

Eclética Química

Print version ISSN 0100-4670 *On-line version* ISSN 1678-4618

Eclet. Quím. vol.23 São Paulo 1998

<http://dx.doi.org/10.1590/S0100-46701998000100001>

Thermal behaviour study of solid state compounds of manganese (II), zinc (II) and lead (II) with cinnamic acid

Marco Aurélio da Silva CARVALHO FILHO*

Massao IONASHIRO*

ABSTRACT: Compounds of cinnamic acid with manganese, zinc and lead have been prepared in aqueous solution. Thermogravimetry, derivative thermogravimetry (TG, DTG), differential scanning calorimetry (DSC), X-ray diffraction and complexometry have been used in the characterization as well as in the study of the thermal stability and interpretation concerning the thermal decomposition.

KEYWORDS: Manganese; zinc; lead; cinnamic acid; thermal decomposition.

Introduction

Several metal ion compounds with 4-dimethylaminobenzylidenepyruvate and 4-methoxybenzylidenepyruvate in solid state, have been prepared and studied by complexometry, TG, DTG, DSC, DTA and X-ray powder diffractometry.²⁻⁵

Compounds of cinnamic acid with cobalt, nickel and copper have been prepared in aqueous solution and characterized by analyses, magnetic moments, vibrational and electronic spectra, as well as the thermal behaviour by thermogravimetry and differential thermal analyses.¹

In this study, solid-state compounds of manganese(II), zinc(II) and lead(II) with cinnamic acid $C_6H_5-CH=CHCOOH$ were prepared. These compounds were characterized and studied by thermogravimetry, derivative thermogravimetry (TG, DTG), differential scanning calorimetry (DSC), X-ray powder diffractometry and other methods of analysis. The data obtained allowed us to acquire information about the thermal stability and thermal decomposition of these compounds.

Experimental

Aqueous suspension of slight excess of cinnamic acid with the corresponding metal carbonates (acid: metal » 2:1) was heated to ebullition until effervescence ceased. The hot solution was filtered and the filtrate evaporated until the volume had decreased and the compounds precipitated. The precipitate was filtered and washed with ethanol until the elimination of the cinnamic acid in excess. The product air dried was kept in desiccator over anhydrous calcium chloride.

The TG, DTG and DSC curves were obtained using a Mettler TA-4000 thermoanalyser system with air flowing at a rate of about 150 mL min⁻¹, and a heating rate of 10°C min⁻¹, with samples weighing about 7-8 mg. Alumina crucible was used to obtain the TG and DTG curves and aluminium crucible with perforated covers 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-Breutano arrangement was adapted using CoK- α_1 radiation ($\lambda = 1.78897\text{\AA}$) and a setting of 38 kV and 20 mA.

Results and discussion

[Table 1](#) presents the analytical and thermoanalytical data for the prepared compounds from which the general formula $ML_2 \cdot nH_2O$ can be established, where M represents Mn(II), Zn(II) and Pb(II), L is cinnamate ($C_6H_5-CH=CH-COO^-$) and $n = 3, 1$ and 0 respectively.

Table 1 - Analytical and thermoanalytical results

Compound	Metal (%)			ΔL (%)		Water (%)		Residue
	Calcd.	TG	EDTA	Calcd.	TG	Calcd.	TG	
$MnL_2 \cdot 3H_2O$	13.62	13.50	13.71	65.04	64.97	13.40	13.66	MnO_2
$ZnL_2 \cdot H_2O$	17.31	17.11	17.32	73.69	73.57	4.77	4.84	ZnO
PbL_2	41.31	41.31	41.42	54.43	54.42			Pb_3O_4

Key: L = cinnamate

The X-ray diffraction powder patterns ([Figure 1](#)) show that the compounds have crystalline structures.

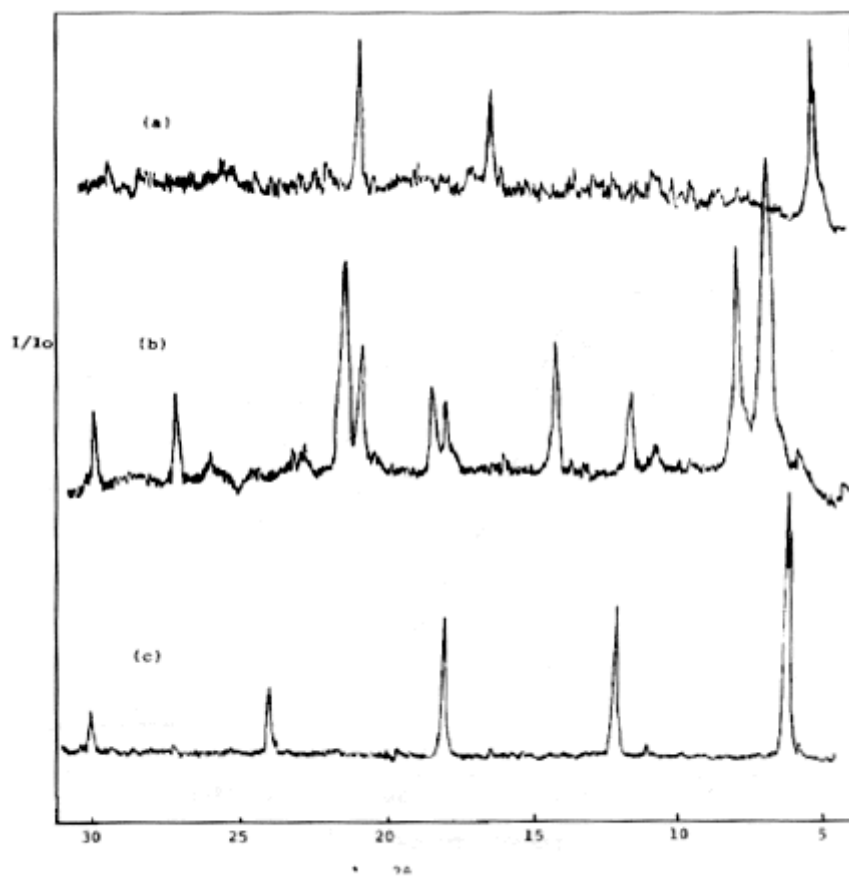


FIGURE 1 - X-ray powder diffraction patterns of the compounds: (a) $MnL_2 \cdot 3H_2O$; (b) $ZnL_2 \cdot H_2O$ and (c) PbL_2 .

The thermal decomposition of these compounds occurs in three steps between 50 and 500°C (Mn, Zn), 250 and 560°C (Pb), as can be seen in the TG and DTG curves, ([Figure 2](#)).

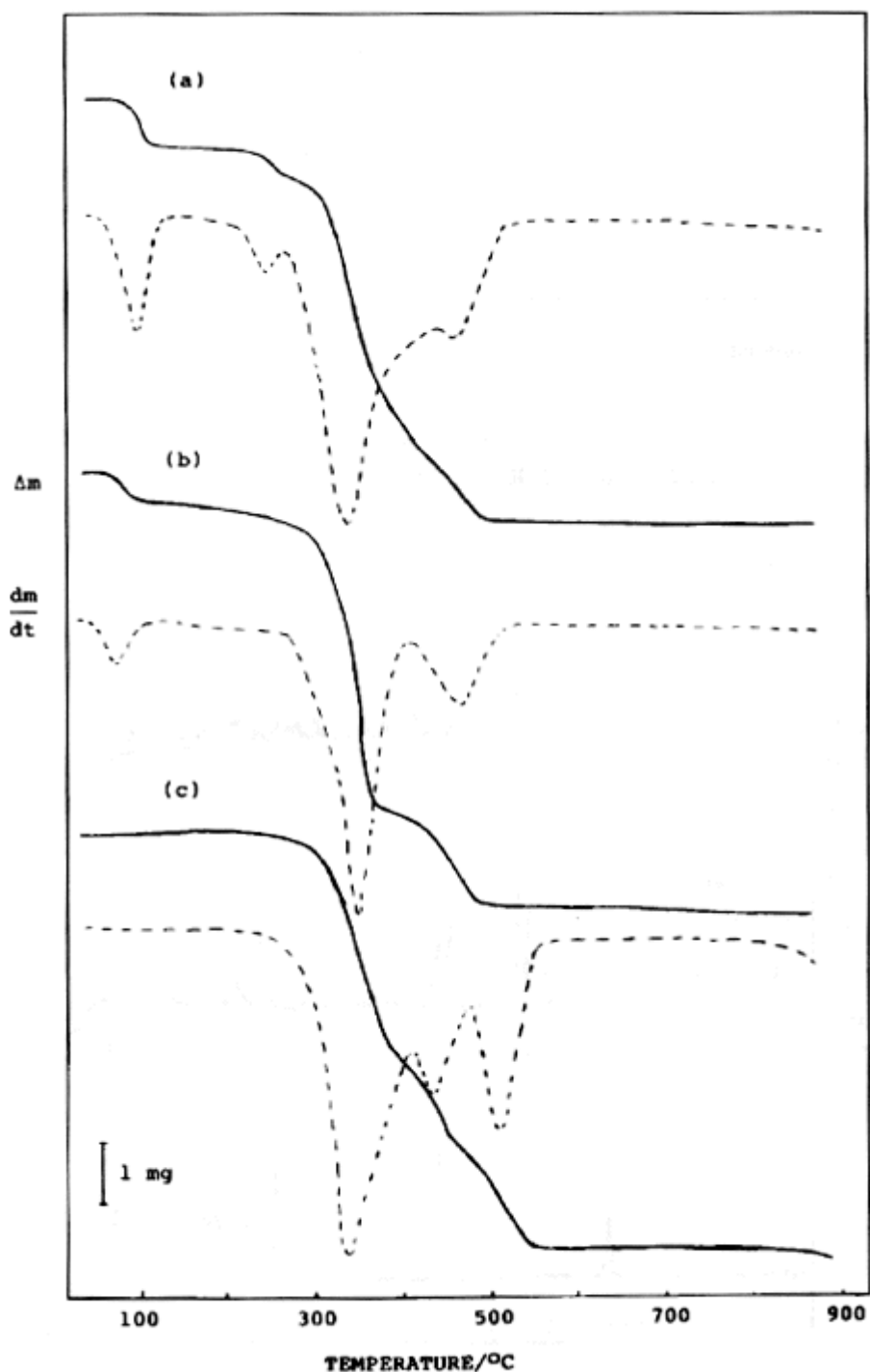


FIGURE 2 - TG and DTG curves of the compounds: (a) $\text{MnL}_2 \cdot 3\text{H}_2\text{O}$ (7.650 mg); (b) $\text{ZnL}_2 \cdot \text{H}_2\text{O}$ (7.370 mg) and (c) PbL_2 (7.503 mg).

For the manganese compound, ([Figure 2\(a\)](#)) the dehydration occurs in two steps and the first step observed up to 100°C is due to the losses of $2\text{H}_2\text{O}$ (Theor. = 8.94%, TG = 8.75%).

The monohydrated compound formed is stable up to 200°C and the loss of this last water occurs between 200 and 270°C (Theor. = 4.47%, TG = 4.45%). The high stability and the temperature at which the final dehydration is observed suggest that this water is strongly binded. The thermal decomposition of the resulting anhydrous compound, although the DTG curve shows mass loss is two consecutive steps, the TG curve suggest one mass loss between 270 and 500°C with formation

of MnO_2 as residue (Theor. = 65.03%, TG = 64.8%).

In the zinc compound the TG and DTG curves, ([Figure 2\(b\)](#)) show mass losses in three steps. The first step observed up to 100°C is due to the dehydration with loss of $1\text{H}_2\text{O}$ (Theor. = 4.77%, TG = 4.84%). The resulting anhydrous compound is stable up to 250°C and between 250 and 500°C the thermal decomposition occurs in two consecutive steps. Calculations based on these mass losses observed in the TG and DTE curves are in agreement with the losses of 2 (C_6H_6) and 2 ($\text{CH}=\text{CH}$) between 250 and 390°C (Theor. = 54.62%, TG = 54.52%) and the remainder of the ligand between 390 and 500°C, with formation of zinc oxide, ZnO as residue (Theor. = 19.07%, TG = 19.27%).

For the lead compound obtained in the anhydrous form, the TG and DTG curves, ([Figure 2\(c\)](#)) show that the thermal decomposition occurs in three consecutive steps. Calculation based on the mass loss observed in each step is in agreement with the loss of 2 (C_6H_6) between 250 and 400°C (Theor. 30.75%, TG = 30.65%); 2($\text{CH}=\text{CH}$) between 400 and 460°C (Theor. = 10.38%, TG = 10.34% and the remainder of the ligand between 460 and 560°C with formation of Pb_3O_4 as residue (Theor. = 13.30%, TG = 13.43%).

The DSC curves of these compounds are shown in [Figure 3](#). For the manganese compound, ([Figure 3\(a\)](#)) the first and second endothermic peaks at 127°C and 238°C respectively, are attributed to the dehydration, in agreement with the first and second mass losses observed in the TG and DTG curves. The sequence of several exothermic peaks observed between 246 and 428°C, in correspondence with the third step indicated by the DTG curve, are very difficult to interpret, probably may be due to the oxidation of the decomposition product accompanied of the oxidation-reduction reactions of the manganese. The broad exotherm between 428 and > 600°C is attributed to the final pyrolysis of the compound.

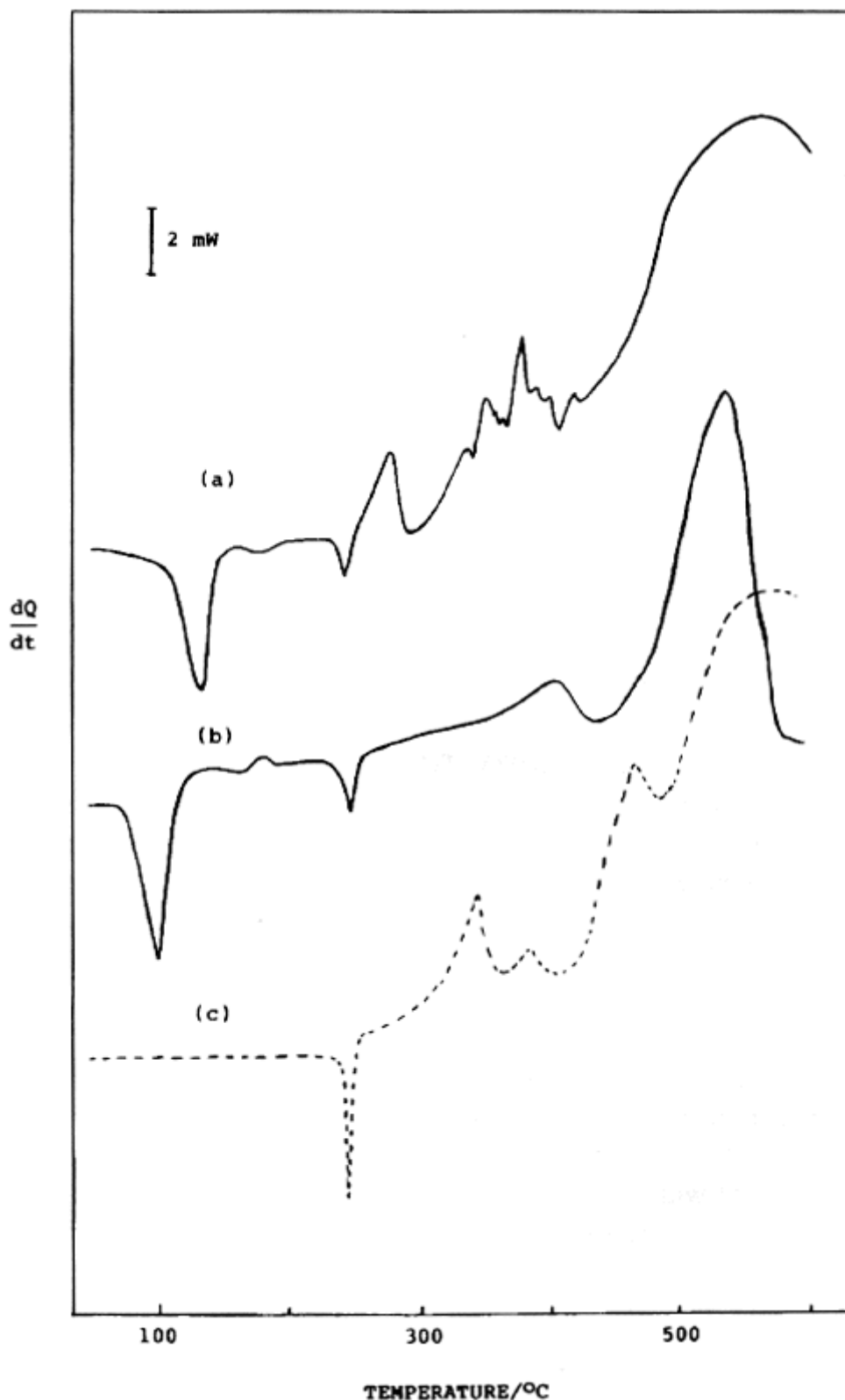


FIGURE 3 - DSC curves of the compounds: (a) $\text{MnL}_2 \cdot 3\text{H}_2\text{O}$; (b) $\text{ZnL}_2 \cdot \text{H}_2\text{O}$ and (c) PbL_2 .

For the zinc compound the DSC curve, ([Figure 3\(b\)](#)) shows an endothermic peak at 96°C due to the dehydration in agreement with the first mass loss observed in the TG and DTG curves. The exothermic peak at 173°C is attributed to a recrystallization process, and the endothermic peak at 240°C is due to the fusion of the compound. The two exothermic peaks observed at 395°C and

525°C are attributed to a recrystallization process, and the endothermic peak at 240°C is due to the fusion of the compound. The two exothermic peaks observed at 395°C and 525°C are attributed to the oxidation reaction of the decomposition products and final pyrolysis of the compound in correspondence with the second and third mass losses observed in the TG and DTG curves.

The DSC curve of the anhydrous lead compound, ([Figure 3\(c\)](#)) shows a first endothermic peak at 244°C due to the fusion of the compound. The sequence of exothermic peaks at 340°C, 380°C and 465°C are attributed to the oxidation reactions of the products eliminated during the thermal decomposition in correspondence with the first and second mass losses of the TG and DTG curves. The broad exothermic peak at 560°C is ascribed to the final pyrolysis of the compound corresponding the third mass loss of the TG and DTG curves.

Conclusion

From the TG and DTG curves, the general formula could be established for these compounds in the solid state and also the partial losses of the ligand during the thermal decomposition could be suggested.

The TG, DTG and DSC curves, and X-ray powder patterns provided previously unreported information about the thermal stability and thermal decomposition of these compounds.

Acknowledgements

The authors thank the Fapesp (Proc. 90/2932-4) and PIBIC/CNPq for financial support and Rosemary Camargo Gabarron for aid in the preparation of this manuscript.

CARVALHO FILHO, M. A. da S., IONASHIRO, M. Estudo do comportamento térmico dos compostos no estado sólido de manganês(II), zinco(II) e de chumbo(II) com ácido cinâmico. *Ecl. Quim. (São Paulo)*, v.23, p.9-16, 1998.

RESUMO: Foram preparados em meio aquoso os cinamatos de manganês, zinco e chumbo. Na caracterização, bem como no estudo da decomposição térmica desses compostos, foram utilizados a termogravimetria, termogravimetria derivada (TG, DTG), calorimetria exploratória diferencial (DSC), difração de raios X e complexometria.

PALAVRAS-CHAVE: Manganês; zinco; chumbo; ácido cinâmico; decomposição térmica.

References

1 ALLAM J. R. et al. Thermal, spectral and magnetic studies of some compounds of cobalt(II), nickel(II) and copper(II) with cinnamic acid. *Thermochim. Acta*, v. 154, p. 315-22, 1989.

2 MIYANO, M. H. et al. The preparation and thermal decomposition of solid state compounds of 4-dimethylaminobenzylidenepyruvate and trivalent lanthanides and yttrium. *Thermochim. Acta*, v. 221, p. 53-62, 1993.

3 OLIVEIRA, L. C. S. et al. Preparation and thermal decomposition of solid state compounds of 4-methoxybenzylidenepyruvate and trivalente lanthanides and yttrium. *Thermochim. Acta*, v. 219, p. 215-24, 1993.

4 _____. Preparation and thermal decomposition of solid state compounds of 4-methoxybenzylidenepyruvate with alkali earth metals, except beryllium and tadium. *Thermochim. Acta*, v. 275, p. 269-78, 1996.

5 RASERA, D. E. et al. The preparation and thermal decomposition of some metal compounds of 4-dimethylaminobenzylidenepyruvate in the solid state. *Thermochim. Acta*, v. 250, p. 151-63, 1995.

Recebido em 8.5.1997.

Aceito em 26.6.1997

* Departamento de Química Analítica - Instituto de Química - UNESP - 14800-900 - Araraquara - SP - Brazil.