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*Dedicated to Professor Ferenc Paulik on the occasion of his 75th birthday*

# THERMAL PROPERTIES OF THE AQUADIMETHYLSULFOXIDE COMPLEXES $[Ln(DMSO)_n(H_2O)_m][Mo_3S_7Br_7]$ WHERE *Ln*=Pr, Nd, Eu, Tm

*O. Geras'ko*[1], *V. Fedorov*[1], *V. Logvinenko*[2], *K. Hegetsweiler*[3], *M. R. J. Elsegood*[4] *and U-Hyon Paek*[5]

[1]Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences,
Novosibirsk, 630090
[2]Novosibirsk Technology Institute, Novosibirsk, 630099, Russia
[3]Saarland University, D–66123 Saarbrücken, Germany
[4]Department of Chemistry, Bedson Building, University of Newcastle-upon-Tyne
Newcastle-upon-Tyne, NE1 7RU, UK
[5]Department of Chemistry, Gyeongsang National University, Chinju 660–701, Korea

## Abstract

Synthesis, X-ray structural investigation, and study of the thermal properties of new aquadimethylsulfoxide complexes $[Ln(DMSO)_n(H_2O)_m][Mo_3S_7Br_7]$ containing the rare earth metals (*Ln*=Pr, Nd, Eu, Tm) were performed. In all complexes DMSO is co-ordinated through the O atoms. Thermal transformations of these salts were studied by quasi-equilibrium thermogravimetry a variant of CRTA (Controlled Rate Thermal Analysis) with constant rate of mass loss (0.3 mg $min^{-1}$); helium flow keeps the partial pressure of self-generated DMSO/$H_2O$ atmosphere ~0.01 atm.

$[Pr(DMSO)_6H_2O)]X$ where *X*=$[Mo_3S_7Br_7]$ decomposes with the formation of the intermediate phases $Pr(DMSO)_5X$ at 100–190°C and $Pr(DMSO)_3X$ at 250–270°C. Thermal decomposition of $[Nd(DMSO)_6(H_2O)X{\cdot}CH_3CN$ leads to the intermediate phase $Nd(DMSO)_5X$ at 200–210°C. $[Eu(DMSO)_7(H_2O)]X$ forms the intermediate phases $Eu(DMSO)_6X$ at 50–150°C and $Eu(DMSO)_5X$ at 190–210°C. Thermal decomposition of $[Tm(DMSO)_6(H_2O)]X$ gives the intermediate phases $Tm(DMSO)_5X$ at 170–200°C and $Tm(DMSO)_4X$ at 240–250°C. The further decomposition takes place continuously for all phases.

**Keywords:** aquadimethylsulfoxide complexes, cluster compounds, CRTA, quasi-equilibrium, rare earth metals, TG

## Introduction

Complexes of the rare earth metals (Ln) with organic sulfoxides, in particular with dimethylsulfoxide (DMSO), have not been extensively studied [1]. Nevertheless there is increasing recent interest in related compounds caused by a variety of their structural and spectral properties.

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Noteworthy structural features of DMSO complexes are mainly due to the nature of the ligand. It is well known that DMSO is an ambidentate ligand: the S atoms exhibits 'soft' base properties, while O exhibits 'hard' ones. The experimental evidence agrees very well with that argument. For example, the 'soft' platinum group metals prefer coordination through the S atom, whereas the 'hard' Ln metals are usually coordinated through the O atom [2]. However, the coordination tendencies of DMSO are considerably more complex and may be changed depending on the situation: DMSO coordination is possible through O and S atoms simultaneously to the same metal atom.

When direct structural data are not available, information from vibrational spectroscopy is most commonly used for a determination of the donor centre for coordinated sulfoxides. In simple cases, IR stretching frequencies are considered fairly reliable [2]. DMSO coordination through the O atom causes a decrease of the S=O stretching frequency by 60–70 wavenumbers, while coordination through the S atom leads to an increase of the frequency by 60–100 cm$^{-1}$ when compared with uncoordinated DMSO (1055–1060 cm$^{-1}$). For O coordinated DMSO the shift of the C–S stretching from 697 cm$^{-1}$ for uncoordinated DMSO to higher values is observed simultaneously. Undoubtedly, the spectroscopic data may be inadequate to distinguish the coordination made in more complicated cases, particularly when the coordination takes place through O and S atoms simultaneously. In such cases the answer may only be obtained through a direct structural investigation.

Several complexes of Ln with DMSO are mentioned in the literature. Dzyubenko *et al.* report the preparation of adducts of Ln *tris*-acetylacetonates with DMSO with compositions $LnA_3 \cdot 2DMSO \cdot H_2O$ and $LnA_3 \cdot DMSO$ for light (*Ln*=La–Tb) and heavy (*Ln*=Dy–Lu) rare earth metals, respectively. Structures of the adducts were not determined, however, the analysis of their IR spectra showed that the stretching bands identified as (S=O) was observed at about 1040 cm$^{-1}$ and 1020 cm$^{-1}$ for $LnA_3 \cdot 2DMSO \cdot H_2O$ and $LnA_3 \cdot DMSO$, respectively.

The structures of some $Ln(NO_3)(DMSO)_n$ ($n$=3, 4) complexes have been studied crystallographically [4–9]; in all of these related complexes the nitrate groups and DMSO ligands are co-ordinated through O atoms; all of the nitrate ligands are bidentate. For these complexes the coordination polyhedra and coordination numbers of the Ln change depending on the nature of the metal: thus, for $La(NO_3)_3(DMSO)_4$ and $Nd(NO_3)_3(DMSO)_4$ the coordination polyhedron of $Ln^{3+}$ is a dodecahedron with two bifurcated vertices, *CN*=10; for $Er(NO_3)_3(DMSO)_3$ and $Lu(NO_3)_3(DMSO)_3$ tri-capped trigonal prismatic coordination geometry is observed, *CN*=9. There is evidence of the $Ln^{3+}$ coordination number changing with ionic radius and DMSO concentration for the series of solvates $[Ln(NO_3)_3(DMSO)_n]$ formed in anhydrous acetonitrile [10]. With DMSO in excess, the large ions (*Ln*=La–Sm) preferred *CN*=10, for Eu–Tm *CN*=9 was typical, while for the smallest ions (*Ln*=Yb, Lu) an average *CN* was between 9 and 8. At lower DMSO concentration a change of coordination number was observed in the region of the atom centrally located in the series (Eu), the co-ordination numbers being 9 and 8 for the first (large ions) and second (small ions) groups, respectively.

The complexes [Ln(DMSO)$_8$[Cr(SCN)$_6$] were prepared for the whole Ln series and for ytterbium [11, 12]. IR data show that for the [Ln(DMSO)$_8$]$^{3+}$ cations the DMSO coordination occurs exclusively through the O atoms as evidenced by the decrease in S=O stretching frequency to 1000–1010 cm$^{-1}$ and the shift in the S–C stretching frequency to 710–720 cm$^{-1}$ [12].

We have recently synthesized a series of new complexes with composition [Ln(DMSO)$_n$(H$_2$O)$_m$][Mo$_3$S$_7$Br$_7$] where *Ln*=Pr, Nd, Eu, and Tm, and solved their crystal structures [13]. The coordination polyhedra for the [Pr(DMSO)$_6$(H$_2$O)$_2$]$^{3+}$, [Nd(DMSO)$_6$(H$_2$O)$_2$]$^{3+}$, [Eu(DMSO)$_7$(H$_2$O)]$^{3+}$ and

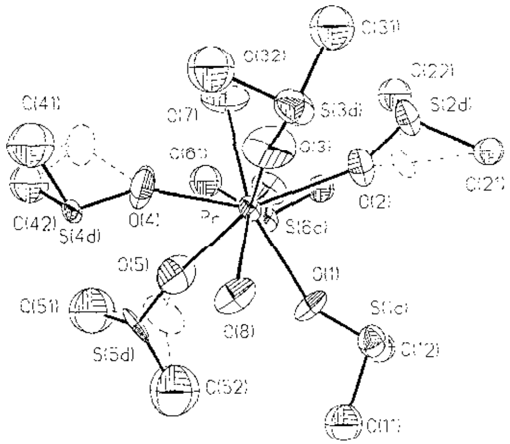

**Fig. 1** The coordination polyhedron for [Pr(DMSO)$_6$(H$_2$O)$_2$]$^{3+}$

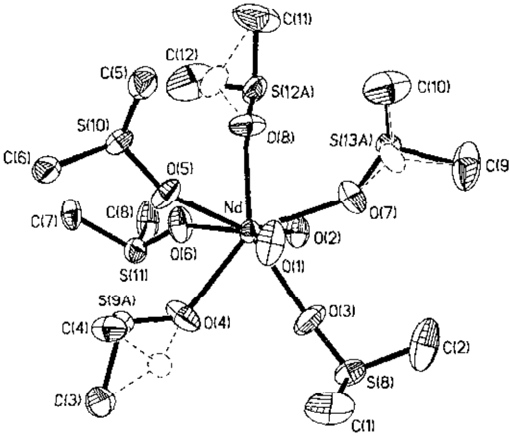

**Fig. 2** The coordination polyhedron for [Nd(DMSO)$_6$(H$_2$O$_2$)]$^{3+}$

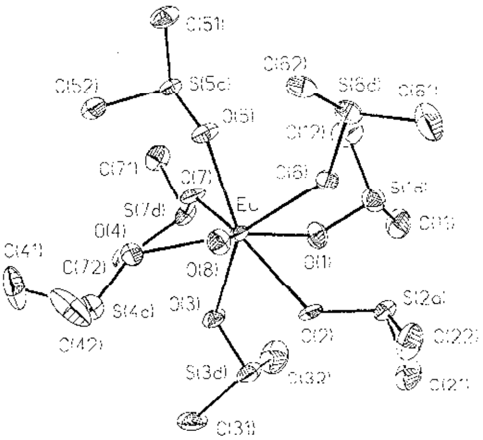

**Fig. 3** The coordination polyhedron for $[Eu(DMSO)_7(H_2O)]^{3+}$

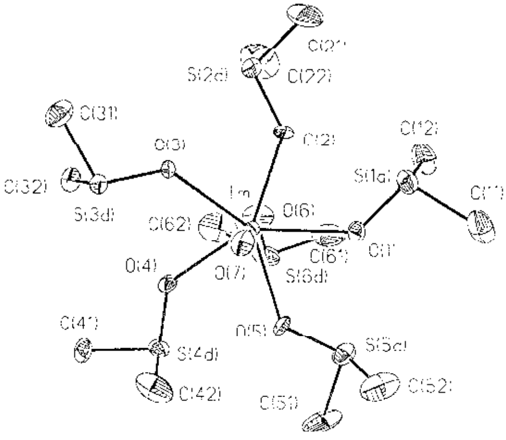

**Fig. 4** The coordination polyhedron for $[Tm(DMSO)_6(H_2O)]^{3+}$

$[Tm(DMSO)_6(H_2O)]^{3+}$ cations are presented in Figs 1–4. The structure of the $[Mo_3S_7Br_7]^{3-}$ anion (Fig. 5) is typical of triangular thiohalogenide clusters of the $[\{Mo_3S_7Y_6\}Z]$ type [14]. The crystal packing in the Tm containing structures is shown in Fig. 6. The most interesting and important feature of these compounds is that the composition and structures of the complex cations are different in each of the four compounds (Figs 1–4). The Ln coordination polyhedron in $[Pr(DMSO)_6(H_2O)_2]^{3+}$, $[Nd(DMSO)_6(H_2O)_2]^{3+}$ and $[Eu(DMSO)_7(H_2O)]^{3+}$, is the distorted square antiprism (*CN*=8) but in $[Tm(DMSO)_6(H_2O)]^{3+}$ it is pentagonal bipyramidal (*CN*=7). For all of the complexes the DMSO ligands are coordinated through O atoms.

IR study of the complexes correlates with the structural data. The shift of the S=O stretching band from 1060 $cm^{-1}$ for uncoordinated DMSO to 1000 $cm^{-1}$ for the complexes fits the traditional concept about the bonding of DMSO with a metal atom through the O atom.

This research is dedicated to the study of the thermal properties of these complexes.

## Experimental

### *Synthesis of the complexes* $[Ln(DMSO)_n(H_2O)_m][Mo_3S_7Br_7]$

The syntheses of the complexes $[Ln(DMSO)_n(H_2O)_m][Mo_3S_7Br_7]$ were carried out in the organic solvent $CH_3CN$ from $(Et_4N)_2Mo_3S_7Br_6$ and $LnBr_3{\cdot}nH_2O$. $(Et_4N)_2Mo_3S_7Br_6$ was prepared using the method described by Fedin *et al.* [15]. $LnBr_3{\cdot}nH_2O$ were prepared by reaction of the rare-earth oxides with hydrobromic acid; the reagents were warmed to 70°C; upon completion of the reaction the solids were filtered off and washed with diethylether and dried in vacuo. The DMSO and $CH_3CN$ were reagent grade and were used without further purification.

The solid starting materials $(Et_4N)_2Mo_3S_7Br_6$ and $LnBr_3{\cdot}nH_2O$ were dissolved in boiling acetonitrile, then dimethylsulfoxide was added drop-wise to the reaction solution until the stoichiometric ratio Ln:DMSO=1:8 was achieved. Addition of DMSO resulted in a colour change from yellow to orange to brown.

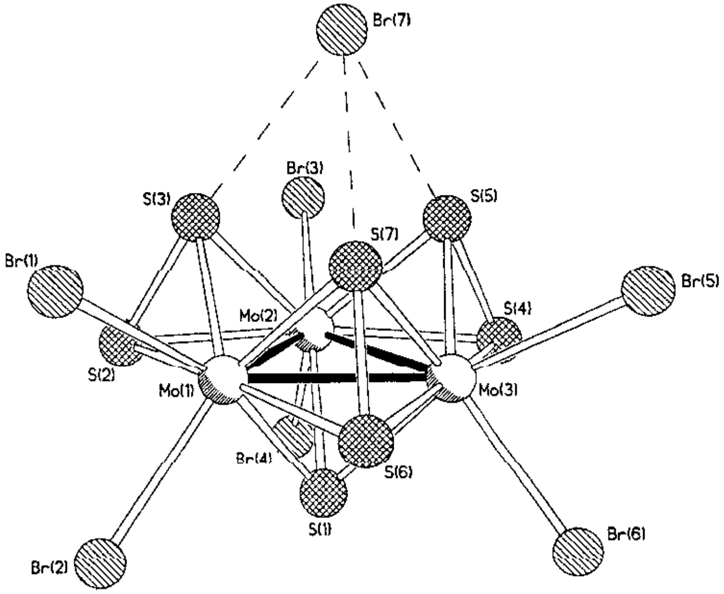

**Fig. 5** The crystal structure of $[Mo_3S_7Br_7]^{3-}$ anion

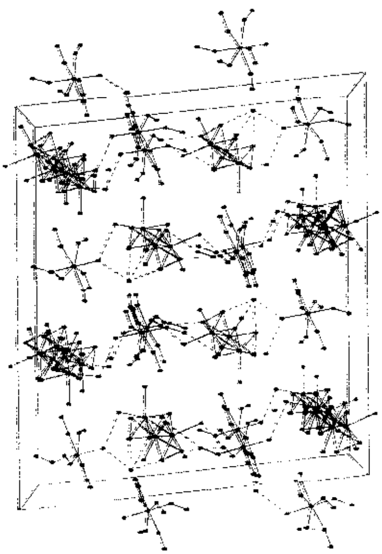

**Fig. 6** The crystal packing in [Tm(DMSO)$_6$(H$_2$O)][Mo$_3$S$_7$Br$_7$]

After cooling the mixtures to room temperature, the solids were filtered off and washed successively with cold acetonitrile and diethylether, and dried in vacuo. Isolated yields of [Ln(DMSO)$_n$(H$_2$O)$_m$][Mo$_3$S$_7$Br$_7$] can be as high as 90%, and we believe that the reaction is essentially quantitative.

For the thermal transformation study of these complexes a variant of Controlled Rate Thermal Analysis (CRTA) [16] was used, so called quasi-equilibrium thermogravimetry. Experimental conditions: quasi-isothermal heating with constant rate of mass loss (0.3 mg min$^{-1}$); TG sensitivity 50 mg or 100 mg, sample mass 150–300 mg; we believe that the slow helium flow (0.08 l min$^{-1}$) keeps the partial pressure of the self-generated DMSO/H$_2$O atmosphere in the standard open crucible near 0.01 atm. The advantages of the method are that the steps of thermal dissociation have high resolution and the intermediate phases formed are thermodynamic equilibrium ones. The latter is important for the expected processes of DMSO and H$_2$O removal which are in competition.

## Results and discussion

The thermogravimetric curves for all complexes (Figs 7–10) indicate several separate mass loss steps. The first step involves a gradual mass loss which begins at about 80°C. This mass change corresponds to the loss of the water only (Tm complex), the water and one molecule of DMSO (Pr and Eu complexes), or the water and uncoordinated CH$_3$CN (Nd complex). The further mass loss steps occur at higher temperatures and correspond to the step-wise loss of further DMSO molecules. The last step is connected with decomposition of the complexes;

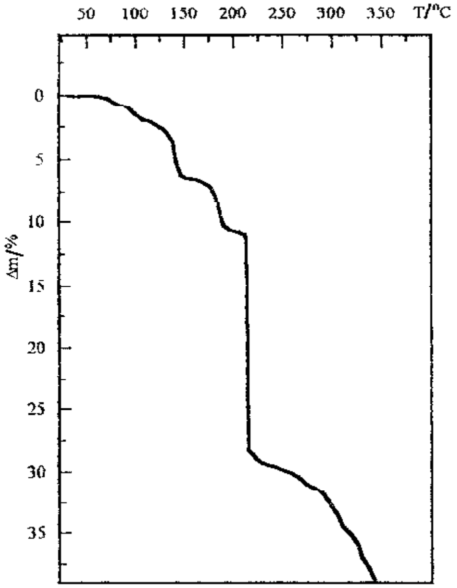

**Fig. 7** Thermal dissociation of $[Pr(DMSO)_6(H_2O)_2][Mo_3S_7Br_7]$ under quasi-equilibrium conditions. Sample holder: open crucible, quasi-isothermal heating, $q$=0.3 mg $min^{-1}$, atmosphere: helium (0.08 l $min^{-1}$), sample mass: 228.3 mg

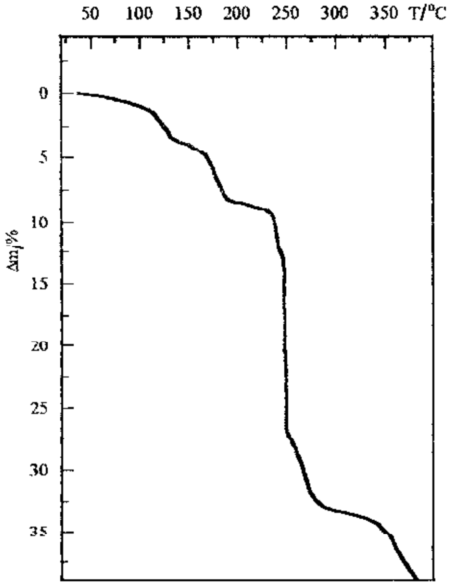

**Fig. 8** Thermal dissociation of $[Nd(DMSO)_6(H_2O)_2][Mo_3S_7Br_7]$ under quasi-equilibrium conditions. Sample holder: open crucible, quasi-isothermal heating, $q$=0.3 mg $min^{-1}$, atmosphere: helium (0.08 l $min^{-1}$), sample mass: 241.0 mg

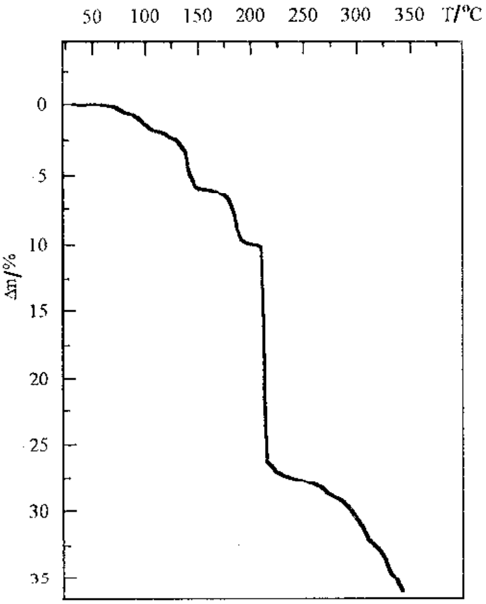

**Fig. 9** Thermal dissociation of [Eu(DMSO)$_7$(H$_2$O)][Mo$_3$S$_7$Br$_7$] under quasi-equilibrium conditions. Sample holder: open crucible, quasi-isothermal heating, $q$=0.3 mg min$^{-1}$, atmosphere: helium (0.08 l min$^{-1}$), sample mass: 227.1 mg

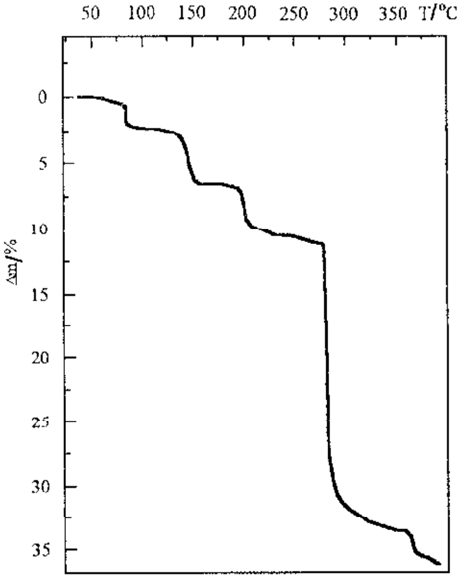

**Fig. 10** Thermal dissociation of [Tm(DMSO)$_6$(H$_2$O)][Mo$_3$S$_7$Br$_7$] under quasi equilibrium conditions. Sample holder: open crucible, quasi-isothermal heating, $q$=0.3 mg min$^{-1}$, atmosphere: helium (0.08 l min$^{-1}$), sample mass: 167.1 mg

among the reaction products $MoS_2$ was observed in all cases above a temperature of 400°C.

The complex $[Pr(DMSO)_6(H_2O)_2]X$ where $X=[Mo_3S_7Br_7]$ decomposes at 80°C to form the stable intermediate phase $Pr(DMSO)_5X$, which in turn gives $Pr(DMSO)_3X$ at 200–250°C. The complex $[Nd(DMSO)_6(H_2O)_2]X{\cdot}CH_3CN$ forms the intermediate phase $Nd(DMSO)_6X$ at 150°C and loses one DMSO molecule at 170–190°C to form Nd(DMSO)5X. The complex $[Eu(DMSO)_7(H_2O)]X$ forms the intermediate phases $Eu(DMSO)_6X$ at 150°C and $Eu(DMSO)_5X$ at 190°C. Thermal decomposition of $[Tm(DMSO)_6(H_2O)]X$ gives intermediate phases $Tm(DMSO)_6X$ at 80°C, $Tm(DMSO)_5X$ at 140–160°C and $Tm(DMSO)_4X$ at 210–240°C. The further decomposition takes place continuously for all phases.

To discuss the common thermal properties of these aquadimethylsulfoxide complexes we would note the following. While the starting complexes have different compositions and structures, the intermediate thermodynamically stable anhydrous phases with six DMSO ligands $\{Ln(DMSO)_6X\}$ exist only for the Eu and Nd complexes; $Ln(DMSO)_4X$ exists only for the Tm complex and $Ln(DMSO)_3X$ exists for only the Pr complex. Only one phase, namely $Ln(DMSO)_5X$, esists for all four complexes (Pr, Nd, Eu, Tm) after their partial decomposition in the vicinity of 200°C. The sequence of thermodynamic stability of $Ln(DMSO)_5X$ phases in the process of thermal decomposition is $Pr{\approx}Nd{\approx}Eu{>}Tm$. So the stabilities of these DMSO complexes for light lanthanides is relatively similar, but decreases for heavier ones.

Aquadimethylsulfoxide complexes of other rare earth metal (*Ln*=Ce, Sm, Gd, Tb, Dy, Ho, Er, Yb, Lu) were synthesized by the same method and processes of thermal decomposition were studied. The common features are: step-wise mass loss (with different stoichiometry), but marked by the existence of the stable $Ln(DMSO)_5X$ phase.

## Conclusions

The expected differences in chemical characteristics of compounds of the light and heavy series of rare earth metals are clearly observed in the different compositions and structures of the complexes studied (different numbers of DMSO and $H_2O$ ligands, the existence of non-coordinated $CH_3CN$, etc.) and different steps in the thermal dissociation pathway. The expected resemblance for all *Ln* atoms is equally important: it is clear that for all rare earth metals it is possible to obtain the same phase $Ln(DMSO)_5X$ during the thermal dissociation under heating. It is of fundamental importance that the steps (the stoichiometry) of the thermal dissociation process do not depend directly on the structure of the decomposing substance. We can not obtain anhydrous $[Pr(DMSO)_6][Mo_3S_7Br_7]$ by simple dehydration of the highest complex $[Pr(DMSO)_6(H_2O)_2][Mo_3S_7Br_7]$, although water molecules are rather weakly bonded: perhaps for the Pr compound such an anhydrous structure is sterically unstable.

We have shown previously that for endothermic processes of thermal dissociation under heating ($\Delta H > 0$) the new intermediate stable phase can be formed spontaneously (that is with $\Delta G < 0$) only if for this process $\Delta S > 0$ and $T\Delta S > \Delta H$ [17]. This is the case when $[Ln(DMSO)_5][Mo_3S_7Br_7]$ is formed regardless for all starting complexes.

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