

# Synthesis, characterization and thermal behavior of solid state 2-methoxybenzylidenepyruvate of alkali earth metals, except beryllium and radium

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## Abstract

Solid state  $M(2\text{-MeO-BP})_2$  compounds, where M stands for bivalent alkali earth metal ions (Mg, Ca, Sr and Ba) and 2-MeO-BP is 2-methoxybenzylidenepyruvate, have been synthesized. Simultaneous thermogravimetry and differential thermal analysis (TG-DTA), differential scanning calorimetry (DSC), infrared spectroscopy, elemental analysis and complexometry, were used to investigate these compounds. The dehydration of magnesium, strontium and barium compounds occurs in a single step, while for calcium compound the dehydration occurs in two steps. The thermal decomposition of the anhydrous compounds occurs with the formation of carbonate as intermediate, except for the magnesium compound. The results also provided information about the composition, coordination mode, thermal behavior and thermal decomposition of isolated compounds.

**Keywords:** alkali earth metals, 2-methoxybenzylidenepyruvate, thermal behavior.

## 1. Introduction

Several works in the literature reports synthesis of benzylidenepyruvic acid (HBP) and its phenyl-substituted derivatives [1,2]. These acids are of continuing interest as intermediates in pharmacological, industries and chemical syntheses, in development of enzyme inhibitors and drugs, as model substrates of enzymes [2-4]. Synthesis and investigation of several metal- ion complexes of phenyl-substituted derivatives of BP, have been carried out in aqueous solutions [5] and in solid state [2, 7-11]. In aqueous solutions, these works reported mainly the thermodynamic stability ( $\beta_1$ ) and spectroscopic parameters ( $\epsilon_{1\text{max}}$ ,  $\lambda_{\text{max}}$ ), associated with 1:1 complex species, analytical applications of the ligands, e.g., in gravimetric analysis and as metalochromic indicators. In solid state, the establishment of the stoichiometry and detailed knowledge of the thermal behaviour of ligands and their metal ion compounds have been the main purposes of the studies.

In the present paper, solid state compounds of some alkali earth metal ions ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ ) with 2-Methoxybenzylidenepyruvate ( $2\text{-CH}_3\text{-O-C}_6\text{H}_4\text{-CH=CH-COCOO}^-$ ) were prepared. The compounds were investigated by complexometry, elemental analysis, infrared spectroscopy, simultaneous thermogravimetry and differential thermal analysis (TG-DTA) and differential scanning calorimetry (DSC). The results allowed us to acquire information concerning these compounds in the solid state, including their thermal stability and thermal decomposition.

## 2. Experimental

The sodium salt of 2-methoxybenzylidenepyruvate acid (Na-2-MeO-BP) was prepared following the same procedure as described in the references [12-14]. Aqueous solution of Na-2-MeO-BP 0,1 Mol L<sup>-1</sup> was prepared by direct weighting of the salt.

Magnesium, calcium, strontium and barium solutions were prepared from the corresponding metal carbonates by treatment with diluted hydrochloric acid. The solutions were transferred to a volumetric flask and diluted in order to obtain ca. 0,1 mol L<sup>-1</sup> solutions, whose pH were adjusted to 5 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 solutions, until total precipitation of metal ions. The precipitates were washed with distilled water until elimination of chloride ion, filtered through and dried on Whatman n° 42 filter paper, and kept in a desiccator over anhydrous calcium chloride, under reduced pressure.

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 solutions, using eriochrome black T as indicator for magnesium, eriochrome blue black R for calcium and methylthymol blue for strontium and barium. Carbon and hydrogen microanalysis were performed by using EA 1110, CHNS-O Elemental analyzer (CE Instruments).

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The diffuse reflectance infrared spectra for Na-2-MeO-BP, as well as for its metal-ion compounds were run on a Nicolet iS10 FT-IR spectrophotometer, using an ATR accessory with Ge window.

Simultaneous TG-DTA and DSC curves were recorded in a models SDT 2960 and Q10, both from TA instruments. The purge gas was an air flow of 100 mL min<sup>-1</sup>. A heating rate of 20 °C min<sup>-1</sup> was adopted, with samples weighting about 7 mg. Alumina and aluminum crucibles, the latter with perforated covers, were used for TG-DTA and DSC, respectively.

### 3. Results and Discussion.

The analytical and thermoanalytical results are shown in Table 1. The results permitted to establish the stoichiometry of the compounds, which is in agreement with the general formula M (2-MeO-BP)<sub>2</sub>. nH<sub>2</sub>O, where M represents alkali earth metal ions, 2-MeO-BP is 2-methoxybenzylidenepyruvate and n= 3.5 (Mg); 4 (Ca); and 1 (Sr and Ba).

**Table 1.** Analytical data for the Ln(L)<sub>3</sub> n H<sub>2</sub>O compounds.

Compound	M (%)			Ligand lost (%)		Water (%)		C (%)		H (%)		Final Residue
	Calcd.	TG	EDTA	Calcd.	TG	Calcd.	TG	Calcd.	EA	Calcd.	EA	
Mg(L) <sub>2</sub> .3.5 H <sub>2</sub> O	4.88	4.78	4.9	79.22	79.11	12.67	12.57	25.16	26.10	1.79	1.82	MgO
Ca(L) <sub>2</sub> .4 H <sub>2</sub> O	7.67	7.15	7.7	75.46	76.40	13.80	13.21	25.27	24.33	1.74	1.60	CaO
Sr(L) <sub>2</sub> .1 H <sub>2</sub> O	16.99	16.85	17.12	76.42	75.82	3.49	4.20	25.59	26.10	1.76	1.80	SrO
Ba(L) <sub>2</sub> .1 H <sub>2</sub> O	24.27	24.37	24.40	61.92	61.58	3.19	3.40	23.34	24.12	1.61	1.66	BaCO <sub>3</sub>

M: Alkali earth metal; Ligand: 2-Methoxybenzylidenepyruvate

Infrared spectroscopic data on 2-methoxybenzylidenepyruvate and its compounds are shown in Table 2. The investigation was focused mainly within the 1700–1400 cm<sup>-1</sup> range because this region is potentially the most informative in attempting to assign coordination sites.

**Table 2.** Spectroscopic data for sodium 2-methoxybenzylidenepyruvate and for its compounds with alkali earth metal.

Compounds	$\nu_{(O-H)}$	$\nu_{s(COO-)}$	$\nu_{as(COO-)}$	$\nu_{(C=O)}$	$\Delta\nu_{(ass-sim)}$
NaL.1.5 H <sub>2</sub> O	3.470 m	1.489 m	1.571 s	1.623 s	82
Mg(L) <sub>2</sub> .3.5 H <sub>2</sub> O	3.385 m	1.486 m	1.577 s	1.591 s	91
Ca(L) <sub>2</sub> .4 H <sub>2</sub> O	3.204 m	1.490 m	1.566 s	1.622 s	76
Sr(L) <sub>2</sub> .1 H <sub>2</sub> O	3.078 m	1.487 m	1.583 s	1.621 s	96
Ba(L) <sub>2</sub> .1 H <sub>2</sub> O	3.075 m	1.486 m	1.582 s	1.629 s	96

L = 2-methoxybenzylidenepyruvate; strong: s; medium: m;  $\nu_{as(O-H)}$  = hydroxyl group stretching frequency;  $\nu_{s(COO-)}$  and  $\nu_{as(COO-)}$  = symmetrical and anti-symmetrical vibrations of the COO- structure;  $\nu_{(C=O)}$  = ketonic carbonyl stretching frequency.

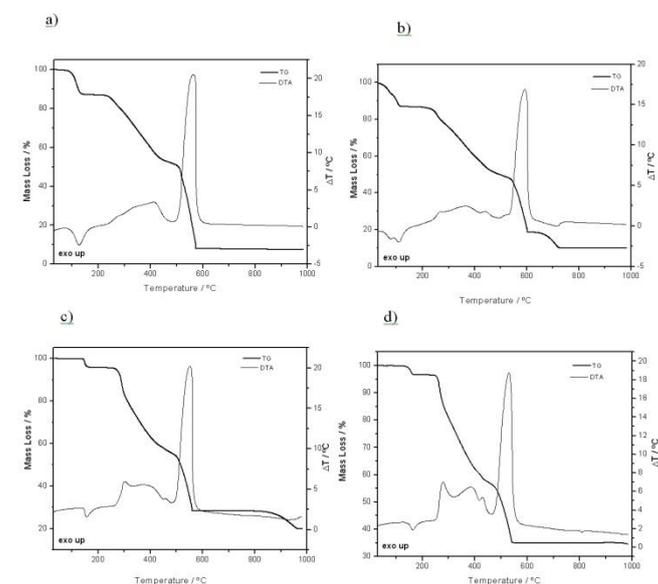
According to Deacon and Phillips [15, 16], the variation in the values of the bands in these regions, in comparison to the corresponding frequencies in 2-MeO-BP itself (sodium salt), indicates that this group act

as coordination center in the metal compounds. The difference between the values of anti-symmetrical and symmetrical carboxylate vibration of the synthesized compounds in comparison with the ones found on 2-MeO-BP itself (sodium salt), can suggest which interaction, between metal and ligands are being made.[15,16]

The bands corresponding to ketonic carbonyl, anti-symmetrical and simetrical carboxylate vibration, found for the studied compounds are in the same region to the ones found for Na-2-MeO-BP. This behavior is in disagreement with 2-MeO-BP compounds with other metals [13, 14, 17, 18], suggesting an ionic interaction between the ligand and the studied metals [15, 16].

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 which are characteristic for each compound.

For magnesium compound, the first mass loss (range: 75 – 171 °C) associated to the endothermic peak at 123 °C in DTA curve and 129°C in DSC one, is ascribed to the dehydration with loss of 3.5 H<sub>2</sub>O, which occurs in a single step. Once dehydrated the compound is stable up to 229°C.



**Figure 1.** Simultaneous TG-DTA curves of the compound: a) Mg(2-MeO-BP)<sub>2</sub>.3.5H<sub>2</sub>O; b) Ca(2-MeO-BP)<sub>2</sub>.4H<sub>2</sub>O; c) Sr(2-MeO-BP)<sub>2</sub>.1H<sub>2</sub>O; d) Ba(2-MeO-BP)<sub>2</sub>.1H<sub>2</sub>O; heating rate: 20°C min<sup>-1</sup>; air flow: 100 mL min<sup>-1</sup>

The second step (range: 229 – 513°C) associated to the exothermic peaks at 270; 325 and 410°C in DTA curve and 270°C; 381°C and 415 °C, in DSC one, is attributed to the

thermal decomposition of the compound. The profiles of DTA curve suggest that the thermal decomposition in this temperature range occurs in three or more consecutive steps. The last step (range: 513 - 583°C) associated with the large exothermic peak at 574°C is attributed to the oxidation of organic matter with the formation of magnesium oxide, as final residue.

For the calcium compound, the first mass loss (range: 30 - 121°C) associated to the exothermic peaks at 75°C and 110 °C (DTA) and 109°C (DSC), is ascribed to the dehydration with loss of 4 H<sub>2</sub>O, which occurs in two steps. The second step (range: 191 - 538°C) associated to the exothermic peaks at 265; 365 and 438°C (DTA) and 267°C; 367°C and 454 °C, (DSC), is attributed to the thermal decomposition of the compound. The DTA curve also suggests that the thermal decomposition of the compounds occurs in three or more consecutive steps. The third step (range: 538 - 604°C) associated with the large exothermic peak at 593°C is attributed to the oxidation of organic matter with the formation of calcium carbonate as intermediate. Tests with hydrochloric acid solution on this intermediate, as indicated by corresponding TG-DTA curves confirmed the evolution of CO<sub>2</sub> and presence of the carbonaceous residue. The last step (range: 604 - 722°C) is due to the thermal decomposition of calcium carbonate and carbonaceous residue with the formation of calcium oxide, as final residue.

For the strontium compound, the first mass loss (range: 145 - 190°C) associated to the exothermic peak at 156°C (DTA) and 160°C (DSC), is ascribed to the dehydration with loss of 1 H<sub>2</sub>O, which occurs in a single step. The second step (range: 266° - 486C) associated to the exothermic peaks at 300; 383 and 462°C (DTA) and 300°C; 396°C and 470 °C, (DSC), are attributed to the thermal decomposition of the compound. The DTA and DSC curves suggest that this decomposition occurs in three or more consecutive steps. The third step (range: 486 - 588°C) associated with the large exothermic peak at 551°C (DTA) is attributed to the oxidation of organic matter with the formation of strontium carbonate as intermediate. Tests with hydrochloric acid solution on this intermediate, as indicated by corresponding TG-DTA curves confirmed the evolution of CO<sub>2</sub> and presence of the carbonaceous residues. The last step (range: 815 - 968°C) is due the thermal decomposition of strontium carbonate and carbonaceous residue with the formation of strontium oxide, as final residue.

For the barium compound, the first mass loss (range: 133 - 204°C) associated to the exothermic peak at 163°C (DTA) and 157°C (DSC), is ascribed to the dehydration with loss of 1 H<sub>2</sub>O, which occurs in a single step. The second step (range: 254 - 438°C) associated to the exothermic peaks at 287; 387 and 428°C (DTA) and 284°C; 383°C and 437 °C, (DSC), is attributed to the thermal decomposition of the compound. The DTA curves suggest that the thermal decomposition of the compound occurs in three or more consecutive steps. The third step (range: 438 - 543°C) associated with the large exothermic peak at 530°C is attributed to the oxidation of organic matter with the formation of barium carbonate as final residue. Tests with hydrochloric acid solution on this residue confirmed the evolution of CO<sub>2</sub>.

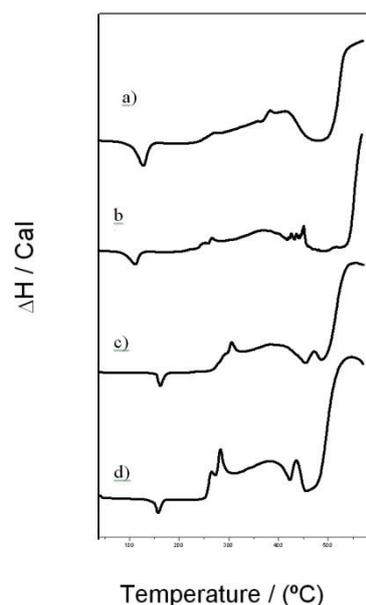
After the dehydration the formation of stable anhydrous compound is observed for all the compounds.

The mass losses, temperature ranges and the peak temperatures observed for each step of the TG – DTA curves are shown in Table 3.

**Table 3.** Temperature ranges  $\theta$ , mass losses (%) and peak temperatures observed for each step of the TG-DTA curves of the compounds. M (L)<sub>3</sub> .nH<sub>2</sub>O, where M = alkali earth metal, L = 2-methoxybenzylidenepyruvate.

Compound	Steps				
	First	Second	Third	Fourth	
Mg L <sub>3</sub> .3.5 H <sub>2</sub> O	$\theta$ °C	75 – 171	229 – 513	513 – 583	-
	Loss (%)	12.57	35.73	21.18	-
	Peak (°C)	123 (endo)	270 (exo) 325 (exo) 410 (exo)	574 (exo)	-
Ca L <sub>2</sub> .4 H <sub>2</sub> O	$\theta$ °C	30 – 121	191 – 538	538-604	604-722
	Loss (%)	13.21	38.93	29,35	8.587
	Peak (°C)	75 (endo) 110 (endo)	265 (exo) 365 (exo) 593 (exo)	593 (exo)	-
Sr L <sub>2</sub> .1 H <sub>2</sub> O	$\theta$ °C	145 – 190	266 – 486	486 – 588	815 - 968
	Loss (%)	4.20	40.42	27.06	8.44
	Peak (°C)	156 (endo)	300 (exo) 383 (exo) 466 (exo)	551 (exo)	-
Ba L <sub>2</sub> .1 H <sub>2</sub> O	$\theta$ °C	133-204	240-438	438 – 543	-
	Loss (%)	3.40	38.88	22.67	-
	Peak (°C)	163 (endo)	287 (exo) 387 (exo) 428 (exo)	530 (exo)	-

The DSC curves of the compounds are shown in Fig. 2 and the dehydration enthalpies found for these compounds (Mg, Ca, Sr and Ba) were: 179.83, 87.7, 48.29 and 66.7 kJ mol<sup>-1</sup>, respectively.



**Figure 2.** DSC curves of the: a) Mg(2-MeO-BP)<sub>2</sub>.3.5H<sub>2</sub>O; b) Ca(2-MeO-BP)<sub>2</sub>.4H<sub>2</sub>O; c) Sr(2-MeO-BP)<sub>2</sub>.1H<sub>2</sub>O; d) Ba(2-MeO-BP)<sub>2</sub>.1H<sub>2</sub>O.

#### 4. Conclusions

From TG curves, elemental analysis and complexometry results, a general formula could be established for these compounds in solid state.

The infrared spectroscopic data suggest that 2-MeO-BP acts as an ionic ligand towards the metal ions considered in this work.

The TG-DTA curves show that the dehydration occurs in a single step, except for the calcium compound and the thermal decomposition of the anhydrous compound occurs with the formation of the metal carbonate except for the magnesium compound.

The TG-DTA and DSC curves also provided previously unreported information concerning the thermal behavior and thermal decomposition of these compounds which have been synthesized and reported for the first time.

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