DSC Investigations of the Phase Transitions of $[M(H_2O)_6](NO_3)_2$, where M = Mn, Co, Ni, Cu and Zn

E. Mikuli, A. Migdał-Mikuli, S. Wróbel[a], and B. Grad

Department of Chemical Physics, Faculty of Chemistry of the Jagiellonian University, ulica Ingardena 3, 30-060 Kraków, Poland

[a] Department of Solid State Physics, M. Smoluchowski Institute of Physics, Jagiellonian University, ulica Reymonta 4, 30-059 Kraków, Poland

Reprint requests to Dr. E. M.; E-mail: mikuli@trurl.ch.uj.edu.pl

Z. Naturforsch. **54 a,** 595–598 (1999); received August 13, 1999

The phase transitions of $[M(H_2O)_6](NO_3)_2$, where M = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} or Zn^{2+} have been studied at 100 - 400 K by DSC. Two phase transitions connected with a two-stage melting process have been found for these five compounds. For the compound with M = Co, besides the two melting points a solid-solid phase transition at 272 K has been found.

Key words: Hexaaquametal(II) nitrates; Phase Transitions; Melting Points; DSC Method.

1. Introduction

As opposed to the isomorphous family of $[M(H_2O)_6](XY_4)_2$ compounds, where M = Mg, Mn, Fe, Co, Ni, Zn or Cd and $XY_4 = ClO_4^-$ or BF_4^- [1], the corresponding $[M(H_2O)_6](NO_3)_2$ compounds crystallize at room temperature in several structures (different space groups). Taking into account only the compounds investigated in this work, two pairs of them are isostructural, namely the pair with M = Mn and Zn, which has the space group Pnma [2, 3], and that with M = Ni and Cu, which has the space group $P\bar{1}$ [4, 5]. The space groups of $[Co(H_2O)_6](NO_3)_2$ and $[Mg(H_2O)_6](NO_3)_2$ are C2/c [6] and $P2_1/c$ [7, 8], respectively. It is not clear yet if the differences in the structure are due to small but different deviations from the perfect octahedral structure of the complex cation, to different strains from hydrogen bonds, or to reorientational motions of the nitrate groups.

The phase transitions of the $[M(H_2O)_6](NO_3)_2$ compounds were detected by calorimetry and dilatometry [9 - 13]. The reported phase transition temperatures are summarized in Table 1. The more precise adiabatic calorimetry studies revealed in $[Mg(H_2O)_6](NO_3)_2$ **two** phase transitions [12]. The transition at T_{C1}, connected with a **large** specific heat anomaly, was interpreted as a melting point, whereas the transition at T_{C2} connected with a **much smaller**

Table 1. Phase transition temperatures (in K) of $[M(H_2O)_6](NO_3)_2$ compounds as measured by different methods.

	— References —						
M	[9]	[10]	[11]	[12]	[13]	[14]	*
Mn							312
	299					299	299
			268				
			236				
Zn	310		311				313
			292		292	299	298
			260				
			157				
					123		
					107		
Ni							362
	330					333	328
		149					
Cu							394
	299					318	301
			268				
			248				
Co							348
	329					336	328
							272
		153					
Mg	363		362	363		371	
			343	343			
			260				
				215			

* this work.

0932–0784 / 99 / 1000–0595 $ 06.00 © Verlag der Zeitschrift für Naturforschung, Tübingen · www.znaturforsch.com

specific heat anomaly was interpreted as a solid-solid phase transition. Apart from these anomalies, the third one was detected at ~215 K, but only in the first run of the measurements for each of the three fillings of the calorimeter. The NMR and QNS measurements [12] gave evidence of 180° angular flips of H_2O groups around the Mg-O axes. The characteristic correlation time for these flips amounts to *ca.* 50 picoseconds at room temperature. A hysteresis of about 8 K was observed for the T_{C2} transition [12]. These two phase transitions, and additionally the third one at 260 K, were observed earlier also by DTA and dylatometry [11]. In $[Co(H_2O)_6](NO_3)_2$ and $[Ni(H_2O)_6](NO_3)_2$ the low temperature phase transitions were observed at 153 and 149 K, respectively, as very small specific heat anomalies (ΔS = 0.4 J/mol K) [10]. Up to now only one high temperature phase transition was detected for all investigated compounds (with the exception of the mentioned $[Mg(H_2O)_6](NO_3)_2$) and was interpreted as melting of these crystals [12, 13]. The aim of this study is to detect anomalies on the DSC curves and hence to determine the thermodynamic parameters of the phase transitions of the five $[M(H_2O)_6](NO_3)_2$ compounds, whith M = Mn, Co, Ni, Cu, and Zn.

2. Experimental

Pure $[Co(H_2O)_6](NO_3)_2$, $[Ni(H_2O)_6](NO_3)_2$, $[Cu(H_2O)_6](NO_3)_2$ and $[Zn(H_2O)_6](NO_3)_2$ were obtained from commercial products by repeated crystallization from water distilled four times in a quartz vessel. $[Mn(H_2O)_6](NO_3)_2$ was synthesized by the reaction of $MnCO_3$ and diluted HNO_3. The solution was concentrated by mild heating, and the crystals obtained after cooling of that solution were purified by repeated crystallization from four times distilled water. Then the crystals were dried in a desiccator over P_2O_5 and stored in a hygrostate. Before the measurements, the composition of the compounds was determined on the basis of the metal content, by titration with natrium wersenate. The average content of metal in each of the investigated compounds was found to be equal to the theoretical value within an error limit of *ca.* 2%.

The DSC measurements were performed with a Perkin-Elmer PYRIS 1 DSC apparatus at the M. Smoluchowski Institute of Physics of the Jagiellonian University. The instrument was calibrated by means of the melting point of indium – for the high temperature region, and the melting point of H_2O – for the low temperature region. High purity dry gases were used as purging gas (helium, 99.999%) and as air shield gas (nitrogen, 99.999%). The nitrogen gas used for transferring liquid nitrogen to the cold finger dewar was also of high purity. Two characteristic temperatures of the DSC peaks obtained on heating were computed: the temperature of the peak maximum (T_{peak}) and the temperature calculated from the slope of the left-hand side of the peak (T_{onset}). These two temperatures differed by 2 to 6 K. As for the transition temperatures, the values of T_{onset} were taken into account. The enthalpy changes (ΔH) connected with the observed phase transitions were calculated by numerical integration of the DSC curves under the peaks of the anomalies. Before the calculations a linear background was subtracted. This was done in a more or less arbitrary though identical way for all the samples. Nevertheless, they are good enough to allow the comparison of the compounds investigated. The entropy changes (ΔS) were calculated using the formula $\Delta S_x = \Delta H/T_{Cx}$. For the sharp peaks of the DSC curves they were computed with high accuracy (± 4%). The masses of the samples amounted to from 8.5 to 31.5 mg. The DSC measurements were performed on heating and cooling the samples with a constant rate of 10 K·min^{-1}. Because all these compounds easily overcool, much slower cooling rate is needed. For that reason the DSC measurements during the cooling of these compounds are not presented in this work. They are now in progress with a very slow rate of cooling and will be published later.

3. Results and Discussion

Figure 1 shows the temperature dependence of the heat flow (DSC curve) obtained during the heating of the $[Co(H_2O)_6](NO_3)_2$ sample at the rate of 10 K·min^{-1}. **Three** anomalies of the DSC curve were detected. The endothermic peak at 272 K corresponds to a solid-solid phase transitions. The next two peaks are connected with two stages of the melting process. This statement was confirmed by visual observation.

The DSC curves (registered on heating the samples at a rate of 10 K·min^{-1}) for $[Mn(H_2O)_6](NO_3)_2$ and $[Zn(H_2O)_6](NO_3)_2$ are shown on Fig. 2, and the DSC curves for $[Ni(H_2O)_6](NO_3)_2$ and $[Cu(H_2O)_6](NO_3)_2$ are shown on Figure 3. In these figures there are **two** anomalies on the DSC curves: a **small** and

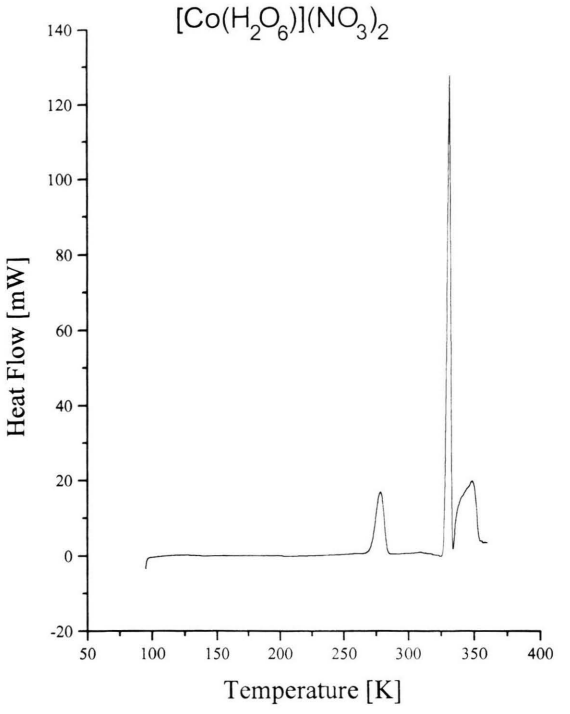

Fig. 1. DSC curves of $[Co(H_2O)_6](NO_3)_2$ on heating the sample at a rate of 10 K·min^{-1}.

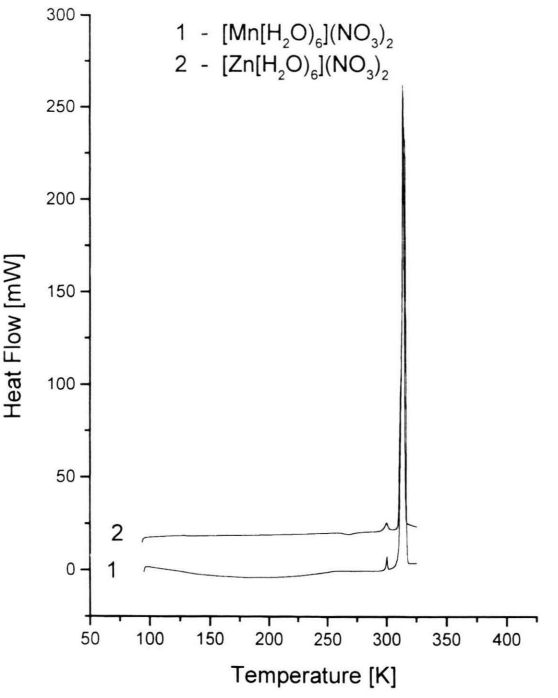

Fig. 2. Comparison of the DSC curves of $[Mn(H_2O)_6](NO_3)_2$ and $[Zn(H_2O)_6](NO_3)_2$ on heating the samples at a rate of 10 K·min^{-1}.

a **large** peak. These peaks are connected with a two-stage melting process, which was confirmed by visual observation. A termogravimetric analysis connected with a mass spectrometric analysis of $[Ni(H_2O)_6](NO_3)_2$ has indicated that at ca. 330 and ca. 364 K the substance loses 8.5% and 10.0% of its water, respectively. Altogether the loss amounts to three water molecules per one $[Ni(H_2O)_6](NO_3)_2$ molecule [15].

The temperature and the enthalpy and entropy changes of the detected phase transitions are presented in Table 2. For $[M(H_2O)_6](NO_3)_2$ with M = Mn, Zn, Ni and Cu, the values of ΔH and ΔS for the large anomaly are much bigger than those for the small one. For the compounds with M = Mn and Zn, the ΔS-value for the small anomaly amounts to 1% and 2 % of the ΔS-value for the large anomaly, respectively. For the compounds with M = Ni and Cu, the ΔS-value for the small anomaly amounts to 15% and 16 % of the ΔS-value for the large anomaly, respectively. The ΔS value for the large anomaly is by about 50% bigger and for the small anomaly it is one order of magnitude lower for compounds with M = Mn and Zn than the corresponding value for the compounds with M = Ni and Cu. For $[Co(H_2O)_6](NO_3)_2$ the ΔS values for all three anomalies of the DSC curve are of the same order of magnitude.

It should be pointed out that the polymorphism of the $[M(H_2O)_6](NO_3)_2$ compounds is quite different than that of $[M(H_2O)_6](ClO_4)_2$ [16] and $[M(H_2O)_6](BF_4)_2$ [17].

4. Conclusions

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

1. The character of the DSC curves and the enthalpy- and entropy-changes of the investigated compounds, which are isostructural, are very similar.

2. The investigated compounds melt in two steps. Only in the case of $[Co(H_2O)_6](NO_3)_2$ there exists besides the two melting points a solid state transition.

3. For the $[M(H_2O)_6](NO_3)_2$ compounds with M = Mn, Zn, Ni, and Cu the enthalpy- and entropy-changes connected with the first melting point are much lower than those for the second melting point, while for

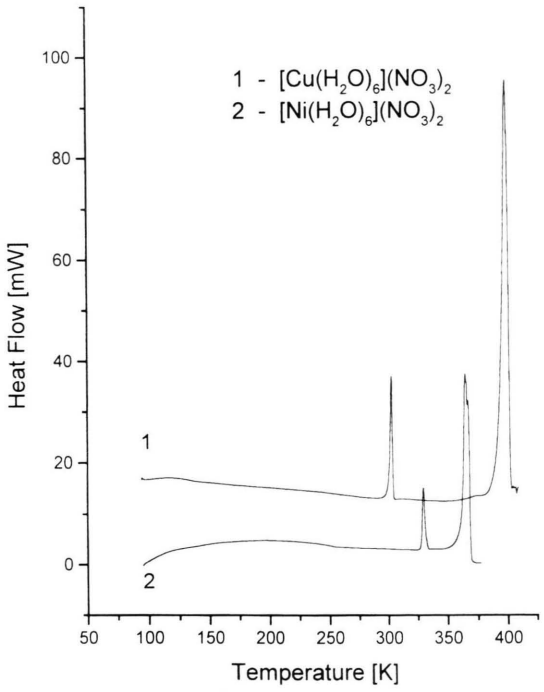

Fig. 3. Comparison of the DSC curves of $[Ni(H_2O)_6](NO_3)_2$ and $[Cu(H_2O)_6](NO_3)_2$ on heating the samples at a rate of 10 $K \cdot min^{-1}$.

$[Co(H_2O)_6](NO_3)_2$ they are of the same order of magnitude.

4. The entropy changes connected with the first melting point are by about one order of magnitude lower and those connected with the second melting point are by about 50% bigger for $[Mn(H_2O)_6](NO_3)_2$ and $[Zn(H_2O)_6](NO_3)_2$ than for $[Ni(H_2O)_6](NO_3)_2$ and $[Cu(H_2O)_6](NO_3)_2$.

5. In the case of $[Ni(H_2O)_6](NO_3)_2$ the two-stage melting process is probably connected with a two-stage release of 50% of the water molecules from the crystal lattice.

Table 2. Thermodynamic parameters of the phase transitions of $[M(H_2O)_6](NO_3)_2$ compounds.

M	T_C [K]	ΔH [$kJ \cdot mol^{-1}$]	ΔS [$J \cdot mol^{-1} \cdot K^{-1}$]	Ref.
Mn	312.31	49.68	159.1	*
	299.4	0.47	1.6	*
Zn	312.9	47.45	151.7	*
	297.7	1.04	3.5	*
Ni	362.0	42.11	116.3	*
	327.8	6.08	18.5	*
Cu	394.1	39.69	100.7	*
	300.7	4.80	16.0	*
Co	348.4	16.65	47.8	*
	327.8	28.71	87.6	*
	271.7	8.8	32.4	*
Mg	363.23	41.349	113.88	[12]
	342.8	5.263	12.93	[12]
	215	?	?	[12]

* this work.

Acknowledgements

One of us (S. W.) would like to express his gratitude to the Polish Foundation for Science for purchasing the PYRIS 1 DSC calorimeter.

[1] C. D. West, Z. Kristall. **91A**, 480 (1935).
[2] B. Ribar, B. Prelesnik, and S. Caric, Z. Kristall. **137**, 318 (1973).
[3] A. Ferrari, A. Braibanti, A. M. Manotti Lanfredi, and A. Tiripicchio, Acta Cryst. **22**, 240 (1967).
[4] F. Bigoli, A. Braibanti, A. Tiripicchio, and M. Tiripicchio Camellini, Acta Cryst. **B27**, 1427 (1971).
[5] R. W. Wyckoff, Crystal Structures, Interscience, New York 1965.
[6] A. Jayaraman, Proc. Indian Acad. Sci. **47A**, 147 (1958).
[7] A. Braibanti, A. Tiripicchio, A. M. Manotti Lanfredi, and F. Bigoli, Acta Cryst. **B25**, 354 (1969).
[8] J. Schefer and M. Grube, Mat. Res. Bull. **30**, 1235 (1995).
[9] E. H. Riesenfeld and C. Milchsack, Z. anorg. Chem. **85**, 401 (1914).
[10] H. D. Vasileff and H. Grayson-Smith, Can. J. Research A **28**, 367 (1950).
[11] P. Pouillen, C. R. Acad. Sci. Paris **250**, 3318 (1960).
[12] J. M. Janik, E. Mikuli, A. Migdał-Mikuli, M. Rachwalska, T. Stanek, J. A. Janik, K. Otnes, and I. Svare, Phys. Scripta **28**, 569 (1983).
[13] B. Borzęcka-Prokop, E. Kapturkiewicz, A. Wesełucha-Birczyńska, and S. A. Hodorowicz, Cryst. Res. Technol. **25**, 1311 (1990).
[14] Poradnik fizykochemiczny, WNT, Warszawa 1980.
[15] E. Mikuli, A. Migdał-Mikuli, R. Dziembaj, and R. Chyży, to be published.
[16] E. Mikuli, A. Migdał-Mikuli, and J. Mayer, J. Thermal Anal. **54**, 93 (1998).
[17] E. Mikuli, A. Migdał-Mikuli, and S. Wróbel, Z. Naturforsch. **54a**, 225 (1999).