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THE COUPLED TG-MS INVESTIGATIONS OF LANTHANIDE(III) NITRATE COMPLEXES WITH HEXAMETHYLENETETRAMINE

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Abstract

New transition metal compounds of the general formula $Ln(NO_3)_3{\cdot}2[N_4(CH_2)_6]{\cdot}nH_2O$, where Ln = La, Nd, Sm, Gd, Tb, Dy, Er, Lu, and n = 7–12, were obtained. The compounds and the gases evolved in the course of their thermal decomposition were characterised by thermogravimetric analysis. The measurements were carried out in air and argon environment in order to compare the intermediate products, final products and the mechanism of the thermal decomposition. The combined TG-MS system was used to identify the main volatile products of thermal decomposition and fragmentation processes of the obtained compounds.

Keywords: hexamethylenetetramine, lanthanide complexes, mass spectroscopy, thermogravimetry

Introduction

The lanthanides (*Ln*) chemistry is a field of the science, which has developed rapidly in the recent years because of their huge and versatile applications [1–5]. Their important feature is a relatively steady variations of properties across the group, which results from the 'lanthanide contraction' (the lanthanides have large ionic radii, which decrease continually with the increasing of the element atomic number). This affects the coordination numbers (CN) and the coordination geometry of their complexes. The CN of a Ln^{n+} ion is very rarely six, and higher coordination numbers (7–12) appear to dominate. The most common ligands existing in lanthanide compounds are these ones containing oxygen atom.

The present work is a continuation of our study on properties of lanthanide compounds with hexamethylenetetramine (HMTA) [6–14]. The aim was to obtain lanthanide nitrates complexes with HMTA in the solid state. The TG-MS analysis was performed on complexes in order to obtain information about their thermal stability and propose the scheme for their thermal decomposition in the air and argon atmosphere.

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Experimental

Materials, synthesis and analysis of the complexes

The following reagents were used for the syntheses: analytically pure hexamethylenetetramine (Fluka AG), 99% pure lanthanide oxides and cerium carbonate (Aldrich and Fluka AG), concentrated HNO_3 (Chempur).

The lanthanide complexes of higher hydration state were prepared by crystallisation from water solutions. The samples of lanthanide oxides were dissolved in possible smallest amount of nitric acid (1:1) (the salt of cerium nitrate was prepared by dissolving the cerium carbonate in HNO_3). The obtained solutions were cooled and then mixed with cooled saturated aqueous solutions of hexamethylenetetramine (molar ratio 1:2). The mixtures were placed in a refrigerator and left to crystallise at 5°C. The crystals were filtered and dried in air. The content of lanthanides was determined by complexometric titration using EDTA *vs*. xylenol orange [15].

Physical measurement

The thermal analysis was carried out in a TG/DTA-SETSYS-16/18 thermoanalyser coupled with ThermoStar (Balzers) mass spectrometer. The samples (9.5–14.8 mg) were heated in corundum crucibles up to 1000°C at the heating rate $10°\text{C min}^{-1}$ in air and argon atmosphere. The products of decomposition were calculated from TG curves. The temperature ranges were determined by means of thermoanalyser Data Processing Module [16]. The thermogravimetric analysis in argon atmosphere of the neodymium salt was not carried out because of the rapidly proceeding decomposition process in air atmosphere, which caused the contamination of the apparatus.

Results and discussion

Thermal decomposition in air atmosphere

The thermoanalytical curves TG, DTA, DTG of lanthanum decahydrate salt decomposition are presented in Fig. 1a. The decomposition is multi-stage process. The first endothermic step of thermal decomposition occurs within the temperature range 61–180°C. The initial mass loss is attributed to the removal of water molecules. The DTA curve indicates that it is multi-stage dehydration process, but the overlapping peaks make it impossible to distinguish individual steps. The mass spectrum of the thermal decomposition of lanthanide nitrates complexes with HMTA shows the ion current signals m/z=17, 18, which correspond to the molecular mass of OH^+ and H_2O^+. The succeeding stages are exothermic. The next step of decomposition is characterised by strong, narrow peaks on the DTA, DTG curves and the biggest mass loss. According to the detected gaseous products, in the range 180–400°C the decomposition of the nitrates, hexamethylenetetramine molecules and removal of water molecules begins simultaneously. Such high temperature of the dehydration can indicate that some oxygen atom of the water molecules (m/z=16, 17, 18 corresponds to

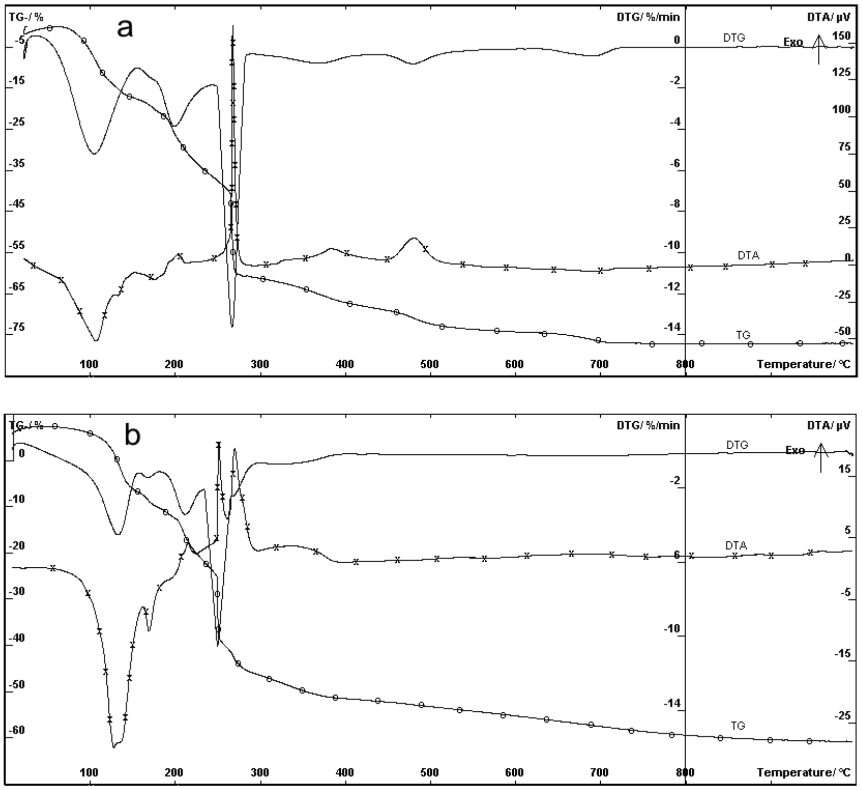

Fig. 1 TG, DTG and DTA curves of a – $La(NO_3)_3 \cdot 2[N_4(CH_2)_6] \cdot 9H_2O$ (in air) and b – $Er(NO_3)_3 \cdot 2[N_4(CH_2)_6] \cdot 10H_2O$ (in argon)

O^+, OH^+ and H_2O^+) must be coordinated directly to the lanthanum ion. The exothermic effect connected with combustion of organic ligand is so strong that it can mask the endothermic effect attached with the decomposition of the nitrates and dehydration process. The main volatile products include ammonium (m/z=17) and formaldehyde (m/z=30), probably as a result of HMTA decomposition. The hydrated hexamethylenetetramine decomposes into ammonia and formaldehyde by heating over 60°C [17]. According to the Guo *et al.* [18] one of the HMTA decomposition product may be the hydrazine but the MS peaks with m/z=32, which corresponds to the $N_2H_4^+$, does not appear for investigated compounds. The signal with m/z=44 can be attributed to CO_2^+, which comes from the HMTA decomposition. This is supported by the fact that the parallel peak for CO^+ (m/z=28) is observed in the mass spectrum for the thermal decomposition in argon. The nitrates decompose gradually with releasing nitrogen oxide (m/z=30), dinitrogen oxide (m/z=44) and probably oxygen (m/z=16). These oxides were reported as products of transition metal hydrated nitrates thermal decomposition in previous works [19–21]. The MS spectra do not display the presence of other typical nitrate decomposition products such as NO_2 or HNO_3. Even if NO_2 is formed, the existence of NO instead of NO_2 is observed probably due to the fragmentation process of NO_2 to NO or following reaction $NO_2 + O \rightarrow NO + O_2$ takes place. According to Małecki *et al.* [20] the amount of nitrogen releasing during heating in the form of the nitric acid does not exceed 5% of the total nitrogen. The thermal decomposition intermediate products may include $La(NO_3)_2(OH)$ and $LaO(NO_3)$ respectively in the two next steps. The presence of such hydroxo- and oxonitrates is observed in previous works [22, 23] concerning the thermal decomposition of transition metal hydrated nitrates. Creating of *Ln*OX (X = CO_3, Cl) compounds was detected during thermal decomposition of lanthanide complexes [24–28]. During heating over 400°C the solid decomposes with forming the La_2O_3 (final product) at 725°C. The two gaseous product were liberated over 400°C, the NO (m/z=30) and the N_2O (m/z=44) as a result of thermal decomposition of hydro- and oxo-species. The previous investigations of the bromide salts of lanthanides(III) with HMTA [7], especially the results of X-ray powder studies, confirm the final forming of lanthanide oxide.

The mechanisms of the thermal decomposition in air environment of all lanthanide nitrates complexes with HMTA differ from each other in the temperature ranges, the number of stages and the values of mass loss. However they have a few features in common: in the first stage the dehydration occurs, in the temperature range 240–270°C the rapid decomposition of hexamethylenetetramine molecule (deamination process) takes place, the intermediate products are $Ln(NO_3)_2(OH)$, $LnO(NO_3)$ and the final product in all cases is lanthanide oxide. The thermal decomposition data are collected in Table 1. The temperatures of the oxides formation are high and change in the lanthanide series from 550°C (Tb_4O_7) to 725°C (La_2O_3). These temperatures are similar to these found during thermal analysis of lanthanide complexes [24, 29].

Thermal decomposition in argon atmosphere

The thermal decompositions of lanthanide nitrates complexes with HMTA were carried out in argon atmosphere in order to eliminate the reaction of principle volatile products with air constituents. The TG, DTA, DTG curves of erbium decahydrate salt decomposition in argon environment are presented in Fig. 1b. The complex is stable up to 65°C. The decomposition is multi-stage. In the range 66–190°C the water molecules are released from the outer and inner coordination sphere. In the DTA curve such dehydration process appears as an endothermic peaks. The MS spectrum displays the presence of OH^+ (m/z=17) and H_2O^+ (m/z=18) in this step of decomposition process. All succeeding steps are exothermic. According to the detected gaseous products, in the range 190–420°C the decomposition of the nitrates, hexamethylenetetramine molecules and removal of water molecules begins simultaneously. The HMTA decomposes to NH_3^+ (m/z=17), $HCOH^+$ (m/z=30). The signal with m/z=28 can be attributed to N_2^+ CO^+ or CH_2N^+, which come also from the HMTA decomposition. There are the ion current signals m/z=17, 18, which corre-

Table 1 The thermal decomposition in air atmosphere [$L = N_4(CH_2)_6$, $A = NO_3$]

Complex	ΔT_1/°C	Mass loss/%	nH$_2$O	ΔT_2/°C	Mass loss/%	ΔT_3/°C	Mass loss/%	DTA endo/°C	DTA exo/°C
$LaA_3{\cdot}2L{\cdot}10H_2O$	61–180	21.06	9	181–513	72.17	514–725	77.07	107, 176	267, 382, 480
$NdA_3{\cdot}2L{\cdot}9H_2O$	59–182	21.61	7	183–445	72.13	446–700	76.65	88, 124, 179	258, 390
$SmA_3{\cdot}2L{\cdot}9H_2O$	48–182	19.40	8.5	183–457	70.98	458–660	76.85	88, 113, 176	252, 471
$GdA_3{\cdot}2L{\cdot}10H_2O$	55–181	20.46	9	182–455	72.43	456–650	77.74	98, 137, 170	249, 425, 474
$TbA_3{\cdot}2L{\cdot}9H_2O$	50–181	19.00	8.5	182–431	71.40	431–550	75.50	94, 142	246, 385, 446
$DyA_3{\cdot}2L{\cdot}7H_2O$	47–174	17.90	5	175–438	72.50	439–600	76.00	90, 143	236, 406
$ErA_3{\cdot}2L{\cdot}10H_2O$	53–126	18.32	8	184–467	72.43	467–580	75.81	84, 121, 142	238, 432, 486
$LuA_3{\cdot}2L{\cdot}12H_2O$	50–184	20.90	10	185–454	70.99	454–640	75.80	85, 149, 179	232, 238, 417

ΔT_1–temperature range in which the dehydration process takes place, ΔT_2–temperature range of decomposition to intermediate products, ΔT_3–temperature range of decomposition to oxides

Table 2 The thermal decomposition in argon atmosphere [$L = N_4(CH_2)_6$, $A = NO_3$]

Complex	ΔT_1/°C	Mass loss/%	nH$_2$O	ΔT_2/°C	Mass loss/%	DTA endo/°C	DTA exo/°C
LaA_3•2L•10H_2O	64–186	21.75	9.5	187–987	80.14	108, 175	266, 366, 598, 874
SmA_3•2L•9H_2O	55–181	10.07	4.5	182–1000	68.80	99, 176	255, 356
GdA_3•2L•10H_2O	50–185	21.12	9.5	186–954	80.70	133	270, 356, 518
TbA_3•2L•9H_2O	50–184	19.80	8.5	185–862	78.80	98, 142, 181	241
DyA_3•2L•7H_2O	55–161	13.91	6	162–901	68.95	96, 146	250, 350
ErA_3•2L•10H_2O	66–190	18.29	8	191–1000	68.06	126, 170	250, 269, 341
LuA_3•2L•12H_2O	40–188	23.60	11.5	189–852	75.20	90, 150, 183	225, 236, 357

ΔT_1–temperature range in which the dehydration process takes place, ΔT_2–temperature range of decomposition to final products (La_2O_3, $Sm(OH)_2NO_3$, Gd_2O_3, Tb_2O_3, $DyO(NO_3)$, $Er(OH)_2NO_3$, Lu_2O_3)

spond to the molecular mass of OH^+ and H_2O^+. The nitrates decompose to NO^+ (m/z=30), N_2O^+ (m/z=44) and probably O^+ (m/z=16). During heating over 420°C the compound decomposes gradually. In the MS spectrum only one strong signal for m/z=28 is observed. It may correspond to N_2^+ CO^+ or CH_2N^+. Over this temperature there are also two small signals for m/z=16, 44, which correspond to O^+ and N_2O^+. It suggests that the decomposition of nitrate ions and hexamethylenetetramine molecules still takes place. The product which forms at 1000°C is $Er(NO_3)_2(OH)$.

The thermoanalytical curves show a different pattern of decomposition in argon atmosphere (Table 2), distinct from the decomposition pattern in the air and different for each lanthanide compound. For example, in case of lutetium compound decomposition, the dehydration process starts at 40°C and the Lu_2O_3 forms at 860°C. However, in the range 40–190°C the MS spectrum displays the presence of OH^+ (m/z=17) and H_2O^+ (m/z=18) among the volatile products next to the broad peak for m/z=28, which may corresponds to N_2^+ CO^+ or CH_2N^+. It may suggest that the HMTA molecule starts to decompose at the lower temperature, probably because organic compound was weaker bounded in the crystal lattice. The complexes of lanthanum, gadolinium, terbium and lutetium de-

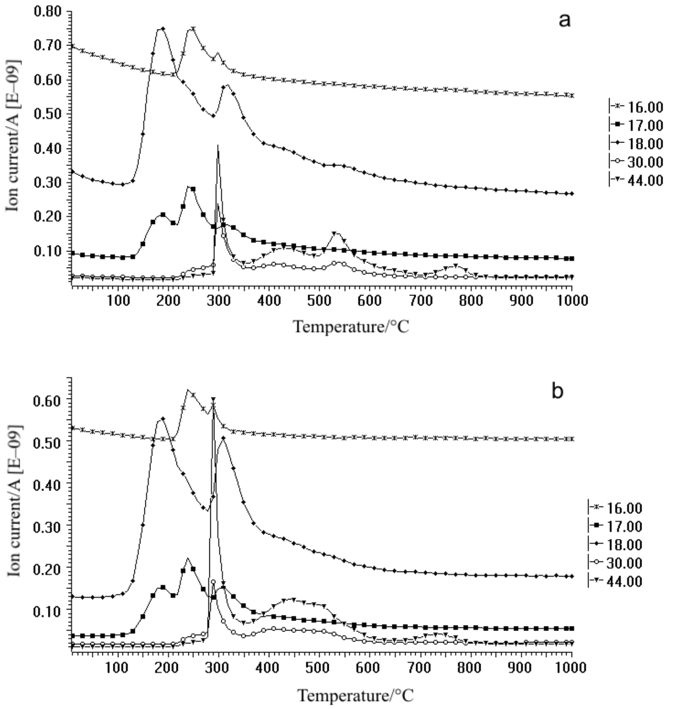

Fig. 2 Gaseous products of a – $La(NO_3)_3 \cdot 2[N_4(CH_2)_6] \cdot 10H_2O$ and b – $Nd(NO_3)_3 \cdot 2[N_4(CH_2)_6] \cdot 9H_2O$ the thermal decomposition in air (heating rate 10°C/cyc)

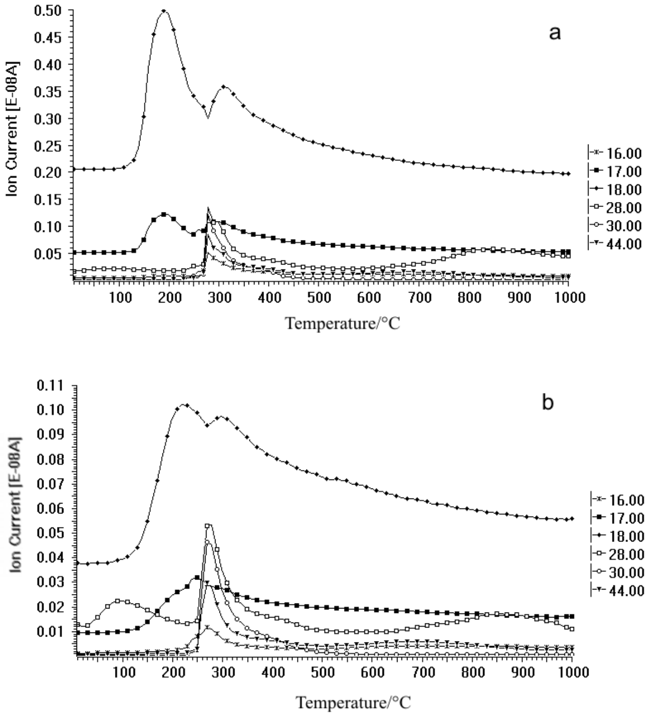

Fig. 3 Gaseous products of a – $Er(NO_3)_3 \cdot 2[N_4(CH_2)_6] \cdot 10H_2O$ and b – $Lu(NO_3)_3 \cdot 2[N_4(CH_2)_6] \cdot 12H_2O$ the thermal decomposition in argon (heating rate 10°C/cyc)

compose to the lanthanide oxides while the samarium, dysprosium and erbium compound form the hydroxo- and oxonitrates at 1000°C.

Conclusions

New lanthanide compounds of the general formula $Ln(NO_3)_3 \cdot 2[N_4(CH_2)_6] \cdot nH_2O$, where Ln = La, Nd, Sm, Gd, Tb, Dy, Er, Lu, and n = 7–12, were obtained and characterised by thermogravimetric analysis in conjunction with evolved gases. The measurements were carried out in air and argon environment in order to determine the intermediate and final products, to establish the terms of the dehydration reaction and to compare the main volatile products of the thermal decomposition.

The mechanisms of the thermal decomposition in air environment of all lanthanide nitrates complexes with HMTA are similar to each other while the schemes for their thermal decomposition in argon atmosphere are different. In all cases of decomposition carried out in air, the dehydration process takes place in the initial stages and the compounds decompose probably via $Ln(OH)_2NO_3$ and $LnO(NO_3)$ to the lanthanide oxides. In the case of decomposition carried out in argon the only common feature is the initial removal of water molecules. The decomposition of the nitrates and HMTA molecules is multi-stage combined process and generally it succeeds at higher temperatures, which makes it impossible to distinguish precisely the stages and the intermediate products from the TG curves. The complexes of lanthanum, gadolinium, terbium and lutetium decompose to the lanthanide oxides while the samarium, dysprosium and erbium compound form the hydroxo- and oxonitrates at 1000°C.

It is worth stressing that the maxima of strong, narrow, exothermic peaks on the DTA curves corresponding to the biggest mass loss are shifted to the side of higher temperatures in case of decomposition carried out in argon. For instance, the DTA peak (air) occurs at 249°C for the gadolinium salt and at 236°C for the dysprosium salt. When the decomposition occurs in argon atmosphere the gaseous products can not react with oxygen and the DTA peak occurs at 270°C and 250°C respectively. It indicates that the simultaneous decomposition of nitrate ions and organic molecules takes place earlier in air environment. Taking into account the fact of existence of the signals for m/z=44, which correspond to N_2^+, CO^+ or CH_2N^+ in the MS spectra in argon at higher temperatures, it can be assumed that the decomposition hexamethylenetetramine molecules takes place over 500°C.

According to the X-ray investigations [30], there is the change in the composition of the lanthanide coordination sphere, adopted polyhedron and coordination number with changing the size of *Ln* ions. The inner coordination spheres of the lanthanum and neodymium [9] salts consist of two nitrate ions and six water molecules. The complexes of samarium and gadolinium include one nitrate ion and seven water molecules in the inner coordination sphere. In the inner coordination sphere of the dysprosium, erbium and lutetium complexes, there are only water molecules, probably due to the steric effects. The decrease of the ionic radius leads to the narrowing of the coordination sphere and enhances the interaction of the Ln^{3+}–OH_2 bonds. The mechanisms of the thermal decomposition in air environment of all lanthanide nitrates complexes with HMTA are the same besides their different conformation. This can be explained by the fact that the HMTA molecules and the nitrate ions may migrate from the outer coordination sphere to the inner coordination sphere of the complex and bond directly to the *Ln* ion after the dehydration process, due to absence of the steric hindrance caused by the water molecules. This is consistent with the presence of the absorption peaks from the vibration of the *Ln*-N (HMTA) and O-*Ln*-O (NO_3^-) bonds in the infrared spectra of the complex of lower hydration state (n = 0.5–3.5) [14].

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