Melting and thermal decomposition of $[Ni(H_2O)_6](NO_3)_2$

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Abstract

The two-stage melting process and the thermal decomposition of $[Ni(H_2O)_6](NO_3)_2$ was studied by DSC, DTA and TG. The first melting point at 328 K is connected with the small and the second melting point at 362 K with the large enthalpy and entropy changes. The thermal dehydration process starts just above ca. 315 K and continues up to ca. 500 K. It consists of three well-separated stages, but the sample mass loss at each stage depends on the experimental regime. However, irrespective of the chosen regime, the total of registered mass losses in stage one and two amounts to three H_2O molecules per one $[Ni(H_2O)_6](NO_3)_2$ molecule. The remaining three H_2O molecules are gradually freed in the temperature range of 440–500 K in the third stage of the dehydration. Above 580 K, anhydrous $Ni(NO_3)_2$ decomposes into NO and NiO. The gaseous products were identified by quadrupole mass spectrometer (QMS), and the solid product was identified by X-ray diffraction (XRD) analysis. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Crystalline compounds of the type $[M(H_2O)_6](NO_3)_2$, where M = Mg, Mn, Co, Ni, and Zn, are subject to an interesting two-stage melting process [1]. Also, they have recently become of particular interest as potentially valuable media for isothermal heat storage [2,3]. As the range between the two melting points is relatively wide ($T_{m1} = 328$ K and $T_{m2} = 362$ K), $[Ni(H_2O)_6](NO_3)_2$ may be useful as a model substance in the study of the nature of a two-stage melting process by different measurements. Because the dehydration of the compound was found to start as

low as 315 K [4], and due to its multistage character, it is interesting to determine its connection with the two-stage melting process, which can also be understood as the dissolution of the sample in its own water of crystallization (or rather coordinated water). The melting and the thermal decomposition of nickel hexahydrate has been the subject of many papers [5–12]. However, there is considerable disagreement concerning the proposed mechanism of these processes. The aim of this study is to gain a greater understanding of the mechanism of the melting and the thermal decomposition of $[Ni(H_2O)_6](NO_3)_2$, especially in the dehydration process.

Crystals of $[Ni(H_2O)_6](NO_3)_2$ are triclinic, space group no. $2\text{-}P\bar{1}\text{-}C_i^1$, with the following unit cell constants: $a = 7.694$ Å, $b = 11.916$ Å, $c = 5.817$ Å, $\alpha = 102.3°$, $\beta = 102.4°$, $\gamma = 105.9°$, $Z = 2$ [13]. The structure of $[Ni(H_2O)_6](NO_3)_2$ crystals is made of

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hexaaquanickel cations and nitrate anions joined with one another by a network of hydrogen bonds. The coordination of six water molecules around Ni^{2+} is only approximately octahedral. In fact, there are two kinds of six different Ni–O distances in the $[Ni(H_2O)_6]^{2+}$ cation: three short (2.021, 2.045 and 2.058 Å) and three long (2.078, 2.082 and 2.095 Å). It means that in the crystal lattice there are such three H_2O molecules that are stronger bonded than the other three. Also, the two crystallographically independent nitrate anions show a significant deviation from the trigonal symmetry. Through averaging adequate bonds in the both anions: two short (1.23 Å) and one long (1.28 Å) N–O bonds are developed. Almost all hydrogen bonds formed by the water molecules are directed toward the nitrate groups. However, not all water molecules form equal hydrogen bonds, either in direction or in strength. Four water molecules (nos. 1, 2, 5 and 6) form two hydrogen bonds with nitrate anions. There are three possible hydrogen bonds with NO_3^- formed by H_2O no. 4, but two of them could result from the presence of a bifurcated hydrogen bond or two possible orientations of the H_2O molecule. The water molecule no. 3 forms one strong hydrogen bond with NO_3^- and one weak hydrogen bond with H_2O of another $[Ni(H_2O)_6]^{2+}$ cation [13].

2. Experimental

$[Ni(H_2O)_6](NO_3)_2$ were obtained from the commercial product by repeated crystallization from four-time-distilled water (twice in a silver vessel and twice in a quartz vessel). The composition of the compound was determined on the basis of the metal content by titration with dinatrium wersenate and the infrared spectrum confirmed the purity of the sample.

The differential scanning calorimetric (DSC) measurements were performed with a Perkin-Elmer PYRIS 1 DSC apparatus. Details of the experiment were published elsewhere [1]. The sample was heated and cooled at a constant rate of 10 K/min.

The differential thermal analytic (DTA) measurements were performed using a MOM-Budapest apparatus. The sample with of 102.00 mg mass was placed in the corundum crucible and heated in the flowing air (4 dm³/h) at a constant rate of 2 K/min. 100.00 mg of Al_2O_3 was used as the reference substance.

A characterization of the decomposition process of $[Ni(H_2O)_6](NO_3)_2$ was performed using a Mettler Toledo TGA/SDTA 851^e. Samples I–IV of masses equal to respectively, 9.220, 9.644, 25.819 and 56.422 mg, were placed in 150 µl crucibles. The thermogravimetric (TG) measurements were made in a flow of Argon from 300 up to 800 K, with the on-line analysis of the evolved gases by a quadrupole mass spectrometer (QMS) using a Balzer GSD 300T apparatus. The measurements were performed at two different experimental regimes: at a constant heating rate of 2 K/min (for samples I and III) and at a constant decomposition rate-quasi-isothermal conditions (for samples II and IV). At a constant heating rate, the temperature was measured by Pt–Pt/Rh thermocouple with the accuracy of ± 0.5 K. Constant decomposition rate (quasi-isothermal conditions) means that the heating rate decreased as the process speeded up and increased when it slowed down. The thermo-balance controlling software uses the DTG curve to observe the speed of processes and lower heating rate when the process arises to create quasi-isothermal conditions. The parameters used in this case were the following: minimum heating rate $= 0.2°C/min$, maximum heating rate $= 2.0°C/min$, high threshold $= 8$ µg/s (if the current DTG value exceeds this value during the threshold check the heating rate will be reduced), low threshold $= 3$ µg/s (if the current DTG value falls below this value during the threshold check the heating rate will be increased), factor (by which the heating rate is divided or multiplied when the threshold is reached) equals to 2. At a constant decomposition rate, the temperature was measured by same Pt–Pt/Rh thermocouple.

The X-ray diffraction (XRD) analysis of the solid decomposition product was made with a Seifert XRD-7 apparatus using filtrated Cu Kα radiation.

3. Results and discussion

Fig. 1 shows the DSC results obtained for $[Ni(H_2O)_6](NO_3)_2$ in the temperature range of 100–375 K on heating and cooling the sample at a rate of 10 K/min. During heating (see Fig. 1a), two anomalies on the DSC curve were registered: one small and one large endothermic peak. These two peaks are connected with the two-stage melting of the sample. The
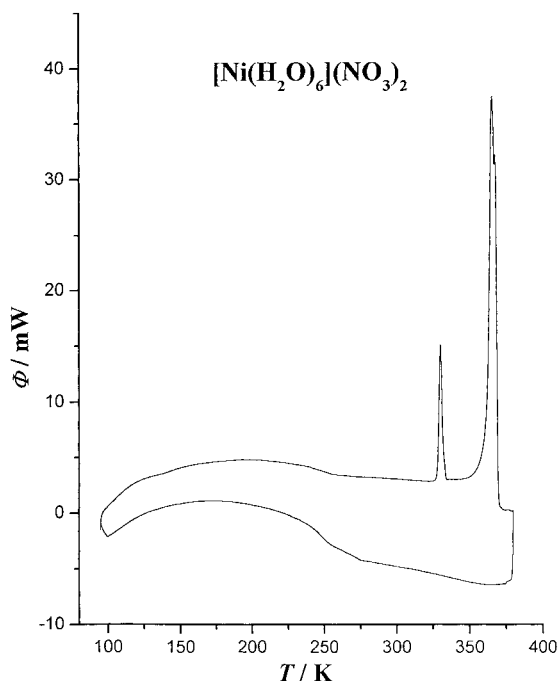
Fig. 1. DSC curves for [Ni(H₂O)₆](NO₃)₂ obtained in the range of 100–375 K during the heating (upper curve) and cooling (lower curve) at a constant rate of 10 K/min.

Fig. 2. DTA signal recorded in the range of 300–475 K during the heating of the $[Ni(H_2O)_6](NO_3)_2$ sample at a constant rate of 2 K/min.

first melting point at 328 K is connected with the small enthalpy and entropy changes ($\Delta H = 6.08$ kJ/mol, $\Delta S = 18.5$ J/mol K) and the second melting point at 362 K with the large enthalpy and entropy changes ($\Delta H = 42.11$ kJ/mol, $\Delta S = 116.3$ J/mol K). The melting process was also observed visually using a microscope. While the sample was heated, at the temperature that corresponded to the first melting point, one could see how the water phase was appearing among the crystallites. It can be particularly clear when the sample is mixed with oil (nujol). In spite of the subsequent heating, the crystallites did not dissolve completely in the water. Scarcely, at the temperature that corresponded to the second melting point, they started to dissolve rapidly and clear liquid could be observed. Thus, one can suppose that the two-stage melting of $[Ni(H_2O_6](NO_3)_2$ is connected with the two-stage partial dehydration. The reversible process cannot be observed, if the sample is not hermetically closed, because it systematically loses its water through evaporation. While the hermetically closed sample is cooled (see Fig. 1b), no peaks on the
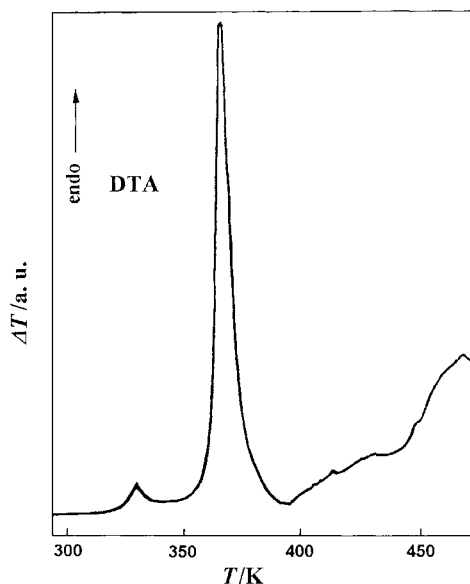
DSC curve can be observed, as the substance is easily super-cooled and terns into a glass. Even relatively slow cooling (1 K/min) leads only to a partial crystallization of the sample.

Fig. 2 shows the DTA results obtained for [Ni(H₂O)₆](NO₃)₂ in the temperature range of 300–475 K. Two endothermic peaks clearly seen at 328 K (small) and at 367 K (large), very well coincide with the DSC results. Additionally, some broad signal above 400 K (with the maximum at 466 K) can be also observed. It can be interpreted as connected with the next stage of the sample dehydration, what will be shown below by means of the thermal analysis.

Thermal analysis of [Ni(H₂O)₆](NO₃)₂ was performed for four samples. Two of them (nos. I and III) were measured at a constant heating rate and the other two (nos. II and IV) at a constant decomposition rate, i.e. at quasi-isothermal conditions. The TG and DTG signals recorded for sample no. III at a constant heating rate of 2 K/min in the temperature range of 300–800 K are presented on Fig. 3a. Four main stages of the sample decomposition can be seen. The temperatures and percentage mass losses for samples I and III at particular stages are presented in Table 1.
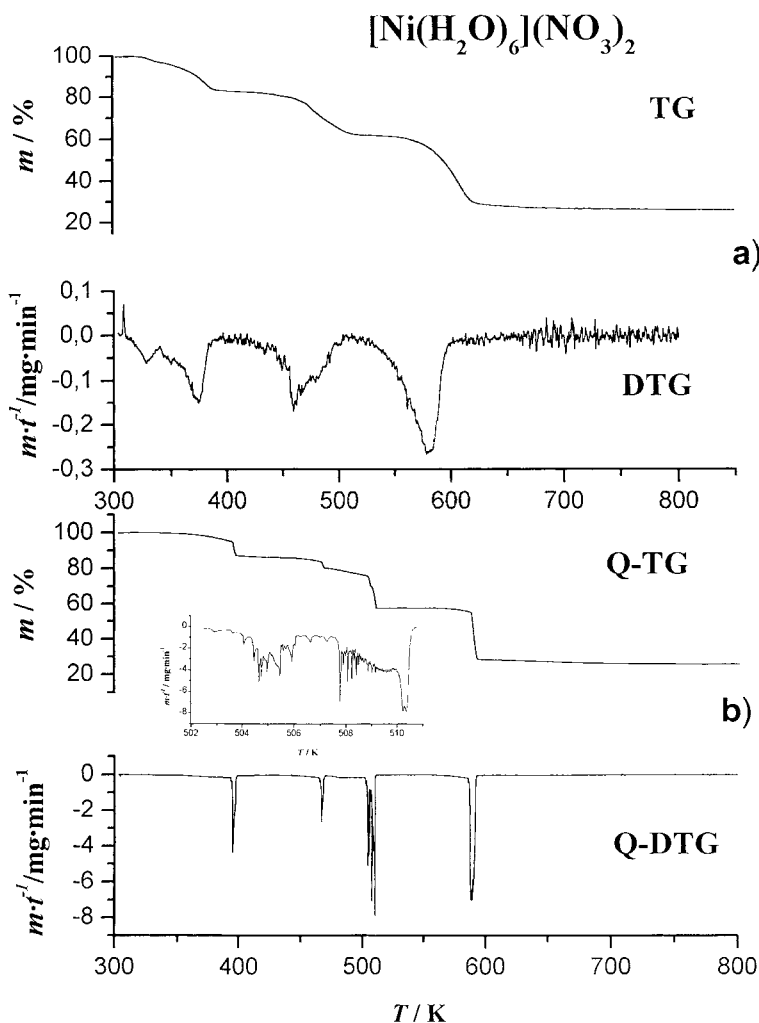
Fig. 3. (a) TG and DTG curves for [Ni(H$_2$O)$_6$](NO$_3$)$_2$ in the range of 300–800 K, heated at a constant rate of 2 K/min. (b) Q-TG and Q-DTG curves for [Ni(H$_2$O)$_6$](NO$_3$)$_2$ in the range of 300–800 K, heated at a constant decomposition rate (quasi-isothermal conditions). Insertion shows more precisely the third step of the dehydration.

Fig. 3b shows quasi-isothermal Q-TG and Q-DTG curves for sample no. IV in the range of 300–800 K. In that quasi-isothermal experimental regime, it could be clearly observed that the whole thermal decomposition of the sample took effect in the four well-separated stages, though in fact the third stage seems to be split into three steps. More precise analysis shows, however, that it should be described as differences between total dehydration of the particular grains than stepwise dehydration of the whole sample (see insertion on Fig. 3b).

Fig. 4 shows Q-TG, Q-DTG and QMS signals versus temperature for sample no. II, recorded at quasi-isothermal conditions. During the Q-TG experiment, the spectrum of masses were followed from $m/e = 1$ to $m/e = 100$, however, for reasons of graphic readability, only the masses of $m/e = 18$ — representing water and $m/e = 30$ — representing the decomposition of the nitrous species are shown. The products of the decomposition at particular stages are presented in Table 1. It can be observed that the first three stages involve mainly the freeing of H$_2$O

Table 1
Parameters of $[Ni(H_2O)_6](NO_3)_2$ thermal analyses

Sample no. and mass (mg)	Stage no.	T (K)	Mass loss at stage (%)	Mass after decomposition (%)	Calculated values (%)	Products of decomposition
I, 9.2203	1	330	8.43		6.195	1 H_2O
	2	364	10.06		12.390	2 H_2O
III, 25.8186	1	328	3.91	25.51	6.195	1 H_2O
	2	370	13.06		12.390	2 H_2O
	3	458	21.04		18.585	3 H_2O
	4	578	36.49		37.145	N_xO_y[a]
					25.685	NiO
II, 9.6440	1	334	10.68	27.89	12.390	2 H_2O
	2	358	6.01		6.195	1 H_2O
	3	451	19.62		18.585	3 H_2O
	4	502	35.80		37.145	N_xO_y
		575			25.685	NiO
IV, 56.4220	1	380	13.97	25.57	12.390	2 H_2O
	2	450	6.76		6.195	1 H_2O
	3	492	21.85		18.585	3 H_2O
	4	496	31.85		37.145	N_xO_y
		574			25.685	NiO

[a] N_xO_y indicates mixture of nitrogen oxides.

molecules, whereas the forth stage — the decomposition of anhydrous $Ni(NO_3)_2$ to gaseous nitrogen oxides and solid NiO. The temperatures and percentage mass losses for samples II and IV at particular stages of the decomposition are presented in Table 1. It should be noticed here that the temperatures of particular stages of the sample decomposition at quasi-isothermal conditions are, of course, systematically higher that those registered at a constant heating rate.

Interestingly, at a constant heating rate, at the temperatures of the maxima of the DTG curve equal to 329 K (stage 1) and 360 K (stage 2), coinciding very well with the DSC and DTA results, the mean value of the weight loss for samples I and III amounted to 6.17 and 11.56% of the initial mass, respectively. However, at quasi-isothermal regime, the mean value of the weigh loss for samples II and IV amounted to 12.32 and 6.38%, respectively, at the stages 1 and 2. The mean value of the total weight loss for all measured samples in the two dehydration stages, amounting to 18.22% of their initial mass, corresponds well to one-half of the water contaminated by the crystals (theoretical value = 18.58%). It means that the $Ni(NO_3)_2 \cdot 3H_2O$ is obtained after the two-stage dehydration of $[Ni(H_2O)_6](NO_3)_2$. Thus, the mechanism of

$[Ni(H_2O)_6](NO_3)_2$ dehydration observed in this study is more similar to that proposed by Funk [5] and Mu and Perlmutter [9] than to that one proposed by Sievert and Schreiner [7] and Weigel et al. [8].

The third stage of the dehydration is connected with the mass loss amounts to 20.88% (theoretical value: 18.58%). The sum of registered mass losses in the three stages of the dehydration amounted to 39.06%. The theoretical weight loss connected with all water contaminated by the sample amounts to 37.17%. The correction for the eventually absorbed by the sample water gives no more than 0.5% of the initial mass. On the other hand, the mass loss in the fourth stage of the decomposition amounted to 34.71% (the theoretical value amounts to 37.14%) and was connected with gaseous products of the decomposition of nitrate ions. The obtained results suggested that partial decomposition of nickel nitrate also took place during the dehydration process.

26.14% of the initial mass of the samples remained on average after the fourth stage of the decomposition and this figure corresponds to the amount of nickel oxide (theoretical value: 25.68%). The XRD analysis of the solid decomposition product for sample no. III confirmed that it was NiO, which has the structure of
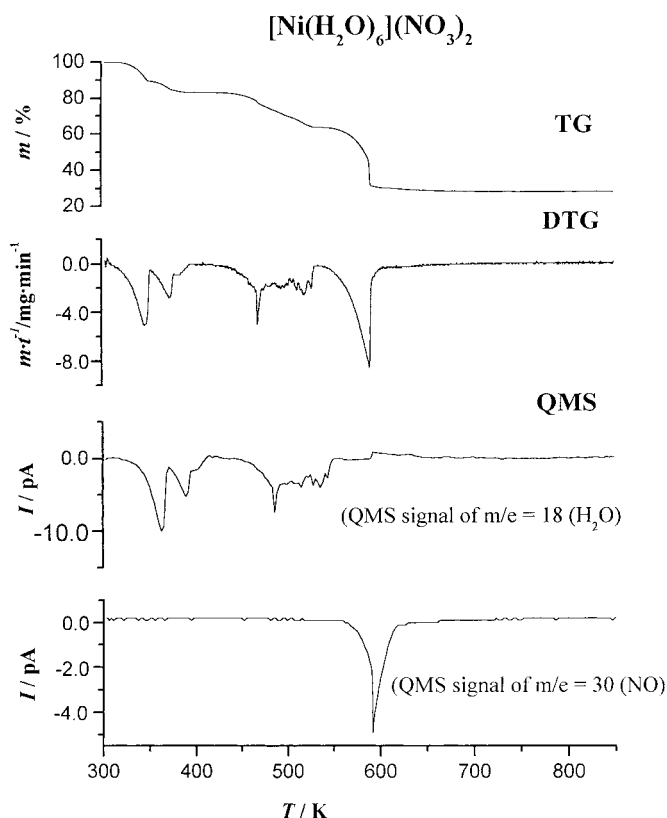
$$[Ni(H_2O)_6](NO_3)_2$$

Fig. 4. Q-TG, Q-DTG and QMS curves for $[Ni(H_2O)_6](NO_3)_2$ at quasi-isothermal conditions as a function of temperature.

bunsenite, as identified using JCPDS–ICDD data. The diffraction pattern of NiO obtained by us is very similar to that obtained by Llewellyn et al. [12].

4. Conclusions

$[Ni(H_2O)_6](NO_3)_2$ crystals exhibit an interesting two-stage melting process. The first melting point (fmp) at 328 K and the second melting point (smp) at 362 K are connected with the respective small and large enthalpy and entropy changes. The melted substance is easily super-cooled and turns into glass, even if cooled slowly.

The thermal dehydration process starts just above ca. 315 K and proceeds up to ca. 500 K. It is composed of three well-separated stages, but the sample mass loss at particular stages depends on the chosen experimental regime. At the constant heating rate regime, in the first stage at ca. 329 K (fmp), the substance loses

6.17% of the initial mass, and in the second stage at ca. 367 K (smp), it loses 11.56% of the initial mass (average value for two samples). However, at quasi-isothermal regime, the mass loss amounts to 12.32% in the first stage, and 6.38% in the second stage, and temperature values corresponding to these two DTG maxima are obviously significantly higher than those registered at a constant heating rate. Nevertheless, in both regimes, the total of the registered mass losses in these two stages (18.22%) corresponds well to three H_2O molecules per one $[Ni(H_2O)_6](NO_3)_2$ molecule. The remaining three H_2O molecules are loosen in the temperature range of 440–500 K, in the third stage of dehydration. Above 580 K in the fourth stage of decomposition, anhydrous $Ni(NO_3)_2$ decomposes into nitrogen oxides and NiO. The stages 3 and 4 are connected with the mass losses of 20.88 and 34.71%, respectively. The comparison with theoretical values (18.58 and 37.14%) suggests that the partial decomposition of nickel nitrate takes place already

during the dehydration process. The gaseous products were identified by QMS, and the solid product was identified by XRD analysis.

Acknowledgements

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