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SOLID-STATE 2-METHOXYBENZOATES OF LIGHT TRIVALENT LANTHANIDES
Synthesis, characterization and thermal behaviour

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Solid-state LnL_3 compounds, where *L* is 2-methoxybenzoate and *Ln* is light trivalent lanthanides, have been synthesized. Thermogravimetry (TG), differential scanning calorimetry (DSC), X-ray powder diffractometry, infrared spectroscopy and elementary analysis were used to characterize and to study the thermal behaviour of these compounds. The results led to information on the composition, dehydration, thermal stability and thermal decomposition of the isolated compounds. On heating these complexes decompose in three (Ce, Pr) or five (La, Nd, Sm) steps with the formation of the respective oxide: CeO_2, Pr_6O_{11} and Ln_2O_3 (*Ln*=La, Nd, Sm) as final residues. The theoretical and experimental spectroscopic study suggests predominantly the ionic bond between the ligand and metallic center.

Keywords: *light trivalent lanthanides, 2-methoxybenzoate, thermal decomposition, thermal stability*

Introduction

Benzoic acid and some of their derivatives have been used as conservant, catalyst precursor polymers in pharmaceutical industries, beyond other applications. A survey of literature shows that the complexes of rare earth and d-block elements with benzoic acid and some of its derivatives have been investigated in aqueous solutions and in the solid-state.

In aqueous solutions, the papers reported the magnetic, physical and chemical properties, thermodynamics of complexation, the spectroscopic study and the influence of pH surfactant and synergic agent on the luminescent properties of terbium chelates with benzoic acid derivatives [1–3].

In the solid-state the papers reported the preparation, thermal behaviour, thermal decomposition, vibrational and electronic spectroscopy, spectral and magnetic studies of several metal-ion complexes of phenyl substituted derivatives of benzoates [4–17].

In an endeavour to extend the literature works, the present paper deals with the synthesis of La(III), Ce(III), Pr(III), Nd(III) and Sm(III) 2-methoxybenzoates, studied by means of infrared spectroscopy, X-ray powder diffractometry, thermogravimetry (TG), differential scanning calorimetry (DSC) and other analytical methods. The results permitted to obtain information concerning the thermal stability, thermal decomposition and information on the bond between the ligand and metallic center.

Experimental

Materials and methods

The 2-methoxybenzoic acid (HL) 99% was obtained from Aldrich and purified by recrystallization. Aqueous solution of NaL 0.1 mol L^{-1} was prepared from aqueous HL suspension by treatment with sodium hydroxide solution 0.1 mol L^{-1}.

Lanthanide chlorides were prepared from the corresponding metal oxides (except for cerium) by treatment with concentrated hydrochloric acid. The resulting solutions were evaporated to obtain an almost dry substance. 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 by adding diluted sodium hydroxide solution. Cerium(III) was used as its nitrate and ca. 0.1 mol L^{-1} aqueous solutions of this ion were prepared by direct weighing of the salt.

The solid-state compounds were prepared by adding slowly with continuous stirring the solution of the ligand to the respective metal chloride or nitrate solutions. No precipitate was observed during the addition of sodium benzoate; however the precipitate was obtained when the solution was evaporated in a water bath. The precipitates were washed with distilled water until elimination of the chloride (or nitrate) ions, filtered through and dried on Whatman n° 42 filter paper, and kept in a desiccator over anhydrous calcium chloride.

In the solid-state compounds metal ions, hydration water and 2-methoxybenzoate contents were de-

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termined from TG curves. The metal ions were also determined by complexometry with standard EDTA solution [18, 19] after igniting the compounds to the respective oxides and their dissolution in hydrochloric acid solution.

X-ray powder patterns were obtained by using a Siemens D-5000 X-ray diffractometer using CuK_α radiation (λ=1.541 Å) and setting of 40 kV and 20 mA.

Infrared spectra for sodium benzoate as well as for its metal-ion compounds were recorded on a Nicolet model Impact 400 FTIR instrument, within the 4000–400 cm^{-1} range. The solid samples were pressed into KBr pellets.

TG curves were obtained by using a Mettler TA-4000 thermal analysis system. The purge gas was air at a flow rate of 100 mL min^{-1} applying 20 K min^{-1} of heating rate and about 7 mg of initial sample masses in alumina crucibles.

DSC curves were obtained with thermal analysis system model DSCQ10 from TA Instruments. The purge gas was air (flow rate: 50 mL min^{-1}). The heating rate was 20 K min^{-1} and the sample mass was about 5 mg in aluminium crucibles with perforated cover.

Computational strategy

Calculation of theoretical infrared spectrum of lanthanum 2-methoxybenzoate has been necessary to evaluate the structure and wave function computed by the ab initio SCF Hartree–Fock–Roothan method [20] using a split valence (3–21 g) basis set [21]. The performed molecular calculations in this work were done by using the Gaussian 98 routine [22] and the hardware IBM power 3. The geometry optimization was carried out without any constraints. The molecule of 2-methoxybenzoate contains rings with conformational flexibility and all variables optimized. The optimization proceeded more uniformly when all variables were optimized.

Results and discussion

The X-ray diffraction powder patterns, Fig. 1 show that the 2-methoxybenzoates of the metal ions considered in this work have a crystalline structure without evidence for formation of an isomorphous series.

Infrared spectroscopic data on 2-methoxybenzoate and their compounds with trivalent ions considered in this work are shown in Table 1. The investigation was focused mainly within the 1700–1400 cm^{-1} range because this region is the potentially most informative to assign coordination sites. In sodium 2-methoxybenzoate strong band at 1576 cm^{-1} and a medium intensity band located at 1404 cm^{-1} are attributed to the anti-symmetrical and symmetrical frequencies of the carboxylate groups, respectively [8]. In all the complexes considered in this work the symmetrical and anti-symmetrical vibrations of the COO^- groups when compared to the sodium salt, suggest that the compounds have a bidentate bond with an incomplete equalization of bond lenghts in the carboxylate anion, which is in agreement with the literature [5].

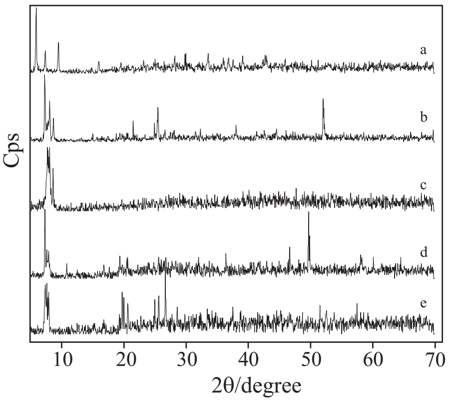

Fig. 1 X-ray powder diffraction patterns of the compounds: a – $LaL_3·4H_2O$; b – $CeL_3·4H_2O$; c – PrL_3; d – $NdL_3·4H_2O$; e – $SmL_3·4H_2O$

Table 1 Spectroscopic data for Na(I) and some light lanthanide ions (III) 2-methoxybenzoate. IR spectra cm^{-1}

Compound	$\nu_{(O–H)}H_2O^b$	$\nu_{asym(COO^-)}{}^c$	$\nu_{sym(COO^-)}{}^c$	$\Delta\nu(\nu_{asym}–\nu_{sym})$
NaL	–	1576_s	1404_m	172
$LaL_3·4H_2O$	3489_{br}	1541_s	1398_m	143
$CeL_3·4H_2O$	3489_{br}	1544_s	1396_m	148
PrL_3	3471_{br}	1544_s	1404_m	140
$NdL_3·4H_2O$	3483_{br}	1545_s	1398_m	147
$SmL_3·4H_2O$	3481_{br}	1546_s	1398_m	148

L=2-methoxybenzoate; ^{a}m – medium; s – strong; br – broad; $^b\nu_{(O–H)}$: hydroxyl group stretching frequency;
$^c\nu_{sym(COO^-)}$ and $\nu_{asym(COO^-)}$: symmetrical and antisymmetrical vibrations of the COO^- group, respectively.

The theoretical infrared spectrum of the LaL_3 was calculated by using an anharmonic field [23] and the obtained frequencies were not scaled. The geometry optimization was computed by optimized algorithm of Berny [24]. The obtained geometry from calculations is presented in Fig. 2 and Table 2.

The theoretical infrared spectrum of the LaL_3 (electronic state ^1A) was obtained with frequency values (cm^{-1}), relative intensities, assignments and description of vibrational modes. The theoretical frequency, assignments and description was visualized by using graphic software Molden 4.2 for Linux [25]. It was compared to the experimental infrared spectrum of the LaL_3.

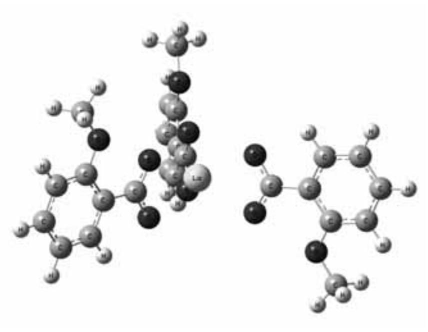

Fig. 2 Proposed structure 3D of solid-state anhydrous compound of lanthanum 2-methoxybenzoate (optimized using Hartree–Fock–Roothan method, LanL2DZ basis set of Gaussian 98)

Table 2 Theoretical geometries parameters of LaL_3 compound

d	$La - O_{COO^-}$	2.49 Å
d	$C_{COO^-} - O_{COO^-}$	1.25 Å
d	$C_{COO^-} - C_{ring}$	1.49 Å
d	$C_{ring} - C_{ring}$	1.40 Å
d	$C_{ring} - H_{ring}$	1.07 Å
<	$C_{COO^-} - O_{COO^-} - La$	95.01°
<	$O_{COO^-} - C_{COO^-} - O_{COO^-}$	118.97°
<	$O_{COO^-} - La - O_{COO^-}$	51.59°
<	$C_{ring} - C_{ring} - C_{ring}$	119.85°

La=lanthanum; *L*=2-methoxybenzoate; *d*=atoms distance; <=atoms angle; COO^-=carboxylate; ring=benzene ring

A comparative analysis between the experimental and theoretical spectrum permitted to verify that: (a) the first assignment shows a strong contribution at 1541 cm^{-1} suggesting a $\nu_{asym(COO^-)}$ assignment, while the theoretical results show the corresponding peak at 1550 cm^{-1} with discrepancies of 0.5 %; (b) the second assignment shows a strong contribution at 1398 cm^{-1} suggesting a $\nu_{sym(COO^-)}$ assignment, while the theoretical results show the corresponding peak at 1410 cm^{-1} with discrepancies of 0.8%. The theoretical data are in agreement with experimental ones.

The analytical and thermoanalytical (TG) data are shown in Table 3. These results establish the stoichiometry of these compounds, which are in agreement with the general formula $LnL_3 \cdot nH_2O$, where *Ln* represents La, Ce, Pr, Nd or Sm, L is 2-methoxybenzoate and *n*=4, 4, 0, 4, 4, respectively.

The TG curve of these compounds shows that the thermal decomposition of the anhydrous compounds occurs in consecutive and/or overlapping steps and the evolved product in the first step was identified by infrared spectrum and qualitative test as 2-methoxybenzoic anhydride. For the lanthanum, neodymium and samarium compounds the formation of dioxycarbonate as intermediate was observed during the thermal decomposition of these compounds. All the residues were confirmed by X-ray powder diffractometry.

The thermal behaviour of the compounds is heavily dependent on the nature of the metal ion and so the features of each of these compounds are discussed individually. The mass losses and temperature ranges observed for each step of the TG curves are shown in Table 4.

Lanthanum compound

TG curve is shown in Fig. 3a. The TG curve indicates mass losses in five steps. The first mass loss observed between 316 and 383 K is due to dehydration with loss of $4H_2O$ (calcd.=10.85%; TG=10.33%). The anhydrous compound is stable up to 523 K and above this temperature up 823 K the thermal decomposition occurs in three steps being the two first overlapping ones.

Table 3 Analytical and thermoanalytical (TG) data of the compounds

Compound	Metal/%			ΔL/%		H_2O/%		Final residue
	Calcd.	TG	EDTA	Calcd.	TG	Calcd.	TG	
$LaL_3 \cdot 4H_2O$	20.41	21.14	21.11	64.63	64.89	10.85	10.33	La_2O_3
$CeL_3 \cdot 4H_2O$	21.05	21.27	21.46	63.31	63.67	10.83	10.21	CeO_2
PrL_3	23.71	23.81	23.71	71.36	71.17	–	–	Pr_6O_{11}
$NdL_3 \cdot 4H_2O$	21.54	21.51	22.22	64.12	64.37	10.76	10.67	Nd_2O_3
$SmL_3 \cdot 4H_2O$	22.25	22.21	22.62	63.54	63.45	10.66	10.78	Sm_2O_3

L means 2-methoxybenzoate

Table 4 Temperature ranges θ and mass losses (%) observed for each step of TG curves of the compounds

Compound	Steps					
	first	second	third	fourth	fifth	
$LaL_3·4H_2O$	θ/K	316–383	523–573	573–703	703–823	823–1013
	loss/%	10.33	28.06	8.18	25.73	2.92
$CeL_3·4H_2O$	θ/K	333–393	523–573	573–683	–	–
	loss/%	10.21	26.87	36.8	–	–
PrL_3	θ/K	503–573	573–693	693–838	–	–
	loss/%	29.61	9.35	32.21	–	–
$NdL_3·4H_2O$	θ/K	323–383	508–573	573–653	653–853	853–1058
	loss/%	10.67	23.78	10.44	28.42	1.73
$SmL_3·4H_2O$	θ/K	333–393	493–573	573–663	663–843	843–1063
	loss/%	10.78	28.26	8.08	25.38	1.73

L=2-methoxybenzoate

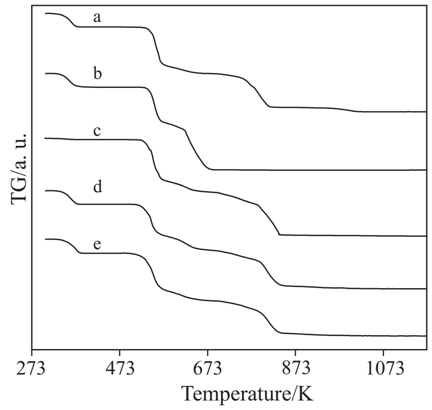

Fig. 3 TG curves of the compounds: a – $LaL_3·4H_2O$ (*m*=7.250 mg); b – $CeL_3·4H_2O$ (*m*=7.250 mg); c – PrL_3 (*m*=7.390 mg); d – $NdL_3·4H_2O$ (*m*=7.290 mg); e – $SmL_3·4H_2O$ (*m*=7.325 mg)

Tests with hydrochloric acid solution on samples heated up to 823 K confirmed the elimination of CO_2 and calculations based on the mass loss up to this temperature suggest the formation of lanthanum dioxycarbonate ($La_2O_2CO_3$) as intermediate. The last step that occurs between 823 and 1013 K is attributed to the thermal decomposition intermediate to the lanthanum oxide as final residue (calcd.=75.48%; TG=75.22%).

Cerium compound

TG curve is shown in Fig. 3b. The TG curve shows three mass loss steps. The first mass loss observed between 333 and 393 K is due to dehydration with loss of $4H_2O$ (calcd.=10.83%; TG=10.21%). The anhydrous compound is stable up to 523 K and the thermal decomposition occurs in two consecutive steps between 523 and 683 K. The total mass loss up to 683 K is in agreement with the formation of CeO_2 as final residue (calcd.=74.14%; TG=73.98%).

Praseodymium compound

TG curve is shown in Fig. 3c. The thermal decomposition of this compound occurs in three steps. The anhydrous compound is stable up to 503 K and above this temperature the thermal decomposition occurs in three overlapping steps, being the first and third ones fast processes and the second step slow process. The total mass loss up to 838 K is in agreement with the formation of Pr_6O_{11}, as final residue (calcd.=71.36%; TG=71.17%).

Neodymium compound

TG curve is shown in Fig. 3d. The thermal decomposition of this compound occurs in five steps. The first mass loss observed between 323 and 383 K, is due to dehydration with loss of $4H_2O$ (calcd.=10.76%; TG=10.67%). The anhydrous compound is stable up to 508 K and above this temperature up to 1058 K the mass loss occurs in four steps being the three first up to 853 K overlapping ones. Tests with hydrochloric acid solution on samples heated up to 853 K, confirmed the elimination of CO_2 and calculations based on the mass loss suggest the formation of a mixture of neodymium oxide and dioxycarbonate in no simple stoichiometric relation. The last step that occurs between 853 and 1058 K is ascribed to the thermal decomposition of dioxycarbonate to neodymium oxide Nd_2O_3, as final residue (calcd.=74.88%; TG=75.04%).

Samarium compound

TG curve is shown in Fig. 3e. The thermal decomposition of this compound also occurs in five steps. The first mass loss observed between 333 and 393 K, is due to dehydration with loss of $4H_2O$ (calcd.=10.66%; TG=10.78%). The anhydrous compound is stable up to 493 K and between 493–1063 K the thermal decomposition occurs in four steps being the three first overlapping ones. Tests with hydrochloric acid solution on samples heated up to 843 K, confirmed the elimination of CO_2 and calculations based on the mass loss up to this temperature also suggest the formation of a mixture of samarium oxide and dioxycarbonate in no simple stoichiometric relation. The last step that occurs between 843 and 1063 K corresponding to the thermal decomposition of the dioxycarbonate to samarium oxide Sm_2O_3 as final residue (calcd.=74.20%; TG=74.23%).

DSC curves of the compounds are shown in Fig. 4. These curves show thermal events corresponding to the mass losses observed in TG curves or due to physical phenomenon.

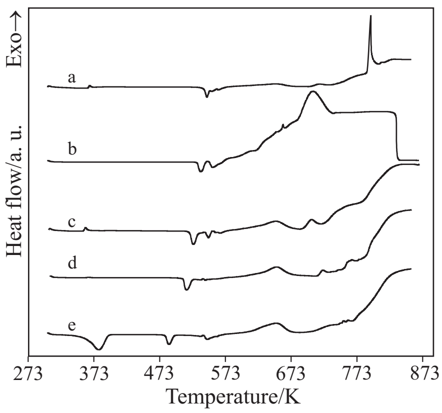

Fig. 4 DSC curves of the compounds: a – LaL_3 (m=4.959 mg); b – CeL_3 (m=4.917 mg); c – PrL_3 (m=5.132 mg) ; d – NdL_3 (m=4.800 mg); e – $SmL_3 \cdot 4H_2O$ (m=4.930 mg)

Only the samarium compound shows an endothermic peak at 383 K, ΔH=120.5 kJ mol^{-1}, due to dehydration in agreement with the first mass loss of the TG curve. For the other compounds no endothermic peak due to dehydration is observed in the DSC curves, and in disagreement with the TG curves. This disagreement undoubledly is because the DSC curves were obtained six months after TG curves, showing that the crystalline water is easily removed by drying the salt in a desiccator over anhydrous calcium chloride and in agreement with the literature data [6].

The small exothermic peaks of the DSC curves at 367 K (La), 360 K (Pr) and 364 K (Nd) is attributed to the increase of the degree of crystallinity which was confirmed by X-ray powder diffractometry.

The endothermic peaks at 545, 553, 562 K (La); 536, 554 K (Ce); 525, 547, 566 K (Pr); 514, 543 K (Nd); and 487, 546 K (Sm) are attributed to the thermal decomposition of the anhydrous compounds, corresponding to the first step of the TG curves.

The exotherm above 643 K (La), 573 K (Ce), 623 K (Pr, Nd, Sm) up to 873 K, with three or four peaks are attributed to oxidation of organic matter that occurs during the thermal decomposition.

Conclusions

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

The thermal decomposition of the compounds occurred in three (Ce, Pr) or five (La, Nd, Sm) steps with formation of the respective oxide: La_2O_3, CeO_2, Pr_6O_{11}, Nd_2O_3 and Sm_2O_3 as final residue.

The X-ray powder patterns pointed out that the 2-methoxybenzoates of the metal ions have a crystalline structure, without evidence concerning the formation of isomorphous compounds.

The theoretical and experimental infrared spectroscopic data suggest that the ligand acts as a bidentate bond with an incomplete equalization of bond lenghts in the carboxylate anion.

TG and DSC provided previously unreported information about the thermal stability, thermal decomposition and physical phenomenon of these compounds.

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