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THERMAL AND SPECTRAL PROPERTIES OF 2,3-, 2,4- AND 3,4- DIMETHOXYBENZOATES OF LIGHT LANTHANIDES

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Abstract

The physico-chemical properties and thermal stability in air of light lanthanide 2,3-, 2,4- and 3,4-dimethoxybenzoates were compared and the influence of $-OCH_3$ substituent on their thermal stability was investigated. The complexes of these series are crystalline, hydrated or anhydrous salts with colours typical of Ln^{3+} ions. The carboxylate group is a bidentate, chelating (2,4- and 3,4-dimethoxybenzoates) or tridentate chelating and bridging ligand (2,3- dimethoxybenzoates). The thermal stability of 2,4- , 3,4- and 2,3- dimethoxybenzoates of light lanthanides was studied in the temperature range 273–1173 K.

The positions of methoxy groups in benzene ring influence the thermal properties of the complexes and their decomposition mechanism.

Keywords: complexes of rare earth elements, influence of methoxy-substituents, light lanthanide dimethoxybenzoates, properties of dimethoxybenzoates, thermal stability of 2,3- , 2,4- and 3,4-dimethoxybenzoates

Introduction

2,3- , 2,4- and 3,4-dimethoxybenzoic acids are crystalline solids sparingly soluble in cold water [1–8]. The literature survey shows that there is no information about the complexes of these acids with various cations. Papers exist only on their compounds with rare earth elements in solution [9] and in solid states [10–15].

We decided to obtain the complexes of the light lanthanides with 2,3- , 2,4- and 3,4-dimethoxybenzoic acids as solids, to examine some of their physico-chemical properties and to compare them.

In our previous papers [10–15] we characterized these complexes by elemental analysis, IR spectra data, thermogravimetric studies and X-ray diffraction measurements but now taking into account the presence and positions of two methoxy groups in benzene ring we decided to compare the properties of dimethoxybenzoates of light lanthanides in order to investigate the influence of substituent positions on their properties.

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Experimental

2,3-, 2,4- and 3,4-dimethoxybenzoates of light lanthanides were prepared by the addition of the equivalent quantities of 0.1 M ammonium 2,3-, 2,4- or 3,4-dimethoxybenzoate (pH~5) to a hot solution containing the light lanthanide element chlorides (and nitrate in the case of cerium ion) and by crystallizing at 293 K. The formed solids were filtered off, washed with hot 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 analyzer. The contents of the Ln(III) ions and crystallization water molecules were determined by oxalic acid method and from the TG curves, respectively.

The IR spectra of complexes were recorded over the range 4000–400 cm^{-1} using M-80 spectrophotometer. Some of the results are presented in Table 1 and Fig. 1.

Table 1 Frequencies of the maxima of the absorption bands of COO$^-$ and M–O vibrations for 2,3-, 2,4- and 3,4-dimethoxybenzoates of light lanthanides and sodium (cm^{-1}) and their solubility products in water (at 293 K)

	Complex L=$C_9H_9O_4$	ν_{asCOO-}	ν_{sCOO-}	$\Delta\nu_{COO-}$	ν_{M-O}	Solubility products/(mol dm^{-3})^4
I	LaL_3	1546	1392	154	413	$6.2\cdot10^{-6}$
	CeL_3	*1546	1389	157	415	$1.3\cdot10^{-7}$
	PrL_3	1546	1391	155	417	$2.5\cdot10^{-6}$
	NdL_3	*1547	1390	157	417	$3.1\cdot10^{-6}$
	SmL_3	1548	1393	155	421	$2.1\cdot10^{-6}$
	EuL_3	*1547	1393	154	419	$3.7\cdot10^{-6}$
	GdL_3	1549	1394	155	423	$1.2\cdot10^{-5}$
	NaL	1602	1396	206	–	–
II	$LaL_3\cdot3H_2O$	1520	1400	120	430	$2.0\cdot10^{-10}$
	CeL_3	1520	1400	120	430	$7.9\cdot10^{-9}$
	PrL_3	1520	1400	120	410	$6.7\cdot10^{-9}$
	NdL_3	1530	1400	130	440	$5.5\cdot10^{-8}$
	$SmL_3\cdot2H_2O$	1530	1400	130	440	$3.2\cdot10^{-10}$
	$EuL_3\cdot2H_2O$	1520	1400	120	440	$8.7\cdot10^{-9}$
	$GdL_3\cdot3H_2O$	1520	1410	110	440	$2.8\cdot10^{-9}$
	NaL	1560	1400	160	–	–
III	$LaL_3\cdot4H_2O$	1520	1400	120	420	$2.7\cdot10^{-12}$
	$CeL_3\cdot4H_2O$	1520	1400	120	420	$1.4\cdot10^{-10}$
	$PrL_3\cdot4H_2O$	1520	1400	120	420	$7.0\cdot10^{-13}$
	$NdL_3\cdot4H_2O$	1530	1400	130	420	$1.0\cdot10^{-11}$
	$SmL_3\cdot4H_2O$	1530	1400	130	420	$2.5\cdot10^{-11}$
	$EuL_3\cdot4H_2O$	1520	1400	120	420	$9.0\cdot10^{-13}$
	$GdL_3\cdot4H_2O$	1520	1410	110	430	$1.0\cdot10^{-13}$
	NaL	1560	1400	160	–	–

*Splitting bands

I – complexes with 2,3-dimethoxybenzoic acid, II – complexes with 2,4-dimethoxybenzoic acid, III – complexes with 3,4-dimethoxybenzoic acid

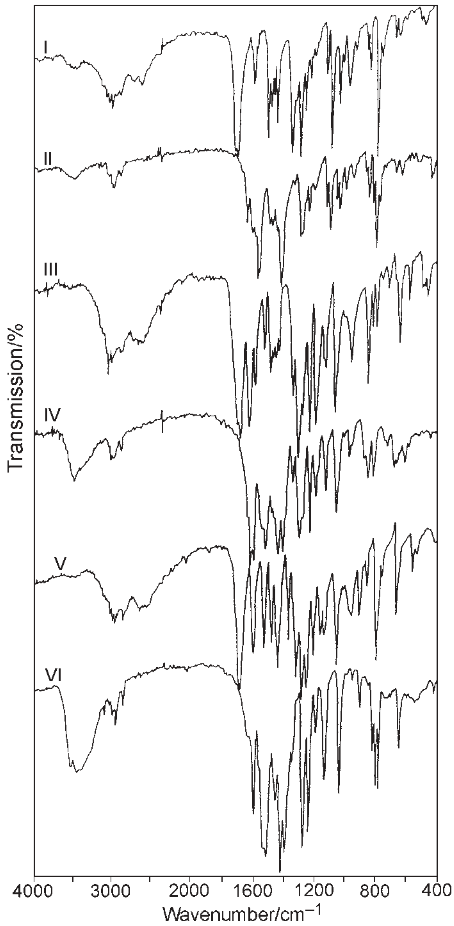

Fig. 1 Infrared spectra of I – 2,3- and III – 2,4- and V – 3,4-dimethoxybenzoic acids; II – 2,3-, IV – 2,4- and VI – 3,4-dimethoxybenzoates of Eu

The X-ray diffraction patterns were recorded on an HZG-4 (Carl Zeiss Jena) diffractometer using Ni filtered CuK$_\alpha$ radiation. The measurements were made within the range 2θ=4–80 by means of the Debye–Scherrer–Hull method.

The thermal stability and decomposition of the prepared complexes were investigated using a Paulik–Paulik–Erdey Q-1500 D derivatograph connected to 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 samples (100 mg) were heated in platinum crucibles in static air to 1173 K, with a sensitivity of the TG to 100 mg. The DTG and DTA sensitivities were regulated by the Derill computer programme. The paper speed was 2.5 mm min^{-1} and Al_2O_3 was used as a reference material. The products of decomposition were calculated from the TG curves and verified by registration of the diffraction patterns (Table 2).

Table 2 Temperature ranges of the dehyration and decomposition processes of 2,3-, 2,4- and 3,4-dimethoxybenzoates of light lanthanides in an air atmosphere

	Complex L=$C_9H_9O_4$	ΔT_1/K	Mass loss/%		n	ΔT_2/K	Mass loss/%		T_K/K
			calcd.	found			calcd.	found	
I	LaL_3	–	–	–	–	516–1118	76.11	76.00	1178
	CeL_3	–	–	–	–	518–1074	74.81	75.00	1148
	PrL_3	–	–	–	–	520–1048	75.10	75.00.	1123
	NdL_3	–	–	–	–	519–1080	75.51	75.00.	1148
	SmL_3	–	–	–	–	503–1073	74.85	74.80	1098
	EuL_3	–	–	–	–	513–1093	74.68	74.50.	1123
	GdL_3	–	–	–	–	513–1073	74.11	74.00	1163
II	$LaL_3\cdot 3H_2O$	363–383	7.16	7.30	3	513–1053	78.39	77.90	1098
	CeL_3	–	–	–	–	508–1003	74.80	74.90	1063
	PrL_3	–	–	–	–	483–1003	75.10	75.60	1048
	NdL_3	–	–	–	–	498–1043	75.52	76.20	1098
	$SmL_3\cdot 2H_2O$	368–398	4.93	4.60	2	478–1023	76.09	76.20	1073
	$EuL_3\cdot 2H_2O$	363–403	4.92	4.90	2	488–1013	75.93	76.20	1073
	$GdL_3\cdot 3H_2O$	358–398	7.20	7.00	3	498–923	77.57	77.60	978
III	$LaL_3\cdot 4H_2O$	333–413	10.50	10.40	4	573–933	75.76	75.56	1083
	$CeL_3\cdot 4H_2O$	313–393	10.50	10.45	4	533–933	78.00	77.99	943
	$PrL_3\cdot 4H_2O$	368–408	9.50	9.24	4	553–893	75.10	75.20	923
	$NdL_3\cdot 4H_2O$	353–413	10.40	10.30	4	573–953	75.76	75.76	1073
	$SmL_3\cdot 4H_2O$	343–413	10.40	10.35	4	573–953	78.00	78.00	973
	$EuL_3\cdot 4H_2O$	358–393	9.30	9.40	4	553–898	74.98	75.00	993
	$GdL_3\cdot 4H_2O$	363–393	9.30	9.20	4	563–943	74.10	74.00	1003

I – complexes with 2,3-dimethoxybenzoic acid, II – complexes with 2,4-dimethoxybenzoic acid, III – complexes with 3,4-dimethoxybenzoic acid, ΔT_1 – temperature range of the dehydration process, n – number of molecules of crystallization water being lost in one endothermic process, The solubilities of the 2,3- and 3,4-dimethoxybenzoates of light lanthanides in water at 298 K were determined by measuring the concentration of Ln^{3+} ions in a saturated solution by the oxalic acid method (Table 1, Fig. 6).

The solubilities of the 2,4-dimethoxybenzoates of light lanthanides in water at 298 K were determined by measuring the concentration of Ln^{3+} ions in a saturated solution by a spectrophotometrical method using the spectrophotometer Specord M-40 (Table 1, Fig. 6). The absorbance of the complexes was measured by using the Arsenazo III in the formic buffer (pH~3.5) and the wavelength λ=650 nm, and with the use of the blank as reference.

Results and discussion

2,3-, 2,4- and 3,4-dimethoxybenzoates of light lanthanides were obtained as hydrated or anhydrous crystalline products with a metal to ligand ratio of 1:3. 2,3-dimethoxybenzoates of light lanthanides and 2,4-dimethoxybenzoates of Ce(III), Pr(III), Nd(III) were obtained as anhydrous salts. 3,4-dimethoxybenzoates of light lanthanides form tetrahydrates, 2,4-dimethoxybenzoates of La(III) and Gd(III) trihydrates and those of Sm(III) form dihydrates.

In these three series of dimethoxybenzoates being compared the number of crystallization water molecules changes with the change of $-OCH_3$ group positions in benzene ring. The colours of the complexes are typical of the appropriate trivalent lanthanide ions which is connected with the structure of molecules and electron density in benzene ring. In these molecules the $f \rightarrow f$ electronic transitions of the central ions are those of the lowest energy and absorption occurs at relatively high wavelengths which depends on the nature of metal ions [16]. The compositions of the complexes were established on the basis of elemental analysis and IR spectra data and their external crystalline forms were also estimated [10–15].

From the IR spectra analysis of light lanthanide 2,3-, 2,4- and 3,4-dimethoxybenzoates it appears that the carboxylate ion is a symmetrical, bidentate chelating ligand in 2,4- and 3,4-dimethoxybenzoates of those elements and also in 2,3-dimethoxybenzoates of La(III), Pr(III), Sm(III) and Gd(III). In the case of 2,3-dimethoxybenzoates of Ce(III), Nd(III) and Eu(III) it is bidentate chelating or tridentate bridging and chelating ligand [17–21].

The magnitudes of separation, $\Delta\nu_{OCO}$ ($\Delta\nu=\Delta\nu_{asOCO}-\Delta\nu_{symOCO}$) which characterized the metal-oxygen bond change in the range from 157–154 cm^{-1} for 2,3-dimethoxybenzoates to 130–110 cm^{-1} for 2,4-and 3,4-dimethoxybenzoates. In these complexes being compared the participation of M–O ionic bond is presumably the largest in the case of 2,3-dimethoxybenzoates while the least one in the case of 2,4- and 3,4-dimethoxybenzoates. The bands of metal–oxygen group are being changed depending on the position of $-OCH_3$ substituents in aromatic ring. Accordingly in the case of 2,3-dimethoxybenzoates of light lanthanides these bands appear in the range 423–413 cm^{-1} while for 2,4- and 3,4-dimethoxybenzoates they are shifted to higher frequencies to be equal to 440–420 cm^{-1} [22]. The frequencies of the bands due to ν_{asOCO} vibration are changed depending on the position of –OCH_3 groups in aromatic ring and they are at 1549–1546 cm^{-1} for 2,3-dimethoxybenzoates, at 1530–1520 cm^{-1} for 2,4-dimethoxybenzoates and at 1520 cm^{-1} for 3,4-dimethoxybenzoates. Similarly, the frequencies of the bands of ν_{sOCO} vibrations have various values being equal to: 1394–1390 and 1410–1400 cm^{-1} for 2,3-, 2,4- and 3,4-dimethoxybenzoates of light lanthanides, respectively. The changes in the values of these band frequencies result from the various position of –OCH_3 groups in aromatic ring and various influences of inductive and mesomeric effects on electron densities in the molecules of those complexes.

The X-ray spectra of 2,3-, 2,4- and 3,4-dimethoxybenzoates of light lanthanides were recorded. Their analysis suggests that the complexes are polycrystalline compounds with low symmetry, large size of the unit cells and different structures [23].

The thermal stability of these complexes was studied in air in the range 273–1173 K by TG, DTG and DTA techniques. The obtained results are presented in Figs 2–5 and in Table 2. When heated at 273–1173 K the complexes decompose in various steps. The anhydrous 2,3-dimethoxybenzoates of La(III) and Nd(III) are decomposed in two steps: first the oxycarbonates are formed and next they are decomposed to La_2O_3 and Nd_2O_3, respectively. 2,3-dimethoxybenzoates of Ce(III), Pr(III), Sm(III), Eu(III) and Gd(III) are stable up to 503–520 K and then at 503–1093 K they form the oxides of the respective metals. These oxides as the final products of 2,3-dimethoxybenzoate decompositions are formed at 1098 K (Sm_2O_3)–1178 K (La_2O_3) (Table 2, Fig. 2). Tetrahydrates of La(III) and Nd(III) 3,4-dimethoxybenzoates decompose in three steps while those of Ce(III), Pr(III), Sm(III), Eu(III) and Gd(III) only in the two ones. The dehydration process occurring at 313–413 K and connected with the endothermic effect in DTA curves yield the anhydrous complexes. In the range 533–953 K they are decomposed to oxide of the respective metals with the intermediate formation of the oxycarbonates (complexes of La(III) and Nd(III)). The oxides of the appropriate metals are formed in the range 923 K (Pr_6O_{11}) –1083 K (La_2O_3) (Table 2, Fig. 5).

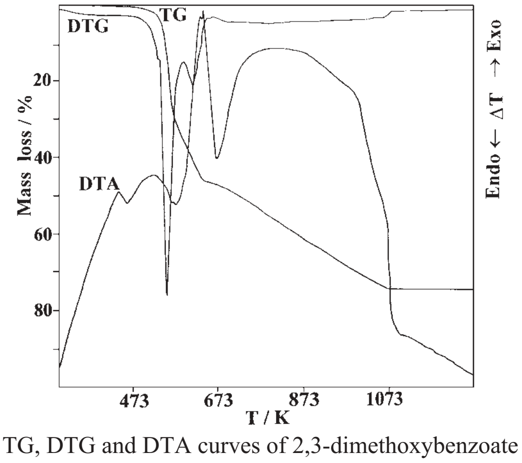

Fig. 2 TG, DTG and DTA curves of 2,3-dimethoxybenzoate of Gd

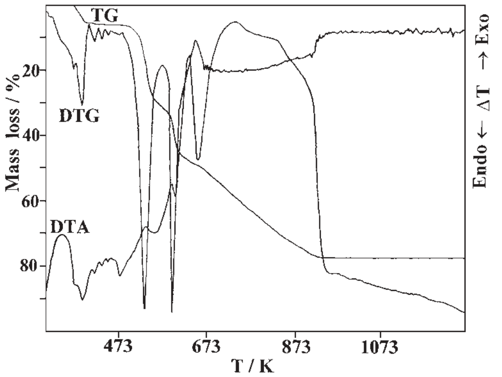

Fig. 3 TG, DTG and DTA curves of 2,4-dimethoxybenzoate of Gd

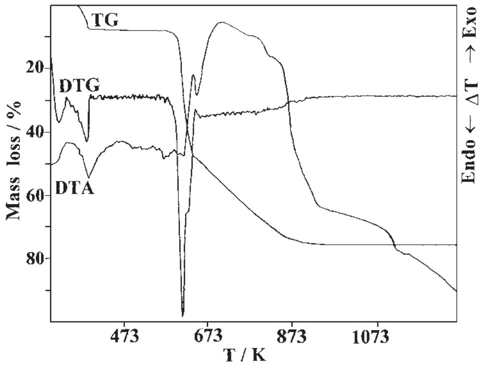

Fig. 4 TG, DTG and DTA curves of 3,4-dimethoxybenzoate of Gd

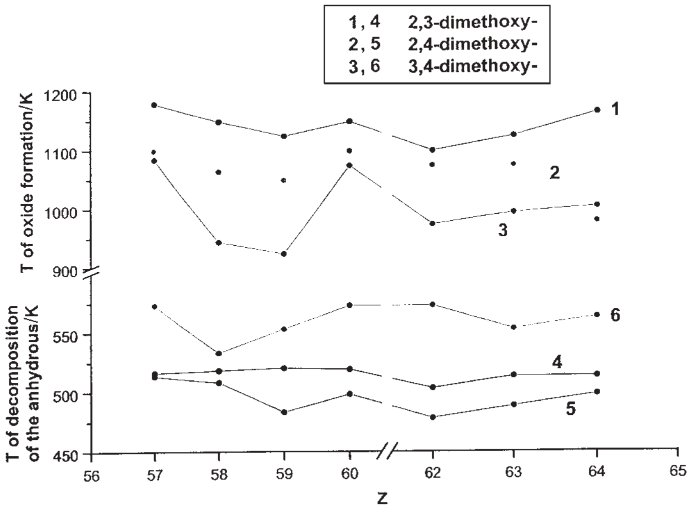

Fig. 5 Dependence of decomposition of the anhydrous complexes and oxide formation temperatures of 2,3- , 2,4- and 3,4-dimethoxybenzoates of lanthanides and *Z*

The complexes of Ce(III) and Pr(III) with 2,4-dimethoxybenzoic acid decompose in one step. In the temperature range 483–1003 K they are decomposed to CeO_2 and Pr_6O_{11}, respectively, which are the ultimate products of decomposition. The anhydrous Nd(III) 2,4-dimethoxybenzoate is decomposed to oxycarbonate that next in the second step of its decomposition forms Nd_2O_3.

Trihydrates of La(III) and Gd(III) and dihydrates of Sm(III) and Eu(III) 2,4-dimethoxybenzoates dehydrate in the range 358–403 K and form anhydrous complexes, which in the temperature range 478–1053 K are decomposed to the oxides of respective metals. The temperatures of the oxide formation change in the series of light lanthanides from 978 K (Gd_2O_3) to 1098 K (La_2O_3, Nd_2O_3) (Table 2, Fig. 5).

In the complexes being compared the dehydration process is connected with an endothermic effect in DTA curves whereas the combustion of the organic ligand with an exothermic one.

From the obtained results concerning the dehydration process of the hydrated 2,4- and 3,4-dimethoxybenzoates of light lanthanides it is possible to assume that the water molecules may be differently bound in the complex coordination sphere and it may be lattice or coordination water [24–28].

From the comparison of the mechanism of decomposition of 2,3-, 2,4- and 3,4-dimethoxybenzoates it appears that thermal decompositions of 2,3-, 2,4- and 3,4-dimethoxybenzoates of La(III) and Nd(III) proceed through oxycarbonates. The anhydrous complexes of 2,3-, 2,4- and 3,4-dimethoxybenzoic acids with Ce(III) are directly decomposed to CeO_2. In the series of dimethoxybenzoates being compared the temperatures of the oxide formations are the highest for La_2O_3 (1173–1083 K) while the lowest ones are for Sm_2O_3, Gd_2O_3 and Pr_6O_{11} (formed by Sm 2,3-, Gd 2,4- and Pr 3,4-dimethoxybenzoate decompositions, respectively).

From the comparison of the decomposition mechanism results for the three series of dimethoxybenzoates of light lanthanides it follows that the various position of $–OCH_3$ substituents in benzene ring influences the decomposition process being strongly connected with the various participations of the inductive and mesomeric effects of methoxy-groups in the electron density of the system [29–31]. The thermal stability of anhydrous dimethoxybenzoates increases in order: 2,4-<2,3-<3,4-. The various position of methoxy groups influence the number of crystallization water molecules in the complexes and the positions of the bands of M–O and asymmetrical vibrations of carboxylate groups in their IR spectra. The number of crystallization water molecules increases in the following sequence: 2,3-<2,4-<3,4-. The positions of asymmetrical vibration bands of carboxylate groups in the IR spectra of dimethoxybenzoates and the values of the temperatures of oxide formations increase in the order: 3,4-<2,4-<2,3-. The positions of the bands of M–O vibrations change in the sequence: 2,3-<3,4-<2,4-.

The solubilities of 2,3-, 2,4- and 3,4-dimethoxybenzoates of light lanthanides in water at 293 K were measured and their values were compared (Table 1, Fig. 6). The values of solubilities in these three series of dimethoxybenzoates being compared increase in the order: 3,4-<2,4-<2,3-. The changes in the values presented above are probably connected with the various influences of inductive, mesomeric and steric ef-

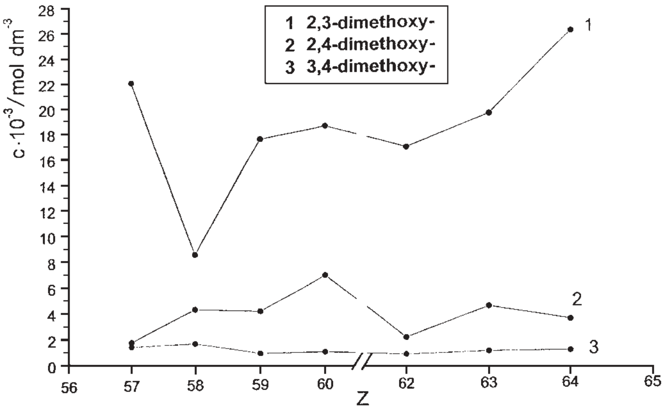

Fig. 6 Relationship between the values of solubilities of 2,3- , 2,4- and 3,4-dimethoxybenzoates of light lanthanides and *Z*

fects of methoxy groups on the electron density of the system depending on their position in benzene ring. The inductive effects of each methoxy groups cause the delocalization of the electrons in the molecule and the change of its energy state brought about the conjugation of electrons. It leads to the stabilization of the system [29–31]. The appearance of the mesomeric effect causes the characteristic changes in the molecule of the organic compound. Therefore, the lengths of some of the σ bonds may be changed. This can be observed in the positions of the bands of the characteristic group vibrations in the IR spectra complexes and in their various thermal stability in air during heating from 273 to 1173 K.

The obtained results also reveal that irrespective of the methoxy group positions in benzene ring the ratio of metal : ligand in the complexes, their colours stay the same for all 2,3-, 2,4- and 3,4-dimethoxybenzoates of light lanthanides.

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