

Synthesis, characterisation and thermal behaviour of solid state compounds of 4-methylbenzylidenepyruvate with heavier trivalent lanthanides and yttrium(III)

R.N. Marques, C.B. Melios, M. Ionashiro*

Instituto de Química, UNESP, SP, CP 355, CEP 14801-970, Araraquara, SP, Brazil

Received 24 October 2001; received in revised form 28 February 2002; accepted 28 February 2002

Abstract

Solid state Ln-4-Me-BP compounds, where Ln stands for heavier trivalent lanthanides (gadolinium to lutetium) and yttrium(III) and 4-Me-BP is 4-methylbenzylidenepyruvate ($\text{CH}_3\text{-C}_6\text{H}_4\text{-CH=CH-COCOO}^-$), have been synthesized. Elemental analysis, complexometry, X-ray powder diffractometry, infrared spectroscopy and simultaneous thermogravimetry-differential thermal analysis (TG-DTA), have been used to characterise and to study the thermal behaviour of these compounds. The results provided information concerning the stoichiometry, crystallinity, ligand's denticity, thermal stability and thermal decomposition. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Heavier trivalent lanthanides; Yttrium(III); 4-Methylbenzylidenepyruvate; Complexes; Characterization; Thermal behaviour

1. Introduction

Several metal-ion complexes of phenyl-substituted derivatives of benzylidenepyruvate, $\text{C}_6\text{H}_5\text{-CH=CH-COCOO}^-$ (BP), have been investigated in aqueous solutions [1–5] and in the solid state [6–12]. In aqueous solutions these works reported the thermodynamic stability (β_1), and spectroscopic parameters ($\epsilon_{1\text{max}}$, λ_{max}), associated with 1:1 complex species, as well as analytical applications of sodium 4-dimethylamino-BP for the gravimetric determination of Cu(II), and as indicator in the complexometric titration of Th(IV) and Al(III), with EDTA. In the solid state, the works reported the synthesis and investigation

of the compounds by means of thermogravimetry, derivative thermogravimetry (TG, DTG), differential thermal analysis (DTA), differential scanning calorimetry (DSC), X-ray powder diffractometry, and other methods of analysis. Establishment of stoichiometry and the details of the thermal decomposition were the main purposes of these studies.

In this paper, the object of the present research was to prepare solid state compounds of heavier trivalent lanthanides (i.e. Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) and yttrium(III) with 4-methylbenzylidenepyruvate (4-Me-BP) and to investigate by means of complexometry, elemental analysis, X-ray powder diffractometry, infrared spectroscopy 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.

* Corresponding author. Tel. +55-16-201-6617;
fax: +55-16-222-7932.
E-mail address: rosemarq@posgrad.iq.unesp.br (M. Ionashiro).

2. Experimental

The sodium salt of 4-methylbenzylidenepyruvic acid, was prepared following the same procedure described in the literature [13]. Aqueous solutions of 0.10 M Na-4-Me-BP were prepared by direct weighing of the salt.

Lanthanide and yttrium chlorides were prepared from the corresponding metal oxides by treatment with concentrated hydrochloric acid. The resulting solutions were evaporated to near dryness, the residues dissolved in distilled water, and the solutions again evaporated to near dryness to eliminate the excess of hydrochloric acid. The residues were redissolved in distilled water, transferred to a volumetric flask and diluted in order to obtain ca. 0.10 M solutions, whose pH were adjusted to 5.0 by adding diluted sodium hydroxide or hydrochloric acid solutions.

The solid state compounds were prepared by adding slowly, with continuous stirring, the solution of the ligand to the respective metal chloride solution, until total precipitation of the metal ions. The precipitates were washed with distilled water until elimination of the chloride ion, filtered through and dried on Whatman no. 42 filter paper, and kept in a desiccator over anhydrous calcium chloride, under reduced pressure, to constant mass.

In the solid state compounds, hydration water, ligand and metal ion contents were determined from the TG curves. The metal ions were also determined by complexometric titrations with standard EDTA solution, using xylenol orange as indicator [14]. Carbon and

hydrogen microanalysis were performed by using EA 1110, CHNS-O Elemental Analyser (CE Instruments).

X-ray powder patterns were obtained by using a Siemens D-500 X-ray diffractometer, employing Cu K α radiation ($\lambda = 1.541 \text{ \AA}$) and settings of 40 kV and 20 mA. Infrared spectra for 4-Me-BP (sodium salt) as well as for its trivalent lanthanide and yttrium(III) compounds, were run on a Nicolet mod. Impact 400 FT-IR instrument, within the 4000–400 cm^{-1} range. The solid samples were pressed into KBr pellets.

Simultaneous TG-DTA curves, were recorded on a model SDT 2960 thermal analysis system from TA Instruments. The purge gas was an air flow of 150 ml min^{-1} . A heating rate of 20 $^{\circ}\text{C min}^{-1}$ was adopted, with samples weighing about 7–8 mg. Alumina crucibles were used for recording the TG-DTA curves.

3. Results and discussion

The analytical results of the synthesised compounds are shown in Table 1. These results permitted to establish the stoichiometry of the compounds, which is in agreement with the general formula $\text{Ln}(\text{4-Me-BP})_3 \cdot 1.5\text{H}_2\text{O}$, where Ln represents trivalent lanthanides and yttrium and 4-Me-BP is 4-methylbenzylidenepyruvate.

The X-ray powder patterns showed that all the compounds were obtained in amorphous state. The amorphous state is undoubtedly related to the low solubility of these compounds, as already observed for

Table 1
Analytical data for the $\text{LnL}_3 \cdot 1.5\text{H}_2\text{O}$ compounds

Compound	Ln (%)			Ligand lost (%)		Water (%)		Carbon (%)		Hydrogen (%)	
	Calculated	TG	EDTA	Calculated	TG	Calculated	TG	Calculated	EA	Calculated	EA
GdL ₃ ·1.5H ₂ O	20.91	20.83	21.02	72.30	72.32	3.59	3.67	52.71	52.13	4.02	4.17
TbL ₃ ·1.5H ₂ O	21.10	21.05	21.00	71.61	71.56	3.59	3.68	52.60	52.85	4.02	4.16
DyL ₃ ·1.5H ₂ O	21.46	21.62	21.42	71.80	71.59	3.57	3.60	52.35	52.91	4.00	4.07
HoL ₃ ·1.5H ₂ O	21.71	21.82	21.89	71.57	71.50	3.56	3.50	52.18	51.39	3.99	4.05
ErL ₃ ·1.5H ₂ O	21.95	21.89	21.82	71.35	71.40	3.55	3.57	52.02	51.97	3.98	4.03
TmL ₃ ·1.5H ₂ O	22.12	22.19	22.38	71.19	71.03	3.54	3.63	51.91	51.46	3.97	4.06
YbL ₃ ·1.5H ₂ O	22.54	22.70	22.79	70.81	70.70	3.52	3.44	51.63	51.33	3.95	4.01
LuL ₃ ·1.5H ₂ O	22.68	22.77	22.92	70.68	70.57	3.51	3.53	51.53	51.72	3.94	4.01
YL ₃ ·1.5H ₂ O	13.01	13.03	13.27	79.53	79.44	3.95	4.02	57.98	58.26	4.43	4.55

Ln: trivalent lanthanides and yttrium(III); L: 4-methylbenzylidenepyruvate.

Table 2

Spectroscopic data for sodium 4-methylbenzylidenepyruvate and for its compounds with heavier trivalent lanthanides and yttrium(III)

Compounds	$\nu_{(\text{O}-\text{H})} (\text{H}_2\text{O})$	$\nu_{\text{s}(\text{COO}^-)}$	$\nu_{\text{as}(\text{COO}^-)}$	$\nu_{(\text{C}=\text{O})}$
4MeBP—Na·0.5H ₂ O	3425 m	1406 m	1635 s	1670 s
Gd(4-MeBP) ₃ ·1.5H ₂ O	3347 m	1412 m	1590 s	1644 s
Tb(4-MeBP) ₃ ·1.5H ₂ O	3352 m	1407 m	1589 s	1631 s
Dy(4-MeBP) ₃ ·1.5H ₂ O	3344 m	1410 m	1589 s	1644 s
Ho(4-MeBP) ₃ ·1.5H ₂ O	3361 m	1415 m	1590 s	1643 s
Er(4-MeBP) ₃ ·1.5H ₂ O	3359 m	1410 m	1589 s	1641 s
Tm(4-MeBP) ₃ ·1.5H ₂ O	3344 m	1403 m	1587 s	1640 s
Yb(4-MeBP) ₃ ·1.5H ₂ O	3333 m	1402 m	1586 s	1634 s
Lu(4-MeBP) ₃ ·1.5H ₂ O	3355 m	1410 m	1588 s	1645 s
Y(4-MeBP) ₃ ·1.5H ₂ O	3360 m	1414 m	1590 s	1643 s

Strong: s; medium: m, 4-MeBP: 4-methylbenzylidenepyruvate; $\nu_{(\text{O}-\text{H})}$ = hydroxyl group stretching frequency; $\nu_{\text{s}(\text{COO}^-)}$ and $\nu_{\text{as}(\text{COO}^-)}$ = symmetrical and anti-symmetrical vibrations of the COO⁻ structure; $\nu_{(\text{C}=\text{O})}$ = ketonic carbonyl stretching frequency.

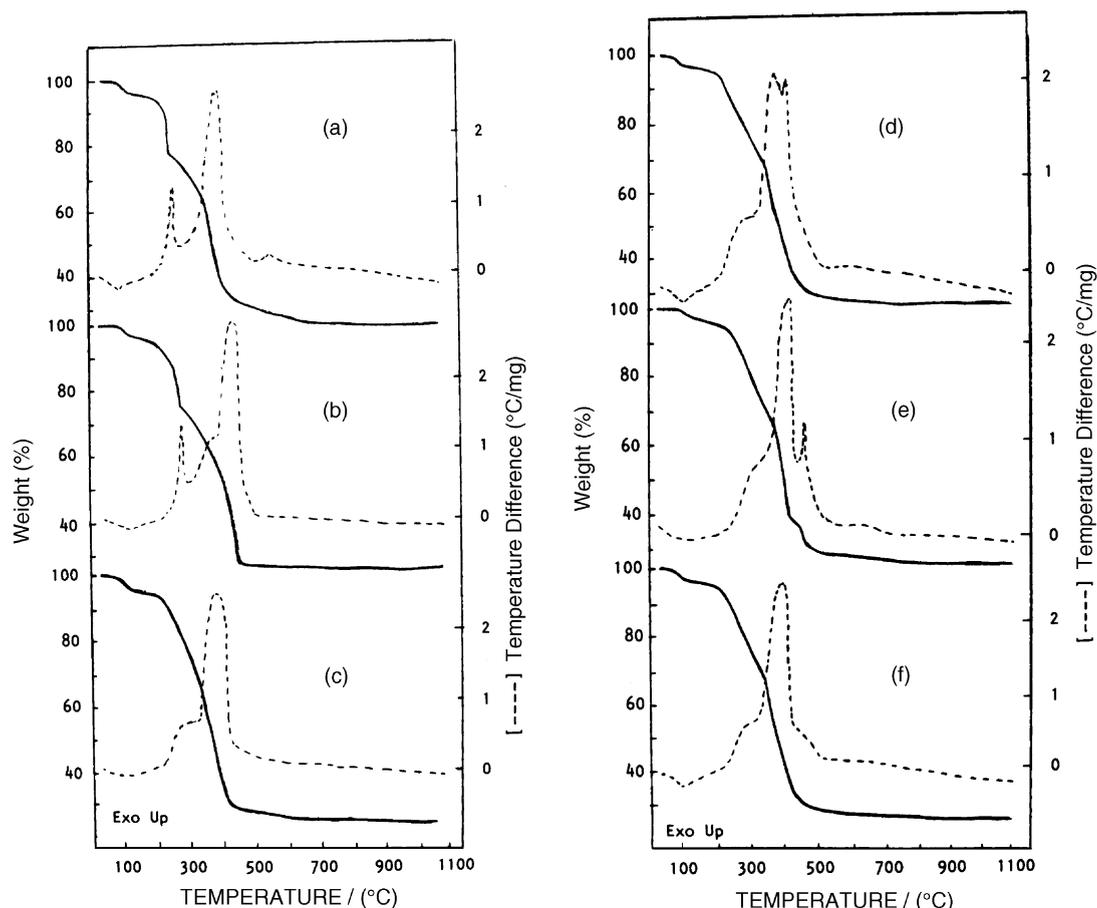


Fig. 1. Simultaneous TG-DTA curves of the compounds: (a) Gd(4-Me-BP)₃·1.5H₂O (7.601 mg); (b) Tb(4-Me-BP)₃·1.5H₂O (7.319 mg); (c) Dy(4-Me-BP)₃·1.5H₂O (8.032 mg); (d) Ho(4-Me-BP)₃·1.5H₂O (8.573 mg); (e) Er(4-Me-BP)₃·1.5H₂O (7.839 mg); (f) Tm(4-Me-BP)₃·1.5H₂O (7.391 mg); (g) Yb(4-Me-BP)₃·1.5H₂O (7.612 mg); (h) Lu(4-Me-BP)₃·1.5H₂O (7.335 mg); (i) Y(4-Me-BP)₃·1.5H₂O (7.898 mg).

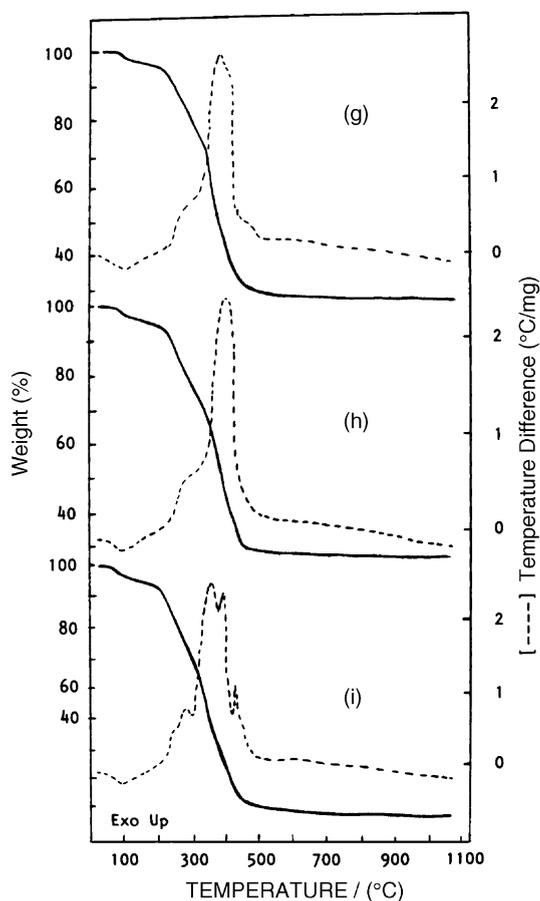


Fig. 1. (Continued).

the lanthanides and yttrium compounds with other phenyl-substituted derivatives of BP [6,7].

Infrared spectroscopic data on 4-methylbenzylidene-pyruvate and its compounds with heavier trivalent lanthanides and yttrium(III) are shown in Table 2. The bands found for 4-Me-BP (sodium salt), centred at 1670 cm^{-1} (ketonic carbonyl stretching) and 1635 cm^{-1} (anti-symmetrical carboxylate vibration) are both shifted to lower frequencies in the complexes, namely, $1645\text{--}1631$ and $1590\text{--}1586\text{ cm}^{-1}$, respectively, suggesting lanthanides and yttrium co-ordination both by the α -ketonic carbonyl and carboxylate groups of the ligand. This behaviour is in line with that observed for the 1:1 complexes of the same ligand with lanthanides in aqueous solution, where linear free energy relationships, as applied to oxygen donor

substances, also suggest the -COCOO^- moiety as the bidentate metal binding site of 4-Me-BP [5].

Simultaneous TG-DTA curves of the compounds are shown in Fig. 1. These curves exhibit mass losses in three or four consecutive and/or overlapping steps and thermal events corresponding to these losses. Two patterns of thermal behaviour are observed up to $400\text{ }^\circ\text{C}$. Firstly, a close similarity is noted concerning the TG-DTA profiles of the gadolinium and terbium compounds, Fig. 1a and b. On the other hand, dysprosium to lutetium and yttrium compounds display another set of very similar TG-DTA profiles, Fig. 1c–i.

These curves also show that the first mass loss for all the compounds occurs within the same temperature range (i.e. $50\text{--}140\text{ }^\circ\text{C}$); the second mass loss also begins at the same temperature ($155\text{ }^\circ\text{C}$), showing that the thermal behaviour up to this step is not dependent on the nature of the lanthanide ion. However, the features shown by the next steps of thermal decomposition as well as the mass lost in each step are characteristic of each compound, and no depend on the lanthanide ion present. Probably this behaviour is because all the compound was obtained in the amorphous state.

For all the compounds, the first mass loss (range: $55\text{--}140\text{ }^\circ\text{C}$), associated to endothermic peaks at $95\text{--}100\text{ }^\circ\text{C}$, is ascribed to the dehydration, which occurs in a single step and through a slow process. This behaviour was also observed during the dehydration of lanthanides and yttrium compounds with other phenyl-substituted derivatives of BP, and it seems to be characteristic of compounds obtained in amorphous state [6,7,12].

Once dehydrated, the anhydrous compounds are stable up to $155\text{ }^\circ\text{C}$, and above this temperature up to $415\text{ }^\circ\text{C}$ (Gd, Er, Yb); $455\text{ }^\circ\text{C}$ (Tb); $410\text{ }^\circ\text{C}$ (Dy); $490\text{ }^\circ\text{C}$ (Ho); $420\text{ }^\circ\text{C}$ (Tm, Y) and $430\text{ }^\circ\text{C}$ (Lu), the mass losses corresponding to exothermic events are attributed to the oxidation of organic matter. For the gadolinium and terbium compounds, the mass losses occur in two consecutive steps through fast processes, without a plateau between the steps. The similarity of the TG-DTA curves up to this point suggests that the decomposition mechanism is the same, for both compounds. For the other compounds (Dy–Lu, Y), the mass losses occur in a single step. The change in slope that occurs in the TG curves above $320\text{ }^\circ\text{C}$, is due to

the increase of the reactions' rates. The similarity among these curves, also suggests that the decomposition mechanism should be the same for the aforementioned compounds.

For each of the considered compounds, the oxidation of the organic matter yields an intermediate derivative, accompanied by a carbonaceous residue. The intermediate is probably the corresponding dioxycarbonate, as already observed for the complexes of other phenyl-substituted derivatives of BP with trivalent lanthanides and yttrium(III) [6,7]. Tests with hydrochloric acid solution on samples heated up to the temperatures of formation of these intermediates, as indicated by the corresponding TG-DTA curves,

confirmed, in all cases, evolution of CO₂ and presence of the carbonaceous residues.

For the Dy, Ho, Tm, Yb, Lu and Y compounds, the thermal decomposition of the corresponding intermediates and of the carbonaceous residues occurs simultaneously and slowly in a single step; for the Gd, Tb and Er compounds, two steps are observed. In correspondence with the mass losses, the DTA curves show small and broad exothermic events only for the Ho and Er compounds, while for the other compounds these thermal events are not observed. This is probably due to the balance between in exothermic process (oxidation of the carbonaceous residue) and an endothermic one (decomposition of the metal dioxycarbonates); the

Table 3

Temperature ranges (θ), mass losses (%) and peak temperatures observed for each step of the TG-DTA curves of the compounds LnL₃·1.5H₂O where Ln = trivalent lanthanides and yttrium(III); L = 4-methylbenzylidenepyruvate

Compound		Steps			
		First	Second	Third	Fourth
GdL ₃ ·1.5H ₂ O	θ (°C)	55–140	155–265	265–415	415–720
	Loss (%)	3.67	20.09	41.32	10.91
	Peak (°C)	95 (endo)	260 (exo)	390 (exo)	545 (exo)
TbL ₃ ·1.5H ₂ O	θ (°C)	55–140	155–290	290–455	455–710
	Loss (%)	3.68	21.10	50.47	1.99
	Peak (°C)	100 (endo)	280 (exo)	435 (exo)	–
DyL ₃ ·1.5H ₂ O	θ (°C)	55–140	155–410	410–715	
	Loss (%)	3.60	65.90	5.69	
	Peak (°C)	100 (endo)	390 (exo)	–	
HoL ₃ ·1.5H ₂ O	θ (°C)	55–140	155–490	490–730	
	Loss (%)	3.50	68.64	2.86	
	Peak (°C)	100 (endo)	385, 415 (exo)	620 (exo)	
ErL ₃ ·1.5H ₂ O	θ (°C)	55–140	155–415	415–500	500–750
	Loss (%)	3.57	57.79	10.20	3.41
	Peak (°C)	100 (endo)	400 (exo)	445 (exo)	635 (exo)
TmL ₃ ·1.5H ₂ O	θ (°C)	55–140	155–420	420–750	
	Loss (%)	3.63	63.07	7.96	
	Peak (°C)	100 (endo)	385 (exo)	–	
YbL ₃ ·1.5H ₂ O	θ (°C)	55–140	155–415	415–760	
	Loss (%)	3.44	63.29	7.41	
	Peak (°C)	100 (endo)	380 (exo)	–	
LuL ₃ ·1.5H ₂ O	θ (°C)	55–140	155–430	430–770	
	Loss (%)	3.53	65.45	5.12	
	Peak (°C)	100 (endo)	400 (exo)	–	
YL ₃ ·1.5H ₂ O	θ (°C)	55–140	155–420	420–730	
	Loss (%)	4.02	75.26	4.18	
	Peak (°C)	100 (endo)	370, 400, 440 (exo)	–	

resulting net heats produce only small exothermic peak or no thermal event at all.

For all the compounds, the final thermal decomposition residues were the respective oxides, Tb_4O_7 and Ln_2O_3 ($Ln = Gd, Dy-Lu, Y$), as proven by X-ray powder diffraction analyses of these residues.

The mass losses, temperature ranges and the peak temperatures observed for each step of the TG-DTA curves are shown in [Table 3](#).

4. Conclusions

From the TG curves and elemental analysis, a general formula could be established for these compounds in the solid state. The infrared spectroscopic data suggest that 4-Me-BP acts as a bidentate ligand towards trivalent lanthanides and yttrium(III).

The TG-DTA curves and X-ray powder patterns provided previously unreported information concerning crystallinity, thermal stability and thermal decomposition of these compounds.

Acknowledgements

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

References

- [1] C.B. Melios, V.R. Torres, M.H.A. Mota, J.O. Tognolli, M. Molina, *Analyst* 109 (1984) 385.
- [2] C.B. Melios, J.T.S. Campos, M.A.C. Mazzeu, L.L. Campos, M. Molina, J.O. Tognolli, *Inorg. Chim. Acta* 139 (1987) 163.
- [3] C.B. Melios, H. Redigolo, M. Molina, *J. Inorg. Biochem.* 36 (1989) 307.
- [4] C.B. Melios, M. Ionashiro, H. Redigolo, M.H. Miyano, M. Molina, *Eur. J. Solid State Inorg. Chem.* 28 (1991) 291.
- [5] R.N. Marques, C.B. Melios, N.C.S. Pereira, O.S. Siqueira, M. de Moraes, M. Molina, M. Ionashiro, *J. Alloys Comps.* 249 (1997) 102.
- [6] L.C.S. Oliveira, C.B. Melios, C.A. Ribeiro, M.S. Crespi, M. Ionashiro, *Thermochim. Acta* 219 (1993) 215.
- [7] M.H. Miyano, C.B. Melios, C.A. Ribeiro, H. Redigolo, M. Ionashiro, *Thermochim. Acta* 221 (1993) 53.
- [8] D.E. Rasera, L.C.S. de Oliveira, C.B. Melios, M. Ionashiro, *Thermochim. Acta* 250 (1995) 151.
- [9] L.C.S. Oliveira, D.E. Rasera, O.S. Siqueira, J.R. Matos, C.B. Melios, M. Ionashiro, *Thermochim. Acta* 275 (1996) 269.
- [10] L.C.S. Oliveira, D.E. Rasera, J.D.S. Oliveira, C.B. Melios, M. Ionashiro, *An. Assoc. Bras. Quím.* 47 (1998) 75.
- [11] R.A. Mendes, M.A. Carvalho Filho, N.S. Fernandes, L.M. D'Assunção, C.B. Melios, M. Ionashiro, *An. Assoc. Bras. Quím.* 47 (1998) 329.
- [12] N.S. Fernandes, M.A.S. Carvalho Filho, C.B. Melios, M. Ionashiro, *J. Thermal Anal. Cal.* 59 (2000) 663.
- [13] C.B. Melios, A.M. Delsin, J.O. Tognolli, M. Molina, *Ecl. Quím.* 6 (1981) 51.
- [14] M. Ionashiro, C.A.F. Graner, J. Zuanon Netto, *Ecl. Quím.* 8 (1983) 29.