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Synthesis, characterization and thermal behaviour of solid state compounds of 2-
chlorobenzylidenepyruvate with trivalent aluminium, gallium, indium and scandium metals
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SYNTHESIS, CHARACTERIZATION AND THERMAL BEHAVIOUR OF SOLID STATE COMPOUNDS OF 2-CHLOROBENZYLIDENEPYRUVATE WITH TRIVALENT ALUMINIUM, GALLIUM, INDIUM AND SCANDIUM METALS.

G. BANNACH ¹; E. SCHNITZLER ²; M. IONASHIRO ¹

Abstract

Solid state compounds M-2-Cl-BP, where 2-Cl-BP is 2-chlorobenzylidenepyruvate and M represents Al, Ga, In, and Sc were prepared. X-ray powder diffractometry, infrared spectroscopy and simultaneous thermogravimetry-differential thermal analysis (TG-DTA), have been used to characterize and to study the thermal behavior of these compounds. The results provided information concerning the stoichiometry, crystallinity, thermal stability and thermal decomposition of the compounds.

Keywords: 2-chlorobenzylidenepyruvate, characterization, thermal behaviour.

Introduction

Preparation and investigation of several metal ion complexes with 4-dimethylaminobenzylidenepyruvate (DMBP), 2-chloro-4-dimethylaminobenzylidenepyruvate (2-Cl-DMBP), 4-methoxybenzylidenepyruvate (4-MeO-BP), cinnamylidenepyruvate (CP) have been investigated in aqueous solution [5-8, 13, 17]. In the solid state, several metal-ion complexes with DMBP, 4-MeO-BP and CP, have also been prepared and investigated by using thermoanalytical techniques (TG, DTA, DSC), elemental analysis and X-ray powder diffractometry. The establishment of the stoichiometry, thermal stability as well as the thermal decomposition has been the main purposes

of the aforementioned studies.

In this work, solid-state compounds of the trivalent ions with 2-chlorobenzylidenepyruvate, 2-Cl-C₆H₄-CH=CH-COCOO- (2-Cl-BP) were prepared. The compounds were investigated by means of X-ray powder diffractometry, infrared spectroscopy and simultaneous TG-DTA. The results of the present study improve the knowledge on these compounds including their thermal stability and thermal decomposition.

Experimental

The sodium salt of 2-chlorobenzylidenepyruvic acid, was prepared following the same procedure described in the literature [14]. Scandium and gal-

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lithium nitrates were prepared from the scandium oxide and metallic gallium by treatment with concentrated nitric acid. The resulting solutions were transferred to a volumetric flask, and their pH values were adjusted to 5 and 3, respectively, by the use of a solution of diluted nitric acid solution. Aqueous solutions of aluminium and gallium nitrates were prepared from the dissolution of the solid salts in water following by the adjustment of the pH value by using a solution of the diluted nitric acid adjusted to 3. The solid-state compounds were prepared by mixing with continuous stirring, the solution of the ligand with the respective metal nitrate solution until total precipitation of the metallic (III) pyruvates. The precipitates were washed with distilled water until elimination of the nitrate ions filtered through and dried on Whatman n° 42 filter paper, and kept in a desiccator over anhydrous calcium chloride.

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

X-ray powder patterns were obtained by using a Siemens D-500 X-ray diffractometer, employing $\text{CuK}\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$) and settings of 40 kV and 20 mA. Infrared spectra for 2-Cl-BP (sodium salt) as well as for the Al, Ga, In and Sc compounds, were run on a Nicolet mod. Impact 400 FT-IR instrument, within 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 100 mL min^{-1} . A heating rate of 20°C min^{-1} was adopted, with samples weighing about 7mg. Alumina crucibles were used for recording the TG-DTA curves.

Results and discussion

The thermoanalytical data of the synthesized compounds are shown in Table 1. These results permitted to establish the stoichiometry of the compounds which is in agreement with the general formula $\text{M}(2\text{-Cl-BP})_3 \cdot n\text{H}_2\text{O}$, where M represents Al, Ga, In, Sc; 2-Cl-BP is 2-chlorobenzylidenepyruvate and $n = 2, 2, 1.5$ and 2.5, respectively.

Compounds	Metal (%)		Ligand loss (%)		Water (%)	
	Calcd.	TG	Calcd.	TG	Calcd.	TG
Al(2-Cl-BP) ₃ ·2H ₂ O	3.90	3.73	87.42	87.86	5.21	5.10
Ga(2-Cl-BP) ₃ ·2H ₂ O	9.49	9.44	82.34	82.55	4.91	4.76
In(2-Cl-BP) ₃ ·1.5H ₂ O	14.90	15.03	78.48	78.20	3.51	3.62
Sc(2-Cl-BP) ₃ ·2.5H ₂ O	6.25	6.27	84.14	84.23	6.27	6.17

Key: 2-Cl-BP is 2-chlorobenzylidenepyruvate

Table 1: Thermoanalytical data of the compound M (2-Cl-BP)₃·nH₂O.

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 compounds with other phenyl-substituted derivative of BP [8, 13].

Main IR data on the sodium 2-chlorobenzylidenepyruvate and its compounds with the metal ions considered in this work are shown in table 2.

From the bands observed for 2-Cl-BP (sodium salt) one centered at 1686 cm^{-1} (ketonic carbonyl stretching) and another at 1618 cm^{-1} (anti-symmetrical carboxylate vibration) it is only the anti-symmetrical carboxylate vibration that is shifted to lower frequencies in the compounds, namely 1590-1608 cm^{-1} , suggesting that the binding between the metal and the ligand occurs via the oxygen atom of the carboxylate group without participation of the oxygen atom of the α -ketonic carbonyl group.

Compounds	$\nu_{\text{as}}\text{COO}^- (\text{cm}^{-1})$	$\nu_{\text{sym}}\text{COO}^- (\text{cm}^{-1})$	$\nu\text{C=O}$
Na(2-Cl-BP) ₃ ·0.5H ₂ O	1618 _s	1401 _s	1686 _s
Al(2-Cl-BP) ₃ ·2H ₂ O	1608 _s	1441 _m	1759 _s
Ga(2-Cl-BP) ₃ ·2H ₂ O	1590 _s	1439 _m	1767 _s
In(2-Cl-BP) ₃ ·1.5H ₂ O	1599 _s	1433 _m	1765 _s
Sc(2-Cl-BP) ₃ ·2.5H ₂ O	1595 _s	1437 _m	1765 _s

Table 2: Main IR data for sodium and trivalent metallic 2-chlorobenzylidenepyruvates
s: strong, m: medium, nsy COO⁻ and nas COO⁻: symmetrical and anti-symmetrical vibrations of the COO⁻ group, respectively.

The simultaneous TG-DTA and TG/DTG curves of the synthesized compounds are shown in figures 1-4. In all TG-DTA curves the first mass loss corresponding to the endothermic peak is due to the loss of hydration water, which occurs in a single step. Immediately after the dehydration the TG curves indicate mass losses in two or three consecutive and/or overlapping steps, however the DTG curves show that the thermal decomposition

occurs with a large number of steps and through a more complex pathway than that observed from the TG curves.

For the aluminium compound the TG-DTA curves Figure 1, show that the thermal decomposition occurs in three steps between 30 and 600°C. The first mass loss that occurs up to 140°C, corresponding to the endothermic peak at 110°C is due to the loss of 2 H₂O (Calcd. = 5.21%; TG = 5.10%). The thermal decomposition of the anhydrous compound occurs in two steps between 140-430°C and 430-600°C, corresponding to the exotherm (280-400°C) and exothermic peak (555°C), with loss of 43.78% and 44.08%, respectively. The total mass loss up to 600°C is in agreement with formation of Al₂O₃, as final residue (Calcd. = 92.63%; TG = 92.96%).

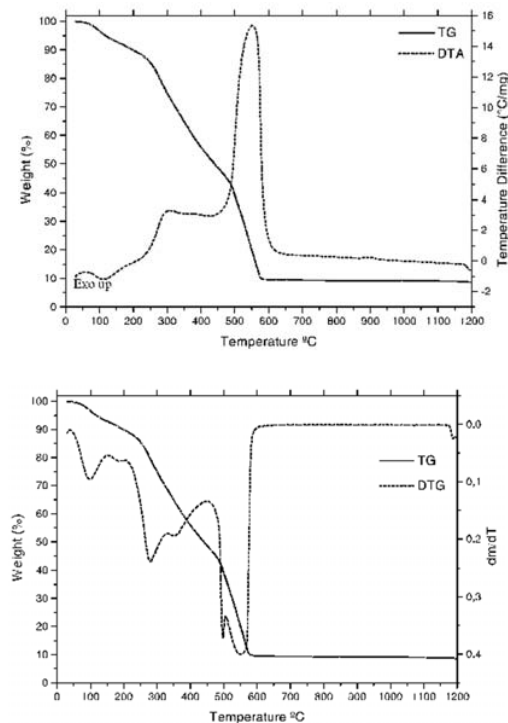


Figure 1. TG-DTA and TG/DTG curves of Al(2-Cl-BP)₃·2H₂O, (crucible = Al₂O₃, purge gas: air 100 mL min⁻¹, heating rate: 20°C min⁻¹, m = 7.043 mg).

For the gallium compound the TG-DTA curves, Figure 2, show mass losses between 40 and 600°C. The first mass loss up to 130°C, correspond-

ing to the endothermic peak at 100°C is due to the loss of 2 H₂O of hydration water (Calcd. = 4.91%; TG = 4.76%). The thermal decomposition of the anhydrous compound occurs in two steps between 130-400°C and 400-600°C, corresponding to the exothermic peaks at 310°C and 590°C, with loss of 42.06% and 40.49%, respectively. The total mass loss up to 600°C is in agreement with formation of Ga₂O₃, as final residue (Calcd. = 87.25%; TG = 87.31%).

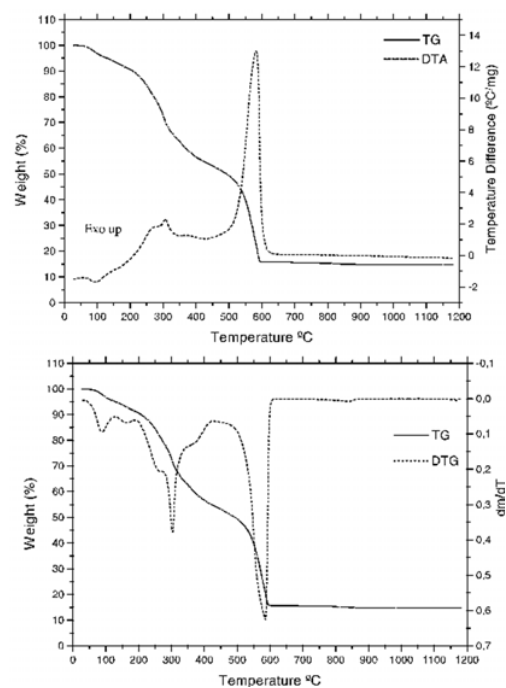


Figure 2. TG-DTA and TG/DTG curves of Ga(2-Cl-BP)₃·2H₂O, (crucible = Al₂O₃, purge gas: air 100 mL min⁻¹, heating rate: 20°C min⁻¹, m = 7.021 mg).

For the indium compound the TG-DTA curves Figure 3, show mass losses between 40-620°C. The first mass loss up to 130°C, corresponding to the endothermic peak at 90°C is attributed to the dehydration with loss of 1.5 H₂O (Calcd. = 3.51%; TG = 3.62%). The thermal decomposition of the anhydrous compound occurs in two steps between 130-400°C and 400-620°C, corresponding to the exothermic peaks at 320°C and 580°C, with loss of 38.34% and 39.86%, respectively. The total mass loss up to 620°C is in agreement with formation of

In_2O_3 , as final residue (Calcd. = 81.99%; TG = 81.82%).

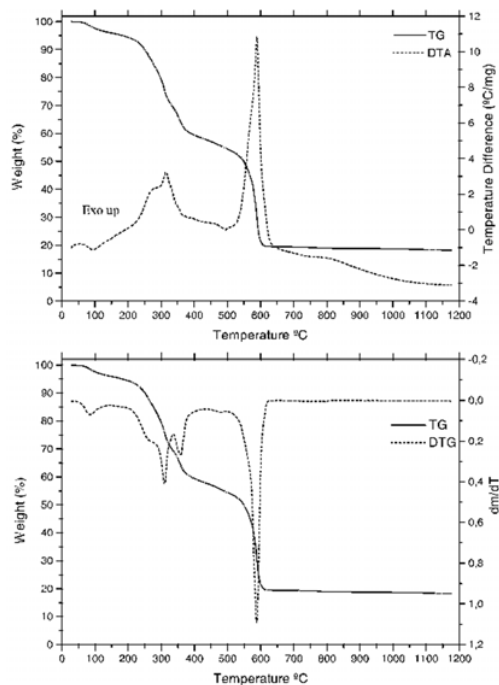


Figure 3. TG-DTA and TG/DTG curves of $\text{In}(2\text{-Cl-BP})_3 \cdot 1.5\text{H}_2\text{O}$, (crucible = Al_2O_3 , purge gas: air 100 mL min^{-1} , heating rate: $20^\circ\text{C min}^{-1}$, $m = 7.542 \text{ mg}$).

In the scandium compound the TG-DTA curves, Figure 4, show mass loss between 40 and 540°C . The first mass loss up to 140°C , corresponding to the endothermic peak at 100°C is ascribed to the dehydration with loss of $2.5 \text{ H}_2\text{O}$ (Calcd. = 6.27%; TG = 6.17%). The thermal decomposition of the anhydrous compound occurs in two steps between $140\text{-}460^\circ\text{C}$ and $460\text{-}540^\circ\text{C}$, corresponding to the exothermic peaks at 287°C and 510°C , with loss of 52.54% and 31.69%, respectively. The total mass loss up to 540°C is in agreement with formation of Sc_2O_3 , as final residue (Calcd. = 90.41%; TG = 90.40%).

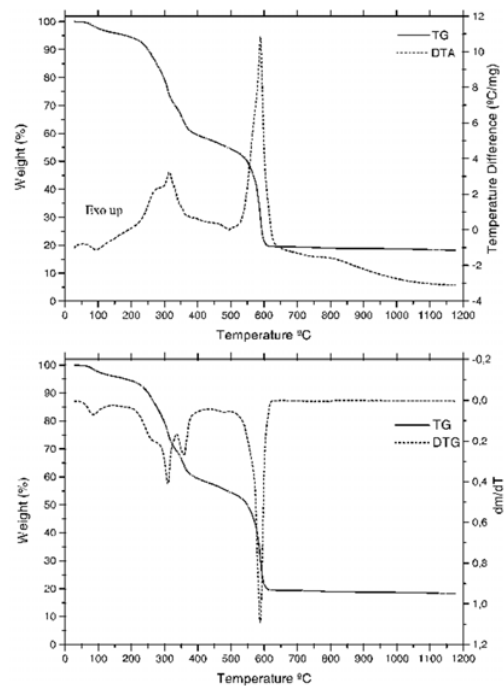


Figure 4. TG-DTA and TG/DTG curves of $\text{Sc}(2\text{-Cl-BP})_3 \cdot 2.5\text{H}_2\text{O}$, (crucible = Al_2O_3 , purge gas: air 100 mL min^{-1} , heating rate: $20^\circ\text{C min}^{-1}$, $m = 6.949 \text{ mg}$).

Conclusions

From TG curves, a general formula could be established for these compounds in the solid state.

The TG-DTA curves, X-ray powder patterns and infrared spectroscopic data provided previously unreported information concerning these compounds in the solid state.

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BANNACH, G., SCHNITZLER, E., IONASHIRO, M. Síntese, caracterização e comportamento térmico dos compostos 2-clorobenzalpiruvatos de alumínio, gálio, índio e escândio, no estado sólido.

Resumo

Foram preparados compostos sólidos $M(2\text{-Cl-BP})_3 \cdot n\text{H}_2\text{O}$, onde 2-Cl-BP é o ânion 2-clorobenzalpiruvato e M representa os íons metálicos trivalentes: alumínio, gálio, índio e escândio. Esses compostos foram caracterizados e estudados utilizando-se as técnicas de difração de raios X, pelo método do pó, espectroscopia de absorção na região do infravermelho e termogravimetria-análise térmica diferencial simultâneas (TG-DTA). Os resultados permitiram obter informações com respeito a estequiometria, cristalinidade, estabilidade e decomposição térmica.

Palavras-chave: 2-clorobenzalpiruvato, caracterização, comportamento térmico.

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