SYNTHESIS, CHARACTERIZATION AND THERMAL BEHAVIOUR OF HEMIMELLITIC ACID COMPLEXES WITH LANTHANIDES(III)

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The complexes of lanthanides(III) with hemimellitic acid (1,2,3-benzenetricarboxylic acid, H_3btc) of the formula $Ln(btc)\cdot nH_2O$, where *Ln*=lanthanide(III) ion and *n*=2–6 were prepared and characterized by elemental analysis, infrared spectra, X-ray diffraction patterns and thermal analysis. The IR spectra of the complexes indicate coordination of lanthanides(III) through all carboxylate groups. The complexes of La(III), Ce(III), Pr(III) and Er(III) are amorphous. On heating in air atmosphere all complexes lose water molecules and next anhydrous compounds decompose to corresponding metal oxides.

Introduction

Recently, a great attention has been paid to the construction of metal-organic frameworks as promising materials for applications in gas storage, separation and catalysis [1–4]. Their useful properties arises from desirable pore shapes and sizes, high porosity and flexible frameworks. For construction of coordination polymers are chosen appropriate polydentate ligands as bridges between several metal centres. The benzenepolycarboxylate acids [3] are commonly used in the synthesis of such new materials. Polycarboxylate ligands exhibit a variety of coordination fashions and the capability of forming coordination architectures of diverse sizes and shapes. Symmetric benzenepolycarboxylate acids such as 1,4-benzenedicarboxylic acid [5] 2,6-naphthalenedicarboxylic acid [6], 1,3,5-benzenetricarboxylic acid [7, 8] and 1,2,4,5-benzenetetracarboxylic acid [9, 10] are intensively employing to construct coordination polymers due to theirs bridging abilities. On the other hand asymmetric ligands such as 1,2,4- and 1,2,3-benzenetricarboxylic acids can form fascinating structures by reason of the special orientation of carboxylate groups. In the molecule of 1,2,3-benzenetricarboxylic acid (hemimellitic acid) none of carboxyl groups is coplanar with the benzene ring [11]. In literature are known only a few examples of coordination polymers with hemimellitic acid. Two-dimensional coordination polymer with the zinc ions and three-dimensional coordination polymer with copper(II) were obtained by Ling Xu *et al.* [12, 13]. Both complexes form networks with channels. Hemimellitic acid form also solvent-inclusion clathrates with the brick-wall, herringbone or lamellar architectures [14].

The lanthanides are explored in the construction of coordination polymer due to their high coordination number and flexible coordination geometry in comparison to the transition metal frameworks that is led to unusual molecular architectures.

The aim of this work was to synthesize complexes of lanthanides(III) with 1,2,3-benzenetricarboxylic acid as potential coordination polymers and investigations some of their properties.

Experimental

1,2,3-benzenetricarboxylic acid hydrate (98%) and cerium(III) nitrate hexahydrate (99.99%) were purchased from Aldrich. Lanthanide chlorides were prepared from lanthanide oxides (99.9%), Sigma.

The complexes of lanthanide from La(III) to Eu(III) with hemimellitic acid were prepared by dropwise adding of aqueous ammonium hemimellitate solution (2 mmol, 20 mL, pH=5.5) to aqueous solution of lanthanide chloride(III) (2 mmol, 150 mL, pH=4.5) (for cerium(III) complex nitrate solution was used). The precipitates of complexes were left for 2 h in mother solution at 60°C, and then filtered off, washed with water and dried at 30°C to constant mass. The complexes of lanthanide(III) from Gd(III) to Lu(III) were synthesized by addition of freshly precipitated lanthanide hydroxide (2 mmol) to aqueous solution of hemimellitic acid (2 mmol, 100 mL). The complexes of Gd(III), Er(III), Tm(III), Yb(III) and

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Lu(III) were immediately precipitated and next were kept for an 1 h in mother solution and then isolated by filtration, washed with water and dried at 30°C to constant mass. The complexes of Tb(III), Dy(III) and Ho(III) were obtained by evaporation of reaction mixture for several days at room temperature. The prepared compounds were dried at 30°C to constant mass. The yields of synthesis are in the range: 60–80%.

The prepared complexes were identified by means of elemental analysis and thermogravimetry. The contents of C and H were determined by using a Perkin Elmer 2400 CHN elemental analyzer.

The infrared spectra of the obtained complexes and 1,2,3-benzenetricarboxylic acid were recorded in KBr discs on a SPECORD M80 spectrophotometer over the range 4000–400 cm^{-1}.

The X-ray powder diffraction patterns were collected on a HZG 4 diffractometer, using Ni filtered CuK$_\alpha$ radiation. Measurements were taken over the range of 2θ=5–70°.

Thermal analysis was carried out by the TG-DTA method using SETSYS 16/18 analyser from Setaram. Samples of about 7–8 mg were heated in ceramic crucible up to 850°C at a heating rate of 10°C min^{-1} in dynamic air atmosphere (0.75 dm^3 h^{-1}).

Results and discussion

The studied complexes of lanthanide with hemimellitic acid have general formula Ln(btc)·nH$_2$O where Ln=lanthanide(III) ion, btc=C$_6$H$_3$(COO)$_3^{3-}$ and n=2–6. The detail formula are given in Table 1. The X-ray

powder diffractions showed that the complexes of La(III), Ce(III), Pr(III) and Er(III) are amorphous. The remaining compounds were obtained as polycrystalline substances. Depending on number of water molecules in the complex they are isostructural in several groups: Nd–Eu, Gd–Ho and Tm–Lu.

Spectroscopic analysis

The infrared spectra of the 1,2,3-benzenetricarboxylic acid and its lanthanide complexes were recorded in purpose to establish ligating behaviour of hemimellitate ligand. The presence of water molecules in all investigated complexes is confirmed by broad band in the region 3800–2500 cm^{-1} with strong maximum at about 3500 cm^{-1} originating from stretching vibrations of OH group from water molecules influenced by extensive hydrogen-bonding network. In the spectra of dihydrate complexes of Nd(III), Sm(III) and Eu(III) strong absorption peak at 3632 cm^{-1} was found besides a broad absorption band about 3420 cm^{-1}. This band corresponds to very weakly hydrogen bonded OH groups in the water molecules. Moreover in these spectra are present broad bands with maxima at 2550 and 2232 cm^{-1} resulting from overtones of hydrogen bonds [15]. Appearing of these band in the studied complexes may point to presence of water molecules bonding in different way.

The infrared spectrum of free 1,2,3-benzenetricarboxylic acid is characterized by strong double band at 1728 and 1700 cm^{-1} due to stretching vibrations of unequivalent C=O groups. Additionally, carboxylic group COOH give strong

Table 1 Characteristic IR bands (cm^{-1}) of 1,2,3-benzenetricarboxylic acid and its lanthanide(III) compounds

	ν_{OH}	$\nu_{as(COO^-)}$	$\nu_{(C-C)_{ar}}$	$\nu_{s(COO^-)}$	$\beta_{(C-H)_{ar}}$	γ_{OH}	$\gamma_{(C-H)_{ar}}$	$\nu_{(C-C)_{ar}}$
H$_3$btc	3800–2000	–	1464	–	1064	–	776, 756	578, 540
La(btc)·4H$_2$O	3700–2800	1552	1464	1384	1072	940	772, 712	544
Ce(btc)·4.5H$_2$O	3800–2500	1544	1464	1380	1072	940	772, 712	544
Pr(btc)·4H$_2$O	3800–2500	1552	1464	1380	1072	940	768, 712	544
Nd(btc)·2H$_2$O	3632, 3000–2300	1532, 1484	1400	1360	1064	936	768, 708	568
Sm(btc)·2H$_2$O	3632, 3600–3000	1532, 1484	1400	1360	1064	936	704	568
Eu(btc)·2H$_2$O	3632, 3600–3100	1532, 1484	1400	1364	1064	936	768, 720	568
Gd(btc)·5.5H$_2$O	3800–2500	1537	1458	1365	1068	938	767, 716	572
Tb(btc)·6H$_2$O	3800–2500	1552	1448	1384	1072	936	768, 712	590
Dy(btc)·5H$_2$O	3800–2500	1556	1457	1381	1069	940	769, 713	580
Ho(btc)·5H$_2$O	3800–2500	1559	1456	1381	1069	940	769, 714	581
Er(btc)·4.5H$_2$O	3800–2500	1553	1461	1386	1070	942	769, 708	560
Tm(btc)·4H$_2$O	3800–2500	1552	1464	1384	1070	940	772, 708	560
Yb(btc)·4H$_2$O	3800–2500	1536	1480	1380	1070	936	772, 712	570
Lu(btc)·4H$_2$O	3800–2500	1537	1460	1376	1075	939	771, 699	576

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

absorption band at 1280 cm^{-1} corresponds to stretching vibrations of C–OH group. When the metal complexes are formed the absorption peaks arised from COOH groups are replaced by asymmetric and symmetric stretching vibrations of carboxylate group COO. In the spectra of lanthanide hemimellitates the asymmetric stretching vibrations of COO group are hardly distinguishable because in the same wavenumber range appear vibrations arised from stretching vibrations of benzene ring as well as deformation vibrations of water molecules. It was assumed that asymmetric stretching vibrations of carboxylate group are in the range 1552–1532 cm^{-1} while the symmetric vibrations are in range 1360–1384 cm^{-1}. It is not possible to determine the coordination mode of COO group based only the IR data. The carboxylate group shows the significant diversity of mode of metal bonding. The most utilised the coordination mode by carboxylate group is: monodentate, bidentate-bridging and bidentate-chelating [16]. The known crystal structures of hemimellitate metal complexes present different types of metal bonding. In the structure of nickel(II) complex with 1,2,3-benzenetricarboxylic acid only ionic interactions appears between hexaaquanickel(II) ion and fully deprotonated anions of hemimellitic acid [17]. On the other hand in the copper(II) complex, the investigated acid behaves as monodentate ligand in which only carboxylate group in position 2 is engaged in metal bonding while two remaining COOH groups remain protonated [18]. In the copper(II) complex with 1,2,3-benzene-

tricarboxylic acid and 4,4`-bipyridine ligand only carboxylate groups from 1 and 3 position in hemimellitic acid take part in Cu atom binding. Both carboxylate groups act as bidentate-bridging [13].

Lack of the crystal structure of the investigated complexes makes interpretation of infrared spectra hardly possible. It is worth to note that in the case of dihydrate complexes the band arising from asymmetric stretching vibrations of COO group is splitted into the two peaks with maxima at 1532 and 1484 cm^{-1}, respectively. Splitting of ν_{asym} (COO) absorption band has been attributed to many causes e.g. two coordination modes, polymer–dimer equilibrium or coupling between neighbouring carboxylate groups [16]. That suggest quite different mode of carboxylate coordination in these complexes in comparison to remaining compounds. The IR spectral data and possible assignments are listed in Table 1.

Thermal analysis

Thermal data of the lanthanide 1,2,3-benzenetricarboxylates are given in Table 2. The studied complexes are stable up to about 30°C. During heating of the complexes in the air atmosphere multi-stage decomposition is observed (Figs 1–4). The first mass loss observed on the TG curve is associated with dehydration process similarly as in 1,2,4-benzenetricarboxylates of lanthanides [19, 20]. The loss of water molecules occurs in wide temperature range (30–270°C) and in different way in depending on their number. The shape of TG

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

Complex	T_1/°C	T_{endo}^*/°C	Mass loss/%		Intermediate solid product	T_2/°C	Mass loss/%		Residue
			found	calcd.			found	calcd.	
La(btc)·4H$_2$O	30–200	97	17.50	17.22	La(btc)	390–760	61.36	61.03	La$_2$O$_3$
Ce(btc)·4.5H$_2$O	30–180	91	19.80	18.91	Ce(btc)	335–500	59.47	59.81	CeO$_2$
Pr(btc)·4H$_2$O	30–210	95	16.90	17.14	Pr(btc)	380–600	59.07	59.47	Pr$_6$O$_{11}$
Nd(btc)·2H$_2$O	40–235	75*, 227	10.00	9.28	Nd(btc)	380–660	56.20	56.57	Nd$_2$O$_3$
Sm(btc)·2H$_2$O	30–255	76*, 250	10.00	9.15	Sm(btc)	380–650	56.45	55.69	Sm$_2$O$_3$
Eu(btc)·2H$_2$O	40–250	80*, 250	9.80	9.11	Eu(btc)	350–650	55.32	54.58	Eu$_2$O$_3$
Gd(btc)·5.5H$_2$O	30–235	115, 215*	22.00	21.36	Gd(btc)	400–700	60.76	60.89	Gd$_2$O$_3$
Tb(btc)·6H$_2$O	30–270	112, 220*	22.50	22.78	Tb(btc)	380–570	60.97	60.57	Tb$_4$O$_7$
Dy(btc)·5H$_2$O	30–240	98, 130	20.97	19.58	Dy(btc)	410–580	59.51	59.42	Dy$_2$O$_3$
Ho(btc)·5H$_2$O	40–210	105,130	19.24	19.47	Ho(btc)	400–580	58.54	59.11	Ho$_2$O$_3$
Er(btc)·4.5H$_2$O	40–190	95	18.20	17.78	Er(btc)	380–570	57.35	58.00	Er$_2$O$_3$
Tm(btc)·4H$_2$O	30–270	95, 240	17.00	16.07	Tm(btc)	400–590	55.24	59.94	Tm$_2$O$_3$
Yb(btc)·4H$_2$O	30–185	158	15.90	15.92	Yb(btc)	400–565	54.66	56.42	Yb$_2$O$_3$
Lu(btc)·4H$_2$O	30–105	165	16.30	15.86	Lu(btc)	390–570	55.55	56.19	Lu$_2$O$_3$

T_1 – temperature range of dehydration; T_2 – temperature range of degradation of anhydrous complexes to suitable oxides;
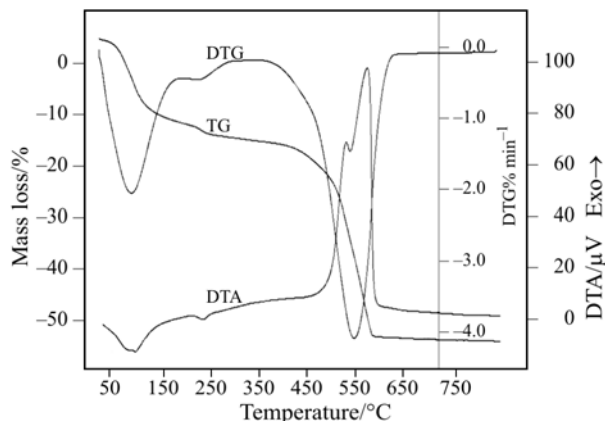T_{endo}^* – very weak endothermic effects
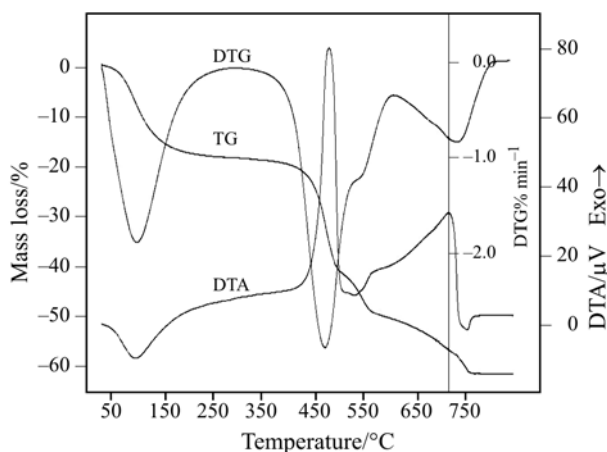
Fig. 1 TG, DTG and DTA curves of thermal decomposition of La(btc)·4H₂O
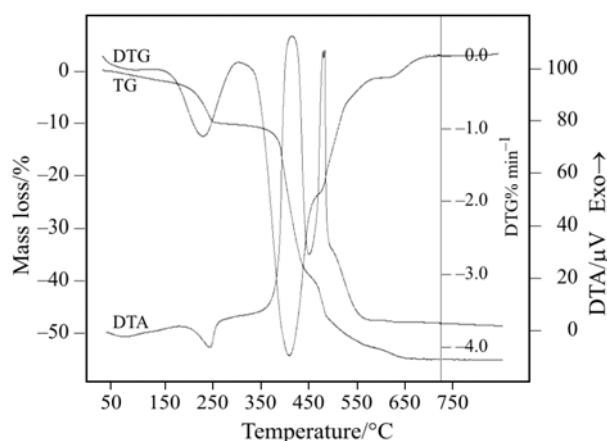
Fig. 2 TG, DTG and DTA curves of thermal decomposition of Eu(btc)·2H₂O

Fig. 3 TG, DTG and DTA curves of thermal decomposition of Tm(btc)·4H₂O
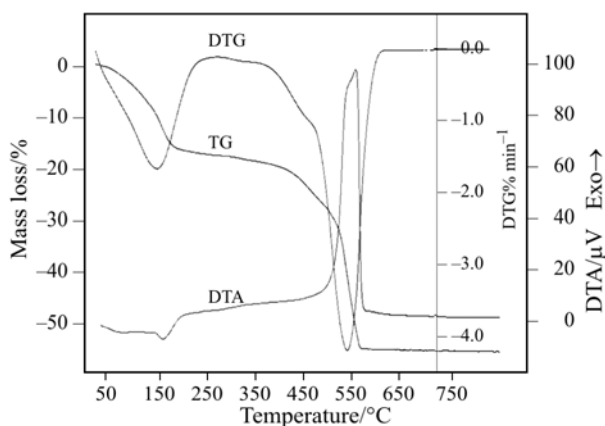

Fig. 4 TG, DTG and DTA curves of thermal decomposition of Lu(btc)·4H₂O

and DTG curves of tetrahydrate 1,2,3-benzene-tricarboxylates of La(III), Ce(III), Pr(III) and Er(III) indicates a single-step dehydration connected with endothermic effect at about 95°C (Fig. 1). In the case of dihydrate hemimellitates of Nd(III), Sm(III) and Eu(III) dehydration process occurs in entirely different way. Heating of the complexes above 30°C resulting in slowly mass loss connected with hardly distinguishable endothermic effect at about 80°C (Fig. 2). This DTA effect is connected with liberation of very weakly hydrogen bonded water molecules. The second step of dehydration proceeds with distinct mass loss detected on the TG curve and strong endothermic effect at 250°C. Relatively high temperature of water molecules liberating point to their strong bonding in structures of complexes. It may suggest that water molecules appear in inner coordination sphere being directly bonded with lanthanide ions [21]. In different ways dehydration of 1,2,3-benzenetricarboxylates of Gd(III), Tb(III), Dy(III), Ho(III) and Tm(III) occurs

(Fig. 3). On the DTG and DTA curves recorded at temperature range of water molecules losing are present double peaks at about 90–130°C and very weak peak at 230°C. Such course of thermal decomposition indicate multi-step dehydration process. Endothermic effects recorded at lower temperature probably correspond to water molecules which occupy position in outer coordination sphere being hydrogen bonded with organic ligand. The second endothermic effect at higher temperature is connected with releasing of small amount of water that is clearly reflected on the TG curve. Relatively high temperature of water liberating points to tightly bonding of water molecules in the complexes. In the case of tetrahydrate complexes of Yb(III) and Lu(III) dehydration process is characterized by asymmetric broad DTG peak associated with endothermic effects recorded at 158 and 165°C, respectively (Fig. 4).

As can be seen from thermal decomposition data water molecules are removed at different temperatures in accordance of strength of their bonding. Anhydrous hemimellitates are formed in the range 185–270°C. The next decomposition stage is

connected with degradation of anhydrous complexes that begins in the temperature range 335–400°C. The decomposition process of the complexes is associated with burning of organic ligand resulting in strong exothermic effect. Such way of degradation mechanism is characteristic for complexes of lanthanide benzoates [22]. As the final solid products of thermal decomposition suitable metal oxides (Ln_2O_3, CeO_2, Pr_6O_{11}, Tb_4O_7) are formed in the range 565–760°C.

Conclusions

The new complexes of lanthanide(III) with hemimellitic acid were obtained as hydrates. The 1,2,3-benzene-tricarboxylate ligand is entirely deprotonated in the studied complexes. As can be seen from infrared spectra, the dihydrate complexes show different mode of coordination in comparison to remaining compounds. The decomposition process of the studied complexes in the air atmosphere proceeds in two main stages: dehydration and degradation of organic ligand. Amorphous complexes lose water molecules in one step. Dehydration process in crystalline compounds occurs in overlapped stages.

Further synthesis in the gel medium and hydrothermal conditions are provided in purpose to obtaining monocrystals of lanthanide(III) hemimellitates for X-ray structural investigations. Additionally, examination of reversibility of dehydration process for hydrated complexes will be done.

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