

Thermal behaviour of nicotinic acid, sodium nicotinate and its compounds with some bivalent transition metal ions



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ABSTRACT

Solid-state $M(L)_2 \cdot nH_2O$ compounds, where M stands for bivalent transition metals (Mn, Fe, Co, Ni, Cu and Zn), L is nicotinate and $n = 0-4.5$, have been synthesized. Characterization and thermal behaviour of these compounds were investigated employing elemental analysis based on the mass losses observed in the TG-DTA curves, complexometry, X-ray diffractometry, infrared spectroscopy (FTIR), simultaneous thermogravimetric and differential thermal analysis (TG-DTA) and TG-DSC coupled to FTIR. The thermal behaviour of nicotinic acid and its sodium salt was also investigated. For the hydrated transition metal compounds, the dehydration and thermal decomposition of the anhydrous compounds occur in a single step. For the sodium nicotinate, the final residue up to 765 °C is sodium carbonate and for the transition metal nico tinates, the final residues are Mn_3O_4 , Fe_2O_3 , Co_3O_4 , NiO, CuO and ZnO. The results also provided information concerning the thermal stability, thermal decomposition and identification of the gaseous products evolved during the thermal decomposition of the compounds.

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1. Introduction

Pyridine-3-carboxylic acid ($C_6H_5NO_2$), also called 3-picoline or nicotinic acid is an organic acid whose melting point is 236.6 °C. It is the biological precursor of the co-enzymes nicotinamide adenine dinucleotide (NAD) and nicotinamide adenine dinucleotide phosphate (NADP). A survey of the literature shows that papers involving bivalent transition metals and nicotinic acid reported the spectroscopic, thermogravimetric and magnetic studies on some metal complexes with pyridine carboxylic acid [1], thermochemical behaviour of solid nicotinic hydrazide metal complexes in correlation with their stoichiometry [2], the thermal decomposition of copper(II) nicotinate and isonicotinate [3], the polymeric structure of aqua cadmium bisnicotinate [4], a new 2-D chiral coordination polymer of $[Zn(nicotinate)_2]_n$ [5], synthesis and characterization of copper(II) complexes with nicotinate in different coordination style [6], simultaneous thermal analysis of a cobalt(II) complex with nicotinate [7], hydrothermal synthesis, crystal structures of two 3-D network nickel nicotinate coordination polymers [8], hydrothermal synthesis, structural determination properties of 2-D-cobalt-and-nickel-based coordination polymers incorporating pendant-arm-3-pyridinecarboxylate ligands [9], a pioneer study on the anti-nuclear activities of copper nicotinate complex $[CuCl(NHA)_2]$ in experimental gastric ulcer induced by

aspirin-pylorus ligation model (shay model) [10] and grow and characterization of a novel polymer of manganese(II) nicotinate single crystal [11].

In this paper, the object of the present research was to investigate the thermal behaviour of nicotinic acid and its sodium salt, as well as to prepare solid-state compounds of some bivalent transition metal ions (i.e. Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II)) with nicotinate and to characterize and to investigate by means of complexometry, elemental analysis, X-ray diffractometry, infrared spectroscopy (FTIR), simultaneous thermogravimetry and differential thermal analysis (TG-DTA), differential scanning calorimetry (DSC) and TG-DSC coupled to FTIR which make possible a correct interpretation for the mechanism of a thermally induced reactions involving the formation of gaseous species, evolved during the thermal decomposition [12]. The thermal studies were performed in dynamic air atmosphere.

2. Experimental

The nicotinic acid ($C_6H_5NO_2$) with 99.5% purity was obtained from Sigma and it was used as received. Aqueous solution of sodium nicotinate 0.1 mol L^{-1} was prepared by neutralization of an aqueous solution of nicotinic acid with sodium hydroxide solution 0.1 mol L^{-1} . Aqueous solutions of bivalent metal ions 0.1 mol L^{-1} were prepared by dissolving the corresponding chloride (Mn(II), Co(II), Ni(II)) or sulphate (Fe(II), Cu(II), Zn(II)).

The solid-state compounds were obtained by adding slowly with stirring 100 mL of sodium nicotinate solution 0.1 mol L^{-1} to

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50 mL of the respective metal ions solutions 0.1 mol L^{-1} heated up to near ebullition. The system was cooled up to ambient temperature and the precipitates were filtered off, washed with distilled water until chloride or sulphate ions were eliminated (qualitative test with $\text{AgNO}_3/\text{HNO}_3$ solution for chloride ions or BaCl_2 solution for sulphate), dried at 50°C in a forced circulation air oven during 12 h and kept in a desiccator over anhydrous calcium chloride. To avoid the oxidation of Fe(II), all the solutions, as well the water employed for washing the precipitate were purged with nitrogen gas, even during the heating up to near ebullition and cooling up to ambient temperature.

In the solid-state metal ions, hydration water and nicotinate contents were determined from TG curves. The metal ions were also determined by complexometry with standard EDTA solution after igniting the compounds to the respective oxides and their dissolution in hydrochloric acid solution [13,14].

Carbon, hydrogen and nitrogen contents were determined 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 oxides with stoichiometry known, as final residue.

The X-ray powder patterns were obtained by using a Siemens D-5000 X-ray diffractometer, employing $\text{Cu K}\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$) and setting of 40 kV and 20 mA.

The attenuate total reflectance infrared spectra for nicotinic acid, sodium nicotinate and its metal-ion compounds were run on a Nicolet iS10 FTIR spectrophotometer, using an ATR accessory with Ge window.

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 gas was an air flow of 100 mL min^{-1} and 50 mL min^{-1} for DSC experiments. A heating rate of $10^\circ\text{C min}^{-1}$ was adopted, with samples weighing about 7 mg for TG–DTA and 3 mg for DSC. Alumina and aluminium crucibles, the latter with perforated cover, were used for recording the TG–DTA and DSC curves, respectively.

The measurements of the gaseous products were carried out using a Thermogravimetric Analyzer Mettler TG–DSC coupled to a FTIR spectrometer Nicolet with gas cell and DTGS KBr detector. The furnace and heated gas cell (250°C) were coupled through a heated ($T = 225^\circ\text{C}$) 120 cm stainless steel line transfer 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 TG–DTA and DSC curves of nicotinic acid are shown in Fig. 1a and b. These curves show total mass loss in a single step between 181 and 260°C (TG) and endothermic peaks at 183 , 235 and 254°C (DTA) or 183 , 237 and 283°C (DSC). The beginning of the mass loss between 181 and 185°C suggests that the endothermic peak at 183°C is due to this mass loss. However, DSC curve of nicotinic acid heated up to 205°C and cooled up to 100°C showed that this thermal event is due to a reversible transition phase, Fig. 1c and sample heated in a glass tube up to 190°C during 15 min, sublimation of the compound was observed. Infrared spectrum of the sublimated product was the same as that of original sample. The second and third endothermic peaks are attributed to the melting and evaporation of the sample, respectively. In other experiment, sample heated in a tube glass up to 260°C , as indicated by TG–DTA curves, melting followed by evaporation of the compound were also observed and infrared spectrum of the condensation product of evaporation was also the same as that of original sample, in agreement with Ref. [16] and in disagreement with Ref. [15].

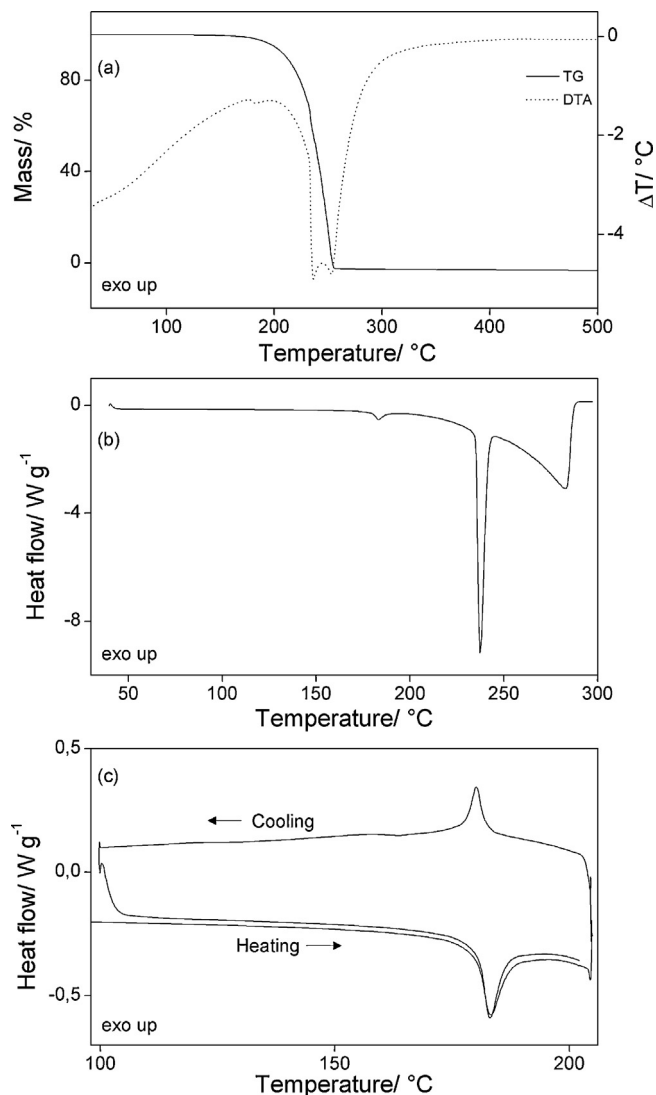


Fig. 1. (a) Simultaneous TG–DTA ($m = 5.155 \text{ mg}$), (b) DSC curve ($m = 5.155 \text{ mg}$) and (c) cycle DSC curve ($m = 4.817 \text{ mg}$) of the nicotinic acid.

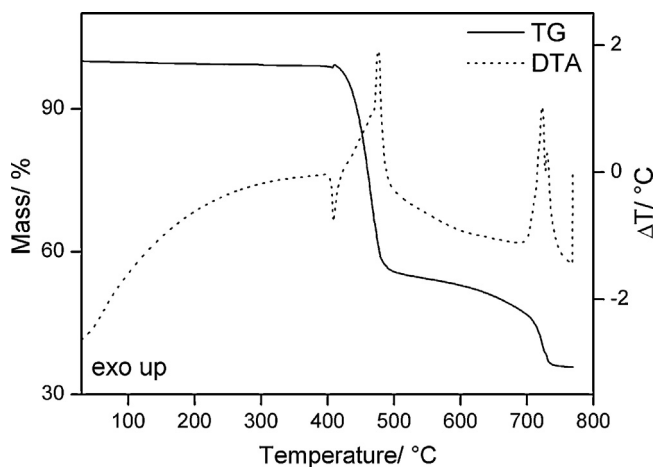


Fig. 2. Simultaneous TG–DSC curves of the sodium nicotinate ($m = 3.0298 \text{ mg}$).

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