Journal of Thermal Analysis and Calorimetry, Vol. 74 (2003) 511–519

COMPARISON OF SOME PROPERTIES OF 2,3- AND 3,5-DIMETHOXYBENZOATES OF LIGHT LANTHANIDES

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Abstract

The physico-chemical properties and thermal stability in air of the light lanthanide 2,3- and 3,5-dimethoxybenzoates were studied and compared in order to observe if there is influence of the position of $-OCH_3$ substituents in benzene ring on their properties, mainly on their thermal stability. The complexes of both of two series are crystalline, hydrated or anhydrous salts with colours typical of Ln^{3+} ions. The carboxylate group shows the different coordination modes. It may coordinate as a bidentate, chelating or tridentate chelating-bridging ligand. The thermal stabilities of 2,3- and 3,5-dimethoxybenzoates of light lanthanides were studied in the temperature range 293–1173 K. The solubilities of 2,3- and 3,5-dimethoxybenzoates of these elements in water at room temperature are in the orders of 10^{-3}–10^{-2} mol dm^{-3} and 10^{-4} mol dm^{-3}, respectively. The various positions of $-OCH_3$ groups in benzene ring influences some physico-chemical properties of these compounds.

Keywords: 2,3-dimethoxybenzoates of light lanthanides, 3,5-dimethoxybenzoates of light lanthanides, solubility of complexes, thermal stability of complexes

Introduction

According to literature survey the compounds of various metal ions with different carboxylic acid ligands have been scarcely studied. There are papers on the complexes of rare earth elements with 2,4-, 3,4-dimethoxy-, 4-chloro-2-nitro- and 4-chloro-3-nitrobenzoic acids [1–4]. Papers exist also on the complexes of 2,3- and 3,5-dimethoxybenzoic acids with the following cations only: Cu(II), Ag(I), Zn(II), Pb(II), La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III) and Gd(III) [5–8]. They were obtained as solids or were investigated in solution. Some of their physico-chemical properties were studied. There is no information about the comparison of properties of solid complexes of 2,3- and 3,5-dimethoxybenzoic acids with the light lanthanides. Therefore, we decided to prepare these complexes in the solid-state in order to examine some of their physico-chemical properties, such as their thermal stability in air, solubility in water at room temperature, to present their IR spectral characterisation and crystalline forms. The influence of the positions of methoxy-groups in the benzene ring on the properties of the formed compounds was also investigated by com-

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1388–6150/2003/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

paring the thermal stability, the solubility, dentates of carboxylate groups and colours of complexes.

Experimental

2,3- and 3,5-dimethoxybenzoates of light lanthanides were prepared by the addition of the equivalent quantities of 0.1 M ammonium 2,3- and 3,5-dimethoxybenzoates ($pH \approx 5$) to a hot aqueous solution containing the lanthanide chlorides and crystallization at room temperature. The solids formed were filtered off, washed with hot water to remove ammonium ions and dried at 303 K to a constant mass. The carbon, and hydrogen contents were determined by elemental analysis using a CHN 2400 Perkin Elmer analyser. The contents of metal(III) ions were determined by the oxalic acid method.

The IR spectra of the complexes, the spectra of 2,3- and 3,5-dimethoxybenzoic acids and their sodium salts were recorded in the 4000–400 cm^{-1} on an M-80 spectrophotometer, using KBr discs.

X-ray powder patterns were recorded on a HZG-4 (Carl Zeiss Jena) diffractometer using Ni filtered CuK_{α} radiation. The measurements were made within the 2θ range 4–80° by means of the Debye–Scherrer–Hull method.

The thermal stability of these complexes in air in the temperature range 293–1173 K was studied using a Paulik–Paulik–Erdey 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 TG sensitivity of 100 mg (it means that the whole scale in the balance is 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 gaseous products of thermal decompositions of 2,3- and 3,5-dimethoxybenzoates of light lanthanides were identified by the registration of TG-FTIR spectra in the range 4500–500 cm^{-1} in the TG-FTIR system using Mettler–Toledo Star System. The measurements were carried out in argon atmosphere at a heating rate of 20°C min^{-1}. The samples of masses ranging from 10.7254 to 16.9180 mg were heated to 1273 K. The argon flowed at a rate of 50 mL min^{-1}.

The solubilities of the 2,3- and 3,5-dimethoxybenzoates of the 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.

Results and discussion

The 2,3- and 3,5-dimethoxybenzoates of the light lanthanides were obtained as crystalline compounds with metal:ligand ratio of 1:3 (Table 1). Their general formula is $Ln(C_9H_9O_4)_3$, (where *Ln*=La(III)–Gd(III)), except in the case of the La(III) complex with 3,5-dimethoxybenzoic acid, which crystallizes with two molecules of water. The colours of the compounds are typical of the particular Ln(III) ion i.e., white for La, Ce, Eu, Gd, cream for Sm, green for Pr and violet for Nd.

Table 1 Elemental analysis data of light lanthanide 2,3- and 3,5-dimethoxybenzoates and their solubilities in water (at 293 K)

Complex L=$C_9H_9O_4$		H/%		C/%		Ln/%		Solubility/ mol dm^{-3}
		calcd.	found	calcd.	found	calcd.	found	
I	LaL_3	3.96	3.87	47.51	47.67	20.36	20.71	$2.19\cdot 10^{-2}$
	CeL_3	3.95	3.87	47.43	47.43	20.51	20.67	$8.4\cdot 10^{-3}$
	PrL_3	3.94	3.87	47.37	47.42	20.60	20.94	$1.74\cdot 10^{-2}$
	NdL_3	3.92	3.83	47.14	47.07	20.98	21.00	$1.84\cdot 10^{-2}$
	SmL_3	3.89	3.81	46.72	47.04	21.68	21.56	$1.67\cdot 10^{-2}$
	EuL_3	3.88	3.84	46.62	46.76	21.86	21.59	$1.93\cdot 10^{-2}$
	GdL_3	3.85	3.77	46.27	46.42	22.56	22.59	$2.58\cdot 10^{-2}$
II	$LaL_3\cdot 2H_2O$	4.31	4.17	45.13	45.25	19.35	19.35	$8.6\cdot 10^{-4}$
	CeL_3	3.95	3.73	47.43	47.53	20.51	20.19	$1.8\cdot 10^{-4}$
	PrL_3	3.94	3.76	47.37	47.89	20.60	20.69	$3.0\cdot 10^{-4}$
	NdL_3	3.92	3.73	47.14	47.38	20.98	21.09	$3.6\cdot 10^{-4}$
	SmL_3	3.89	3.70	46.72	46.93	21.68	21.90	$9.2\cdot 10^{-4}$
	EuL_3	3.88	3.67	46.62	46.62	21.86	22.02	$7.2\cdot 10^{-4}$
	GdL_3	3.85	3.65	46.27	46.13	22.45	22.21	$5.0\cdot 10^{-4}$

I – complexes with 2,3-dimethoxybenzoic acid; II – complexes with 3,5-dimethoxybenzoic acid

Table 2 Frequencies of the maxima of the absorption bands of COO^- for the 2,3- and 3,5-dimethoxybenzoates of light lanthanides and Na (cm^{-1})

Complex L=$C_9H_9O_4$	2,3-dimethoxybenzoates			Complex L=$C_9H_9O_4$	3,5-dimethoxybenzoates		
	$^*\nu_{asCOO^-}$	ν_{sCOO^-}	$\Delta\nu_{COO^-}$		ν_{asCOO^-}	ν_{sCOO^-}	$\Delta\nu_{COO^-}$
LaL_3	1546	1392	154	$LaL_3\cdot 2H_2O$	1530	1397	133
CeL_3	1546	1388	158	CeL_3	1522	1382	140
PrL_3	1545	1391	154	PrL_3	1521	1381	140
NdL_3	1546	1389	157	NdL_3	1522	1378	144
SmL_3	1547	1393	154	SmL_3	1525	1384	141
EuL_3	1547	1392	155	EuL_3	1525	1381	144
GdL_3	1549	1394	155	GdL_3	1527	1384	143
NaL	1602	1396	206	NaL	1577	1399	178

[*] The strongest intensity of the split band

The compositions of the complexes were also established by IR spectral analysis (Table 2). All the 2,3- and 3,5-dimethoxybenzoates of the light lanthanides 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 bands due to the

COOH group at 1686 $\mathrm{cm^{-1}}$ for the 2,3-dimethoxybenzoic acid and 1684 $\mathrm{cm^{-1}}$ for the 3,5-dimethoxybenzoic acid are replaced in the spectra of the complexes by two bands: asymmetric (1549–1546 $\mathrm{cm^{-1}}$ for 2,3- and 1530–1521 $\mathrm{cm^{-1}}$ for 3,5-dimethoxybenzoates) and symmetric vibrations of $\mathrm{COO^-}$ group (1394–1388 $\mathrm{cm^{-1}}$ for 2,3- and 1397–1378 $\mathrm{cm^{-1}}$ for 3,5-dimethoxybenzoates), respectively [9–15]. The magnitudes of the separation, $\Delta\nu_{\mathrm{OCO^-}}$ (where $\Delta\nu_{\mathrm{OCO^-}}=\nu_{\mathrm{asOCO^-}}-\nu_{\mathrm{sOCO^-}}$), which characterize the metal–oxygen bond, change from 158–154 $\mathrm{cm^{-1}}$ for the 2,3- to 144–133 $\mathrm{cm^{-1}}$ for the 3,5-dimethoxybenzoates. According to the spectroscopic criteria and with regard to Nakamoto [11, 15, 16], the carboxylate ion shows in the complexes the different modes of coordination. In the 3,5-dimethoxybenzoates it may function as a bidentate chelating ligand. From a detailed analysis of the bands of the asymmetric and symmetric vibrations of the $\mathrm{COO^-}$ group in the 2,3-dimethoxybenzoate of the light lanthanides it follows that the bands of the $\nu_{\mathrm{as}\,\mathrm{OCO^-}}$ vibrations are significantly split. It suggests, that the carboxylate group may coordinate as a tridentate chelating ligand and as well as a bidentate bridging one.

The X-ray diffraction patterns spectra of 2,3- and 3,5-dimethoxybenzoates of the light lanthanides were recorded and some of their interpretations were presented in our previous paper [17]. The analysis of the diffractograms suggests that the complexes are polycrystalline compounds with different structures [18, 19]. Their structures have not been examined as attempts to obtain single crystals have failed.

The thermal stability of complexes under study in air in the range 293–1173 K were examined by the TG, DTG and DTA techniques. The obtained results are presented in Figs 1, 2 and in Table 3. The dihydrate of lanthanum 3,5-dimethoxybenzoate decomposes in three steps: first the water molecules are removed with the formation of the anhydrous complex, which next decomposes to $\mathrm{La_2O_3}$ with the intermediate formation of the oxycarbonate $\mathrm{La_2O_2CO_3}$. The dehydration process is connected with the endo-effect observed in the DTA curve. Anhydrous complexes of lanthanum and neodymium 2,3- and 3,5-dimethoxybenzoates decompose to $\mathrm{La_2O_3}$ and $\mathrm{Nd_2O_3}$ with the intermediate formation of the oxycarbonates while 2,3- and 3,5-dimethoxybenzoates of cerium(III), praseodymium(III), samarium(III), europium(III) and gadolinium(III) decompose directly to oxides ($\mathrm{CeO_2}$, $\mathrm{Pr_6O_{11}}$, $\mathrm{Sm_2O_3}$, $\mathrm{Eu_2O_3}$ and $\mathrm{Gd_2O_3}$) (Table 3). Generally 3,5-dimethoxybenzoates of light lanthanides are more thermally stable in air than 2,3-dimethoxybenzoates.

The decomposition process with the gas product analysis was recorded for 2,3- and 3,5-dimethoxybenzoates of light lanthanides. For example the FTIR spectrum of gaseous products of decomposition process of gadolinium 2,3-dimethoxybenzoate is presented in Fig. 3. FTIR spectra of the gas phase products indicate that the decomposition of complexes is connected with the release of $\mathrm{CO_2}$, CO, $\mathrm{H_2O}$ ($\mathrm{H_2O}$ in the case of 3,5-dimethoxybenzoate of lanthanum) and hydrocarbons. The characteristic valence and deformation vibration bands of water molecules in FTIR spectra appear in the wavenumber ranges of 3900–3400 and 1580–1350 $\mathrm{cm^{-1}}$, respectively. The bands characteristic for $\mathrm{CO_2}$ molecule vibrations occur in the following ranges: 3800–3500, 2400–2200 and 700–670 $\mathrm{cm^{-1}}$. The bands of hydrocarbon vibrations are observed at: 3100–2700, 1700–1640 and 1500–1300 $\mathrm{cm^{-1}}$. The double peak of band characteristic for CO molecule vibrations appears in the range of 2220–2060 $\mathrm{cm^{-1}}$ [20–23].

Table 3 Temperature ranges of the thermal decomposition of the 2,3- and 3,5-dimethoxybenzoates of the light lanthanides in air

Complex L=$C_9H_9O_4$	ΔT_1/ K	Mass loss/%		n	ΔT_2/ K	Mass loss/%		Product of decomposition
		calcd.	found			calcd.	found	
3,5-Dimethoxybenzoates of light lanthanides								
$LaL_3{\cdot}2H_2O$	341–405	5.01	4.8	2	596–987	74.24	74.0	$La_2O_2CO_3$
CeL_3								
PrL_3								
NdL_3					616–976	72.32	72.7	$Nd_2O_2CO_3$
SmL_3								
EuL_3								
GdL_3								
2,3-Dimethoxybenzoates of light lanthanides								
LaL_3					673–1044	72.88	72.5	$La_2O_2CO_3$
CeL_3								
PrL_3								
NdL_3					673–1023	72.32	72.5	$Nd_2O_2CO_3$
SmL_3								
EuL_3								
GdL_3								

ΔT_1 – temperature range of the dehydration process; n – number of crystallization water molecules lost in one endothermic step; ΔT_2, ΔT_3 – temperature ranges of the decomposition of the anhydrous complex; T_{endo} – temperature of the maximum of the endo-effect; T_K – temperature of oxide formation

Table 3 Continued

Complex L=$C_9H_9O_4$	ΔT_3/ K	Mass loss/%		T_{endo} DTA/ K	T_K/ K	Fional product of decomposition
		calcd.	found			
3,5-Dimethoxybenzoates of light lanthanides						
$LaL_3 \cdot 2H_2O$	1004–1053	77.31	77.3	661	1100	La_2O_3
CeL_3	589–953	74.81	75.2	655	976	CeO_2
PrL_3	611–963	75.10	75.0	658	1006	Pr_6O_{11}
NdL_3	994–1033	75.51	75.4	660	1069	Nd_2O_3
SmL_3	616–973	74.85	74.6	660	996	Sm_2O_3
EuL_3	596–973	74.68	74.5	663	1021	Eu_2O_3
GdL_3	608–1003	74.11	74.4	675	1030	Gd_2O_3
2,3-Dimethoxybenzoates of light lanthanides						
LaL_3	1080–1118	76.11	76.0	630	1178	La_2O_3
CeL_3	518–1074	74.81	75.0	655	1148	CeO_2
PrL_3	520–1048	75.10	75.0	629	1123	Pr_6O_{11}
NdL_3	1044–1080	75.51	75.0	627	1148	Nd_2O_3
SmL_3	503–1073	74.85	74.8	627	1098	Sm_2O_3
EuL_3	513–1093	74.68	74.5	625	1123	Eu_2O_3
GdL_3	513–1073	74.11	74.0	637	1163	Gd_2O_3

ΔT_1 – temperature range of the dehydration process; n – number of crystallization water molecules lost in one endothermic step; ΔT_2, ΔT_3 – temperature ranges of the decomposition of the anhydrous complex; T_{endo} – temperature of the maximum of the endo-effect; T_K – temperature of oxide formation

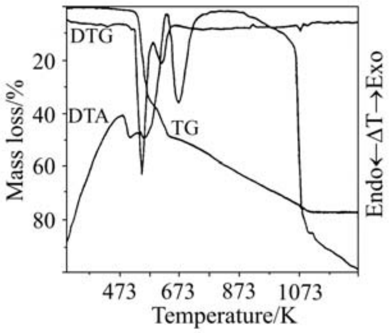

Fig. 1 TG, DTG and DTA curves of lanthanum 2,3-dimethoxybenzoate in air

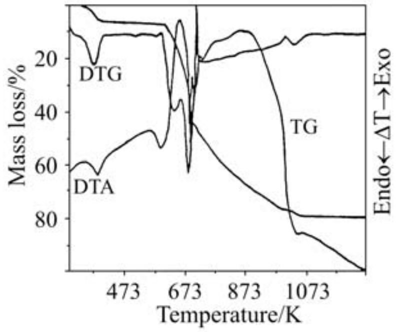

Fig. 2 TG, DTG and DTA curves of dihydrate of lanthanum 3,5-dimethoxybenzoate in air

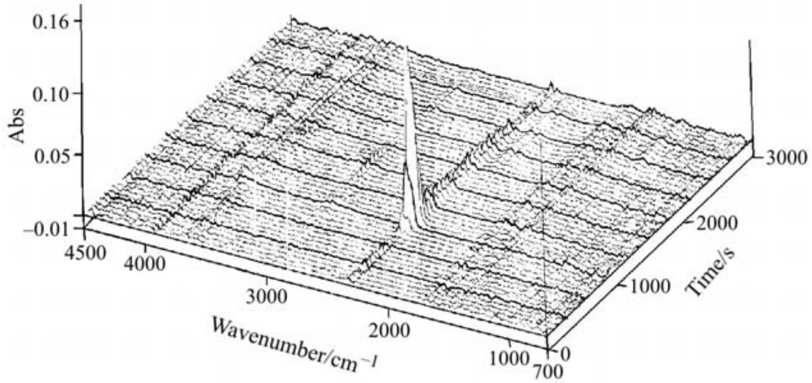

Fig. 3 FTIR spectrum of gaseous products of thermal decomposition of gadolinium 2,3-dimethoxybenzoate

The solubilities of the 2,3- and 3,5-dimethoxybenzoates of light lanthanide in water at room temperature were determined (Table 1). They are of the order of 10^{-3}–10^{-2} mol dm^{-3} for 2,3- and of 10^{-4} mol dm^{-3} for 3,5-dimethoxybenzoates. The 2,3-dimethoxybenzoates are better soluble than the 3,5-dimethoxybenzoates of the light lanthanide (Fig. 4).

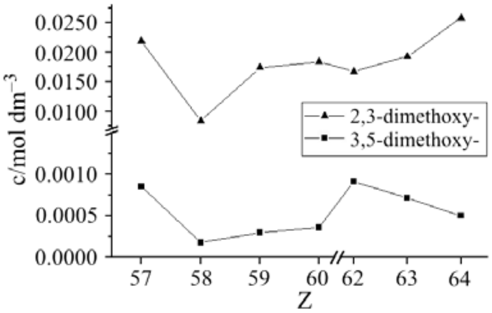

Fig. 4 Relationship between solubilities of 2,3- and 3,5-dimethoxybenzoates of light lanthanides and *Z*

Conclusions

Concluding, the various positions of methoxy-groups in the benzene ring do not influence the metal: ligand ratio, colours of complexes and the kinds of the gas products. Moreover results show that their position influence the temperature of the oxide formations, the mode of the carboxylate group coordination and their solubility in water (at 293 K). These differences are connected with the various influence of an inductive and mesomeric effects of the $-OCH_3$ substituent positions on the electron density in the benzene ring.

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This work is financially supported by the grant (N 4 T09A 157 22) from Committee of Scientific Researches in Poland.

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