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Synthesis, characterization and thermal behaviour of solid-state compounds of europium(III) and gadolinium(III) 3-methoxybenzoate

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Abstract Solid-state Ln–$C_8H_7O_3$ compounds, where Ln stands for Eu(III) and Gd(III) and $C_8H_7O_3$ is 3-methoxybenzoate, have been synthesized. Simultaneous thermogravimetry and differential thermal analysis (TG-DTA), differential scanning calorimetry (DSC), X-ray powder diffractometry, infrared spectroscopy, elemental analysis and complexometry were used to characterize and to study the thermal behaviour of these compounds. The results led to information about the composition, dehydration, thermal stability and decomposition of the isolated compounds.

Keywords Eu(III) · Gd(III) · 3-Methoxybenzoate · Thermal behaviour

Introduction

Benzoic acid and some of its derivatives are used as preservative, catalyst precursors, in pharmaceutical industries, beyond other applications. A survey of the literature shows that the complexes of rare earth elements with benzoic acid and some of its derivatives have been investigated in solid state. These works reported the thermal and spectral behaviour on solid compounds of benzoates and its derivatives with rare earth elements [1–8], the vibrational and electronic spectroscopic study of lanthanides and effect of sodium on the aromatic system of benzoic acid [9, 10].

In this work the 3-methoxybenzoates of europium(III) and gadolinium(III) were synthesized and characterized by X-ray powder diffractometry, infrared spectroscopy, simultaneous TG-DTA, DSC, elemental analysis and complexometry.

Experimental

The 3-methoxybenzoic acid ($C_8H_8O_3$) with 99% purity was obtained from Aldrich. Aqueous solution of Na–$C_8H_7O_3$ 0.1 mol L^{-1} was prepared from aqueous ($C_8H_8O_3$) suspension by adding sodium hydroxide solution 2.5 mol L^{-1} up to near total neutralization, followed by NaOH solution 0.1 mol L^{-1} up to pH 8.7.

Europium(III) and gadolinium(III) chlorides were prepared from the corresponding metal oxides by treatment with concentrated hydrochloric acid. The resulting solutions were evaporated to near dryness, the residues were again dissolved in distilled water, transferred to a volumetric flask and diluted in order to obtain ca. 0.1 mol L^{-1} solutions, whose pH were adjusted to 5.5 by adding diluted sodium hydroxide or hydrochloric acid solutions.

The solid state compounds were prepared by adding slowly, with continuous stirring, the aqueous solution of the ligand (Na–$C_8H_7O_3$) to the respective metal chloride until total precipitation of the metal ions. The precipitates were washed with distilled water until elimination of chloride ions, filtered through and dried on Whatman no. 42 filter paper and kept in a desiccator over anhydrous calcium chloride.

In the solid state compounds hydration water, ligand and metal ion content were determined from TG curves. The metal ions were also determined by complexometric titrations with standard EDTA solution using xylenol orange as indicator [11].

X-ray powder patterns were obtained by using a SIEMENS D-5000 X-ray diffractometer employing Cu K_α radiation ($\lambda = 1.541$ Å) and setting of 40 kV and 20 mA.

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Infrared spectra for Na–$C_8H_7O_3$ as well as for its metal ion compounds were run on a Nicolet model Impact 400 FT-IR Instrument, within the 4000–400 cm^{-1} range. The solid samples were pressed into KBr pellets.

Simultaneous TG-DTA curves and DSC curves were obtained with two thermal analysis systems, models 2960 and Q10 both from TA Instruments, respectively. The purge gas was an air flow of 100 mL min^{-1} (TG-DTA) and 50 mL min^{-1} (DSC). A heating rate of 20 K min^{-1} and with samples weighing about 7 mg (TG-DTA) and about 5 mg (DSC). Alumina and aluminium crucibles, the latter with perforated cover were used for TG-DTA and DSC, respectively.

Carbon and hydrogen contents were determined by microanalytical procedures, with an EA 1110 CHNS-O Elemental Analyser from CE Instruments.

Results and discussion

The analytical and thermoanalytical (TG) results are shown in 1. These results establish the stoichiometry of these compounds, which are in agreement with the general formula, Ln $(C_8H_7O_3)_3 \cdot nH_2O$, where Ln represents europium(III) or gadolinium(III), $C_8H_7O_3$ is 3-methoxybenzoate and $n = 2$ (Gd).

The X-ray diffraction powder patterns (1) show that the europium(III) and gadolinium(III) compounds have a crystalline structure, without evidence for formation of isomorphous compounds.

Infrared spectroscopic data on sodium-3-methoxybenzoate (Na–$C_8H_7O_3$) and its compounds with europium(III) and gadolinium(III) are shown in 2. The investigation was focused mainly within the 1700–1400 cm^{-1} range because the region is potentially most informative in attempting to assign coordination sites. In the Na–$C_8H_7O_3$, strong bands located at 1568 and 1400 cm^{-1} are attributed to anti-symmetrical (ν_{as}) and symmetrical (ν_{sym}) frequencies of the carboxylate groups, respectively [12, 13]. In the Eu(III) and Gd(III) compounds, analysis of the frequencies of the ν_{as} and ν_{sym} (COO^-) bands, where $\nu_{as} - \nu_{sym} = 129$, shows that the lanthanides are linked to the carboxylate group by a bidentate bond with an incomplete equalization of bond lengths in the carboxylate anion [6–9].

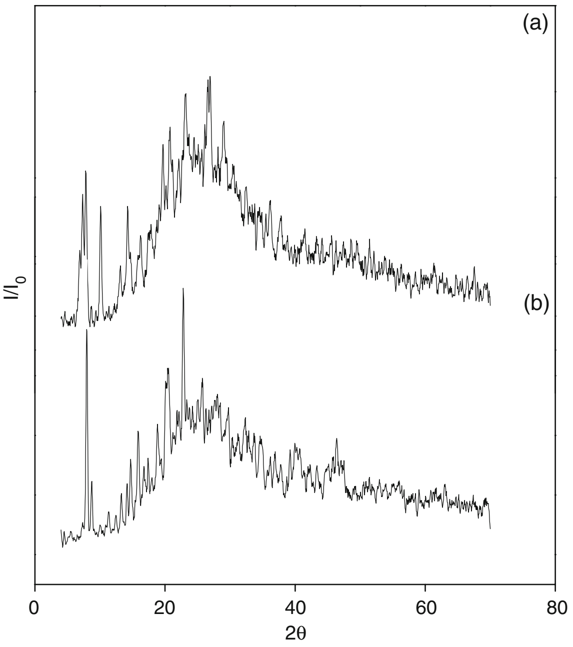

Fig. 1 X-ray powder diffraction patterns of: (*a*) $Eu(C_8H_7O_3)_3$, (*b*) $Gd(C_8H_7O_3)_3 \cdot 2H_2O$. $C_8H_7O_3$ = 3-methoxybenzoate

Table 2 Spectroscopic data for sodium 3-methoxybenzoate and compounds with lighter trivalent lanthanides

Compound	$\nu_{(O–H)}$ H_2O (cm^{-1})	$\nu_{as(COO^-)}$ (cm^{-1})	$\nu_{sym(COO^-)}$ (cm^{-1})	$\Delta\nu(\nu_{as} - \nu_{sym})$ (cm^{-1})
$Na(C_8H_7O_3)$	–	1568_s	1402_s	166
$Eu(C_8H_7O_3)_3$	3439_{br}	1529_s	1400_s	129
$Gd(C_8H_7O_3)_3 \cdot 2H_2O$	3501_{br}	1537_s	1408_s	129

br Broad, *s* strong, $C_8H_7O_3$ 3-methoxybenzoate, $\nu_{(O–H)}$ hydroxyl group stretching frequency, $\nu_{sym(COO^-)}$ and $\nu_{as(COO^-)}$ symmetrical and anti-symmetrical vibrations of the COO^- group, respectively

The TG-DTA curves of the europium(III) and gadolinium(III) complex are shown in 2. The first mass loss up to 363 K(Eu) and 373 K(Gd), corresponding to the endothermic peak at 353 K(Eu) and 362 K(Gd) is due to the release of 0.25 hygroscopic water molecule and two hydration water molecules, respectively.

Table 1 Analytical data for $Ln(L)_3 \cdot nH_2O$

Compound	Water (%)		Ligand lost (%)		Metal oxide (%)			Carbon (%)		Hydrogen (%)		Residue
	Calcd.	TG	Calcd.	TG	Calcd.	TG	EDTA	Calcd.	E.A.	Calcd.	E.A.	
$Eu(L)_3$	–	–	70.93	71.25	29.07	28.75	29.57	47.61	47.85	3.50	3.52	Eu_2O_3
$Gd(L)_3 \cdot 2H_2O$	5.57	5.64	66.40	66.51	28.03	27.85	28.41	44.57	44.68	3.90	3.79	Gd_2O_3

Ln Europium(III) or gadolinium(III), *L* 3-methoxybenzoate

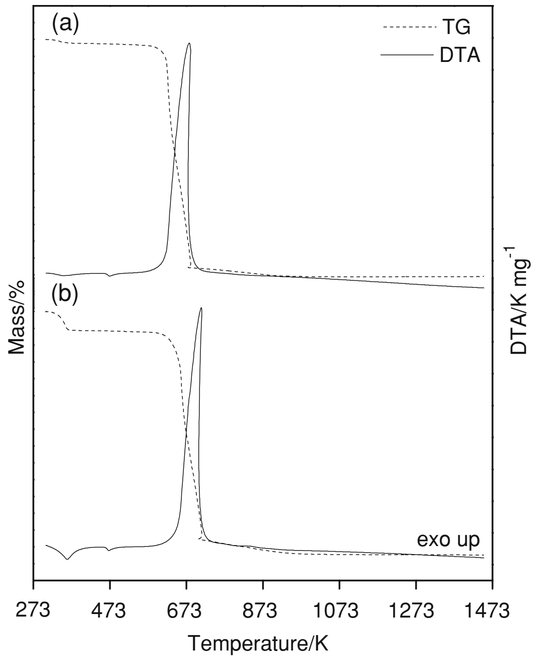

Fig. 2 TG-DTA curves of: (*a*) $Eu(C_8H_7O_3)_3$, (*b*) $Gd(C_8H_7O_3)_3 \cdot 2H_2O$. $C_8H_7O_3$ = 3-methoxybenzoate

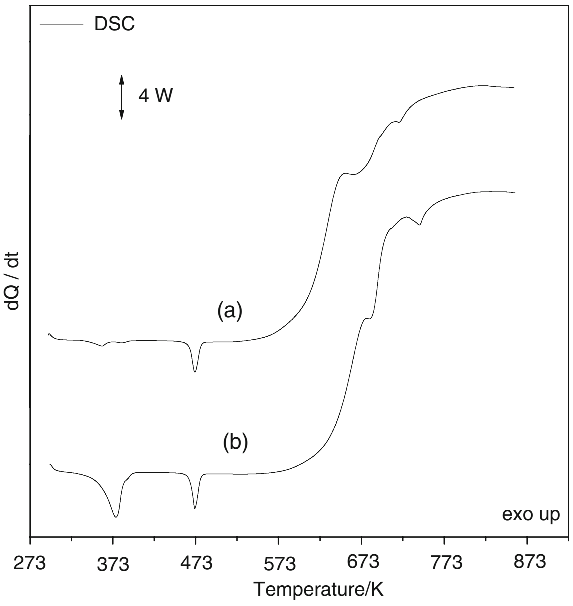

Fig. 3 DSC curves of: (*a*) $Eu(C_8H_7O_3)_3$, (*b*) $Gd(C_8H_7O_3)_3 \cdot 2H_2O$. $C_8H_7O_3$ = 3-methoxybenzoate

After their dehydration the anhydrous compounds are stable up to 583 K and the endothermic peak at 471 K(Eu) and 470 K(Gd) are attributed to the reversible crystalline phase transition confirmed by X-ray powder diffraction and DSC analysis.

The thermal decomposition of the anhydrous compounds occurs in two steps. The first mass loss that occurs through a fast process with loss of 68.72% up to 693 K(Eu) and 62.18% up to 723 K(Gd), corresponding to exothermic peaks at 683 and 703 K, respectively, is attributed to the oxidation of the organic matter. The TG-DTA profiles also show that the oxidation of the organic matter is accompanied by combustion, with formation of a mixture of Ln_2O_3 and $Ln_2O_2CO_3$ (Ln = Eu, Gd) in no simple stoichiometric composition. The formation of dioxycarbonate as intermediate was based on the mass losses observed in the TG curves and tests with hydrochloric acid solution on samples heated up to the formation temperature of the intermediate as indicated by the TG curves, confirming the elimination of CO_2. The last mass loss step is attributed to the thermal decomposition of the dioxycarbonate to the respective oxides, Eu_2O_3 and Gd_2O_3. The formation of lanthanides oxides was confirmed by X-ray diffraction. No peak was observed in the DTA curves under the applied experimental settings, which is probably due to the small heat effect of this step.

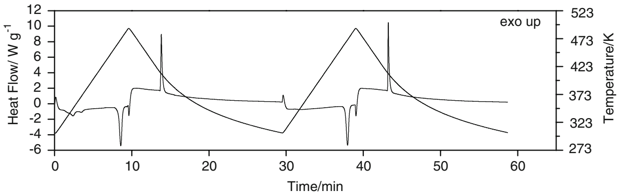

Fig. 4 DSC curves of heating and cooling of the compound $Eu(C_8H_7O_3)_3$. $C_8H_7O_3$ = 3-methoxybenzoate

The DSC curves of the compounds are shown in 3. These curves show endothermic and exothermic events that are in agreement with the mass losses observed in the TG curves and endothermic peaks due to the reversible crystalline phase transition (4). The endothermic peak at 360 K(Eu) and 377 K(Gd) is due to dehydration. The dehydration enthalpy found for the gadolinium(III) compound was: 49.8 kJ mol^{-1}, respectively.

The broad exothermic event observed above 573 K(Eu) and 623 K(Gd), without appearance of definitive peaks are ascribed to the thermal decomposition of the anhydrous compounds where the oxidation of the organic matter takes place in overlapping steps.

The endothermic peak at 472 K (Eu, Gd) are due to crystalline phase transition and the enthalpies found were: 27.9 and 28.0 kJ mol^{-1}, respectively.

Conclusions

From analytical and thermoanalytical (TG) results a general formula could be established for these compounds in the solid state.

The X-ray powder patterns showed that the europium and gadolinium compounds exist in crystalline state, without evidence for formation of isomorphous compounds.

The infrared spectroscopic data suggest that the $C_8H_7O_3$ acts as a bidentate ligand towards the europium and gadolinium ions.

The TG-DTA and DSC curves provided information about the thermal stability and thermal behaviour of these compounds.

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