

Spectral and thermal behaviours of rare earth element complexes with 3,5-dimethoxybenzoic acid

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Abstract: The conditions for the formation of rare earth element 3,5-dimethoxybenzoates were studied and their quantitative composition and solubilities in water at 293 K were determined. The complexes are anhydrous or hydrated salts and their solubilities are of the orders of 10^{-5} – 10^{-4} mol dm⁻³. Their FTIR, FIR and X-ray spectra were recorded. The compounds were also characterized by thermogravimetric studies in air and nitrogen atmospheres and by magnetic measurements. All complexes are crystalline compounds. The carboxylate group in these complexes is a bidentate, chelating ligand. On heating in air to 1173 K, the 3,5-dimethoxybenzoates of rare earth elements decompose in various ways. The hydrated complexes first dehydrate to form anhydrous salts which then decompose in air to the oxides of the respective metals while in nitrogen to mixtures of carbon and oxides of the respective metals. The complexes are more stable in air than in nitrogen.

Keywords: 3,5-dimethoxybenzoates, rare earth elements, thermal stability of 3,5-dimethoxybenzoates, magnetic properties of complexes.

INTRODUCTION

The compounds of 3,5-dimethoxybenzoic acid with various cations are little known. Papers exist on its complexes with cations such as: Cu(II) and Ag(I), Zn(II) and Pb(II). The compounds were obtained as solids or were investigated in solution.^{1,2} The 3,5-dimethoxybenzoate of Cu(II) was isolated in the solid state and its thermal stability was studied¹ while those of Ag(I), Zn(II) and Pb(II) were only investigated in solution.²

The physico-chemical properties of 2,3-dimethoxybenzoic acid were also studied and the parameters of its unit cell in the solid state were determined.^{2,3} There is no information about the solid-state properties of complexes of 3,5-dimethoxybenzoic acid with rare earth elements. Therefore, it was decided to synthesize them in the solid state and to examine some of their properties, such as thermal stability in air and nitrogen, solubility in water at room temperature, IR spectral characteristics and crystalline form in order to determine whether they are crystalline or amorphous compounds. The thermal stability investiga-

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tions enabled the evaluation of the mechanism of the complex decomposition. The determination of the solubility is valuable because it gives information about the practical use of the acid for the separation of rare-earth elements by extraction or ion-exchange chromatographic methods.

EXPERIMENTAL

The 3,5-dimethoxybenzoates of rare earth elements were prepared by the addition of equivalent quantities of 0.1 M ammonium 3,5-dimethoxybenzoate (pH \approx 5) to a hot solution containing the chloride of the rare earth elements followed by crystallization at 293 K. The solids formed were filtered off, washed with water to remove ammonium ions and dried at 303 K.

The contents of carbon and hydrogen were determined by elemental analysis using a CHN 2400 Perkin-Elmer analyser. The contents of metal (III) ions were determined by the oxalic acid method³ (Table I).

TABLE I. Analytical data of rare earth element 3,5-dimethoxybenzoates

Complex L = C ₉ H ₉ O ₄	C / %		H / %		Ln / %		Solubility mol/dm ³
	Calcd.	Found	Calcd.	Found	Calcd.	Found	
LaL ₃ · 2H ₂ O	45.13	45.25	4.31	4.17	19.35	19.35	8.6 · 10 ⁻⁴
CeL ₃	47.43	47.53	3.95	3.73	20.51	20.19	1.8 · 10 ⁻⁴
PrL ₃	47.37	47.89	3.94	3.76	20.60	20.69	3.0 · 10 ⁻⁴
NdL ₃	47.14	47.38	3.92	3.73	20.98	21.09	3.6 · 10 ⁻⁴
SmL ₃	46.72	46.93	3.89	3.70	21.68	21.90	9.2 · 10 ⁻⁴
EuL ₃	46.62	46.62	3.88	3.67	21.86	22.02	7.2 · 10 ⁻⁴
GdL ₃	46.27	46.13	3.85	3.65	22.45	22.21	5.0 · 10 ⁻⁴
TbL ₃	46.16	45.67	3.85	3.63	22.64	22.95	3.4 · 10 ⁻⁴
DyL ₃	45.92	45.63	3.82	3.60	23.03	23.35	4.5 · 10 ⁻⁴
HoL ₃	45.76	44.92	3.81	3.56	23.30	23.30	3.4 · 10 ⁻⁴
ErL ₃	45.61	45.16	3.80	3.53	23.55	23.26	2.3 · 10 ⁻⁴
TmL ₃	45.51	44.66	3.79	3.64	23.73	23.64	1.5 · 10 ⁻⁴
YbL ₃	45.25	45.62	3.77	3.57	24.16	24.50	1.3 · 10 ⁻⁴
LuL ₃	45.12	44.64	3.76	3.51	24.37	24.44	6.5 · 10 ⁻⁵
YL ₃ · H ₂ O	49.77	51.74	4.46	4.11	13.81	13.89	3.2 · 10 ⁻⁴

The FTIR and FIR spectra of complexes were recorded over the range 4000–400 cm⁻¹ and 400–100 cm⁻¹ using an FTIR 1725X Perkin-Elmer spectrometer and a Nicolet MAGNA FTIR 760 spectrometer, respectively. The samples for the FTIR spectra measurements were prepared as KBr discs and those for the FIR spectra with polyethylene of masses from 0.8 to 1.0 mg. Some of the results are presented in Table I and Figs. 1 and 2.

The X-ray diffraction patterns were taken on a HZG-4 (Carl Zeiss-Jena) diffractometer using Ni filtered CuK α radiation. The measurements were made within the range $2\theta = 4-80^\circ$ by means of the Debye-Scherrer-Hull method. The relationships between I/I_0 and 2θ for some of 3,5-dimethoxybenzoates of rare earth elements are presented in Fig. 3.

The thermal stability and decomposition of the prepared complexes were studied in air using a Paulik-Paulik-Erday θ -1500 D derivatograph with a Derill converter recording TG, DTG and DTA curves (Figs. 4 and 5). The measurements were made at a heating rate of 10 K min⁻¹ with a full scale. The 100 mg

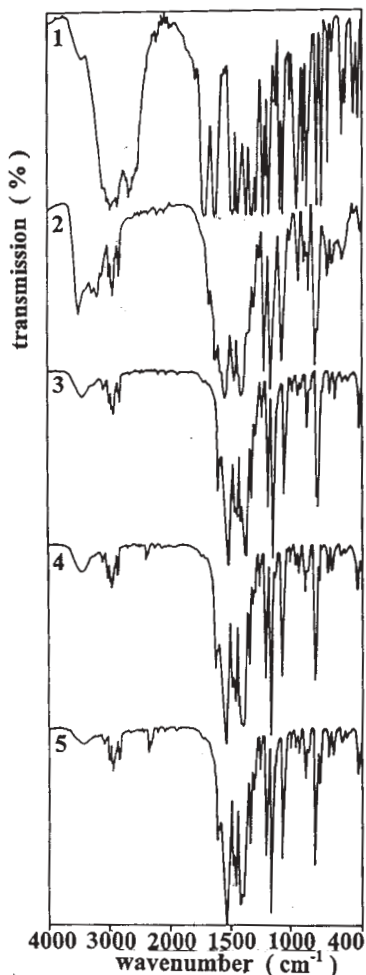


Fig. 1. FTIR spectra of 3,5-dimethoxybenzoic acid (1), 3,5-dimethoxybenzoates of La (2), Eu (3), Tb (4) and Lu (5).

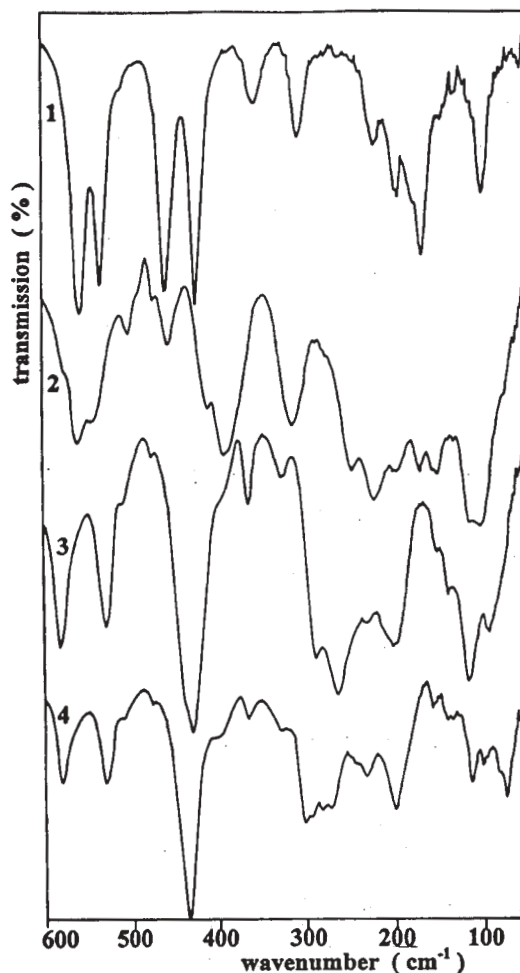


Fig. 2. FIR spectra of 3,5-dimethoxybenzoic acid (1), 3,5-dimethoxybenzoates of La (2), of Gd (3), and of Lu (4).

samples were heated in platinum crucibles in static air to 1173 K with a TG sensitivity of 100 mg (this means that the whole scale of the balance was 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 the standard. The products of decomposition were calculated from the TG curves and verified by X-ray powder diffraction. The data are presented in Table III.

The measurements in nitrogen were made on an OD-102 derivatograph at a heating rate of 10 deg/min. 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 $115 \text{ cm}^3/\text{min}$. The results are presented in Table III and Fig. 6. The nature of the solid decomposition products was established from the TG curves and confirmed by IR and X-ray spectroscopy.

Magnetic susceptibilities of the polycrystalline complexes of 3,5-dimethoxybenzoates of rare earth elements were measured by the Gouy method using a sensitive Cahn RM-2 balance. Measurements were made

at a magnetic field strength of 9.9 kOe. The calbrant employed was $\text{CoHg}(\text{SCN})_4$ for which a magnetic susceptibility of $16.44 \times 10^{-6} \text{ cm}^{-3} \text{ g}^{-1}$ was taken.⁴

TABLE II. Frequencies (cm^{-1}) of the absorption bands of COO^- for 3,5-dimethoxybenzoates of rare earth elements and sodium and that of CO for 3,5-dimethoxybenzoic acid ($\text{L} = \text{C}_9\text{H}_9\text{O}_4$)

Complex $\text{L} = \text{C}_9\text{H}_9\text{O}_4$	$\nu_{\text{C=O}}$	$\nu_{\text{as COO}^-}$	$\nu_{\text{s COO}^-}$	$\Delta\nu_{\text{COO}^-}$	$\nu_{\text{M-O}}$
$\text{LaL}_3 \cdot 2\text{H}_2\text{O}$	—	1530	1397	133	391.05
CeL_3	—	1522	1382	140	429.49
PrL_3	—	1521	1381	140	430.52
NdL_3	—	1522	1378	144	431.42
SmL_3	—	1525	1384	141	432.61
EuL_3	—	1525	1381	144	432.93
CdL_3	—	1527	1384	143	433.39
TbL_3	—	1527	1387	140	433.63
DyL_3	—	1527	1386	141	434.10
HoL_3	—	1527	1386	141	434.31
ErL_3	—	1529	1386	143	434.57
TmL_3	—	1529	1408	121	435.54
YbL_3	—	1531	1412	119	436.38
LuL_3	—	1531	1412	119	436.42
$\text{YL}_3 \cdot \text{H}_2\text{O}$	—	1528	1387	141	436.92
HL	1684	—	—	—	—
NaL	—	1577	1399	178	—

TABLE III. Temperature range of thermal stability of rare earth element 3,5-dimethoxybenzoates in air and nitrogen atmospheres

Complex $\text{L} = \text{C}_9\text{H}_9\text{O}_4$	$\Delta T_1 / \text{K}$	Mass loss / %		n	A (Air) N (N_2)	$\Delta T_2 / \text{K}$	Mass loss / %		T_K / K
		Calcd.	Found				Calcd.	Found	
$\text{LaL}_3 \cdot 2\text{H}_2\text{O}$	341–405	5.01	4.80	2	A	596–1053	77.31	73.3	1100
	333–373	5.01	4.92	2	N	593–1163		85.6	1273
CeL_3	—	—	—	—	A	589–953	74.81	75.2	976
	—	—	—	—	N	673–1093		61.18	1123
PrL_3	—	—	—	—	A	611–963	75.10	75.0	1006
	—	—	—	—	N	693–993		72.2	1073
NdL_3	—	—	—	—	A	616–1033	75.51	75.4	1069
	—	—	—	—	N	633–1113		78.94	1133
SmL_3	—	—	—	—	A	616–973	74.85	74.6	996
	—	—	—	—	N	613–913		81.39	973
EuL_3	—	—	—	—	A	596–973	74.68	74.5	1021

TABLE III. Continued

Complex L = C ₉ H ₉ O ₄	ΔT_1 / K	Mass loss / %		<i>n</i>	$\frac{A \text{ (Air)}}{N \text{ (N}_2)}$	ΔT_2 / K	Mass loss / %		T_K / K
		Calcd.	Found				Calcd.	Found	
GdL ₃	–	–	–	–	N	613–1183		75.22	1203
					A	608–1003	74.11	74.4	1030
TbL ₃	–	–	–	–	N	613–1253		74.4	1273
					A	602–1013	73.37	73.0	1045
DyL ₃	–	–	–	–	N	613–1273		71.96	1273
					A	599–1036	73.56	73.2	1053
HoL ₃	–	–	–	–	N	793–1273		66.3	1273
					A	593–1023	73.31	73.3	1037
ErL ₃	–	–	–	–	N	613–1273		78.57	1273
					A	595–1049	73.07	73.4	1073
TmL ₃	–	–	–	–	N	673–1273		72.72	1273
					A	603–1050	72.90	73.0	1073
YbL ₃	–	–	–	–	N	583–1273		63.58	1273
					A	573–973	72.48	72.1	1023
LuL ₃	–	–	–	–	N	593–1143		71.11	1173
					A	573–1013	72.29	72.2	1023
YL ₃ ·H ₂ O	437–537	2.76	2.90	1	A	604–1003	82.50	82.4	1023
	303–473		3.00		N	593–1153		82.2	1203

ΔT_1 = Temperature range of the dehydration process; *n* = the number of molecules water lost in one endothermic step; ΔT_2 = temperature range of anhydrous complex decomposition; T_K = temperature of the final decomposition process

Correction for diamagnetism of the constituent atoms was calculated by use of Pascal's constants.⁵ The temperature independent paramagnetism of the rare earth ions was assumed to be zero. Magnetic moments were calculated from the equations:

$$\mu = 2.83 (\chi M \cdot T)^{1/2} \quad (1)$$

$$\mu = 2.83 [\chi M(T - \theta)]^{1/2} \quad (2)$$

The results are presented in Table IV.

RESULTS AND DISCUSSION

The 3,5-dimethoxybenzoates of rare earth elements were obtained as crystalline hydrated products with a metal to ligand ratio of 1:3 and a general formula: Ln(C₉H₉O₄)₃ · *n*H₂O 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 Ln = La(III), *n* = 1 for Ln = Y(III) and *n* = 0 for Ln = Ce(III) – Lu(III).

The colours of the complexes were those typical for the corresponding trivalent Ln^{3+} ions, *i.e.*, white for La, Ce, Eu, Gd, Tb, Dy, Yb, Lu and Y, cream for Sm, Ho, green for Pr, greenish for Tm, violet for Nd and pink for Er and originate from lowest energy f-f electronic transitions of the central ion.⁶

The complexes were characterized by elemental analysis (Table I) and IR spectroscopy (Table II, Figs. 1 and 2).

All the 3,5-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 the acid to the salts. The band of the COOH group at 1684 cm^{-1} present in the spectrum of the acid disappears in the spectra of the complexes and two bands arising from the asymmetric and symmetric vibrations of the COO^- group occur at $1530\text{--}1527\text{ cm}^{-1}$ and $1412\text{--}1381\text{ cm}^{-1}$, respectively.⁷⁻¹³ The bands of the C-H antisymmetric and symmetric stretching of the $-\text{OCH}_3$ group are observed at $2944\text{--}2938\text{ cm}^{-1}$ and $2843\text{--}2839\text{ cm}^{-1}$, re-

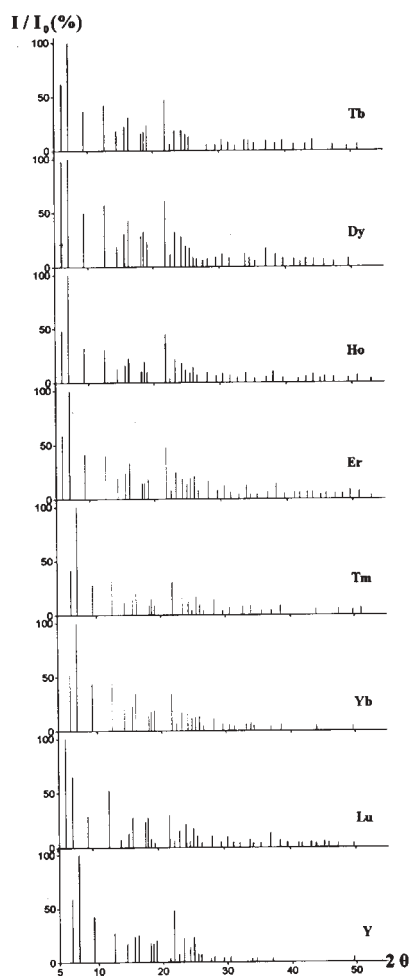


Fig. 3. Relationships between I/I_0 and 2θ for 3,5-dimethoxybenzoates of heavy lanthanides and yttrium.

spectively. The bands of the $\gamma(\text{C}-\text{C})$ ring vibrations appear at 1612–1597 cm^{-1} and its out of plane deformation modes at 1198–1157 cm^{-1} . The $\gamma(\text{C}-\text{H})$ vibrations are observed at 1397–1378 cm^{-1} and 1062–638 cm^{-1} . The bands typical for the aromatic ring vibrations are shifted insignificantly in the complexes compared to the respective bands in 3,5-dimethoxybenzoic acid, which indicates that the Ln(III) ions only weakly influence the benzene ring. Bands due to the metal–oxygen bond appear at 436–391 cm^{-1} for the whole series of complexes.^{8–13} Therefore, it is possible to suppose that 3,5-dimethoxybenzoic acid forms complexes with rare earth elements of similar stability.⁸

In the FIR spectra of 3,5-dimethoxybenzoates of rare earth elements the bands at 116–101 cm^{-1} and at 170–150 cm^{-1} confirm the presence of water molecules and hydrogen bonds O–H ... O in the complexes of La(III) and Y(III). They are also caused by the torsional vibration of the aromatic ring. The bands at 222–220 cm^{-1} result from the internal vibration of the molecule. The bands at 365–314 cm^{-1} are indicative of the $\nu(\text{M}-\text{O})$ vibrations. The FIR spectra for the 3,5-dimethoxybenzoates of La(III), Gd(III) and Lu(III) are shown in Fig. 2.

The frequency of the maxima of the absorption bands of the COO^- group for the 3,5-dimethoxybenzoates of rare earth elements and of sodium, as well as, of the CO group for 3,5-dimethoxybenzoic acid are presented in Table II. The magnitudes of the separation, $\Delta\nu_{\text{COO}^-}$, between the frequencies $\nu_{\text{as COO}^-}$ and $\nu_{\text{s COO}^-}$ in the complexes are lower ($\Delta\nu_{\text{OCO}^-} = 143\text{--}119 \text{ cm}^{-1}$) than in the sodium salt ($\Delta\nu_{\text{OCO}^-} = 178 \text{ cm}^{-1}$), which indicates a lower degree of ionic bond in the rare earth element 3,5-dimethoxybenzoates. According to the spectroscopic criteria^{9,13,14} and with regard to the Nakamoto criterion, the carboxylate ion appears to be a bidentate chelating ligands.

Analysis of the diffractograms suggests that the rare earth element 3,5-dimethoxybenzoates are crystalline compounds. The structures of the compounds have not been determined because single crystals have not been obtained.

The thermal stability of yttrium and lanthanum 3,5-dimethoxybenzoate was studied in air and nitrogen atmospheres (Table III, Figs. 4–6). When heated in air to 1173 K, the 3,5-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.^{15,16}

The thermal stabilities of the rare earth element 3,5-dimethoxybenzoates were studied in air in the temperature range 293–1173 K (Table III). The results obtained from their thermal decompositions 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 573–616 K and then they decompose (with the exception of 3,5-dimethoxybenzoates of La and Nd) to the oxides of the respective metal which are formed between 976–1100 K. The weight loss calculated from the TG curves are equal to 72.1–82.40 % (the theoretical values are 72.2–82.5 %). The oxides of the rare earth elements were identified by X-ray powder diffraction analysis.¹⁶ The 3,5-dimethoxybenzoates of La(III) and Nd(III) decompose to $\text{La}_2\text{O}_2\text{CO}_3$ and $\text{Nd}_2\text{O}_2\text{CO}_3$.^{17,18} 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 weight loss of the complexes during heating.

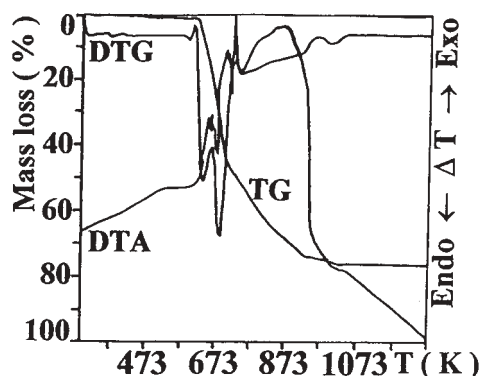


Fig. 4. TG, DTG and DTA curves of neodymium 3,5-dimethoxybenzoate in air.

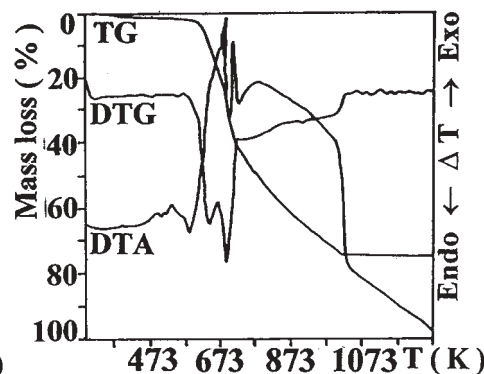


Fig. 5. TG, DTG and DTA curves of holmium 3,5-dimethoxybenzoate in air.

The hydrated 3,5-dimethoxybenzoates of rare earth elements lose one or two molecules of water of crystallization in one step in the range 341–537 K and form anhydrous complexes (405–537 K). The found weight losses estimated for dehydration process from TG curves are equal to 2.9–4.8 % (the theoretical: 2.76–5.01 %). The dehydration process is connected with an endothermic effect shown in the DTA curves.^{17,18}

The derivatogram of neodymium 3,5-dimethoxybenzoate is presented in Fig. 4. The complex decomposes in two steps. The weight loss of the complex starts at 616 K. The decrease in weight occurs in the range 616–976 K. The weight loss determined from the TG curve is equal to 72.7 % (the calculated value is 72.32 %), which corresponds to the formation of $\text{Nd}_2\text{O}_2\text{CO}_3$. Accordingly, the peak ascribed to this loss of the weight is also recorded in the DTG curve, which is the first derivative of the weight loss. Next, the oxycarbonate of neodymium is finally decomposed to Nd_2O_3 (994–1033 K). The weight loss determined from the TG curve is equal to 75.4 % (the calculated value is 75.51 %). The oxidation process is associated with a strong exothermic effect reflected in the DTA curve. Subsequently, the TG curve reaches a plateau as the formed Nd_2O_3 is thermally stable.

The thermal stability of the rare earth element 3,5-dimethoxybenzoates was also studied in a nitrogen atmosphere (Table III, Fig. 6). The complexes were found to be anhydrous or hydrated salts. The 3,5-dimethoxybenzoates of lanthanum and yttrium were obtained as mono- and dihydrates while those of the remaining ones are anhydrous salts. In the case of yttrium and lanthanum 3,5-dimethoxybenzoate the found mass losses calculated from the TG curves are equal to 2.9–4.92 % and theoretical 2.76–5.01 %. This corresponds to the loss of one and two molecules of water.

On heating to 1173 K, the complexes decompose in various ways. The anhydrous 3,5-dimethoxybenzoates of Ce(II), Pr(III), Nd(III), Sm(II), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III) and Lu(II) are stable up to 573–793 K when they then decompose to a mixture of the respective metal oxides and carbon (Table III).

The hydrates of lanthanum and yttrium 3,5-dimethoxybenzoates, first dehydrate in

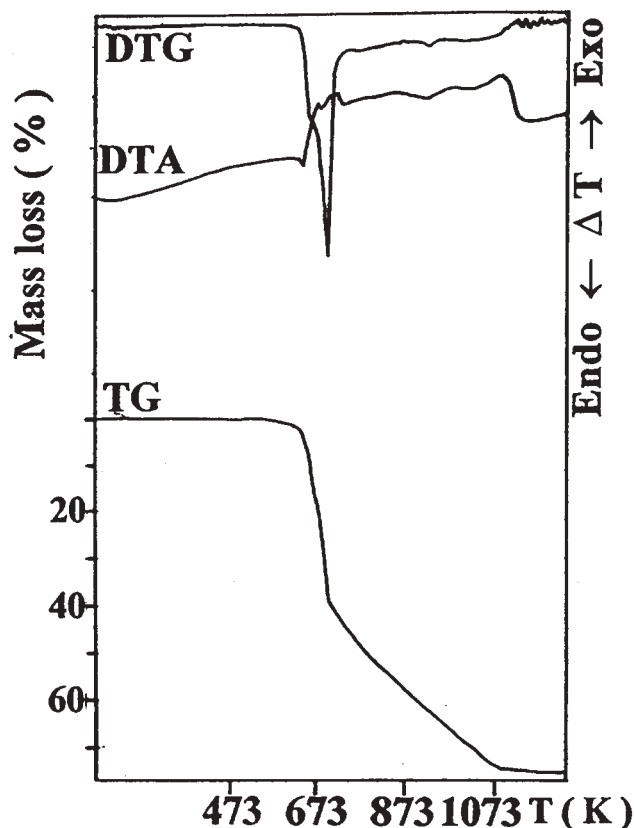


Fig. 6. TG, DTG and DTA curves of neodymium 3,5-dimethoxybenzoate in nitrogen.

the range 303–473 K to form anhydrous complexes. The dehydration process is accompanied by an endothermic effect observed in the DTA curves. Next, in the range 593–1163 K, the anhydrous complexes decompose further. The combustion of the organic ligand is connected with an exo-effect seen in the DTA curves. The TG, DTG and DTA curves of the 3,5-dimethoxybenzoate of Nd during heating in a nitrogen atmosphere are presented in Fig. 6.

The values of the initial decomposition temperatures of the anhydrous complexes of La, Nd, Sm, Tm, Y, Lu in nitrogen are lower (573–633 K) than those in air, which suggests that they are more stable in air than in nitrogen. The final products of decomposition of 3,5-dimethoxybenzoates of rare earth elements are mixtures of the respective metal oxides and carbon. The content of the mixtures were identified by X-ray powder diffraction,^{16,19}

From the obtained results it follows that the molecules of water may bind in different ways in the coordination spheres of the complexes.^{20–23} Water of crystallization is removed from various compounds over a broad temperature range.^{17,18,20–22} According to Nikolaev *et al.*^{20–22} and Singh *et al.*²³ water eliminated below 413–423 K can be considered as water of crystallization and water eliminated above 423 K may be coordinated to the central ion. In the present investigation, the water of the lanthanum complex is eliminated

below 413 K and FTIR spectral studies revealed it to be water of crystallization. In the case of yttrium 3,5-dimethoxybenzoate the water is eliminated above 423 K and so may be considered as water coordinated to the central ion. 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.

TABLE IV. Values of μ_{eff} for the lanthanides determined by Hund and by Van Vleck at room temperature*

Ln^{3+}	Ground term	Calcd. μ_{eff} by Hund	μ_{eff} by Van Vleck	μ_{eff} (BM*)
La^{3+}	$^1\text{S}_0$	0.00	0.00	0.00
Ce^{3+}	$^2\text{F}_{5/2}$	2.54	2.56	2.64
Pr^{3+}	$^3\text{H}_4$	3.58	3.62	3.68
Nd^{3+}	$^4\text{J}_{9/2}$	3.62	3.68	3.70
Sm^{3+}	$^6\text{H}_{5/2}$	0.84	1.55–1.65	1.82
Eu^{3+}	$^7\text{F}_0$	0.00	3.40–3.51	6.00
Gd^{3+}	$^8\text{S}_{7/2}$	7.94	7.94	7.90
Tb^{3+}	$^6\text{H}_{15/2}$	9.70	9.70	9.28
Dy^{3+}	$^6\text{H}_{15/2}$	10.60	10.60	10.32
Ho^{3+}	$^5\text{J}_8$	10.60	10.60	10.61
Er^{3+}	$^4\text{I}_{15/2}$	9.60	9.60	9.23
Tm^{3+}	$^3\text{H}_6$	7.60	7.60	6.90
Yb^{3+}	^2F	4.50	4.50	4.31
Lu^{3+}	$^1\text{S}_0$	0.00	0.00	0.00

In order to estimate the nature of the metal ligand bonding in the rare earth element complexes and to attempt to establish why the colours of 3,5-dimethoxybenzoates of rare earth elements are typical of Ln(III), the magnetic susceptibility of the 3,5-dimethoxybenzoates was determined over the range 77–330 K. The complexes obey the Curie-Weiss law. For all the complexes the values of the Weiss constants, θ , have a negative sign. This is probably the consequence of antiferromagnetic spin interaction or crystal field splitting of the paramagnetic spin state.^{24–29} 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 IV). The paramagnetic behaviour of the tripositive lanthanide ions is due to the presence of unpaired 4f electrons. Since these electrons are well shielded from external influence, both their spin and 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 4f electrons are involved in bond formation. The complexes discussed herein show little deviation from the Van Vleck values although the Curie equation has been used. This was to 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 whose degenerate levels have been split by the crystal field.^{29–31} The values of the magnetic moments (Table IV) indicate that the La(III) and Lu(III) complexes are diamagnetic, as may be expected from their closed shell electronic configurations and the absence of unpaired electrons.^{32–34} The higher value of μ_{eff} for europium 3,5-dimethoxybenzoate compared with that given by Hund may suggest a possible interaction of the ligand field with the central ion or may be associated with a multistep 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.^{29,35,36} Since the excited states possess higher J values than the ground state, the actual magnetic moment is larger than that 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 ($kT = 200 \text{ cm}^{-1}$) 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 for a ${}^7\text{F}$ term²⁹ it appears (Eq.(3))

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

$$J_{\text{min}} + 1 = 1$$

In the complexes of 3,5-dimethoxybenzoates, the paramagnetic central ions remain virtually unaffected by the surrounding diamagnetic 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 surrounding atoms.³⁷ Their energy levels are the same as in the free ions due to 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 behave in the same manner 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 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 3,5-dimethoxybenzoates is mainly electrostatic in nature, since the 4f orbitals of the lanthanide ions are effectively shielded by the $5s^25p^6$ octet.

The solubilities of 3,5-dimethoxybenzoates of rare earth elements in water at 293 K were measured (Table I). They are in the order of $10^{-5} - 10^{-4} \text{ mol dm}^{-3}$. Samarium 3,5-dimethoxybenzoate is the most soluble salt while that of lutetium the least soluble one. Taking into account the values of the complex solubilities, it is possible to state that 3,5-dimethoxybenzoic acid cannot be used for the separation of rare earth elements by ion exchange chromatography because it forms not readily soluble complexes with these elements.

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ИЗВОД

СПЕКТРАЛНО И ТЕРМИЧКО ПОНАШАЊЕ КОМПЛЕКСА ЕЛЕМЕНАТА РЕТКИХ
ЗЕМАЉА СА 3,5-ДИМЕТОКСИБЕНЗОЕВОМ КИСЕЛИНОМWIESŁAWA FERENC¹, AGNIESZKA WALKÓV-DZIEWULSKA¹ and JANUSZ CHRUSCIEL²¹Faculty of Chemistry, Maria Curie-Skłodowska University, Pl 20-031 Lublin, Poland and ²Institute of Chemistry, University of Podlasie, Pl 08-110 Siedlce, Poland

Проучавани су услови за образовање 3,5-диметоксибензоата са елементима ретких земаља као и њихов квантитативан састав и растворљивост у води на 293 К. Комплекси су анхидроване или хидратисане соли, а њихове растворљивости су реда величине $10^{-5} - 10^{-4}$ mol dm⁻³. Снимљени су и њихови FTIR, FIR и рендгенски спектри. Једињења су такође карактерисана термогравиметријском анализом у ваздуху и азоту, као и магнетним мерењима. Сви комплекси су кристална једињења. Карбоксилне групе у овим комплексима су бидентатни, хелатни лиганди. Грејањем на ваздуху до 1173 К 3,5-диметоксибензоати елемената ретких земаља разлажу се на различите начине. Хидратисани комплекси се прво дехидратишу уз стварање анхидрованих соли које се затим на ваздуху разлажу до оксида одговарајућег метала, док се у азоту добијају смеше угљеника и оксида одговарајућег метала. Комплекси су стабилнији на ваздуху него у азоту.

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