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Thermal study and characterization of nicotinates of some alkaline earth metals using TG–DSC–FTIR and DSC-system photovisual

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ABSTRACT

Characterization, thermal stability and thermal decomposition of alkaline earth nicotinates M $(C_6H_5NO_2)_2{\cdot}nH_2O$ (M = Mg(II), Ca(II), Sr(II) and Ba(II)), were investigated employing simultaneous thermogravimetry and differential thermal analysis (TG–DTA), Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), DSC-photovisual system, elemental analysis, complexometry and TG-DSC coupled to FTIR. These compounds were obtained as: mono (Ba), hemi three (Mg), and di (Ca, Sr) hydrated and the TG curve shows that the dehydration occurs in a single step for all the compounds, also for magnesium compound the DTA curve shows to overlap step.

In all the compounds the thermal decomposition occurs with the formation of carbonate as intermediate and the respective oxides as final residue, except magnesium one which the thermal decomposition occurs with the formation of magnesium oxide, without formation of carbonate. For the barium compound the TG curve shows that the thermal decomposition of the barium carbonate the mass loss is still being observed up to 1000 °C. The results also provided information concerning the thermal stability, thermal behavior and identification of the gaseous products evolved during the thermal decomposition of these compounds.

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1. Introduction

The niacin although it can be defined more expansively as "nicotinamide (nicotinic acid amide), nicotinic acid (pyridine-3-carboxylic acid), nicotinamide 3-picoline, and derivatives that exhibit the biological activity of nicotinamide" [1]. This acid of molecular formula $C_6H_5NO_2$, is a crystalline solid soluble in water, whose melting point is 236.6 °C.

Next, we describe some biological activities of nicotinic acid that motivated the synthesis and characterization of nicotinates of some alkaline earth metals. In doses large enough to produce pharmacological effects, nicotinic acid and extended-release nicotinic acid are potent lipid-modifying agents with a broad spectrum of effects, including effects aimed at attenuating the risks associated with low high-density lipoprotein cholesterol (HDL), high low-density lipoprotein cholesterol (LDL), high lipoprotein (a), and hypertriglyceridemia [1,2]. Magnesium is essential to maintain glucose homeostasis and insulin action. Studies in animal models and humans have demonstrated that insulin resistance and diabetes are associated with decreased plasma magnesium levels, especially in those with poorly controlled diabetes with increased urinary loss. Magnesium deficiency was shown to disrupt tyrosine kinase activity on the insulin receptor and lead to an increase in intracellular calcium concentration all of which lead to development of insulin resistance [3–9]. The literature shows that the papers involving bivalent transition metal and nicotinic acid, reported the spectroscopic, thermogravimetric and magnetic studies [10], thermogravimetric behavior [11], thermal decomposition [12], polymeric structure [13], synthesis and characterization [14], simultaneous thermal analysis [15], study on the antinuclear activities [16] and synthesis and thermal behavior [17]. Were also found the papers involving the lanthanides reported the crystal structure [18] and structural characterization and luminescence studies [19–21]. While for alkaline earth only one paper that reported the synthesis and structure of calcium and magnesium nicotinates was found [22].

Thus, the present papers deals with the preparation of solid-state alkaline earth except beryllium and radium nicotinates, and to investigate by means of complexometry, elemental analysis, infrared spectroscopy (FTIR), simultaneous thermogravimetry and

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differential thermal analysis (TG–DTA), differential scanning calorimetry (DSC), DSC-photovisual system and TG–DSC coupled to FTIR.

2. Experimental

2.1. Synthesis

The nicotinic acid ($C_6H_5NO_2$) with 99.5% purity was obtained from Sigma and it was used as received. The calcium, strontium and barium carbonates were obtained from Fluka (Ca, 99.5%) and Merck (Sr, Ba, 99% purity). The magnesium carbonate was prepared by adding slowly with continuous stirring, saturated sodium hydrogen carbonate solution to the magnesium sulphate solution, until precipitation of the metal ion. The precipitate was washed with a mixture of ethanol-distilled water (1:1) until the elimination of sulphate ion (qualitative test with $BaCl_2$ solution).

Solid-state Mg(II), Ca(II), Sr(II) and Ba(II) compounds were prepared by mixing stoichiometric amount of the corresponding metal carbonates in aqueous suspension with nicotinic acid solution, and heated slowly to near ebullition, until total neutralization of the respective metal carbonate. The resulting solution was evaporated in circulation air oven during 24 h and kept in desiccator over anhydrous calcium chloride.

2.2. Experimental equipment and conditions

In the solid-state compounds, metal ions and nicotinate contents were determined from TG curves. The metal ions were also determined by complexometry with standard EDTA solution using eriochrome black T (Mg(II), eriochrome blue black R (Ca(II)), methyl thymol blue, (Sr(II), Ba(II)), as indicator [23,24].

Carbon, hydrogen and nitrogen contents were determined by microanalytical procedures, with a CHN Elemental Analyser from Perkin Elmer, model 2400 and also by calculations based on the mass losses of the TG curves, since the ligand lost in the thermal decomposition occurs with the formation of the respective carbonate and/or oxides with stoichiometry known, as final residue.

The attenuate total reflectance infrared spectra were run on a Nicolet iS10 Fourier transform infrared spectrophotometer (FTIR), using an ATR accessory with Ge window. The FTIR spectra were recorded in the region of 4000–600 cm^{-1} with 32 scans per spectrum at the resolution of 4 cm^{-1}.

Simultaneous TG–DTA and DSC curves were obtained with two thermal analysis systems, model SDT 2960 and DSC Q10, both from TA Instruments. The purge gases were air and nitrogen flow of 100 mL min^{-1} for TG–DTA and nitrogen flow of 50 mL min^{-1} for DSC experiments. A heating rate of 10 °C min^{-1} was adopted with samples weighing about 5 mg for TG–DTA and 3 mg for DSC. Alumina and aluminum crucibles, the latter with perforated cover, were used for recording the TG–DTA and DSC curves, respectively.

The images were obtained on equipment Mettler–Toledo DSC 1 stare system coupled to OLYMPUS camera digital, model SC 30 which incorporates a 3.3 megapixel CMOS sensor, optical sub-assembly mechanic Navitar 1-6232D with 6.5X zoom. The experimental conditions were similar to those used to obtain the DSC curve.

The measurements of the gaseous products were carried out using a thermogravimetric analyzer Mettler TG–DSC coupled to a FTIR spectrophotomer Nicolet with gas cell and DTGS KBr detector. The furnace and heated gas cell (250 °C) were coupled through a heated (225 °C) 120 cm stainless steel line transform with diameter of 3.0 mm, both purged with dry air (50 mL min^{-1}). The FTIR spectra were recorded with 16 scans per spectrum at a resolution of 4 cm^{-1}.

3. Results and discussion

The analytical and thermoanalytical (TG) results for the synthesized compounds are shown in Table 1. These data permitted to establish the stoichiometry of these compounds, which are in agreement with general formula: $M(L)_2{\cdot}nH_2O$, where M represents Mg(II), Ca(II), Sr(II) and Ba(II), L is nicotinate and $n = 1$ (Ba), 1.5 (Mg) and 2 (Ca, Sr).

3.1. Thermal analysis

The Simultaneous TG/DTG–DTA curves of the compounds are shown in Figs. 1–4. These curves show mass losses in three or four steps and thermal events corresponding to these losses or due to physical phenomenon.

These curves also show that the thermal stability of the anhydrous compounds, depend on the nature of the metal ion, and they follow the order:

$$\text{Air)}\ Ca > Mg = Sr > Ba\ (N_2)\ Ca > Sr > Mg > Ba \quad (1)$$

The thermal behavior of the compound is also dependent on the nature of the metal ion and so the features of each of these compounds are discussed individually.

3.1.1. Magnesium compound

The simultaneous TG/DTG–DTA curves in air and N_2 atmospheres are shown in Fig. 1a and b, respectively. The first mass loss between 55 and 220 °C, corresponding to two endothermic peaks at 105 and 125 °C (DTA) in both atmospheres is due to dehydration with loss of 1.5 H_2O. The exothermic peak at 285 °C without mass loss observed in both atmospheres is assigned to a physical phenomenon.

The anhydrous compound in air atmosphere is stable up to 420 °C and above this temperature the thermal decomposition occurs in two consecutive steps between 420 and 490 °C and 490–560 °C, corresponding to an exothermic peak at 470 °C and 540 °C attributed to oxidation of the organic matter and/or of gaseous products evolved during the thermal decomposition. The total mass loss up to 560 °C is in agreement with the formation of magnesium oxide, MgO, as final residue (Calc. = 86.36%, TG = 86.58%).

For the N_2 atmosphere, to an increase of the thermal stability of the anhydrous compound (25 °C more stable than in air

Table 1
Analytical and thermoanalytical (TG) data for the $M(C_6H_4NO_2)_2{\cdot}nH_2O$ compounds.

Compounds	Metal oxide/%			L (Lost)/%		Water/%		C/%		N/%		H/%		Final residue
	Calc.	TG	EDTA	Calc.	TG	Calc.	TG	Calc.	EA	Calc.	EA	Calc.	EA	
$Mg(L)_2{\cdot}1.5H_2O$	13.64	13.42	13.50	77.22	77.63	9.14	9.07	48.76	48.88	9.48	9.46	4.44	4.45	MgO
$Ca(L)_2{\cdot}2H_2O$	17.51	17.16	17.80	71.42	71.46	11.25	11.38	44.99	44.80	8.75	9.80	4.41	4.39	CaO
$Sr(L)_2{\cdot}2H_2O$	28.17	28.16	28.31	62.03	61.89	9.80	9.95	39.18	38.27	7.62	7.60	3.84	3.80	SrO
$Ba(L)_2{\cdot}H_2O$	38.38	38.59	38.25	57.11	57.05	4.51	4.36	30.07	29.91	7.01	6.97	3.03	3.00	$BaCO_3$

L = nicotinate.

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