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NEW 2,2'-BIPYRIDINE–CHLOROACETATO COMPLEXES OF TRANSITION METALS(II)

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The new mixed–ligand complexes of *d*–electron metals (*M*(II)=Mn, Ni, Cu) with 2,2'-bipyridine (2-bpy) and mono- or dichloroacetates were prepared as crystalline solids. The general formulae of the synthetized complexes are: $Cu(2\text{-}bpy)_2(CClH_2COO)_2\cdot 2H_2O$, $Mn(2\text{-}bpy)_2(CCl_2HCOO)_2$, $M(2\text{-}bpy)_2(CCl_2HCOO)_2\cdot 2H_2O$ (*M*(II)=Ni, Cu). The compounds were characterized by chemical analysis, IR and VIS spectroscopy. Their magnetic, molar conductivity and thermal properties also were studied. During heating in air complexes decompose via different intermediate products to metal oxides. A coupled TG-MS system was used to analyse the principal volatile thermal decomposition (or fragmentation) products of 2,2'-bipyridine–chloroacetato complexes.

Keywords: *2,2'-bipyridine–dichloroacetato complexes, 2,2'-bipyridine–monochloroacetato complexes, complexes of transition metals(II), IR-VIS spectra, TG-MS data, thermal analysis*

Introduction

Coordination compounds of transition metals with 2,2'-bipyridine (2-bpy) are current interest for their rich physico-chemical properties, reactivity patterns and potential application in catalysis, analysis, bioorganic systems and as new types of materials [1–7]. The 2,2'-bipyridine–carboxylate complexes of metal ions have been extensively investigated during many years [8–10]. However, there is scan information on the mixed-ligand complexes of metal(II) with 2-bpy and chloroacetates [11]. In our earlier works [12–14] complexes formed between 2-bpy and metal(II) trichloroacetates (*M*(II)=Mn, Co, Ni, Zn, Cd), dichloroacetates (Zn, Cd) or monochloroacetates (Mn) were prepared. We also obtained some metal(II) complexes containing other isomers of bipyridine (4,4'- or 2,4'-bipyridine) and mono-, di- or trichloroacetates [15–17]. They have been characterized by IR and VIS spectra, thermal and other properties. The influence of chloroacetate anions and structure of N–donors on the formation of the compounds in the process of thermal decomposition and of the types metal–ligand bonds was examined. This work is continuation of our studies. In the present paper we describe the synthesis and properties of new 2,2'-bipyridine–monochloroacetato complex of Cu(II) and 2,2'-bipyridine–dichloroacetato compunds of Mn(II), Ni(II) and Cu(II). They were studied by chemical and thermal analysis, IR and VIS spectra, magnetic and molar conductivity measurements.

Experimental

Preparation of complexes

Mono- and dichloroacetates of metal(II) as hydrate products were prepared by method described in the literature [15, 16]; 2,2'-Bipyridine (*m.p.* 72°C) was obtained from Aldrich; other chemicals were the same as described in our previous papers [15, 16]. The complexes were prepared by reacting cold water solutions of $Cu(CClH_2COO)_2$ and $M(CCl_2HCOO)_2$ (where *M*(II)=Mn, Ni, Cu) with 2,2'-bipyridine in 96% *v*/*v* ethanol. Over a period of several minutes precipitates of complexes:

$$Cu(2\text{-}bpy)_2(CClH_2COO)_2\cdot 2H_2O \quad (1)$$

$$Mn(2\text{-}bpy)_2(CCl_2HCOO)_2 \quad (2)$$

$$Ni(2\text{-}bpy)_2(CCl_2HCOO)_2\cdot 2H_2O \quad (3)$$

and $$Cu(2\text{-}bpy)_2(CCl_2HCOO)_2\cdot 2H_2O \quad (4)$$

were obtained. Final products were removed by filtration, washed with cool EtOH, Et_2O and EtOH mixture (1:1) and dried at room temperature. In the case of the reaction mixture containing $Co(CClH_2COO)_2$ or $Co(CCl_2HCOO)_2$ and 2-bpy, two liquid phases are formed. After 2–3 days no homogeneous precipitate were formed. The metal analyses in mineralized samples of obtained complexes were carried out by complexometric method. The content of C, H, and N were determined by elemental analysis with V_2O_5-as an oxidizing agent. The theoretical decomposition was confirmed by analysis in limits 0.05/0.5%. These analytical results are presented in Table 1.

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Methods

IR spectra of complexes were determined using FTIR 8501 Shimadzu spectrometer. The samples were prepared as KBr discs. Electronic spectra were recorded on a Specord M40 spectrometer (12000–26000 cm^{-1}) in Nujol mulls. The molar conductivities (Λ_M) of the complexes were measured on $1.0\cdot10^{-3}$ mol L^{-1} solutions in MeOH, DMF and DMSO at 25±0.05°C; OK-102/1 conductivity meter equipped with an OK 902 electrode. The magnetic measurements were carried out at room temperature by Gouy's method using $Hg[Co(NCS)_4]$ as a calibrant. The correction for the diamagnetism of the consistent atoms was calculated by the Pascal's constants [18]. The X-ray diffractograms were recorded using a D-5000 diffractometer and CuK_α (Ni-filtered) radiation. The measurements were made in the $2\theta=2\theta$–80° range. Thermal decomposition studies were carried out on a derivatograph type Q-1500 over a temperature range of 20–1000°C, at heating rate of 10 K min^{-1}, in static air atmosphere. The sample mass was 100 mg; α-Al_2O_3 served as the reference. The solid thermal decomposition products in different temperatures were identified using derivatographic curves and were confirmed by recording the IR spectra of sinters (prepared during heating of samples of complexes up to definite temperature from TG). In the sinters presence of anions Cl^- was also investigated. The final solid products of decomposition were verified by X-ray diffraction patterns registration. Obtained X-ray diffractometric results were analyzed using the Powder Diffraction File [19]. TG-MS system was used to analyse the principal volatile products formed during thermal decomposition (or degradation) process of complexes [20, 21]. TG-MS system, consisting of derivatograph TG/DTA-SETSYS-16/18, coupled to a mass spectrometer (QMS-422), model ThermoStar Balzers Instruments; dynamic measurements were carried out in air atmosphere, with flow rate of 1 L h^{-1} between 20–1000°C. The samples were heated in platinum crucible 100 μL at heating rate 10°C min^{-1}. Sample of masses in the range ca 8–11 mg. An ion source temperature of ca 150°C by using 70 eV electron impact ionization.

Results and discussion

Mixed-ligand complexes

$Cu(2\text{-}bpy)_2(CClH_2COO)_2\cdot2H_2O$
$Mn(2\text{-}bpy)_2(CCl_2HCOO)_2$,
$M(2\text{-}bpy)_2(CCl_2HCOO)_2\cdot2H_2O$ (M(II)=Ni, Cu)
were prepared as crystalline solids. The analysis of the diffractograms proved that obtained compounds are small crystalline and non-isostructural. Magnetic moments, molar conductivity data and solubility in water at 21°C of obtained complexes are listed in Table 1. The experimental magnetic moments (at room temperature) of complexes (1)–(3) are closed to the values observed for the metal ions with octahedral stereochemistry [22]. Only the μ_{eff} value for complex (4) is 1.63 M.B; which is a little lower than observed range for octahedral complexes of Cu(II) ($\mu_{eff\ cald.}$=1.73 M.B, observed in the range 1.70–2.20 M.B). This suggests the possibility of at best a very weak magnetic interaction between the paramagnetic centres of Cu^{++} (which are practically magnetical isolated in this complex) [23]. The molar conductivity of all complexes in DMSO, (1)–(2) in DMF and (2) in MeOH presented behaviour intermediate between non- and 1:1 electrolytes; complexes (1), (3), (4) in MeOH and (3)–(4) in DMF are 1:1 electrolytes [24].

All obtained compounds have very similar IR spectra in solid state, only the absorption bands of water are not observed in $Mn(2\text{-}bpy)_2(CCl_2HCOO)_2$. IR spectra of obtained complexes exhibit several absorption bands characteristic for 2-bpy and OCO groups. The fundamental vibration modes of these ligands are summarized in Table 2. The absorption bands were identified in accordance with the literature [25, 26]. In spectra of complexes the bands assigned as ring stretching modes: CC, CN, $CC_{i.r.str.}$ (A_1 symmetry), CN, $CC_{str.}$ (B_1 symmetry) and ring 'breathing' modes are observed in the range 1606.6–1598.9, 1578.0–1566.1 cm^{-1} and 1024.1–1014.5 cm^{-1}, respectively. They are shifted to higher frequencies in comparison to free ligand. The characteristic aromatic out-of-plane hydrogen deformation modes in unbonded 2-bpy are observed at 753 and 738 cm^{-1} (satellite). The complexes exhibit very strong absorption in the range 779.2–757.6 cm^{-1}; the satellite of this band gains intensity and is clearly splitted. Thus, the obtained complexes are 2,2'-bipyridine chelate compounds [27].

The asymmetric $\nu_{as}(OCO)$ bands of carboxylate group in complexes lie between 1684.3–1637.5 cm^{-1}. The bands of symmetric vibrations $\nu_s(OCO)$ for complexes appear in the range 1420.0–1340.4 cm^{-1}. The $\nu_{as}(OCO)$ are shifted to higher frequencies; $\nu_s(OCO)$– to the smaller values, compared to the bands of sodium salts. The separation $\Delta\nu=\nu_{as}(OCO)-\nu_s(OCO)$ of these bands varies between 319.3–234.8 cm^{-1} and is in all cases, higher than the $\Delta\nu$ of corresponding sodium salts (Table 2). It is reasonable to suggest that in obtained complexes the therminal carboxylate groups exist [28–31]. In these complexes showed a few bands of $\nu_{as}(OCO)$ and $\nu_s(OCO)$, as well as, in several mixed metal(II) complexes with N-donors and carboxylates [16, 32, 33]. This would seen to indicate that the

Table 1 Analytical data: solubility (S) in water at 21°C, molar conductivity (Λ_M) in MeOH, DMF and DMSO ($c=1\cdot10^{-3}$ mol L^{-1}) and effective magnetic moments (μ_{eff}) at 25°C

No.	Complex	Analysis: found (calculated)/%				S 10^2/	Λ_M /Ω^{-1} cm^2 mol^{-1}			μ_{eff}/
	(colour)	M	C	N	H	mol L^{-1}	MeOH	DMF	DMSO	M.B
(1)	$Cu(2\text{-}bpy)_2(CClH_2COO)_2\cdot2H_2O$	10.61	48.13	9.08	4.04	♦	83.3	31.6	28.7	1.88
	(blue)	(10.42)	(48.08)	(9.05)	(4.01)					
(2)	$Mn(2\text{-}bpy)_2(CCl_2HCOO)_2$	8.82	46.26	8.99	3.23	0.1	74.7	46.0	48.1	6.08
	(yellow)	(8.86)	(46.19)	(9.04)	(3.20)					
(3)	$Ni(2\text{-}bpy)_2(CCl_2HCOO)_2\cdot2H_2O$	8.86	43.48	8.58	3.65	♦	114.6	65.2	47.5	3.08
	(green)	(9.01)	(43.51)	(8.45)	(3.61)					
(4)	$Cu(2\text{-}bpy)_2(CCl_2HCOO)_2\cdot2H_2O$	9.51	43.17	8.00	3.62	♦	80.8	63.6	33.3	1.63
	(blue)	(9.13)	(43.09)	(8.39)	(3.59)					

♦ – very right soluble

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

Assignment	2-bpy [23]	Complex			
		(1)	(2)	(3)	(4)
		Coordination 2-bpy modes			
ν_1	1579	1606.6sh 1598.5	1595.8	1604.7sh 1598.9	1600.0
ν_2	1553	1566.1	1575.7 1566.1	1575.7 1566.1	1578.0
ν_3	991	1012.6	1014.5	1024.1	1015.5
ν_4	753 738sh	769.5 731.0	771.5 738.7	757.6 736.8	779.2 732.9
		Coordination carboxylate modes			
		$NaCClH_2COO$ $(NaCCl_2HCOO)$ [24]			
$\nu_{as}(OCO)$	1603 (1640)	1654.8	1666.4 1640.0	1668.3 1637.5	1684.3 1640.3
$\nu_s(OCO)$	1418 (1399)	1420.0	1382.9 1350.1	1340.4	1365.0 1355.9 } pd
$\Delta\nu=\nu_{as}(OCO)\text{-}\nu_s(OCO)$	185 (241)	234.8	283.5 289.9	327.9 297.1	319.3 284.4
$\nu(M\text{–}O)+\delta(OCO)$		439.7 592.1	624.9	437.8	588.2

complexes have a cis–configuration [32] or forms non-equivalent bonds between metal(II) and carboxylate ligands [34–36]. In the IR spectra of complexes (1), (3), (4) there are broad absorption bands with maximum at ca 3400 cm^{-1}, confirming the presence of water molecules in the compounds.

The ligand–field spectra of Ni(II) complexes are typical for six–coordination Ni(II) in pseudooctahedral environment. This complex has magnetic and spectral behaviours with octahedral geometry consistent. Three spin–allowed bands corresponding to the ^1E_g, $^3T_{1g}(F)$ and $^3T_{1g}(P)$ transitions in O_h symmetry [37] are observed in complex (3) at ca 17700 and 26700 cm^{-1} (with a shoulder at 13300 cm^{-1}). The shoulder at ca 13300–13400 cm^{-1} was observed in several complexes of Ni(II) with pyridine and halogenoacetates [32]. The copper(II) complexes exhibit one asymmetric band in the visible spectrum (broad maximum at 13000–14000 cm^{-1}), associated with three transitions lying within one broad envelope: ^2E_g, $^2B_{2g}$ and $^2A_{1g}$ [38]. The position of these bands indicates probably a pseudooctahedral environment around Cu(II).

Thermal behaviour of complexes

The obtained complexes are stable in air at room temperature. Thermal decomposition of the compounds is a multi–stage process. The TG, DTG and DTA curves for Cu(II) complexes are shown in Figs 1 and 2. The thermal data obtained from thermal curves, supported by other investigation (see experimental) are collected in Table 3. The hydrated complexes begin to lose water between 60–85°C; the complexes of Cu(II) lose water molecules in one step, whereas the complex (3) in two steps. The thermal curves exhibit clearly defined dehydration processes. The dehydration processes of complexes are connected with endothermic effects. The anhydrous compounds decompose in very similar way. On increase of the temperature, decomposition of the chloroacetates ligand takes place, and the stepwise liberation of 2-bpy begins. During these processes, intermediate species of the type $M(2\text{-bpy})_{2-x}Cl_2$ probably are formed. In the sinters of complexes heated up to definite temperature from TG (Table 3), only absorption bands for 2-bpy and chlorine ions were evident. In the temperature range 275–700°C, during decomposition of $Mn(2\text{-bpy})_{1.5}Cl_2$, Mn_2O_3 is formed (Fig. 3a). Above 900°C only diffraction lines characteristic of Mn_3O_4 were detected (Fig. 3b). Anhydrate complex $Ni(2\text{-bpy})_2(CCl_2HCOO)_2$ lost 2-bpy in two steps, and intermediate products with formulae $Ni(2\text{-bpy})_2Cl_2$, $Ni(2\text{-bpy})Cl_2$ are formed. Next, process of decomposition $Ni(2\text{-bpy})Cl_2$ takes place. A plateau for pure NiO in the TG curve being obtained at 740°C. In case of the copper(II) complexes, total decomposition of organic ligands is connected with the formation and volatilization of Cu_xCl_x and only 4.5–5% CuO is formed as a final product. The existence of pure $MnCl_2$ and $NiCl_2$ as intermediate solid products, was not proved from TG and DTG curves and analytical data.

DTA curves of these complexes in the presence of air may be a mixture of both endo and exo peaks (Table 3).

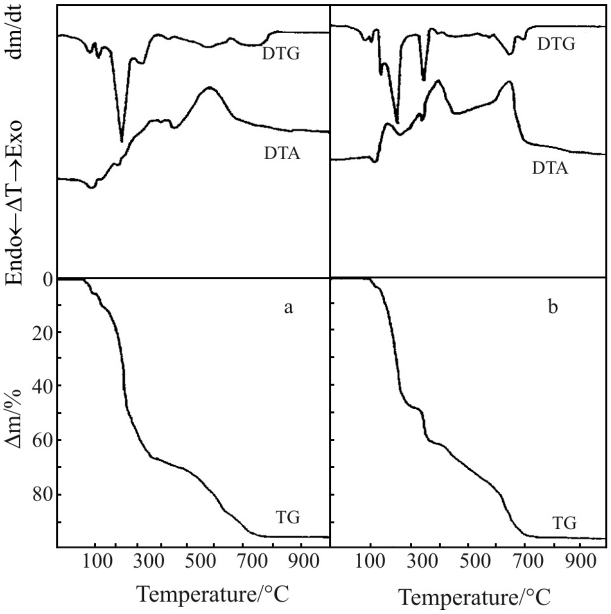

Fig. 1 TG, DTG, DTA curves of a – $Mn(2\text{-bpy})_2(CClH_2COO)_2$; b – $Ni(2\text{-bpy})_2(CCl_2HCOO)_2 \cdot 2H_2O$; sample mass 100 mg, heating rate: 10° min^{-1}

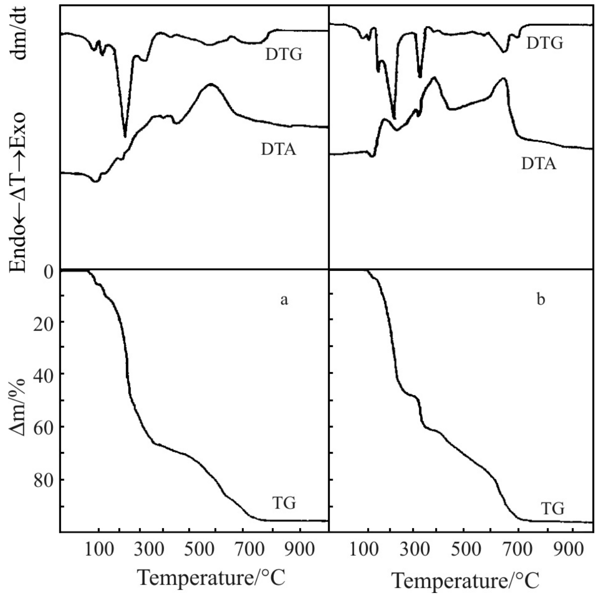

Fig. 2 TG, DTG, DTA curves of a – $Cu(2\text{-bpy})_2(CClH_2COO)_2 \cdot 2H_2O$; b – $Cu(2\text{-bpy})_2(CCl_2HCOO)_2 \cdot 2H_2O$; sample mass 100 mg, heating rate: 10° min^{-1}

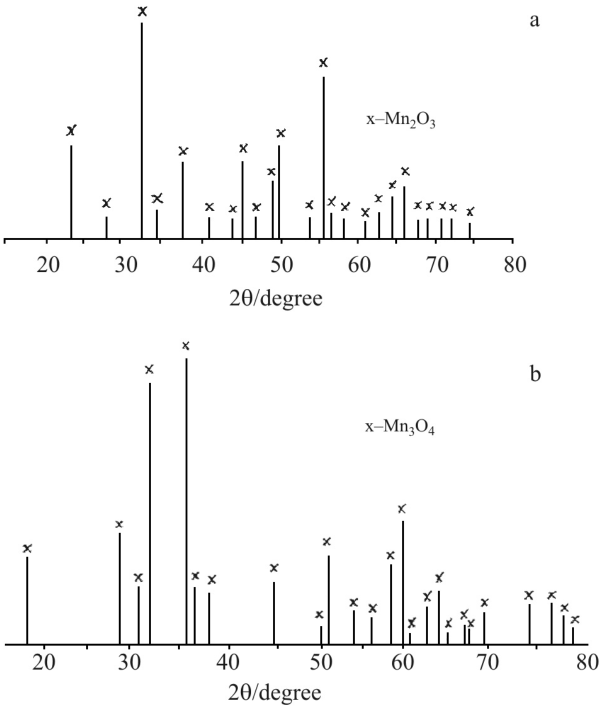

Fig. 3 X-ray diffraction patterns of decomposition of complex $Mn(2\text{-bpy})_2(CCl_2HCOO)_2$ a – sintered at 720°C; b – sintered at 920°C

Table 3 Thermal decomposition data, sample 100 mg; heating rate of 10°C min^{-1} in air

Starting, intermediate and final products	Temperature range/°C	Temperature peak of DTA/°C	Mass loss/%	
			found.	cald.
(1) $Cu(2\text{-}bpy)_2(CClH_2COO)_2\cdot 2H_2O$				
$\downarrow$	60–100	100 endo	5.5	6.02
$Cu(2\text{-}bpy)_2(CClH_2COO)_2$				
$\downarrow$	120–300	195 exo, 200 endo	46.0	45.45
$Cu(2\text{-}bpy)Cl_2$				
$\downarrow$	300–370	335 endo	13.0	13.04
$Cu(2\text{-}bpy)_{0.5}Cl_2$				
$\downarrow^a$	370–700	400, 600 exo	34.0	22.21
CuO				
(2) $Mn(2\text{-}bpy)_2(CCl_2HCOO)_2$				
$\downarrow$	165–275	220 exo	43.0	42.21
$Mn(2\text{-}bpy)_{1.5}Cl_2$				
$\downarrow$	275–700	465, 540, 630, 680 exo	44.0	45.12
Mn_2O_3				
$\downarrow$	>900	760 exo	~1.0	0.43
Mn_3O_4				
(3) $Ni(2\text{-}bpy)_2(CCl_2HCOO)_2\cdot 2H_2O$				
$\downarrow$	60–100	80 endo	2.7	2.72
$Ni(2\text{-}bpy)_2(CCl_2HCOO)_2\cdot H_2O$				
$\downarrow$	100–138	120 endo	3.0	2.72
$Ni(2\text{-}bpy)_2(CCl_2HCOO)_2$				
$\downarrow$	138–260	220 exo	28.3	27.89
$Ni(2\text{-}bpy)_2Cl_2$				
$\downarrow^b$	260–405	320 endo	24.0	23.56
$Ni(2\text{-}bpy)Cl_2$				
$\downarrow^b$	405–740	460, 620 exo, 500 endo,	32.5	31.84
NiO				
(4) $Cu(2\text{-}bpy)_2(CCl_2HCOO)_2\cdot 2H_2O$				
$\downarrow$	85–145	130 endo	5.0	5.40
$Cu(2\text{-}bpy)_2(CCl_2HCOO)_2$				
$\downarrow$	145–258	190 exo, 240 endo	40.0	39.39
$Cu(2\text{-}bpy)_{1.5}Cl_2$				
$\downarrow$	258–375	330 endo	17.5	17.54
$Cu(2\text{-}bpy)_{0.75}Cl_2$				
$\downarrow^a$	375–700	400, 600 exo	34.0	25.76
~4,5% CuO				

[a] total decomposition of organic ligands and probably gradual volatilization of Cu_xCl_x take place; [b] probably *via* $Ni(2\text{-}bpy)_{2\text{-}x}Cl_2$, TG curve shows bending at 340° and 500°C

The endothermic effects are due to decomposition of intermediate complexes and chloroacetate ligands and exothermic to the ligand combustion. The very strong and broad exothermic maxima with centers at: 400° (1), 465, 540° (2), 460° (3) and 400°C (4) were observed on the DTA curves.

Thermogravimetry coupled with mass spectroscopy (TG-MS) was used to characterize only complexes

((2)–(4)) containing 2-bpy and dichloroacetate ligands. The mass spectra of all these complexes present the similar signals. The principal ion current may indicate for: H^+, C^+, OH^+, H_2O^+, CN^+ (or $C_2H_2^+$), CHO^+, NO^+ (or CH_2O^+), Cl^+, HCl^+, Cl_2^+, CO_2^+, $bpy^{\bullet +}$ (*m/z*=1, 12, 17, 18, 27, 29, 30, 35, 36, 70, 44, 78), additionally *m/z*=50, 76 and 84 and traces of other. Figure 4 (as an example) presents the chemogram for selected profiles of ion current of $Ni(2\text{-}bpy)_2(CCl_2HCOO)_2{\cdot}2H_2O$. Many signals are observed at ca: 200–209, 450–460, 700°C (2), 150, 210–220, 465°C (3), 190, 340–360 and 550°C (4). The characteristic MS peaks for crystalline water appeared at 138°C for (3) and at 150°C for (4). The absence of *m/z*=18–signal to elimination of H_2O crystalline for (2) is stated. Maximum rates of forming H_2O during decomposition of organic ligands at: 456, 629, 689° (2), 467° (3) and 358°C (4) are observed. The ion signals intensities of CO_2^+ have centres at: 188, 270, 428, 447, 533° (2), 208, 466, 561° (3), 196, 362 and 547°C for (4). The species containing halogen (Cl^+, HCl^+, Cl_2^+, CCl^+, $CClH^+$, $CCl_2H_2^+$ and *m/z*=50) have several centres on chemograms with maximum at: 182–225°, 196–228°, 192–276°, 188–466° and 176–269°C, respectively. Correlation of MS data with the mass loss in the TG curves and IR measurements (for sinters), shows that in the first step the molecules of crystalline H_2O^+ are released; followed the decomposition of dichloroacetate ligands takes place. Maximum rates of forming NO^+ (or CH_2O^+) at: 456, 545° for (2), 474, 561° for (3) and 565°C for complex (4) are observed. In case of *m/z*=76 and $bpy^{\bullet +}$ were detected very low intensities with several peaks (majority at ca: 682, 700° (2), 465° (3) and 360, 670° (4). Nitrogen–containing ions observed by MS coincide with decomposition of intermediate products of the type $M(2\text{-}bpy)_{2-x}Cl_2$. TG-MS curves for selected ions current are presented, as an example, in Fig. 5.

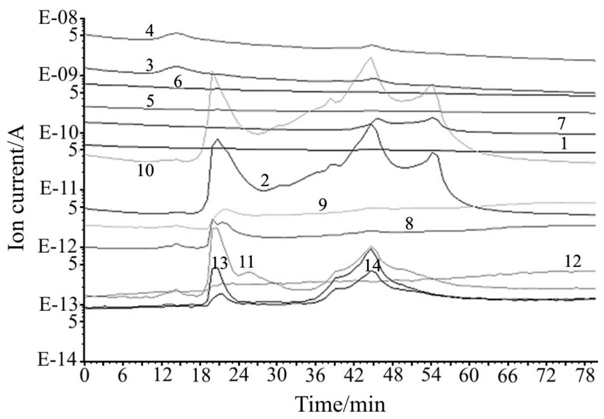

Fig. 4 The principal ion current detected in the mass spectrometer *vs.* time, in air, for complex $Ni(2\text{-}bpy)_2(CCl_2HCOO)_2{\cdot}2H_2O$; heating rate 10 K min^{-1}; mass sample 11.07 mg, *m/z*: 1–1; 2–12; 3–17; 4–18; 5–27; 6–29; 7–30; 8–35; 9–36; 10–44; 11–50; 12–70; 13–76; 14–78

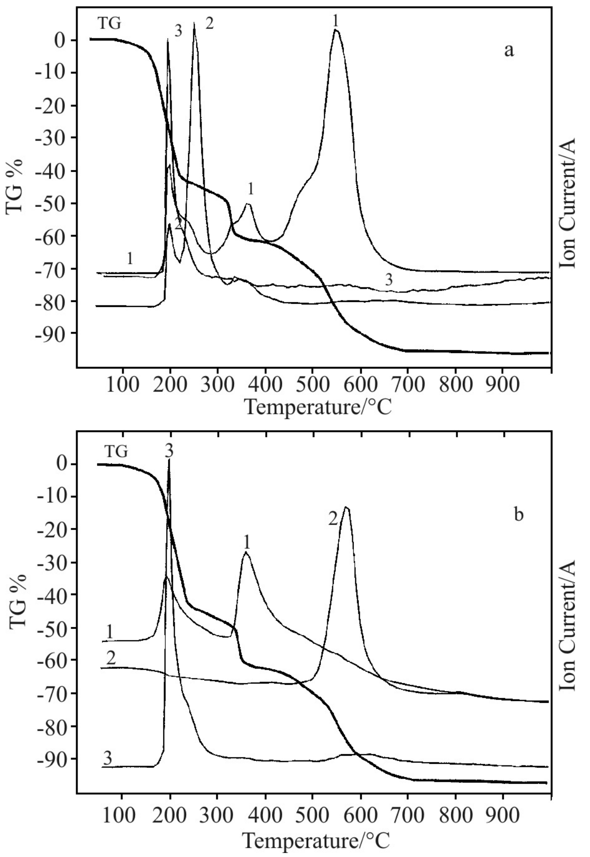

Fig. 5 TG curve and ion current detected by the MS in air for $Cu(2\text{-}bpy)_2(CCl_2HCOO)_2{\cdot}2H_2O$ mass sample 8.02 mg a – *m/z*: 1–44; 2–50; 3–70 with sensitivities of: E-09, E-12, E-12 A, respectively; b – *m/z*: 1–18; 2–30; 3–35 with sensitivities of: E-09, E-10, E-11 A, respectively

Conclusions

New mixed-ligand complexes of general formulae: $Cu(2\text{-}bpy)_2(CClH_2COO)_2{\cdot}2H_2O$, $Mn(2\text{-}bpy)_2(CCl_2HCOO)_2$, $M(2\text{-}bpy)_2(CCl_2HCOO)_2{\cdot}2H_2O$ (*M*(II)=Ni, Cu) were prepared. The influence of nitrogen atom position in the bipyridine causes changes in the composition of the mixed-complexes with halogenoacetates. Obtained in this work complexes have analogous molar ratio of metal(II) to organic ligands 1:2:2 as complexes of the types: $M(2\text{-}bpy)_2(CCl_3COO)_2{\cdot}nH_2O$ and $M(2,4'\text{-}bpy)_2(CCl_2HCOO)_2{\cdot}nH_2O$ [13]. The coordination compounds with 4,4'-bipyridine (4-bpy) have the general formulae $M(4\text{-}bpy)(hac)_2{\cdot}nH_2O$, without complexes of Ni(II) [13, 16], (where: hac=mono-, di- or trichloroacetate) [13, 15, 16]. The IR data show that 2-bpy coordinated in obtained complexes as bidentate–chelating ligand. Carboxylate groups in these compounds are bonded as monodentate. The isolated complexes $M(2\text{-}bpy)_2(CCl_2HCOO)_2{\cdot}2H_2O$

(*M*(II)=Ni, Cu) are ligand–isomeric with the 2,4'-bipyridine complexes [13].

The stability of the hydrate compounds synthesized in this work is very similar. They begin to lose water at 60–85°C. The anhydrated complexes containing dichloroacetate ligands are thermally more stable; $Mn(2\text{-}bpy)_2(CCl_2HCOO)_2$ has the highest stability (165°C). After dehydration of mono- and dichloroacetates takes place. The intermediate products of $M(2\text{-}bpy)_{2-x}Cl_2$ are formed. The species of the types $M(bpy)_{2-x}Cl_2$ (where: *bpy*=2-bpy; 4-bpy and 2,4'-bpy) also occurs during pyrolysis of 2,2'-bipyridine–trichloroacetato, 2,4'-bipyridine (or 4,4'-bipyridine)–dichloroacetato complexes of metal(II) [13]. The resultant final products were the Mn_3O_4 and NiO, respectively. These conclusions are in agreement in the literature on other metal carboxylate complexes [39–40]. During decomposition of Cu(II) complexes, the volatile Cu_xCl_x are formed and only trace of CuO was observed as residue solid product. The volatile species produced during pyrolysis (or fragmentation) of metal(II) complexes with bipyridine isomers (2-bpy, 4-bpy and 2,4'-bpy) and dichloroacetates are similar, only major maxima of ions current are shifted.

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