Phase Polymorphism of $[Cd(DMSO)_6](ClO_4)_2$ Studied by Differential Scanning Calorimetry

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Five phase transitions of $[Cd(DMSO)_6](ClO_4)_2$ have been detected by differential scanning calorimetry, namely the three reversible transitions: stable KIa ↔ stable KIb at $T_{C4} = 242$ K, due to a change of the crystal structure, metastable KII ↔ metastable KIII at $T_{C3} = 318$ K, and metastable KII ↔ overcooled K0 at $T_{C2} = 347$ K, one irreversible transition: KIa → K0 at $T_{C1} = 376$ K, and melting at $T_t = 465$ K. From the enthalpy changes of these transitions it can be concluded that K0 is a solid rotational phase and KII and KIII are most probably solid phases with a high degree of orientational disorder. The phases K0, KII, and KIII form an enantiotropic system, but they are metastable in relation to the phases KIa and KIb in the whole temperature range, so they form the monotropic system with them.

Key words: Hexadimethylsulphoxidecadmium(II) chlorate(VII); Phase Transitions; Molecular Motions; DSC.

1. Introduction

Hexadimethylsulphoxidecadmium(II) chlorate(VII) (called HC) crystallizes in a rhombic system at ambient temperature and belongs to the Fdd2 space group (No. 43, C_{2v}^{19}) [1]. The crystals form a face centred lattice with eight molecules in the elementary cell. The lattice parameters are $a = 12.54$ Å, $b = 20.23$ Å and $c = 25.53$ Å [1]. HC consists of complex ions: $[Cd((CH_3)_2SO)_6]^{2+}$ and ClO_4^-. The cation is a slightly deformed octahedron, the cadmium atom being surrounded by six oxygen atoms coming from the dimethylsulphoxide (DMSO) ligands. The distance between cadmium and the oxygen atoms is $2.25 – 2.27$ Å. The DMSO ligands are built like C_{2v} pyramids, which are $0.72 – 0.73$ Å high. Two of the six DMSO groups may be in two different crystallographic positions. There are some atoms located in position I and others located in position II. The two DMSO ligands are connected to each other through a mirror image plane in a way that the positions of the carbon atoms C5 and C6 remain unchanged. However, this changes the positions of the oxygen atoms O3 and O4 and those of the sulphur atoms S3 and S4. There are two types of ClO_4^- tetrahedral ions. One of them has got two alternative crystallographic positions of oxygen atoms [1].

X-ray diffraction measurements for polycrystalline HC, made by Ljubiezniova and Ponomarieva [2], showed that there is a phase transition during sample cooling at 246 K, related to a crystal symmetry reduction from a rhombic crystallographic system (Fdd2) to a monoclinic system (C2/c). Because of a continuous change of the order parameter (deviation of the β angle from 90°) with temperature, the authors classify this transition as a second order one. It was also found that the reorientation of the ClO_4^- groups freezes below 246 K [2].

The purpose of this work was to check carefully the polymorphism of $[Cd(DMSO)_6](ClO_4)_2$ at $153 – 483$ K using differential scanning calorimetry (DSC).

2. Experimental

A few grams of $[Cd(H_2O)_6](ClO_4)_2$ were dissolved while being slowly heated up in DMSO of high chemical purity, which was previously additionally purified by vacuum distillation at low pressure. Then this solution was chilled and the precipitated crystals of HC were filtered. HC was then dried in a desiccator over phosphorous pentaoxide for a few hours. After desiccation, it was put in a sealed vessel and stored in a desiccator with barium oxide as a desiccant.

RS this work	RS [3]	IR this work in KBr pellet	IR this work ^{a}in Apiezon ^{b}in Nujol	IR [3]	DMSO RS [4,5]	DMSO IR	Assignment
			54 w^a				ν_L (lattice)
70 sh			72 w^a				ν_L (lattice)
116 m			106 w^a				ν_L (lattice)
			144 m^a				ν_L (lattice)
			186 m^a	191 w			ν_d (CdO)
195 w	197 m						ν_d (CdO)
312 m	315 st				313 m	313 m	δ_{as} (CSC)
341 w	343 st		310 m^a	320 w	338 m	338 m	δ_{as} (CSO)
			336 m^a	370 w	388 m	381 m	δ_s (CSO)
411 w	412 w						ν_s(CdO)
			418 m^a	418 m			ν_{as}(CdO)
459 m	460 m						δ_d(OClO)E
625 m	626 m	631 st	624 st^b	621 vst			δ_d(OClO)F_2
			669 vw^b			612 sh	ν_s(CS)
679 vst	681 vst	674 w	677 w^b	665 vw	663 vst	663 m	ν_s(CS)
716 st	717 st	705 m	716 m^b	695 w	700 m	700 st	ν_{as}(CS)
910 w	912 m	899 w			900 vw	900 w	ρ(CH$_3$)
932 st	932 vst	937 sh					ν_s(ClO)A_1
			940 st^b		925 vw	931 m	ρ(CH$_3$)
959 w	962 m	954 st	952 st^b	947 m	954 w	955 st	ρ(CH$_3$)
1003 w	1007 m		999 st^b				ρ(CH$_3$)
1026 m	1028 st	1026 vst	1034 sh^b	1019 m			ν_s(SO)
1039 sh					1050 m	1050 vst	ν_s(SO)
			1058 sh^b				ν_d(ClO)F_2
1096 m	1100 m	1103 sh	1098 vst^b	1088 m			ν_d(ClO)F_2
		1123 st	1126 vst^b				ν_d(ClO)F_2
	1305 vw	1295 vw	1300 sh^b			1303 m	δ_s(HCH)
		1313 m	1319 m^b	1304 w	1313 w		δ_s(HCH)
		1343 vw	1377 st^b	1395 m			δ_{as}(HCH)
1422 st	1425 st	1405 m	1414 sh^b	1418 m		1404 st	δ_{as}(HCH)
1432 sh		1436 m	1457 vst^b		1425 m	1440 st	δ_{as}(HCH)
2814 vw		2855 w	2854 vst^b		2885 br	2825 br	ν_s(CH)
2867 vw			2871 sh^b	2899 vw			ν_s(CH)
2922 vst		2914 m	2921 vst^b		2913 vst	2910 st	ν_s(CH)
		2955 sh	2959 vst^b	2970 wv			ν_{as}(CH)
3007 st		2995 m			2999 m	2999 st	ν_{as}(CH)

Frequencies in cm^{-1} — [Cd(DMSO)$_6$](ClO$_4$)$_2$

Table 1. The list of band positions of the Raman and infrared spectra of solid [Cd(DMSO)$_6$](ClO$_4$)$_2$ and liquid DMSO at room temperature; (vw – very weak, w – weak, sh – shoulder, m – medium, st – strong, vst – very strong, br – broad).

To check the chemical composition of the synthesised HC, the percentage content of cadmium ions was checked using a complexometric method, using a solution of the sodium salt of ethylenediaminetetraacetic acid (EDTA) as a titrant. The content of carbon and hydrogen, that form the DMSO ligand, was determined using an elementary analysis done with an EURO EA 3000 apparatus. The theoretical content of cadmium (14.41%) and its content found by the titration analysis (15.45% ± 0.12) differ by about 1% between themselves. For carbon atoms, the difference between the theoretical value (18.48%) and the test value (18.67% ± 0.01) does not exceed 0.2%. For hydrogen atoms, the theoretical value is 4.65% and the test value is 4.69% ± 0.01. Therefore, the elementary analysis of the complex confirmed presence of six molecules of DMSO in this compound.

To identify this compound further, its infrared absorption spectra (FT-FIR and FT-MIR) and its Raman spectrum (FT-RS) were recorded at ambient temperature. The FT-FIR and FT-MIR spectra were made using the Digilab FTS-14 and the EQUINOX-55 from Bruker Fourier transform infrared spectrometers, respectively, with a resolution of 2 cm^{-1}. The FT-FIR spectrum for powder samples, suspended in apiezon grease, was recorded. Polyethylene and silicon windows were used. The FT-MIR spectrum was recorded for a sample suspended in Nujol between the KBr pel-

Table 2. Thermodynamics parameters of the detected phase transitions (on heating).

| T_c [K]	ΔH [kJ·mol^{-1}]	ΔS [J·mol^{-1}·K^{-1}]
465	34.88	75.0
376	31.30	83.2
347	6.63	19.1
318	13.42	42.2
242	0.64	2.6

lets. The FT-RS spectrum was recorded using a Bio-Rad spectrometer with a YAG neodymium laser (λ = 1064 nm) at 10– 4000 cm^{-1} with a resolution of 4 cm^{-1}. Table 1 contains a list of the obtained and literature data [3–5] of band frequencies and their assignments. The recorded spectra additionally identify HC as [Cd(DMSO)$_6$](ClO$_4$)$_2$.

The DSC measurements of HC were made using a Perkin-Elmer DSC-7 apparatus at 153–483 K for three samples airtight closed in 30 μl aluminium containers. The weights of these samples were: sample **a:** 23.15 mg, **b:** 3.45 mg, **c:** 6.00 mg. Details of the DSC experiment are the same as described in [6].

3. Results and Discussion

The dependence on temperature of the difference of the thermal power supplied to the two calorimeters (the so called thermal stream), in short named the DSC curve or thermogram, was obtained for each of the samples **a**, **b** and **c** of HC at different scanning rates and initial and final heating and cooling conditions. The samples weights were chosen to check if the observed phase transition depends on the sample weight. The DCS curves were recorded while the sample was heated and cooled. All thermodynamic parameters of the phase transitions are given in Table 2.

All DSC measurements result in the dependence of the free enthalpy G on temperature, as shown in Figure 1. Samples not yet subjected to any "thermal history" are in a crystalline phase called KIa. Measurements on a sample **a** started with cooling it to 153 K, holding it at this temperature for 1 minute, recording the DSC curve while heating it to 293 K and then cooling it again to 153 K. This procedure was repeated three times. Thermograms obtained while heating (upper curve) and cooling (lower curve) a sample **a** with a scanning rate of 20 K/min are shown in Figure 2. As seen, there is a small endothermic and exothermic anomaly at ca. 242 K, both on a sample heating and cooling which is connected with the reversible phase transition KIa ↔ KIb (compare with Fig. 1). For sam-
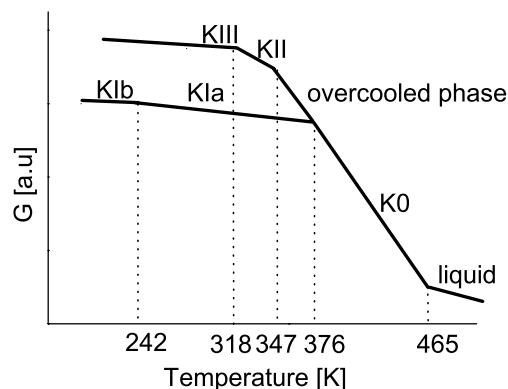
Fig. 1. Dependence of the free enthalpy G of [Cd(DMSO)$_6$](ClO$_4$)$_2$ (HC) on temperature.
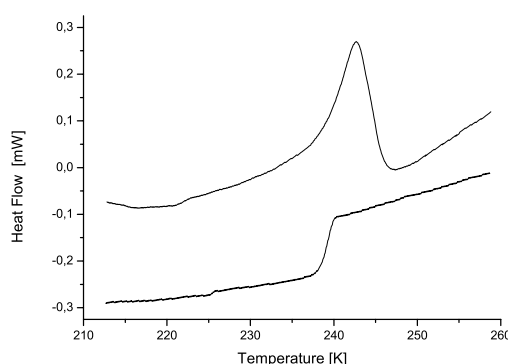
Fig. 2. Differential scanning calorimetry (DSC) curves obtained during heating (upper curve) and cooling (lower curve) of HC with a scanning rate of 20 K/min at 212–258 K.

ple **c** it was a thermogram recorded only on heating. Again a slight anomaly was observed at ca. 242 K. This anomaly was also recorded for samples **a** and **c** that were heated to 393 K and then cooled to 153 K. This transition temperature was marked as T_{C4} = 242 K. It is probably due to the same structural phase transition as recorded using the X-ray diffraction [2] at 246 K.

While heating a sample from 273 to 383 K, being initially in the KIa phase, it undergoes a phase transition at T_{C1} = 376 K into a phase which was named K0 phase (see Fig. 1). Due to this transition, a distinct anomaly on the DSC curves was recorded for the samples **a**, **b** and **c**. For example, Fig. 3 shows this for sample **a** at a heating rate of 10 K/minute (upper curve). While cooling sample **a**, being in a K0 phase, from 383 to 283 K it undergoes a deep over-cooling. As seen in Fig. 3, there is no anomaly on cooling at
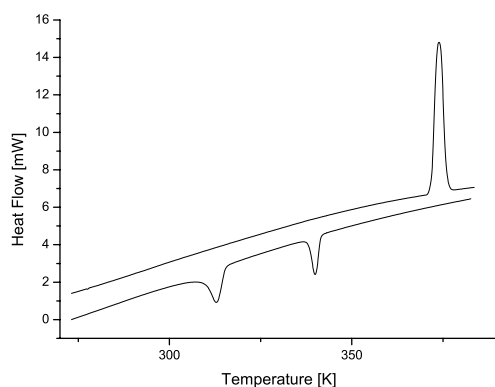
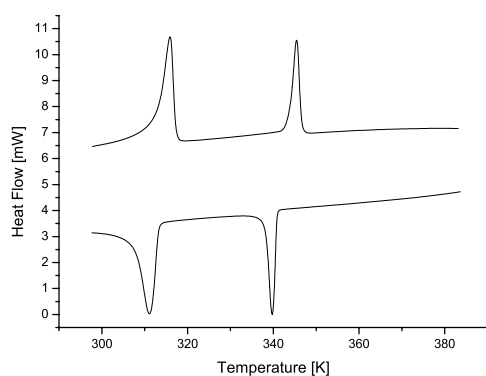Fig. 3. DSC curves at 273 – 383 K during heating and cooling of HC with a scanning rate of 10 K/min.

Fig. 5. DSC curves at 300 – 393 K during heating of HC with a scanning rate of 25 K/min.

Fig. 4. DSC curves at 295 – 383 K during heating and cooling of HC with a scanning rate of 10 K/min.

Fig. 6. DSC curves at 273 – 383 K during heating and cooling of HC with a scanning rate of 10 K/min.

temperatures even much below T_{C1}. When the sample is cooled only a bit further down, the over-cooled K0 phase undergoes a phase transition at $T_{C2} = 347$ K into a metastable phase, called KII phase. On further cooling the KII phase, it goes at $T_{C3} = 318$ K into the KIII phase (see Fig. 1). The phase transitions at T_{C2} and T_{C3} were recorded on the thermograms as anomalies connected with exothermic processes for all three samples, for example, for sample **a** in Fig. 3 (lower curve).

The transitions from the over-cooled K0 phase to the KII (at T_{C2}) and KIII (at T_{C3}) phase are reversible. This is clearly seen in Fig. 4, showing two distinct anomalies on the DSC curves both on heating and cooling of sample **c** at 295 – 383 K with a rate of 10 K/minute.

It is not possible to determine the nature of the observed phases on the basis of DSC measurements. Using a microscope, it was observed that there are solid phases. It is concluded from the change of the enthalpy of transitions (see Table 2), that the K0, KII,
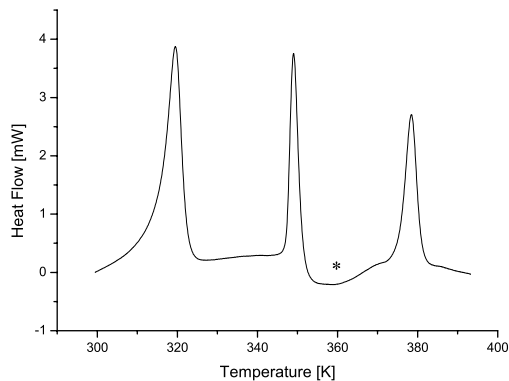
and KIII phases are likely to be rotational phases or phases of a high degree of rotational disorder, so called "plastic crystals" or "orientationally disordered crystals" (ODIC). The KIII and KII phases form mutually an enantiotropic system but, in respect to the KIa and KIb phases, are metastable in the whole temperature range, and thus form a monotropic system with them.

The metastable nature of the KII and KIII phases is also suggested by the DSC measurements that are given in Figs. 5 and 6. There is a distinct depreciation of the DSC curve (marked with an asterisk in Fig. 5), that was recorded during heating of sample **b** at a rate of 25 K/minute, just after an anomaly that is due to the phase transition: phase KII $\rightarrow$ over-cooled phase K0, i. e. above T_{C2}. The observed depreciation of the DSC curve is probably due to an exothermic process that is caused by relatively slow spontaneous conversion of the metastable K0 phase into the stable KIa phase. This stable KIa phase undergoes a phase transition into the
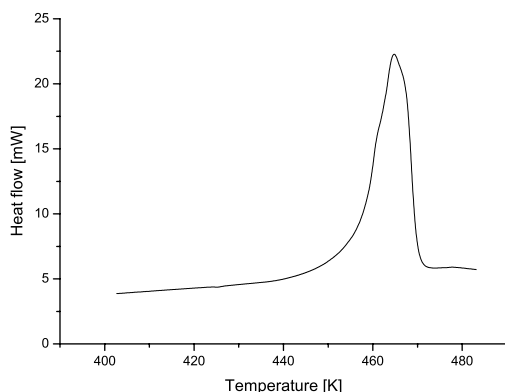
Fig. 7. DSC curves obtained in the temperature range of 400 – 485 K during heating of [Cd(DMSO)$_6$](ClO$_4$)$_2$ with a scanning rate of 20 K/min.

stable K0 phase during further heating to a temperature T_{C1} = 376 K. Thus an anomaly is also visible due to a transition at T_{C1}, besides the anomalies at T_{C3} and at T_{C2}, in Figure 5. This anomaly is rather small, as only a small part of this sample managed to convert from the K0 phase to the KIa phase due to the high heating speed used in this measurement (25 K/minute).

A transition into the stable phase KIa can also occur at lower temperatures, namely from the phase KII. Figure 6 presents such an event, occurring while a spontaneous transition (an exothermic anomaly marked with an asterisk in Fig. 6) occurs at approximately 340 K. It can be seen in Fig. 6 that besides this exothermic anomaly, there are only two endothermic anomalies at T_{C3} and T_{C1}, and the latter is much bigger than the T_{C1} anomaly that is shown in Figure 5. It follows that practically the whole sample managed to convert from a metastable KII phase into a stable KIa phase, since the scan ratio was slower in this measurement (10 K/minute).

While heating up above the T_{C1} temperature, the sample melts at T_t = 465 K. A DSC curve showing the anomaly resulting from the melting process can be seen in Figure 7.

4. Conclusions

1. The thermodynamic parameters for the following phase transitions of HC have been determined:
- Melting of the crystals at T_t = 465 K.
- Irreversible phase transition: KIa → K0 at T_{C1} = 376 K.
- Reversible phase transition: metastable KII ↔ overcooled K0 at T_{C2} = 347 K.
- Reversible phase transition: metastable KII ↔ metastable KIII at T_{C3} = 318 K.
- Reversible phase transition: stable KIa ↔ stable KIb at T_{C4} = 242 K, due to a change of a crystallographic structure.

2. It can be concluded from the enthalpy changes of the transitions that the K0 phase is a rotational solid phase and the KII and KIII phases are most probably solid phases with a high degree of orientational disorder, so called "plastic crystals" and "orientationally disordered crystals", respectively. The phases K0, KII and KIII form an enantiotropic system, but KII and KIII are metastable with respect to the phases KIa and KIb in the whole temperature range, so they form a monotropic system with them.

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