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THERMAL AND SPECTRAL FEATURES OF YTTRIUM AND HEAVY LANTHANIDE COMPLEXES WITH 2,4-DIMETHOXYBENZOIC ACID

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Abstract

The complexes of yttrium and heavy lanthanides with 2,4-dimethoxybenzoic acid of the formula: $Ln(C_9H_9O_4)_3 \cdot nH_2O$, where Ln=Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III) and Y(III), n=2 for Tb(III), Dy(III), Ho(III), Er(III), Tm(III) and Y(III), and n=0 for Yb(III) and Lu(III), have been synthesized and characterized by elemental analysis, IR spectroscopy, themogravimetric studies, as well as X–ray and magnetic susceptibility measurements. The complexes have a colour typical of Ln^{3+} salts (Tb, Dy, Tm, Yb, Lu, Y – white, Ho – cream, Er – pink). The carboxylate group in these complexes is a bidentate, chelating ligand. The compounds form crystals of various symmetry. 2,4-Dimethoxybenzoates of Yb(III) and Lu(III) are isostructural. 2,4-Dimethoxybenzoates of yttrium and heavy lanthanides decompose in various ways on heating in air to 1173 K. The hydrated complexes first lose water to form anhydrous salts and then decompose to the oxides of respective metals. The ytterbium and lutetium 2,4-dimethoxybenzoates decompose in one step to form Yb_2O_3 and Lu_2O_3.

The solubilities of the 2,4-dimethoxybenzoates of yttrium and heavy lanthanides in water and ethanol at 293 K are of the order of: 10^{-3} and 10^{-3}–10^{-2} mol dm^{-3}, respectively. The magnetic moments for the complexes were determined over the range of 77–298 K. They obey the Curie–Weiss law. The results show that there is no influence of the ligand field on the 4f electrons of lanthanide ions.

Keywords: 2,4-dimethoxybenzoates of heavy lanthanides thermal stability, IR spectroscopy, magnetic moments, X-ray diffraction

Introduction

A literature survey indicates that the compounds of 2,4-dimethoxybenzoic acid with various cations have been relatively seldom studied. Papers concerning complexes of the following cations: Cu(II), La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Dy(III) and Yb(III) can only be found. The compounds were often obtained as solids or were investigated in solution [1–3].

The 2,4-dimethoxybenzoate of Cu(II) was obtained in the solid state and its magnetic properties were determined [1], while those of La(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Yb(III) were investigated in solution and their dissociation

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constants were established potentiometrically [2]. The 2,4-dimethoxybenzoates of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III) and Gd(III) were also obtained in the solid state and their properties such as thermal stability in air during heating to 1173 K, and solubilities in water and ethanol at 293 K were studied [3].

2,4-Dimethoxybenzoic acid is a crystalline solid, which easily sublimates under high vacuum [4] and is sparingly soluble in water [5]. The pK_a value relating to its dissociation constant is equal to 9.29 (298 K) and its melting point is 382 K [2, 5]. 2,4-Dimethoxybenzoic acid is often used for preparation of resins [6].

There is no information in literature concerning solid-state properties of the complexes of 2,4-dimethoxybenzoic acid with yttrium and heavy lanthanides. Therefore, we synthesized them and examined some of their properties, such as thermal stability in air or solubility in water and ethanol at 293 K. Furthermore, IR spectral characteristics, and X-ray powder investigations were carried out in order to know whether the compounds appear in crystalline or amorphous phases. Last magnetic features of the compounds were investigated in order to reveal the nature of metal ligand bonding.

The thermal stability investigations enabled to reveal the role and location of crystallization water molecules, i.e. indicate in which, sphere of coordination (outer or inner) these molecules appear, and pathways of complexes decomposition, as well as, to determine the endothermic or exothermic effects accompanying such processes as: dehydration, melting, crystallization, oxidation, reduction, and to estimate the strength of the bonding between atoms or groups of atoms and ions.

The determination of the solubility is valuable because it furnishes information on the practical use of the respective acid for the separation of rare-earth elements by extraction or ion-exchange chromatographic methods.

If the magnetic moment is known, the number of unpaired electrons can be determined. This may provide information on the oxidation state of the metal ion or the central atom of a complex, the electronic configuration, and hence, the nature of the bonding between the metal and ligands.

Experimental

The 2,4-dimethoxybenzoates of yttrium and heavy lanthanides were prepared by the addition of equivalent quantities of 0.1 M ammonium 2,4-dimethoxybenzoate (pH 5) to a hot solution containing the chlorides of the yttrium and heavy lanthanides followed by crystallization at 293 K. The formed solids were filtered off, washed with hot water to remove ammonium ions and dried at 303 K to constant mass.

The contents of carbon and hydrogen were determined by elemental analysis using a CHN 2400 Perkin Elmer analyser. The contents of metal(III) ions and crystallization water molecules were determined spectrophotometrically, and from the TG curves (Table 1).

The IR spectra of complexes were recorded over the range 4000–400 cm^{-1} using a M-80 spectrophotometer. Samples were dispersed in KBr. Some of the results are presented in Fig. 1.

Table 1 Elemental analysis data of yttrium and heavy lanthanide 2,4-dimethoxybenzoates and solubilities in water and ethanol (at 293 K) (L=$C_9H_9O_4$)

Complex	H/%		C/%		Ln/%		Solubility/mol dm^{-3}	
	calcd.	found	calcd.	found	calcd.	found	water	ethanol
$TbL_3·2H_2O$	4.20	4.17	43.90	43.36	21.53	21.32	$2.20·10^{-3}$	$4.09·10^{-3}$
$DyL_3·2H_2O$	4.18	4.13	43.69	43.23	21.91	21.85	$2.46·10^{-3}$	$5.23·10^{-3}$
$HoL_3·2H_2O$	4.16	4.11	43.55	43.24	22.17	21.89	$2.18·10^{-3}$	$5.15·10^{-3}$
$ErL_3·2H_2O$	4.15	4.01	43.41	42.75	22.41	22.51	$2.27·10^{-3}$	$8.07·10^{-3}$
$TmL_3·2H_2O$	4.14	4.11	43.31	42.85	22.58	22.62	$2.19·10^{-3}$	$1.10·10^{-3}$
YbL_3	3.77	3.65	45.23	45.33	24.16	23.76	$4.33·10^{-3}$	$6.35·10^{-3}$
LuL_3	3.76	3.59	45.12	44.68	24.36	23.79	$2.23·10^{-3}$	$6.00·10^{-3}$
$YL_3·2H_2O$	4.61	4.63	48.43	48.05	13.43	13.54	$2.78·10^{-3}$	$3.95·10^{-3}$

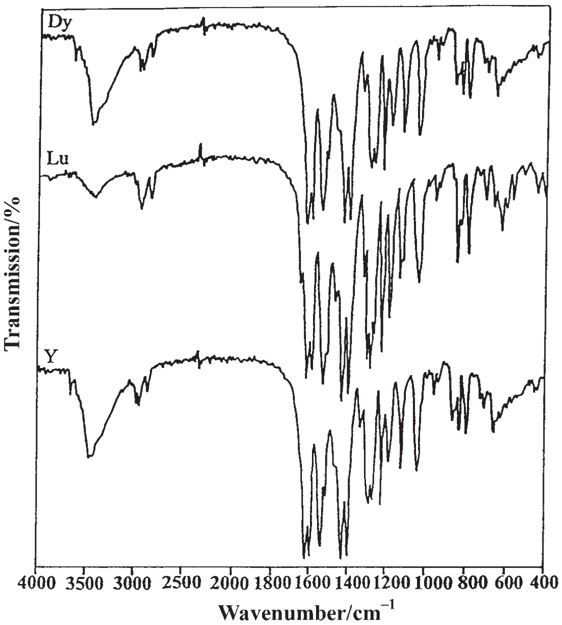

Fig. 1 Infrared spectra of 2,4-dimethoxybenzoates of dysprosium, lutetium and yttrium

The X-ray diffraction patterns were taken on a HZG-4 (Zeiss Jena) diffractometer using Ni filtered CuK$_\alpha$ radiation. The measurements were carried out within the range 2Θ=4–80° by means of the Debye–Scherrer–Hull method. The radiograms of the complexes are presented in Fig. 2.

The thermal stability and decomposition of the prepared complexes were determined using a Paulik–Paulik–Erdey Q-1500 D derivatograph with a Derill converter recording TG, DTG and DTA curves. The measurements were carried out at a heating rate of 10 K min^{-1}. 100 mg samples were heated in platinum crucibles in static air to 1173 K. Sensitivity of TG was 100 mg (it means that the whole scale in the balance is equal to 100 mg). DTG and DTA sensitivities were regulated by the Derill computer programme. The paper speed was 2.5 mm min^{-1}, and Al_2O_3 was used as the reference material. The products of decomposition were identified on the basis of X-ray diffraction pattern (Table 2), and their amounts were estimated on the basis of mass losses (from TG curves).

The solubilities of 2,4-dimethoxybenzoates of yttrium and the heavy lanthanides in water and ethanol at 293 K were determined spectrophotometrically by measuring the concentration of Ln^{3+} ions in a saturated solution using SPECORD M-40 spectrophotometer (Table 1). The aborbance of the complexes was measured by using the Arsenazo III in the formic buffer (pH~3.5) and the wavelength λ=650 nm [7, 8].

Magnetic susceptibilities of polycrystalline samples of 2,4-dimethoxybenzoates were measured by the Gouy method using a sensitive Cahn RM-2 balance. Measurements were carried out at a magnetic field strength of 9.9 KΘe. The calibrant employed was $CoHg(SCN)_4$, for which the magnetic susceptibility was assumed to be $1.644\cdot 10^{-5}$ cm^{-3} g^{-1} [9]. Correction for diamagnetism of the constituent atoms was calculated by the use of Pascal's constants [10]. The magnetism of the samples was found to be field independent. The temperature-independent paramagnetism of rare earth was assumed to be zero. Magnetic moments were calculated according to Eqs (1) and (2),

$$\mu=2.83(\chi_M T)^{1/2} \tag{1}$$

$$\mu=2.83[\chi_M (T-\Theta)]^{1/2} \tag{2}$$

The results are given in Table 3.

The surface distributions of the atoms of 2,4-dimethoxybenzoates of yttrium and heavy lanthanides were determined using the scanning microscope LEO 1430 VP (Leica and Zeiss) with beam current 80 μA and the chamber pressure of $5.34\cdot 10^{-1}$ Pa. X-ray analyses were carried out with the use of X-ray detector (Röntec) in the time 200 s (Fig. 4).

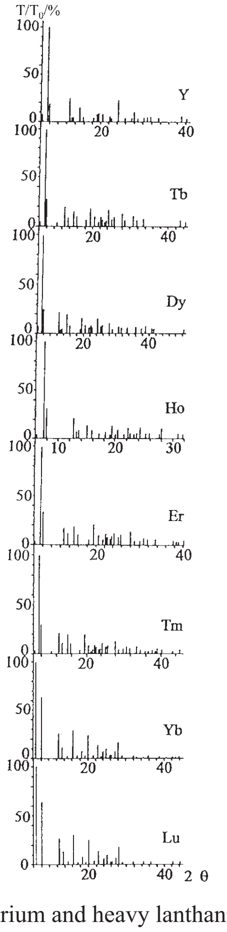

Fig. 2 Diffractograms of yttrium and heavy lanthanide 2,4-dimethoxybenzoates

Table 2 Temperatures of dehydration and decomposition of 2,4-dimethoxybenzoates of yttrium and heavy lanthanides, their mass losses and products of their decompositions and activation energy of dehydration reaction

Complex	ΔT_1/K	T_{max}/ K	Mass loss/%		n	ΔT_2/K	Mass loss/%		T_K/K	Product of decomp.	E_a/ kJ mol^{-1}
			calcd	found			calcd	found			
$TbL_3\cdot 2H_2O$	383–413	408	4.87	4.62	2	533–983	74.66	74.92	998	Tb_4O_7	65.56
$DyL_3\cdot 2H_2O$	388–408	403	4.85	4.62	2	538–998	74.85	74.92	1048	Dy_2O_3	51.21
$HoL_3\cdot 2H_2O$	383–403	398	4.84	4.62	2	548–973	74.60	74.92	1098	Ho_2O_3	81.68
$ErL_3\cdot 2H_2O$	378–398	398	4.82	4.62	2	543–983	74.37	74.26	1073	Er_2O_3	109.07
$TmL_3\cdot 2H_2O$	373–393	393	4.81	4.62	2	548–963	74.20	74.16	1053	Tm_2O_3	79.94
YbL_3	–	–	–	–	–	563–973	72.48	72.94	1023	Yb_2O_3	–
LuL_3	–	–	–	–	–	543–988	72.28	72.94	998	Lu_2O_3	–
$YL_3\cdot 2H_2O$	383–403	403	5.38	5.28	2	548–998	82.97	82.84	1073	Y_2O_3	70.61

L=$C_9H_9O_4$; ΔT_1=temperature range of dehydration process, T_{max}=temperature of the endothermic effect in the DTA curve, n=number of crystallization water molecules being lost in first endothermic step, ΔT_2=temperature range of anhydrous complex decomposition, T_K=temperature of lanthanide oxide formations, E_a=activation energy of the dehydration reaction

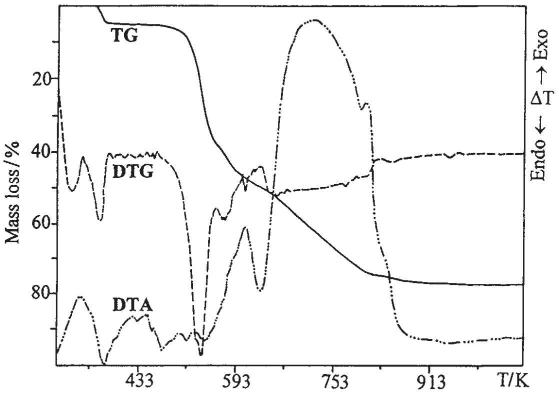

Fig. 3 TG, DTG and DTA curves of dysprosium 2,4-dimethoxybenzoate

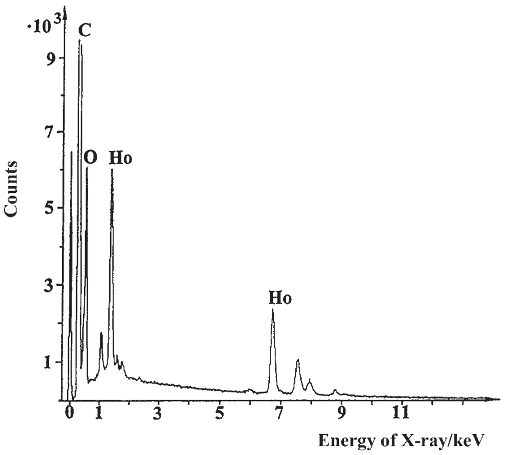

Fig. 4 The number of countings *vs.* X-ray energy emitted by Ho, O and C in 2,4-dimethoxybenzoate of Ho

Results and discussion

The 2,4-dimethoxybenzoates of yttrium and heavy lanthanides were obtained as crystalline hydrates or anhydrous solids of the general formula: $Ln(C_9H_9O_4)_3{\cdot}nH_2O$, where Ln=Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III) and Y(III), $n=0$ in the case of Yb(III) and Lu(III), and $n=2$ for other compounds. The colour of the complexes is typical of the particular *Ln*(III) salts i.e., is white in the case of Tb, Dy, Tm, Yb, Lu and Y, cream for Ho and pink for Er and originates from the lowest-energy f–f electronic transitions of the central atom.

The complexes were characterized by elemental analyses (Table 1) and IR spectroscopy (Fig. 1). All the 2,4-dimethoxybenzoates of yttrium and the heavy lanthanides exhibit in solid state similar IR spectra; some of them are presented in

Table 3 Magnetic susceptibility data for the heavy lanthanide 2,4-dimethoxybenzoates (L=$C_9H_9O_4$)

$TbL_3\cdot 2H_2O$			$DyL_3\cdot 2H_2O$			$HoL_3\cdot 2H_2O$			$ErL_3\cdot 2H_2O$			$TmL_3\cdot 2H_2O$			YbL_3		
Θ= –10 K			Θ= –20 K			Θ= –15 K			Θ= –3 K			Θ= –13 K			Θ= –35 K		
T/K	$\chi_M\cdot 10^6$	μ/BM	T/K	$\chi_M\cdot 10^6$	μ/BM	T/K	$\chi_M\cdot 10^6$	μ/BM	T/K	$\chi_M\cdot 10^6$	μ/BM	T/K	$\chi_M\cdot 10^6$	μ/BM	T/K	$\chi_M\cdot 10^6$	μ/BM
77	140507	10.17	77	142671	10.52	77	147601	10.42	77	143583	9.58	77	70520	7.12	77	22470	4.48
122	88853	9.69	120	93732	10.25	124	97013	10.39	124	94330	9.79	131	45920	7.27	124	15310	4.41
136	84321	9.92	135	86317	10.35	134	90318	10.38	136	86860	9.83	140	41430	7.12	133	15160	4.51
146	76308	9.76	147	80385	10.36	146	86598	10.56	146	76420	9.54	148	38440	7.04	144	14596	4.57
155	72619	9.79	158	74453	10.30	156	81391	10.55	152	71942	9.45	158	36200	7.04	148	13880	4.51
168	66715	9.75	166	68521	10.10	170	76183	10.62	164	67465	9.49	170	34700	7.13	165	13164	4.59
179	63764	9.82	178	66993	10.30	180	68744	10.56	169	65970	9.53	178	33950	7.20	175	12448	4.57
187	59336	9.67	185	65550	10.37	188	65768	10.34	185	60000	9.50	200	33210	7.52	183	12090	4.59
194	57860	9.72	192	62589	10.45	196	61305	10.17	194	57764	9.54	210	31715	7.52	198	11016	4.53
224	51957	9.86	220	56657	10.43	202	58329	10.06	216	52540	9.59	222	30182	7.53	207	11176	4.65
235	49005	9.80	234	53691	10.45	220	53865	10.06	226	48800	9.46	230	28688	7.47	218	10443	4.60
240	47529	9.75	242	52208	10.46	236	52378	10.26	235	46570	9.42	248	27194	7.53	226	10300	4.64
248	44578	9.59	246	50691	10.39	248	50890	10.35	240	45077	9.36	252	25730	7.38	239	9576	4.58
257	43102	9.60	258	49242	10.47	254	49402	10.31	244	43570	9.28	260	24230	7.27	247	8890	4.48
269	40888	9.55	266	47759	10.45	262	47914	10.31	255	40580	9.15	268	22739	7.15	262	8724	4.55
277	37199	9.24	274	46276	10.43	278	46426	10.43	260	37600	8.89	274	21244	6.98	272	8152	4.47
286	36461	9.25	290	43281	10.36	298	44938	10.61	263	38348	9.03	278	20490	6.91	281	7436	4.33
298	34985	9.28	298	41827	10.32				298	35360	9.23				294	7078	4.31

Fig. 1. As anticipated, the characteristic wavenumbers corresponding to the carbonyl group are altered markedly when going from the acid to the *Ln*(III) salts. The band at 1668 $\mathrm{cm^{-1}}$ originating from the COOH group, present in the IR spectrum of the acid, is replaced in the spectra of the complexes by two bands at 1528–1520 and 1415–1400 $\mathrm{cm^{-1}}$, which can be ascribed to the asymmetric and symmetric vibrational modes of the $\mathrm{COO^-}$ group, respectively [11–16]. The bands with maxima at 3464–3424 $\mathrm{cm^{-1}}$, characteristic of γ(OH) vibrations, and the narrow $\delta(H_2O)$ band at 1584 $\mathrm{cm^{-1}}$ confirm the presence of lattice water molecules in the complexes of Tb(III), Dy(III), Ho(III), Er(III), Tm(III) and Y(III). The bands attributed to asymmetric and symmetric C–H stretching modes of the CH_3 groups are observed at 2936 $\mathrm{cm^{-1}}$ and 2840–2830 $\mathrm{cm^{-1}}$, respectively. Bands relevant to symmetric deformation modes of the CH_3 group appear at 1392–1388 $\mathrm{cm^{-1}}$. The presence of the methoxy-substituents at the benzene ring is confirmed by the bands at 1276 $\mathrm{cm^{-1}}$. The skeletal benzene ring modes are observed at 1616–1450 $\mathrm{cm^{-1}}$. The stretching vibrations of the =C–H bond appear at 3440–3424 $\mathrm{cm^{-1}}$ and the out-of plane bending vibrations of this bond in the 945–645 $\mathrm{cm^{-1}}$ range. The bands typical of the aromatic ring vibrations in the complexes are not shifted significantly relative to those of the 2,4-dimethoxybenzoic acid, that indicates that the influence of the *Ln*(III) ions on the benzene ring is not significant. The bands corresponding to the metal–oxygen stretching appear probably at 466–460 $\mathrm{cm^{-1}}$ for the whole series of the complexes. It is therefore reasonable to assume that 2,4-dimethoxybenzoic acid form with the heavy lanthanides and yttrium complexes of similar stability [17].

The separation of the $\nu_{\mathrm{asCOO^-}}$ and $\nu_{\mathrm{sCOO^-}}$ modes of the complexes is smaller ($\Delta\nu_{\mathrm{COO^-}}$ =112–96 $\mathrm{cm^{-1}}$) than that of the sodium salt ($\Delta\nu_{\mathrm{COO^-}}$ =125 $\mathrm{cm^{-1}}$), which indicates a weaker ionic bonding in the heavy lanthanide 2,4-dimethoxybenzoates. Trivalent ions due to stronger electrostatic potential sorrounding them deform the ligand stronger than the smaller sodium ion. The shifts of the $\nu_{\mathrm{asCOO^-}}$ and $\nu_{\mathrm{sCOO^-}}$ wavenumbers are smaller in the heavy lanthanide complexes ($\nu_{\mathrm{asCOO^-}}$ =1528–1520 $\mathrm{cm^{-1}}$; $\nu_{\mathrm{sCOO^-}}$ =1415–1400 $\mathrm{cm^{-1}}$) than in the sodium 2,4-dimethoxybenzoate ($\nu_{\mathrm{asCOO^-}}$ =1550 $\mathrm{cm^{-1}}$, $\nu_{\mathrm{sCOO^-}}$ =1430 $\mathrm{cm^{-1}}$). This implies that the carboxylate ion behaves in the complexes as bidentate chelating ligand [11, 13, 18].

In order to know whether the heavy lanthanide 2,4-dimethoxybenzoates were prepared as crystalline or anhydrous compounds, their X-ray powder diffractograms were recorded. Their interpretation reveals, that only 2,4-dimethoxybenzoates of ytterbium and lutetium seem to be isostructural. The complete crystal stuctures of the complexes have not been determined, as attempts to obtain single crystals failed.

On heating to 1173 K, the 2,4-dimethoxybenzoates of yttrium and heavy lanthanides form oxides of relevant metals, having the same structures as the oxides obtained by roasting the rare-earth element oxalates [20].

The thermal stabilities of yttrium and the heavy lanthanide 2,4-dimethoxybenzoates were studied in air in the temperature range 293–1173 K (Table 2). The results of thermoanalytical investigations on these salts correspond generally well to the elemental analysis data (Table 1) and indicate which of them are hydrated and which anhydrous. All the complexes are stable in air at room temperature and do not change their mass on storage. When heated in air, they decompose in one or two steps. Dihydrates of Tb(III), Dy(III), Ho(III), Er(III), Tm(III) and Y(III) decompose in two steps. The compounds are stable up to 373–388 K. In the first step they lose two water molecules (373–408 K) and form anhydrous complexes. In the second step at 533–998 K, they decompose to the oxides of the relevant metals (Eq. (3)). The mass loss estimated from TG curves is equal to 74.16–82.84%, while calculated is 74.20–82.97%.

$$\mathrm{LnL_3{\cdot}2H_2O\rightarrow LnL_3\rightarrow Ln_2O_3\ (+Tb_4O_7);}\quad Ln\mathrm{(III)=Tb,\ Dy,\ Ho,\ Er,\ Tm,\ Y} \tag{3}$$

The oxides of the heavy lanthanides formed at 998–1098 K were identified by X-ray powder diffraction [20, 21]. The anhydrous complexes of Yb(III) and Lu(III) are stable up to 543–563 K and decompose in one step (543–988 K) to the oxides of the respective metals between 998–1023 K. The mass losses calculated from the TG curves are equal to 72.94% (the theoretical values are 72.28% and 72.48% respectively). An example of thermoanalytical data is presented in Fig. 3. Decomposition of dysprosium 2,4-dimethoxybenzoate begins at 388 K. The mass loss occurring in the range 383–408 K equals to 4.62% and corresponds to the release of two water molecules (the theoretical value is 4.85%). The dehydration process is associated with endothermic effect observed in the DTA curve [22, 23]. The anhydrous compound decomposes between 538–998 K to Dy_2O_3, which corresponds to the 74.92% mass loss. The oxidation process is associated with a strong exothermic effect reflected in the DTA curve.

As temperatures of the dehydration process are relatively low (373–408 K), and water molecules are released in a single step, it is reasonable to assume that water is bounded in the outer coordination sphere of the heavy lanthanide 2,4-dimethoxybenzoate [24, 25]. Water from crystals of various substances is removed in a broad temperature range [22, 23]. According to Nikolaev *et al.* [24] and Singh *et al.* [25], water released below 423 K can be considered as crystallization water, whereas that eliminated above 423 K, as chemically bounded to the central ion through weak ionic or partially covalent bonds [11]. The exact assignment of the position and bonding interaction of the water molecules in the dihydrate complexes investigated requires determination of their crystal structures. Unfortunately, we were unable to do so.

From the TG and DTA curves, the activation energies of the dehydration reactions (E_a in Table 2) were calculated by the Fotieev and Pletniev method [26] according to Eq. (4).

$$E_a = RT_{\max}^2 \Delta m m_o^{-1} \Delta T^{-1} \tag{4}$$

where R is the gas constant, $T_{\max}$ – the temperature of maximum of the mass loss, m_o – the mass loss at $T_{\max}$, m – the mass loss at T and T – the temperature; $\Delta m = m_o - m$; $\Delta T = T_{\max} - T$.

The different E_a values may suggest that the water molecules in the studied complexes are bounded with different strength, depending on their position in the coordination sphere. The lowest E_a value applies to dysprosium 2,4-dimethoxybenzoate, whereas the highest to the erbium complex.

The solubilities of the 2,4-dimethoxybenzoates of yttrium and the heavy lanthanides in water and ethanol (at 293 K) are given in Table 1. They are of the order of: 10^{-3} and 10^{-3}–10^{-2} mol dm^{-3} in water and ethanol, respectively. 2,4-dimethoxybenzoate of thulium is among the compounds investigated the best soluble in ethanol,while 2,4-dimethoxybenzoate of ytterbium is the best soluble in water. Poorly soluble in both water and ethanol are complexes of holmium and yttrium. Solubility data indicate that 2,4-dimethoxybenzoic acid is not suitable for the separation of the heavy lanthanides by ion-exchange chromatography or by extraction methods, because relevant complexes are relatively soluble.

The magnetic susceptibility of the heavy lanthanide 2,4-dimethoxybenzoates was measured in the temperature range of 77–298 K. The values of the Weiss constant, Θ, are negative for all the complexes [27–30]. The paramagnetic central ions in the compounds investigated remain virtually unaffected by the sorrounding ligands. The 4f electrons causing their paramagnetism are well protected from outside influences and do not participate in the formation of the *Ln*–O bond. Instead, they only weakly interact with the electrons of the sorrounding atoms and are located in an inner shell of a radius of 0.35 Å [31]. This value is very small in comparison with the radius of the $5s^25p^6$ closed shell equals to ca 1 Å. The ground state of the lanthanide ions is separated by several hundreds of cm^{-1} from the first higher-lying state. Hence, the magntic properties in the ground state can be expected to be identical for bounded and non-bounded lanthanide ions. The 2,4-dimethoxybenzoates of the heavy lanthanides obey the Curie–Weiss law. The values of μ_{eff} determined for all the complexes are close to those calculated for *Ln*(III) ions by Hund and van Vleck (Table 4). Lutetium 2,4-dimethoxybenzoate is, as expected, diamagnetic. The above data indicate that the *Ln*–O bond in the heavy lanthanide 2,4-dimethoxybenzoates is predominantly of an electrostatic nature, since the 4f orbitals of the lanthanide ions are effectively polarized by the $5s^25p^6$ octet [31, 32].

The distribution of the atoms on the surface of 2,4-dimethoxybenzoate of rare earth elements confirms the composition of the complexes. The dependence of the number of the countings *vs.* X-ray energy for 2,4-dimethoxybenzoate of holmium is presented, as an example, in Fig. 4.

Table 4 Value of μ_{eff} for the heavy lanthanides determined by Hund and van Vleck (μ/B.M.)

Ln(III)	Ground term	Hund μ_{eff}	Van Vleck μ_{eff}
Tb(III)	$^7F_6$	9.70	9.70
Dy(III)	$^6H_{15/2}$	10.60	10.60
Ho(III)	$^5J_8$	10.60	10.60
Er(III)	$^4J_{15/2}$	9.60	9.60
Tm(III)	$^3H_6$	7.60	7.60
Yb(III)	$^2F_{7/2}$	4.50	4.50
Lu(III)	$^1S_0$	0.00	0.00

Concluding, 2,4-dimethoxybenzoates of yttrium and heavy lanthanides were synthesized as hydrated or anhydrous complexes. The compounds exhibit colours arising from the relevant *Ln*(III) ion, i.e. white in the case of Tb, Dy, Tm, Yb, Lu and Y, cream for Ho and salmon for Er, having their origin in the lowest energy of f–f electronic transitions of the central atom. The energy levels do not change substantially in bounded and non-bounded lanthanide ions, which causes that the colours of the compounds and the free lanthanide ions are similar.

The Ln–O bond is predominantly of electrostatic nature. 2,4-dimethoxybenzoates of heavy lanthanides and yttrium are crystalline compounds that decompose in two steps on heating in air up to 1173 K. In the first step dehydration takes place and anhydrous complexes formed decompose in the second step to the oxides of the appropriate metals.

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