THERMAL BEHAVIOUR OF HYDRATED LANTHANIDE COMPLEXES WITH HEPTANEDIOIC ACID

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The multi-step dehydration and decomposition of trivalent lanthanum and lanthanide heptanediate polyhydrates were investigated by means of thermal analysis completed with infrared study. Further more, X-ray diffraction data for investigated heptanediate complexes of general stoichiometry $Ln_2(C_7H_{10}O_4)_3 \cdot nH_2O$ (where $n = 16$ in the case of La, Ce, Pr, Nd and Sm pimelates, $n = 8$ for Eu, Gd, Tb, Dy, Er and Tm pimelates, $n = 12$ for Ho, Yb and Lu pimelates) were also reported.

The last discoveries of new properties and occurence of heptanedioic acid (usually called pimelic acid) and its compounds have indicated many possibilities of their practical use [1-7]. It is well known that heptanedioic acid durint heating undergoes a variety of transformations such as decarboxylation, cyclization and polymerization. Its complexes play a dominant role in biochemical systems and are used for preparation of some sorts of bactericides and antibiotic substances [8, 9]. The salts of heptanedioic acid show the antidiabetic activity [10]. Pimelic acid inhibits the development of saprophytic microflora, and for that reason is used now for biological purification of wastewater from the production of synthetic fat [11].

Heptanedioic acid as bidentate ligand forms easily complexes with a vide variety of metals; however only few data exist in literature on lanthanide pimelates. The preparation of these complexes and their solubility in water are published by Ryabchikov [12], Brzyska and Hubicki [13]. The brief thermal study only of Ce, Nd, Eu and Lu dicarboxylates have been reported by Azikov and Serebrennikov [14]. Turova and Serebrennikov [15] have indicated one-step dehydration process of Gd, Tb, Dy, Ho, Yb and Lu pimelates at exceptionally low total dehydration temperature (about 125-175°). These

results inspired to controversy and did not find the confirmation with preliminary data received in our researches concerning thermal dissociation of Ce, Pr, Er and Tm pimelates [16].

This paper reports the results of broaden researches on all lanthanide (excluding promethium) pimelate polyhydrates of stoichiometry $Ln_2(C_7H_{10}O_4)_3 \cdot nH_2O$, where $n = 16$ in the case of La, Ce, Pr, Nd and Sm heptanediates, $n = 8$ for Eu, Gd, Tb, Dy, Er and Tm heptanediates; $n = 12$ for Ho, Yb and Lu heptanediates. So high-hydrated rare earth pimelates are obtained and investigated for the first. The characterization of these complexes, their thermal stability and behaviour are being reported and discussed.

Experimental

Chemical reagents: lanthanide oxides were 99.6-99.8% purity, and pimelic acid $HO_2C(CH_2)_5CO_2H$ over 99% (Fluka A. G., Buchs S. G. Switzerland).

Preparation of rare earth metal heptanediates and their elemental analysis

To an aqueous solution of ammonium heptanediate (0.3 M, $pH = 5.2$) was added slowly with stirring the equivalent amount of lanthanide chloride solution (0.2 M, $pH = 3$-4). The resulting precipitate was left for 24 hours in mother solutions ($pH = 4.4$-4.0) at 289-291 K. The product was subsequently filtered, washed to remove ammonium and chloride ions, and dried in the air to constant mass at 289 K for 3-4 days.

The carbon and hydrogen contents of obtained lanthanide heptanediate hydrates were determined by elemental analysis with V_2O_5 as oxiding agent. The rare earth metal contents were determined by ignition of the complexes to corresponding rare earth oxides at 1273 K. The elemental analysis data are collected in Table 1.

Apparatus

Infrared spectra of free heptanedioic acid and obtained lanthanide heptanediates (all prepared as potassium bromide discs) were recorded using Spectrophotometer UR-20 (Carl Zeiss, Jena) in the range 4000-400 cm^{-1}.

X-ray spectra of rare earth element heptanediates were recorded using DRON-2 diffractometer (with Ni filtered Cu $K\alpha$ radiation) in the range of angle 2θ 4-80°, by means of powder Debey-Scherrer method.

Table 1 Analytical data

$Ln_2(C_7H_{10}O_4)_3 \cdot nH_2O$		Ln, %		C, %		H, %	
Ln	n	calcd.	found	calcd.	found	calcd.	found
La	16	26.70	26.5	24.24	24.2	6.01	5.9
Ce	16	26.87	26.8	24.18	24.1	5.99	5.9
Pr	16	26.98	26.8	24.15	24.3	5.98	5.8
Nd	16	27.44	27.6	23.99	24.1	5.94	5.8
Sm	16	28.28	28.6	23.72	24.0	5.88	6.0
Eu	8	32.95	33.1	27.34	27.2	5.03	5.1
Gd	8	33.71	33.4	27.03	26.8	4.97	5.1
Tb	8	33.54	33.5	26.94	27.0	4.95	4.8
Dy	8	34.44	34.4	26.73	26.9	4.91	5.0
Ho	12	32.32	37.2	24.27	24.4	5.33	5.1
Er	8	35.10	35.0	26.46	26.8	4.86	5.0
Tm	8	35.32	35.1	26.37	26.2	4.84	5.0
Yb	12	34.37	34.3	24.33	24.5	5.25	5.0
Lu	12	33.63	33.4	24.24	24.5	5.23	5.1

TG, DTG and DTA curves were obtained using a Derivatograph OD-102, system Paulik-Paulik-Erdey. All measurements were carried out on un-diluted powder samples of 100 mg initial mass in platinum crucibles, composed from five small shallow dishes, heated over the temperature range 289-1200 K in static air and in dynamic nitrogen atmosphere. The heating rate was 9 deg min^{-1}; the sensitivities of TG was 100 mg. α-Al_2O_3 was used as reference material.

Results and discussion

Analytical data (Table 1), tested also by means of derivatograph showed that the complexes of rare earth metal heptanediates (obtained at 289 K) crystallize with 16, 8 or 12 water molecules, depending on the coordination centre. The increase of synthetic preparation temperature caused the formation of the less hydrated pimelates.

The recorded IR spectra of all prepared complexes show great similarities. Analysis of their IR spectra, in comparison with IR spectrum of free heptanedioic acid, has confirmed the purity and composition of

prepared rare earth pimelates. Both the intensive broad absorption band in their IR spectra, between 3700-300 cm^{-1} (max. 3370 cm^{-1} - characteristic for OH from water stretching vibration) and the weak band in the range 1640-1660 cm^{-1} (bond bending deformation) confirm the presence of crystallization water in complex molecules. The other more characteristic frequencies (cm^{-1}) of maximum infrared absorption bands of investigated lanthanide heptanediates are in the ranges: 2940-2935, 2860; 1460, 1305 and 1203 cm^{-1} (anti- and symmetric valence; scissoring, wagging, twisting vibrations of CH2); 720-715 cm–1 (skeletal breathing of $(CH_2)_5$-); 1560-1540, 1440-1430 cm^{-1} (asymmetric and symmetric vibrations of COO^-) and 420 cm^{-1} (metal-to-oxygen bond vibration).
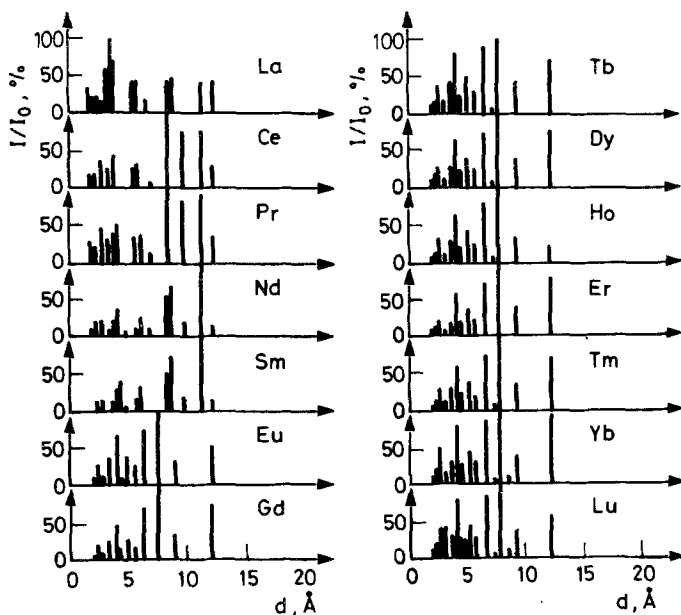

Fig. 1 Radiogram sheets of lanthanide heptanediate polyhydrates

In order to examine the instructurality of prepared lanthanide heptanediate polyhydrates, their diffractograms were recorded with DRON-2. Powder X-ray spectra of these compounds showed that all investigated complexes have crystalline form of large sizes unit cells and low symmetry. The presented radiogram sheets of lanthanide pimelates (Fig. 1) evidently indicate, that heptanediate octa- or dodeca-hydrates of heavy lanthanide (from europium to lutetium) seem to be isostructural compounds; their strongest

interference reflections are recorded at an angle $2\theta = 11.6°$ ($d = 0.76$ nm). And the analysis of other diffractograms proofs that hexadecahydrate light lanthanide pimelates indicate different structurality. The obtained cerium and praseodymium complexes are isostructural. It was noticed that the calculated crystallinity degrees of the neodymium and samarium complexes have the lowest values (386 and 410) in comparison with crystallinity degrees of all investigated lanthanide pimelate polyhydrates (496-600). The crystalline structure of lanthanum pimelate hexadecahydrate differs most from others.
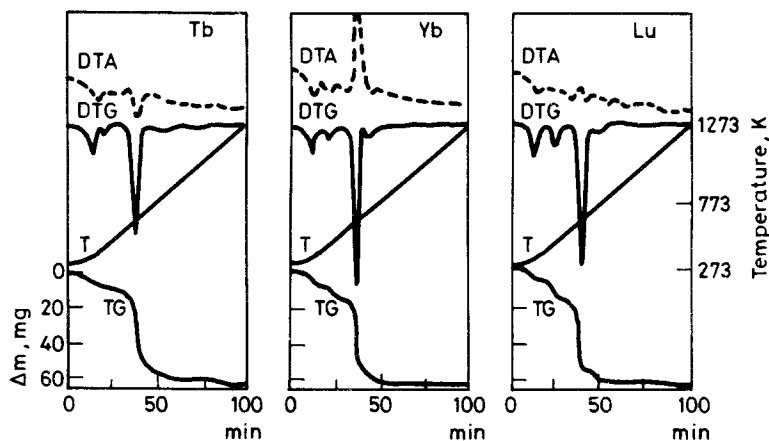

Fig. 2 TG, DTG and DTA curves of some lanthanide heptanediate polyhydrates (Tb and Lu - in nitrogen, Yb - in air)

TG, DTG and DTA curves for selected lanthanide heptanediate polyhydrates (100 mg samples of $[Tb_2(C_7H_{10}O_4)_3.3H_2O].5H_2O$ and $[Lu_2(C_7H_{10}O_4)_3.2H_2O].10H_2O$ - heated in nitrogen atmosphere and 100 mg $[Yb_2(C_7H_{10}O_4)_3.3H_2O].9H_2O$ - heated in static air) are shown in Fig. 2. Detailed TG, DTA and DTG data, concerning measurements in static air for all investigated $Ln_2(C_7H_{10}O_4)_3.nH_2O$ complexes, are summarized in Tables 2 and 3.

It has been found that the recorded curves of respective samples of lanthanide pimelate polyhydrates, heated both in the air and in nitrogen atmosphere, indicate correspondent similarity of thermal dissociation processes in respect of analogous intermediate decomposition product formation. Only small differences are noticed in temperature regions of particular dissociation steps.

Table 2a Thermal stabilities of rare earth pimelate polyhydrates and the corresponding intermediate products of decomposition

Ln	H2O n	$Ln_2(C_7H_{10}O_4)_3 \cdot n\ H_2O$ Stability range, K	Residue mass found, %	calc., %	$Ln_2O_2CO_3$ Stability range, K	Residue mass found, %	calcd., %	Ln oxide Temp., K		Residue mass found %	calcd. %
La	16	293 – 353	100	100							
	12	403 – 443	93.0	93.07							
	3	553 – 563	78.0	77.49							
	2	603 – 623	76.0	75.76	848 – 913	35.3	35.54	1043	La_2O_3	31.0	31.31
Ce	16	293 – 353	100	100							
	12	413 – 463	93.0	93.09							
	3	573 – 583	78.0	77.54				733	CeO_2	33.0	33.01
Pr	16	293 – 358	100	100							
	12	413 – 463	93.0	93.10							
	4	578 – 588	79.0	79.30							
	3	613 – 618	77.0	77.58				953	Pr_6O_{11}	33.0	32.60
Nd	16	293 – 348	100	100							
	12	408 – 463	93.0	93.14							
	3	603 – 623	77.0	77.72	873 – 883	36	36.20	953	Nd_2O_3	32.0	32.01

Table 2b Thermal stabilities of rare earth pimelate polyhydrates and the corresponding intermediate products of decomposition

Ln	H_2O	$Ln_2(C_7H_{10}O_4)_3 \cdot n\ H_2O$			$Ln_2O_2CO_3$			Ln oxide			
		Stability range,	Residue mass		Stability range,	Residue mass		Temp.,		Residue mass	
			found,	calcd.,		found,	calcd.,			found,	calcd.,
	n	K	%	%	K	%	%	K		%	%
Sm	16	293 – 343	100	100							
	12	393 – 453	93.0	93.22							
	10	493 – 533	89.5	89.84							
	2	593 – 613	76.5	76.28	833 – 843	37	36.94	913	Sm_2O_3	33	32.8
Eu	8	293 – 363	100	100							
	4	433 – 453	92.0	92.19							
	3	513 – 533	90.0	90.24							
	2	553 – 583	89.0	88.28	833 – 838	43	42.92	903	Eu_2O_3	38	38.15
Gd	8	293 – 353	100	100							
	2	508 – 608	88.0	88.42	818 – 823	43	43.53	1033	Gd_2O_3	38.5	38.84

Table 3a Thermal stabilities of heavy lanthanide pimelate polyhydrates and the corresponding intermediate products of decomposition

Ln	H_2O n	$Ln_2(C_7H_{10}O_4)_3 \cdot nH_2O$			$Ln_2O_2CO_3$			Ln oxide			
		Stability range, K	Residue mass found, %	calcd., %	Stability range, K	Residue mass found, %	calcd., %	Temp., K		Residue mass found, %	calcd., %
Tb	8	293–353	100	100							
	4	413–433	92	92.30							
	3	493–583	90	90.38	768–778	43	43.77	943–1163	Tb_4O_7	40	39.32
								1188	Tb_2O_3	39	39.07
Dy	8	293–353	100	100							
	4	393–423	92.5	92.36							
	2	523–593	89	88.54	813–823	44	44.19	973	Dy_2O_3	39.5	39.53
Ho	12	293–353	100	100							
	8	393–423	92.6	92.94							
	3	523–593	84	84.11	753–758	42	41.34	973	Ho_2O_3	37	37.03
Er	8	293–363	100	100							
	4	393–433	92	92.44							
	3	513–593	90.5	90.55	813–823	44	44.75	953	Er_2O_3	40	40.13

Table 3b Thermal stabilities of heavy lanthanide pimelate polyhydrates and the corresponding intermediate products of decomposition

| Ln	H₂O n	$Ln_2(C_7H_{10}O_4)_3 \cdot nH_2O$ Stability range, K	Residue mass found, %	calcd., %	$Ln_2O_2CO_3$ Stability range, K	Residue mass found, %	calcd. %	Ln oxide Temp., K		Residue mass found, %	calcd., %
Tm	8	293 – 363	100	100							
	4	393–433	92	92.46							
	3	513–593	90.5	90.58	813–818	45	44.94	953	Tm₂O₃	40.5	40.34
Yb	12	293–353	100	100							
	8	393–453	93	93.05							
	3	533–593	84.5	84.36	733–738	42	42.26	933	Yb₂O₃	38	38.01
Lu	12	293–353	100	100							
	8	393–453	93	93.07							
	2	533–593	82.5	82.69	733–738	42.5	42.47	893	Lu₂O₃	38	38.24

Generally, all prepared complexes, containing 16, 8 or 12 water molecules, are thermally stable from 289 K to 353-363 K. Exceptionally the hexadecahydrates of Nd and Sm compounds indicate the little less stability to only 343-348 K (they had also lower degrees of crystallinity) in comparison to other investigated lanthanide pimelate polyhydrates.

Dehydration of all lanthanide heptanediates proceeds via 3-4 stages, what indicates on various bond forces of particular water molecules. At first, at below 393 K only four molecules are liberated from heated samples, which transform into dodecahydrates (of light lanthanide) and tetra- or octahydrates of heavier lanthanide pimelates (Tables 2-3). The next dehydration stage begins over about 423-453 K and is stopped when di- or trihydrates are formed at about 513-533 K.

It is noticed, that the last two or three H_2O are bonded in inner corrdination sphere of lanthanide ion. So formed complexes $[Ln_2(C_7H_{10}O_4)_3 \cdot (2\text{-}3)H_2O]$, chiefly of heavy lanthanide, indicate very wide range of thermal stability. Within this series, gadolinium pimelate dihydrate is the most thermally stable (508-608 K). The di- or trihydrates of light lanthanide pimelates indicate narrower range stability.

The last loss of rest water molecules occurs simultaneously with rapid decomposition of pimelate ions at over about 600 K. During the decomposition of pimelate, predominant volatile products are cyclohexanone [17] and CO_2, according to general equation

$$[Ln_2(C_7H_{10}O_4)_3.(2\text{-}3)H_2O] \rightarrow$$
$$\rightarrow (2\text{-}3)H_2O + 3\ CH_2(CH_2)_4CO + Ln_2O_2CO_3 + 2CO_2$$
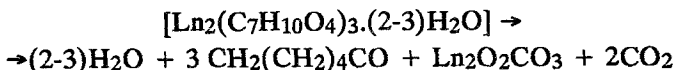
The liberated cyclohexanone undergoes exothermic combustion in air, what is appeared by a strong exothermic DTA peak above 600 K (Fig. 2 "Yb"). In the used crucible remains only the corresponding lanthanide (excluding Ce) dioxycarbonate as unstable or low stable (5-10 degree range) intermediate decomposition product. Exceptionally lanthanum dioxycarbonate indicates high thermal stability (893-913 K). This conclusion is confirmed by obtained infrared absorption spectra of intermediate decomposition products of samples heated isothermally at 733 and 833 K. There are recorded characteristic absorption bands in the ranges 1440-1410 cm^{-1} and 880-860 cm^{-1}, indicating on CO_3^{2-} vibrations [18].

The final stage of thermal decomposition of lanthanide heptanediate polyhydrate complexes is the total transformation to correspondent rare earth metal oxides. The cerium dioxide is formed in the lowest temperature.

Generally, the sequence of obtaining the oxides of particular rare earth elements from their pimelates during the gradual heating runs as follows (in given experimental conditions):

Temp. K	$733 < 893 < 903 < 913 < 933 < 943$
Oxide	$CeO_2 \ Lu_2O_3 \ Eu_2O_3 \ Sm_2O_3 \ Yb_2O_3 \ Tb_4O_7$
	$< 953 < 973 < 1033 < 1043 < 1188$
	$Pr_6O_{11} \ Dy_2O_3 \ Gd_2O_3 \ La_2O_3 \ Tb_2O_3$
	Nd_2O_3
	Er_2O_3
	Tm_2O_3

The X-ray powder data were helpful to explain partially the differences of thermal behaviour of particular rare earth metal heptanediate polyhydrates. The recorded plateaux on TG and DTG curves, indicating the intermediate dehydration and decomposition products of investigated heptanediate polyhydrates, became more visible owing to the use of special thermocrucibles permitting faster diffusion of gases liberated from samples.

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Zusammenfassung — Mittels TG, DTG, DTA wurde in Verbindung mit IR-Methoden der mehrstufige Dehydratations- und der Zersetzungsvorgang der Polyhydrate der Pimelinsäuresalze von dreiwertigem Lanthan und dreiwertigen Lanthanoiden untersucht. Röntgendiffraktionsdaten der untersuchten Heptandiat-Komplexe mit der allgemeinen Formel $Ln_2(C_7H_{10}O_4)_3 \cdot nH_2O$ (mit $n = 16$ für Ln = La, Ce, Pr, Nd und Sm, $n = 8$ für Ln = Eu, Gd, Tb, Dy, Er und Tm sowie $n = 12$ für Ln = Ho, Yb und Lu) werden ebenfalls gegeben.