

# Phase Polymorphism of $[\text{Mn}(\text{DMSO})_6](\text{BF}_4)_2$ Studied by Differential Scanning Calorimetry

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The tetrafluoroborate of hexadimethylsulfoxidemanganese(II) was synthesized and studied by differential scanning calorimetry. Five solid phases of  $[\text{Mn}(\text{DMSO})_6](\text{BF}_4)_2$  were revealed. Specifically, four phase transitions of the first order were detected between the following solid phases: stable K1b  $\leftrightarrow$  stable K1a at  $T_{C4} = 215$  K; metastable KIII  $\leftrightarrow$  overcooled K0 at  $T_{C3} = 354$  K; metastable KII  $\leftrightarrow$  overcooled K0 at  $T_{C2} = 377$  K; stable K1a  $\rightarrow$  stable K0 at  $T_{C1} = 385$  K.  $[\text{Mn}(\text{DMSO})_6](\text{BF}_4)_2$  starts to decompose at 400 K with a loss of one DMSO molecule per formula unit and forms  $[\text{Mn}(\text{DMSO})_5](\text{BF}_4)_2$  which next decomposes in one step to  $\text{MnF}_2$  at the temperature range of 460–583 K. From the entropy changes it can be concluded that the phases K0 and metastable KII are orientationally dynamically disordered (ODDIC) crystals. The stable phases K1b and K1a are ordered solid phases.

**Key words:** Hexadimethylsulfoxidemanganese(II) Tetrafluoroborate; Phase Transitions; DSC.

## 1. Introduction

Hexadimethylsulfoxidemanganese(II) tetrafluoroborate (called HMnTF) consists of two kinds of coordinate complex ions:  $[\text{Mn}((\text{CH}_3)_2\text{SO})_6]^{2+}$  and  $\text{BF}_4^-$ . The cation is a slightly deformed octahedron, the manganese atom being surrounded by six oxygen atoms coming from the dimethylsulfoxide (DMSO) ligands. The DMSO ligands are built like  $C_{2v}$  pyramids. Unfortunately, the crystal structure of HMnTF is unknown. However, a similar compound, namely hexadimethylsulfoxidemanganese(II) chlorate(VII)  $[\text{Mn}(\text{DMSO})_6](\text{ClO}_4)_2$ , crystallizes at room temperature in the orthorhombic system (space group: No. 43;  $Fd2d$ ;  $C_{2v}^{19}$ ) [1]. We have recently investigated the polymorphism of  $[\text{Mn}(\text{DMSO})_6](\text{ClO}_4)_2$  by differential scanning calorimetry (DSC) [2] and found six solid phases. From these measurements we could conclude that four phases were stable and two were metastable phases. It could be concluded from entropy changes that the metastable phase KIII and stable phases K1c, K1b are more or less ordered solids whereas the metastable phase KII, stable phase K1a and high-temperature phases K0 and K0' are more or less orientationally dynamically disordered crystals (ODDIC).

The aim of the work was to examine the polymorphism of  $[\text{Mn}(\text{DMSO})_6](\text{BF}_4)_2$  at 93–400 K using DSC and compare it with that of  $[\text{Mn}(\text{DMSO})_6](\text{ClO}_4)_2$ .

## 2. Experimental

### 2.1. Sample Preparation

A few grams of  $[\text{Mn}(\text{H}_2\text{O})_6](\text{BF}_4)_2$  were dissolved, while being slowly heated, in DMSO of high chemical purity [3], which was previously purified by vacuum distillation at low pressure. This solution was then chilled and the precipitated crystals of HMnTF were filtered and washed with acetone. They were then dried in a desiccator over phosphorous pentaoxide for a few hours. After desiccation, they were put in a sealed vessel and stored in a desiccator with barium oxide as a desiccant. To check the chemical composition of the synthesized HMnTF, the percentage content of manganese ions was checked using a complexometric method with a solution of the sodium salt of ethylenediaminetetraacetic acid (EDTA) as a titrant. The contents of carbon and hydrogen in the DMSO ligand were determined using elementary analysis on an EURO EA 3000 apparatus. The theoretical content

of manganese equalled 7.88%, and its content found by the titration analysis amounted to  $(7.79 \pm 0.12)\%$ . For carbon atoms, the difference between the theoretical value (20.67%) and the test value  $[(20.73 \pm 0.01)\%]$  did not exceed 0.1%. For hydrogen atoms the theoretical value was 5.20% and the test value was  $(5.25 \pm 0.01)\%$ . Therefore, the elementary analysis of the title compound confirmed the presence of the stoichiometric number of six DMSO molecules in the complex cation.

## 2.2. Sample Characteristics

In order to further identify the title compound, its infrared absorption (FT-MIR) and Raman spectra (FT-RS) were recorded at ambient temperature. The FT-MIR spectrum was recorded using an EQUINOX-55 Bruker Fourier transform infrared spectrometer with a resolution of  $2 \text{ cm}^{-1}$ ; the sample was suspended in Nujol between KBr pellets. The FT-RS spectrum was recorded using a Bio-Rad spectrometer with a YAG neodymium laser ( $\lambda = 1064 \text{ nm}$ ) at  $10\text{--}4000 \text{ cm}^{-1}$  with a resolution of  $4 \text{ cm}^{-1}$ . For all recorded spectra there were assigned literature data of band frequencies and their assignments [4–7]. Thus, the recorded spectra additionally identified the investigated compound as  $[\text{Mn}(\text{DMSO})_6](\text{BF}_4)_2$ .

Thermal analysis of the examined compound was made in order to further verify its composition. The differential thermal analysis (DTA) and thermogravimetry (TG) measurements were performed using a Mettler Toledo TGA/SDTA 851e apparatus. The sample weighing 27.1821 mg was placed in a  $70 \mu\text{l}$  corundum crucible. The thermogravimetric measurements were made in a flow of argon ( $80 \text{ ml min}^{-1}$ ) from 293 K up to 600 K at a constant heating rate of  $5 \text{ K min}^{-1}$ . The temperature was measured by a Pt-Pt/Rh thermocouple with the accuracy of  $\pm 0.5 \text{ K}$ . It could be seen from the TG and DTG curves that during heating the sample up to 400 K it lost only ca. 2% of its initial mass. This means that the compound practically did not change its composition, even when the sample was not hermetically closed.

## 2.3. Heat Flow Measurements

We checked the phase polymorphism in the title compound using a Perkin-Elmer Pyris 1 DSC apparatus at 93–400 K for sample of 11.72 mg. The details of our DSC experiment were described in [8]. After

Table 1. Thermodynamic parameters of the detected phase transitions in  $[\text{Mn}(\text{DMSO})_6](\text{BF}_4)_2$ .

$T \text{ (K)}$	$\Delta H \text{ (kJ mol}^{-1}\text{)}$	$\Delta S \text{ (J mol}^{-1} \text{ K}^{-1}\text{)}$
$T_{C4} = 215 \pm 1$	$0.28 \pm 0.03$	$1.29 \pm 0.13$
$T_{C3} = 354 \pm 1$	$3.17 \pm 0.27$	$8.99 \pm 0.79$
$T_{C2} = 377 \pm 1$	$3.53 \pm 0.06$	$9.36 \pm 0.17$
$T_{C1} = 385 \pm 1$	$33.87 \pm 0.62$	$87.90 \pm 1.62$

the measurements the masses of the samples did not change.

## 3. Results and Discussion

The temperature dependences of differences in thermal power supplied by two calorimeters (the so-called thermal stream or heat flow), named DSC curves, were obtained for HMnTF at different scanning rates and at different initial and final sample heating and cooling conditions. The thermodynamic parameters of the detected phase transitions are presented in Table 1. The results of all DSC measurements are also schematically presented as temperature dependence of the free enthalpy  $G$  (Gibbs free energy) and shown in all figures.

The measurements start by cooling the sample from room temperature (RT) to 93 K, holding it at this temperature for 1 min, and next heating it up to 400 K. During cooling the sample a phase transition from stable phase KIa to low-temperature phase KIb at  $T_{C4} = 215 \text{ K}$  (see Fig. 1A, curve no. 1) can be observed. While heating the sample with the scanning rate of  $30 \text{ K min}^{-1}$  (Fig. 1A, curve no. 2), being initially in the KIb phase, from 93 K to 400 K, a phase transition into an intermediate phase, which is named KIa, can be observed at  $T_{C4} = 215 \text{ K}$ , which is manifested as a small anomaly on the DSC curve no. 2 (Fig. 1A). Phase KIa next transforms into the phase K0 at  $T_{C1} = 385 \text{ K}$ , what is manifested as a big anomaly on the same curve (see Fig. 1A curve no. 2 and compare with Fig. 1B).

Later, while cooling the sample from 400 K with a scanning rate of  $30 \text{ K min}^{-1}$ , being in the K0' phase, it transforms partially to the metastable phase KII at  $T_{C2}$ . The rest of the sample undergoes deep overcooling and transforms to the metastable phase KIII at  $T_{C3}$ . Next cooling the sample causes a spontaneous phase transition from the metastable phase KIII to the metastable phase KII and the stable phase KIa. The part of the sample in the metastable phase KII undergoes a spontaneous transformation to the stable phase KIa too. The DSC curve, obtained during cooling the sample after

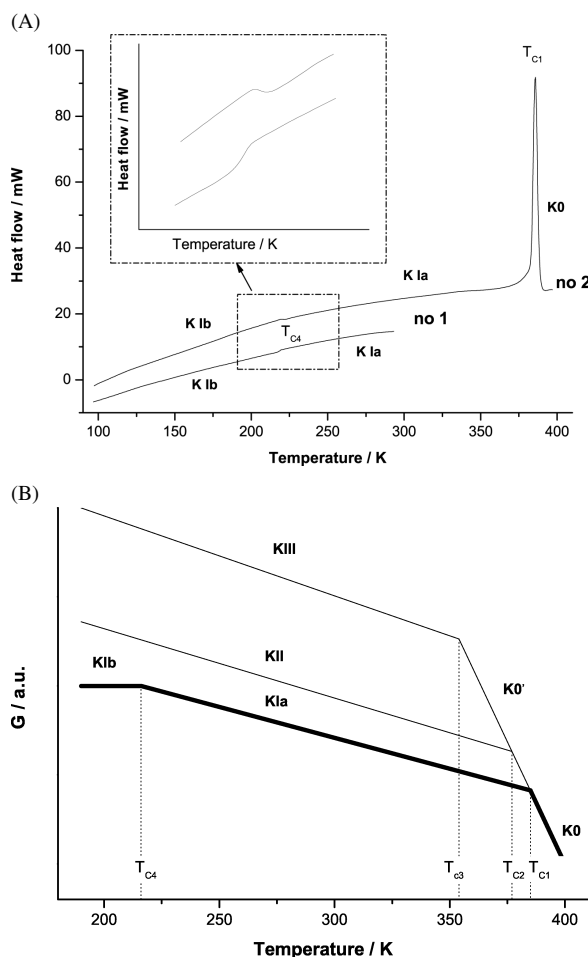


Fig. 1. (A) DSC curves obtained during cooling of HMnTF from RT to 93 K (curve No. 1) and during heating it from 93 K to 400 K (curve No. 2) with a scanning rate of  $30 \text{ K min}^{-1}$ . (B) Schema of HMnTF phase polymorphism deduced from DSC curves presented in Fig. 1A.

the spontaneous phase transition, shows a phase transition from phase KIa to phase Klb at  $T_{C4}$  (see Fig. 2A and compare with Fig. 2B).

Heating again gave the same results as present in Fig. 1A, curve no. 2; so the following process of cooling was stopped at 340 K just before the above described spontaneous phase transition. In Fig. 3A the obtained results are presented. As can be seen the sample which is in phase K0 undergoes deep overcooling and transforms to the metastable phase KIII at  $T_{C3}^C = 354 \text{ K}$  (curve no. 4). We do not observed a phase transition at  $T_{C2}$ ; this suggests that the metastable phases KIII and KII are monotropic phases. Heating again gives the results presented in Fig. 3A, curve no. 5. The

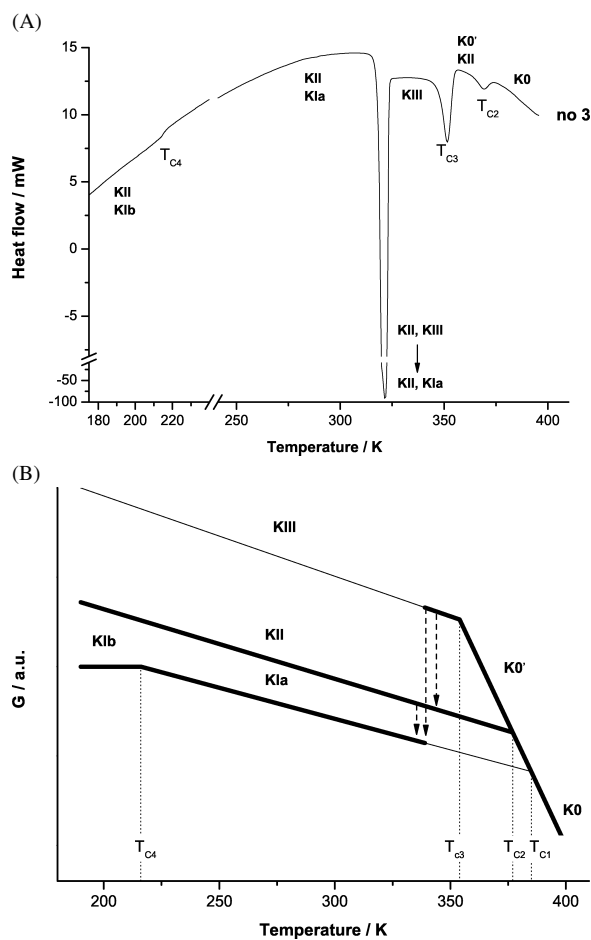


Fig. 2. (A) DSC curves obtained during cooling of HMnTF from 400 K to 93 K (curve No. 3). (B) Schema of HMnTF phase polymorphism deduced from DSC curves presented in Fig. 2A.

sample which is in the metastable phase KIII transforms to the overcooled phase K0' at  $T_{C3}^H$ .

Cooling the sample again was stopped just after a spontaneous phase transition. In Fig. 4A, curve no. 6, two anomalies can be seen. The first is connected with a phase transition at  $T_{C3}$  (stable phase K0'  $\rightarrow$  metastable phase KIII), the second with the spontaneous phase transition metastable phase KIII  $\rightarrow$  metastable phase KII and stable phase KIa. The sample is heated up to 400 K. The obtained results are presented in Fig. 4A, curve no. 7. Part of the sample which is in the metastable phase KII transforms to the overcooled phase K0' at  $T_{C2} = 377 \text{ K}$ , whereas part of the sample which is in the stable phase KIa transforms to the high-temperature phase K0 at  $T_{C1} = 385 \text{ K}$ .

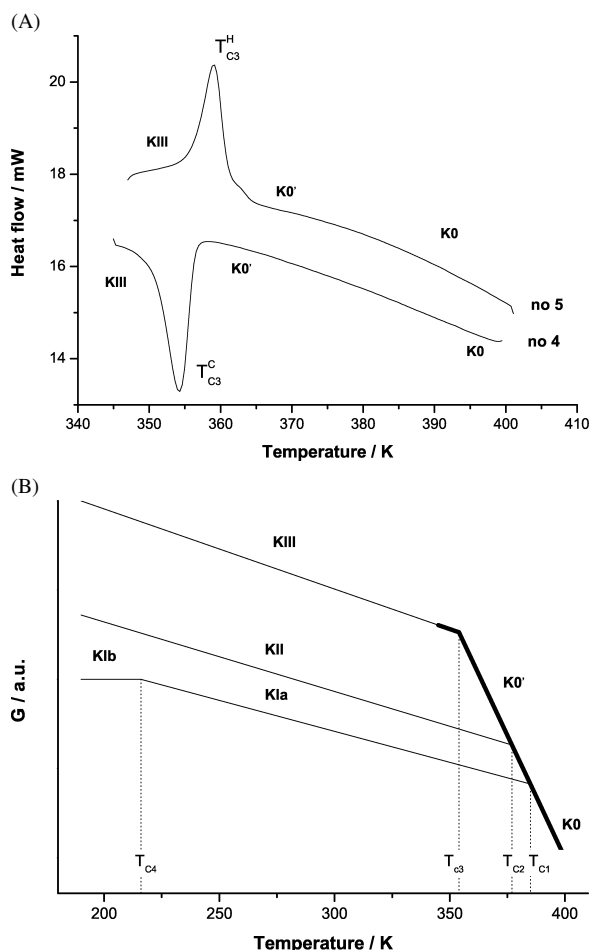


Fig. 3. (A) DSC curves obtained during cooling of HMnTF from 400 K to 345 K (curve No. 4) and during heating it from 345 K to 400 K (curve No. 5) with a scanning rate of  $20 \text{ K min}^{-1}$ . (B) Schema of HMnTF phase polymorphism deduced from DSC curves presented in Fig. 3A.

Using a microscope it was observed that all of the five detected phases were solid phases. Of course, it was not possible to determine the nature of the observed phases only on the base of DSC measurements and microscope observation. However, it was concluded from the change of the entropy of transitions,  $\Delta S$  (see Table 1), that the metastable phases KII, KIII and the stable phase K0 are orientationally dynamically disordered phases. Investigations by complementary methods, like for example X-ray diffraction, are now in progress.

The above described phase polymorphism of the title compound HMnTF is similar to that of  $[\text{Mn}(\text{DMSO})_6](\text{ClO}_4)_2$  (called HMnC) [2] as far as the

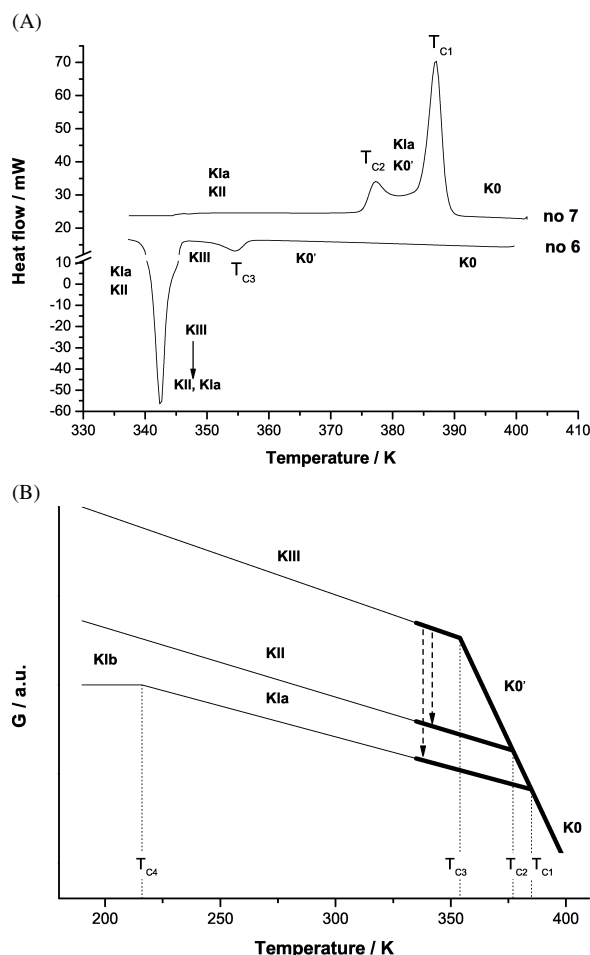


Fig. 4. (A) DSC curves obtained during cooling of HMnTF from 400 K to 335 K (curve No. 6) and during heating it from 335 K to 400 K (curve No. 7) with a scanning rate of  $20 \text{ K min}^{-1}$ . (B) Schema of HMnTF phase polymorphism deduced from DSC curves presented in Fig. 4A.

character of the phase transitions is concerned. However, the most important difference is the following: the metastable phases KII and KIII in HMnTF are monotropic phases, whereas in HMnC there is an enantiotropic system of phases. Moreover in HMnC there exists one more stable phase.

#### 4. Conclusions

1. The thermodynamic parameters for the following phase transitions of HMnTF have been determined both on heating and on cooling:
  - reversible phase transition: stable KIb  $\leftrightarrow$  stable KIa at  $T_{C4} = 215 \text{ K}$ ;

- reversible phase transition: metastable KIII  $\leftrightarrow$  overcooled K0 (K0') at  $T_{\text{C}3} = 354$  K;
  - reversible phase transition: metastable KII  $\leftrightarrow$  overcooled K0 (K0') at  $T_{\text{C}2} = 377$  K;
  - irreversible phase transition: stable KIa  $\rightarrow$  stable K0 at  $T_{\text{C}1} = 385$  K.
2. It can be concluded from the entropy changes of the phase transitions that the phases K0, K0' and the metastable phase KII are more likely so-called "orientationally dynamically disordered crystals" (ODDIC) or plastic crystals, whereas the stable phases KIa, KIb and the metastable phase KIII are orientationally ordered solid phases.
3. The phase polymorphism of the title compound is in general similar to that of  $[\text{Mn}(\text{DMSO})_6](\text{ClO}_4)_2$ . Also the phase transition parameters have similar values. However, there also exist important differences. Namely the metastable phases KII and KIII in HMnTF are monotropic phases, whereas in HMnC there is an enantiotropic system of these phases. Moreover, in HMnC there exists an additional ordered stable phase (KIc).

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