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SYNTHESIS AND CHARACTERIZATION OF METAL POLYCARBOXYLATES CONSTRUCTED FROM LANTHANIDES(III) AND 1,2,4,5-BENZENETETRACARBOXYLIC ACID

Z. Rzączyńska[*], *A. Ostasz, M. Sikorska-Iwan, H. Głuchowska, E. Olszewska and S. Pikus*

Faculty of Chemistry, Maria Curie-Skłodowska University, M.C. Skłodowska Sq. 2, 20-031 Lublin, Poland

The complexes of yttrium(III) and lanthanides(III) with 1,2,4,5-benzenetetracarboxylic acid were prepared as crystalline solids of the general formula $Ln_4(C_{10}H_2O_8)_3 \cdot 14H_2O$. They are insoluble in water. On heating in air or inert gas atmosphere all compounds lose water molecules; next anhydrous compounds decompose to oxides. The yttrium complex and heavy lanthanide (from Ho to Lu) ones crystallize in monoclinic crystal system. The dehydration does not change the crystal structure of the compounds.

Keywords: *1,2,4,5-benzenetetracarboxylates, lanthanide complexes, pyromellitates, TG-DSC, TG-DTA, X-ray powder analysis*

Introduction

The construction of coordination polymeric complexes has developed rapidly in recent years, owing to their interesting molecular topologies and potential applications as functional materials [1, 2]. The synthetic strategy of coordination polymers is needed to build up by functional organic ligands such as pyridine, carboxylate and phosphonate which much interests as microporous materials [3, 4]. Porous coordination polymers with open channels have potential applications in heterogeneous catalysts, separations, preparation of sensors, storage materials, sorption and ion exchange [4].

Various polycarboxylate ligands have been used to prepare coordination polymer compounds of transition metals or lanthanides: 1,4-benzenedicarboxylates, 1,3,5-benzenetricarboxylate, 1,3,5,7-adamantanetetracarboxylate, 1,3,5-cyclohexanetricarboxylate [4–7]. As compared to the reports of *d*-block transition metal polymers, lanthanide polymeric complexes are less common, because the high coordination numbers of lanthanide ions may cause difficulty in controlling the synthetic reactions and thereby the structures of the products. Lanthanide ions have high affinity for hard donor atoms and ligands containing oxygen or hybrid oxygen-nitrogen atoms, especially multicarboxylate ligands are usually employed in the architectures for lanthanide polymeric complexes.

1,2,4,5-benzenetetracarboxylic acid (H_4BTEC; pyromellitic acid) possesses several interesting characteristic:

- it has four carboxyl groups that may be completely or partially deprotonated, including rich coordination modes and allowing interesting structures with higher dimensions
- it can act not only as hydrogen-bond acceptor but also as hydrogen-bond donor, depending upon the number of deprotonated carboxyl group [1, 8]

Benzenetetracarboxylate (or pyromellitate) ligand has a very versatile coordination behavior, since it can form bridges between metallic centers, generating various and sometimes surprising molecular architectures. Pyromellitate complexes have been reported with several transition metals [9–12]. In some of these compounds, the carboxylate ligand is capable of forming one-, two-, or three-dimensional networks, where the metal centers are coordinated by two to four carboxylate groups. In compounds, four types of coordination were observed:

- the carboxylate group of the ligand is monodentate
- one carboxylate group of the ligand forms a four-membered chelate ring with the metal center
- the ligand bridges two different metal centers and
- two different carboxylate groups form a seven-membered chelate with the metal center

The acid form of the ligand contains four H protons, which can be deprotonated in various degrees. The most common are the $[C_6H_2(COO)_4]^{4-}$ and $[C_6H_2(COO)_2(COOH)_2]^{2-}$ anions.

The aim of this work was to examine properties and thermal stability of new lanthanide compounds with potential polymeric structure. The results of investigations of the metal carboxylates show that polycarboxylates ligands such as 1,2,4,5-benzenetetracarboxylates ions create complexes of desired properties. Cao *et al*. [1] have described structures and some

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[*] Author for correspondence: rzacz@hermes.umcs.lublin.pl

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properties of pyromellitates of Tb(III), Er(III) and Yb(III) obtained by hydro- or solvothermal reaction. We decided to use a simpler way of synthesis and to extend the study to the all lanthanides expecting interesting properties in complete series of compounds.

Experimental

The complexes of Y(III) and lanthanides(III) from La to Lu (except Pm) were prepared adding stoichiometric amounts of 0.05 M solution of ammonium 1,2,4,5-benzenetetracarboxylate (pH 5.5) to the hot solution of lanthanide chlorides; in the case of cerium(III) the nitrate solution was used. The precipitates formed were heated at 50°C in mother solution for 3 h, then filtered off, washed with hot water to remove ammonium ions and dried at 30°C to a stable mass.

The percentage of carbon and hydrogen were determined with Perkin-Elmer CHN 2400 elemental analyzer.

IR spectra of the complexes were recorded over the range of 4000–400 cm^{-1} by using a FTIR 1725X Perkin Elmer spectrophotometer. The samples were dispersed in KBr discs.

The X-ray diffraction patterns were taken on a Seifert-DRON automated X-ray diffractometer ($2\theta=5–72°$) at ambient temperature. Pattern indexing was carried out with the PC-version of TREOR program [13].

The solubility of the prepared complexes in water at room temperature was determined spectrophotometrically on a Specord M40 (Carl Zeiss, Jena) spectrometer using arsenazo III. Complexes are sparingly soluble in water. The solubilities are of the order 10^{-7}–10^{-6} mol L^{-1} and they increase from lanthanum to lutetium. The solubility of yttrium complex and heavy lanthanide ones are comparable.

The thermal stability and decomposition of the complexes was investigated with the aid of a Setsys 16/18 (Setaram) thermal analyzer, recording TG, DTA and DTG curves. Samples (9–10 mg) were heated in ceramic crucible between 30–1000°C in flowing air atmosphere (v=1 L h^{-1}) with a heating rate of 10°C min^{-1}. The products of decomposition were postulated on the basis of the TG curves (Table 1). The dehydration process of complexes was studied in detail by TG-DSC technique on the Setsys 16/18 analyzer. Samples of 5 mg were heated in ceramic crucible up to 450°C with a heating rate of 2.5, 5, 7.5 and 10°C min^{-1} in flowing air.

Gaseous products of decomposition were identified using a Netzsch TG 209 apparatus coupled to a Brucker FTIR IFS 66 spectrophotometer. The samples were heated in a dynamic argon atmosphere using a ceramic crucible and heating with a rate of 20°C min^{-1} up to 1000°C (Fig. 1).

Results and discussion

The 1,2,4,5-benzenetetracarboxylates of Y(III) and lanthanides(III) from La(III) to Lu(III) were obtained as crystalline compounds with metal:ligand ratio of

Table 1 Thermoanalytical data of Y(III) and lanthanide(III)1,2,4,5-benzenetetracarboxylates

Complexes	ΔT_1/°C	Mass loss/%		ΔT_2/°C	Mass loss/%	
		calc.	found		calc.	found
$Y_4L_3\cdot14H_2O$	30–250	18.56	18.5	400–680	66.75	66.2
$La_4L_3\cdot14H_2O$	30–400	16.17	15.9	620–760	58.18	58.8
$Ce_4L_3\cdot14H_2O$	30–250	16.13	15.8	400–520	55.96	56.2
$Pr_4L_3\cdot14H_2O$	30–300	16.10	15.9	425–620	56.52	55.6
$Nd_4L_3\cdot14H_2O$	30–300	15.97	15.8	620–710	57.40	57.8
$Sm_4L_3\cdot14H_2O$	30–300	15.74	15.8	450–660	56.48	56.2
$Eu_4L_3\cdot14H_2O$	30–310	15.66	15.7	390–675	56.29	55.9
$Gd_4L_3\cdot14H_2O$	30–310	15.45	15.5	450–660	55.56	54.8
$Tb_4L_3\cdot14H_2O$	30–270	15.39	15.4	440–580	54.36	53.5
$Dy_4L_3\cdot14H_2O$	30–230	15.26	15.3	420–650	54.86	54.3
$Ho_4L_3\cdot14H_2O$	30–285	15.17	15.1	440–660	54.54	53.6
$Er_4L_3\cdot14H_2O$	30–260	15.09	15.1	450–660	54.24	54.4
$Tm_4L_3\cdot14H_2O$	30–290	15.02	15.0	445–635	54.01	54.4
$Yb_4L_3\cdot14H_2O$	30–290	14.80	14.9	410–680	53.49	53.9
$Lu_4L_3\cdot14H_2O$	30–290	14.82	15.0	460–640	53.25	53.4

$L=C_{10}H_2O_8^{4-}$; ΔT_1 – temperature range of dehydration process; ΔT_2 – temperature range of decomposition of anhydrous complexes or intermediates to oxides: Ln_2O_3, CeO_2, Pr_6O_{11} and Tb_4O_7

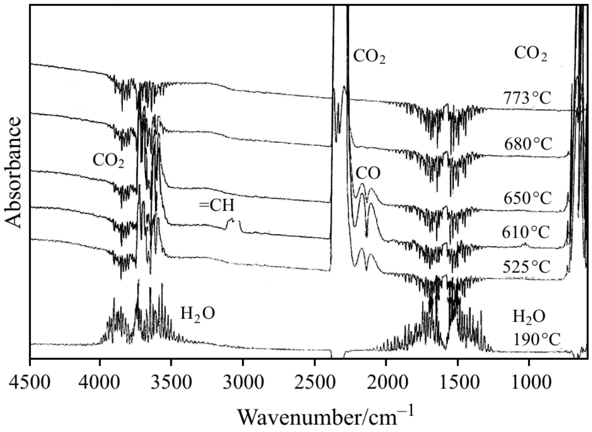

Fig. 1 FTIR spectra of gaseous products of thermal decomposition of $Eu_4(C_{10}H_2O_8)_3\cdot 14H_2O$

4:3. Their general formula is $Ln_4(C_{10}H_2O_8)_3\cdot 14H_2O$. The contents of carbon and hydrogen found on the basis of elemental analysis are in a very good agreement with calculated values for 14-hydrated pyromellitates.

The complexes were characterized by FTIR spectroscopy. The spectra of complexes were compared with a spectrum of pyromellitic acid. The 1,2,4,5-benzenetetracarboxylates of yttrium and lanthanides exhibit in solid state similar IR spectra. The bands with the maximum at 3230–3435 cm^{-1} are characteristic for ν(OH) vibrations which confirm the presence of water molecules in the complexes. The band at 1702 cm^{-1} originating from the COOH group, present in the spectrum of acid, is replaced in the spectra of complexes by two bands which can be ascribed to the asymmetric and symmetric vibration modes of the COO^- groups [14]. The asymmetric band forms submaxima at the region of 1602–1565 cm^{-1}. Single symmetric band is present at 1398–1387 cm^{-1} . The splitting of asymmetric COO^- bands suggests the different mode of coordination of carboxylate groups. These results are in good agreement with ones obtained by Cao *et al.* [1]. The authors had observed several types of coordination modes of COO^- groups in structures of studied Tb, Er and Yb pyromellitates: a monodentate mode, bidentate chelating or bridging modes and a tridentate chelating-bridging one. Two coordination modes, at least, had been presented in each complex.

The thermal stability of Y(III) and lanthanide(III) 1,2,4,5-benzenetetracarboxylates was studied in air atmosphere. The hydrated complexes are not stable above 30°C. They are dehydrated to form anhydrous compounds near 350°C. The anhydrous complexes are stable up to 400–450°C (Table 1) and decompose on heating to oxides (Ln_2O_3, CeO_2, Tb_4O_7 and Pr_6O_{11}) directly or with formation intermediates in the case of La(III) and Nd(III) complexes. The temperature of oxide formations varies from 520°C (CeO_2) to 760°C (La_2O_3).

The decomposition process with the gas product analysis was recorded for 1,2,4,5-benzenetetracarboxylates of some lanthanides. For example the FTIR spectrum of gaseous products of decomposition process of europium 1,2,4,5-benzenetetracarboxylate is presented on Fig. 1. The spectra confirm that dehydration is the first decomposition stage. The characteristic valence and deformation vibration bands of water molecules in the wavenumber ranges of 3900–3400 and 1900–1300 cm^{-1} are observed. The anhydrous complex is stable up to 450°C. The bands characteristic for CO_2 molecule vibrations occur in the following ranges: 3750–3550, 2400–2250 and 750–600 cm^{-1} [15]. At 610°C bands in the wavenumber range of 3100–3025 cm^{-1} are observed. This region is characteristic of stretching =C–H vibrations of gaseous hydrocarbons. Upon further heating they disappear at 650°C. The double peak of band characteristic of CO molecule vibrations appears in the range of 2200–2050 cm^{-1} and 500–650°C [16].

X-ray diffraction patterns indicate that all 14-hydrated pyromellitates of Y(III) and lanthanides(III) are crystalline. The yttrium compound and heavy lanthanide ones (from Ho to Lu) are isostructural.

It was decided to investigate structural changes of lanthanide pyromellitates caused by dehydration process. The loss of water molecules without changes of structure gives the possibility to obtain a material of desired properties: porous with open channels, capable of sorption of gases or other small molecules. The detailed studies of dehydration of selected complexes were carried out with TG-DSC method. The results show that dehydration occurs in several overlapping stages (Table 2). The first step (30–60°C) is not clearly visible on TG curves. A shape of DTG curves and a change of heat capacity recorded on DSC curves indicate the presence of this stage of dehydration. It is connected with loss of weekly bonded water molecules (about 1 mole of water per 1 mole of complex; this water is lost in ambient temperature when the complexes are heated in vacuum). Next, the coordination water molecules are lost. In the case of majority of complexes (except yttrium and erbium compounds) the dihydrate appears as intermediate at about 150°C. Unfortunately, the dehydration stages overlap. The decrease of heating rate from 10 to 2.5°C min^{-1} does not allow to separate completely the particular dehydration steps. However at heating rate of 2.5°C min^{-1} the DSC peaks are sufficiently separated to determine the enthalpy of dehydration of certain steps (Table 2). Dehydration is finished at about 250–300°C, but a small quantity of water rests in products up to 350°C (in the case of La compound the dehydration is finished at 400°C).

In order to determine the structural changes during dehydration anhydrous lanthanide pyromellitates

Table 2 The results of dehydration process of yttrium and lanthanide(III) pyromellitates ($L=C_{10}H_2O_8^{4-}$; air atmosphere; β=2.5°C min^{-1}; enthalpy values counted over mol of $Ln_4L_3\cdot 14H_2O$)

Compound	T_{range}/°C	Mass loss/%		Product of dehydration	Enthalpy/kJ mol^{-1}
		calc.	found		
$Y_4L_3\cdot 14H_2O$	30–270	18.56	18.72	Y_4L_3	526.7
$La_4L_3\cdot 14H_2O$	30–95	8.09	7.85	$La_4L_3\cdot 7H_2O$	140.0
	95–150	11.55	11.65	$La_4L_3\cdot 4H_2O$	
	150–280	13.86	14.10	$La_4L_3\cdot 2H_2O$	
	280–400	16.17	16.50	La_4L_3	
$Nd_4L_3\cdot 14H_2O$	30–115	9.12	9.42	$Nd_4L_3\cdot 6H_2O$	320.8
	115–160	13.68	13.55	$Nd_4L_3\cdot 2H_2O$	
	160–300	15.97	16.40	Nd_4L_3	
$Eu_4L_3\cdot 14H_2O$	30–115	11.18	10.80	$Eu_4L_3\cdot 4H_2O$	417.1
	115–150	13.42	13.40	$Eu_4L_3\cdot 2H_2O$	
	150–320	15.66	15.90	Eu_4L_3	
$Dy_4L_3\cdot 14H_2O$	30–145	13.08	13.40	$Dy_4L_3\cdot 2H_2O$	505.7
	145–250	15.26	15.30	Dy_4L_3	
$Ho_4L_3\cdot 14H_2O$	30–130	13.00	12.72	$Ho_4L_3\cdot 2H_2O$	506.7
	130–280	15.17	15.40	Ho_4L_3	
$Er_4L_3\cdot 14H_2O$	30–260	15.09	14.68	Er_4L_3	503.3
$Lu_4L_3\cdot 14H_2O$	30–110	8.46	8.60	$Lu_4L_3\cdot 6H_2O$	329.4
	110–135	12.69	12.20	$Lu_4L_3\cdot 2H_2O$	
	135–300	14.82	14.52	Lu_4L_3	

were obtained by heating of 14-hydrates in air up to 350°C (400°C in the case of La complex) with a heating rate of 5°C min^{-1}. The products were identified by TG technique and elemental analysis. The X-ray diffractograms show that anhydrous pyromellitates of light lanthanides (from La to Dy) are amorphous and anhydrous complexes of Y and heavy lanthanides are crystalline and isostructural.

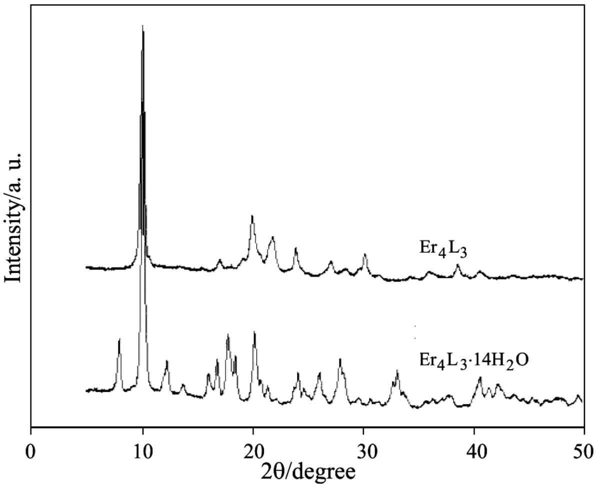

Fig. 2 X-ray powder diffraction patterns of $Er_4L_3\cdot 14H_2O$ and Er_4L_3 obtained at 350°C ($L=C_{10}H_2O_8^{4-}$)

The hydrated complexes of Er(III) and Lu(III) are representative for isostructural group of lanthanide complexes from Ho to Lu. The 14-hydrated complexes crystallize in monoclinic crystal system with decreasing elemental cell volume from 1936 Å^3 for Er(III) to 1780 Å^3 for Lu(III) complex (elemental cell parameters are given in Table 3 and X-ray diffraction patterns of erbium pyromellitate is shown on Fig. 2). The decreasing of elemental cell volume in the isostructural series of lanthanide complexes is due to decreasing of radii of lanthanide ions.

The anhydrous compounds characterize also monoclinic crystal system with similar values elemental cell parameters (Table 3). This fact shows that heating of complexes up to 350°C causes removing of coordination and hydrogen bonded water molecules, but lanthanide-organic framework does not change. Despite of absence of 14 water molecules in the framework, the volume of elemental cell is quite the same; the change is equal of 1.5% in the case of erbium complex and about 5% in the case of lutetium one (Table 3).

Although the 14-hydrated and anhydrous pyromellitates of erbium and lutetium are isostructural, the way of loss of water molecules is not the same (Fig. 3). The dehydration of lutetium complex is multistage (independently from heating rate and atmosphere of furnace). The erbium complex loss coordination water molecules in one step. This fact shows that comparison of crystal structures of hydrates and anhydrous compounds does not allow to draw conclusions about mechanism of dehydration process. The same structures can be obtained by different way of dehydration.

Take to consideration the powder diffraction data of Ho, Tm, Yb and Y pyromellitates one can say that removing of the crystallization water molecules does

Table 3 The unit cell parameter for hydrated and unhydrous pyromellitates of erbium and lutetium ($L=C_{10}H_2O_8^{4-}$)

	$Er_4L_3\cdot14H_2O$	Er_4L_3	$Lu_4L_3\cdot14H_2O$	Lu_4L_3
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
a/Å	17.93	11.39	17.19	10.32
b/Å	9.77	17.47	9.35	17.08
c/Å	11.33	9.63	11.16	9.65
α/degree	90.00	90.00	90.00	90.00
β/degree	102.86	95.63	97.51	95.43
γ/degree	90.00	90.00	90.00	90.00
Volume/Å^3	1936	1907	1780	1695

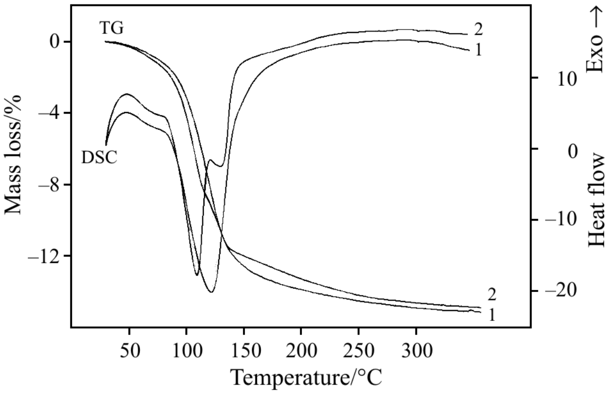

Fig. 3 TG and DSC curves of dehydration of 1 – $Er_4L_3\cdot14H_2O$ and 2 – $Lu_4L_3\cdot14H_2O$ ($L=C_{10}H_2O_8^{4-}$, β=5°C min^{-1}, air atmosphere)

not cause a structure modification and the framework formed by lanthanide ions and carboxylate ligands changes insignificantly. Further study on application of yttrium and heavy lanthanide pyromellitates as storage or sorption materials is now in progress.

Conclusions

We succeeded in obtaining the hydrates of heavy lanthanide pyromellitates which did not change their crystal structure after dehydration. It indicates the complexes may be used to generated porous materials. The synthesis method used is particularly simple. The main problem is the necessity to heat the hydrates up to 350°C. Only at such temperature totally anhydrous products are obtained.

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