

Phase polymorphism and thermal decomposition of hexadimethylsulphoxidemagnesium(II) chlorate(VII)

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Abstract Differential scanning calorimetry (DSC) measurements were performed over the temperature range 93–480 K and three enantiotropic (at 323, 409, and 461 K) and one monotropic (at 271 K) phase transitions were detected. Thus, four solid phases (three of them stable and one metastable) and one liquid phase were found. It was concluded, from the entropy change (ΔS) values of these phase transitions that two of them are stable rotational phases and two are crystalline phases (one stable and one metastable). The thermal decomposition of $[\text{Mg}((\text{CH}_3)_2\text{SO})_6](\text{ClO}_4)_2$, which was studied using thermogravimetry (TG) with simultaneous differential thermal analysis (SDTA), takes place in two main stages. The gaseous products of the decomposition were identified on-line by a quadruple mass spectrometer (QMS). In the first stage, which starts just above ca. 432 K, the compound loses two dimethylsulphoxide (DMSO) molecules per one formula unit. In the second stage (502–673 K) $[\text{Mg}(\text{DMSO})_4](\text{ClO}_4)_2$ decomposes explosively and Cl_2 , O_2 , H_2 , and MgSO_4 are finally produced.

Keywords DSC · Hexadimethylsulphoxidemagnesium(II) chlorate(VII) · Phase transitions SDTA · TG/QMS · Thermal decomposition

Introduction

We recently investigated the phase polymorphism of several $[\text{M}(\text{DMSO})_6](\text{ClO}_4)_2$ compounds, where $\text{M} = \text{Cd}, \text{Co}, \text{Mn}, \text{Zn}, \text{Ni}$ and $\text{DMSO} = (\text{CH}_3)_2\text{SO}$ using the DSC

method [1–5] and found that all these substances had crystalline and rotational solid phases, some of them being stable and some metastable phases. The compounds with $\text{M} = \text{Ni}, \text{Co}$ and Zn crystallize in an orthorhombic system (S.G.: P31c (No. 159), $Z = 2$) [6, 7] and those with $\text{M} = \text{Mn}$ and Cd crystallize in a trigonal system (space group: Fdd2, No. 43, $Z = 2$) [8–10]. Their crystal lattices consist of two kinds of complex ions: $[\text{M}((\text{CH}_3)_2\text{SO})_6]^{2+}$ and ClO_4^- . The cation is a slightly deformed octahedron in which the metal(II) cation is coordinated by six oxygen atoms derived from the dimethylsulphoxide ligands. The DMSO ligands are built like C_{2v} pyramids. Unfortunately, the crystal structure of $[\text{Mg}(\text{DMSO})_6](\text{ClO}_4)_2$ is so far unknown, but it is probably similar to that of $[\text{Ni}(\text{DMSO})_6](\text{ClO}_4)_2$. Theoretical and experimental studies of molecular structure and vibrational spectrum of $[\text{Mg}(\text{DMSO})_6](\text{ClO}_4)_2$ we will publish elsewhere [11].

The aim of the present study was to discover the polymorphism of $[\text{Mg}(\text{DMSO})_6](\text{ClO}_4)_2$ in the temperature range 93–480 K using differential scanning calorimetry (DSC) in order to compare the results with those obtained earlier for the similar compounds mentioned above. Additionally, we tried to establish the mechanism of the thermal decomposition of $[\text{Mg}(\text{DMSO})_6](\text{ClO}_4)_2$ using thermal analysis methods (TG, DTG, QMS, SDTA, and DSC).

Experimental

Synthesis, identification of compound and used methods

The compound to be examined was obtained from hexa-aquamagnesium(II) chlorate(VII) which had earlier been synthesised by the reaction of magnesium carbonate

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(www.sigmaaldrich.com, CAS number: 546-93-0) with diluted HClO_4 (in the molar ratio 1:6). The $[\text{Mg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ was dissolved (in the molar ratio 1:6) while slowly being heated in dimethylsulphoxide, which had previously been purified by vacuum distillation at low pressure. This solution was then chilled and the precipitated crystals of $[\text{Mg}(\text{DMSO})_6](\text{ClO}_4)_2$ were filtered. The compound was then dried in a desiccator over phosphorous oxide(V) for few hours. After this time it was put in a sealed vessel and stored in a desiccator with barium oxide.

To check the chemical composition of the synthesised compound the percentage content of magnesium ions was checked using a complexometric method with a solution of sodium salt of ethylenediaminetetraacetic acid (EDTA) as a titrant. The carbon and hydrogen content in the DMSO ligand was determined using elementary analysis in a EURO EA 3000 apparatus. The theoretical content of magnesium is 3.51%, and the content found by titration analysis was 3.42 (± 0.12) %. For the carbon atoms, the difference between the theoretical (20.83%) and test value 20.94 (± 0.01) % did not exceed 1%. For the hydrogen atoms, the theoretical value is 5.24% and the test value was 5.38 (± 0.01) %. Therefore, elementary analysis of the title compound confirmed the presence of the stoichiometric number of six DMSO molecules in the complex cation.

Fourier transform Raman scattering measurements (FT-RS) were performed at room temperature with a Nicolet NXR 96/50 spectrometer with a resolution of 4 cm^{-1} . The incident radiation ($\lambda = 1,064 \text{ nm}$) was from a YAG Spectra-Physics Neodymium laser. Fourier transform middle-infrared absorption measurements (FT-MIR) were performed using a Bruker EQUINOX-55 spectrometer, with a resolution of 2 cm^{-1} . The FT-MIR spectrum was recorded for a sample suspended in Nujol between KBr pellets. Figure 1 shows the infrared and Raman spectra of $[\text{Mg}(\text{DMSO})_6](\text{ClO}_4)_2$. The recorded and calculated [11] spectra and their comparison with the respective spectra of similar compounds [1–5] and with literature data [12, 13] also confirmed the identification of the investigated compound as $[\text{Mg}(\text{DMSO})_6](\text{ClO}_4)_2$.

Thermogravimetry (TG) and simultaneous differential thermal analysis were performed using a Mettler-Toledo TGA/SDTA 851^c instrument. The measurements were made in a flow (80 mL min^{-1}) of high purity dry argon (99.999%) over the temperature range 300–675 K. TG measurements were performed at a constant heating rate of 10 K min^{-1} . Additionally, gases evolved during the experiment were analyzed with an on-line quadruple mass spectrometer (QMS) using a Balzer GSD 300T instrument. The temperature was measured by a Pt–Pt/Rh thermocouple with an accuracy of $\pm 0.5 \text{ K}$. Thermal decomposition measurements were made for a sample weighing 6.67 mg, which was placed in a 150 μL open corundum ($\alpha\text{-Al}_2\text{O}_3$) crucible.

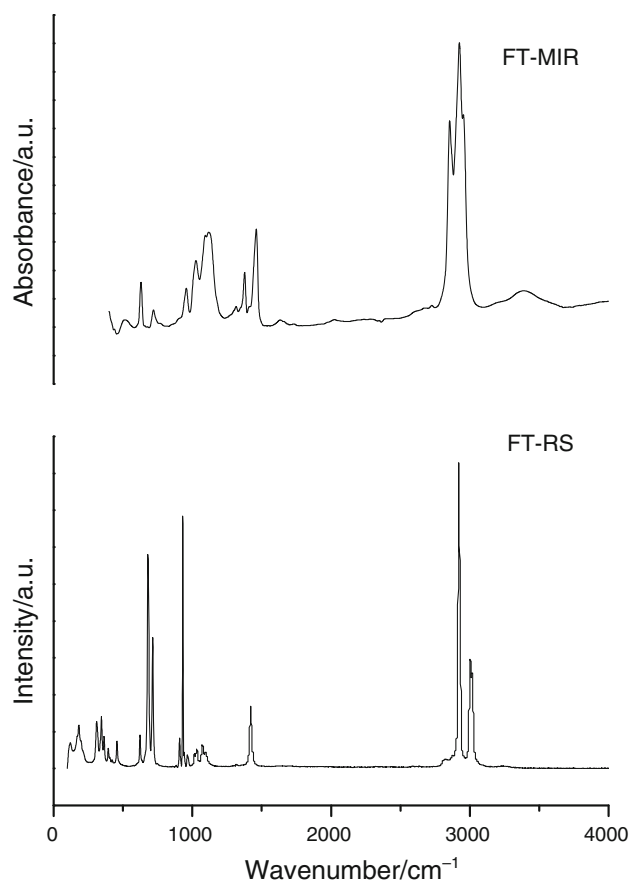


Fig. 1 Infrared (FT-MIR) and Raman (FT-RS) spectra of $[\text{Mg}(\text{DMSO})_6](\text{ClO}_4)_2$

Differential scanning calorimetry (DSC) measurements were made using two types of DSC apparatus: the first was a Perkin-Elmer PYRIS 1 DSC apparatus on which four samples were investigated over the temperature range 93–423 K. The mass of these samples was, respectively, 8.07, 10.07, 13.29, and 16.68 mg. The experimental details were the same as published in [14]. The second apparatus was a Mettler-Toledo DSC 821e instrument used over the temperature range 218–556 K. The DSC measurements were made by heating samples of massing 9.88, 14.06, and 15.95 mg. Measurements were performed under a constant flow of argon (80 mL min^{-1}), with a heating rate equal to 5 K min^{-1} . The obtained DSC curves were fully reproducible, so the results will be discussed for the representative samples only.

Results and discussion

DSC measurements

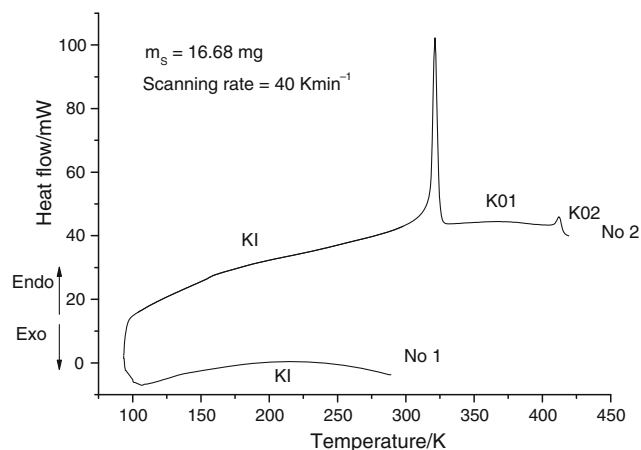
The temperature dependence of the difference between the thermal power supplied to the two calorimeters (the

Table 1 Thermodynamics parameters of the detected phase transitions on heating T_{Cn}^h (and at cooling T_{Cn}^c) in $[\text{Mg}(\text{DMSO})_6](\text{ClO}_4)_2$

	Phase transition	$[\text{Mg}(\text{DMSO})_6](\text{ClO}_4)_2$		
		T_c/K	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{J mol}^{-1} \text{K}^{-1}$
T_{m1}^h	K02 \rightarrow L0	461 ± 1	7.73 ± 0.98	16.8 ± 2.3
T_{C1}^h (T_{C1}^c)	K01 \leftrightarrow K02	409 ± 1 (406 ± 1)	1.08 ± 0.22	2.6 ± 0.5
T_{C2}^h (T_{C2}^c)	KI \leftrightarrow K01	323 ± 2 (315 ± 2)	17.13 ± 2.90	53.1 ± 8.7
T_{C3}^h (T_{C3}^c)	KII \leftrightarrow K0'	287 ± 1 (271 ± 1)	3.95 ± 0.41	1.5 ± 0.2

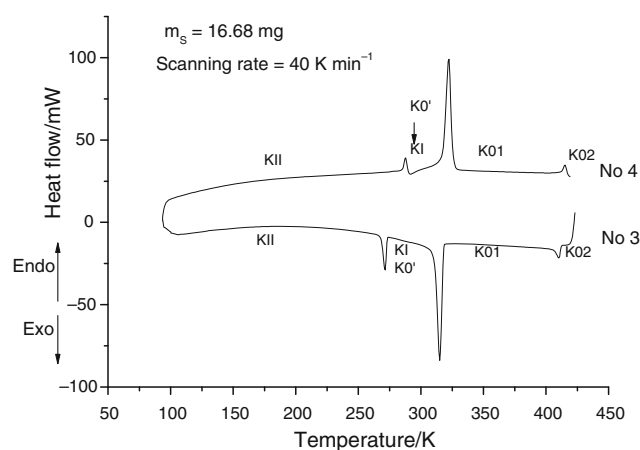
so-called heat flow), in short the DSC curve, were obtained for each of the six independent samples of the title compound at different scanning rates and at initial and final heating and cooling conditions. The masses of the samples were chosen so as to determine whether the observed phase transition is dependent on mass. We did not notice significant differences between the results for all the samples. All the thermodynamic parameters of the detected phase transitions are shown together in Table 1.

Measurements on the representative sample with a mass of 16.68 mg were started by cooling the sample, with a scanning rate of 40 K min^{-1} , from room temperature (298 K) to 93 K (first cooling). As can be seen in Fig. 2 there was no anomaly on the DSC curve obtained over the temperature range 298–93 K (curve No 1). After holding the sample at 93 K for 1 min, it was heated to 423 K. While heating, with a scanning rate of 40 K min^{-1} , this sample being initially in the ordered crystalline phase named by us KI underwent a phase transition at $T_{C2}^h = 323 \text{ K}$ into the intermediate phase, which was named by us K01, and which is evident as a large anomaly on DSC curve No 2 in Fig. 2. On further heating phase K01 transforms at $T_{C1}^h = 409 \text{ K}$ into the high temperature phase, named K02, which is evident as a small anomaly also on curve No 2.

**Fig. 2** Differential scanning calorimetry (DSC) curves obtained for $[\text{Mg}(\text{DMSO})_6](\text{ClO}_4)_2$ during cooling from 298 to 93 K and during heating at 93–423 K with a scanning rate of 40 K min^{-1}

The total enthalpy (or entropy) value changes associated with the observed phase transitions were quite large at T_{C2}^h and small at T_{C1}^h suggesting that phases K01 and K02 are the rotational phases [15]. Of course, it is not possible to determine the nature of the observed phases using the DSC (or TG/SDTA) method only. Therefore, X-ray powder diffraction (XRPD) measurements at different temperatures were recently performed and the preliminary results, which will be published soon, confirmed that phases K01 and K02 are crystalline phases with great rotational disorder.

During cooling of the sample in the K02 phase, with a scanning rate of 40 K min^{-1} , it underwent (at T_{C1}^c) a transition to phase K01. The sample, then partially in phase K01, was overcooled to phase K0' and underwent partially (phase transition at T_{C2}^c) to phase KI (see curve No 3 in Fig. 3). The overcooled phase K0' underwent transition to the metastable phase KII at $T_{C3}^c = 271 \text{ K}$. Heating of the same sample, with a scanning rate of 40 K min^{-1} , gave DSC curve No 4 presented in Fig. 3. The sample, then in the metastable phase KII, partially transformed by an endothermic process into the overcooled phase K0' at $T_{C3}^h = 287 \text{ K}$ (the small but sharp endothermic anomaly on the DSC curve) and, at a slightly higher temperature, the overcooled phase K0' converted via an exothermic process

**Fig. 3** DSC curves obtained during cooling from 423 to 93 K and during heating at 93–423 K of $[\text{Mg}(\text{DMSO})_6](\text{ClO}_4)_2$ with a scanning rate of 40 K min^{-1}

to the stable phase KI (the sharp but very small exothermic anomaly denoted as arrow on DSC No 4 in Fig. 3). When heating of the sample was continued a phase transition was occurred from phase KI to K01 at T_{C2}^h (the very large endothermic anomaly on the DSC curve No 4). Finally the stable K01 phase also endothermically converted at T_{C1}^h to the stable phase K02 (manifested as small anomaly on DSC curve No 4).

DSC measurement during heating of a new sample of mass 9.88 mg from 300 to 480 K, with a scanning rate of 10 K min^{-1} , gave DSC curve presented in Fig. 4. As can be seen on this DSC curve, the phase transitions into the high temperature phases occurred at $T_{C2}^h = 323 \text{ K}$ (KI \rightarrow K01) and $T_{C1}^h = 409 \text{ K}$ (K01 \rightarrow K02) with temperature values identical to our earlier measurements. Additionally, heating the sample above $T_{C1}^h = 409 \text{ K}$ stimulated a phase transition from the stable phase K02 to the partially liquid phase named L0 at $T_{m1}^h = 461 \text{ K}$. Taking into account the results of thermal analysis, which are presented below, we can postulate that, at $T_{m1}^h = 461 \text{ K}$, the sample is partially dissolved in DMSO because two DMSO molecules per one formula unit are liberated during the decomposition of $[\text{Mg}(\text{DMSO})_6](\text{ClO}_4)_2$ to $[\text{Mg}(\text{DMSO})_4](\text{ClO}_4)_2$ (see chapter below: TG/SDTA measurements).

TG/SDTA measurements

Figure 5 shows TG, DTG, and SDTA curves recorded for the sample over the temperature range 300–675 K. During the TG experiment the QMS spectra of masses were followed from $m/e = 1$ to 140, however, for reasons of graphic clarity, only the masses of $m/e = 15, 18, 16, 28, 32, 17, 29, 14, 44, 64, 48, 45, 13, 35,$ and 31 representing:

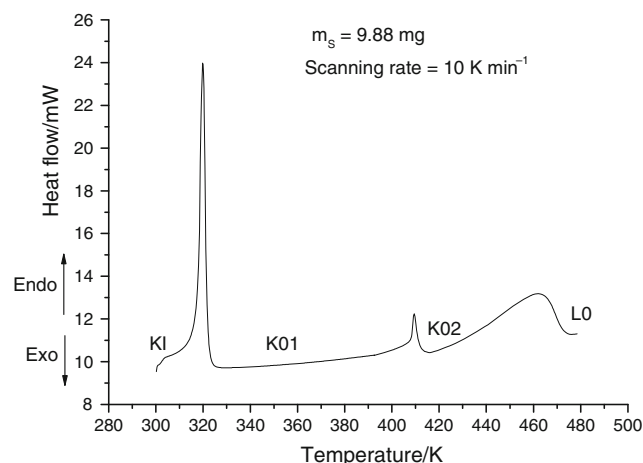


Fig. 4 DSC curves registered in the temperature range of 300–480 K during heating of $[\text{Mg}(\text{DMSO})_6](\text{ClO}_4)_2$ with a scanning rate of 10 K min^{-1}

$\bullet\text{CH}_3, \text{H}_2\text{O}, \bullet\text{O}$ or CH_4, CO or $\text{C}_2\text{H}_4, \text{O}_2$ or $\text{S}, \bullet\text{OH}, \bullet\text{C}_2\text{H}_5, \bullet\text{CH}_2, \text{CO}_2, \text{SO}_2, \text{SO}, \text{C}_2\text{H}_5\text{O}, \bullet\text{CH}, \text{Cl}\bullet,$ and CH_3O are shown in Fig. 6. The TG, DTG, and QMS curves show that

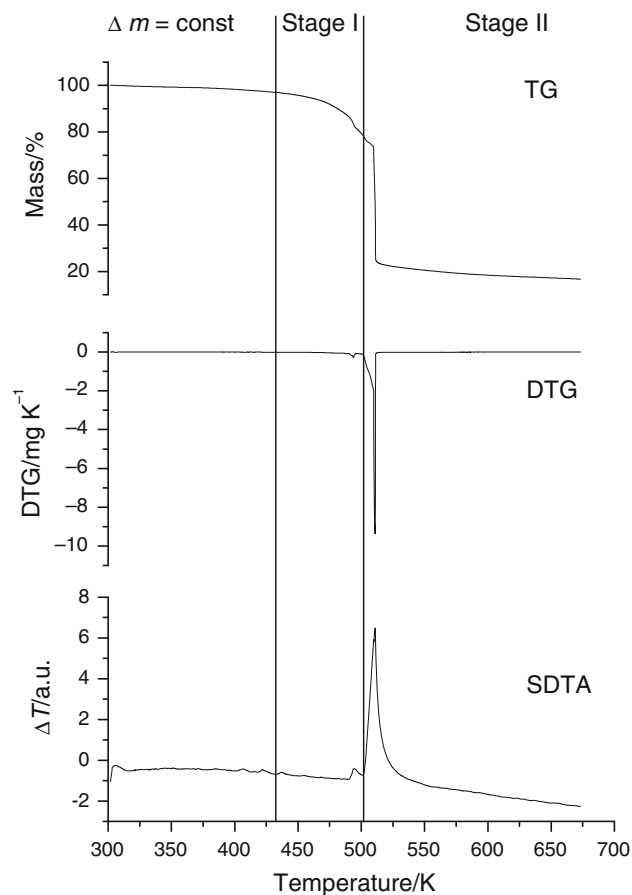


Fig. 5 TG, DTG, and SDTA curves registered for $[\text{Mg}(\text{DMSO})_6](\text{ClO}_4)_2$ in the temperature range of 300–675 K

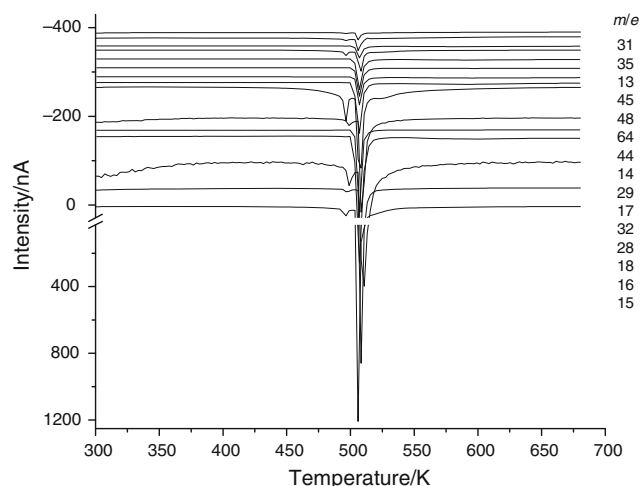


Fig. 6 QMS curves for $[\text{Mg}(\text{DMSO})_6](\text{ClO}_4)_2$ in the range of 300–675 K

Table 2 Progress of thermal analysis of $[\text{Mg}(\text{DMSO})_6](\text{ClO}_4)_2$

Stage number	Reaction	References
I	$[\text{Mg}((\text{CH}_3)_2\text{SO})_6](\text{ClO}_4)_2 \rightarrow [\text{Mg}((\text{CH}_3)_2\text{SO})_4](\text{ClO}_4)_2 + 2(\text{CH}_3)_2\text{SO}$	This study
II	$(\text{CH}_3)_2\text{SO} + \bullet\text{OH} \rightarrow \text{CH}_3\text{S}(\text{O})\text{OH} + \bullet\text{CH}_3$	[16, 17]
	$\text{CH}_3\text{S}(\text{O})\text{OH} + \bullet\text{OH} \rightarrow \text{CH}_3\text{S}(\text{O})(\text{OH})_2 + \text{O}_2 \rightarrow \text{CH}_3\text{S}(\text{O})_2\text{OH} + \text{HO}_2$	[16, 17]
	$\text{CH}_3\text{S}(\text{O})_2\text{OH} + \bullet\text{OH} \rightarrow \text{H}_2\text{SO}_4 + \bullet\text{CH}_3$	[16, 17]
	$[\text{Mg}((\text{CH}_3)_2\text{SO})_4](\text{ClO}_4)_2 + \text{H}_2\text{SO}_4 \rightarrow 4(\text{CH}_3)_2\text{SO} + \text{MgSO}_4 + \text{Cl}_2 + 4\text{O}_2 + \text{H}_2$	[18]

Table 3 Parameters of $[\text{Mg}(\text{DMSO})_6](\text{ClO}_4)_2$ thermal decomposition; initial sample mass = 6.67 mg

Stage number	Temperature range/K	Mass loss/%	Mass after decomposition/%	Calculated values/%	Products of decomposition
I	432–502	22.5		22.6	$2(\text{CH}_3)_2\text{SO}$
II	502–673	60.8	16.7	60.0	$4(\text{CH}_3)_2\text{SO}, \bullet\text{CH}_3, \text{Cl}_2, \text{O}_2, \text{H}_2$
				17.4	MgSO_4

the decomposition of the sample takes place in two main stages (I and II). The proposed progress of the thermal decomposition of the title compound is presented in Table 2 and the thermogravimetric data are gathered in Table 3. It can be seen that the first stage of thermolysis, which begins slowly above ca. 430 K, only releases two DMSO ligands per one formula unit until ca. 495 K. In the second stage, which occurs over the temperature range 502–675 K, we can observe melting and decomposition of newly created $[\text{Mg}(\text{DMSO})_4](\text{ClO}_4)_2$. In this process DMSO molecules react with $\bullet\text{OH}$ radicals derived from DMSO fragmentation [16, 17]. According to Rachwalska and Majda [18] H_2SO_4 created in this process can react with $[\text{Mg}(\text{DMSO})_4](\text{ClO}_4)_2$ giving magnesium sulphate and chloric(VII) acid and the newly created HClO_4 immediately decomposes to Cl_2 , O_2 , and H_2 .

Conclusions

- TG, DTG, SDTA, and QMS curves show that the decomposition of the sample takes place in two main stages
 - the first stage (432–502 K) of thermolysis, which starts just above 432 K, involves the release of two DMSO ligands per one formula unit;
 - in the second stage, which occurs over the temperature range 502–675 K, melting point and decomposition of newly created $[\text{Mg}(\text{DMSO})_4](\text{ClO}_4)_2$ are observed.
- $[\text{Mg}(\text{DMSO})_6](\text{ClO}_4)_2$ over the temperature range 93–480 K indicates four phase transitions:
 - rotational K02 \rightarrow L0, at $T_{m1} = 461$ K, with $\Delta S = 16.8 \pm 2.3 \text{ J mol}^{-1} \text{ K}^{-1}$;

- rotational K01 “rotational K02, at $T_{C1} \approx 407$ K, with $\Delta S = 2.6 \pm 0.5 \text{ J mol}^{-1} \text{ K}^{-1}$;
- KI “K01, at $T_{C2} \approx 319$ K, with $\Delta S = 53.1 \pm 8.7 \text{ J mol}^{-1} \text{ K}^{-1}$;
- metastable KII “overcooled K0’, at $T_{C3} \approx 279$ K, with $\Delta S = 1.5 \pm 0.2 \text{ J mol}^{-1} \text{ K}^{-1}$.

- It can be concluded from a comparison between the values of the entropy changes of the melting and the reversible phase transition KI phase “K01 phase, that phases K01, K02 and the overcooled K0 (K0’) are so-called “plastic crystals—(PC)” or “orientationally dynamically disordered crystals—(ODDIC)”. Phases KI and KII are more-or-less ordered phases.

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