Spectral, Thermal, and Magnetic Properties of 2,3-Dimethoxybenzoates of Rare Earth Elements

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The complexes of rare earth elements with 2,3-dimethoxybenzoic acid of the formula $\mathrm{Ln(C_9H_9O_4)_3 \cdot }n\mathrm{H_2O}$, where Ln = La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III), and Y(III), and $n = 2$ for Tb, Dy, Ho, Y, $n = 1$ for Er, Tm, $n = 0$ for La, Gd, Yb, and Lu have been synthesized and characterized by elemental analysis, IR spectroscopy, thermogravimetric studies, as well as by X-ray and magnetic measurements. The complexes have colours typical for $\mathrm{Ln^{3+}}$ ions. The carboxylate group is a bidentate, chelating ligand or tridentate chelating and bridging one. The complexes are crystalline compounds characterized by low symmetry. On heating in air to 1173 K they decompose in various ways.

2,3-Dimethoxybenzoates of Ce(III), Pr(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III), and Y(III) decompose directly to oxides of the respective metals while those of La(III) and Nd(III) *via* the formation of $\mathrm{La_2O_2CO_3}$ and $\mathrm{Nd_2O_2CO_3}$. Their thermal stabilities were also studied in nitrogen. The complexes are more stable in air than in nitrogen.

The magnetic moments of the complexes were determined over the range 77—300 K. They obey the Curie—Weiss law. The results show that there is no influence of the ligand field on the 4*f* electrons of lanthanide ions in the polycrystalline compounds and probably 4*f* electrons do not take part in the formation of M—O bonding.

A literature survey indicated that the compounds of 2,3-dimethoxybenzoic acid with various cations had been relatively seldom studied. Papers exist on its complexes with such cations as $\mathrm{Cu^{2+}}$ and some lanthanide ions which were obtained as solids or were investigated in solution [1—6].

The 2,3-dimethoxybenzoate of Cu(II) was obtained in the solid state and its thermal stability was studied [3] while those of $\mathrm{Ln^{3+}}$ were mainly investigated in solution [4, 5]. The light lanthanide 2,3-dimethoxybenzoates were obtained in the solid state and some of their properties were studied [6]. 2,3-Dimethoxybenzoic acid is a solid sparingly soluble in water [7—12] and its melting point is equal to 395 K. There is no information about the solid state properties of the complexes of 2,3-dimethoxybenzoic acid with rare earth elements. Therefore we decided to synthesize them as solids and to examine some of their physico-chemical properties such as their thermal stability in air, IR spectral characteristic and crystalline form in order to determine whether they are crystalline or amorphous compounds. The thermal stability investigations enabled the evaluation of the mechanism of the complex decomposition.

The 2,3-dimethoxybenzoates of rare earth elements were obtained as crystalline anhydrous (light lanthanides) or hydrated (heavy lanthanides and yttrium) products with a metal to ligand ratio of 1:3 and general formula $\mathrm{Ln(C_9H_9O_4)_3 \cdot }n\mathrm{H_2O}$ where Ln = La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III), and Y(III), and $n = 2$ for Tb(III), Dy(III), Ho(III), $n = 1$ for Er(III), Tm(III), $n = 0$ for La(III), Gd(III), Yb(III), and Lu(III). The colours of the complexes are those typical for the corresponding trivalent $\mathrm{Ln^{3+}}$ ions, *i.e.* white for La, Ce, Eu, Gd, Tb, Dy, Yb, Lu, Y, cream for Sm, Ho, green for Pr, greenish for Tm, violet for Nd, pink for Er and originate from the lowest energy of *f*—*f* electronic transitions of the central atom [13].

The complexes were characterized by elemental analysis and IR spectroscopy (Tables 1 and 2). All the 2,3-dimethoxybenzoates of rare earth elements show similar solid state IR spectra.

However, the characteristic frequencies related to the carbonyl group are altered markedly in going from

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Table 1. Analytical Data of Rare Earth Element 2,3-Dimethoxybenzoates

Complex L = $C_9H_9O_4$	w(C)/%		w(H)/%		w(Ln)/%	
	calc.	found	calc.	found	calc.	found
LaL_3	47.51	47.67	3.96	3.87	20.36	20.71
CeL_3	47.43	47.43	3.95	3.87	20.51	20.67
PrL_3	47.37	47.42	3.94	3.87	20.60	20.94
NdL_3	47.14	47.07	3.92	3.81	20.98	21.00
SmL_3	46.72	47.04	3.89	3.84	21.68	21.56
EuL_3	46.62	46.76	3.88	3.81	21.86	21.59
GdL_3	46.27	46.42	3.85	3.77	22.56	22.59
$TbL_3 \cdot 2H_2O$	43.90	44.05	4.20	4.21	21.53	21.21
$DyL_3 \cdot 2H_2O$	43.69	43.80	4.18	4.08	21.91	22.13
$HoL_3 \cdot 2H_2O$	43.55	43.68	4.16	4.07	22.17	22.52
$ErL_3 \cdot H_2O$	44.48	44.36	3.98	4.07	22.96	23.35
$TmL_3 \cdot H_2O$	44.38	44.61	3.97	4.13	23.14	22.76
YbL_3	45.24	46.04	3.77	3.71	24.16	23.97
LuL_3	45.13	45.28	3.76	3.69	24.36	24.62
$YL_3 \cdot 2H_2O$	48.44	48.71	4.63	4.61	13.43	13.42

Table 2. Frequencies of the Absorption Bands of COO^- and M—O Group Vibrations for 2,3-Dimethoxybenzoates of Rare Earth Elements and Sodium and that of CO for 2,3-Dimethoxybenzoic Acid

Complex	$\tilde{\nu}$/cm^{-1}				
	ν(C=O)	$\nu_{as}(COO^-)$	$\nu_s(COO^-)$	$\Delta\nu(COO^-)$	ν(M—O)
LaL_3	–	1546*	1392	154	413
CeL_3	–	1546*	1388	158	415
PrL_3	–	1545*	1391	154	417
NdL_3	–	1546*	1389	157	417
SmL_3	–	1547*	1393	154	421
EuL_3	–	1547*	1392	155	419
GdL_3	–	1549*	1394	155	423
$TbL_3 \cdot 2H_2O$	–	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
HL	1684	–	–	–	–
NaL	–	1602	1396	206	436

*The strongest intensity of the split band.

the acid to the salts. The band of the COOH group at 1684 cm^{-1}, present in the spectrum of acid, disappears in the spectra of the complexes and two bands arising from the asymmetric and symmetric vibrations of the COO^- group occur at 1536—1559 cm^{-1} and 1388—1421 cm^{-1}, respectively [14—18]. The bands of the C—H antisymmetric and symmetric stretching of the —CH_3 group are observed at 2928—2944 cm^{-1} and 2834—2850 cm^{-1}, respectively. The bands of the ν(C—C) ring vibrations appear at 1593—1624 cm^{-1} and their out-of-plane deformation modes at 1064—1172 cm^{-1}. The ν(C—H) vibrations are observed at 1388—1421 cm^{-1} and 608—1016 cm^{-1}. The bands typical for the aromatic ring vibrations are shifted insignificantly in the complexes compared to the respective bands in the 2,3-dimethoxybenzoic acid, which indicates that the Ln(III) ions only weakly influence the benzene ring. Bands due to the metal—oxygen bond appear at 407—423 cm^{-1} for the whole series of complexes [15, 18]. Therefore it is possible to suppose that 2,3-dimethoxybenzoic acid forms complexes with rare earth elements of similar stability [15]. Table 2 presents the frequency of maxima of the absorption bands of the asymmetric and symmetric vibrations of the COO^- group for the 2,3-dimethoxybenzoates of rare earth elements and of sodium, as well as of the CO group for 2,3-dimethoxybenzoic acid. The magnitudes of the separation, $\Delta\tilde{\nu}$, between the frequencies

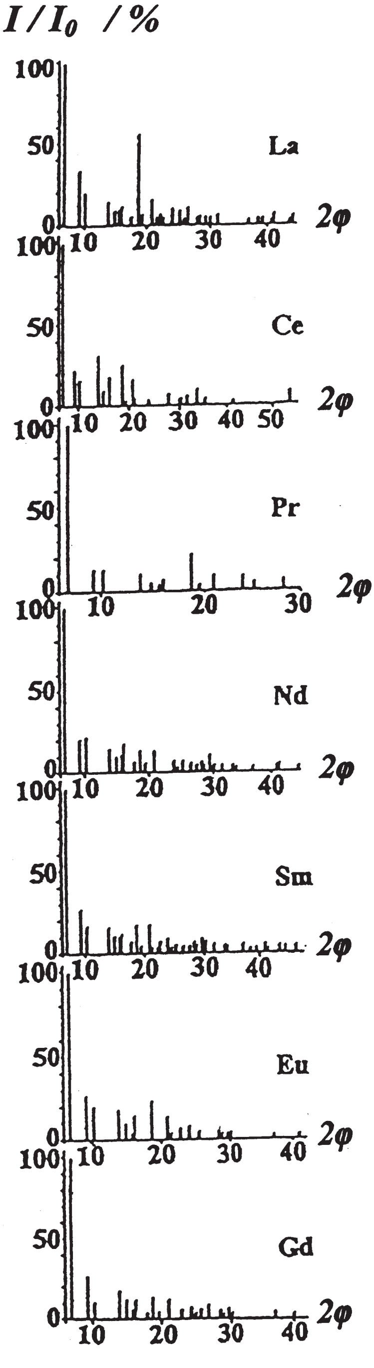

Fig. 1. Dependence between I/I_0 and 2φ for light lanthanide 2,3-dimethoxybenzoates.

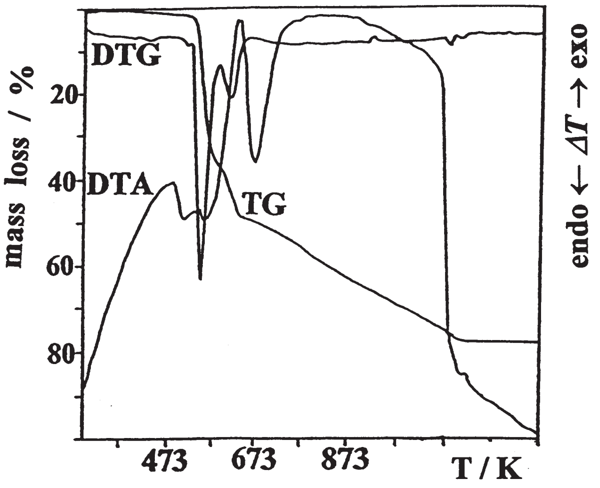

Fig. 2. TG, DTG, and DTA curves of lanthanum 2,3-dimethoxybenzoates in air.

$\tilde{\nu}_{\mathrm{as}}$(OCO) and $\tilde{\nu}_{\mathrm{s}}$(OCO) in the complexes are lower ($\Delta\tilde{\nu}$(OCO) = 117—158 cm^{-1}) than in the sodium salt ($\Delta\tilde{\nu}$(OCO) = 206 cm^{-1}), which indicates a lower degree of ionic bonding in the rare earth element 2,3-dimethoxybenzoates. According to the spectroscopic criteria [16, 18, 19] and with regard to Nakamoto criterion, in the case of the heavy lanthanides, the carboxylate ion appears to be a bidentate chelating ligand. However, from a detailed analysis of the bands of the asymmetric and symmetric vibrations of the COO^- group it follows that in the case of the light lanthanide 2,3-dimethoxybenzoates the bands of the $\tilde{\nu}_{\mathrm{as}}$(OCO) vibrations are significantly split. It suggests, on the one hand, that the carboxylate group may be a tridentate, chelating and bridging ligand or, on the other hand, that the carboxylate group may coordinate in various ways being chelating or bridging ligand. These types of coordination lead to polymerization in these solid compounds making the coordination number of Ln(III) ions equal to 9 in the case of light lanthanide complexes and to 8 for those of the heavy ones.

Analysis of the diffractograms suggests that the rare earth element 2,3-dimethoxybenzoates are polycrystalline compounds (Fig. 1). The structures of the compounds have not been determined because single crystals have not been obtained.

The thermal stability of yttrium and lanthanide 2,3-dimethoxybenzoates was studied in air and nitrogen atmospheres (Table 3, Figs. 2—4). Heated in air to 1173 K, the 2,3-dimethoxybenzoates of rare earth elements form oxides of the respective metal having the same structures as the oxides obtained by roasting the rare earth element oxalates [20, 21]. The thermal stabilities of the rare earth element 2,3-dimethoxybenzoates were studied in air in the temperature range 293—1173 K (Table 3). The results obtained from their thermal decomposition showed them to be anhydrous or hydrated salts. When heated in air they decompose in one or two steps. The anhydrous complexes are stable up to 403—520 K and then they decompose (with the exception of the 2,3-dimethoxybenzoates of La(III) and Nd(III)) to the oxides of the respective metal, which are formed at 973—1178 K. The mass loss calculated from the TG curves is equal to 72.00—83.00 % (the theoretical value is 72.29—82.97 %). The oxides of the rare earth elements were also identified by X-ray powder diffraction [21]. The 2,3-

Table 3. Temperature Ranges of Thermal Stability of Rare Earth Element 2,3-Dimethoxybenzoates in Air and Nitrogen Atmospheres

Complex	ΔT_1/K	Mass loss/%		n	A(air) N(N_2)	ΔT_2/K	Mass loss/%		T_K/K
		calc.	found				calc.	found	
LaL_3	–	–	–	–	A	516—655	76.11	76.00	1178
					N	473—613			
CeL_3	–	–	–	–	A	518—1074	74.81	75.00	1148
					N	483—593			
PrL_3	–	–	–	–	A	520—1048	75.10	75.00	1123
					N	473—603			
NdL_3	–	–	–	–	A	519—645	75.51	75.00	1148
					N	473—593			
SmL_3	–	–	–	–	A	503—1073	74.85	74.80	1098
					N	473—593			
EuL_3	–	–	–	–	A	513—1093	74.68	74.50	1123
					N	473—593			
GdL_3	–	–	–	–	A	513—1073	74.11	74.00	1163
					N	473—603			
$TbL_3 \cdot 2H_2O$	375—415	4.87	4.80	2	A	493—1078	74.67	74.80	1213
	343—373		4.80		N	473—653			
$DyL_3 \cdot 2H_2O$	360—393	4.85	4.80	2	A	503—971	74.85	74.70	1026
	323—373		4.93		N	463—573			
$HoL_3 \cdot 2H_2O$	357—385	4.83	4.70	2	A	496—947	74.60	74.20	973
	333—373		4.48		N	473—633			
$ErL_3 \cdot H_2O$	363—388	2.47	2.30	1	A	453—941	73.74	73.30	973
	333—373		2.34		N	438—573			
$TmL_3 \cdot H_2O$	355—368	2.46	2.40	1	A	403—943	73.57	74.00	973
	333—353		3.42		N	433—613			
YbL_3	–	–	–	–	A	436—933	72.48	72.70	1003
					N	433—593			
LuL_3	–	–	–	–	A	439—951	72.29	72.00	1003
					N	433—613			
$YL_3 \cdot 2H_2O$	377—435	5.38	5.30	2	A	518—1073	82.97	83.00	1088
	333—383		5.17		N	473—593			

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 the oxide formation.

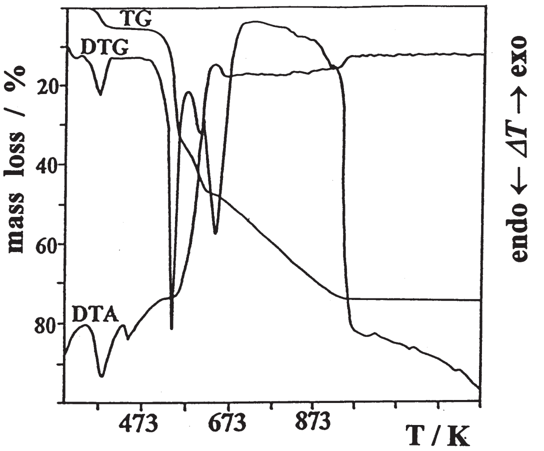

Fig. 3. TG, DTG, and DTA curves of holmium 2,3-dimethoxybenzoates in air.

dimethoxybenzoates of La(III) and Nd(III) decompose to La_2O_3 and Nd_2O_3 *via* the intermediate formation of the oxycarbonates of lanthanum $La_2O_2CO_3$ and neodymium, $Nd_2O_2CO_3$ [22, 23]. The peaks ascribed to the losses of mass seen in TG curves in the interval 473—673 K are also recorded in the DTG curves, which is the first derivative of the formation of the various intermediate products of decomposition.

The combustion of the organic ligands is accompanied by strong exo-effects seen in the DTA curves. The large peaks recorded in the curves of the DTG correspond to the gradual mass loss of the complexes during heating.

The hydrated 2,3-dimethoxybenzoates of heavy lanthanides and yttrium lose two or one molecule of water of crystallization in one step in the range 355—435 K and form anhydrous complexes (368—435 K). The found mass losses estimated for dehydration process from TG curves are equal to 2.30—5.30 % (theoretical: 2.46—5.38 %). The dehydration process is connected with an endothermic effect shown by the DTA curves [22, 23].

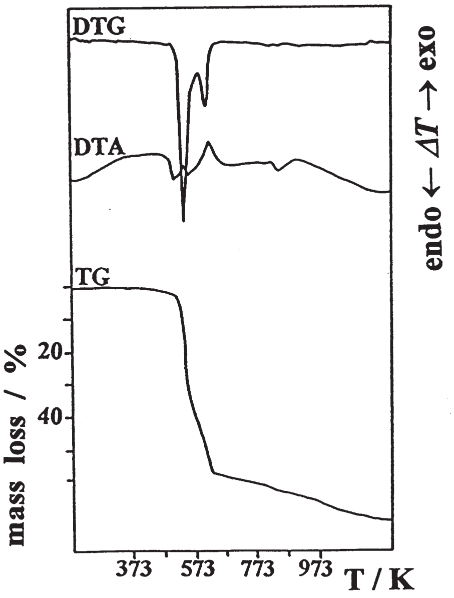

Fig. 4. TG, DTG, and DTA curves of neodymium 2,3-dimethoxybenzoates in nitrogen.

The derivatogram of lanthanum 2,3-dimethoxybenzoate is presented in Fig. 2. The complex decomposes in two steps. The mass loss of the complex starts at 516 K. The decrease in mass occurs in the range 516—655 K and therefore the TG curve deviates from the horizontal. The mass loss determined from the TG curve is equal to 46.00 % (the calculated value is 45.77 %), which corresponds to the formation of $La_2O_2CO_3$. Accordingly, the peak ascribed to this loss of mass is also recorded in the DTG curve, which is the first derivative of the mass loss. The $La_2O_2CO_3$ was also identified by X-ray powder diffraction, elemental and IR spectra analysis. Next, the oxycarbonate of lanthanum is finally decomposed to La_2O_3 (673—1118 K). The mass loss determined from the TG curve is equal to 76.00 % (the calculated value is 76.11 %). The oxidation process is associated with a strong exothermic effect reflected in the DTA curve. Subsequently, above 1080 K the TG curve reaches a plateau as the formed La_2O_3 is thermally stable.

The thermal stability of rare earth element 2,3-dimethoxybenzoates was studied also in nitrogen atmosphere (Table 3, Fig. 4). The complexes were found to be anhydrous (light lanthanides) or dihydrates (heavy lanthanides and yttrium). In the case of yttrium and heavy lanthanide 2,3-dimethoxybenzoates the found mass losses calculated from TG curves are equal to 2.34—5.17 % (theoretical: 2.46—5.38 %).

The complexes being heated to 1173 K decompose in various ways. The light lanthanide 2,3-dimethoxybenzoates are stable up to 473—483 K and then they decompose to the mixture of the respective metal oxides and carbon (Table 3). The yttrium and heavy lanthanide 2,3-dimethoxybenzoates, in the first step in the range 323—383 K, are dehydrated to form anhydrous complexes. The dehydration process is accompanied by endo-effect observed in DTA curves. Next, in the range 433—653 K, all anhydrous complexes further decompose. The combustion of organic ligands is connected with an exo-effect seen in DTA curves. Fig. 4 presents the TG, DTG, and DTA curves of 2,3-dimethoxybenzoate of Nd during heating in nitrogen atmosphere. The values of initial decomposition temperatures of anhydrous complexes of 2,3-dimethoxybenzoates of rare earth elements in nitrogen are lower (433—613 K) than those in air, which suggests them to be more stable in air than in nitrogen. The final products of decomposition of 2,3-dimethoxybenzoates of rare earth elements are the mixtures of the respective metal oxides and carbon. The contents of mixture were identified by X-ray powder diffraction [21, 24].

From the obtained results it follows that the molecules of water bind in the outer coordination sphere of the complexes [25, 26]. Water of crystallization is removed from various compounds in a broad temperature range [22, 23, 25, 26]. According to *Nikolaev et al.* [25, 26] and *Singh et al.* [27] water being eliminated below 413—423 K may be the one coordinated to the central ion. In the present investigations water is eliminated below 413 K and FTIR studies revealed it to be water of crystallization. The exact assignment of the position and bonding interaction of the water molecules in the studied complexes demands determination of their crystal structures, this has unfortunately been hindered by the lack of suitable single crystals.

The gaseous products of thermal decompositions of rare earth element 2,3-dimethoxybenzoates were identified by the registration of TG-FTIR spectra. Some of the results are presented in Table 4 and

Table 4. Frequencies of Absorption Bands in FTIR Spectra of Gaseous Products Liberated during Decomposition of Rare Earth Element 2,3-Dimethoxybenzoates

Frequency range $\Delta\tilde{\nu}/\mathrm{cm}^{-1}$	Gaseous products
3400—3900 1350—1580	H_2O molecules
3500—3800 2200—2400 670—700	CO_2 molecules
2700—3100 1640—1700 1300—1500	Molecules of hydrocarbons
3580—3670 2800—3100 900—1400	Molecules of monohydroxy alcohols
2060—2220	CO molecules

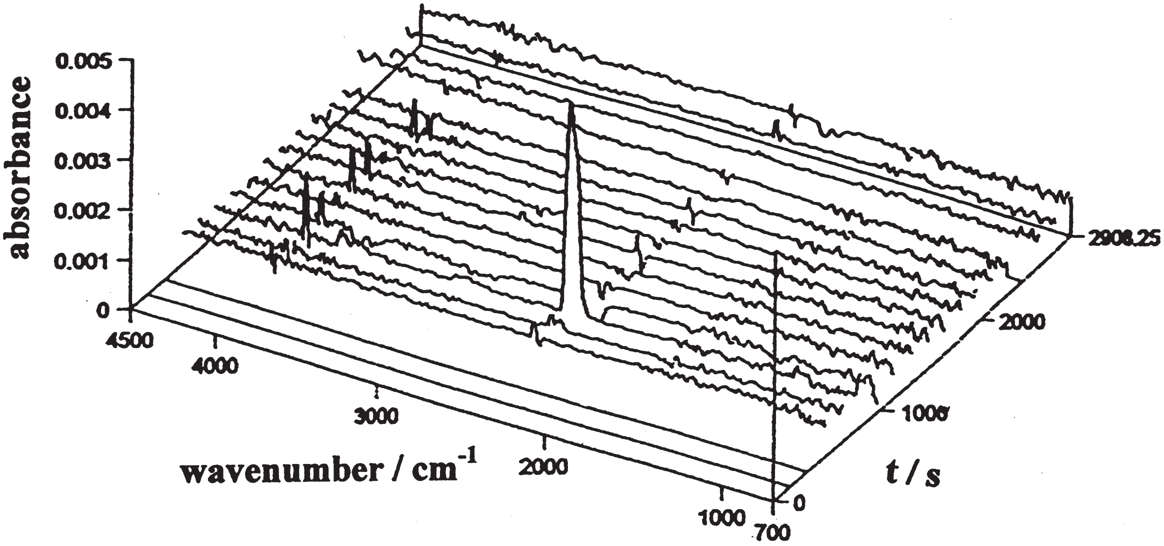

Fig. 5. FTIR spectrum of gaseous products of decomposition process of lanthanum 2,3-dimethoxybenzoate.

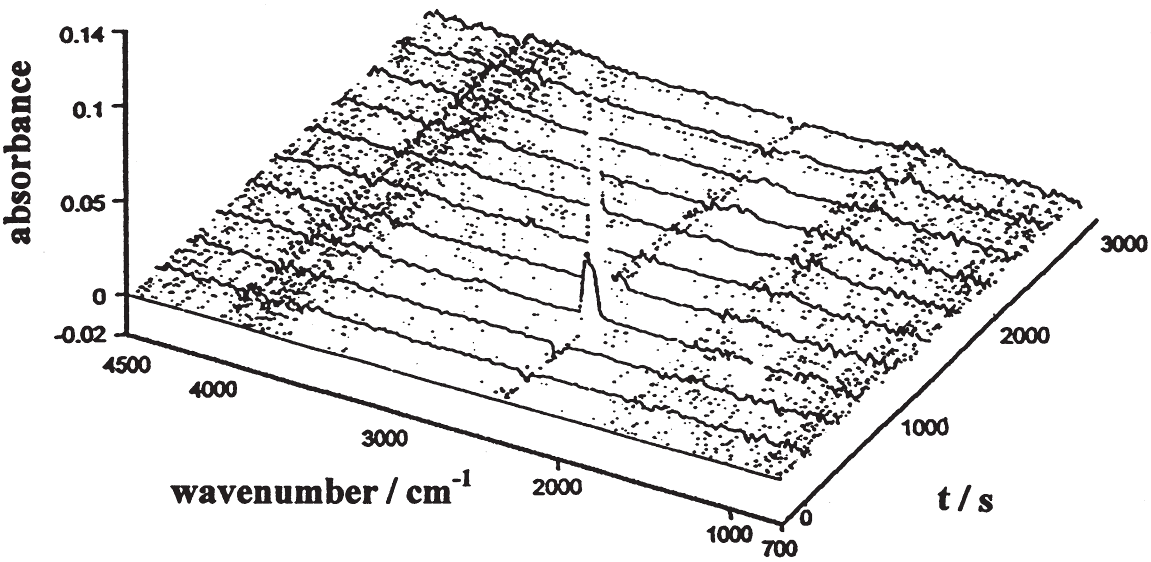

Fig. 6. FTIR spectrum of gaseous products of holmium 2,3-dimethoxybenzoate decomposition process.

Figs. 5 and 6. From the FTIR spectra analysis of the hydrated complexes it follows that during heating to 1173 K, in the first step, the molecules of water are released (353—493 K). It is confirmed by the bands in the intervals 3400—3900 cm^{-1} and 1350—1580 cm^{-1} [28]. The beginning of the decomposition process of the anhydrous complexes is connected with the liberation of CO_2 molecules. The greatest intensity of the absorption bands was observed at 627—700 K. In the FTIR spectra of gaseous products the bands of CO_2, hydrocarbons, and monohydroxy alcohol molecules occur. In the ranges 3500—3800 cm^{-1}, 2200—2400 cm^{-1}, and 670—700 cm^{-1} the bands resulting from the stretching and deformation vibrations of CO_2 molecules are observed and the bands at 2700—3100 cm^{-1}, 1640—1700 cm^{-1}, and 1300—1500 cm^{-1} confirm the presence of hydrocarbons in the gaseous products of thermal decomposition of 2,3-dimethoxybenzoates [17, 28]. The bands resulting from the monohydroxy alcohols appear in the ranges 3580—3670 cm^{-1}, 2800—3100 cm^{-1}, and 900—1400 cm^{-1} [28, 29]. With increasing temperature the molecules of CO are released and their characteristic absorption bands occur in the range 2060—2220 cm^{-1} [17, 28, 29]. The analysis of FTIR spectra of hydrated and anhydrous complexes shows that with the rise of temperature the dihydrates release the water molecules the presence of which in the gaseous mixture is confirmed by the bands in the range 3400—3900 cm^{-1}. During further heating the organic ligand decomposes and the molecules of CO_2, CO, hydrocarbons, and monohydroxy alcohols are released.

Table 5. Magnetic Data of Light Lanthanide 2,3-Dimethoxybenzoates

CeL_3 $\Theta = -46.6$ K			PrL_3 $\Theta = -42.2$ K			NdL_3 $\Theta = -25$ K			SmL_3 $\Theta = -73$ K			EuL_3 $\Theta = -730$ K			GdL_3 $\Theta = -7.6$ 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	6920	2.67	77	14962	3.82	77	17396	3.80	77	21002	1.70	77	5084	5.92	77	83042	7.59
125	4720	2.64	130	10158	3.81	122	10990	3.76	130	1596	1.74	130	5012	6.05	130	49122	7.40
137	4482	2.65	140	9450	3.84	140	10282	3.74	139	1378	1.72	139	4650	5.86	140	46858	7.48
144	4169	2.70	152	9136	3.85	152	9963	3.82	150	1628	1.70	150	4505	5.83	150	43055	7.36
162	3776	2.64	161	8585	3.82	160	8854	3.72	161	1232	1.70	156	4504	5.85	160	39401	7.32
170	3540	2.60	164	8427	3.82	170	8384	3.73	173	1230	1.74	170	4430	5.84	168	38304	7.32
178	3383	2.59	172	7796	3.74	184	8064	3.73	186	1084	1.72	179	4503	5.90	177	37248	7.46
183	3383	2.63	185	7640	3.80	194	7826	3.76	200	1016	1.70	189	4360	5.86	187	33220	7.24
196	3225	2.65	195	7320	3.82	201	7118	3.80	202	1015	1.71	198	4285	5.82	196	32166	7.26
210	2989	2.61	206	7002	3.81	212	6960	3.72	207	1015	1.73	206	4215	5.80	205	30733	7.26
220	2912	2.63	208	6928	3.82	228	6644	3.74	221	1015	1.76	218	4215	5.86	216	29418	7.28
232	2832	2.56	218	6690	3.83	240	6328	3.78	232	1016	1.80	228	4140	5.86	226	27802	7.23
242	2674	2.64	229	6534	3.86	249	6168	3.78	240	942	1.76	236	4070	5.84	240	26462	7.30
250	2598	2.64	236	6140	3.84	257	5932	3.80	251	940	1.80	246	4070	5.86	250	24852	7.20
262	2517	2.65	248	6140	3.86	266	5615	3.78	258	942	1.82	256	3934	5.83	259	24140	7.22
272	2438	2.63	255	5822	3.83	276	5380	3.74	270	650	1.62	278	3920	5.84	267	23538	7.24
277	2360	2.64	267	5668	3.85	298	5062	3.70	294	582	1.62	298	3849	5.86	277	22538	7.24
296	2280	2.68	278	5432	3.83										298	21199	7.25
			298	5196	3.86												

Table 6. Magnetic Data of Heavy Lanthanide 2,3-Dimethoxybenzoates

$TbL_3 \cdot 2H_2O$ $\Theta = -12$ K			$DyL_3 \cdot 2H_2O$ $\Theta = -10$ K			$HoL_3 \cdot 2H_2O$ $\Theta = -10.2$ K			$ErL_3 \cdot H_2O$ $\Theta = -8$ K			$TmL_3 \cdot H_2O$ $\Theta = -6$ K			YbL_3 $\Theta = -45$ 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	133861	9.70	77	164002	10.37	77	154436	10.38	77	134290	9.46	77	73228	7.26	77	24462	4.94
120	88262	9.64	128	101202	10.34	124	98546	10.30	130	78862	9.24	132	47517	7.36	124	17069	4.84
132	80904	9.68	132	96500	10.30	134	91074	10.32	138	72612	9.18	140	42590	7.22	135	15732	4.82
142	74288	9.60	146	90200	10.46	142	87184	10.40	148	67930	9.20	152	39780	7.25	148	14159	4.76
152	70606	9.62	154	84000	10.32	158	82042	10.42	159	64026	9.22	162	36734	7.16	168	13374	4.82
164	64726	9.56	168	74720	10.18	170	73950	10.30	168	59342	9.14	178	32824	7.15	185	12660	4.80
177	62298	9.68	176	72292	10.30	180	65540	10.01	180	53096	8.97	216	26574	7.12	198	12192	4.98
184	58842	9.60	198	70202	10.68	188	66162	10.29	192	52315	9.18	226	25790	7.02	208	11644	4.92
194	57370	9.65	202	69342	10.78	200	63828	10.32	213	47630	9.17	232	25006	7.08	228	11012	5.00
220	50015	9.62	218	60020	10.32	208	59470	10.22	225	45288	9.16	252	22665	7.12	250	10145	4.98
234	47070	9.59	224	58526	10.40	226	55190	10.20	243	41384	9.12	262	21880	7.09	260	9285	4.86
238	45600	9.53	236	54560	10.22	240	52770	10.30	252	39820	9.46	274	21102	7.06	270	9048	4.54
256	42660	9.53	245	52624	10.22	250	50592	10.26	264	38260	9.10	298	19540	7.00	280	8730	4.84
278	38980	9.48	258	50124	10.26	262	47870	10.24	284	35138	9.10				298	8334	4.88
289	37512	9.47	278	47492	10.34	278	44210	10.14	298	33574	9.08						
298	35304	9.62	298	45228	10.34	298	41870	10.22									

In order to estimate the nature of metal ligand bonding in rare earth element complexes and try to know the reason why the colours of 2,3-dimethoxybenzoates of rare earth elements are typical of Ln^{3+} the magnetic susceptibility of 2,3-dimethoxybenzoates was determined over the range 77—300 K. The complexes obey the Curie—Weiss law (Tables 5 and 6). For all complexes the values of the Weiss constants, Θ, have a negative sign. It probably results from the antiferromagnetic spin interaction or from a crystal field splitting of the paramagnetic spin state [30—33].

The values of μ_{eff} determined for all the complexes (except that for europium) are close to those calculated for Ln(III) ions by Hund and Van Vleck (Table 7). Paramagnetic behaviour among the Ln^{3+} ions is due to the presence of unpaired 4*f* electrons. Since these electrons are well shielded from external influence, both their spin orbital motions are significant in determining the overall observed magnetic moment of a complex compound. It follows, therefore, that the magnetic moment of a complex should indicate whether or not these 4*f* electrons are involved in bond formation. The complexes discussed herein show little deviation from the Van Vleck values although the

Table 7. Value of μ_{eff} for the Lanthanides Determined by Hund and *Van Vleck* [33]

Ln^{3+}	Ground term	Calc. μ_{eff}/BM by Hund	μ_{eff}/BM by Van Vleck
La^{3+}	$^1S_0$	0.00	0.00
Ce^{3+}	$^2F_{5/2}$	2.54	2.56
Pr^{3+}	$^3H_4$	3.58	3.62
Nd^{3+}	$^4I_{9/2}$	3.62	3.68
Sm^{3+}	$^6H_{5/2}$	0.84	1.55—1.65
Eu^{3+}	$^7F_0$	0.00	3.40—3.51
Gd^{3+}	$^8S_{7/2}$	7.94	7.94
Tb^{3+}	$^7F_6$	9.70	9.70
Dy^{3+}	$^6H_{15/2}$	10.60	10.60
Ho^{3+}	$^5J_8$	10.60	10.60
Er^{3+}	$^4J_{15/2}$	9.60	9.60
Tm^{3+}	$^3H_6$	7.60	7.60
Yb^{3+}	$^2F_{7/2}$	4.50	4.50
Lu^{3+}	$^1S_0$	0.00	0.00

Curie equation has been used. This could be expected as the crystal field splitting of the *f*-orbitals is of the order of 100 cm^{-1}, a value quite inadequate to bring about electron pairing or even an altered magnetic moment due to thermal population of excited state the degenerate levels of which have been split by the crystal field [33, 34]. The values of magnetic moments (Tables 5 and 6) indicate that La(III) and Lu(III) complexes are diamagnetic, as may be expected from their closed shell electronic configurations and the absence of unpaired electrons [35]. The higher value of μ_{eff} for europium 2,3-dimethoxybenzoate compared with that given by Hund [33] may suggest a possible interaction of the ligand field with central ion or may be associated with the multiplet splitting. The lowest three excited states of the europium ion are sufficiently close in energy to the ground states to be appreciably populated at room temperature [33, 36]. Since the excited states possess higher J values than the ground state, the actual magnetic moment is larger than those calculated by using the J value for the ground state. With the exception of Sm and Eu, the multiplet widths for the lanthanide elements are very large compared with kT ($kT \Rightarrow 200$ cm^{-1}) at room temperature, whereas those for Sm and Eu are not really infinitely large compared to kT. For Eu the interval between the lowest multiplet components is only 1/21 of the overall width as it appears for a ^7F term [33].

$$\frac{1}{2} \times [J_{\max}(J_{\max}+1) - J_{\min} \cdot (J_{\min}+J)] = \\ = \frac{1}{2} \times 6 \times 7 - 0 = 21 \quad (3) \\ J_{\min}+1 = 1$$

In the complexes of 2,3-dimethoxybenzoates, the paramagnetic central ions remain virtually unaffected by the surrounding diamagnetic ligands. The 4*f* 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 [37]. Their energy levels are the same as in the free ions due to the very effective shielding by the overlapping $5s^25p^6$ shell. For the lanthanide ions the ground state is separated by several hundreds of cm^{-1} from the next higher-lying state. Hence, the magnetic properties can be considered identical to those of the ground state alone, making bonded lanthanide ions act in the same way as the free ions. Therefore, the colours of the complexes remain the same as those in the free lanthanide ions. The electron density in the molecules makes the *f*→*f* electronic transitions of central ions to be those of the lowest energy and the absorption occurs at relatively high wavelengths.

Concluding, from the obtained results it appears that the Ln—O bond in rare earth element 2,3-dimethoxybenzoates is mainly electrostatic in nature, since the 4*f*-orbitals of the lanthanide ions are effectively shielded by the $5s^25p^6$ octet.

The analytical, magnetic, and spectral data suggest that in 2,3-dimethoxybenzoates of rare earth elements the lanthanide ions exhibit a coordination number 9 or 8 depending on the dentates of the carboxylate group and the position of water molecules in the complex. The coordination numbers of Ln^{3+} ions could be established on the basis of the complete crystal structure determination of monocrystals but they have not been obtained. The trivalent lanthanide ions exhibit a wide variety of stereochemical arrangements on the basis of their varying coordination numbers from six to twelve. This coordination variation in lanthanide complexes is well established and may be ascribed to the steric factors and electrostatic force of attraction and repulsion rather than to the direction of bonds by the deep-seated 4*f*-orbitals of metal ions.

EXPERIMENTAL

For the preparation of the complexes the following oxides of rare earth elements were used: La_2O_3,

Pr_6O_{11}, Nd_2O_3, Sm_2O_3, Eu_2O_3, Gd_2O_3, Tb_4O_7, Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, Lu_2O_3, and Y_2O_3 (Aldrich Chemical Company); only cerium was used as $Ce(NO_3)_3$. The 2,3-dimethoxybenzoic acid used for the preparation was produced by Aldrich Chemical Company. In the experiments the solutions of NH_3 aq (25 %), HCl (36 %) and of the oxalic acid, $H_2C_2O_4$ were also used for preparation of the complexes. They were produced by Polish Chemical Reagents in Gliwice (Poland).

The contents of carbon and hydrogen were determined by elemental analysis using a CHN 2400 Perkin—Elmer analyzer. The contents of metal(III) ions were determined by the oxalic acid method. The FTIR spectra of complexes were recorded over the range 400—4000 cm^{-1} using FTIR 1725X Perkin—Elmer spectrometer. The samples were prepared as KBr discs.

The X-ray diffraction patterns were taken on a HZG-4 (Zeiss, Jena) diffractometer using Ni filtered CuK_α radiation. The measurements were made within the range $2\varphi = 4$—$80°$ by means of the Debye—Scherrer—Hull method.

The thermal stability and decomposition of the prepared complexes were determined in air using a Paulik—Paulik—Erday Q-1500 D derivatograph with a Derill converter recording TG, DTG, and DTA curves. The measurements were made at a heating rate of 10 K min^{-1} with a full scale. The 100 mg samples were heated in platinum crucibles in static air to 1173 K with the sensitivity of the TG 100 mg (this means that the whole scale in the balance was equal to 100 mg). The DTG and DTA sensitivities were regulated by the Derill computer program. The paper speed was 2.5 mm min^{-1} and Al_2O_3 was used as the standard. The products of decomposition were calculated from TG curves and verified by the registration of the diffraction pattern.

The measurements in nitrogen were made on OD-102 derivatograph at a heating rate of 10 K min^{-1}. The samples were heated to 1173 K at the following sensitivities: TG – 100 mg, 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 nature of the solid products of decomposition was established from the TG curves and confirmed by IR and X-ray spectra.

The gaseous products of thermal decompositions of 2,3-dimethoxybenzoates of rare earth elements were identified by the registration of TG-FTIR spectra in the range 500—4500 cm^{-1} in the TG-FTIR system using the Mettler—Toledo Star System. The measurements were carried out in argon atmosphere at a heating rate of 20 K min^{-1}. The samples of masses ranging from 10.7254 mg to 16.9180 mg were heated to 1273 K. The argon flowed at a rate of 50 cm^3 min^{-1}.

Magnetic susceptibilities of polycrystalline samples of 2,3-dimethoxybenzoates of rare earth elemnts were measured by the Gouy method using a sensitive Cahn RM-2 balance. Measurements were made at a magnetic field strength of 9.9×79.58 A m^{-1}. The calibrant employed was $CoHg(SCN)_4$ for which the magnetic susceptibility of 16.44×10^{-6} cm^3 g^{-1} was taken [1].

The correction for diamagnetism of the constituent atoms was calculated by the use of Pascal's constants [2]. The temperature-independent paramagnetism of rare earth ions was assumed to be zero. Magnetic moments were calculated from the equations

$$\mu = 2.83(\chi_\mathrm{M}T)^{1/2} \qquad (1)$$

$$\mu = 2.83(\chi_\mathrm{M}T)^{1/2} \times 1.257 \times 10^{-6}\ \mathrm{m\ kg\ s^{-2}\ A^{-2}} \qquad (1^*)$$

$$\mu = 2.83[\chi_\mathrm{M}(T-\theta)]^{1/2} \qquad (2)$$

$$\mu = 2.83[\chi_\mathrm{M}(T-\theta)]^{1/2} \times \times 1.257 \times 10^{-6}\ \mathrm{m\ kg\ s^{-2}\ A^{-2}} \qquad (2^*)$$

The 2,3-dimethoxybenzoates of rare earth elements were prepared by the addition of equivalent quantities of 0.1 M ammonium 2,3-dimethoxybenzoate (pH ≈ 5) to a hot solution containing the chloride of the rare earth elements 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.

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