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THERMAL DECOMPOSITION OF $Cs_2Hg_3I_8 \cdot H_2O$

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ABSTRACT

Studies of the thermal decomposition of $Cs_2Hg_3I_8 \cdot H_2O$ at constant heating rates and with isothermal heating have been carried out using the TG technique. Up to four steps were observed for the decomposition when heating rates of 10 °C min^{-1} (I) and 5 °C min^{-1} (II) were used in the temperature interval 35–605 °C. In the first step, dehydration takes place. In the second step, the anhydrous compound releases HgI_2 forming an intermediate, probably $CsHgI_3$. The third step for I may give Cs_2HgI_4, while the last step yields the end product CsI. For II, the third step is accompanied by further release of HgI_2 with the formation of CsI. When isothermal heating at 155 °C was used, only two decomposition steps were observed. First, dehydration occurs and then release of HgI_2 gives the stable crystalline end product Cs_2HgI_4. Weight loss studies at 65, 135 and 440 °C were performed to verify the decomposition models. The end products were characterized by X-ray powder diffraction and EDX analysis.

INTRODUCTION

The present work is part of a project concerned with structural studies of double iodides of Cs with Hg or Cd. Recently, accurate structure determinations at room temperature were published for four compounds in the $CsI–MI_2$ system, $M \equiv Cd$, Hg [1,2]. The compounds are $Cs_2Hg_3I_8 \cdot H_2O$, Cs_2HgI_4, Cs_3HgI_5 and Cs_2CdI_4. A limited number of structure determinations for hydrates of double iodides with an alkali metal ion and a metal ion have been reported in the literature [3–10]. The hydrates are: $KZnI_3 \cdot 2H_2O$ [3]; $KHgI_3 \cdot H_2O$ [4]; $RbCdI_3 \cdot H_2O$ [5]; $Rb_5I(I_3)(BiI_6) \cdot 2H_2O$ [6]; $KPbI_3 \cdot 2H_2O$ and $RbPbI_3 \cdot 2H_2O$ [7]; $KTlI_4 \cdot 2H_2O$, $RbTlI_4 \cdot 2H_2O$ and $CsTlI_4 \cdot 2H_2O$ [8]; $K_2PtI_5 \cdot 2H_2O$ and $Rb_2PtI_5 \cdot 2H_2O$ [9]; and $K_2PbI_4 \cdot 2H_2O \cdot 0.237KI_3 \cdot 0.37H_2O$ [10]. One of these, $CsTlI_4 \cdot 2H_2O$ [8], dehydrates between 70 and 100 °C with formation of $CsTlI_4$ [11]. In this paper a TG study is undertaken in order to describe the mechanism of the thermal decomposition of $Cs_2Hg_3I_8 \cdot H_2O$.

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EXPERIMENTAL

Yellow transparent crystals of $Cs_2Hg_3I_8 \cdot H_2O$ were grown from a water solution with HgI_2 and CsI in excess. The crystals were washed in *n*-hexane and dried in air. The TG was carried out on a Mettler TG-50 thermobalance. Substances released when heating the samples were removed by a gas stream. Corrections were made for the excess weight caused by this dynamic atmosphere of pure air and nitrogen. The experimental conditions are summarized in Table 1. X-ray powder photographs were taken at 19 °C by means of a Guinier–Hägg focusing camera [$\lambda(\mathrm{Cu}\ K\alpha_1) = 1.540598$ Å]. Silicon was used as internal standard [$a(\mathrm{Si}) = 5.430975$ Å]. Microstructural studies and EDX analyses were carried out on a JSM-840A scanning electron microscope equipped with a LINK AN10000 energy dispersive X-ray detector system.

RESULTS AND DISCUSSION

Structural background

$Cs_2Hg_3I_8 \cdot H_2O$ [1], monoclinic *Cm*, $a = 7.451(1)$, $b = 21.721(3)$, $c = 7.685(1)$ Å, $\beta = 108.03(1)°$, consists of stacked two-dimensional networks of almost regular HgI_4 tetrahedra with Cs^+ and H_2O situated in between (Fig. 1a, b). The Cs^+ is coordinated by eight iodides and a water oxygen forming a tri-capped trigonal prism, with the water oxygen as one of the capping atoms. There are five different Hg–I bond distances in the range 2.680(1)–2.952(1) Å [1]. These distances, except that of 2.952(1) Å, are similar to those found in Cs_2HgI_4, 2.738(1)–2.819(1) Å, and Cs_3HgI_5, 2.729(1)–2.804(1) Å [1]. The structure of Cs_2HgI_4 [1], monoclinic $P2_1/m$, $a = 7.734(1)$, $b = 8.386(1)$, $c = 11.019(1)$ Å, $\beta = 110.06(1)°$, has isolated HgI_4 tetrahedra (Fig. 1c). The two independent Cs^+ ions have eight- and

TABLE 1

Experimental conditions for TG analysis of $Cs_2Hg_3I_8 \cdot H_2O$

Experiment	Weight (mg)	Heating	Protective gas (ml min^{-1})	Crystals
I	13.816	10 °C min^{-1}, 35–605 °C	100 air + 140 N_2	ground
II	9.613	5 °C min^{-1}, 35–500 °C	100 air + 120 N_2	ground
III	3.970	5 °C min^{-1}, 30–155 °C, then isothermal at 155 °C for 7.5 h	290 air + 290 N_2	as grown
IV	1.835	Isothermal at 65 °C for 48 h	no	as grown
V	1.361	Isothermal at 135 °C for 14 h	no	as grown
VI	2.023	Isothermal at 440 °C for 24 h	no	as grown

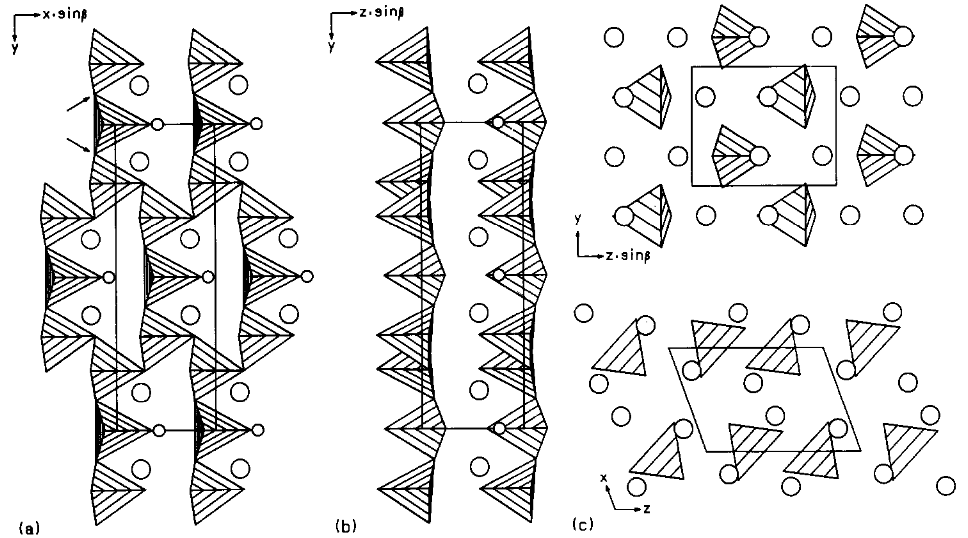
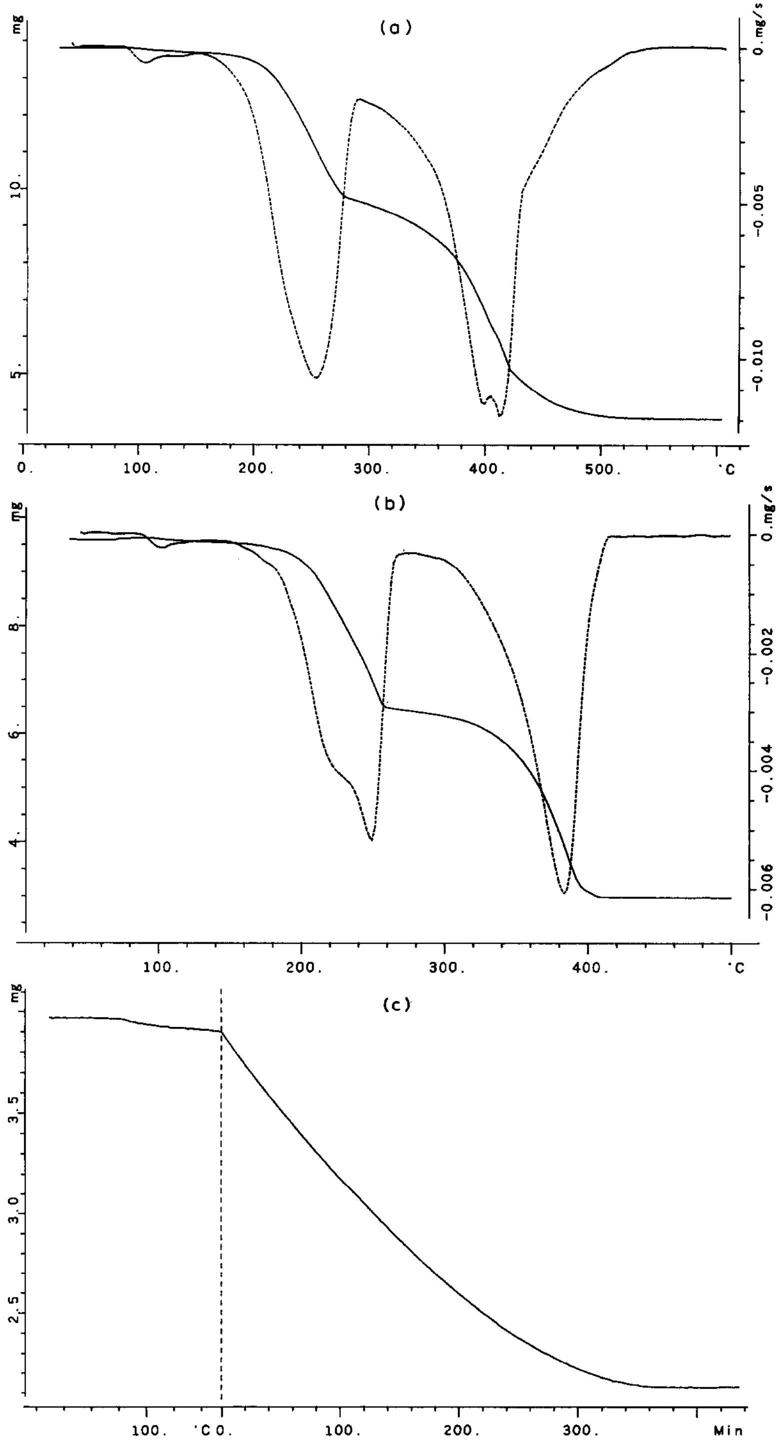


Fig. 1. Structure plots showing the unit cell packing of $Cs_2Hg_3I_8 \cdot H_2O$ (a) along [001]; (b) along [100]; and (c) that of Cs_2HgI_4, upper half along [100] and lower half along [010]. Hg is inside and I atoms are at corners of the tetrahedra. Cs^+ are marked with large circles and H_2O with small ones. The arrows mark the iodides in the longest Hg–I bonds.

nine-coordination of iodides, respectively. Three compounds are observed in the $CsI–HgI_2$ phase diagram [12], Cs_2HgI_4 (m.p. 380 °C), $CsHgI_3$ (melts with decomposition in the range 160–200 °C) and $CsHg_2I_5$ (m.p. 210 °C, decomposes in air). Like $KHgI_3 \cdot H_2O$ [4], $CsHgI_3$ is probably formed of chains of corner-sharing HgI_4 tetrahedra.

Experiments I and II

$Cs_2Hg_3I_8 \cdot H_2O$ is stable up to 89 °(85 °C) (here and below the data from Experiment II are given in parentheses). The compound loses the water molecule in one step between 89 and 154 °C (85–140 °C) (Fig. 2a, b). The DTG curves (Fig. 2a, b) give the observed peak temperature 107 °C (104 °C). The observed weight loss is 0.98% (1.08%) compared with the calculated value of 0.95%. The anhydrous compound undergoes a small weight loss up to 202 °C (184 °C). Then a large weight loss occurs between 202 (184) and 278 °C (257 °C) with a peak temperature of 255 °C (251 °C). This weight loss is accompanied by the release of 1 mole HgI_2 with formation of the intermediate compound, $CsHgI_3$. A probable mechanism for this reaction is a break of the longest Hg–I bonds in anhydrous $Cs_2Hg_3I_8$ (2.952(1) Å in the hydrated crystal), forming an HgI_2 molecule which diffuses out of the crystal. However, the observed and calculated values do not agree very well, they are 28.93% (29.71%) and 24.85%, respectively. The large difference could be the result of the formation of some Cs_2HgI_4 (I) or CsI (I,II) before


(a)
mg
10.
5.
0. mg/s
-0.005
-0.010
0.
100.
200.
300.
400.
500.
°C
(b)
mg
8.
6.
4.
0. mg/s
-0.002
-0.004
-0.006
100.
200.
300.
400.
°C
(c)
mg
3.5
3.0
2.5
100.
°C 0.
100.
200.
300.
Min

the formation of $CsHgI_3$ is completed. No explanation has emerged so far for the shoulder on the second peak (150–270 °C) in Fig. 2b. In the DTG curve (Fig. 2a) the last peak is split in two, with peak temperatures of 399 °C and 413 °C, respectively. The first peak is probably due to Cs_2HgI_4 formation. The weight loss is 51.30%, compared with 48.76% for the calculated value. The second peak is concerned with the end product, CsI. The corresponding peak for II is 387 °C. Observed and calculated values differ somewhat depending on adhesion of Hg to the lead-through chain. The values are 72.45% (71.45%) and 72.66%, respectively. CsI formation is complete by 550 °C (412 °C). Thus, the complete reaction between 35 and 605 °C occurs in the following steps

$$Cs_2Hg_3I_8 \cdot H_2O(s) \xrightarrow{89\text{–}154(85\text{–}140)^\circ C} Cs_2Hg_3I_8(s) + H_2O(g) \quad (1)$$

$$Cs_2Hg_3I_8(s) \xrightarrow{154\text{–}278(140\text{–}257)^\circ C} 2CsHgI_3(s) + HgI_2(g) \quad (2)$$

$$2CsHgI_3(s) \xrightarrow{278\text{–}404(I)^\circ C} Cs_2HgI_4(s) + HgI_2(g) \quad (3)$$

$$Cs_2HgI_4(s) \xrightarrow{404\text{–}550(I)^\circ C} 2CsI(s) + HgI_2(g) \quad (4)$$

$$2CsHgI_3(s) \xrightarrow{257\text{–}412^\circ C(II)} 2CsI(s) + 2HgI_2(g) \quad (5)$$

Experiment III

Heating at 5 °C min^{-1} up to 155 °C and then isothermal heating for 7.5 h at 155 °C (Fig. 2c), first results in dehydration between 70 and 124 °C. The observed weight loss is 1.43%, the calculated value is 0.95%. Then a decomposition with release of 2 moles of HgI_2 occurs. The total observed weight loss is 48.38%, the calculated value is 48.76%. Formation of the end product was complete after 6 h. The compound Cs_2HgI_4 was confirmed by X-ray powder diffraction and EDX analysis. Micrographs of crystals before and after heating showed that the shapes were not changed but a lot of large holes (1 μm in diameter) were observed on the surfaces (Fig. 3a, b). The end product, Cs_2HgI_4, is stable up to 380 °C. No hint of $CsHgI_3$ formation was seen on the TG curve (Fig. 2c). The reactions for isothermal conditions at

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Fig. 2. TG (———) and DTG (- - - - - -) curves for $Cs_2Hg_3I_8 \cdot H_2O$ at heating rates of (a) 10 °C min^{-1} and (b) 5 °C min^{-1}. (c) TG curve with a heating rate of 5 °C min^{-1} up to 155 °C and then isothermal heating for 7.5 h. The left vertical axis marks the weight loss, w (mg), and the right marks the $\Delta w/\Delta t$ (mg s^{-1}). The horizontal axis marks the temperature, T (° C), or the isothermal heating time, t (min).

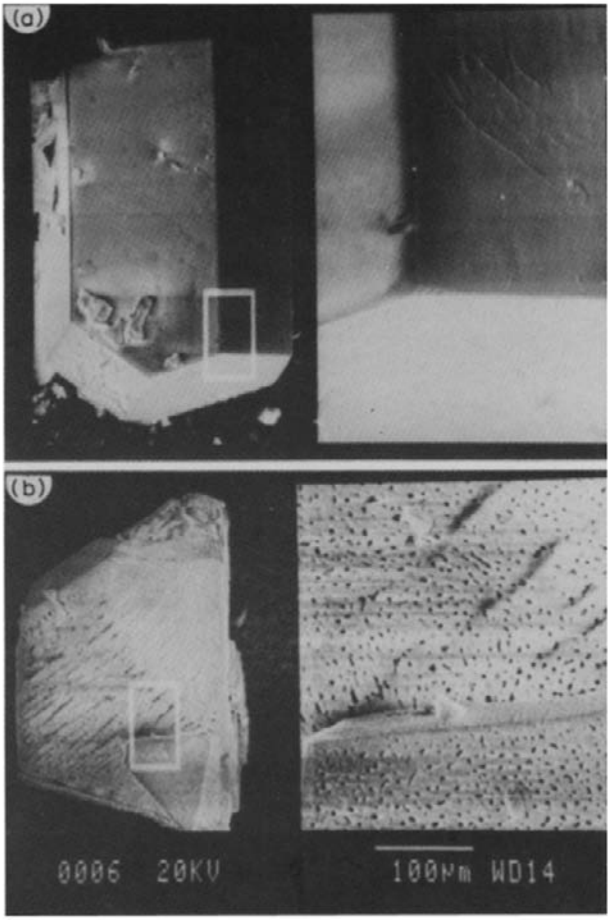

Fig. 3. Scanning electron micrographs showing crystals (a) before ($Cs_2Hg_3I_8 \cdot H_2O$) and (b) after isothermal heating at 155° C for 7.5 h (Cs_2HgI_4). The bar in (b) is also valid for (a). The inserted micrographs show the surfaces at higher magnification.

155° C are

$$Cs_2Hg_3I_8 \cdot H_2O(s) \xrightarrow{70-124^\circ C} Cs_2Hg_3I_8(s) + H_2O(g) \tag{6}$$

$$Cs_2Hg_3I_8(s) \xrightarrow{0-6 \text{ hours}} Cs_2HgI_4(s) + 2HgI_2(g) \tag{7}$$

Experiments IV, V and VI

The crystals in Experiments IV and V lost their transparency following heating, although their shapes were not affected. Large holes were observed on the surfaces. The weight loss for IV and V were 2.13% (0.95%) and 48.93% (48.76%), respectively. Some formation of Cs_2HgI_4 or $CsHgI_3$ probably occurred in IV. Calculated values are in parentheses. When large single crystals of $Cs_2Hg_3I_8 \cdot H_2O$ were kept at 135° C for 14 h, they were only

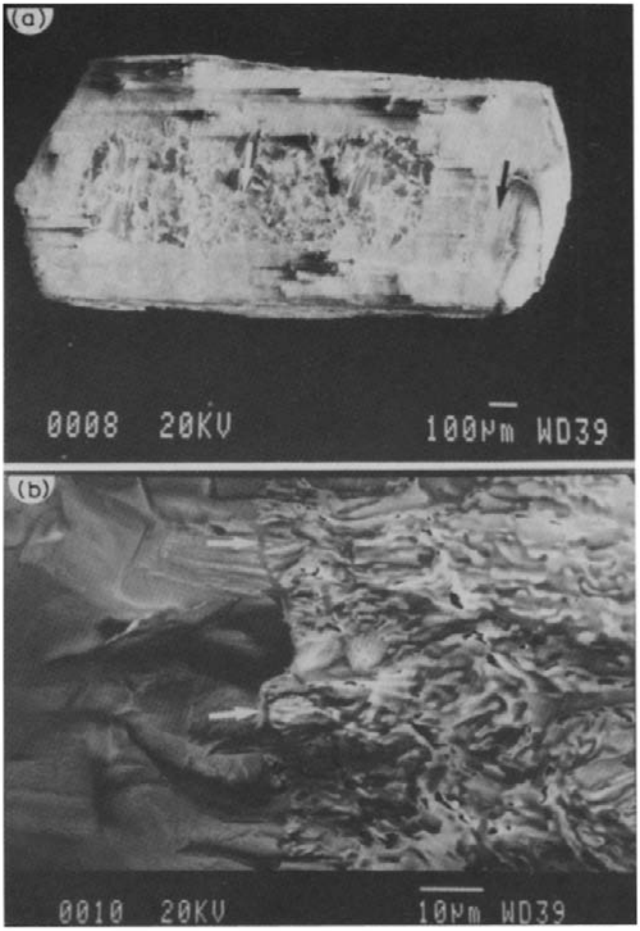

Fig. 4. Micrograph (a) shows a $Cs_2Hg_3I_8 \cdot H_2O$ crystal (inner part, white arrow) partly converted to Cs_2HgI_4 (outer part, black arrow). In (b) the phase boundary is shown (white arrows). Crystalline $Cs_2Hg_3I_8 \cdot H_2O$ to the left and porous Cs_2HgI_4 to the right.

partly converted to Cs_2HgI_4. In Fig. 4a, a crystal is shown where the inner part contains crystalline $Cs_2Hg_3I_8 \cdot H_2O$ and the outer part, porous Cs_2HgI_4. There is an obvious phase boundary (Fig. 4b). In Experiment VI no well-defined crystals were obtained following heating. X-ray powder diffraction and EDX investigations were performed on samples IV–VI in the experiments. The same powder pattern was observed for IV and $Cs_2Hg_3I_8 \cdot H_2O$. The end products in V and VI were Cs_2HgI_4 and CsI, respectively.

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