Journal of Thermal Analysis and Calorimetry, Vol. 78 (2004) 501–511

TG-MS, TG, DTG AND DTA METHODS IN STUDY OF THERMAL DECOMPOSITION OF SOME *d*-METAL COMPLEXES WITH *4,4'-BPY* AND PROPIONATES

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Abstract

The new mixed ligand complexes with formulae $M(4\text{-bpy})(C_2H_5COO)_2 \cdot 2H_2O$ (where *M(II)*=Mn, Co, Ni; *4,4'-bpy* or *4-bpy*=4,4'-bipyridine) and $Cu(4\text{-bpy})_{0.5}(C_2H_5COO)_2 \cdot H_2O$ were prepared and characterized by VIS (for solid compounds of Co(II), Ni(II), Cu(II) in Nujol), IR spectroscopy, X-ray powder diffraction and molar conductance in MeOH, DMF or DMSO. Thermal behaviour of complexes was studied under static conditions in air atmosphere. Corresponding metal oxides were identified as final products of pyrolysis. A coupled TG-MS system was used to analysis of principal volatile thermal decomposition and fragmentation products of isolated complexes under dynamic air and argon atmosphere. The principal species correspond to: C^+, OH^+, H_2O^+, NO^+, CO_2^+ and other; additionally CO^+ in argon atmosphere.

Keywords: 4,4-bipyridine-propionato complexes, conductivity, TG-MS data, thermal decomposition, VIS-IR spectra

Introduction

Synthesis and properties of transition metals(II) complexes with 4,4'-bipyridine (4-*bpy*) and carboxylates is extensively studied. Investigations of new types of materials with potential functions as: microporous solid for molecular adsorption, ion exchange, materials for gas storage and potential catalysts are especially interesting. Final products of thermal decomposition of this type of compounds have important electronic surface properties [1, 2]. Ahuja *et al*. [3] prepared of some d^n metal complexes with 4-*bpy* and acetates where thermal properties were not determined. Recently, data concerning compounds of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with 4-*bpy* and formates were published by us [4]. The comparative study of corresponding 4.4'-bipyridine – propionato compounds seemed of interest. A survey of literature shows that only complexes of Cu(II) with 4-*bpy* and propionates have been studied [5]. In this paper we describe the synthesis of new mixed ligand complexes of

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1388–6150/2004/ $ 20.00

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Mn(II), Co(II), Ni(II) and Cu(II) with 4-*bpy* and propionates. The obtained compounds were characterized by chemical and elemental analysis, IR and VIS (for compounds of Co(II), Ni(II), Cu(II)) spectroscopic and molar conductivity investigations. Thermal behaviour was studied under static conditions in air. A coupled TG-MS system was used to analysis of principal species evolved during dynamic thermal decomposition or fragmentation processes of all synthesized complexes.

Experimental

Materials, synthesis and analysis

Propionic acid p. a. was obtained from Aldrich; other chemicals were the same as those described in our previous paper [6]. Water solution of $M(C_2H_5COO)_2$ (*M*(*II*)=Mn, Co, Ni and Cu) were prepared by method published in [4]. The complexes of *M*(*II*) with 4-*bpy* and propionates were isolated from ethanol (75% *v*/*v*)-water solutions according to procedure used for 4,4'-bipyridine-formato compounds of *M*(*II*) [4]. The metal contents in synthesized complexes and solutions of $M(C_2H_5COO)_2$ were determined complexometrically; C, H and N by elemental analysis with V_2O_5 as oxidizing agent. Solid decomposition products were determined on the ground of mass losses recorded on TG curves and results of XRD analysis.

Physical measurements

Thermal behaviour of all obtained compounds was studied by means of DTA, DTG, TG techniques under static conditions in air on derivatograph Q-1500 using 100 mg mass sample in ceramic crucibles with α-Al_2O_3 as reference. A coupled TG-MS system was used to analysis of principal species evolved during the dynamic thermal decomposition or fragmentation processes of all investigated complexes in air and argon atmosphere (flow rate 1 L h^{-1}); for studies 5–12 mg of mass samples were used. Data were performed by on line connected computer system with commercial (TG/DTA-SETSYS 16/18 apparatus, mass spectrometer QMS-422, model Thermostar from Balzers) software; an ion source temperature of ca. 150°C by using 70 eV electron impact ionization. All thermal investigations were carried between 20–1000°C at the heating rate of 10 K min^{-1}. The *m*/*z* values are given based on ^{1}H, ^{12}C, ^{14}N, ^{16}O (additionally ^{13}C and ^{18}O for CO_2). Molar conductivities (Λ_M) of investigated complexes were measured [7] using $1.0\cdot10^{-3}$ mol L^{-1} solutions in MeOH, DMSO and DMF at 25±0.5°C. Other apparatus and conditions of measurements were the same as reported in [8].

Results and discussion

The new mixed 4,4'-bipyridyne-propionato complexes with formulae $M(4\text{-bpy})(C_2H_5COO)_2\cdot 2H_2O$ (*M*(*II*)=Mn, Co, Ni) and $Cu(4\text{-bpy})_{0.5}(C_2H_5COO)_2\cdot H_2O$ were prepared in the solid-state. The analytical, conductivity and solubilities data are listen in Table 1. All compounds are stable in air. Their solubility in water at 21°C as

Table 1 Analytical data, molar conductivity Λ_M (Ω^{-1} cm^2 mol^{-1}) in MeOH, DMF and DMSO (concentration $1\cdot10^{-3}$ mol L^{-1}) at 25°C, solubility *S* (mol L^{-1}) in water at 25°C of obtained complexes

Complex	Analysis found (calculated)/%				Λ_M/Ω^{-1} cm^2 mol^{-1}			
	M	C	N	H	MeOH	DMF	DMSO	$S\cdot10^2$
$Mn(4\text{-}bpy)(C_2H_5COO)_2\cdot2H_2O$	14.69 (13.97)	43.01 (42.75)	7.27 (7.12)	5.64 (5.62)	53.0	18.3	23.2	2.2
$Co(4\text{-}bpy)(C_2H_5COO)_2\cdot2H_2O$	14.74 (14.83)	42.30 (42.33)	7.11 (7.05)	5.57 (5.58)	45.0	17.2	17.2	2.2
$Ni(4\text{-}bpy)(C_2H_5COO)_2\cdot2H_2O$	14.70 (14.78)	42.37 (42.35)	7.15 (7.05)	5.59 (5.58)	44.4	18.6	16.5	1.3
$Cu(4\text{-}bpy)_{0.5}(C_2H_5COO)_2\cdot H_2O$	21.54 (20.78)	35.33 (35.35)	4.69 (4.58)	5.25 (5.27)	26.9	*	6.1	0.5

*practically insoluble in DMF

found to be in range of 10^{-2}–10^{-3} mol L^{-1}. The obtained complexes are isostructural in the group: Mn(II), Co(II) and Ni(II) (Fig. 1). These isostructural compounds presented intermediate behaviour between those of non-electrolytes and 1:1 electrolytes [9] in Me(OH), DMF and DMSO. Higher than anticipated Λ_M values are due of displacement of propionato ligand by solvent molecules. Similar results were noted for complexes of Mn(II), Co(II), Ni(II) with bipyridine and other ligands [10, 11]. Conductivity data proved that $Cu(4\text{-bpy})_{0.5}(C_2H_5COO)_2\cdot H_2O$ in MeOH and DMSO is non-electrolyte [9]. It is practically insoluble in DMF.

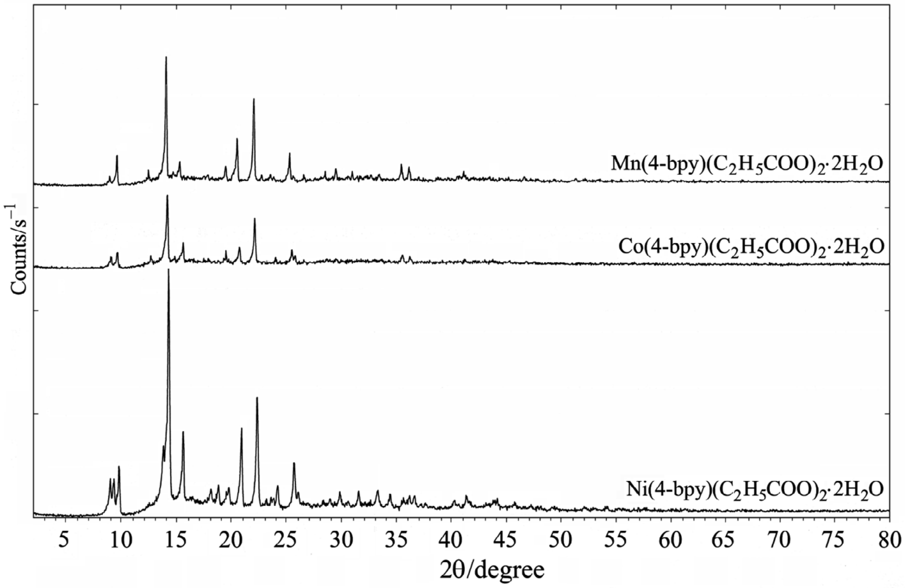


Fig. 1 X-ray diffraction patterns for isostructural complexes of type $M(4\text{-bpy})(C_2H_5COO)_2\cdot 2H_2O$ (*M(II)*=Mn, Co and Ni)

Spectroscopic characteristic

VIS spectra for solid complexes of Co(II), Ni(II) and Cu(II) in Nujol mulls (Fig. 2) were investigated (22000–12000 cm^{-1}). The ligand field spectra of complexes $M(4\text{-bpy})(C_2H_5COO)_2\cdot 2H_2O$ (*M(II)*=Co, Ni) are consisted with distorted octahedral environment around the metal atoms [12]. $Co(4\text{-bpy})(C_2H_5COO)_2\cdot 2H_2O$ exhibit only unsymmetric band at 21100 cm^{-1} which corresponds to the transition $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$. The electronic spectrum of Ni(II) complex shows only one spin allowed band attributed to the $^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$ at ca. 15600 cm^{-1}. The single band observed for Cu(II) compound at 14050 cm^{-1} can be indicated that all three transitions ($^2B_{1g}\rightarrow{}^2E_g$, $^2B_{1g}\rightarrow{}^2B_{2g}$, $^2B_{1g}\rightarrow{}^2A_{1g}$). The position and shape of this suggested a rhombic octahedral environment around Cu(II) [13]. The characteristic ring vibration stretching mode CC, CN, $CC_{\text{inter ring}}$ (A_1 symmetric) [14] (at 1595 cm^{-1} [14] in unbonded ligand) is shifted by about 10–15 cm^{-1} towards higher values. The pyridine 'breathing' frequency appearing

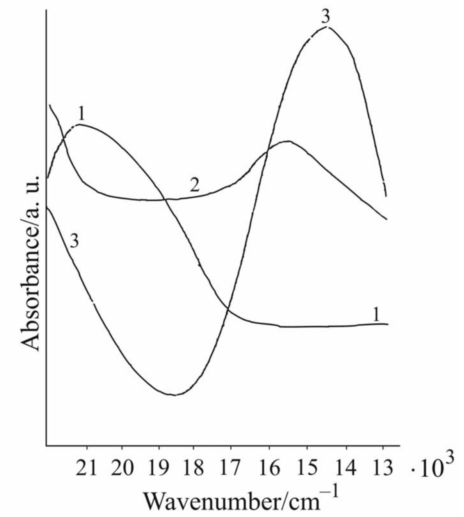


Fig. 2 VIS spectra for solid complexes of 1 – $Co(4\text{-}bpy)(C_2H_5COO)_2{\cdot}2H_2O$, 2 – $Ni(4\text{-}bpy)(C_2H_5COO)_2{\cdot}2H_2O$ and 3 – $Cu(4\text{-}bpy)_{0.5}(C_2H_5COO)_2{\cdot}2H_2O$ (in Nujol)

at 988 cm^{-1} [15] in free ligand is observed in the range 1002.9–1014.5 cm^{-1}. It is partly superimposed on the CH_3 wagging vibration of propionate groups. These bathochromic shifts of principal absorption bands suggested that 4-*bpy* was coordinated to metal ions [16]. The IR spectra of investigated complexes in the range of carboxylate groups absorption show the presence of bands, which are assigned as asymmetric (ν_{as}(OCO)) and symmetric (ν_s(OCO)) stretching vibration of OCO groups. In the case of Cu(II) complex, the bands of ν_{as}(OCO) and ν_s(OCO) occur at 1560.3 and 1434.9 cm^{-1}, respectively; the value $\Delta\nu=\nu_{as}-\nu_s$ is smaller than this for sodium propionate salt ($\Delta\nu_{C_2H_5COONa}$=142 cm^{-1} [17]). Thus, according to the spectroscopic criterion [18, 19] and other works [20, 21], carboxylate groups in this compound act as bidentate chelating ligands. The modes of ν_{as}(OCO) for isostructural complexes $M(4\text{-}bpy)(C_2H_5COO)_2{\cdot}2H_2O$ (*M*(*II*)=Mn, Co, Ni) are observed in the range 1542.9–1550.7 cm^{-1}. The ν_s(OCO) are partly masked by absorption of 4-*bpy*. Thus, it is difficult to discuss the nature of the metal-propionate bonds. A strong and broad band in water stretching region (with maximum at 3400 cm^{-1}) was present in the IR spectra.

Thermal behaviour of complexes in air

The data obtained from thermoanalytical curves are presented on respective Schemes. The DTA, TG and DTG curves for $Ni(4\text{-}bpy)(C_2H_5COO)_2{\cdot}2H_2O$ and $Cu(4\text{-}bpy)_{0.5}(C_2H_5COO)_2{\cdot}H_2O$ in static air atmosphere are shown as an example, in Fig. 3. Solid decomposition products were determined on the ground of mass losses recorded on TG curves and results of XRD analysis. The pyrolysis of all studied complexes start by the release of water molecules, which is demonstrated by the loss of mass on TG curve and weak endothermic peak on DTA curve. Compounds

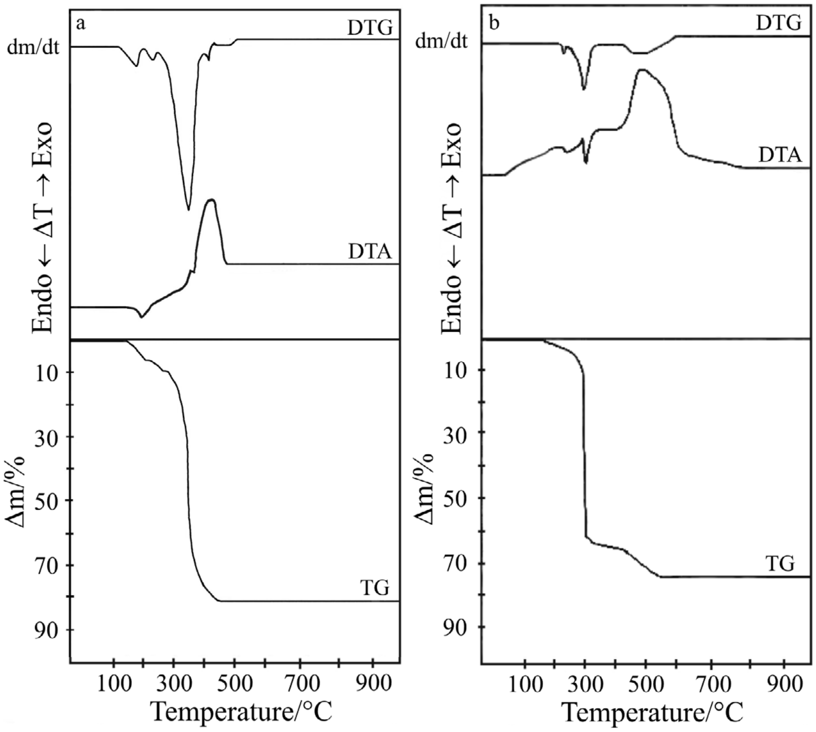
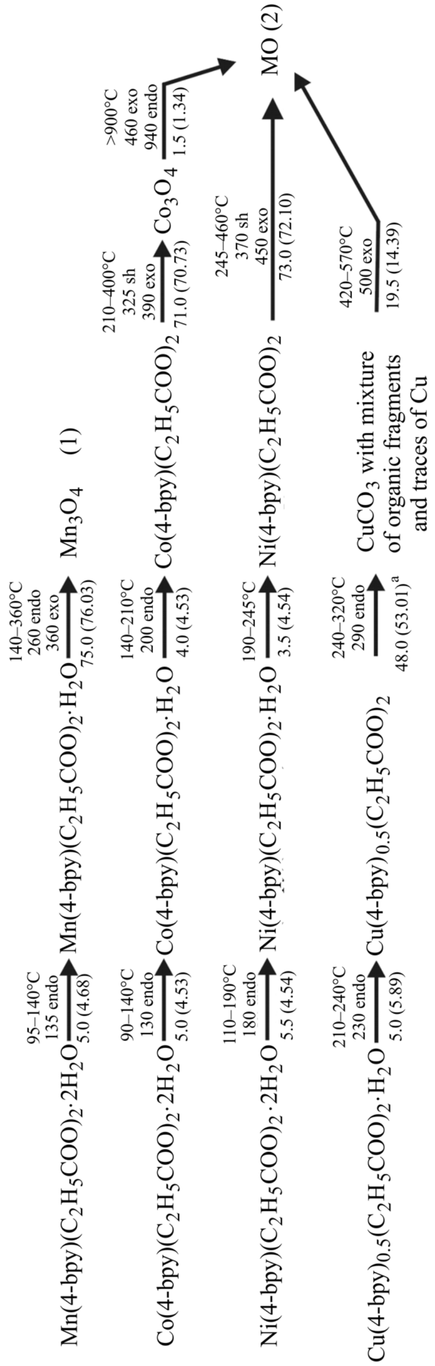


Fig. 3 Thermoanalytical curves of a – $Ni(4\text{-bpy})(C_2H_5COO)_2{\cdot}2H_2O$ and b – $Cu(4\text{-bpy})_{0.5}(C_2H_5COO)_2{\cdot}2H_2O$; mass sample 100 mg

of Co(II), Ni(II) and Cu(II) dehydrated in similar way. They are stable up to 90, 110 and 210°C, respectively. Complexes of Co(II) and Ni(II) eliminate H_2O in double stage. On heating, $Ni(4\text{-bpy})(C_2H_5COO)_2$ decomposes directly to final product NiO between 245–460°C. $Co(4\text{-bpy})(C_2H_5COO)_2$ begins to decompose at ca. 210°C and formation of Co_3O_4 occurs. Above 900°C stoichiometric CoO is formed. Anhydrous compound of Cu(II) deaminates and the process of carboxylate groups decomposition takes place; forms $CuCO_3$ with mixture of organic fragments and traces of Cu. Pyrolysis terminated at 570°C (CuO was found: 26.0%; calcd: 26.01%); In the case of $Mn(4\text{-bpy})(C_2H_5COO)_2{\cdot}2H_2O$, TG and DTG curves show two well resolved stages of decomposition. The dehydration starts at 95°C. Monohydrate $Mn(4\text{-bpy})(C_2H_5COO)_2{\cdot}H_2O$ decomposed directly to Mn_3O_4; the endo and exoeffects appear on DTA curve at 260 and 360°C, respectively.

Found mass loss values (% without brackets) and those calculated (in brackets) are shown below arrows (Schemes 1–2). Ranges of decomposition and peaks from DTA (°C) are presented above arrows.



^{a}calculated for pure $CuCO_3$

Schemes 1 and 2

Mass spectrometric thermal analysis

MS coupled with TG system has been used to study of volatile species of thermal decomposition and fragmentation processes for all obtained complexes. Dynamic measurements were carried out in air and argon atmosphere. Figure 4 (as an example) presents the ion current for *m*/*z* detected in the mass spectrometer *vs*. temperature for Co(4-bpy)$(C_2H_5COO)_2{\cdot}2H_2O$ in these atmospheres. In air atmosphere major signals are observed in the range 130–170 and 200–370°C for Mn; 110–180 and 290–380°C for Co; 110–210 and 300–400°C for Ni; 280–320 and 380–500°C for Cu. The first MS peak for H_2O^+ (with *m*/*z*=18) appeared at 140 (Mn), 147 (Co), 180 (Ni) and 215°C (Cu). These data are coincided with mass loss observed on TG curve. Fur-

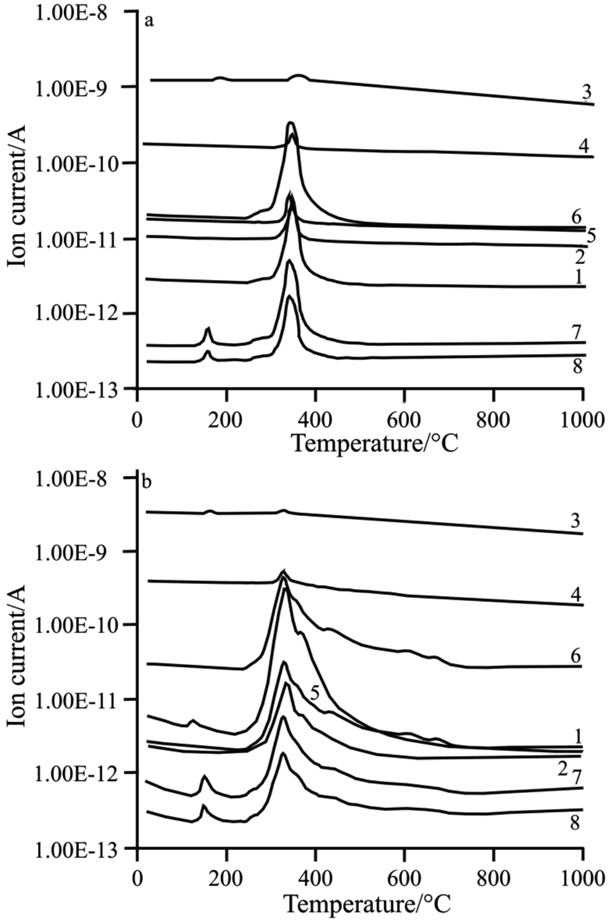


Fig. 4 MS profiles of gaseous products of decomposition for complex Co(4-bpy)$(C_2H_5COO)_2{\cdot}2H_2O$; a – in air; mass sample 7.62 mg; *m*/*z*=1–12; 2–15; 3–18; 4–29; 5–30; 6–44; 7–45; 8–46 ; b – in argon; mass sample 8.36 mg; *m*/*z*=1–12; 2–15; 3–18; 4–28; 5–29; 6–44; 7–45; 8–46

ther, the H_2O^+ was produced during decomposition of organic ligands; MS maxima occurred at 322 (Mn), 350 (Co), 373 (Ni) and 313°C (Cu). The rates of elimination of CO_2^+ during pyrolysis decrease when temperature increased. Maxima rates of forming CO_2^+ (m/z=44) have centres at 317 for Mn, 345 for Co and 374 for Ni. Additionally, maxima of signals with m/z=45 and 46 are observed (which correspond $^{13}C^{16}O_2^+$ or $^{12}C^{16}O^{18}O^+$). The profiles are similar only intensities of ion currents are lower. In the case of $Cu(4\text{-bpy})_{0.5}(C_2H_5COO)_2{\cdot}H_2O$ clearly resolved maxima of ion current in the elimination of CO_2^+ at 305 and 458°C are observed. The last peak caused by consecutive decomposition of $CuCO_3$ and combustion of residues of organic fragments takes place. This line of ion current for CO_2^+ is correlated with TG

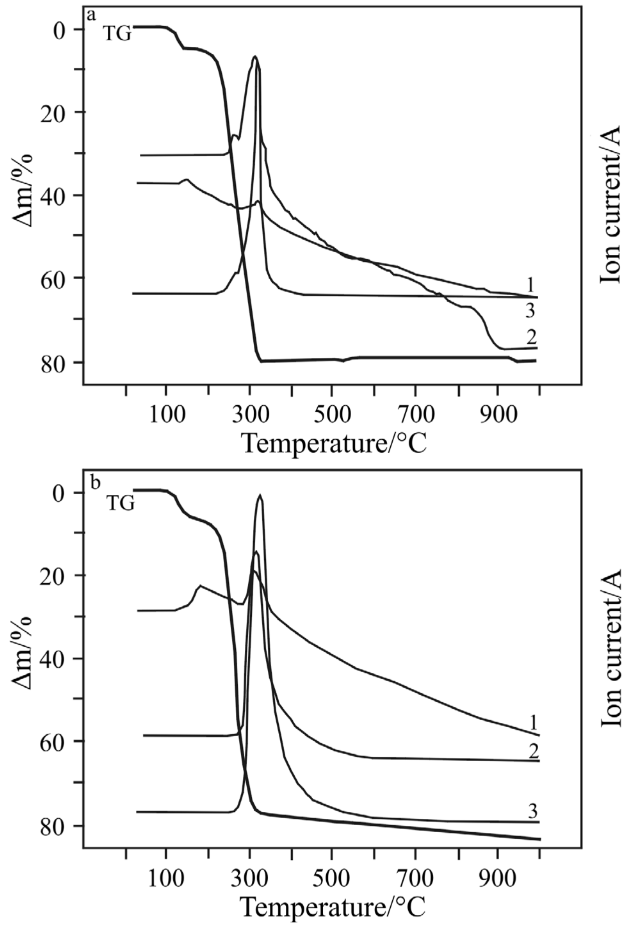


Fig. 5 TG curve for $Mn(4\text{-bpy})(C_2H_5COO)_2{\cdot}2H_2O$ and ion current detected by MS; a – in air; mass sample 5.60 mg; m/z=1–18; 2–30; 3–44; with sensitivity of ion current: E-9; E-11; E-10 A, respectively; b – in argon; mass sample 8.36 mg; m/z=1–18; 2–28; 3–44, with sensitivity of ion current: E-9; E-10; E-10A, respectively

curve. The MS peaks for *m*/*z*=30 (NO^+ or $HCHO^+$) occur in the range 310–500°C. Also MS peaks for ion fragments with *m*/*z*=12 (C^+), 15 (CH_3^+), 17 (OH^+), 26 (CN^+ or $C_2H_2^+$), 27 (HCN^+) and 29 ($C_2H_5^+$) of investigated compounds were detected. The MS curve for *m*/*z*=32 (O_2 from air atmosphere) shows a minimum in the range 320–370°C. When a dynamic argon atmosphere was used profiles of volatile species produced during pyrolysis (or fragmentation) of investigated complexes were very similar to those of detected for air. Though peaks of MS in argon are shifted towards higher temperatures at about 20–40°C for complexes of Mn(II), Co(II) and Ni(II). In the case of $Cu(4\text{-bpy})_{0.5}(C_2H_5COO)_2 \cdot H_2O$, the maxima of elimination of volatile species occur at 280°C (strong) and between 320–360°C (blurry). In argon the ion signal intensities with *m*/*z*=28 (CO^+ or N_2) at ca. 315°C take place. TG coupled with MS data for some ions current are shown, as an example in Fig. 5.

Conclusions

The new mixed ligand complexes of empirical formulae $M(4\text{-bpy})(C_2H_5COO)_2 \cdot 2H_2O$ (*M*(*II*)=Mn, Co, Ni) and $Cu(4\text{-bpy})_{0.5}(C_2H_5COO)_2 \cdot H_2O$ were prepared as crystalline compounds. The analysis of the powder diffractin patterns proved that complexes of type $M(4\text{-bpy})(C_2H_5COO)_2 \cdot 2H_2O$ (*M*(*II*)=Mn, Co, Ni) were isostructural. The ligand field spectra of Co(II) and Ni(II)) are characteristic of distorted octahedral environment around metal ions [12]. IR spectra of investigated compounds indicate that 4-*bpy* coordinated to metal ions [16]. The complexes of Cu(II) and Ni(II) are more thermal stable. All compounds decompose progressively. The temperature of the oxide formation increases as following: Mn_3O_4<NiO<CuO<CoO. Generally, the MS detected during pyrolysis of complexes of type $M(4\text{-bpy})(C_2H_5COO)_2 \cdot 2H_2O$ and $Cu(4\text{-bpy})_{0.5}(C_2H_5COO)_2 \cdot H_2O$ are very similar, only in argon the presence of the signal *m*/*z*=28 (CO^+) has been observed. The ion currents correspond to C^+, OH^+, H_2O^+, CN^+ (or $C_2H_2^+$), HCN^+, $C_2H_5^+$, NO^+, CO_2^+ as well as $^{13}C^{16}O_2^+$ and $^{12}C^{16}O^{18}O^+$ (*m*/*z*=12, 17, 18, 26, 27, 29, 30, 44, 45 and 46, respectively) were detected; also for *m*/*z*=13 and 15. The maxima of ion currents are associated with mass decrease observed on TG curve.

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