

SYNTHESIS, CHARACTERIZATION AND THERMAL ANALYSIS OF 1:1 AND 2:3 LANTHANIDE(III) CITRATES

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The synthesis and characterization of lanthanide(III) citrates with stoichiometries 1:1 and 2:3; $[\text{LnL}\cdot x\text{H}_2\text{O}]$ and $[\text{Ln}_2(\text{LH})_3\cdot 2\text{H}_2\text{O}]$, $\text{Ln}=\text{La, Ce, Pr, Nd, Sm}$ and Eu are reported. L stands for $(\text{C}_6\text{O}_7\text{H}_5)^{3-}$ and LH for $(\text{C}_6\text{O}_7\text{H}_6)^{2-}$. Infrared absorption spectra of both series evidence coordination of carboxylate groups through symmetric bridges or chelation. X-ray powder patterns show the amorphous character of $[\text{LnL}\cdot x\text{H}_2\text{O}]$. The compounds $[\text{Ln}_2\text{LH}_3\cdot 2\text{H}_2\text{O}]$ are crystalline and isomorphous. Emission spectra of Eu compounds suggest C_{2v} symmetry for the coordination polyhedron of $[\text{LnL}\cdot x\text{H}_2\text{O}]$ and C_{4v} for $[\text{Ln}_2(\text{LH})_3\cdot 2\text{H}_2\text{O}]$. Thermal analyses (TG-DTG-DTA) were carried out for both series. The thermal analysis patterns of the two series are quite different and both fit in a 4-step model of thermal decomposition, with lanthanide oxides as final products.

Keywords: characterization, crystalline citrate, emission spectra, lanthanide citrate, thermal analysis

Introduction

The first reports on lanthanide citrate chemistry are lanthanides separations [1–8]. Until now lanthanides separations remain still an active field [9]. Nemukhin's studies of the stability of rare lanthanides citrates in aqueous solution started the studies on coordination chemistry of these salts [10]. Yamakawa published the determinations of citrate and hydrogen citrate constants in ion exchange systems [11]. Saratov published the first report on thermal analysis of solid lanthanides complexes and X-ray diffraction patterns of thermal analysis products [12]. Brittain and Spaulding reported energy transfer between Eu^{3+} and Tb^{3+} citrate complexes as probes for evaluating polynuclear species formation [13]. Kakihana and Popa reported the identification of $[\text{Pr}_2(\text{III})\text{O}(\text{CO}_3)_2]$ as a main intermediate in a thermal study of praseodymium citrate [14]. Nowadays the amorphous lanthanide citrate method is extensively used to synthesize highly pure multicomponent oxides [15, 16]. In the last decade, there has been a tremendous interest in the synthesis of modulated organic-metal frameworks (MOF), because these structures yield new potential materials [17–19]. Indeed, a variety of organic molecules, including bi-, tri- and tetradentate ligands have been used for the construction of many interesting structures [20–24], bringing lanthanide citrates to the focus of materials research [25–28].

In this work, the synthesis and characterization by elemental analysis (CH), infrared absorption spectra (FTIR), X-ray powder patterns (XRD), emission spec-

troscopy and thermal analysis (TG/DTG/DTA) of the two series of lanthanides(III) citrates with distinct stoichiometry are reported, 1:1, $[\text{LnL}\cdot x\text{H}_2\text{O}]$ and 2:3, $[\text{Ln}_2(\text{LH})_3\cdot 2\text{H}_2\text{O}]$, where $L=(\text{C}_6\text{O}_7\text{H}_5)^{3-}$, $\text{LH}=(\text{C}_6\text{O}_7\text{H}_6)^{2-}$ and $\text{Ln}=\text{La, Ce, Pr, Nd, Sm}$ and Eu . The last series has not been reported in the literature to date.

Experimental

Lanthanide hydroxycarbonates were prepared reacting lanthanide oxide, (Aldrich), with hydrochloric acid (Merck) followed by precipitation, using urea (Merck).

Synthesis of $[\text{Ln}_2(\text{LH})_3\cdot 2\text{H}_2\text{O}]$: 1 g of $[\text{Ln}(\text{OH})\text{CO}_3]$ were dissolved in 50 mL of 1.2 mol L^{-1} citric acid (Merck) solutions at 373 K. After 30 min, the suspensions were centrifuged. The precipitates were washed with distilled water and centrifuged three times. The solids were dried at 373 K and kept in a desiccator with anhydrous calcium chloride.

Synthesis of $[\text{LnL}\cdot x\text{H}_2\text{O}]$: 1 g of $[\text{Ln}(\text{OH})\text{CO}_3]$ were added to 200 mL of 0.2 mol L^{-1} citric acid at 373 K. After homogenization, 600 mL of ethanol (Merck) were added, yielding colloidal precipitates, which were centrifuged. The precipitates were redispersed in ethanol, centrifuged three times and dried at 373 K. The solids were kept in a desiccator with anhydrous calcium chloride.

Elemental analyses were carried out in a Perkin Elmer model 240 microanalyzer (CHN). Ln(III) contents were calculated from thermal analysis data. FTIR spectra were recorded in KBr pellets on a

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Bomem model 100 spectrophotometer. X-ray powder patterns were recorded on a Rigaku Miniflex diffractometer, using $\text{CuK}\alpha$, $\lambda=1.54 \text{ \AA}$ radiation and a Ni filter. Thermogravimetric measurements were carried out in a TG/DTA Shimadzu model DTG-60/DTG-60A thermal analyzer. Typically, 10 mg of a sample were placed in a platinum crucible and 10 mg of ignited alumina used as reference with heating rate of 10 K min^{-1} in the temperature range of 398 to 1473 K, in 50 L min^{-1} of atmospheric air flow. Emission and excitation spectra of $[\text{Eu}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$ and $[\text{EuL} \cdot x\text{H}_2\text{O}]$ were recorded on a SPEX Model 1934 D spectrofluorimeter at 77 K.

Results and discussion

The synthesized salts are not soluble in any solvents tested. Elemental analyses data are shown in Table 1. These data suggest the general formulae $[\text{Ln}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$ and $[\text{LnL} \cdot x\text{H}_2\text{O}]$ as representative of the two salts series, respectively. The salts $[\text{LnL} \cdot x\text{H}_2\text{O}]$ show variable crystallization water amounts for minimal formula along the series. This fact agrees with their amorphous nature [12]. $[\text{Ln}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$ salts are crystalline. Therefore, the crystalline energy controls the crystallization water amount. Following the lanthanides series, beyond $[\text{Eu}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$, these salts could not be obtained, probably due to steric factors which increase with lanthanide ionic radii contraction. Attempts of hydrothermal syntheses of salts beyond europium yield already reported compounds: $[\text{LnL} \cdot 3\text{H}_2\text{O}]$ [28, 29]. The fact that $[\text{Y}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$ could not be obtained agrees with the above hypothesis.

X-ray patterns of $[\text{Ln}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$ salts show the isomorphous and crystalline nature of this series. $[\text{LnL} \cdot x\text{H}_2\text{O}]$ are amorphous.

Infrared absorption spectra of all synthesized salts were recorded. Figure 1 shows spectra of $[\text{CeL} \cdot x\text{H}_2\text{O}]$ and $[\text{Ce}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$ as typical examples of these two series. $[\text{Ln}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$ salts ex-

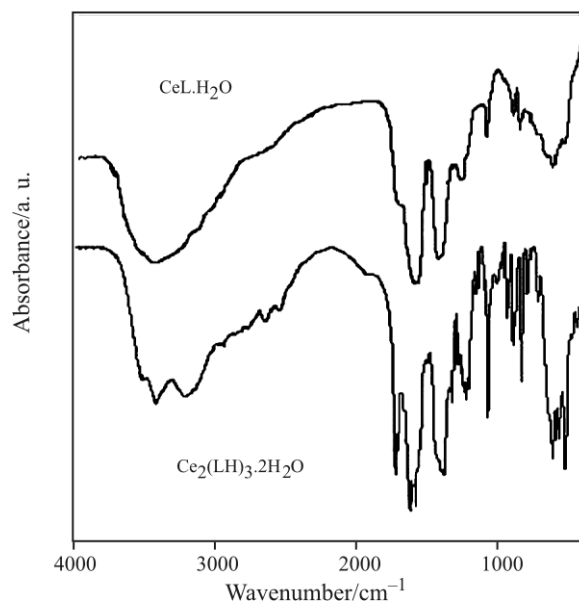


Fig. 1 FTIR spectra of $[\text{Ce}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$ and $[\text{CeL} \cdot x\text{H}_2\text{O}]$ in KBr pellets

hibit relatively narrow peaks; $[\text{LnL} \cdot x\text{H}_2\text{O}]$ salts exhibit broad peaks, reflecting their amorphous character; due to the lack of crystalline restrictions on bond orientation, broad absorption bands appear in infrared spectra [31]. Table 2 reports carboxyl and carboxylate frequencies. Table 3 reports infrared selected frequencies for $[\text{Ln}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$, since this series has not been previously characterized.

IR spectra of $[\text{Ln}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$ show the presence of a protonated carboxyl group (ν_{COOH} at 1728 cm^{-1}), four peaks due to an asymmetric stretching ($\nu_{\text{COO-M}}$) in the region 1380 to 1460 cm^{-1} and three peaks due to symmetric stretching ($\nu_{\text{COO-M}}$) in the region 1563 to 1624 cm^{-1} . Differences between the values of frequencies of asymmetric and symmetric stretchings: $\Delta = [\nu_{(\text{COO}^-)_{\text{asym}}} - \nu_{(\text{COO}^-)_{\text{sym}}}]$, of coordinated carboxylate groups can suggest how the carboxylate groups are coordinated. For $[\text{Ln}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$, these values are 164 cm^{-1} and for $\text{LnL} \cdot x\text{H}_2\text{O}$, 150 cm^{-1} . Since these values are

Table 1 Elemental analyses results for lanthanide citrates

RE	$[\text{Ln}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$				$[\text{LnL} \cdot x\text{H}_2\text{O}]$				
	carbon/%		hydrogen/%		carbon/%		hydrogen/%		H ₂ O
	theor.	exp.	theor.	exp.	theor.	exp.	theor.	exp.	x
La	24.5	24.3	2.5	2.4	20.8	21.2	2.0	2.6	0.6
Ce	24.4	24.5	2.5	2.5	20.7	21.1	2.0	2.5	0.6
Pr	24.3	24.4	2.3	2.4	20.2	20.2	2.4	2.5	1.5
Nd	24.1	24.3	2.4	2.6	20.5	20.3	2.0	2.6	1.0
Sm	23.8	23.9	2.4	2.4	20.2	20.3	1.7	2.0	0.8
Eu	23.7	22.2	2.4	2.3	20.0	20.2	1.9	2.4	0.8

Table 2 Carboxylate and carboxyl frequencies for $[\text{Ln}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$ and $[\text{LnL} \cdot x\text{H}_2\text{O}]$ salts (cm^{-1})

Compound	$\nu_{(\text{COO}^-)_{\text{sym}}}$	$\nu_{(\text{COO}^-)_{\text{asym}}}$	$\nu_{(\text{COOH})_{\text{asym}}}$
$[\text{La}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$	(1388 – 1410 – 1441 – 1460) s	(1624 – 1590 – 1563) s	1728 s
$[\text{Ce}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$	(1388 – 1402 – 1417 – 1441) s	(1629 – 1595 – 1569) s	1728 s
$[\text{Pr}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$	(1391 – 1404 – 1435 – 1460) s	(1628 – 1596 – 1571) s	1728 s
$[\text{Nd}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$	(1389 – 1403 – 1437 – 1455) s	(1625 – 1597 – 1569) s	1728 s
$[\text{Sm}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$	(1390 – 1402 – 1427 – 1450) s	(1628 – 1595 – 1567) s	1728 s
$[\text{Eu}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$	(1390 – 1404 – 1430 – 1452) s	(1627 – 1596 – 1566) s	1728 s
$[\text{LaL} \cdot x\text{H}_2\text{O}]$	1439 s	1590 s	
$[\text{CeL} \cdot x\text{H}_2\text{O}]$	1438 s	1592 s	
$[\text{PrL} \cdot x\text{H}_2\text{O}]$	1440 s	1590 s	
$[\text{NdL} \cdot x\text{H}_2\text{O}]$	1437 s	1592 s	
$[\text{SmL} \cdot x\text{H}_2\text{O}]$	1439 s	1591 s	
$[\text{EuL} \cdot x\text{H}_2\text{O}]$	1439 s	1591 s	

Table 3 Selected frequencies from $[\text{Ln}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$ (cm^{-1})

Compound	$\nu_{(\text{OH})_{\text{H}_2\text{O}}}$	OH_{coord}	$\text{H}_2\text{O}_{\text{coord}}$	$\text{r}(\text{CH}_2)$, $\text{t}(\text{CH}_2)$, $\text{o}(\text{CH}_2)$
$[\text{La}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$	3196 m	3450 m	3415 m	(1295 – 1282 – 1296) w
$[\text{Ce}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$	3196 m	3450 m	3415 m	(1264 – 1283 – 1296) w
$[\text{Pr}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$	3196 m	3450 m	3415 m	(1265 – 1284 – 1295) w
$[\text{Nd}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$	3196 m	3450 m	3415 m	(1264 – 1285 – 1296) w
$[\text{Sm}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$	3196 m	3450 m	3415 m	(1265 – 1284 – 1296) w
$[\text{Eu}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$	3196 m	3450 m	3415 m	(1265 – 1284 – 1295) w

Table 4 Assignments of $[\text{EuL} \cdot x\text{H}_2\text{O}]$ and $[\text{Eu}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$ emission spectra bands

	Transitions				
	${}^7\text{D}_0 \rightarrow {}^7\text{D}_0$	${}^7\text{D}_0 \rightarrow {}^7\text{D}_1$	${}^7\text{D}_0 \rightarrow {}^7\text{D}_2$	${}^7\text{D}_0 \rightarrow {}^7\text{D}_3$	${}^7\text{D}_0 \rightarrow {}^7\text{D}_4$
$[\text{EuL} \cdot x\text{H}_2\text{O}]$	1 peak	3 peaks	3 peaks		5 peaks
Species	A ₁	A ₂ , B ₁ , B ₂	A ₁ , B ₁ , B ₁		3A ₁ , 2A ₂ , B ₁ , B ₁
wavelengths/nm	581	593, 594, 596	616, 617, 619		690, 691, 696, 698, 701
$[\text{Eu}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$	1 peak	3 peaks	5 peaks		5 Peaks
Species	A ₁	1E, 1A ₂	1A ₁ , 2E		2E, 2A ₁
wavelengths/nm	582	593, 595, 596	616, 617, 618, 620, 621		690, 692, 697, 699, 701

significantly smaller than the values for ionic sodium citrate (180 cm^{-1}), this suggests that these carboxylate groups are coordinated either as symmetrical bridges or chelated [28, 30–32].

Spectra of $[\text{Ln}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$ show $\text{r}(\text{CH}_2)$, $\text{t}(\text{CH}_2)$, $\text{o}(\text{CH}_2)$ respectively at 1295, 1282, 1296 cm^{-1} , coordinated OH stretching frequencies in the region of 3450 cm^{-1} , coordinated water at 3415 cm^{-1} and hydration water at 3196 cm^{-1} , as can be seen in Table 3 [28–31].

Eu(III) salts are strongly luminescent. Their emission spectra are shown in Fig. 2. Table 4 reports the observed peaks in the emission spectra and their assignments. The presence of a ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ band indi-

cates C_n , C_{nv} or C_s as possible symmetries for the coordination polyhedron [33]. The relative ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ intensity is larger than ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$, indicating that only symmetries without inversion centres can take place [33]. Taking into account that the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ band is split into three components (one A₂ and one E species) and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ band is split into three components in $[\text{EuL} \cdot x\text{H}_2\text{O}]$ (one A and two B) and is split in five peaks for $[\text{Eu}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$ (2E and 1A), the symmetry C_{2v} is proposed for $[\text{EuL} \cdot x\text{H}_2\text{O}]$ and C_{4v} for $[\text{Eu}_2(\text{LH})_3 \cdot 2\text{H}_2\text{O}]$ [33–36]. Excitation spectra present a broad band with superimposed europium narrow absorption peaks, for both salts. The broad band is due to ligand (citrate anion) absorption.

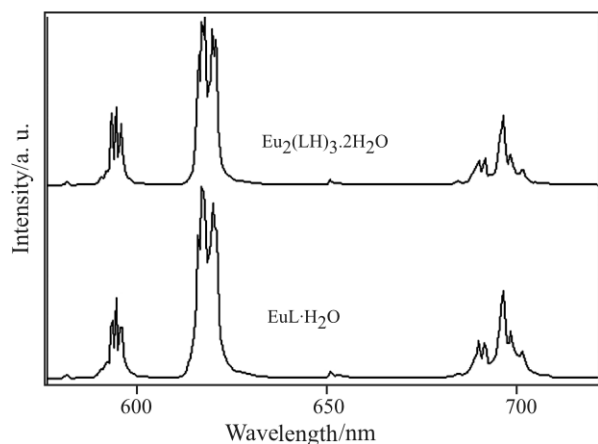


Fig. 2 Emission spectra of $[EuL \cdot xH_2O]$ and $[Eu_2(LH)_3 \cdot 2H_2O]$, at 77 K, $\lambda_{exc}=394$ nm

Thermal decomposition patterns of the two citrate series were investigated by TG, DTG and DTA, in the conditions indicated in the experimental chapter for both $[LnL \cdot xH_2O]$ and $[Ln_2(LH)_3 \cdot 2H_2O]$. These curves present four distinct steps, with the exception of cerium, as discussed below. Figure 3 shows TG, DTA, DTG of 1:1 and 2:3 europium citrates as examples.

$[LnL \cdot xH_2O]$

In the first step (Fig. 3a) it can be observed one endothermic mass loss at around 298 K, attributed to adsorbed water elimination. In the second step, at about 493 K, there is another endothermic mass loss attributed to both crystallization water evolution and citrate dehydration. The water amounts were variable depending on each lanthanide [12]. The products were suggested to be lanthanide itaconates and itaconate anhydride. In a third step, two strong exothermic peaks were attributed to oxidation of itaconate anhydrides and itaconates to lanthanide carbonates [28, 37].

The fourth step is the decomposition of lanthanide carbonates. This decomposition can proceed by five different thermal reactions with the same intermediate, oxycarbonate, and lanthanide oxides as final products, as shown in Fig. 4 [37–41]. Ln_2CO_3 and $Ln_2O(CO_3)_2$ were identified by IR spectroscopy and mass losses.

$[Ln_2(LH)_3 \cdot 2H_2O]$

This series has a somewhat different decomposition pattern (Fig. 3b). In step one, at around 393 K, one endothermic process and the mass loss evidence elimination of two water molecules per minimal formula. Step two shows two convoluted mass losses. They are one endothermic and one exothermic process, respectively. DTG shows two convoluted peaks and DTA shows a very broad and asymmetric endothermic resulting band. The products were suggested to be

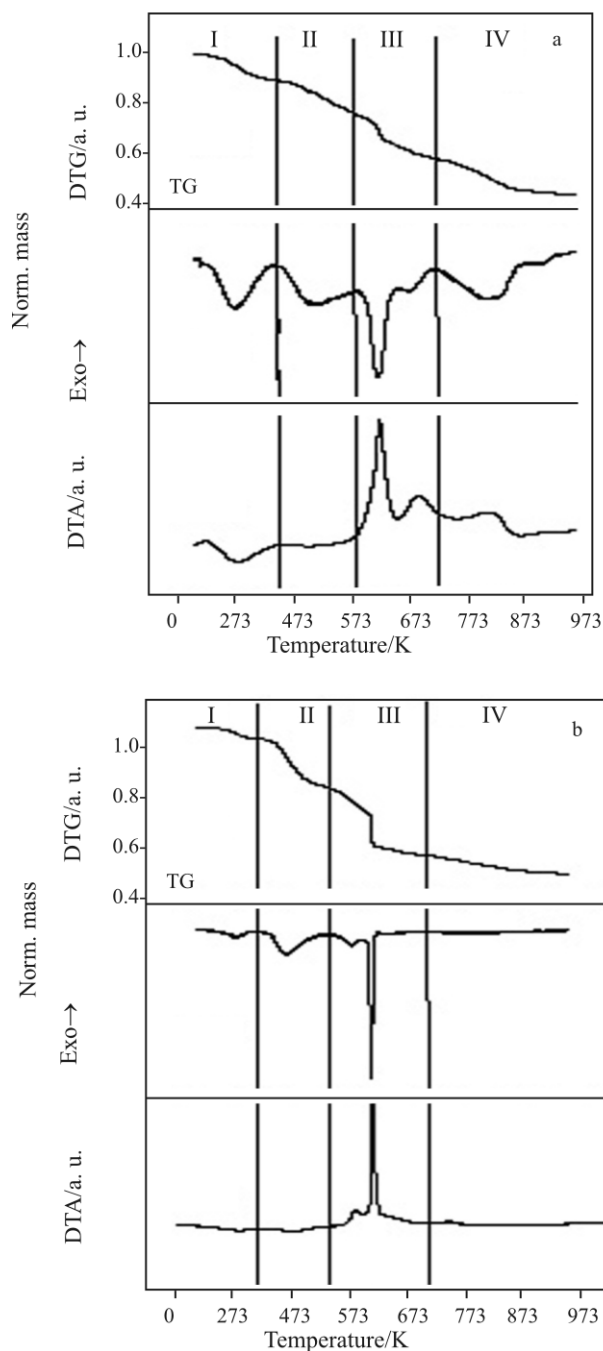


Fig. 3 TG, DTG and DTA curves of a – $[EuL \cdot xH_2O]$ and b – $[Eu_2(LH)_3 \cdot 2H_2O]$

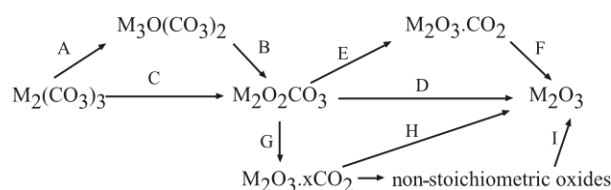


Fig. 4 Thermal decomposition scheme of lanthanide(III) carbonates [Apud 38]

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Table 5 Results of TG analysis for [LnL·xH₂O]

Steps	I	II	III	IV	total	Ln/%	L/%	H ₂ O/%	Obs. stoichiometry/%			
						exp.	exp.	exp.	Ln ³⁺	L	H ₂ O	
La	Temp./K	373	493	571	813	–	33.8	45.0	21.8	1.0	1.0	5.1
	Calc./%	10.0	20.0	18.0	14.7	61						
	Exper./%	10.0	19.5	18.4	13.8	61.7						
Ce	Temp./K	373	505				38.7	52.2	8.9	1.0	1.0	1.8
	Calc./%	9.1	52.4			61.5						
	Exper./%	9.4	54.2			63.6						
Pr	Temp./K	373	480	610	–		36.9	49.5	13.6	1.0 :	1.0:	2.8
	Calc./%	8.6	19.6	36.5	–	64.7						
	Exper./%	8.6	19.3	33.4	–	61.3						
Nd	Temp./K	371	482	608	784		38.9	50.9	10.2	1.0	1.0	2.1
	Calc./%	7.09	13.8	20.7	15.9	57.5						
	Exper./%	7.09	13.2	21.2	16.4	57.9						
Sm	Temp./K	373	499	617	803		39.0	49.0	11.9	1.0	1.0	2.5
	Calc./%	8.92	13.4	19.6	15.9	57.8						
	Exper./%	8.92	13.2	20.0	14.8	56.9						
Eu	Temp./K	373	493	617	808		39.8	49.7	10.4	1.0	1.0	2.2
	Calc./%	10.0	12.0	19.5	15.9	53.6						
	Exper./%	10.0	12.1	19.5	14.3	55.9						

Table 6 Results of TG analysis for [Ln₂(LH)₃·2H₂O]

Steps	I	II	III	IV	total	Obs. stoichiometry/%			
						Ln	LH	H ₂ O	
La	Temp./K	392	559	633					
	Calc./%	4.1	22.81	37.7	62.8	32.7	64.4	3.9	
	Exper./%	4.5	21.2	36.5	62.2				
Ce	Temp./K	395	511						
	Calc./%	3.0	59.3		61.0	32.8	64.1	3.8	
	Exper./%	3.9	60.8		63.4				
Pr	Temp./K	397	546	610	787				
	Calc./%	4.0	22.3	30.0	5.1	62.7	32.1	62.8	5.0
	Exper./%	4.3	22.2	31.0	5.7	63.3			
Nd	Temp./K	400	550	608	784				
	Calc./%	4.0	22.1	29.3	5.1	62.1	32.4	63.5	3.6
	Exper./%	3.9	22.6	30.1	4.0	61.6			
Sm	Temp./K	386	459	650	836				
	Calc./%	4.0	22.2	28.7	5.2	61.1	33.2	62.2	4.5
	Exper./%	4.8	24.6	27.5	4.9	61.8			
Eu	Temp./K	383	462	571	814				
	Calc./%	4.0	21.8	27.3	5.0	61.1	33.4	62.0	4.5
	Exper./%	5.5	22.7	28.4	62.3				

lanthanide itaconates. Step three shows two mass losses, both exothermic, attributed to the sequential formation of lanthanide oxalate and oxycarbonate. FTIR spectra could identify only the oxycarbonate, due mainly to technical limitations [41, 42].

The fourth step is decomposition of oxycarbonates. They decompose in a very broad and slightly exothermic process yielding lanthanides oxides as final products, as follows: La_2O_3 , CeO_2 , Pr_6O_{11} , Nd_2O_3 , Sm_2O_3 and Eu_2O_3 . These same final products are observed for $[\text{LnL}\cdot x\text{H}_2\text{O}]$.

Tables 5 and 6 present all data relevant to thermal analysis of $[\text{LnL}\cdot x\text{H}_2\text{O}]$ and $[\text{Ln}_2(\text{LH})_3\cdot 2\text{H}_2\text{O}]$, respectively.

Cerium compounds

Cerium compounds behave rather differently with respect to other salts. They loose water at around 393 K; and at ca. 503 K they decompose totally to cerium oxide, CeO_2 , in only one step, as shown in Tables 5 and 6. This is due to the $\text{Ce}^{3+}/\text{Ce}^{4+}$ variable oxidation state, which makes cerium compounds good catalysts for organic compounds combustion [43, 44].

On the other hand, $[\text{PrL}\cdot x\text{H}_2\text{O}]$ and $[\text{La}_2(\text{LH})_3\cdot 2\text{H}_2\text{O}]$ can fit the four-step decomposition scheme, but steps 3 and 4 are convoluted.

The final products are always lanthanide oxides, as mentioned above. They were characterized by X-ray powder diffraction patterns, presenting the usual crystalline habits. The morphology of the oxides generated from $[\text{LnL}\cdot x\text{H}_2\text{O}]$ are strikingly different from the oxides generated from $[\text{Ln}_2(\text{LH})_3\cdot 2\text{H}_2\text{O}]$. We have evidences that point out the influence of the precursor morphology in the final products properties. This study is currently under way in our laboratory.

Conclusions

Two series of lanthanide citrate salts were synthesized and characterized. Their thermal decomposition processes are different and both can fit four-step decomposition patterns. Cerium citrates decompose in only one step and at lower temperature with respect to the other lanthanide citrates. In all cases the final products are lanthanide oxides, with morphologies related to the respective precursor salts.

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References

- 1 F. H. Spedding, A. F. Voigt, E. M. Gladrow, N. R. Sleight, J. E. Powell, J. M. Wright, T. A. Butler and P. Figard, *J. Am. Chem. Soc.*, 69 (1947) 2786.
- 2 F. H. Spedding, E. I. Fulmer, T. A. Butler, E. M. Gladrow, M. Gobush, P. E. Porter, J. E. Powell and J. M. Wright, *J. Am. Chem. Soc.*, 69 (1947) 2812.
- 3 F. H. Spedding, E. I. Fulmer, J. E. Powell and T. A. Butler, *J. Am. Chem. Soc.*, 72 (1950) 2354.
- 4 F. H. Spedding, E. I. Fulmer, J. E. Powell, T. A. Butler and I. S. Yaffe, *J. Am. Chem. Soc.*, 73 (1951) 4840.
- 5 J. A. Marinsky and J. X. Khym, Oak Ridge Natl. Lab., Oak Ridge, TN, National Nuclear Energy Series, Manhattan Project Technical Section, Division 4: Plutonium Project (1951), 9 (Radiochem. Studies: The Fission Products, Book 3), 1747.
- 6 E. I. Onstott, *J. Am. Chem. Soc.*, 81 (1959) 4451.
- 7 D. B. James, J. E. Powell and H. Spedding, *J. Inorg. Nucl. Chem.*, 19 (1961) 133.
- 8 N. A. Skorik, V. V. Serebrennikov and T. Tomskogo, *Gos. Univ. Ser. Khim.*, 157 (1963) 307.
- 9 Y. L. Juncai, T. Z. Zili and D. Shiming, *H. Kexue*, 26 (2005) 169.
- 10 V. I. Spitsyn, L. I. Martynenko, Z. M. Rivina, K. N. Rivin, N. A. Dobrynina and A. V. Nemukhin, *Doklady Akademii Nauk SSSR*, 179 (1968) 1348.
- 11 A. Ohyoshi, E. Ohyoshi, H. Ono and S. Yamakawa, *J. Inorg. Nucl. Chem.*, 34 (1972) 1955.
- 12 V. Khraov, V. G. Egorova and A. Bolshakov, *F. Mat. Fiz. Khim.*, 7 (1973) 174.
- 13 L. Spaulding and H. G. Brittain, *J. Lum.*, 28 (1983) 385.
- 14 M. Popa and M. Kakihana, *J. Therm. Anal. Cal.*, 65 (2001) 281.
- 15 M. P. Pechini, U.S. Pat. No. 3, 231, 328, (1966).
- 16 R. S. M. Silva, C. L. O. Miranda, M. R. C. Santos, S. J. G. Lima, L. E. B. Soledade, E. Longo, C. A. Paskocimas, A. G. Souza and I. M. G. Santos, *J. Therm. Anal. Cal.*, 87 (2007) 753.
- 17 M. E. Davis, *Nature*, 417 (2002) 813.
- 18 E. Tsuchida and K. Oyaizu, *Coord. Chem. Rev.*, 237 (2003) 213.
- 19 C. Skovic, B. Colette, K. Euan, W. E. Streib, K. Foltling, J. C. Bollinger, D. N. Hendrickson and G. J. Christou, *J. Am. Chem. Soc.*, 124 (2002) 3725.
- 20 M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, O'Keeffe and M. O. M. Yaghi, *Science*, 295 (2002) 469.
- 21 C. R. Finn and J. Zubieta, *Inorg. Chem.*, 40 (2001) 2466.
- 22 S. Feng and R. Xu, *Acc. Chem. Res.*, 34 (2001) 239.
- 23 L. Pan, N. Zheng, Y. Wu, S. Han, R. Yang, X. Huang and J. Li, *Inorg. Chem.*, 40 (2001) 828.
- 24 S. Neogi and K. Bharadwaj, *Polyhedron*, 25 (2006) 1491.
- 25 C. W. Yount, D. M. Loveless and S. L. Craig, *J. Am. Chem. Soc.*, 127 (2005) 14488.
- 26 R. Baggio and M. Perec, *Inorg. Chem.*, 43 (2004) 6965.
- 27 W. C. Yount, D. M. Loveless and S. L. Craig, *Inorg. Chem.*, 127 (2005) 14489.
- 28 G. Vanhoylanda, J. Pagnaera, J. D'Haenb, S. Mullensa and S. J. Mullensa, *J. Solid State Chem.*, 178 (2005) 166.
- 29 R. Baggio and M. Perec, *Inorg. Chem.*, 43 (2004) 6965.
- 30 R. Baggio, R. Calvo, M. T. Garland, O. Pena, M. Perec and A. Rizzi, *Inorg. Chem.*, 44 (2005) 8979.

1:1 AND 2:3 LANTHANIDE(III) CITRATES

- 31 M. Wu, W. Li, M. Zhang and K. Tao, *Acta Physico-Chimica Sinica*, 23 (2007) 1311.
- 32 G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, 33 (1980) 227.
- 33 P. Porcher and P. Caro, *Semin. Chim. d'État Solide*, 5 (1972) 141.
- 34 J. H. Forsberg, *Coord. Chem. Rev.*, 10 (1973) 195.
- 35 J. C. G. Bünzli and G. R. Choppin, *Lanthanide Probes in Life, Chemical and Earth Sciences*, Elsevier, Amsterdam 1989, p. 219.
- 36 M. F. P. da Silva, J. Zukerman-Schpector, G. Vicentini and P. C. Isolani, *Inorg. Chim. Acta*, 358 (2005) 796.
- 37 D. Hennings and W. Mayr, *J. Solid State Chem.*, 26 (1978) 329.
- 38 G. A. M. Hussein, *J. Anal. Appl. Pyrolysis*, 37 (1996) 111.
- 39 A. F. Clitford and P. A. Faeth, *Rare Earth Research II*, Gordon and Breach, New York 1963, p. 36.
- 40 R. L. N. Etry, S. R. Yoganarasimhan, P. L. Mehrorta and C. N. R. Rao, *J. Inorg. Nucl. Chem.*, 2 (1966) 1165.
- 41 L. M. D'Assunção, I. Giolito and M. Ionashiro, *Thermochim. Acta*, 137 (1989) 319.
- 42 C. Joseph, G. Varghese and M. A. Ittyachen, *J. Thermal Anal.*, 52 (1998) 517.
- 43 N. Imanaka, T. Masui, Y. Mayama and K. Koyabu, *J. Solid State Chem.*, (2005) 3601.
- 44 K. Krishna, A. Bueno-López, M. Makkee and J. A. Moulijna, *Appl. Catal. B*, 75 (2007) 189.

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