J Therm Anal Calorim (2010) 101:213–219
DOI 10.1007/s10973-009-0326-7

Structural and thermal properties of rare earth complexes with 2,2′-biphenyldicarboxylic acid

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Received: 26 June 2009 / Accepted: 2 July 2009

Abstract Rare earth complexes with 2,2′-biphenyldicarboxylic acid (diphenic acid = H_2dpa) were obtained as hydrated precipitates of the general formula $Ln_2(C_{14}H_8O_4)_3 \cdot nH_2O$, where $n = 3$ for the of Y(III) and Ce(III)–Er(III) and $n = 6$ for La(III), Tm(III), Yb(III) and Lu(III) complexes. On heating in air atmosphere complexes lose all water molecules in the temperature range 30–210 °C in one step and form anhydrous compounds, which are stable up to 315–370 °C. During further heating they decompose to oxides. The trihydrated compounds are crystalline powders whereas the hexahydrated are amorphous solids. The trihydrated complexes crystallize in the monoclinic (Pr(III) and Ce(III) complexes) and triclinic (Y(III) and Nd(III)–Er(III) complexes) crystal systems.

Keywords 2,2′-biphenyldicarboxylates · Thermal analysis · X-ray powder diffraction analysis

Introduction

In recent years, the synthesis and construction of multidimensional coordination polymers have attracted curiosity in the area of new functional materials of unique and useful properties, which appears from eligible pore shapes and sizes, high porosity and flexible frameworks [1, 2]. Typically they consist of metal centers, tethered by rigid, functional organic linkers, giving rise to a variety of building units and overall topologies [3]. The most frequently used organic ligands in these constructions are aromatic polycarboxylates. Carboxylic acid ligands have been used for preparation lanthanide carboxylates, which exhibit exploitable applications in catalysis, ion exchange, gas separation, gas adsorption and storage [4]. Polycarboxylate acid ligands show diversity of coordination modes of carboxylate, such as monodentate, bridging and chelating [5, 6]. The carboxylate groups can bridge metal ions through M–O–M and M–O–C–O–M bridges to generate one-dimensional chain, two-dimensional layer and three-dimensional framework structures [7]. Rare earth elements are widely applied in miscellaneous fields of modern technology [8]. Their compounds have been used in high-performance luminescent devices, magnets, photocatalysts and pigments [9]. Lanthanide ions can construct high-dimension coordination polymers because they are characterized by high and variable coordination numbers and high affinity for hard donor atoms and ligands containing oxygen or nitrogen atoms [10, 11].

2,2′-Biphenyldicarboxylic acid (diphenic acid) is an aromatic dicarboxylate ligand, which is composed of two benzene rings and two carboxylic groups. H_2dpa can bridge metal centers to form one-dimensional single- or double helical-chain complexes because two phenyl rings are not coplanar with each other owing to the steric hindrance of 2,2′-positioned carboxylate groups [12]. Two carboxylic groups may be completely or partially deprotonated, in view of that H_2dpa exhibits diverse types of coordination modes with multiple coordination sites [13].

Several novel complexes of lanthanide(III) with diphenic acid have been synthesized by using hydrothermal synthesis technique. The structures of Sm(III), Dy(III) [14], Nd(III), Dy(III) and Y(III) [15], La(III), Pr(III), Eu(III), Tb(III) [16], Gd(III) [17] and Nd(III) [18] 2,2′-biphenyldicarboxylate, were reported. All complexes were prepared as dihydrates, which crystallize in the monoclinic

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crystal system with the space group C2/c. Complexes are composed of one-dimensional chains consist of two crystallographically independent Ln(III) ions [14–18]. The Ln(III) atoms are coordinated to oxygen atoms from carboxylate groups of diphenate ligand and to oxygen atoms from water molecules. Complexes exhibit various coordination modes of diphenate ligand, for example a diphenate ligand may be tetradentate or pentadentate [14–18].

The aim of our paper was to prepare the complexes of Y(III) and the series of lanthanides(III) with 2,2′-biphenyldicarboxylic acid by classical precipitation method to study their properties especially their thermal dehydration and decomposition in air atmosphere and to investigate the range of complete durability of anhydrous compounds. The anhydrous compounds should to be a good materials to the next syntheses of coordination polymers.

Table 1 The results of elemental analysis of some 2,2′-biphenyldicarboxylates obtained under classical conditions

Complexes	C/%		H/%		Ln/%	
	Found	Calc.	Found	Calc.	Found	Calc.
$La_2(C_{14}H_8O_4)_3 \cdot 6H_2O$	44.72	45.55	3.15	3.25	25.51	25.11
$Pr_2(C_{14}H_8O_4)_3 \cdot 3H_2O$	47.44	47.70	2.79	2.84	25.28	26.67
$Sm_2(C_{14}H_8O_4)_3 \cdot 3H_2O$	46.88	46.87	2.75	2.79	27.96	27.96
$Gd_2(C_{14}H_8O_4)_3 \cdot 3H_2O$	46.22	46.27	2.71	2.75	29.10	28.87
$Dy_2(C_{14}H_8O_4)_3 \cdot 3H_2O$	45.53	45.83	2.74	2.73	28.58	29.55
$Er_2(C_{14}H_8O_4)_3 \cdot 3H_2O$	44.69	45.44	2.67	2.70	29.79	30.16

Experimental

Synthesis

The lanthanide(III) complexes with diphenic acid were prepared by classical precipitation method. As diphenic acid is insoluble in water, first we had to prepare its ammonium salt (pH = 5.5–5.8) to obtain a soluble form of the ligand (except Ce). The next stage of synthesis was addition of the ammonium salt to the hot aqueous solution of lanthanide chloride (pH = 4.5–6.0) while stirring. In the case of cerium(III), the nitrate solution was used. The resulting precipitates of lanthanide complexes were filtered, washed with hot water, subjected to Nessler control to remove ammonium ions and dried at 30 °C to constant mass for couple of days. All reagents were used in the commercial form. Lanthanide oxides (99.9% purity) and diphenic acid (97% purity) were produced by Aldrich.

Measurement methods

The C, H, N elemental analyses were made for all lanthanide complexes using the Perkin Elmer 2400 instrument. The forthcoming results for the selected compounds are presented in Table 1.

The complexes were examined by FT-IR spectroscopy. The samples in the form of KBr discs were recorded in the range 4,000–400 cm^{-1} by using a FT-IR 1725X Perkin Elmer spectrometer.

Table 2 Frequencies for characteristic absorption bands in the IR spectra of lanthanides(III) and Y(III) complexes with diphenic acid ($L = C_{14}H_8O_4^{2-}$)

Complex	ν_{OH}[a] + $\nu_{(Ar–H)}$	$\nu_{C=O}$	δ_{H_2O}[a]	$\nu_{s(Ar)}$	$\nu_{as(COO)}$	$\nu_{as(Ar)}$	δ_{COH}	$\nu_{s(COO)}$	$\nu_{C–O}$	$\gamma_{C–O–H}$	$\gamma_{Ar–H}$	$\nu_{M–O}$	$\Delta\nu$
H_2L	3,000–2,360	1685 s		1598, 1578		1476, 1454	1,412		1,295 s	921	753 s		
$La_2L_3 \cdot 6H_2O$	3,600–2,700		1,604	1576	1544 s	1536, 1440		1,400vs			752	424	144
$Ce_2L_3 \cdot 3H_2O$	3,632–2,700		1,615	1571	1544 s	1521, 1442		1,402vs			761	428	142
$Pr_2L_3 \cdot 3H_2O$	3,633–2,700		1,618	1570	1548 s	1521, 1443		1,407vs			761	428	141
$Nd_2L_3 \cdot 3H_2O$	3,632–2,700		1,617	1568	1548 s	1522, 1443		1,404vs			761	426	144
$Sm_2L_3 \cdot 3H_2O$	3,636–2,700		1,620	1568	1553 s	1524, 1443		1,407vs			762	427	146
$Eu_2L_3 \cdot 3H_2O$	3,637–2,700		1,622	1579	1556 s	1524, 1443		1,409vs			763	429	147
$Gd_2L_3 \cdot 3H_2O$	3,638–2,700		1,624	1597, 1574	1554 s	1528, 1444		1,408vs			764	430	146
$Tb_2L_3 \cdot 3H_2O$	3,639–2,700		1,625	1598, 1571	1555 s	1527, 1444		1,409vs			764	430	146
$Dy_2L_3 \cdot 3H_2O$	3,640–2,700		1,627	1598, 1572	1557 s	1528, 1444		1,409vs			764	430	148
$Ho_2L_3 \cdot 3H_2O$	3,640–2,700		1,627	1598, 1574	1558 s	1528, 1444		1,408vs			764	431	150
$Er_2L_3 \cdot 3H_2O$	3,641–2,700		1,630	1599, 1579	1557 s	1531, 1445		1,411vs			764	433	146
$Tm_2L_3 \cdot 6H_2O$	3,622–2,700		1,604	1580	1553 s	1530, 1444		1,412vs			752	427	141
$Yb_2L_3 \cdot 6H_2O$	3,600–2,700		1,604	1572	1552 s	1536, 1440		1,412vs			752	428	140
$Lu_2L_3 \cdot 6H_2O$	3,600–2,700		1,604	1580	1548 s	1536, 1440		1,408vs			752	428	140
$Y_2L_3 \cdot 3H_2O$	3,642–2,700		1,631	1598, 1572	1558 s	1531, 1445		1,412vs			764	433	146

[a] Only for complexes

The thermal stability of the lanthanide complexes were investigated using a Setsys 16/18 analyzer, recording the TG, DTG and DTA curves. The samples (6–8 mg) of all complexes were heated in an Al_2O_3 melting pot at 30–750 °C in air atmosphere with a heating rate 5 °C min^{-1}. The samples of La(III), Tm(III) and Lu(III) complex were heated between 30–1,000 °C in air atmosphere with a heating rate 10 °C min^{-1}. The products of dehydration and decomposition process were calculated from the TG curve. Gaseous products of decomposition were identified on a Netzsch TG 209 instrument coupled to a Brucker FT-IR IFS 66 spectrometer. The sample of gadolinium(III) complex was heated in dynamic argon atmosphere using a ceramic crucible and heating with a rate of 15 °C min^{-1} up to 1,000 °C min^{-1}.

The X-ray diffraction patterns were taken at ambient temperature on a HZG-4 (Carl Zeiss, Jena) diffractometer in the range $2\theta = 4$–70° with a step equal to 0.5°. The powder diffraction data of Pr(III), as a representative of trihydrated complexes, was carried out on a Philips Xpert Pro automated X–ray diffractometer ($2\theta = 4$–64° with a step equal to 0.02°). The apparatus was calibrated by using a SRM 1976 standard. The X-rayan program was used for determining positions and peak intensities. The TREOR program was used for calculating the unit cell parameters from the collection of data, which had been obtained from the X-rayan program [19].

Results and discussion

Solid complexes of lanthanide(III) 2,2′-biphenyldicarboxylates were obtained as hydrated compounds with the metal:ligand ratio of 2:3 and the general formula $Ln_2(C_{14}H_8O_4)_3{\cdot}nH_2O$ ($n = 3$ for Ce–Er and Y and $n = 6$ for Tm–Lu and La). The complexes, which contain three water molecules, are crystalline powders. The hexahydrated compounds are amorphous solids. All complexes exhibit a typical colors, which are characteristic of the trivalent lanthanide ions, i.e. *Pr* green, *Nd* violet,

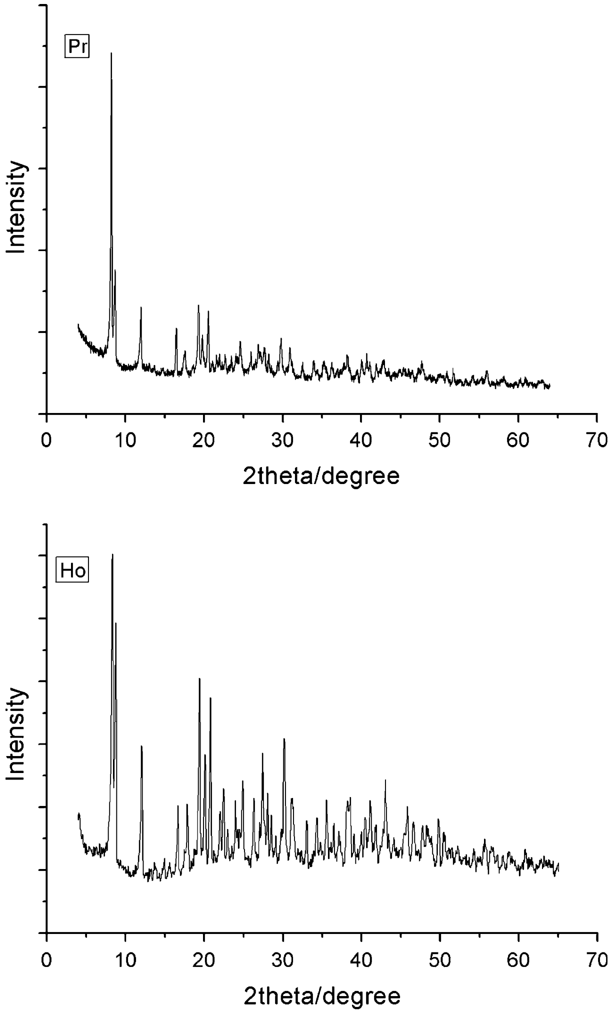

Fig. 1 X-ray powder diffraction patterns of $Pr_2L_3{\cdot}3H_2O$ (monoclinic) and $Ho_2L_3{\cdot}3H_2O$ (triclinic) ($L = C_{14}H_8O_4^{2-}$)

Table 3 The unit cell parameters for the crystalline series of 2,2′-biphenyldicarboxylates

Complexes	Crystal system	a/Å	b/Å	c/Å	α/°	β/°	γ/°	Volume/Å^3
$Ce_2(C_{14}H_8O_4)_3{\cdot}3H_2O$	monoclinic	11.75	10.79	8.35	90.00	119.93	90.00	917
$Pr_2(C_{14}H_8O_4)_3{\cdot}3H_2O$	monoclinic	10.45	10.77	8.34	90.00	103.80	90.00	911
$Nd_2(C_{14}H_8O_4)_3{\cdot}3H_2O$	triclinic	12.80	13.16	13.48	68.24	64.00	55.98	1666
$Sm_2(C_{14}H_8O_4)_3{\cdot}3H_2O$	triclinic	11.95	14.34	17.26	44.95	124.29	110.37	1719
$Eu_2(C_{14}H_8O_4)_3{\cdot}3H_2O$	triclinic	11.96	12.62	17.88	73.78	55.91	58.40	1903
$Gd_2(C_{14}H_8O_4)_3{\cdot}3H_2O$	triclinic	12.42	16.38	14.47	77.87	89.32	136.32	1928
$Tb_2(C_{14}H_8O_4)_3{\cdot}3H_2O$	triclinic	10.20	10.85	18.36	92.42	60.45	83.36	1745
$Dy_2(C_{14}H_8O_4)_3{\cdot}3H_2O$	triclinic	10.59	16.32	18.08	99.34	75.65	47.45	1977
$Ho_2(C_{14}H_8O_4)_3{\cdot}3H_2O$	triclinic	8.59	13.97	19.45	61.45	59.56	51.91	1536
$Er_2(C_{14}H_8O_4)_3{\cdot}3H_2O$	triclinic	7.81	11.68	16.51	72.76	99.48	109.03	1355
$Y_2(C_{14}H_8O_4)_3{\cdot}3H_2O$	triclinic	8.44	11.36	15.48	70.31	110.22	96.55	1312

Sm cream, *Ho* peach, *Er* pink and the remaining compounds are white.

FT-IR spectroscopy

All the complexes were analyzed by FT-IR spectroscopy. The IR spectra of lanthanide complexes were compared with those of free 2,2′-biphenyldicarboxylic acid (Table 2). The following notation is used: ν = stretching vibration, δ = in-plane deformation vibration, γ = out-of-plane deformation vibration and Ar = aromatic carbon atom vibration. The strongest band, observed in the IR spectrum of free acid is characteristic of carboxylic groups. This band is at 1,684 cm^{-1} and responds to the stretching vibrations of the carboxyl part $\nu(C=O)$. The band of carboxylic groups near such frequency is characteristic of linked groups –COOH, which participate in creating hydrogen bonds. The following bands, which are attributed to carboxylic groups are located at: 1412 cm^{-1}, 1273 cm^{-1} and 921 cm^{-1}. The first band corresponds to the in-plane deformation vibration δ(C–O–H), the second band is characteristic of the stretching ν(C–O) fragment and the last one represents the out-of-plane deformation vibrations γ(C–O–H). When the acid is converted into salts, all above mentioned vibrations of –COOH group disappear, whereas the stretching asymmetric and symmetric vibrations of $–COO^-$ group appear. The intensive bands corresponding to the stretching asymmetric vibrations $\nu_{as}(COO^-)$ in the IR spectra of complexes are observed at 1,544–1,558 cm^{-1} and at 1,412–1,400 cm^{-1} for the symmetric stretching vibrations $\nu_s(COO^-)$ of carboxylate anions [20, 21]. The lack of stretching and deformation vibrations of –COOH groups in salts indicates that all carboxylate groups are deprotonated. The differences between the position of the $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ modes ($\Delta\nu(COO^-)$) in the complexes of lanthanides is similar ($\Delta\nu(COO^-)$ = 140–150 cm^{-1}, Table 2)), so carboxylate groups may be chelated in these complexes [22].

In a high energy region in the IR spectra there are broad absorption bands in the range 3,642–2,700 cm^{-1}, which are attributed to ν(O–H) bonds of water molecules. In the same energy region, the wide peak consisting of several maxima was found. This absorption band appears at 3,100–2,700 cm^{-1} and represents the stretching vibrations ν(Ar–H). In the IR spectra of complexes the center of the above mentioned band is situated at 3,061–3,055 cm^{-1} and overlaps to some extent on the right wing of the stretching ν(O–H) vibrations of water molecules [20, 21].

X-ray diffraction patterns

The X-ray diffraction patterns were made for all lanthanide(III) 2,2′–biphenyldicarboxylates. The X-ray analysis shows that the complexes containing three water molecules are crystalline solids and they crystallize in the monoclinic or triclinic crystal system. The unit cell parameters for all crystalline complexes are presented in Table 3. Compounds with six molecules of water are amorphous. The

Table 4 Thermal decomposition of lanthanides(III) and Y(III) complexes with 2,2′-biphenyldicarboxylic acid (air atmosphere)

Complexes	M_{mol}	ΔT_1/°C	Mass loss/%		T_2/°C	T_3/°C	Residue/%	
			Calc.	Found			Calc.	Found
$La_2L_3 \cdot 6H_2O$	1106.51	30–190	9.76	10.02	345	630	29.45	29.92
$Ce_2L_3 \cdot 3H_2O$	1054.93	30–175	5.12	5.46	315	410	32.63	31.58
$Pr_2L_3 \cdot 3H_2O$	1056.51	30–175	5.11	5.70	350	560	32.23	30.54
$Nd_2L_3 \cdot 3H_2O$	1063.17	30–180	5.08	5.28	360	510	31.65	31.94
$Sm_2L_3 \cdot 3H_2O$	1075.41	30–190	5.02	5.55	355	495	32.43	32.42
$Eu_2L_3 \cdot 3H_2O$	1078.63	30–195	5.01	5.46	345	475	32.62	32.21
$Gd_2L_3 \cdot 3H_2O$	1089.19	30–200	4.96	4.38	370	500	33.28	33.54
$Tb_2L_3 \cdot 3H_2O$	1092.55	30–185	4.94	5.08	360	490	34.22	34.33
$Dy_2L_3 \cdot 3H_2O$	1099.69	30–200	4.91	4.75	365	500	33.92	32.80
$Ho_2L_3 \cdot 3H_2O$	1104.55	30–210	4.89	5.53	360	505	34.21	34.56
$Er_2L_3 \cdot 3H_2O$	1163.21	30–170	4.87	4.98	365	500	34.20	34.07
$Tm_2L_3 \cdot 6H_2O$	1165.55	30–170	9.26	9.54	360	500	33.08	33.57
$Yb_2L_3 \cdot 6H_2O$	1174.77	30–155	9.12	9.48	360	495	33.55	33.72
$Lu_2L_3 \cdot 6H_2O$	1178.63	30–180	9.16	9.26	355	510	33.76	35.28
$Y_2L_3 \cdot 3H_2O$	954.51	30–210	5.66	5.91	365	515	23.66	23.92

$L = (C_{14}H_8O_4)^{2-}$

ΔT_1 Temperature range of dehydration process; *T_2* Temperature of beginning of decomposition; *T_3* Temperature of beginning of oxide formation

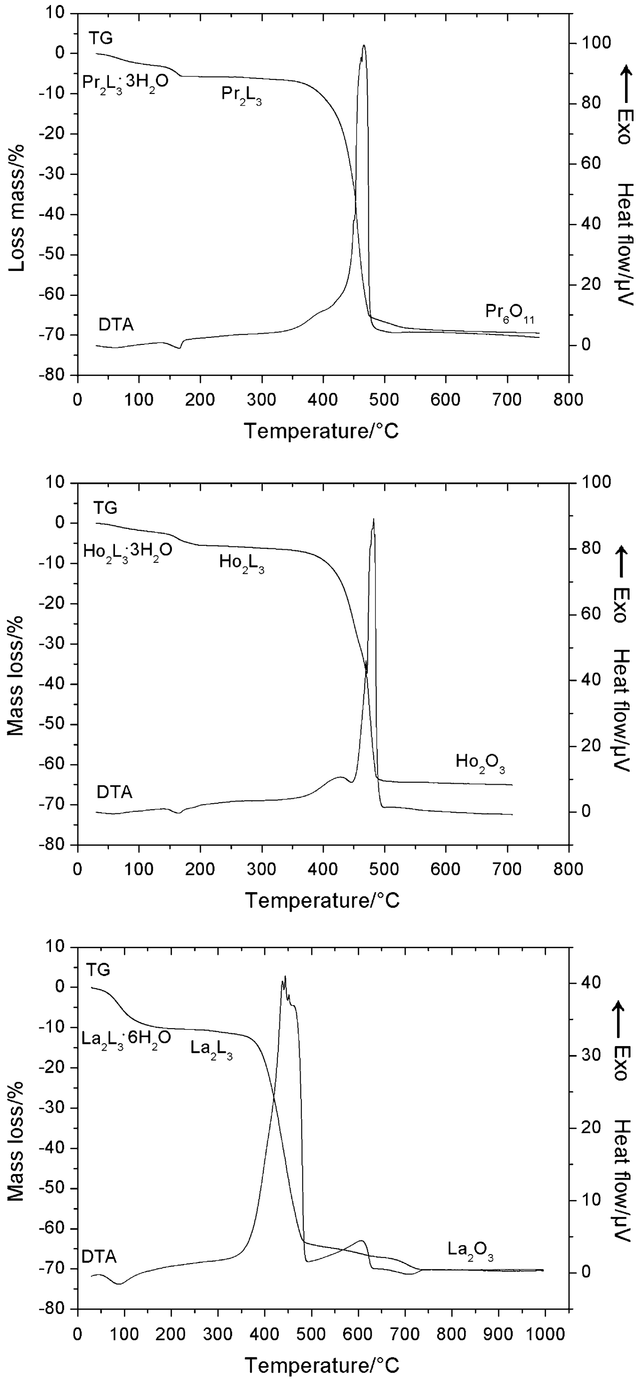

Fig. 2 TG and DTA curves of $Pr_2(C_{14}H_8O_4)_3{\cdot}3H_2O$, $Ho_2(C_{14}H_8O_4)_3{\cdot}3H_2O$ ($\beta = 5$ °C min^{-1}) and $La_2(C_{14}H_8O_4)_3{\cdot}6H_2O$ ($\beta = 10$ °C min^{-1}) in air

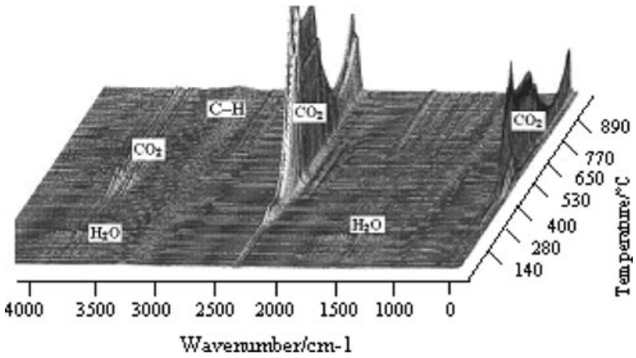

Fig. 3 FTIR spectra of gaseous products of thermal decomposition of $Gd_2(C_{14}H_8O_4)_3{\cdot}3H_2O$

first group contains the compounds from Ce(III) to Er(III) and Y(III) with three water molecules. The second group contains hexahydrated complexes, i.e. Tm(III), Yb(III), Lu(III) and additionally La(III). The first group of complexes consists of two kinds of crystal powders, that is: Ce(III) and Pr(III) complexes crystallize in the monoclinic crystal system whereas the compounds from Nd(III) to Er(III) crystallize in the triclinic crystal system. Figure 1 shows the X-ray diffraction patterns for both types of trihydrated compounds $Pr_2(C_{14}H_8O_4)_3{\cdot}3H_2O$ and $Ho_2(C_{14}H_8O_4)_3{\cdot}3H_2O$. The praseodymium(III) complex crystallizes in the monoclinic crystal system with the elemental cell parameters: $a = 10.45$; $b = 10.77$; $c = 8.34$ Å and $\beta = 103.80°$, the volume of elemental cell is equal to 911 Å^3. In the series of lanthanide(III) complexes only the values of volume and unit cell parameters for compounds with holmium(III), erbium(III) and yttrium(III) differ significantly from other compounds which crystallize in the same triclinic crystal system. For the above mentioned complexes the values of volume and unit cell parameters (that is a/Å) are much smaller than for the complexes from Nd(III) to Dy(III) (Table 3). The holmium(III) complex crystallizes in the triclinic crystal system with the elemental cell parameters: $a = 8.59$; $b = 13.97$; $c = 19.45$ Å and $\alpha = 61.45$, $\beta = 59.56$, $\gamma = 51.91°$. The elemental cell volume is equal to 1,536 Å^3. The values of cell volume for the complexes with yttrium(III) and erbium(III) are 1,355 and 1,312 Å^3 respectively. The values of cell volume for the series of complexes with lanthanides from Nd(III) to Dy(III) are in the range 1,666–1,977 Å^3.

Thermal analysis

The thermogravimetric analysis technique (TG) is used to investigate the behavior of materials are subjected to temperature change [23]. Thermogravimetric analyses were recorded (in air atmosphere) for all lanthanide(III) complexes to find out their behavior with the increasing temperature. The results of thermal analyses are collected in Table 4. The lanthanides(III) complexes include three or six molecules of water on two metal ions. The 2,2′–biphenyldicarboxylates are stable up to 30 °C. On further heating the complexes lose all water molecules in one step. The dehydration processes proceed in accordance with the following schemes and go off up to 155–210 °C:

$$Ln_2L_3 \cdot 3H_2O \rightarrow Ln_2L_3 + 3H_2O,$$
$$\text{where Ln} = \text{Y(III) and Ce(III)} - \text{Er(III)};$$
$$Ln_2L_3 \cdot 6H_2O \rightarrow Ln_2L_3 + 6H_2O,$$
$$\text{where Ln} = \text{La(III) and Tm(III)} - \text{Lu(III)}$$

The TG curves in the aforementioned temperature range show loss of mass by about 4–6% and 9–10% which corresponds to the loss of three and six water molecules per a dimeric unit of polymeric structure (Table 4). The DTA curves show that dehydration processes are presented as endothermic effects which results from the heat absorption in order to remove water molecules from the structure of hydrated complexes. The loss of all water molecules leads to creation of anhydrous compounds, which are stable up to 315–370 °C. The anhydrous compounds decompose on heating directly to oxides (Ln_2O_3, CeO_2, Tb_4O_7 and Pr_6O_{11}). In the case of the La(III) complex the corresponding oxide is formed by the intermediate forms (Fig. 2). The anhydrous La(III) complex is stable up to about 345 °C and next it decomposes by intermediate formation (between 345–630 °C) and then La_2O_3 (in the range 630–725 °C). The temperature of oxide formation changes from 410 °C, for CeO_2, to 560 °C for Pr_6O_{11}. The oxidation of the organic ligand is accompanied by the exothermic effects.

The IR spectrum of gaseous products of decomposition was obtained for the gadolinium(III) complex as the representative complex for compounds with three water molecules. As follows from Fig. 3. only the dehydration process takes place below 200 °C. The characteristic stretching and deformation vibrations of water molecules occur at about 3,900–3,400 and 1,900–1,300 cm^{-1}. The lack of absorption bands between 200–350 °C indicates that the anhydrous complex is stable in this temperature range. When the complex is heated above 350 °C the decomposition of the compound with degradation of organic ligand is observed. In the FTIR spectrum of gaseous products, the absorption bands corresponding to the emission of CO_2 appear. The absorption bands attributed to carbon dioxide molecules are situated round 2,350 and 670 cm^{-1}. The first one comes from the stretching asymmetric vibrations and the second one presents the deformation vibration of CO_2 molecules. Around 650 °C the weak absorption bands in the wavenumber range of 3,100–3,000 cm^{-1} are observed. These bands probably come from the stretching vibrations of gaseous hydrocarbons.

Conclusions

Lanthanide(III) 2,2′-biphenyldicarboxylates were obtained as hydrated solids. Trihydrated complexes crystallize in the monoclinic (Ce(III) and Pr(III)) and triclinic (Y(III) and Nd(III)–Er(III)) crystal systems. All hexahydrated compounds are amorphous solids. Lanthanide(III) 2,2′-biphenyldicaroxylates are stable at room temperature and during heating lose all water molecules in one step. The anhydrous compounds are the products of dehydration and they are stable in the wide temperature range about 150 °C. The FTIR spectra of gaseous products show that the dehydration process is associated only with emission of H_2O. The complexes, which may create the microporous coordination polymers must be crystalline compounds, their dehydration process must be absolute and the temperature range of the stability of anhydrous form must be wide. On the basis of these, the complexes from Ce(III) to Er(III) may be promising compounds for creation of microporous coordination polymers.

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