DSC Investigations of the Phase Transitions of $[M(NH_3)_6](ClO_4)_2$ and $[M(NH_3)_6](BF_4)_2$, where M = Co and Cd

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Solid polymorphism of four compounds of the type $[M(NH_3)_6](XY_4)_2$, where $M = Co^{2+}$ or Cd^{2+}, and $XY_4 = ClO_4^-$ or BF_4^- has been studied at 100 - 300 K by DSC. One or two phase transitions of the investigated compounds have been found. For the compounds with M = Co the phase transitions have not yet been described in the literature. For the compounds with M = Cd the phase transition-temperature is in good agreement with the results obtained by NMR and EPR. Generally, for $[M(NH_3)_6](BF_4)_2$ compounds (M = Mg, Fe, Co, or Ni) the phase transition temperature T_{C1} is lower than that for the corresponding $[M(NH_3)_6](ClO_4)_2$, but for compounds with M = Cd it is higher. However, the enthalpy and entropy changes at the T_{C1} phase transitions of $[M(NH_3)_6](BF_4)_2$ are always lower than those for $[M(NH_3)_6](ClO_4)_2$. Moreover, for the compounds of this type a correlation between the transition temperature T_{C1} and the crystal lattice parameter a has been found.

Key words: Phase Transitions; DSC Method; Chlorate(VII) and Tetrafluoroborate of Hexaaminacobalt(II) and Hexaaminacadmium(II).

1. Introduction

Adiabatic calorimetry studies of $[M(NH_3)_6](XY_4)_2$, where $M = Ni^{2+}$ or Mg^{2+}, and $XY_4 = ClO_4^-$ or BF_4^-, revealed two phase transitions [1 - 3]. The transition from high temperature to the intermediate phase shows at T_{C1} a *large* specific heat anomaly, whereas the transition from the intermediate to the low temperature phase shows at T_{C2} a *much smaller* specific heat anomaly. Extensive studies by various methods [3 - 22] established that these phase transitions are associated both with a change of the crystal structure and with an abrupt change in the rate of reorientational motion of the tetrahedral anions. Fast reorientational motions of the NH_3 groups take place in all three phases of these compounds and are only slightly distorted by the phase transitions. Their characteristic correlation time amounts to several picoseconds even at liquid nitrogen temperature [21]. The phase transition at T_{C1} was also observed in $[M(NH_3)_6](XY_4)_2$ compounds with M = Fe or Cd by Mössbauer [23], NMR [24, 25] and EPR [26] methods. For the compounds with M = Mn or Co neither phase transitions nor reorientational motions have yet been studied.

So far a few theoretical attempts at a description of the phase transitions in the discussed compounds have been done [27 - 31]. Unfortunately, none of them has predicted correctly the phase transition temperatures and the observed monoclinic distortion of the crystal. However, taking into account the symmetry of the anion, it is possible to correlate T_{C1} of the highest temperature phase transition with the lattice parameters of these crystals [28].

The $[M(NH_3)_6](XY_4)_2$ crystalline compounds, have at room temperature a face centered cubic structure (space group Fm3m - O_h^5, no. 225) with four molecules in the unit cell [32 - 34]. The high symmetry of the crystal lattice is possible because the NH_3 groups perform fast reorientational motions around the threefold axis. Both the intermediate and low temperature phases of these compounds are monoclinic (space group $P2_1/c$ - C_{2h}^5, no. 14) with four molecules in the unit cell [3, 6, 14, 16, 17].

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The aim of this study is to detect anomalies of the DSC curves and hence to determine the thermodynamic parameters of the phase transitions in $[M(NH_3)_6](ClO_4)_2$ and $[M(NH_3)_6](BF_4)_2$, where M = Co or Cd. Additionally, we will present the correlation between T_{C1} and the lattice parameter a for $[M(NH_3)_6](XY_4)_2$ compounds with M = Mg, Fe, Co, Ni or Cd.

2. Experimental

The examined compounds were obtained from corresponding hexaaquametal(II) chlorates(VII) and tetrafluoroborates which were earlier synthesized by reaction of the corresponding carbonates with diluted $HClO_4$ and HBF_4, respectively, and recrystallized several times from water distilled four times in a quartz vessel. The adequate hexaaquametal(II) complex placed in a quartz vessel was put in a glass tube through which dry gaseous ammonia was blown, and the tube was placed inside an oven. First the tube was heated for several hours at about 390 K until all the water from the hexaaquacomplex had been lost. Then the corresponding hexaammine complex that formed was cooled to room temperature and kept at this temperature for several days. All hexaammine compounds exhibit poor stability at room temperature if they are not kept in a container filled with dry ammonia. Before the measurements, the composition of the compounds was determined on the basis of their metal and ammonia content, by titration by means of natrium wersenate and hydrochloric acid, respectively. The average contents of metal and NH_3 were found to be equal to the theoretical values within the error limit of *ca.* 10%.

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. In the case of second order transitions also the T_{end} temperature was computed from the right-hand side peak slope. For first order transitions the T_{onset} and T_{end} temperatures obtained may differ by 1 to 3 K, whereas for the second order transitions the difference may be as high as 10 K, or even greater. For sharp peaks the value of T_{onset} and for diffuse peaks the value of T_{peak} as the phase transition temperature was taken into account, respectively. 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 ($\pm$ 4%), whereas for the diffuse peaks they could be considered as estimates only. The DSC measurements were performed on heating and cooling the samples with a constant rate of 10 K·min^{-1}. The masses of the samples amounted to 8 to 28 mg.

3. Results and Discussion

Figure 1 shows as an example the temperature dependencies of the heat flow (DSC curves) obtained during the heating and cooling of the $[Cd(NH_3)_6](ClO_4)_2$ sample at the rate of 10 K·min^{-1}. A sharp peak on both DSC curves is seen. It corresponds to a solid-solid phase transition. The difference between the T_{onset} temperatures obtained on heating and cooling is *ca.* 5 K, so a **small hysteresis** of the phase transition temperature T_{C1} was detected. It indicates that this phase transition is of **first order**. Similar DSC curves were registered for $[Cd(NH_3)_6](BF_4)_2$, $[Co(NH_3)_6](ClO_4)_2$ and $[Co(NH_3)_6](BF_4)_2$ samples.

The comparison of the DSC curves (registered on heating the samples at a rate of 10 K·min^{-1}) for $[M(NH_3)_6](BF_4)_2$ and $[M(NH_3)_6](ClO_4)_2$ is shown in Figs. 2 (M = Cd) and 3 (M = Co), respectively. Evidently the phase transition of $[Cd(NH_3)_6](BF_4)_2$ takes place at a higher temperature than that of $[Cd(NH_3)_6](ClO_4)_2$. For the corresponding cobalt compounds it is the opposite. We believe that for these there exists also a very small and diffused anomaly on the DSC curve in the low temperature region. For

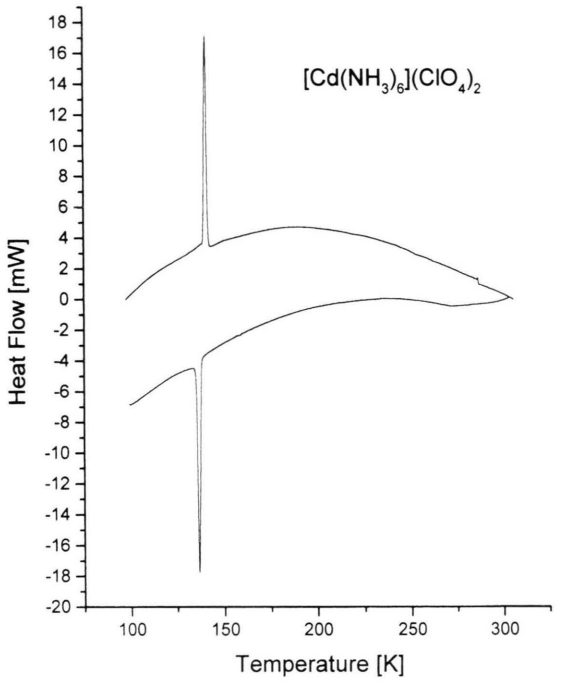

Fig. 1. DSC curves for $[Cd(NH_3)_6](ClO_4)_2$ registered on cooling and heating at a rate of 10 $K \cdot min^{-1}$.

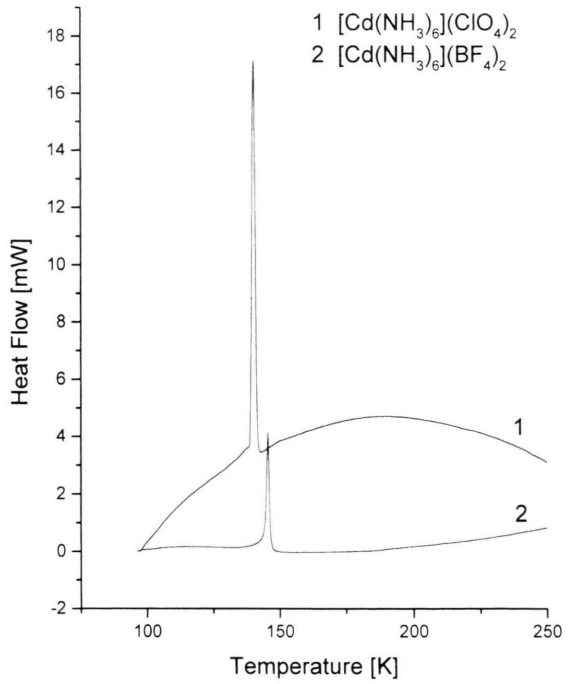

Fig. 2. Comparison of the DSC curves for $[Cd(NH_3)_6](ClO_4)_2$ and $[Cd(NH_3)_6](BF_4)_2$ registered on heating at a rate of 10 $K \cdot min^{-1}$.

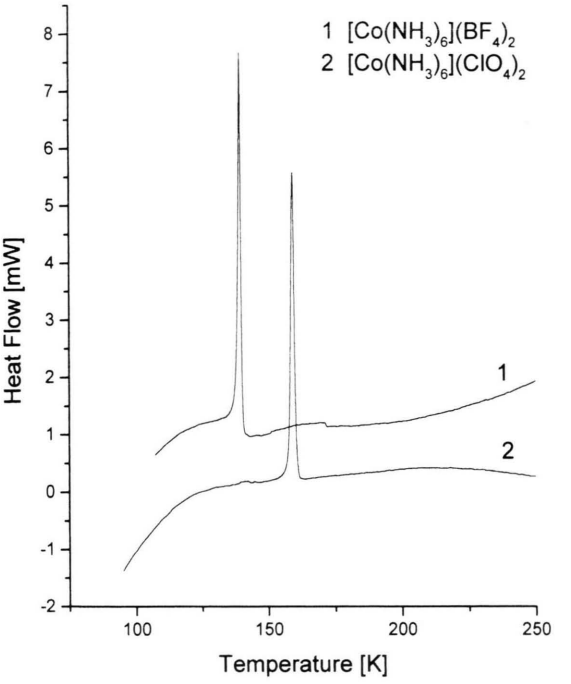

Fig. 3. Comparison of the DSC curves for $[Co(NH_3)_6](ClO_4)_2$ and $[Co(NH_3)_6](BF_4)_2$ registered on heating at a rate of 10 $K \cdot min^{-1}$.

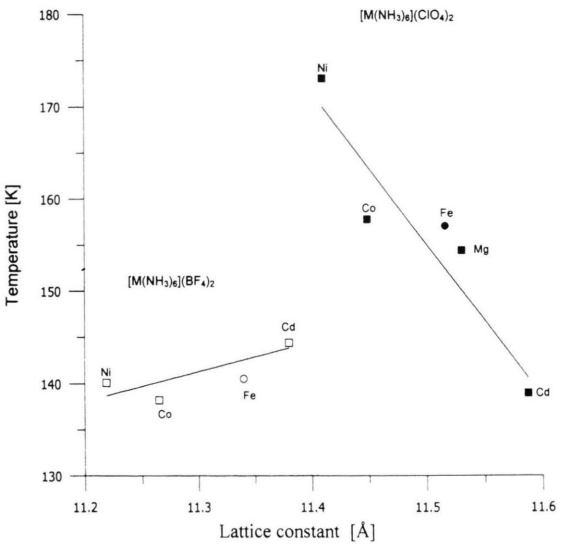

Fig. 4. Phase transition temperature T_{C1} vs. lattice constant a for $[Me(NH_3)_6](XY_4)_2$ compounds.

$[Co(NH_3)_6](ClO_4)_2$ this very small anomaly at *ca.* 140 K is quite evident on the DSC curve of Fig. 3. This observation will be a subject of our further

Table 1. Thermodynamic parameters of the phase transitions of $[M(NH_3)_6](ClO_4)_2$ and $[M(NH_3)_6](BF_4)_2$.

M	T_C [K]	ΔH [kJ·mol^{-1}]	ΔS [J·mol^{-1}·K^{-1}]	Ref.	T_C [K]	ΔH [kJ·mol^{-1}]	ΔS [J·mol^{-1}·K^{-1}]	Ref.
	— $[M(NH_3)_6](ClO_4)_2$ —				— $[M(NH_3)_6](BF_4)_2$ —			
Mg	154.35	4.68	30.35	[3]				
	139.5	0.76	5.43	[3]				
Fe	159			[23]	142			[23]
Co	157.7	3.90	24.7	this work	138.2	1.91	13.8	this work
	141	0.10	0.7	this work	?			this work
Ni	173.05	5.65	32.64	[2]	140.1	2.46	17.56	[1]
	143	0.54	3.76	[2]	115	?	?	[1]
Cd	138.9	4.12	29.6	this work	144.4	1.87	13.0	this work
Cd	125			[25]	147			[24, 26]

investigations. The temperature and enthalpy- and entropy-changes for the phase transitions detected for all the investigated compounds are presented in Table 1 together with the literature data on the analogous compounds with M = Mg, Fe and Ni. Table 1 shows that ΔH and ΔS for the $[M(NH_3)_6](BF_4)_2$ compounds are distinctly lower than those for the $[M(NH_3)_6](ClO_4)_2$ ones. For compounds with M = Cd there is a possibility of a comparison of the transition temperatures obtained in this work with those obtained by NMR [24, 25] and EPR [26]. The agreement of the results is much better for $[Cd(NH_3)_6](BF_4)_2$ than for $[Cd(NH_3)_6](ClO_4)_2$. Figure 4 shows a correlation between the high phase transition temperature (T_{C1}) and the crystal lattice parameter (a) for all the compounds presented in Table 1. A similar correlation for $[M(NH_3)_6]X_2$ compounds with different anions and different metal cations was noticed by Stankowski [31]. Our work improves this correlation for $[Cd(NH_3)_6](BF_4)_2$ and $[Cd(NH_3)_6](ClO_4)_2$ and adds two new points, namely for $[Co(NH_3)_6](BF_4)_2$ and $[Co(NH_3)_6](ClO_4)_2$. It can be seen in Fig. 4 that for the $[M(NH_3)_6](BF_4)_2$ compounds T_{C1} slightly increases with increasing lattice constant a, while for $[M(NH_3)_6](ClO_4)_2$ it is quite the opposite: T_{C1} strongly decreases with increasing a. $[M(H_2O)_6](ClO_4)_2$ behaves in an other way than most $[M(NH_3)_6]X_2$ compounds. We are yet unable to explain this difference. We did not observe such a difference in the case of the similar families $[M(H_2O)_6](ClO_4)_2$ and $[M(H_2O)_6](BF_4)_2$ [35], either.

4. Conclusions

The results of this work and their comparison with the literature data lead to the following conclusions:

1. The DSC curves of all the investigated compounds are very similar to the temperature dependence of the heat capacity of $[Ni(NH_3)_6](ClO_4)_2$, $[Mg(NH_3)_6](ClO_4)_2$ and $[Ni(NH_3)_6](BF_4)_2$.
2. The phase transition temperatures for the $[M(NH_3)_6](BF_4)_2$ compounds are generally lower than those for the compounds with ClO_4^- anions. However, for compounds with M = Cd it is quite the opposite.
3. The enthalpy and entropy changes detected for the $[M(NH_3)_6](BF_4)_2$ compounds are always significantly smaller than those for the compounds with ClO_4^- anions.
4. For both $[M(NH_3)_6](ClO_4)_2$ and $[M(NH_3)_6](BF_4)_2$ there exists a correlation between T_{C1} and the crystal lattice parameter a. However, whereas T_{C1} of $[M(NH_3)_6](ClO_4)_2$ decreases with increasing a, that of $[M(NH_3)_6](BF_4)_2$ increases with increasing a.

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