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THERMAL DECOMPOSITION OF RARE EARTH COMPLEXES WITH 2-AMINO-3,5-DICHLOROBENZOIC ACID

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ABSTRACT

The conditions of the thermal decomposition of the 2-amino-3,5-dichlorobenzoates of Y and lanthanides have been studied. During heating in air, the dihydrated complexes $Ln(C_6H_2Cl_2NH_2COO)_3 \cdot 2H_2O$ decompose in three steps, with the exception of the yttrium(III) and cerium(III) complexes, which decompose in two steps. In the first step the complexes lose two molecules of water and next decompose to the oxides with intermediate formation of LnOCl. The complexes of Y(III) and Ce(III), when heated, are dehydrated and then decompose to the oxides. The mode of metal-ligand coordination is discussed.

INTRODUCTION

Our investigations of lanthanide complexes with aminobenzoic acids concern the formation and thermal stability of the coordination sphere of lanthanide ions.

The coordination sphere of the metal is formed by the organic anions, bonded by oxygen atoms of the carboxylate group and water molecules. The water molecules complete the coordination number to 9 for the light, and to 8 for the heavier lanthanides. With a high degree of complex hydration, some water molecules are in the outer coordination sphere of the complexes for lack of free coordination sites around the central atom. The position of water molecules in the benzoate complexes of lanthanides does not always influence the shape of the dehydration curve.

The aim of this work was to examine the thermal stability series of new compounds as continuation of our study on the thermal stability and properties of chloro-[1-4], amino-[5-7] and aminochlorobenzoates of lanthanides[8, 9].

RESULTS AND DISCUSSION

The 2-amino-3,5-dichlorobenzoates of Y(III) and lanthanides(III) were prepared by the reaction of equivalent amounts of 0.1 M ammonium 2-amino-3,5-dichlorobenzoate (pH 7.2-7.6) and rare earth element chloride solutions (Ce(III) was used as nitrate). The reaction mixture was heated at 70°C and the solids formed were filtered off, washed with hot water to remove the NH_4^+ and Cl^- ions and dried at 30°C to a constant weight.

The complexes of Y, La and the lanthanides with 2-amino-3,5-dichlorobenzoic acid of the formula $Ln(C_6H_2NH_2Cl_2COO)_3 \cdot 2H_2O$ where Ln = Y, La-Lu (Table I) were obtained as light grey powders. The small size of particles probably caused the color of the compounds. The powder patterns of the complexes obtained at various conditions of temperature indicate that the whole series of complexes is amorphous. It is worth noting that the previously

TABLE I
Analytical Data

Empirical formula[a]	Formula weight	% M		% H		% C		% Cl		% N		Yield %	Dec. point/°C
		Calcd.	Found	Calcd	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found		
$C_{21}H_{16}Cl_6N_3O_8Y$	739.99	12.02	11.81	2.16	2.25	34.05	34.12	28.67	28.65	5.67	5.70	76.8	270
$C_{21}H_{16}Cl_6LaN_3O_8$	790.00	17.58	17.21	2.02	1.95	31.89	32.02	26.96	26.89	5.30	5.42	77.5	267
$C_{21}H_{16}Cl_6CeN_3O_8$	791.21	17.71	17.91	2.02	2.10	31.85	31.86	26.92	26.82	5.31	5.44	78.1	205
$C_{21}H_{16}Cl_6N_3O_8Pr$	792.00	17.81	17.73	2.02	2.11	31.82	31.88	26.89	26.77	5.30	5.35	78.0	276
$C_{21}H_{16}Cl_6N_3O_8Nd$	795.33	18.13	18.89	2.01	2.08	31.69	31.62	26.78	26.67	5.28	5.37	77.5	240
$C_{21}H_{16}Cl_6N_3O_8Sm$	801.44	18.76	18.97	1.99	2.03	31.44	31.60	26.57	26.72	5.24	5.15	77.8	261
$C_{21}H_{16}Cl_6EuN_3O_8$	803.05	18.93	18.14	1.99	2.05	31.38	31.28	26.52	26.47	5.23	5.30	78.2	287
$C_{21}H_{16}Cl_6GdN_3O_8$	808.34	19.45	19.08	1.97	1.96	31.17	31.33	26.35	26.23	5.19	5.24	78.0	348
$C_{21}H_{16}Cl_6N_3O_8Tb$	810.02	19.62	19.55	1.97	1.98	31.11	31.26	26.29	26.35	5.18	5.26	78.0	347
$C_{21}H_{16}Cl_6DyN_3O_8$	813.59	19.97	19.78	1.96	2.04	30.97	31.00	26.18	26.25	5.16	5.15	77.5	349
$C_{21}H_{16}Cl_6HoN_3O_8$	816.02	20.21	20.07	1.96	2.00	30.88	30.92	26.10	25.99	5.15	5.21	77.8	346
$C_{21}H_{16}Cl_6ErN_3O_8$	819.02	20.44	20.12	1.95	2.03	30.79	29.96	26.03	26.02	5.13	5.25	77.1	347
$C_{21}H_{16}Cl_6N_3O_8Tm$	820.02	20.59	20.13	1.95	2.07	30.73	30.43	25.97	25.76	5.12	5.22	77.5	309
$C_{21}H_{16}Cl_6N_3O_8Yb$	824.13	20.99	21.07	1.94	2.00	30.57	30.96	25.84	25.50	5.09	5.03	77.5	377
$C_{21}H_{16}Cl_6LuN_3O_8$	826.06	21.18	21.11	1.93	1.89	30.51	30.76	25.78	26.07	5.08	5.13	76.0	332

[a] The formulas of the complexes are $Ln(C_6H_2NH_2Cl_2COO)_3 \cdot 2H_2O$, where Ln is either Y or lanthanides.

investigated series of chlorobenzoates[1-4], aminobenzoates[5-7] as well as complexes of lanthanides with 3-amino-4-chlorobenzoic acid[8] and 2-amino-4-chlorobenzoic acid[9] are crystalline. The series of 2-amino-3,5-dichlorobenzoates is unique inasmuch as it represents the first series of amorphous lanthanide benzoates. Their solubility in water at 20°C is in the range of 1.96 to $6.79 \cdot 10^{-5}$ mol/dm^3 (Table II), which is much smaller than those of the chloro-[1-3] and aminobenzoates [6,7].

The analytical (Table I) data show that the metal ions, as a central atom of the complexes, are coordinated by three organic ligands and two molecules of water. The 2-amino-3,5-dichlorobenzoate anions may coordinate with the lanthanide ions first of all through the oxygen atoms of the carboxylate group. The coordination by the nitrogen atom of the amino group is rather unlikely because of strong preference of the lanthanides for oxygen atoms. Up to now, coordination of aminobenzoate anions to lanthanide ions by a nitrogen atom of amino group was observed in the polymeric structure of neodymium(III) complex with 4-aminobenzoic acid[10].

IR Studies

In the IR spectra of the complexes, the main effect of coordination of the carboxylate group of the ligand with a metal ion is observed at the C-O frequencies[11] $\nu 3,5,8,11,15$, but the most useful are the $\nu 3$ frequency corresponding to the C-O symmetric stretching and the $\nu 8$ frequency corresponding to the antisymmetric stretching vibrations. After metal coordination, a change of the O-C-O angle of the carboxylate group takes place; increasing this angle decreases the $\nu 3$ and increases the $\nu 8$ frequencies and hence the increase of $\Delta\nu = \nu 8 - \nu 3$. The value of $\Delta\nu$ may be used with extreme caution to predict the mode of carboxylate group coordination[12].

TABLE II

Solubility of Y and Lanthanide 2-Amino-3,5-Dichlorobenzoates in Water at 20°C

Compound	Solubility [mol/dm^3]	Compound	Solubility [mol/dm^3]
$YL_3 \cdot 2H_2O$[a]	$2.29 \cdot 10^{-5}$	$TbL_3 \cdot 2H_2O$	$3.95 \cdot 10^{-5}$
$LaL_3 \cdot 2H_2O$	$3.67 \cdot 10^{-5}$	$DyL_3 \cdot 2H_2O$	$5.16 \cdot 10^{-5}$
$CeL_3 \cdot 2H_2O$	$3.53 \cdot 10^{-5}$	$HoL_3 \cdot 2H_2O$	$1.96 \cdot 10^{-5}$
$PrL_3 \cdot 2H_2O$	$3.97 \cdot 10^{-5}$	$ErL_3 \cdot 2H_2O$	$4.88 \cdot 10^{-5}$
$NdL_3.2H_2O$	$2.01 \cdot 10^{-5}$	$TmL_3 \cdot 2H_2O$	$6.09 \cdot 10^{-5}$
$SmL_3 \cdot 2H_2O$	$2.62 \cdot 10^{-5}$	$YbL_3 \cdot 2H_2O$	$6.79 \cdot 10^{-5}$
$EuL_3 \cdot 2H_2O$	$2.36 \cdot 10^{-5}$	$LuL_3 \cdot 2H_2O$	$6.05 \cdot 10^{-5}$
$GdL_3.2H_2O$	$3.71 \cdot 10^{-5}$		

[a] $L = (C_6H_2NH_2Cl_2COO)^-$

In the IR spectra of the 2-amino-3,5-dichlorobenzoate complexes of the lanthanides (Table III) the bands of symmetric vibrations of the carboxylate group (ν_s) at 1380-1392 cm^{-1} are slightly shifted to higher frequencies compared to those of the sodium salt. The antisymmetric vibration bands (ν_{as}) are split into two bands at 1508-1530 cm^{-1} and 1532-1545 cm^{-1}. The first of these is slightly shifted to low frequencies but the second one is close to that of the sodium salt. The values of $\Delta\nu = \nu_{as} - \nu_s$ are 120-142 cm^{-1} and 144-157 cm^{-1}, while for the sodium salt it is 152 cm^{-1}. Considering the IR spectral criterion for the mode of carboxylate bonding based on the direction of the shifts as well as magnitude of $\Delta\nu$[11,12] and our own experience concerning the crystal structure and properties of lanthanide aminobenzoates[13-18], one can assume that some of the carboxylate groups in 2-amino-3,5-dichlorobenzoate complexes have bidentate-chelating and others

TABLE III

Relevant IR Bands for C-Cl, N-H and C-O Bonding of 2-Amino-3,5-Dichlorobenzoic Acid and its Compounds

Complex	ν C-Cl	ν C-N	tw N-H	ν_s NH_2	ν_{as} NH_2	$\nu_s COO$	$\nu_{as} COO$	$\Delta\nu$
HL[a]	705;752	1312	1152	3368	3488	-	1676	-
NaL	724;792	1304	1150	-	-	1380	1532	152
$YL_3 \cdot 2H_2O$[a]	735;752	1312	1160	3368	3488	1388	1512;1532	124/144
$LaL_3 \cdot 2H_2O$	705;752	1312	1160	3368	3488	1384	1512;1530	128/146
$CeL_3 \cdot 2H_2O$	744;752	1312	1160	3368	3488	1384	1512;1535	128/151
$PrL_3 \cdot 2H_2O$	744;752	1320	1160	3368	3496	1388	1508	120
$NdL_3 \cdot 2H_2O$	740;752	1312	1160	3360	3488	1384	1520	136
$SmL_3 \cdot 2H_2O$	744;752	1312	1160	3368	3488	1388	1512;1535	124/147
$EuL_3 \cdot 2H_2O$	744;752	1320	1160	3368	3496	1392	1512	120
$GdL_3 \cdot 2H_2O$	744;756	1320	1160	3368	3496	1388	1512	124
$TbL_3 \cdot 2H_2O$	756;770	1320	1160	3368	3496	1392	1525;1540	133/148
$DyL_3 \cdot 2H_2O$	745;756	1320	1160	3368	3488	1388	1512;1535	124/147
$HoL_3 \cdot 2H_2O$	730;752	1312	1160	3360	3480	1388	1525;1540	137/152
$ErL_3 \cdot 2H_2O$	740;752	1312	1160	3368	3488	1388	1512;1532	124/144
$TmL_3 \cdot 2H_2O$	730;745;752	1312	1160	3376	3488	1388	1512;1532	124/144
$YbL_3 \cdot 2H_2O$	730;752;765	1316	1164	3376	3488	1388	1530;1545	142/157
$LuL_3 \cdot 2H_2O$	730;752;765	1316	1160	3376	3496	1388	1528;1540	140/152

[a] L - $(C_6H_2NH_2Cl_2COO)^-$

bidentate-bridging character. The chelating and bridging character of carboxylate groups suggests that in the investigated complexes the metal ions must be joined by bridging the carboxylate groups in dimer units similar to tetraaqua-bis(μ-4-aminobenzoato-*O,O'*)tetrakis(4-aminobenzoato-*O,O*)diytterbium(III) dihydrate[3,13] or polymer chains similarly to catena-diaquabis(μ-3,5-diamino-benzoato-*O,O'*)(3,5-diaminobenzoato-*O,O*)yttrium(III) tetrahydrate[14]. Additionally, each metal ion must join with two[1,3] or one[4] chelating carboxylate groups and two molecules of water. In this case, the coordination number of the rare earth ions must be 8 in the whole series. Carboxylate groups may also be chelating-bridging, similarly to the dimers of octaaquabis(μ-2,6-dichlorobenzoato-*O,O,O'*)-tetrakis(2,6-dichloro-benzoato-*O*)dilanthanide(III) dihydrates[18] joining two metal ions in the dimeric unit or polymeric chain. The coordination number of the metal is 9. In the latter model of complexes, two molecules of water are always in the inner sphere.

Thermal Studies

All the complexes are stable at room temperature. Upon the heating in air all compounds, except the cerium(III) and yttrium(III) complexes, decompose to oxides in three steps. At first, the hydrated complexes lose the molecules of coordination water and turn into the anhydrous form. The temperature of dehydration is about 50°C for the light and about 60°C for heavy lanthanide and yttrium(III) complexes (Table IV, Figs. 1, 2). The anhydrous compounds are stable during further heating. At the temperature of about 260°C decomposition of the light, and about 340°C decomposition of the heavy lanthanide compounds occurs. One of the stable intermediate products of decomposition are oxychlorides of the lanthanides - LnOCl. These compounds were identified by X-ray diffraction

TABLE IV

Temperature Range of Decomposition of Y and Lanthanide 2-Amino-3,5-Dichlorobenzoates in Air

Complex	ΔT_1/°C	T_2/°C	Weight loss/ %		ΔT_3/°C	Weight loss/ %		ΔT_4/°C	Weight loss/ %	
			Calcd.	Found		Calcd.	Found		Calcd.	Found
$YL_3 \cdot 2H_2O^a$	60 -260	95	4.68	4.50	-	-	-	260 - 915	84.63	85.00
$LaL_3 \cdot 2H_2O$	50 - 260	73	4.55	4.50	260 - 770	75.90	76.50	1085 - 1360	79.38	81.00
$CeL_3 \cdot 2H_2O$	40 - 125	60	4.55	4.50	-	-	-	195 - 540	78.25	78.00
$PrL_3 \cdot 2H_2O$	50 - 265	120	4.54	4.00	265 - 693	75.71	78.00	975 - 1238	78.50	81.00
$NdL_3 \cdot 2H_2O$	50 - 230	80	4.52	5.00	230 - 680	75.39	76.00	990 - 1265	78.85	76.00
$SmL_3 \cdot 2H_2O$	40 - 160	73	4.49	4.50	250 - 803	74.82	75.00	900 - 1157	74.82	75.00
$EuL_3 \cdot 2H_2O$	50 - 275	90	4.48	4.00	275 - 575	74.67	75.50	800 - 1055	78.09	79.00
$GdL_3 \cdot 2H_2O$	90 - 275	90	4.45	4.00	275 - 690	74.18	74.50	690 - 1115	77.58	78.00
$TbL_3 \cdot 2H_2O$	60 - 340	70	4.42	4.20	340 - 557	74.02	74.00	557 - 730	76.93	77.00
$DyL_3 \cdot 2H_2O$	60 - 340	80	4.42	5.00	340 - 580	73.70	74.00	580 - 980	76.57	77.00
$HoL_3 \cdot 2H_2O$	70 - 340	80	4.41	4.50	340 - 560	73.48	74.00	560 - 940	76.85	77.00
$ErL_3 \cdot 2H_2O$	50 - 340	90	4.40	4.50	340 - 535	73.27	73.00	535 - 990	77.08	77.00
$TmL_3 \cdot 2H_2O$	70 - 340	70	4.39	4.50	300 - 550	73.32	73.00	550 - 795	76.47	77.00
$YbL_3 \cdot 2H_2O$	60 - 370	144	4.37	4.50	370 - 600	72.76	73.00	600 - 900	76.09	76.00
$LuL_3 \cdot 2H_2O$	50 - 320	90	4.36	3.80	320 - 600	72.58	73.00	600 - 820	75.92	76.00

[a] $L = (C_6H_2NH_2Cl_2COO)^-$. ΔT_1 = temperature range of dehydration. T_2 = endothermic DTA peaks.

ΔT_3 = temperature range of decomposition to LnOCl. ΔT_4 = temperature range of decomposition to oxides.

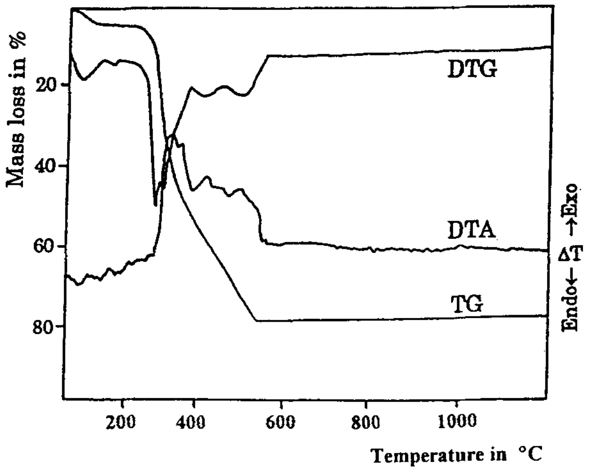

FIG. 1. The TG, DTG and DTA Curves of $Ce(C_6H_2NH_2Cl_2COO)_3 \cdot 2H_2O$

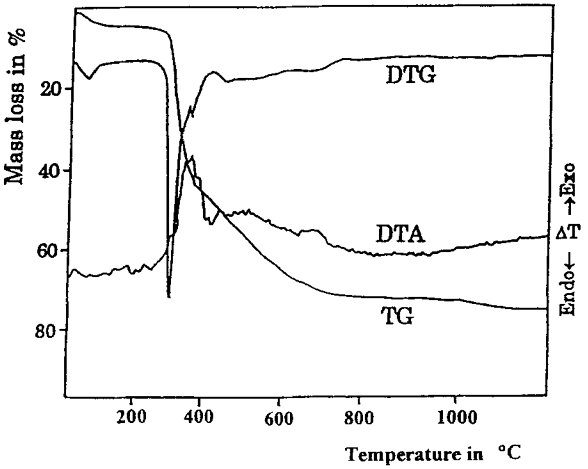

FIG. 2. The TG,DTG and DTA Curves of $Sm(C_6H_2NH_2Cl_2COO)_3 \cdot 2H_2O$

patterns. The patterns were in agreement with the data from the catalogue of International Centre for Diffraction Data[19,20]. Oxychloride formation was observed by a decomposition process of lanthanide 3-chlorobenzoates[1], 4-chlorobenzoates[2] or 2,4- [3], 2,5-dichlorobenzoate[4] complexes.

The Ce(III) and Y(III) complexes decompose in two steps, and the anhydrous compounds on further heating decompose directly to the oxides. The final products of decomposition of the Y(III) and Ln(III) 2-amino-3,5-dichlorobenzoates are the oxides: Y_2O_3, CeO_2, Pr_6O_{11}, Tb_4O_7 and oxides of type Ln_2O_3 for other lanthanides. The temperature of oxide formation is considerably higher in the case of the light lanthanide complexes: 1360°C for the La(III) to 1055°C for the Eu(III) complexes and for the complexes of Y(III) are at 820°C and the heavy lanthanide(III) complexes at 730-990°C. The temperature of CeO_2 formation has the lowest value at 540°C. In the case of Ce(III) complexes with other organic ligands[1-4] the direct decomposition to CeO_2 without oxy compound formation was observed.

The scheme of the thermal decomposition of the rare earth 2-amino-3,5-dichlorobenzoates may be presented as follows:

$LnL_3 \cdot 2H_2O \rightarrow LnL_3 \rightarrow LnOCl \rightarrow Ln_2O_3$
(for Ln = La to Lu except Ce)
$YL_3 \cdot 2H_2O \rightarrow YL_3 \rightarrow Y_2O_3$
$CeL_3 \cdot 2H_2O \rightarrow CeL_3 \rightarrow CeO_2$

The dehydration processes are accompanied with a very weak endothermic effect in the range of 60-144°C. The endothermic effects of decomposition are masked by the exothermic effect of burning the organic ligand, thus in the range of 240-400°C one can observe strong exothermic effects.

EXPERIMENTAL

2-Amino-3,5-dichlorobenzoic acid, >96% (Merck, Germany); $NH_3 \cdot H_2O$ p.a., 25% solution, HCl p.a., 36% solution, Lu_2O_3 99.9% (POCh Gliwice, Poland), Y_2O_3 99.9%, La_2O_3 99.5%, $Ce(NO_3)_3 \cdot 6H_2O$ 99%, Pr_6O_{11} 99.5%, Nd_2O_3 99.9%, Sm_2O_3 99%, Gd_2O_3 99.5% (prepared at our laboratory); Eu_2O_3 99.9%, Tb_4O_7 99.9%, Dy_2O_3 99.9% (Koch Light Laboratories Ltd., England); Ho_2O_3 99.9% (Union Chimique Belge); Er_2O_3 99.9% (Fluka AG, Buch GS, Switzerland); Tm_2O_3 99.9% (Research Organic/Inorganic Chemical Corp., USA); Yb_2O_3 99.9% (prepared in the laboratory of the I. Franko University, Lvov, Ukraine) were used.

The ammonium 2-amino-3,5-dichlorobenzoate solution and the solution of suitable lanthanide(III) salts (chlorides or nitrate in the case of cerium(III)) were employed in the molar ratio 3:1 for the synthesis of lanthanide(III) 2-amino-3,5-dichlorobenzoates. In each synthesis 1 g (0.0048 mole) of 2-amino-3,5-dichlorobenzoic acid, dissolved in 50 mL of 0.1 M ammonia solution, was used. The pH of the ammonium salt solution was 7.2-7.6.

In the synthesis of cerium(III) 2-amino-3,5-dichlorobenzoate, 0.69 g (0.0016 mole) of cerium(III) nitrate hexahydrate, dissolved in 50 mL of water, was used. In the synthesis of yttrium(III) and the other lanthanide(III) 2-amino-3,5-dichlorobenzoates, 0.0008 mole amounts of Y_2O_3 and Ln_2O_3 (Ln = La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu), 0.00027 mole of Pr_6O_{11} or 0.0004 mole of Tb_4O_7 were employed. The oxides were dissolved in 20 mL of 3 M HCl solution and evaporated. The obtained crystals of lanthanide(III) chlorides were dissolved in 50 mL of water. The pH of the solutions obtained was 4.5.

The yields of the yttrium(III) and lanthanide(III) 2-amino-3,5-dichlorobenzoates were about 78% (Table I).

The contents of carbon, nitrogen, chlorine and hydrogen in the compounds were determined by the elemental analyses. The rare earth elements were determined by ignition of the complexes to Ln_2O_3, CeO_2, Pr_6O_{11} or Tb_4O_7 (Table I). The contents of water were established from the TG curves and elemental analyses.

The IR spectra of the prepared complexes were recorded over the range 4000-400 cm^{-1} (Table III). X-ray patterns of the prepared complexes were recorded on a DRON 2 diffractometer by the Debye-Scherrer method using CuK_α radiation. The solubility of the prepared complexes in water at 20°C was examined. Saturated solutions were prepared under isothermal conditions. The concentration of Y(III) and lanthanide(III) ions was determined spectrophotometrically on a Specord M40 spectrometer using arsenazo III[21,22]. The results are presented in Table II.

The thermal stability of the complexes of Y and lanthanides with 2-amino-3,5-dichlorobenzoic acid was studied. TG, DTG and DTA curves were recorded using a Q 1500D derivatograph. The complexes of the light lanthanides were heated to 1500°C at the rate of 7.5 deg/min and heavy lanthanides and Y were heated to 1000°C at the rate of 10 deg/min in air atmosphere. The samples of 100 mg were heated in platinum crucibles with the following sensitivity: TG-100 mg, DTG-500 μV, DTA-500 μV, using Al_2O_3 as the reference material. As an example, the curves obtained for the Ce(III) and Sm(III) complexes are presented in Figs. 1 and 2. From the thermal curves of the prepared complexes the temperatures of the thermal decomposition were evaluated. They are presented in Table IV.

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