

Preparation and properties of yttrium and lanthanide complexes with *m*-methoxybenzoic acid

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Abstract

The preparation and properties of yttrium and lanthanide (from La to Lu) complexes with *m*-methoxybenzoic acid are described.

INTRODUCTION

m-Methoxybenzoic acid $C_6H_4(OCH_3)COOH$ is a crystalline solid, sparingly soluble in water [1]. A survey of the literature shows that *o*-methoxybenzoates of lanthanides from La to Ho have been prepared [2, 3]. In earlier work, we described the preparation of Y and lanthanide (from La to Lu) *p*-methoxybenzoates and presented some of their properties [4, 5]. Makushova and Pirkes [6] have described the properties of anhydrous *m*-methoxybenzoates of lanthanides from La to Er. *m*-Methoxybenzoates of Y, Tm, Yb and Lu were previously unknown.

As a continuation of our work on the rare earth element benzene-carboxylates, we now report on the preparation and properties of Y and lanthanide (from La to Lu) complexes with *m*-methoxybenzoic acid in solid state.

EXPERIMENTAL

The reagents used were HCl p.a. (POCh Gliwice), NH_3 25% solution p.a. (POCh Gliwice), *m*-methoxybenzoic acid p. (Merck-Schuchardt), La_2O_3 (99.8%), $Ce(NO_3)_3 \cdot 6H_2O$ (99.8%), Pr_6O_{11} (99.9%), Nd_2O_3 (99.9%), Sm_2O_3 (99.9%) (made in our laboratory), Eu_2O_3 (99.9%) (International Enzymes Ltd., Windsor Berkshire), Gd_2O_3 (99.9%), (VEB

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Laborchemie Apolde), Tb_4O_7 (99.9%), Dy_2O_3 (99.9%) (Koch-Light Laboratories Ltd.), Ho_2O_3 (99.9%) (POCh Gliwice), Er_2O_3 (99.9%) (Fluka AG), Tm_2O_3 (99.9%), Yb_2O_3 (99.9%), Lu_2O_3 (99.9%) (Rare Earth Products Limited), oxalic acid p.a. and NaOH p.a. (POCh Gliwice).

Preparation of the complexes

m-Methoxybenzoates of Y and lanthanides from La(III) to Lu(III) (without Pm) were prepared by reaction of stoichiometric quantities of hot 0.2 M solution of ammonium *m*-methoxybenzoate (pH 5.5–6.0) and solutions of lanthanide chlorides (Ce(III) was used as its nitrate). The precipitate was formed during heating the mixture for 0.5 h at 343–353 K; it was then filtered off, washed with hot water to remove Cl^- and NH_4^+ ions, and dried at 303 K to a constant mass. The sodium salt was prepared by adding stoichiometric quantities of 3-methoxybenzoic acid to a solution of NaOH and crystallizing at room temperature.

Elemental analysis

The carbon and hydrogen contents were determined by elemental analysis using V_2O_5 as oxidizing agent. The metal content was determined from the TG curve and by ignition of the complexes to the oxides at 1253 K. The content of crystallization water was determined from the TG curve and by heating the samples isothermally at 473 K to a constant mass.

IR spectra and diffractograms

The IR spectra of *m*-methoxybenzoic acid, and of the separated Y and lanthanide complexes and the sodium salt were recorded over the range 4000–400 cm^{-1} with a UR-20 spectrophotometer. The samples were prepared as KBr discs. The X-ray patterns were recorded with a DRON-2 diffractometer by the Debye–Schörrer powder method using Mn-filtered Fe K_α radiation. The measurements were made over the range $2\theta = 5-80^\circ$.

Derivatographic measurements

The thermal stability of the prepared *m*-methoxybenzoates was determined using a Paulik–Paulik–Erdey Q-1500 derivatograph. The TG, DTG and DTA curves were recorded. Measurements were made at a sensitivity of 100 mg (TG), 500 μV (DTG), and 500 μV (DTA). Samples (100 mg) were heated in platinum crucibles to 1273 K at a heating rate of

10 K min⁻¹. The hydrated complexes were heated isothermally at set temperatures to a constant mass and the products obtained were confirmed by the IR spectra and X-ray diffractograms.

Determination of solubility

The solubility of the prepared complexes in water was determined at 293 K. The saturated solutions were prepared under isothermal conditions. The content of the Ln(III) ions was determined by the oxalate method. The solubilities were determined on the basis of oxide mass (see Table 3, below).

RESULTS AND DISCUSSION

Complexes of Y and lanthanides from La(III) to Lu(III) with *m*-methoxybenzoic acid were prepared as crystalline solids with the color characteristics of the lanthanide(III) ions. From the elemental analyses, it was found that complexes of yttrium and lanthanides from Ce(III) to Tm(III) with *m*-methoxybenzoic acid were prepared as hydrates with a molar ratio of metal to organic ligand of 1:3 and various degrees of hydration which do not change regularly with decreasing ionic radius of the lanthanide series (Table 1). Only the complexes of La, Yb and Lu were prepared as anhydrous compounds. The complexes described in ref.

TABLE 1
Analytical data

Complex ^a	Ln (%)		C (%)		H (%)	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
Y(C ₈ H ₇ O ₃) ₃ · 3H ₂ O	14.90	14.80	48.29	48.30	4.52	4.60
La(C ₈ H ₇ O ₃) ₃	23.45	23.50	48.62	48.15	3.54	3.52
Ce(C ₈ H ₇ O ₃) ₃ · 2H ₂ O	22.25	22.30	45.74	45.44	3.97	4.08
Pr(C ₈ H ₇ O ₃) ₃ · H ₂ O	23.00	23.10	47.03	47.21	3.75	3.71
Nd(C ₈ H ₇ O ₃) ₃ · 4H ₂ O	21.53	21.58	43.00	43.20	4.33	4.30
Sm(C ₈ H ₇ O ₃) ₃ · 2H ₂ O	23.49	23.52	45.01	45.60	3.90	3.84
Eu(C ₈ H ₇ O ₃) ₃ · 4H ₂ O	22.43	22.40	42.51	42.55	4.28	4.21
Gd(C ₈ H ₇ O ₃) ₃ · 4H ₂ O	23.03	23.00	42.18	42.00	4.24	4.20
Tb(C ₈ H ₇ O ₃) ₃ · 3H ₂ O	23.84	23.88	43.22	43.30	4.05	4.00
Dy(C ₈ H ₇ O ₃) ₃ · 4H ₂ O	23.62	23.60	41.86	41.48	4.21	3.95
Ho(C ₈ H ₇ O ₃) ₃ · 3H ₂ O	24.52	24.50	42.83	42.80	4.01	4.05
Er(C ₈ H ₇ O ₃) ₃ · 4H ₂ O	24.14	24.18	41.57	41.43	4.18	4.19
Tm(C ₈ H ₇ O ₃) ₃ · H ₂ O	26.42	26.50	44.94	44.11	3.59	3.67
Yb(C ₈ H ₇ O ₃) ₃	27.62	27.60	45.96	45.59	3.35	3.40
Lu(C ₈ H ₇ O ₃) ₃	27.84	27.80	45.82	45.80	3.34	3.28

^a (C₈H₇O₃)⁻ is *m*-(C₆H₄(CH₃O)COO)⁻.

6 were obtained in anhydrous form. Therefore, we have prepared previously unknown complexes with *m*-methoxybenzoic acids.

In order to confirm the composition of the prepared *m*-methoxybenzoates and to determine the metal–ligand coordination, the IR spectra of *m*-methoxybenzoic acid of the prepared Y, lanthanide and sodium *m*-methoxybenzoates were recorded. The IR absorption spectra of *m*-methoxybenzoates are similar to each other and have many bands. When the acid is converted to complexes the absorption band of C=O at 1690 cm^{-1} disappears and the bands of asymmetrical (ν_{as}) and symmetrical (ν_{s}) vibrations of the COO group appear at $1545\text{--}1525\text{ cm}^{-1}$ and $1400\text{--}1395\text{ cm}^{-1}$, respectively, together with the broad absorption bands of $\nu(\text{OH})$ with a maximum at 3490 cm^{-1} and the narrow bands of $\delta(\text{H}_2\text{O})$ at 1600 cm^{-1} that are characteristic for hydrates, the bands of O–CH₃ with a maximum at 1320 , 1280 and 1250 cm^{-1} , and the bands of the M–O bond at $425\text{--}410\text{ cm}^{-1}$. In the IR spectra of the prepared *m*-methoxybenzoates, there are numerous bands of the aromatic ring at $1185\text{--}1175$, $1130\text{--}1105$, $1045\text{--}1025$ and $995\text{--}990\text{ cm}^{-1}$, and of the CH bond at $880\text{--}870$, $800\text{--}790$, $770\text{--}750$ and $685\text{--}670\text{ cm}^{-1}$. These bands are shifted insignificantly ($10\text{--}5\text{ cm}^{-1}$) compared to the respective bands of *m*-methoxybenzoic acid; this indicates that the La(III) ions have only a weak influence on the benzene ring.

The frequencies of the M–O bond for all the complexes studied have similar values (Table 2). Accordingly, it may be suggested that *m*-methoxybenzoic acid forms complexes with Y and lanthanides that have similar stabilities. Comparison of the stabilities of the prepared complexes is possible because these complexes are of the same type. The separation values ($\Delta\nu$) of $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ in the IR spectra of the prepared complexes ($\Delta\nu = 145\text{--}125\text{ cm}^{-1}$) are smaller than that of the sodium salt ($\Delta\nu = 160\text{ cm}^{-1}$); this is due to the smaller degree of ionic bonding in the complexes studied than in the sodium salt. The rare earth element ions are characterized by a higher ionic potential than the Na⁺ ion; therefore, they influence the organic ligand more strongly, causing its greater deformation.

From the shifts of $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ in the IR spectra of the complexes, compared to the bonds of the sodium salt, it can be suggested that the --COO^- group is bonded in different ways in the same complex molecule, probably bidentate bridging and chelating.

The rare earth element *m*-methoxybenzoates are crystalline solids of low symmetry with large unit cells (Figs 1 and 2). They are isostructural in the groups: Ce, Pr–Gd; Y, Dy, Ho; Er–Lu. The degree of crystallinity changes irregularly in the lanthanide series and does not depend on the degree of hydration of the complexes (Table 3).

m-Methoxybenzoates of Y and lanthanides are stable in air and can be stored without change. When heated in air, the complexes decompose in

TABLE 2
Frequencies (cm⁻¹) of the most important bands for the IR spectra of *m*-methoxybenzoic acid sodium salt and lanthanide complexes

Complex ^a	$\nu(\text{OH})$	$\delta(\text{H}_2\text{O})$	$\nu(\text{CO})$	$\nu_{\text{as}}(\text{OCO})$	$\nu_s(\text{OCO})$	$\Delta\nu = \nu_{\text{as}} - \nu_s$	$\nu(\text{CH}_3\text{-O-Ar})$	$\nu(\text{M-O})$
C ₆ H ₄ (CH ₃ O)COOH			1690				1305, 1285, 1240	—
YL ₃ · 3H ₂ O	3425	1595		1545	1400	145	1315, 1280, 1245	415
LaL ₃	—	—		1535	1415	120	1310, 1285, 1255	425
CeL ₃ · 2H ₂ O	3420	1600		1540	1400	140	1315, 1280, 1245	415
PrL ₃ · H ₂ O	3400	1600		1545	1410	135	1310, 1280, 1250	425
NdL ₃ · 4H ₂ O	3480	1600		1525	1410	115	1315, 1280, 1250	410
SmL ₃ · 2H ₂ O	3480	1595		1525	1400	125	1310, 1280, 1250	410
EuL ₃ · 4H ₂ O	3490	1605		1535	1405	130	1315, 1285, 1250	410
GdL ₃ · 4H ₂ O	3460	1600		1530	1395	135	1315, 1280, 1250	410
TbL ₃ · 3H ₂ O	3420	1600		1540	1405	135	1320, 1280, 1250	415
DyL ₃ · 4H ₂ O	3450	1600		1540	1410	130	1320, 1280, 1250	420
HoL ₃ · 3H ₂ O	3400	1600		1540	1410	130	1320, 1280, 1250	410
ErL ₃ · 4H ₂ O	3450	1600		1540	1410	130	1315, 1285, 1250	420
TmL ₃ · H ₂ O	3440	1600		1535	1410	125	1315, 1285, 1250	420
YbL ₃				1540	1410	130	1320, 1290, 1250	410
LuL ₃				1535	1410	125	1320, 1280, 1250	425
NaL				1570	1410	160	1317, 1282, 1248	430

^a L is *m*-C₆H₄(CH₃O)COO⁻.

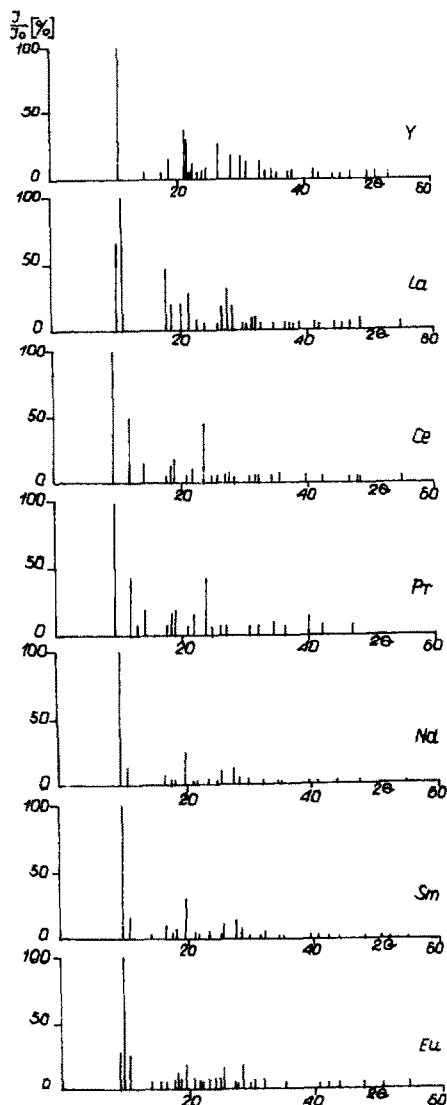


Fig. 1. X-ray diffractograms of Y and light-lanthanide *m*-methoxybenzoates.

various ways (Figs 3–9). The anhydrous complexes of La, Yb, and Lu are stable up to 523–563 K and then decompose directly to the oxides. The hydrates of Pr, Sm and Tm are stable up to 313–353 K, and then lose crystallization water in one step; the anhydrous complexes then decompose directly to the oxides. The hydrates of Y, Ce, Eu, Gd, Dy, Ho, and Er decompose in two steps. In the first step they lose some crystallization water molecules, and then simultaneously lose the remaining water molecules and decompose directly to oxides.

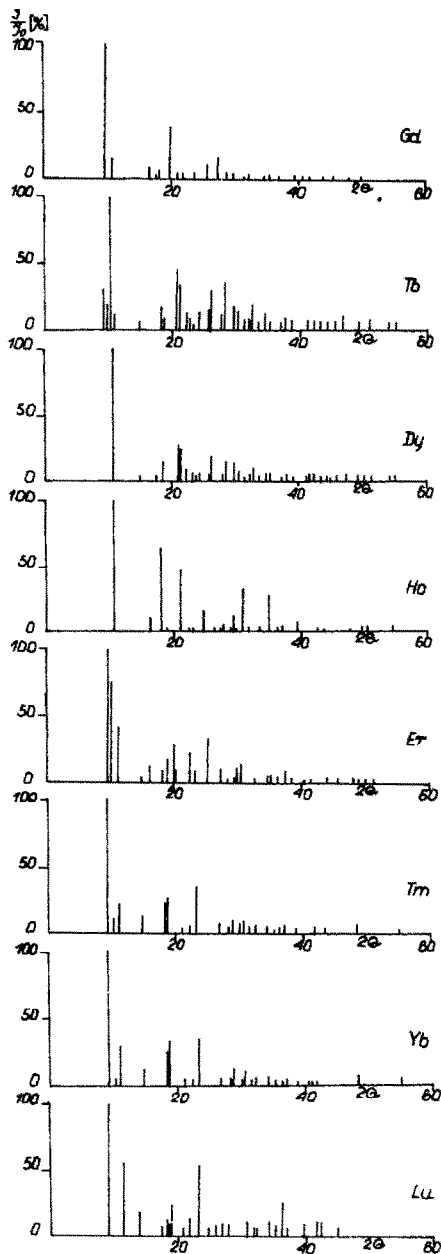


Fig. 2. X-ray diffractograms of heavy-lanthanide *m*-methoxybenzoates.

The tetrahydrated neodymium complex loses 2 water molecules at 343–393 K and is then stable up to 553 K when the dihydrate decomposes to oxide with intermediate formation of the oxocarbonate (Fig. 6).

TABLE 3

Crystallinity degrees and solubilities of yttrium and lanthanide *m*-methoxybenzoates in water at 293 K

Complex ^a	Crystallinity degree	Solubility (10 ⁻³ mol dm ⁻³)
YL ₃ · 3H ₂ O	300	1.74
LaL ₃	317	2.60
CeL ₃ · 2H ₂ O	288	1.38
PrL ₃ · 4H ₂ O	113	1.46
NdL ₃ · 4H ₂ O	337	1.78
SmL ₃ · 2H ₂ O	485	2.04
EuL ₃ · 4H ₂ O	196	1.97
GdL ₃ · 4H ₂ O	523	2.12
TbL ₃ · 3H ₂ O	346	1.28
DyL ₃ · 4H ₂ O	303	1.47
HoL ₃ · 3H ₂ O	733	1.27
ErL ₃ · 4H ₂ O	769	1.97
TmL ₃ · H ₂ O	417	2.00
YbL ₃	374	1.60
LuL ₃	203	1.21

^a L is *m*-C₆H₄(CH₃O)COO⁻.

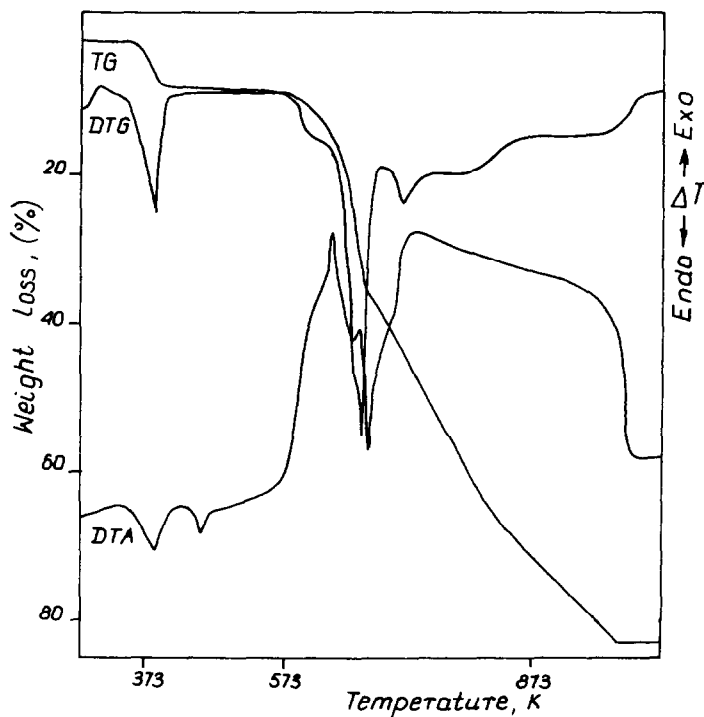


Fig. 3. TG, DTG, and DTA curves of $Y(C_6H_4(OCH_3)COO)_3 \cdot 3H_2O$.

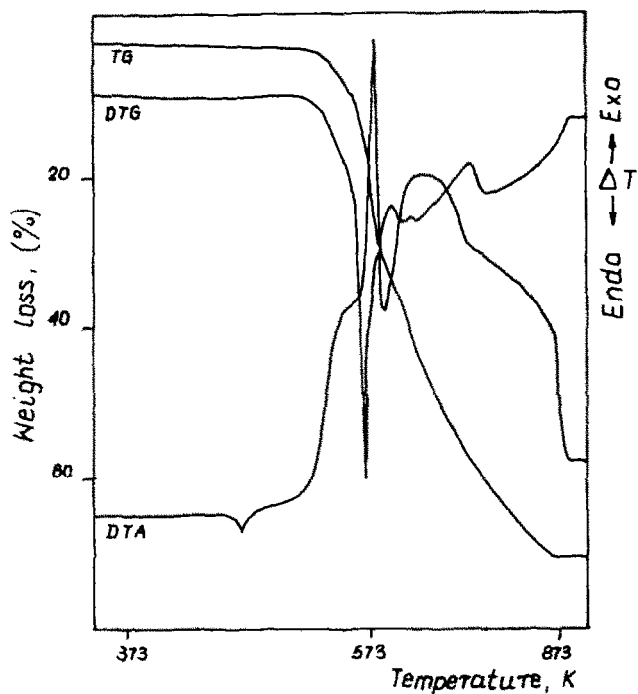


Fig. 4. TG, DTG, and DTA curves of $\text{La}(\text{C}_6\text{H}_4(\text{OCH}_3)\text{COO})_3$.

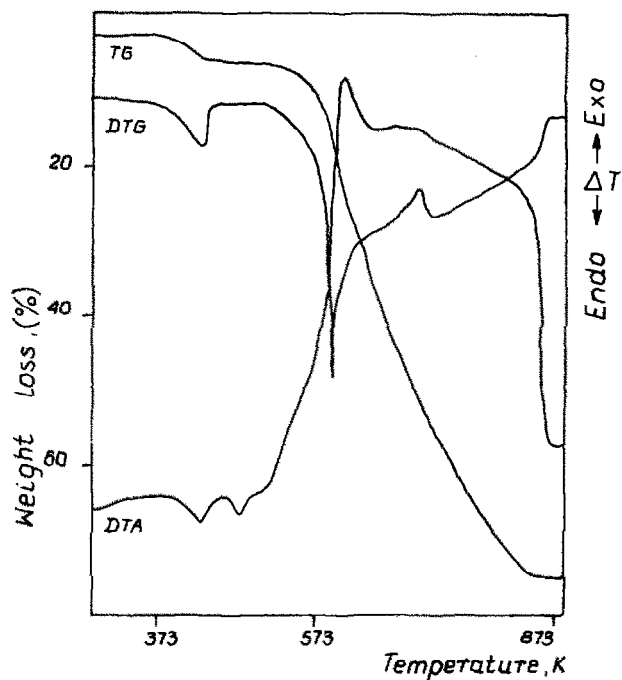


Fig. 5. TG, DTG, and DTA curves of $\text{Ce}(\text{C}_6\text{H}_4(\text{OCH}_3)\text{COO})_3 \cdot 4\text{H}_2\text{O}$.

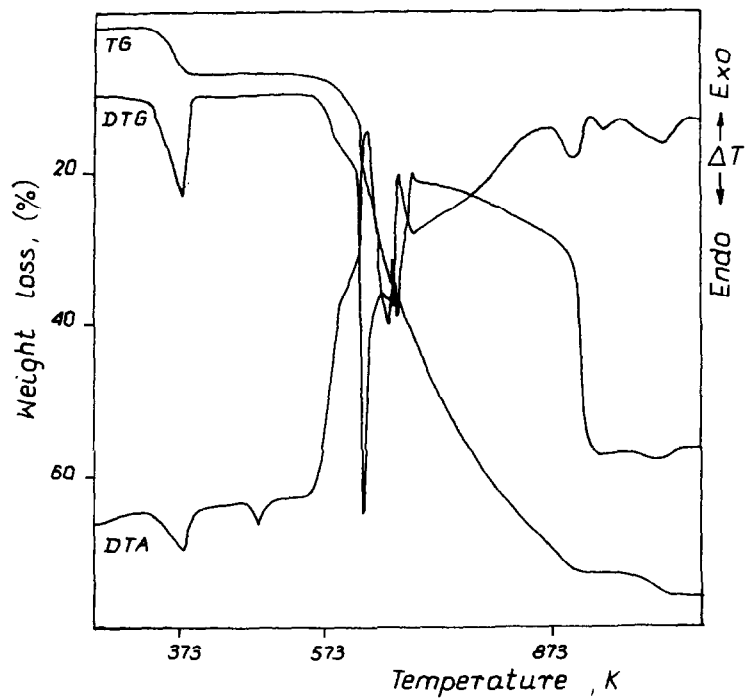


Fig. 6. TG, DTG, and DTA curves of $\text{Nd}(\text{C}_6\text{H}_4(\text{OCH}_3)\text{COO})_3 \cdot 4\text{H}_2\text{O}$.

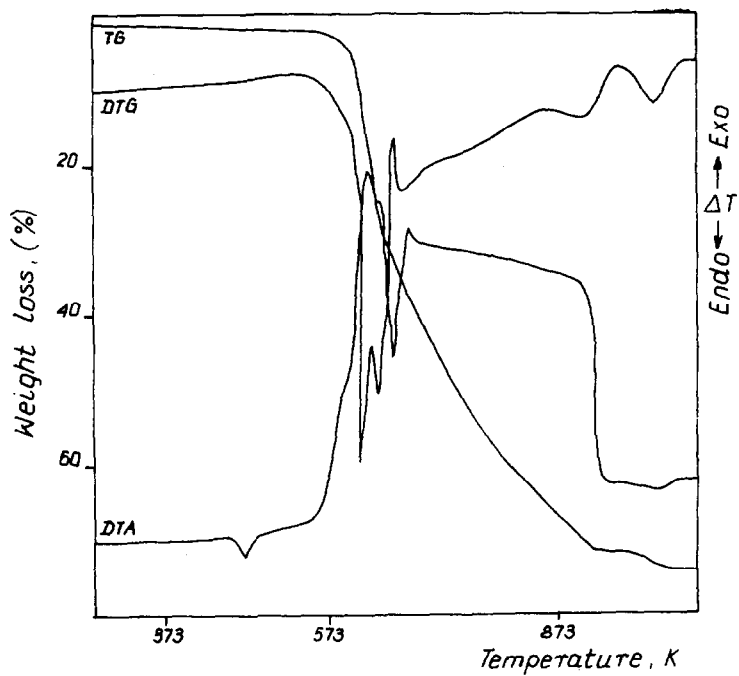


Fig. 7. TG, DTG, and DTA curves of $\text{Nd}(\text{C}_6\text{H}_4(\text{OCH}_3)\text{COO})_3 \cdot 2\text{H}_2\text{O}$.

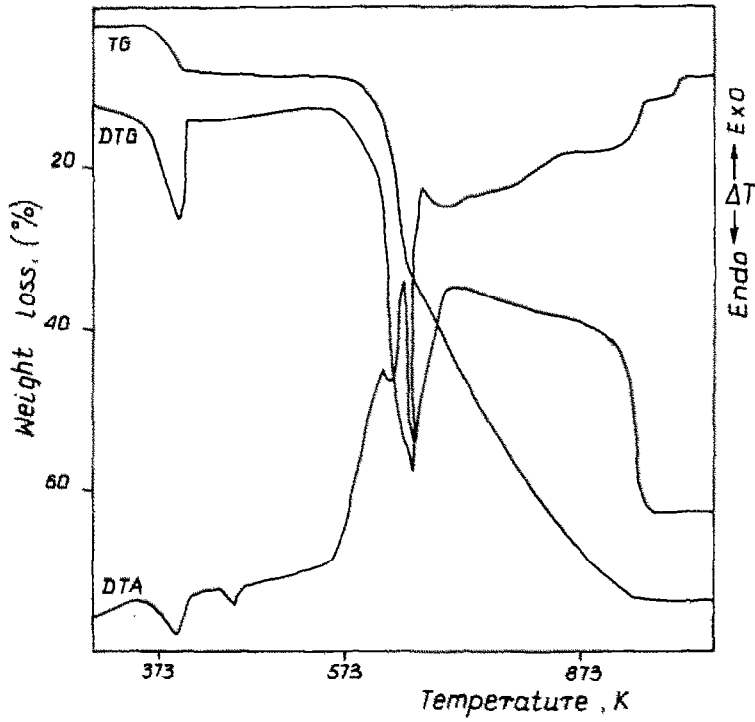


Fig. 8. TG, DTG, and DTA curves of $\text{Ho}(\text{C}_6\text{H}_4(\text{OCH}_3)\text{COO})_3 \cdot 3\text{H}_2\text{O}$

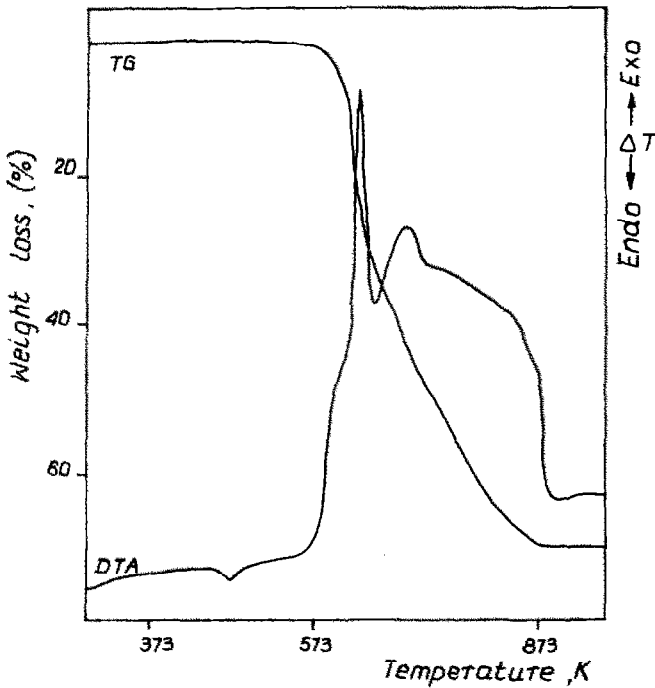
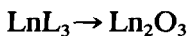


Fig. 9. TG, DTG, and DTA curves of $\text{Lu}(\text{C}_6\text{H}_4(\text{OCH}_3)\text{COO})_3$.

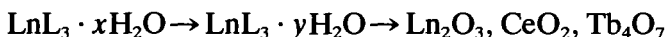
The results indicate the the thermal decomposition of Y and lanthanide *m*-methoxybenzoates can be presented in the following manner.



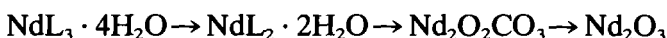
for Ln = La, Yb, Lu



for Ln = Pr, Sm, Tm



for Ln = Y, Ce, Eu, Gd, Tb, Dy, Ho, Er and $x > y$



In general, it can be suggested that anhydrous *m*-methoxybenzoates, when heated in air, decompose directly to the oxides, whereas the hydrated complexes dehydrate, losing all or some water molecules, and then decompose to the oxides either directly or with intermediate formation of oxycarbonate (Nd).

The complexes heated at 473 K lose all or some water molecules forming stable compounds; this was confirmed by the IR spectra and the derivatograms and the results obtained are in accord with the previous data. For example, Fig. 7 shows the derivatogram of neodymium *m*-methoxybenzoate dihydrate obtained by heating at 473 K.

The dehydration and decomposition of the complexes are connected with a strong endothermic effect, whereas the combustion of the organic ligand shows an exothermic effect. The endothermic effect (DTA) associated with the dehydration and simultaneous decomposition is larger than that for the dehydration alone. At 433–483 K, the DTA curves indicate an endothermic effect without weight loss which is connected with a polymorphic transformation.

On the basis of the IR spectra and the thermal curves, it is possible to suggest that the water molecules present in Y and lanthanide *m*-methoxybenzoates are bonded in different ways. The water molecules in the Pr, Sm and Tm complexes are probably outer-sphere water, and those in the complexes of Y, Ce, Eu, Gd, Tb, Dy, Ho and Er are outer- and inner-sphere water.

The temperatures of dehydration (T_0), the temperatures of decomposition (T_1) of the complexes and the temperatures of oxide formation (T_K) change irregularly with increasing atomic number Z of the metal (Fig. 10). The T_0 values are in the same range (313–363 K). The decomposition of the anhydrous complexes begins at 523–563 K, and that of the hydrates at 513–593 K. The temperature of oxide formation changes insignificantly in

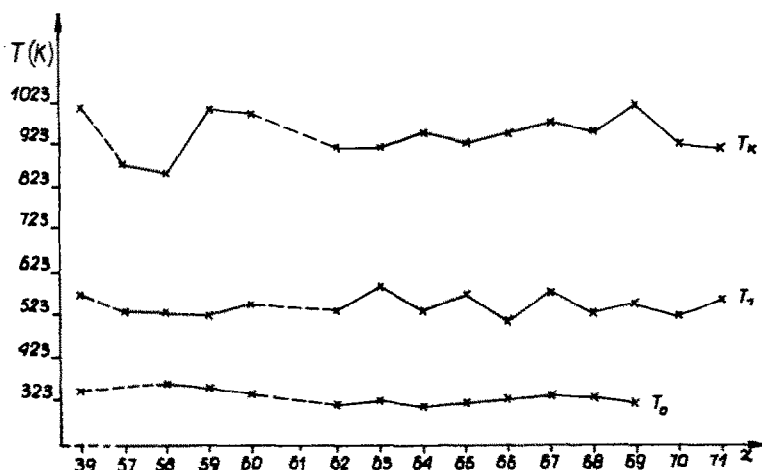


Fig. 10. Relationship between T_0 , T_1 , T_x , and Z .

the lanthanide series: Tm_2O_3 forms at the highest temperature (1023 K) and CeO_2 at the lowest (853 K). These results are listed in Table 4.

m-Methoxybenzoates of Y and lanthanides are soluble in water. Their solubilities are in the order of $10^{-3} \text{ mol dm}^{-3}$ (Table 1) and change irregularly with change in the ionic potential (Fig. 11). The degree of crystallinity does not influence the solubility: the *m*-methoxybenzoate complex of La(III) is most soluble and Lu the least.

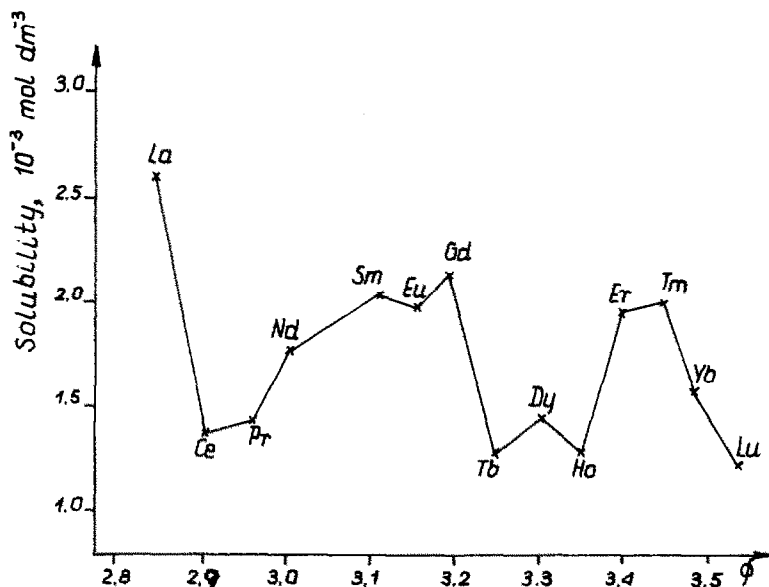


Fig. 11. Relationship between solubility and ionic potential ϕ of Ln(III).

TABLE 4
Data on dehydration and decomposition of Y and lanthanide complexes with 3-methoxybenzoic acid

Complex ^a	Temp. range of dehydration (K)	Weight loss (%)		Loss of H ₂ O (moles)	Temp. range of decomposition (K)	Weight loss (%)		Temp. of oxide formation (K)	Temp. of polymorphic transformation (K)
		Calcd.	Found			Calcd.	Found		
YL ₃ · 3H ₂ O	343-393	6.00	6.2	2	573-993	79.85	79.74	993	443
LaL ₃	-	-	-	-	533-893	72.49	72.50	893	473
CeL ₃ · 2H ₂ O	363-413	2.80	3.0	1	533-853	71.85	72.10	853	463
PrL ₃ · H ₂ O	353-413	2.95	3.0	1	523-993	71.39	71.15	993	433
NdL ₃ · 4H ₂ O	343-393	5.37	5.5	2	553-1003	73.92	73.55	1003	483
SmL ₃ · 2H ₂ O	313-393	5.62	5.6	2	533-913	71.43	71.39	913	473
EuL ₃ · 4H ₂ O	323-393	5.30	5.5	2	593-913	72.56	72.48	913	483
GdL ₃ · 4H ₂ O	313-393	5.30	5.5	2	533-953	71.97	71.95	953	473
TbL ₃ · 3H ₂ O	323-393	5.40	5.5	2	573-923	70.34	70.37	923	473
DyL ₃ · 4H ₂ O	333-393	5.23	5.3	2	513-953	71.39	71.48	953	453
HoL ₃ · 3H ₂ O	333-393	5.35	5.5	2	573-973	70.31	70.37	973	453
ErL ₃ · 4H ₂ O	333-393	5.20	5.3	2	533-953	70.88	70.57	953	453
TmL ₃ · H ₂ O	323-413	2.80	2.8	1	553-1023	68.95	69.10	1023	433
YbL ₃	-	-	-	-	523-923	68.55	69.00	923	473
LuL ₃	-	-	-	-	563-913	68.36	69.00	913	463

^a L is *m*-[C₆H₄(CH₃O)COO]⁻.

CONCLUSIONS

m-Methoxybenzoates of Y and lanthanides from La(III) to Lu(III) were prepared, and their quantitative composition and solubility in water at 293 K (10^{-3} mol dm⁻³) were determined. The complexes are solid hydrates (except those of La, Yb and Lu) with the ratio of metal to organic ligand being 1:3. On the basis of X-ray diffractograms and IR spectra, it was found that these complexes are crystalline and that the metal–ligand bonds are ionic. Upon heating, the anhydrous complexes decompose directly to the oxides, whereas the hydrated complexes lose all or some of the crystallization water molecules and then decompose directly to the oxides or with intermediate formation of an oxocarbonate (Nd). At 433–483 K, the complexes undergo a polymorphic transformation.

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