reactions of the antimony complex salts with the admixture of lead was followed by heating samples of these compounds (ca. 100 mg) in a silite furnace at 10 °C min^{-1} in air; i.e. the conditions were similar to those under which the thermal analysis curves were prepared, and up to appropriate temperatures determined from the thermal analysis curves. For compounds **I**–**IV** these temperatures corresponded to the end of the second stage of decomposition; thus the results obtained from sinter analyses provide information on the global decomposition products of both stages of the reaction. A more detailed analysis of the first stage of the reaction was not possible because the second stage followed immediately. Compound **V** was heated to a temperature corresponding to the end of the first stage of the decomposition reaction.

Sinter samples were dissolved in hot concentrated H_2SO_4, and antimony, lead and chloride were determined by the methods described above. The results of the analyses are presented in Table 4.

DISCUSSION

In this work we examined a number of complex salts of the general formula $Cs_3[Sb_xPb_yCl_z]$ which were obtained by gradual replacement of antimony by different amounts of lead(II), the radius and formal charge of which are different from those of the central ion (Sb). Compounds of this type can easily be obtained by crystallization from hydrochloric acid, but their stoichiometric composition is sometimes considerably different from that which is expected. The assumed and real formulae of the complex salts, determined on the basis of chemical analysis, are presented in Table 1. In all the compounds obtained the total of moles of the central atom (Sb) and admixtured atom (Pb) is higher than the assumed value (2) and it increases as more lead atoms are introduced. For the compounds **I**–**V** it equals the Sb content (mol) is 2, 2.05, 2.23, 2.33 and 5.64, respectively. The stoichiometric content of chlorides, calculated on the assumption that the other elements were determined correctly, is a little higher than the real content, which most probably results from systematic analytical error.

The first (**I**) and last (**V**) compounds in the series are colourless. The introduction of more lead atoms into the mother compound increases the colour intensity.

X-ray diffraction studies of the chloroantimonates with the admixture of lead indicate that the introduction into $Cs_3[Sb_2Cl_9]$ of amounts of lead such as in salts **II**–**IV** does not basically change the crystalline structure, but causes only slight deformations of the lattice. Higher amounts of lead, as in complex **V**, causes a change in the type of structure.

Thermoanalytical studies of chloroantimonates(III) with the admixture of lead confirm the conclusions following from the analysis of diffraction patterns. Thermal analysis curves for compounds **II**–**IV** are similar to the analogous curves for $Cs_3[Sb_2Cl_9]$ and indicate a two-stage thermal decomposition of these complexes. Thermal analysis curves for compound **V** show an entirely different reaction course: only one stage of thermal decomposition reaction is observed.

It was found experimentally that the only volatile product of the thermal decomposition of all the complex salts under investigation at temperatures up to ca. 700 °C is $SbCl_3$; CsCl was found only in the decomposition products of $Cs_3[Sb_2Cl_9]$.

The thermal stability of the chloroantimonates(III) having a low lead content increase in the order **I** < **II** < **III**. Complexes **IV** and **V** begin to decompose at a temperature ca. 60 °C lower than compound **III**; their thermal stabilities are similar. The thermoanalytical data for the decomposition of the compounds examined are presented in Table 3.

Chemical analysis of sinters obtained by heating the examined complex salts to appropriate temperatures (determined from thermal analysis curves and corresponding with the end of the first and second stages for compounds **I**–**IV** and with the end of the first stage for compound **V**) and the analysis of the results of thermal examinations and X-ray diffraction studies allow the following summary schemes of thermal decomposition reactions to be suggested:

I $Cs_3[Sb_2Cl_9] = Cs_3[Sb_{0.16}Cl_{3.48}] + 1.84SbCl_3$

II $Cs_3[Sb_{1.80}Pb_{0.25}Cl_{8.90}] \rightarrow Cs_3[Sb_{0.24}Pb_{0.25}Cl_{4.15}] + 1.56SbCl_3$

III $Cs_3[Sb_{1.72}Pb_{0.51}Cl_{9.06}] \rightarrow Cs_3[Sb_{0.34}Pb_{0.51}Cl_{5.06}] + 1.38SbCl_3$

IV $Cs_3[Sb_{1.12}Pb_{1.21}Cl_{8.42}] \rightarrow Cs_3[Sb_{0.14}Pb_{1.21}Cl_{5.65}] + 0.98SbCl_3$

V $Cs_3[Sb_{0.53}Pb_{5.31}Cl_{15.06}] \rightarrow Cs_3[Sb_{0.38}Pb_{5.24}Cl_{14.28}] + 0.15SbCl_3$

The above formulae result from the chemical analyses and, therefore, there is no equality sign between the left- and right-hand sides of the decomposition reaction. X-ray studies have shown that part of the CsCl in the sinter of $Cs_3[Sb_2Cl_9]$ occurs in a free form and not bound in the complex.

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