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PHASE TRANSITION AND THERMAL DECOMPOSITION OF $[Cd(H_2O)_6](BF_4)_2$*

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Abstract

Phase transition and thermal decomposition of $[Cd(H_2O)_6](BF_4)_2$ were studied by differential scanning calorimetry (DSC), differential thermal analysis (DTA) and thermogravimetry (TG) methods. The solid-solid phase transition at T_{C1}=324 K and the melting point at $T_{melt.}$=391 K were registered. The thermal dehydration process starts just above T_{C1} and continues up to $T_{melt.}$, where $[Cd(H_2O)_4](BF_4)_2$ in the liquid phase is formed. Then, dehydration and decomposition take place simultaneously until CdF_2 is obtained. Final products of the thermal decomposition were identified using quadrupole mass spectrometry (QMS) and X-ray diffraction methods.

Keywords: DSC, DTA, hexaaquacadmium tetrafluoroborate, phase transition, QMS, TG, thermal decomposition

Introduction

Crystalline compounds of the type $[M(H_2O)_6](BF_4)_2$, where M=Mn, Fe, Co, Ni and Zn, exhibit several phase transition both below and above room temperature [1]. In $[Cd(H_2O)_6](BF_4)_2$ two phase transition proceeding in the solid state were discovered: at T_{C1}=329 K and at T_{C2}=176 K [2,3]. According to West [4, 5], the crystal structure of $[Cd(H_2O)_6](BF_4)_2$ is trigonal at room temperature (space group no. 156=P3m1=C_{3v}^{1}) with one molecule per unit cell, and it is isomorphic with $[Cd(H_2O)_6](ClO_4)_2$. The lattice constants, determined by Moss *et al.* [6] for hexaaquacadmium tetrafluoroborate are quite close to those for hexaaquacadmium chlorate(VII). However, Johansson and Sandström [7] proposed the space group no. 164=P$\bar{3}$m1=D_{3d}^{3} for $[Cd(H_2O)_6](ClO_4)_2$. Unfortunately, the structures of the high- and low-temperature phases of both $[Cd(H_2O)_6](ClO_4)_2$ and $[Cd(H_2O)_6](BF_4)_2$ are still unknown. Since, according to Georgiev and Maneva [8], the dehydration process of the $[Cd(H_2O)_6](BF_4)_2$ starts already at ca 320 K, it is interesting to find its connection with T_{C1} phase transition and also with the melting point of the crystals. In addition,

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results of the thermal decomposition of the investigated compound, will also be presented for different experimental conditions.

Experimental

$[Cd(H_2O)_6](BF_4)_2$ was synthesized by treating cadmium carbonate with dilute tetrafluoroborate acid. The solution was concentrated by mild heating, and the colorless crystals obtained after cooling of the solution were purified several times by repeated crystallization from four-times-distilled water. Then, the crystals were dried for several days in a desiccator over BaO and later stored in a hygrostat. The composition of the compound was established through chemical analysis. The infrared and Raman spectra certified the purity of the sample.

Differential scanning calorimetric (DSC) measurements were performed with a TA Instruments DSC 2010 apparatus.

Thermogravimetry (TG) and differential thermal analytic (DTA) measurements were performed using a TA Instruments SDT 2960 apparatus. They were made in the flow of air, helium and argon at a constant heating rate of 2 and 3 K min^{-1}, up to 500 K, under atmospheric pressure, with the on-line analysis of the evolved gases by a Balzers ThermoStar GDS 300T3 quadrupole mass spectrometer (QMS).

The X-ray analysis of the solid decomposition product was made with a Sefert XRD-7 apparatus by applying filtrated CuK_α radiation.

Results and discussion

Figure 1 presents heat flow *vs.* temperature (DSC curve) for $[Cd(H_2O)_6](BF_4)_2$ as registered on heating the sample at a rate of 10 K min^{-1} in the temperature range of 300–400 K. There are two endothermic peaks on the DSC curve: at T_{C1}=324 K and at

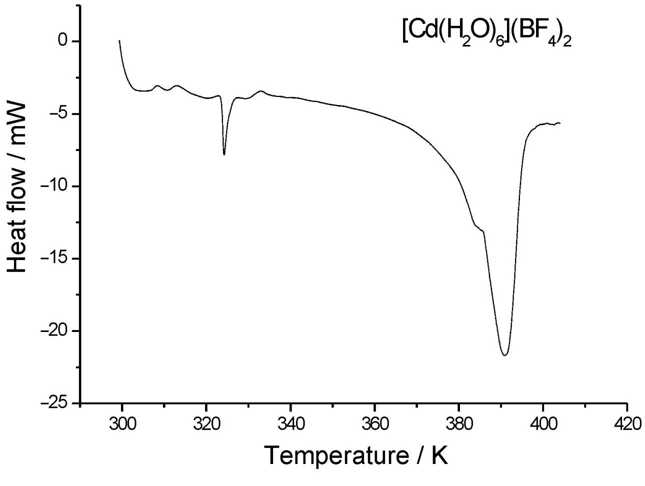

Fig. 1 DSC curve obtained for $[Cd(H_2O)_6](BF_4)_2$ at a constant heating rate of 10 K min^{-1}

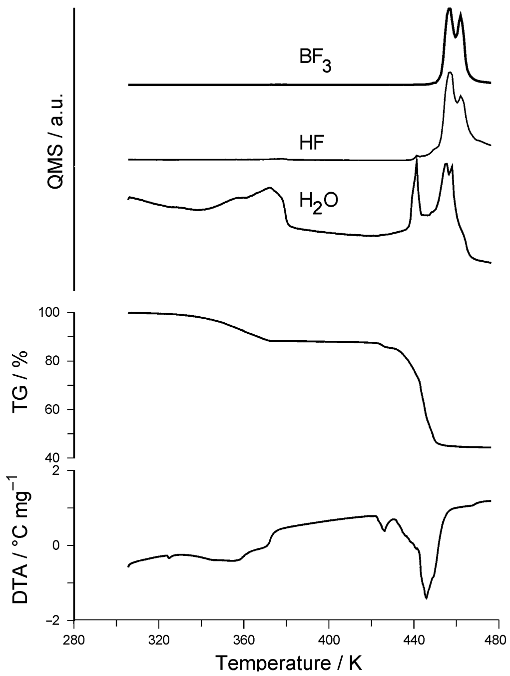

Fig. 2 DTA, TG and QMS curves obtained for $[Cd(H_2O)_6](BF_4)_2$ at a constant heating rate of 2 K min^{-1} in the flow of air

$T_{melt.}$=391 K. The first one is connected with the phase transition proceeding in the frame of the solid state (ΔH=0.6 kJ mol^{-1}) and the second one is sample melting (ΔH=18.9 kJ mol^{-1}).

A thermal analysis of seven $[Cd(H_2O)_6](BF_4)_2$ samples of different masses was made under different experimental conditions. The results were similar, regardless the varying sample masses, the kind of the flowing medium and as well as the applied heating rate. The only difference was that particular steps of the sample decomposition took place at slightly lower temperatures whereas the heating rate was slower. Figure 2 presents exemplarily DTA, TG and QMS curves for a $[Cd(H_2O)_6](BF_4)_2$ sample of 9.97 mg measured in the flow of air at constant heating rate of 2 K min^{-1}. A small (but very well reproducible) endothermic peak of the DTA curve at ca 325 K, which was not connected with any mass loss (TG curve) was detected. It was connected with the T_{C1} phase transition which took place in the solid state, as we discovered earlier [3] and also registered by the above mentioned DSC measurements. One can see in Fig. 2 that the thermal decomposition of $[Cd(H_2O)_6](BF_4)_2$ started just at the T_{C1} phase transition, and it took effect in two main stages. The first one was connected with a very broad endothermic peak on the DTA curve, which was extended from ca 330 to 380 K. DSC measurements as well as the microscopic observation of the sample proved that this peak was connected with sample melting. Moreover, the QMS results proved the connection with sample dehydration. The average mass loss in the first stage of the decomposition, as calculated from the TG curve, equaled 9.6±2.4% of the initial sample mass. The calculated value for freeing two water molecules per one formula of $[Cd(H_2O)_6](BF_4)_2$ equaled 9.1%. Therefore, we suggest that the first stage of the $[Cd(H_2O)_6](BF_4)_2$ decomposition should be connected with its dehydration to $[Cd(H_2O)_4](BF_4)_2$, which, while being subsequently heated, melted at ca 391 K. Later, in the second stage, the subsequent decomposition of $[Cd(H_2O)_4](BF_4)_2$ at a liquid phase took place, in fact, in the three steps, as indicated by the QMS curves presented in Fig. 2. In the first step, at ca 425 K, only H_2O molecules were released, and at ca 445 K, BF_3 and HF molecules were released as well as along with water. The average sample mass loss after the second stage of the decomposition equal to 58.7±2.5% of the initial sample mass, implies the formation of CdF_2 (theoretical value: 61.8%). The X-ray diffraction patterns for the solid decomposition product confirmed CdF_2, as was identified using JCPDS-ICDD data.

Conclusions

- The solid-solid phase transition from room temperature to the high-temperature phase of $[Cd(H_2O)_6](BF_4)_2$ proceeds at T_{C1}=324 K.
- The dehydration process of $[Cd(H_2O)_6](BF_4)_2$ starts just at T_{C1} and, after freeing two H_2O molecules per one formula unit, the crystals of a new complex – $[Cd(H_2O)_4](BF_4)_2$ – melt at $T_{\text{melt.}}$=391 K. Subsequent heating of the melted sample at first leads only to the subsequent dehydration, and later prompts the simultaneous freeing of H_2O, HF and BF_3 molecules, until nothing else but solid CdF_2 remains.
- $[Cd(H_2O)_4](BF_4)_2$ obtained in the course of this experiment, as an intermediate product of the decomposition of $[Cd(H_2O)_6](BF_4)_2$, is not consistent with the results of some previous studies, [8] and [9], which described the formation of $Cd(BF_4)_2\cdot$
- $3H_2O$ and $Cd(BF_4)_2\cdot 2H_2O$, respectively.

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