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STUDIES ON THE THERMAL DECOMPOSITION OF COMPLEX SALTS OF THE $Cs_3[Bi_{2-x}Pb_xCl_{9-x}]$ TYPE

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ABSTRACT

Thermoanalytical studies have been carried out on crystalline complex salts of the $Cs_3[Bi_{2-x}Pb_xCl_{9-x}]$ type formed between $BiCl_3$, $PbCl_2$ and CsCl in hydrochloric acid solution. Some conclusions concerning the thermal stability of these compounds have been drawn. From chemical and X-ray analyses of the solid decomposition products thermal decomposition reaction schemes have been established.

INTRODUCTION

This work is a continuation of an investigation to determine the influence of foreign atoms introduced into the lattice of the matrix compound on the thermal stability of complex salts. The subject of the investigation is a series of compounds obtained by replacing bismuth atoms in the lattice of caesium(III) nonachlorodibismuthate $Cs_3[Bi_2Cl_9]$ with different numbers of lead(II) atoms. Lead has an ionic radius and oxidation number different from those of the central atom of the matrix compound.

Thermal investigations of the complex salts of $Cs_3[Sb_xBi_{2-x}Cl_{9-x}]$ and $Cs_3[Sb_{2-x}Pb_xCl_{9-x}]$ have been reported previously [1,2].

EXPERIMENTAL

Apparatus

The apparatus used for the investigation and the conditions under which the measurements were performed were the same as used in the examination of compounds of the $Cs_3[Sb_{2-x}Pb_xCl_{9-x}]$ type [2].

Preparation and chemical analysis of the compounds

Complex salts with the general formula $Cs_3[Bi_{2-x}Pb_xCl_{9-x}]$ were obtained by dissolving $(BiO)_2CO_3$ and $PbCO_3$ in the appropriate proportions

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TABLE 1

Results of analyses and theoretical and actual formulae of compounds

Theoretical formula	Results of analyses (%)			Actual formula	Colour of compound
	Sb	Pb	Cl		
I $Cs_3[Bi_2Cl_9]$	36.90	–	27.85	$Cs_3[Bi_2Cl_9]$	Colourless
II $Cs_3[Bi_{1.78}Pb_{0.22}Cl_{8.78}]$	34.30	3.10	27.65	$Cs_3[Bi_{1.87}Pb_{0.17}Cl_{8.91}]$	Colourless
III $Cs_3[Bi_{1.60}Pb_{0.40}Cl_{8.60}]$	29.75	9.10	27.45	$Cs_3[Bi_{1.68}Pb_{0.52}Cl_{9.14}]$	Pale yellow
IV $Cs_3[Bi_{1.0}Pb_{1.0}Cl_{8.0}]$	19.10	20.20	25.85	$Cs_3[Bi_{1.04}Pb_{1.11}Cl_{8.39}]$	Intense yellow
V $Cs_3[Bi_{0.40}Pb_{1.60}Cl_{7.42}]$	–	58.20	24.55	$Cs_3[Pb_{6.48}Cl_{16.0}]$	Colourless

in a hot 2 M solution of hydrochloric acid. A solution of $Cs_2CO_3 \cdot 2\ H_2O$ in 2 M hydrochloric acid was added slowly and the mixture was stirred at high speed. The precipitate formed was immediately dissolved by heating it in the matrix solution and was recrystallized by very slow cooling of the solution. The well-formed crystals obtained were filtered off and dried in air at room temperature. To prevent the possible precipitation of caesium chloroplumbate(II) slightly less caesium carbonate was used for the synthesis of the compounds under study than required for the stoichiometric composition.

In the successive crystallizations of the complex salts the amounts of starting compounds used correspond to the molar ratios Bi : Sb of 8 : 1, 4 : 1, 1 : 1 and 1 : 4. These are identical with those used for the compound series $Cs_3[Sb_{2-x}Pb_xCl_{9-x}]$. These proportions correspond to the theoretical formulae presented in column 1 of Table 1.

The actual formulae of the compounds examined were determined on the basis of the results of chemical analysis, i.e. the determination of bismuth, lead and chloride. To determine the content of bismuth and chloride, the compounds were dissolved in nitric acid (1 + 1). To determine the content of lead the compounds were dissolved in hot concentrated sulphuric acid. Bismuth was determined by complexometry, i.e. by titration of EDTA in the presence of thiourea. Lead was precipitated in the form of $PbSO_4$; the precipitate was dissolved in ammonium acetate and was precipitated again in the form of $PbCrO_4$. Chlorides were determined by the method of Volhard. The content of caesium was calculated from the percentage difference. The results of the analyses, the actual formulae and the colours of the compounds under study are presented in Table 1. On the basis of the known $Cs_3[Bi_2Cl_9]$ crystal structure and the X-ray study presented below the formulae of the examined complexes can be presented in the general form $Cs_3[Bi_xPb_yCl_z]$.

The content of chloride in the complex salts under investigation is slightly different from that expected from stoichiometry in relation to the other elements. This may be due to analytical error, to the non-stoichiometric composition of the compounds or to both of these factors.

X-ray diffraction study

The crystal structure of $Cs_3[Bi_2Cl_9]$ has been reported [3]. In the structure the $Bi_2Cl_9^{3-}$ ion constitutes a separate structural unit. The *d/n* and intensity *I* values of the chlorobismuthates(III) containing lead are presented in Table 2. The diffraction patterns for compounds **II** and **III** are very similar to that of compound **I**, which indicates that the structure of the matrix compound has been retained. The *d/n* values decrease slightly in the order **I** > **II** > **III**.

The diffraction pattern of complex **IV** differs considerably from those of compounds **I**–**III**. The diffraction pattern of complex **V** is entirely different from the others, which implies that a distinct compound is formed. This was confirmed by chemical analysis.

Thermoanalytical studies

The data on the thermal decomposition of the complex salts are presented in Table 3. The thermal curves of compounds **I**–**III** are similar to the curves characteristic of $Cs_3[Bi_2Cl_9]$. The only differences observed are in the temperatures corresponding to the peaks on the DTA and DTG curves and in the mass loss associated with the first stage of the decomposition reaction, calculated from the TG curves. It is possible to observe and identify only one stage of the decomposition reaction. At higher temperatures, a fast and continuous mass loss occurs caused by the evolution of gaseous products of further decomposition and by the evaporation or sublimation of the final products of decomposition. The mass loss decreases considerably in the order **I** > **II** $\gg$ **III**. The thermal stability of the compounds, measured as the temperature at which the decomposition begins and as the temperature of the peak on the DTA curve corresponding to the first stage of the decomposition reaction, decreases in the same order. The thermal curves of compounds **IV** and **V** are entirely different. The first stage of the decomposition of $Cs_3[Bi_{1.04}Pb_{1.11}Cl_{8.39}]$ is hardly visible on either the TG or the DTA curve. A continuous, rapid mass loss is observed in the TG curve of $Cs_3[Pb_{6.48}Cl_{16}]$ at temperatures higher than 550 ° C, until all products of the decomposition of the compound are exhausted. The small endothermic peak on the DTA curve of salt **V** at 265 ° C, which is not accompanied by a change in mass on the TG curve, is probably associated with the change in the crystal structure of this compound. Peaks on the DTG curves of chlorobismuthates containing lead are broad and difficult to identify. The peaks corresponding to the first stage of decomposition of compounds **I**–**III** are exceptions.

TABLE 2

X-ray diffraction data

$Cs_3[Bi_2Cl_9]$			$Cs_3[Bi_{1.87}Pb_{0.17}Cl_{8.91}]$			$Cs_3[Bi_{1.68}Pb_{0.52}Cl_{9.14}]$			$Cs_3[Bi_{1.04}Pb_{1.11}Cl_{8.39}]$			$Cs_3[Pb_{6.48}Cl_{16.0}]$		
2θ(deg)	d/n	I	2θ(deg)	d/n	I	2θ(deg)	d/n	I	2θ(deg)	d/n	I	2θ(deg)	d/n	I
9.3	9.509	10	9.3	9.509	10	9.4	9.408	15	13.1	6.102	8	10.8	8.192	5
11.5	7.694	4	11.7	7.550	73	11.9	7.437	47	15.6	5.680	2	12.0	7.375	200
15.6	5.680	7	15.6	5.680	4	18.9	4.695	35	18.8	4.720	11	15.25	5.494	7
16.2	5.471	4	18.9	4.695	37	23.3	3.818	22	19.8	4.484	8	17.3	5.257	12
18.8	4.720	41	19.4	4.575	4	24.0	3.708	50	22.3	3.986	23	19.6	4.529	6
19.4	4.575	6	23.2	3.834	10	28.7	3.110	100	28.6	3.121	22	21.75	4.095	3
23.2	3.834	20	24.0	3.708	41	33.2	2.867	10	31.8	2.814	8	24.15	3.684	150
28.6	3.121	100	28.7	3.110	100	36.4	2.468	15	33.5	2.675	9	25.15	3.534	10
33.1	2.706	10	33.1	2.706	7	41.1	2.196	10	35.7	2.315	2	28.8	3.097	4
36.2	2.481	6	36.4	2.468	10	47.8	1.903	5	39.3	2.292	9	30.65	2.918	19
40.8	2.211	10	40.9	2.206	6	49.3	1.851	11	40.5	2.226	4	31.15	2.876	4
43.6	2.076	6	47.7	1.906	4	49.9	1.827	7	45.7	1.985	3	34.95	2.571	6
47.6	1.910	8	48.7	1.810	37				48.6	1.873	7	36.55	2.462	25
48.7	1.870	18	49.3	1.851	18				51.5	1.774	2	39.3	2.292	17
59.3	1.558	37	59.3	1.558	82				59.2	1.561	9	39.8	2.265	7
												42.95	2.108	7
												49.4	1.845	35
												56.2	1.637	2
												59.45	1.556	2

TABLE 3

Thermal decomposition data

Formula of compound	Temperature range of decomposition (°C)	DTA peak temperature (°C)	DTG peak temperature (°C)	Mass loss from TG (%)
I $Cs_3[Bi_2Cl_9]$ I step	440–610	595 [a]	581	10.0
$Cs_3[Bi_2Cl_9]$ II step	610	681		
II $Cs_3[Bi_{1.87}Pb_{0.17}Cl_{8.91}]$ I step	430–610	595	595	8.0
$Cs_3[Bi_{1.87}Pb_{0.17}Cl_{8.91}]$ II step	610	670	[b]	
III $Cs_3[Bi_{1.68}Pb_{0.52}Cl_{9.14}]$ I step	360–460	427	440	2.0
$Cs_3[Bi_{1.68}Pb_{0.52}Cl_{9.14}]$ II step	460	546	[b]	
IV $Cs_3[Bi_{1.04}Pb_{1.11}Cl_{8.39}]$	420	565	[b]	
V $Cs_3[Pb_{6.48}Cl_{16.0}]$	500	440	[b]	

[a] All peaks on DTA curve are endothermic.

[b] Diffuse peak, difficult to localize.

Examination of the products of the decomposition reactions

To trace the course of the thermal decomposition reactions of the complex salts of bismuth containing lead, samples of these compounds (100 mg) were heated in a furnace with a thermoregulator at a rate of 10 °C min^{-1} in an air atmosphere, i.e. under conditions similar to those under which thermal analysis curves were prepared. The samples of compounds **I**–**III** were heated up to temperatures corresponding to the end of the first stage of the reaction, since only these temperatures could be determined with sufficient accuracy. As it is impossible to determine any temperatures of transformations (except at the beginning of the decomposition) from the thermal curves of salts **IV** and **V**, the compounds were heated up to 720 °C, a temperature which was chosen arbitrarily. Bismuth, lead and chloride were determined in the sinters by the methods described above. The results of the analyses are presented in Table 4.

TABLE 4

Results of analyses of thermal decomposition products (%)

Compound	Temperature of heating (°C)	Bi	Pb	Cl
I	610	34.85	–	27.30
II	610	31.10	5.60	27.00
III	460	30.80	9.40	26.90
IV	720	15.00	21.95	24.90
V	720	–	54.45	24.30

DISCUSSION

A series of complex salts of the $Cs_3[Bi_xPb_yCl_z]$ type have been examined. The salts were obtained by partial replacement of the central atom (Bi) with different amounts of lead(II), a cation whose radius and formal oxidation number are different from those of Bi^{3+}. Compounds of this type (similar to the salts of the $Cs[Sb_xPb_yCl_z]$ type) are easy to obtain by crystallization from a 2 M solution of hydrochloric acid. Their compositions are sometimes considerably different from those expected. The theoretical and actual formulae of the complexes examined are presented in Table 1. The total number of moles of the central atom (Bi) plus the admixtured atom (Pb) is always higher than the theoretical value ($=2$) and it increases (with one exception) as more atoms of lead are introduced. For the successive compounds of the series the values are 2, 2.04, 2.20, 2.15 and 6.48. These values are slightly lower than in the analogous compounds of antimony. The stoichiometric content of chloride calculated on the assumption that the other elements were determined correctly is slightly different from the actual content. This is probably due to a systematic error in determination. In the antimony complexes which were studied previously the differences were considerably larger. The matrix compound $Cs_3[Bi_2Cl_9]$ and the last compound of the series examined are colourless, whereas the other compounds are yellow. The intensity of the colour increases as the amount of lead increases. If small amounts of lead are introduced into the matrix compound the type of crystal structure remains unchanged. The slight changes in the diffraction patterns probably result from the deformation of the lattice caused by the replacement of bismuth atoms with atoms of lead, which have a different size and different formal oxidation number. The changes are less significant than those observed in the analogous complex salts of antimony.

The thermal decomposition of compounds **II** and **III** is similar to the decomposition of $Cs_3[Bi_2Cl_9]$. Only one stage of the decomposition can be observed on the thermal curves. The thermal stability diminishes in the order $\mathbf{I} > \mathbf{II} \gg \mathbf{III}$. The thermal curves of compounds **IV** and **V** are entirely different. The first stage of the decomposition reaction is not clearly visible and the continuous and fairly rapid mass loss observed on the TG curves results from the evolution of $BiCl_3$ and the evaporation or sublimation of other decomposition products. The data for the thermal decomposition of the complex salts are presented in Table 3. From these data and those previously published, it follows that the thermal decomposition of caesium chlorobismuthates(III) containing lead(II) begins at temperatures several tens of degrees higher than the decomposition of the analogous antimony compounds; thus their thermal stabilities are considerably higher. Chemical analysis of the sinters obtained by heating the examined compounds to the appropriate temperatures determined from the thermal analysis curves (corresponding to the end of the first stage of the reaction for compounds **I**–**III**, and to 720 °C for the other two) and the analysis of the results of the thermal examinations and the X-ray diffraction study indicate the following thermal decomposition reactions for the complexes

I $Cs_3[Bi_2Cl_9] \rightarrow Cs_3[Bi_{1.76}Cl_{8.1}] + 0.24\ BiCl_3$

II $Cs_3[Bi_{1.87}Pb_{0.17}Cl_{8.91}] \rightarrow Cs_3[Bi_{1.59}Pb_{0.18}Cl_{8.43}] + 0.28\ BiCl_3$

III $Cs_3[Bi_{1.68}Pb_{0.52}Cl_{9.14}] \rightarrow Cs_3[Bi_{1.46}Pb_{0.49}Cl_{7.71}] + 0.22\ BiCl_3$

IV $Cs_3[Bi_{1.04}Pb_{1.11}Cl_{8.39}] \rightarrow Cs_3[Bi_{0.75}Pb_{1.11}Cl_{7.34}] + 0.29\ BiCl_3$

V $Cs_3[Pb_{6.48}Cl_{16.0}] \rightarrow Cs_3[Pb_{4.93}Cl_{12.84}] + 1.55\ PbCl_2$

The compositions of the decomposition products were obtained from the chemical analysis of the sinters; hence, there is no equality sign between the left and right sides of the decomposition reaction equations.

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