

## DSC STUDY OF THE PHASE TRANSITIONS IN [Ni(D<sub>2</sub>O)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> AND [Ni(H<sub>2</sub>O)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub>

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### Abstract

DSC measurements were carried out for [Ni(H<sub>2</sub>O)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> (sample *H*) and [Ni(D<sub>2</sub>O)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> (sample *D*) in the temperature range 300–380 K. For both compounds two anomalies on the DSC curves were detected. The results for sample *H* are compared to those previously obtained using adiabatic calorimetry method. For both compounds studied in this work the high-temperature transition appears at the same temperature while the low-temperature one is shifted towards higher temperatures in sample *D*. Disorder connected with H<sub>2</sub>O or D<sub>2</sub>O groups is suggested in the intermediate phase between the low- and high-temperature transitions.

**Keywords:** DSC, phase transitions in [Ni(D<sub>2</sub>O)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> and [Ni(H<sub>2</sub>O)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub>

### Introduction

Isomorphous compounds of the type of [Me(H<sub>2</sub>O)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub>, where *M* = Mg, Mn, Co, Ni and Zn, have at room temperature the pseudohexagonal structure (space group *C*<sub>2v</sub>-*Pmn*2<sub>1</sub>) with two molecules in an orthorhombic unit cell [1, 2]. Mössbauer investigations of [Ni(H<sub>2</sub>O)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> [3] indicate that at about 83 K there is a phase transition between the phase with the axially compressed [Ni(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> octahedrons and the phase with the axially elongated octahedrons (at higher temperatures). The magnetic susceptibility measurements [4–7] have shown the anomaly at 225 K. The authors of [4–7] relate this transition to the transition from pseudohexagonal (*Pmn*2<sub>1</sub>) to monoclinic (*P*2<sub>1</sub>/*c*) phase. Investigations by the EPR method [8] carried out for [Ni(H<sub>2</sub>O)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> showed the existence of phase transitions at 361, 310, 245 and 100 K and by the NMR method [9] at 250 K. Other EPR works [10, 11] report only one transition at 224 K. The adiabatic calorimetry measurements [12] performed for [Ni(H<sub>2</sub>O)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> in the temperature range between 100 K and 370 K revealed the existence of two distinct phase transitions at 311.40±0.93 K and 361.05±0.01 K and of only a weak trace of an anomaly at 225 K. The two high-temperature phases have been interpreted as disordered phases where the disorder is connected with ClO<sub>4</sub> groups [13]. It seemed interesting to study how deuteration influences the phase situation in [Ni(H<sub>2</sub>O)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub>. Therefore the

aim of the present work was the calorimetric study of polymorphism in  $[\text{Ni}(\text{D}_2\text{O})_6](\text{ClO}_4)_2$  and  $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  and the comparison of the results.

## Experimental

$[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  was produced by dissolving spectrally pure powdered Ni in diluted  $\text{HClO}_4$  (70%). Next, the crystallization process of  $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  was performed under reduced pressure because the substance is highly hygroscopic.

$[\text{Ni}(\text{D}_2\text{O})_6](\text{ClO}_4)_2$  was produced in several stages:

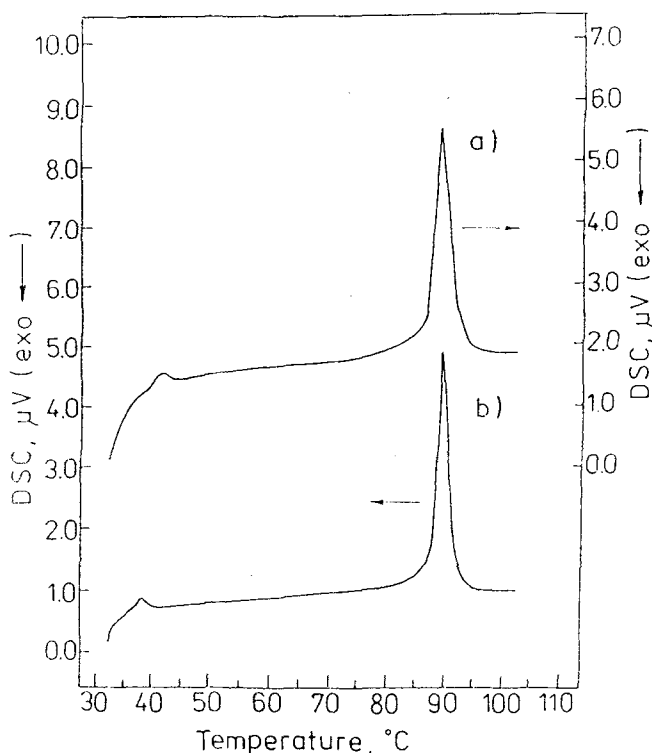
- 1)  $\text{SO}_3$  was distilled from oleum.
- 2)  $\text{SO}_3$  obtained in that way was introduced into  $\text{D}_2\text{O}$  while cooling the receiver in which  $\text{D}_2\text{SO}_4$  was formed, with ice.
- 3)  $\text{D}_2\text{SO}_4$  and  $\text{KClO}_4$  were mixed together, and next the obtained  $\text{DClO}_4$  was distilled from the mixture.
- 4) The acid was diluted with  $\text{D}_2\text{O}$  to about 70%. In this solution of  $\text{DClO}_4$  spectrally pure Ni was dissolved at the temperature of 353–368 K using an oil bath. The crystallization process of  $[\text{Ni}(\text{D}_2\text{O})_6](\text{ClO}_4)_2$  was performed under reduced pressure.

The number of hydrogen atoms (resulting mainly from using 94%  $\text{D}_2\text{O}$ ) in the obtained compound was estimated by NMR method to be about 6%.

The DSC measurements for  $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  and  $[\text{Ni}(\text{D}_2\text{O})_6](\text{ClO}_4)_2$  were made using High-Temperature Heat Flux Differential Calorimeter DSC 404 produced by NETZSCH. The measurements were carried out in air atmosphere in the temperature range 300–380 K for freshly prepared samples. Several experimental series were performed with various heating rates and various masses of the samples. The samples were placed in aluminum crucibles. Empty aluminum crucible was used as a reference. The sensitivity curve of the instrument was obtained using synthetic sapphire as a standard material. The temperatures of anomalies are given with the accuracy of 0.5 K and the enthalpy changes at the transitions with the accuracy of about 10%.

## Results and discussion

Figure 1 presents the results obtained for  $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  (sample *H*) and  $[\text{Ni}(\text{D}_2\text{O})_6](\text{ClO}_4)_2$  (sample *D*) on heating of the samples with the heating rate equal to  $5 \text{ deg}\cdot\text{min}^{-1}$ . The mass of sample *H* was 7 mg and of sample *D* 10.6 mg. Figure 2 shows heating and cooling curves for sample *D*. As is seen from Fig. 1 two phase transitions appear in both substances. The low-temperature transition is much weaker than the high-temperature one and is shifted towards lower temperatures in sample *H* (peak temperature:  $38.2^\circ\text{C}$  for sample *H*



**Fig. 1** DSC curves obtained for a)  $[\text{Ni}(\text{D}_2\text{O})_6](\text{ClO}_4)_2$  (sample *D*) and b)  $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  (sample *H*). Heating rate was  $5 \text{ deg}\cdot\text{min}^{-1}$ . Left-hand scale corresponds to sample *H*, right-hand scale to sample *D*

and  $41.5^\circ\text{C}$  for sample *D*). The temperature of the second transition is practically the same for both compounds (peak temperatures:  $89.7$ ,  $89.3^\circ\text{C}$  for sample *H* and *D* respectively). To make a better comparison of peak positions between sample *H* and sample *D*, the accurate data from the adiabatic calorimetry measurements for sample *H* [12] were taken into account. For this comparison peak temperatures for  $[\text{Ni}(\text{D}_2\text{O})_6](\text{ClO}_4)_2$ , recorded at various heating rates (Fig. 3), were extrapolated to zero heating rate which corresponds to adiabatic calorimetry results obtained in equilibrium conditions. The temperatures determined in this way for  $[\text{Ni}(\text{D}_2\text{O})_6](\text{ClO}_4)_2$  are following: the low-temperature transition:  $41.0 \pm 0.3^\circ\text{C}$  and the high-temperature transition:  $87.8 \pm 0.2^\circ\text{C}$ . The transition temperatures for  $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  obtained in [12] are equal to:  $38.25 \pm 0.93^\circ\text{C}$  and  $87.05 \pm 0.01^\circ\text{C}$  for the low-temperature transition and the high-temperature transition respectively. The comparison of the transition temperatures confirms that the temperature of the high-temperature transition is practically the same for both compounds. The temperature of the low-temperature transition is higher in sample *D* by about  $3^\circ\text{C}$ . Therefore it is reasonable to assume that in this transition a change of the dynamics of  $\text{H}_2\text{O}$  (or

D<sub>2</sub>O) groups plays a significant role. In the literature [12, 13] only the ClO<sub>4</sub> groups configurational disorder was taken into account. On the basis of the entropy changes, a multi-configurational situation of ClO<sub>4</sub> anions in the high temperature phase and bi-configurational disorder of ClO<sub>4</sub> anions were suggested in the intermediate phase between low- and high-temperature transitions [13]. It seems now that ClO<sub>4</sub> anions disorder plays an important role mainly in the high-temperature transition and that in the low-temperature one a role of H<sub>2</sub>O (or D<sub>2</sub>O) groups cannot be neglected.

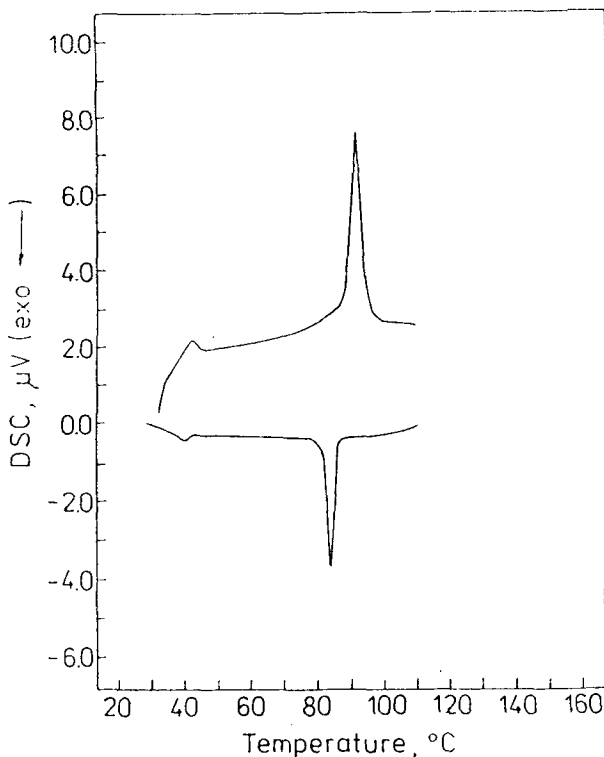


Fig. 2. DSC curves obtained on heating (upper curve) and cooling (lower curve) of sample *D*

It is interesting to give here some comments on the enthalpy values calculation. The comparison with the adiabatic calorimetry measurements turned out to be very important here. The results of the specific heat measurements for [Ni(H<sub>2</sub>O)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> using adiabatic calorimetry [12] are presented in Fig. 4. From the figure it is clearly seen that both anomalies appear on a systematically increasing background. In Fig. 1 which presents the DSC data obtained in a much narrower temperature range this fact is not evident. Only after adjusting the scale of the DSC results to that of the adiabatic ones was it possible to notice this fact and choose the appropriate limits for peak integration. From the comparison of the DSC and adiabatic results it is clear that for the low-temperature

transition it is not possible to calculate the enthalpy from the DSC measurements with a reasonable accuracy as they start at too high temperature.

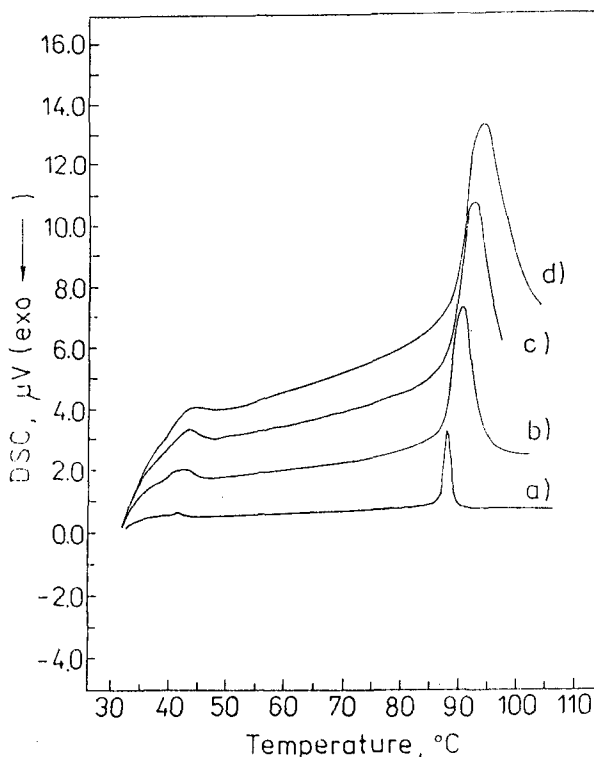


Fig. 3 DSC curves for  $[\text{Ni}(\text{D}_2\text{O})_6](\text{ClO}_4)_2$  measured at various heating rates: a)  $1 \text{ deg}\cdot\text{min}^{-1}$ , b)  $5 \text{ deg}\cdot\text{min}^{-1}$ , c)  $10 \text{ deg}\cdot\text{min}^{-1}$  and d)  $15 \text{ deg}\cdot\text{min}^{-1}$

The enthalpy value for the high-temperature transition obtained in this work for sample *H* taking into account peak integration limits resulting from the comparison with the results of [12] is following:

the high-temperature transition:  $\Delta H = 8.8 \text{ kJ}\cdot\text{mol}^{-1}$ .

The data obtained in [12] are given below:

the high-temperature transition:  $\Delta H = 9.10 \pm 0.20 \text{ kJ}\cdot\text{mol}^{-1}$

the low-temperature transition:  $\Delta H = 2.94 \pm 0.20 \text{ kJ}\cdot\text{mol}^{-1}$ .

As one can see the agreement with the results of [12] is very good. For sample *D* the enthalpy of the high-temperature transition calculated in a similar way as for sample *H* has the value of  $\Delta H = 7.8 \text{ kJ}\cdot\text{mol}^{-1}$ . So,  $\Delta H$  values are comparable in both substances. In addition, also the entropy changes at the high-temperature transition will be comparable in both substances as the transition

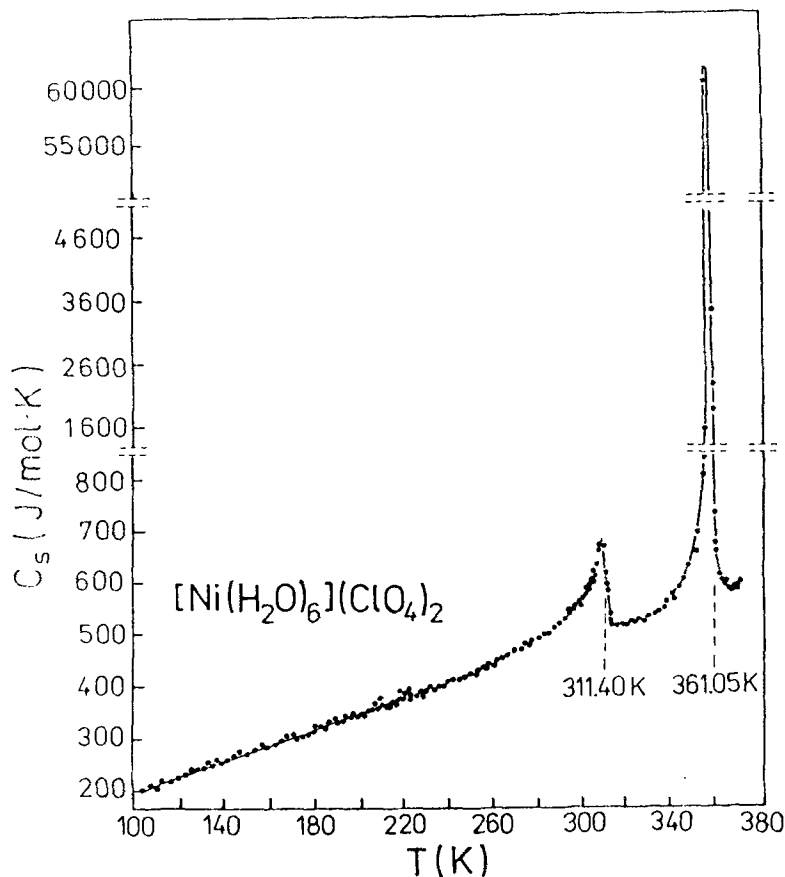


Fig. 4 Specific heat vs. temperature for  $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  [12]

temperatures are practically the same. For the low-temperature transition, as was explained above, it did not seem reasonable to calculate the enthalpy because of too short 'tail' on the low temperature side of the transition. However, the similar shape and only a small temperature shift of the transition justifies the assumption that here also the thermodynamic parameters, in particular the entropy change at the transition, have similar values. One can therefore expect that the disorder connected with  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  groups is the same in the intermediate phase of both substances.

## Conclusions

1.  $[\text{Ni}(\text{D}_2\text{O})_6](\text{ClO}_4)_2$  similarly to  $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  has two phase transitions in the temperature range 300–380 K: the high-temperature one at 362.4 K

(362.8 K for sample *H*) and the low-temperature transition at 314.6 K (311.3 K in sample *H*).

2. The high-temperature transition appears at the same temperature in both compounds. The low-temperature one appears in  $[\text{Ni}(\text{D}_2\text{O})_6](\text{ClO}_4)_2$  at the temperature higher by about 3°C than in  $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ . On the basis of this temperature shift one can expect that  $\text{H}_2\text{O}$  ( $\text{D}_2\text{O}$ ) groups play a role in the low-temperature transition.

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**Zusammenfassung** — An  $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  (Probe *H*) und  $[\text{Ni}(\text{D}_2\text{O})_6](\text{ClO}_4)_2$  (Probe *D*) wurden DSC-Messungen im Temperaturintervall 300–380°C durchgeführt. Für beide Verbindungen wurden an den DSC-Kurven zwei Anomalien festgestellt. Die Ergebnisse für die Probe *H* wurden mit denen verglichen, die unlängst mittels adiabatischer Kalorimetrie ermittelt wurden. Für beide in vorliegender Studie untersuchten Verbindungen erscheint die Umwandlung bei höherer Temperatur bei der gleichen Temperatur, während die bei niedriger Temperatur im Falle der Probe *D* in Richtung höherer Temperaturen verschoben wird. Für die Übergangphase zwischen den Nieder- und Hochtemperaturumwandlungen wird eine Fehlordnung bezüglich der  $\text{H}_2\text{O}$  oder  $\text{D}_2\text{O}$  Gruppen angenommen.