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Synthesis, characterization and thermal behaviour of solid-state compounds of 2-methoxybenzoate with some bivalent transition metal ions

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Abstract: Solid-state M-2-MeO-Bz compounds, where *M* stands for bivalent Mn, Co, Ni, Cu and Zn and 2-MeO-Bz is 2-methoxybenzoate, have been synthesized. Simultaneous thermogravimetry-differential thermal analysis (TG-DTA), thermogravimetry, derivative thermogravimetry (TG/DTG), 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 have information about the composition, dehydration, thermal stability and thermal decomposition of the isolated compounds.

Keywords: bivalent transition metals; 2-methoxybenzoate; thermal behaviour.

Introduction

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

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

Several papers reported the thermal stability and thermal decomposition of solid-state salts as thorium with several organic acids, including 4-methoxybenzoic acid [6], as well as benzoic and m-hydroxybenzoic acids [7]; the thermal decomposition of nickel benzoate and of the nickel salt of ciclohexane carboxylic acid [8]; the thermal and spectral behaviour on solid compounds of benzoates and its methoxy derivates with rare earth elements [9-12, 14, 15-17] ; the vibrational and electronic spectroscopic study of lanthanides and effect of sodium on the aromatic system of benzoic acid [13, 16]; the reaction of bivalent cooper, 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 [18]; the thermal decomposition of thorium salts of benzoic and 4-methoxybenzoic acids in air atmosphere [19]; the thermal and spectral behaviour on solid compounds of 5-chloro-2-methoxybenzoate with rare earth and d-block elements [20-23]; the synthesis and characterization of 2,3-dimethoxybenzoates of heavy lanthanides and yttrium [24]; the spectral and magnetic studies of 2-chloro-5-nitrobenzoates of rare earth elements [25] and thermal behaviour of solid state 4-methoxybenzoates of some bivalent transition metal ions [26].

In this work 2-methoxybenzoates of Mn(II), Co(II), Ni(II) and Zn(II) were synthetized. The compounds were investigated by means of infrared spectroscopy, X-ray powder diffractometry, simultaneous thermogravimetry and differential thermal analysis (TG-DTA), thermogravimetry, derivative thermogravimetry (TG/DTG), differential scanning calorimetry (DSC) and other methods of analysis.

Experimental

Carbonates of Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) were prepared by adding slowly with continuous stirring saturated sodium hydrogen carbonate solution to the corresponding metal chloride solutions (except copper), until total precipitation of the metal ions. The precipitates were washed with distilled water until elimination of chloride ions (qualitative test with $AgNO_3/HNO_3$ solution) and maintained in aqueous suspension.

Solid state Mn (II), Co (II), Ni (II) and Zn (II) compounds were prepared by mixing the respective metal carbonates with 2-methoxybenzoic acid 99% (2-MeO-HBz) obtained from Aldrich, in slight excess. The aqueous suspension was heated slowly up to near ebullition, until total neutralization of the respective carbonates. The resulting solutions after cooled were maintained in an ice bath to recrystallize the acid in excess and filtered through a Whatman nº 40 filter paper. Thus, the aqueous solutions of the respective metal 2-methoxybenzoates were evaporated in a water bath until near dryness and kept in a desiccator over calcium chloride.

The copper compound due to its low solubility was prepared by adding slowly, with continuous stirring, the aqueous solution of Na-2-MeO-Bz 0.1 mol L^{-1} to the respective metal sulphate solution, until total precipitation of the metal ions. The precipitate was washed with distilled water until elimination of the sulphate ion, filtered through and dried on Whatman nº42 filter paper, and kept in a desiccator over anhydrous calcium chloride, under reduced pressure to constant mass.

In the solid-state compounds, metal ions, hydration water and 2-methoxybenzoate contents were determined from TG curves. The metal ions were also determined by complexometry with standard EDTA solution [27] 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 Cu Kα radiation (lλ= 1.541 Å) and setting of 40 kV and 20 mA.

Infrared spectra for sodium 2-methoxybenzoate 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 and TG/DTG curves were obtained with thermal analysis system model SDT 2960 from TA Instruments. The purge gas was an air flow of 100 mL min^{-1}. A heating rate of 20 ºC min^{-1} was adopted with samples weighing about 7 mg. Platinum crucibles were used for TG-DTA.

DSC curves were obtained with thermal analysis systems model DSC 25 from Mettler Toledo. The purge gas was an air flow of 100 mL min^{-1}. A heating rate of 20 ºC min^{-1} was adopted with samples weighing about 5 mg. Aluminium crucibles, with perforated cover, were used for DSC.

Results and discussion

The TG-DTA curves, infrared spectra and chemical analysis of the compounds synthesized through the reaction of the metal carbonates with 2-methoxybenzoic acid (2-MeO-HBz) permitted to verify that the binary compounds were obtained contaminated with 2-MeO-HBz. The contamination must be due to aggregation phenomenon, and that the procedure used to eliminate the acid in excess was not efficient, probably because the 2-MeO-Bz

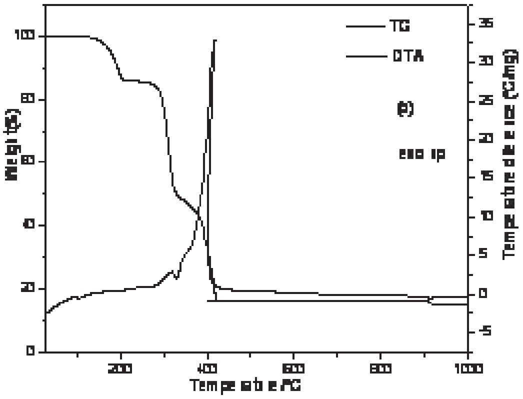


Figure 1. TG-DTA curves of cobalt compound.

must be more soluble in 2-methoxibenzoate solution and it no recrystallize, even in an ice bath. However, the TG-DTA curves, showed that the elimination of 2-MeO-HBz occurs up to 200 ºC, without thermal event corresponding to this loss and before the thermal decomposition of these compounds.

The TG-DTA curves of cobalt compound, as representative of these compounds, are shown in Fig. 1. Thus, these compounds were heated up to 200 ºC, and the manganese, cobalt, nickel and zinc 2-methoxybenzoate were obtained. The analytical and thermoanalytical (TG) data for the synthesized compounds are shown in Table 1. These results establish the stoichiometry of these compounds, which are in agreement with the general formula $M(2\text{-MeO-Bz})_2$, where M represents Mn, Co, Ni and Zn, 2-MeO-Bz is 2-methoxybenzoate or $Cu(2\text{-MeO-Bz})_2.H_2O$.

Table 1: Spectroscopic data for sodium 2-metoxybenzoate (2-MeO-Bz) and compounds with some bivalent metal ions [a] (cm^{-1})

Compound	$\nu_{(O-H)}H_2O$ [b]	$\nu_{sym\,(COO^-)}$ [c]	$\nu_{asym\,(COO^-)}$ [c]	$\Delta\nu$ [d]
Na(2-MeOBz)	-	1399_s	1595_s	196
$Mn(2\text{-MeOBz})_2$	-	1380_s	1619_s	239
$Co(2\text{-MeOBz})_2$	-	1373_m	1619_s	246
$Ni(2\text{-MeOBz})_2$.	-	1379_s	1625_s	246
$Cu(2\text{-MeOBz})_2.1H_2O$	3452_{br}	1394_s	1607_s	213
$Zn(2\text{-MeOBz})_2$	-	1412_s	1618_s	206

[a] br, broad; w, weak; m, medium; s, strong;

[b] $\nu_{(O-H)}$: hydroxyl group stretching frequency;

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

[d] $\Delta\nu = \nu_{asym\,(COO^-)} - \nu_{sym\,(COO^-)}$

The X- ray powder diffraction patterns, Fig. 2, show that all the compounds tend towards a crystalline structure with, except for the copper compound, evidence for formation of isomorphous ones.

Infrared spectroscopic data on 2-methoxybenzoate and its compounds with the metal ions considered in this work are shown in Table 2. The investigation was focused mainly in the 1700 – 1400 cm^{-1} range, because this region is potentially most informative to assign coordination sites. In the sodium–2–methoxybenzoate, the strong bands at 1595 and 1399 cm^{-1} are attributed to the anti–symmetrical and symmetrical stretching frequencies of the carboxylate group, respectively [28]. For the synthesized compounds, the anti-symetrical and symetrical stretching frequencies are located between 1625-1607 cm^{-1} and 1394-1373 cm^{-1}, respectively. These results show that the anti-symetrical and symetrical carboxylate stretching vibrations are shifted to higher and to slightly lower frequencies, respectively, when compared with the sodium salt, suggesting that the carboxylate group is acting as unidentate bonded to the metal ion.

Simultaneous TG-DTA and TG/DTG curves of the compounds are shown in Fig.3. These curves show mass losses in consecutive and/or overlapping steps with partial losses wich are characteristic for each compound.

For the copper compound the TG-DTA curves, Fig. 3(d) show that the thermal decomposition occurs in three steps between 110 and 349 ºC although the DTG curve shows four

Compound	Metal Oxide (%)			Δ (2-MeO-Bz) (%)		H_2O (%)		Final Residue
	Calcd.	TG	EDTA	Calcd.	TG	Calcd.	TG	
$Mn(2\text{-}MeO\text{-}Bz)_2$	15.38	15.62	15.50	78.65	78.31	-	-	Mn_3O_4
$Co(2\text{-}MeO\text{-}Bz)_2$	16.31	15.96	16.31	77.78	78.03	-	-	CoO
$Ni(2\text{-}MeO\text{-}Bz)_2$	16.25	16.45	16.17	79.31	78.85	-	-	NiO
$Cu(2\text{-}MeO\text{-}Bz)_2.1\ H_2O$	16.55	16.57	16.20	79.28	79.26	4.69	4.67	CuO
$Zn(2\text{-}MeO\text{-}Bz)_2$	17.78	17.97	17.45	77.87	77.63	-	-	ZnO

Key: 2-MeO-Bz = 2-methoxybenzoate

Table 2: Analytical and thermoanalytical (TG) data of the compounds.

steps, being the two last overlapping ones. The first mass loss observed up to 150 ºC, corresponding to the endothermic peak at 140 ºC is due to dehydration with loss of 1 H_2O (Calcd= 4.69%; TG= 4.67%). The anhydrous compounds is stable up to 220 ºC and above this temperature the thermal decomposition occurs in two steps between 220-270 ºC and 270-349 ºC with loss of 29.60 % and 45.00% , respectively, corresponding to the endothermic peak at 226 ºC, followed by an exothermic one at 246 ºC attributed to the thermal decomposition and oxidation reaction and the exothermic peak at 349 ºC attributed to the oxidation and combustion of the organic matter. The total mass loss up to 349 ºC is agreement with formation of copper oxide, CuO, as final residue (Calcd= 79.28%; TG= 79.26%).

For the manganese and cobalt compounds the TG-DTA and TG/DTG curves, Fig. 3(a, b), show mass losses in two consecutive steps and exothermic peaks corresponding to these losses. The first step that occurs between 230-330 ºC (Mn) and 260-350 ºC (Co) with loss of 38.60% (Mn) and 42.02% (Co), corresponding to exothermic peaks at 309 ºC and 340 ºC, respectively, is attributed to the partial thermal decomposition of these compounds. In this step the DTA curve suggests that the endothermic and exothermic events occur simultaneously, prevailing a small endothermic peak, since the mass loss in the first step is slightly smaller (Mn) or greater (Co) than the observed for the second step. The second step observed between 330-415 ºC (Mn) and 350-420 ºC (Co), corresponding to the exothermic peaks at 415 ºC and 420 ºC, respectively, is attributed to the final thermal decomposition. The TG-DTA and TG/DTG profiles in this step show that the oxidation of the organic matter occurs with combustion. The total mass loss up to 415 ºC (Mn) and 420 ºC (Co) is in agreement with the formation of Mn_3O_4 (Calcd= 78.65%; TG= 78.31%) and Co_3O_4 (Calcd= 77.78%;

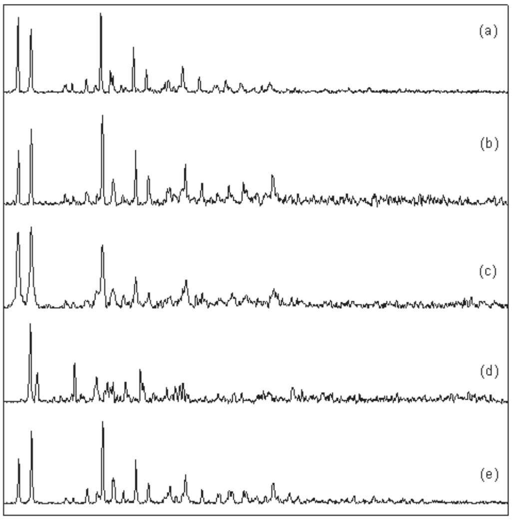


Figure 2. X-ray powder diffraction patterns of the compounds: (a)$Mn(2\text{-}MeOBz)_2$, (b)$Co(2\text{-}MeO\text{-}Bz)_2$, (c)$Ni(2\text{-}MeO\text{-}Bz)_2$, (d)$Cu(2\text{-}MeO\text{-}Bz).1H_2O$ and (e)$Zn(2\text{-}MeO\text{-}Bz)_2$. 2-MeO-Bz = 2-metoxybenzoate.

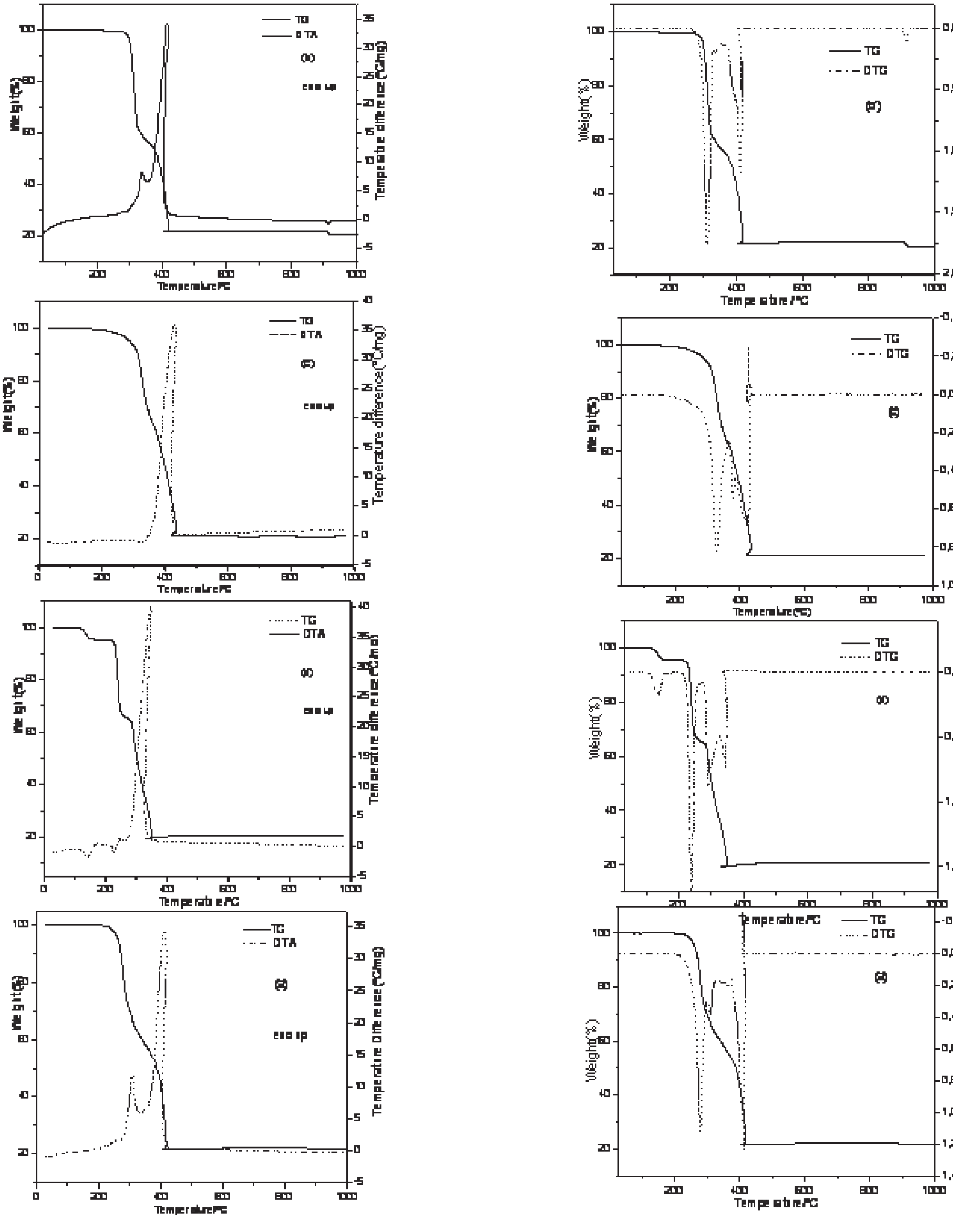
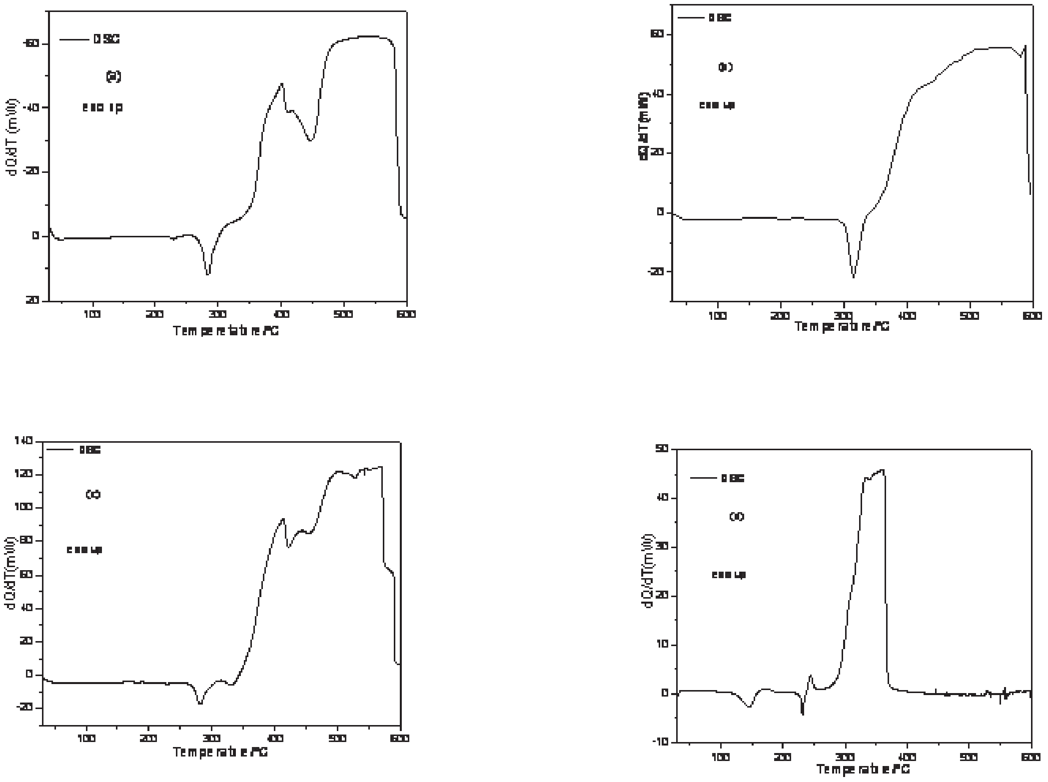
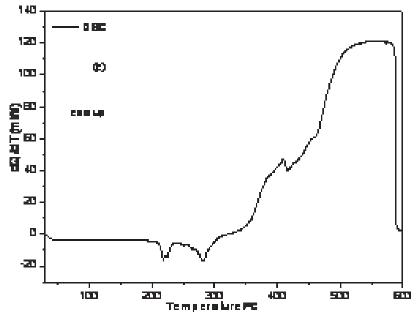


Figure 3. TG-DTA and TG/DTG curves of: (a) Mn(2-MeO-Bz)$_2$ (7,860 mg), (b) Co(2-MeO-Bz)$_2$ (7,760 mg), (c) Ni(2-MeO-Bz)$_2$ (7,538 mg), (d) Cu(2-MeO-Bz)$_2$.1H$_2$O (7,290 mg) and (e)Zn(2-MeO-Bz)$_2$ (7,090mg). 2-MeO-Bz =2-metoxybenzoate.

Figure 4. DSC curves of: (a) Mn(2-MeO-Bz)$_2$ (5.239 mg), (b) Co(2-MeO-Bz)$_2$ (5.100 mg), (c) Ni(2-MeO-Bz)$_2$ (5.430 mg), (d) Cu(2-MeO-Bz)$_2$.1H$_2$O (1.0490 mg) and (e) Zn(2-MeO-Bz)$_2$ (5.366 mg). 2-MeO-Bz =2-metoxybenzoate.





TG= 78.03%), as final residue. For the cobalt compound the mass loss observed between 900-930 ºC, corresponding to the endothermic peak at 915 ºC is due to the reduction of the Co_3O_4 to CoO (Calcd= 1.47%; TG= 1.45%) and in agreement with the literature [29].

For the nickel and zinc compounds, the TG-DTA and TG/DTG curves are shown in Fig.3 (c, e). Although the DTG curves show mass losses in several steps, the TG curves suggest two consecutive steps, the first mass loss observed between 220-340 ºC (Ni) and 220-280 ºC (Zn) with loss of 39.40% and 31.18%, respectively, is attributed to the partial thermal decomposition of these compounds. In this step no thermal event is observed in the DTA curve, probably due to the balance between an endothermic process (thermal decomposition) and an exothermic one (oxidation of organic matter).

The second mass loss that occurs between 340-430 ºC (Ni) and 280–490 ºC (Zn), corresponding to the exothermic peak at 429 ºC and 459 ºC with shoulder at 470 ºC, respectively, is attributed to the final thermal decomposition. The TG-DTA and TG/DTG profiles in this step also show that the oxidation of the organic matter occurs with combustion. The total mass loss up to 430 ºC (Ni) and 490 ºC (Zn) is in agreement with the formation of NiO (Calcd= 79.31%; TG= 78.85%) and ZnO (Calcd= 77.87%; TG= 77.63 %) as final residue. For the zinc compound the two overlapped endothermic peaks at 216 ºC and 223 ºC is attributed to fusion and elimination of the methoxy group, respectively.

The DSC curves of the compounds are shown in Fig. 4. Theses curves show endothermic and exothermic peaks or exotherm corresponding to the mass losses observed in TG curves.

For the copper compound the DSC curve, fig. 4(d) shows an endothermic peak at 145 ºC, attributed to the dehydration and in agreement with the DTA curve. The two small endothermic and exothermic peaks at 232 ºC and 245 ºC, respectively, are attributed to partial thermal decomposition, corresponding to the first mass loss of the anhydrous compound. The exotherm between 280 and 370 ºC is ascribed to the final thermal decomposition corresponding to the last mass loss of TG curve.

For the manganese, cobalt, nickel and zinc compounds, the DSC curves, Fig. 4 (a, b, c, e) show an endothermic peaks at 283 ºC, 315 ºC, 282 ºC and 280 ºC, respectively, attributed to the partial thermal decomposition, corresponding to the first mass loss of the TG curves. The exothermic events above 350 ºC (Mn, Ni) and 360 ºC (Co, Zn) are ascribed to the final thermal decomposition of these compounds, corresponding to the last mass loss of the TG curves.

The differences concerning the thermal events obtained by DTA and DSC are undoubtedly due to the perforated cover to obtain the DSC curves, while the TG-DTA ones are obtained without cover.

Conclusions

The TG-DTA curves, infrared spectra and chemical analysis, showed that the binary compounds synthesized by the reaction of metallic carbonate with 2-methoxybenzoic acid, were obtained with contamination.

The DTG-DTA, also showed that the 2-MeO-HBz is eliminated before the thermal decomposition of these compounds. Thus binary compounds would be obtained by thermosynthesis.

The X-ray powder patterns pointed out that the synthesized compounds have a crystalline structure, with except for the copper one, evidence concerning the formation of isomorphous compounds.

The infrared spectroscopy data suggest that in the compounds considered in this work, the carboxylate group is acting as unidentate in its bonding to the metal ion.

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

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C.T. Carvalho, A. B. Siqueira, E. C. Rodrigues, M. Ionashiro. Síntese, caracterização e comportamento térmico dos 2-metoxibenzoatos de alguns íons metálicos bivalentes de transição, no estado sólido.

Resumo: compostos M-2-MeO-Bz foram sintetizados no estado sólido, onde M representa os íons bivalentes Mn, Co, Ni, Cu e Zn e 2-MeO-Bz é o anion 2-metoxibenzoato. Esses compostos foram caracterizados e estudados, utilizando-se técnicas de difração de raios X pelo método do pó, espectroscopia na região do infravermelho, complexometria e analise térmica diferencial simultânea (TG-DTA), thermogravimetry, derivative thermogravimetry (TG/DTG) e calorimetria exploratória diferencial (DSC). Os resultados permitiram obter informações com respeito a estequiometria, desidratação, estabilidade térmica e decomposição térmica.

Palavras-chave: metais de transição bivalente; 2-metoxibenzoato; comportamento térmico.

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