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A THERMAL ANALYSIS STUDY OF LANTHANIDE ADIPATE HYDRATES

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The multi-step dehydration and decomposition of trivalent lanthanide adipate hydrates has been investigated by TG, DTG and DTA, together with infrared study of these compounds and the corresponding intermediate decomposition products. X-ray diffraction data for adipate complexes of general stoichiometry $Ln_2(C_6H_8O_4)_3 \cdot 10H_2O$, where Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu are also reported.

Adipic acid, $HOOC(CH_2)_4COOH$, behaves as dicarboxylic acid and on heating undergoes a variety of transformations such as cyclisation, decarboxylation and polymerization. Adipic acid and adipates are used in the polymer and food industries. Adipic acid exhibits a sharp melting point at 424.56 K and is recommended as a temperature standard for DTA calibration [1]. Adipic acid is also used as an analytical reagent for the quantitative precipitation of aluminium, zirconium and uranium [2].

Adipic acid functions as bidentate ligand and forms complexes with a wide variety of metals. However few data exist on lanthanide adipates [3]. Stability constants of ion association complexes of several rare earth metal adipates [4–6], and a brief thermal dehydration study of $Ce_2(C_6H_8O_4)_3 \cdot 2H_2O$, $Eu_2(C_6H_8O_4)_3 \cdot 6H_2O$ and $Nd_2(C_6H_8O_4)_3 \cdot 5H_2O$ [8–10] have been reported. Wynne and Roberts [11] have reported a TG study of Pr and Nd adipate dihydrates.

This paper reports the synthesis and characterization of lanthanide (excluding promethium) adipate decahydrates and the thermal behaviour of these complexes $Ln_2(C_6H_8O_4)_3 \cdot 10H_2O$ (where Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) is reported and discussed. Thermal stability ranges for these complexes and the corresponding intermediate pyrolysis products are deduced for conditions prevailing.

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Experimental

Chemical reagents: Lanthanide oxides were 99.6–99.8% purity, and adipic acid, 99.5% (Fluka A. G., Buch S. G., Switzerland).

Preparation of rare earth metal adipates

To an aqueous solution of ammonium adipate (0.3 M, pH = 5) was added slowly with stirring the equivalent amount of a lanthanide chloride solution (0.2 M, pH = 3–4). The resulting precipitate was left for 2 hours in mother solution (pH = 3.7–4.0) at 288 K. The product was subsequently filtered, washed copiously with water to remove ammonium and chloride ions, and dried to constant mass in the air at 288 K for 3–4 days.

The carbon and hydrogen contents of obtained lanthanide adipate hydrates were determined by elemental analysis with V_2O_5 as oxiding agent. The rare earth metal contents (M) 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 weighed samples (2.22×10^{-6} Mole) of obtained lanthanide adipates $Ln_2(C_6H_8O_4)_3 \cdot nH_2O$ (prepared as pellets with KBr) were recorded using Spectrometer Specord 75 IR (Carl Zeiss, Jena) in the range 4000–400 cm^{-1}.

Table 1 Analytical data

Rare earth metal adipate hydrate	M, %		C, %		H, %	
	calcd.	found.	calcd.	found.	calcd.	found.
$La_2(C_6H_8O_4)_3 \cdot 10H_2O$	31.20	31.1	24.28	24.4	4.98	5.1
$Ce_2(C_6H_8O_4)_3 \cdot 10H_2O$	31.39	30.9	24.21	24.2	4.97	5.0
$Pr_2(C_6H_8O_4)_3 \cdot 10H_2O$	31.51	31.5	24.17	24.2	4.96	5.0
$Nd_2(C_6H_8O_4)_3 \cdot 10H_2O$	32.02	32.5	24.60	23.9	4.92	4.9
$Sm_2(C_6H_8O_4)_3 \cdot 10H_2O$	32.93	33.7	23.67	23.5	4.86	5.0
$Eu_2(C_6H_8O_4)_3 \cdot 10H_2O$	33.16	33.2	23.59	23.7	4.84	4.9
$Gd_2(C_6H_8O_4)_3 \cdot 10H_2O$	33.93	33.8	23.32	23.3	4.78	4.7
$Tb_2(C_6H_8O_4)_3 \cdot 10H_2O$	34.16	34.4	23.24	23.1	4.77	4.7
$Dy_2(C_6H_8O_4)_3 \cdot 10H_2O$	34.67	34.4	23.06	23.0	4.73	4.8
$Ho_2(C_6H_8O_4)_3 \cdot 10H_2O$	35.00	35.3	22.94	22.9	4.71	4.6
$Er_2(C_6H_8O_4)_3 \cdot 10H_2O$	35.32	35.8	22.83	22.9	4.68	4.6
$Tm_2(C_6H_8O_4)_3 \cdot 8H_2O$	36.95	36.8	23.64	23.8	4.41	4.3
$Yb_2(C_6H_8O_4)_3 \cdot 10H_2O$	36.10	36.0	22.55	22.4	4.63	4.5
$Lu_2(C_6H_8O_4)_3 \cdot 10H_2O$	36.35	36.0	22.46	22.4	4.61	4.5

X-ray spectra of rare earth metal adipates were recorded using DRON-2 diffractometer (with Ni filtered Cu K_α radiation) in the range 4–80° by means of powder Debye–Scherrer method.

TG, DTG and DTA curves were obtained using a MOM Derivatograph OD–102, system F. Paulik–J. Paulik–L. Erdey. All measurements were carried out on undiluted powdered samples of 50 mg and 100 mg initial mass in platinum crucibles, heated over the temperature range 288–1200 K in static air, and in dynamic nitrogen atmosphere. The heating rate was 9 $\mathrm{deg \cdot min^{-1}}$; the sensitivities used were TG 50 or 100 mg, DTG 1 : 5 and DTA 1 : 10. α-Al_2O_3 was used as reference material.

Results and discussion

TG, DTG and DTA curves for selected lanthanide adipate hydrates (100 mg samples heated in air atmosphere) are shown in Fig. 1. Detailed TG, DTA and DTG data for $Ln_2(C_6H_8O_4)_3 \cdot 10H_2O$ complexes and corresponding temperature ranges, mass losses and residue masses of the corresponding intermediate decomposition products are summarised in Tables 2 and 3.

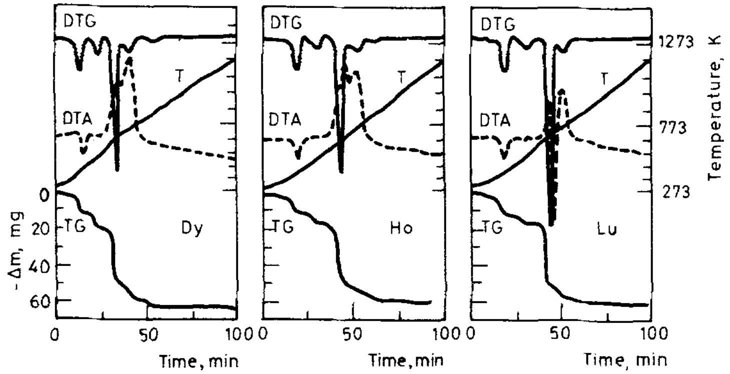


Fig. 1 TG, DTG and DTA curves of dysprosium, holmium and lutetium adipates $Ln_2(C_6H_8O_4)_3 \cdot 10H_2O$

Generally, the thermal decomposition pathway of these rare earth metal adipate decahydrates proceeds via 4–6 stages; the number of such stages appears to depend on the rare earth metal involved.

Lanthanum adipate decahydrate is the most thermally stable (within the broadest range of temperature: from room temperature to 533 K) in comparison to thermal stabilities of all lanthanide adipate decahydrates, which are stable only to 313–343 K.

Table 2 Thermal stabilities of rare earth adipate decahydrates and the corresponding intermediates products of decomposition

Ln	$Ln_2(C_6H_8O_4)_3 \cdot nH_2O$				$Ln_2O_2CO_3$			Ln Oxide			
	H_2O	Stability range	Residue mass		Stability range	Residue mass		From temperature, K		Residue mass	
	n	K	found. %	calc. %	K	found. %	calc. %			found. %	calc. %
La	10	293–533	100	100							
	2	623–633	84	83.80	833–993	43	41.53	1093	La_2O_3	36.5	36.59
Ce	10	293–353	100	100							
	2	393–443	83.5	83.8							
	0	493–583	79.5	79.8	—			813	CeO_2	38	38.55
Pr	10	293–333	100	100							
	6	393–398	90.5	91.9							
	4	433–443	87.2	87.9							
	3	463–523	86	86.17	723	44	41.79	813–853	Pr_6O_{11}	38	38.6
								893	Pr_2O_3	36.6	36.87
Nd	10	293–333	100	100							
	6	383–403	92	92.01							
	4	493–593	88	88.01	838–893	45	42.33	993	Nd_2O_3	38	37.45
Nd*	4	293–393	100	100							
	2	483–573	95	95.44	833–903	48	47.97	973	Nd_2O_3	42.5	42.43
Sm	10	293–333	100	100							
	4	473–478	88	88.17							
	3	483–603	86	86.20	873–883	43	43.01	943	Sm_2O_3	39	38.14
Eu	10	293–333	100	100							
	4	343–393	88.5	88.19							
	2	553–603	84.5	84.26	818–873	43	43.31	913	Eu_2O_3	38.5	38.39
Gd	10	293–333	100	100							
	4	353–503	88.5	88.36							
	1	553–583	83	82.53	813–833	43.5	43.86	923	Gd_2O_3	39	39.11

* Neodymium adipate dried at 303 K

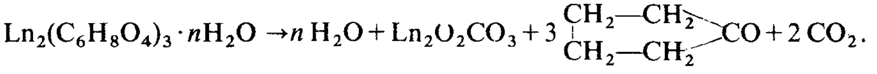
Dehydration of these complexes proceeds in several steps (Tables 2, 3). Among intermediate products, thermally stable tetrahydrates or trihydrates are formed in all cases, except lanthanum and cerium adipate decahydrates, which form a dihydrate as a decomposition product. The steps of dehydration of investigated particular samples in air and in nitrogen were similar. Total dehydration to thermally stable anhydrous adipates are noted only for cerium and dysprosium

Table 3 Thermal stabilities of heavy lanthanide adipate decahydrates and the corresponding intermediates products of decomposition (air atmosphere)

		$Ln_2(C_6H_8O_4)_3 \cdot nH_2O$			$Ln_2O_2CO_3$			Ln Oxide			
Ln	H_2O	Stability range	Residue mass		Stability range	Residue mass		From temperature, K		Residue mass	
	n	K	found. %	calc. %	K	found. %	calc. %			found. %	calc. %
Tb	10	293-323	100	100							
	4	443–498	88.5	88.40							
	2	553–608	84.5	84.52	633–634	43.5	44.06	993–1173	Tb_4O_7	40.5	40.19
								1183	Tb_2O_3	39.5	39.33
Dy	10	293-323	100	100							
	4	443–463	89	88.50							
	0	563–603	81	80.81	773–783	43	44.45	903	Dy_2O_3	39.5	39.76
Ho	10	293-313	100	100							
	4	423–473	89	89.52							
	2	543–603	84.5	84.70	793–803	44.5	44.76	883	Ho_2O_3	40.5	40.10
Er	10	293-313	100	100							
	4	433–453	89	88.59							
	3	533-583	86.5	86.69	803-813	44.5	45.04	913	Er_2O_3	41	40.39
Tm*	8	293-353	100	100							
	4	433–473	90	90.09							
	1	543-593	86.5	86.16	788	46	46.99	913	Tm_2O_3	42	42.20
Yb	10	293-313	100	100							
	4	433–473	89	88.71							
	2	523–633	84.5	84.95	793–798	44	45.69	923	Yb_2O_3	41	41.10
Lu	10	293-333	100	100							
	4	433–473	88.3	88.77							
	1	573–643	83	83.15	773–783	44	45.91	913	Lu_2O_3	41	41.35

* Only thulium adipate precipitate was dried at 303 K

adipates. Generally, the thermal analysis data for these complexes indicate, that the loss of the last molecules of water (3, 2 or 1 H_2O) occurs simultaneously with the stepwise-decomposition of the adipate ion. During the decomposition of adipate, predominant volatile products are cyclopentanone [12] and CO_2, according to general equation:



$$Ln_2(C_6H_8O_4)_3 \cdot nH_2O \rightarrow n\,H_2O + Ln_2O_2CO_3 + 3\begin{matrix} CH_2-CH_2 \\ | \\ CH_2-CH_2 \end{matrix}\!\!>CO + 2\,CO_2.$$

The formed cyelopenthanone undergoes exothermic combustion in air, as shown by a strong exothermic peak above 600 K.

Wynne and Roberts [11] have postulated at least three thermal decomposition steps for unhydrous praseodymium- or neodymium-adipates (heating rate 5 deg·min^{-1}) between temperatures 453–713 K, involving intermediates $Ln_2O_{0.5}C_6H_8O_4$, $Ln_2O_{0.5}CO_3C_6H_8O_4$ (with carbon residue) and $Ln_2O_2CO_3$ respectively. In contrast, our data suggest, that at first (earlier) rapid decomposition of adipic radicals occurs, and formation and combustion of cyclopentanone are also rapid. The subsequent oxidation of residual carbon occurs slowly over temperature ranges varying according to the lanthanide complex. This conclusion is confirmed by obtained infrared absorption spectra.

The most characteristic infrared absorption bands of the rare earth adipates are in the range 3480–3320 cm^{-1} and 1660–1680 cm^{-1} (OH water, strech.; H_2O, bend.); 2960, 2870, 1460, 1330, 1200 cm^{-1} (CH_2, anti- and symmetrical, scissoring, wagging, twisting); 720–710 cm^{-1} ($(CH_2)_4$, skeletal breathing); 1430, 1400, 670 cm^{-1} (COO^-, anti- and symmetrical deformation); 640 cm^{-1} (metal-to-oxygen bond vibration), and 1530–1550 cm^{-1} (ionic valence vibrations). Similar IR bands are recorded for free adipic acid, of course, without obvious vibrations of water and Ln–O bond and without strong ionic valence vibration; very strong bands appear at 1695 and 1280 cm^{-1}, which are characteristic of carboxyl group COOH antisymmetric and symmetric vibrations.

In the obtained IR spectra for intermediate decomposition products of adipates (heated isothermally at 623, 703, and 793 K—$LnO(CO_3)_2$ or $Ln_2O_2CO_3$) are absent characteristic absorption bands, which could indicate on adipic moiety vibrations, there are recorded new bands in the ranges 1450–1410 cm^{-1} and 880–850 cm^{-1}, which indicate on CO_3^{2-} vibrations [13].

The final stage of thermal decomposition of these complexes is the transformation of dioxycarbonates (excluding cerium adipate) to corresponding rare earth metal oxides. Within this series, lanthanum dioxycarbonate is the most thermally stable (833–993 K range). The other rare earth dioxycarbonates exhibit lower thermal stability extending over 5–10 degree range. The thermal stability range of the $Ln_2O_2CO_3$ phase decreases with increasing atomic number of the lanthanon.

The thermal stability sequence of the oxides obtained from the corresponding rare earth metal adipates is

$$CeO_2, Pr_6O_{11} \gg Ho_2O_3 > Pr_2O_3, Dy_2O_3 > Eu_2O_3, Er_2O_3, Tm_2O_3,$$

$$Lu_2O_3 > Gd_2O_3, Yb_2O_3 > Sm_2O_3 > Nd_2O_3, Tb_4O_7 \gg La_2O_3 \gg Tb_2O_3.$$

The temperatures corresponding to total transformation of Ln-adipates to rare earth metal oxides are lower by comparison with the transformation temperatures of the corresponding lanthanide oxalate decahydrates [14, 15].

Powder X-ray spectra of $Ln_2(C_6H_8O_4)_3 \cdot 10H_2O$ showed that investigated complexes have crystalline form of large sizes unit cells and low symmetry. The heavy lanthanide adipate decahydrates are isostructural compounds. The crystalline structure of lanthanum adipate decahydrate differs most from other. The detailed results will be described [16].

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Zusammenfassung — Die in mehreren Schritten verlaufende Dehydratisierung und Zersetzung von Adipat-Hydraten der dreiwertigen Lanthanide wurden mittels TG, DTG und DTA untersucht. Diese Verbindungen und bei deren Zersetzung auftretende Zwischenprodukte wurden auch infrarotspektroskopisch charakterisiert. Röntgendiffraktometrische Daten sind für Adipatkomplexe der allgemeinen Stöchiometrie $Ln_2(C_6H_8O_4)_3 \cdot 10H_2O$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb und Lu) angegeben.

Резюме — Методом ТГ, ДТГ, ДТА и ИК спектроскопии изучена многоступенчатая дегидратация и разложение декагидратов лантаноидов адипиновой кислоты с общей формулой $Ln_2(C_6H_8O_4)_3 \cdot 10H_2O$. Метод ИК спектроскопии был использован также для идентификации промежуточных продуктов разложения. Для всех исходных солей представлены также данные рентгеноструктурного анализа.