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THERMOANALYTICAL STUDY OF THE COMPLEXES OF 4-DIMETILAMINOCINNAMYLIDENEPIRUVATE WITH MANGANESE (II), COBALT (II), NICKEL (II), CUPPER (II), ZINC (II) AND LEAD (II), IN THE SOLID STATE

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ABSTRACT: Solid state compounds M-4-DMCP, where 4-DMCP is 4-dimethylaminocinnamylidenepyruvate and M represents Mn (II), Co (II), Ni (II), Cu (II), Zn (II) and Pb (II) were prepared.
These compounds were studied by thermoanalitycal techniques: thermogravimetry (TG), derivative thermogravimetry (DTG), differential scanning calorimetry (DSC), X-ray diffraction powder patterns and complexometric titration with EDTA.
From the results obtained by the complexometric titration with EDTA, TG, DTG and DSC curves, was possible to establish the hydration degree, stoichiometry and thermal stability of the prepared compounds.
KEYWORDS: 4-dimethylaminocynnamylidenepyruvate, thermal analysis, TG, DSC.

Introduction

The preparation and investigation of metal ion complexes with 4-dimethylaminobenzylidenepyruvate (4-DMBP$^-$), 2-chloro-4-dimethylamino- benzylidenepyruvate (2-Cl-4-DMBP$^-$), 4-methoxybenzylidenepyruvate (4-MeO-BP$^-$), cynnamylidenepyruvate (CP$^-$) and 4-dimethylaminocinnamylidene- pyruvate, (4-DMCP$^-$) have been investigated in aqueous solution[5-8,13,17].

In the solid state, several metal-ion complexes with 4-DMBP$^-$, 4-MeO-BP$^-$ and CP$^-$, have also been prepared and investigated using TG, DTG, DSC, DTA and X-ray powder diffractometry[9-12,14]. The establishment of the stoichiometry, thermal stability as well as the thermal decomposition have been the main purposes of the aforementioned studies.

As an extension of the works of Refs. 4, 15, 16, in this present paper, solid state compounds of Mn (II), Co (II), Ni (II), Cu (II), Zn (II) and Pb (II) with 4-dimethylaminocynnamylidenepyruvate, $(CH_3)_2N\text{-}C_6H_4\text{-}(CH)_4COCOO^-$, (4-DMCP$^-$) were prepared. The compounds were characterized and studied by complexometric titration with EDTA, thermogravimetry (TG), derivative thermogravimetry (DTG), differential scanning calorimetry (DSC) and X-ray diffractometry. The data obtained allowed us to acquire new information concerning these compounds in the solid state.

Experimental

4-dimethylaminocynnamylidenepyruvic acid (H-4-DMCP) was prepared following the same procedure adopted for 4-DMBP$^-$, as previously described[6]. The sodium salt (4-DMCP$^-$) was prepared by neutralizing the aqueous suspension of H-4-DMCP with aqueous solution of sodium hydroxide (0,1 mol L^{-1}) exempt of carbonate. The solid state compounds were prepared by mixing solutions of the ligand with a solution of the respective metal nitrate, until total precipitation. The precipitates were washed until elimination of nitrate ions, filtered and dried in a Whatman nº 42 filter papers, and stored in a desiccator over anhydrous calcium chloride.

After igniting the compounds to the respective oxides, metal contents were determined by complexometric titration with standard EDTA solution, using xylenol orange as metalochromic indicator[2-3] . TG, DTG and DSC curves were obtained by using a Mettler TA 4000 thermal analysis system with an air flow of about 150 mL min^{-1} , a heating rate of 10 ºC min^{-1} and samples weighing about 7 mg. A platinum crucible was used for TG / DTG curves and a aluminium crucible with perforated cover was used to obtain the DSC curves.

X-ray powder patterns were obtained with an HGZ 4 / B horizontal diffractometer (GDR) equipped with a proportional counter and pulse height discriminator. The Bragg-Brentano arrangement was adopted using Cu Ka (l = 1,5418 Å)and a setting of 38 KV and 20 mA.

Results and Discussion

Table 1 presents the analytical and thernoanalytical (TG) results on the prepared compounds, from which the general formula $M(4\text{-}DMCP)_2.nH_2O$ canbe established, where M represents Mn, Co, Ni, Cu, Zn and Pb, 4-DMCP is 4-dimethylaminocinnamylidenepyruvate, and n = 0.5 – 2.

Table 1: *Analytical and thermoanalytical data of the compounds $M(4\text{-DMCP})_2.nH_2O$*

Compounds	Metal (%)			Ligand Loss (%)		Water (%)	
	Theor.	EDTA	TG	Theor.	TG	Theor.	TG
$Mn(L)_2.1{,}5H_2O$	9.63	9.78	9.62	81.43	81.74	4.74	4.70
$Co(L)_2.H_2O$	10.42	10.24	10.42	82.62	82.60	3.19	3.13
$Ni(L)_2.2H_2O$	10.06	9.99	10.06	81.01	81.00	6.18	6.18
$Cu(L)_2.H_2O$	11.14	11.00	11.13	82.89	82.69	3.16	3.12
$Zn(L)_2.H_2O$	11.42	11.17	11.44	82.62	82.64	3.15	3.12
$Pb(L)_2.0{,}5H_2O$	29.39	29.72	29.38	67.05	67.04	1.28	1.28

Key: L = 4-dimethylaminocinamylidenepyruvate

The X-ray powder diffraction patterns of these compounds indicate amorphous state.

The TG and DTG curves of the compounds are shown in Figures 1 – 6. In all the TG and DTG curves, the first mass loss up to 108 ºC (Mn); 160 ºC (Co); 120 ºC (Ni); 112 ºC (Cu); 100 ºC (Zn) and 104 ºC (Pb) is due to the hydration water with loss of 1.5; 1; 2; 1; 1 and 0.5 H_2O respectively. After the dehydration, the TG/DTG curves indicate mass losses in two or three consecutive and/or overlapping steps.

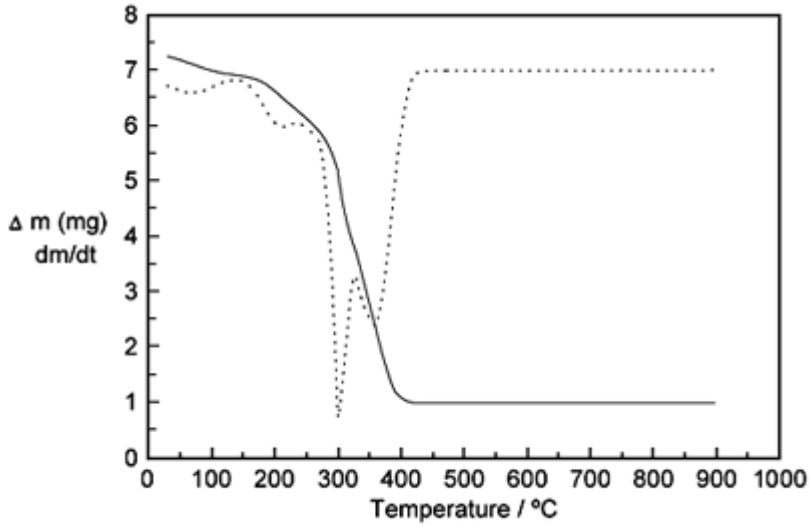

Fig. 1: TG and DTG curves of $Mn(4\text{-DMCP})_2.1{,}5H_2O$

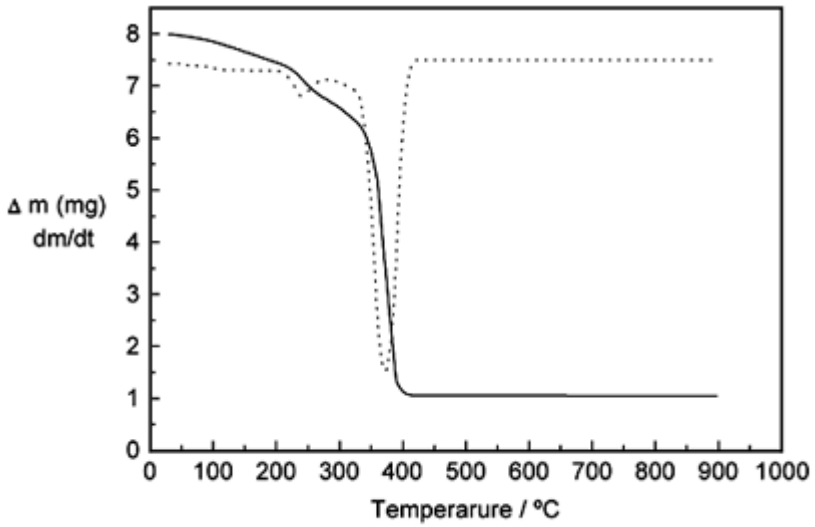

Fig. 2: TG and DTG curves of $Co(4\text{-}DMCP)_2.H_2O$

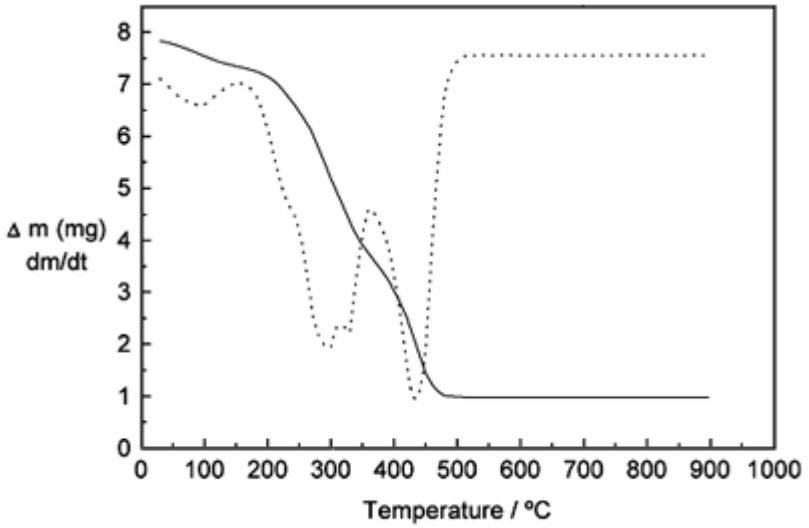

Fig. 3: TG and DTG curves of $Ni(4\text{-}DMCP)_2\ 2H_2O$

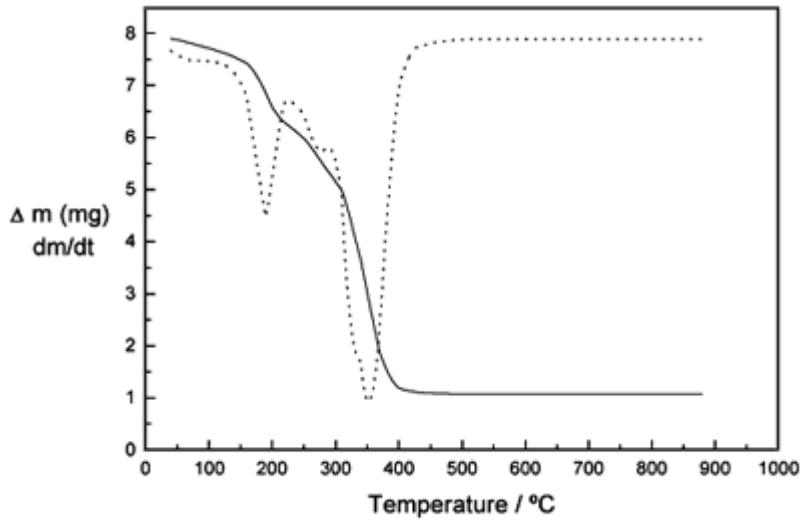

Fig. 4: TG and DTG curves of $Cu(4\text{-}DMCP)_2.H_2O$

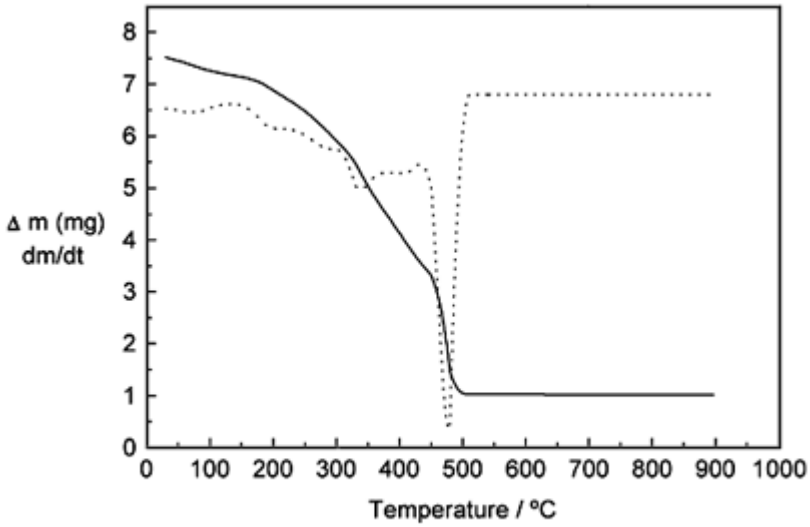

Fig. 5: TG and DTG curves of $Zn(4\text{-}DMCP)_2.H_2O$

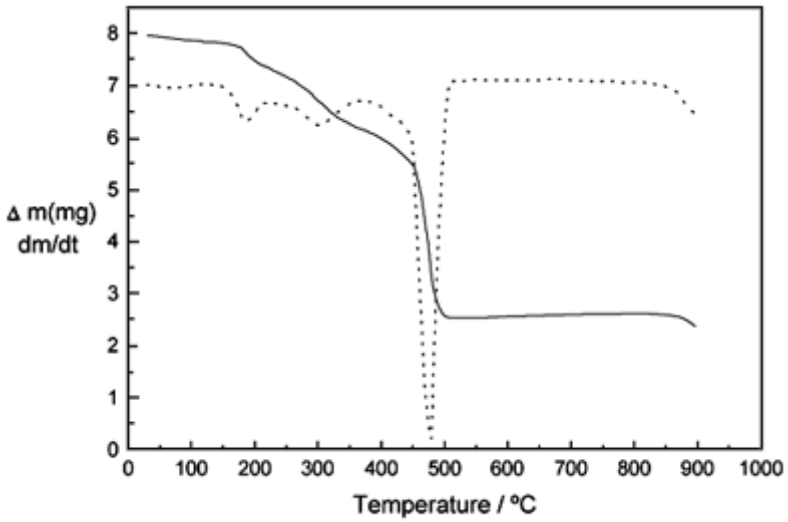

Fig. 6: TG and DTG curves of $Pb(4\text{-}DMCP)_2.0{,}5H_2O$

For the anhydrous manganese compounds, the TG and DTG curves, Figure 1, show that the thermal decomposition occurs in the temperature range 108 – 408 ºC, and begins with a slow process, followed by fast process. The total mass loss up to 408 ºC is in agreement with formation of Mn_2O_3 as final residue, (calcd. = 95.80%; TG = 95.79%).

For the anhydrous cobalt compound the TG and DTG curves, Figure 2, show that the thermal decomposition occurs in two consecutive steps between 160 and 402 ºC, and begins with a slow process followed by a fast process, too. The total mass loss up to 402 ºC is in agreement with formation of Co_3O_4, as a final residue, (calcd. = 96.23%; TG = 96.13%).

In the anhydrous nickel compound, Figure 3, the TG curve show mass loss in two overlapping steps between 120 and 482 ºC, although the DTG curve suggest three overlapping steps. The mass loss up to 482 ºC is in agreement with the formation of NiO, as final residue, (calcd. = 97.25%; TG = 97.24%).

For the anhydrous copper compound the TG and DTG curves, Figure 4, show mass losses in three consecutive and overlapping steps between 112 and 420 ºC. The mass loss up to 320 ºC (first and second steps) occurs through a slow process, followed by a fast process. The total mass loss up to 420 ºC is in agreement with the formation of CuO, as final residue, (calcd. = 97.19%; TG = 97.14%).

For the anhydrous zinc compound the TG and DTG curves, Figure 5, suggest mass losses in three consecutive and overlapping steps between 100 and 500 ºC. The mass loss in slow up to 450 ºC, followed by a fast process. The mass loss up to 500 ºC is in agreement with formation of ZnO, as final residue, (calcd. = 97.19%; TG = 97.20%).

In the anhydrous lead compound the TG and DTG curves, Figure 6, show mass losses in three consecutive steps between 104 and 510 ºC. The first and the second steps, the mass loss occurs slowly up to 450 ºC, followed by a fast process. The mass loss up to 510 ºC is in agreement with formation of PbO, as a final residue, (calcd. = 97.72%; TG = 97.70%). The mass gain between 510 and 850°C is attributed to a new oxidation and gives rise to minium (Pb_3O_4), which in turn loses

oxygen beyond 860°C.

The DSC curves for all the studied compounds are shown in Figure 7. These curves show endothermic and exothermic peaks that agree with the mass losses observed in the TG and DTG curves. The endothermic peaks about 100 ºC are due to dehydration, in agreement with the mass losses observed in TG and DTG curves. The broad exotherms observed for all the compounds, are attributed to the thermal decomposition of the anhydrous compounds, where the oxidation of organic matter takes place in consecutive steps. The DSC curves also show that the final thermal decomposition of these compounds occurs above 600 ºC, although the TG and DTG curves indicate below this temperature. This difference is undoubtedly due to the crucible with perforated cover used to obtain the DSC curves.

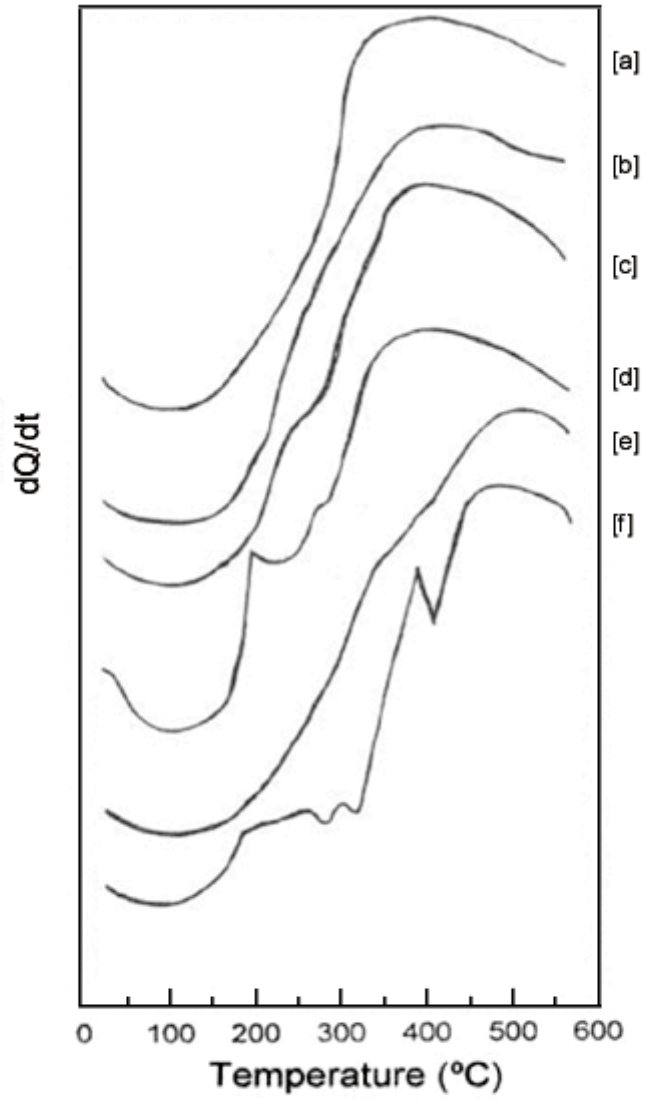

Figure7: DSC curves of: [a] $Mn(4\text{-}DMCP)_2 .1.5\ H_2O$; [b] $Co(4\text{-}DMCP)_2 . H_2O$; [c] $Ni(4\text{-}DMCP)_2 . 2H_2O$; [d] $Cu(4\text{-}DMCP)_2 . H_2O$; [e] $Zn(4\text{-}DMCP)_2 . H_2O$; [f] $Pb(4\text{-}DMCP)_2 . 0.5\ H_2O$; obtained in a aluminium crucible with perforated cover, heating rate = 10 °C / min; dynamic atmosphere of synthetic air with flow of 150 mL / min.

The final residue of the thermal decomposition of these compounds, due to the small quantity, no information was possible to obtain from the X-ray diffraction powder patterns.

Conclusions

The results obtained from the complexometric titration with EDTA and TG and DTG curves, were possible to establish the hidration degree and the stoichiometry of the prepared compounds, having the general formula:

$M(4\text{-DMCP})_2 \cdot n\ H_2O$

Where: M = Mn, Co, Ni, Cu, Zn or Pb; 4-DMCP = 4-dimethylaminocinamylidenepyruvate and n = 0,5 – 2.

The DSC curves, up to 600 ºC show endothermic peaks due to dehydration and exotherm attributed to the oxidation of organic matter, wich are in correspondence with the mass losses observed in the TG and DTG curves, showing that the thermal decomposition process occurs through consecutive reactions.

The X-ray powder patterns of these compounds indicate amorphous state.

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SCHNITZLER, E., LAZZAROTTO, M., CARVALHO FILHO, M. A. S., IONASHIRO, M. Estudo termoanalítico dos complexos 4-dimetilaminocinamalpiruvatos (4-DMCP) de manganês(II), cobalto(II), níquel(II), cobre(II), zinco(II) e de chumbo(II), no estado sólido. *Ecl. Quím. (São Paulo),* v.27, p. , 2002.

RESUMO: *Os compostos dos 4-dimetilaminocinamalpyruvatos (4-DMCP) de Mn (II), Co (II), Ni (II), Cu (II), Zn (II) e Pb (II) foram preparados.*
Estes compostos foram estudados pelas técnicas termoanaliticas: termogravimetria (TG), termogravimetria derivada (DTG), calorimetria exploratória diferencial (DSC), difratometria de raios – X pelo método do pó e titulação complexométrica com EDTA.
Através dos resultados obtidos pela titulação complexométrica com EDTA, TG, DTG e DSC foi possível estabelecer o grau de hidratação, estequiometria e estabilidade térmica dos compostos preparados.
PALAVRAS-CHAVE: *4-dimetilaminocinamalpiruvato, análise térmica, TG, DSC.*

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