

Spectroscopic, magnetic and thermal behaviour of the 2,3,4-trimethoxybenzoates of heavy lanthanides(III) and yttrium(III)

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Abstract: The complexes of 2,3,4-trimethoxybenzoic acid with Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III) and Y(III) are crystalline, anhydrous salts with colours typical of the M(III) ions. The carboxylate group is probably a bidentate, chelating ligand. The thermal stabilities of the complexes were examined under an air atmosphere in the temperature range 293–1273 K. The solubility in water at 293 K for all the heavy lanthanide(III) and yttrium(III) complexes are in the order of 10^{-3} mol dm⁻³. The magnetic moments of the complexes were determined in the temperature range 77–300 K.

Keywords: heavy lanthanides(III), yttrium(III), thermal stability, IR spectra, complexes of 2,3,4-trimethoxybenzoic acid, magnetic moments.

INTRODUCTION

Lanthanide(III) carboxylates have been widely studied in recent years due to their physico-chemical properties, variety of structural types and potential uses as fluorescent sensors. The isomers of mono-, di- and trimethoxybenzoates of rare earth elements(III) have been examined.^{1–8} The –COOH group, as an electron acceptor substituent, decreases the electronic density of the benzene ring and the –OCH₃ group, as an electron donor, decreases the acidity of benzoic acid derivatives. The opposed properties of these two kinds of substituents influence the properties of the isomers of methoxybenzoic acids and their compounds.

In our previous articles,^{9–12} the physico-chemical properties of 2,3,4-, 2,4,5-, and 3,4,5-trimethoxybenzoates of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III) (heavy lanthanides(III) and yttrium(III) in the case of 3,4,5-trimethoxybenzoates) were described. Continuing this research, the complexes of 2,3,4-trimethoxybenzoic acid with Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III),

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Lu(III) and Y(III) were examined. The aim of this work was to prepare 2,3,4-trimethoxybenzoates of heavy lanthanides(III) and Y(III) and to characterise their properties: thermal stability in air during heating to 1273 K, IR spectral data, X-ray powder investigations, solubility in water at room temperature and magnetic properties. Thermal stability investigations give information about the mechanism of complex decomposition and the endo- or exo-effects connected with such processes, such as: dehydration, melting, polymorphic changes, crystallization, oxidation or reduction. The determination of 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 chromatography. The magnetic measurements give information about the nature of the metal-oxygen bond.

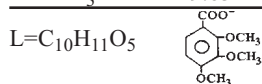
EXPERIMENTAL

The complexes of 2,3,4-trimethoxybenzoic acid with Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III) and Y(III) were prepared by addition of equivalent quantities of 0.1 M ammonium 2,3,4-trimethoxybenzoate ($\text{pH} \approx 5$) to a hot aqueous solution containing the chloride of the required metal ion and crystallizing at 293 K. The solids were filtered off, washed with hot water and methanol to remove ammonium ions and dried at 303 K.

The C, H analysis was performed using a CHN 24000 Perkin-Elmer analyser. The contents of M^{3+} metals were established by the oxalic acid method (Table I).

TABLE I. Elemental analysis of heavy lanthanides(III) and yttrium(III) 2,3,4-trimethoxybenzoates

Complex	C/%		H/%		M/%	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
TbL ₃	45.47	45.57	4.19	4.26	20.05	20.08
DyL ₃	45.26	45.27	4.17	4.19	20.41	21.09
HoL ₃	45.13	44.96	4.17	4.16	20.65	20.81
ErL ₃	44.99	45.06	4.16	4.17	20.89	20.73
TmL ₃	44.90	45.06	4.14	4.19	21.05	20.87
YbL ₃	44.63	44.62	4.09	4.07	21.45	21.25
LuL ₃	44.52	44.45	4.08	4.05	21.64	21.39
YL ₃	49.83	49.96	4.57	4.56	12.31	12.05



The IR spectra of the complexes (KBr discs) were recorded over the range 4000–400 cm^{-1} using a M-80 spectrophotometer (Carl-Zeiss, Jena) (Table II).

The X-ray diffraction patterns were taken on a HZG-4 (Carl Zeiss, Jena) diffractometer using Ni filtered $\text{CuK}\alpha$ radiation. The measurements were made within the range $2\theta = 4 - 80^\circ$ by means of the Debye-Scherrer-Hull method.

The thermal stability and decomposition of the complexes were studied in air by Q-1500D derivatograph with a Derill converter, simultaneously recording TG, DTG and DTA curves. The measurements were made at a heating rate of 10 $\text{K}\cdot\text{min}^{-1}$. The 100 mg samples (50 mg in the case of

Lu(III)) were heated in platinum crucibles in static air to 1273 K with a TG sensitivity of 100 mg, full scale. The DTG and DTA sensitivities were regulated by the Derill computer programme. Some results are presented in Table III.

TABLE II. Spectroscopic data of the 2,3,4-trimethoxybenzoates of sodium and heavy lanthanides(III) and yttrium(III) complexes and of 2,3,4-trimethoxybenzoic acid (cm^{-1}) and the solubility of the complexes (mol dm^{-3}) in water at 293 K

Complex $L = \text{C}_{10}\text{H}_{11}\text{O}_5$	$\nu(\text{C}=\text{O})$	$\nu_{\text{as}}(\text{COO}^-)$	$\nu_{\text{s}}(\text{COO}^-)$	$\Delta\nu(\text{COO}^-)$	$\nu(\text{M}-\text{O})$	Solubility mol dm^{-3}
TbL ₃	–	1540	1395	145	420	2.31×10^{-3}
DyL ₃	–	1540	1395	145	420	2.92×10^{-3}
HoL ₃	–	1540	1395	145	420	8.18×10^{-3}
ErL ₃	–	1540	1395	145	420	3.71×10^{-3}
TmL ₃	–	1540	1395	145	420	4.10×10^{-3}
YbL ₃	–	1536	1416	120	420	3.88×10^{-3}
LuL ₃	–	1536	1416	120	420	4.51×10^{-3}
YL ₃	–	1536	1416	120	420	3.21×10^{-3}
NaL	–	1560	1380	180	–	–
HL	1680	–	–	–	–	–

The DSC/TG analysis was also performed in the temperature range 303–1173 K using a SETARAM differential thermoanalyser Setsys 16/18. The experiments were carried out under a dynamic air atmosphere. The values of the enthalpy of polymorphic changes were determined and are presented in Table III.

TABLE III. Decomposition data for heavy lanthanides(III) and yttrium(III) 2,3,4-trimethoxybenzoates

Complex $L = \text{C}_{10}\text{H}_{11}\text{O}_5$	ΔT_1^{a} K	Weight loss/%		Final compound	T_2^{b} K	ΔH^{c} kJ mol ⁻¹	T_3^{d} K
		Calcd.	Found				
TbL ₃	555–895	76.40	77.00	Tb ₄ O ₇	935	47.95	530.40
DyL ₃	545–925	76.60	76.00	Dy ₂ O ₃	978	44.10	522.50
HoL ₃	540–947	76.30	77.60	Ho ₂ O ₃	1003	44.48	514.80
ErL ₃	512–925	76.10	77.70	Er ₂ O ₃	990	42.87	503.30
TmL ₃	500–947	75.90	75.90	Tm ₂ O ₃	725	41.81	488.20
YbL ₃	494–940	75.60	75.50	Yb ₂ O ₃	940	33.56	470.00
LuL ₃	492–709	75.40	75.50	Lu ₂ O ₃	790	11.37	453.00
						16.47	468.00
YL ₃	523–976	84.40	84.50	Y ₂ O ₃	976	35.05	504.00

^a ΔT_1 = temperature range of anhydrous complex decomposition; ^b T_2 = final temperature of decomposition; ^c ΔH = enthalpy of the polymorphic change; ^d T_3 = maximum temperature of the endo-effect

The gaseous decomposition products were analysed over the range 4500–700 cm^{-1} using the Mettler Toledo Star System (Fig. 2, Table IV).

TABLE IV. Frequencies of the absorption bands of some of the gaseous products evolved during the decomposition of the 2,3,4-trimethoxybenzoates of heavy lanthanides(III) and yttrium(III) (cm^{-1})

Range of frequency	Identified gaseous products
3800 – 3500	CO ₂
2400 – 2280	
670	
2060 – 2220	CO
3100 – 1420	Hydrocarbons
1000	
905	

The magnetic susceptibilities measurements of polycrystalline samples of the 2,3,4-trimethoxybenzoates of the heavy lanthanides were carried out at a magnetic field strength of 9.9 kOe. The calibrant was $\text{Co}[\text{Hg}(\text{SCN})_4]$ with a magnetic susceptibility of $1.64 \times 10^{-5} \text{ cm}^{-3} \text{ g}^{-1}$. Correction for diamagnetism of the constituent atoms was calculated by the use of Pascal's constants.^{13,14} The magnetism of the samples was found to be field independent. The temperature-independent paramagnetism of the heavy lanthanides was assumed to be zero. Magnetic moments were calculated according to Eqs. (1) and (2).

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

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

The results are given in Tables V and VI.

RESULTS AND DISCUSSION

The 2,3,4-trimethoxybenzoate complexes of Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III) and Y(III) were obtained as polycrystalline solids with a metal to ligand ratio of 1:3 with the general formula $\text{M}(\text{C}_{10}\text{H}_{11}\text{O}_5)_3$. Their colours were typical for the corresponding trivalent ions.

Some of the results of IR analysis are presented in Table II. The IR spectrum of 2,3,4-trimethoxybenzoic acid shows the following absorption bands: a strong band of COOH at 1680 cm^{-1} , and bands assigned to the asymmetric and symmetric vibrations of the OCH_3 groups at 2944 and 2840 cm^{-1} , respectively. The bands of ring vibrations appear at 1592 cm^{-1} , $1500\text{--}1420 \text{ cm}^{-1}$, 1176 cm^{-1} and 1020 cm^{-1} . The C–H deformation vibration bands $\delta(\text{C-H})$, are observed in the region $1144\text{--}1100 \text{ cm}^{-1}$. The –C–O–C–symmetric vibration, $\nu_s(\text{COC})$, bands occur at $1020\text{--}1035 \text{ cm}^{-1}$. The bands observed at $940\text{--}650 \text{ cm}^{-1}$ are associated with out of plane deformation ring vibrations, $\phi(\text{CC})$, and the C–H wagging vibrations, $\gamma(\text{C-H})$. The bands at $830\text{--}800 \text{ cm}^{-1}$ have been assigned to the $\gamma(\text{C-H})$ vibrations (in the 1,2,3,4-substituted ring).^{9–12,15–28}

In the IR spectra of the 2,3,4-trimethoxybenzoates of heavy lanthanides(III), the band at 1680 cm^{-1} disappears, which indicates that COOH groups are not present in the analysed complexes. Two bands arising from asymmetric and symmetric vibrations of the COO^- group occur at $1540\text{--}1536\text{ cm}^{-1}$ and $1395\text{--}1416\text{ cm}^{-1}$, respectively. Bands assigned to asymmetric and symmetric vibrations of the OCH_3 groups, $\nu_{\text{as}}(\text{CH}_3)$ and $\nu_{\text{s}}(\text{CH}_3)$, are observed at the $2950\text{--}2944$ and 2840 cm^{-1} , respectively. The bands of $\nu(\text{C}=\text{C})$ ring vibrations appear at $1600\text{--}1592\text{ cm}^{-1}$, $1500\text{--}1416\text{ cm}^{-1}$, $1185\text{--}1180\text{ cm}^{-1}$ and $1040\text{--}1032\text{ cm}^{-1}$. The bands in the region of $1160\text{--}1100\text{ cm}^{-1}$ are attributed to $\delta(\text{C-H})$ deformation vibrations and those of the $-\text{C-O-C}-$ symmetric vibrations, $\nu_{\text{s}}(\text{COC})$, occur at $1040\text{--}1032\text{ cm}^{-1}$. The bands observed at $940\text{--}650\text{ cm}^{-1}$ are associated to out of plane deformation ring vibration, $\phi(\text{CC})$, and out of plane C-H bond vibrations, $\gamma(\text{C-H})$. The bands at $830\text{--}800\text{ cm}^{-1}$ have been assigned to $\gamma(\text{C-H})$ vibrations (in the 1,2,3,4-substituted ring). The band at 420 cm^{-1} results from $\nu(\text{M-O})$ stretching vibrations.^{9-12,15-27} Table II presents the maximum of the frequencies of the absorption bands of asymmetric and symmetric vibrations of the COO^- group of 2,3,4-trimethoxybenzoates of heavy lanthanides(III) and sodium. The differences between the frequencies of ν_{asCOO^-} and ν_{sCOO^-} , $\Delta\nu_{\text{COO}^-}$, in these complexes are smaller ($\Delta\nu_{\text{COO}^-} = 145\text{--}120\text{ cm}^{-1}$) than in the sodium salt ($\Delta\nu_{\text{COO}^-} = 180\text{ cm}^{-1}$). For the 2,3,4-trimethoxybenzoates of heavy lanthanides(III) and Y(III), the shifts of the frequencies ν_{asCOO^-} and ν_{sCOO^-} are lower and higher, respectively, than those for sodium 2,3,4-trimethoxybenzoate. Accordingly, the carboxylate ion in the analysed complexes appears to be a symmetrical, bidentate, chelating ligand.^{27,28} Probably the methoxy- group is also coordinated with the central ion. This conclusion results from the interpretation of the IR spectra. The band positions of the $-\text{OCH}_3$ group vibrations in the spectra of the complexes are changed in comparison with those in the acid spectrum.

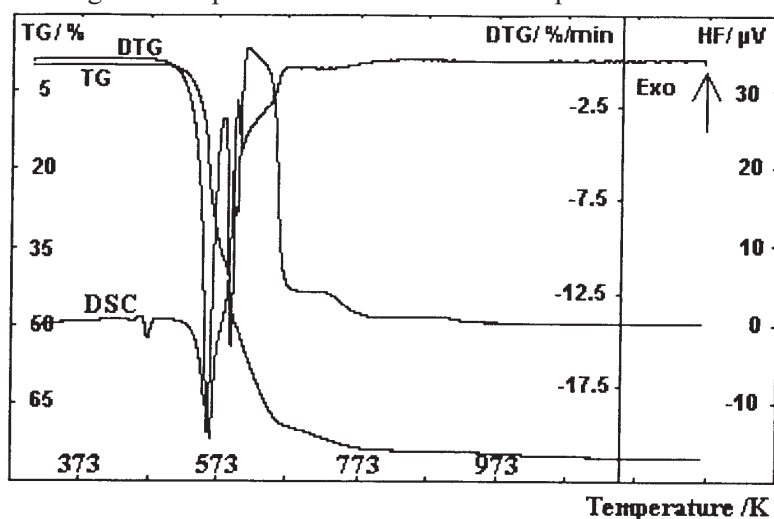


Fig. 1. TG and DSC curves of 2,3,4-trimethoxybenzoate of Yb(III).

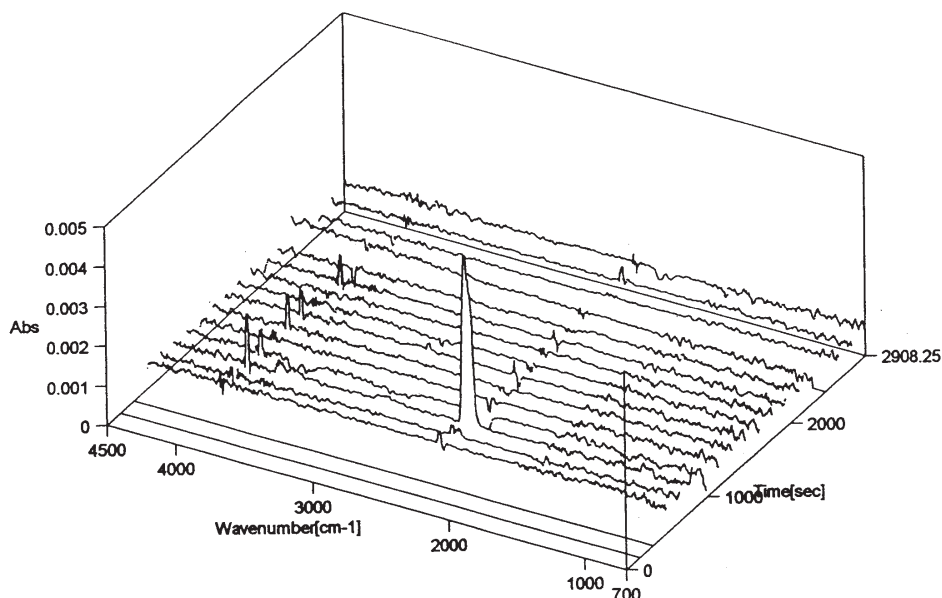


Fig. 2. The FTIR spectrum of the gaseous products evolved during the decomposition of the 2,3,4-trimethoxybenzoate of Dy(III).

The analysis of the diffractograms suggests that the heavy lanthanides(III) and yttrium(III) 2,3,4-trimethoxybenzoates are polycrystalline compounds. It was not possible to determine the structures of the compounds because single crystals were not obtained.

The thermal stabilities of the 2,3,4-trimethoxybenzoates of Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III) and Y(III) were studied under an air atmosphere in the temperature range 293–1273 K. Some results are presented in Table III and Fig. 1. The results revealed that the complexes of heavy lanthanides(III) and yttrium(III) are anhydrous compounds. These results were also confirmed by elemental analysis (Table I) and IR spectroscopy. 2,3,4-Trimethoxybenzoates of heavy lanthanides(III) and yttrium(III) heated in air to 1273 K are stable up to 492–555 K. In the temperature range 453–530 K, polymorphic changes in these complexes were observed. The polymorphic changes were confirmed by endo-effects seen on the DSC curves (Fig. 1). The values of the enthalpy of the polymorphic changes of the 2,3,4-trimethoxybenzoates of Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III) and Y(III), ΔH , were determined using the DSC technique (Table III). The obtained values were in the range 11.37–47.95 kJ mol⁻¹. Having various stabilities, the anhydrous complexes decomposed at temperatures between 492–976 K. The weight loss calculated from the TG curves lay in the 75.50–84.50 % (the theoretical values are 75.40–84.40 %). The combustion of the organic ligands was accompanied by a strong exo-effect. The temperatures of the thermal stability of the complexes change regularly with increasing atomic number of the element. The 2,3,4-trimetho-

TABLE V. Magnetic data for heavy lanthanide 2,3,4-trimethoxybenzoates (L = C₁₀H₁₁O₅)

TbL ₃		DyL ₃		HoL ₃		ErL ₃		TmL ₃		YbL ₃	
Θ = - 10 K		Θ = - 22 K		Θ = - 15 K		Θ = - 14 K		Θ = - 12 K		Θ = - 34 K	
T/K	χ _M ·10 ⁶ μ/BM	T/K	χ _M ·10 ⁶ μ/BM	T/K	χ _M ·10 ⁶ μ/BM	T/K	χ _M ·10 ⁶ μ/BM	T/K	χ _M ·10 ⁶ μ/BM	T/K	χ _M ·10 ⁶ μ/BM
77	140503	77	142670	78	147598	77	14583	77	70520	77	22470
120	88847	122	93730	123	97011	122	94330	130	45920	124	15310
132	84300	134	86315	132	90317	134	86858	140	41432	133	15160
146	76301	146	80382	146	86598	146	76420	146	38441	144	14594
155	72611	158	74450	154	81391	152	71942	158	36202	146	13882
164	66712	162	68520	170	76182	164	67465	170	34701	162	13162
179	63759	178	66991	182	68744	169	65970	178	33952	173	12444
187	59331	184	65550	186	65768	186	60002	202	33212	183	12092
194	57658	192	62585	196	61305	193	57764	210	31704	196	11014
224	51956	220	56654	203	58328	216	52540	222	30158	207	11174
235	49001	234	53692	220	53860	226	48884	230	28682	218	10440
241	47524	241	52204	236	52374	298	35360	274	21240	272	8152
247	44577	246	50692	248	50894			278	20488	281	7436
260	43100	258	49241	254	49402					294	7076
264	40883	264	47753	262	47915						
275	37197	272	46275	278	46424						
285	36457	290	43282	298	44936						
297	34980	298	41824	10.32							

xybenzoate of Tb(III) is the most thermally stable ($T_1 = 555$ K) while the least thermally stable is the complex of Lu(III) ($T_1 = 492$ K). Heavy lanthanide(III) and yttrium(III) 2,3,4-trimethoxybenzoates decompose directly to the oxides of the respective metals as the final product of their decomposition. The oxides of these elements are formed at 725–1004 K. The temperature of oxide formation is the highest for Ho_2O_3 (1003 K) and the lowest for Tm_2O_3 (725 K).

The FTIR spectra of the gaseous products evolved during the decomposition of the 2,3,4-trimethoxybenzoates of heavy lanthanides(III) and yttrium(III) are presented in Table IV and in Fig. 2. Their interpretation reveals the presence of CO_2 , CO and hydrocarbons.^{16–18,24–27}

The solubilities of the 2,3,4-trimethoxybenzoates of heavy lanthanides(III) and Y(III) in water were measured at 293 K (Table II). They are in the order to 10^{-3} mol dm^{-3} . The terbium(III) 2,3,4-trimethoxybenzoate is the most soluble salt while that of holmium(III) is the least soluble one.

TABLE VI. Values 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	$^7 F_6$	9.70	9.70
Dy	$^6 H_{15/2}$	10.60	10.60
Ho	$^5 I_8$	10.60	10.60
Er	$^4 J_{15/2}$	9.60	9.60
Tm	$^3 H_6$	7.60	7.60
Yb	$^2 F_{7/2}$	4.50	4.50
Lu	$^1 S_0$	0.00	0.00

The magnetic susceptibilities of the heavy lanthanide 2,3,4-trimethoxybenzoates were 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 (higher at room temperature than at lower ones) or a crystal field splitting of the paramagnetic spin state.^{29–32} This may also result from the presence of superexchange magnetic interactions between the paramagnetic centres of different molecules of the complexes in the crystal lattice. The paramagnetic central ions in the compounds investigated remain virtually unaffected by the surrounding ligands. The 4f electrons causing their paramagnetism bond. Instead, they interact only weakly with the electrons of the surrounding atoms and are located in an inner shell with a radius of 0.35 Å.³³ This value is very small in comparison with the radius of the $5s^2 5p^6$ closed shell (ca. 1 Å). The ground states of the lanthanide ions are separated by several hundreds of cm^{-1} from the first higher-lying state. Hence the magnetic properties in the ground state are expected to be identical for bonded and non-bonded lanthanide

ions. The 2,3,4-trimethoxybenzoates of 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 VI). Lutetium 2,3,4-trimethoxybenzoate is, as expected, diamagnetic.

The above data indicate that the Ln–O bond in the heavy lanthanide 2,3,4-trimethoxybenzoates is predominantly electrostatic in nature since the 4f orbitals of the lanthanide ions are effectively polarized by the $5s^25p^6$ octet.^{33,34}

ИЗВОД

СПЕКТРОСКОПСКО, МАГНЕТНО И ТЕРМИЧКО ПОНАШАЊЕ 2,3,4-ТРИМЕТОКСИБЕНЗОАТА ТЕШКИХ ЛАНТАНИДА(III) И ИТРИЈУМА(III)

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Комплекси 2,3,4-триметоксибензоєве киселине са Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III) и Y(III) су кристалне анхидроване соли боја карактеристичних за одговарајуће M(III) јоне. Карбоксилатна група је вероватно бидентатни, хелатни лиганд. Термичка стабилност комплекса испитивана је у ваздуху у области температуре 293 – 1273 К. Растворљивости свих тешких лантанида(III) и итријум(III) комплекса су реда величине 10^{-3} mol dm⁻³. Магнетни моменти комплекса одређивани су у области температуре 77 – 300 К.

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