

Synthesis, characterization and thermal behaviour of solid state compounds of 4-methoxybenzoate with Manganese, Nickel and Copper.

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Abstract: Solid state M-L compounds, where M stands for bivalent Mn, Ni, Cu and L is 4-methoxybenzoate, have been synthesized. Simultaneous thermogravimetry – differential thermal analysis (TG-DTA), 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 thermal decomposition of the isolated compounds.

Keywords: Mn, Ni, Cu, 4-methoxybenzoate, thermal behaviour

Introduction

Several metal-ion salts of benzoic acid, as well as benzoic acid derivatives, have been reported. Wendlandt synthesized thorium salts with several organic acids, including 4-methoxybenzoic acid [1], benzoic and m-hydroxybenzoic acids [2], and studied the thermal stability and the thermal decomposition of these compounds. Glowiac and co-workers [3] studied the reaction of bivalents copper, cobalt and nickel with 3-hydroxy-4-methoxy and 3-methoxy-4-hydroxybenzoic acids. Brzyska and Karasinski [4] studied the thermal decomposition of thorium salts of benzoic and 4-methoxybenzoic acids in air atmosphere. The complexation of trivalent lanthanides cations with various aromatic monocarboxylate ligands has also been described [5-7].

In this study, solid state compounds of bivalent manganese, nickel and copper with 4-methoxybenzoate were prepared. These compounds were characterized and studied by complexometric titration, simultaneous TG-DTA, X-ray powder diffractometry, infrared spectroscopy and elemental analysis. The data obtained allowed us to acquire new information concerning these compounds in

the solid state, including their thermal stability and thermal decomposition.

Experimental

The 4-methoxybenzoic acid (98%) was obtained from Acros organics and used without further purification. The hydrated basic carbonates of Mn (II), Ni (II) and Cu (II) were prepared by adding slowly with continuous stirring, saturated sodium carbonate solution to the corresponding metal chloride solutions, until complete precipitation of the metal ions; except for copper, where the sulphate was used. The precipitates were washed with distilled water until elimination of chloride or sulphate ions. (negative tests with $\text{AgNO}_3/\text{HNO}_3$ or BaCl_2 solutions).

Solid state Mn (II), Ni (II) and Cu (II) compounds were prepared by neutralizing the corresponding aqueous suspensions of hydrated basic carbonates with 4-methoxybenzoic acid in excess. The suspensions were heated slowly up to ebullition, until total neutralization of the respective basic carbonates. The resulting solutions after cooled were maintained in an ice bath to precipitated the acid in excess. Thus, the suspensions were filtered

through a Whatman n° 40 filter paper and the filtered evaporated in a water bath until near dryness and kept in a desiccator over anhydrous calcium chloride.

In the solid state compounds, metal ion, water and 4-methoxybenzoate contents were determined from the TG curves. The metal ions were also determined by complexometry with standard EDTA solution [8, 9] after igniting the compounds of the respective oxides and their dissolution in hydrochloric acid. Carbon and hydrogen contents were determined by microanalytical procedures, with an EA 1110 CHNS-O Elemental Analyzer from CE Instruments.

X-ray powder patterns were obtained with a SIEMENS D-5000 X-ray diffractometer using Cu K α radiation ($\lambda = 1.544 \text{ \AA}$) and setting of 40 kV and 20 mA.

Infrared spectra for sodium 4-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 curves were obtained with thermal analysis system model SDT 2960 from TA instruments. The purge gas was an air flow of 150 mL min^{-1} . A heating rate of 10 $^{\circ}\text{C min}^{-1}$ was adopted with samples weighing about 7 mg. Alumina crucible was used for TG-DTA.

Results and discussion

The analytical data are shown in Table 1. This results establish the stoichiometry of these compounds, which are in a agreement with the general formula $\text{ML}_2 \cdot n\text{H}_2\text{O}$, where M represents Mn (II), Ni (II) or Cu (II), L is 4-methoxybenzoate and $n = 2, 3.5$ and 3 respectively. The X-ray diffraction powder patterns (Fig.1) show that all the compounds have a crystalline structure, without evidence for formation of an isomorphous series.

Table 1. Analytical data for the $\text{ML}_2 \cdot n\text{H}_2\text{O}$ compounds

Compounds	M (%)		L (lost) (%)		H ₂ O (%)		C (%)		H (%)		Final Residue	
	Calcd	EDTA	TG	Calcd	TG	Calcd	TG	Calcd	EA	Calcd		EA
Mn(L) ₂ ·2H ₂ O	13.97	13.79	14.18	71.44	71.08	9.16	9.28	48.86	48.54	4.62	4.85	Mn ₃ O ₄
Ni(L) ₂ ·3.5 H ₂ O	13.84	13.90	13.76	67.51	67.60	14.87	14.89	45.31	46.04	5.00	5.12	NiO
Cu(L) ₂ ·3H ₂ O	15.13	14.88	15.21	68.18	68.08	12.87	12.99	45.76	45.52	4.81	5.02	CuO

L = 4-methoxybenzoate

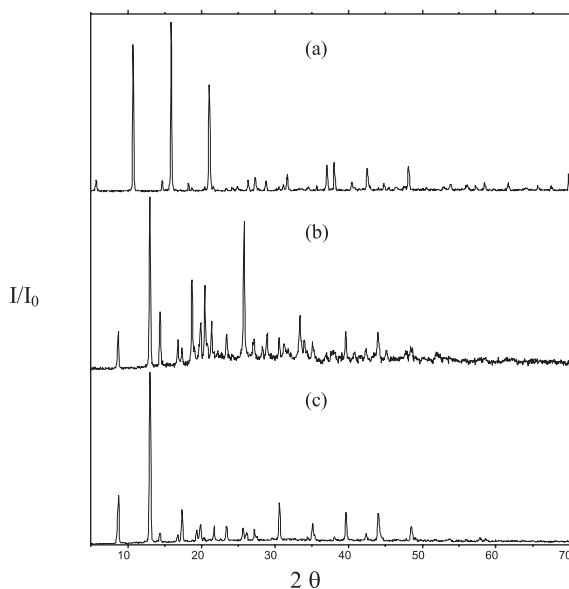


Figure 1. X-ray powder diffraction patterns of the compounds: (a) $\text{Mn(L)}_2 \cdot 2\text{H}_2\text{O}$, (b) $\text{Ni(L)}_2 \cdot 3.5\text{H}_2\text{O}$ and (c) $\text{Cu(L)}_2 \cdot 3\text{H}_2\text{O}$. (L=4-methoxybenzoate).

Infrared spectroscopic data on 4-methoxybenzoate and its compounds with the metal ions considered in this work are shown in table 2. The investigation was focused mainly within the 1700 – 1400 cm⁻¹ range because this region is potentially most informative to assign coordination sites. In sodium 4-methoxybenzoate, strong band at 1543 cm⁻¹ and a medium intensity band located at 1416 cm⁻¹ are attributed to the anti-symmetrical and

symmetrical frequencies of the carboxylate groups, respectively [10,11]. The manganese, nickel and copper compounds, presented practically the same symmetrical and anti-symmetrical vibrations of the COO⁻ groups, and with the DN very mean when compared with the sodium salt, indicating that compounds have ionic character. The DN values also indicate a decrease of the ionic character with the increase of the atomic number of these metal ions.

Table 2. Spectroscopy data for sodium 4-methoxybenzoate and compounds with manganese, nickel and copper.^(c); ^av as and N sym = anti-symmetrical and symmetrical vibrations of the COO⁻ group, respectively.; ^b Δv = N as - N sym; ^c s = strong; m = medium

Compound	v as (COO ⁻) ^a (cm ⁻¹)	v sym (COO ⁻) ^a (cm ⁻¹)	Δv ^b
Na.4.MeO.Bz	1543 _s	1416 _m	127
Mn (4.MeO.Bz) ₂	1533 _s	1408 _m	125
Ni (4.MeO.Bz) ₂	1547 _s	1439 _m	108
Cu (4.MeO.Bz) ₂	1531 _s	1435 _m	96

Simultaneous TG-DTA curves of the compounds are shown in Figs. 2 - 4. These curves show mass losses in steps, corresponding to endothermic peaks due to dehydration and the exothermic peaks attributed to oxidation of the organic matter. In all the TG-DTA curves, the final mass loss profile shows that the sample temperature is greater than the oven temperature, indicating that the oxidation of the organic matter is accompanied by the combustion.

The thermal stability of the anhydrous compounds (I), as well the final temperature of thermal decomposition (II) as shown by the TG-DTA curves, depend on the nature of the metal ion, and they follow the order:



The thermal behaviour of the compounds is heavily dependent on the nature of the metal ion and so the features of each these compounds are discussed individually.

Manganese compound. The simultaneous TG-DTA curves are shown in Fig. 2. The first mass loss observed between 80 and 150°C, corresponding to an endothermic peak at 139°C is due to dehydration with loss of 2 H₂O (Calcd = 9.16%; TG = 9,28%). The thermal decomposition of the anhydrous compound occurs in two overlapping steps between 240 – 390°C, and 390 and 456°C, with losses of 32.70 and 38.38%, respectively, corresponding to the exothermic peak at 456°C, attributed to oxidation and combustion of the organic matter. The total mass loss up to 456°C, is in agreement with the formation of Mn₃O₄ as final residue (calcd. = 80.60%, TG. = 80.36%) and confirmed by X-ray powder diffractometry.

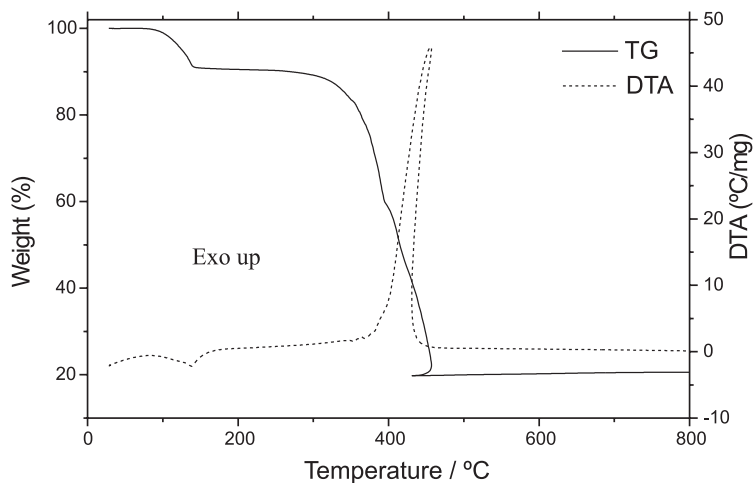


Figure 2. TG and DTA curves of the $\text{Mn}(\text{L})_2 \cdot 2\text{H}_2\text{O}$ (L=4-methoxybenzoate).

Nickel compound. The TG-DTA curves are shown in Fig. 3. The mass loss that occurs between 100 and 160°C, corresponding to the endothermic peak at 143°C, is due to dehydration with loss of 3.5 H_2O (Calcd. = 14.87%; TG = 14.89%). Immediately after the dehydration, the anhydrous compound shows mass loss that begins with a slow process (up to 320°C), followed by a fast process to give the oxide level beginning at 430°C, with losses of 5.60 and 62.00%, respectively, corresponding

to the exothermic event with two peaks at 410 and 415 °C, attributed to the oxidation and combustion of the organic matter. In both temperatures (410 and 415 °C), the anomaly observed in the TG-DTA curves is due to the combustion of the organic matter, where the sample temperature exceeded the oven one. The total mass loss up to 430°C, is in agreement with the formation of NiO as final residue (Calcd. = 82.38%; TG = 82.49%) and confirmed by X-ray powder diffractometry.

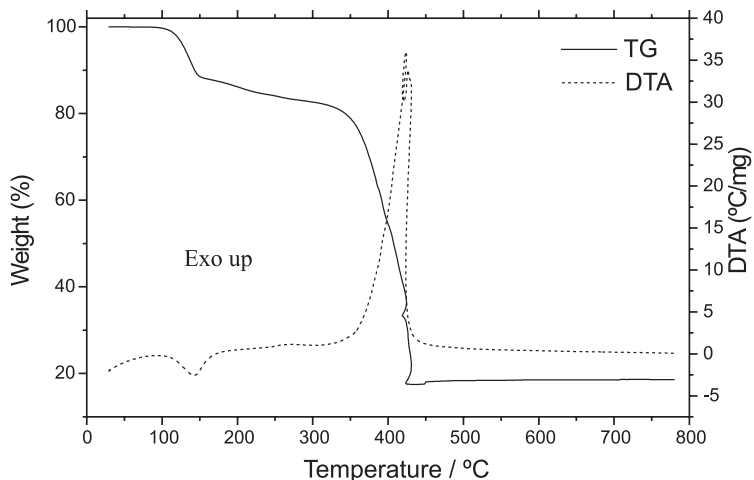


Figure 3. TG and DTA curves of the $\text{Ni}(\text{L})_2 \cdot 3.5\text{H}_2\text{O}$ (L=4-methoxybenzoate).

Copper compound. The TG-DTA curves are shown in Fig.4. The first mass loss observed between 70 and 120°C, corresponding to the endothermic peak is due to dehydration water with loss of 3 H₂O (Calcd. 12.87%; TG = 12.99%) the anhydrous compounds is stable up to 235°C, and above this temperature the thermal decomposition occurs in three overlapping steps with losses of 14.50% (235-262°C), 21.76% (262-

350°C) and 31.82% (350-415°C), corresponding to exothermic peaks at 278°C, 319°C and 415°C, respectively, attributed to the oxidation and for the last step, oxidation and combustion of the organic matter. The total mass loss up to 415°C is in agreement with the formation of CuO, as final residue (Calcd = 81.05%; TG=81.07%), and confirmed by X-ray powder diffractometry.

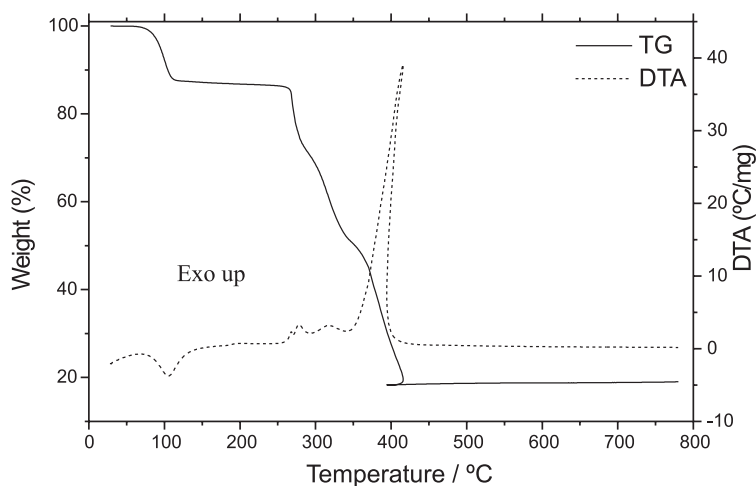


Figure 4. TG and DTA curves of the Cu(L)₂ · 3H₂O (L=4-methoxybenzoate).

Conclusions

From TG, complexometry and elemental analysis data, a general formula could be established for the binary compounds involving Mn (II), Ni (II) and Cu (II), and 4-methoxybenzoate.

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

The infrared spectroscopy data suggest that the 4-methoxybenzoate of manganese, nickel and copper are compound of ionic nature.

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

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E. C. Rodrigues, A. C. Vallejo, E. Y. Ionashiro, G. Banach, M. Ionashiro. Síntese, caracterização e comportamento térmico dos 4-metoxibenzoatos de manganês, níquel e cobre, no estado sólido.

Resumo: Compostos M–L foram sintetizados no estado sólido, onde M representa os íons bivalentes Mn, Ni, Cu e L é o ânion 4–metoxibenzoato. Esses compostos foram caracterizados e estudados, utilizando-se as técnicas de difração de raios x pelo método do pó, espectroscopia na região do infravermelho, análise elementar, complexometria e termogravimetria – análise térmica diferencial simultânea (TG – DTA). Os resultados permitiram obter informações com respeito à estequiometria, desidratação, estabilidade térmica e decomposição térmica.

Palavras-chave: Mn, Ni, Cu, 4–metoxibenzoato, comportamento térmico.

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