Phase Polymorphism of $[Co(DMSO)_6](BF_4)_2$ Studied by Differential Scanning Calorimetry

Anna Migdał-Mikuli, Łukasz Skoczylas, and Elżbieta Szostak

Department of Chemical Physics, Faculty of Chemistry, Jagiellonian University, Ingardena 3,
30-060 Kraków, Poland

Reprint requests to Dr. A. M.-M.; Fax: +48 12 634 0515; E-mail: migdalmi@chemia.uj.edu.pl

Z. Naturforsch. **61a,** 180 – 188 (2006); received February 1, 2006

Five solid phases of $[Co(DMSO)_6](BF_4)_2$ have been detected by differential scanning calorimetry (DSC). Phase transitions were detected between the following solid phases: stable KIb ↔ stable KIa at $\overline{T}_{C4} = (328 \pm 2)$ K, metastable KIII ↔ undercooled phase K0 at $\overline{T}_{C3} = (383 \pm 4)$ K, metastable KII ↔ undercooled K0 at $\overline{T}_{C2} = (399 \pm 2)$ K and stable KIa ↔ stable K0 at $\overline{T}_{C1} = (404 \pm 1)$ K. The title compound melts at $T_m = 440$ K. From the entropy changes at the melting point and at phase transitions it can be concluded that the phases K0 and undercooled K0 are orientationally dynamically disordered crystals. The stable phases KIa, KIb are ordered solid phases. The metastable phases KII and KIII are probably solid phases with a high degree of orientational dynamical disorder.

Key words: Hexadimethylsulphoxidecobalt(II) Tetrafluoroborate; Phase Transitions; Melting Point; DSC.

1. Introduction

Hexadimethylsulphoxidecobalt(II) tetrafluoroborate (called HCoBF) consists of two kinds of ions: $[Co((CH_3)_2SO)_6]^{2+}$ and $BF_4{}^-$. The cation is a slightly deformed octahedron, where Co^{2+} is surrounded by six oxygen atoms coming from dimethylsulphoxide (DMSO) ligands, which are built like C_{2v} pyramids. The crystal structure of HCoBF is unknown. However, analogous $[Zn(DMSO)_6](ClO_4)_2$ crystallizes in the trigonal system (space group: No. 159; $P31c$; C_{3v}) [1, 2]. We have recently investigated the polymorphism of four coordinated compounds of the type: $[M(DMSO)_6](ClO_4)_2$, where M = Cd, Mn, Co and Zn, using differential scanning calorimetry (DSC) [3 – 6]. For example, for the hexadimethylsulphoxide-cobalt(II) chlorate(VII) we found five solid phases. Three of them are stable and two are metastable. It can be concluded that the phases K0 and undercooled K0 are orientationally dynamically disordered (ODDIC) [7]. This stable phases KIa, KIb and the metastable phase KIII are ordered solid phases. The metastable phase KII is probably a solid phase with a high degree of orientational dynamical disorder.

The purpose of the present work was to carefully examine the polymorphism of $[Co(DMSO)_6](BF_4)_2$ at 97 – 440 K using DSC in order to compare it with that of $[Co(DMSO)_6](ClO_4)_2$ [5].

2. Experimental

2.1. Sample Preparation

A few grams of $[Co(H_2O)_6](BF_4)_2$ were dissolved while being slowly heated in DMSO of high chemical purity, which was previously additionally purified by vacuum distillation at low pressure. This solution was then chilled and the precipitated crystals of HCoBF were filtered and washed with acetone. The crystals were 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 HCoBF, the percentage content of cobalt ions was checked using a complex metric method, with a solution of the sodium salt of ethylenediaminetetraacetic acid (EDTA) as a titrante. The content of carbon and hydrogen in the DMSO ligand was determined using elementary analysis in an EURO EA 3000 apparatus. The theoretical content of cobalt equaled 8.40%, and its content found by the titration analysis amounted to (8.22 ± 0.12)%. For the carbon atoms, the difference between the theoretical (20.57%) and test value [$(20.67 \pm 0.01\%)$] did not exceed 0.1%. For the hydrogen atoms the theoretical value was 5.18% and the test value (4.99 ± 0.01)%. Therefore, the elementary analysis of the ti-

0932–0784 / 06 / 0300–0180 $ 06.00 © 2006 Verlag der Zeitschrift für Naturforschung, Tübingen · http://znaturforsch.com

Table 1. The list of band positions of the infrared (IR) and Raman spectra (RS) of solid $[Co(DMSO)_6](BF_4)_2$ at room temperature.

Frequencies in cm^{-1}					Assignments
IR			RS		
This work in KBr	This work in Nujol	Literature [7 – 11]	This work	Literature [7 – 11]	
			129 w	123	ν_L(lattice)
			315 m	311	δ_{as}(CSC)
			345 m	338	δ_{as}(CSO)
	430 st	429 s	417 w	422 w	ν_s(CoO)
450 m	443 st	444 s			ν_{as}(CoO)
522 m	521 st	525 m	520 w	530 w	δ_d(FBF)
		661 m			ν_s(CS)
677 w	678 m	690 s	683 vst	683 vst	ν_s(CS)
714 m	718 st	717 m	718 st	718 st	ν_{as}(CS)
	795 w		765 m	772	ν(BF)
	902 sh	887 w	905 w	910 w	$\rho(CH_3)$
		921 m			$\rho(CH_3)$
953 vst	954 m	946 m	945 m		$\rho(CH_3)$
			962 sh	961 w	$\rho(CH_3)$
	1008 br	1000 st	998 sh	996 w	$\rho(CH_3)$
1020 vst	1026 br	1012 m	1016 m	1024 m	ν_s(SO)
	1042 br	1037 vst	1038 br		ν_{as}(BF)
		1051 vst		1076 w	ν_{as}(BF)
	1056 br	1055 vs			ν_s(SO)
	1148 br	1150 w			
1300 br	1299 w	1306 m			δ_s(HCH)
1318 m	1321 m	1325 w			δ_s(HCH)
		1404 m			δ_{as}(HCH)
1411 st	1410 sh	1416 m	1423 st	1420 st	δ_{as}(HCH)
1432 st	1449 vst	1436 s			δ_{as}(HCH)
	2858 sh	2871 vst			ν_s(CH)
	2878 sh	2885 vst			ν_s(CH)
2914 w		2918 m	2926 vst	2924 vst	ν_s(CH)
		2955 vst			ν_{as}(CH)
3001 w		3000 m	3012 st	3015 st	ν_{as}(CH)

vw, very weak; w, weak; sh, shoulder; m, medium; st, strong; vst, very strong; br, broad.

Table 2. Thermodynamics parameters of the detected phase transitions (on heating) in $[Co(DMSO)_6](BF_4)_2$ (this work) and in $[Co(DMSO)_6](ClO_4)_2$ [5].

	$[Co(DMSO)_6](BF_4)_2$				$[Co(DMSO)_6](ClO_4)_2$		
	T_c (K)	ΔH $(kJ \cdot mol^{-1})$	ΔS $(J \cdot mol^{-1} \cdot K^{-1})$		T_c (K)	ΔH $(kJ \cdot mol^{-1})$	ΔS $(J \cdot mol^{-1} \cdot K^{-1})$
T_m	440	9.69	22.0	T_m	495 ± 1	14.75 ± 0.53	29.8 ± 1.1
T_{C1}	403 ± 2	46.49 ± 1.72	115.7 ± 4.3	T_{C1}	377 ± 1	28.03 ± 1.06	74.3 ± 2.8
T_{C2}	399 ± 3	5.31 ± 0.79	13.4 ± 1.9	T_{C2}	363 ± 1	2.36 ± 0.22	6.4 ± 0.7
T_{C3}	388 ± 1	0.90 ± 0.04	2.3 ± 0.1	T_{C3}	350 ± 1	2.13 ± 0.08	6.1 ± 0.2
T_{C4}	329 ± 1	1.09 ± 0.09	3.3 ± 0.3	T_{C4}	324 ± 1	21.74 ± 0.13	67.1 ± 0.4

tle compound confirmed the presence of the stoichiometric number of six DMSO molecules in the complex cation.

2.2. Sample Characteristics

For further identification of the title compound its infrared absorption spectrum (FT-IR) was recorded at ambient temperature using EQUINOX-55 Bruker Fourier transform infrared spectrometers with a resolution of 2 cm^{-1}. The FT-IR spectrum was recorded in the frequency range 500 – 4000 cm^{-1} for the sample in a KBr pellet and also for the sample suspended in Nujol placed between the KBr windows. Fourier transform Raman scattering measurements (FT-RS) were performed at room temperature with a Bio-Rad spectrometer of resolution 4 cm^{-1}. The incident radiation (λ = 1064 nm) was from a Neodymium laser YAG Spectra-Physics. Figure 1 presents a comparison of the infrared and Raman spectra of HCoBF. Table 1 contains a list of the obtained and literature data [8 – 11] of band frequencies and their assignments. The recorded spectra additionally identify the investigated compound as $[Co(DMSO)_6](BF_4)_2$.

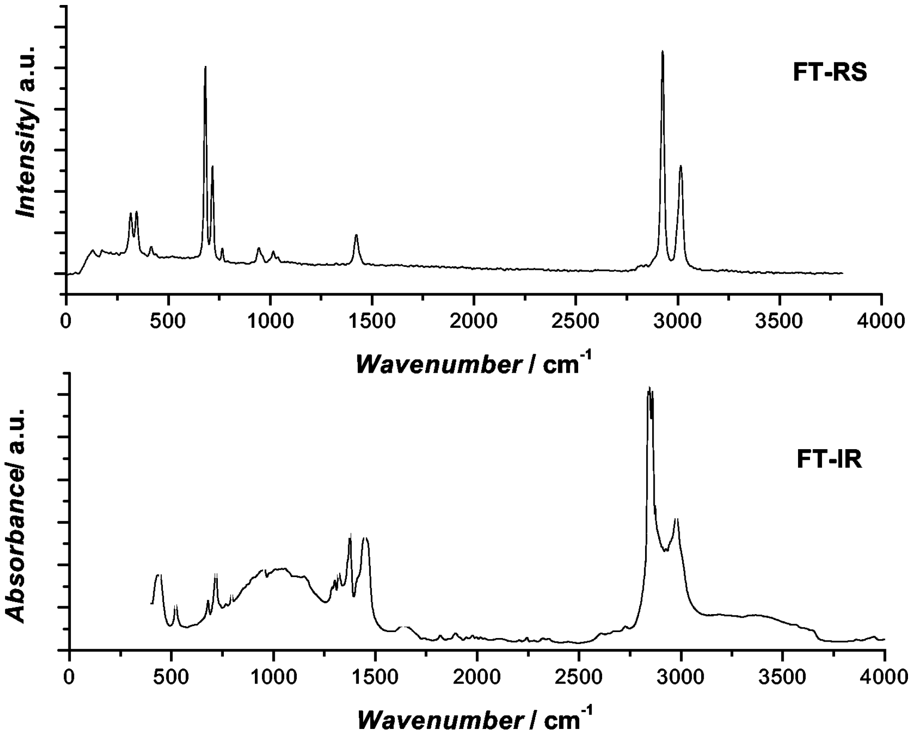

Fig. 1. FT-RS and FT-IR spectra of $[Co(DMSO)_6]$-$(BF_4)_2$.

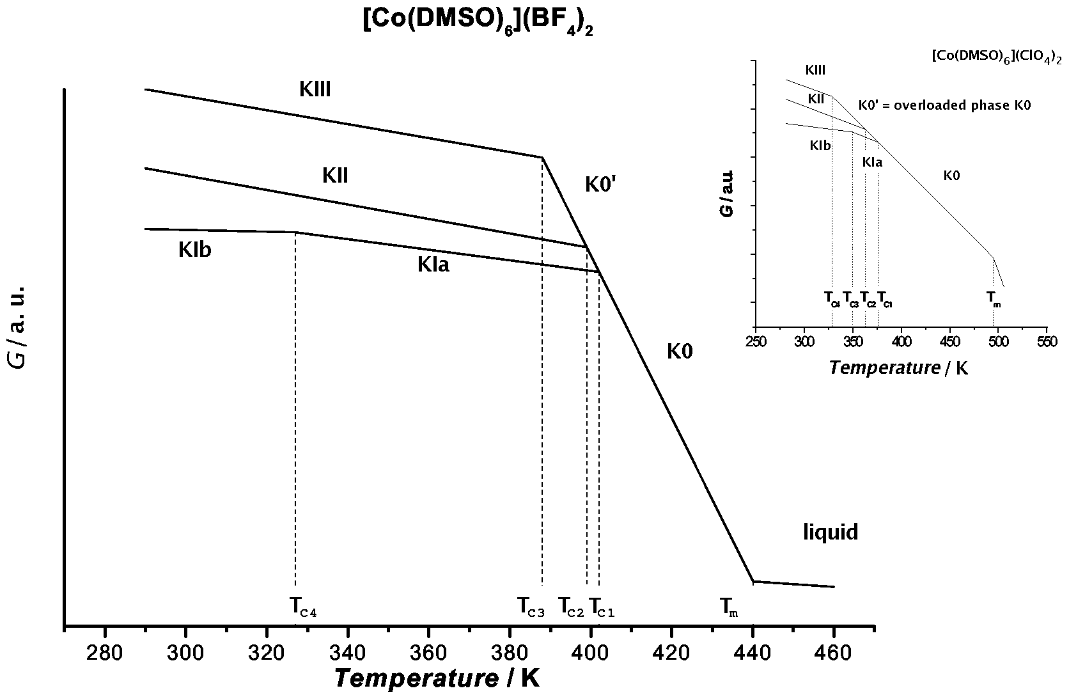

Fig. 2. Scheme of temperature dependence of the free enthalpy G of $[Co(DMSO)_6](BF_4)_2$. Insertion: G vs. T for $[Co(DMSO)_6](ClO_4)_2$.

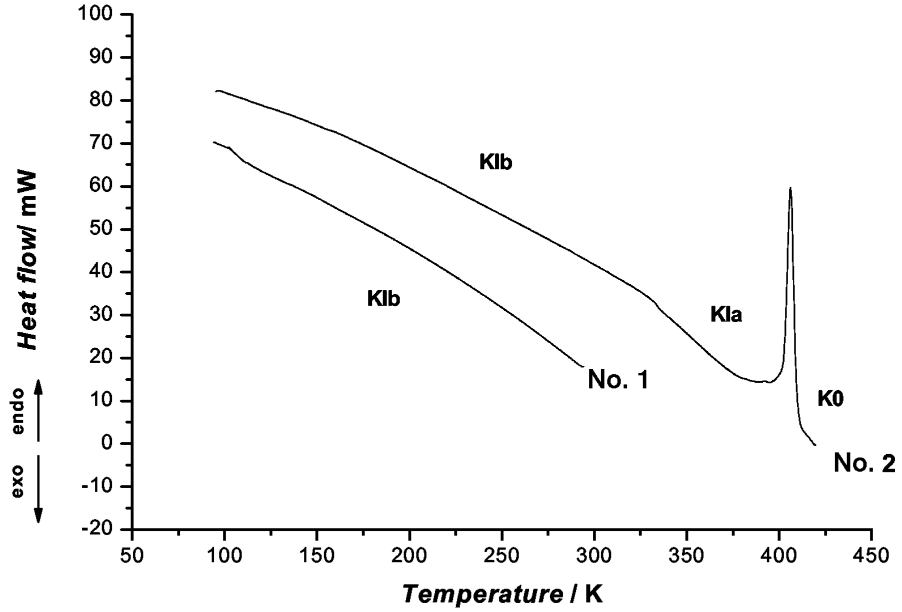

Fig. 3. Differential scanning calorimetry (DSC) curves of $[Co(DMSO)_6]$-$(BF_4)_2$, obtained during cooling from RT to 93 K (curve No. 1), and during heating from 93 to 425 K (curve No. 2) and subsequent cooling from 425 K to RT, with a scanning rate of $40\ K \cdot min^{-1}$.

Thermal analysis of the examined compound was performed in order to further verify its composition. The differential thermal analysis (DTA) and thermogravimetric (TG) measurements were performed using a Mettler Toledo TGA/SDTA 851e apparatus. A sample weighing 20.0667 mg was placed in a 70 μl open corundum crucible. The thermogravimetric measurements were made in a flow of argon $(80\ ml \cdot min^{-1})$ from 293 K up to 473 K at a constant heating rate of $5\ K \cdot min^{-1}$. The temperature was measured by a Pt–Pt/Rh thermocouple with an accuracy of ±0.5 K. It can be seen from the TG and DTG curves that, when the sample is heated up to 410 K, it loses only ca. 2% of its initial mass. This means that the compound practically does not change its composition, even when it is not hermetically closed.

2.3. Heat Flow Measurements

At the beginning we checked the phase polymorphism of the examined compound using a Perkin-Elmer Pyris 1 DSC apparatus at 93–425 K for a sample of 10.02 mg (sample A). However, major DSC measurements of HCoBF were made using a Mettler-Toledo 821e apparatus at 293–425 K for two samples (B and C), hermetically closed in 40 μl aluminium containers. The weights of these samples were as follows: 14.91 mg for sample B and 8.87 mg for sample C. By the measurements the masses of the samples did not change.

3. Results and Discussion

Temperature dependences of the difference in thermal power supplied to the two calorimeters (one empty and the second with a sample), the so-called thermal stream or heat flow, named also DSC curves, were obtained by us for each of three HCoBF samples (A, B and C) with different masses, at different scanning rates and under different initial and final sample heating and cooling conditions. We did not notice any differences between the results obtained for the samples A, B and C. Thus, the mean values of the thermodynamic parameters of the detected phase transitions have been presented in Table 2, together with the results for $[Co(DMSO)_6](ClO_4)_2$ [5]. The results of all DSC measurements are also schematically presented as a temperature dependence of the free enthalpy *G* (Gibbs free energy) and shown in Figure 2. As an insertion in Fig. 2 we have introduced such a scheme for $[Co(DMSO)_6](ClO_4)_2$.

The sample without any "thermal history" is in a crystalline phase called KIb. The measurement was started by cooling the sample from room temperature (RT) to 93 K, holding it at this temperature for 1 min, then heating it up to 425 K and then cooling it again down to RT. DSC curves obtained for first sample cooling (No. 1) and its subsequent heating (No. 2) with a scanning rate of $40\ K \cdot min^{-1}$ are shown in Figure 3. As can be seen in Fig. 3, while cooling the sample

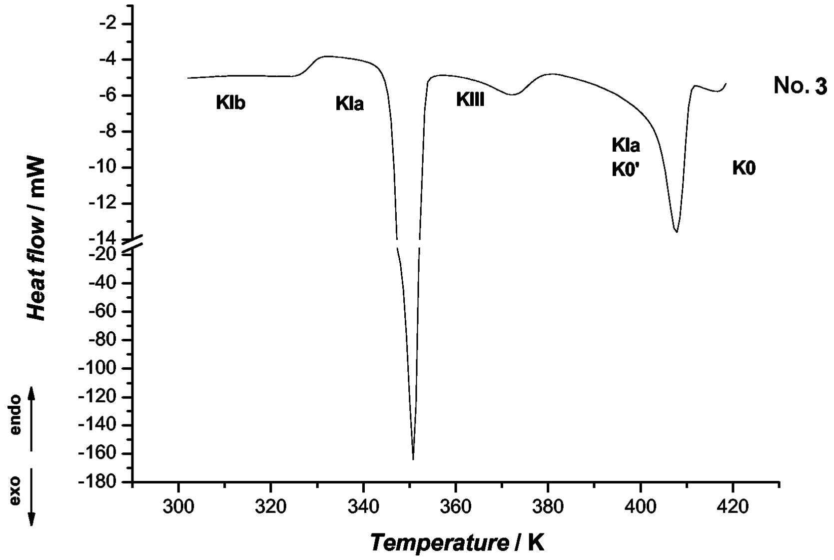

Fig. 4. DSC curve obtained during cooling of $[Co(DMSO)_6]$-$(BF_4)_2$ from 425 K to RT (curve No. 3), with a scanning rate of 40 K · min^{-1}.

from RT to 93 K no anomaly was recorded on the DSC curve No. 1. During subsequent heating of this sample, being initially in the KIb phase, from 93 to 425 K, a phase transition at $T^{h}_{C4} = 331$ K into an intermediate phase, which was named KIa, can be observed above RT, which is manifested in a small and broad endothermic anomaly on the DSC curve No. 2. While next heating, phase KIa transforms into the high temperature phase K0 at $T^{h}_{C1} = 406$ K, what is manifested on this curve as a big endothermic anomaly (compare it with the scheme in Fig. 2).

At subsequent cooling of the sample from 425 K, being in the K0 phase, with a scanning rate of 40 K · min^{-1}, we obtained the DSC presented in Figure 4. As can be seen in Fig. 4 (curve No. 3), when the sample was cooled, a part of the K0 phase experienced a phase transition at $T^{c}_{C1} = 407$ K into the stable phase KIa, which was connected with a big anomaly on the DSC curve No. 3. The rest of the sample underwent a deep overcooling (36 K), forming a phase K0', which transformed at $T^{c}_{C3} = 372$ K to a metastable phase, called KIII phase, which was connected with a small and broad exothermic anomaly on the DSC curve No. 3. On further cooling, at ca. 350 K the KIII phase underwent a spontaneous transformation (exothermic process) into the stable phase KIa, which is manifested in a very big anomaly on the DSC curve. Further cooling showed the phase transition KIa → KIb at $T^{c}_{C4} = 325$ K (compare it with the scheme in Fig. 2). This sequence of the phase transitions of the title compound we denoted as transformations I.

Heating of a new sample from 300 to 425 K, with a scanning rate of 10 K · min^{-1}, gave the DSC curve No. 4 presented in Figure 5. This curve is very similar to the DSC curve No. 2 in Figure 3. The sample which was in the stable phase KIb was transformed into the phase KIa at $T^{h}_{C4} = 328$ K (small and broad endothermic anomaly on the DSC curve). When the heating of the sample was continued, the phase transition occurred from phase KIa to phase K0 at $T^{h}_{C1} = 402$ K (big endothermic anomaly). Next, when cooling the sample from 425 to 300 K, with a scanning rate of 5 K · min^{-1}, we registered the DSC curve No. 5 presented also in Figure 5. However this curve is not exactly similar to the DSC curve No. 3. Namely, the sample being in the K0 phase during cooling became undercooled (phase K0'), and at $T^{c}_{C2} = 399$ K nearly the entire sample transformed into the metastable phase KII. Continuation of cooling induced the spontaneous transformation of the metastable phase KII into the stable phase KIa at ca. 359 K. The stable phase KIa was transformed at $T^{c}_{C4} = 326$ K into the KIb phase. The above drawn sequence of the phase transitions of the title compound was denoted as transformations II.

Subsequent heating of the sample did not give any new information, thus cooling of the next sample with a constant cooling rate of 5 K · min^{-1} was stopped at 387 K, i.e. before the temperature of the spontaneous transformation KII → KIa, which takes place at 360 K. The registered DSC curve No. 6 is shown in Figure 6. We can see a small but sharp anomaly connected with the phase transition from phase K0' to phase KII

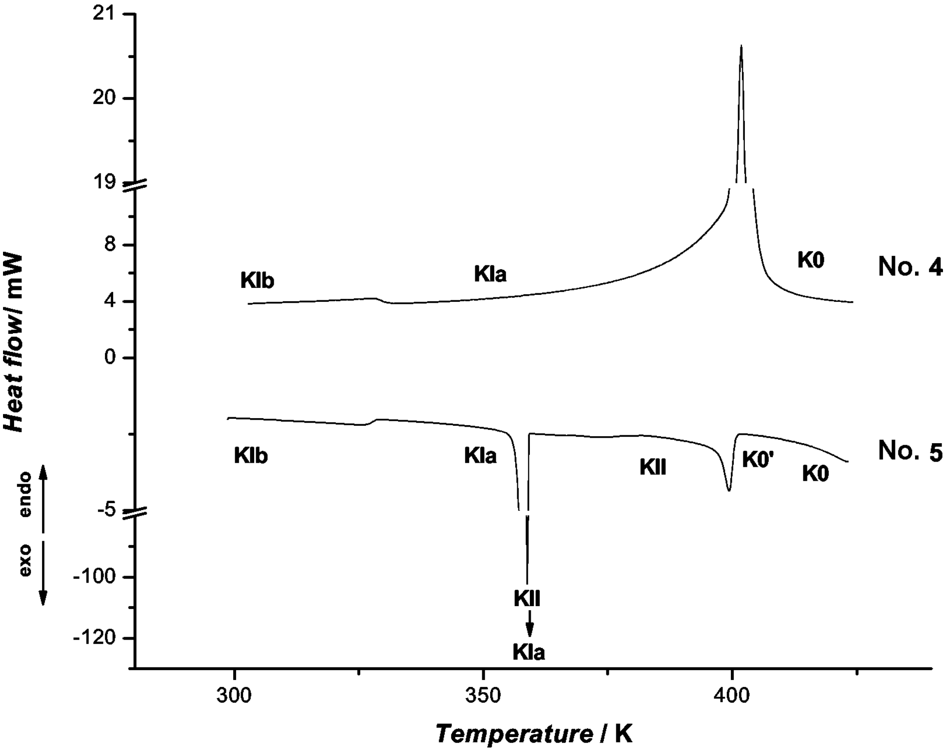

Fig. 5. DSC curves obtained during heating of [Co(DMSO)$_6$](BF$_4$)$_2$ from 300 to 425 K (curve No. 4), with a scanning rate of 10 K · min^{-1}, and during cooling from 425 to 300 K, with a scanning rate of 5 K · min^{-1} (curve No. 5).

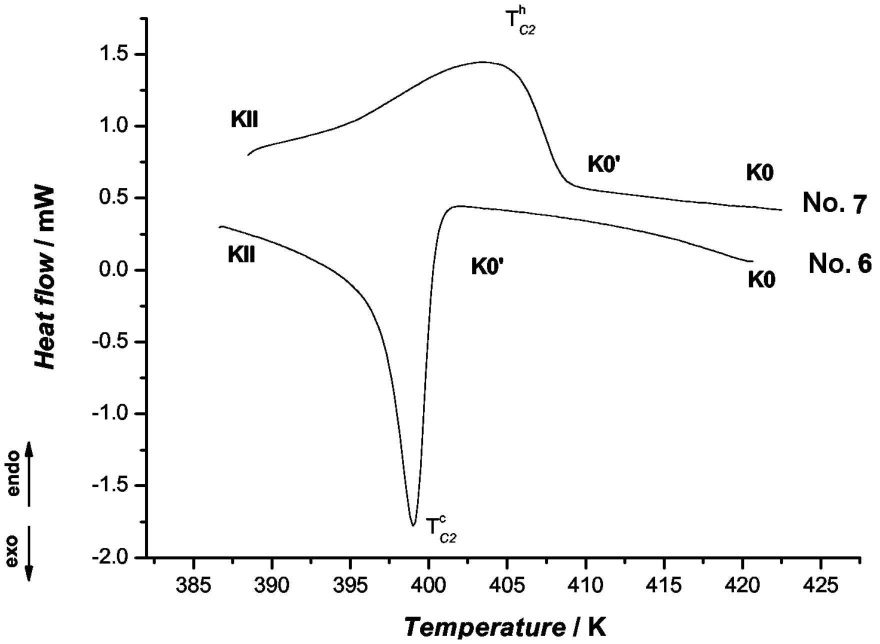

Fig. 6. DSC curves obtained during cooling of [Co(DMSO)$_6$](BF$_4$)$_2$ from 425 to 388 K (curve No. 6) and during heating from 388 to 425 K (curve No. 7), with a scanning rate of 5 K · min^{-1}.

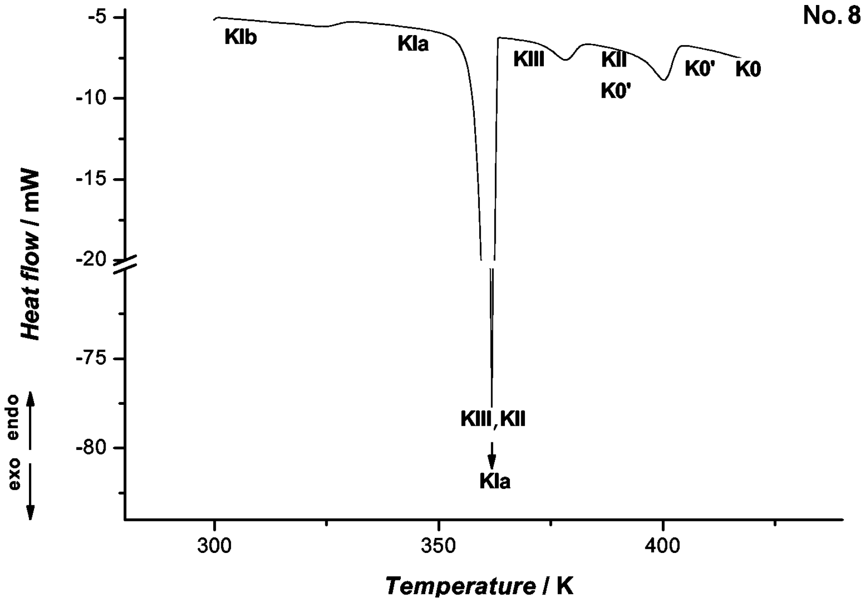

Fig. 7. DSC curve obtained during cooling of $[Co(DMSO)_6]$ $(BF_4)_2$ from 420 to 300 K (curve No. 8), with a scanning rate of 5 K · min^{-1}.

at $T^{c}_{C2} = 399$ K. When the sample was subsequently heated up from 388 K to 425 K, at a constant heating rate of 5 K · min^{-1}, the phase transition occurred from phase KII to phase K0', which was manifested by a very small and broad anomaly on the DSC curve No. 7 at $T^{h}_{C2} = 402$ K.

Subsequent cooling of the sample from 420 K down to 300 K with a scanning rate of 5 K · min^{-1} gave the DSC curve No. 8 presented in Figure 7. It provides a somewhat different sequence of the phase transformations than that presented above in Fig. 4 (curve No. 3) and in Fig. 5 (curve No. 5). Namely, while the sample in the K0 phase was cooled from 420 K, it became slightly undercooled (phase K0'), and at $T^{c}_{C2} = 400$ K only part of the K0' phase underwent a phase transition into a metastable phase KII. On further cooling, the rest of the K0' phase – at $T^{c}_{C3} = 378$ K – transformed into the metastable KIII phase (compare with Fig. 2). Continuation of cooling induced the spontaneous transformation of both metastable phases KIII and KII into the stable phase KIa at ca. 362 K, which was manifested as a big and sharp exothermic anomaly. On further cooling, the stable phase KIa at $T^{c}_{C4} = 325$ K was transformed into the stable KIb phase, and this was manifested as a very small anomaly (compare with Fig. 2). This sequence of the phase transitions of the title compound we denoted as transformations III.

The next cooling of the sample from 425 to only 370 K gave the DSC curve No. 9 presented in Figure 8, which more precisely confirms the phase transformations III. As can be seen when the sample was cooled, part of the K0 phase experienced a phase transition at $T^{c}_{C1} = 404$ K into phase KIa, and the rest of the sample underwent a deep overcooling and then transformed at $T^{c}_{C3} = 379$ K into the metastable phase KIII. These phase transitions are reversible, and this can be seen as two small and broad anomalies at $T^{h}_{C3} = 388$ K and at $T^{h}_{C1} = 408$ K on the DSC curve No. 10, obtained during subsequent sample heating (Fig. 8).

In spite of the very small differences between the phase transition temperatures and enthalpy changes, the phase transitions occurring at T^{c}_{C2} and at T^{c}_{C1} are actually two different phase transitions. Figure 9 presents the comparison of two DSC curves obtained upon sample cooling, both with a scanning rate of 5 K · min^{-1}; but each of these was registered after different "thermal histories", which represent the following transformations: I and II (or III), respectively. Thus, in Fig. 9 we can see two different anomalies: one at $T^{c}_{C1} = 403$ K and the second at $T^{c}_{C2} = 399$ K.

If the sample is heated to a temperature above 425 K, it melts at $T_m \approx 440$ K, with $\Delta H_m = 14.75$ kJ · mol^{-1}.

It is not possible to determine the nature of the observed phases solely on the basis of DSC measurements. Measurements utilizing complementary methods, for example X-ray diffraction and infrared and Raman spectroscopy, are now in progress. However,

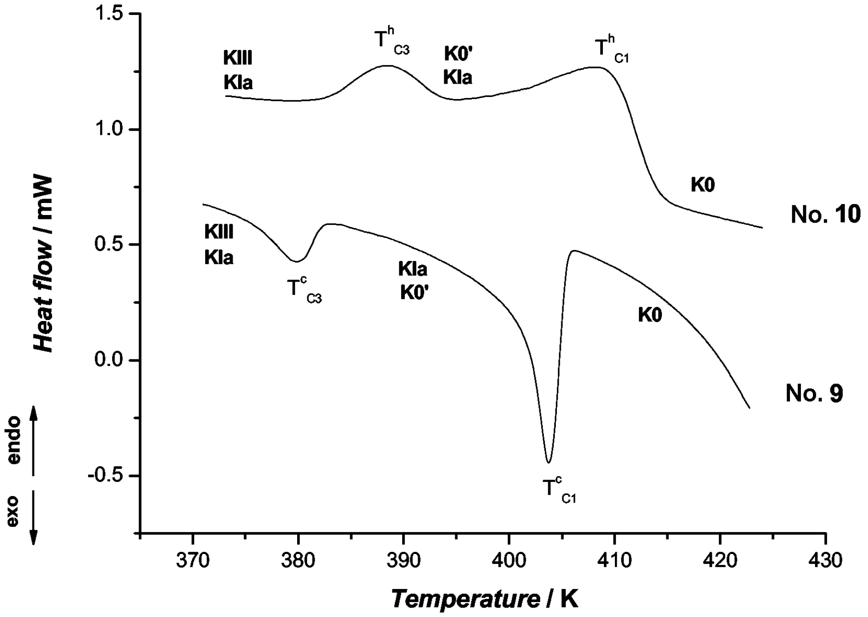

Fig. 8. DSC curves obtained during cooling of $[Co(DMSO)_6](BF_4)_2$ from 425 to 370 K (curve No. 9) and during heating from 370 to 425 K (curve No. 10), with a scanning rate of 5 K · min^{-1}.

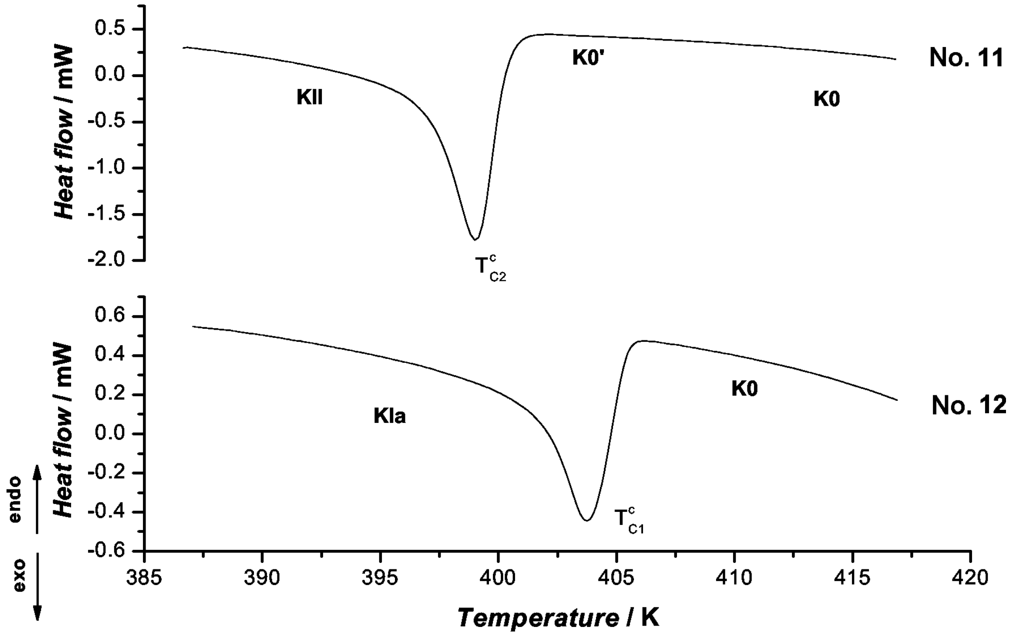

Fig. 9. Two DSC curves obtained during cooling of $[Co(DMSO)_6](BF_4)_2$ in the temperature range 385 – 420 K, with a scanning rate of 5 K · min^{-1}.

it was concluded from the change of the entropy of transitions ΔS (see Table 2) that phases K0 and undercooled K0 are more likely to be orientationally dynamically disordered crystals, so-called “ODIC” or “ODDIC” ones. We have preliminary evidence that stochastic reorientations of the CH_3 groups of dimethylsulphoxide ligands, of the $BF_4{}^-$ anions and also of the $[Co(DMSO)_6]^{2+}$ cations take place in the title compound, with reorientational correlation times τ_R of the order from 10^{-12} s across 10^{-11} s to 10^{-7} s, respectively. The entropy change connected with melting ($\Delta S_m = 22.0\ J \cdot K^{-1} \cdot mol^{-1}$) is very low and nearly fulfills Timmermans criterion [12] for so-called plastic crystals. It is very probable that also the metastable phases KII and KIII are of a high degree of rotational disorder, because of the low values of ΔS for the KII ↔ K0 phase transition at T_{C2} ($13.4\ J \cdot K^{-1} \cdot mol^{-1}$) and KII ↔ K0' phase transition at T_{C3} ($2.34\ J^{-1} \cdot mol^{-1}$). The phases KIa and KIb are more or less ordered ones (the very big value of $\Delta S = 115.7\ J \cdot K^{-1} \cdot mol^{-1}$ connected with the phase transition KIa ↔ K0 at T_{C1}, and the small value of $\Delta S = 3.3\ J \cdot K^{-1} \cdot mol^{-1}$ connected with the KIb ↔ KIa phase transition at T_{C4}, see Table 2).

The polymorphism of the title compound described above is very similar to that of $[Co(DMSO)_6](ClO_4)_2$ (also called HCC) [3] (see also Fig. 2 and Table 2). However, the most important difference is the following: For HCoBF the phase transition undercooled phase K0 ↔ metastable phase KIII at $T_{C3} = (382 \pm 6)$ K occurred at a higher temperature than the phase transition between the stable phases KIa ↔ KIb, which occurred at $T_{C4} = (326 \pm 1)$ K, whereas in the case of HCC it is the opposite, phase transition undercooled phase K0 ↔ metastable phase KIII occurred at a lower temperature [at $T_{C4} = (324 \pm 1)$ K] than the phase transition between the stable phases KIa ↔ KIb, which occurred at $T_{C3} = (350 \pm 1)$ K (see Table 2). Additionally, in the case of the title compound phase KIII is ordered ($\Delta S = 3.3\ J \cdot mol^{-1} \cdot K^{-1}$) and in the case of HCC it is disordered ($\Delta S = 67.1\ J \cdot mol^{-1} \cdot K^{-1}$). Moreover, in the case of the title compound the disordered K0 phase is not as deeply undercooled ($\Delta T = 36$ K) as for HCC ($\Delta T = 53$ K).

4. Conclusions

1. The following reversible phase transitions of HCoBF have been discovered:
   - stable phase KIb ↔ stable phase KIa at $\overline{T}_{C4} = (328 \pm 2)$ K;
   - metastable phase KIII ↔ undercooled phase K0 at $\overline{T}_{C3} = (383 \pm 4)$ K;
   - metastable phase KII ↔ undercooled phase K0 at $\overline{T}_{C2} = (399 \pm 2)$ K;
   - stable phase KIa ↔ stable phase K0 at $\overline{T}_{C1} = (404 \pm 1)$ K;
   - melting of the crystals at $T_m = 440$ K.

   The phase transition temperatures were calculated as the mean values of those determined on heating and cooling of HCoBF.
2. It can be concluded from the small values of the entropy change on melting that the phases K0 and undercooled K0 are so-called “orientationally dynamically disordered crystals” (ODDIC). Probably, the metastable phases KII and KIII are the crystals with a high degree of rotational disorder too because of the low values of ΔS for the phase transitions at T_{C2} and at T_{C3}. The phases KIa and KIb are more or less ordered phases.
3. The polymorphism of HCoBF and HCC is very similar. Only small differences were observed in the transitions metastable phase KIII ↔ undercooled phase K0 and stable phase KIb ↔ stable phase KIa.

Acknowledgements

We thank Dr. E. Mikuli from our faculty for stimulating discussions and Drs. D. Majda and A. Wesełucha-Birczyńska from the Regional Laboratory of Physicochemical Analysis and Structural Research in Kraków for help in the DSC measurements and in recording the FT-RS spectrum, respectively.

[1] I. Person, Acta Chem. Scand. A **36**, 1 (1982).
[2] M. Calligaris and O. Corugo, Coord. Chem. Rev. **153**, 83 (1996).
[3] A. Migdał-Mikuli, E. Mikuli, E. Szostak, and J. Serwońska, Z. Naturforsch. **58a**, 341 (2003).
[4] A. Migdał-Mikuli and E. Szostak, Z. Naturforsch. **60a**, 289 (2005).
[5] A. Migdał-Mikuli and E. Szostak, Thermochim. Acta **426**, 191 (2005).
[6] A. Migdał-Mikuli and E. Szostak, Thermochim. Acta (in press).
[7] J. Selbin, W. E. Bull, and L. H. Holmes Jr., J. Inorg. Nucl. Chem. **16**, 219 (1961).
[8] F. A. Cotton, R. Francis, and W. D. Horrocks Jr., J. Phys. Chem. **64**, 1534 (1960).
[9] M. Sandström, I. Persson, and St. Ahrland, Acta Chem. Scand. A **32**, 607 (1978).
[10] J. E. Connet, J. A. Creighton, J. H. S. Green, and W. Kynaston, Spectrochim. Acta **22**, 1859 (1966).
[11] Raman IR Atlas, Verlag Chemie GmbH, Weinheim 1974.
[12] J. Timmermans, J. Phys. Chem. Solids **18**, 1 (1961).