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NEW COMPLEXES OF Mn(II), Co(II), Ni(II) AND Cu(II) WITH 2,2'- OR 2,4'-BIPYRIDINE AND FORMATES
Synthesis, thermal and other properties

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New mixed-ligand complexes with empirical formulae: $Mn(2\text{-}bpy)_{1.5}L_2\cdot 2H_2O$, $M(2\text{-}bpy)_2L_2\cdot 3H_2O$ (M(II)=Co, Cu), $Ni(2\text{-}bpy)_3L_2\cdot 4H_2O$ and $M(2,4'\text{-}bpy)_2L_2\cdot 2H_2O$ (where 2-bpy=2,2'-bipyridine, 2,4'-bpy=2,4'-bipyridine; L=$HCOO^-$) have been obtained in pure solid-state. The complexes were characterized by chemical and elemental analysis, IR and VIS spectroscopy, conductivity (in methanol and dimethylsulfoxide). The way of metal-ligand coordination discussed. The formate and 2,4'-bpy act as monodentate ligands and 2-bpy as chelate ligand. The new complexes with ligand isomerism were identified. During heating the complexes lose water molecules in one or two steps. Thermal decomposition after dehydration is multistage and yields corresponding metal oxides as final products. A coupled TG-MS system was used to analysis principal volatile thermal decomposition (or fragmentation) products of $Ni(2,4'\text{-}bpy)_2(HCOO)_2\cdot 2H_2O$ under dynamic air or argon atmosphere.

Keywords: *bipyridine formate complexes, TG-MS data, thermal decomposition, transition-metal complexes, VIS-IR spectra*

Introduction

The synthesis and characterization of bipyridine metal complexes attract much attention during the many years due to their various applications [1]. As an example: in molecular separation [2, 3], catalysis [4, 5], storage of solar energy [6, 7]. Many metal complexes containing bipyridine isomers are of interest from biological and material chemistry [5, 8–10]. Mixed ligand complexes of metal containing bipyridine isomers and biologically active carboxylates are especially attractive [11–17]. Several studies of transition metal(II) complexes with formates have been reported [18–20]. Very little is known on mixed ligand complexes of d^n metal with bipyridine isomers and formates. Hathaway *et al.* [21] prepared complexes with formulae:

$$Cu(2\text{-}bpy)_2(HCOO)_2\cdot 4H_2O$$
$$[Cu(2\text{-}bpy)_2(HCOO)]\cdot ClO_4$$

where 2-bpy=2,2'-bipyridine.

Also the complex

$$[Cu(2\text{-}bpy)_2(HCOO)_2]BF_4\cdot 0.5H_2O$$

was described [22]. We have recently reported [23] the synthesis and characterization of 4,4'-bipyridine-formato complexes of M(II) ions (M(II)=Mn, Co, Ni, Cu, Zn and Cd). Herein, we describe the synthesis of mixed ligand complexes of Mn(II), Co(II), Ni(II) and Cu(II) with 2,2'-bipyridine or 2,4'-bipyridine (2,4'-bpy) and formates in the solid-state and their physico-chemical properties. The obtained mixed-ligand compounds were characterized by chemical and elemental analysis, molar conductivity investigations, IR and VIS spectra (for complexes of Co(II), Ni(II), Cu(II)) and thermal decomposition in air. A coupled TG-MS system was used to investigation of the principal volatile products of thermal decomposition or fragmentation of $Ni(2,4'\text{-}bpy)_2(HCOO)_2\cdot 2H_2O$ complex under dynamic air or argon atmosphere.

Experimental

Materials

2,2'-Bipyridine, 2,4'-bipyridine, HCOOH, manganese powder, dimethylsulfoxide (DMSO), dimethylformamide (DMF) and methanol (MeOH) (anhydrous) p.a. were obtained from Aldrich and Lab-Scan, respectively. Water solutions of $M(HCOO)_2$ (M(II)=Co, Ni, Cu) were prepared following: to 20 mL water solution of HCOOH (60 mmol) freshly precipitated carbonates of metal(II) in ca. stoichiometric ratio were slowly added with stirring and heating. Water solution of $Mn(HCOO)_2$ was prepared by dissolving pure Mn in 20 mL of 2 mol L^{-1} HCOOH (warm) in ca. equimolar ratio. The solution contained 1 mL of 10% v/v hydroxylamine (to stop

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the oxidation process of Mn(II)). The contents of *M*(II) ions in obtained solutions were complexometrically (EDTA) determined. Other chemicals were p.a. products from POCh-Gliwice.

Complex synthesis

2-Bpy complexes of Mn(II), Co(II), Ni(II) and Cu(II) prepared by mixing 12.8 mmol of 2-bpy in 96% *v*/*v* ethanol (26 mL) with the solution of 6.4 mmol metal formates in 24 mL of water. The mixture was heated up to 80°C for ca. 30 min and allowed to cool. During several days the compounds crystallized. The obtained compounds were filtered off; washed with 40% *v*/*v* ethanol and then with EtOH and Et_2O mixture (1:1). The products were air dried at room temperature.

2,4'-Bpy complexes: H_2O solution (14.7 mL) of 2,4'-bpy (12.9 mmol) containing 0.2 mL of 96% *v*/*v* EtOH was added to water solutions of $M(HCOO)_2$ (4.3 mmol in 15 mL). The resulting mixture of molar ratio M:2,4'-bpy=1:3 was heated to 80°C ca. 30 min and then allowed to cool. The small crystalline products were obtained after 1–2 days at room temperature. The products were filtered, washed with small portions of water next with ethanol and diethyl ether mixture (1:1) and dried in open air.

Methods

Carbon, hydrogen and nitrogen analysis were performed with a Carbo-Erba analyser with V_2O_5 as an oxidizing agent. Metal content in mineralized sample determined by EDTA titration. IR spectra were recorded with a Shimadzu spectrometer (4000–400 cm^{-1}) using KBr pellets. The VIS spectra were obtained in Nujol mulls; they recorded on a Specord M40 spectrometer (30000–12000 cm^{-1}). Molar conductances were measured on a conductometer of the OK-102/1 type equipped with an OK 902 electrode at 25±0.5°C. Molar conductivity of complexes was measured using $1.0\cdot10^{-3}$ mol L^{-1} solutions in MeOH and DMSO; for Cu(II) compounds also in DMF.

Thermal studies were performed on a derivatograph Q-1500 at a heating rate 10°C min^{-1} under a static air atmosphere. α-Al_2O_3 served as the reference; mass sample of 100 mg. The analysis of some solid decomposition products was performed using TG and DTG curves and supported by X-ray diffractograms (diffractometer D-5000, CuK_α, Ni filtered radiation). The measurements were made in the 2θ=2–80° range. Obtained X-ray diffractometric results were analysed using the Powder Diffraction File [24]. The system TG-MS was used to analysis of principal volatile products of pyrolysis and fragmentation processes of complex $Ni(2,4'\text{-bpy})_2(HCOO)_2\cdot2H_2O$ in air and argon atmosphere (flow rate 1 L h^{-1}). 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°C 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).

Results and discussion

Results of the elemental and chemical analysis are listed in Table 1. The complexes are small crystalline

Table 1 Analytical data, molar conductivity Λ_M in MeOH and DMSO (concentration $1\cdot10^{-3}$ mol L^{-1})

No.	Complex (colour)	Analysis: found (calculated)/%				Λ_M/Ω^{-1} cm^2 mol^{-1}	
		M	C	N	H	MeOH	DMSO
I	$Mn(2\text{-bpy})_{1.5}(HCOO)_2\cdot2H_2O$ (yellow)	13.09 (13.23)	49.68 (49.17)	9.84 (10.12)	4.22 (4.37)	76.0	31.1
II	$Co(2\text{-bpy})_2(HCOO)_2\cdot3H_2O$ (orange)	11.33 (11.43)	51.91 (51.27)	10.56 (10.87)	4.50 (4.69)	104.0	27.3
III	$Ni(2\text{-bpy})_3(HCOO)_2\cdot4H_2O$ (blue)	8.64 (8.52)	56.02 (55.75)	11.75 (12.19)	4.79 (4.97)	165.1	34.6
IV	$Cu(2\text{-bpy})_2(HCOO)_2\cdot3H_2O$ (blue)	12.30 (12.22)	51.01 (50.82)	10.35 (10.77)	4.51 (4.65)	75.3	20.8
V	$Mn(2,4'\text{-bpy})_2(HCOO)_2\cdot2H_2O$ (yellow)	11.21 (11.13)	53.92 (53.56)	11.61 (11.36)	4.37 (4.49)	66.2	29.7
VI	$Co(2,4'\text{-bpy})_2(HCOO)_2\cdot2H_2O$ (pink)	11.47 (11.85)	53.70 (53.13)	11.26 (11.26)	4.37 (4.46)	64.6	24.2
VII	$Ni(2,4'\text{-bpy})_2(HCOO)_2\cdot2H_2O$ (pink)	12.05 (11.81)	53.67 (53.15)	11.73 (11.27)	4.38 (4.46)	58.1	15.4
VIII	$Cu(2,4'\text{-bpy})_2(HCOO)_2\cdot2H_2O$ (blue)	12.88 (12.66)	53.01 (52.64)	11.52 (11.16)	4.31 (4.42)	34.3	10.2

solids. The analytical data indicate, in general, 1:2:2 (M:bpy:$HCOO^-$) stoichiometry. Only Mn(II) and Ni(II) with 2-bpy were obtained as

$$Mn(2\text{-}bpy)_{1.5}(HCOO)_2{\cdot}2H_2O$$

and

$$Ni(2\text{-}bpy)_3(HCOO)_2{\cdot}4H_2O$$

2,2'-Bipyridine complexes are hydrates with different degree of hydration. The complexes with 2,4'-bpy were prepared as dihydrates. In solid state all complexes are stable in air. The compounds dissolved fairly in H_2O, MeOH, DMSO, decompose in aqueous acids and alkali and are insoluble in most organic solvents (CCl_4, CH_3Cl, C_2H_5OH). The observed molar conductivities values in MeOH and DMSO are given in Table 1. The high molar conductivity value observed for the $Ni(2\text{-}bpy)_3(HCOO)_2{\cdot}4H_2O$ in MeOH (165.1 Ω^{-1} cm^2 mol^{-1}) feel into the range expected for 1:2 electrolytes [25]. The remaining complexes in MeOH have intermediate behaviour between non- and 1:1 electrolytes except complex **II**, which is 1:1 electrolyte. Also Λ_M for complexes **I–VII** in DMSO (Table 1) and **IV** in DMF (16.9 Ω^{-1} cm^2 mol^{-1}) solutions corresponded intermediate those non- and 1:1 electrolytes. The low molar conductivity values indicate the non-electrolytic nature of $Cu(2,4'\text{-}bpy)_2(HCOO)_2{\cdot}2H_2O$ in DMSO (10.2 Ω^{-1} cm^2 mol^{-1}) and DMF (9.0 Ω^{-1} cm^2 mol^{-1}).

Electronic and IR spectra

The spectra in VIS region of the cobalt(II) and nickel(II) complexes are all consistent with a distorted octahedral environment around metal atom (for these compounds chromophores have been indicated) [26]. We ascribe the observed band in the cobalt(II) complexes to the following transition: ${}^4T_{1g}(P){\leftarrow}{}^4T_{1g}(F)$. The calculated values of $\overline{\nu}_{calcd}$ by the rule of average environment (RAE) [26] for ${}^4T_{1g}(P)$ are comparable with experimental $\overline{\nu}_{exp.}$, which indicate the following chromofores in the solid complexes CoN_4O_2 ($\overline{\nu}_{exp.}$ 21000 cm^{-1}, $\overline{\nu}_{calcd}$ 21130 cm^{-1}) for compound **II** and $CoN'_2O_2O'_2$ ($\overline{\nu}_{exp.}$ 20250 cm^{-1}, $\overline{\nu}_{calcd}$ 20260 cm^{-1}) in case **VI** (where *N*=from 2-bpy, *N'*=(4')N from 2,4'-bpy, *O*=from monodentate carboxylate groups, *O'*=from water. The ${}^4A_{2g}{\leftarrow}{}^4T_{1g}(F)$ band has been observed only for the complex $Co(2,4'\text{-}bpy)_2(HCOO)_2{\cdot}2H_2O$. The ligand field spectra of nickel(II) compounds were observed at $\overline{\nu}_{exp.}$ 19000 cm^{-1} for **III** and $\overline{\nu}_{exp.}$ 15000 cm^{-1} for **VII**, it is assigned to the ${}^3T_{1g}(F){\leftarrow}{}^3A_{2g}$ transition. The comparison of the values of $\overline{\nu}_{calcd}$ for this transition with $\overline{\nu}_{exp.}$, indicates that the following chromophores are probably presented in solid compounds: NiN_6 in **III** ($\overline{\nu}_{calcd}$ 19200 cm^{-1}) and $NiN'_2O_2O'_2$ in **VIII** ($\overline{\nu}_{calcd}$ 15600 cm^{-1}). The complex **VII** exhibits also band at 12400 cm^{-1} (${}^1E_g{\leftarrow}{}^3A_{2g}$). The electronic spectra of Cu(II) complexes have similar profiles. They exhibit one broad ligand field band at: 15250 cm^{-1} for **IV** and 15000 cm^{-1} for **VIII**. The band can be attributed to the ${}^2E_g{\leftarrow}{}^2B_{1g}$, ${}^2B_{2g}{\leftarrow}{}^2B_{1g}$, ${}^2A_{1g}{\leftarrow}{}^2B_{1g}$ transitions, in which the three levels are close so that they are not resolved in the VIS spectra. The position of this band suggest pseudooctahedral geometry (probably compressed rhombic-octahedral) in the copper complex [27].

For consistency, only IR fundamental vibration modes of 2-bpy, 2,4'-bpy and OCO groups for obtained compounds are listed in Tables 2–3. The IR spectrum of free 2-bpy and 2,4'-bpy owing to complex formation. The bands $\nu_{CC,CN,CC_{ir}}$ (symmetry A_1) and $\nu_{CN,CC}$ (symmetry B_1) for 2-bpy complexes appear at 1602.7–1595.0 and 1570.0–1559.3 cm^{-1}, respectively. These bands are shifted towards higher frequencies in comparison to free 2-bpy [28]. In all complexes, the pyridine 'breathing' mode shift also to higher wave number about 29.3–23.5 cm^{-1}. The γ_{CH} out-of-plane deformation modes (in free 2-bpy are observed at 753 cm^{-1}) shift by ca. 30.8–16.5 cm^{-1} to higher frequency, also weak satellite of this band (at 738 cm^{-1}) gains intensity and is strongly split away from parent [29]. In summary, the 2-bpy behaves as bidentate ligand with the formation 2,2'-bipyridine chelate complexes [29]. Due to formation of complexes with metal ions, IR spectrum of 2,4'-bpy undergoes a change only in the region of the ring vibration $\nu_{CC,CN,CC_{ir}}$, $\nu_{CN,CC}$ and ring 'breathing' modes of 4-substituted pyridine (4-sub) (Table 2) [30]. These observations permit to presume that 2,4'-bpy coordinates via the least hindered (4')N atom as a monodentate ligand [31].

The IR spectra of 2-bpy complexes show asymmetric $\nu_{as(OCO)}$ and symmetric $\nu_{s(OCO)}$ vibrations of OCO group in the range 1639.1–1612.2 and 1352.0–1313.4 cm^{-1}, respectively (Table 3). Comparison of these bands with those of HCOONa shows that $\nu_{as(OCO)}$ are shifted to higher and $\nu_{s(OCO)}$ to lower frequencies. The separation values $\Delta\nu$ of $\nu_{as(OCO)}$ and $\nu_{s(OCO)}$ in the IR spectra of these complexes are higher than those for the sodium salt ($\Delta\nu$=240 cm^{-1} [32]). The region of frequencies of these bands and separation modes indicate that the carboxylate groups act probably as monodentate formate groups in the obtained 2-bpy complexes [33–35]. However conductivity and VIS data suggest, that in $Ni(2\text{-}bpy)_3(HCOO)_2{\cdot}4H_2O$ complex carboxylate groups act as 'pseudomonodentate' ligand in results the interaction of the formate ions and water molecules in solid-state of $Ni(2\text{-}bpy)_3(HCOO)_2{\cdot}4H_2O$. The $\nu_{s(OCO)}$ for all complexes and bands $\nu_{as(OCO)}$ for Co(II)

Table 2 Principal IR bands for 2-bpy and 2,4'-bpy in free ligand and their complexes, (cm^{-1})

Compound	2-bpy complexes			
	$\nu_{CC,CN,CC_{ir}}^{a}$	$\nu_{CN,CC}^{b}$	Ring 'breathing'	γ_{CH}
2-bpy [28]	1579	1553	991	753 738 sh
$Mn(2\text{-}bpy)_{1.5}(HCOO)_2{\cdot}2H_2O$	1602.7 1598.2	1570.0 1560.0 sh	1015.5	770.5 737.7
$Co(2\text{-}bpy)_2(HCOO)_2{\cdot}3H_2O$	1598.2	1560.0 sh	1019.3	776.3 737.7
$Ni(2\text{-}bpy)_3(HCOO)_2{\cdot}4H_2O$	1598.0 1596.9	1559.3	1020.3	783.8 738.7
$Cu(2\text{-}bpy)_2(HCOO)_2{\cdot}3H_2O$	1595.0	1560.3	1014.5	769.5 731.0

Compound	2,4'-bpy complexes				
	$\nu_{CC,CN,CC_{ir}}^{a}$ 4 sub	$\nu_{CC,CN,CC_{ir}}^{a}$ 2 sub	$\nu_{CN,CC}^{b}$ 4 sub	$\nu_{CN,CC}$ 4 sub	Ring 'breathing'
2,4'-bpy [30]	1595	1586	1575	1405	990 sh
$Mn(2,4'\text{-}bpy)_2(HCOO)_2{\cdot}2H_2O$	1609.5	1585.0	1550.0	1415.7	1010.6
$Co(2,4'\text{-}bpy)_2(HCOO)_2{\cdot}2H_2O$	1611.4	1585.0	1550.0	1414.7	1014.5
$Ni(2,4'\text{-}bpy)_2(HCOO)_2{\cdot}2H_2O$	1613.3	1585.0	1558.0	1416.6	1017.4
$Cu(2,4'\text{-}bpy)_2(HCOO)_2{\cdot}2H_2O$	1616.2	1585.0 sh	1554.5	1417.9	1026.1

ir – inter ring, a – A_1 symmetry, b – B_1 symmetry, γ_{CH} – out-of-plane, sh – shoulder

complex are splitted into doublet. From here is probable that non-completely equivalent bonds between *M*(II) and carboxylate groups of the formate ligands exist [33]. The bands $\pi_{CH}+\rho_{r(OCO)}$ in complexes appear at 1386.7–1376.1 cm^{-1}. In case of complexes $M(2,4'\text{-}bpy)_2(HCOO)_2{\cdot}2H_2O$ (where *M*(II)=Co, Ni) carboxylate groups are bonded as monodentate ligands. The $\nu_{as(OCO)}$ and $\nu_{s(OCO)}$ bands in these complexes are not splitted (Table 3).

The frequency $\nu_{as(OCO)}$ for $Mn(2,4'\text{-}bpy)_2(HCOO)_2{\cdot}2H_2O$ is superimposed by the absorption of 2,4'-bpy; also in $Cu(2,4'\text{-}bpy)_2(HCOO)_2{\cdot}2H_2O$ the band $\nu_{s(OCO)}$ is masked by the absorption $\pi_{CH}+\rho_{r(OCO)}$. Thus, it is dif-

Table 3 Principal IR bands for OCO^- groups in free ligand and obtained complexes

Compound	$\nu_{as(OCO)}$	$\nu_{s(OCO)}$	$\pi_{CH}+\rho_{r(OCO)}$	$\Delta\nu=\nu_{as}-\nu_{s}$
HCOONa [32]	1597	1357	1389	240
Compound	2-bpy complexes			
$Mn(2\text{-}bpy)_{1.5}(HCOO)_2{\cdot}2H_2O$	1612.2	1349.1 1326.0	1384.8 1376.1	263.1 286.2
$Co(2\text{-}bpy)_2(HCOO)_2{\cdot}3H_2O$	1639.1 1631.1	1352.0 1344.0	1379.0	287.1 287.1
$Ni(2\text{-}bpy)_3(HCOO)_2{\cdot}4H_2O$	1631.7	1345.3 1313.4	1380.9	286.4 318.3
$Cu(2\text{-}bpy)_2(HCOO)_2{\cdot}3H_2O$	1631.7	$\left.\begin{matrix}1348.1\\1338.5\end{matrix}\right\}$pd 1319.2	1386.7	283.6 293.2 312.5
Compound	2,4'-bpy complexes			
$Mn(2,4'\text{-}bpy)_2(HCOO)_2{\cdot}2H_2O$	*	1348.1	1370.0	–
$Co(2,4'\text{-}bpy)_2(HCOO)_2{\cdot}2H_2O$	1625.0	1344.3	1362.6	280.7
$Ni(2,4'\text{-}bpy)_2(HCOO)_2{\cdot}2H_2O$	1629.7	1350.1	1364.6	279.6
$Cu(2,4'\text{-}bpy)_2(HCOO)_2{\cdot}2H_2O$	1631.7	**	1369.4	–

*overlaid by 2,4'– absorption; **overlaid by $\pi_{CH}+\rho_{r(OCO)}$; pd – poorly resolved doublet ferent to discuss the nature of metal–formate bonds in these complexes. The IR spectra of the all prepared complexes exhibit broad absorption bands in the range ca. 3500–3400 cm^{-1}, confirming the presence of water molecules in these compounds.

Thermal studies

Results of TG, DTG and DTA analysis are presented in Table 4. Because the complexes are hydrated, as expected, the first mass losses can be assigned to water evaluation in **I–III**, **V–VIII** complexes. The release of water molecules in these complexes is well-defined step which can clearly be observed on the thermal curves. The dehydration occurs in endothermic steps. In the case of complexes **I**, **III** and **VII** elimination of all water molecules in one stage takes place. $Co(2\text{-bpy})_2(HCOO)_2\cdot3H_2O$ loses water molecules in two steps. For compounds **V**, **VI** and **VIII** the lost stage of dehydration is connected with total or partial elimination of bipyridine. The H_2O evaluation (the temperatures of the first peak in DTG curves) decrease in the sequence: Cu (125°C, elimination of 3 mole of H_2O and 0.75 mole 2-bpy)>Ni (120°C)>Mn (95°C)≈Co (95°C) for 2-bpy complexes; Ni(II) (160°C)>Mn (150°C)>Co (125°C)>Cu (105°C) for 2,4'-bpy complexes. The thermal analytical curves of

$$Mn(2\text{-bpy})_{1.5}(HCOO)_2\cdot2H_2O$$
$$Mn(2,4'\text{-bpy})_2(HCOO)_2\cdot2H_2O$$

and

$$Co(2\text{-bpy})_2(HCOO)_2\cdot3H_2O$$
$$Ni(2\text{-bpy})_3(HCOO)_2\cdot4H_2O$$

complexes, as an example are presented in Figs 1 and 2. The thermal decompositions of anhydrous compounds are different. $Mn(2\text{-bpy})_{1.5}(HCOO)_2\cdot2H_2O$ decompose progressively. In temperature ranges: 115–220 and 220–250°C formation of $Mn(2\text{-bpy})(HCOO)_2$ and $Mn(2\text{-bpy})_{0.5}(HCOO)_2$ takes place, respectively. Further mass loss is observed within temperature 250–350°C. It is attributed to the loss of remaining 2-bpy, decomposition of formates and formation of Mn_2O_3. Formation of Mn_3O_4 begins above 900°C. For the anhydrous complexes $Co(2\text{-bpy})_2(HCOO)_2$ and $Ni(2\text{-bpy})_3(HCOO)_2$ the curves show a very rapid mass loss, which is connected with decomposition of organic ligands and the formation of Co_3O_4 (130–420°C) and NiO (150–460°C) via traces of ca. 2% organic fragments. Above 420 and 460°C pure Co_3O_4 and NiO are identified. Figure 3 presents X-ray diffraction patterns of the sinters of complexes **II** and **III** heated up to 420 and 460°C, respectively. The intermediate compound

$$Cu(2\text{-bpy})_{1.25}(HCOO)_2$$

in the temperature range 130–250°C decompose to the CuO+residue organic fragments. In the range 250–700°C mixture of $CuO+Cu_2O$ forms. In the sinter of **IV** heated up 710°C these compounds are observed (Fig. 4). On temperature elevation intermediate compound $Mn(2,4'\text{-bpy})_2(HCOO)_2\cdot1/2H_2O$ forms Mn_3O_4 via $Mn(HCOO)_2$ and Mn_2O_3. Monohydrate complex $Co(2,4'\text{-bpy})_2(HCOO)_2\cdot H_2O$ in the temperature range: 150–265°C decompose to $Co(HCOO)_2$; at 420°C pure Co_3O_4 occurs. Above 800°C CoO is slowly formed. The anhydrous complex $Ni(2,4'\text{-bpy})_2(HCOO)_2$ eliminates 1 mole of 2,4'-bpy

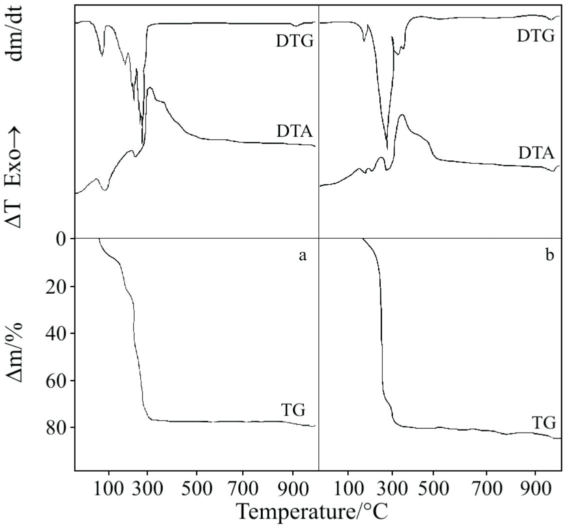

Fig. 1 Thermoanalytical curves of
a – $Mn(2\text{-bpy})_{1.5}(HCOO)_2\cdot2H_2O$ and
b – $Mn(2,4'\text{-bpy})_2(HCOO)_2\cdot2H_2O$; sample mass: 100 mg

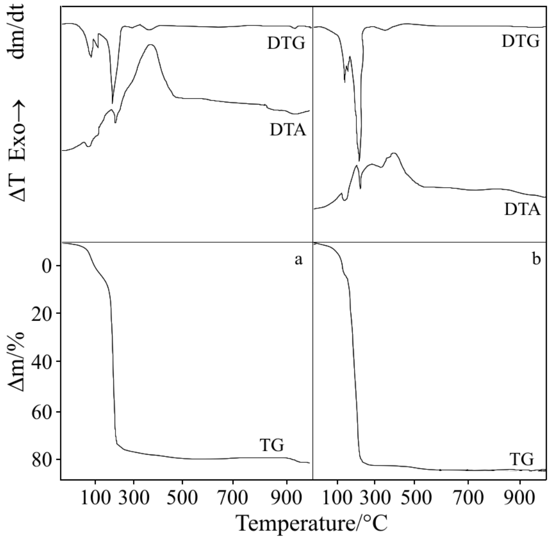

Fig. 2 Thermoanalytical curves of
a – $Co(2\text{-bpy})_2(HCOO)_2\cdot3H_2O$ and
b – $Ni(2\text{-bpy})_3(HCOO)_2\cdot4H_2O$; sample mass: 100 mg

Table 4 Thermal decomposition in air; sample mass 100 mg

No.	Complex	Ranges of decomposition/°C	DTA peak/°C	Mass loss/%		Intermediates and final solid products
				found	calc.	
I	$Mn(2\text{-}bpy)_{1.5}(HCOO)_2\cdot 2H_2O$	60–115	105 endo	8.5	8.68	$Mn(2\text{-}bpy)_{1.5}(HCOO)_2$
		115–220		18.0	18.80	$Mn(2\text{-}bpy)(HCOO)_2$
		220–250	240 endo	18.0	18.80	$Mn(2\text{-}bpy)_{0.5}(HCOO)_2$
		250–350	330 exo	36.5	34.70	Mn_2O_3
		>900		1.0	0.64	Mn_3O_4
II	$Co(2\text{-}bpy)_2(HCOO)_2\cdot 3H_2O$	50–100	95 endo	7.0	6.99	$Co(2\text{-}bpy)_2(HCOO)_2\cdot H_2O$
		100–130	105 endo sh	3.5	3.50	$Co(2\text{-}bpy)_2(HCOO)_2$
		130–420	200, 395 exo	74.0	73.94	pure Co_3O_4**
		>900	910 endo	1.5	1.03	CoO (slowly)
III	$Ni(2\text{-}bpy)_3(HCOO)_2\cdot 4H_2O$	60–150	140 endo	10.5	10.45	$Ni(2\text{-}bpy)_3(HCOO)_2$
		150–460	240 exo	78.0	78.71	pure NiO**
			360 endo, 420 exo			
IV	$Cu(2\text{-}bpy)_2(HCOO)_2\cdot 3H_2O$	60–130	85, 118 endo	33.5	32.92	$Cu(2\text{-}bpy)_{1.25}(HCOO)_2$
		130–250	215 endo	50.5	51.78	CuO**
		250–700	~400 exo br			mixture of $CuO+Cu_2O$
V	$Mn(2,4'\text{-}bpy)_2(HCOO)_2\cdot 2H_2O$	118–160	160 endo	5.0	5.48	$Mn(2,4'\text{-}bpy)_2(HCOO)_2\cdot 1/2H_2O$
		160–295	190, 285 endo	65.0	65.14	$Mn(HCOO)_2$
		295–500	355 exo, 440 exo br	14.0	13.79	pure Mn_2O_3**
		>900	960 endo	~0.5	0.14	Mn_3O_4
VI	$Co(2,4'\text{-}bpy)_2(HCOO)_2\cdot 2H_2O$	100–150	140 endo	4.0	3.62	$Co(2,4'\text{-}bpy)_2(HCOO)_2\cdot H_2O$
		150–265	200 exo, 250 endo	66.0	66.42	$Co(HCOO)_2$*
		265–420	320, 420 exo	13.5	13.82	Co_3O_4
		>800	920 endo	~1.0	1.08	CoO (slowly)
VII	$Ni(2,4'\text{-}bpy)_2(HCOO)_2\cdot 2H_2O$	140–200	170 endo	6.5	7.24	$Ni(2,4'\text{-}bpy)_2(HCOO)_2$
		200–250	230 exo, 250 endo	32.0	31.42	$Ni(2,4'\text{-}bpy)(HCOO)_2$*
		250–450	290 endo, 440 exo	46.5	46.31	pure NiO***
VIII	$Cu(2,4'\text{-}bpy)_2(HCOO)_2\cdot 2H_2O$	85–115	115 endo	3.6	3.59	$Cu(2,4'\text{-}bpy)_2(HCOO)_2\cdot H_2O$
		115–160	138 endo	19.0	19.15	$Cu(2,4'\text{-}bpy)_{1.5}(HCOO)_2$
		160–400	215 endo sh, 280 endo	62.0	61.41	pure CuO**
			320 exo, 400 exo br			
		>750				mixture of $CuO+Cu_2O$

*by projecting minimum of DTG curve on TG curve; br – broad; sh – shoulder, **via mixture suitable metal oxides+organic residue, ***via mixture NiO+ca. 1.5% Ni

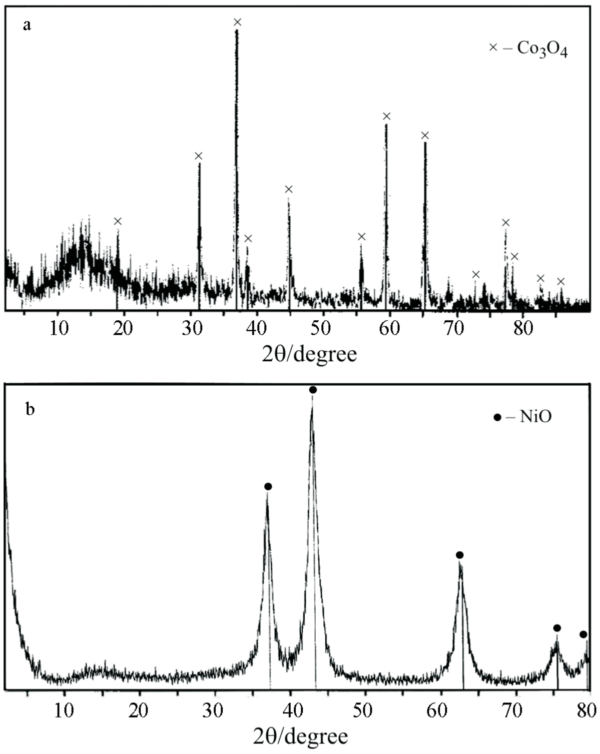

Fig. 3 X-ray diffraction patterns of decomposition product of a – $Co(2\text{-bpy})_2(HCOO)_2{\cdot}3H_2O$ heated up to 420°C and b – $Ni(2\text{-bpy})_3(HCOO)_2{\cdot}4H_2O$ heated up to 460°C

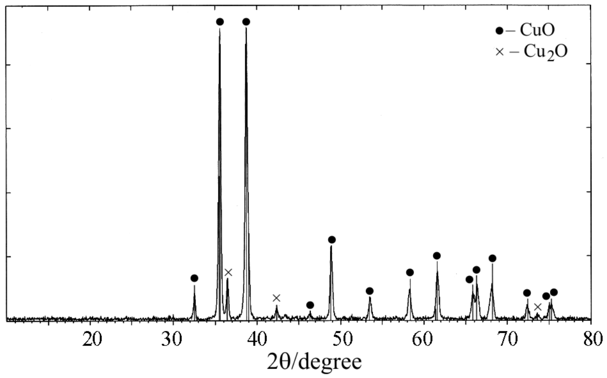

Fig. 4 X-ray diffraction patterns of decomposition product of $Cu(2\text{-bpy})_2(HCOO)_2{\cdot}3H_2O$ heated up to 710°C

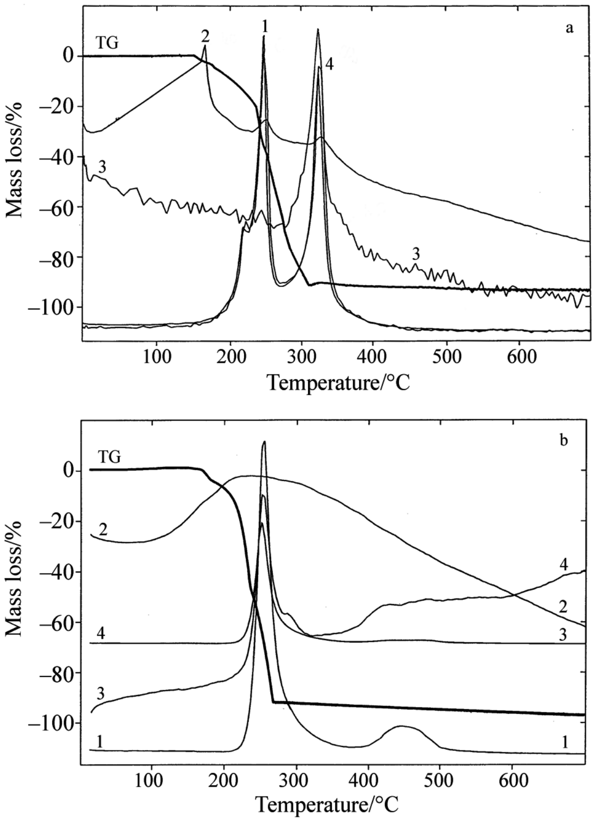

Fig. 5 TG curve and ion current detected by the MS for $Ni(2,4'\text{-bpy})_2(HCOO)_2{\cdot}2H_2O$; a – in air, mass sample 5.35 mg, *m*/*z*: 1–12; 2–18; 3–30; 4–44 with sensitivities of: E-12, E-09, E-11, E-10 A, respectively; b – in argon, mass sample 9.85 mg, *m*/*z*: 1–12; 2–18; 3–28; 4–44 with sensitivities of: E-11, E-09, E-10, E-09 A, respectively

and decompose to $Ni(2,4'\text{-bpy})(HCOO)_2$. In the range 250–450°C was forming pure NiO (via mixture NiO+ca. 1.5% Ni). Similar mixture was obtained during pyrolysis of $Ni(C_{17}H_{10}O_4){\cdot}H_2O$ [36]. For intermediate compound $Cu(2,4'\text{-bpy})_{1.5}(HCOO)_2$ in the interval of temperature 160–400°C the deamination overlaps the process of full decomposition of formates. The products of this stage of pyrolysis are CuO with ca. 1.5% organic residue. Futher heating causes oxidation of the organic residue and result is pure CuO, which converts to mixture $CuO+Cu_2O$. The DTA curves are mixtures of several endo and exo peaks. Very strong and broad exothermic effects are as usually [37] caused by the oxidation of organic fragments observed with maxima at ca.: 330°C (**I**), 395°C (**II**), 420°C (**III**), 400°C (**IV**), 355 and 440°C (**V**), 320 and 420°C (**VI**), 440°C (**VII**), 320 and 400°C (**VIII**).

Mass spectrometric thermal analysis

In this paper a coupled TG-MS system was used to study of gaseous species evolved during dynamic thermal decomposition (or fragmentation) processes only of $Ni(2,4'\text{-bpy})_2(HCOO)_2{\cdot}2H_2O$ in air and argon atmosphere. Ion current intensities were noted with sensitivity between E-9–E-13. Figure 5 (as an example) presents ion currents and TG curves for same *m*/*z* detected by the mass spectrometer *v*/*s* temperature for this complex in air and argon atmosphere. Complex $Ni(2,4'\text{-bpy})_2(HCOO)_2{\cdot}2H_2O$ in inert atmosphere presents the higher thermostability (the mass losses starting at ca. 180°C) than in air. Generally many signals of ion currents are observed in the ranges: 140–270 and 310–360°C (for air) and between 180–300 and ca. 450°C (for argon). In air atmosphere first MS peak for coordination (or crystalline) water occurred at 165°C; maximum rates of H_2O forming during the decomposition of organic ligands at 254 and 326°C are observed. One broad maximum of ion current (218–295°C) corresponding elimination of H_2O appeared in the case of argon atmosphere. The ion signal intensities of CO_2 (m/z 44) as well as $^{13}C^{16}O_2$ and $^{12}C^{18}O^{16}O$ (m/z 45 and 46, respectively) have centers at: 218, 244 and 325°C (in air) and at 251°C (in argon). A low intensity of ion currents were detected for NO^+ (or CH_2O^+) at 324 (in air) and 280°C (in argon). Minima of ion current correspond to O_2 from air atmosphere at 248 and 333°C are observed. In argon maxima rates with m/z 28 (correspond to CO) at 253 and 285°C exist. Also peaks for fragments with m/z 12, 15, 17 were appeared.

Conclusions

The new mixed ligand complexes with empirical formulae:

$$Mn(2\text{-bpy})_{1.5}(HCOO)_2\cdot 2H_2O$$
$$M(2\text{-bpy})_2(HCOO)_2\cdot 3H_2O$$

where M(II)=Co, Cu

$$Ni(2\text{-bpy})_3(HCOO)_2\cdot 4H_2O$$
$$M(2,4'\text{-bpy})_2(HCOO)_2\cdot 2H_2O$$

where M(II)=Mn, Co, Ni and Cu – were prepared as small-crystalline compounds. The

$$Mn(2,4'\text{-bpy})_2(HCOO)_2\cdot 2H_2O$$
$$Mn(4\text{-bpy})_2(HCOO)_2\cdot 2H_2O$$

[23] are new complexes with ligand isomerism. The ligand field spectra of Co(II), Ni(II) and Cu(II) are characteristic of distorted octahedral environment around metal ions. IR data show, that obtained complexes of Co(II), Ni(II) and Cu(II) with 2-bpy and formates are *bis* 2,2'-bipyridine chelates. The 2,4'-bpy coordinates with title metals(II) via least hindered (4')N atom as a monodentate ligand. The carboxylate groups act as monodentate in all obtained complexes. In the case of major metals(II) with 4,4'-bipyridine and formates the carboxylate ions are bonded as bidentate chelating ligands [23]. The mode of metal-carboxylate coordination probably depends on bipyridine structure [29, 31]. During heating in air the hydrated complexes lose water molecules in one or two steps. Dehydration begins at 50–60°C for complexes with 2-bpy and 85–140°C in case of 2,4'-bpy compounds. Next, generally the compounds lose 2-bpy or 2,4'-bpy in several stages and converted to oxides. The intermediate products formed during the thermal decomposition process:

$$Co(2\text{-bpy})_2(HCOO)_2\cdot H_2O \text{ and } Cu(2\text{-bpy})_{1.5}(HCOO)_2$$

are ligand isomeric with 2,4'-bpy complexes; $Ni(2,4'\text{-bpy})(HCOO)_2$ is isomeric with 4-bpy compound [23]. Generally, MS data detected during pyrolysis of $Ni(2,4'\text{-bpy})_2(HCOO)_2\cdot 2H_2O$ indicate, that major of ion signals are similar in air and argon, only in inert atmosphere profil of CO^+ with m/z 28 takes place. The principal ion intensities correspond to: C^+, OH^+, H_2O^+, NO^+, CO_2^+ as well as $^{13}C^{16}O_2^+$ and $^{12}C^{16}O^{18}O_2^+$ (m/z 12, 17, 18, 30, 44 as well as 45 and 46, respectively).

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