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CALORIMETRIC AND THERMAL INVESTIGATION OF METAL DERIVATIVES OF 6-AMINOPICOLINIC ACID

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Abstract

The comparison of thermal and calorimetric properties of metal derivatives of 6-aminopicolinic acid (APH) is presented. The salts and complexes of APH with Cr(III), Cd(II), Cu(II), Ni(II), Pb(II), Co(II) and Ag(I) have been studied by TG-DTA and DSC methods up to 1200°C in a nitrogen atmosphere. Decomposition processes are proposed. The decarboxylation, deamination and carbonation of the organic fragments of molecules take place. The compounds decompose to metal or to metal oxides. The values of the transition enthalpy were determinated.

Keywords: comparison, decomposition, DSC, enthalpy

Introduction

There was no clear effect of the type of the metal ion on the thermal behaviour of 6-aminopicolinic acid (APH) metal derivatives. There seemed to be an interest in examining and comparing the thermal properties of these compounds. According to an IR study, all metal derivatives (except of copper complex) are APH salts [1]. In the present work the derivatives of APH with Cr(III), Cd(II), Cu(II), Ni(II), Pb(II), Co(II) and Ag(I) have been studied by the TG-DTA method, and by the DSC method in nitrogen atmosphere, at temperatures up to 1200°C. The thermal decomposition process was performed by using the Netzsch STA 409 simultaneous thermal analyzer, at a heating rate 10 K min^{-1}. The mass changes and transformation energetics of the samples were measured. Data acquisition and evaluation were carried out by using a standard software package. The analyses of the decomposition processes and those of the solid products were carried out by using X-ray diffraction, qualitative analysis methods, the results obtained by thermal analysis [1] and literature data [2–4]. The results of thermal analysis of Mn, Pb and Cr picolinates, obtained by Setaram thermal analyzer, were reported previously [5, 6].

Results and discussion

The thermodynamic parameters of the main thermal degradation process of the studied compounds are presented in Table 1. The graphs of the TG and DSC measure-

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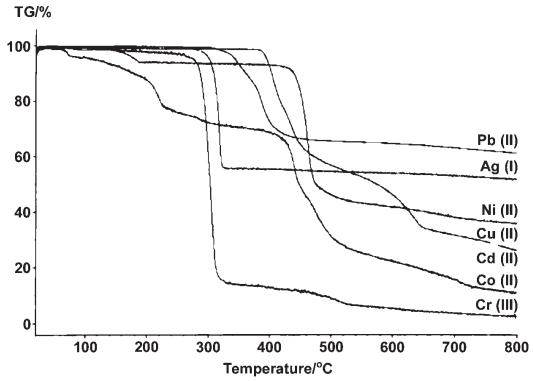

Fig. 1 TG curves of APH metal derivatives

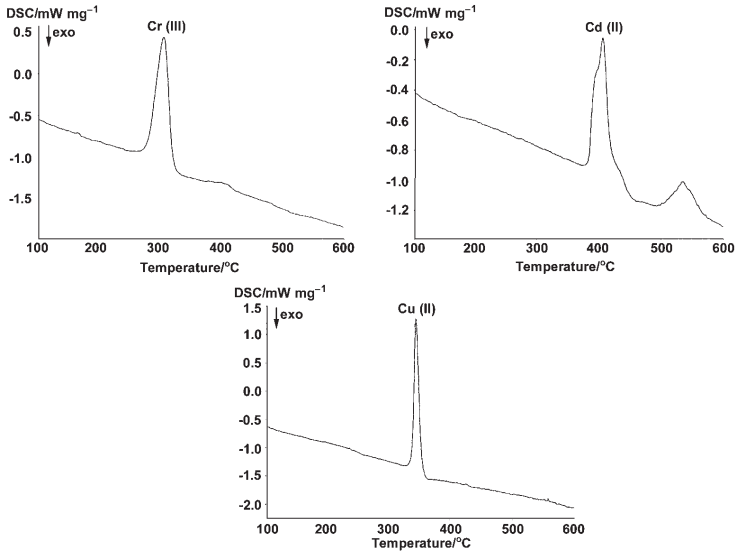

Fig. 2 DSC curves of Cr, Cd, and Cu derivatives with APH

ments are shown in Fig. 1 and Figs 2–4, respectively. The main decomposition process takes places between the temperatures of 280–500°C and its character is always endothermic. The following mode of thermal decomposition of the studied metal picolinates may be proposed:

$$(C_6H_6N_2O_2)_3Cr{\cdot}6APH \xrightarrow[-6APH,\ -CO_2\ ,\ -2\text{-}NH_2Py]{240-350^{\circ}C} (C_6H_6N_2O_2)_2Cr \xrightarrow[\text{determination}]{350-550^{\circ}C} \text{forms } Cr_2O_3\ (0.5)$$

The total mass loss observed on TG curve is 96.5%, the calculated value being 96.1%.

$$(C_6H_6N_2O_2)_2Cu \xrightarrow[-2CO_2\ ,\ -2\ 2\text{-}NH_2Py]{350-500^{\circ}C} \text{forms CuO, partial decomposition to Cu.}$$

The observed total mass loss is 77.3, the calculated 80.0%.

$$(C_6H_6N_2O_2)_2Ni \xrightarrow[-CO]{140-210^{\circ}C} (C_5H_6N_2O)_2Ni \xrightarrow[-CO_2,\,-2\cdot 2\text{-}NH_2Py]{430-520^{\circ}C} \text{forms NiO.}$$

The calculated mass losses in the particular decomposition steps are 8.4 and 62.4%, the recorded values are 7.2 and 60.2%, respectively.

$$C_6H_6N_2O_2Ag \xrightarrow[-CO_2,\,-2\text{-}NH_2Py]{270-360^{\circ}C} \text{forms } Ag_2O\ (0.5), \text{ decomposition } Ag_2O \text{ to Ag}$$

The mass loss, according to TG curve, is 48.4, the calculated one is 51.7%.

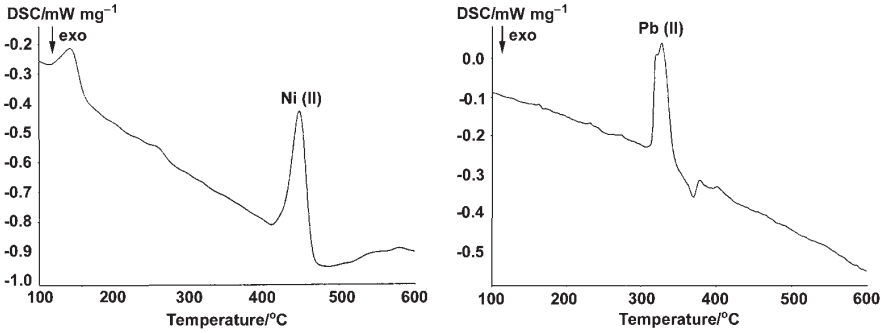

Fig. 3 DSC curves of Ni and Pb picolinates

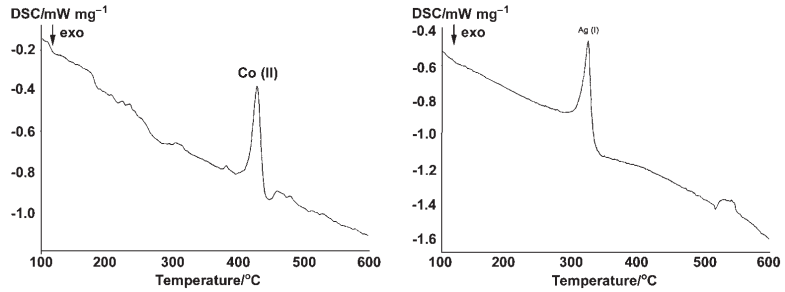

Fig. 4 DSC curves of Co and Ag picolinates

Table 1 Thermodynamic parameters of thermal decomposition from TG and DSC curves

Compound	T_{onset}/°C	T_{max} peak endo/°C	Mass loss/%	Transition enthalpy/kJ mol^{-1}
$(AP)_3Cr\cdot 6APH$	241.4	307.3	82.71	85.19
$(AP)_2Cd$	359.4	408.1	39.07	55.81
$(AP)_2Cu$	281.5	344.8	63.33	50.72
$(AP)_2Ni$	418.3	450.9	48.07	46.97
$(AP)_2Pb$	292.5	326.6	32.35	39.12
$(AP)_2Co\cdot H_2O$	382.5	429.7	45.45	29.59
(AP) Ag	276.2	322.6	42.92	11.49

The thermal stability of metal picolinates is similar in general, the thermal degradation of the studied compounds consists of the following processes: decarboxylation, loss of the organic molecules (mostly 2-NH_2Py) [1], forming metal oxides, carbonation of the organic parts of molecules, and partial decomposition of metal oxides to metal. The decomposition of Cd, Co and Pb derivatives with 6-aminopicolinic acid proceeds more slowly. The differences observed on TG curves of these metal derivatives are probably caused by the difficulties and different intensity in carrying away the gaseous molecules, and the different density of new phases formed during the decomposition processes. The Cd, Co, and Pb picolinates decompose to the mixture of metal and metal oxides. The DSC peak of Cu(II) compound is distinctly different from other DSC peaks, it is the highest and sharpest one. Probably, this fact is due to the complex structure of the Cu derivative, opposite to other metal derivatives which are picolinates.

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