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atadorno@iq.unesp.br

Universidade Estadual Paulista Júlio de  
Mesquita Filho  
Brasil

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## Synthesis, characterization and thermal studies on solid state 3-methoxybenzoate of lighter trivalent lanthanides

P. R. Dametto, A. B. Siqueira, C. T. Carvalho, M. Ionashiro<sup>\*1</sup>

Instituto de Química, UNESP, C. P. 355, CEP 14801 – 970, Araraquara, SP, Brazil.

<sup>\*</sup>massaoi@iq.unesp.br

**Abstract:** Solid-state Ln -3-MeO-Bz compounds, where Ln stands for lighter trivalent lanthanides (La – Sm) and 3-methoxybenzoate, have been synthesized. Thermogravimetry (TG), differential scanning calorimetry (DSC), X-ray powder diffractometry, infrared spectroscopy, and complexometry were used to characterize and to study the thermal behaviour of these compounds. The results led to information concerning the composition, dehydration, polymorphic transformation, thermal behaviour and thermal decomposition of the synthesized compounds.

**Keywords:** Ligther lanthanides; 3-Methoxybenzoate; Characterization; Thermal behaviour.

### Introduction

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

In aqueous solutions, the works reported the thermodynamics of complexation; spectroscopy study; influence of pH; surfactant and synergic agent on the luminescent properties; crystal structure, photophysical and magnetic properties [1-5].

In the solid state, the works reported the thermal and spectral behaviour on solid compounds of benzoates and its derivatives with rare earth elements [6-12]; the vibrational and electronic spectroscopy study of lanthanides and effect of sodium on the aromatic system of benzoic acid [13-14]; the reaction of divalent cooper, cobalt and nickel with 3-hydroxy-4-methoxy and 3-methoxy-4-hydroxybenzoic acid and a structure for these compounds has been proposed on the basis of spectroscopy and thermogravimetric data [15]. The thermal decomposition of thorium salts of benzoic acid 4-methoxybenzoic acids in air atmosphere [16] and thermal behaviour of solid state 4-methoxy; 3-methoxy; 2-methoxybenzoates

and benzoate of some bivalent transition metal ions have also been described [17-20].

In this work the 3-methoxybenzoates of lighter trivalent lanthanides (La-Sm) were synthesized and characterized by X-ray powder diffractometry, infrared spectroscopy, thermogravimetry (TG), differential scanning calorimetry (DSC) and complexometry.

### Experimental details

The 3-methoxybenzoic acid (3-MeO-HBz) 99% was obtained from Aldrich. Aqueous solution of Na-3-MeO-Bz 0.1 mol L<sup>-1</sup> was prepared from aqueous 3-MeO-HBz suspension by adding sodium hydroxide solution 2.5 mol L<sup>-1</sup> up to near total neutralization, followed by NaOH solution 0.1 mol L<sup>-1</sup> up to pH = 8.7.

Lanthanide chlorides were prepared from the corresponding metal oxides (except for cerium) by treatment with hydrochloric acid solution. 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<sup>-1</sup> solutions, whose pH were adjusted to 5.5 by adding diluted sodium hydroxide or hydrochloric acid solutions. Cerium (III) was used as its nitrate and ca 0.1 mol L<sup>-1</sup>

<sup>1</sup> aqueous solution of this ion was prepared by direct weighing of the salt.

The solid state compounds were prepared by adding slowly, under continuous stirring, the solution of the ligand to the respective metal chloride or nitrate solutions, until total precipitation of the metal ions. 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, ligand and metal ion contents were determined from TG curves. The metal ions were also determined by complexometric titrations with standard EDTA solution, using xylenol orange as indicator [21-22].

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

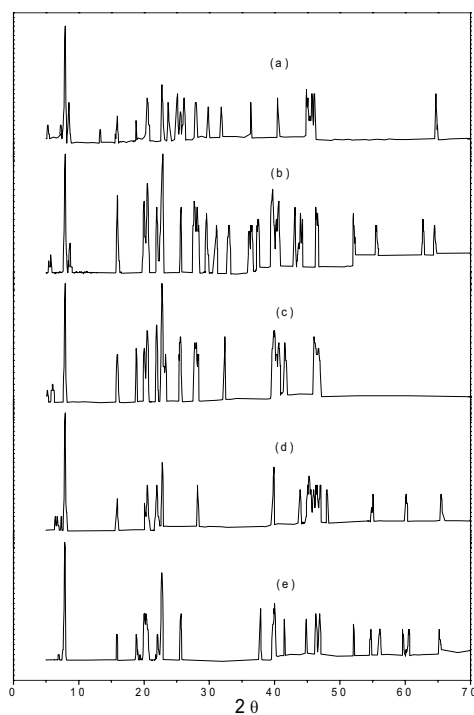
Infrared spectra for Na-3-MeO-Bz as well as for its metal ion compounds were run on a Nicolet model Impact 400 FT-IR Instrument, within the 4000-400  $\text{cm}^{-1}$  range. The solid samples were pressed into KBr pallets.

The TG curves were obtained by using a Mettler TA-4000 thermal analysis system, with air flowing at 100  $\text{mL min}^{-1}$ , a heating rate of 20  $^{\circ}\text{C min}^{-1}$  and with samples weighing about 7 mg. An alumina crucible was used to obtain the TG curve.

The DSC curves were obtained with a thermal analysis system model DSCQ10 from TA Instruments. The purge gas was an air flow of 50  $\text{mL min}^{-1}$ . A heating rate was 20  $^{\circ}\text{C min}^{-1}$  was adopted with samples weighing about 5 mg. Aluminium crucibles with perforated cover were used for recording the DSC curves.

## Results and discussion

The analytical and thermoanalytical (TG) results are shown in Table 1. These results establish the stoichiometry of these compounds, which are in agreement with the general formula,  $\text{Ln}(\text{3-MeO-Bz})_3 \cdot n\text{H}_2\text{O}$ , where Ln represents lighter trivalent lanthanides (La-Sm), 3-MeO-Bz is 3-methoxybenzoate and  $n = 2$  (La, Pr, Nd, Sm), 2.5 (Ce).



**Figure 1:** X-ray powder diffraction patterns of the compounds: (a)  $\text{La}(\text{L})_3 \cdot 2\text{H}_2\text{O}$ , (b)  $\text{Ce}(\text{L})_3 \cdot 2.5\text{H}_2\text{O}$ , (c)  $\text{Pr}(\text{L})_3 \cdot 2\text{H}_2\text{O}$ , (d)  $\text{Nd}(\text{L})_3 \cdot 2\text{H}_2\text{O}$  and (e)  $\text{Sm}(\text{L})_3 \cdot 2\text{H}_2\text{O}$ . (L=3-methoxybenzoate).

**Table 1.** Analytical and thermoanalytical (TG) data of the compounds.

Compound	Metal (%)			Loss (%)		Water (%)		Residue
	Calcd.	TG	EDTA	Calcd.	TG	Calcd.	TG	
$\text{La}(\text{L})_3 \cdot 2\text{H}_2\text{O}$	22.11	21.98	22.67	68.34	68.38	5.74	5.93	$\text{La}_2\text{O}_3$
$\text{Ce}(\text{L})_3 \cdot 2.5\text{H}_2\text{O}$	21.94	21.99	22.05	65.99	66.25	7.05	6.71	$\text{CeO}_2$
$\text{Pr}(\text{L})_3 \cdot 2\text{H}_2\text{O}$	22.35	22.30	21.63	67.28	67.02	5.72	6.12	$\text{Pr}_6\text{O}_{11}$
$\text{Nd}(\text{L})_3 \cdot 2\text{H}_2\text{O}$	22.76	22.76	22.90	67.77	67.63	5.69	5.95	$\text{Nd}_2\text{O}_3$
$\text{Sm}(\text{L})_3 \cdot 2\text{H}_2\text{O}$	23.50	24.10	24.31	67.12	67.07	5.63	5.17	$\text{Sm}_2\text{O}_3$

L means 3-methoxybenzoate

Infrared spectroscopic data on 3-methoxybenzoate sodium salt and its compounds with lighter trivalent lanthanides are shown in Table 2. The investigation was focused mainly within the 1700-1400  $\text{cm}^{-1}$  range, because this region is potentially most informative to assign coordination sites. In the sodium 3-methoxybenzoate, strong bands located at 1568  $\text{cm}^{-1}$  and 1400  $\text{cm}^{-1}$  are attributed to the anti-symmetrical and symmetrical frequencies of the carboxylate groups, respectively [23,24]. In the compounds considered in this work, analysis of the frequencies of the  $\nu_{\text{as}}$  and  $\nu_{\text{sym}}$  ( $\text{COO}^-$ ) bands 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; this is in agreement with the literature [5,11-13].

The TG curves of the compounds are shown in Fig. 2. These curves show mass losses in two (Ce), three (Pr, Sm) or four (La, Nd) steps. In all the TG curves, the first mass loss between 50 and 100  $^{\circ}\text{C}$  is attributed to dehydration, which

occurs in a single step. Once dehydrated, the anhydrous compounds are stable up to 270  $^{\circ}\text{C}$  (Ce), 330  $^{\circ}\text{C}$  (La, Nd, Sm) and 355  $^{\circ}\text{C}$  (Pr) and above these temperatures the TG curves show that the thermal decomposition is characteristic for each compound.

For the lanthanum compound, Fig. 2 (a) the first mass loss is due to dehydration, with loss of 2  $\text{H}_2\text{O}$  (calcd. = 5.74 %, TG = 5.93 %). The thermal decomposition of the anhydrous compound occurs in three steps between 330 and 750  $^{\circ}\text{C}$ , with the two first ones a fast processes and losses of 29.46 and 28.90 %, respectively. In the last step the mass loss occurs through a slow process with formation of lanthanum oxide,  $\text{La}_2\text{O}_3$  as final residue.

For the cerium compound, Fig. 2 (b) the first mass loss is due to dehydration with loss of 2.5  $\text{H}_2\text{O}$  (calcd. = 7.05 %, TG = 6.71 %). The thermal decomposition of the anhydrous compound occurs in a single step between 270 and 570  $^{\circ}\text{C}$ , with loss of 66.25 %. The lower thermal stability of the cerium compound, as compared with the other compounds is undoubtedly related to the exothermic oxidation

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

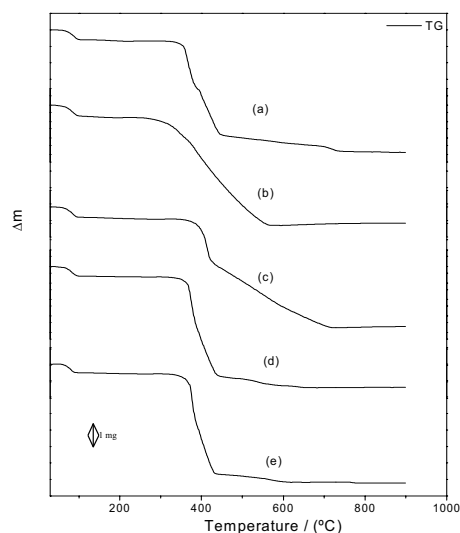
Compound	$\nu_{(\text{O-H}) \text{ H}_2\text{O}}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{as}(\text{COO}^-)}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{sym}(\text{COO}^-)}$ ( $\text{cm}^{-1}$ )	$\Delta\nu(\nu_{\text{as}}-\nu_{\text{sym}})$ ( $\text{cm}^{-1}$ )
Na(3-MeO-Bz)	-	1568 <sub>s</sub>	1402 <sub>s</sub>	168
La(3-MeO-Bz) <sub>3</sub> .2H <sub>2</sub> O	3487 <sub>br</sub>	1529 <sub>s</sub>	1406 <sub>s</sub>	123
Ce(3-MeO-Bz) <sub>3</sub> .2.5H <sub>2</sub> O	3492 <sub>br</sub>	1525 <sub>s</sub>	1400 <sub>s</sub>	125
Pr(3-MeO-Bz) <sub>3</sub> .2H <sub>2</sub> O	3489 <sub>br</sub>	1529 <sub>s</sub>	1406 <sub>s</sub>	123
Nd(3-MeO-Bz) <sub>3</sub> .2H <sub>2</sub> O	3501 <sub>br</sub>	1529 <sub>s</sub>	1409 <sub>s</sub>	120
Sm(3-MeO-Bz) <sub>3</sub> .2H <sub>2</sub> O	3510 <sub>br</sub>	1529 <sub>s</sub>	1409 <sub>s</sub>	120

br: broad; s = strong; 3-MeO-Bz = 3-metoxibenzoate

$\nu_{(\text{O-H})}$ : hydroxyl group stretching frequency;  $\nu_{\text{sym}(\text{COO}^-)}$  and  $\nu_{\text{as}(\text{COO}^-)}$  = symmetrical and anti-symmetrical vibrations of the  $\text{COO}^-$  structure.

reaction that results in the formation of cerium (IV) oxide.

In the praseodymium compound, Fig. 2 (c) the first mass loss is due to the dehydration with loss of 2 H<sub>2</sub>O (calcd. = 5.72 %, TG = 6.12 %). The thermal decomposition of the anhydrous compound occurs in two steps between 355 °C and 720 °C. The mass loss up to 440 °C occurs through a fast process followed by a slow one with losses of 29.36 and 37.66 %, respectively and with formation of praseodymium oxide, Pr<sub>6</sub>O<sub>11</sub> as final residue.



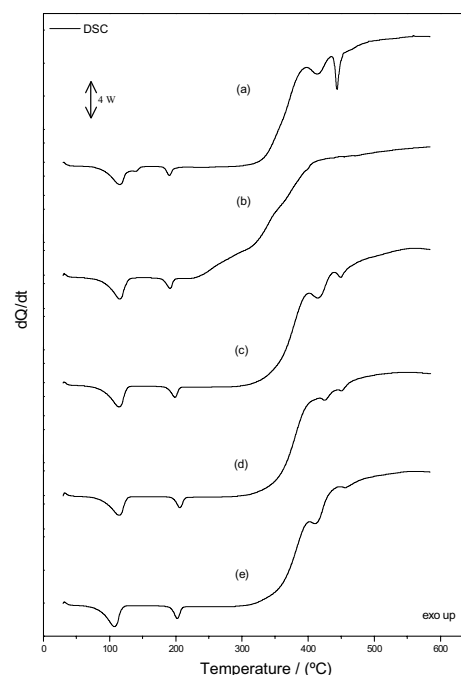
**Figure 2:** TG curves of the compounds: (a) La(L)<sub>3</sub>.2H<sub>2</sub>O (m = 7.090 mg), (b) Ce(L)<sub>3</sub>.2.5H<sub>2</sub>O (m = 7.020 mg), (c) Pr(L)<sub>3</sub>.2H<sub>2</sub>O (m = 6.780 mg), (d) Nd(L)<sub>3</sub>.2H<sub>2</sub>O (m = 6.960 mg) and (e) Sm(L)<sub>3</sub>.2H<sub>2</sub>O (m = 7.030 mg). heating rate: 20° min<sup>-1</sup>; air flow: 100 mL min<sup>-1</sup>. L= 3-methoxybenzoate.

In the neodymium compound, Fig. 2 (d) the first mass loss is attributed to dehydration with loss of 2 H<sub>2</sub>O (calcd. = 5.69 %, TG = 5.95 %). The thermal decomposition of the anhydrous compound occurs in three steps between 330 and 655 °C. The first mass loss up to 440 °C, also occurs through a fast process, followed by two slow processes with losses of 60.54, 6.00 and 1.09 %, respectively resulting in the formation of neodymium oxide, Nd<sub>2</sub>O<sub>3</sub>, as final residue.

For the samarium compound, Fig. 2 (e) the first mass loss is due to dehydration with loss of 2 H<sub>2</sub>O (calcd. = 5.63 %, TG = 5.17 %). The thermal decomposition of the anhydrous compound occurs in two steps between 330 and 620 °C. The first

mass loss up to 435 °C occurs through a fast process followed by a slow process with losses of 61.70 and 5.37 %, respectively, leading to formation of samarium oxide, Sm<sub>2</sub>O<sub>3</sub> as final residue.

The DSC curves of the compounds are shown in Fig. 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 crystalline phase transition. The endothermic peak at 115 °C (La), 117 °C (Ce), 107 °C (Pr), 114 °C (Nd) and 106 °C (Sm) is due to dehydration. The dehydration enthalpies found for the lanthanum to samarium compounds were: 112.2, 105.4, 106.8, 95.5 and 93.3 kJ mol<sup>-1</sup>.



**Figure 3:** DSC curves of the compounds: (a) La(L)<sub>3</sub>.2H<sub>2</sub>O (m = 4.906 mg), (b) Ce(L)<sub>3</sub>.2.5H<sub>2</sub>O (m = 5.091 mg), (c) Pr(L)<sub>3</sub>.2H<sub>2</sub>O (m = 5.227 mg), (d) Nd(L)<sub>3</sub>.2H<sub>2</sub>O (m = 5.052 mg) and (e) Sm(L)<sub>3</sub>.2H<sub>2</sub>O (m = 5.255 mg). heating rate: 20 ° min<sup>-1</sup>; air flow: 50 mL.min<sup>-1</sup>. L= 3-methoxybenzoate.

The broad exothermic event observed for all compounds, except the cerium, between 325 and temperature higher than 600 °C without the appearance of definitive peaks are due to the thermal decomposition of the anhydrous compounds, where the oxidation of the organic matter takes place in consecutive and/or overlapping steps. For the cerium compound the exothermic event between 225 and temperature higher than 600 °C,

the oxidation of the organic matter takes place in a single step.

The endothermic peak at 190 °C (La), 193 °C (Ce), 193 °C (Pr), 205 °C (Nd) and 201 °C (Sm) are due to crystalline phase transition. The crystalline phase transition enthalpies found for the lanthanum to samarium compounds were: 14.9, 22.1, 23.8, 23.8 and 24.4 kJ mol<sup>-1</sup> respectively.

### Conclusion

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

The X-ray powder patterns pointed out that the synthesized compounds have a crystalline structure without evidence for formation of isomorphous compounds.

The infrared spectroscopic data suggest that the 3-MeO-Bz acts as a bidentate ligand toward the metal ions considered in this work.

The TG and DSC curves provided previously unreported information about the thermal behaviour and thermal decomposition of these compounds.

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P. R. Dametto, A. B. Siqueira, C. T. Carvalho, M. Ionashiro<sup>1</sup>. Síntese, caracterização e estudo térmico dos 3-metoxibenzoatos de lantanídeos mais leves no estado sólido.

**Resumo:** Compostos do tipo Ln-3-MeO-Bz foram sintetizados no estado sólido, em que Ln representa os íons trivalentes La, Ce, Pr, Nd e Sm, e 3-MeO-Bz é o ânion 3-metoxibenzoato. Esses compostos foram caracterizados, utilizando-se as técnicas de difração de raios X pelo método do pó, espectroscopia na região do infravermelho, complexometria, e seu comportamento térmico foi avaliado usando termogravimetria (TG) e calorimetria exploratória diferencial (DSC). Os resultados forneceram informações com respeito a estequiometria, desidratação, transformação polimórfica, comportamento e decomposição térmica desses compostos.

**Palavras-chave:** lantanídeos leves; 3-metoxibenzoato; caracterização; comportamento térmico.

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