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COMPLEXES OF Mn(II), Co(II), Ni(II) AND Cu(II) WITH 4,4'-BIPYRIDINE AND DICHLOROACETATES

Synthesis, thermal and other properties

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Abstract

New mixed-ligand complexes with empirical formulae M(4-bpy)$L_2 \cdot 1.5H_2O$ (*M(II)*=Mn, Co), Ni(4-bpy)$_2L_2$ and Cu(4-bpy)$L_2 \cdot H_2O$ (where: *4-bpy*=4,4'-bipyridine, *L*=CCl_2HCOO^-) have been isolated in pure state. The complexes have been characterized by elemental analysis, IR spectroscopy, conductivity (in methanol, dimethylformamide and dimethylsulfoxide solutions) and magnetic and X-ray diffraction measurements. The Mn(II) and Co(II) complexes are isostructural. The way of metal–ligand coordinations discussed. The IR spectra suggest that the carboxylate groups are bonded with metal(II) in the same way (Ni, Cu) or in different way (Mn, Co). The solubility in water is in the order of $19.40 \cdot 10^{-3} \div 1.88 \cdot 10^{-3}$ mol dm^{-3}. During heating the hydrate complexes lose all water in one step. The anhydrous complexes decompose to oxides *via* several intermediate compounds. A coupled TG-MS system was used to analyse the principal volatile products of obtained complexes. The principal volatile products of thermal decomposition of complexes in air are: H_2O^+, CO_2^+, HCl^+, Cl_2^+, NO^+ and other.

Keywords: bipyridine-dichloroacetate complexes, IR spectra, TG-MS data, thermal decomposition, transition-metal complexes

Introduction

This paper is a continuation of our earlier studies on transition metal complexes with bipyridine isomers and halogenoacetates. Previously, we described the compounds of the types M(4-bpy)$(CClH_2COO)_2 \cdot nH_2O$ (where: *M(II)*=Mn, Co, Ni, Cu; *4-bpy*= 4,4'-bipyridine) [1], M(4-bpy)$_2(CCl_3COO)_2 \cdot nH_2O$ *(M(II)*=Co, Ni, Cu) and Mn(4-bpy)$(CCl_3COO)_2 \cdot H_2O$ [2].

The literature survey shows that there are scanty informations about mixed dihalogenoacetates complexes with title metal(II), except informations abount the complexes with copper(II). Coordination compounds of copper(II), with dichloroacetates and several nitrogen donors (for example, pirydine and its derivatives, ethylenodiamine,

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α-picoline) were extensively studied. Spectral, magnetic and structural data of this type complexes of copper(II) are listed in papers [3–5]. Only fragmentary data are available in the literature on the thermal decomposition of metal(II) dichloroacetates [6–8]. Mojumdar *et al.* [9] described the IR spectra and the analytical properties of the compound $Cu(CCl_2HCOO)_2(mpc)$, where: *mpc*=methyl-3-pyridyl carbamate.

This work reports the preparation of new 4,4'-bipyridine and dichloroacetate complexes of Mn(II), Co(II), Ni(II) and Cu(II). Characterization of these complexes has been carried out by chemical analyses, magnetic and molar conductivity measurements. We describe here also IR spectra. The thermal decomposition of obtained compounds was studied in air and discussed. A coupled TG-MS system was used to investigation of the principal gaseous products involved during pyrolysis of the title complexes.

Experimental

Materials and synthesis of complexes

Dichloroacetic acid, dimethylformamide (DMF) and dimethylsulfoxide (DMSO) p.a. were obtained from Aldrich, Reachim and VEB Janapharm Labochem Apolda respectively; other chemicals were the same as was described in our previous papers [1, 2]. Solutions of $M(CCl_2HCOO)_2$ were prepared by addition 20 mL 2M CCl_2HCOOH to freshly precipitated carbonates of the metal(II) in ca. equimolar ratio. The metal contents in obtained solutions, isolated complexes and solid thermal decomposition products were analysed by standard methods [1, 2].

The complexes were prepared by reacting water solutions of $M(CCl_2HCOO)_2$ *(M(II)*=Mn, Co, Ni, Cu) with solution of 4,4'-bipyridine in 96% *v/v* ethanol, according to a procedure described previously [1, 2].

Measurements

The apparatus and measuring conditions (except molar conductivities) were the same as described in our previous papers [1, 2, 10]. Molar conductivity (Λ_M) of complexes were measured [11] using $1.0\cdot10^{-3}$mol dm^{-3} solutions in MeOH, DMF and DMSO.

Results and discussion

The analytical results of the obtained compounds are presented in Table 1 together with other characteristic data. The analysis of the diffractograms proved that the prepared complexes are crystalline and isostructural in the pair: $Mn(4\text{-}bpy)(CCl_2HCOO)_2\cdot1.5H_2O$ and $Co(4\text{-}bpy)(CCl_2HCOO)_2\cdot1.5H_2O$. The compounds are fairy soluble in water ($19.40\cdot10^{-3}$–$1.88\cdot10^{-3}$ mol dm^{-3}). The room temperature effective magnetic moments of the compounds are characteristic for the orbital singlet states [12]. Conductivity data suggested that complexes in methanol and DMF (except $Mn(4\text{-}bpy)(CCl_2HCOO)_2\cdot1.5H_2O$) present intermediate behaviour between those of non-electrolytes and 1:1 electrolytes. The molar conductivity values of all investigated compounds in DMSO and

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

No.	Complex	Analysis: found (calculated)/%				S·10^3/ mol dm^{-3}	Λ_M/Ω^{-1} cm^2 mol^{-1}			μ_{eff}/M.B
		M	C	N	H		CH_3OH	DMF	DMSO	
I	Mn(4-bpy)L_2·1.5H_2O (white)	10.57 (11.12)	33.98 (34.04)	5.76 (5.67)	2.63 (2.65)	19.40	85.1	48.5	50.5	5.83
II	Co(4-bpy)L_2·1.5H_2O (pink)	11.83 (11.84)	34.12 (34.04)	5.93 (5.63)	2.77 (2.65)	5.30	70.7	45.5	51.0	5.15
III	Ni(4-bpy)$_2L_2$ (green)	10.00 (9.36)	46.05 (45.98)	9.85 (8.94)	2.76 (2.89)	8.75	69.7	46.5	44.4	3.02
IV	Cu(4-bpy)L_2·H_2O (blue)	12.73 (12.87)	34.01 (34.07)	6.39 (5.68)	2.34 (2.45)	1.88	12.1[a)]	29.8	32.8	1.75

[a] c=3.0·10^{-4} mol dm^{-3}

Mn(4-bpy)($CCl_2HCOO)_2\cdot1.5H_2O$ in methanol corresponded probably to that of a 1:1 electrolyte [13]. Higher than anticipated Λ_M values are usually due to the displacement of dichloroacetate ligands by a molecule of solvent in complexes. Similar behaviours were observed for several complexes, mainly in DMSO, because this solvent is strong donor with profitable steric properties [14].

IR spectra

The infrared spectra of compounds **I, II, IV** display a broad absorption band in the water stretching region (3600–3400 cm^{-1} range). Table 2 presents the fundamental vibration modes of 4-bpy and of the carboxylate group for obtained compounds and of $CCl_2HCOONa$.

The IR spectrum of free 4-bpy changes owing complex formation [16]. The most characteristic ring vibrations >C=C< and >C=N–, appearing at 1530 and 1590 cm^{-1} in a free ligand are observed in the ranges 1539.1–1535.2 and 1610.5–1600.0 cm^{-1}, respectively. The pyridine ‘breathing’ frequency is shifted by about 28.5–24.8 cm^{-1} towards higher values. These data indicate that 4-bpy is bonded to the metal(II) ions, steric position of the nitrogen atoms in 4-bpy precludes chelation but favours coordinations to two metal ions [17].

Table 2 Principal IR bands (cm^{-1}) for 4-bpy and OCO group in obtained complexes; $L=CCl_2HCOO^-$

Assignment	$NaCCl_2HCOO$ [15]	Complex			
		I	**II**	**III**	**IV**
	Coordinated 4-bpy modes				
ν(CN)	–	1604.7	1600.0	1606.6	1610.5
ν(CC)	–	1537.2	1539.1	1535.2	1535.2
Pyridine ‘breathing’	–	1006.8	1008.7	1010.6	1010.6
	Acetato modes				
$\nu_{as}(OCO)$	1640	1647.1	1647.1	1652.9	1658.7 1627.8
$\nu_s(OCO)$	1399	1404.1 1388.7 1371.3	1405.2 1390.0 1375.0	1383.5 1371.3	1390.6 1355.9
$\Delta\nu=\nu_{as}(OCO)-\nu_s(OCO)$	241	243.0 258.4 275.8	242.0 257.1 272.0	269.4 314.4	268.1 271.9
ν(M–O)+δ(OCO)	–	480.0	478.3	470.0	472.5

In addition, to the 4-bpy frequencies IR spectra of investigated complexes exhibit new absorption bands, which are identified as $\nu_{as}(OCO)$ and $\nu_s(OCO)$ modes of the carboxylate groups. IR spectra of the region characteristic of dichlorocarboxylate absorption for Mn(II) and Co(II) complexes are very similar. The $\nu_{as}(OCO)$ are shifted to higher frequencies compared to those bands for the sodium salt. The ν_s(OCO) is splitted for these complexes; two bands are shifted to lower and one almost the same in comparison to those in ionic salt. The two values $\Delta\nu=\nu_{as}-\nu_s$ are higher and one value $\Delta\nu$ is almost the same as for sodium salt ($\Delta\nu_{Na}$). Due to the spectroscopic criterium [18–19] it is possible to suggest, that in the complexes Mn(II) and Co(II) the dichloroacetates act as monodentate as well as unsymmetric bridging groups [18–23]. From the IR spectra analysis of Ni(II) and Cu(II) complexes it appears that the dichloroacetate ions are a monodentate ligands in these compounds. However, the ν_s(OCO) band is splitted into two (Table 2). It can be said that non-equivalent bonds between these M(II) and carboxylic groups of dichloroacetate ligand are formed [24]. The splitting of ν_{as}(OCO) and ν_s(OCO) bands is observed for cobalt(II), nickel(II) and copper(II) dichloroacetates and their complexes with several N-donors [3]. Above mentioned information suggest, that the structure of investigated complexes can be complicated.

The ν(M–O)+δ(OCO) vibrations are observed as medium or weak bonds in the interval 480.0–470.0 cm^{-1}.

Thermal analyses

The data obtained from the TG, DTG and DTA curves, supported by chemical and the X-ray diffraction pattern investigations, are listed in Table 3. The thermal analysis curves of Mn(II) and Co(II) complexes are presented, as an example, in Fig. 1.

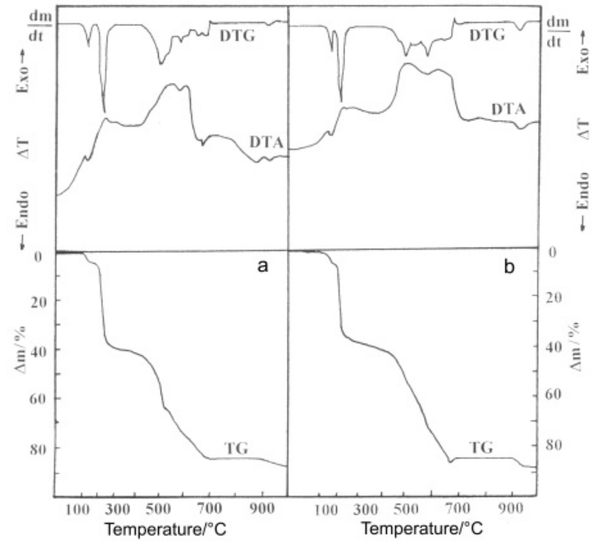

Fig. 1 Thermoanalytical curves of a – Mn(4-bpy)($CCl_2HCOO)_2\cdot1.5H_2O$; b – Co(4-bpy)($CCl_2HCOO)_2\cdot1.5H_2O$; mass sample 100 mg

All the compounds decompose progressively. The character of thermal decomposition of Mn(4-bpy)$L_2\cdot1.5H_2O$ is very similar to those of Co(4-bpy)$L_2\cdot1.5H_2O$.

Table 3 Thermal decomposition data of complexes in *L*=CCl_2HCOO^-; sample mass 100 mg

Starting material	Ranges of decomp./°C	DTA peaks/°C	Mass loss/%		Intermediates and residue solid products
			found	calc.	
$Mn(4\text{-}bpy)L_2\cdot 1.5H_2O$	100–142	140 endo	5.0	5.5	$Mn(4\text{-}bpy)L_2$
	160–420	250 exo	37.5	37.4	$Mn(4\text{-}bpy)Cl_2$
	420–540	540 exo	23.5	23.7	$Mn(4\text{-}bpy)_{0.25}Cl_2$
	540–620	600 exo	8.5	7.9	$MnCl_2$
	620–720	720 exo	9.6	10.1	Mn_2O_3
	720–900	900 exo	~1.0	0.6	Mn_3O_4
$Co(4\text{-}bpy)L_2\cdot 1.5H_2O$	60–160	150 endo	5.5	5.4	$Co(4\text{-}bpy)L_2$
	160–420	210 exo	37.0	37.0	$Co(4\text{-}bpy)Cl_2$
	420–558	500 exo	22.8	23.7	$Co(4\text{-}bpy)_{0.25}Cl_2$[a]
	558–590	585 endo	8.0	7.9	$CoCl_2$[a]
	590–680	610 exo	12.5	10.0	Co_3O_4[b]
	>900	920 endo	1.5	1.0	CoO[c]
$Ni(4\text{-}bpy)_2L_2$	180–200	200 exo	15.0	14.8	$Ni(4\text{-}bpy)_2L(Cl)$
	210–280	280 endo	15.5	14.8	$Ni(4\text{-}bpy)_2Cl_2$
	280–510	500 exo	25.0	24.9	$Ni(4\text{-}bpy)Cl_2$[a]
	510–605	600 exo	24.6	24.9	$NiCl_2$[a]
	>660	755 exo	8.5	8.8	NiO
$Cu(4\text{-}bpy)L_2\cdot H_2O$	65–170	170 endo	3.5	3.7	$Cu(4\text{-}bpy)L_2$
	170–345	200 exo	36.5	37.4	$Cu(4\text{-}bpy)Cl_2$
		350 exo	15.0	15.8	$Cu(4\text{-}bpy)_{0.5}Cl_2$[a]
	345–390	360 endo	–	–	
		400 exo	16.5	15.8	$CuCl_2$[a]
	390–508	580 exo	12.0	11.2	CuO
	508–610		2.0	1.6	Cu_2O
	>610				

[a] By projecting minimum of the DTG curve on TG curve;
[b] Transition with trace of Co;

They lose water in one step. Dehydration is characterized by a weak endothermic effect. The complexes of Mn(II) and Co(II) are stable up to100 and 60°C, respectively. In the temperature range 160–420°C, a sudden decrease in mass occurs. This decrease in mass is ascribed to decomposition of the dichloroacetate ligands (*vide* MS data) and formation of $M(4\text{-}bpy)Cl_2$. This process is connected with the strong exoeffects observed in DTA curve, and sharp DTG peak corresponds to the rapid loss in mass. Next, the stepwise liberation of 4-bpy begins and MCl_2 forms. For Co(II) complex the elimination of 4-bpy processes overlap, but by projecting the minimum of the DTG curve on the TG curve [25] it can be established that 0.75 and 0.25 moles of 4-bpy are lost. $MnCl_2$ forms at 620°C (found 25.5%, cald 25.5%) and $CoCl_2$ at 590°C (found 25.6%, cald 26.1%); peaks appear on DTA curve at 600°C (exo) and 585°C (endo), respectively. On increase of the temperature $MnCl_2$ decompose to Mn_2O_3; the Mn_3O_4 level begins at 700°C. Between 590–680°C the Co_3O_4 with ca 2.5% Co occurs. Formation of CoO begins above 900°C.

Cu(4-bpy)L_2·H_2O displaces very similar behaviour to that of Co(4-bpy)L_2·1.5H_2O. However, according to the DTG curve, the intermediate complex Cu(4-bpy)Cl_2 eliminates 0.5 mol of 4-bpy, and Cu(4-bpy)$_{0.5}$$Cl_2$ is formed. In the range 390–508°C, it loses 0.5 mol 4-bpy and decompose to $CuCl_2$. From 508–610°C CuO is formed. Over a temperature of 610°C, formation of Cu_2O begins. Only high and broad exothermic effects appear clearly in DTA curve.

The pyrolysis of Ni(4-bpy)$_2$$L_2$ occurs in several steps. This complex is thermally stable up to 180°C, when a partial decomposition of dichloroacetates takes place and gives intermediate compounds Ni(4-bpy)$_2$L(Cl) and Ni(4-bpy)$_2$$Cl_2$. The deamination of Ni(4-bpy)$_2$$Cl_2$ begins at 280°C. According to the DTG curve, 4-bpy is released stepwise in two stages. At first 1 mol of 4-bpy is eliminated to form Ni(4-bpy)Cl_2. Next it loses the remaining 4-bpy and is converted to $NiCl_2$. In temperature range 605–658°C the $NiCl_2$ decomposes to pure NiO (found 11.0%, cald 11.9%). The DTA curve shows the presence of mixture of exo and endo peaks.The exothermic effect at 500°C is high and broad. It accompanies the burning of the organic fragments and probably masks other peaks in DTA curve.

Mass spectrometric thermal analysis

A coupled TG-MS was used for characterization of volatile thermal decomposition products of the compounds studied. Dynamic measurements were carried out in air atmosphere for all complexes and for Ni(II) compound also in argon. MS data for all complexes detected several signal intensities. Figure 2a presents the ion current for *m/z* detected by MS *v/s* time for complex Ni(4-bpy)$_2$(CCl_2HCOO)$_2$ in air. The corresponding data in argon atmosphere are shown in Fig. 2b. Generally, in air atmosphere many signals are observed in the range ca 190–250 and 420–550°C for Mn(II) and Ni(II) complexes, ca 172–250, 410–510 and 650°C for Co(II), and ca 250 and 375°C in the case of Cu(II) compound. The corresponding MS peaks for crystalline water appeared at 126 (Mn), 182 (Co) and 143°C (Cu). Maximum rates of forming of H_2O during decomposition of organic ligands at 475, 530 (Mn), 516 (Co), 471 (Ni) and 377°C (Cu) are observed. The ion signal intensities of CO_2^+ (and its isotopes) have centers at 193, 465, 527°C for (Mn); 239, 517, 645°C for (Co); 195, 468°C for (Ni); 238 and 376°C in case of Cu(II) complex. The intensities of major ion signals containing halogen (Cl^+, HCl^+, CH_3Cl^+, Cl_2^+, $CH_2Cl_2^+$) have several centers. The first maximum of these fragments occurs in the range ca 173–260°C (very similar as observed for CO_2^+). Correlation of fragmentation observed by MS with the mass loss in the TG curves show that in the first step the molecules of probably crystalline H_2O are released, followed the decomposition of dichloroacetate anions takes place. Further maxima in the detection of these fragments occur at around 545 (Mn), 308, 540, 645°C (Co), 340, 510–550 (Ni) and 380°C (Cu), coincides with the decomposition of intermediate compounds. Strong maxima in the detection for *m/z*: 30, 46, 76, (probably molecular ions containing nitrogen) occur at around 467, 524 (Mn), 510–546 (Co), 470 (Ni) and 363–381°C (Cu). However, the MS peaks for these *m/z* also at lower temperatures (235–247 for Co and Cu, 190–196°C for Mn and Ni) are observed. It suggests, that some steps of decomposition of studied complexes are weakly separated

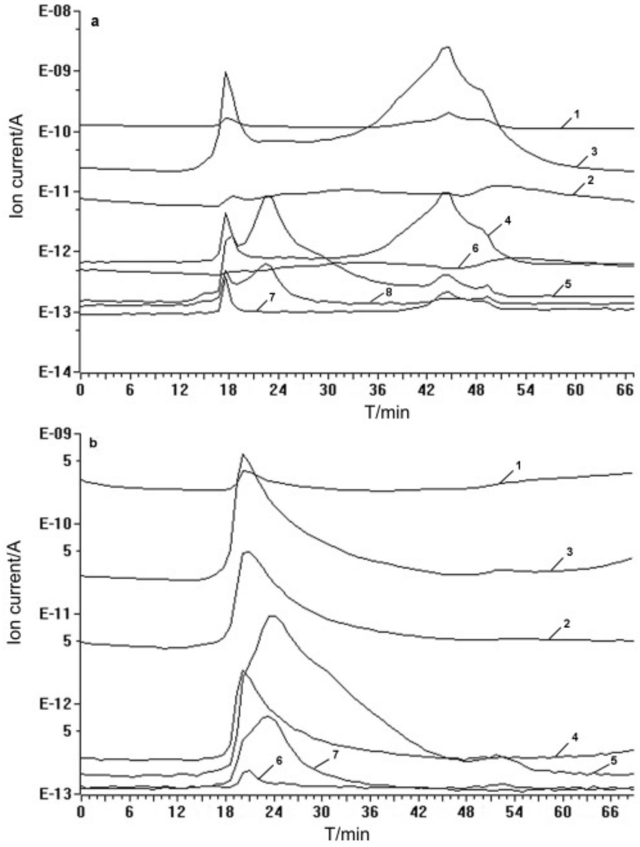

Fig. 2 Ion current detected in the mass spectrometer *vs*. time (without *m/z*: 18) for complex Ni(4-bpy)$_2$(CCl$_2$HCOO)$_2$; heating rate 10°C min^{-1}; In air, a – mass sample 4.66 mg, *m/z*: 1 – 30; 2 – 36; 3 – 44; 4 – 46; 5 – 50; 6 – 70; 7 – 76; 8 – 84. In argon, b – mass sample 4.55 mg, *m/z*: 1 – 28; 2 – 30; 3 – 44; 4 – 46; 5 – 50; 6 – 76; 7 – 84

one from another. TG coupled with MS data for some ions current are presented, as an example, in Figs. 3 and 4.

Figures 2a and 2b compares the MS data for Ni(4-bpy)$_2$(CCl$_2$HCOO)$_2$ in two various atmospheres. They clearly show that main peaks of MS occurs in the argon only in region of lower temperatures (215–260°C), whereas in higher temperatures relatively very weak intensities of ion currents are observed. The types of volatile products detected in the MS during thermal decomposition of Ni(4-bpy)$_2$(CCl$_2$HCOO)$_2$ in inert atmosphere are very similar as in air. Although the species of H_2O^+, Cl_2^+, HCl^+ were not observed; on the other hand additionally with *m/z*=28 exist.

The mass decrease appeared at 658°C for TG curve show that the pure Ni (found: 10.0%, cald: 9.4%) was formed as a final product of pyrolysis of Ni(4-bpy)$_2$(CCl$_2$HCOO)$_2$ in argon atmosphere.

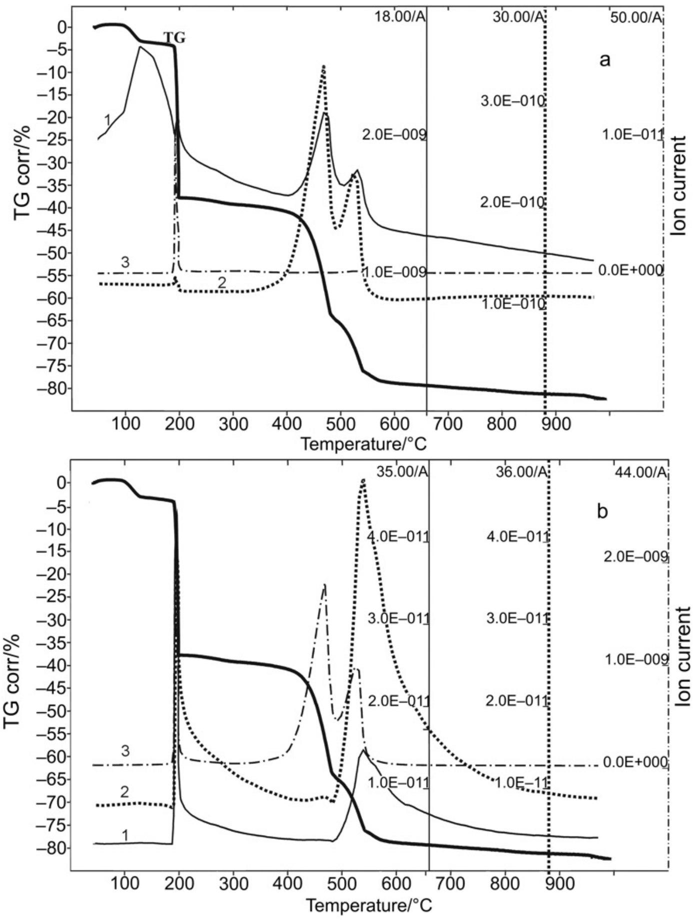

Fig. 3 TG curve for Mn(4-bpy)$(CCl_2HCOO)_2\cdot 1.5H_2O$ and ion current detected by the MS in air a – *m/z*; 1 – 18; 2 – 30; 3 – 50; b – 1 – 35; 2 – 36; 3 – 44; mass sample 5.98 mg

Conclusions

4,4'-bipyridine and chloroacetate ions are very interesting ligands and form several mixed-ligand complexes with nd^m metals. Synthesis and properties of these types of Mn(II), Co(II), Ni(II) and Cu(II) complexes are studied by us in this and previous works [1, 2].

Compounds with stoichiometry: $M(4\text{-bpy})_2(CCl_3COO)_2\cdot nH_2O$ (*M(II)*=Co, Cu), $Mn(4\text{-bpy})(CCl_3COO)_2\cdot H_2O$, $M(4\text{-bpy})(CCl_2HCOO)_2\cdot nH_2O$ (*M(II)*=Mn, Co, Cu), and $M(4\text{-bpy})(CClH_2COO)_2\cdot nH_2O$ (*M(II)*=Mn, Co, Ni, Cu) were obtained as hydrates with different contents of H_2O molecules. Only $Ni(4\text{-bpy})_2(CCl_2HCOO)_2$ complex

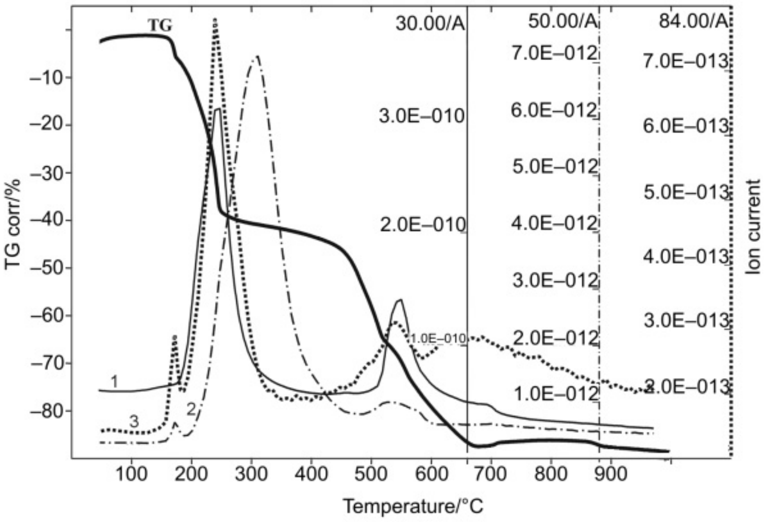

Fig. 4 TG curve for Co(4-bpy)$(CCl_2HCOO)_2\cdot 1.5H_2O$ and ion current detected by the MS in air *m/z*: 1 – 30; 2 – 50; 3 – 84; mass sample 12.06 mg

was obtained as anhydrous one. The compounds Mn(4-bpy)$(CCl_2HCOO)_2\cdot 1.5H_2O$ and Co(4-bpy) $(CCl_2HCOO)_2\cdot 1.5H_2O$ are isostructural with only small differences in their spectral, conductivity and thermal data.

IR spectra of all compounds suggest that 4-bpy is coordinated to a metal ion. In the 4,4'-bipyridine-monochloroacetate and 4,4'-bipyridine-trichloroacetate complexes the OCO groups are bonded in the same way as bidentate chelating ligands, whereas in the Ni$(4\text{-bpy})_2(CCl_2HCOO)_2$ and Cu(4-bpy)$(CCl_2HCOO)_2\cdot H_2O$ as monodentate. In the case of Mn(4-bpy)$(CCl_2HCOO)_2\cdot 1.5H_2O$ and Co(4-bpy)$(CCl_2HCOO)_2\cdot 1.5H_2O$ the carboxylate groups in the same complex probably are bonded in different way as monodentate as well as unsymmetric bridging groups.

During heating in air all complexes decompose in multistep, from which some are weakly separated one from another. Generally, anhydrate complexes containing monochloroacetate ligands are thermically more stable. The hydrated compounds containing other chloroacetates are stable only up to 60–100°C, except Mn(4-bpy)$(CCl_3COO)_2\cdot H_2O$; it begin to lose water at 120°C. Anhydrate complexes Mn(4-bpy)$(CCl_3COO)_2$ (190°C) and Ni(4-bpy)$(CCl_2HCOO)_2$ (180°C) have the higher stability. The initial temperatures of decomposition of other anhydrous complexes are near (140–170°C). The resultant final products were the metal oxide in all cases.

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