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POLYMORPHISM AND THERMAL DECOMPOSITION OF $[Ni(DMSO)_4]I_2$

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Tetrakis(dimethyl sulphoxide)nickel(II) *bis*(iodide) was studied by thermogravimetry (TG) and simultaneous differential thermal analysis (SDTA) and differential scanning calorimetry (DSC). The gaseous products of the decomposition were on-line identified by a quadrupole mass spectrometer (QMS). Thermal decomposition of the title compound proceeds in three main stages. In the first stage, which starts just above ca. 419 K, the compound loses two dimethyl sulphoxide (DMSO) molecules per one formula unit and small amount of iodide ion. In the second stage (464–552 K) the next DMSO ligands and the iodide ion simultaneously are released. In the last stage (552–900 K) $NiSO_4$ is created which next decomposes to NiO and SO_3.

Keywords: *DSC, SDTA, tetrakis(dimethyl sulphoxide)nickel(II) bis(iodide), TG/QMS, thermal decomposition*

Introduction

This kind of compound has been studied regarding to the polymorphism and thermal stability of the compounds of the type: $[M(DMSO)_y](X)_2$, where $DMSO=(CH_3)_2SO$; $X=BF_4^-$, ClO_4^-, NO_3^-; M=Mg, Mn, Co, Ni, Zn and Cd; y=4 or 6 [1–8]. Thermogravimetry (TG, DTG), simultaneous evolved gas analysis with on-line quadrupole mass spectrometer (SEGA/QMS) and simultaneous differential thermal analysis (SDTA) measurements were performed for these substances in order to enable verification of their chemical composition and thermal stability. It has been shown that all these compounds are stable up to temperature of ca. 380 K, whereas just above this temperature they start to loose DMSO molecules.

The crystallization of $[M(DMSO)_y](X)_2$ undergo in a specific way because some of the phases can be very easily overcooled. Namely, in dependence of those how fast and how deep was the sample cooled, on DSC curve were observed from one to six anomalies connected with phase transitions between different stable and different overcooled, metastable phases. It was concluded from the value of the enthalpy changes, that some of these phases are so-called 'orientationally dynamically disordered crystals' (ODIC) and the others are more and less ordered phases. The crystal structure, phase polymorphism and mechanism of thermal decomposition of $[Ni(DMSO)_4]I_2$ is so far unknown.

The main aim of these studies was to establish the mechanism of the thermal decomposition of $[Ni(DMSO)_4]I_2$ using methods of thermal analysis (TG, DTG, QMS, SDTA and DSC).

Experimental

Materials

Examined compound was obtained from hexaaquanickel(II) iodide which was earlier synthesised by the reaction of nickel carbonate (www.sigmaaldrich.com-CAS number: 12607-70-4) with diluted HI (in molar ratio 1:6). The hexaaquanickel(II) iodide was dissolved (in molar ratio 1:6) while being slowly heated up in dimethylsulphoxide (DMSO) which was previously purified by vacuum distillation at low pressure. Then this solution was chilled and the precipitated crystals of $[Ni(DMSO)_4]I_2$ were filtered. This compound was then dried in a desiccator over phosphorous oxide(V) for few hours. After desiccation, it was put in a sealed vessel and stored in a desiccator with barium oxide as a desiccant.

Methods

To check the chemical composition of the synthesised compound, the percentage content of nickel ions was checked using a complexometric method, with a solution of sodium salt of ethylenediaminetetraacetic acid (EDTA) as a titrant. 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 nickel equalled 9.39%, and its content found by the titration analysis amounted to 9.28±0.12%. For the carbon atoms, the difference between the theoretical (15.37%) and test value (15.43±0.01%) did not exceed 1%. For the hydrogen atoms, the theoretical value was 3.87% and the test

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value 3.87±0.01%. Therefore, the elementary analysis of the title compound confirmed the presence of the stoichiometric number of four DMSO molecules in the complex cation.

Fourier transform Raman scattering measurements (FTRS) were performed at room temperature with a Bio-Rad spectrometer with a resolution of 4 cm^{-1}. The incident radiation (λ=1064 nm) was from the Neodymium laser YAG Spectra-Physics. Fourier transform middle-infrared absorption measurements (FT-MIR) were performed using a Bruker EQUINOX-55 spectrometers, with a resolution of 2 cm^{-1}. The FT-MIR spectrum was recorded for a sample suspended in Nujol between KBr pellets.

The thermogravimetry (TG) and simultaneous differential thermal analysis were performed using a Mettler-Toledo TGA/SDTA 851^e instrument. The measurements were made in a flow (80 mL min^{-1}) of high purity dry argon (99.999%) within temperature range 300–900 K. The TG measurements were performed at a constant heating rate of 10 K min^{-1}. Additionally gas evolved during the experiment was analyzed with on-line quadrupole mass spectrometer (QMS) using a Balzer GSD 300T instrument. The temperature was measured by a Pt–Pt/Rh thermocouple with the accuracy of ±0.5 K. The thermal decomposition measurements were made for a sample weighing 19.42 mg which was placed in a 150 μL open corundum α-Al_2O_3 crucible.

The differential scanning calorimetry (DSC) measurements were made using a Mettler Toledo DSC 821^e apparatus used in the temperature range of 300–823 K. The DSC measurements were made by heating the sample of mass of 8.93 mg, measurements were performed under constant flow of argon (80 mL min^{-1}), with the heating rate equals to 5 K min^{-1}.

Results and discussion

In order to further identify of the synthesized compound the FTRS and FTIR spectra were registered [9, 10]. Figure 1 shows a comparison of Raman and infrared spectra of $[Ni(DMSO)_4]I_2$ obtained at room temperature. The cation was considered to have tetrahedral symmetry with nearly freely rotating CH_3 groups of DMSO ligands.

Figure 2 shows TG, DTG and SDTA curves recorded for the sample in the temperature range of 300–900 K, and DSC curve recorded in the temperature range of 300–823 K. We can see small differences between DSC and SDTA profiles because they were performed under different conditions (masses of samples, scanning rates, open and closed crucibles). The DSC measurements were made in different conditions in order to compare results obtained for title compound with data obtained for previously investigated compounds. As an insertion in Fig. 2 were placed the results of the DSC measurement for

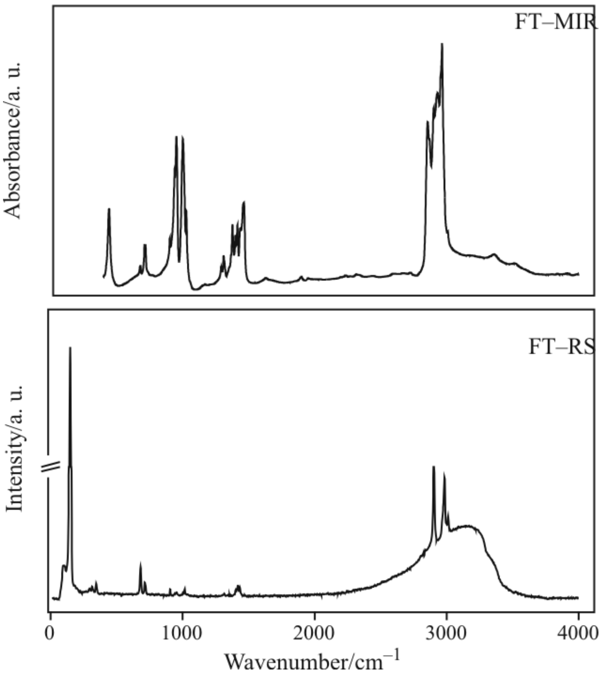

Fig. 1 Comparison of the infrared (FT-MIR) and Raman (FT-RS) spectra of $[Ni(DMSO)_4]I_2$

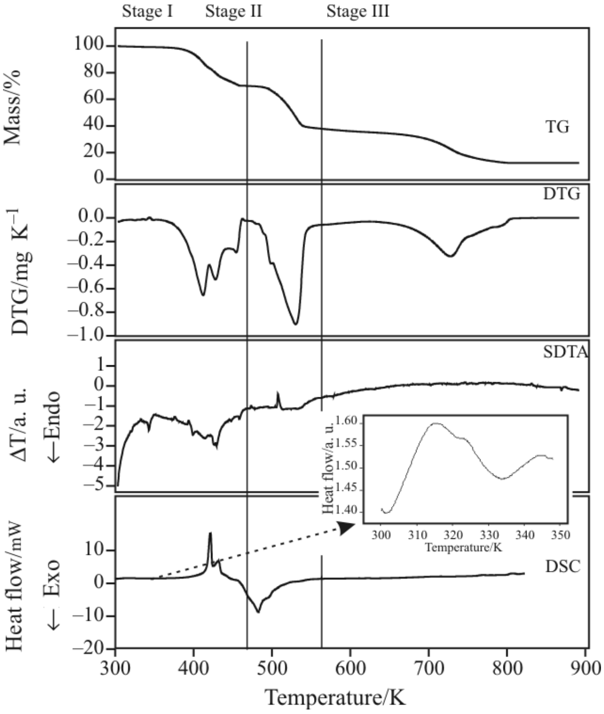

Fig. 2 TG, DTG, SDTA and DSC curves for $[Ni(DMSO)_4]I_2$ in the range of 300–900 K registered at a constant heating rate of 10 K min^{-1} and DSC curves in the range of 300–823 K registered at a constant heating rate of 5 K min^{-1}

$[Ni(DMSO)_4]I_2$ in the temperature range 300–350 K. As can be seen while heating sample from 300 to 350 K, an irreversible phase transition into the high temperature phase can be observed at $T_C=315$ K (small anomaly on the DSC curve).

During the TG experiment, the QMS spectra of masses were followed from $m/e=1$ to 140, however, for reasons of graphic readability, only the masses of $m/e=78$, 61, 45, 127, 63, 44, 29, 15, 32, 17 and 18 representing CH_2SO_2 or $(CH_3)_2SO$, CHSO, C_2H_5O, I, CH_3SO, CO_2, C_2H_5, CH_3, O_2, OH and H_2O are shown in Fig. 3. The TG, DTG and QMS curves show that the decomposition of the sample proceeds in three main stages (I, II and III). The mechanism of thermal analysis of the title compound is presented in Table 1 and the thermogravimetric data are gathered in Table 2. It can be observed that the first stage (300–464 K) of thermolysis, which starts just above 419 K, involves release of two DMSO ligands per one formula unit. This process undergoes very probably in the two steps. At the end of this stage at 455 K also small amount of iodide ion is released (the third anomaly on the DTG curve) [11]. This ion immediately reacts with CH_3 radical derived from DMSO fragmentation and $[(CH_3)_3SO]^+I^-$ (TMSOI) is created [12, 13]. The profile of the DSC curve shows that in the vicinity of 455 K some exothermic process is began. Releasing of small amount of iodide and creation of TMSOI can explained this anomaly. In the second stage, which occurs in the temperature range of 464–552 K, we can observe melting and decomposition of new-created TMSOI to CH_3SO, ${}^{\cdot}CH_3$ and I^- and partial decomposition of resulting $[Ni(DMSO)_2]I_2$ into ${}^{\cdot}[Ni(CH_3)_2SO]I$ radical [11, 12, 14]. The profile of the SDTA curve of $[Ni(DMSO)_4]I_2$ in this temperature range shows one exothermic peak. It is probably because the TMSOI is also created here but immediately decompose to CH_3SO, ${}^{\cdot}CH_3$ radical and I^- [12, 14]. In the third stage (in the temperature range of 552–900 K) the DMSO molecules reacts with ${}^{\cdot}OH$ radical derived from DMSO fragmentation [15]. Created in this process H_2SO_4 and ${}^{\cdot}CH_3$ can react with ${}^{\cdot}[Ni(CH_3)_2SO]I$ giving trimethyl sulphoxonium iodide (TMSOI), nickel sulphate, and hydrogen. New-created TMSOI decomposed immediately to: CH_3SO, ${}^{\cdot}CH_3$ and I^-.

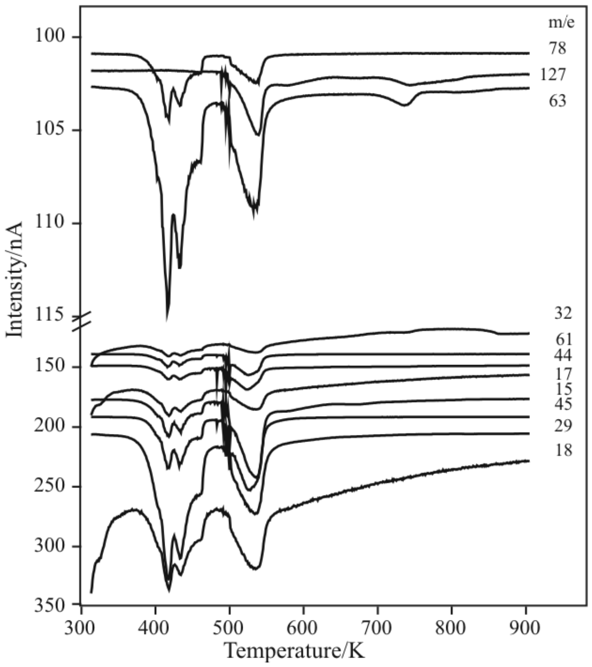

Fig. 3 QMS curves for $[Ni(DMSO)_4]I_2$ in the range of 300–900 K

Table 1 Mechanism of thermal analysis of $[Ni(DMSO)_4]I_2$

Stage number	Reaction	References
Ia	$[Ni((CH_3)_2SO)_4]I_2 \rightarrow [Ni((CH_3)_2SO)_3]I_2+(CH_3)_2SO$	[this work]
Ib	$[Ni((CH_3)_2SO)_3]I_2 \rightarrow [Ni((CH_3)_2SO)_2]I_2+(CH_3)_2SO$	[this work]
Ic	$x([Ni((CH_3)_2SO)_2]I_2) \rightarrow x({}^{\cdot}[Ni((CH_3)_2SO)]I)+x((CH_3)_2SO)+xI^-$	[11]
Id	$x((CH_3)_2SO \rightarrow x({}^{\cdot}CH_3SO)+x({}^{\cdot}CH_3)$	[12]
	$x({}^{\cdot}CH_3)+xI^-+x(CH_3)_2SO \rightarrow x[(CH_3)_3SO]^+I^-$	[13]
IIa	$x[(CH_3)_3SO]^+I^- \rightarrow xCH_3SO+2x({}^{\cdot}CH_3)+xI^-$	[12, 14]
IIb	$(1-x)[Ni((CH_3)_2SO)_2]I_2 \rightarrow (1-x)({}^{\cdot}[Ni(CH_3)_2SO]I)+(1-x)(CH_3)_2SO+(1-x)I^-$	[11]
	$(1-x)(CH_3)_2SO+(1-x)I^- \rightarrow (1-x)[(CH_3)_3SO]^+I^- \rightarrow (1-x)CH_3SO+(2-2x)({}^{\cdot}CH_3)+(1-x)I^-$	[12, 14]
IIIa	$(CH_3)_2SO+{}^{\cdot}OH \rightarrow CH_3S(O)OH+{}^{\cdot}CH_3$	[15]
	$CH_3S(O)OH+{}^{\cdot}OH \rightarrow CH_3S(O)(OH)_2+O_2 \rightarrow CH_3S(O)_2OH+HO_2$	[15]
	$CH_3S(O)_2OH+{}^{\cdot}OH \rightarrow H_2SO_4+{}^{\cdot}CH_3$	[15]
IIIb	$({}^{\cdot}[Ni((CH_3)_2SO)]I)+H_2SO_4+{}^{\cdot}CH_3+ \rightarrow [(CH_3)_3SO]^+I^-+NiSO_4+0.5H_2$	[this work]
	$[(CH_3)_3SO]^+I^- \rightarrow CH_3SO+2({}^{\cdot}CH_3)+I^-$	[12, 14]
IIIc	$NiSO_4 \rightarrow NiO+SO_3$	[this work]

Table 2 Parameters of $[Ni(DMSO)_4]I_2$ thermal decomposition; sample mass=19.42 mg

Stage number	Temp. range/ K	Mass loss/ %	Mass after decomposition/%	Calc. values/%	Products of decomposition
I	300–464	29.8		25.0	$2(CH_3)_2SO$, $x(^{\cdot}[Ni((CH_3)_2SO)]I)$ $x[(CH_3)_3SO]^+I^-$
II	464–552	31.5		32.8	$(1–x)([Ni((CH_3)_2SO)]I)$, CH_3SO, $2(CH_3)$, I^-
III	552–900	26.5		30.2	CH_3SO , $2(CH_3)$, $0.5H_2$, SO_3, I^-
			12.2	12.0	NiO

The decomposition gets completed at 810 K, when created in this stage nickel sulphate decomposes into anhydrous nickel oxide and sulphur trioxide.

Conclusions

1. The DSC measurements of $[Ni(DMSO)_4]I_2$ performed in the temperature range of 300–350 K using a Mettler-Toledo 851^e apparatus allowed to detect one phase transition at T_c=315 K (ΔH=2.43 kJ mol^{-1}, ΔS=7.7 J mol^{-1} K^{-1}). In opposite to our previous investigations the high temperature phase was not orientationally disordered ones.

2. The TG, DTG and QMS curves show that the decomposition of the sample proceeds in three main stages (I, II and III):

- It can be observed that the first stage (300–464 K) of thermolysis, which starts just above 419 K, involves release of two DMSO ligands per one formula unit. This process undergoes very probably in the two steps. At the end of this stage also small amount of iodide ion is released [11]. This ion immediately reacts with $\cdot CH_3$ radical derived from DMSO fragmentation and $[(CH_3)_3SO]^+I^-$ (TMSOI) is created [12, 13].
- In the second stage, which occurs in the temperature range of 464–552 K, we can observe melting and decomposition of new-created TMSOI to $CH_3SO\cdot$, $\cdot CH_3$ and I^- and partial decomposition of resulting $[Ni(DMSO)_2]I_2$ into $\cdot[Ni(CH_3)_2SO]I$ radical [11, 12, 14]. The profile of the SDTA curve of $[Ni(DMSO)_4]I_2$ shows one exothermic peak in this temperature range. It is probably because the TMSOI is also created here but immediately decompose to CH_3SO, CH_3 radical and I^- [12, 14].
- In the third stage (in the temperature range of 552–900 K) the DMSO molecules reacts with •OH radical derived from DMSO fragmentation [15]. Created in this process H_2SO_4 and $\cdot CH_3$ can react with •[Ni(CH3)2SO]I giving trimethyl sulphoxonium iodide (TMSOI), nickel sulphate, and hydrogen. New-created TMSOI decomposed immediately to CH_3SO, $\cdot CH_3$ and I^-. The decomposition gets completed at 810 K when created in this stage nickel sulphate decomposes into anhydrous nickel oxide and sulphur trioxide.

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