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SYNTHESIS, THERMAL AND OTHER STUDIES OF 2,4'-BIPYRIDINE–DICHLOROACETATO COMPLEXES OF Mn(II), Co(II), Ni(II) AND Cu(II)

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Abstract

Four new mixed ligand complexes were prepared by the reaction of title metal dichloroacetates and 2,4'-bipyridine. The general formulae of synthesized compounds are $M(2,4'\text{-bpy})_2(CCl_2HCOO)_2{\cdot}nH_2O$ (where *M*(II)=Mn, Co, Ni, Cu; *2,4'-bpy*=2,4'-bipyridine, *n*=2 or 4). The complexes have been isolated from aqueous media and characterized by chemical analysis, molar conductance (in MeOH, DMSO and DMF), magnetic, IR and VIS spectral studies. The nature of metal(II)–ligand coordination is discussed. The thermal behaviour of obtained complexes was studied by thermal analysis and TG-MS techniques in air. IR, X-ray powder diffraction and thermoanalytical data were used for the determination of solid intermediate products of the thermal decomposition. The principal volatile products of thermal decomposition of complexes were proved by mass spectroscopy: H_2O^+, CO_2^+, HCl^+, Cl_2^+, NO^+ and other.

Keywords: 2,4'-bipyridine-dichloroacetato complexes, IR and VIS spectra, TG-MS data, thermal decomposition, transition metal(II) complexes

Introduction

Synthesis of metal complexes with carboxylates or mixed ligands compounds containing N-donors (as an example: bipyridines and their derivatives) is extensively studied due to not only their complicated structures [1–3] but also as their application. They exhibit biological activity [4, 5] and catalytic properties [6]. Also their application as new materials with potential functions as microporous solids for molecular adsorption, ion exchange, as materials for gas storage [7, 8] and in nonlinear optics [9] is interesting.

The reports on mixed 2,4'-bipyridine-carboxylate complexes with transition metals(II) are very scarce. In our previous papers we described the compounds of the type: $M(2,4'\text{-bpy})_2(ox){\cdot}2H_2O$ (*M*(II)=Mn, Co, Ni, Cu, Zn), $Cd(2,4'\text{-bpy})(ox){\cdot}2H_2O$ [10, 11] and $M(2,4'\text{-bpy})_2(CH_3COO)_2{\cdot}2H_2O$ (*M*(II)=Co, Ni, Cu, Zn, Cd) [12, 13]. Synthesis, characterization, crystal and molecular structures are described for diaquadi(acetato-

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O)-bis(2,4'-bipyridine) manganese(II) [2] and mono- and diaquadi(acetato-O)-bis(2,4'-bipyridine) copper(II) [1]. In these compounds 2,4'-bipyridine coordinated via N(4') atom as a monodentate ligand.

In recent years, several studies have been made on the synthesis and characterization of the mixed ligand complexes of transition metal ions with 2,2'- or 4,4'-bipyridine and mono- or trichloroacetates [13–19]. The complexes of formulae: Cd(2,4'-bpy)$_2$(R'COO)$_2$·2H$_2$O (*R'*=CClH$_2$–, CBrH$_2$–) have been also isolated [12]. We earlier determined the conditions of preparation of Mn(II), Co(II), Ni(II) and Cu(II) complexes with 4,4'-bipyridine and dichloroacetates and studied their thermal decomposition in air and other properties [17]. The compounds of Mn(II), Co(II), Ni(II) and Cu(II) with *2,4'-bpy* and dichloroacetates are unknown. It was thus interest to examine the behaviours of *2,4'-bpy* and dichloroacetate groups in mixed ligand metal(II) complexes and the properties of these compounds. This paper reports the results of study of this problem.

Here we describe the synthesis, IR and VIS spectra, magnetic and molar conductivity investigations and thermal decomposition in air of mixed 2,4'-bipyridine-dichloroacetato complexes of title metals(II).

Experimental

Physical measurements and materials

The thermal decomposition was studied by means of derivatograph Q-1500. The samples of 100 mg were heated in ceramic crucible in static air atmosphere. α-Al$_2$O$_3$ has used as standard material. TG-MS system consisting of derivatograph TG/DTA SETSYS-16/18, coupled to a mass spectrometer (QMS-422), model ThermoStar Balzers Instruments; platinium crucible 100 μL; dynamic measurements were carried out in air at flow rate of 1 L h^{-1}; sample of mass in the range ca. 5–8 mg; 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 heating rate 10°C min^{-1}. The other apparatus, experimental conditions and materials were described in previous papers [12, 13, 17]. Preparation and analyses of complexes of Mn(II), Co(II), Ni(II) and Cu(II) with *2,4'-bpy* and dichloroacetates were performed according to a procedure described in [17], only *2,4'-bpy* dissolved in water, containing few drops of 96 *v/v*% EtOH. The contents of C, H and N were determined by elemental analysis with V$_2$O$_5$ as oxidizing agent; *M*(II) were complexometrically determined.

Results and discussion

The empirical formulae of the obtained complexes, analytical results and other characteristic data are collected in Table 1. All complexes were small crystalline solids and are not isostructural. The obtained compounds are soluble in water (Table 1). The solubilities of the complexes increase in the order Mn(II)<Cu(II)<Ni(II)<Co(II). The magnetic moments (in room temperature) of the Co(II), Ni(II) and Cu(II) complexes show that these compounds are paramagnetic. The observed magnetic mo-

ment values are in the range expected for the orbital singlet states for pseudo-octahedral geometry of around these metal(II) ions [20]. The molar conductivities (Λ_M) for obtained complexes in DMF, DMSO (except Co(II) in DMSO) and in MeOH (except Mn(II) and Co(II) in MeOH) show behaviour intermediate between those of non-electrolytes and 1:1 electrolytes. Conductivity data (Table 1) of Mn(II) and Co(II) complexes in methanol and Co(II) compound in DMSO fall within the general acceptable range for 1:1 electrolytes [21]. Λ_M increase in the sequence: DMF≈DMSO<MeOH. Higher than anticipated Λ_M values (vide IR data) are usually due to the displacement of dichloroacetato ligands by solvent molecules. Similar behaviours were observed for metal(II) complexes with other bipyridine isomers and halogenoacetates [14, 15, 17].

Electronic and IR spectra

VIS spectra were obtained in Nujol mulls within the 27 000–12 000 cm^{-1}. The cobalt(II) complex exhibit broad band with maximum at 20 400 cm^{-1}, which corresponds to the transition $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$. Two bands have been observed at 26 300 and 16 000 cm^{-1} for Ni(II) complex. The bands are assigned to $^3A_{2g}\rightarrow{}^3T_{1g}(P)$ and $^3A_{2g}\rightarrow{}^3T_{1g}(F)$ transitions. These bands are in accordance with a distorted octahedral geometry around the metal ions [22]. The values $\overline{\nu}_{calcd}$ calculated by the rule of average environment (RAE) for chromophore MN_2O_4 are 20 300 cm^{-1} for $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ and 15 600 cm^{-1} for $^3A_{2g}\rightarrow{}^3T_{1g}(F)$ transitions, respectively in the cobalt(II) and nickel(II) complexes. The comparison of the $\overline{\nu}_{calcd}$ with the experimental $\overline{\nu}$ and according to IR data, indicates that the following chromophores are present in solid-state: $CoN_2O_2'O_2''$ and $NiN_2O_2'O_2''$ (where O'=atom from $(OCO)^-$ group, O''=atom from H_2O). The electronic spectrum of Cu(II) complex shows a broad band in the region ca. 15 600 cm^{-1}. This band can be assigned to three transitions lying within one broad envelope ($^2B_{1g}\rightarrow{}^2E_g$, $^2B_{1g}\rightarrow{}^2B_{2g}$, $^2B_{1g}\rightarrow{}^2A_{1g}$). The position of this band indicates probably a rhombic-octahedral environment around Cu(II) [23].

The IR spectra of all complexes exhibit a strong and broad bands in the water stretching region (ca. 3050–3600 cm^{-1}). The water bending vibration is observed only for Mn(II) (1630 cm^{-1}) and for Co(II) (at 1635 cm^{-1}) complexes. Selected IR bands of *2,4'-bpy* and of dichloroacetate group, as well as assignments of their frequencies are presented in Table 2.

The IR spectrum of *2,4'-bpy* is the sum of characteristic patterns of 2- and 4-substituted pyridines [24]. Upon coordination with title metals(II), the IR spectrum of free *2,4'-bpy* undergoes a change only in the ring vibration modes of 4-substituted pyridine (4-sub). A bathochromic shift of the bands attributed to a stretching ring vibration and ring 'breathing' frequency for 4-sub pyridine takes place. It is thus possible to assume that *2,4'-bpy* coordinates via the least hindered (4')N atom [25]. This conclusion is in good agreement with those reported for other metal(II) complexes with *2,4'-bpy* [2, 10–13, 26].

The principal IR bands $\nu_{as}(OCO)^-$ and $\nu_s(OCO)^-$ of $CCl_2HCOONa$ and obtained complexes are also listed in Table 2. The spectra of region characteristic of

Table 1 Analytical data, solubility S (mol dm^{-3}) in water at 21°C, molar conductivity Λ_M (Ω^{-1} cm^2 mol^{-1}) in MeOH, DMF and DMSO c=1 10^{-3} mol dm^{-3} and effective magnetic moments μ_{eff} (MB) at 25°C

Complex	Analysis found (calculated)/%				S·10^3	Λ_M			μ_{eff}
	M	C	N	H		MeOH	DMF	DMSO	
Mn(2,4'-bpy)$_2$(CCl$_2$HCOO)$_2$·2H$_2$O	8.12	43.98	8.76	3.33	0.46	82.1	49.5	47.3	–
(white)	(8.33)	(43.73)	(8.50)	(3.36)					
Co(2,4'-bpy)$_2$(CCl$_2$HCOO)$_2$·4H$_2$O	8.44	41.12	8.12	3.77	17.6	74.7	46.5	52.5	4.78
(pink)	(8.43)	(41.23)	(8.10)	(3.75)					
Ni(2,4'-bpy)$_2$(CCl$_2$HCOO)$_2$·2H$_2$O	8.74	43.55	8.98	3.41	8.18	66.5	42.5	39.5	2.92
(green)	(8.86)	(43.48)	(8.45)	(3.34)					
Cu(2,4'-bpy)$_2$(CCl$_2$HCOO)$_2$·2H$_2$O	9.86	43.01	8.87	3.34	4.40	50.5	27.3	30.8	1.68
(blue)	(9.78)	(34.17)	(8.62)	(3.32)					

Table 2 Principal IR bands (cm^{-1}) for *2,4'-bpy* and $(OCO)^-$ group in obtained complexes

Assignment of bends [24, 31]	*2,4'-bpy* [24]	$NaCCl_2HCOO$ [33]	Complex			
			Mn(II)	Co(II)	Ni(II)	Cu(II)
Coordinated 2,4'-bpy modes (4-sub)						
C–C, C–N, $C–C_{i.r}$ str.	1595s	–	1610.5vs	1614.3vs	1614.3vs	1614.3vs
C–C, C–N, $C–C_{i.r}$ str. 2-sub.	1585s	–	1587.3	1593.0	1591.3	1586.1
H bend+ring str.	1405m	–	1415.7s	1417.6s	1417.6s	1417.6s
Ring 'breathing'	990sh	–	1012.6vs	999.1s	999.1w	989.4s 1010.0vw
Carboxylate group modes						
$\nu_{as}(OCO)^-$	–	1640	1639.4vsd 1630.0sd	1683.7s 1647.1vs	1681.8s 1645.2vw	1637.5vs
$\nu_s(OCO)^-$	–	1399	1404.1s 1386.7s 1365.5s	1375.2vs	1383.5 1371.3	1390.6vs 1367.4vs
$\Delta\nu=\nu_{as}(OCO)^- - \nu_s(OCO)^-$	–	241	235.3 252.7 273.9	308.5 271.9	306.6 270.0 263.0	246.9 270.1
ν M–O)+$\delta(OCO)^-$	–		465.8w	460.0w	468.7w	457.1w

i.r – inter ring; vs, s, m, w, sh – very strong, strong, medium, weak, shoulder; d – doublet

$\nu_{as}(OCO)^-$ and $\nu_s(OCO)^-$ vibrations are analogous for cobalt(II) and nickel(II) complexes. The magnitudes of the separation $\Delta\nu$ between the $\nu_{as}(OCO)^-$ and $\nu_s(OCO)^-$ in these compounds are higher than in sodium salt. On the basis of the Nakamoto criterion [27] and other papers [5, 12–15, 28–30], the carboxylate groups in Co(II) and Ni(II) are monodentate. Probably non-completely equivalent bonds between Co(II) and Ni(II) and dichloroacetate ligands are formed ($\nu_{as}(OCO)^-$ is splitted) [29]. The $\nu_s(OCO)^-$ of the Mn(II) and Cu(II) complexes are clearly splitted into three (Mn) and two (Cu); bands $\nu_{as}(OCO)^-$ of Mn(II) compound is splitted into poorly resolved doublet. In case of Mn(II) complex the $\Delta\nu$ values are 253 and 274 cm^{-1} and are higher than for sodium salt. The carboxylate groups here appear as unidentate (non-equivalent) groups. In addition, $\Delta\nu$ for Mn(II) complex has also value (235 cm^{-1}) lower than for the sodium salt. This fact, as well as splitting $\nu_s(OCO)^-$ into three bands suggests, that in Mn(II) complex the dichloroacetate act also as bidentate asymmetrical bridging group; probably strong intermolecular hydrogen bonds exist [1]. The $\Delta\nu$ for Cu(II) have values 247 and 270 cm^{-1}. The separation of these modes shows the presence of coordinated monodentate dichloroacetate group. The bands $\nu_s(OCO)^-$ is splitted into two, and $\Delta\nu$ are higher than for sodium salt, probably that non-equivalent bonds between Cu(II) and carboxylate groups exists [28–30].

Thermal decomposition

The obtained complexes are stable at room temperature. The solid intermediate products of decomposition were determined from TG curve and were confirmed by recording the IR spectra of sinters. IR spectra for sinters (prepared during the heating of sample of complex up to definite temperature from TG) occur the bands of *2,4'-bpy* and carboxylate group or only bands of *2,4'-bpy*. In the sinters presence of anions Cl^- was investigated. The final solid products of decomposition were calculated from TG curve and verified by X-ray diffraction patterns registration. The thermal decomposition data of the obtained complexes are collected in Table 3.

The thermoanalytical curves of Mn(II) and Ni(II) complexes are presented, as an example in Fig. 1. All the complexes decompose progressively. Hydrated compounds are stable up to the temperature 60–70°C. During heating the Ni(II) and Cu(II) complexes lose water molecules in one step. $Co(2,4'\text{-bpy})_2(CCl_2HCOO)_2\cdot 4H_2O$ dehydrates in two steps. First it eliminates 3 mol of water (60–120°C) and at 120–170°C all water is lost. $Mn(2,4'\text{-bpy})_2(CCl_2HCOO)_2\cdot 2H_2O$ – at first 1 mol of water (60–120°C) is eliminated, while by 170–238°C it loses all water producing $Mn(2,4'\text{-bpy})_2(CCl_2HCOO)Cl$. The dehydration processes are accompanied by small endothermic effects. The decomposition of the anhydrous compounds to corresponding oxides is the multi-stage process. The decomposition of dichloroacetates and subsequent detachment of *2,4'-bpy* was observed. At first stage partial decomposition of dichloro- acetates takes place to give intermediate products: $Mn(2,4'\text{-bpy})_2\text{-}(CCl_2HCOO)Cl$ (170–238°C), $Co(2,4'\text{-bpy})_2(CCl_2HCOO)Cl$ (170–220°C), $Cu(2,4'\text{-bpy})_2\text{-} (CCl_2HCOO)_{0.5}Cl_{1.5}$ (170–200°C). The IR spectra of all the sinters (prepared during heating of complexes up to temperature 238° (Mn), 220° (Co) and 200°C (Cu)) indicated the presence of bands characteristic of *2,4'-bpy* and carboxylate

Table 3 Thermal decomposition data in air; sample mass 100 mg

Starting material	Ranges of decomposition/°C	DTA peaks/°C	Mass loss/%		Intermediates and residue solid products
			found	calcd	
$Mn(2,4'\text{-}bpy)_2(RCOO)_2\cdot 2H_2O$	60–120	95 endo	2.3	2.7	$Mn(2,4'\text{-}bpy)_2(RCOO)_2\cdot H_2O$
	170–238	185 endo	17.0	16.8	$Mn(2,4'\text{-}bpy)_2(RCOO)Cl$
		200 exo			
	238–360	325 endo	38.0	37.7	$Mn(2,4'\text{-}bpy)Cl_2$
	360–800	562 exo	31.0	31.8	Mn_3O_4
		618 endo			
		660 exo			
$Co(2,4'\text{-}bpy)_2(RCOO)_2\cdot 4H_2O$	60–120	95 endo	8.0	7.7	$Co(2,4'\text{-}bpy)_2(RCOO)_2\cdot H_2O$
	120–170	175 sh endo	2.8	2.6	$Co(2,4'\text{-}bpy)_2(RCOO)_2$
	170–220	200 endo	13.8	13.2	$Co(2,4'\text{-}bpy)_2(RCOO)Cl$
	220–380	242 exo	33.0	35.6	$Co(2,4'\text{-}bpy)Cl_2$
		320 endo			
	380–780	380 exo	30.5	29.4	Co_3O_4
		700 exo			
	930	930 exo	~1.0	0.6	CoO

Table 3 Continued

Starting material	Ranges of decomposition/°C	DTA peaks/°C	Mass loss/%		Intermediates and residue solid products
			found	calcd	
$Ni(2,4'\text{-bpy})_2(RCOO)_2\cdot 2H_2O$	60–140	98 endo	6.0	5.4	$Ni(2,4'\text{-bpy})_2(RCOO)_2$
	140–260	200 exo	28.0	27.9	$Ni(2,4'\text{-bpy})_2Cl_2$
		250 endo			
	260–340	320 endo	23.0	23.6	$Ni(2,4'\text{-bpy})Cl_2$
	340–480	470 exo	23.0	23.6	$NiCl_2$
	480–660	700 exo	9.0	8.3	NiO
$Cu(2,4'\text{-bpy})_2(RCOO)_2\cdot 2H_2O$	70–125	70 endo	3.0	2.8	$Cu(2,4'\text{-bpy})_2(RCOO)_2$
	170–200	190 exo	22.5	22.9	$Cu(2,4'\text{-bpy})_2(RCOO)_{0.5}Cl_{1.5}$
	200–820[b]	230 exo	71.0	62.1	CuO (~3.5%)
		460 endo			
		720–800 exo br			

[a] – $R=CCl_2H$–; [b] – total decomposition of organic ligands and probably gradual volatilization of copper compounds take place; br – broad

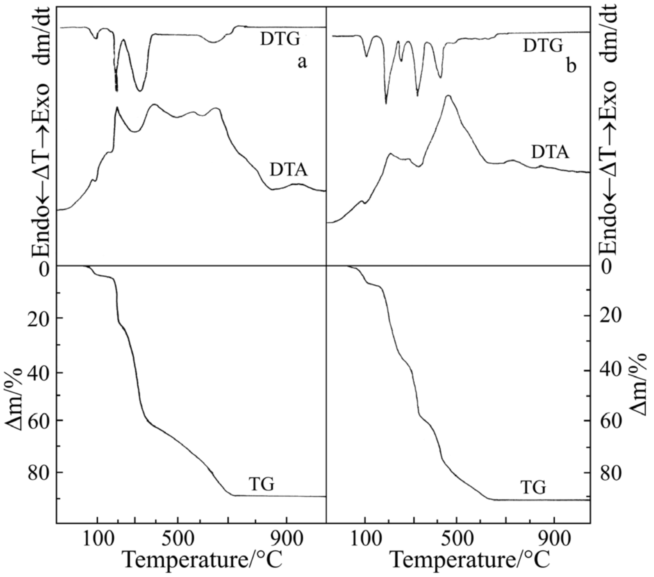

Fig. 1 TG/DTG and DTA curves of a – $Mn(2,4'\text{-}bpy)_2(CCl_2HCOO)_2{\cdot}2H_2O$; b – $Ni(2,4'\text{-}bpy)_2(CCl_2HCOO)_2{\cdot}2H_2O$; mass sample 100 mg

groups. Also in these sinters presence of chlorine ions were identicated. Above these temperatures remaining molecules of dichloroacetate decompose and release of *2,4'-bpy* begins. During these processes, only the intermediate compounds $M(2,4'\text{-}bpy)Cl_2$ (*M*(II)=Mn, Co) were detected from thermal curves (in sinters obtained at 360°C for Mn(II) and 380°C for Co(II)), chlorine ions and absorption bands only for 2,4'-bpy were evident. The $Mn(2,4'\text{-}bpy)Cl_2$ transformed exothermically (DTA peaks at 562 and 660°C) to Mn_3O_4, probably via Mn_2O_3. Above 800°C, only diffraction lines characteristic of Mn_3O_4 were detected. Between 380–780°C, $Co(2,4'\text{-}bpy)Cl_2$ was transformed to pure Co_3O_4. The X-ray diffraction pattern of $Co(2,4'\text{-}bpy)_2(CCl_2HCOO)_2{\cdot}4H_2O$ heated up to 780°C is similar to that of the original Co_3O_4. Above 930°C Co_3O_4 decompose to CoO very slowly. DTA curve exhibited several exo- and endoeffects. Process of decomposition of the intermediate compound $Cu(2,4'\text{-}bpy)_2(CCl_2HCOO)_{0.5}Cl_{1.5}$ is very complicated. TG curve shows bending at ca. 340°C. However, in the sinters of $Cu(2,4'\text{-}bpy)_2\text{-}(CCl_2HCOO)_2{\cdot}2H_2O$ heated up to 340°C indicate only very weak IR bands for *2,4'-bpy*. On increase of the temperature molecules of organic ligands decomposed and volatile compounds of copper are formed, only ca. 3.5% CuO is as the final product (theor. 11.9%). (The volatile products also occur during thermal decomposition of $Cu(CCl_2HCOO)_2$ [32]). The DTA curve presents several exoeffects. A strong broad exothermic effect is observed in the temperature range ca. 720–800°C with center at about 760°C. The endothermic effects associated with volatilization of volatile compounds of copper and other decomposition processes are masked by these exoeffect. Clearly endo peak is demonstrated on the DTA curve only at 460°C.

The anhydrous complex $Ni(2,4'\text{-}bpy)_2(CCl_2HCOO)_2$ decomposes in different way. During heating it was transformed to NiO, with intermediate formation ($Ni(2,4'\text{-}bpy)_2Cl_2$

(140–260°C), Ni(2,4'-bpy)Cl_2 (260–340°C) and $NiCl_2$ (340–480°C). The IR bands of *2,4'-bpy* are observed only in products obtained during heating of Ni(2,4'-bpy)$_2$(CCl_2HCOO)$_2$·2H_2O up to 260 and 340°C; the characteristic modes for carboxylate groups were not noted. A horizontal mass level in the TG curve begins at 660°C, corresponding to pure NiO (verified by X-ray diffraction pattern). DTA curve exhibits several exo- and endoeffects.

Mass spectrometric thermal analysis

A coupled TG-MS system was used to analyse of volatile species which are forming during the dynamic thermal decomposition of M(2,4'-bpy)$_2$(CCl_2HCOO)$_2$·$n$$H_2O$ in air atmosphere. MS data for all obtained complexes detected several signal intensities. The registered mass spectra of lines based on: ^{1}H, ^{12}C, ^{14}N, ^{16}O and ^{35}Cl were

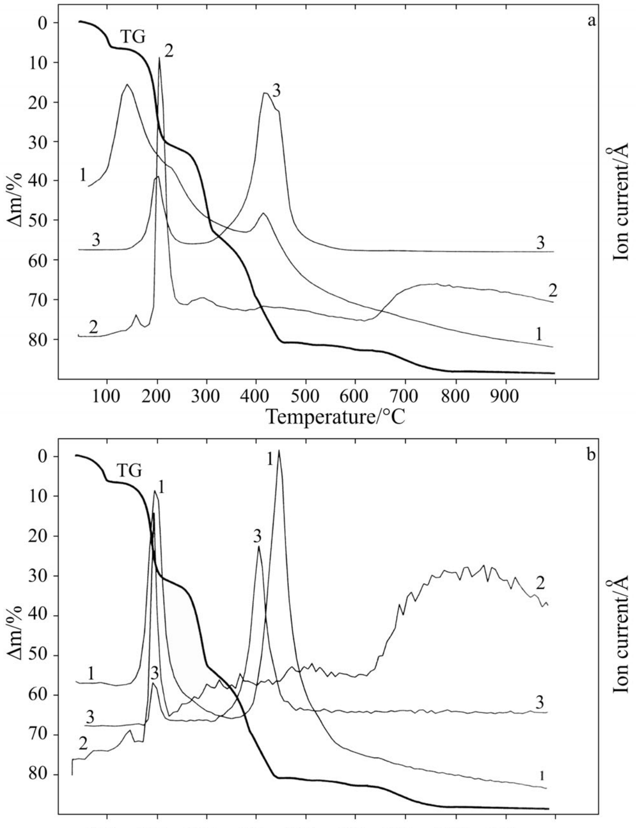

Fig. 2 TG curve and ion current detected by the MS in air for Ni(2,4'-bpy)$_2$(CCl_2HCOO)$_2$·2H_2O mass sample 8.02 mg: a – m/z: 1–18; 2–36; 3–44 with sensitivities of: E-09, E-12, E-09 A, respectively; b – m/z: 1–30; 2–70; 3–76 with sensitivities of: E-10, E-12, E-13 A, respectively

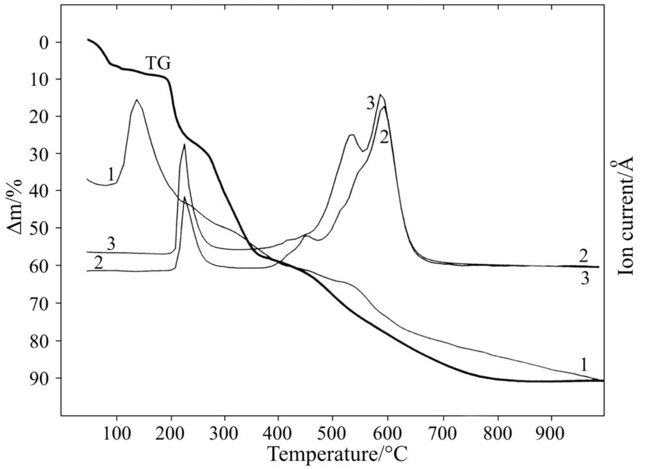

Fig. 3 TG curve and ion current detected by the MS in air for $Co(2,4'\text{-bpy})_2(CCl_2HCOO)_2\cdot 4H_2O$ mass sample 5.60 mg, *m*/*z*: 1–18; 2 – 30; 3 – 44 with sensitivities of: E-09, E-10, E-09 A, respectively

only examined. Generally, MS data are very similar. Many MS signals are observed by ca. 160, 250, 430°C for Mn(II), 220, 350°C for Co(II), 150–200, 390°C for Ni(II) and ca. 190, 270°C in case of Cu(II) complex. The corresponding MS peaks for coordination (or crystalline) water appeared at 117° (Mn), 120° (Co), 139° (Ni) and 125°C (Cu). These MS peaks coincide with the mass decrease appeared on TG. When the temperature of the sample raised, maximum rates of H_2O forming during decomposition of organic ligands at 321–367° for (Mn), 538 in (Co), 226, 411° for (Ni) and 290° (Cu) are observed. The ion intensities of CO_2^+ have centers at 194, 381, 459° (Mn), 227, 538, 588° (Co), 197, 416° (Ni) and 192, 271, 428, 529°C in case of Cu(II) complex. The first maxima of CO_2^+ coincide with begin of decomposition of dichloroacetato ligands; further peaks with the total decomposition of ligands and the burning of organic residues. MS measurement presents also volatile species containing halogen Cl_2^+, HCl^+, with centres in temperature range: 192–227°C (and additionally at 307°C for Mn(II) complex). Profiles for *m*/*z*=30 (NO^+) and *m*/*z*=76 ($N_2O_3^+$) were clearly shown by MS, during heating of all complexes at range ca. 210°, 440–473° (additionally 381, 502° (Mn), 594° (Co) and 530°C (Cu)). MS data presented also several ion signals from fragmentation which were not analysed. TG coupled with MS data for some ion current are shown in Figs 2 and 3.

Conclusions

The composition and several properties of Mn(II), Co(II), Ni(II) and Cu(II) complexes with dichloroacetates and isomers of bipyridine depend on the position of the nitrogen atoms in bipyridine. In case of *2,4'-bpy* compounds, molar ratio of metal(II) to N-donors is 1:2, whereas with *4-bpy* is 1:3 (only complex of Ni(II) with formula

$Ni(4\text{-}bpy)_2(CCl_2HCOO)_2$ was obtained) [17]. Many complexes of these types are hydrated and stable in air. The *2,4'*- and *4-bpy* are bonded to the title metal(II) ions. Due to spherical position of nitrogen atoms *2,4'-bpy* coordinated with metal(II) via the least hindered (4')N atom [1], when *4-bpy* is mainly bonded as bridging ligand [3]. Carboxylate groups [1] in mixed complexes with *2,4'-bpy* (Mn(II), Co(II), Ni(II), Cu(II)) and *4-bpy* (Ni(II), Cu(II)) are bonded as monodentate; in other complexes in different way (monodentate and bidentate bridging) [17].

Thermal decomposition of our new synthetized hydrated compounds begins with the release of a water above 60–70°C. After dehydration pyrolysis of the dichloroacetates takes place. The intermediate products of the types $M(2,4'\text{-}bpy)_2(CCl_2HCOO)_{2-n}Cl_n$ (where n=0, 1 or 1.5), $M(2,4'\text{-}bpy)Cl_2$ (*M*(II)=Mn, Co, Ni) and $Ni(2,4'\text{-}bpy)_2Cl_2$ are formed. The fragmentary thermal decomposition of halogenoacetates was observed in other mixed ligand complexes containing bipyridine isomers (*2-bpy*, *4-bpy*) and halogenoacetates [13–15, 17]. Next, the *2,4'-bpy* is released and conversion into pure Mn_3O_4 (via Mn_2O_3), CoO (via Co_3O_4) and NiO takes place. In the case of Cu(II) complex during decomposition of organic ligands, the volatile products copper are formed and only trace of CuO was observed. The principal volatile species produced during pyrolysis of metal(II) complexes with *4-bpy* [17] and *2,4'-bpy* are similar, only major maxima of ion current are shifted.

Generally, the process and products of thermal decomposition of the new synthesized complexes of Mn(II), Co(II), Ni(II) and Cu(II) with *2,4'-bpy* and dichloroacetates is near to correspond for previously studied complexes with *4-bpy* [17, 18]. Only differences were observed in the temperature ranges of decomposition and certain differences in composition of intermediate compounds as well as in the temperature of elimination of maximum rate of volatile thermal decomposition products.

The anhydrous complexes $Ni(2,4'\text{-}bpy)_2(CCl_2HCOO)_2$ and $Ni(4\text{-}bpy)_2(CCl_2HCOO)_2$ [17] are new examples of complexes with ligand isomerism.

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