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Synthesis and thermal studies of solid state 2-chloro-benzylidenepyruvic acid and its compounds with sodium, aluminium (III), gallium (III) and indium (III) cations.

*G. Bannach[1], E. Schnitzler[2], C. B. Melios[1] and M. Ionashiro[1]**
[1]Instituto de Química – UNESP – Araraquara - CEP 14801-970 – SP - Brasil
[2]Departamento de Química – UEPG – CEP 84030-000 - Ponta Grossa – PR - Brasil

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Abstract: The synthesis of sodium 2-chlorobenzylidenepyruvate and its corresponding acid as well as binary, binary together with it's acid or hydroxo-2-chorobenzylidenepyruvate of aluminium (III), gallium (III) and indium (III), were isolated. Chemical analysis, thermogravimetry, derivative thermogravimetry (TG/DTG), simultaneous thermogravimetry-differential thermal analysis (TG-DTA) and X-ray powder diffractometry have been employed to characterize and to study the thermal behaviour of these compounds. The results provided information concerning the stoichiometry, crystallinity, thermal stability and thermal decomposition.

Keywords: 2-chlorobenzylidenepyruvic acid; 2-chlorobenzylidenepyruvate; sodium; aluminium; gallium; indium: thermal behaviour.

Introduction

Solid-state compounds of 4-methoxybenzylidenepyruvate (4-MeO-BP), 4-dimethylaminobenzylidenepyruvate (DMBP), 4-chlorobenzylidenepyruvate (4-Cl-BP) and 4-methylbenzylidenepyruvate (4-Me-BP) with several metallic ions, including trivalent lanthanides [1, 2, 6-8], alkaline-earth cations [4] and some bivalent transition metals [3,5] have been isolated and characterized.

In all these studies, no major difficulties were faced in obtaining binary complexes of general formula $M^{m+}L_m.nH_2O$, where M stands for the metal ion and L for the ligand under consideration. These compounds are very slightly soluble in aqueous media as well as in most organic solvents. Preliminary attempts directed towards the preparation of the analogous Al(III), Ga(III) and In(III) complexes from aqueous solutions by the already described procedures [1-8] presented difficulties: only solid materials with no definite stoichiometry were invariably obtained. It was soon depicted that the main drawback could be ascribed to the very pronounced tendency of these metal ions to hydrolyse and especially begin uniformly at a pH of 3.8 (Al), 3.4 (Ga) [9] and 3.4(In) [9, 10] and this competition between hydroxide ions and the ligand 2-chorobenzylidenepyruvate for these metal ions becomes quite significant at the usual working pH ranges (i. e., between 3.5 and 5.5). On the other hand for pH<2, occurs the simultaneous precipitation of 2-chlobenzylidenepyruvic acid together with binary complexes.

Thus, the present work deals with the synthesis of sodium 2-chloro-benzylidenepyruvate and its corresponding acid not yet described in the literature, as well as solid-state compounds of aluminium, gallium and indium with 2-chloro-benzylidenepyruvate obtained by their interaction in solution at three different pH values.

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*corresponding author

Experimental

Synthesis of sodium 2-chlorobenzylidenepyruvate and its corresponding acid

Sodium 2-chlorobenzylidenepyruvate and its corresponding acid were synthesized and purified as follows: an aqueous solution of sodium pyruvate (22g per 500 ml) was added dropwise, with continuous stirring, to a methanol solution of 2-chlorobenzaldehyde (29g per 500 ml). Sixty milliliters of an aqueous sodium hydroxide solution (18 % m/v) was slowly added 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 10 and 12ºC. The formation of a pale yellow precipitate was observed during the addition of the sodium hydroxide solution.

The system is left to stand for about 14 hours at room temperature (23-28ºC). The pale yellow precipitate (impure sodium 2-chlorobenzylidenepyruvate) is filtered, washed with five 100 ml portions of methanol, to remove most of the unreacted aldehyde and secondary products and left standing at room temperature for about 24 hours. This crude product (21.5g) was recrystallized from 50% (v/v) methanol-water. The purified product was dried in an oven at 110ºC, to constant mass (6.5g).

A portion of 2.5g of the purified sodium 2-chlorobenzylidenepyruvate was dissolved in 50 ml of water, adding to this solution, under continuous stirring, 10 ml of concentrated (12 mol L^{-1}) hydrochloric acid. A finely divided yellow precipitate separated immediately; the supernatant liquid remained clear and pale yellow. The system was kept in a refrigerator (4-5ºC) for about 4 hours. The precipitate was then filtered and washed with cooled water, until chloride free. It was left air-drying spontaneous for about 3 days and then transferred to a desiccator over anhydrous P_2O_5, under reduced pressure (2-5 mm Hg) during 2 days. Impure 2-chlorobenzylidenepyruvic acid was obtained (1.63g). It was recrystallized from boiling benzene in yellow plates (0.61g), m.p. 94.3-95.0ºC.

Preparation of solid-state compounds of aluminium, gallium and indium with 2-chlorobenzylidenepyruvate

Aqueous solutions of the ligand, whose pH was adjusted to 3.0, 3.5 and 4.0 by adding diluted nitric acid solution, were prepared by direct weighing of the sodium salt. Gallium nitrate was prepared from metallic gallium by treatment with concentrated nitric acid. The resulting solution was transferred to a volumetric flask, whose pH was adjusted to 2.0 by adding diluted sodium hydroxide solution. Aqueous aluminium and indium nitrates solutions were prepared by direct weighing of aluminium nitrate nonahydrate and indium nitrate pentahydrate, their pH values being adjusted to 2.0 by adding diluted nitric acid solution. The solid-state compounds were prepared adding, with continuous stirring, the solution of the respective metallic ion to the solution of the ligand until complete precipitation of the metallic ion present in the solution. The precipitates were washed with distilled water until total elimination of nitrate ions, filtered through and dried on Whatman nº 42 filter paper, and kept in a desiccator over anhydrous calcium chloride.

In the solid-state compounds, hydration water, ligand and metal ion contents were determined from the TG curves.

X-ray powder patterns were obtained by using a Siemens D-500 X-ray diffractometer, employing Cu K? radiation (?=1.541 Å) and setting of 40 kV and 20 mA.

Simultaneous TG-DTA and DSC curves were recorded on a model SDT 2960 and 2010 thermal analysis system from TA Instruments. The purge gas was an air flow of 100 mL min^{-1}. A heating rate of 20ºC min^{-1} was adopted, with samples weighing about 7 mg. Alumina crucibles for TG-DTA and aluminium crucibles for DSC were used for recording these curves.

Results and Discussion

The presence of water in the 2-chlorobenzylidenepyruvic acid (2-Cl-HBP), recrystallized from boiling benzene was strongly suggested by its infrared spectrum. Elemental analysis yielded: C= 55.91%, H= 3.60%; equivalent mass found by potentiometric titration = 216.2. These values, coupled with the infrared spectrum evidence were consistent with the formula $C_{10}H_7O_3Cl.1/3H_2O$ (calculated carbon and hydrogen contents: 55.45 and 3.57%, respectively; calculated equivalent mass: 216.6). Strong retention of crystallization solvents is well-known features of benzylidenepyruvic acids [11, 12].

The TG-DTA and DSC curves of 2-Cl-HBP are shown in Figs 1(a) and 2(a), respectively. The first mass loss observed between 50 and 100ºC, corresponding to the broad endothermic peak at 80ºC is ascribed to dehydration with loss of 0.39 H_2O (Calcd= 3.23%; TG= 3.21%), in spite of the DSC curve to suggest overlapping events. For that very reason TG-DTA and DSC curves of the anhydrous compounds were obtained up to 200ºC and they are shown in Figs 1(b) and 2(b). These curves show an endothermic peak at 92ºC (DTA) or 97ºC (DSC) due to the fusion of the compound and also confirmed that the dehydration and fusion occur simultaneously.

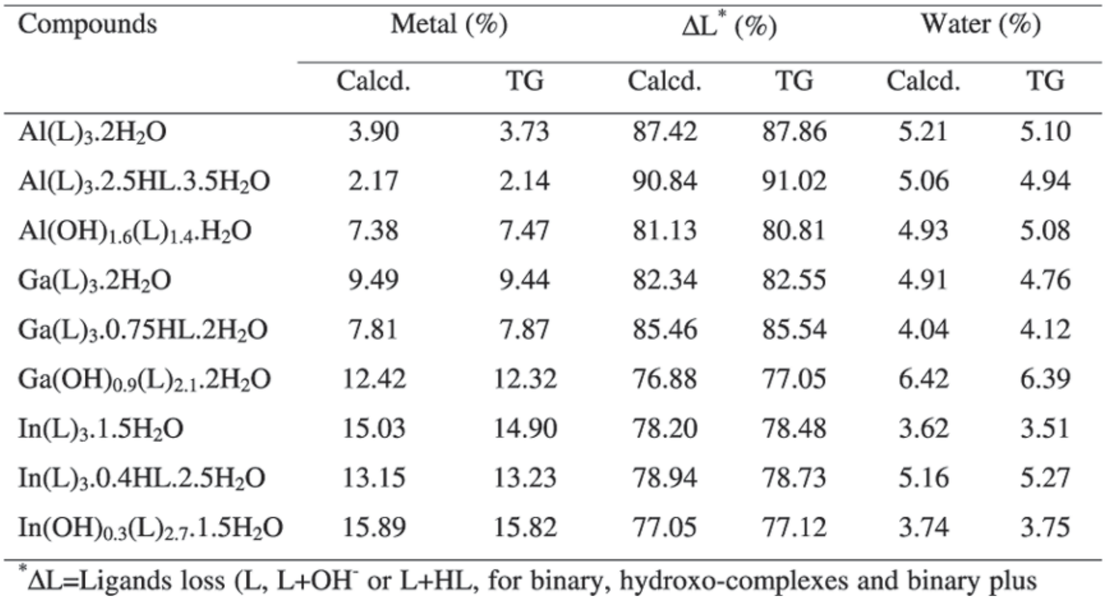
The anhydrous compound is stable up to 110ºC and above this temperature the thermal decomposition occurs in two consecutive steps between 100-480ºC and 480-630ºC with loss of 64.41% and 32.32%, respectively. Only a rough draft of an exotherm event is associated to the first mass loss, suggesting that the thermal decomposition (endothermic) and oxidation of evolved products (exothermic) occur almost simultaneously, with formation of carbonaceous residue. The second step corresponding to the large exothermic peak is ascribed to the oxidation of carbonaceous residue.

The TG-DTA curves of sodium salt of 2-Cl-HBP are shown in Fig. 3. The first mass loss in the temperature range 95 – 130ºC associated to endothermic peak at 123ºC is ascribed to dehydration, with loss of 0.5 H_2O. (Calcd= 3.73%; TG= 4.08%). The anhydrous compound is stable up to 230ºC, and above this temperature up to 700ºC, the mass loss (70.15%) occurs in four steps corresponding to exothermic events that are attributed to oxidation of organic matter with formation of sodium carbonate and small amount of carbonaceous residue. Test with hydrochloric acid solution on sample heated up to the temperature of formation of the intermediate, as indicated by the TG-DTA curves (700ºC), confirmed evolution of CO_2 and presence of carbonaceous residue. The last step between 700 and 850ºC is attributed to the thermal decomposition of the carbonaceous residue and thermal decomposition/evaporation of sodium carbonate in spite of the TG curve yet to show mass loss. The endothermic peak at 793ºC is ascribed to the fusion of sodium carbonate.

For the Al, Ga and In with 2-Cl-BP compounds the thermoanalytical (TG) results are shown in Table 1. These results show a good agreement between calculated and experimental contents, thereby supporting the proposed formula. These results also show that the formation of hydroxo-complexes occur when the precipitation of the metal ions was realized by using aqueous solution of the ligand whose pH was adjusted to a value of 4.0, while binary compound or a mixture of binary compound with 2-chlobenzylidenepyruvic acid were obtained when pH of the aqueous solution of the ligand was adjusted to 3.5 and 3.0, respectively.

The TG/DTG and TG-DTA curves of the compounds are shown in Figs. 4-12. These curves show mass losses in consecutive or overlapping consecutive steps between 30 and 640ºC. For each metal ion, a great similarity is observed in the TG/DTG profiles of these compounds; however the mass losses, as well as the temperature ranges observed for each step are characteristic of each compound. In all the TG and DTG curves, the first mass loss up to 120ºC or 130ºC ascribed to dehydration, was firstly pointed out by their DTG curves and subsequently confirmed by the broad endothermic peaks centered at 60-120ºC or 70-130ºC in the respective DTA curves. This procedure was necessary because no evidence concerning the formation of stable anhydrous compounds is observed in the TG curves. For all the compounds the dehydration occurs in a single step and through slow mass loss; this behaviour seems to be characteristic of compounds obtained in amorphous state, as already observed during the dehydration of compounds with other phenyl-substituted derivatives of BP [1, 2, 6, and 8].

Table 1 - Thermoanalytical (TG) Results



Compounds	Metal (%)		ΔL^* (%)		Water (%)	
	Calcd.	TG	Calcd.	TG	Calcd.	TG
$Al(L)_3.2H_2O$	3.90	3.73	87.42	87.86	5.21	5.10
$Al(L)_3.2.5HL.3.5H_2O$	2.17	2.14	90.84	91.02	5.06	4.94
$Al(OH)_{1.6}(L)_{1.4}.H_2O$	7.38	7.47	81.13	80.81	4.93	5.08
$Ga(L)_3.2H_2O$	9.49	9.44	82.34	82.55	4.91	4.76
$Ga(L)_3.0.75HL.2H_2O$	7.81	7.87	85.46	85.54	4.04	4.12
$Ga(OH)_{0.9}(L)_{2.1}.2H_2O$	12.42	12.32	76.88	77.05	6.42	6.39
$In(L)_3.1.5H_2O$	15.03	14.90	78.20	78.48	3.62	3.51
$In(L)_3.0.4HL.2.5H_2O$	13.15	13.23	78.94	78.73	5.16	5.27
$In(OH)_{0.3}(L)_{2.7}.1.5H_2O$	15.89	15.82	77.05	77.12	3.74	3.75

[*] ΔL=Ligands loss (L, L+OH^- or L+HL, for binary, hydroxo-complexes and binary plus

Immediately after the dehydration the TG curves suggest mass losses in two overlapping consecutive steps, although the DTG curves show mass losses in three or four overlapping consecutive or simultaneous steps through a rather complex pathway, as can be seen in the Figs. 4(a)–12(a).

For all the aluminium compounds, after the dehydration the TG curves, Figs. 4-6 show that the mass losses begin with a slow process, followed by fast processes without a plateau between the steps. In correspondence with the mass losses the DTA curves, Figs. 4(b)-6(b) show an exotherm between 250-600ºC suggesting overlapping peaks. These curves also show that in the first step the mass loss is greater than that observed for the second step, however the evolved heat is on the contrary. This is an indication that the first mass loss is due to the simultaneous thermal decomposition (endothermic event) and oxidation of the evolved materials (exothermic event), with formation of carbonaceous residue, where the resulting net heats produce only small exotherm without formation of a definite peak. In the last step the mass loss is ascribed to the oxidation of the carbonaceous residue that produces a great quantity of heat, as shown by the second exothermic peak. The similarity among these curves, suggests that the thermal decomposition should be the same for the aforementioned compounds.

In all the gallium and indium compounds, after the dehydration the TG curves, Figs. 7-12 show mass losses in two consecutive steps. For both of them the thermal decomposition begins with a slow process followed by a fast one. In the first step the mass loss is slightly smaller than the second step, on the contrary of the mass losses observed in the TG curves of the aluminium compounds, nevertheless the first exothermic peak is very smaller than the second exothermic one showing the same behaviour of the DTA curves of the aluminium compounds. Thus, the first mass loss is also ascribed to the simultaneous thermal decomposition and oxidation of evolved materials, with formation of carbonaceous residue, while the second mass loss is ascribed to the oxidation of the carbonaceous material formed in the previous step. A close similarity is also observed in the TG-DTA curves of these compounds, suggesting that the thermal decomposition mechanism must to be the same, too.

For all the compounds, the final thermal decomposition residues were the respective oxides, Al_2O_3, Ga_2O_3 and In_2O_3, as indicated by the TG curves and proven by X-ray powder diffraction analyses of these residues.

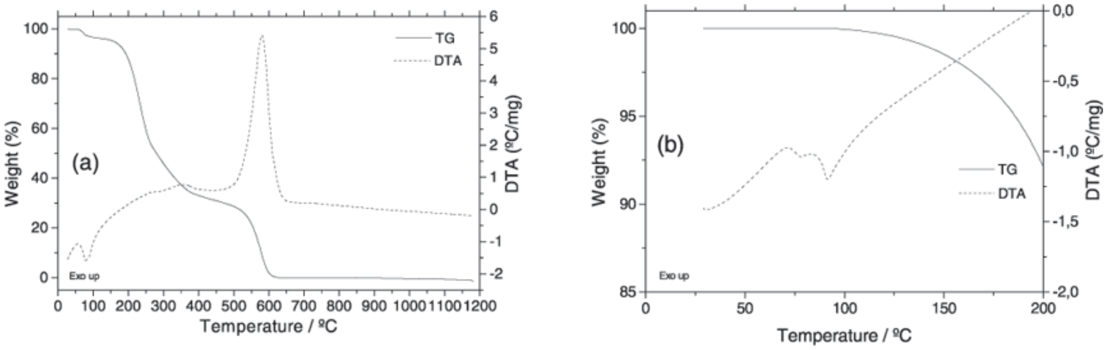


Figure 1 - TG-DTA curves of 2-chlorobenzylidenepyruvic acid. [(a) 0.39H_2O m_i= 2.9744 mg; (b) anhydrous m_i= 5.3013 mg].

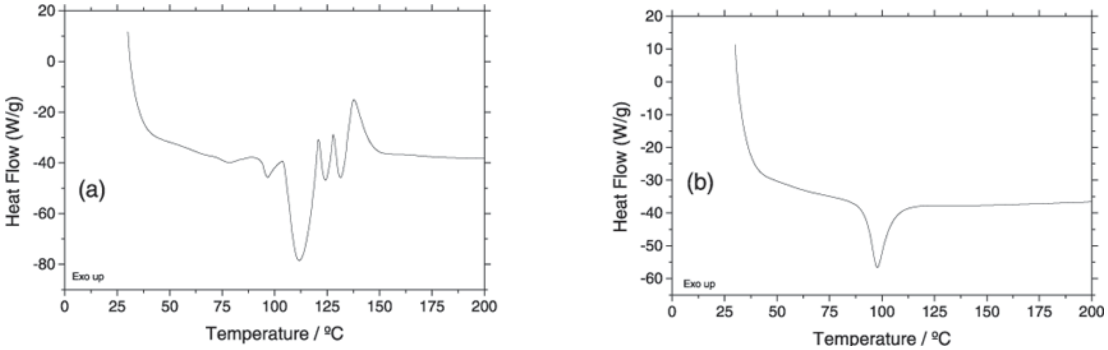


Figure 2 - DSC curves of 2-chlorobenzylidenepyruvic acid. [(a) 0.39H_2O m_i= 5.2310 mg; (b) anhydrous m_i= 5.0154 mg].

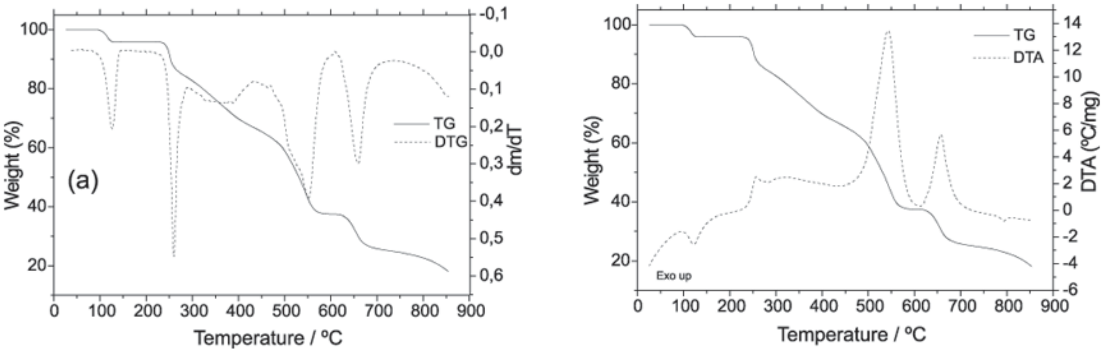


Figure 3 - (a) TG/DTG and (b) simultaneous TG-DTA curves of Na-2-Cl-BP.1/2H_2O (m_i=7.0597 mg).

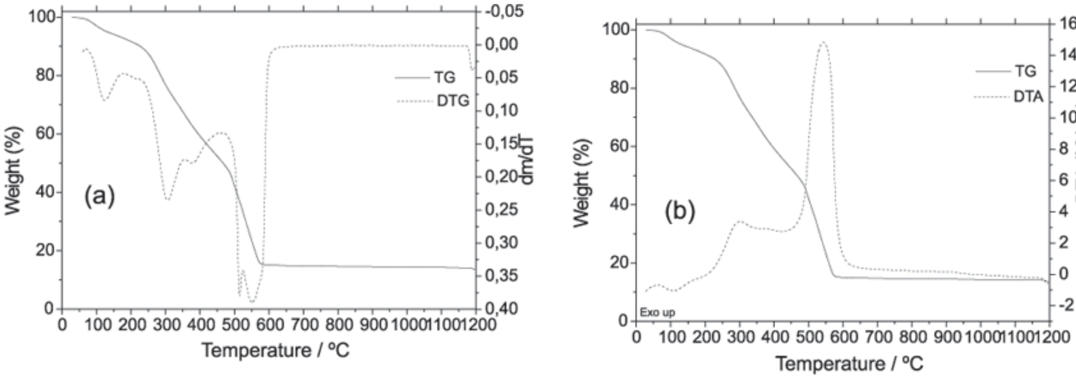


Figure 4 - (a) TG/DTG and (b) simultaneous TG-DTA curves of $Al(OH)_{1.6}(2\text{-}Cl\text{-}BP)_{1.4}.H_2O$ (m_i=7.029 mg).

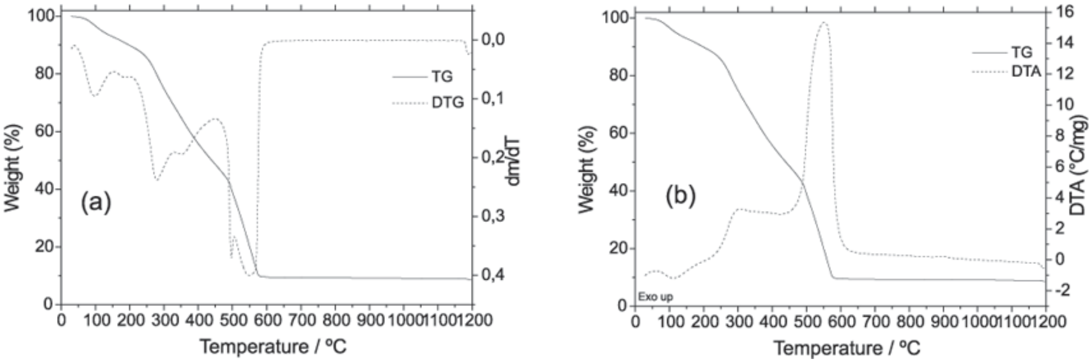


Figure 5 - (a) TG/DTG and (b) simultaneous TG-DTA curves of $Al(2\text{-}Cl\text{-}BP)_3.2H_2O$ (m_i=7.043 mg).

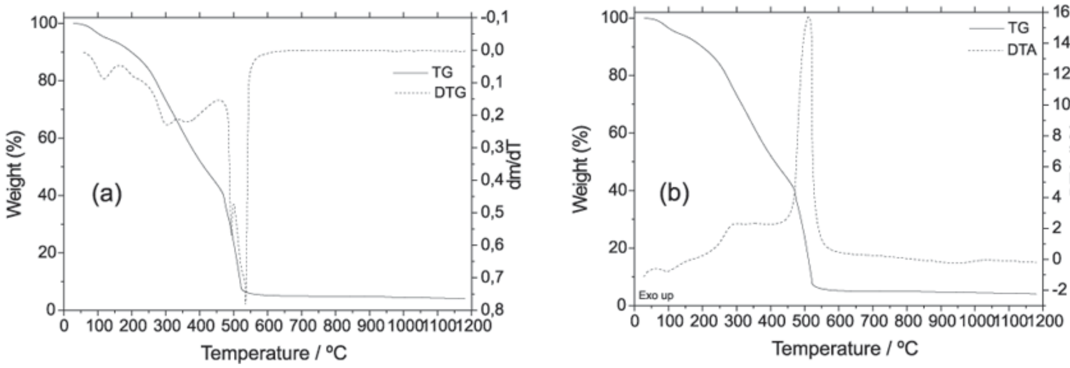


Figure 6 - (a) TG/DTG and (b) simultaneous TG-DTA curves of $Al(2\text{-}Cl\text{-}BP)_3.2.5(2\text{-}Cl\text{-}HBP).3.5H_2O$ (m_i=6.719 mg).

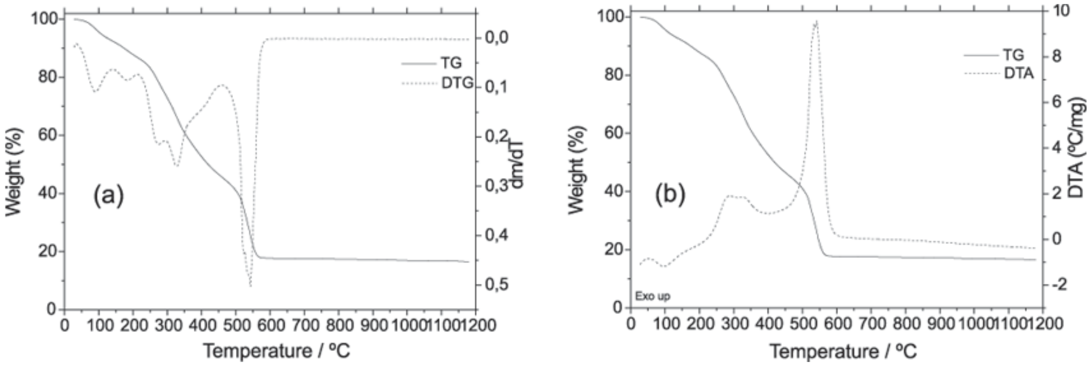


Figure 7 - (a) TG/DTG and (b) simultaneous TG-DTA curves of Ga(OH)$_{0.9}$(2-Cl-BP)$_{2.1}$.2H$_2$O (m$_i$=6.587 mg).

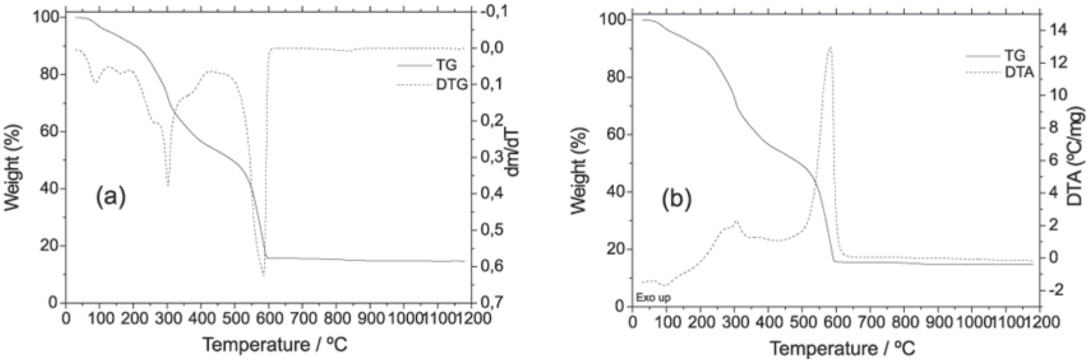


Figure 8 - (a) TG/DTG and (b) simultaneous TG-DTA curves of Ga(2-Cl-BP)$_3$.2H$_2$O (m$_i$=7.021 mg).

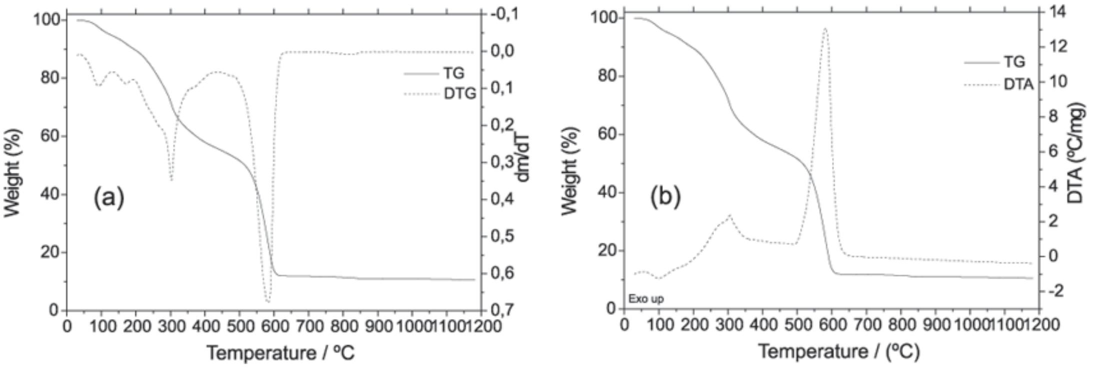


Figure 9 - (a) TG/DTG and (b) simultaneous TG-DTA curves of Ga(2-Cl-BP)$_3$.0.75 (2-Cl-HBP).2H$_2$O (m$_i$=7.047 mg).

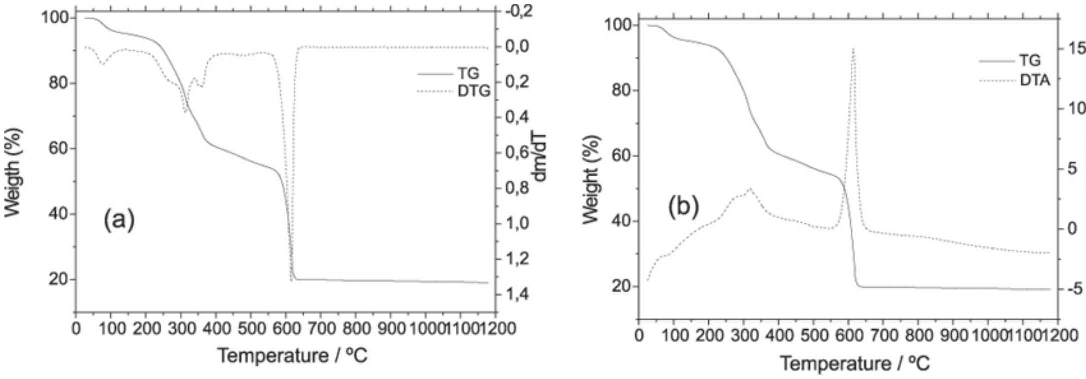


Figure 10 - (a) TG/DTG and (b) simultaneous TG-DTA curves of In$(OH)_{0.3}$(2-Cl-BP)$_{2.7}$.1.5H_2O (m_i=6.933 mg).

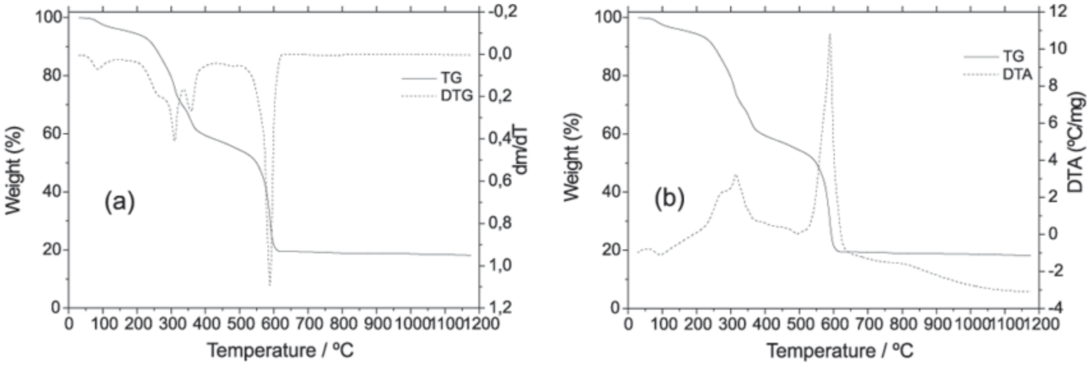


Figure 11 - (a) TG/DTG and (b) simultaneous TG-DTA curves of In(2-Cl-BP)$_3$.1.5H_2O (m_i=7.542 mg).

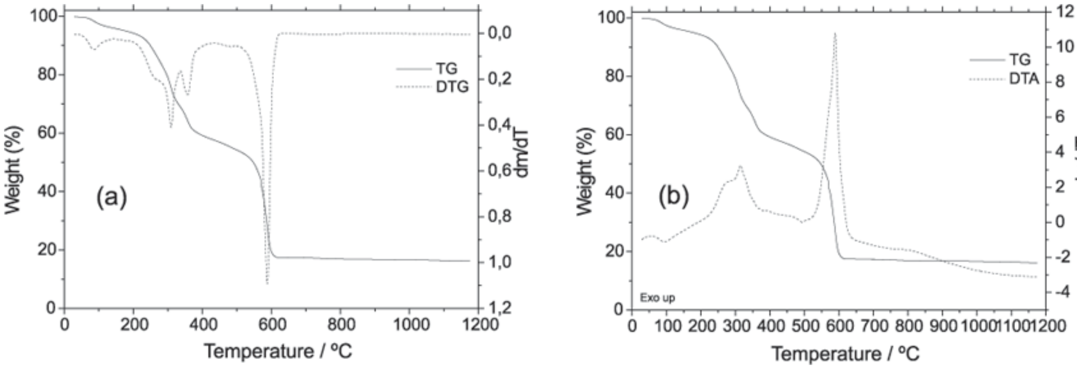
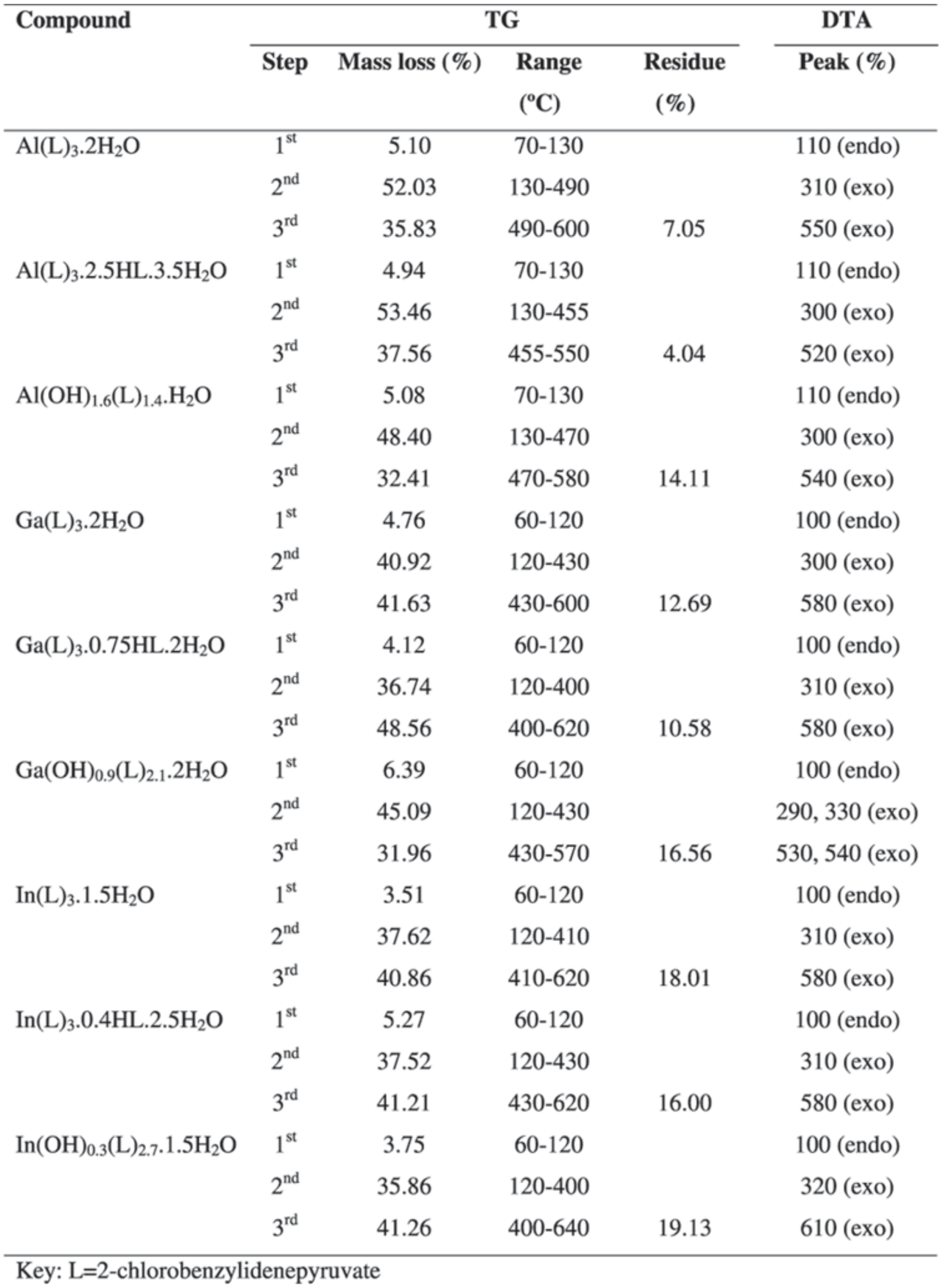


Figure 12 - (a) TG/DTG and (b) simultaneous TG-DTA curves of In(2-Cl-BP)$_3$.0.4(2-Cl-HBP).2.5H_2O (m_i=7.543 mg).

The mass losses, temperature ranges, residues and peak temperatures observed for each step of the TG-DTA curves of Al, Ga and In compounds are shown in Table 2.

Table 2 - Mass losses, temperature ranges, residues and peak temperatures observed in the TG-DTA curves of Al, Ga and In compounds.



Compound	TG				DTA
	Step	Mass loss (%)	Range (ºC)	Residue (%)	Peak (%)
Al(L)$_3$.2H$_2$O	1st	5.10	70-130		110 (endo)
	2nd	52.03	130-490		310 (exo)
	3rd	35.83	490-600	7.05	550 (exo)
Al(L)$_3$.2.5HL.3.5H$_2$O	1st	4.94	70-130		110 (endo)
	2nd	53.46	130-455		300 (exo)
	3rd	37.56	455-550	4.04	520 (exo)
Al(OH)$_{1.6}$(L)$_{1.4}$.H$_2$O	1st	5.08	70-130		110 (endo)
	2nd	48.40	130-470		300 (exo)
	3rd	32.41	470-580	14.11	540 (exo)
Ga(L)$_3$.2H$_2$O	1st	4.76	60-120		100 (endo)
	2nd	40.92	120-430		300 (exo)
	3rd	41.63	430-600	12.69	580 (exo)
Ga(L)$_3$.0.75HL.2H$_2$O	1st	4.12	60-120		100 (endo)
	2nd	36.74	120-400		310 (exo)
	3rd	48.56	400-620	10.58	580 (exo)
Ga(OH)$_{0.9}$(L)$_{2.1}$.2H$_2$O	1st	6.39	60-120		100 (endo)
	2nd	45.09	120-430		290, 330 (exo)
	3rd	31.96	430-570	16.56	530, 540 (exo)
In(L)$_3$.1.5H$_2$O	1st	3.51	60-120		100 (endo)
	2nd	37.62	120-410		310 (exo)
	3rd	40.86	410-620	18.01	580 (exo)
In(L)$_3$.0.4HL.2.5H$_2$O	1st	5.27	60-120		100 (endo)
	2nd	37.52	120-430		310 (exo)
	3rd	41.21	430-620	16.00	580 (exo)
In(OH)$_{0.3}$(L)$_{2.7}$.1.5H$_2$O	1st	3.75	60-120		100 (endo)
	2nd	35.86	120-400		320 (exo)
	3rd	41.26	400-640	19.13	610 (exo)

Key: L=2-chlorobenzylidenepyruvate

Conclusions

The presence of water in the 2-chlorobenzylidenepyruvic acid, even recrystallized from boiling benzene was confirmed by infrared, elemental analysis and thermoanalytical techniques. Fusion and dehydration of this compound occurs in the same temperature range.

The X-ray powder patterns showed that all the compounds of Al, Ga and In with 2-Cl-BP were obtained in amorphous state and from TG/DTG and TG-DTA curves, a general formula could be established for these compounds in the solid state. These results show that the very pronounced tendency of Al(III), Ga(III) and In(III) to hydrolysis, binary compounds are obtained only with a close control of the pH value of the aqueous solution of the ligand as well as, that of the aqueous solution of the metallic ions.

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G. Bannach, E. Schnitzler, C. B. Melios, M. Ionashiro. Síntese e estudo térmico do ácido 2-clorobenzalpirúvico e dos benzalpiruvatos de sódio, alumínio (III), gálio (III) e índio (III) no estado sólido.

Resumo: A síntese do 2-clorobenzalpiruvato de sódio e seu respectivo ácido, bem como compostos binários, compostos binários junto com seu respectivo ácido ou hidroxo-2-clorobenzalpiruvato de alumínio (III), gálio (III) e de índio (III), foram isolados.

Na caracterização e estudo do comportamento térmico desses compostos foram utilizados a termogravimetria, termogravimetria derivada (TG/DTG), termogravimetria-analise térmica diferencial simultânea (TG-DTA), difratometria de raios X pelo método do pó e análise química. Os resultados forneceram informações com respeito a estequiometria, cristalinidade, estabilidade e decomposição térmica.

Palavras-chave: ácido 2-clorobenzalpirúvico, 2-clorobenzalpiruvato, sódio, alumínio, gálio, índio, comportamento térmico.

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