Phase Transitions in Crystalline $[Me(H_2O)_6](BF_4)_2$. Part I (Me = Mn, Fe, Co, Ni and Zn)

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

Department of Chemical Physics, Faculty of Chemistry of the Jagiellonian University,
Ingardena Street 3, 30-060 Kraków, Poland
[a] Department of Solid State Physics, Smoluchowski Institute of Physics, Jagiellonian University,
Reymonta Street 3, 30-059 Kraków, Poland

Z. Naturforsch. **54 a,** 225–228 (1999); received December 12, 1998

Solid polymorphism in five compounds of the type $[Me(H_2O)_6](BF_4)_2$, where Me = Mn, Fe, Co, Ni and Zn, have been studied in the temperature range 120 - 330 K by DSC. For each substance at least three solid modifications have been found. In addition, for compounds with Me = Mn, Fe and Zn some new low temperature phase transitions have been observed. The transition temperatures for the $[Me(H_2O)_6](BF_4)_2$ compounds are distinctly lower than those for the $[Me(H_2O)_6](ClO_4)_2$ compounds. The entropy- and enthalpy-changes at the phase transitions of the hexaaquametal(II) tetrafluoroborates are significantly lower than those for the corresponding chlorates(VII). Linear correlations between the highest transition temperature and the crystal density are found for both series of these isomorphous compounds.

Key words: Hexaaquametal(II) tetrafluoroborates; Phase Transitions; DSC Method.

1. Introduction

The hexaaquametal(II) tetrafluoroborates $[Me(H_2O)_6](BF_4)_2$, where Me = Mg, Mn, Fe, Co, Ni and Zn, form at room temperature a body centered orthorhombic-pseudohexagonal structure (space group $Pmn2_1$ – C^7_{2v}) with two molecules per unit cell and are isomorphous to the analogue hexaaquametal(II) chlorates(VII) [1 - 3]. The lattice parameters of $[Me(H_2O)_6](BF_4)_2$ were determined at room temperature by Moss et al. [3] and were found to be quite close to those of the corresponding $[Me(H_2O)_6](ClO_4)_2$ crystals.

Phase transitions of $[Me(H_2O)_6](BF_4)_2$ have been studied by EPR [4 - 6] and Mössbauer [7, 8] methods. The reported transition temperatures are summarized in Table 1 and compared with the data obtained in this work. In principle, in these compounds there could be several phase transitions associated with a change of the crystal structure, disorder of the BF_4^- ions, rearrangement of the H_2O groups and tumbling of the $[Me(H_2O)_6]^{2+}$ cations, but up to now experimental data are only available for the isomorphous $[Me(H_2O)_6](ClO_4)_2$ compounds. The high temperature phases of $[Mg(H_2O)_6](ClO_4)_2$ and $[Ni(H_2O)_6](ClO_4)_2$ have been interpreted [9 - 13] as disordered phases where the ClO_4^- anions and the H_2O groups perform fast stochastic reorientation at picosecond rate. During cooling of these compounds, the relatively large motions of the ClO_4^- anions stop abruptly at the transition point (T_{C1}) from the high temperature phase to the intermediate one [11]. In the intermediate phase there still exists some disorder connected with the H_2O groups, which has been suggested [14] on the basis of the temperature shift of the second phase transition (T_{C2}) after deuteration of the $[Ni(H_2O)_6](ClO_4)_2$ sample. Phase transitions to the low temperature phases (T_{C3} and T_{C4}) of $[Me(H_2O)_6](ClO_4)_2$, with Me = Mn, Fe, Co, and Ni,

Table 1. Temperature [K] of the phase transitions of $[Me(H_2O)_6)](BF_4)_2$.

Me	Mn	— Fe —			— Co —			— Zn —		— Ni —	
Ref.	*	*	[6]	[7, 8]	*	[6]	[8]	*	[6]	*	[6]
T_{C1}	250	271	269	273	281	281		285	286	304	301
T_{C2}	223	244			262	257		276	277	294	294
T_{C3}					(223)	189	185	(255)			
T_{C4}	162				177	172		161			
					168						

* this work; ( ) concerns anomalies that are extremely small.

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

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are probably connected with the symmetry lowering of the crystal structure [15, 16]. However, contrary to the above proposed mechanism of the phase transitions, the X-ray investigations at various temperatures [17], done for single crystals of $[Zn(H_2O)_6](ClO_4)_2$ and $[Ni(H_2O)_6](ClO_4)_2$, showed no unusually high thermal parameters of any atom and also no change of the overall hexagonal nature of the crystals throughout the range of temperature covering the T_{C1}, T_{C2} and T_{C3} phase transitions. The aim of this study is to detect the phase transitions of $[Me(H_2O)_6](BF_4)_2$ with Me = Mn, Fe, Co, Ni, Zn and to compare the results with those obtained earlier [18, 19] for the corresponding isomorphous $[Me(H_2O)_6](ClO_4)_2$ compounds.

2. Experimental

The compounds with Me = Mn and Co were synthesized by treating the corresponding carbonates with dilute HBF_4, and those with Me = Ni and Zn by dissolving the corresponding granulated metals in this acid. The solutions were concentrated by mild heating and the crystals obtained after the cooling of these solutions were purified several times by recrystallization from distilled water in a quartz vessel. The crystals were then dried for several days in a desiccator first over P_2O_5 and then over BaO, since they are extremely hygroscopic. The composition of these compounds was established on the basis of chemical and thermal analysis [20]. The commercial product of Aldrich Chemical Company was used for the investigations of $[Fe(H_2O)_6](BF_4)_2$.

The DSC measurements were performed with a Perkin-Elmer PYRIS 1 DSC apparatus at the Smoluchowski Institute of Physics of the Jagiellonian University. The instrument was calibrated by means of the melting point of indium and nitrochloroaniline for the high temperature region, and the melting point of H_2O for the low temperature region. Two temperatures of the DSC peaks were registered: the temperature of the maximum of the peak (T_{peak}) and the temperature calculated from the slope of the peak (T_{onset}). These two values differ by 2 to 6 K. As transition temperatures the values of T_{onset} for sharp peaks (first order transitions) and of T_{peak} for diffuse peaks (second order transitions) were 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. Before calculations, a linear background was subtracted. This was done in a more or less arbitrary way, but identically for all samples. Nevertheless, they are good for a comparison of the compounds. The entropy changes (ΔS) were calculated using the formula: $\Delta S_x = \Delta H / T_{Cx}$. For the first order phase transitions they were computed with high accuracy (± 4%), whereas for the second order phase transitions they could be seen as estimated only. The DSC measurements were performed on heating the samples with a constant rate of 10 K/min.

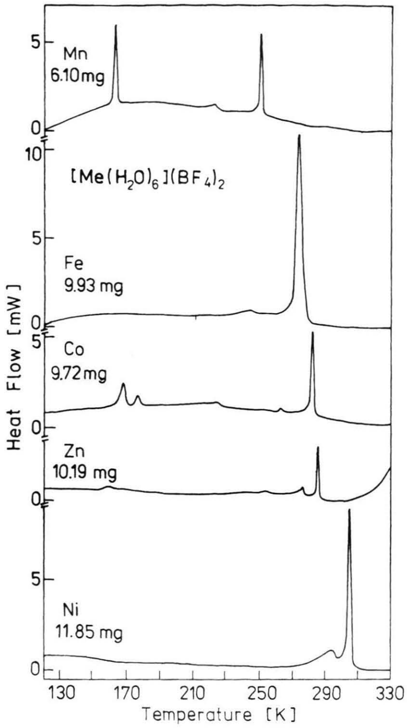

Fig. 1. DSC curves obtained for $[Me(H_2O)_6)](BF_4)_2$, where Me = Mn, Fe, Co, Zn and Ni.

3. Results and Discussion

Two DSC runs for two independent samples of each of the five investigated compounds were performed and the obtained results are fully consistent. Figure 1 presents the DSC results obtained for $[Me(H_2O)_6](BF_4)_2$ with Me = Mn, Fe, Co, Zn and Ni at 120 - 330 K, on heating the samples. The masses of the samples are given in the Figure 1. It can be seen that the character of the anomalies is very similar. Namely, in the high temperature region (above 200 K) there is always *one small* and *one sharp* anomaly. The temperature of these two anomalies (T_{C1} and T_{C2})

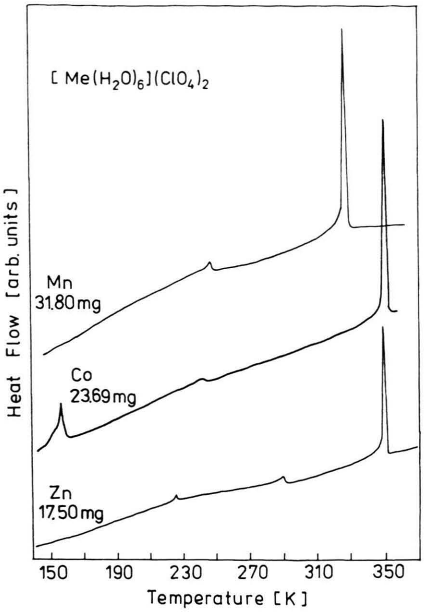

Fig. 2. DSC curves for $[Me(H_2O)_6](ClO_4)_2$, where Me = Mn, Co and Zn. Recalculated experimental data from [21].

increases moving from the compound with Me = Mn to Me = Fe, Co, Zn and Ni. In the low temperature region there exist also other anomalies, but only for compounds with Me = Mn, Co and Zn. The transition temperatures for all the detected phase transitions are gathered, together with the literature data, in Table 1. For the compounds with Me = Mn, Fe and Zn a few new phase transitions have been revealed. The transition temperatures of the other phase transitions are in a good agreement with the literature data obtained by EPR [6] and Mössbauer [7, 8] methods.

One should also point out that the heat flow temperature dependence of these compounds resembles that obtained by us earlier [18, 21] for the corresponding isomorphous $[Me(H_2O)_6](ClO_4)_2$ compounds. The DSC results for three $[Me(H_2O)_6](ClO_4)_2$ compounds with Me = Mn, Co and Zn obtained by us earlier [18] are compared in Figure 2. Table 2 presents a comparison of the transition temperatures and the entropy- and enthalpy-changes for the phase transitions of $[Me(H_2O)_6](BF_4)_2$ and $[Me(H_2O)_6](ClO_4)_2$. Table 2 shows that the adequate transition temperatures T_{C1} for the $[Me(H_2O)_6](BF_4)_2$ compounds are distinctly lower than those for the corresponding $[Me(H_2O)_6](ClO_4)_2$ compounds. Also the entropy- and enthalpy-changes connected with the phase transitions for the hexaaquametal(II) tetrafluoroborates are significantly lower than those for the corresponding chlorates(VII) [21]. An analogical effect was observed earlier [22, 23] in the adiabatic calorimetry measurements for $[Ni(NH_3)_6](BF_4)_2$ (T_{C1} = 140 K, ΔS = 17.6 J mol^{-1} K^{-1}) and $[Ni(NH_3)_6](ClO_4)_2$ (T_{C1} = 173 K, ΔS = 32.6 J mol^{-1} K^{-1}) crystals. The only exception are the ΔH and ΔS values for the phase transition of $[Fe(H_2O)_6](BF_4)_2$, which are by about 50% larger than those of $[Fe(H_2O)_6](ClO_4)_2$. We are yet unable to explain this phenomenon.

Table 2. Thermodynamics parameters of the phase transitions of isomorphous $[Me(H_2O)_6)](ClO_4)_2$ and $[Me(H_2O)_6)](BF_4)_2$ compounds.

— $[Me(H_2O)_6)](ClO_4)_2$ —			— $[Me(H_2O)_6)](BF_4)_2$ —		
T_C [K]	ΔS [J mol^{-1}K^{-1}]	ΔH [kJ mol^{-1}]	T_C [K]	ΔS [J mol^{-1}K^{-1}]	ΔH [kJ mol^{-1}]
Me = Mn:					
323.5	23	7.4	249.9	8	2.0
247	14	3.5	223	2	0.4
			162	17	2.8
Me = Fe:					
337.5	20	6.7	270.6	35	9.5
244	29	7.1	244	2	0.4
210	2	0.4			
Me = Co:					
347.5	19	6.6	281.4	6	1.8
241	15	3.6	262	0.2	0.06
			(223)		
156	18	2.8	177	2	0.3
			168	5	0.9
Me = Zn:					
348.0	19	6.6	285	3	0.7
290	6	1.7	276	1	0.3
226	1	0.2	(255)		
70	4	0.3	161	1	0.2
Me = Ni:					
361.0	25.2	9.1	303.6	11	3.2
311.4	9.5	2.9	294	3	0.9

( ) concerns anomalies that are extremely small.

Similarly as for the series of isomorphous $[Me(H_2O)_6](ClO_4)_2$, also for the $[Me(H_2O)_6](BF_4)_2$ series one can observe a correlation between the temperature of the highest phase transition (T_{C1}) and the density of the crystal. Namely, T_{C1} increases with the increase of the density of the crystal, as can be seen in Figure 3. This suggests that the highest temperature phase transition (T_{C1}), which is connected with a disorder of the anions (ClO_4^- or BF_4^-), should also be connected with changes in crystal structure. Because of the analogy between the $[Me(H_2O)_6](ClO_4)_2$ and

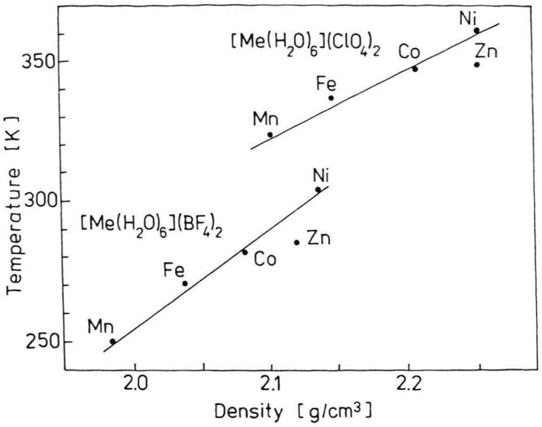

Fig. 3. Phase transition temperature T_{C1} vs. density of $[Me(H_2O)_6)](BF_4)_2$ and $[Me(H_2O)_6](ClO_4)_2$, where in both cases Me = Mn, Fe, Co, Ni and Zn.

$[Me(H_2O)_6](BF_4)_2$ compounds we could also suggest that the transition from the intermediate to the lowest temperature phase (T_{C2}) in $[Me(H_2O)_6](BF_4)_2$ is connected with disorder of the H_2O groups.

4. Conclusions

The isomorphous $[Me(H_2O)_6](BF_4)_2$ and $[Me(H_2O)_6](ClO_4)_2$ compounds, where in both cases Me = Mn, Fe, Co, Ni and Zn, exhibit similar DSC curves, but the highest temperature (T_{C1}) phase transitions and the enthalpy- and entropy-changes are systematically lower for the tetrafluoroborates than for the corresponding chlorates(VII). The highest temperature (T_{C1}) phase transitions in both series, which are related to an abrupt change in the rate of reorientation of the anions, exhibit a linear increase with the density of the crystals. The transition from the intermediate to the low temperature phase at T_{C2} in both series is connected with an abrupt change of the rate of reorientation of the H_2O groups.

Acknowledgements

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

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