

## **THERMAL AND OTHER PROPERTIES OF COMPLEXES OF Mn(II), Co(II) AND Ni(II) WITH 2,2'-BIPYRIDINE AND TRICHLOROACETATES**

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### **Abstract**

Complexes of the general formulae  $Mn(2-bpy)_2(CCl_3COO)_2$ ,  $Co(2-bpy)_2(CCl_3COO)_2 \cdot H_2O$  and  $Ni(2-bpy)_2(CCl_3COO)_2 \cdot 2H_2O$  (where: *2-bpy*=2,2'-bipyridine) have been prepared and characterized by VIS and IR spectroscopy, conductivity and magnetic measurements. The thermal properties of complexes in the solid state were studied under non-isothermal conditions in air atmosphere. During heating the complexes decompose *via* different intermediate products to the oxides  $Mn_3O_4$ ,  $CoO$  and  $NiO$ . A coupled TG-MS system was used to detection the principal volatile products of thermal decomposition and fragmentation processes of obtained compounds. The principal volatile products of thermal decomposition of complexes are:  $H_2O^+$ ,  $CO_2^+$ ,  $Cl_2^+$  and other.

**Keywords:** 2,2'-bipyridine complexes, conductivity, mass spectrometry, thermal decomposition, trichloroacetate, VIS-IR spectra

### **Introduction**

In earlier publications, we have reported the synthesis and characterization of mixed-ligand complexes of Mn(II), Co(II), Ni(II) and Cu(II) with 4,4'-bipyridine (4-bpy) and mono- and trichloroacetates [1, 2]. Some conclusions of their structure were drawn. The thermal behaviours of these compounds (in the temperature range 20–1000°C) were studied using TG/DTA, and TG-MS techniques in air.

In connection with our investigation into the 4,4'-bipyridine–trichloroacetato complexes of the transition metals [2] a comparative study of the corresponding 2,2'-bipyridine–trichloroacetato compounds seemed of interest.

The influence of bipyridine isomers and halogenoacetates species on the several behaviours of these type of complexes was not studied. The bipyridine isomers favour mainly types of coordination: as an example, 2-bpy is potential bidentate chelating ligand; 4-bpy can coordinate as bidentate bridging ligand; 2,4'-bipyridine acts as monodentate ligand [3, 4]. The influence of nitrogen atom position from the bipyridine was observed on thermal stability of mixed bipyridine–oxalato complexes with several metals(II) [5, 6]. The complexes of 2-bpy and 4-bpy are more stable, than those containing 2,4'-bipyridine.

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The interesting aspect of title complexes lies also in the fact, that the halogenoacetate ion can coordinate metal(II) ions in various ways: as a simple unidentate ligand, or as a bidentate bridging or chelating, symmetric or asymmetric group [7–12]. However, studies on the metal(II) complexes with 2,2'-bipyridine and trichloroacetates are not reported yet in literature. Only the complex of Zn(II) with 2-bpy and trichloroacetates was described in [13]. Several mixed-ligand complexes of Co(II), Ni(II) and Cu(II) with trichloroacetates and other N-donors also have been synthesized and characterized [12, 14–16]. Shova *et al.* [17, 18] prepared trichloroacetates of manganese(II) and cobalt(II). The molecular structure of these compounds was determined. Therefore, in this paper we describe the results of our investigations on Mn(II), Co(II) and Ni(II) complexes with 2,2'-bipyridine and trichloroacetates. This report is concerned predominantly on the nature of metal-ligand bond and thermal decomposition of obtained compounds.

## Experimental

### *Materials, synthesis and analysis*

2,2'-Bipyridine (*m.p.* 72°C) and other chemicals were the same as described in our previous papers [2, 6].

The complexes were synthesized by reacting water solutions of  $M(\text{CCl}_3\text{COO})_2$  ( $M(\text{II})=\text{Mn, Co, Ni}$ ) with solution of 2,2'-bipyridine in 96% *v/v* ethanol. The procedure was similar to that used for the 4,4'-bipyridine compounds [2]. The chemical formulae of obtained complexes have been established analytically. The solid thermal decomposition products at different temperatures were identified using derivatographic curves, analytical and IR data or X-ray diffractograms. Obtained X-ray diffractometric results were analyzed using the Powder Diffraction File [19]. Metal(II) in mineralized samples was determined complexometrically; C, H and N – by standard elemental analysis with  $\text{V}_2\text{O}_5$  as oxidizing agent.

### *Physical measurements*

Molar conductivities ( $\Lambda_M$ ) of complexes were measured [20] on  $1.0 \cdot 10^{-3}$  mol  $\text{L}^{-1}$  solutions in methanol, DMSO and DMF at  $25 \pm 0.05^\circ\text{C}$ . The magnetic susceptibility of prepared complexes was measured on a magnetic balance (Sherwood scientific MSB MK I) using  $\text{Co}[\text{Hg}(\text{SCN})_4]$  as a calibrant, and experimental magnetic susceptibilities were corrected for diamagnetism [21]. Thermal behaviours of title complexes were investigated by techniques: TG/DTA, DTG with derivatograph OD-102/1  $500^\circ\text{C}$ . The samples of 100 mg were heated in ceramic crucible in air static atmosphere.  $\alpha\text{-Al}_2\text{O}_3$  was 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; platinum crucible 100  $\mu\text{L}$ ; dynamic measurements were carried out in air or in argon atmosphere at flow rate of 1  $\text{L h}^{-1}$ ; sample of mass in the range ca. 9–11 mg (Figs 2 and 3);

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<sup>-1</sup>.

## Results and discussion

Reactions of metal trichloroacetates with 2,2'-bipyridine in ethanol (75% v/v) – water solution yield solid complexes of the composition Mn(2-bpy)<sub>2</sub>(CCl<sub>3</sub>COO)<sub>2</sub>, Co(2-bpy)<sub>2</sub>(CCl<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O and Ni(2-bpy)<sub>2</sub>(CCl<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O. The analytical, conductivity and magnetic data of compounds are collected in Table 1. The complexes of Co(II) and Ni(II) are right soluble in water; the compound of Mn(II) is fairly soluble (1.25·10<sup>-2</sup> mol L<sup>-1</sup>). The analysis of the diffractograms proved that these complexes are crystalline. Complex Ni(2-bpy)<sub>2</sub>(CCl<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O shows higher symmetry than other compounds. The molar conductance values of complexes in methanol fall within the generally acceptable range for electrolytes 1:1 [22]. Conductivity data suggested that all compounds in DMSO and Co(II) and Ni(II) complexes in DMF present intermediate behaviour between those of non- and 1:1 electrolytes. Higher than anticipated  $\Lambda_M$  values are usually due to the displacement of trichloroacetate ligand by a molecule of solvent. Similar behaviours were observed for Mn(II), Co(II) and Ni(II) complexes with 4-bpy and mono- or trichloroacetates [1, 2], and other metal(II) complexes with several amines [20, 23]. The very low molar conductance value indicate the non- electrolytic nature of the Mn(2-bpy)<sub>2</sub>(CCl<sub>3</sub>COO)<sub>2</sub> in DMF. The room temperature effective magnetic moment  $\mu_{\text{eff}}$  of Ni(II) complex corresponds to two unpaired electrons. The Ni(II) complex shows magnetic moment value of 3.84 M.B., which is in the range expected for octahedral complexes [12, 24]. The  $\mu_{\text{eff}}$  value for the Co(II) complex is 3.65 M.B., which is lower than observed range for octahedral complexes ( $\mu_{\text{eff, calcd}}$  3.88 M.B., observed in the range 4.30–5.20 M.B.). Sub-normal magnetic moment in the present compound suggests the possibility of at best a very weak interaction between the paramagnetic centres [25].

### *Electronic absorption spectra*

These spectra of solid Co(II) and Ni(II) complexes in Nujol mulls exhibit strong band above 26 000 cm<sup>-1</sup> which may be assigned to charge transfer transition. The ligand field spectra of these complexes are entirely consistent with a distorted octahedral donor environment around the metal ions [26]. The main absorption band at 20 800 cm<sup>-1</sup>, observed in spectra of Co(II) complex, can be attributed to the <sup>4</sup>T<sub>1g</sub>(P)←<sup>4</sup>T<sub>1g</sub>(F) and shoulder at 16 000 cm<sup>-1</sup> as <sup>4</sup>A<sub>2g</sub>←<sup>4</sup>T<sub>1g</sub>(F) transitions. The *d-d* bands of the Ni(II) complex are assigned to the following transitions: <sup>3</sup>T<sub>1g</sub>(F)←<sup>3</sup>A<sub>2g</sub> (17600 cm<sup>-1</sup>) and <sup>1</sup>E<sub>g</sub>←<sup>3</sup>A<sub>2g</sub> (12 800 cm<sup>-1</sup>, shoulder). The Rule of Average Environment (RAE) [26] has been applied to indicate of chromophores in the obtained solid complexes of cobalt(II) and nickel(II). The comparison of the values of  $\bar{\nu}_{\text{calcd}}=21\ 000\ \text{cm}^{-1}$  (for transition <sup>4</sup>T<sub>1g</sub>(P)←<sup>4</sup>T<sub>1g</sub>(F)) and  $\bar{\nu}_{\text{calcd}}=17\ 400\ \text{cm}^{-1}$  (for <sup>3</sup>T<sub>1g</sub>(F)←<sup>3</sup>A<sub>2g</sub>) with the experimental  $\bar{\nu}$  and supported by IR data, indicate that the following chromophores are presented in the compounds: CoN<sub>4</sub>O<sub>2</sub> and NiN<sub>4</sub>O<sub>2</sub> (where: O-form carboxylate groups).

**Table 1** Analytical data, molar conductivity,  $\kappa_m$  in MeOH, DMF and DMSO (concentration  $1 \cdot 10^{-3}$  mol L $^{-1}$ ) and effective magnetic moments,  $\mu_{\text{eff}}$  at 25°C

Complex	Colour	Analysis: found (calculated)/%				$\kappa_m$ / $\text{cm}^2 \text{mol}^{-1}$			$\mu_{\text{eff}}$ / M.B.
		M	C	N	H	MeOH	DMF	DMSO	
Mn(2-bpy) $_2$ (CCl $_3$ COO) $_2$	white	7.94 (7.42)	41.09 (41.65)	8.10 (8.52)	2.29 (2.33)	90.4	4.34	24.14	–
Co(2-bpy) $_2$ (CCl $_3$ COO) $_2$ ·H $_2$ O	orange	8.11 (8.25)	41.07 (40.37)	8.03 (8.05)	2.65 (2.54)	99.0	42.9	27.8	3.65
Ni(2-bpy) $_2$ (CCl $_3$ COO) $_2$ ·2H $_2$ O	green	7.90 (8.02)	40.05 (39.39)	8.00 (7.66)	2.89 (2.75)	111.6	48.8	32.8	3.84

### Infrared spectra

The IR spectrum of free 2-bpy changes owing to complex formation [27]. The most characteristic ring stretching C–C, C–N, C–C<sub>i.r.</sub> str. (symmetry  $A_1$ ) and C–N, C–C str. (symmetry  $B_1$ ) frequencies, appearing at 1579 and 1553  $\text{cm}^{-1}$  in a free ligand are observed in these compounds in the ranges 1604.7–1596.6  $\text{cm}^{-1}$  and 1575.7–1568.4  $\text{cm}^{-1}$ , respectively. The pyridine ‘breathing’ frequency is shifted by about 33–24  $\text{cm}^{-1}$  towards higher values. The characteristic out-of-plane hydrogen deformation modes in unbonded 2-bpy are observed of 753 and 738  $\text{cm}^{-1}$ ; the complexes exhibit very strong absorptions at 769.5–761.3 and 736.8–731.0  $\text{cm}^{-1}$ . The IR data at all isolated complexes show that they are *cis*-2,2’-bipyridine chelates [27, 28].

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

Assignment	CCl <sub>3</sub> COONa [29]	Complex		
		Mn(II)	Co(II)	Ni(II)
Coordinated 2-bpy modes				
C–C, C–N, C–C <sub>i.r.</sub> str.	–	1604.7	1604.7	1598.9
		1596.6	1600.8	
C–N, C–C str.	–	1569.0	1575.7	1575.7
			1568.8	1568.4
C–H out of plane bend	–	761.3	765.7	769.5
		731.0	732.9	736.8
Pyridine ‘breathing’	–	1014.5	1020.3	1024.1
Carboxylate group modes				
$\nu_{\text{as}}(\text{OCO})$	1677.0	1700.3	1708.8 pd	1718.8
			1688.5	1688.7
$\nu_{\text{s}}(\text{OCO})$	1353.0	1354.9	1350.1	1363.6
			1329.2	1317.3
$\Delta\nu = \nu_{\text{as}}(\text{OCO}) - \nu_{\text{s}}(\text{OCO})$	324.0	348.1	358.7	353.2
			358.4	371.2

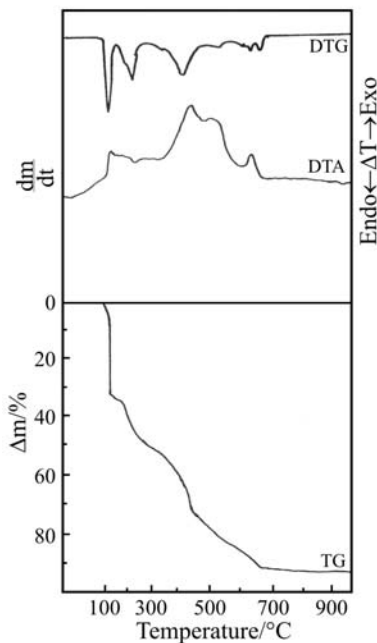
pd – poorly resolved doubler; i.r. – inter-ring bands

The IR spectra of studied complexes revealed also absorptions of the carboxylate group. Principal concern are the positions of the asymmetric ( $\nu_{\text{as}}$ ) and symmetric ( $\nu_{\text{s}}$ ) stretching frequencies and their separation ( $\Delta\nu = \nu_{\text{as}} - \nu_{\text{s}}$ ). These are listed in Table 2 for complexes, together with data for sodium salt. The asymmetric bands lie between 1718.8–1687.6  $\text{cm}^{-1}$  and are in all complexes, higher than the  $\nu_{\text{as}}(\text{OCO})$  of the CCl<sub>3</sub>COONa. Calculated from examined spectra values of  $\Delta\nu$  of complexes are in the range 348–371  $\text{cm}^{-1}$  and are higher than for sodium salt. This suggests the presence of thermal carboxylate groups in obtained complexes [7–12]. IR spectra of all complexes exhibit two clearly separated bands in the symmetric stretching frequency  $\nu_{\text{s}}(\text{OCO})$  region. This would seem to indicate that the complexes have a *cis*-configuration [12]. A

strong and broad band in the water stretching region (ca. 3050–3450  $\text{cm}^{-1}$ ) and only the shoulder in the water bending region (ca. 1625  $\text{cm}^{-1}$ ) for  $\text{Ni}(2\text{-bpy})_2(\text{CCl}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  complex are observed.

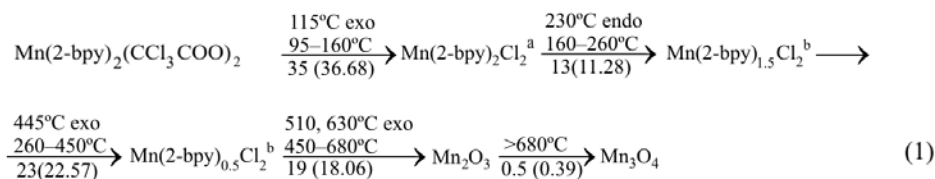
#### *Thermal properties of complexes in air*

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-bpy and carboxylate groups (for intermediate products of  $\text{Co}(2\text{-bpy})_2\text{Cl}_{1.5}(\text{CCl}_3\text{COO})_{0.5}$ ) or only bands of 2-bpy products of the type  $\text{M}(2\text{-bpy})_n\text{Cl}_2$ . In the sinters presence of anions  $\text{Cl}^-$  was investigated. They were in all intermediate products. 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 2. All the complexes decompose progressively. The anhydrous complex  $\text{Mn}(2\text{-bpy})_2(\text{CCl}_3\text{COO})_2$  begin decompose at about 95°C. Thermoanalytical curves of  $\text{Mn}(2\text{-bpy})_2(\text{CCl}_3\text{COO})_2$  in air is shown, as an example, in Fig. 1. A sudden mass loss was observed between 95–160°C, which corresponded to the composition,  $\text{Mn}(2\text{-bpy})_2\text{Cl}_2$  with trace of not burned carbon. The appropriate exothermic peak on DTA is at 115°C. Next, the step-



**Fig. 1** Thermoanalytical curves of  $\text{Mn}(2\text{-bpy})_2(\text{CCl}_3\text{COO})_2$ ; mass sample 100 mg

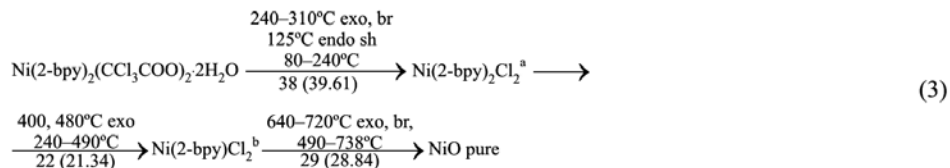
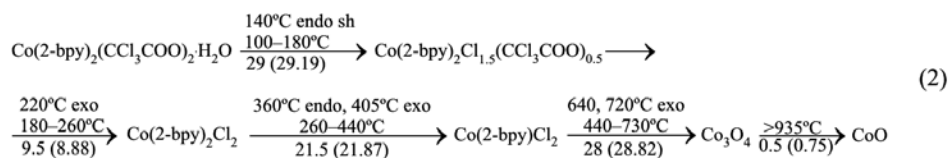
wise elimination of 2-bpy begins and  $\text{Mn}_2\text{O}_3$  forms. The deamination processes are partly overlap; on TG curve show only the bendings. According to the DTG curve [30] is probably, than 2-bpy is lost in three stages and intermediate forms  $\text{Mn}(2\text{-bpy})_{1.5}\text{Cl}_2$  and  $\text{Mn}(2\text{-bpy})_{0.5}\text{Cl}_2$ . Above  $680^\circ\text{C}$  the slow conversion  $\text{Mn}_2\text{O}_3$  to  $\text{Mn}_3\text{O}_4$  takes place (only diffraction lines characteristic of  $\text{Mn}_3\text{O}_4$  were detected). The very strong and broad exothermic effect on the DTA curve with centers is associated with the combustion of the organic ligands. The Scheme 1 of thermal decomposition of Mn(II) compound in air is:



<sup>a</sup>with ca. 1.5% C; <sup>b</sup>by projecting minimum of the DTG curve on TG curve

On Schemes 1–3 are shown below the arrows the mass values (%) found (without brackets) and those calculated (in brackets). Above the arrows there are presented ranges of decomposition and peaks from DTA ( $^\circ\text{C}$ ).

Hydrate complexes are stable up to  $100^\circ\text{C}$  (Co) and up to  $80^\circ\text{C}$  (Ni). The rapid mass loss observed on TG in range  $100\text{--}180^\circ\text{C}$  (Co) and  $80\text{--}240^\circ\text{C}$  (Ni) is connected with the dehydration and decomposition of trichloroacetates. Following intermediate compounds were detected:  $\text{Co}(2\text{-bpy})_2\text{Cl}_{1.5}(\text{CCl}_3\text{COO})_{0.5}$  (clearly separated step) and  $\text{Ni}(2\text{-bpy})_2\text{Cl}_2$  with trace of ca. 1.5% C. Between  $180\text{--}260^\circ\text{C}$   $\text{Co}(2\text{-bpy})_2\text{Cl}_2$  is formed. This stage of decomposition is followed by exothermic peak at  $220^\circ\text{C}$  for Co and broad exoeffect with center at ca.  $300^\circ\text{C}$  for the nickel complex. The intermediate complexes  $\text{M}(2\text{-bpy})_2\text{Cl}_2$  (where:  $M(\text{II})=\text{Co}, \text{Ni}$ ) appeared to more stable than the corresponding  $\text{Mn}(2\text{-bpy})_2\text{Cl}_2$  complex. The intermediate compounds  $\text{M}(2\text{-bpy})_2\text{Cl}_2$  deaminate in two stages. At first 1 mol of 2-bpy was eliminated to form  $\text{M}(2\text{-bpy})\text{Cl}_2$  (temperature range  $260\text{--}440^\circ\text{C}$  for Co and  $240\text{--}490^\circ\text{C}$  for Ni). In the case of the nickel compound this step is not clearly separated on the TG curve. On temperature elevation,  $\text{Co}(2\text{-bpy})\text{Cl}_2$  decompose via  $\text{Co}_3\text{O}_4$  to CoO. A horizontal mass level for NiO begins at  $738^\circ\text{C}$ . These oxides of metals(II) were verified by X-ray diffraction patterns registration. DTA curves present mixture of several endo- and exothermic peaks. The very strong exothermic maxima with center at:  $405, 640, 720^\circ\text{C}$  (Co) and broad exothermic effects in the range  $240\text{--}310, 640\text{--}720^\circ\text{C}$  (Ni) correspond to pyrolysis of organic ligands. Schemes of thermal decomposition of Co(II) and Ni(II) complexes can be expressed as:



<sup>a</sup>with trace of ca. 1.5% C; <sup>b</sup>by projecting minimum of the DTG curve on TG curve; sh-shoulder; br-broad

Thermal stability of obtained complexes in argon atmosphere was not analyzed.

#### Mass spectrometric analysis

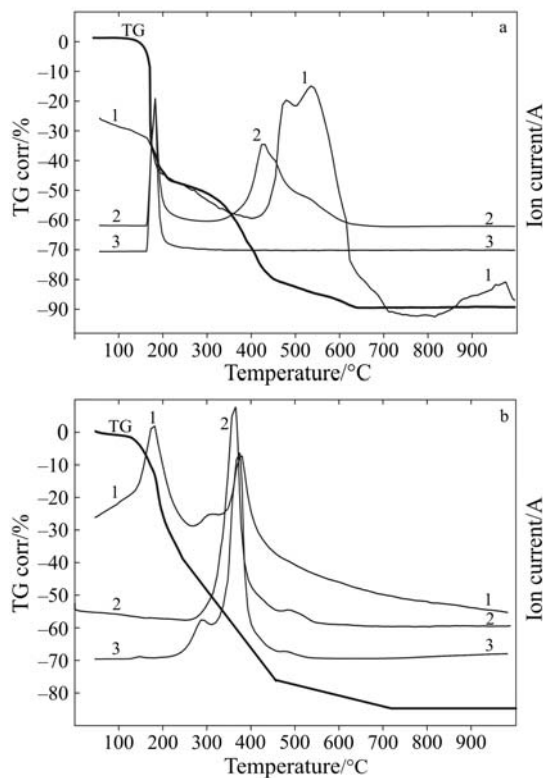
Mass spectrum measured obtained during thermal decomposition and fragmentation processes in air of complexes showed presence of several ion signals intensities. The  $m/z$  values are given based on:  $^1\text{H}$ ,  $^{12}\text{C}$ ,  $^{16}\text{O}$ ,  $^{14}\text{N}$  and  $^{35}\text{Cl}$ .

In air atmosphere major maxima of ion current signals are observed at ca. 183 and 430–450°C for Mn(II) compound. The MS peaks coincide with mass decrease appeared on TG. In the temperature ca. 183°C, dominate in gases the molecular ions  $\text{CO}_2^+$  ( $m/z=44$ ), formed probably by decomposition of carboxylate groups. In this region of temperatures, ion signals was detected also for:  $\text{Cl}_2^+$  ( $m/z=70$ ) and traces of other signals. At higher temperatures ca. 430–450°C further maxima for  $\text{CO}_2^+$  occur; additional signals with  $m/z=30, 76, 78$  ( $\text{NO}^+$ ,  $\text{N}_2\text{O}_3^+$  and 2-bpy $\cdot^+$  radical) were observed. Many ion signals in these temperatures correspond to total decomposition of trichloroacetate anions; next probably release and pyrolysis of 2-bpy takes place. Maximum rates of forming  $\text{NO}^+$  at 478, 536°C and  $\text{N}_2\text{O}_3^+$  at 451°C are observed.

The total amount and relative abundance of ions current for Co(II) and Ni(II) complexes are sufficiently similar to those detected for Mn(II) complex. In the case of Co(II) compound many maxima of signals take place at ca. 164–180 and 385–420°C, and for Ni(II) complex at ca. 148 and 359–376°C. Generally, varieties in the ion currents for Mn(2-bpy) $_2$ (CCl $_3$ COO) $_2$ , Co(2-bpy) $_2$ (CCl $_3$ COO) $_2$ ·H $_2$ O and Ni(2-bpy) $_2$ (CCl $_3$ COO) $_2$ ·2H $_2$ O complexes are following: in the case of Co(II) complex many maxima for ion currents are shifted by ca. 20°C for Ni(II) complex by ca. 50–70°C to lower temperatures. MS peaks of H $_2$ O $^+$  ( $m/z=18$ ) appeared at ca. 164, 500°C (Co) and 179, 376°C (Ni). The strong peaks  $\text{CO}_2^+$  ( $m/z=44$ ) were observed at: 242, 421, 551°C for Co(II) complex and 290, 372 and 480°C (Ni). The peaks of  $\text{NO}^+$  appeared at 425, 555°C (Co) and 373°C (Ni). Correla-

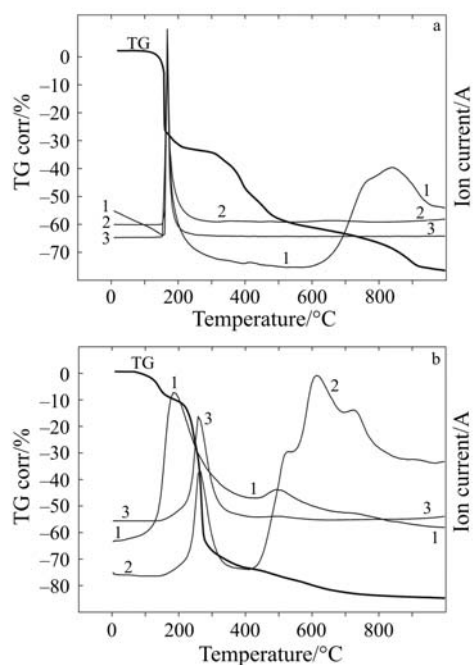


tion of some  $m/z$  observed by MS with TG curves for Mn(II) and Ni(II) compounds is shown as an example in Fig. 2.



**Fig. 2** TG curve and ion current detected by the MS in air for:  
 Mn(2-bpy)<sub>2</sub>(CCl<sub>3</sub>COO)<sub>2</sub>, sample mass 11.61 mg,  $m/z$ : 1–30; 2–44; 3–70;  
 a – order of the magnitude of ion currents/A: E-10, E-09, E-12, respectively,  
 Ni(2-bpy)<sub>2</sub>(CCl<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O, sample mass 9.04 mg,  $m/z$ : 1–18; 2–30; 3–44;  
 b – order of the magnitude of ion currents/A: E-09, E-10, E-09, respectively

In argon the main peaks of MS occur in region of lower temperatures at ca. 165–170°C (Mn), 243–268°C (Co), 167–193 and 278–284°C for Ni(II) complex. MS data detected only some ions signal. Major profiles for ions current are observed with  $m/z$ : 18 (only for Co(II) and Ni(II)), 27, 44 and traces of 70 and 78. At higher temperatures only certain smaller peaks are observed. Additionally in argon atmosphere the elimination of signal with  $m/z=28$  (which corresponds to CO<sup>+</sup> or N<sub>2</sub><sup>+</sup>) is observed. The MS peaks with  $m/z=28$  appeared at: 168, 843°C (Mn), 265, 520, 613, 731°C (Co) and 278, 517°C for Ni(II) complex; on the other hand, the main peaks of CO<sub>2</sub><sup>+</sup> appeared at: 168°C (Mn), 260°C (Co) and 282, 511°C for Ni(II) compounds. The maximum



**Fig. 3** TG curve and ion current detected by the MS in argon for:  
 Mn(2-bpy)<sub>2</sub>(CCl<sub>3</sub>COO)<sub>2</sub>, sample mass 8.47 mg, *m/z*: 1–28; 2–44; 3–70;  
 a – order of the magnitude of ion currents/A: E-09, E-09, E-12, respectively,  
 Co(2-bpy)<sub>2</sub>(CCl<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O, sample mass 9.37 mg, *m/z*: 1–18; 2–28; 3–44;  
 b – order of the magnitude of ion currents/A: E-09, E-10, E-09, respectively

rate of elimination of H<sub>2</sub>O<sup>+</sup> occurs at around 188°C (Co) and 193°C (Ni). TG coupled with MS data for some *m/z* are presented in Fig. 3.

## Conclusions

New mixed-ligand complexes of general formulae M(2-bpy)<sub>2</sub>(CCl<sub>3</sub>COO)<sub>2</sub>·*n*H<sub>2</sub>O (where *n*=0 for Mn, *n*=1 for Co and *n*=2 for Ni) were prepared as crystalline compounds. The complexes of M(II) with trichloroacetate and 2-bpy or 4-bpy have analogous molar ratio of metal to organic ligands 1:2:2 (anhydrous or hydrate) except Mn(4-bpy)(CCl<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O. The obtained compound Ni(2-bpy)<sub>2</sub>(CCl<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O is new complex with ligand isomerism. Previously we described a similar complex with 4-bpy [2].

IR data show, that obtained compounds M(2-bpy)<sub>2</sub>(CCl<sub>3</sub>COO)<sub>2</sub>·*n*H<sub>2</sub>O are *cis*-bis 2,2'-bipyridine chelates. The carboxylate group acts as monodentate in these complexes. In the case of mixed-ligand complexes of Mn(II) and Co(II) with 4,4'-bipyridine and trichloroacetates, the carboxylate ion is bonded as a bidentate chelating ligand [2]. The way of metal-carboxylate coordination probably depends on bipyridine structure. Hence

the complexes have different structures and different thermal properties. The complex  $\text{Ni}(2\text{-bpy})_2(\text{CCl}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  is thermally more stable than analogous complex with 4-bpy; for complex with 2-bpy the step of elimination of water was not observed. The stoichiometry of intermediate products of thermal decomposition also depends on the nature metal-ligand bonds. In the case of mixed-ligand 2-bpy complexes  $\text{M}(2\text{-bpy})_2\text{Cl}_2$  as intermediate solid compounds were detected. These compounds lose 2-bpy in several stages, and convert to oxides. The mixed 4-bpy complexes decompose to oxides *via* unidentified products and  $\text{MnCl}_2$  or  $\text{CoCl}_2$  (formation of  $\text{NiCl}_2$  was not observed). The MS data show, that the principal profiles with  $m/z$  detected at the temperature range 20–1000°C for metal(II) complexes with 2-bpy (or 4-bpy) and trichloroacetates are very similar only major maxima of ion current are a little shifted. Other observations made in this paper are similar to those made in the case of metal(II) complexes with 4-bpy and trichloroacetates [2, 31].

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