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THERMAL AND SPECTROSCOPIC INVESTIGATIONS OF NEW LANTHANIDE COMPLEXES WITH 1,2,4-BENZENETRICARBOXYLIC ACID

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The new 1,2,4-benzenetricarboxylates of lanthanide(III) of the formula Ln(btc)$\cdot n$H$_2$O, where *btc* is 1,2,4-benzenetricarboxylate; *Ln* is La–Lu, and n=2 for Ce; n=3 for La, Yb, Lu; and n=4 for Pr–Tm were prepared and characterized by elemental analysis, infrared spectra and X-ray diffraction patterns. Polycrystalline complexes are isotructural in the two groups: La–Tm and Yb, Lu. IR spectra of the complexes show that all carboxylate groups from 1,2,4-benzenetricarboxylate ligands are engaged in coordination of lanthanide atoms.

The thermal analysis of the investigated complexes in air atmosphere was carried out by means of simultaneous TG-DTA technique. The complexes are stable up to about 30°C but further heating leads to stepwise dehydration. Next, anhydrous complexes decompose to corresponding oxides. The combined TG-FTIR technique was employed to study of decomposition pathway of the investigated complexes.

Keywords: *1,2,4-benzenetricarboxylic acid, dehydration, lanthanide complexes, TG-DTA, TG-FTIR*

Introduction

In recent years, porous coordination polymers are intensively studied for their fascinating structural properties and potential applications in a lot of fields such as catalysis, separation at molecular level, gas storage and high-technology optics [1–5]. The metal coordination polymers are constructed by binding of metal ions to bridging multidentate ligands such as bipyridyls [6, 7] or carboxylic acids [8–11]. The metal-ligand coordinate bond and the hydrogen bond between donor and acceptor molecules have both been exploited to generate infinite framework structures. The use of lanthanide ions as central atom for the construction of coordination polymers is more difficult than their transition metal analogues for the high and variable coordination number and flexible coordination geometry of lanthanide ions [12].

Among carboxylate ligands, aromatic symmetrical polycarboxylate acids such as: 1,4-benzenedicarboxylic acid [13, 14]; 1,3,5-benzenetricarboxylic acid [15–20] and 1,2,4,5-benzenetetracarboxylic [21–24] acid are widely explored to synthesis of high-dimensional metal organic architectures.

Asymmetric ligand such as 1,2,4-benzenetricarboxylic acid (trimellitic acid, H$_3$btc) is also a good candidate for constructing of microporous materials with novel topological features. 1,2,4-benzenetricarboxylate ligand exhibits many coordination modes, which were summarized by Wang *et al*. [23]. Molecule of trimellitic acid may appear as three, four, five or six-dentate ligand. So far, only monocrystals of complexes of transition metals with 1,2,4-benzenetricarboxylic acids were synthesized. In the three-dimensional metal organic coordination polymers of zinc(II) and cobalt(II), btc ligand is hexadentate and all carboxylate groups demonstrate different mode of metal bonding [25, 26]. In the complex of copper(II) with 1,2,4-benzenetricarboxylic acid the carboxylate group in position 1 demonstrate monodentate character while group in position 2 is bidentate-bridging. The carboxylate group in position 4 is not engaged in coordination of copper atom [27].

The complexes of unsymmetrical carboxylate ligands with lanthanides are rather neglected. Only, the structure of 1,2,4-benzenetricarboxylic acid with praseodymium(II) has been determined from X-ray powder diffraction data. In this complex each carboxylate group exhibits a different mode of connection to the rare earth. One carboxylate group is chelating a single Pr atom, one group is bridging two different atoms while the third group is both bridging and chelating two and one praseodymium atom, respectively [28].

This paper deals with the spectroscopic and thermal properties of new 1,2,4-benzenetricarboxylates of lanthanide(III), according to their potential microporous properties.

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Experimental

1,2,4-benzenetricarboxylic acid was purchased from Aldrich (99%). Lanthanide chlorides were prepared from lanthanide oxides (Sigma, 99.9%).

The complexes of lanthanides(III) with 1,2,4-benzenetricarboxylic acid were prepared by adding aqueous ammonium 1,2,4-benzenetricarboxylate solution (pH 5.3) to aqueous solution of lanthanide(III) chloride (pH 4.5) (for cerium complex, nitrate solution was used) heated to 50°C. The precipitates of lanthanide(III) complexes were left for 2 h in solution at 60°C, then filtered off, washed with water and dried at 30°C to constant mass.

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 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 $2\theta=5–70°$.

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 850°C at a heating rate of 10°C min^{-1} in dynamic air atmosphere (v=0.75 $dm^3\ h^{-1}$). To study dehydration process, the samples were heated up to temperature of obtaining of anhydrous compounds with heating rate 2.5°C min^{-1}.

The TG-FTIR coupled measurements have been carried out using a Netzsch TG apparatus coupled with a Bruker FTIR IFS66 spectrophotometer. The samples of about 30 mg were heated up to 950°C at a heating rate of 15°C min^{-1} in flowing argon atmosphere.

Results and discussion

The investigated complexes of lanthanide(III) with 1,2,4-benzenetricarboxylic acid were obtained as polycrystalline powders of characteristic colour for lanthanide(III) ions. Based on analytical (Table 1) and thermogravimetric data their formulae were deduced as: Ln(btc)·$n$$H_2O$ where btc is 1,2,4-benzenetricarboxylate ligand ($C_6H_3(COO)_3^{3-}$); *Ln* is La–Lu, and n=2 for Ce; n=3 for La, Yb and Lu and n=4 for Pr–Tm. The compounds are hardly soluble in water as well as common organic solvents (methanol, ethanol, acetone, dimethyl sulfoxide).

X-ray powder diffraction patterns of the studied complexes confirm their crystalline form. The compounds are isostructural in the two groups: La–Tm and Yb, Lu. Despite of different number of water molecules in the complexes of lanthanum and cerium, they have the same structure as remaining compounds in first isostructural group. Representative X-ray pattern diffractions are shown in Fig. 1.

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

Complex	C/%		H/%	
	calc.	found	calc.	found
La(btc)·3H_2O	27.00	26.49	1.75	2.05
Ce(btc)·2H_2O	28.19	27.56	1.83	1.98
Pr(btc)·4H_2O	25.72	26.42	2.62	2.81
Nd(btc)·4H_2O	25.51	25.23	2.60	2.89
Sm(btc)·4H_2O	25.15	25.24	2.56	2.23
Eu(btc)·4H_2O	25.05	25.00	2.55	2.73
Gd(btc)·4H_2O	24.75	24.03	2.52	2.29
Tb(btc)·4H_2O	24.71	24.93	2.51	2.23
Dy(btc)·4H_2O	24.45	25.04	2.49	2.75
Ho(btc)·4H_2O	24.36	24.95	2.48	2.66
Er(btc)·4H_2O	24.20	24.87	2.46	2.81
Tm(btc)·4H_2O	24.11	24.28	2.45	2.43
Yb(btc)·3H_2O	24.88	24.75	2.07	2.15
Lu(btc)·3H_2O	24.77	24.67	2.06	2.11

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

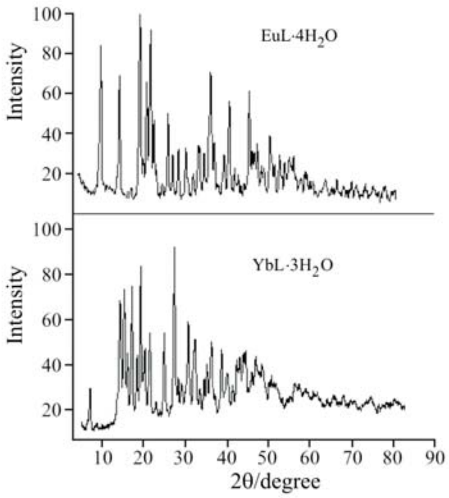

Fig. 1 XRD patterns of europium(III) and ytterbium(III) complexes of 1,2,4-benzenetricarboxylic acid

Spectroscopic analysis

Evidence for complex formation was obtained by comparing the infrared spectra for the free ligand and complexes in the wavenumber region 4000–400 cm^{-1}. The most characteristic bands and their assignments are given in Table 2. All the infrared spectra of the studied complexes are characterized by broad band in the region 3800–2600 cm^{-1} due to presence of

Table 2 Most characteristic IR bands (cm^{-1}) of 1,2,4-benzenetricarboxylic acid and its lanthanide(III) compounds

Complex	ν_{OH}	$\nu_{as(COO)}$	$\nu_{sym(COO)}$	$\beta_{C_{Ar}H}$	$\gamma_{C_{Ar}H}$			
H_3btc	–	–	–	1084	860	776		660
La(btc)·3H_2O	3800–2600	1580, 1528	1404	1080	840	784	740	616
Ce(btc)·2H_2O	3800–2600	1584, 1528	1396	1080	856	776	740	648
Pr(btc)·4H_2O	3800–2600	1580, 1540	1412	1080	840	784	744	672
Nd(btc)·4H_2O	3800–2600	1570, 1536	1412	1080	840	784	744	672
Sm(btc)·4H_2O	3600–2800	1580, 1536	1412	1080	840	788	744	672
Eu(btc)·4H_2O	3800–2600	1580, 1540	1412	1080	840	792	744	672
Gd(btc)·4H_2O	3700–2800	1580, 1536	1412	1080	844	792	744	672
Tb(btc)·4H_2O	3800–2600	1580, 1536	1416	1080	848	792	744	688
Dy(btc)·4H_2O	3600–2800	1580, 1540	1416	1080	848	792	744	680
Ho(btc)·4H_2O	3600–2800	1580, 1540	1416	1080	844	772	744	664
Er(btc)·4H_2O	3800–2600	1580, 1540	1416	1080	848	792	744	680
Tm(btc)·4H_2O	3800–2600	1560, 1540	1420	1080	848	784	740	670
Yb(btc)·3H_2O	3700–3000	1530, 1512	1430, 1416	1080	856	784	740	672
Lu(btc)·3H_2O	3700–3000	1536, 1520	1428, 1410	1080	856	784	740	672

ν – stretching vibrations, β – in-plane bending vibrations, γ – out-of-plane deformation vibrations

stretching vibrations, ν_{OH} of the hydroxyl group in hydrogen bonded water molecules [29]. Only the spectrum of free acid shows strong band at 1696 cm^{-1} driving from stretching vibrations of CO carbonyl group. When coordination of metal atom takes place, this band is replaced by stretching asymmetric and symmetric vibrations of carboxylate group [30]. The absence of $\nu_{C=O}$ band in the IR spectra of the investigated compounds indicates the complete deprotonation of 1,2,4-benzenetricarboxylic acid and participation of all carboxylate groups in Ln binding [31]. The splitted bands driving from asymmetric vibrations of COO groups appear in the range 1584–1512 cm^{-1}. The splitting of carboxylate band is indicative for present of unequivalent carboxylate groups. That point to different mode of lanthanide ions bonding COO groups. Such fact has found the confirmation in the praseodymium(III) 1,2,4-benzenetricarboxylate complex where various modes of coordination were postulated [28]. The stretching symmetric vibrations of carboxylate groups are observed in the wavenumber range 1420–1396 cm^{-1} for complexes from lanthanum to thulium. For complexes of ytterbium and lutetium this band is splitted and absorption peaks are observed at 1430, 1416 and 1428, 1410 cm^{-1}, respectively. The IR spectra of these complexes indicate different manner of metal coordination through carboxylate groups in comparison to remaining complexes. The characteristic bands of benzene ring vibrations are in similar position in comparison to free acid.

Thermal analysis

The investigated lanthanide(III) 1,2,4-benzenetricarboxylates are stable up to about 30°C. Heating of the complexes resulting in multi-stage decomposition (Figs 2 and 3). The scheme of compounds decomposition consists of two general stages. The first one is connected with dehydration process whereas the second stage is related with degradation of anhydrous complexes (Table 3). The greatest differences in the decomposition way of the investigated complexes are observed during release of water molecules (Table 4).

The dehydration process of cerium(III) 1,2,4-benzenetricarboxylate dihydrate occurs in two steps. In each step, one water molecule is lost. Very weak endothermic effects accompany releasing of water molecules at 120 and 260°C, respectively. In effect unstable anhydrous complex is formed which immediately decomposes.

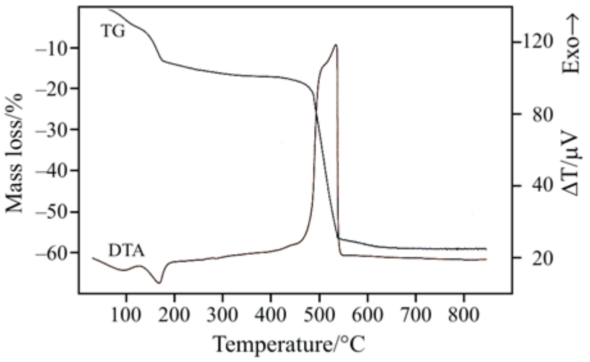

Fig. 2 TG and DTA curves of thermal decomposition of europium(III) 1,2,4-benzenetricarboxylate tetrahydrate

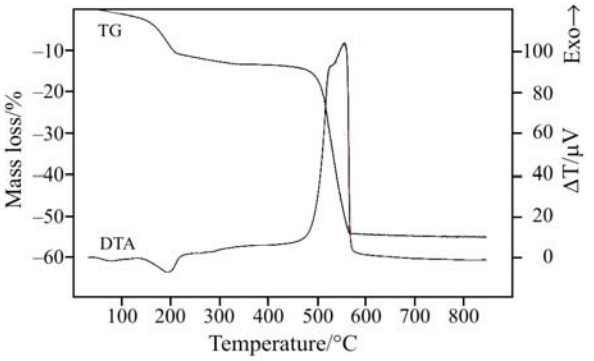

Fig. 3 TG and DTA curves of thermal decomposition of ytterbium(III) 1,2,4-benzenetricarboxylate trihydrate

Dehydration process of trihydrate lanthanum(III) complex proceeds in two following steps. The first mass loss accompanied by endothermic effect at 100°C, corresponds to the release of two water molecules yielding the unstable hydrate 1,2,4-benzenetricarboxylate lanthanum(III). The second step of dehydration process is connected only with hardly distinguishable endothermic effect at about 200°C.

Trihydrate complexes of ytterbium and lutetium 1,2,4-benzenetricarboxylate are dehydrated in three steps. At about 30°C half water molecule is releasing. After that two water molecules are lost. The third mass loss of dehydration corresponds to loss of half water molecule resulting in anhydrous complex formation. Weak and strong endothermic effects accompany two first steps at about 50 and 160°C, respectively (Fig. 4).

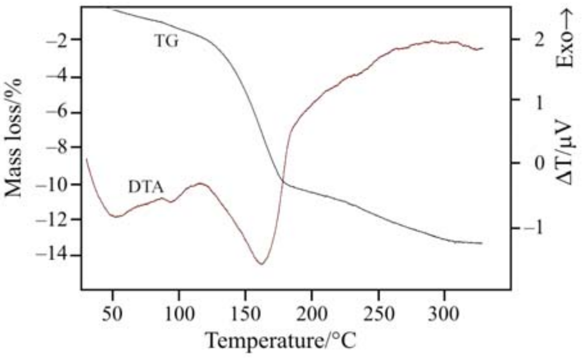

Fig. 4 TG and DTA curves of dehydration of Yb(btc)·3H_2O

TG and DTA curves of thermal decomposition of tetrahydrate 1,2,4-benzenetricarboxylate complexes show that dehydration proceeds in three stages. The first step is connected with loss of one water molecule. This process is accompanied by endothermic peak at about 75°C. Further heating of compounds resulting in removing of next two water molecules (or 2.5 water molecules for complexes of Ho and Tm). On the DTA curves strong endothermic effects at about 140°C are observed. On further heating the TG curves show the next mass losses connected with removing of one water molecule (or 0.5 water molecule for Ho and Tm complexes). This stage is accompanied by very weak endothermic effect (Fig. 5), which is not detectable by used DTA thermocouple.

Stepwise of dehydration process point to different mode of water molecules bonding. It can be concluded that first stage of complexes dehydration is

Table 3 Thermogravimetric data obtained during heating complexes of lanthanide(III) with 1,2,4-benzenetricarboxylic acid in air atmosphere

Complex	T_1/°C	Intermediate solid product	T_2/°C	Mass loss/%		Residue
				found	calc.	
La(btc)·3H_2O	30–250	La(btc)	450–750*	58.48	59.28	La_2O_3
Ce(btc)·2H_2O	30–290	Ce(btc)	300–460	56.65	55.05	CeO_2
Pr(btc)·4H_2O	30–290	Pr(btc)	445–580	57.70	59.47	Pr_6O_{11}
Nd(btc)·4H_2O	30–320	Nd(btc)	460–670	59.00	60.26	Nd_2O_3
Sm(btc)·4H_2O	30–350	Sm(btc)	470–670	58.58	59.40	Sm_2O_3
Eu(btc)·4H_2O	30–350	Eu(btc)	400–640	59.00	59.18	Eu_2O_3
Gd(btc)·4H_2O	35–310	Gd(btc)	470–630	56.73	58.47	Gd_2O_3
Tb(btc)·4H_2O	30–300	Tb(btc)	470–570	57.80	57.33	Tb_4O_7
Dy(btc)·4H_2O	30–340	Dy(btc)	460–590	55.53	57.77	Dy_2O_3
Ho(btc)·4H_2O	30–275	Ho(btc)	420–670	55.85	57.15	Ho_2O_3
Er(btc)·4H_2O	30–250	Er(btc)	400–570	55.80	57.15	Er_2O_3
Tm(btc)·4H_2O	30–250	Tm(btc)	430–570	55.61	56.92	Tm_2O_3
Yb(btc)·3H_2O	30–300	Yb(btc)	450–570	53.92	54.60	Yb_2O_3
Lu(btc)·3H_2O	30–350	Lu(btc)	470–560	54.23	54.36	Lu_2O_3

T_1 – temperature range of dehydration; T_2 – temperature range of degradation of anhydrous complexes to suitable oxides;
*degradation to oxide occurs with formation of intermediate $La_2O_2CO_3$

Table 4 Detailed data of dehydration process of lanthanide(III) 1,2,4-benzenetricarboxylates

Complex	T/°C	T_{endo}/°C	Mass loss/%		Loss	Residue
			found	calc.		
$La(btc)\cdot 3H_2O$	30–120	100	8.77	9.00	$2H_2O$	$La(btc)\cdot H_2O$
	120–250	200	12.77	13.50	H_2O	La(btc)
$Ce(btc)\cdot 2H_2O$	30–140	120	4.77	4.69	H_2O	$Ce(btc)\cdot H_2O$
	140–280	260	10.85	9.39	H_2O	Ce(btc)
$Pr(btc)\cdot 4H_2O$	30–100	75	4.38	4.29	H_2O	$Pr(btc)\cdot 3H_2O$
	100–150	128	13.14	12.86	$2H_2O$	$Pr(btc)\cdot H_2O$
	150–290		16.88	17.14	H_2O	Pr(btc)
$Nd(btc)\cdot 4H_2O$	30–105	75	5.04	4.25	H_2O	$Nd(btc)\cdot 3H_2O$
	105–150	140	13.15	12.75	$2H_2O$	$Nd(btc)\cdot H_2O$
	150–320		17.57	17.00	H_2O	Nd(btc)
$Sm(btc)\cdot 4H_2O$	30–90	78	4.23	4.19	H_2O	$Sm(btc)\cdot 3H_2O$
	90–150	142	12.97	12.57	$2H_2O$	$Sm(btc)\cdot H_2O$
	150–300		16.75	16.76	H_2O	Sm(btc)
$Eu(btc)\cdot 4H_2O$	30–95	75	4.21	4.17	H_2O	$Eu(btc)\cdot 3H_2O$
	95–145	142	12.36	12.53	$2H_2O$	$Eu(btc)\cdot H_2O$
	145–350		16.30	16.70	H_2O	Eu(btc)
$Gd(btc)\cdot 4H_2O$	30–120	75	4.63	4.12	H_2O	$Gd(btc)\cdot 3H_2O$
	120–170	140	12.50	12.37	$2H_2O$	$Gd(btc)\cdot H_2O$
	170–310		15.69	16.39	H_2O	Gd(btc)
$Tb(btc)\cdot 4H_2O$	30–100	73	4.49	4.11	H_2O	$Tb(btc)\cdot 3H_2O$
	100–145	140	12.17	12.33	$2H_2O$	$Tb(btc)\cdot H_2O$
	145–300		16.36	16.44	H_2O	Tb(btc)
$Dy(btc)\cdot 4H_2O$	30–85	75	4.53	4.08	H_2O	$Dy(btc)\cdot 3H_2O$
	85–145	140	11.82	12.23	$2H_2O$	$Dy(btc)\cdot H_2O$
	145–340		16.29	16.30	H_2O	Dy(btc)
$Ho(btc)\cdot 4H_2O$	30–100	75	4.42	4.05	H_2O	$Ho(btc)\cdot 3H_2O$
	100–150	143	14.31	14.18	$2.5H_2O$	$Ho(btc)\cdot 0.5H_2O$
	150–275		15.71	16.21	$0.5H_2O$	Ho(btc)
$Er(btc)\cdot 4H_2O$	30–90	70	4.31	4.03	H_2O	$Er(btc)\cdot 3H_2O$
	90–140	134	12.98	13.00	$2H_2O$	$Er(btc)\cdot H_2O$
	140–250		16.11	16.30	H_2O	Er(btc)
$Tm(btc)\cdot 4H_2O$	30–95	72	4.32	4.02	H_2O	$Tm(btc)\cdot 3H_2O$
	95–140	134	13.90	14.07	$2.5H_2O$	$Tm(btc)\cdot 0.5H_2O$
	140–250		15.47	16.07	$0.5H_2O$	Tm(btc)
$Yb(btc)\cdot 3H_2O$	30–115	50. 93	1.71	2.07	$0.5H_2O$	$Yb(btc)\cdot 2.5H_2O$
	115–180	162	9.92	10.36	$2H_2O$	$Yb(btc)\cdot 0.5H_2O$
	180–300		13.30	12.44	$0.5H_2O$	Yb(btc)
$Lu(btc)\cdot 3H_2O$	30–130	50	2.00	2.06	$0.5H_2O$	$Lu(btc)\cdot 2.5H_2O$
	130–190	167	9.78	10.32	$2H_2O$	$Lu(btc)\cdot 0.5H_2O$
	190–350		11.88	12.39	$0.5H_2O$	Lu(btc)

connected with releasing of weakly bonded water molecules. Probably, these molecules occupied position in other coordination sphere of lanthanide atoms being hydrogen bonded with organic ligand. The water molecules removing in the second step of dehydration are more tightly bonded and they are releasing in significantly higher temperature. It is assumed that these water molecules are probably directly bonded with metal atoms being in inner coordination sphere [32].

As the result of dehydration process, anhydrous lanthanide 1,2,4-benzenetricarboxylate complexes are formed. As can be seen from Table 3 these compounds show different thermal stability. Complex of lanthanum(III) demonstrates the widest temperature range of stability (250–450°C). Only anhydrous complex of cerium(III) is unstable

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 300–670°C and strong exothermic effects observed at DTA curves accompany them. The solid residues obtained during thermal decomposition of lanthanide(III) 1,2,4-benzenetricarboxylate complexes are suitable metal oxides: CeO_2, Pr_6O_{11}, Tb_4O_7 and Ln_2O_3 (for La, Nd–Lu com-

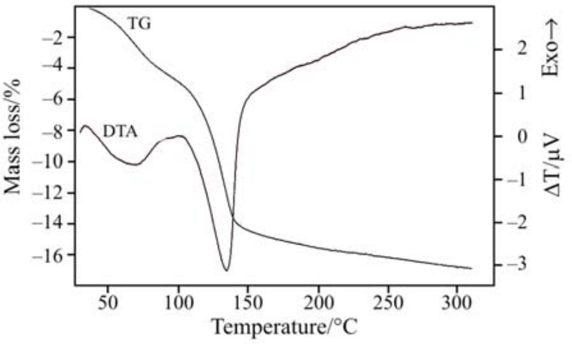

Fig. 5 TG and DTA curves of dehydration of Eu(btc)·4H_2O

plexes). The temperature of oxide formation is in the range 460–750°C. Only in the case of lanthanum complex formation of unstable oxycarbonate $La_2O_2CO_3$ is observed.

TG-FTIR spectra of gaseous products

The FTIR spectra of evolved gas products of thermal decomposition of neodymium(III) and lutetium(III) 1,2,4-benzenetricarboxylates as representatives of isostructural groups were recorded. The FTIR spectra of gaseous products of decomposition of both complexes are quite similar. The recorded spectra clearly confirm that the first step of complexes thermal decomposition is dehydration process. The spectra recorded up to 300°C show bands in the wavenumber ranges 3750–3500 and 1900–1300 cm^{-1} corresponding to stretching and deformations vibrations of liberating water molecules, respectively [33]. Further heating up to about 500°C does not cause releasing any gaseous products. This fact confirms formation of anhydrous stable complexes. Heating upon 500°C lead to degradation of 1,2,4-benzenetricarboxylate ligand with evolution of a mixture of several different products. The FTIR spectra recorded at 540°C show characteristic absorption bands in frequencies ranges: 2300–2250 and 750–600 cm^{-1} corresponding to the carbon dioxide vibrations. Apart from that, a small amount of carbon monoxide can be observed. Vibrations of CO molecules give easily detectable double-band in the range 2250–2050 cm^{-1} [34]. Upon 590°C, besides carbon oxides in the FTIR spectra other gaseous compounds are observed. They give several distinct absorption bands. The absorption peaks at 3084, 3057 and 3046 cm^{-1} were attributed to valence C–H vibrations from evolved hydrocarbons (aliphatic as well as aromatic hydrocarbons). The band at 1950 cm^{-1} is connected with stretching vibrations of CC (for example from propadiene). The bands at 1480, 1464 cm^{-1} can be attributed to the several modes: deformation vibrations of CH_3 groups, scissoring vibrations of CH_2 groups or deformation and stretching vibrations of aromatic ring. The band recorded at 1036 cm^{-1} was ascribed to the CH bending deformation of benzene ring or rocking vibrations of CH_3 groups [35–37] (Fig. 6).

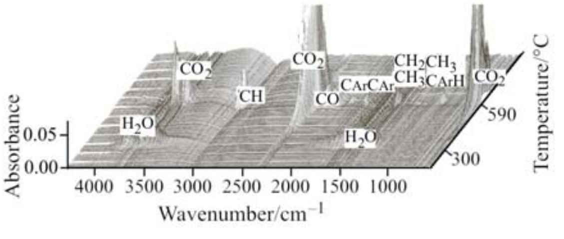

Fig. 6 Stacked plot of the FTIR spectra of the evolved gases for Lu(btc)·3H_2O

Conclusions

Complexes of lanthanide(III) with 1,2,4-benzenetricarboxylic acid are polycrystalline hydrates. All carboxylate groups from organic ligand are deprotonated and engaged in different manner in coordination of lanthanide atoms. In the air atmosphere complexes decompose in the two main stages. The first one is connected with multi-steps dehydration whereas the second stage with degradation and combustion of organic ligand. The schemes of releasing of water molecules are presented on following schemes:

$$\mathrm{Ce(btc)\cdot 2H_2O \xrightarrow{-H_2O} Ce(btc)\cdot H_2O \xrightarrow{-H_2O} Ce(btc)}$$

$$\mathrm{La(btc)\cdot 3H_2O \xrightarrow{-2H_2O} La(btc)\cdot H_2O \xrightarrow{-H_2O} La(btc)}$$

$$\mathrm{Ln(Yb,Lu)(btc)\cdot 3H_2O \xrightarrow{-0.5H_2O}}$$
$$\mathrm{Ln(btc)\cdot 2.5H_2O \xrightarrow{-2H_2O}}$$
$$\mathrm{Ln(btc)\cdot 0.5H_2O \xrightarrow{-0.5H_2O} Ln(btc)}$$

$$\mathrm{Ln(btc)\cdot 4H_2O \xrightarrow{-H_2O} Ln(btc)\cdot 3H_2O \xrightarrow{-2H_2O}}$$
$$\mathrm{Ln(btc)\cdot H_2O \xrightarrow{-H_2O} Ln(btc)}$$

$$\mathrm{Ln(Ho,Tm)(btc)\ \cdot 4H_2O \xrightarrow{-H_2O}}$$
$$\mathrm{Ln(btc)\cdot 3H_2O \xrightarrow{2.5H_2O}}$$
$$\mathrm{Ln(btc)\cdot 0.5H_2O \xrightarrow{-0.5H_2O} Ln(btc)}$$

The FTIR spectra of gaseous products of thermal decomposition confirm formation of solid intermediate products in the form of anhydrous complexes. Degradation of 1,2,4-benzenetricarboxylate moieties is connected with evolution of carbon oxides and hardly distinguishable aliphatic and aromatic hydrocarbons.

Further investigations of lanthanide 1,2,4-benzenetricarboxylates are provided in purpose to examination of reversibility of dehydration process of the complexes. Moreover complexes are prepared in hydrothermal synthesis for obtaining in the monocrystal form with purpose of structure investigations.

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