Journal of Thermal Analysis and Calorimetry, Vol. 71 (2003) 375–386

2,3-DIMETHOXYBENZOATES OF HEAVY LANTHANIDES AND YTTRIUM

W. Ferenc[*] *and A. Walków-Dziewulska*

Faculty of Chemistry, Maria Curie Skłodowska University 20-031 Lublin, Poland

(Received May 12, 2002; in revised form July 25, 2002)

Abstract

The complexes of heavy lanthanides and yttrium with 2,3-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), Y(III), and n=2 for Tb(III), Dy(III), Ho(III), Y(III), n=1 for Er(III), Tm(III), n=0 for Yb(III) and Lu(III) have been synthesized and characterized by elemental analysis, IR spectroscopy, thermogravimetric studies and X-ray diffraction measurements. The complexes have colours typical for Ln^{3+} ions (Tb(III), Dy(III), Tm(III), Yb(III), Lu(III), Y(III) – white; Ho(III) – cream and Er(III) – salmon). The carboxylate groups in these complexes are a symmetrical, bidentate, chelating ligand or tridentate chelating-bridging. They are isostructural crystalline compounds characterized by low symmetry.

On heating in air to 1273 K the 2,3-dimethoxybenzoates of heavy lanthanides and yttrium decompose in various ways. The complexes of Tb(III), Dy(III), Ho(III), Er(III), Tm(III) and Y(III) at first dehydrate to form anhydrous salts which next are decomposed to the oxides of the respective metals. 2,3-Dimethoxybenzoates of Yb(III) and Lu(III) are directly decomposed to oxides. When heated in nitrogen the hydrates also dehydrate in one step to form the anhydrous complexes that next form the mixture of carbon and oxides of respective metals or their carbonates.

The solubility of the yttrium and heavy lanthanide 2,3-dimethoxybenzoates in water at 293 K is of the order of 10^{-2} mol dm^{-3}.

Keywords: 2,3-dimethoxybenzoates, rare earth complexes, thermal stability investigations

Introduction

2,3-Dimethoxybenzoic acid is a white solid of melting point being equal to 395 K. It crystallizes from water in the prism form [1] in monoclinic system [2, 3]. The pK_a value of 2,3-dimethoxybenzoic acid and its thermodynamic parameter values were determined potentiometrically in the aqueous solutions and the energy of its combustion was calculated as well [4–6].

A literature survey indicates that the compounds of 2,3-dimethoxybenzoic acid with various cations have been relatively seldom studied. Papers concerning complexes of

---

[*] Author for correspondence: E-mail: WETAFER @hermes.umcs.lublin.pl

1388–6150/2003/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

some of the Ln^{3+} ions with 2,3-dimethoxybenzoic acid in the solution can only be found and their dissociation constants at 318 K were potentiometrically determined [7, 8]. The complex of Cu(II) with 2,3-dimethoxybenzoic acid was synthesized as solid and its thermal stability studied [9]. The complexes of 2,3-dimethoxybenzoic acid with the light lanthanides have been also prepared as solids and some of their physico-chemical properties have been studied [10]. 2,3-Dimethoxybenzoates of yttrium and heavy lanthanides have not been obtained so far. Therefore we decided to synthesize them and to examine some of their thermal stability in air and in nitrogen during heating, solubility in water (at 293 K) to record their FTIR spectra and X-ray powder diffractograms and to study their magnetic properties.

The aim of the thermal stability investigation is to estimate the position of the crystallization water molecules, i.e., in outer or inner coordination spheres, (ii) to resolve the mechanism of complex decomposition and to determine the endothermic or exothermic effects associated with the processes involved, such as dehydration, melting, crystallization, oxidation, reduction and (iii) to compare the relative strength of the bonding between the central Ln(III) ions and the surrounding molecules. The determination of the solubility provides valuable information about the practical use of the employed acid for the separation of rare-earth elements by extraction or ion-exchange chromatographic methods.

Experimental

The 2,3-dimethoxybenzoates of yttrium and heavy lanthanides were prepared by the addition of the equivalent quantities of 0.1 M ammonium 2,3-dimethoxybenzoate (pH~5) to a hot solution containing the rare-earth element chlorides followed by crystallization at 293 K. The formed solids were filtered off, washed with water to remove ammonium ions and dried at 303 K to constant mass.

Table 1 Elemental analysis data of yttrium and heavy lanthanide 2,3-dimethoxybenzoates and their solubilities in water (at 293 K)

Complex	C/%		H/%		Ln/%		Solubility/ mol dm^{-3}
L=$C_9H_9O_4$	calcd.	found	calcd.	found	calcd.	found	
$TbL_3 \cdot 2H_2O$	43.90	44.05	4.20	4.21	21.53	21.21	$2.1 \cdot 10^{-2}$
$DyL_3 \cdot 2H_2O$	43.69	43.80	4.18	4.08	21.91	22.13	$2.1 \cdot 10^{-2}$
$HoL_3 \cdot 2H_2O$	43.55	43.68	4.16	4.07	22.17	22.52	$1.9 \cdot 10^{-2}$
$ErL_3 \cdot H_2O$	44.48	44.36	3.98	4.07	22.96	23.35	$2.2 \cdot 10^{-2}$
$TmL_3 \cdot H_2O$	44.38	44.61	3.97	4.13	23.14	22.76	$2.2 \cdot 10^{-2}$
YbL_3	45.24	46.04	3.77	3.71	24.16	23.97	$1.6 \cdot 10^{-2}$
LuL_3	45.13	45.28	3.76	3.69	24.36	24.62	$1.2 \cdot 10^{-2}$
$YL_3 \cdot 2H_2O$	48.44	48.71	4.63	4.61	13.43	13.42	$2.6 \cdot 10^{-2}$

The contents of carbon and hydrogen were determined by elemental analysis using a CHN 2400 Perkin Elmer analyzer. The contents of metal(III) ions and crystallization water molecules were determined by oxalic acid method (Table 1).

The IR and FTIR spectra of complexes were recorded over the range 4000–400 cm^{-1} using M-80 and FTIR 1725 X Perkin Elmer spectrophotometers, respectively. Some of the results are presented in Table 2 and Fig. 1.

Table 2 Frequencies of the absorption bands of COO^- and M–O group vibrations for 2,3-dimethoxybenzoates of yttrium and heavy lanthanides and sodium (cm^{-1})

Complex $L=C_9H_9O_4$	$\nu_{as\,COO^-}$	$\nu_{s\,COO^-}$	$\Delta\nu_{COO^-}$	$\nu_{M–O}$
$TbL_3\cdot 2H_2O$	1554	1408	146	407
$DyL_3\cdot 2H_2O$	1558	1412	146	407
$HoL_3\cdot 2H_2O$	1558	1413	145	408
$ErL_3\cdot H_2O$	1559	1415	144	408
$TmL_3\cdot H_2O$	1538	1408	130	409
YbL_3	1536	1419	117	419
LuL_3	1539	1421	118	421
$YL_3\cdot 2H_2O$	1559	1413	146	412
NaL	1602	1396	206	436

$\nu_{C=O}=1686$ cm^{-1} for 2,3-dimethoxybenzoic acid

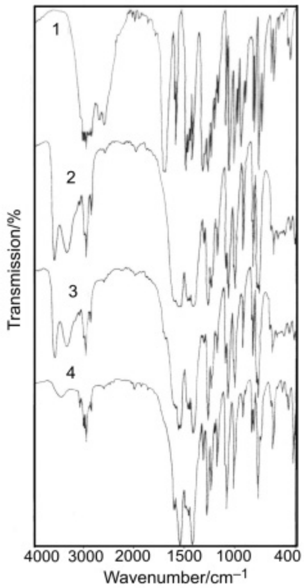

Fig. 1 Infrared spectra of 2,3-dimethoxybenzoic acid (1), 2,3-dimethoxybenzoates of Tb (2), Er (3), Yb (4)

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

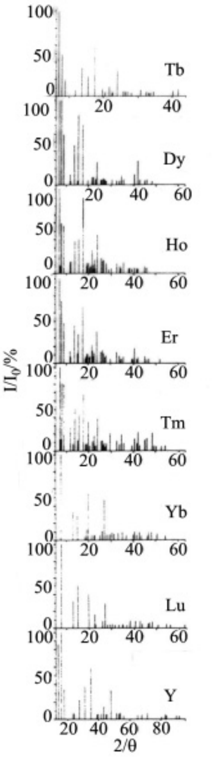

Fig. 2 Diffractograms of heavy lanthanides and yttrium 2,3-dimethoxybenzoates

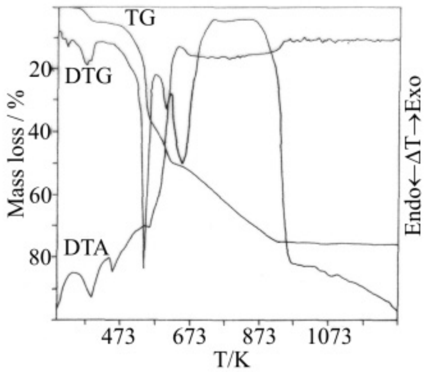

Fig. 3 TG, DTG and DTA curves of erbium 2,3-dimethoxybenzoate in air

The thermal stability and decomposition of the prepared complexes were determined using a Q-1500 D derivatograph with a Derill converter recording TG, DTG and DTA curves (Fig. 3). The measurements were carried out at a heating rate of 10 K min^{-1} with a full scale. The 100 mg samples were heated in platinum crucibles in a static air atmosphere to 1173 K. Sensitivity of the TG was 100 mg (it means that whole scale in the balance is equal to 100 mg). The 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 a reference material. The products of decomposition were identified on the basis of X-ray diffraction pattern (Table 3) and their amounts were estimated on the basis of the mass losses from TG curves.

The measurements in nitrogen were made on an OD-102 derivatograph at a heating rate of 10 deg min^{-1}. The samples were heated to 1173 K at the following sensitivities: TG-100g, DTA-1/10, DTG-1/5. The nitrogen flowed through gas washers filled with pyrogallol and silica gel at a rate of 115 cm^3 min^{-1}. The results are presented in Table 3 and in Fig. 4. The solubilities of 2,3-dimethoxybenzoates of yttrium and the heavy lanthanides in water at 293 K were determined by measuring the concentration of Ln^{3+} ions in a saturated solution by the oxalic acid method (Table 1).

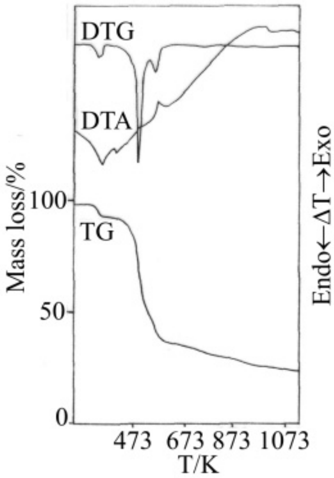

Fig. 4 TG, DTG and DTA curves of erbium 2,3-dimethoxybenzoate in nitrogen

Magnetic susceptibilities of polycrystalline samples of 2,3-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 $1.644\cdot10^{-5}$ cm^{-3} g^{-1} [11]. Correction for diamagnetism of the constituent atoms was calculated by the use of Pascal's constants [12]. The magnetism of the samples was found to be field independent.

Table 3 Temperature range of thermal stability of heavy lanthanides and yttrium 2,3-dimethoxybenzoates in air and nitrogen atmospheres

Complex	ΔT_1/K	Mass loss/%		n	Air	ΔT_2/K	Mass loss/%		T_k/K	T_{exo}/K	Ln_2O_3, Tb_4O_7/%		Residue/ %
		calcd.	found		N_2		calcd.	found			calcd.	found	
$TbL_3\cdot 2H_2O$	375–415 343–373	4.87	4.80 4.80	2	A N	493–1078 473–653	74.67	74.80	1213	764	25.33	24.95	47.84
$DyL_3\cdot 2H_2O$	360–393 323–373	4.85	4.80 4.93	2	A N	503–971 463–573	74.85	74.70	1026	647	25.15	25.40	50.73
$HoL_3\cdot 2H_2O$	357–385 333–373	4.83	4.70 4.48	2	A N	496–947 473–633	74.60	74.20	973	640	25.39	25.80	52.56
$ErL_3\cdot H_2O$	363–388 333–373	2.47	2.30 3.34	1	A N	453–941 438–573	73.74	73.30	973	613	26.26	26.70	48.95
$TmL_3\cdot H_2O$	355–368 333–353	2.46	2.40 3.42	1	A N	403–943 433–613	73.57	74.00	973	611	26.43	26.00	49.31
YbL_3	– –	–	– –	–	A N	436–933 433–593	72.48	72.70	1003	616	27.51	27.30	53.11
LuL_3	– –	–	– –	–	A N	439–951 433–613	72.29	72.00	1003	620	27.71	28.00	53.51
$YL_3\cdot 2H_2O$	377–435 333–383	5.38	5.30 5.17	2	A N	518–1073 473–593	82.97	83.00	1088	633	17.03	17.00	44.82

L=$C_9H_9O_4$; ΔT_1=temperature range of dehydration process; n=number of crystallization water molecules being lost in one endothermic step; ΔT_2=temperature range of anhydrous complex decomposition; T_k=temperature of oxide formation

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

$TbL_3 \cdot 2H_2O$ $\Theta = -10$ K			$DyL_3 \cdot 2H_2O$ $\Theta = -22$ K			$HoL_3 \cdot 2H_2O$ $\Theta = -16$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
77	140504	10.15	77	142670	10.50	78	147598	10.41
120	88848	9.72	122	93730	10.24	123	97011	10.38
132	84300	9.90	134	86315	10.32	133	90318	10.38
146	76302	9.70	146	80382	10.30	146	86598	10.56
155	72612	9.68	158	74450	10.31	156	81391	10.55
164	66710	9.75	162	68520	10.12	170	76183	10.62
179	63760	9.82	178	66991	10.28	180	68744	10.56
187	59330	9.65	184	65550	10.35	188	65768	10.34
194	57658	9.72	192	62585	10.44	196	61305	10.17
224	51956	9.86	220	56655	10.42	202	58329	10.04
235	49000	9.80	234	53692	10.44	220	53860	10.06
240	47525	9.75	241	52206	10.46	236	52376	10.24
248	44578	9.59	246	50690	10.38	248	50892	10.36
260	43100	9.60	258	49240	10.46	254	49402	10.30
268	40884	9.52	264	47754	10.44	262	47915	10.32
277	37198	9.24	272	46274	10.43	278	46424	10.41
286	36458	9.25	290	43280	10.34	298	44936	10.61
298	34982	9.28	298	41825	10.32	–	–	–
$ErL_3 \cdot 2H_2O$ $\Theta = -15$K			$TmL_3 \cdot 2H_2O$ $\Theta = -13$K			YbL_3 $\Theta = -35$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
77	14583	9.58	77	70520	7.12	77	22470	4.48
122	94330	9.78	130	45920	7.27	124	15310	4.41
134	86858	9.83	140	41432	7.12	133	15160	4.50
146	76420	9.54	148	38440	7.02	144	14596	4.57
152	71942	9.45	158	36202	7.04	146	13882	4.51
164	67465	9.49	170	34700	7.13	162	13162	4.58
169	65970	9.52	178	33952	7.22	173	12446	4.57
185	60000	9.50	202	33212	7.52	183	12092	4.56
193	57764	9.54	210	31715	7.52	196	11014	4.65
216	52540	9.59	222	30158	7.52	207	11176	4.64
226	48800	9.46	230	28682	7.45	218	10440	4.60

Table 4 Continued

$ErL_3 \cdot 2H_2O$ $\Theta = -15$ K			$TmL_3 \cdot 2H_2O$ $\Theta = -13$ K			YbL_3 $\Theta = -35$ 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
298	35360	9.23	274	21240	6.98	272	8152	4.47
–	–	–	278	20488	6.90	281	7436	4.33
–	–	–	–	–	–	294	7076	4.31

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 4a and b.

Results and discussion

The 2,3-dimethoxybenzoates of yttrium and heavy lanthanides were obtained as crystalline hydrated or anhydrous solids of 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), Y(III), and n=2 for Tb(III), Dy(III), Ho(III), Y(III), n=1 for Er(III), Tm(III), n=0 for Yb(III) and Lu(III). The colour of the complex is typical of the particular Ln(III) salts i.e., is white in the case of Tb, Dy, Tm, Yb, Lu, Y, cream for Ho and salmon for Er and originates from the lowest energy f–f electronic transitions of the central atom [13].

The complexes were characterized by elemental analyses (Table 1) and FTIR spectroscopy (Table 2, Fig. 1). The 2,3-dimethoxybenzoates of yttrium and the heavy lanthanides exhibit in solid state similar IR spectra; some of them are presented in 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 1686 cm^{-1} originating from the RCOOH group, presented in the spectrum of the acid, is replaced in the spectra of complexes, by two bands at 1559–1536 and 1421–1408 cm^{-1}, which can be ascribed to the asymmetric and symmetric vibration of modes of the COO^- group, respectively [14–20]. The bands attributed to asymmetric and symmetric C–H stretching modes of the CH_3 groups are observed at 2944–2928 and 2838–2834 cm^{-1}, respectively. The bands with the maxima at 3570–3564 and 3328–3318 cm^{-1} are characteristic for ν(OH) vibrations [21, 22]. The bands of ν(C–C) ring vibrations appear at 1599–1593, 1467–1445, 1172–1064, 938–813 and 648–619 cm^{-1}.

The bands corresponding to metal-oxygen stretching appear at 421–407 cm^{-1} and they shift to higher frequencies from Tb to Lu. It is therefore reasonable to assume that 2,3-dimethoxybenzoic acid forms with the heavy lanthanides complexes of various stability [15]. The Table 2 presents the values of the band frequencies of asymmetrical and symmetrical vibrations for carboxylate group of 2,3-dimethoxybenzoates of heavy lanthanides, yttrium and sodium salt. The separation of the $\nu_{\text{as COO}^-}$ and $\nu_{\text{s COO}^-}$ modes of the complexes ($\Delta\nu_{\text{COO}^-}$) is smaller ($\Delta\nu_{\text{COO}^-}$= 146–117 cm^{-1}) than that of the sodium salt $\Delta\nu_{\text{COO}^-}$=206 cm^{-1}) which indicates a weaker ionic bonding in the heavy lanthanide 2,3-dimethoxybenzoates.

Trivalent ions due to the stronger electrostatic potential surrounding them deform the ligand stronger than the sodium ion. According to the spectroscopic criteria [16, 20, 23] and the data presented in Table 2 carboxylate ion behaves in the anhydrous complexes as bidentate chelating ligand. In the spectra of hydrated 2,3-dimethoxybenzoates the bands of asymmetrical vibrations of carboxylate group are splitting. Therefore the carboxylate groups may act as bidentate chelating and bidentate bridging ones.

In order to know wheather the yttrium and heavy lanthanide 2,3-dimethoxybenzoates were prepared as crystalline or amorphous compounds their X-ray powder diffractograms were recorded. The analysis of diffractograms reveals them to be polycrystalline compounds of low symmetry [24, 25]. They form two groups of isostructural compounds; in the first one there are 2,3-dimethoxybenzoates of Tb, Dy, Ho, Er, Tm, Y and in the second one there are those of Yb and Lu.

The thermal stability of the yttrium and heavy lanthanide 2,3-dimethoxybenzoates was studied in air and nitrogen atmospheres (Table 3, Figs 3 and 4). When heated in air they decompose in one or two steps. The hydrated complexes decompose in two steps. They are stable up to 355–377 K. Next in the temperature range 355–435 K they are dehydrated in one step losing two (Tb, Dy, Ho, Y) or one (Er, Tm) molecules of crystallization water and form anhydrous complexes. The mass loss calculated from TG curves being equal to 2.30–5.30% corresponds to the loss of 1 or 2 molecules of water (theoretical values are 2.46–5.38%). The anhydrous 2,3-dimethoxybenzoates of yttrium and heavy lanthanides in the temperature range 403–1078 K are decomposed to the oxides of appropriate lanthanides. The temperature of oxide formations are changed from 1213 K (Tb_4O_7) to 973 K (Ho_2O_3, Er_2O_3, Tm_2O_3).

The dehydration process is connected with an endothermic effect seen in DTA curves whereas the combustion of the organic ligand with exothermic one. Considering the temperature at which the dehydration process of the complexes takes place and the way by which it proceeds it is possible to assume that the water molecules are in the outer sphere of complex coordination [26].

The anhydrous complexes of ytterbium and lutetium are stable up 436-439 K. Next in the temperature range 436–951 K they are directly decomposed to the oxides Yb_2O_3 and Lu_2O_3 which are formed at 1003 K.

The results indicate that the thermal decomposition of 2,3-dimethoxybenzoates of yttrium and heavy lanthanides in air may proceed in the following ways:

$$LnL_3\cdot 2H_2O \rightarrow LnL_3 \rightarrow Ln_2O_3 \quad \text{(for } \mathit{Ln}\text{=Dy, Ho)} \tag{3}$$

$$Tb_4O_7 \quad \text{(for Tb)}$$

$$LnL_3\cdot H_2O \rightarrow LnL_3 \rightarrow Ln_2O_3 \quad \text{(for } \mathit{Ln}\text{=Er, Tm)} \tag{4}$$

$$LnL_3 \rightarrow Ln_2O_3 \quad \text{(for } \mathit{Ln}\text{=Yb, Lu)} \tag{5}$$

The thermal stability of heavy lanthanide 2,3-dimethoxybenzoates was studied also in nitrogen atmosphere (Table 3, Fig. 4). The complexes of Tb(III), Dy(III), Ho(III), Er(III), Tm(III) and Y(III) were found to be di- and monohydrates (the found mass loss calculated from TG curves are equal to 2.40–5.00% and the theoretical 2.46–5.38%). The complexes being heated to 1173 K decompose in one or two stages. The hydrated complexes, in the first step in the range 323–383 K, are dehydrated to form anhydrous complexes. The dehydration process is accompanied by endoeffect in DTA curves [27, 28]. The initial dehydration temperature values are lower (with the exception of Tb complex) compared to those in air, which suggest that during heating to 1173 K the heavy lanthanide 2,3-dimethoxybenzoates are more stable in air than in nitrogen. Next in the range 433–1073 K the anhydrous complexes are being further decomposed to the mixtures of the respective metal oxides and carbon or carbon and carbonates of the respective metals. The contents of mixture were roentgenographically established [29]. On heating 2,3-dimethoxybenzoates of Yb(III) and Lu(III) are directly decomposed to the mixtures of carbon and oxides of respective metals or their carbonates.

The solubilities of 2,3-dimethoxybenzoates of yttrium and heavy lanthanides in water at 293 K were measured (Table 1). They are in the order of 10^{-2} mol dm^{-3}. The yttrium 2,3-dimethoxybenzoate is the most soluble salt while that of lutetium the least soluble one.

The magnetic susceptibility of the heavy lanthanide 2,3-dimethoxybenzoates was measured in the temperature range of 77–300 K. The values of the Weiss constant, θ, are negative for all the complexes which may be caused by small antiferromagnetic spin interactions in the complexes that are higher at room temperatures than at lower ones or a crystal field splitting of the paramagnetic spin state [30–33]. This may probably also result from the presence of superexchange magnetic interactions between paramagnetic centers of different molecules of the complexes in the crystal lattice. The paramagnetic central ions in the compounds investigatied remain virtually unaffected by the surrounding ligands.

Table 5 Value of μ_{eff} for the heavy lanthanides determined by Hund and van Vleck (μ/BM)

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

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 surrounding atoms and are located in an inner shell of a radius of 0.35 Å [34]. This value is very small in comparison with the radius of the $5s^2 5p^6$ 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 magnetic properties in the ground state can be expected to be identical for bounded and non-bounded lanthanide ions. The 2,3-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 5). Lutetium 2,3-dimethoxybenzoate is, as expected, diamagnetic.

The above data indicate that the Ln–O bond in the heavy lanthanide 2,3-dimethoxybenzoates is predominantly of an electrostatic nature, since the 4f orbitals of the lanthanide ions are effectively polarized by the $5s^2 5p^6$ octet [34, 35].

Conclusions

On the basis of the results obtained it appears that 2,3-dimethoxybenzoates of heavy lanthanides and yttrium were synthesized as hydrated or anhydrous complexes. Their colours are typical of the particular Ln(III) ion, i.e. white for Tb, Dy, Tm, Yb, Lu and Y, cream for Ho and salmon for Er; having their origin in the lowest energy of $f \rightarrow f$ electronic transitions of the central ions. Their energies are not radically changed in comparison with the free lanthanide ions, therefore the colours of the compounds are the same as those for the free lanthanide ions.

The Ln–O bond is mainly electrostatic in nature. The complexes are crystalline compounds that on heating in air and nitrogen to 1173 K decompose in two steps. In the first step they dehydrate to anhydrous complexes that next in air decompose to the oxides of the appropriate metals or in nitrogen to the mixtures of metal oxides and carbon or metal oxides, carbon and carbonates of the respective metals.

References

1 Beilsteins Handbuch der organischen Chemie, Bd. X, Springer Verlag, Berlin 1932, p. 174.
2 S. Swaminathan and K. Sarangapani, Struct. Commun., 6 (1977) 369.
3 R. F. Bryan and H. D. White, Acta Crystallogr., 38 (1982) 1012.
4 M. Georgieva, Anal. Chim. Acta, 101 (1978) 139.
5 M. Colomina, M. V. Roux and J. J. Turrian, Chem. Thermodyn., 13 (1981) 1169.
6 L. D. Pethe and B. D. Mali, Indian J. Chem., 16 (1978) 364.
7 Yun Sock Sung, Bae Sung Hee, Hong Sung Wan, Kang Sung Kwan, Kim Inn Hoe and Park Joan Talk, Thermochim. Acta, 246 (1994) 39.
8 Gmelin Handbuch of Inorganic Chemistry, Springer Verlag, Berlin 1984, p. 105.
9 S. Erre, L. Micera and G. Cariati G, Polyhedron, 6 (1987) 1869.
10 W. Ferenc and A. Walków-Dziewulska, J. Serb. Chem. Soc., 66 (2001) 543.
11 B. N. Figgs and R. S. Nyholm, J. Chem. Soc., (1958) 4190.
12 E. König, Magnetic Properties of Coordination and Organometallic Transition Metal Compounds, Springer Verlag, Berlin 1966.

13 A. Bartecki, Electronic Spectroscopy of Inorganic and Coordination Compounds, PWN, Warsaw 1993, p. 87.
14 L. J. Bellamy, The Infrared Spectra of Complex Molecules, Chapman and Hull, London 1975.
15 K. Burger, Coordination Chemistry: Experimental Methods, Akadémiai Kiadó, Budapest 1973.
16 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, Toronto 1997.
17 R. M. Silverstein and G. C. Bassler, Spectroscopic Methods of Inorganic Compound Identifications, PWN, Warsaw 1970.
18 A. Cross and A. R. Jones, An Introduction to Practical Infrared Spectroscopy, Butterworths, London 1969.
19 K. Nakamoto and P. J. McCarthy, Spectroscopy and Structure of Metal Chelate Compounds, Wiley, New York 1986.
20 R. C. Mehrotra and R. Bohra, Metal Carboxylates Academic Press, London 1983.
21 G. E. Walfaren, J. Chem. Phys., 40 (1964) 3249.
22 W. A. Senior and W. K. Thomson, Nature, 205 (1965) 170.
23 B. S. Manhas and A. K. Trikha, J. Indian Chem. Soc., 59 (1982) 315.
24 E. Łagiewka and Z. Bojarski, X-ray structural analysis, PWN, Warsaw, 1988.
25 P. Pascal, Noveau Traité de Chimie Minérale, VII Mason et C^{ie}, Paris, 1959.
26 A. V. Nikolaev, V. A. Logvinenko and L. I. Myachina, Thermal Analysis, Vol. 3, Academic Press, New York 1989.
27 D. N. Todor, Thermal Analysis of Minerals, Abacus Press, Tunbridge, Wells Kent 1976.
28 F. Paulik, Special Trends in Thermal Analysis, Wiley, Chichester 1995.
29 M. Van Meersche and I. Feneau-Dupont, Introduction à la Crystallographie et à la Chimie Structurale, OYEZ, Leuven, Bruxelles, Paris 1976.
30 C. I. O'Conner, Progress in Inorganic Chemistry, Vol 29., Wiley, New York 1982.
31 C. Benelli, A. Caneschi, D. Gatteschi, J. Laugier and P. Rey, Angew. Chem., 26 (1989) 913.
32 C. Benelli, A. Caneschi, D. Gatteschi, J. Laugier and L. Pardi, Inorg. Chem., 28 (1989) 275.
33 C. Benelli, A. Caneschi, D. Gatteschi, J. Laugier, L. Pardi and P. Rey, Inorg. Chem., 28 (1989) 320.
34 S. P. Sinha, Systematics and Properties of the Lanthanides, Reidel, Dordrecht 1983.
35 D. J. Karraker, J. Chem. Educ., 47 (1970) 424.