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# THERMAL BEHAVIOUR OF $[Ca(H_2O)_4](NO_3)_2$

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Melting process and thermal decomposition of $[Ca(H_2O)_4](NO_3)_2$ was studied by thermogravimetry analysis (TG), differential scanning calorimetry (DSC) and simultaneous differential thermal analysis (SDTA) at a constant heating rate. The gaseous products of the decomposition were on-line identified by a quadruple mass spectrometry (QMS). Tetraaquacalcium nitrate(V) melts at $T_m$=320 K. The decomposition of the sample proceeds in three main stages. In the first stage dehydration of $[Ca(H_2O)_4](NO_3)_2$ to anhydrous $Ca(NO_3)_2$ undergoes in two steps, in which consecutively 1/4 and 3/4 of all $H_2O$ molecules are liberated. The thermal dehydration process starts just above ca. 302 K and continues up to ca. 475 K. In the second stage (475–775 K) anhydrous $Ca(NO_3)_2$ remains unchanged. The third stage is connected with the melting of anhydrous $Ca(NO_3)_2$ at $T_m$=816 K and next with its decomposition in the liquid phase to nitrogen oxide, oxygen, nitrogen and solid CaO.

**Keywords:** *anhydrous calcium nitrate(V), DSC, DTA, melting points, tetraaquacalcium nitrate(V), TG, thermal decomposition*

## Introduction

The melting and thermal decomposition of $[Ni(H_2O)_6](NO_3)_2$ were the subject of our former studies [1]. A review of the thermal decomposition of other hexaaquametal(II) nitrates(V) was given by Małecka [2] and Małecki *et al*. [3]. The same subject matter was studied also for $[Mg(H_2O)_6](NO_3)_2$ by Odochian [4] and for anhydrous calcium nitrate $Ca(NO_3)_2$ by Ettarh and Galwey [5]. As a natural extension of those studies we present here the results for $[Ca(H_2O)_4](NO_3)_2$.

The title compound crystallizes in monoclinic crystal system in the space group No. 14=$P2_1/n$. The unit cell contains two $[Ca_2(H_2O)_8](NO_3)_4$ dimers, joined by hydrogen bonds [6–9].

The general aim of this study was to gain a better understanding of mechanism of thermal decomposition of the tetraaquacalcium nitrate(V), particularly of the dehydration process, and to compare obtained results with those for $[Mg(H_2O)_6](NO_3)_2$ and $[Ni(H_2O)_6](NO_3)_2$. Additionally, we draw attention to how experimental conditions can influence for obtained results.

## Experimental

### *Materials and methods*

Tetraaquacalcium nitrate(V) was synthesized by treating calcium carbonate with water-diluted nitric acid(V). The solution was concentrated by mild heating and colorless crystals, obtained after cooling 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 stored in hygrostat. The composition of the compound was established through a chemical analysis and verified by infrared and Raman spectra [9].

The thermogravimetry analyses (TG) with simultaneous differential thermal analyses (SDTA) measurements were performed using a Mettler Toledo 851$^e$ apparatus. Sample of mass around 27 mg was placed in a 150 μL open corundum crucible. The measurements were made in a flow of argon (60 mL $min^{-1}$), within temperature range of 300–873 K. The TG measurements were performed at a constant heating rate of 5 K $min^{-1}$. The simultaneous evolved gas analysis (SEGA) was performed during the experiments by a joined on-line quadruple mass spectrometer (QMS) using a Thermostar-Balzers apparatus. The temperature was measured by a Pt–Pt/Rh thermocouple with an accuracy of ±0.5 K.

The differential scanning calorimetry (DSC) measurements at 95–300 K were performed with a Perkin-Elmer PYRIS 1 DSC apparatus. The samples of masses: 19.49 and 17.54 mg were placed in an aluminum vessel and closed by compressing. Another empty aluminum vessel was used as a reference holder. Two characteristic temperatures of the DSC peaks obtained on heating and on cooling the sample were computed: temperature of the peak maximum ($T_{peak}$) and temperature calculated from a slope of the left-hand side of the peak ($T_{onset}$).

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DSC measurements in temperature range of 300–873 K were performed using a Mettler Toledo 821$^e$ calorimeter. The sample of mass equals to 16.18 mg was placed in 40 μL aluminum open crucible, under constant flow of argon (80 mL min$^{-1}$), with the heating rate equals to 5 K min$^{-1}$.

## Results and discussion

Figure 1 shows the DSC results obtained in the temperature range of 90–330 K on cooling and heating of $[Ca(H_2O)_4](NO_3)_2$ sample in hermetically closed vessel at the scanning rate of 20 K min$^{-1}$. During the heating, three peaks on DSC curve (upper curve) were registered as two small and one large endothermic peak. These two small peaks are connected with the reversible phase transitions in solid-state at $T_{C1}^{h}$=243.7 K and $T_{C2}^{h}$=203.3 K (on heating) and at $T_{C1}^{c}$=222.0 K and $T_{C2}^{c}$=201.5 K (on cooling). Studies of these phase transitions are the subject of our next paper [9]. Third large peak is connected with the melting of the sample at $T_m$=318 K. The melting point is connected with the large enthalpy and entropy changes ($\Delta H$=34.28 kJ mol$^{-1}$, $\Delta S$=107.94 J mol$^{-1}$ K$^{-1}$). The melting process was also observed visually using a microscope.

Next, while cooling the liquid sample from 330 to 90 K, at a rate of 20 K min$^{-1}$, no peaks on the DSC curve were recorded, as can be seen in Fig. 2. One can observe the changes of baseline during the cooling and heating at temperature $T_g$≈220 K. Very probably, it is a vitreous transition and a metastable glass phase was formed. Subsequent heating of this glass sample from 90 to 330 K, a spontaneous re-crystallization into a crystalline phase can be observed at ca. 247 K, as an exothermic sharp peak. Subsequent heating leads to the melting of the crystal at ca. 318 K [9].

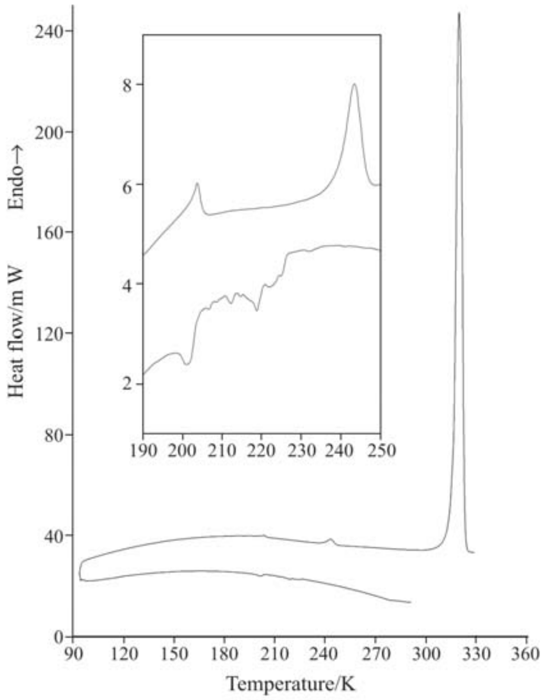

**Fig. 1** DSC curves registered on cooling and heating of $[Ca(H_2O)_4](NO_3)_2$ sample at a rate of 20 K min$^{-1}$ in the temperature range of 90–330 K. Insertion shows an enlargement of heat flow *vs*. *T* dependence in 190–250 K range

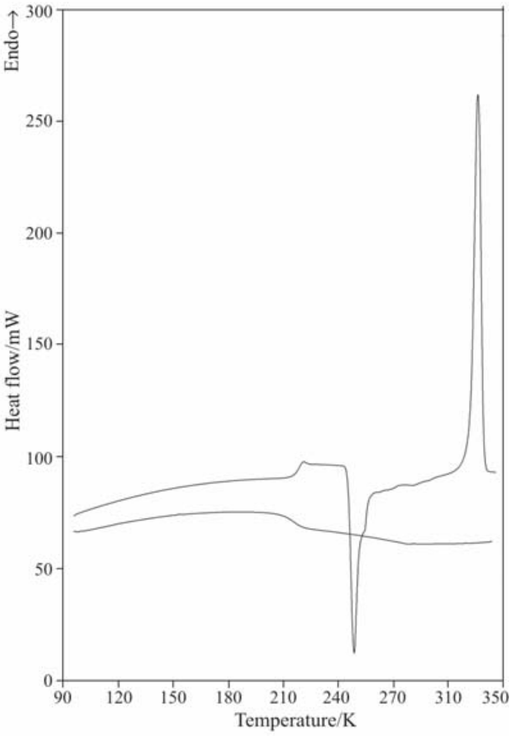

**Fig. 2** DSC curves registered on cooling and subsequent heating of the melted $[Ca(H_2O)_4](NO_3)_2$ sample at a rate of 20 K min$^{-1}$ in the temperature range of 90–330 K

Figure 3 shows the DSC results obtained in the temperature range of 300–873 K with the scanning rate of 5 K min$^{-1}$ for $[Ca(H_2O)_4](NO_3)_2$ sample in non-hermetically closed aluminum vessel. This measurement was performed just before TG analysis in order to check the stability of the compound and to qualitative comparison of these results with thermal analysis. Endothermic peak clearly seen at 320 K very well coincide with this from DSC results registered at a rate of 20 K min$^{-1}$ for hermetically closed vessel. This anomaly can be interpreted as the melting of $[Ca(H_2O)_4](NO_3)_2$ (melting I in Fig. 3). Additionally, some endothermic peaks above 400 and 430 K can be also observed. They can be interpreted as connected with the sample dehydration, what will be shown below by means of the thermal analysis. In the vicinity of 816 K one can see the endothermic peak connected with melting of anhydrous $Ca(NO_3)_2$ (melting II in Fig. 3). Next to this huge endothermic peak is corresponding to decomposition of the sample.

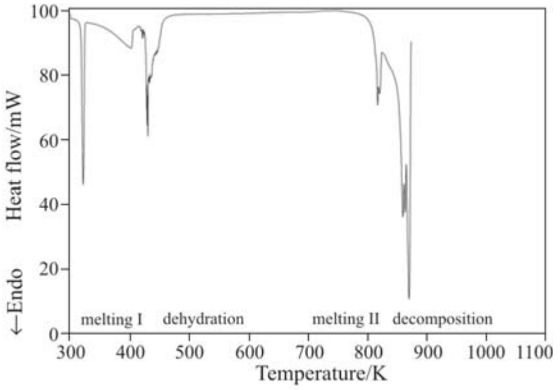

**Fig. 3** DSC curve for $[Ca(H_2O)_4](NO_3)_2$ in the range of 300–873 K

Figure 4 shows TG, DTG, QMS and SDTA curves recorded for $[Ca(H_2O)_4](NO_3)_2$ at a constant heating rate of 5 K $min^{-1}$ in the temperature range of 300–873 K. During the TG experiment, the QMS spectrum of masses were followed from $m/e=1$ to 100, however, for reasons of graphic readability, only the masses of $m/e=17$, 18, 28, 30 and 32 – representing OH, $H_2O$, $N_2$, NO and $O_2$ are shown.

TG, DTG and QMS curves show that the decomposition of the sample proceeds in three main stages (I, II and III). It can be observed that the first stage involves freeing all of $H_2O$ molecules. The dehydration undergo in the two steps (Ia and Ib). Statistically at step Ia 1.3 molecules of water per one formula unit are freeing and the rest 2.7 molecules of water are freeing at step Ib. Summary in the temperature range of 300–475 K all molecules of water are freeing and the anhydrous $Ca(NO_3)_2$ is formed. In the temperature range of 475–775 K (stage II) the investigated anhydrous compound $Ca(NO_3)_2$ remains unchanged. It means that $Ca(NO_3)_2$ is very stable in the mentioned above temperature range. However, it is not very common feature, because for example the anhydrous gallium nitrate does not form at any temperature as the reaction consists of coupled dehydration/decomposition processes [10]. The third stage is connected with decomposition of resulting $Ca(NO_3)_2$ to nitrogen oxide, oxygen, nitrogen and solid CaO. 23.9% of the initial mass of the sample remained after the third stage of the decomposition and this quite well corresponds to the theoretical amount of calcium oxide (Table 1). The temperatures, percentage mass of losses and the products of the decomposition of $[Ca(H_2O)_4](NO_3)_2$ at particular stages are presented in Table 1.

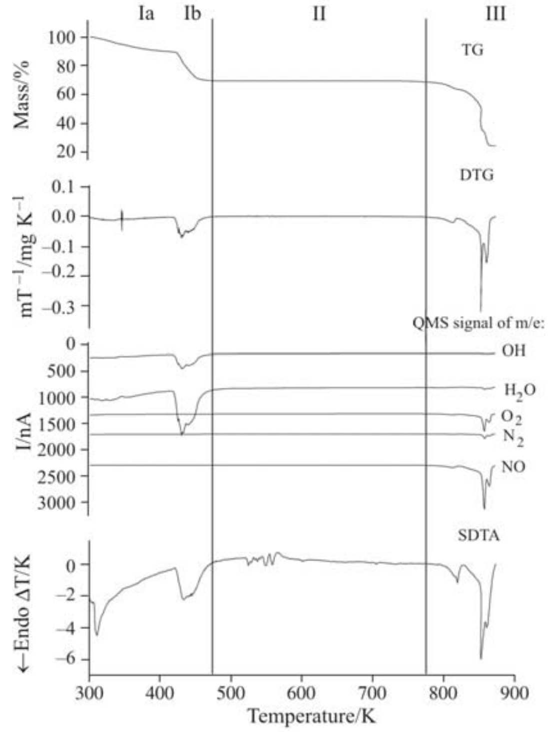

**Fig. 4** TG, DTG, QMS and SDTA curves for $[Ca(H_2O)_4](NO_3)_2$ in the range of 300–873 K, at a constant heating rate of 5 K $min^{-1}$

The profile of the SDTA curve of $[Ca(H_2O)_4](NO_3)_2$ shows four endothermic peaks. The first endothermic peak can be explained as a melting process of tetraaquacalcium nitrate(V) (melting I). Immediately after this melting $[Ca(H_2O)_4](NO_3)_2$ starts loosing $H_2O$ molecules. This process can be described by the two steps of the dehydration (stages Ia and Ib). The first step corresponds to liberation statistically of 1.3 $H_2O$ molecules and the second corresponds to liberation of the rest 2.7 $H_2O$ molecules per one formula unit. The process of dehydration undergoes according to the following reactions:

$$\text{Ia: } [Ca(H_2O)_4](NO_3)_2\text{®}[Ca(H_2O)_3](NO_3)_2+H_2O$$
$$\text{Ib: } [Ca(H_2O)_3](NO_3)_2\text{®}Ca(NO_3)_2+3H_2O \quad (1)$$

**Table 1** Parameters of $[Ca(H_2O)_4](NO_3)_2$ thermal analysis; sample mass=27 mg

| Stage number | Temperature range/K | Mass loss at the stage/% | Mass after decomposition/% | Calculated values/% | Products of the decomposition |
|---|---|---|---|---|---|
| Ia | 302–424 | 10.5 | | 7.6 | $H_2O$ |
| Ib | 424–475 | 20.0 | | 22.9 | $3H_2O$ |
| II | 475–775 | 0 | | 0 | |
| III | 775–871 | 45.5 | | 45.7 | $CaO+0.5N_2+NO+2O_2$ |
| | | | 23.9 | 23.7 | CaO |

Next endothermic peak present in SDTA curve at 816 K corresponds to melting of anhydrous compound. The last broad endothermic peak (at 860 K) can be explained as connected with the process of the $Ca(NO_3)_2$ decomposition, according to the following reactions:

$$\begin{aligned} \text{III: } & Ca(NO_3)_2 \leftrightarrow Ca(NO_2)_2+O_2\text{®} \\ & CaO+0.5N_2+NO+2O_2 \qquad (2) \end{aligned}$$

According to Doumeng [11], formation of $Ca(NO_2)_2$ and $O_2$ is the most probable first step of $Ca(NO_3)_2$ decomposition and it may occur just during reactant melting. However, other concurrent or subsequent reactions undoubtably participate. Among others, there are reactions which yields to the reformation of $Ca(NO_3)_2$ from $Ca(NO_2)_2$ and NO or $NO_2$, with production of $N_2$ or NO, respectively. Reaction (2) proposed by us for the stage III are consistent with the information derived from QMS measurement (Fig. 4). However, these reactions are not compatible with the results obtained by Ettarh and Galwey [5] on heating of $Ca(NO_3)_2$ (dehydrated compound, but retaining a small amount of water) at 10 K $min^{-1}$ in a flowing nitrogen atmosphere. They proposed the following mechanism of the decomposition:

$$Ca(NO_3)_2\text{®}CaO+0.25N_2+O_2+1.5NO_2 \qquad (3)$$

This reaction seems us to be not correct because one should remember that the nitrogen oxides: $N_2O_5$, $N_2O_4$ and $NO_2$ are unstable in the temperature of nitrates decomposition, which is about 800 K, and can not be taken into consideration in this mechanism. Moreover the temperatures both of the melting (836 K) and of the decomposition (949 K) of $Ca(NO_3)_2$ obtained by these authors are even a little higher than those determined by us.

Careful comparison of SDTA and DSC curves shows their great similarity, however DSC results presented in Fig. 3 are more detailed. The main difference is fact that on the DSC curve one can see five endothermic peak instead of four peaks registered on SDTA curve. Dehydration process is better visible on the DSC curve. Namely, in the temperature range of 330–470 K two endothermic peaks clearly show two stages of dehydration resulting in the formation of $[Ca(H_2O)_3](NO_3)_2$ and $Ca(NO_3)_2$, according to Reaction (1).

The melting and thermal decomposition of $[Ca(H_2O)_4](NO_3)_2$ is somewhat different than these of $[Ni(H_2O)_6](NO_3)_2$ [1] and $[Mg(H_2O)_6](NO_3)_2$ [4]. Firstly, contrary to $[Ca(H_2O)_4](NO_3)_2$, which melts in its own coordination water in one stage, they both indicate an interesting two-stage melting process [12]. Moreover, dehydration of $[Ni(H_2O)_6](NO_3)_2$ undergoes in three main stages and that of $[Mg(H_2O)_6](NO_3)_2$ in two main stages. In the case of $[Ca(H_2O)_4](NO_3)_2$ it undergoes in two stages. The particular dehydration temperatures of $[Ni(H_2O)_6](NO_3)_2$ and $[Mg(H_2O)_6](NO_3)_2$ are higher than those of $[Ca(H_2O)_4](NO_3)_2$. Process of the decomposition of hexaaquanickel(II) nitrate(V) leads directly to the final products ($H_2O$, NO, $N_2O$ and $N_2$), without the formation of $Ni(NO_3)_2$ as an intermediate product, whereas in the case of $[Ca(H_2O)_4](NO_3)_2$ the decomposition is followed by the formation of anhydrous $Ca(NO_3)_2$, which firstly indicates melting process and just next decomposes to the final products. However, decomposition process of $[Mg(H_2O)_6](NO_3)_2$ undergoes similarly and anhydrous $Mg(NO_3)_2$ decomposes to final products. The thermal decomposition process of $[Ca(H_2O)_4](NO_3)_2$ is more similar to that for $[Mg(H_2O)_6](NO_3)_2$ than to that for $[Ni(H_2O)_6](NO_3)_2$.

We studied also the thermal decomposition of $[Ni(NH_3)_6](NO_3)_2$, $[Ni(ND_3)_6](NO_3)_2$, $[Mg(NH_3)_6](NO_3)_2$ [13] and $[Cd(NH_3)_6](NO_3)_2$ [14], where after the deammination the very similar decomposition of a corresponding nitrates(V) takes place.

## Conclusions

The results obtained in this work and their comparison with the literature data have led us to the following conclusions:

- Tetraaquacalcium nitrate(V) has two solid-solid phase transitions at: $T_{C1}^{h}$=243.7 K and $T_{C2}^{h}$=203.3 K (on heating) and at $T_{C1}^{c}$=222.0 K and $T_{C2}^{c}$=201.5 K (on cooling). Additionally one vitreous phase transition at $T_g$»220 K is observed. The compound melts at $T_m$=318 K. The melting point is connected with the large enthalpy and entropy changes ($\Delta H$=34.28 kJ $mol^{-1}$, $\Delta S$=107.94 J $mol^{-1}$ $K^{-1}$).
- The thermal decomposition of the title compound proceeds in three main stages. In first stage dehydration of tetraaquacalcium nitrate(V) to calcium nitrate(V) undergoes in two steps and all (0.25 and 0.75) of $H_2O$ molecules are liberated. In the second stage the investigated anhydrous $Ca(NO_3)_2$ remains unchanged. The third stage is connected with the melting of anhydrous calcium nitrate(V) at $T_m$=816 K and subsequent decomposition, which occurs in the liquid phase, to nitrogen oxide, oxygen, nitrogen and solid CaO.

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