Journal of Thermal Analysis and Calorimetry, Vol. 93 (2008) 3, 833–838

COMPARISON OF THERMAL PROPERTIES OF LANTHANIDE TRIMELLITATES PREPARED BY DIFFERENT METHODS

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By diffusion in gel medium new complexes of formulae: $Nd(btc)\cdot 6H_2O$, $Gd(btc)\cdot 4.5H_2O$ and $Er(btc)\cdot 5H_2O$ (where btc= $(C_6H_3(COO)_3^{3-})$ were obtained. Isomorphous compounds were crystallized in the form of globules. During heating in air atmosphere they lose stepwise water molecules and then anhydrous complexes decompose to oxides.

Hydrothermally synthesized polycrystalline lanthanide trimellitates form two groups of isomorphous compounds. The light lanthanides form very stable compounds of the formula $Ln(btc)\cdot nH_2O$ (where *Ln*=Ce–Gd and *n*=0 for Ce; *n*=1 for Gd; *n*=1.5 for La, Pr, Nd; *n*=2 for Eu, Sm). They dehydrate above 250°C and then immediately decomposition process occurs. Heavy lanthanides form complexes of formula $Ln(btc)\cdot nH_2O$ (*Ln*=Dy–Lu). For mostly complexes, dehydration occurs in one step forming stable in wide range temperature compounds. As the final products of thermal decomposition lanthanide oxides are formed.

Keywords: *1,2,4-benzenetricarboxylic acid, lanthanides(III), TG-DTA analysis, X-ray diffraction patterns*

Introduction

Recently, particular interest has been focused on the design and synthesis of metal-organic materials for their fascinating structures and favourable properties. They have various applications in heterogeneous catalysis, molecular recognization, ion exchange, gas storage, etc. [1–3]. Metal coordination polymers are built from metal centers and bridging ligand, which form rigid multidimensional structures with network of open channels.

Benzenopolycarboxylate ligands are widely employed as building blocks in the construction of microporous coordination polymers [4–7]. Also 1,2,4-benzenetricarboxylic acid (trimellitic acid) can be used to construction of new coordination polymers with potential microporous properties. Previously, I have reported results of investigations of lanthanide 1,2,4-benzenetricarboxylates and 1,2,3-benzenetricarboxylates obtained by classical method [8, 9]. In order to synthesis of complexes in the form of monocrystals with purpose of structure investigations, two further methods have been applied.

This paper deals with the synthesis and thermal properties of lanthanide trimellitates obtained by hydrothermally method and crystallization in gel medium.

Experimental

Materials

1,2,4-benzenetricarboxylic acid (99%), sodium metasilicate and lanthanide(III) nitrates (99.9%) were purchased from Aldrich. Glacial acetic acid and ammonia solution were purchased from POCH Lublin. Lanthanide chlorides were prepared from lanthanide oxides (Sigma, 99.9%).

Methods

Hydrothermal synthesis

The stoichiometric amounts of solid trimellitic acid, aqueous solution of lanthanide chloride and 50 mL of distilled water were filled in Teflon-lined autoclave at 160°C under autogeneous pressure. After 5 days autoclaves were cooled with a rate of $5°C\ h^{-1}$ and the polycrystalline solid products were separated by filtration.

Anhydrous lutetium trimellitate was obtained by heating of $Lu(btc)\cdot 2H_2O$ at 120°C during 1 h.

Crystallization in gel medium

U-tube technique was used. The silica gel was used as a growth medium. The silica gel was prepared by mixing glacial acetic acid with solution of sodium meta-silicate. Aqueous solutions of selected lanthanide nitrate (neodymium, gadolinium and erbium and

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1388–6150/$20.00

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ammonium trimellitate were poured over the gel in different arms of U-tube. After several weeks complexes in the form of the globules were separated from the gel media and washed by distilled water.

The contents of C and H were obtained by means of elemental analysis using a Perkin-Elmer CHN 2400 apparatus. The infrared spectra of the lanthanide(III) complexes and 1,2,4-benzenetricarboxylic acid were recorded in KBr discs on a SPECORD M80 spectrophotometer over the range 4000–400 cm^{-1}. The X-ray powder diffractions of the studied complexes were recorded on a HZG 4 diffractometer, using Ni filtered CuK_{α} radiations. Measurements were taken over the range of 2θ= 5–70°.

Thermal analysis of prepared complexes was carried out by the TG-DTA method using SETSYS 16/18 analyser (Setaram). Samples (about 7 mg) were heated in ceramic crucible up to 700–800°C at a heating rate of 10°C min^{-1} in dynamic air atmosphere (v=0.75 $dm^3 h^{-1}$).

Results and discussion

Complexes of lanthanide(III) with 1,2,4-benzenetricarboxylic acid were prepared by hydrothermal method and crystallization in gel medium (Table 1). Unfortunately, in spite of applications of two new methods of synthesis, the obtaining of complexes in the form of monocrystals was failed.

Table 1 Elemental analysis data of lanthanide(III) 1,2,4-benzenetricarboxylates

Complex	C/%		H/%	
	calc.	found	calc.	found
$Nd(btc)\cdot 6H_2O$	23.52	23.10	3.27	3.19
$Gd(btc)\cdot 4.5H_2O$	26.78	26.22	2.96	3.10
$Er(btc)\cdot 5H_2O$	25.69	25.10	3.09	2.94
$La(btc)\cdot 1.5H_2O$	29.16	28.80	1.75	1.65
Ce(btc)	33.43	32.98	0.93	0.90
$Pr(btc)\cdot 1.5H_2O$	31.31	30.86	1.74	1.60
$Nd(btc)\cdot 1.5H_2O$	31.02	30.77	1.75	1.85
$Sm(btc)\cdot 2H_2O$	29.88	29.55	1.94	1.82
$Eu(btc)\cdot 2H_2O$	29.75	29.31	1.93	1.83
$Gd(btc)\cdot H_2O$	30.48	30.80	1.41	1.35
$Dy(btc)\cdot 2H_2O$	28.92	28.08	1.87	1.77
$Ho(btc)\cdot 2H_2O$	28.73	28.43	1.86	1.80
$Er(btc)\cdot 2H_2O$	28.55	28.50	1.85	1.71
$Tm(btc)\cdot 2H_2O$	28.43	28.05	1.84	1.77
$Yb(btc)\cdot 2H_2O$	28.13	28.51	1.83	1.69
$Lu(btc)\cdot 2H_2O$	27.98	26.67	1.81	1.75

btc=$C_6H_3(COO)_3^{3-}$

By diffusion of substracts in silica gel, three complexes of the formulae: $Nd(btc)\cdot 6H_2O$, $Gd(btc)\cdot 4.5H_2O$ and $Er(btc)\cdot 5H_2O$ (where btc= $(C_6H_3(COO)_3^{3-})$ were obtained. The compounds were crystallized in the form of globular crystallites of color characteristic for lanthanide ions. The complexes are isomorphous as arised from their X-ray powder diffraction patterns.

The IR spectra of the complexes (Table 2) show sharp absorption band at 3640 cm^{-1} assigned to stretching vibrations ν_{OH} of coordination water molecules [10]. The broad band with maximum at 3432 cm^{-1} is due to stretching vibrations ν_{OH} of hydrogen bonded water molecules. The complexation process of lanthanide ions by trimellitate ligand is confirmed by the IR spectra of the complexes. The spectra of all compounds show intense bands with maximum at 1536 cm^{-1} assigned to the asymmetric stretching vibrations of carboxylate groups $\nu_{as(COO)}$. The symmetric stretching vibrations of carboxylate groups $\nu_{sym(COO)}$ are located at 1408, 1412 and 1416 cm^{-1}, respectively for complexes of Nd, Gd and Er complexes. The positions of these characteristic bands indicate the existence of similar coordination mode in the complexes. The application of magnitude of Δν as spectral criterion for the prediction of the mode of carboxylate bonding in the case of lanthanide trimellitates is impossible because sodium salt of 1,2,4-benzenetricarboxylic acid do not has ionic character as can be clearly seen from the crystal structure [11]. For achieving the coordination number 9 or 8 (for heavier lanthanides) some water molecules and carboxylate oxygen atoms form coordination environments of Ln(III) ions. Moreover, positions of carboxylate groups in trimellitate molecule force the bridging or bridging–chelating character of COO groups.

The studied compounds have been investigated by thermal methods in the temperature range 30–800°C. The results showed that their thermal behaviors are similar and the thermal data are summarized in Table 3. Heating of the compounds above 40°C resulting in dehydration process, which as can be seen from Figs 1–3 occurs in two stages. The first mass loss accompanied by endothermic effect (at 171.3, 185.9, 172.7°C for complexes of Nd, Gd and Er, respectively) corresponds to the release of weaker bonding water molecules yielding the unstable hydrated lanthanide(III) trimellitate. The second step of dehydration corresponds to loss of remaining water molecules resulting in anhydrous complex formation. Heating of anhydrous complexes causes decomposition. In oxidative air atmosphere degradation of trimellitic ligand is accompanied by strong exothermic effect connected with burning of organic ligand. The solid residues obtained during thermal decompo-

Table 2 Most characteristic IR bands (cm^{-1}) of lanthanide 1,2,4-benzenetricarboxylates prepared by crystallization in gel medium and hydrothermal method

	ν_{OH}	$\nu_{as(COO)}$	$\nu_{sym(COO)}$
Nd(btc)·6H_2O	3800–2600, 3640	1536	1408
Gd(btc)·4.5H_2O	3800–2600, 3640	1536	1412
Er(btc)·5H_2O	3800–2600, 3640	1536	1416
La(btc)·1.5H_2O	3700–2600	1530, 1504	1440, 1404
Ce(btc)	3700–2600	1530, 1504	1440, 1404
Pr(btc)·1.5H_2O	3700–2700	1530, 1504	1440, 1404
Nd(btc)·1.5H_2O	3800–2600	15730, 1504	1440, 1404
Sm(btc)·2H_2O	3700–2700	1530, 1508	1440, 1404
Eu(btc)·2H_2O	3700–2700	1530, 1504	1440, 1400
Gd(btc)·H_2O	3700–2800	1530, 1508	1440, 1408
Dy(btc)·2H_2O	3700–2800	1575, 1536	1432, 1420
Ho(btc)·2H_2O	3600–2800	1572, 1540	1430, 1408
Er(btc)·2H_2O	3600–2800	1572, 1536	1420
Tm(btc)·2H_2O	3600–2900	1560, 1536	1420
Yb(btc)·2H_2O	3800–2600	1560, 1540	1420
Lu(btc)·2H_2O	3700–2600	1572, 1536	1420

btc=$C_6H_3(COO)_3^{3-}$, ν – stretching vibrations

Table 3 Thermal decomposition data of lanthanide trimellitates obtained in a gel medium

Complex	T_1/°C	nH$_2$O	T_{endo}/°C	Mass loss/%		T_2/°C	Mass loss/%	
				found	calc.		found	calc.
Nd(btc)·6H_2O	45–180 180–340	–5H_2O –H_2O	171.3	17.59 4.10	18.17 3.63	440–770	64.73	63.34
Gd(btc)·4.5H_2O	60–200 200–390	–3.5H_2O H_2O	185.9	13.64 4.36	14.44 3.96	470–630	57.81	58.46
Er(btc)·5H_2O	40–185 185–300	–3.5H_2O –1.5H_2O	172.7	13.23 6.15	13.57 5.82	470–600	58.21	58.80

btc=$C_6H_3(COO)_3^{3-}$; T_1 – temperature range of dehydration; T_2 – temperature range of decomposition of anhydrous complex

sition of lanthanide(III) 1,2,4-benzenetricarboxylate complexes are suitable metal oxides: Nd_2O_3, Gd_2O_3 and Er_2O_3. The temperature of oxides formation is in the range 600–770°C.

In hydrothermal synthesis two groups of polycrystalline powders of lanthanide(III) trimellitates have been obtained. The lanthanides from La(III) to Gd(III) form compounds (group I) with 1,2,4-benzenetricarboxylic acid of the formula Ln(btc)·nH$_2$O (where *Ln*=Ce-Gd and n=0 for Ce; n=1 for Gd; n=1.5 for La, Pr, Nd; n=2 for Eu, Sm). The lanthanides from Dy(III) to Lu(III) form 1,2,4-benzenetricarboxylates (group II) of the formula Ln(btc)·2H_2O (where btc=($C_6H_3(COO)_3^{3-}$)). Some results concerning complexes of cerium, neodymium and erbium have been presented earlier [12]. The X-ray pattern diffractions indicate that studied complexes are isomorphous in groups I and II.

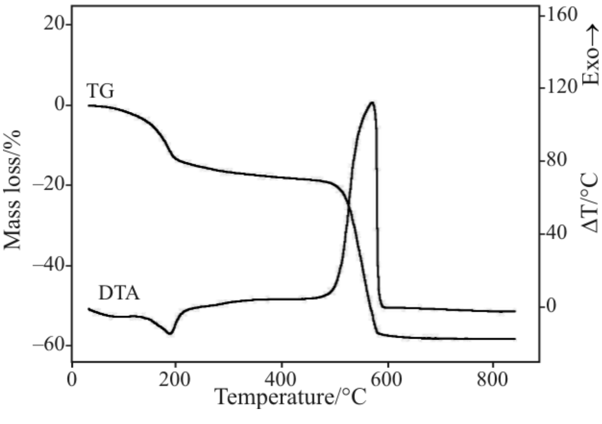

Fig. 1 TG and DTA curves of thermal decomposition of Nd(btc)·6H_2O (crystallization in gel medium)

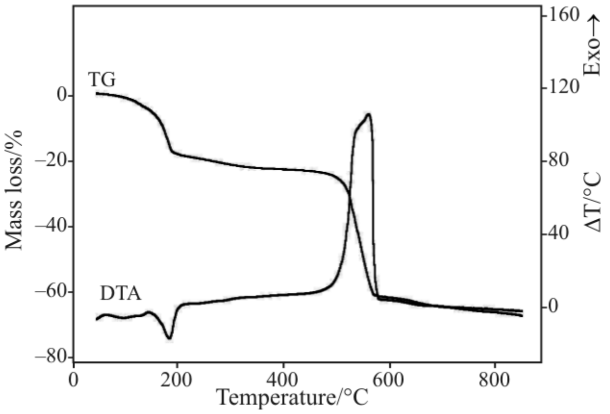

Fig. 2 TG and DTA curves of thermal decomposition of Gd(btc)·4.5H_2O (crystallization in gel medium)

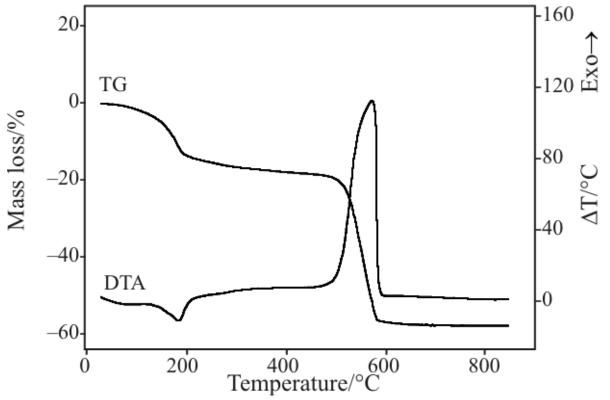

Fig. 3 TG and DTA curves of thermal decomposition of Er(btc)·5H_2O (crystallization in gel medium)

The IR spectra of the complexes of group I are characterized by broad band in the range 3800–2600 with maximum at 3350 cm^{-1} due to stretching vibrations of hydrogen bonded hydroxyl group from water molecules. Deprotonation process of trimellitic acid in the studied complexes is confirmed by lack of stretching vibrations of carbonyl group at 1696 cm^{-1}. The IR spectra of group I complexes show splitted bands derived from asymmetric and symmetric stretching vibrations of carboxylate groups which appear at 1530, 1504 and 1440, 1404 cm^{-1}, respectively. On the other hand for complexes of group II (without complexes of Ho and Dy), bands from asymmetric and symmetric stretching vibrations of carboxylate groups are at about 1560, 1540 and 1420 cm^{-1}, respectively (Table 2). Splitting of absorption bands derived from stretching vibrations of carboxylate groups may be attributed to the different coordination modes of particular COO groups. Such conclusion is confirmed by the analysis of the crystal structure and IR data of the sodium trimellitate tetrahydrate. In this compound, carboxylate groups which coordinates sodium atoms in: tetradentate-bridging, tetradentate bridging-chelating and hexadentate chelating-bridging fashions give splitting stretching absorption bands of COO group on the IR spectrum.

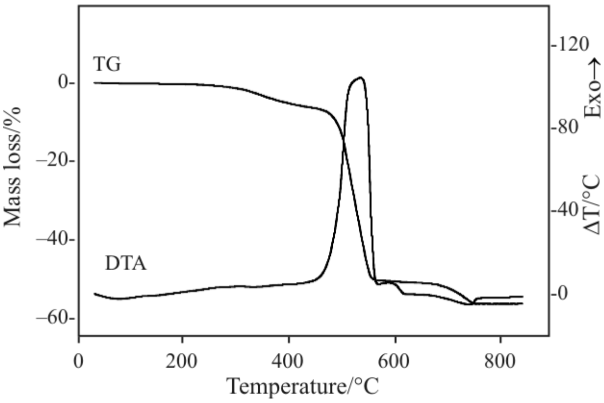

Fig. 4 TG and DTA curves of thermal decomposition of La(btc)·1.5H_2O (hydrothermal method)

Further confirmation of differences between trimellitates of light and heavy lanthanides are results from thermal investigations. The light lanthanides form complexes that are characterized by high thermal stability in the air atmosphere as can be seen from Fig. 4. The thermal decomposition of the complexes begins in the range 250–350°C (Table 4). Above this temperature, the mass loss connected with dehydration process is observed. Anhydrous compounds are unstable, and further heating resulting in the decomposition to the suitable oxides. As final solid products suitable lanthanide oxides have been obtained (Ln_2O_3, CeO_2, Pr_6O_{11}).

High temperature of dehydration process indicates strong bonding of water molecules. It may suggest that water molecules are directly connected with lanthanide ions and they are in the inner coordination sphere of metal ion. Such behavior of water molecules is observed in the lanthanide trimellitates from La to Gd (except Ce which is anhydrous). This conclusion is confirmed by the work of Ferey [13] who presented crystal structure of praseodymium 1,2,4-benzenetrimellitate monohydrate. In this isomorphous complex with the investigated compounds, the water molecule occupies terminal position in the square antiprism.

The trimellitates of the heavier lanthanides (from Dy to Lu) form dihydrate complexes under hydrothermal conditions (Fig. 5). They show different behavior during dehydration process. The complex of dysprosium losses water molecules in the wide temperature range 44–200°C. On the other hand dehydration process of the holmium compound occurs in the two stages. The remaining complexes (from Er to Lu) form stable dihydrate compounds. The investigated complexes are stable up to about 120°C. Further heating resulting in the removing of the two water molecules from the complex structure. It is assumed that

Table 4 Thermal decomposition data of lanthanide trimellitates obtained under hydrothermal condition

Complex	T_1/°C	Mass loss/%		T_2/°C	Mass loss/%		Product
		found	calc.		found	calc.	
La(btc)·1.5H_2O	250–460	7.02	7.28	460–760	56.74	53.33	La_2O_3
Ce(btc)	–	–	–	250–520	53.20	50.43	CeO_2
Pr(btc)·1.5H_2O	300–470	6.98	7.20	470–580	58.24	54.61	Pr_6O_{11}
Nd(btc)·1.5H_2O	260–470	7.51	6.93	470–580	53.62	56.83	Nd_2O_3
Sm(btc)·2H_2O	350–510	9.20	9.15	510–650	56.00	55.69	Sm_2O_3
Eu(btc)·2H_2O	250–400	8.90	9.15	400–700	54.55	55.46	Eu_2O_3
Gd(btc)·H_2O	330–470	4.52	4.71	470–650	52.90	52.60	Gd_2O_3
Dy(btc)·2H_2O	44–200	8.60	8.88	460–660	55.37	54.02	Dy_2O_3
Ho(btc)·2H_2O	150–200 300–500	2.05 6.50	2.21 6.61	500–610	53.66	53.66	Ho_2O_3
Er(btc)·2H_2O	134–250	8.50	8.78	460–650	54.50	53.41	Er_2O_3
Tm(btc)·2H_2O	132–230	8.55	8.74	470–600	53.17	53.18	Tm_2O_3
Yb(btc)·2H_2O	126–200	8.63	8.61	480–650	52.55	52.41	Yb_2O_3
Lu(btc)·2H_2O	126–200	8.62	8.65	460–650	52.36	53.66	Lu_2O_3

btc=$C_6H_3(COO)_3^{3-}$; T_1 – temperature range of dehydration; T_2 – temperature range of decomposition of anhydrous complex

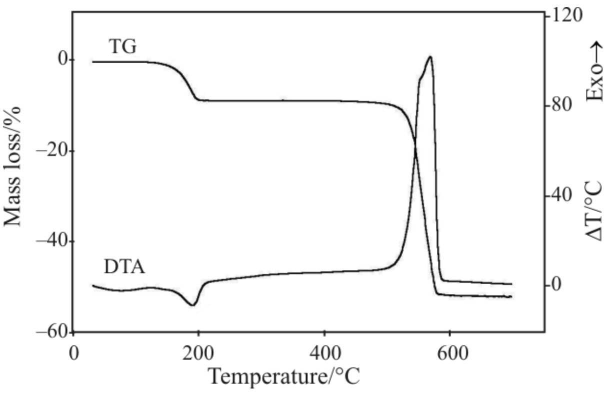

Fig. 5 TG and DTA curves of thermal decomposition of Lu(btc)·2H_2O (hydrothermal method)

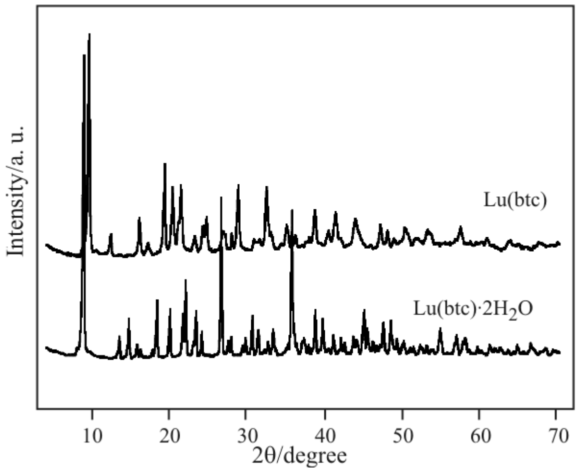

Fig. 6 XRD patterns of Lu(btc)·2H_2O and Lu (btc)

these water molecules are directly bonded with metal atoms being in inner coordination sphere. This conclusion is confirmed by X-ray diffraction investigations of powder europium-doped yttrium trimellitate dihydrate [14]. Anhydrous complexes are stable in wide temperature range (about 200–460°C). The next distinct mass loss observed on the TG curves is associated with degradation and combustion of 1,2,4-benzenetricarboxylate ligand. These reactions occur in the temperature range 460–650°C and strong exothermic effects observed at DTA curves accompany them. As the final products of thermal decomposition metal oxides are observed (Ln_2O_3) [15]. Thermal data are summarized in Table 4.

Additionally, diffraction pattern for anhydrous lutetium complex has been recorded. As can be seen from Fig. 6, this complex also appears in the crystalline form. This fact point to the presence of rigid framework in the studied complexes of heavy lanthanides. These results are very promising for further investigations of these compounds under their microporous properties.

Conclusions

- Compounds obtained by crystallization in gel medium are more hydrated in comparison to hydrothermally prepared complexes.
- Thermal behavior of complexes of light as well as heavy lanthanides is very similar in the case of compounds obtained in gel medium.

- Dehydration process of compounds obtained from crystallization occurs gradually in two steps.
- Hydrothermally obtained lanthanide trimellitates contain less amount of water molecules in comparison to complexes obtained by diffusion.
- The light lanthanide complexes hydrothermally prepared lose water molecules above 250°C after that directly decomposition process occurs.
- The heavy lanthanide trimellitates lose water molecules above 120°C forming in wide range temperature stable anhydrous complexes.
- The trimellitates of heavy lanthanides obtained by hydrothermal method are more suitable for further investigations of sorption properties due to the crystalline form of dehydrated compounds that point to present of stable framework.

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DOI: 10.1007/s10973-008-9203-z