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PHASE TRANSITION AND THERMAL DECOMPOSITION OF $[Al(DMSO)_6]Cl_3$

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Phase transition and thermal decomposition of hexadimethylsulfoxidealuminium chloride were studied by differential scanning calorimetry (DSC), thermogravimetry (TG) and simultaneous differential thermal analysis (SDTA). The gaseous products of the decomposition were on-line identified by a quadrupole mass spectrometer (QMS). In the temperature range of 95–300 K, $[Al(DMSO)_6]Cl_3$ indicates one phase transition at T_c^h=244.96 K (on heating) and at T_c^c=220.87 K (on cooling). Large thermal hysteresis of the phase transition (~24 K) indicates its first order character. Large value of transition entropy ($\Delta S\approx40$ J mol^{-1} K^{-1}) suggests its configurational character. Thermal decomposition of the title compound proceeds in four main stages. In the first stage, which starts just above ca. 300 K, the compound loses two DMSO molecules per one formula unit and undergoes into $[Al(DMSO)_4]Cl_3$. In the second stage, the next three DMSO ligands are released and simultaneously decomposed. The third stage, which continues up to ca. 552 K, is connected with a loss of the last DMSO ligand and the formation of $AlCl_3$. In the fourth stage $AlCl_3$ reacts with carbon monoxide that originates from the decomposition of DMSO, and first aluminium oxychloride and next solid Al_2O_3 plus carbon are created.

Keywords: *DSC, hexadimethylsulfoxidealuminium chloride, phase transition, SDTA, TG/QMS, thermal decomposition*

Introduction

Both stable and metastable phases have been identified by Migdał-Mikuli *et al.* [1–4] in their studies of polymorphism of $[M(DMSO)_6](ClO_4)_2$ compounds, where DMSO=$(CH_3)_2SO$ and M=Cd, Co, Mn and Zn, with DSC in the temperature range of 300–390 K. Some of these phases are orientationally dynamically disordered crystals (ODDIC) or plastic crystals. Additionally, one low temperature solid-solid structural phase transition was detected for both $[Cd(DMSO)_6](ClO_4)_2$ at 242 K [1] and $[Mn(DMSO)_6](ClO_4)_2$ at 225 K [2], when the compounds were heated up. The thermogravimetry (TG, DTG), the simultaneous evolved gas analysis with on-line quadrupole mass spectrometer (SEGA/QMS) and simultaneous differential thermal analysis (SDTA) were also performed for these substances in order to enable verification of their chemical composition and 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 crystal structure, phase polymorphism and mechanism of thermal decomposition of $[M(DMSO)_6]Cl_3$ compounds is so far unknown. However, Boström *et al.* [5] have determined the structure of the low temperature phase of $[Al(DMSO)_6]Cl_3$ (at 150 K) as the trigonal (space group $R\bar{3}$), with lattice parameters: a=10.3760(6) Å, c=22.0210(12) Å and Z=3. Six oxygen atoms of six DMSO ligands are bonded to the Al^{3+} ion in the form of trigonally distorted octahedron. There is a distorted rhombododecahedral arrangement of Cl^- ions around the Al^{3+} ions [5]. Furthermore, thermal decomposition of $[Ln(DMSO)_3]Cl_3$, where Ln=Dy, Ho, Er, Tm, Yb and Lu, were studied by Matos *et al.* [6] using oxygen or nitrogen dynamic atmosphere. All the compounds first melt (at 404–428 K) and then decompose (at 472–488 K). In all cases the residues at ca. 820 K were identified as lanthanide oxychlorides and at ca. 1170 K as Ln_2O_3. There was no evidence of formation of anhydrous lanthanide chlorides [6].

The main aims of these studies were to detect the phase polymorphism of $[Al(DMSO)_6]Cl_3$ by DSC and to establish the mechanism of the thermal decomposition of this compound using methods of thermal analysis (TG, DTG, QMS, SDTA and DSC).

Experimental

Materials

A few grams of $[Al(H_2O)_6]Cl_3$ were dissolved while being slowly heated up in dimethyl sulfoxide, later called DMSO, of high chemical purity, which was previously purified by vacuum distillation at low pressure. The solution was then chilled and small, white col-

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oured crystals of hexadimethylsulfoxidealuminium chloride were precipitated, filtered and washed with acetone. The obtained crystals were then dried in a desiccator over P_2O_5 for a few days. After desiccation, they were put in a sealed vessel and stored in a desiccator over barium oxide as a desiccant.

Methods

Before the measurements, the composition of the investigated compound was determined on the basis of carbon and hydrogen content in the DMSO ligand, using elementary analysis on a EURO EA 3000 instrument. Elementary analysis confirmed the proper composition of the investigated compound. The average contents of the DMSO ligands were found to be equal to the theoretical values within the error limit of ca. 0.3%.

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 far and middle-infrared absorption measurements (FT-FIR and FT-MIR) were performed using a Bio-Rad FTS60V and Bruker EQUINOX-55 spectrometers, respectively, with a resolution of 2 cm^{-1}. The FT-FIR spectrum for a powdered sample suspended in polyethylene dust was recorded. The FT-MIR spectrum was recorded for a sample suspended in Nujol between KBr pellets.

The thermogravimetry (TG/DTG) measurements were performed using a Mettler-Toledo 851^e instrument. Three series of measurements for three samples of different masses were performed. The measurements were made in a flow (60 mL min^{-1}) of high purity dry argon (99.999%) within temperature range 300–640 K. The TG measurements were performed at a constant heating rate of 10 K min^{-1}. At a constant heating rate beside TG and DTG curves, the simultaneous differential thermal analysis (SDTA) curve and the simultaneous evolved gas analysis (SEGA), with on-line quadrupole mass spectrometer (QMS) using a Balzer GSD 300T instrument, were also registered. The temperature was measured by a Pt–Pt/Rh thermocouple with the accuracy of ±0.5 K.

The DSC measurements at 95–300 K were performed with a Perkin-Elmer PYRIS 1 DSC instrument. The powdered sample was placed in an aluminium vessel and was closed by compression. Another empty vessel was used for reference. The instrument was calibrated by means of the melting point of indium and melting point of water, for the high and the low temperature region, respectively. High purity dry helium (99.999%) was used as the purging gas. As the air shield gas, nitrogen 99.999% was used. The nitrogen gas used for transfer of liquid nitrogen to the cold finger dewar was of high purity as well. Two characteristic temperatures of the DSC peaks, obtained on heating, were computed: the temperature of the peak maximum (T_{peak}) and the temperature calculated from the slope of the left-hand side of the peak (T_{onset}). The difference between these two temperatures ranged usually from 2 to 6 K. The enthalpy changes (ΔH) linked up with observed transitions were calculated by numerical integration of the DSC curves under the peaks of the anomalies. A linear background was subtracted prior to the calculations. It was done in an arbitrary manner, however, for every sample the procedure was the same. The entropy changes (ΔS) were calculated using the following formula: $\Delta S=\Delta H/T_c$. The sharp peaks of the DSC curves were computed with high accuracy reaching ±4%, whereas the diffuse peaks could be regarded as mere estimates. Details of the DSC experiment are the same as described in [7].

Results and discussion

In order to further identify the synthesized compound and certify its purity, the FTRS and FTIR spectra were performed. Figure 1 shows a comparison of Raman and infrared spectra of $[Al(DMSO)_6]Cl_3$ obtained at room temperature. The cation was considered to have octahedral symmetry with nearly freely rotating CH_3 groups of DMSO ligands. Table 1 presents a list of the bands' positions, observed in the FTRS and FTIR

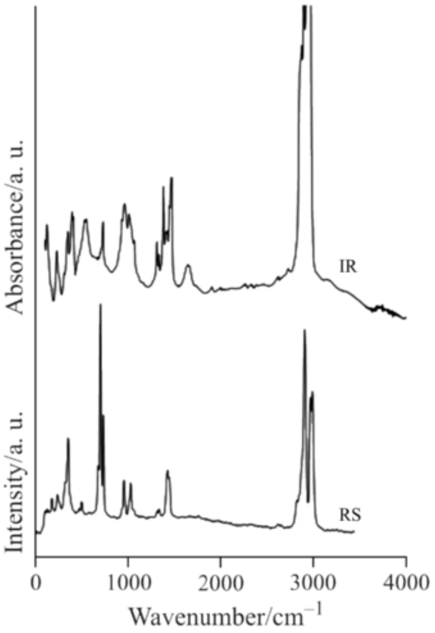

Fig. 1 Comparison of the room temperature Raman and infrared spectra of $[Al(DMSO)_6]Cl_3$

Table 1 The list of bands' positions of the Raman and infrared spectra of $[Al(DMSO)_6]Cl_3$ at room temperature, comparison with literature data

Frequencies/cm^{-1}					Assignments
RS		IR			
this work	DMSO [9]	this work	[8]	DMSO [9]	
2990st	2997m	*		2985st	$\nu_{as(CH)}$
2967st					$\nu_{as(CH)}$
2905vst	2913vst	*		2902st	$\nu_{s(CH)}$
2820w					$\nu_{s(CH)}$
1441wv		1441st		1432st	$\delta_{as(HCH)}$
1422m	1420m	1421m			$\delta_{as(HCH)}$
		1405m		1401st	$\delta_{as(HCH)}$
1331vw		1330w			$\delta_{s(HCH)}$
1312vw	1310w	1307m		1305m	$\delta_{s(HCH)}$
1056vw	1045vs	1062m		1048vst	$\nu_{s(SO)}$
1024m		1007vst			$\nu_{s(SO)}$
	997vw	961vst		949m	$\rho_{r(CH_3)}$
953m	995m	930st			$\rho_{r(CH_3)}$
~930vw	928vw				$\rho_{r(CH_3)}$
729st		727st			$\nu_{as(CS)}$
698vst	699st			690m	$\nu_{as(CS)}$
675m	670vs			660w	$\nu_{s(CS)}$
		544st	544st		ν_{AlO}
		527st	535sh		ν_{AlO}
496w					$\nu_{s(AlO)}$
471w					$\nu_{s(AlO)}$
		405m			$\delta_{s(CSO)}$
~380m	382m	392m	389m	378m	$\delta_{s(CSO)}$
351st	332st	349m	335w	327m	$\delta_{as(CSO)}$
320m	308m	311w	303w		$\delta_{as(CSC)}$
237w		230m			$\nu_{d(AlO)}$
177w		~170w			$\nu_{d(AlO)}$
125vw		123m			ν_L (lattice)
102vw					ν_L (lattice)

*position of Nujol bands, vw – very weak, w – weak, sh – shoulder, m – medium, st – strong, vst – very strong, br – broad

spectra of $[Al(DMSO)_6]Cl_3$, their relative intensities and assignments denoted by comparing with the literature data [8–11] for several $[M(DMSO)_6]X_2$ and $[M(DMSO)_6]X_3$ complexes. These assignments proved that both the composition and the structure of the investigated compound were as expected.

The DSC measurements were made both by heating and cooling the samples of masses of 10.20 and 12.83 mg at constant rates of: 20 and 30, 40 and 60 K min^{-1}, respectively. Figure 2 shows two temperature dependencies of the heat flow (two DSC curves) obtained on heating and cooling of $[Al(DMSO)_6]Cl_3$ in the range of 95–300 K at the scanning rate of 20 K min^{-1}. One anomaly on each of these DSC curves was registered at T^{h}_{peak}=244.28 K (on heating) and at T^{c}_{peak}=210.65 K (on cooling). The temperatures of the phase transition T_c^{h}=244.96 K and T_c^{c}= 220.87 K were obtained by linear extrapolation of the dependence of T^{h}_{peak} and T^{c}_{peak} values *vs*. the rate of heating and cooling to the zero, respectively. Large thermal hysteresis of the phase transition (~24 K) indicates its first order character. The thermodynamic parameters of the detected phase transition are presented in Table 2. The relatively large value of the entropy change connected with the observed phase tran-

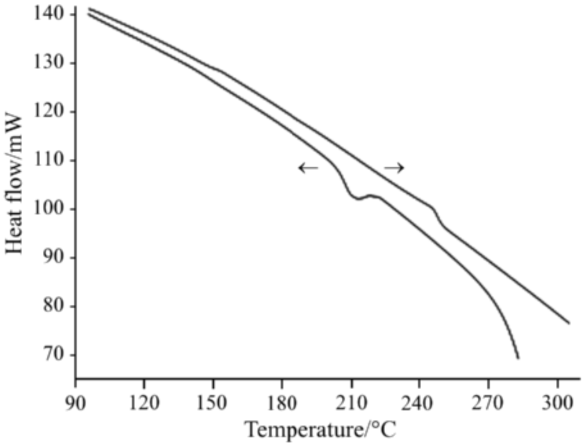

Fig. 2 DSC curves registered on heating and cooling of $[Al(DMSO)_6]Cl_3$ in the range of 95–300 K at a rate of 20 K min^{-1}

sition (mean value of ΔS is ca. 40 J mol^{-1} K^{-1}) is noteworthy as it indicates its configurational character.

To sum up, the temperature of the phase transition discovered in $[Al(DMSO)6]Cl_3$ at T_c^h=244.96 K is similar to the temperature of the low temperature structural phase transitions registered for $[Mn(DMSO)_6](ClO_4)_2$ (T_c^h=225.40 K) [2] and $[Cd(DMSO)_6](ClO_4)_2$ (T_c^h=242.0 K) [1]. However, the enthalpy and entropy change values (ΔH and ΔS) for the phase transition in $[Al(DMSO)_6]Cl_3$ are distinctly larger than the corresponding values for the aforementioned compounds. It confirms the configurational character of the discovered in $[Al(DMSO)_6]Cl_3$ phase transition. So the high temperature phase of the title compound is probably the phase with a high degree of orientational dynamical disorder (ODDIC). Moreover, contrary to the investigations of $[M(DMSO)_6](ClO_4)_2$ compounds to date, the compound under study has no metastable phases above room temperature.

The thermal decomposition measurements were made for three samples with masses of 33.1555, 96.2831 and 37.0941 mg, at a constant heating rate of 10 K min^{-1}. The first two samples were placed in a 150 μL open corundum crucible, while the third one was placed in a 150 μL open platinum crucible. The results obtained for all three samples are nearly identical. Figure 3 shows TG, DTG and SDTA curves recorded for the sample of mass 37.0941 mg placed in the platinum crucible in the temperature range of 300–640 K. 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=16, 64, 44, 32, 48, 14, 17, 18, 78, 63 and 36 representing CH_4, SO_2, CO_2, O_2, SO, CH_2, OH, H_2O, CH_2SO_2 or $(CH_3)_2SO$, CH_3SO and Cl are shown in Fig. 4.

The TG, DTG and QMS curves show that the decomposition of the sample proceeds in four main stages

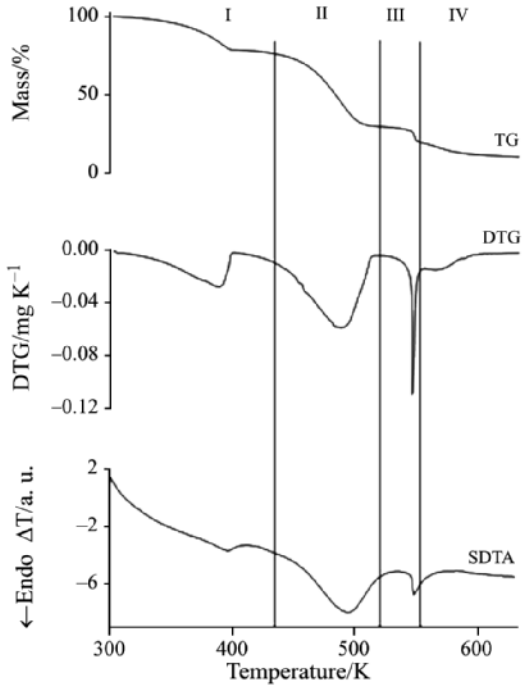

Fig. 3 TG, DTG and SDTA curves for $[Al(DMSO)_6]Cl_3$ in the range of 300–640 K registered at a constant heating rate of 10 K min^{-1}

Table 2 Thermodynamic parameters of the phase transition of $[Al(DMSO)_6]Cl_3$

Scanning rate/K min^{-1}	20	30	40	60
Mass/mg	10.20	12.83	12.83	12.83
		heating		
ΔH/kJ mol^{-1}	9.37	9.96	8.75	7.74
ΔS/J mol^{-1} K^{-1}	38.34	40.54	35.56	31.39
T_c^h/K	244.28	245.78	245.99	246.57
		cooling		
ΔH/kJ mol^{-1}	10.26	8.99	7.95	7.17
ΔS/J mol^{-1} K^{-1}	48.71	41.94	38.71	35.13
T_c^c/K	210.65	214.22	205.32	204.03

Table 3 Parameters of [Al(DMSO)$_6$]Cl$_3$ thermal decomposition; sample mass=37.0941 mg

Stage number	Temperature range/K	Mass loss/%	Mass after decomposition/%	Calculated values/%	Products of decomposition
I	300–433	24.0		26.0	2DMSO
II	433–519	43.3		39.0	3DMSO
III	519–552	11.2		13.0	1DMSO
IV	552–640	10.9		11.3	3/2Cl$_2$
			10.6*	10.7*	1/2Al$_2$O$_3$+3/2C

*mass calculated after reaction of AlCl$_3$ with CO according to Eq. (2)

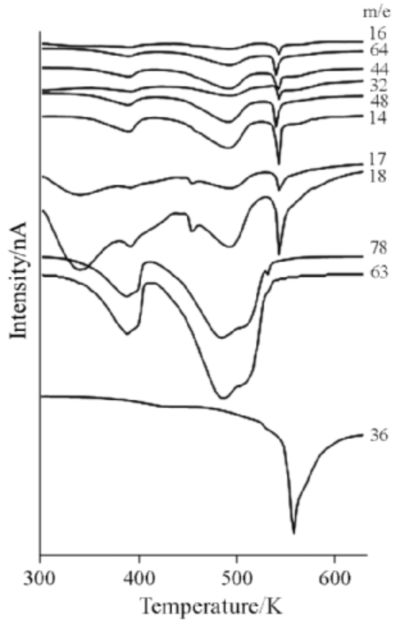

Fig. 4 QMS curves for [Al(DMSO)$_6$]Cl$_3$ in the range of 300–640 K

(I, II, III and IV). It can be observed that the first stage, which takes place in the temperature range of 300–433 K, involves release of two DMSO ligands included in coordination sphere of aluminium atom, per one formula unit. In the second stage, which occurs in the temperature range of 433–519 K, three DMSO ligands are released. The third stage (in the temperature range of 519–552 K) is connected with the loss of the last DMSO ligand. In summary, in the temperature range of 300–552 K, six molecules of dimethylsulfoxide are released and AlCl$_3$ is formed. Immediately after aluminium chloride is created in the temperature range of 552–608 K (stage IV), it reacts with CO derived from DMSO fragmentation and Al$_2$O$_3$, Cl$_2$ and C are created. After the fourth stage of the decomposition 10.6% of the initial mass of the sample remained. The temperature ranges, percentage of mass loss and the products of thermal decomposition of [Al(DMSO)$_6$]Cl$_3$ at particular stages are presented in Table 3.

The profile of the SDTA curve of [Al(DMSO)$_6$]Cl$_3$ shows three endothermic peaks. All of them correspond to the liberation of the DMSO molecules. This process can be described by the following reactions:

stage I

$$[Al(DMSO)_6]Cl_3 \rightarrow [Al(DMSO)_4]Cl_3 + 2DMSO$$

stage II (1)

$$[Al(DMSO)_4]Cl_3 \rightarrow [Al(DMSO)]Cl_3 + 3DMSO$$

stage III

$$[Al(DMSO)]Cl_3 \rightarrow AlCl_3 + DMSO$$

At the second stage, the evolved dimethyl sulfoxide simultaneously decomposes to mainly paraformaldehyde. Dimethyl sulfide, dimethyl disulfide, bis(methylthio)methane and water are other volatile products. A small amount of dimethyl sulfone can also be found [12]. At higher temperatures or after the fragmentation of the above mentioned molecules, mass spectrum of DMSO contains five main groups of lines. The most intense lines in each group are situated at *m/z* values equal to: 15, 29, 45, 63 and 78. They may correspond to CH$_3$, C$_2$H$_5$, C$_2$H$_5$O, CH$_3$SO and CH$_2$SO$_2$, respectively [13, 14]. At the third stage, solid AlCl$_3$ is also formed.

The fourth and last stage, which cannot be observed in the SDTA curve, but is clearly seen in DTG curve, can be explained by the instant reaction between AlCl$_3$ and CO, derived from the DMSO ligands, according to the following reaction:

stage IV

$$AlCl_3 + 3/2CO \rightarrow AlClO + Cl_2 + 3/2C + 1/4O_2 \rightarrow 3/2Cl_2 + 3/2C + 1/2Al_2O_3 \quad (2)$$

The above presented mechanism of thermal decomposition of [Al(DMSO)$_6$]Cl$_3$ is highly consistent with the results which we obtained from the DSC measurement. The DSC curve obtained for the studied compound by heating the sample in the temperature range of 300–650 K is presented in Fig. 5. The profile of the DSC curve shows four endothermic and one exothermic peaks. The first four endothermic peaks can be explained by the three stages of the lib-

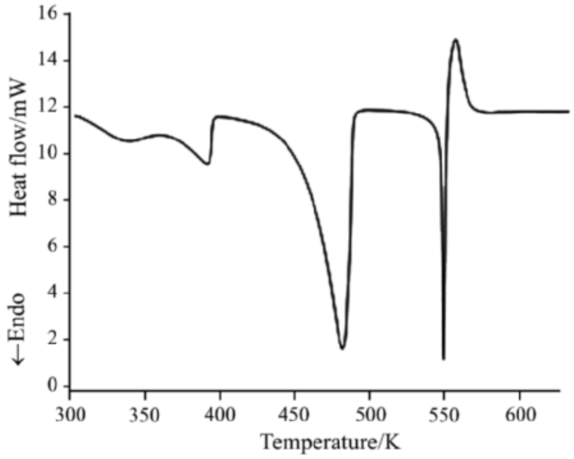

Fig. 5 DSC curve registered on heating of $[Al(DMSO)_6]Cl_3$ in the range of 300–650 K at a rate of 10 K min^{-1}

eration of the DMSO ligands resulting in the formation of the tetra- and monodimethylsulfoxidealuminium chloride and $AlCl_3$ according to Reactions (1). Finally, one distinct exothermic peak at ca. 560 K can be explained on the basis of $AlCl_3$ oxidation process, which takes place during the decomposition of DMSO, according to Reaction (2), with the formation of amorphous Al_2O_3 [15].

Conclusions

- The DSC measurements of $[Al(DMSO)_6]Cl_3$ performed in the temperature range of 95–300 K allowed one phase transition to be discovered. The temperature of the phase transition amounts to T_c^h=244.96 K (on heating) and T_c^c=220.87 K (on cooling). The large value of transition entropy ($\Delta S \approx 40$ J mol^{-1} K^{-1}) indicates its configurational character.
- The phase polymorphism of the hexadimethylsulfoxidemetal(II) chlorates(VII) family: $[Mn(DMSO)_6](ClO_4)_2$, $[Co(DMSO)_6](ClO_4)_2$, $[Cd(DMSO)_6](ClO_4)_2$ and $[Zn(DMSO)_6](ClO_4)_2$, is quite different than that of $[Al(DMSO)_6]Cl_3$.
- The thermal decomposition of the investigated compound proceeds in four main stages. In the first stage two, and in the second stage three, DMSO ligands are liberated. In the third stage, the last molecule of DMSO is liberated and aluminium chloride is created. In the fourth and last stage, Al_2O_3 and carbon are formed as a result of the reaction of $AlCl_3$ with CO, which was derived from DMSO decomposition.

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