Journal of Thermal Analysis and Calorimetry, Vol. 79 (2005) 323–328

SYNTHESIS, CHARACTERIZATION AND THERMAL BEHAVIOUR OF SOLID-STATE COMPOUNDS OF 4-METHOXYBENZOATE WITH SOME BIVALENT TRANSITION METAL IONS

*E. C. Rodrigues, A. B. Siqueira, E. Y. Ionashiro, G. Bannach and M. Ionashiro**

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

Solid-state M-4-MeO-Bz compounds, where *M* stands for bivalent Mn, Co, Ni, Cu and Zn and 4-MeO-Bz is 4-methoxybenzoate, have been synthesized. Simultaneous thermogravimetry-differential thermal analysis (TG-DTA), differential scanning calorimetry (DSC), 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 have information about the composition, dehydration, thermal stability and thermal decomposition of the isolated compounds.

Keywords: *bivalent transition metals, 4-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 *et al.* [1] reported the thermodynamics of complexation of lanthanides by some benzoic acid derivatives. Wang *et al.* [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 *et al*. [4] reported the thermodynamic of complexation of lanthanides by benzoic and isophthalic acids. Lam *et al*. [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 *et al*. [8] reported the reaction of bivalent copper, cobalt and nickel with 3-hydroxy-4-methoxy and 3-methoxy-4-hydroxybenzoic 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] wrote about the synthesis and characterization of 2,3-dimethoxybenzoates of heavy lanthanides and yttrium using elemental analysis, IR spectroscopy, thermogravimetric studies and X-ray diffraction measurements. Ionashiro *et al*. [11, 12] reported the thermal studies on solid compounds of phenyl substituted derivatives of benzylidenepyruvates with several metal ions.

In the present paper, solid-state compounds of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with 4-methoxybenzoate were prepared and investigated using complexometric titration, elemental 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.

Experimental

The 4-methoxybenzoic acid (4-MeO-Bz) 98% was obtained from Acros organics and purified by recrystallization. Thus, aqueous suspension of 4-MeO-Bz was heated near ebullition until total dissolution and cooled to ambient temperature. The crystal in needle form was isolated and after kept in dry in a plastic flask. The hydrated basic carbonates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were prepared by adding slowly with continuous stirring satured sodium carbonate solution to the corresponding metal chloride solutions, sulphate for copper, until total precipitation of the metal ions. The precipitates were washed with distilled water until elim-

---

* Author for correspondence: massaoi@iq.unesp.br

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

ination of chloride or sulphate ions and maintained in an aqueous suspension.

Solid-state Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) compounds were prepared by mixing the corresponding metal basic carbonates with 4-methoxybenzoic acid, in slight excess. The aqueous suspension was heated slowly up to near ebullition, until total neutralization of the respective basic carbonates. The resulting solutions after cooling 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-4-methoxybenzoates were evaporated in a water bath until near dryness and kept in a desiccator over anhydrous calcium chloride. All attempts to synthesize the iron(II) compound were unsuccessful, due to the oxidation reaction of Fe(II) to Fe(III) during the drying of the compound, even by using nitrogen atmosphere.

In the solid-state compounds, metal ions, water and 4-methoxybenzoate contents were determined from TG curves. The metal ions were also determined by complexometry with standard EDTA solution [13, 14] after igniting the compounds of the respective oxides and their dissolution in hydrochloric acid solution. 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-500 X-ray diffractometer using CuK_α radiation (λ=1.544 Å) 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 and DSC curves were obtained with two thermal analysis systems models SDT 2960, and DSC 2010, both from TA instruments. The purge gas was an air flow of 150 mL min^{-1}. A heating rate of 20°C min^{-1} was adopted with samples weighing about 7 mg. Alumina and aluminium crucibles, the latter with perforated covers, were used for TG-DTA and DSC, respectively.

Results and discussion

The analytical data are shown in Table 1. These results establish the stoichiometry of these compounds, which are in agreement with the general formula $ML_2{\cdot}nH_2O$, where M represents Mn(II), Co(II), Ni(II), Cu(II) or Zn(II), L is 4-methoxybenzoate and n=2; 2; 3.5; 3 and 1.75, 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.

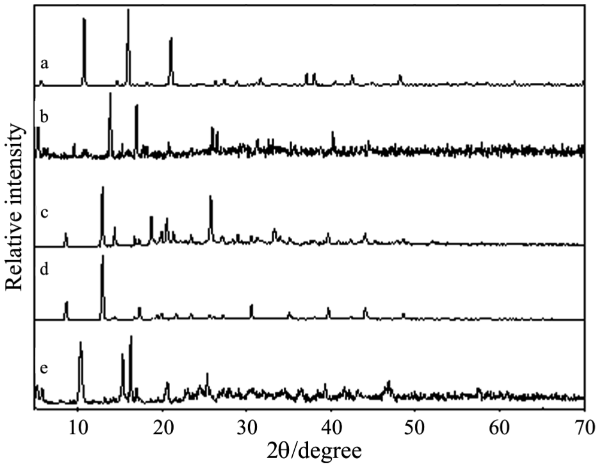

Fig. 1 X-ray powder diffraction patterns of the compounds: a – $MnL_2{\cdot}2H_2O$; b – $CoL_2{\cdot}2H_2O$; c – $NiL_2{\cdot}3.5H_2O$; d – $CuL_2{\cdot}3H_2O$; e – $ZnL_2{\cdot}1.75H_2O$

Infrared spectroscopic data on 4-methoxybenzoate and its compounds with the bivalent 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 inten-

Table 1 Analytical, thermoanalytical (TG) and elemental analysis data of the compounds, $ML_2{\cdot}nH_2O$

Compounds	Metal/%			L loss/%		Water/%		Carbon/%		Hydrogen/%		Residue[a]
	calcd	EDTA	TG	calcd	TG	calcd	TG	calcd	EA	calcd	EA	
$Mn(L)_2{\cdot}2H_2O$	13.97	13.79	14.18	71.44	71.08	9.16	9.28	48.86	48.54	4.62	4.85	Mn_3O_4[b]
	13.97	13.79	13.70	70.77	71.08	9.16	9.28	48.86	48.54	4.62	4.85	Mn_2O_3[b]
$Co(L)_2{\cdot}2H_2O$	14.83	15.20	14.52	70.73	71.08	9.07	9.08	48.37	48.77	4.58	4.38	Co_3O_4[c]
$Ni(L)_2{\cdot}3.5\ H_2O$	13.84	13.90	13.76	67.51	67.60	14.87	14.89	45.31	46.04	5.00	5.12	NiO
$Cu(L)_2{\cdot}3H_2O$	15.13	14.88	15.21	68.18	68.08	12.87	12.99	45.76	45.52	4.81	5.02	CuO
$Zn(L)_2{\cdot}1.75H_2O$	16.38	16.01	16.61	71.71	71.33	7.90	7.99	48.13	48.53	4.43	4.23	ZnO

L – means 4-methoxybenzoate

[a]all the residues was confirmed by X-ray powder diffractometry; [b]mixture of Mn_3O_4 and Mn_2O_3; [c]Co_3O_4 up to 800°C

Table 2 Spectroscopic data for sodium 4-methoxybenzoate and compounds with some bivalent metal ions. IR spectra/cm^{-1}

Compound	νOH(H_2O)	$\nu_{asym}COO^-$	$\nu_{sym}COO^-$
Na4MeO-Bz	3383 br	1543 s	1416 m
Mn(4MeO-Bz)$_2$·2H_2O	3472 br	1533 s	1408 s
Co(4MeO-Bz)$_2$·2H_2O	3179 br	1562 m	1421 m
Ni(4MeO-Bz)$_2$·3.5H_2O	3469 br	1547 s	1439 s
Cu(4MeO-Bz)$_2$·3H_2O	3167 br	1531 s	1435 s
Zn(4MeO-Bz)$_2$·1.75H_2O	3547 br	1560 m	1412 s

br – broad; m – medium; s – strong; 4MeO-Bz=4-methoxybenzoate; νOH=hydroxyl group stretching frequency; ν_{sym} COO^- and $\nu_{asym}COO^-$=symmetrical and anti-symmetrical vibrations of the COO^- structure.

sity band located at 1416 cm^{-1} are attributed to the anti-symmetrical and symmetrical frequencies of the carboxylate groups, respectively [15, 16]. The manganese, cobalt, nickel, copper and zinc compounds, presented practically the same symmetrical and anti-symmetrical vibrations of the COO^- groups, when compared with the sodium salt, suggesting that the compounds have ionic character. The data displayed in Table 2 show that these shifts are dependent on the metal ions and the magnitudes of the shifts do not follow the well-known Irving–Williams series.

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 as 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:

(I) Mn≈Zn>Cu>Co>Ni

(II) Zn>Co>Mn>Ni>Cu

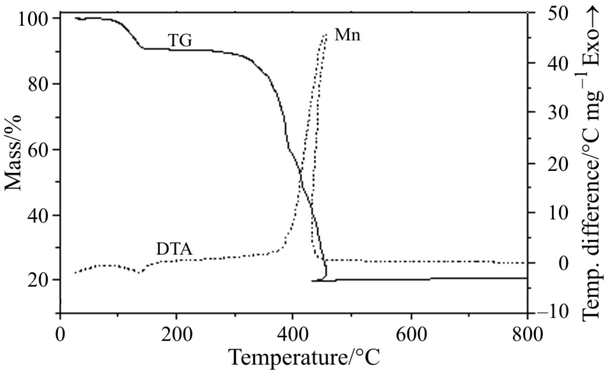

Fig. 2 TG-DTA curves of $MnL_2·2H_2O$ (L=4-methoxybenzoate) m=7.1425 mg

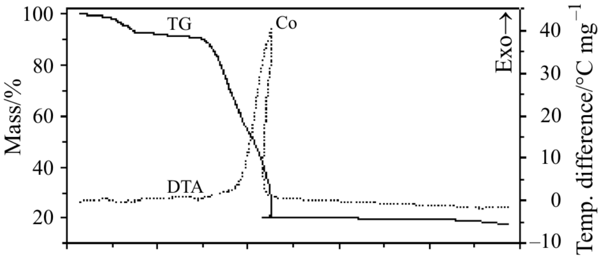

Fig. 3 TG-DTA curves of the $Co(L)_2·2H_2O$ (L=4-methoxybenzoate) m=7.1170 mg

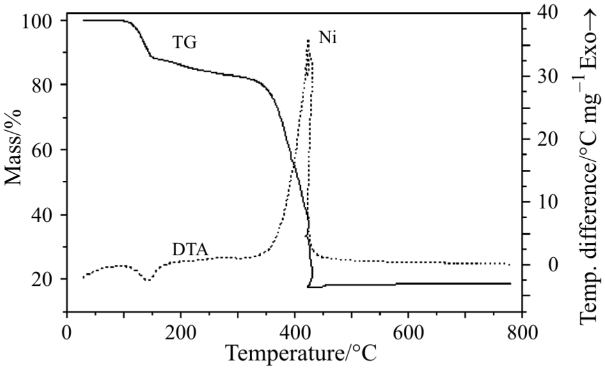

Fig. 4 TG-DTA of $NiL_2·3.5H_2O$ (L=4-methoxybenzoate) m=7.0521 mg

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

Manganese compound

The simultaneous TG-DTA curves are shown in Fig. 2. These curves show mass losses in three steps between 80 and 456°C and thermal events corresponding to these losses. The first mass loss observed between 80 and 150ºC, corresponding to an endothermic peak at 139ºC is due to dehydration with loss of 2H_2O (calcd.=9.16%;

TG=9.28%). The thermal decomposition of the anhydrous compound occurs in two overlapping steps between 240–390°C, and 390–456°C, with losses of 32.70% and 38.38%, respectively, corresponding to the exothermic peak at 456°C. The profiles of the TG and DTA curves, in these steps show that the oxidation of the organic matter is accompanied by combustion. The total mass loss up to 456ºC is in agreement with the formation of Mn_3O_4 or Mn_2O_3 as final residue (calcd.=80.60% – Mn_3O_4, 79.93% – Mn_2O_3; TG=80.36%). The X-ray powder diffractometry showed that the final residue of the thermal decomposition is a mixture of Mn_3O_4 and Mn_2O_3.

Cobalt compound

The TG-DTA curves are shown in Fig. 3. The mass loss observed between 30 and 170°C corresponding to endothermic peaks at 120 and 160°C is due to dehydration that occurs in two steps, with loss of $1H_2O$ in each step (calcd.=9.07%; TG=9.08%). After dehydration, the thermal decomposition of the anhydrous compound occurs in a single step between 170 and 460°C, with loss of 71.08%, corresponding to exothermic peak at 455°C, attributed to oxidation and combustion of the organic substance. The total mass loss up to 460°C is in agreement with the formation of Co_3O_4, as final residue (calcd.=79.82%; TG=80.16%) and confirmed by X-ray powder diffractometry. The small endothermic peak at 290°C is attributed to the fusion of the compound. The last mass loss that occurs between 900 and 930°C corresponding to the endothermic peak at 920°C, is attributed to reduction of Co_3O_4 to CoO, as already observed during the thermal decomposition of the cobalt 4-methylbenzylidenepyruvate [17].

Nickel compound

The TG-DTA curves are shown in Fig. 4. The mass loss that occurs between 100 and 160ºC, corresponding to the endothermic peak at 143ºC, is due to dehydration with loss of $3.5H_2O$ (calcd.=14.87%; TG=14.89%). Immediately after the dehydration, the anhydrous compound shows mass loss that begins with a slow process (up to 320ºC), 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 exceed the oven's 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.

Copper compound

The TG-DTA curves are shown in Fig. 5. These curves show mass losses in four steps between 70 and 415°C and thermal events corresponding to these losses. The first mass loss observed between 70 and 120°C, corresponding to the endothermic peak at 105°C is due to dehydration with loss of $3H_2O$ (calcd.=12.87%; TG=12.99%). The anhydrous compound is stable up to 235ºC, and above this temperature the thermal decomposition occurs in three 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 of the organic matter and for the last step oxidation and combustion of the carbonaceous material. 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.

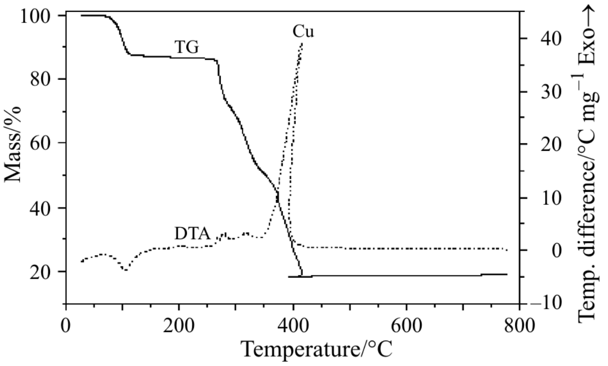

Fig. 5 TG-DTA curves of the $Cu(L)_2 \cdot 3H_2O$ (*L*=4-methoxybenzoate) *m*=7.0498 mg

Zinc compound

The TG-DTA curves are shown in Fig. 6. The mass loss observed between 100 and 200°C, corresponding to the endothermic peaks at 120 and 180°C is attributed to dehydration with loss of 0.75 and $1H_2O$, respectively (calcd.=7.90%; TG=7.99%). After dehydration the anhydrous compound shows mass loss in two overlapping steps with losses of 17.58% (240–350°C) and 53.75% (350–470°C), corresponding to exothermic peak at 335 and 450°C, attributed to oxidation of organic matter and oxidation followed by combustion of the carbonaceous residue, respectively. The total mass loss up to 470°C is in agreement with the formation of ZnO, as final residue (calcd.=79.61%; TG=79.32%).

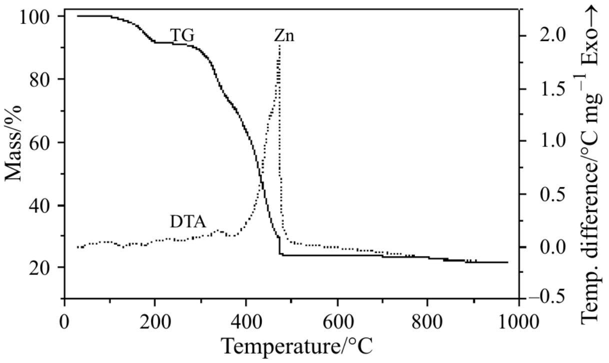

Fig. 6 TG-DTA curves of the $ZnL_2\cdot 1.75\ H_2O$ (L=4-methoxybenzoate) m=7.2888 mg

The temperature range and the percentage mass loss observed in each step of the thermal decomposition are shown in Table 3.

The DSC curves of the compounds are shown in Fig. 7 These curves show endothermic and exothermic peaks that all accord with the mass losses observed in TG curves. The endothermic peaks are in the range 110–160°C (Mn); 105–140 and 140–170°C (Co); 110–180°C (Ni); 85–150°C (Cu) and 105–150 and 150–195°C (Zn) is ascribed to dehydration. The dehydration enthalpies found were: 111.2 kJ mol^{-1} (Mn); 16.3 kJ and 20.9 kJ mol^{-1} (Co); 144.7 kJ mol^{-1} (Ni); 118.3 kJ mol^{-1} (Cu); 10.4 kJ and 8.8 kJ mol^{-1} (Zn).

The endothermic peaks observed only for cobalt, nickel and zinc compounds are in the temperature range of 275–305, 340–365 and 250–280°C, are ascribed to

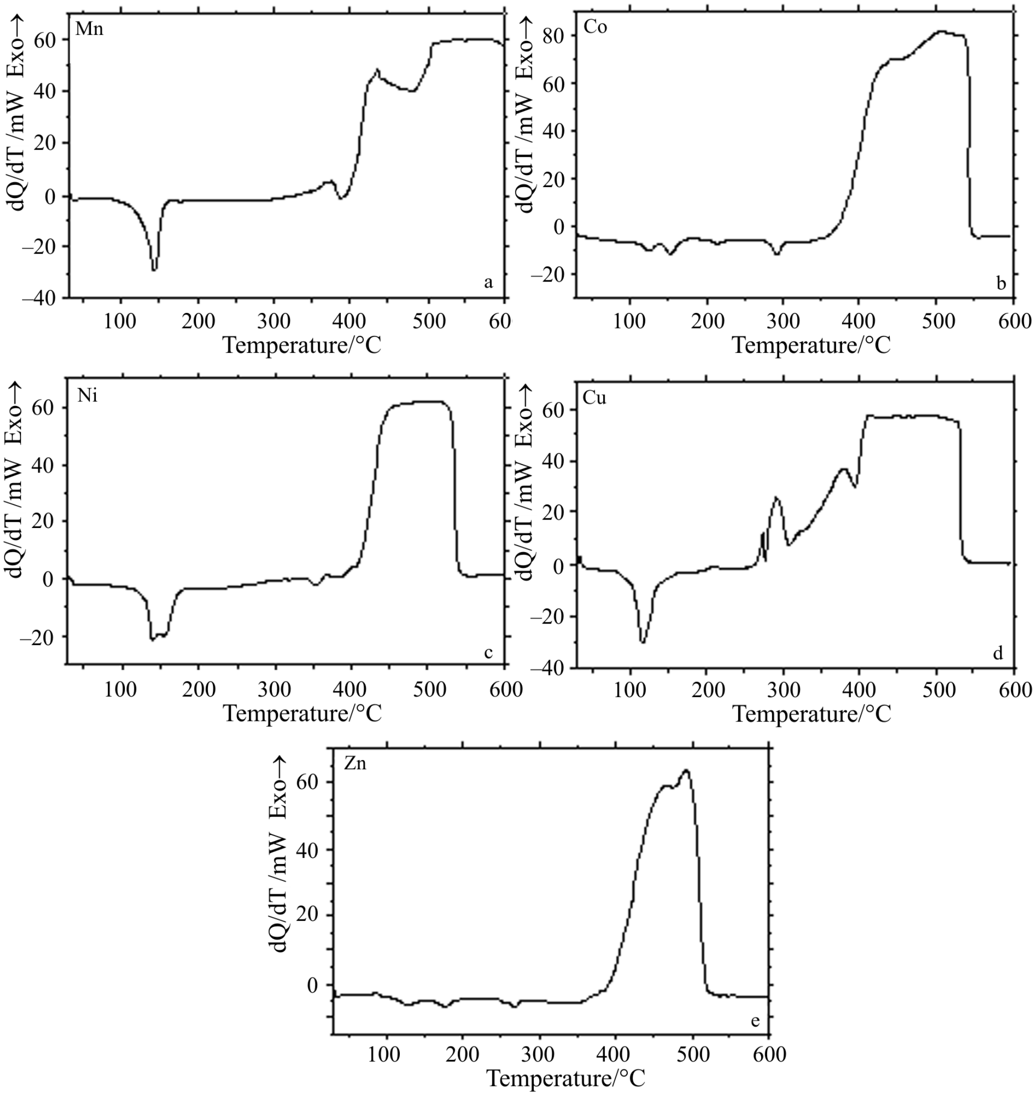

Fig. 7 DSC curves of the compounds: a – $MnL_2\cdot 2H_2O$ (5.4 mg); b – $CoL_2\cdot 2H_2O$ (4.8 mg); c – $NiL_2\cdot 3.5H_2O$ (5.3 mg); d – $CuL_2\cdot 3H_2O$ (5.6 mg) and e – $ZnL_2\cdot 1.75H_2O$ (4.5 mg)

Table 3 Temperature ranges (ΔT), mass losses (%) and peak temperatures observed for each step of the TG-DTA curves of the compounds, $ML_2\cdot nH_2O$, where M=metal and L=4–methoxybenzoate

Compound		Steps				
		First	Second	Third	Fourth	Fusion
$MnL_2\cdot 2H_2O$	ΔT/°C	80–150	240–390	390–456	–	–
	Loss/%	9.28	32.70	38.38	–	–
	Peak/°C	139 (endo)	–	456 (exo)	–	–
$CoL_2\cdot 2H_2O$	ΔT/°C	30–170	170–460	–	–	–
	Loss/%	9.08	71.08	–	–	–
	Peak/°C	120, 160 (endo)	455 (exo)	–	–	290 (endo)
$NiL_2\cdot 3.5H_2O$	ΔT/°C	100–160	160–320	320–430	–	–
	Loss/%	14.89	5.60	62.00	–	–
	Peak/°C	143 (endo)	–	410, 415 (exo)	–	–
$CuL_2\cdot 3H_2O$	ΔT/°C	70–120	235–262	262–350	350–415	–
	Loss/%	12.99	14.50	21.76	31.82	–
	Peak/°C	105 (endo)	278 (exo)	319 (exo)	415 (exo)	–
$ZnL_2\cdot 1.75H_2O$	ΔT/°C	100–200	240–350	350–470	–	–
	Loss/%	7.99	17.58	53.75	–	–
	Peak/°C	120, 180 (endo)	335 (exo)	450 (exo)	–	270 (endo)

the fusion of the compound the corresponding enthalpies are: 20.5, 17.8, and 8.1 kJ mol^{-1}, respectively. The exothermic peaks observed above 350°C (Mn, Co, Zn); 390°C (Ni) and 260°C (Cu), are attributed to the thermal decomposition of the anhydrous compounds, where the oxidation of the organic matter takes place in consecutive and/or overlapping steps.

Conclusions

From TG, complexometric titration and elemental analysis data, a general formula could be established for the binary compounds involving Mn(II), Co(II), Ni(II), Cu(II) and Zn(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 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.

Acknowledgements

The authors thank FAPESP (Proc. 97/12646-8), CNPq and CAPES foundations (Brazil) for financial support.

References

1 S. J. Yun, S. K. Kang and S. S. Yun, Thermochim. Acta, 331 (1999) 13.
2 Z. M. Wang, L. J. van de Burgt and G. R. Choppin, Inorg. Chim. Acta, 293 (1999) 167.
3 N. Arnaud and J. Georges, Analyst, 125 (2000) 1487.
4 G. R. Choppin, P. A. Bertrand, Y. Hasegawa and N. Rizalla, Inorg. Chem., 21 (1982) 3722.
5 A. W. H. Lam, W. T. Wang, S. Gao, G. Wen and X. X. Zhang, Eur. J. Inorg. Chem., (2003) 149.
6 W. W. Wendlandt, Anal. Chem., 17 (1957) 295.
7 W. W. Wendlandt, Anal. Chem., 29 (1957) 800.
8 T. Glowiak, H. Kozlowski, L. Strinna Erre, B. Gulinati, G. Micera, A. Pozzi and S. Brunni, J. Coord. Chem., 25 (1992) 75.
9 W. Brzyska and S. Karasinski, J. Therm. Anal. Cal., 39 (1993) 429.
10 W. Ferenc and A. Walkow-Dziewulska, J. Therm. Anal. Cal., 71 (2003) 375.
11 N. S. Fernandes, M. A. S. Carvalho Filho, C. B. Melios and M. Ionashiro, J. Therm. Anal. Cal., 73 (2003) 307.
12 N. S. Fernandes, M. A. S. Carvalho Filho, R. A. Mendes, C. B. Melios and M. Ionashiro, J. Therm. Anal. Cal., 76 (2004) 193.
13 H. A. Flaschka, EDTA Titrations, Pergamon Press, Oxford 1964.
14 C. N. de Oliveira, M. Ionashiro and C. A. F. Graner, Ecl. Quim., 10 (1985) 7.
15 G. Socrates, Infrared Characteristic Group Frequencies, 2nd Ed., Wiley, New York 1994, pp. 91 and 236–237.
16 R. M. Silverstein and F. X. Webster, Spectrometric Identification of Organic Compounds, 6th Ed., Wiley, New York 1998, pp. 92, 93, 96 and 97.
17 I. A. Petroni, F. L. Fertonani, C. B. Melios and M. Ionashiro, Thermochim. Acta, 400 (2003) 187.