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THERMAL BEHAVIOR OF $[Ca(H_2O)_4](ClO_4)_2$ AND $[Ca(NH_3)_6](ClO_4)_2$

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Melting processes and thermal decompositions of $[Ca(H_2O)_4](ClO_4)_2$ and $[Ca(NH_3)_6](ClO_4)_2$ were studied by thermogravimetry analysis (TG) and differential scanning calorimetry (DSC). The gaseous products of the decomposition were on-line identified by a quadruple mass spectrometry (QMS).

In both compounds the processes of loss of the ligands start at ca. 340–350 K and continue up to ca. 600 K. Tetraaquacalcium perchlorate dissolves in own coordination water (melts) at T_m=350 K. The decomposition of the sample proceeds in three main stages. In stage I (351–602 K) dehydration of $[Ca(H_2O)_4](ClO_4)_2$ to anhydrous $Ca(ClO_4)_2$ undergoes in two steps, in which consecutively 2/4 and 2/4 of all H_2O molecules are liberated. In stage II (602–701 K) anhydrous $Ca(ClO_4)_2$ has one solid–solid phase transition at T_c=619 K and then melts at T_m=689 K. Stage III (above 700 K) is connected with decomposition of melted $Ca(ClO_4)_2$ to oxygen and solid $CaCl_2$. The decomposition of the $[Ca(NH_3)_6](ClO_4)_2$ proceeds also in three main stages. In stage I (341–601 K) deamination of $[Ca(NH_3)_6](ClO_4)_2$ to $Ca(ClO_4)_2$ undergoes in two steps, in which consecutively 3/6 and 3/6 of all NH_3 molecules are liberated. Stages II and III (601–868 K) are exactly the same as they were observed for $[Ca(H_2O)_4](ClO_4)_2$.

Keywords: *anhydrous calcium perchlorate, DSC, hexaamminecalcium perchlorate, melting points, tetraaquacalcium perchlorate, TG, thermal decomposition*

Introduction

Melting and thermal decomposition processes of dozen or so aquametal(II) perchlorates have been investigated up to now [1–6]. The enthalpies of dissolution of anhydrous $Mg(ClO_4)_2$ and $Sr(ClO_4)_2$ and also of hydrated $M(ClO_4)_2$, where M=Mg, Ca, Sr and Ba, in water have been measured and the standard enthalpies of their formation have been determined [7]. The melting temperature of the $[Ca(H_2O)_4](ClO_4)_2$ has been measured by Dobrynina *et al*. [8, 9]. Unfortunately, there is a lack in the literature of the data concerning thermal decomposition process of hexaamminemetal(II) and tetraaquametal(II) perchlorates. As a natural extension of those studies we present here the results for $[Ca(H_2O)_4](ClO_4)_2$ and for $[Ca(NH_3)_6](ClO_4)_2$.

Crystals of tetraaquacalcium perchlorate are triclinic, space group No. 2=P-1, with the following unit cell constants: a=5.582 Å, b=7.817 Å, c= 11.769 Å, α=79.271°, β=89.672°, γ=88.924° and Z=2 [10]. The structure of $[Ca(H_2O)_4](ClO_4)_2$ crystals is built from tetraaquacalcium cations and perchlorate anions joined with one another by a network of hydrogen bonds. $[Ca(H_2O)_4](ClO_4)_2$ has four solid phases in the temperature range of 95–295 K [11].

At room temperature hexaamminecalcium perchlorate crystallizes in the cubic system ($Fm\bar{3}m$ space group) with cell parameter: a=11.685 Å and four molecules per unit cell and is isostructural with many other hexaamminemetal(II) complexes [12]. $[Ca(NH_3)_6](ClO_4)_2$ has between 95 and 295 K one solid phase transition at T_C^h=123.3 K (on heating). According to Fourier transform middle infrared spectra (FT-MIR) measurements the observed phase transition is probably connected with the change of the crystal structure [13].

The general aim of these studies was to gain a better understanding of a mechanism of thermal decomposition of the tetraaquacalcium perchlorate and hexaamminecalcium perchlorate, particularly of the dehydration and deammination processes, respectively. We would like also to make a comparison between the results obtained for these both compounds. The next aim was to compare obtained results for $[Ca(H_2O)_4](ClO_4)_2$ with those for $[M(H_2O)_6](ClO_4)_2$, where M=Mg, Ni, Mn, Fe, Co, Cu, Zn, Cd and Hg.

Experimental

The tetraaquacalcium perchlorate $[Ca(H_2O)_4](ClO_4)_2$ was purchased from Aldrich Chemical Company, Inc. and used without further purification. The examined compound $[Ca(NH_3)_6](ClO_4)_2$ was obtained from tetraaquacalcium perchlorate. The tetraaquacalcium perchlorate complex placed in a quartz vessel and put in a

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glass tube, through which dry gaseous ammonia was blown, and the tube was placed in an oven, according to the method proposed by Smith and Koch [14]. First the tube was heated for several days up to about 400 K until all the water from $[Ca(H_2O)_4](ClO_4)_2$ was lost and and hexaamine complex was composed. Then, after cooling the tube to room temperature, the obtained compound was put into a desiccator for several hours in order to get rid of ammonia excess.

Before the measurements were taken, the composition of the compounds under study was determined based on its calcium and ammonia content by titration using EDTA and HCl, respectively. The average calcium content was found to be equal to the theoretical value within an error margin of ca. 0.3% for $[Ca(H_2O)_4](ClO_4)_2$ and of ca. 1% for $[Ca(NH_3)_6](ClO_4)_2$. The average contents of NH_3 was found to be equal to the theoretical values within the error limit of ca. 2%. Figures 1 and 2 present the comparison of FT-MIR and FT-RS spectra of $[Ca(H_2O)_4](NO_3)_2$ and $[Ca(NH_3)_6](ClO_4)_2$, respectively. The list of the band positions of the Raman and infrared spectra at room temperature and their assignments for investigated compounds are presented in Table 1. Assignments of the bands of all spectra are with good agreement with literature data [15–17]. Thus, chemical analysis confirmed proper composition of the investigated compounds $[Ca(H_2O)_4](ClO_4)_2$ and $[Ca(NH_3)_6](ClO_4)_2$.

Fourier transform middle-infrared absorption measurements (FT-MIR) were performed using a

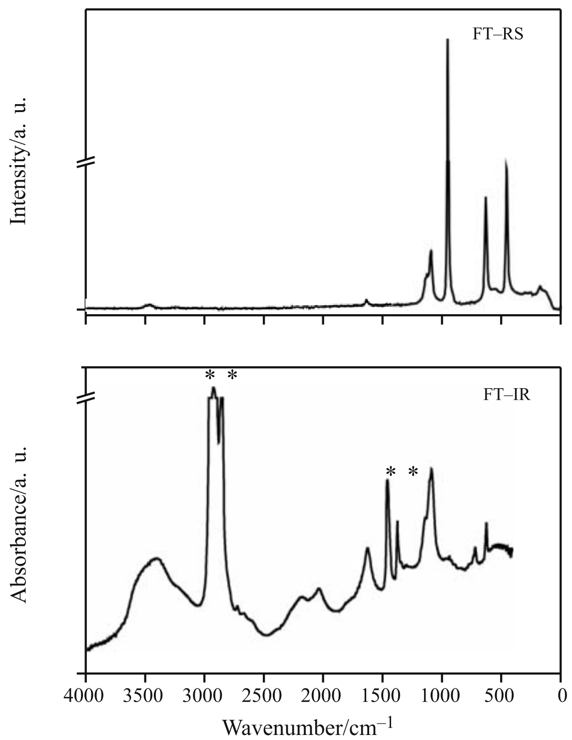

Fig. 1 Comparison of the room temperature Raman and infrared spectra of $[Ca(H_2O)_4](ClO_4)_2$

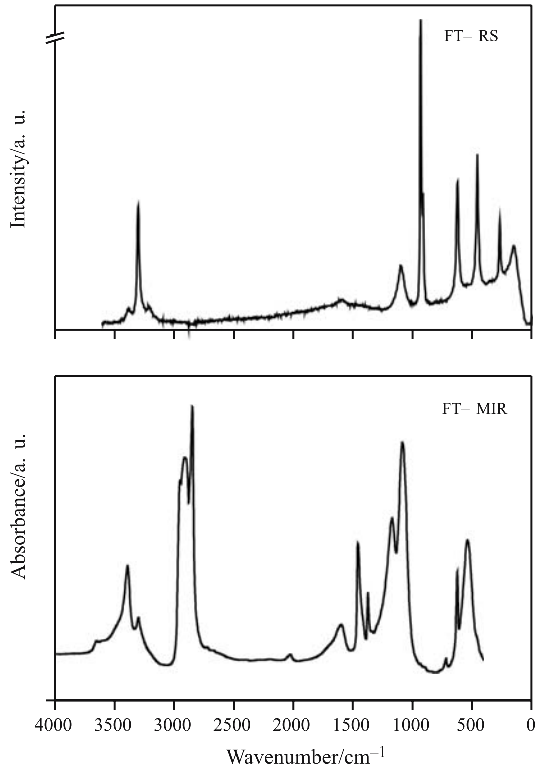

Fig. 2 Comparison of the room temperature Raman and infrared spectra of $[Ca(NH_3)_6](ClO_4)_2$

Bruker EQUINOX-55 spectrometer. The FT-MIR measurements in room temperature were performed in the frequency range of 4000–400 cm^{-1} with a resolution of 2 cm^{-1}. Title powdered compounds were mixed with Nujol and drifted on KBr pellet.

Fourier transform Raman scattering measurements (FT-RS) were performed at room temperature with a Bio-Rad spectrometer, resolution 4 cm^{-1}. The incident radiation (λ=1064 nm) was from the Neodymium laser YAG Spectra-Physics.

To sum up, the FT-RS and FT-MIR spectra, X-ray diffraction and chemical analysis proved the purity, proper composition and crystal structure of the examined compounds.

The thermogravimetry analyses (TG) with simultaneous differential thermal analyses (SDTA) measurements were performed using a Mettler-Toledo 851^e apparatus. Samples of masses equal to 9.9321 mg of $[Ca(H_2O)_4](ClO_4)_2$ and 6.7381 mg of $[Ca(NH_3)_6](ClO_4)_2$ were placed in 150 μL platinum crucibles. The measurements were made in a flow of argon (60 mL min^{-1}), within temperature range of 312–883 K. TG measurements were performed at a constant heating rate of 10 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.

Table 1 List of band positions of the Raman (FT-RS) and infrared (FT-MIR) spectra of $[Ca(H_2O)_4](ClO_4)_2$ and $[Ca(NH_3)_6](ClO_4)_2$ at room temperature

$[Ca(H_2O)_4](ClO_4)_2$			$[Ca(NH_3)_6](ClO_4)_2$		
Frequency/cm^{-1}		Assignments	Frequency/cm^{-1}		Assignments
RS	IR		RS	IR	
				3649	$\nu_{as(NH)}F_{1u}$
	3498	$\nu_{s(OH)}$		3392	$\nu_{s(NH)}F_{1u}$
3477	3409	$\nu_{as(OH)}$	3387		$\nu_{as(NH)}F_{2g}$
			3302		$\nu_{s(NH)}A_{1g}$
				3301	$\nu_{s(NH)}F_{1u}$
			3207		$\nu_{s(NH)}E_g$
				1600	$\delta_{as(HNH)}F_{1u}$
1634	1628	$\delta_{d(HOH)}$	1602		$\delta_{as(HNH)}F_{2g}$
1125	1141	$\nu_{as(ClO)}F_2$		1173	$\nu_{as(ClO)}F_2$
1094	1089	$\nu_{as(ClO)}F_2$	1103	1088	$\nu_{as(ClO)}F_2$
953		$\nu_{s(ClO)}A_1$	937		$\nu_{s(ClO)}A_1$
			916		$2\delta_{(OClO)}E+A_1$
	721	$\rho_{r(H_2O)}$		722	$\rho_{r(NH_3)}F_{1u}$
634	627	$\delta_{d(OClO)}F_2$	627	627	$\delta_{d(OClO)}F_2$
				542	
459		$\delta_{d(OClO)}E$	463		$\delta_{d(OClO)}E$
			274		
177		$\nu_{L(lattice)}$	156		$\nu_{L(lattice)}E_g$

DSC measurements in temperature range of 253–883 K were performed using a Mettler-Toledo 821^e calorimeter. The samples of masses equal to 8.61 mg for $[Ca(H_2O)_4](ClO_4)_2$ and 3.33 mg for $[Ca(NH_3)_6](ClO_4)_2$ were placed in 40 μL aluminum open crucibles, measurements were performed under constant flow of argon (80 mL min^{-1}), with the heating rate equals to 10 K min^{-1}.

Results and discussion

Figures 3a and b show the DSC results obtained in the temperature range of 253–883 K with the scanning rate of 10 K min^{-1} for $[Ca(H_2O)_4](ClO_4)_2$ and $[Ca(NH_3)_6](ClO_4)_2$ samples, respectively, in non-hermetically closed aluminum vessel. Endothermic peak clearly seen at 350 K in Fig. 3a can be interpreted as connected with the dissolving of $[Ca(H_2O)_4](NO_3)_2$ in own coordinated water (denotes as melting I in Fig. 3a). This is in excellent agreement with the data obtained by Dobrynina [8, 9]. It should be pointed out that the melting process of $[Ca(H_2O)_4](ClO_4)_2$ is quite different from melting processes registered for compounds of the type: $[M(H_2O)_6](ClO_4)_2$, where M=Mg, Ni, Mn, Fe, Co, Cu, Zn, Cd and Hg. All of these compounds melt in higher temperatures (above 420 K). Below 350 K all of them indicated at least one solid-state phase transition.

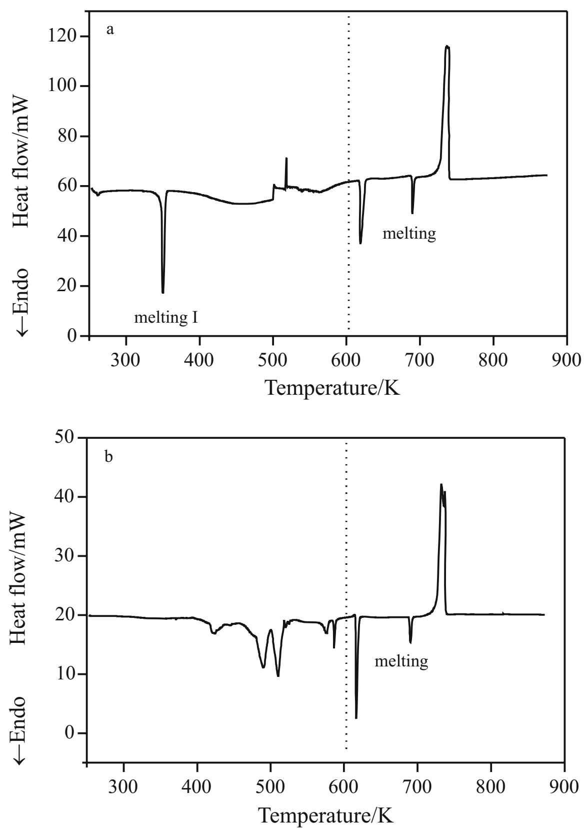

Fig. 3 DSC curves for a – $[Ca(H_2O)_4](ClO_4)_2$ and for b – $[Ca(NH_3)_6](ClO_4)_2$ in the range of 253–873 K. The vertical dashed line denotes temperature above which anhydrous $Ca(ClO_4)_2$ is formed in both cases

Additionally, two very broad endothermic peaks above 457 and 560 K can be also observed in Fig. 3a. They can be interpreted as connected with the sample dehydration, what will be proved below by means of the TG results. The process of dehydration undergoes according to the following reactions:

Ia $[Ca(H_2O)_4](ClO_4)_2 \rightarrow [Ca(H_2O)_2](ClO_4)_2 + 2H_2O$ (1)

Ib $[Ca(H_2O)_2](ClO_4)_2 \rightarrow Ca(ClO_4)_2 + 2H_2O$ (2)

Endothermic peak registered in DSC curve at 619 K is connected with the phase transition in the solid phase of $Ca(ClO_4)_2$. Successive endothermic peak on DSC curve at 689 K corresponds to melting of anhydrous compound. The last broad and large exothermic peak (at 735 K) can be explained as connected with the process of the $Ca(ClO_4)_2$ decomposition with formation of $CaCl_2$ and production of oxygen, according to the following reaction:

III $Ca(ClO_4)_2 \leftrightarrow CaCl_2 + 4O_2$ (3)

Five endothermic peaks clearly visible in DSC curve for $[Ca(NH_3)_6](ClO_4)_2$ at the temperature range of 300–601 K (Fig. 3b) are connected with the liberation of all NH_3 ligands. The process of deamination undergoes according to the following reactions:

Ia $[Ca(NH_3)_6](ClO_4)_2 \rightarrow [Ca(NH_3)_3](ClO_4)_2 + 3NH_3$ (4)

Ib $[Ca(NH_3)_3](ClO_4)_2 \rightarrow Ca(ClO_4)_2 + 3NH_3$ (5)

Endothermic peak registered in DSC curve at 616 K is connected with the phase transition in solid-state of $Ca(ClO_4)_2$. Successive endothermic peak present in DSC curve at 690 K corresponds similarily to melting of $Ca(ClO_4)_2$, as former. The last large and broad exothermic peak (at 733 K) can be explained as connected with the process of the $Ca(ClO_4)_2$ decomposition with forming $CaCl_2$ and production of oxygen, according to presented already above reaction (3).

Figure 4 shows TG, DTG and QMS curves recorded for $[Ca(H_2O)_4](ClO_4)_2$ at a constant heating rate of 10 K min^{-1} in the temperature range of 312–883 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=16, 17, 18 and 32 – representing O, OH and O_2 are shown. The 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 2 molecules of water per one formula unit are freeing and the rest 2 molecules of water are freeing at step Ib. Summary in the temperature range of 351–602 K all molecules of water are freeing and the anhydrous $Ca(ClO_4)_2$ is formed. In the temperature range of 602–883 K (stage II) the investigated anhydrous compound $Ca(ClO_4)_2$ has one phase transition in solid phase at T_c=619 K and then melts at T_m=689 K. The third stage is connected with decomposition of resulting $Ca(ClO_4)_2$ to oxygen and solid $CaCl_2$. 36.7% 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 chloride (Table 2). The temperatures, percentage mass of losses and the products of the decomposition of $[Ca(H_2O)_4](ClO_4)_2$ at particular stages are presented in Table 1.

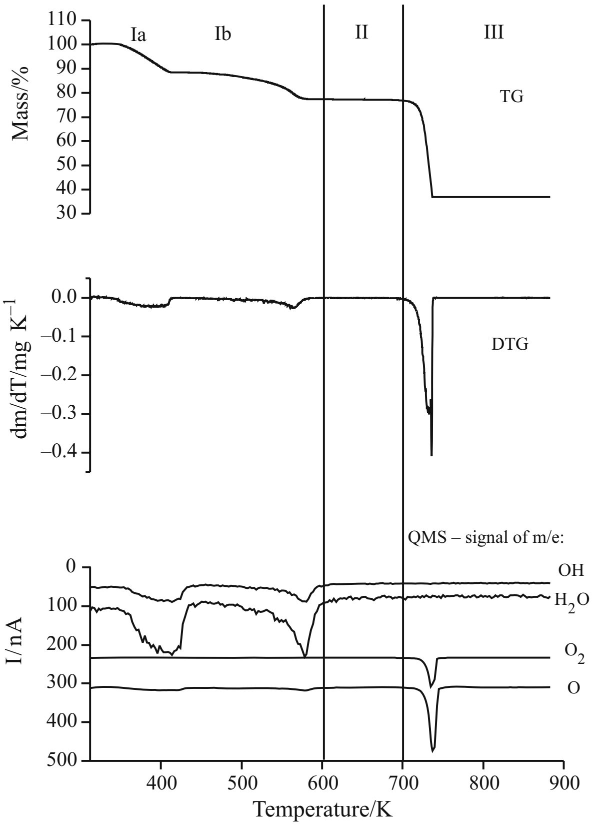

Fig. 4 TG, DTG and QMS curves for $[Ca(H_2O)_4](ClO_4)_2$ in the range of 312–883 K, at a constant heating rate of 10 K min^{-1}

Figure 5 shows TG, DTG and QMS curves recorded for $[Ca(NH_3)_6](ClO_4)_2$ at a constant heating rate of 10 K min^{-1} in the temperature range of 312–868 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=15, 16, 17 and 32 – representing NH, NH_2/O, NH_3 and O_2 are shown. The TG, DTG and QMS curves show that the decomposition of the sample proceeds in three main stages too (I, II and III). It can be observed that the first stage involves freeing all of NH_3 molecules. The deamination undergo in the two steps

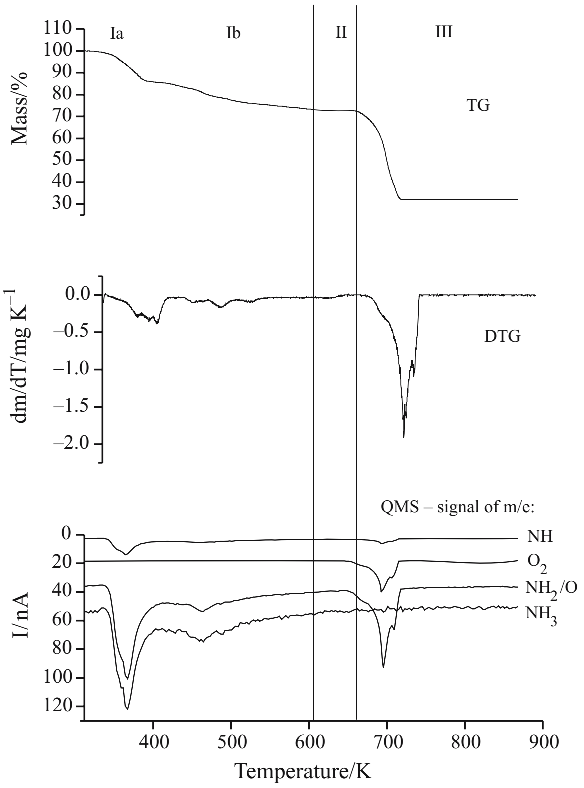

Fig. 5 TG, DTG and QMS curves for $[Ca(NH_3)_6](ClO_4)_2$ in the range of 312–868 K, at a constant heating rate of 10 K min^{-1}

(Ia and Ib). Statistically at step Ia 3 molecules of ammonia per one formula unit are freeing and the rest 3 molecules of ammonia are freeing at step Ib. Summary in the temperature range of 312–601 K all molecules of ammonia are freeing and the anhydrous $Ca(ClO_4)_2$ is formed. In the temperature range of 601–657 K (stage II) the investigated anhydrous compound $Ca(ClO_4)_2$ has one phase transition in solid state at T_c=616 K and then melts at T_m=690 K. The third stage is connected with decomposition of resulting $Ca(ClO_4)_2$ to oxygen and solid $CaCl_2$. 32.2% 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 chloride (Table 3). The temperatures, percentage mass of losses and the products of the decomposition of $[Ca(NH_3)_6](ClO_4)_2$ at particular stages are presented in Table 3.

Up to now from all known perchlorates of aquametal(II) complexes only for $[Ni(H_2O)_6](ClO_4)_2$ the TG and DSC curves were registered in the temperature range of 300–700 K [6]. Thus we were able to compare these results with obtained by us for $[Ca(H_2O)_4](ClO_4)_2$. Thermal decomposition of $[Ca(H_2O)_4](ClO_4)_2$ is somewhat different than this of $[Ni(H_2O)_6](ClO_4)_2$ [5, 6]. In the temperature range of 300–520 K $[Ni(H_2O)_6](ClO_4)_2$ is loss of 3 water molecules per formula unit and $[Ni(H_2O)_3](ClO_4)_2$ is formed. Further process of the decomposition of triaquanickel(II) perchlorate leads directly to the final products (O_2, Cl_2 and NiO is the solid remainder of this process), without the formation of $Ni(ClO_4)_2$ as an intermediate product. In the case of $[Ca(H_2O)_4](ClO_4)_2$ the decomposition is followed by the formation of anhydrous $Ca(ClO_4)_2$, which firstly has one phase transition in solid state, and next melts and finally decomposes to the final products $CaCl_2$ with oxygen releasing. The thermal decomposition process of $[Ca(H_2O)_4](ClO_4)_2$ is more similar to that one for $[Ca(H_2O)_4](NO_3)_2$ [18]. Namely, both of them dissolve in its own coordination water in one stage and next anhydrous products are formed ($Ca(ClO_4)_2$ and $Ca(NO_3)_2$, respectively). In turn, these anhydrous products firstly melt and just next decompose to the final products ($CaCl_2$ and CaO, respectively).

Table 2 Parameters of $[Ca(H_2O)_4](ClO_4)_2$ thermal analysis. Initial sample mass equaled to 9.9321 mg

Stage	T_{range}/K	Mass loss/%	Mass after decomposition/%	Mass $loss_{calc}$/%	Products of decomposition
Ia	351–465	11.6		11.6	$2H_2O$
Ib	465–602	11.3		11.6	$2H_2O$
II	602–701	0		0	
III	701–883	40.4		41.1	$CaCl_2$+$4O_2$
			36.7	35.7	$CaCl_2$

Table 3 Parameters of $[Ca(NH_3)_6](ClO_4)_2$ thermal analysis. Initial sample mass equaled to 6.7381 mg

Stage	T_{range}/K	Mass loss/%	Mass after decomposition/%	Mass $loss_{calc}$/%	Products of decomposition
Ia	341–417	14.1		14.8	$3NH_3$
Ib	417–601	13.9		14.8	$3NH_3$
II	601–657	0		0	
III	657–868	39.8		37.8	$CaCl_2$+$4O_2$
			32.2	32.6	$CaCl_2$

Conclusions

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

- $[Ca(H_2O)_4](ClO_4)_2$ melts at T_{ml}=350 K. The melting point is connected with the large enthalpy and entropy changes (ΔH=41.17±0.8 kJ mol^{-1}, ΔS=117.6±2.3 J mol^{-1} K^{-1}).
- The thermal decomposition of both title compounds is similar and proceeds in three main stages. In both compounds the first stage (ca. 340–600 K) is connected with loss of the ligands. In the second stage (ca. 600–700 K) anhydrous $Ca(ClO_4)_2$ undergoes one phase transition in the solid state at T_c=619 K and next it melts at T_m=689 K. The third stage (above 700 K) is connected with decomposition of the liquid phase of calcium perchlorate to oxygen and solid $CaCl_2$.

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