ECLÉTICA química

www.scielo.br/eq
Volume 35, número 4, 2010

Artigo/Article

SYNTHESIS, CHARACTERIZATION AND THERMAL BEHAVIOUR OF SOLID 2-METHOXYCINNAMYLIDENEPYRUVATE OF SOME BIVALENT METAL IONS IN CO2 AND N2 ATMOSPHERES

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Abstract: Solid State M-2-MeO-CP compounds, where M stands for bivalent metals (Mn, Fe, Co, Ni, Cu and Zn) and 2-MeO-CP is 2-methoxycinnamylidenepyruvate, were synthesized. Simultaneous thermogravimetry and differential thermal analysis (TG-DTA), differential scanning calorimetry (DSC), elemental analysis and complexometry were used to establish the stoichiometry and to study the thermal behaviour of these compounds in CO_2 and N_2 atmospheres. The results were consistent with the general formula: $M(L)_2 \cdot H_2O$. In both atmospheres (CO_2, N_2) the thermal decomposition occurs in consecutive steps which are characteristic of each compound. For CO_2 atmosphere the final residues were: Mn_3O_4, Fe_3O_4, Co_3O_4, NiO, Cu_2O and ZnO, while under N_2 atmosphere the thermal decomposition is still observed at 1000 °C.

Keywords: bivalent metals, 2-methoxycinnamylidenepyruvate, thermal behaviour, CO_2, N_2.

Introduction

Several metal-ion complexes of phenyl-substituted derivatives of cinnamylidenepyruvate, C_6H_5-$(CH)_4$-$COCOO^-$(CP), have been investigated in aqueous solutions [1-2] and in the solid state [3-11]. These works reported the thermodynamic stability (β_1), and spectroscopic parameters (ε_{1max}, λ_{max}) in aqueous solutions associated with 1:1 complex species. The works also report the synthesis and investigation of the compounds in the solid state by means of thermogravimetry, differential thermal analysis (DTA), differential scanning calorimetry (DSC), and other methods of analysis.Establishment of the stoichiometry and the details of the thermal decomposition were the main purpose of the studies. However, the thermal behaviour of 2-methoxycinnamylidenepyruvate of Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) in CO_2 and N_2 atmospheres have not been reported.

In this paper, the objective of the present research was to prepare sodium2-methoxycinnamylidenepyruvate and 2-methoxycinnamylidenepyruvate of some bivalent metal ions in the solid state and too investigated by means of complexometry, elemental analysis, simultaneous thermogravimetry and differential thermal analysis (TG-DTA) and differential scanning calorimetry (DSC). The results allowed us to acquire information concerning the thermal behaviour in an atmosphere of CO_2 and N_2.

Experimental

The 2-methoxycinnamaldehyde, ($CH_3O\text{-}C_6H_4\text{-}(CH)_2\text{-}CHO$) 96% pure predominantly trans, was obtained from Aldrich and sodium pyruvate ($H_3C\text{-}CO\text{-}COONa$) 99% pure was obtained from Sigma.

Sodium 2-methoxycinnamylidenepyruvate (Na-2-MeO-CP) and its corresponding acid were both synthesized following the same procedure as described in literature [12], with some modifications, which were as follows: an aqueous solution of sodium pyruvate (1.5g per 10 mL) was added dropwise with continuos stirring to a methanolic solution of 2-methoxycinnamaldehyde (2.0g per 50mL). Five millilitres of an aqueous sodium hydroxide solution 1.25 mol. L^{-1} was added slowly while the reacting system was stirred and cooled in an ice bath. The rate of addition of alkali was regulated so that the temperature remained between 5 and 9 ºC. The system was stirred at ambient temperature (~28 ºC) for about 5h. To the pale yellow solution was added dropwise with continuous stirring with a glass rod, twenty millilitres of chilled concentrated (12 mol.L^{-1}) hydrochloric acid. The system was left to stand for ca. 16h in a freezer (-6 ºC) and the yellow orange precipitate (impure 2-methoxycinnamylidenepyruvic acid) was filtered, washed with distilled water to remove most of the unreacted aldehyde and secondary products and dried on Whatman nº 41 filter paper. The aqueous suspension of the impure acid was dissolved with 5 mL of aqueous sodium hydroxide solution 2 mol L^{-1} and filtered on Whatman nº 44 filter paper. The yellow solution was stirred with a glass rod and added slowly 20 mL of chilled concentrated (12 mol L^{-1}) hydrochloric acid and left to stand for ca. 16h in freezer (-6ºC). The orange precipitate of 2-methoxycinnamylidenepyruvic acid was filtered and washed with distilled water until elimination of chloride ions and dried on Whatman nº 41 filter paper and kept in desiccators over anhydrous calcium chloride.

Aqueous solution of Na-MeO-CP 0.1 mol L^{-1} was prepared from aqueous 2-MeO-HCP suspension by treatment with sodium hydroxide solution 0.1 mol L^{-1}., whose pH were adjusted around 8. Aqueous solutions of the bivalent metal ions were prepared by dissolving of the chlorides.

The solid-state compounds were prepared by slowly adding the solution of the ligand to the respective metal chloride under continuous stirring until total precipitation of the metal ions. To avoid oxidation of Mn(II) and Fe(II), all their solutions as well as the water employed for washing their precipitates were purged with nitrogen gas. The precipitates were washed with distilled water until the chloride ions were totally eliminated. This was then filtered through and dried on Whatman nº 42 filter paper and kept in desiccators over anhydrous calcium chloride.

For the compounds in the solid state, TG curves were used to determine the hydration water, ligand and metal contents. The metal ions were also determined by complexometric tritration with standard EDTA solution [13, 14] after igniting the compounds to their respective oxides and then dissolving them in hydrochloric acid solution.

Carbon and hydrogen contents were determined by microanalytical procedures, with an EA 1110 CHNS-O Elemental Analyzer from CE instruments.

Simultaneous TG-DTA and DSC curves were obtained with two thermal analysis systems, model SDT 2960 and DSC Q10, both from TA Instruments. The purge gas was CO2 flow of 100 mL min^{-1} for the TG-DTA and 50 mL min^{-1} for the DSC. A heating rate of 20 ºC min^{-1} for the TG-DTA and DSC, with samples weighing about 5 mg for the TG-DTA and 2 mg for the DSC. Alumina and aluminium crucibles, the latter with perforated covers, were used for the TG-DTA and the DSC, respectively.

Results and Discussion

The analytical and thermoalytical (TG) results of the synthesized compounds are shown in Table 1. These results permitted to establish the stoichiometry of the compounds, which is in agreement with the general formula $M(L)_2 .nH_2O$, where M represents bivalent Mn, Fe, Co, Ni, Cu and Zn, L is 2-methoxycinnamylidene pyruvate and n=2.

TG-DTA

The simultaneous TG-DTA curves of the compounds in CO_2 and N_2 atmospheres are shown in Fig. 1 in CO_2 (a - f) and N_2 (a*- f*), respectively. These curves show mass losses in three (Fe), four (Mn, Co, Zn) and five (Cu, Ni) steps in CO_2 atmosphere and three (Co, Ni), four (Mn, Fe, Zn) and five (Cu) steps in N_2 atmosphere. In both atmospheres a great

Table 1. Analytical and thermoanalytical (TG) data for M(L)2.nH2O, where M = metal and L: 2-methoxycinnamylidenepyruvate.

Compound	Metal oxide (%)			L (lost) (%)		Water (%)		Residue
	Calcd.	TG*	EDTA	Calcd.	TG*	Calcd	TG*	
Mn(L)$_2$·2H$_2$O	13.78	13.97	13.47	79.71	79.62	6.51	6.41	Mn$_3$O$_4$
Fe(L)$_2$·2H$_2$O	13.92	13.89	14.15	79.58	79.40	6.50	6.71	Fe$_3$O$_4$
Co(L)$_2$·2H$_2$O	14.40	14.43	13.96	79.13	78.98	6.47	6.59	Co$_3$O$_4$
Ni(L)$_2$·2H$_2$O	13.41	13.09	13.55	80.12	80.52	6.47	6.39	NiO
Cu(L)$_2$·2H$_2$O	12.73	12.50	12.89	80.86	81.25	6.41	6.25	Cu$_2$O
Zn(L)$_2$·2H$_2$O	14.43	14.19	14.14	79.18	79.51	6.39	6.30	ZnO

similarity is observed in the TG-DTA curves up to the second (Fe, Co), third (Mn, Ni, Zn) and four (Cu) steps. This similarity suggests that as much in CO$_2$ as in N$_2$ atmospheres the thermal decomposition mechanism for each compound must be the same. The TG curve in N$_2$ atmosphere also shows that the mass loss are still being observed up to 1000 ºC, in all the compounds.

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

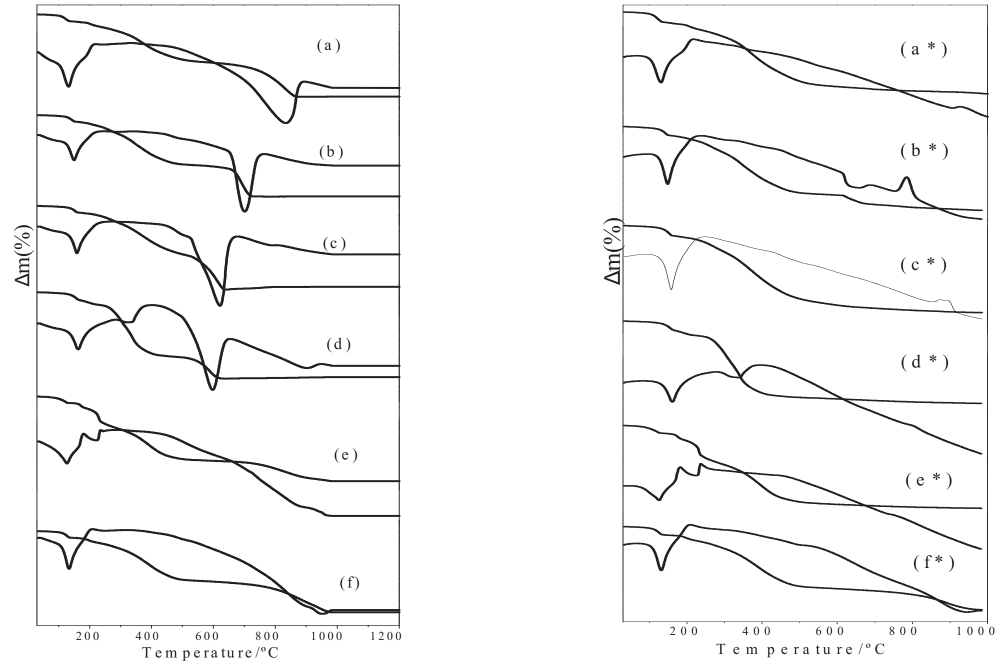

Figure 1. TG-DTA curves of the compounds in CO$_2$ and N$_2^*$: (a, a*) Mn(L)$_2$·2H$_2$O (m = 4,94mg; 5,04 mg *), (b,b*) Fe(L)$_2$·2H$_2$O (m = 5,07 mg;5.08mg*), (c,c*) Co(L)$_2$·2H$_2$O (m =5.13mg; 5,14mg*), (d,d*) Ni(L)$_2$·2H$_2$O (m = 5,00mg; 5,12mg*), (e,e*) Cu(L)$_2$·2H$_2$O (m = 4.88mg; 5,13mg*) and (f,f*) Zn(L)$_2$·2H$_2$O (m= 5.03mg; 5.05mg*). L= 2-methoxycinnamylidenepyruvate.

Manganese compound. The simultaneous TG-DTA curves in CO_2 and N_2 atmospheres are shown in Fig. 1 (a, a*). The first mass loss observed between 50 – 145 ºC (CO_2) and 50 – 140 ºC (N_2) corresponding to the endothermic peak at 135 ºC (CO_2) and 130 (N_2) is attributed to dehydration with loss of 2 H_2O (Calcd. = 6.51%, TG = 6.41% (CO_2), 6,65% (N_2)). For the CO_2 atmosphere, the thermal decomposition of the anhydrous compound occurs in three steps between 145 – 220 ºC, 220 – 555 ºC and 555 – 580 ºC, with losses of 4.64, 37.82 and 37.16% respectively, corresponding to the indicium of exothermic event at 210 ºC and a large endothermic peak at 835 ºC, with formation of Mn_3O_4, as final residue (Calc = 13.78%, TG = 13.97%). For the N_2 atmosphere, the thermal decomposition also occurs in three steps between 140 – 220 ºC, 220 – 565 ºC and 565 ºC – 1000 ºC, with losses of 5.12, 38.92 and 5.51%, respectively, corresponding to the exothermic peak at 210 ºC and small endothermic peak at 895 ºC.

Iron Compound. The simultaneous TG-DTA curves in CO_2 and N_2 atmospheres are shown in Fig. 1 (b, b*). The first mass loss that occurs between 50 – 155 ºC, corresponding to the endothermic peak at 150 ºC, in both atmospheres is attributed to dehydration with loss of $2H_2O$ (Calc. = 6.50 %, TG = 6.71 % (CO_2), 6.65 % (N_2)) The thermal decomposition of the anhydrous compound in CO_2 atmosphere occurs in two steps between 155 º - 540 ºC and 540 – 730 ºC, with losses of 45.99 and 33.41% respectively, corresponding to the endothermic peak at 700 ºC, with formation of Fe_3O_4, as final residue (Calc. = 13.92 %, TG = 13.92 %, 13.89 %). For the N_2 atmosphere, the TG-DTA curves show mass losses in three steps between 155 – 500 ºC, 500 – 690 ºC and 690 – 1000 ºC, with losses of 46.47 %, 9.10 % and 5.14%, respectively, corresponding to the indicium of exothermic event at 220 ºC and endothermic peaks at 650 and 750 ºC.

Cobalt compound. The simultaneous TG-DTA curves in CO2 and N_2 atmospheres are shown in Fig.1 (c, c*). The first mass loss that occurs between 50 – 165 ºC, corresponding to the endothermic peak at 160 ºC in both atmospheres is attributed to dehydration with loss of 2 H_2O. (Calcd. = 6.47%, TG = 6.59% (CO_2), 6.32% (N_2)). The thermal decomposition of the anhydrous compound in CO_2 atmosphere occurs in two steps between 165 – 510 ºC and 510 – 640 ºC, with losses of 43.37 and 38.55%, respectively, corresponding to the endothermic peak 620 ºC, with formation of a mixture of Co and CoO. The mass gain of 2.94% between 640 – 800 ºC is attributed to the oxidation of Co and CoO to Co_3O_4, as final residue (Calcd. = 14.40%, TG = 14.43%). In N_2 atmosphere, the thermal decomposition of the anhydrous compound occurs in two steps between 165 – 610 ºC and 610 – 1000 ºC, with losses of 50.56 % and 4.81 % respectively, corresponding to the endothermic peak at 850 ºC.

Nickel compound. The simultaneous TG-DTA curves in CO_2 and N_2 atmospheres are shown in Fig. 1 (d, d*). The first mass loss observed between 50 – 170 ºC, corresponding to the endothermic peak at 165 ºC, in both atmospheres is ascribed to dehydration with loss of 2 H_2O (Calcd. = 6.47 %, TG = 6.39 % (CO_2), 6.50 % (N_2). The thermal decomposition of the anhydrous compound in CO_2 atmosphere occurs in three steps between 170 – 210 ºC, 210 - 450 ºC and 450 – 640 ºC, with losses of 5.38, 53.70 and 24.10 % respectively, corresponding to the endothermic peaks at 340 and 600 ºC, with formation of a mixture of Ni and NiO. The mass gain of 1.67 % between 640 – 980 ºC corresponding to the exothermic peak at 940 ºC is attributed to the oxidation of Ni to NiO, as final residue (Calcd. = 14.41 %, TG = 13.09 %). The thermal decomposition in N_2 atmosphere occurs in three steps between 170 – 210 ºC, 210 -430 ºC and 430 – 1000 ºC, with losses of 6.07, 53.69 and 7.66 %, respectively, corresponding to the endothermic peak at 340 ºC.

Copper compound. The simultaneous TG-DTA curves in CO_2 and N_2 atmospheres are shown in Fig.1 (e, e*). The first mass loss that occurs between 50 – 130 ºC, corresponding to the endothermic peak at 125 ºC, in both atmospheres is attributed to dehydration with loss of $2H_2O$ (Calcd. = 6.41 %, TG = 6.25 % (CO_2), 6.22 (N_2)). In CO_2 atmosphere, the anhydrous compound shows mass losses in four steps between 130 – 180 ºC, 180 – 240 ºC, 240 – 545 ºC and 545 – 1035 ºC, with losses of 5.66, 13.14, 35.73 and 26.72 %, respectively, corresponding to the exothermic peaks at 175 ºC, 235 ºC and endothermic peaks at 870, 990 ºC, with formation of Cu_2O, as final residue (Calcd. = 12.73 %, TG = 12.50 %). The thermal decomposition in N_2 atmosphere also occurs in four steps between 130 – 190 ºC, 190 – 245 ºC, 245 – 515 ºC and 515 – 1000 ºC, with losses of 5.35, 13.39, 37.20 and 4.29 %, respectively, corresponding to the exothermic peaks at 185 ºC and 240 ºC.

Zinc compound. The simultaneous TG-DTA curves in CO_2 and N_2 atmospheres are shown in Fig.1 (f, f*). The first mass loss between 50 – 140 ºC, corresponding to the endothermic peak at 130 ºC, in both atmospheres is attributed dehydration with loss of

Table 2. Mass losses, temperature ranges and peak temperatures observed in each step of the TG-DTA curves.

Compound	First step	Second step		Third step		Fourth step		Fifth step			
		CO_2	N_2	CO_2	N_2	CO_2	N_2	CO_2	N_2	CO_2	N_2
$Mn(L)_2{\cdot}2H_2O$	θ/ºC	50 - 145	50 -140	145 - 220	140 - 220	220 - 555	220 - 565	555 - 880	565 – 1000	-	-
	Δm/%	6.41	6.65	4.64	5.12	37.82	38.98	37.16	5.51	-	-
	Peak/ºC	135	130	-	-	-	-	835	895	-	-
$Fe(L)_2{\cdot}2H_2O$	θ/ºC	50 - 155	50 -155	155 - 540	155 - 500	540 – 730	500 – 690	-	690 – 1000	-	-
	Δm/%	6.71	6.65	46.47	46.47	33.41	9.1	-	5.14	-	-
	Peak/ºC	150	150	-	-	700	650	-	750	-	-
$Co(L)_2{\cdot}2H_2O$	θ/ºC	50 - 165	50 - 165	165 - 610	165 - 610	510 – 640	610 - 1000	640 – 800	-	-	-
	Δm/%	6.59	6.32	50.56	50.56	38.55	4.81	2.94*	-	-	-
	Peak/ºC	160	160	-	-	620	850	-	-	-	-
$Ni(L)_2{\cdot}2H_2O$	θ/ºC	50 - 170	50 - 170	170 - 210	170 - 210	210 – 450	210 – 430	450 – 640	430 – 1000	640 – 980	-
	Δm/%	6.39	6.50	6.07	6.07	53.70	53.69	24.10	7.66	1.67*	-
	Peak/ºC	165	165	-	-	340	340	600	-	900	-
$Cu(L)_2{\cdot}2H2OO$	θ/ºC	50 - 130	50 -130	130 - 190	130 - 190	190 – 245	190 – 245	240 – 545	245 – 515	545 – 1035	515 - 1000
	Δm/%	6.25	6.22	5.35	5.35	13.39	13.39	35.73	37.20	26.72(CuO)))	4.29
	Peak/ºC	125	125	-	-	225	225	-	-	870, 990	-
$Zn(L)_2{\cdot}2H_2O$	θ/ºC	50 - 140	50 - 140	140 -215	140 – 215	215 – 510	215 – 510	500 – 985	510 – 985	-	-
	Δm/%	6.30	6.28	5.42	5.42	39.53	39.53	34.65	19.50	-	-
	Peak/ºC	130	130	-	-	-	-	950	950	-	-

L: 2-methoxycinnamylidenepyruvate, *mass gain a M: metal.

2 H_2O (Calc. = 6.39 % (CO_2), 6.28 % (N_2)). The thermal decomposition of the anhydrous compound in CO_2 atmosphere occurs in three steps between 140 – 205 ºC, 205 – 500 ºC and 500 – 985 ºC, with losses of 5.10, 39.76 and 34.65%, respectively, corresponding to the exothermic peak at 200 ºC and an endothermic peak at 950 ºC, with formation of ZnO, as final residue (Calc. = 14.43%, TG = 14.19%). In N_2 atmosphere, the thermal decomposition of the anhydrous compound also occurs in three steps between 140 – 215 ºC, 215 – 510 ºC and 510 – 1000 ºC, with losses of 5.42, 39.53 and 19.50 %, respectively, corresponding to the exothermic peak at 210 ºC and an endothermic peak at 950 ºC.

The formation of the respective oxides: Mn_3O_4, Fe_3O_4, Co_3O_4, NiO, Cu_2O and ZnO in CO_2 atmosphere. For N_2 atmosphere the TG-DTA curves show that the thermal decomposition are still being observed up to 1000 ºC, thus do not allowing to verify which oxides are formed, since only 65.4 % (Mn), 78.2 % (Fe), 72.1 % (Co), 8.51 % (Ni), 76.0 % (Cu) and 82.4 % (Zn) of these compounds were lost, when compared with the mass losses of the TG-DTA curves obtained in CO_2 atmosphere.

DSC

The DSC curves of the compounds in CO_2 and N_2 atmospheres are shown in Figs. 2. These curves show endothermic and exothermic peaks that all are in agreement with the mass losses observed in the TG-DTA curves up to 600 ºC.

The endothermic peak in the range 130 - 170 ºC in both atmospheres is assigned to the dehydration which occurs in a single step. The dehydration enthalpies found for these compounds in CO_2 and N_2 atmospheres were: 116.6; 110.8 (Mn), 113.0; 108.9 (Fe), 124.8; 114.5(Co), 119.2; 111.1 (Ni), 91.8; 87.4 (Cu) and 116.2; 116.6 (Zn) kJ mol^{-1}, respectively.

The exothermic peak observed in both atmospheres (except for copper) at 209 ºC (Mn), 213 ºC (Fe), 222 ºC (Co), 285 ºC (Ni) and 200 ºC (Zn), corresponding to the first mass loss of the anhydrous compound, is probably due to the descarboxylation process. For the copper compound two sharps exothermic peaks at 177 ºC and 238 ºC in both atmospheres corresponding to the first two mass losses of the anhydrous compound is probably due to the descarboxylation process and

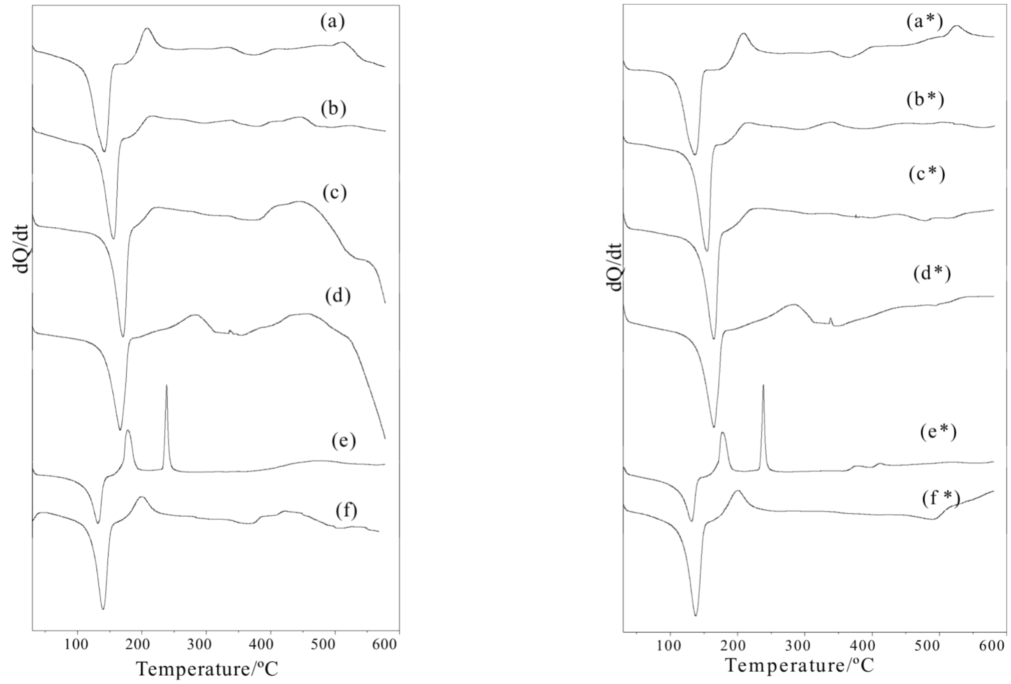

Figure 2. DSC curves of the compounds in CO_2 and N_2^*: (a,a*) $Mn(L)_2{\cdot}2H_2O$ (m = 2.22 mg; 2.24 mg*), (b,b*) $Fe(L)_2{\cdot}2H_2O$ (m = 2.12 mg; 2.29 mg*), (c,c*) $Co(L)_2{\cdot}2H_2O$ (m = 2.29 mg, 2,29 mg*), (d,d*) $Ni(L)_2{\cdot}2H_2O$ (m = 2.46 mg, 2.24 mg*), (e,e*) $Cu(L)_2{\cdot}2H_2O$ (m = 2.22 mg; 2,48 mg*) and (f,f*)$Zn(L)_2{\cdot}2H_2O$ (m = 2.18mg, 2.25mg*). L= 2-methoxycinnamylidenepyruvate.

loss of the methoxy group, respectively (Calcd. = 18.86 %, TG = 18.80 %). The profile of the exothermic peak at 238 ºC, suggest that this step the mass loss is accompanied by a physical phenomenon.

The small endo or exothermic peaks observed above 240 ºC (Mn, Zn), 260 ºC (Fe, Co, Cu) and 320 ºC (Ni) in both atmospheres up to 550 ºC and no observed in the DTA curves, suggest that in this step endo and exothermic events must occur simultaneously, where the net heat produce only small endo or exothermic peaks or no thermal events.

Conclusion

From TG curves (CO_2), and complexometry results, a general formula could be established for these compounds in the solid state, which are in agreement which $M(L)_2{\cdot}2H_2O$.

For CO2 atmosphere the final thermal decomposition occurs at temperature below 1000 ºC with formation of the respective oxide: Mn_3O_4, Fe_3O_4, Co_3O_4, NiO, Cu_2O and ZnO. For N_2 atmosphere the mass loss is still being observed up to 1000 ºC.

The TG-DTA and DSC curves provided information concerning the thermal behaviour and thermal decomposition of these compounds in CO_2 and N_2 atmospheres, which are characteristic of each compound.

Acknowledgements

The authors thank FAPESP, CNPQ and CAPES and Foundations (Brazil) for financial support.

Resumo: Compostos M-2-MeO-CP foram sintetizados no estado sólido, onde M representa os metais bivalentes (Mn(II), Fe(II), Co(II), Ni(II), Cu(II) e Zn(II)) e 2-MeO-CP é o 2-metoxicinamalpiruvato. Para estabelecer a estequiometria e estudar o comportamento térmico desses compostos foram utilizadas termogravimetria, análise térmica diferencial simultânea (TG-DTA), calorimetria exploratória diferencial (DSC), análise elementar e complexometria com EDTA. Os resultados foram concordantes com a fórmula geral: $M(L)_2{\cdot}H_2O$. Em ambas as atmosferas a decomposição térmica ocorre em etapas consecutivas e é característica de cada composto. Em atmosfera de CO_2 os resíduos finais foram: Mn_3O_4, Fe_3O_4, Co_3O_4, NiO, Cu_2O e ZnO, enquanto que em atmosfera de N_2 a decomposição térmica ainda é observada até 1000 ºC.

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