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Synthesis, characterization and thermal studies on solid 3-methoxybenzoate of some bivalent transition metal ions

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Abstract: Solid-state M-3-MeO-Bz compounds, where M stands for bivalent Mn, Co, Ni, Cu and Zn and 3-MeO-Bz is 3-methoxybenzoate, have been synthesized. Simultaneous thermogravimetry and differential thermal analysis (TG-DTA), differential scanning calorimetry (DSC), X-ray powder diffractometry, infrared spectroscopy, and chemical analysis 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 thermal decomposition of the isolated compounds.

Keywords: bivalent transition metals; 3-methoxybenzoate; thermal behaviour.

Introduction

Several metal-ion salts of benzoic acid, as well as some benzoic acid derivatives, have been investigated in aqueous solutions and in solid state.

In aqueous solutions, Yun and co-workers [1] reported the thermodynamics of complexation of lanthanides by some benzoic acid derivatives. Wang and co-workers [2] reported the spectroscopic study of trivalent lanthanides with several carboxylic acids, including benzoic acid. Arnaud and Georges [3] described the influence of pH, surfactant and synergic agent on the luminescent properties of terbium chelates with benzoic acid derivatives. Choppin and co-workers [4] reported the thermodynamic of complexation of lanthanides by benzoic and isophthalic acids. Lam and co-workers [5] described the synthesis, crystal structure and photophysical and magnetic properties of dimeric and polymeric lanthanide complexes with benzoic acid and its derivatives.

In the solid state, Wendlandt synthesized and reported the thermal stability and thermal decomposition of thorium salts with several organic acids, including 4-methoxybenzoic acid [6], as well as benzoic and m-hydroxybenzoic acids [7].

Glowiack and co-workers [8] reported the reaction of bivalent copper, cobalt and nickel with 3-hidroxy-4-methoxy and 3-methoxy-4-hidroxybenzoic acids and a structure for these compounds has been proposed on the basis of spectroscopic and thermogravimetric data. Brzyska and Karasinski [9] described the thermal decomposition of thorium salts of benzoic and 4-methoxybenzoic acids in air atmosphere. Ferenc and Walkow-Dziewulska [10] reported the synthesis and characterization of 2,3-dimethoxybenzoates of heavy lanthanides and yttrium by elemental analysis, IR spectroscopy, thermogravimetric studies and X-ray diffraction measurements.

In the present paper, solid-state compounds of Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) with 3-methoxybenzoate were prepared.

The compounds were investigated by means of chemical analysis, X-ray powder diffractometry, infrared spectroscopy, differential scanning calorimetry (DSC) and simultaneous thermogravimetry-differential thermal analysis (TG-DTA). The results allowed us to acquire information concerning these compounds in the solid state, including their thermal stability and thermal decomposition.

methoxybenzoic acid in these compounds.

Simultaneous TG-DTA curves of the compounds are shown in Fig. 2. These curves show mass losses in consecutive and/or overlapping steps with partial losses which are characteristic for each compound. Only the copper compound shows an endothermic peak corresponding to the first mass loss ascribed to dehydration. For the other compounds, no endothermic peak compatible with the first mass loss due to the dehydration is observed. Based on the information of infrared spectra and DTA curves, samples of these compounds were heated in a long test glass tube up to the temperature corresponding to the first mass loss and under approximately the same conditions as the TG-DTA curves. In these experiments, sublimation for the nickel compound and sublimation followed by fusion and evaporation for manganese, cobalt and zinc compounds were observed. The sublimated materials were identified as 3-methoxybenzoic acid, by infrared spectra and m.p. = 106 – 108°C literature; 105 – 108°C, observed. The presence of 3-MeO-HBz in these compounds must be due to the aggregation phenomenon, indicating that the procedure used to eliminate the acid in excess is not efficient and that the acid is more soluble in 3-methoxybenzoate solution and it no recrystallize even an ice bath. Therefore the first mass loss up to 280°C (Mn), 200°C (Co) and 230°C (Ni, Zn), is due to elimination of 3-methoxybenzoic acid.

Thus, Table 2 presents the analytical and thermoanalytical (TG) results for the prepared compounds, from which the general formula $\text{Cu}(\text{L})_2 \cdot \text{H}_2\text{O}$ or $\text{M}(\text{L})_2 \cdot x\text{HL}$ can be established, where M represents Mn, Co, Ni and Zn, L = 3-methoxybenzoate, HL = 3-methoxybenzoic acid and $x = 0.19(\text{Mn}), 0.28(\text{Co}), 0.13(\text{Ni})$ and $0.081(\text{Zn})$.

Manganese compounds. The TG-DTA and DSC curves are shown in Fig. 2a. These curves show mass losses in two steps between 50-180°C and 180- 500°C (TG), and endothermic peaks at 180°C (DTA, DSC), 100°C (DSC) and exothermic peaks at 360°C, 430°C (DTA, DSC), 474°C (DTA), 500°C and 520°C. The first mass loss that occurs through a slow process is attributed to the loss of 0.19 HL (3methoxybenzoic acid) (calcd. = 7.49%; TG = 7.46%). The second step that occurs through a fast process is ascribed to the thermal decomposition of the compounds that occurs in a single step (Calcd.

= 72,76%; TG = 72.92%), with formation of Mn_3O_4 , as final residue (Calcd. 19.75%; TG=19.57%), and confirmed by X-ray powder diffractometry. The endothermic peaks at 100°C (DSC and 180°C (DTA, DSC), are due to sublimation of 3-MeO-BP and fusion of the compounds, respectively, and in agreement with the experiment already described, with sample heated in a long test tube. The exothermic peaks at 360°C, 430° and 475 °C (DTA, DSC), 500 and 520 °C (DSC) are attributed to the oxidation of the organic matter.

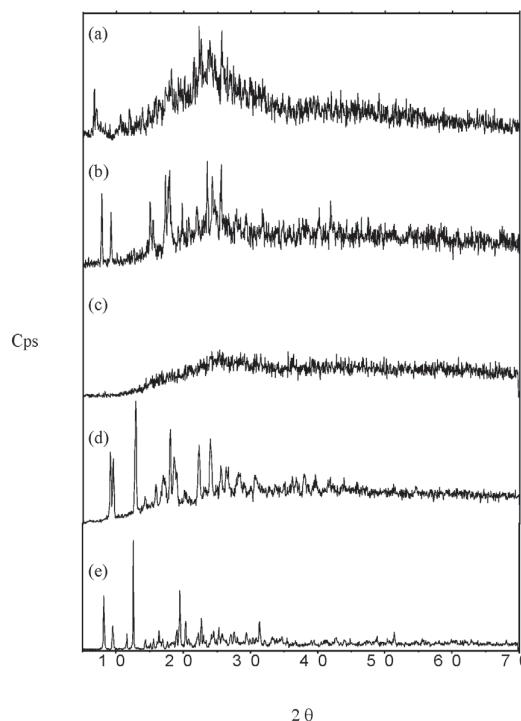


Figure 1. X-ray powder diffraction patterns of the compounds: (a) $\text{Mn}(\text{L})_2 \cdot 0.19\text{HL}$, (b) $\text{Co}(\text{L})_2 \cdot 0.28\text{HL}$, (c) $\text{Ni}(\text{L})_2 \cdot 0.13\text{HL}$, (d) $\text{Cu}(\text{L})_2 \cdot \text{H}_2\text{O}$ and (e) $\text{Zn}(\text{L})_2 \cdot 0.081\text{HL}$ (L=4-methoxybenzoate, HL = 4-methoxybenzoic acid).

Cobalt compound. The TG-DTA and DSC curves are shown in Fig. 2b. These curves show mass losses in four consecutive and/or overlapping steps between 80-200°C, 200-380°C, 380-480°C and 900-920°C (TG) and endothermic peaks at 235°C(DTA, DSC) and 900°C(DTA), and exothermic peaks at 480°C (DTA, DSC) and 490°C(DSC). The first mass loss, without thermal event observed in the DTA and DSC curves is ascribed to the loss of

0.28 HL (3-methoxybenzoic acid) (Calcd. = 10.55%; TG=10.61%). The endothermic peak at 235°C (235°C) DTA, DSC is attributed to the fusion of the compound. The second and third steps with losses of 26.13% and 43.77%, corresponding to the single exothermic peak (DTA) or a broad exothermic between 410-550°C (DSC), are attributed to the thermal decomposition of the compound. The profiles of the TG-DTA curves show that the oxidation of the organic matter occurs with combustion. The total mass loss up to

480°C is in agreement with the formation of Co_3O_4 (Calcd. = 80.13%; TG = 80.51%). The last step corresponding to the small endothermic peak is due to the reduction of Co_3O_4 to CoO (Calcd. = 1.32%; TG = 1.21%) and is in agreement with literature. [15,16]. X-ray powder patterns of the residue obtained at 1000°C is coincident with that obtained for Co_3O_4 ; this is due to the reoxidation reaction of CoO to Co_3O_4 which occurs on cooling the former in an air atmosphere at room temperature [16].

Table 1. Spectroscopic data for 3-methoxybenzoic acid (HL), sodium 3-methoxybenzoate (NaL), and compounds with some bivalent metal ions^a.

Compound	$\nu_{(\text{O}-\text{H})} \text{H}_2\text{O}^b$ (cm^{-1})	$\nu_{\text{as}(\text{COO}^-)}^c$ (cm^{-1})	$\nu_{\text{sym}(\text{COO}^-)}^c$ (cm^{-1})	$\nu_{(\text{C}=\text{O})}^d$ (cm^{-1})
HL	-	-	-	1690
NaL.H ₂ O	3450 _{br}	1568 _s	1402 _s	-
Mn(L) ₂ .0.19HL	-	1556 _s	1404 _s	1682 _m
Co(L) ₂ .0.28HL	-	1529 _s	1385 _s	1691 _m
Ni(L) ₂ .0.13HL	-	1570 _s	1395 _m	1692 _m
Cu(L) ₂ .H ₂ O	3464 _{br}	1595 _s	1418 _s	-
Zn(L) ₂ .0.081HL	-	1581 _s	1404 _s	1693 _m

^a br: broad, m = medium, s = strong.

^b $\nu_{(\text{O}-\text{H})}$: hydroxyl group stretching frequency.

^c $\nu_{\text{sym}(\text{COO}^-)}$ and $\nu_{\text{as}(\text{COO}^-)}$: symmetrical and anti-symmetrical vibrations of the COO^- group, respectively

^d $\nu_{(\text{C}=\text{O})}$: stretching frequency of the dimmer structure.

Table 2. Analytical data for the $\text{M}(\text{L})_2 \cdot \text{H}_2\text{O}$ and $\text{ML}_2 \cdot n\text{HL}$ compounds.

Compound	Metal oxide (%)			ΔL (%)		HL or Water (%)		Residue
	Calcd.	TG	EDTA	Calcd.	TG	Calcd.	TG	
Mn(L) ₂ .0.19HL	19.75	19.57	19.88	72.76	72.92	7.49	7.46	Mn ₃ O ₄
Co(L) ₂ .0.28HL	18.55	18.24	18.31	70.90	71.16	10.55	10.61	CoO
Ni(L) ₂ .0.13HL	19.62	19.31	19.43	75.19	75.42	5.19	5.27	NiO
Cu(L) ₂ .H ₂ O	18.64	19.04	18.28	76.67	76.35	4.69	4.61	CuO
Zn(L) ₂ .0.081HL	21.41	21.20	21.83	75.35	75.59	3.24	3.21	ZnO

ΔL = Ligand lost; HL = 3-metoxibenzoic acid.

M = metal

Nickel Compound. The TG-DTA and DSC curves are shown in Fig.2c. The mass loss that occurs between 50 and 200°C through slow process, without appearing of thermal event in the DTA and DSC curves, is due to the loss of 0.13 HL (3-methoxybenzoic acid) (Calcd. =5.19%; TG = 5.27%). Above this temperature up to 470°C, the thermal decomposition occurs through a fast process, corresponding to the

exothermic peak at 470°C (DTA, DSC) attributed to the oxidation of the organic matter. The profiles of the TG and DTA curves show that this step the oxidation of the organic matter is followed by combustion. The total mass loss up to 470°C is in agreement with the formation of NiO, as final residue (Calcd. =80.29%; TG = 80.69%) and confirmed by X-ray powder diffractometry.

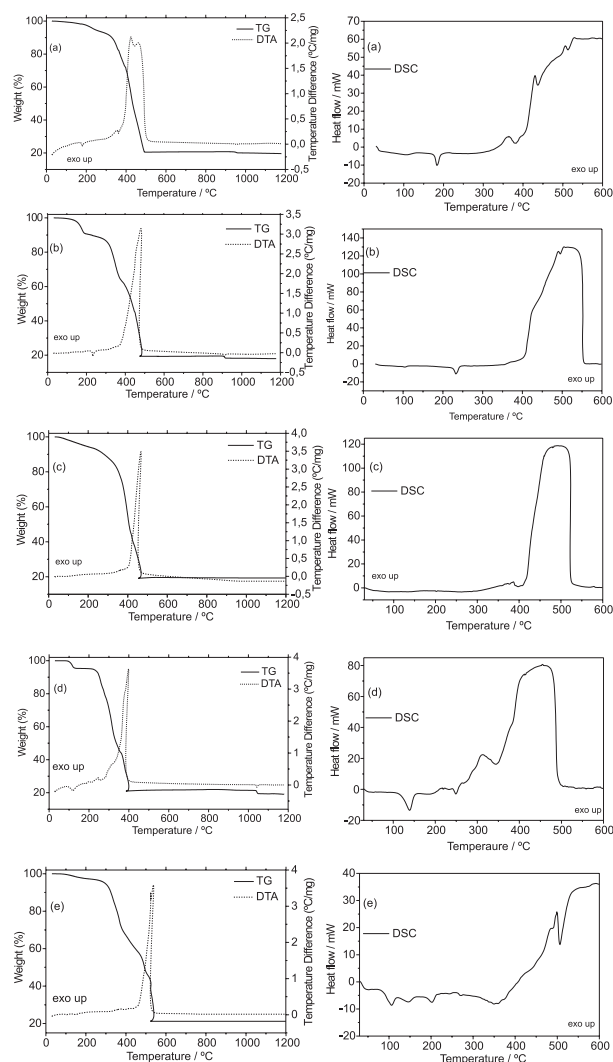


Figure 2. TG-DTA and DSC curves of the compounds: (a) $\text{Mn}(\text{L})_2 \cdot 0.19\text{HL}$ ($m = 6.9788\text{mg}$), (b) $\text{Co}(\text{L})_2 \cdot 0.28\text{HL}$ ($m = 7.0760\text{mg}$), (c) $\text{Ni}(\text{L})_2 \cdot 0.13\text{HL}$ ($m = 7.1162\text{ mg}$), (d) $\text{Cu}(\text{L})_2 \cdot \text{H}_2\text{O}$ ($m = 7.2794\text{ mg}$) and (e) $\text{Zn}(\text{L})_2 \cdot 0.081\text{HL}$ ($m = 7.1821\text{ mg}$). L = 3-methoxybenzoate, HL = 3-methoxybenzoate.

Copper compound. The TG-DTA and DSC curves are shown in Fig. 2d. The mass loss observed between 95 and 130°C, corresponding to an endothermic peak at 120°C (DTA), 140°C (DSC) is due to dehydration with loss of 1 H₂O (Calcd. = 4.69%; TG = 4.61%). The anhydrous compound is stable up to 210°C, and above this temperature the thermal decomposition occurs in two consecutive steps with losses of 48.22% (210-355°C) and 26.13% (355-400°C). These mass losses corresponding to the sharp exothermic peak at 400°C (DTA) or two exothermics between 290-340°C and 360°C (DSC), are attributed to the oxidation followed by combustion of the organic matter. The total mass loss up to 400°C is in agreement with the formation of CuO as the final residue (Calcd. = 79.28%; TG = 78.96%), which was confirmed by X-ray powder diffractometry. The last mass loss between 1034 and 1050°C corresponding to the endothermic peak at 1045°C is attributed to reduction of CuO to Cu₂O (Calcd. = 2.08%; TG = 2.0%).

Zinc compound. The TG-DTA and DSC curves are shown in Fig. 2e. The mass loss observed between 90 and 240°C without appearing of thermal event in the DTA curve is due to the loss of 0.081 HL (3-methoxybenzoic acid) Calcd. 3.24%; TG = 3.21%. In this temperature range the DSC curve shows three endothermic peaks at 110°C, 150°C and 200°C, ascribed to sublimation of 3-methoxybenzoic acid, fusion and evaporation respectively. Above 240°C, the thermal decomposition occurs in three steps with losses of 29.93% (240-380°C), 23.64% (380-500°C) and 26.02% (500-538°C), corresponding to the exothermic peaks at 520 and 538°C (DTA) and 500°C and exothermic between 540-600°C (DSC) attributed to oxidation of organic matter. The profiles of the TG and DTA curves show that the last step the oxidation of the organic matter is accompanied by combustion. The total mass loss up to 538°C is in agreement with the formation of ZnO as final residue (Calcd. = 78.59%; TG = 78.80%) and confirmed by X-ray powder diffractometry.

The differences observed concerning the peak temperatures obtained by DTA and DSC, or

peaks observed only in the DSC curves are undoubtedly due to the perforated cover used to obtain the DSC curves while the DTA ones are obtained without cover and due to the greater sensibility of the DSC.

Conclusions

The TG-DTA curves, infrared spectra and chemical analysis, permitted to verify that the binary compounds were obtained, however contaminated with 3-methoxybenzoic acid, except the copper compound. The procedure used to synthesize these compounds permitted to verify that compound little soluble (copper one) was obtained without contamination, and that the contamination occurs during the evaporation of the compounds solutions, due to the aggregation phenomenon.

The TG-DTA, also permitted verify that the 3-MeO-HBz is eliminated before thermal decomposition of these compounds, thus binary compounds may be obtained by thermosynthesis.

The X-ray powder patterns pointed out that the synthesized compounds have a crystalline structure, except the nickel one, without evidence concerning the formation of isomorphous series.

The infrared spectroscopy data suggest that the compounds considered in this work have an ionic character.

The TG-DTA and DSC provided previously unreported information about the thermal stability and thermal decomposition of these compounds.

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A. C. Vallejo, A. B. Siqueira, E. C. Rodrigues, E. Y. Ionashiro, G. Bannach, M. Ionashiro
Síntese, caracterização e estudo térmico dos 3-metoxibenzoatos de alguns metais de transição, no estado sólido.

Resumo: Compostos M-3-MeO-Bz foram sintetizados no estado sólido, onde M representa os íons bivalentes Mn, Co, Ni, Cu e Zn e 3-MeO-Bz o ânion 3-metoxibenzoato. Esses compostos foram caracterizados e estudados utilizando-se as técnicas de difração de raios x pelo método do pó, espectroscopia de absorção na região do infravermelho, análise química, termogravimetria e análise térmica diferencial simultânea (TG-DTA) e calorimetria exploratória diferencial (DSC). Os resultados forneceram informações com respeito à composição, desidratação, estabilidade térmica e decomposição térmica dos compostos isolados.

Palavras-chave: metais de transição bivalentes; 3-metoxibenzoato; comportamento térmico.

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