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INVESTIGATION OF 5-CHLORO-2-METHOXYBENZOATES OF La(III), Gd(III) AND Lu(III) COMPLEXES

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Abstract

5-Chloro-2-methoxybenzoates of La(III), Gd(III) and Lu(III) were synthesized as penta-, mono- and tetrahydrates with a metal to ligand ratio of 1:3 and with white colour typical of La(III), Gd(III) and Lu(III) ions. The complexes were characterized by elemental analysis, IR and FIR spectra, thermogravimetric and diffractometric studies. The carboxylate group appears to be a symmetrical, bidentate, chelating ligand. The complexes are polycrystalline compounds. Their thermal stabilities were studied in air and inert atmospheres. When heated they dehydrate to form anhydrous salts which next in air are decomposed through oxychlorides to the oxides of the respective metals while in inert atmosphere to the mixture of oxides, oxychlorides of lanthanides and carbon. The most thermally stable in air, nitrogen and argon atmospheres is 5-chloro-2-methoxybenzoate of Gd(III).

Keywords: FIR, FTIR and IR spectra of La (III), Gd(III), Lu(III) complexes, thermal stability of compounds in air and in nitrogen atmospheres, X-ray powder diffraction of lanthanide complexes

Introduction

A literature survey indicates that the compounds of 5-chloro-2-methoxybenzoic acid with various cations are comparatively little known. There are papers that inform about the derivatives of chloro- and dichlorobenzoic acids and their salts [1–3] and also about 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and rare earth elements that have been obtained as solids [4–6]. We decided to synthesize once more the 5-chloro-2-methoxybenzoates of La(III), Gd(III), Lu(III) as solids and to examine their thermal stability in air and inert atmospheres during heating to 1273 (air) and to 1173 K (nitrogen), to compare their crystalline forms at 293 and 403 K, to

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study their IR spectra at above temperatures and to try to examine the influence of number of 4f electrons in central ions on these complex properties.

Experimental

5-Chloro-2-methoxybenzoates of La(III), Gd(III) and Lu(III) were prepared by the addition of equivalent quantities of 0.1 M ammonium 5-chloro-2-methoxybenzoate (pH~5) to a hot solution containing the nitrates of those elements 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 to a constant mass.

The contents of carbon and hydrogen in complexes were determined by elemental analysis using a CHN 2400 Perkin Elmer analyser and the content of chlorine by Schöniger method. The contents of Ln^{3+} metals were established by oxalic method (Table 1).

Table 1 Analytical data of La(III), Gd(III), Lu(III) of 5-chloro-2-methoxybenzoates

Complex	H/%		C/%		Cl/%		M/%	
	calc.	found	calc.	found	calc.	found	calc.	found
$LaL_3\cdot 5H_2O$	3.57	3.40	36.67	36.71	13.56	13.82	17.69	17.67
$GdL_3\cdot H_2O$	2.73	2.64	39.36	39.20	13.56	13.83	21.49	21.49
$LuL_3\cdot 4H_2O$	3.23	3.17	35.84	35.84	13.26	13.18	21.78	21.64

$L=C_8H_6O_3Cl$

IR, FIR and FTIR spectra of complexes were recorded over the ranges 4000–400, 650–100 and 5000–400 cm^{-1}, respectively, using M-80, Digilab FTS-14 and Equinix 55 spectrometers. Samples for IR spectra measurements were prepared as KBr discs. The analysis of the gas products was carried out by applying a TGA-IR detector (Brucker firm) and specially heated (470 K) line connecting the thermobalance and spectrometer. FIR spectra were obtained in Apiezon L mulls sandwiched between poly(ethylene) plates (Table 2, Figs 1–4).

Table 2 Frequencies of the absorption bands of COO^- for 5-chloro-2-methoxybenzoates of La(III), Gd(III), Lu(III) and sodium and that of CO for 5-chloro-2-methoxybenzoic acid (cm^{-1})

Complex	ν(C=O)	ν_{as}(OCO)	ν_s(OCO)	$\Delta\nu$(OCO)	ν(C–Cl)	ν(M–O)
$LaL_3\cdot 5H_2O$	–	1536	1424	112	700	416
$GdL_3\cdot H_2O$	–	1548	1428	120	720-684	412
$LuL_3\cdot 4H_2O$	–	1528	1424	104	712	424
NaL	–	1560	1404	156	670	–
HL	1728	–	–	–	695	–

$L=C_8H_6O_3Cl$

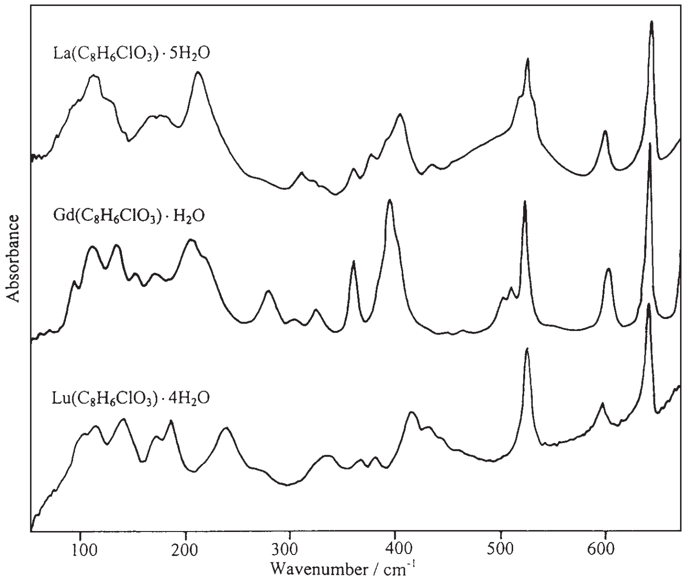

Fig. 1 Far-infrared spectra of 5-chloro-2-methoxybenzoates of La(III), Gd(III) and Lu(III)

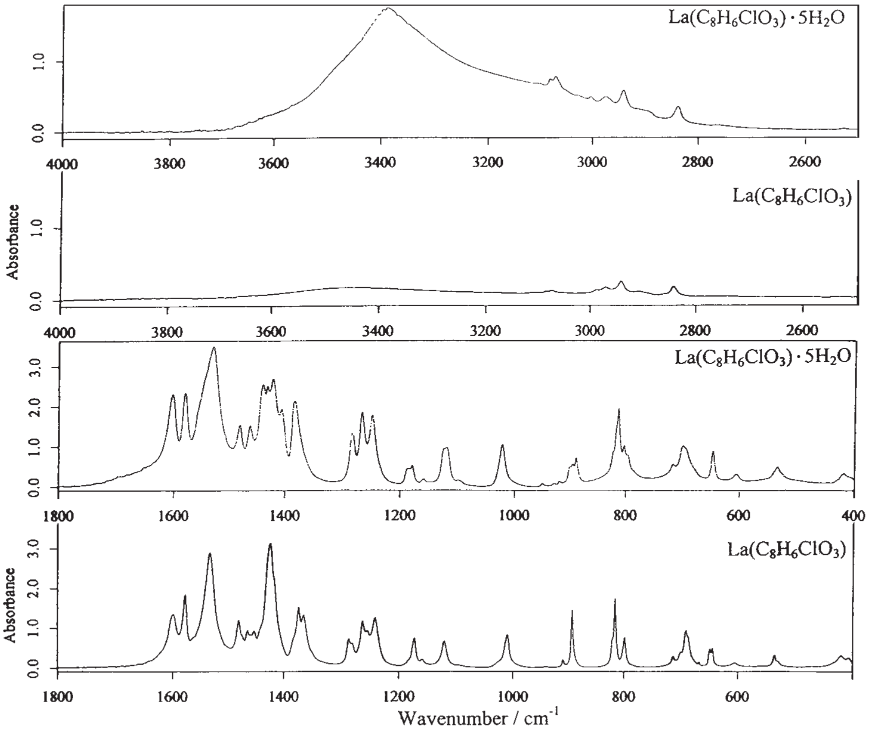

Fig. 2 Infrared spectra of 5-chloro-2-methoxybenzoates of La(III) at 293 and 413 K

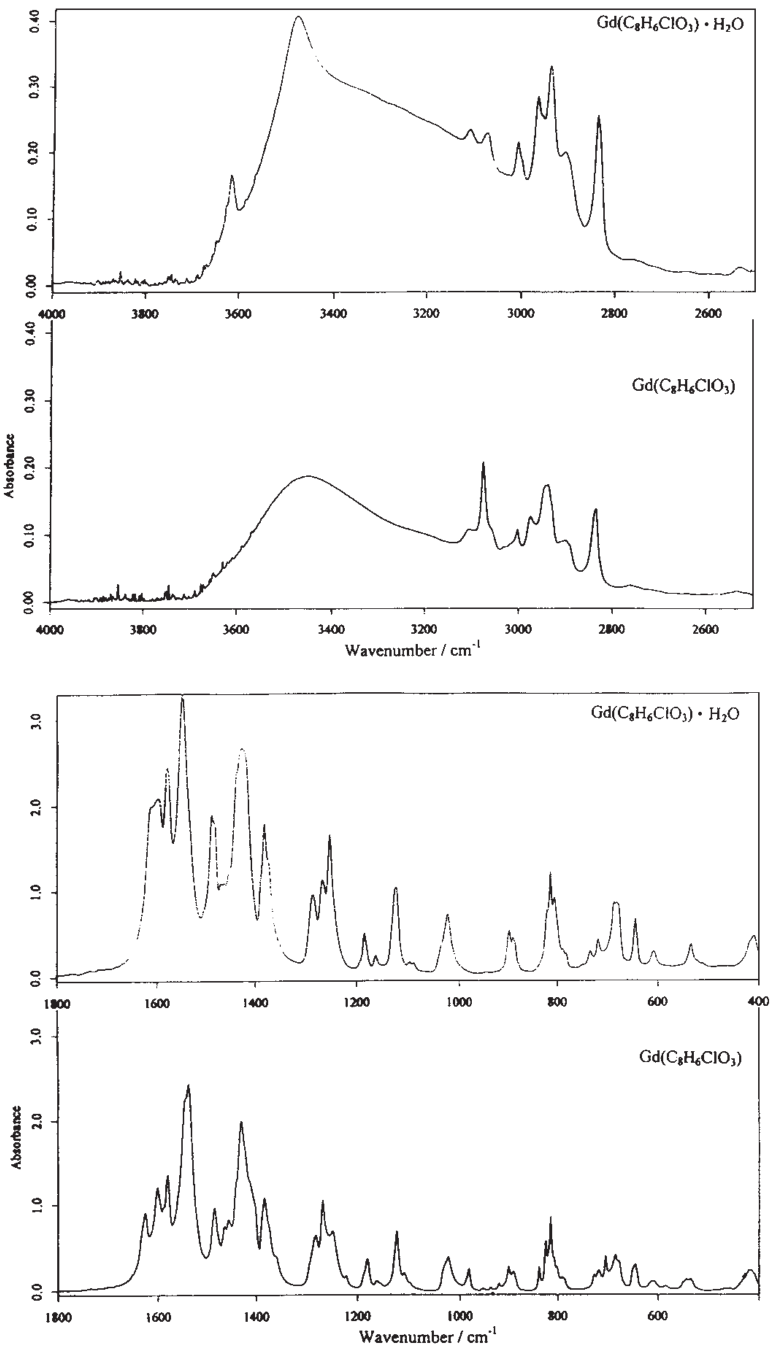

Fig. 3 Infrared spectra of 5-chloro-2-methoxybenzoates of Gd(III) at 293 and 413 K

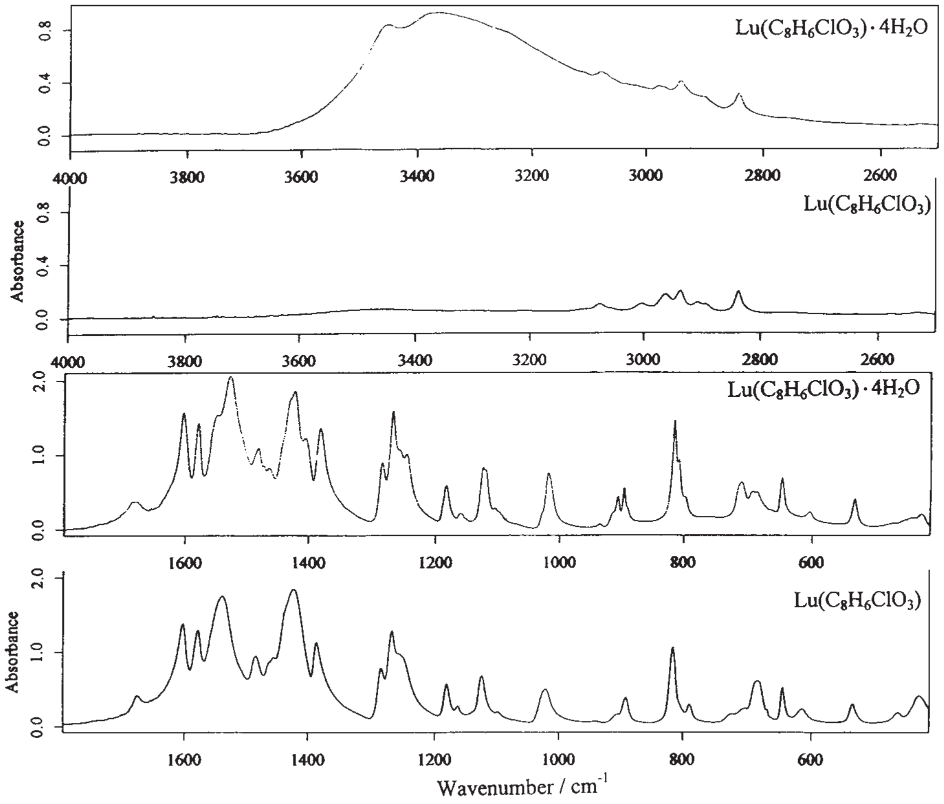

Fig. 4 Infrared spectra of 5-chloro-2-methoxybenzoates of Lu(III) at 293 and 413 K

The X-ray diffraction patterns of the hydrated and dehydrated complexes were taken on a HZG-4 (Carl Zeiss Jena) diffractometer using Ni filtered CuK_α radiation. The X-ray diffraction patterns of the complexes dried at 413 K were made on a PW 1050 Philips diffractometer using Ni filtered CuK_α radiation. The measurements were made within the range $2\Theta = 4–80°$, and $2\Theta = 5–70°$, respectively by means of the Debye–Scherrer–Hull method (Fig. 5).

The thermal stability and decomposition of the prepared complexes were determined by Paulik–Paulik–Erdey Q-1500D 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 samples were heated in platinum crucibles in static air to 1273 K with a sensitivity TG-100 mg, DTG and DTA sensitivities were regulated by a Derill computer programme. The products of decomposition were calculated from TG curves and verified by the diffraction pattern registration. The measurements in nitrogen were made on an OD-102 derivatograph at a heating rate of 10°C min^{-1}. The samples were heated 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 cm^3 min^{-1} (Table 3). The nature of the solid products of decomposition was established from the TG curves and confirmed by IR and X-ray spectra.

The thermogravimetric analysis of DSC/TG was performed at temperatures 303–1150 K using a differential thermoanalyser Netzsch STA 409C 3F. The experiments were carried out under nitrogen flow (99.995% purity) and temperature increase rates of 1–12 K min^{-1}. TG/FTIR coupling of thermobalance and spectrometer was performed using stainless steel gas cell adopted to the IR beam geometry. The spectrometer was installed in coupling unit of additional low noise MCT-IR (Table 4).

Results and discussion

The complexes of 5-chloro-2-methoxybenzoic acid with La(III), Gd(III) and Lu(III) were obtained as crystalline products with a metal to ligand ratio of 1:3 and a general formula $Ln(C_8H_6ClO_3)_3 \cdot nH_2O$ (where Ln=La, Gd, Lu and n=5 for La, n=1 for Gd and n=4 for Lu). Their white colour is typical of the appropriate trivalent ions [7, 8]. The compounds were characterized by elemental analysis (Table 1) FIR, IR and FTIR spectra (Table 2, Figs 1–4). The complexes show similar solid state IR spectra. However, the characteristic frequencies related to the carbonyl group are changed markedly in going from acid to salts. The band of the COOH group at 1728 cm^{-1}, present in the acid spectrum, disappears in the spectra of the complexes and two bands arising from asymmetric and symmetric vibrations of the COO^- group occur at 1528–1548 and 1424–1428 cm^{-1}, respectively. The bands with the maxima at 3384–3480 characteristic for ν(OH) vibrations [9, 10] and narrow bands of $\delta(H_2O)$ at 1600 cm^{-1} confirm the presence of crystallization water molecules in the complexes. The bands of C–H antisymmetric and symmetric stretching vibrations of CH_3 groups are observed at 2944–2950 and 2840 cm^{-1}, respectively [6, 11–21]. The bands of ν(C–C) ring vibrations appear at 1576–1580, 1480–1484, 1180–1184, 1024–1016 and 207–185 cm^{-1}. The valency ν(C–Cl) vibration bands occur at 712–684 and the bands at 424–416 cm^{-1} confirm the metal–oxygen bond [6, 11–13, 20]. Their regular shifts are not observed in the spectra. Accordingly, it is possible to suggest that 5-chloro-2-methoxybenzoic acid forms with the lanthanides complexes having similar stabilities. The bands in the range 120–121 cm^{-1} are connected with the O–H···O vibrations and they are stronger for monohydrate of 5-chloro-2-methoxybenzoate of Gd(III) than those for the rest of the other two. The bands at 226–246 cm^{-1} confirming the aromatic ring vibrations are shifted to lower frequencies from La(III) to Gd(III) and again to higher ones to Lu(III) with the decrease of ionic radii of elements (it can be the influence of the number of 4f electrons). The bands at 533–512 cm^{-1} result probably from the rotational oscillations of the water molecules and they change their shapes in the spectra of complexes depending upon the numbers of water molecules and the modes of their vibrations (wagging, rocking or twisting) [12].

The maxima of frequencies of absorption bands of asymmetric and symmetric vibrations of the COO^- for 5-chloro-2-methoxybenzoates of La(III), Gd(III), Lu(III) and sodium are presented in Table 2. The magnitudes of separation, $\Delta\nu$, between the

Table 3 Temperature range of thermal stability of La(III), Gd(III) and Lu(III) 5-chloro-2-methoxybenzoates in air and nitrogen atmospheres

Complex	ΔT_1/K	Mass loss/%		n	Air	ΔT_2/K	Mass loss/%		T_k/K	Ln_2O_3/%		Residue/ %
		calc.	found.		N_2		calc.	found.		calc.	found.	
$LaL_3 \cdot 5H_2O$	348–388	11.46	11.43	5	A	523–797	79.26	79.21	1435	20.74	20.79	
	333–383		11.50		N	513–733						43.21
$GdL_3 \cdot H_2O$	398–413	2.46	2.64	1	A	513–777	75.24	74.80	1316	24.77	25.20	
	393–413		2.50		N	513–733						19.80
$LuL_3 \cdot 4H_2O$	348–378	8.96	8.91	4	A	533–893	75.24	75.21	1033	24.76	24.79	
	343–373		8.78		N	523–723						25.00

L=$C_8H_6O_3Cl$; ΔT_1=temperature range of dehydration process; n=number of crystallization water molecules being lost in one endothermic step; ΔT_2=temperature range of anhydrous complex decomposition; T_k= temperature of the oxide formation

Table 4 The results of thermogravimetric analysis of 5-chloro-2-methoxybenzoates of La(III), Gd(III) and Lu(III) in the DSC/TG system

Complex	The first peak				The second peak				
	T_{ini}/K	T_{max}/K	T_{fin}/K	Mass loss/%	ΔH/kJ mol^{-1}	T_{ini}/K	T_{max}/K	T_{fin}/K	Mass loss/%
$LaL_3 \cdot 5H_2O$	317.9	335.8	339.9	11.56	263.5	520.3	529.3	539.2	28.97
$GdL_3 \cdot H_2O$	378.7	384.1	389.6	2.47	52.9	515.1	526.2	535.6	27.35
$LuL_3 \cdot 4H_2O$	303.5	332.3	338.6	8.85	250.1	528.9	539.6	551.7	32.78

L=$C_8H_6O_3Cl$

frequencies ν_{as}(COO) and ν_s(OCO) in the complexes are lower ($\Delta\nu$=104–120 cm^{-1}) than in the sodium salt ($\Delta\nu$=156 cm^{-1}) which indicates a smaller degree of ionic bond in the lanthanide 5-chloro-2-methoxybenzoates. The shifts of the frequencies ν_{as}(OCO) and ν_s(OCO) in the complexes are lower and higher, respectively, than those for sodium 5-chloro-2-methoxybenzoate. Accordingly, the carboxylate ion appears to be a symmetrical, bidentate chelating ligand [12, 22, 23].

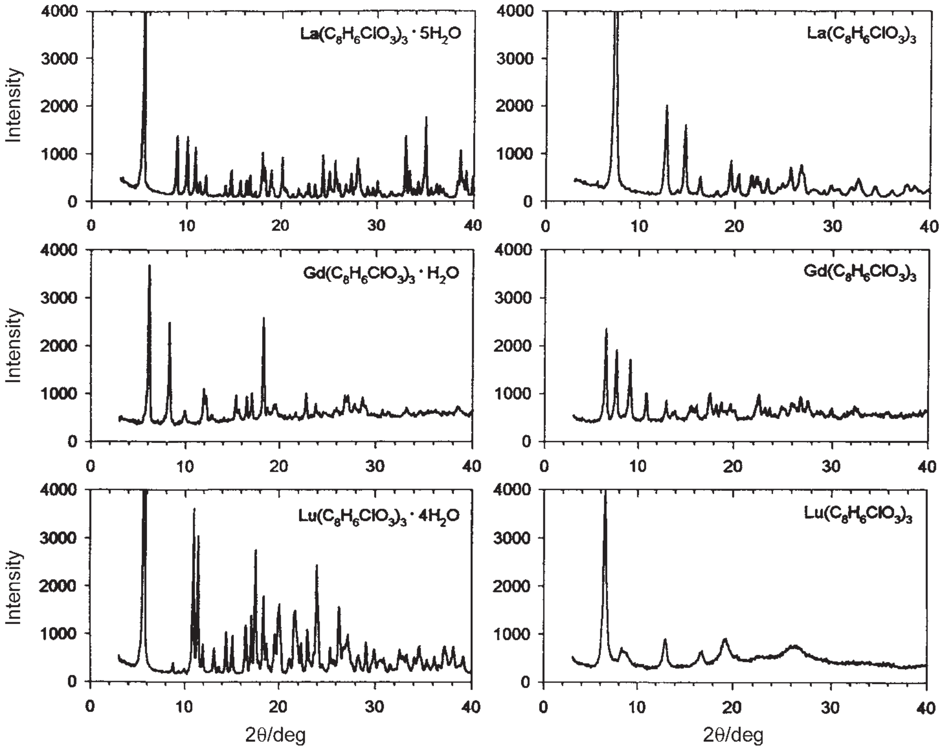

Fig. 5 Diffractograms of 5-chloro-2-methoxybenzoates of La(III), Gd(III), and Lu(III) at 293 and 403 K

The spectra of anhydrous complexes were also recorded (Figs 2–4). They are characterized by many absorption bands with comparatively great intensity but without the changes in their numbers and position compared to those in the spectra of the hydrated ones. In the spectra of anhydrous compounds the disappearance (complexes of La(III), Lu(III)) of the band at 3500–3400 cm^{-1}, and the decrease of its intensity (complex of Gd(III)) is observed. It is indicative of the dehydration process that took place in the hydrated 5-chloro-2-methoxybenzoates of La(III), Gd(III) and Lu(III). These results were also confirmed by the derivatogravimetric and powder diffraction measurements. Comparing the IR spectra of the hydrated and anhydrous complexes it follows that there is a clear influence of the dehydration process on the aromatic system. The intensity of the aromatic bands in the spectra of hydrated complexes is comparatively greater than that of the bands of the aromatic ring vibrations in the spectra of anhydrous compounds. The addition of the water molecule to the central ion causing the weakening of metal ligand interactions with simultaneous increase of coordination number leads to the decrease of electronic cloud deformation of the ring and to the appearance of aromatic ring bands or to the increase of their intensity. In order to determine the crystalline forms of 5-chloro-2-methoxybenzoates of La(III), Gd(III) and Lu(III) their X-ray powder diffractograms were recorded (Fig. 5) within the range $2\Theta=5–40°$. Their comparison shows that complexes are not isostructural but polycrystalline compounds of low symmetry (monoclinic or rhombic systems) and large dimensions of the lattice cells. Their various crystalline forms may be connected with the different number of crystallization water molecules. The powder diffractograms of anhydrous 5-chloro-2-methoxybenzoates of La(III), Gd(III) and Lu(III) dried at 413 K were also recorded. Their comparison with X-ray spectra of hydrated complexes indicates that the removal of crystallization water molecules from hydrated compounds leads to the change of their crystalline and structural forms (Fig. 5).

The arrangement of the interference reflections confirms the low symmetry of crystallographic system in the anhydrous complexes; only anhydrous 5-chloro-2-methoxybenzoate of Lu(III) shows the higher degree of crystallinity compared to those of La(III) and Gd(III). Taking into account the differences in the crystallographic structure of La(III), Gd(III) and Lu(III) complexes it is possible to suppose that the space arrangement of ligands in each complex is not the same irrespectively of the identical M:ligand ratio. The comparison of the powder diffractograms of hydrated and anhydrous 5-chloro-2-methoxybenzoates of La(III), Gd(III) and Lu(III) lets notice that the removal of crystallization water molecules from the hydrated complexes causes the changes in the interference reflection positions from the small angle values to the higher ones [25, 26].

In order to verify the compositions of the complexes, to determine the temperature ranges of their thermal stabilities and decompositions during heating in air, to estimate the intermediate and final products of their decompositions and to evaluate the types of processes that occur during heating, the thermal stability of 5-chloro-2-methoxybenzoates of La(III), Gd(III) and Lu(III) was studied in air and in nitrogen atmospheres. The obtained results are summarized in Table 3. From TG, DTG, DTA and T curves it was found that complexes are hydrates with the ratio of metal:ligand 1:3. 5-Chloro-2-methoxybenzoate of La(III) is pentahydrate, that of Gd(III) monohydrate and that of Lu(III) is tetrahydrate.The complexes are stable up to 348–398 K. Next they dehydrate in one step losing from 1 to 5 molecules of crystallization water and form anhydrous compounds. The losses of mass calculated from TG curves correspond to the losses of 5, 1 and 4 molecules of water. Monohydrate of 5-chloro-2-methoxybenzoate of Gd(III) is the most thermally stable complex since its initial temperature of dehydration, T_1, is equal to 398 K while 5-chloro-2-methoxybenzoates of La(III) and Lu(III) have less thermal stability (T_1=348 K) in comparison with that of Gd(III). The dehydration process is accompanied by endothermic effect in the DTA curves. The values of enthalpy, ΔH, of the dehydration process for complexes of

La(III), Gd(III) and Lu(III) were determined. They are equal to 263.5, 52.9 and 250.1 kJ mol^{-1}, respectively, and they correspond to the energy of the bonding of proper numbers of water molecules. The anhydrous compounds are stable up to 513–533 K. In the temperature range 513–893 K they gradually, one by one, release the parts of ligands and form oxychlorides, LnOCl. The decomposition of organic ligand is connected with strong exothermic effect in DTA curve. In the range 777–1453 K the oxychlorides of lanthanides are decomposed to oxides of respective metals. The theoretical values of mass losses are equal to 75.24–79.26 and those calculated from TG curves 74.80–79.21%. The most thermally stable is the anhydrous complex of Lu(III), the initial temperature of decomposition of which is equal to 533 K whereas the least thermally stable is that of Gd(III) (T_2=513 K). The temperatures of oxide formations change their values from 1435 (La_2O_3) to 1033 K (Lu_2O_3).

In the nitrogen atmosphere, similarly as in the air, the complexes of La(III), Gd(III) and Lu(III) were found to be penta-, mono- and tetrahydrates. They are stable up to 333–393 K and next they dehydrate in one step losing all molecules of crystallization water and form the anhydrous compounds. The most thermally stable in nitrogen atmosphere is monohydrate of 5-chloro-2-methoxybenzoate of Gd(III) since its initial temperature of dehydration (T_1) is equal to 393 K, while the least thermally stable is pentahydrate of La(III). The anhydrous complexes are stable up to 513–523 and next in the range 513–733 K they decompose to the mixture of carbon, oxychlorides and oxides of respective metals. The values of the initial dehydration temperature of the hydrated complexes in air are generally higher (T_1=348–398 K) than in the nitrogen atmosphere (T_1=333–393 K) which testifies their greater stability in air than in nitrogen. The anhydrous 5-chloro-2-methoxybenzoates of La(III) and Lu(III) are more thermally stable in air than in nitrogen. The anhydrous complex of Gd(III) has the same thermal stability both in air and nitrogen atmospheres (T_2=513 K). The final products of decomposition of 5-chloro-2-methoxybenzoates of La(III), Gd(III) and Lu(III) in air are the oxides of respective metals Ln_2O_3 (*Ln*=La, Gd, Lu) but in the nitrogen it is the mixture of carbon, oxides and oxychlorides of the appropriate metals. The final products of decomposition were identified roentgenographically. Taking into account the number of crystallization water molecules in the complexes and the electron configuration of central ions it may be possible to notice the relationship between the electron configuration of central ion and the number of crystallization water molecules. The electron configurations of central ions are following: La^{3+}–$4f^05s^25p^6$, Gd^{3+}–$4f^75s^25p^6$, Lu^{3+}–$4f^{14}5s^25p^6$.

The various number of electrons in the 4f subshell in central ions or their lack may in different manner influence the number of water molecules and the strength of their bonding in the complexes. The lack of electrons in the subshell of 4f (in the case of La^{3+}) or the presence of 7 or 14 electrons in it (in the cases of Gd^{3+} and Lu^{3+}) enable the addition of 5, 4 and 1 molecules of crystallization water in 5-chloro-2-methoxybenzoates of La(III), Lu(III) (in the ions of La^{3+} and Lu^{3+} the 4f subshell is unreactive) and Gd(III), respectively. The thermal stability of 5-chloro-2-methoxybenzoates of rare earth elements were also studied in the DSC/TG system (Table 4). The obtained results confirmed their compositions as hydrates with the formula established previously on the basis of the results obtained from thermal stability investigations in air and nitrogen atmospheres. The thermogravimetric analysis in the DSC/TG system for the complexes was carried out in argon, as well, in 303–1150 K. 5-Chloro-2-methoxybenzoates of La(III), Gd(III) and Lu(III) are stable up to 303.5–389.6 K. The mass losses correspond to the expelling of 5, 1, 4 molecules of crystallization water.

The X-ray powder diffractograms and IR spectra discussed previously confirm the dehydration process of the compounds. From the comparison of the obtained results it follows that in air, nitrogen and argon atmospheres the most thermally stable complex is the monohydrate of Gd(III) (T_1=378.7 K). During further heating the anhydrous complexes decompose to the oxides Ln_2O_3 or to the mixture of oxides, oxychlorides of lanthanides and carbon (in inert atmosphere). The thermal stability investigations of lanthanum, gadolinium and lutetium 5-chloro-2-methoxybenzoates reveal that in air their decomposition process proceeds in the following way:

$$\mathrm{LnL_3{\cdot}}n\mathrm{H_2O} \rightarrow \mathrm{LnL_3} \rightarrow \mathrm{LnOCl} \rightarrow \mathrm{Ln_2O_3}$$

where Ln=La, Gd, Lu; L=$C_8H_6ClO_3$; n=1 for Gd, 5 for La, 4 for Lu.

Conclusions

On the basis of the obtained results it appears that 5-chloro-2-methoxybenzoate of La(III), Gd(III) and Lu(III) were synthesized as hydrated complexes. The carboxylate group appears to be a symmetrical, bidentate, chelating ligand. The complexes are crystalline compounds that on heating in air and inert atmospheres decompose in three steps. In the first step they dehydrate to form anhydrous complexes that next in air decompose to the oxides of the appropriate metals with the intermediate formation of LnOCl or in nitrogen to metal oxides, their oxychlorides and carbon. The complexes are more stable in air than in nitrogen atmosphere.

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