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PHASE TRANSITIONS IN CRYSTALLINE $[M(H_2O)_6](ClO_4)_2$ (M=Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd and Hg)

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Abstract

The results of DSC measurements in the temperature range 140–370 K on nine crystalline compounds of the type $[M(H_2O)_6](ClO_4)_2$, where M=Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd and Hg, are discussed. Anomalies detected in the DSC curves are related to the existence of solid–solid phase transitions and/or to the melting points of these compounds. In consequence of two different hypothetical structural modifications of $[Fe(H_2O)_6](ClO_4)_2$, two DSC curves are obtained. For the compounds with M=Fe, Cd and Hg, new phase transitions have been discovered. The transition temperatures of the other phase transitions are in good agreement with literature data obtained by adiabatic calorimetry. For the compounds with M=Mg, Ni and Cd, DTA measurements were also carried out and the melting points of theses compounds were established.

Keywords: DSC and DTA, phase transitions in hexaaquametal(II) chlorates(VII)

Introduction

The structures of hexaaquametal(II) chlorates(VII) with general formula $[M(H_2O)_6](ClO_4)_2$, where M=Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd and Hg, were first estimated at room temperature by West [1] and were related to that of lithium chlorate(VII) ($LiClO_4{\cdot}3H_2O$, space group: $P6_3mc{-}C^4_{6v}$ [2, 3]) by the removal of every second metal ion along the *c* axis. The metal ions can be removed at either 1/4 *c* or 3/4 *c*. When the unit cell consists of M atoms at 1/4 *c* in the corner columns and at 3/4 *c* in the central column, the lattice can be called type A, following Ghosh and Ray [4]. The lattice type B has metal atoms at 3/4 *c* in the corner columns and at 1/4 *c* in the central column. These two types of cells differ from each other only by a shift of *c*/2. At room temperature, the crystals with M=Mg, Mn, Fe, Co, Ni and Zn form a body-centered orthorhombic-pseudohexagonal structure (space group $Pmn2_1{-}C^7_{2v}$) with two molecules per unit cell [1, 4]. Furthermore, since the unit cell has three equally probable orientations, crystals of these compounds grow as three-component twins. In the crystals with M=Cd and Hg, all the metal ions are at the same height (say, at z=1/4 *c*) in the unit cell. Ac-

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cording to West [1], the crystals form a trigonal structure with the space group $P3m1-C_{3v}^1$ and no twinning has been postulated to describe this structure. However, Johansson and Sandstroem [5, 6] determined the room-temperature structure of these compounds as $P\bar{3}m1-D_{3d}^3$, with one molecule per unit cell. The hydrogen-bonding in all these crystals is weak, which is a common characteristic of chlorate(VII) compounds.

It should be mentioned that there are some interesting peculiarities in the structures of $[M(H_2O)_6](ClO_4)_2$. Ghosh and Ray [7] suggested that the structure of $[Zn(H_2O)_6](ClO_4)_2$ is disordered and can be described in terms of an indefinite periodicity of lattices *A* and *B* such that a sequence of lattice type along the *b* axis undergoes 'random' shifts between *A* and *B*. Those authors [4, 8] also suggested that $[Fe(H_2O)_6](ClO_4)_2$ can crystallize at room temperature not only in a structure similar to that of the corresponding Zn compound, but also in a trigonal structure like that of the corresponding Cd and Hg compounds. $[Cu(H_2O)_6](ClO_4)_2$ occupies an exceptional position among the hexaaquametal(II) chlorates(VII) as it forms monoclinic crystals assigned to the space group $P2_1/c-C_{2h}^5$, with six molecules per unit cell [9, 10] at room temperature. Unfortunately, so far only the room-temperature structure of these compounds is known.

Phase transitions in the compounds investigated in this work have been studied by adiabatic calorimetry [11–15], DSC [16–18], EPR [19–27], NMR [28–30], magnetic susceptibility [31–35], Mössbauer [36–38], infrared and Raman spectroscopy [39–43], X-ray and other [44–46] measurements. The reported transition temperatures are summarized in [17, 18, 29]. In principle, in these compounds there could be several phase transitions associated with a change in structure, disorder of the ClO_4^- ions, rearrangement of the H_2O groups and tumbling of the $[M(H_2O)_6]^{2+}$ units. The high-temperature phases of $[Mg(H_2O)_6](ClO_4)_2$ and $[Ni(H_2O)_6](ClO_4)_2$ have been interpreted [13, 28, 39, 46] as disordered phases where the ClO_4^- anions and H_2O groups perform fast stochastic reorientation at picosecond rate. Relatively large motions of the ClO_4^- anions stop abruptly at the transition point from the high-temperature phase to the intermediate one [39]. In the intermediate phase there still exists disorder connected with the H_2O groups, which has been suggested [16] on the basis of the temperature shift of the second phase transition after deuteration of $[Ni(H_2O)_6](ClO_4)_2$. For $[Zn(H_2O)_6](ClO_4)_2$, $[Cd(H_2O)_6](ClO_4)_2$ and $[Mg(H_2O)_6](ClO_4)_2$, the activation energy for 180° flips of the H_2O groups is 16.3, 13.4 [29] and 13.4 kJ mol^{-1} [28], respectively. The activation energy for 'tumbling' of the whole $[Zn(H_2O)_6]^{2+}$, $[Cd(H_2O)_6]^{2+}$ and $[Mg(H_2O)_6]^{2+}$ cations is 96.3, 74.4 [29] and 50.0 kJ mol^{-1} [28], respectively.

Experimental

The compounds with *M*=Mn, Co, Cu and Cd were prepared by treating the corresponding carbonates with dilute $HClO_4$. The compounds with *M*=Mg, Fe, Ni and Zn were prepared by dissolving the corresponding granulated metals in this acid. $[Hg(H_2O)_6](ClO_4)_2$ was obtained in the reaction of red HgO with $HClO_4$. The solutions were concentrated by mild heating and the needle-shaped 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 over BaO or P_2O_5, since they are highly hygroscopic. The compositions of the compounds were established on the basis of chemical analysis.

The DSC measurements were performed with a Perkin-Elmer DSC-7 apparatus. The instrument was calibrated by means of the melting points of indium and zinc for the high-temperature region, and the melting point of H_2O and the phase transition of NH_4Br for the low temperature region. For the compounds with M=Cu and Hg, a gold vessel had to be used instead of an aluminium one. For all investigated samples, three different scanning rates (cooling and/or heating) were used (typically: 5, 10 and 15°C min^{-1}). 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 calculations, a linear background was subtracted. This was done in a more or less arbitrary way, but identically for all samples. The obtained results are therefore estimated rather than exact. Nevertheless, they are good enough to allow a comparison of the compounds investigated in this work. The entropy changes (ΔS) were calculated by using the formula: $\Delta S=\Delta H/T_c$.

The thermoanalytical curves were recorded on a MOM-Budapest derivatograph at the Regional Laboratory of Physicochemical Analyses and Structural Researches in Cracow. The samples were heated at a constant rate of 2°C min^{-1} and 0.10000 g Al_2O_3 was used as a reference substance. The sensitivity of the galvanometers was TG – 100 mg, DTA – 20 μV, DTG – 5 mg min^{-1}.

Results and discussion

Figure 1 presents the DSC results obtained in the temperature range 140–370 K for $[M(H_2O)_6](ClO_4)_2$ with M=Zn, Mn and Co on heating at a rate of 5°C min^{-1}. The DSC results for the corresponding compounds with M=Ni and Mg are fully compatible with those obtained earlier by adiabatic calorimetry. Figure 2 presents the temperature dependences of the specific heats of $[M(H_2O)_6](ClO_4)_2$ with M=Ni [15] and Mg [13] and, for comparison with Fig. 1, also $[Zn(H_2O)_6](ClO_4)_2$ [11]. With the exception of the positions of the anomalies, the temperature dependences of the heat flow and the specific heats for these five substances are very similar. Figures 1 and 2 reveal that there are one sharp and one (or two) small anomalies in these curves.

Figure 3 presents the DSC curves for the compounds with M=Cd, Fe and Hg on heating at a rate of 5°C min^{-1}. With the exception of the positions of the anomalies, the temperature dependences of the heat flow for these three substances are similar. It can be seen in Fig. 3 that, in contrast with the results shown in Figs 1 and 2, there is not merely one, but two sharp anomalies. Additionally, in the case of $[Cd(H_2O)_6](ClO_4)_2$, there is also one small anomaly. It should be noted here that the ΔH values corresponding to the phase transitions in $[Cd(H_2O)_6](ClO_4)_2$ are nearly one order of magnitude smaller than the respective ΔH values for the corresponding Hg and Fe compounds.

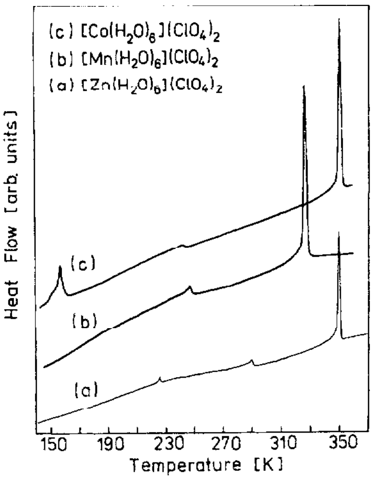

Fig. 1 DSC curves obtained for $[M(H_2O)_6](ClO_4)_2$, where M=Zn, Mn and Co

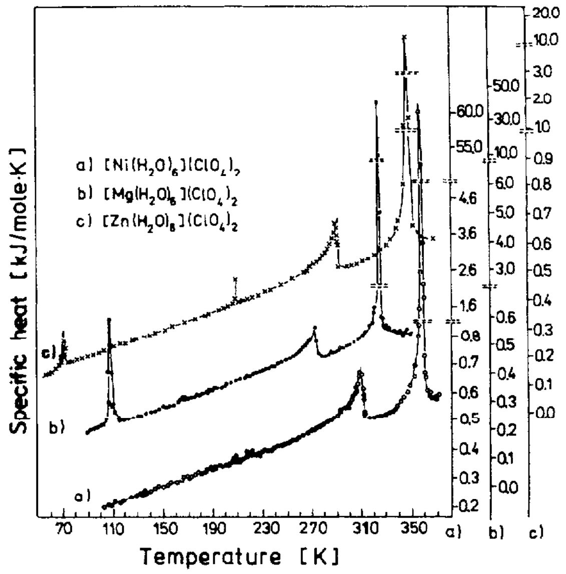

Fig. 2 Specific heats of $[M(H_2O)_6](ClO_4)_2$ *vs.* temperature, where M=Ni [15], Mg [13] and Zn [11]

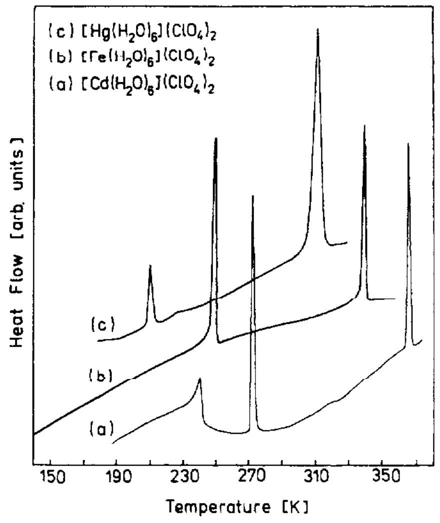

Fig. 3 DSC curves obtained for $[M(H_2O)_6](ClO_4)_2$, where M=Cd, Fe and Hg

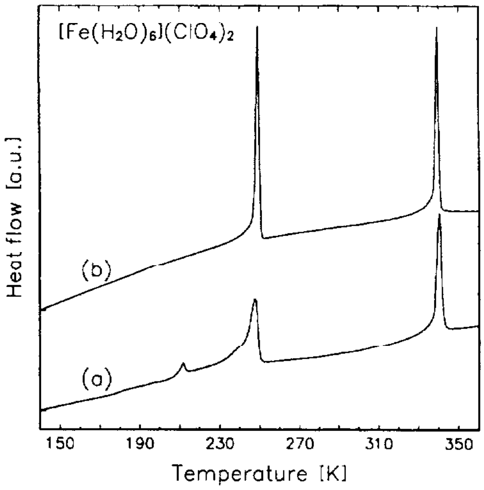

Fig. 4 DSC curves for two specimens of $[Fe(H_2O)_6](ClO_4)_2$

Figure 4 shows the DSC curves for two different specimens of $[Fe(H_2O)_6](ClO_4)_2$. These two specimens differ in the manner of recrystallization from water. It can be seen from Fig. 4 that there are two different temperature dependences of the heat flow. Dependence *b*, the same as that in Fig. 3, indicates two sharp anomalies, while dependence *a* reveals one sharp, and two small anomalies. The explanation may be as follows. Ghosh and Ray [4, 8] report that there exist two modifications of $[Fe(H_2O)_6](ClO_4)_2$ crystals: an ordered one, which has an orthorhombic-pseudohexagonal ($Pmn2_1$) structure like that for the compounds with *M*=Mg, Mn, Co, Ni and Zn, and a disordered one, which probably has a trigonal ($P\bar{3}m1$) structure like that for the compounds with *M*=Cd and Hg. We suppose that specimen *a* of $[Fe(H_2O)_6](ClO_4)_2$ is that which has a pseudohexagonal-orthorhombic structure, and that specimen *b* is that which has a trigonal structure. All anomalies presented in Figs 1–4 are attributed to the existence of the solid–solid phase transitions in the investigated compounds. The transition temperatures and entropy changes for these phase transitions are presented in Table 1.

Table 1 Thermodynamic parameters of $[M(H_2O)_6](ClO_4)_2$

M	Mg	Mn	Fe(a)	Co	Ni	Zn	Cd	Hg	Fe(b)	Cu
References	[13]	[17]	[*]	[17]	[15]	[18]	[18]	[18]	[17]	[18]
$T_{melting}$/K	434*				442*	435	398	333		353
ΔS/J mol^{-1} K^{-1}								149		86
T_1/K	325.0	323.5	337.5	347.5	361.0	348.0	362.7	306.0	336.7	
ΔS/J mol^{-1} K^{-1}	25.4	23	20	19	25.2	19	3	43	23	
T_2/K	273.0	247	244	241	311.4	290	271.0	208	247.0	
ΔS/J mol^{-1} K^{-1}	6.8	14	29	15	9.5	6	6	11	31	
T_3/K	(168)		210		(225)	226	239			
ΔS/J mol^{-1} K^{-1}			2			1	4			
T_4/K	108			156		70	125			
ΔS/J mol^{-1} K^{-1}	8.5			18		4#	20&			

* This work
# From paper [11]
& From paper [12]
() Concerns anomalies that are extremely small

Figure 5 depicts the differential thermal analysis (DTA) curves for the compounds with *M*=Cd, Ni and Mg in the temperature range 298–490 K. The DTA curves are characterized by the appearance of one (or two) small endothermic effects which can be ascribed to the phase transitions connected with structural changes, and one large endothermic effect connected with the melting of the sample. Then there are two small endothermic effects, probably connected with the decomposition of the substance. The low-temperature endothermic effects in the DTA curves correspond quite well to the high-temperature anomalies in the DSC curve or the specific heat curve of the respective compound (Figs 2 and 3).

Figure 6 presents the DSC curve for $[Cu(H_2O)_6](ClO_4)_2$, obtained at a heating rate of 5°C min^{-1}. It can be seen in Fig. 6 that there is only one large anomaly in

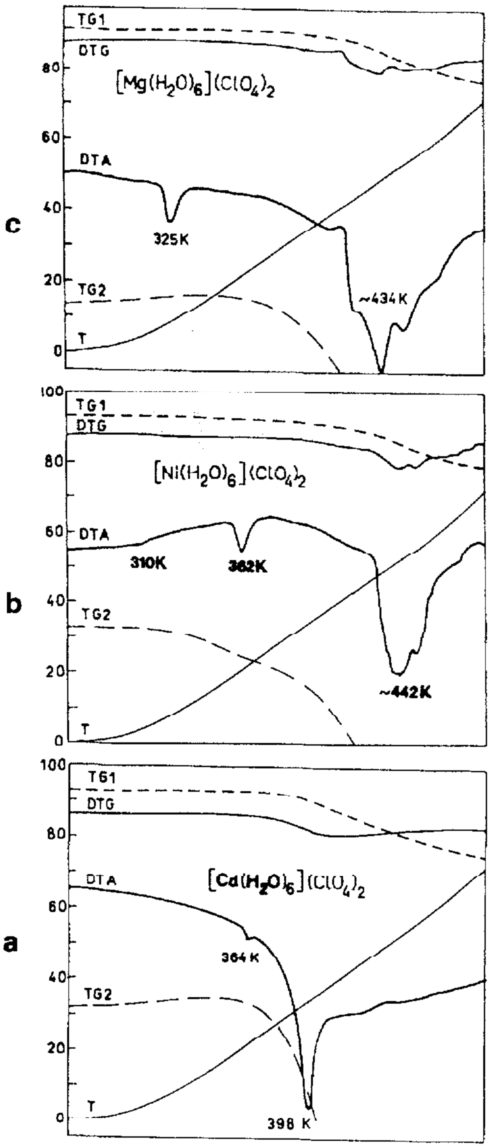

Fig. 5 DTA curves for $[M(H_2O)_6](ClO_4)_2$, where M=Cd, Ni and Mg

the DSC curve, connected with the melting of the substance. There are no anomalies connected with solid–solid phase transitions.

The thermodynamic parameters of the phase transitions for all the compounds investigated in this work are presented in Table 1. In order to obtain the real transition temperatures for the highest temperature anomaly in the DSC curves (T_1), the measurements were made by heating and cooling the investigated compounds at three rates: 5, 10 and 15°C min^{-1}. The values of T_1 pres-ented in Table 1 were determined by extrapolation to zero rate of heating of the sample. It should be pointed out that the value of T_1 obtained for $[Zn(H_2O)_6](ClO_4)_2$ by the DSC method is only ~1 K lower than that obtained by the adiabatic calorimetry method [11]. Extrapolation to zero rate of cooling gives transition temperatures T_1 about 3 K lower than the values obtained when the samples were heated. This phase transition therefore displays a small temperature hysteresis and can thus be treated as of first order.

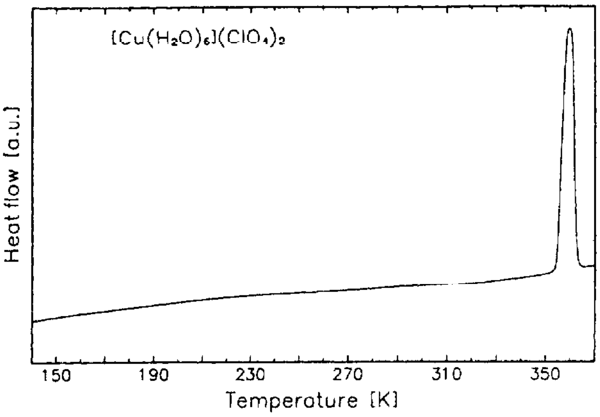

Fig. 6 DSC curve obtained for $[Cu(H_2O)_6](ClO_4)_2$

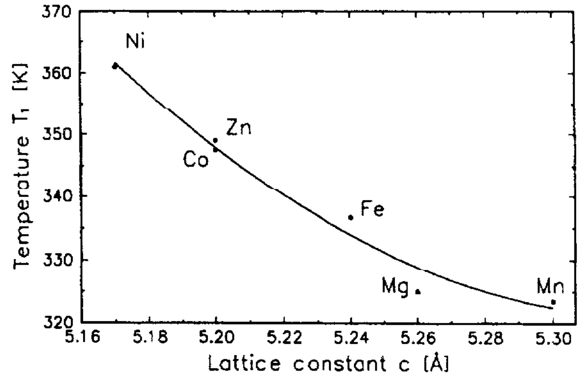

Fig. 7 Transition temperature T_1 *vs.* lattice constant *c* for $[M(H_2O)_6](ClO_4)_2$, where *M*=Ni, Zn, Co, Fe, Mg and Mn

We have also observed a correlation between the value of T_1 and the lattice constant *c* for the isomorphic series of compounds $[M(H_2O)_6](ClO_4)_2$: the value of T_1 decreases with increase in the lattice constant *c*, as can be seen in Fig. 7. This suggests a structural character of the highest-temperature phase transition.

For a better understanding of the polymorphism of the investigated compounds, new DSC investigations into isomorphic compounds $[M(H_2O)_6](BF_4)_2$ are now in progress.

Conclusions

1. The isomorphic compounds $[M(H_2O)_6](ClO_4)_2$ furnish a similar shape for the temperature dependence of the specific heat or the heat flow.
2. $[Fe(H_2O)_6](ClO_4)_2$ exhibits two different temperature dependences of the heat flow, due to its two structural modifications.
3. $[Cu(H_2O)_6](ClO_4)_2$ does not undergo solid–solid phase transitions in the temperature range from 140 K up to the melting point at 353 K.
4. The highest-temperature (T_1) phase transition in $[M(H_2O)_6](ClO_4)_2$ (M=Mg, Mn, Fe, Co, Ni and Zn) is related not only to reorientation of the ClO_4^- anions, but also to a change in their structure.

* * *

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