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Preparation and thermal behavior of mixture of basic carbonate and 4-dimethylaminocinnamylidenepyruvate with lanthanides (III) and yttrium (III) in the solid state.

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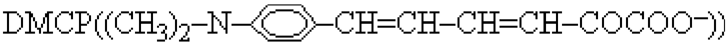
ABSTRACT: Solid Ln-$OHCO_3$-DMCP compounds, where Ln represents lanthanides (III) and yttrium (III) ions and DMCP is the anion 4-dimethylaminocinnamylidenepyruvate, have been prepared. Thermogravimetry, derivative thermogravimetry (TG, DTG), differential scanning calorimetry (DSC), x-ray diffraction powder patterns and elemental analysis have been used to characterize the compounds. The thermal stability as well as the thermal decomposition of these compounds were studied using an alumina crucible in an air atmosphere.

KEYWORDS: Basic carbonate-4-dimethylaminocinnamylidenepyruvate; lanthanides; thermal behavior.

Introduction

Several metal ion complexes with 4-dimethylaminobenzylidenepyruvate (DMBP), 2-chloro-4-dimethylaminobenzylidenepyruvate (2-Cl-DMBP), 4-methoxybenzylidene-pyruvate (4-MeO-BP) and cinnamylidenepyruvate (CP) have been investigated in aqueous solution[3-6,12]. The factors that govern the thermodynamic stability and selectivity of these ligands towards metal ions, as well as analytical applications of the corresponding complexation reactions have been the main purposes of the studies.

Solid state compounds of several metal ion with DMBP and 4-MeO-BP, have also been prepared and studied using TG, DTG, DSC, DTA and X-ray powder diffractometry.[7,9-11] The establishment of the stoichiometry, thermal stability and thermal decomposition mechanism have been the main objective of these studies.

In this study, solid state compounds of lanthanide (III) and yttrium (III) with  characterized and studied by complexometric titration, TG, DTG, DSC, elemental analysis and X-ray powder difractometry. The data obtained allowed us to acquire new information concerning these compounds.

Experimental

The sodium salt of DMCP was prepared following the same procedure for the 4-dimethylaminobenzylidenepyruvate, as previously describe[4]. The neutralization of aqueous suspension of the acid HDMCP in excess, was made with sodium hydrogen carbonate. The excess of the acid was separed by centrifugation. Lanthanides (III) and yttrium (III) chlorides were prepared in accordance with Giesbretch et al.[1]

The solid compounds of trivalent lanthanides and yttrium with DMCP were prepared following the procedure as previously described.[7]

In the solid compounds, the anions contents were determined from the TG curves and elemental analysis and the lanthanide and yttrium contents were determined by complexometric titrations with standard EDTA solutions, using xylenol orange as indicator[2] and from the TG curves.

The TG, DTG and DSC curves were obtained using a Mettler TA-4000 thermoanalyser system with an air flux of » 150 mL min^{-1}, a heating rate of 10°C min^{-1} and with samples weighing about 7 mg. An alumina crucible was used for the TG, DTG curves and an aluminium crucible with a perforated cover was used for the DSC curves.

Diffraction patterns were obtained using an HGZ 4/B horizontal diffractometer (Germany), equipped with a proportional counter and pulse-heigh discriminator. The Bragg-Brentano arrangement was adapted using CuKa radiation (l = 1.541 Å) and settings of 38 KV and 20 mA.

Results and discussion

Table 1 presents the analytical and thermoanalytical (TG) data and Table 2 presents the elemental analysis results for the prepared compounds of general formula $Ln(DMCP)_3.LnOHCO_3.nH_2O$, where Ln represents lanthanides and yttrium, DMCP is 4-dimethylaminocinnamylidenepyruvate, and n = 3-4.5.

Table 1 - Analytical and Thermoanalytical (TG) Results

Compound	Lanthanide (%)			L - L_1 (%)		Water (%)	
	Calcd	EDTA	TG	Calcd	TG	Calcd	TG
$La_2L(L_1)_3.4.5H_2O$	23.77	23.50	23.45	65.19	65.64	6.94	6.85
$Ce_2L(L_1)_3.4H_2O$	24.11	23.87	23.72	64.18	64.17	6.20	6.65
$Pr_2L(L_1)_3.4H_2O$	24.22	23.62	24.00	64.55	64.77	6.19	6.19
$Nd_2L(L_1)_3.4H_2O$	24.65	24.15	24.71	65.09	65.09	6.16	6.10
$Sm_2L(L_1)_3.4H_2O$	25.43	26.03	25.36	64.42	64.55	6.09	6.04
$Eu_2L(L_1)_3.4H_2O$	25.63	25.14	25.54	64.25	64.26	6.08	6.16
$Gd_2L(L_1)_3.4H_2O$	26.23	25.95	26.29	63.68	63.72	6.02	6.04
$Tb_2L(L_1)_3.3H_2O$	27.36	27.91	27.39	63.17	62.87	4.65	4.91
$Dy_2L(L_1)_3.3H_2O$	27.34	26.64	27.56	64.08	63.75	4.55	4.61
$Ho_2L(L_1)_3.3.5H_2O$	27.42	26.98	27.23	63.34	63.42	5.24	5.38
$Er_2L(L_1)_3.3.5H_2O$	27.70	27.05	27.65	63.10	62.97	5.22	5.41
$Tm_2L(L_1)_3.3.5H_2O$	27.90	27.25	27.92	62.92	62.92	5.20	5.19
$Yb_2L(L_1)_3.3H_2O$	28.60	28.90	28.32	62.96	63.18	4.47	4.30
$Lu_2L(L_1)_3.3.5H_2O$	28.61	28.50	28.23	63.30	62.81	5.16	5.08
$Y_2L(L_1)_3.3.5H_2O$	16.92	16.49	16.77	72.51	72.58	6.00	6.13

Key: L, basic carbonate; L_1, 4-dimethylaminocinnamylidenepyruvate.

Table 2 - Elemental Analysis Results

Compound	C (%)		H (%)		N (%)	
	Calcd.	E.A.	Calcd.	E.A.	Calcd.	E.A.
$La_2L(L_1)_3.4.5H_2O$	44.18	43.67	3.71	3.53	3.59	3.43
$Ce_2L(L_1)_3.4H_2O$	44.13	44.30	3.73	4.09	3.49	3.34
$Pr_2L(L_1)_3.4H_2O$	44.37	44.39	3.73	3.34	3.60	3.61
$Nd_2L(L_1)_3.4H_2O$	44.12	43.97	3.71	3.97	3.60	3.43
$Sm_2L(L_1)_3.4H_2O$	43.69	43.39	3.67	3.33	3.55	3.42
$Eu_2L(L_1)_3.4H_2O$	43.55	43.93	3.66	3.87	3.54	3.44
$Gd_2L(L_1)_3.4H_2O$	43.16	42.97	3.63	3.22	3.51	3.37
$Tb_2L(L_1)_3.3H_2O$	44.45	44.21	3.74	3.43	3.60	3.48
$Dy_2L(L_1)_3.3H_2O$	43.44	42.98	3.65	3.87	3.53	3.59
$Ho_2L(L_1)_3.3.5H_2O$	42.93	42.38	3.61	3.27	3.49	3.32
$Er_2L(L_1)_3.3.5H_2O$	42.47	42.21	3.60	3.74	3.48	3.56
$Tm_2L(L_1)_3.3.5H_2O$	42.65	42.77	3.59	3.30	3.48	3.44
$Yb_2L(L_1)_3.3H_2O$	42.68	42.44	3.59	3.97	3.47	3.49
$Lu_2L(L_1)_3.3.5H_2O$	42.23	42.51	3.55	3.21	3.36	3.69
$Y_2L(L_1)_3.3.5H_2O$	49.15	49.30	4.13	4.09	3.39	3.91

Key: L, basic carbonate; L_1, 4-dimethylaminocinnamylidenepyruvate.

The X-ray powder patterns showed that all the compounds are amorphous.

The TG and DTG curves of the compounds are shown in Figure 1. These curves show mass losses in steps between 30 and 730°C. In all the curves a great similarity are observed and the first mass loss observed up to 150°C is due to hydration water. The formation of the intermediate dioxycarbonate, $Ln_2O_2CO_3$, is observed only for La, Nd - Gd, compounds, Figure 1(a), (d-g). In the cerium, praseodymium and terbium compounds, the TG, DTG curves, Figure 1(b), (c) and (h), show that this intermediate is not formed, probably because the exothermic oxidation reaction that results in the formation of the respective oxides (CeO_2, Pr_6O_{11} and Tb_4O_7), as already observed[7]. For the dysprosium - lutetium and yttrium compounds the TG-DTG curves, Figure 1(i) - (o), also show that this intermediate, $Ln_2O_2CO_3$ is not formed, probably because the thermal stability of this intermediate decrease with the increase of the atomic number of the lanthanide ion.[8]

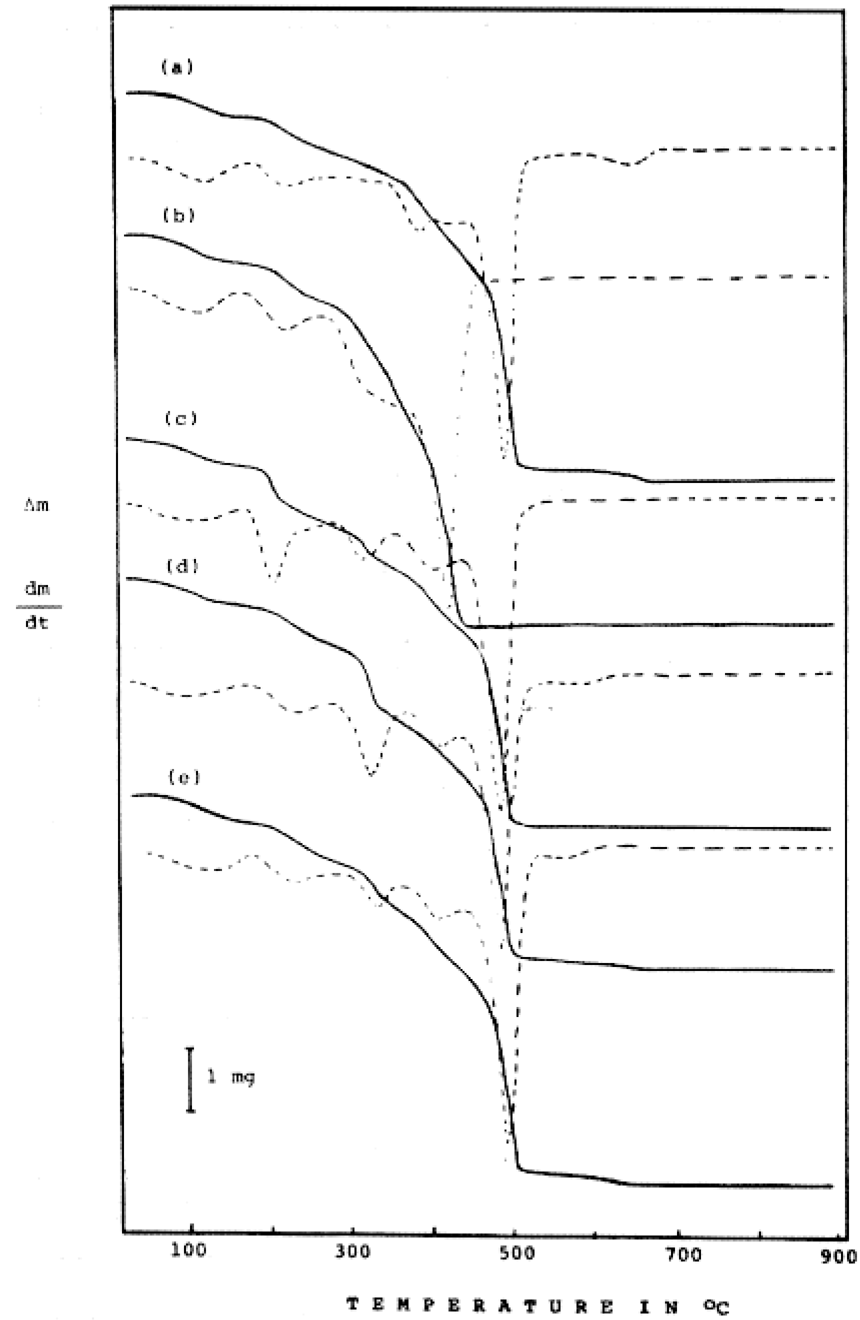


FIGURE 1

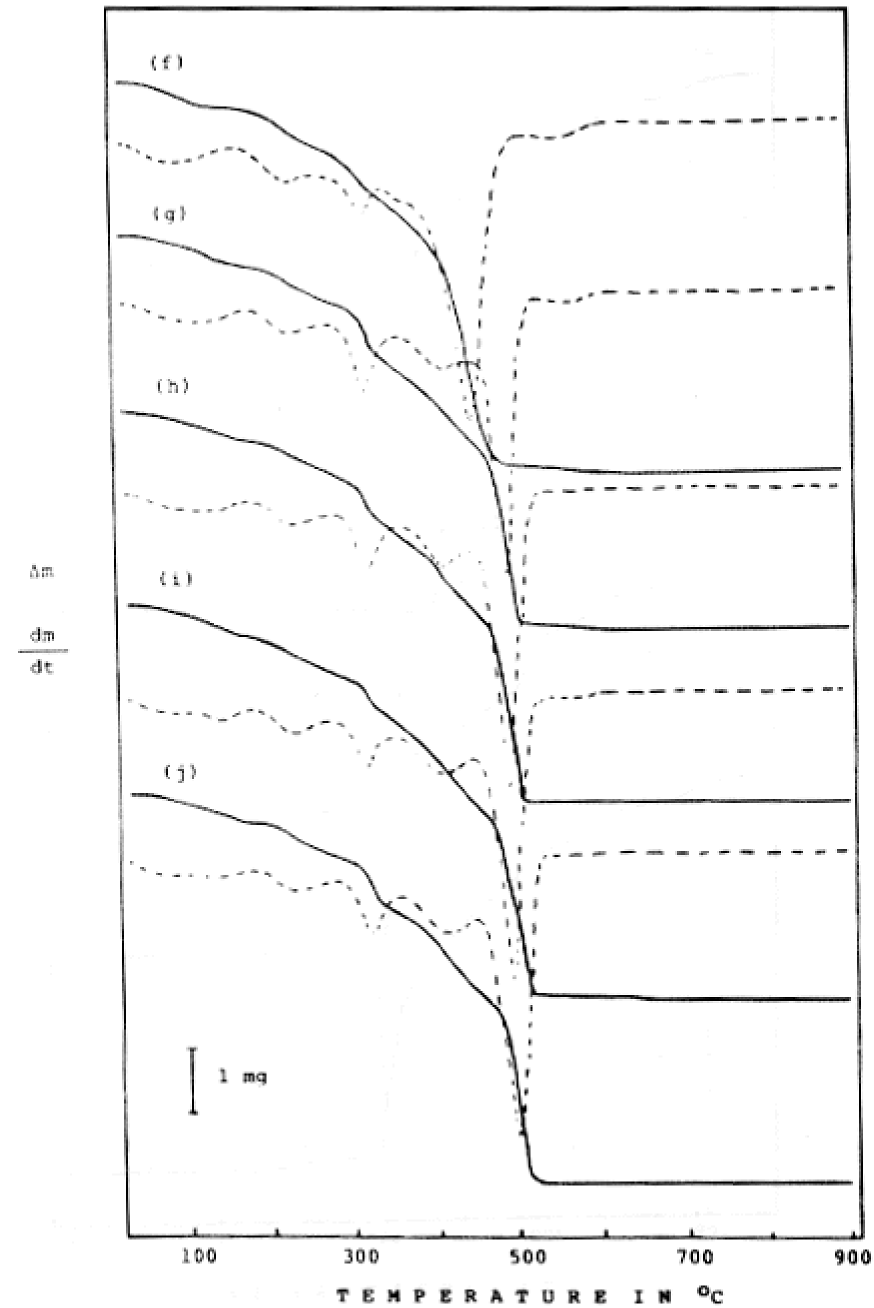


FIGURE 1

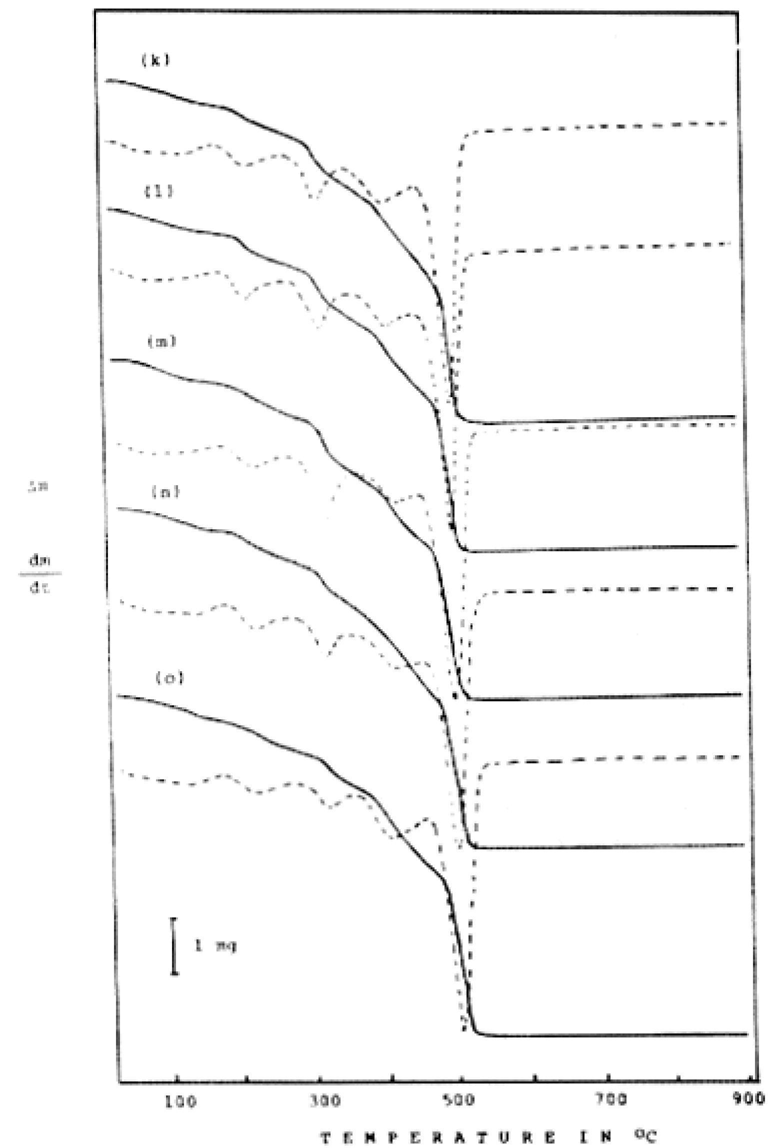
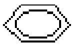
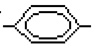


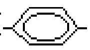
FIGURE 1 - TG-DTG curves of the compounds: (a) La(DMCP)$_3$LaOHCO$_3$.4.5H$_2$O (7.443 mg); b) Ce(DMCP)$_3$CeOHCO$_3$.4H$_2$O (7.415 mg); c) Pr(DMCP)$_3$PrOHCO$_3$.4H$_2$O (7.421 mg); d) Nd(DMCP)$_3$NdOHCO$_3$.4H$_2$O (7.384 mg); e) Sm(DMCP)$_3$SmOHCO$_3$.4H$_2$O (7.367 mg); f) Eu(DMCP)$_3$EuOHCO$_3$.4H$_2$O (7.505 mg); g) Gd(DMCP)$_3$GdOHCO$_3$.4H$_2$O (7.490 mg); h) Tb(DMCP)$_3$TbOHCO$_3$.3H$_2$O (7.428 mg); i) Dy(DMCP)$_3$DyOHCO$_3$.3H$_2$O (7.351 mg); j) Ho(DMCP)$_3$HoOHCO$_3$.3.5H$_2$O (7.437 mg); k) Er(DMCP)$_3$ErOHCO$_3$.3.5H$_2$O (7.528 mg); l) Tm(DMCP)$_3$TmOHCO$_3$.3.5H$_2$O (7.258 mg); m) Yb(DMCP)$_3$YbOHCO$_3$.3H$_2$O (7.318 mg); n) Lu(DMCP)$_3$LuOHCO$_3$.3.5H$_2$O (7.233 mg) and o) Y(DMCP)$_3$YOHCO$_3$.3.5H$_2$O (7.393 mg).

For all anhydrous compounds the mass loss begins with a slow process, followed by a fast process. Although the DTG curves show mass losses in several steps, the TG curves suggest two or three mass losses except for the cerium compound.

For the anhydrous cerium compound, the TG and DTG curves show mass losses in two consecutive steps between 150 and 450°C. Calculations based on the mass losses observed in the TG curves are in agreement with the losses of 3(CH$_3$)$_2$-N; 0.5H$_2$O (first step) and the rest of the ligand DMCP and the thermal decomposition of the cerium monoxycarbonate formed during the dehydration of basic carbonate with formation of $2CeO_2$ (second step).

For the anhydrous lanthanium compound, the TG curve indicates that the thermal decomposition occurs in three steps with losses of $3(CH_3)_2N$-,2  and $0.5H_2O$ (first step), rest of the ligand DMCP and thermal decomposition of the lanthanium monoxycarbonate formed during the dehydration of basic carbonate with formation of the dioxycarbonate (second step) and elimination of CO_2 with formation of La_2O_3 (last step).

For the anhydrous neodymium - gadolinium compounds, the TG curves also show mass losses in three steps with osses of $3(CH_3)_2$-N--and).$5H_2O$ of the ligand DMCP and thermal decomposition of the respective monoxycarbonate formed during the dehydration of basic carbonate with formation of the dioxycarbonate (second step) and elimination of CO_2 with formation of Ln_2O_3.

Finally, for the anhydrous praseodimium, terbium - lutetium and yttrium compounds, the TG curves show mass losses in two steps with losses of $3(CH_3)_2H$--and 0.5 H_2O (first step), rest of the ligand DMCP and thermal decomposition of the respectives monoxycarbonates formed during the dehydration of basic carbonate with formation of the oxides, Pr_6O_{11}, Tb_4O_7 and Ln_2O_3 (second step).

The mass losses and the corresponding temperature ranges, for the partial thermal decompositions for all the compounds are shown in Table 3.

Table 3 – Mass loss m and temperature range θ corresponding to the partial thermal decomposition of the compounds $Ln(DMCP)_3.LnOHCO_3.nH_2O$, where Ln represents lanthanides and yttrium and DMCP is 4-dimethylaminocinnamylidenepyruvate

Compound		Partial thermal decomposition	Loss %	
m/mg	θ/°C		Theor	Exp
$La(DMCP)_3LaOHCO_3.4.5H_2O$				
0.510	30-120	4.5 H_2O	6.94	6.85

continuação

Compound		Partial thermal decomposition	Loss %	
m/mg	θ/°C		Theor	Exp
1.902	150-454	$3(CH_3)_2N$–⬡–;2–⬡–,$0.5H_2O$	25.10	25.55
2.711	454-545	Rest of the compound with formation of dioxycarbonate	36.32	36.42
0.273	600-725	CO_2 with formation of La_2O_3	3.77	3.67
$Ce(DMCP)_3.CeOHCO_3.4H_2O$				
0.495	30-150	$4H_2O$	6.20	6.65
3.852	160-300	$3(CH_3)_2$-N: $0.5H_2O$	51.96	51.89
0.906	300-450	Rest of the compound with formation of $2CeO_2$	12.2	12.28
$Pr(DMCP)_3.PrOHCO_3.4H_2O$				
0.459	30-150	$4H_2O$	6.19	6.19
2.362	160-490	$3(CH_3)_2N$–⬡–; $0.5H_2O$	31.74	31.84
2.444	490-580	Rest of the compound with formation of $1/3Pr_6O_{11}$	32.81	32.93
$Nd(DMCP)_3.NdOHCO_3.4H_2O$				
0.450	30-130	$4H_2O$	6.16	6.10
2.337	170-484	$3(CH_3)_2N$–⬡–; $0.5H_2O$	31.56	31.65
2.469	484-538	Rest of the compound with formation of dioxycarbonate	29.88	29.86
0.264	538-700	CO_2 with formation of Nd_2O_3	3.65	3.58
$Sm(DMCP)_3.SmOHCO_3.4H_2O$				
0.445	30-150	$4H_2O$	6.09	6.04
2.311	170-484	$3(CH_3)_2N$–⬡–; $0.5H_2O$	31.23	31.36
2.199	484-528	Rest of the compound with formation of dioxycarbonate	29.47	29.85
0.246	528-700	CO_2 with formation of Sm_2O_3	3.72	3.34
$Eu(DMCP)_3.EuOHCO_3.4H_2O$				
0.463	30-150	$4H_2O$	6.08	6.16
2.341	170-450	$3(CH_3)_2N$–⬡–; $0.5H_2O$	31.15	31.16
2.202	450-520	Rest of the compound with formation of dioxycarbonate	29.38	29.38
0.279	520-700	CO_2 with formation of Eu_2O_3	3.72	3.72

continuação

Compound		Partial thermal decomposition	Loss %	
m/mg	θ/°C		Theor	Exp
$Gd(DMCP)_3.GdOHCO_3.4H_2O$				
0.453	30-150	$4H_2O$	6.02	6.04
2.319	170-490	$3(CH_3)_2N$-⌬-; $0.5H_2O$	30.87	30.96
2.173	490-530	Rest of the compound with formation of dioxycarbonate	29.13	29.01
0.281	530-700	CO_2 with formation of Gd_2O_3	3.68	3.75
$Tb(DMCP)_3.TbOHCO_3.3H_2O$				
0.364	30-150	$3H_2O$	4.65	4.91
2.337	160-476	$3(CH_3)_2N$-⌬-; $0.5H_2O$	31.79	31.46
2.333	476-540	Rest of the compound with formation of $0.5Tb_4O_7$	31.38	31.41
$Dy(DMCP)_3.DyOHCO_3.3H_2O$				
0.339	30-150	$3H_2O$	4.55	4.61
2.280	150-478	$3(CH_3)_2N$-⌬-; $0.5H_2O$	31.07	31.01
2.407	478-580	Rest of the compound with formation of Dy_2O_3	33.01	32.74
$Ho(DMCP)_3.HoOHCO_3.3.5H_2O$				
0.400	30-150	$3.5H_2O$	5.24	5.38
2.303	150-484	$3(CH_3)_2N$-⌬-; $0.5H_2O$	30.72	30.97
2.413	484-590	Rest of the compound with formation of Ho_2O_3	32.62	32.45
$Er(DMCP)_3.ErOHCO_3.3.5H_2O$				
0.407	30-150	$3.5H_2O$	5.22	5.41
2.311	150-480	$3(CH_3)_2N$-⌬-; $0.5H_2O$	30.59	30.70
2.429	480-590	Rest of the compound with formation of Er_2O_3	32.51	32.27
$Tm(DMCP)_3.TmOHCO_3\ 3.5H_2O$				
0.376	30-150	$3.5H_2O$		
2.237	150-480	$3(CH_3)_2N$-⌬-; $0.5H_2O$	5.20	5.19
2.330	480-590	Rest of the compound with formation of Tm_2O_3	32.41	32.10

continuação

Compound		Partial thermal decomposition	Loss %	
m/mg	θ/°C		Theor	Exp
$Yb(DMCP)_3.YbOHCO_3.3H_2O$				
0.315	30-150	$3H_2O$	4.47	4.30
2.247	150-463	$3(CH_3)_2N$-⬡-; $0.5H_2O$	30.53	30.71
2.356	463-550	Rest of the compound with formation of Yb_2O_3	32.43	32.47
$Lu(DMCP)_3.LuOHCO_3.3.5H_2O$				
0.368	30-150	$3.5H_2O$	5.16	5.08
2.193	150-466	$3(CH_3)_2N$-⬡-; $0.5H_2O$	30.21	30.32
2.350	466-550	Rest of the compound with formation of Lu_2O_3	33.09	32.49
$Y(DMCP)_3.YOHCO_3.3.5H_2O$				
0.453	30-150	$3.5H_2O$	6.00	6.13
2.598	150-482	$3(CH_3)_2N$-⬡-; $0.5H_2O$	35.15	35.14
2.768	482-580	Rest of the compound with formation of Y_2O_3	37.36	37.44

The DSC curves of these compounds (Figure 2) show endothermic and exothermic peaks up to 600°C, in correpondence with the mass losses observed in the TG curves. The broad endothermics that occur in all the compounds between 30 and 200°C, are due to the loss of hydration water. The sequence of broad exotherms observed after the dehydration between 200 and 600°C are attributed to the thermal decomposition of these compounds.

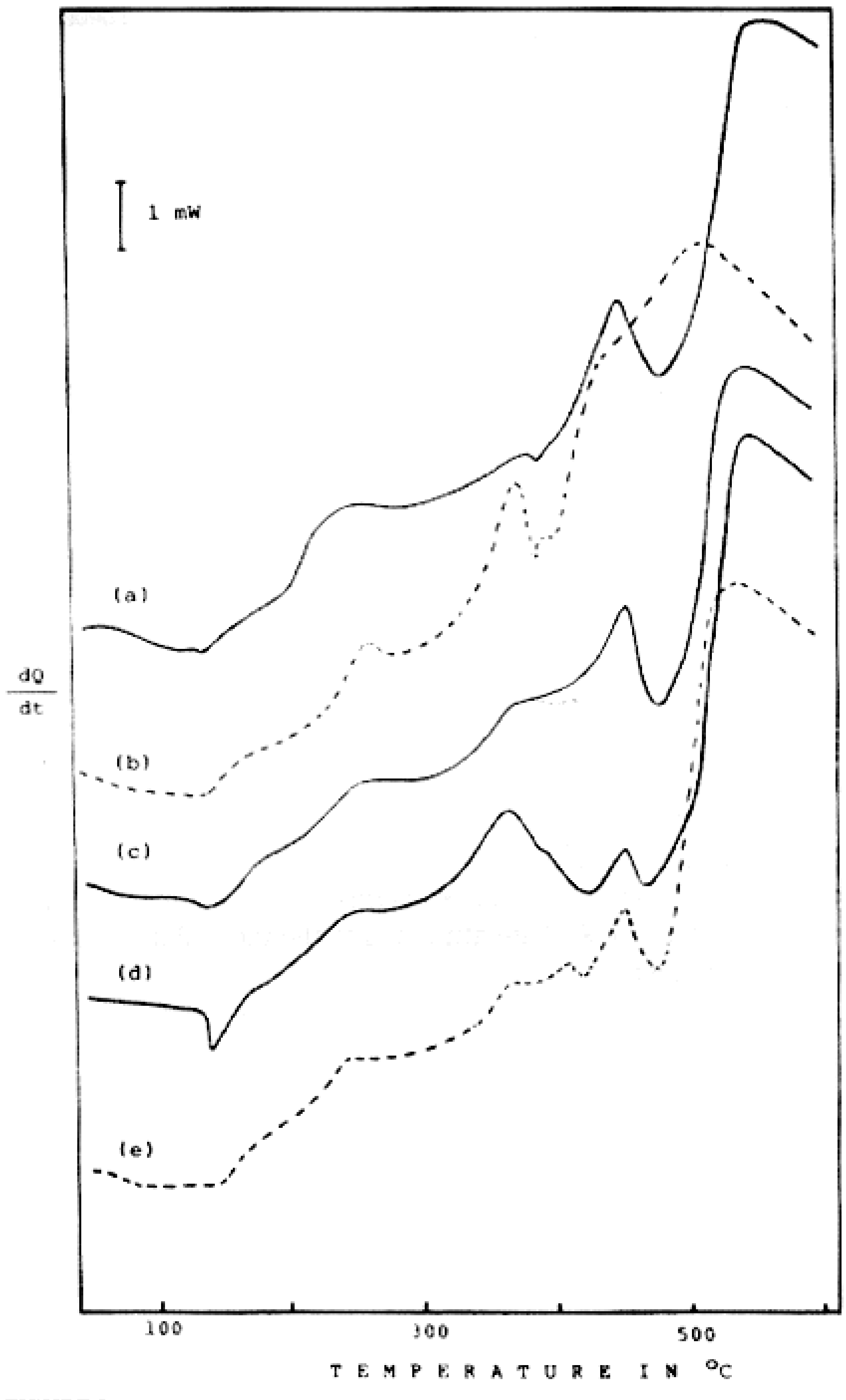


FIGURE 2

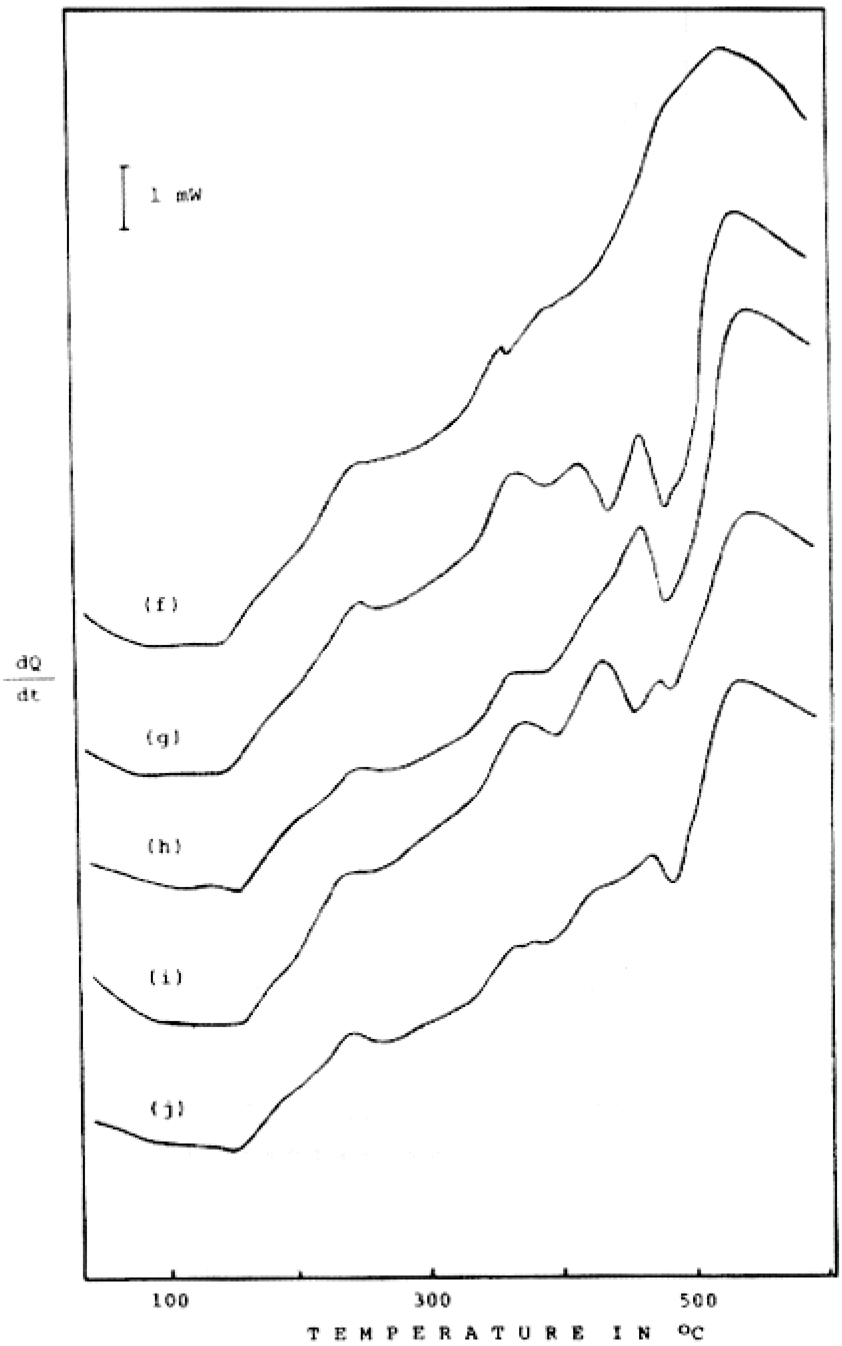


FIGURE 2

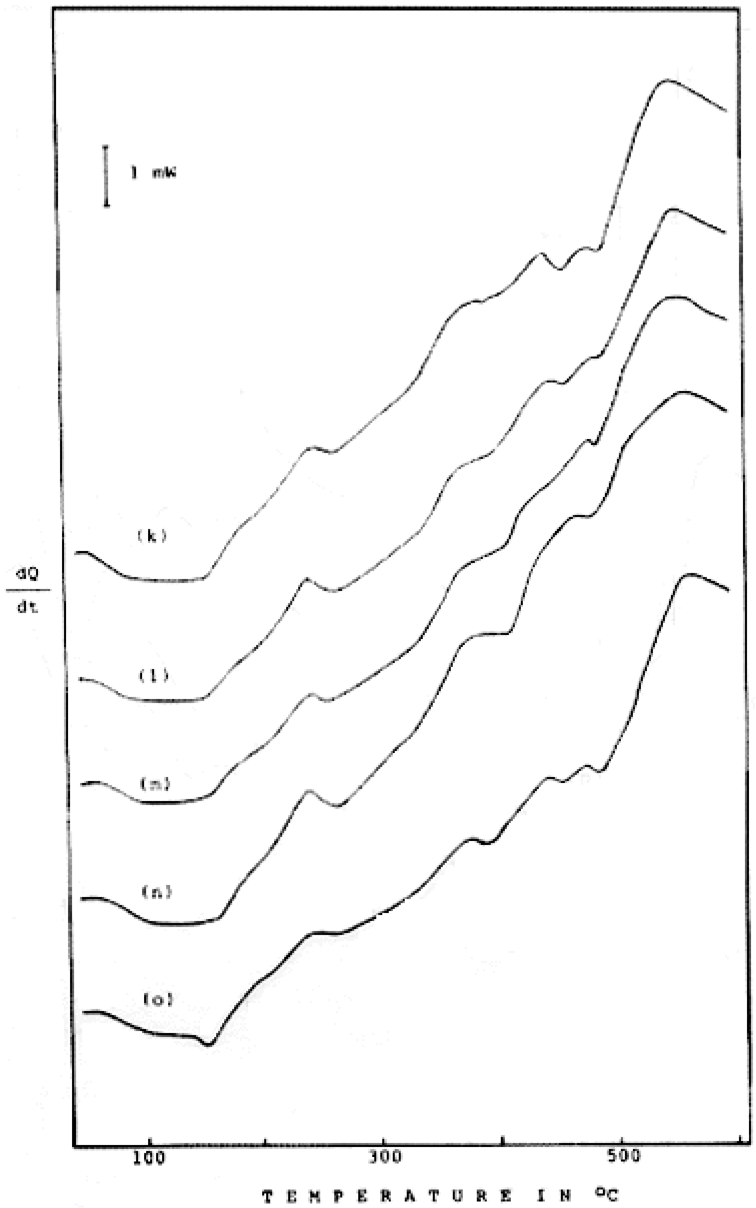


FIGURE 2 - DSC curves of the compounds: (a) $La(DMCP)_3LaOHCO_3.4.5H_2O$; b) $Ce(DMCP)_3CeOHCO_3.4H_2O$; c) $Pr(DMCP)_3PrOHCO_3.4H_2O$; d) $Nd(DMCP)_3NdOHCO_3.4H_2O$; e) $Sm(DMCP)_3SmOHCO_3.4H_2O$; f) $Eu(DMCP)_3EuOHCO_3.4H_2O$; g) $Gd(DMCP)_3GdOHCO_3.4H_2O$; h) $Tb(DMCP)_3TbOHCO_3.3H_2O$; i) $Dy(DMCP)_3DyOHCO_3.3H_2O$; j) $Ho(DMCP)_3HoOHCO_3.3.5H_2O$; k) $Er(DMCP)_3ErOHCO_3.3.5H_2O$; l) $Tm(DMCP)_3TmOHCO_3.3.5H_2O$; m) $Yb(DMCP)_3YbOHCO_3.3H_2O$; n) $Lu(DMCP)_3LuOHCO_3.3.5H_2O$ and o) $Y(DMCP)_3YOHCO_3.3.5H_2O$.

Conclusions

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

During the preparation of the NaDMCP, the neutralization of the acid with sodium hidrogen carbonate, even with excess of the acid HDMCP, mixture of compounds were obtained, indicating a diferent behaviour of DMCP with relation to DMBP and 4-MeO-BP.

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

Acknowledgements

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LELES, M. I. G. et al. Preparação e decomposição térmica de mistura de carbonato básico e 4-dimetilaminocinamalpiruvato com lantanídios(III) e ítrio(III) no estado sólido. *Ecl. Quím. (São Paulo)*, v.24, p.29-44, 1999.

RESUMO: Foram preparados compostos no estado sólido Ln-$OHCO_3$-DMCP, onde Ln representa os íons lantanídios(III) e ítrio(III) e DMCP é o ion 4-dimetilaminocinamalpiruvato. Na caracterização, bem como no estudo da decomposição térmica desses compostos, foram utilizados as técnicas termoanalíticas (TG, DTG, DSC) difratometria de raios X e análise elementar. A estabilidade bem como a decomposição térmica foram estudadas em atmosfera de ar utilizando cadinho de alumina.

PALAVRAS-CHAVE: Carbonato básico e 4-dimetilaminocinamalpiruvato; lantanídios; decomposição térmica.

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