Journal of Thermal Analysis and Calorimetry, Vol. 67 (2002) 667–678

THERMAL AND OTHER PROPERTIES OF NEW 4,4’-BIPYRIDINE-TRICHLOROACETATO COMPLEXES OF Mn(II), Ni(II) AND Zn(II)

D. Czakis-Sulikowska, A. Czylkowska and A. Malinowska

Institute of General and Ecological Chemistry, Technical University of Łódź, 90-924 Łódź, Poland

(Received May 3, 2001)

Abstract

New mixed-ligand complexes of general formulae $Mn(4\text{-bpy})(CCl_3COO)_2{\cdot}H_2O$, $Ni(4\text{-bpy})_2(CCl_3COO)_2{\cdot}2H_2O$ and $Zn(4\text{-bpy})_2(CCl_3COO)_2{\cdot}2H_2O$ (where *4-bpy*=4,4’-bipyridine) were obtained and characterized. The IR spectra, conductivity measurements and other physical properties of these compounds were discussed. The central atoms M(II) form coordinate bonds with title ligands. The thermal behaviour of the synthesized complexes was studied in air. During heating the complexes decompose *via* different intermediate products to Mn_3O_4, NiO and ZnO; partial volatilization of $ZnCl_2$ was observed. A coupled TG-MS system was used to the analysis of the principal volatile thermal decomposition products of Mn(II) and Ni(II) complexes. The principal volatile mass fragments correspond to: H_2O^+, OH^+, CO_2^+, HCl^+, Cl_2^+, CCl^+ and other.

Keywords: 4,4’-bipyridine, IR spectra, mass spectrometry, thermal decomposition, transition-metal complexes, trichloroacetate

Introduction

The work presented here is a continuation of our studies on transition–metal complexes with bipyridine isomers and carboxylates [1–7]. The properties of mixed acetato-bipyridine complexes of metal(II) have been the subject of extensive investigations during the last years. The nature of bonds between M(II) ions and acetate ions and bipyridine isomers (2,2’-, 4,4’-, 2,4’-bpy) is discussed in [1, 2, 7–10]. Thermal behaviour of the mixed complexes of the formula $M(CH_3COO)_2(2,4'\text{-bpy})_2{\cdot}2H_2O$ (where *M*(II)=Mn, Co, Ni, Cu, Zn, Cd) also was studied [1, 2, 7]. However, there is scanty information on the mixed-ligand complexes of metal(II) with bipyridine and chloroacetates. The presence of halogen atoms in the carboxylate ligands does not take place in the coordination of metal ion but their influence on the structure and properties of the complexes is considerable. The complexes of the formulae $[Zn(\mu\text{-}4\text{-bpy})(4\text{-bpy})_2(CCl_3COO)_2(H_2O)_4]_n$ and $[Zn(2\text{-bpy})(CCl_3COO)_2{\cdot}(H_2O)]$ were described by Sen *et al*. [11]. Shova *et al*. [12] have prepared trichloroacetate of manganese(II) and its molecular structure has been determined. Thermal decomposition of some copper(II) halogenoacetates was carried out by Obier *et al*. [13] and described in

1418–2874/2002/ $ 5.00
© 2002 Akadémiai Kiadó, Budapest
Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

other papers [14, 15]. Thermal properties of zinc(II) monochloroacetates and its complexes with nicotinamide and caffeine were reported by Zeleňák *et al*. [16].

In our earlier papers [17, 18] we described the preparation, IR and VIS spectra and thermal decomposition of complexes: M(4-bpy)$_2$(ClCH$_2$COO)$_2$·nH$_2$O (where *M*(II)= Mn, Co, Ni, Cu), M(4-bpy)$_2$(CCl$_3$COO)$_2$·nH$_2$O (*M*(II)=Co, Cu) and Cd(4-bpy)(CCl$_3$COO)$_2$·H$_2$O. IR studies of mixed 4,4'-bipyridine–trichloroacetato complexes of Co(II), Cu(II) and Cd(II) indicate that 4-bpy is coordinated with metal ions and the trichloroacetate groups are bonded as bidentate chelating ligands. The principal volatile thermal decomposition products in air of those complexes were identified. It was thus of interest to examine the behaviour of 4-bpy and trichloroacetate groups in other mixed-ligand complexes.

In this paper we present the results of the synthesis and properties of new mixed-ligand complexes of Mn(II), Ni(II) and Zn(II) with 4-bpy and trichloroacetates. The thermal decomposition of obtained compounds was investigated in air. The TG-MS system was used to analyse the principal volatile thermal decomposition products of these complexes.

Experimental

Materials

4,4'-bipyridine (*m.p.* 69.9°C) and trichloroacetic acid p.a. were obtained from Aldrich; methanol (anhydroscan) was from Lab. Scan. Hydroxyloamine (50% v/v water solution) was purchased from Fluka. The remaining starting materials were p.a. from POCh-Gliwice. Water solutions of metal(II) trichloroacetates were prepared by adding 20 mL 2 M trichloroacetic acid to freshly precipitated metal(II) carbonate in ca. stoichiometric quantities. In the case of the preparation of Mn(CCl$_3$COO)$_2$ the reaction mixture contains 2 mL of 10% *v/v* hydroxyloamine (to stop the oxidation process of Mn(II)). The metal(II) contents in solutions of trichloroacetates were analysed by complexometry.

Table 1 Analytical data, effective magnetic moments μ_{eff} (B.M.) at room temperature, solubility S (mol L^{-1}) in water at 21°C and molar conductivity Λ_M (Ω^{-1} cm^2 mol^{-1}) in methanol (concentration $1\cdot10^{-3}$ mol L^{-1}) at 25°C of the complexes (where L=CCl$_3$COO$^-$)

Complex (colour)	Analysis found (calculated)/%				μ_{eff}	$S\cdot10^3$	Λ_M
	M	C	N	H			
Mn(4-bpy)L$_2$·H$_2$O (white)	10.15 (9.92)	30.66 (30.36)	5.26 (5.06)	1.78 (1.82)	5.72	1.48	96.9
Ni(4-bpy)$_2$L$_2$·2H$_2$O (light-green)	7.60 (7.66)	39.50 (39.39)	8.05 (8.02)	2.62 (2.75)	3.61	0.30	62.1
Zn(4-bpy)$_2$L$_2$·2H$_2$O (white)	9.33 (8.85)	39.22 (39.03)	8.00 (7.59)	2.80 (2.73)	–	0.13	75.3

Synthesis of complexes

A solution of 4-bpy (12.8 mmol) in 96% *v/v* ethanol (31.3 mL) was added to freshly obtained solution of metal(II) trichloroacetate (4.3 mmol) in water (8.7 mL) at room temperature. The precipitate was filtered off, washed with 40% *v/v* ethanol and then with ethanol-diethyl ether mixture (1:1) and dried in open air. The contents of C, H and N were determined by elemental analysis with V_2O_5 as oxidizing agent; metal(II) in mineralized samples of the obtained compounds was determined complexometrically. These analytical results are presented in Table 1.

Measurements

The thermal stability of the complexes was studied by TG, DTG and DTA. Measurements were made by using a derivatograph Q-1500 at heating rate 10°C min^{-1}. α-Al_2O_3 served as reference material. The samples (100 mg) were heated in the range 25–1000°C in air atmosphere. Mass spectrometer was used for the characterization of volatile thermal decomposition products of the Mn(II) and Ni(II) complexes (with samples of mass 5.18 and 8.73 mg, respectively). The TG-MS system: derivatograph TG/DTA-SETSYS-16/18, mass spectrometer ThermoStar from Balzers, platinum crucible 100 μL. The other apparatus and experimental conditions were described in previous papers [1, 2, 19].

Results and discussion

The analytical results for the obtained compounds are collected in Table 1, together with other characteristic data. All of the complexes are air stable. The solubilities of compounds in water at 21°C are in the order of 10^{-3} mol L^{-1}. All the complexes dissolved fairly in methanol, decomposed in aqueous acid and alkali and were insoluble in most organic solvents (CCl_4, $CHCl_3$, $(CH_3)_2CO$). The molar conductivities in methanol indicate that the complex $Mn(4\text{-bpy})(CCl_3COO)_2{\cdot}H_2O$ behaves as 1:1 electrolyte, while the remaining complexes show intermediate behaviour between those of non- and 1:1 electrolytes [20]. Higher than the expected values of molar conductivities are possible due to the substitute of trichloroacetate ligands by solvent molecules. Similar situation was observed in metal complexes with bipyridine and other ligands [4, 17, 18]. The experimental magnetic moments of $Mn(4\text{-bpy})(CCl_3COO)_2{\cdot}H_2O$ (5.72 M.B.) and $Ni(4\text{-bpy})_2(CCl_3COO)_2{\cdot}2H_2O$ (3.61 M.B.) are close to the values calculated for the metal ion in octahedral environment [21].

Spectroscopic characteristics

For consistency, only fundamental vibration modes of 4-bpy and OCO groups for synthesized complexes are reported in Table 2. Infrared spectra of Mn(II), Ni(II) and Zn(II) complexes with 4-bpy have several absorption bands characteristic of CC, CN and CH of the bipyridine and are in good accord with the previous observations on their complexes with metal salts [3, 8, 17, 18]. IR spectra of these compounds suggest that 4-bpy is coordinated to a metal ion.

Table 2 Principal IR bands (cm^{-1}) for 4-bpy and OCO groups in free ligands and their complexes

Assignment	4-bpy	CCl_3COONa [22]	Complexes		
			Mn(II)	Ni(II)	Zn(II)
		4-bpy modes			
$\nu_{(C=N)}$	1596.9 vs		1604.7 vs	1610.5 vs	1608.5 vs
$\nu_{(C=C)}$	1531.4 s		1533.3 s	1537.2 s	1535.2 s
$\gamma_{(CH)}$	810.0 vs		825.5 vs	812.0 s	810.0 vs
γ_r^a	993.3 vs		1006.8 m	1010.6 w	1010.6 w
		carboxylate group modes			
$\nu_{as(OCO)}$		1677.0	1676.4 vs 1666.4 vs	1693.4 vs	1691.5 vs, pd 1683.7 vs, pd
$\nu_{s(OCO)}$		1353.0	1384.8 vs 1352.0 vs	*	1375.0 vw
$\nu_{(MO)}+\delta_{(OCO)}$			432.0 w 466.7 w	455.2 s pd 474.5 s pd	472.5s
$\Delta\nu$		324.0	291.2 314.4	–	316.5 308.7

${}^a\gamma_r$ – ring 'breathing' mode; $\Delta\nu=\nu_{as(OCO)}-\nu_{s(OCO)}$; * – overlaid by 4-bpy absorption;
v, s, m, w, pd – very, strong, medium, weak, poorly resolved doublet

The principal absorption bands $\nu_{as(OCO)}$ and $\nu_{s(OCO)}$ of CCl_3COONa and its complexes are also given in Table 2. The compounds present carboxylate stretching frequencies, $\nu_{as(OCO)}$ at the range 1693.4–1666.4 cm^{-1} and $\nu_{s(OCO)}$ at 1384.8–1352.0 cm^{-1}. The analysis of OCO group bands frequencies allowed the determination of parameter $\Delta\nu=\nu_{as(OCO)}-\nu_{s(OCO)}$, whose magnitude is used as a criterion of the carboxylate bonding with metal ions. Calculations from the examined spectra of Mn(II) and Zn(II) complexes give $\Delta\nu$ values in the range 316.5–291.2 cm^{-1}, less than for the sodium salt ($\Delta\nu$=324 cm^{-1}). According to this fact it is possible to assume that the carboxylate ion is bonded as a bidentate chelating ligand [23–26]. However, the $\nu_{as(OCO)}$ and $\nu_{s(OCO)}$ bands of Mn(II) complex and $\nu_{as(OCO)}$ band of Zn(II) complex are splitted into doublet. From here is probable that non-completely equivalent degree of ionity of bonds formed between M(II) and carboxylate groups of the trichloroacetate ligand exist [27, 28]. The frequency $\nu_{s(OCO)}$ for Ni(II) complex is superimposed by the absorption of the 4-bpy. Thus, it is difficult to discuss the nature of the nickel-trichloroacetate bonds. The $\nu_{(M-O)}+\delta_{(OCO)}$ vibrations are observed in the interval ca. 474.5–432.0 cm^{-1}.

IR spectra of complexes exhibit broad absorption bands in the water stretching region (3440–3500 cm^{-1}). The H_2O wagging vibration of coordinated water is observed at 536.2 cm^{-1} only for Mn(II) complexes.

VIS spectra was obtained in Nujol mulls for the nickel(II) complex within the 26 000–12 000 cm^{-1} region. The observed bands at 12 200, 16 800 and 25 000 cm^{-1} we ascribe to the following transitions: ${}^1E_g$, ${}^3T_{1g}(F)$ and ${}^3T_{1g}(P)$, respectively. The electronic spectrum of this complex is consistent with a distorted octahedral environment around the nickel atom [21, 29].

Thermal behaviour of synthesized compounds

Based on the thermal and chemical analysis, supported by powder X-ray diffraction and TG-MS investigations, the following data for thermal decomposition of obtained complexes are deduced. The hydrated complexes with Ni(II) and Zn(II) are very unstable and begin to lose water between 65–150 and 60–95°C, respectively. The dehydration processes are accompanied by small endothermic effects. The $Mn(4\text{-bpy})(CCl_3COO)_2{\cdot}H_2O$ is thermally the most stable. It starts to elimination of H_2O at 120°C.

Anhydrous compounds decompose to oxides *via* intermediate formation of different products. X-ray analysis of decomposition residue showed that Mn_3O_4, NiO and ZnO are formed as final products. The TG curves for all anhydrous complexes exhibit multiple, overlapping mass loss steps, from which only some can be defined. The first step of decomposition is characterized by a sudden mass loss between 190–230 (Mn), 150–200 (Ni) and 100–180°C (Zn). In this step the pyrolysis of organic ligands begins; probably decomposition of carboxylate anions takes place (TG–MS measurements). The strong exothermic peaks appear on the DTA curves. The further mass loss observed in the TG curves within the temperature interval 230–610 (Mn), 200–610 (Ni) and 180–300°C (Zn) is caused by consecutive thermal decomposition of the residues of organic ligands. The DTA curves show several exothermic peaks in this stage.

In the case of Mn(II) complex at 610°C, the $MnCl_2$ was identified. On temperature elevation, $MnCl_2$ decomposes *via* Mn_2O_3 to Mn_3O_4. The thermal decomposition of the $Mn(4\text{-bpy})(CCl_3COO)_2{\cdot}H_2O$ complex can be expressed by the Scheme 1:

$$Mn(4\text{-bpy})(CCl_3COO)_2{\cdot}H_2O \xrightarrow[3.4\ (3.25)]{120-190\,^{\circ}C} Mn(4\text{-bpy})(CCl_3COO)_2$$

$$\xrightarrow[40]{\substack{225\,\text{exo}\\ 190-230\,^{\circ}C}} \text{intermediate solid products} \xrightarrow[33.5]{\substack{500,590\,\text{exo}\\ 230-610\,^{\circ}C}} MnCl_2 \xrightarrow[8.5\ (8.47)]{\substack{650\,\text{exo}\\ 610-700\,^{\circ}C}} \qquad (1)$$

$$Mn_2O_3 \xrightarrow[0.5\ (0.48)]{>700\,^{\circ}C} Mn_3O_4$$

On Schemes 1–3 are shown below the arrows the mass loss values (%) found (without brackets) and those calculated (in brackets). Above the arrows there are presented ranges of decomposition and peaks from DTA (°C).

The anhydrous complex $Ni(4\text{-bpy})_2(CCl_3COO)_2$ decomposed directly to NiO *via* the formation of undefined intermediate products. The TG curve shows two bendings at 200 and 430°C. The exothermic effects on DTA curve are very strong and broad. A constant mass level for pure NiO (found 10.0%; calcd 10.21%) begins at 610°C. The Scheme of thermal decomposition of Ni(II) compound is:

$$Ni(4\text{-bpy})_2(CCl_3COO)_2{\cdot}2H_2O \xrightarrow[5.0\ (4.92)]{\substack{100\,\text{endo}\\ 65-150\,^{\circ}C}} Ni(4\text{-bpy})_2(CCl_3COO)_2 \qquad (2)$$

$$8.5\ (8.47) \xrightarrow[32.0]{\substack{200-300\,\text{exo}^{a}\\ 150-200\,^{\circ}C}} \text{intermediate solid products} \xrightarrow[53.5]{\substack{480-520\,\text{exo}^{a}\\ 200-610\,^{\circ}C,53.5}} NiO$$

[a] very strong and broad

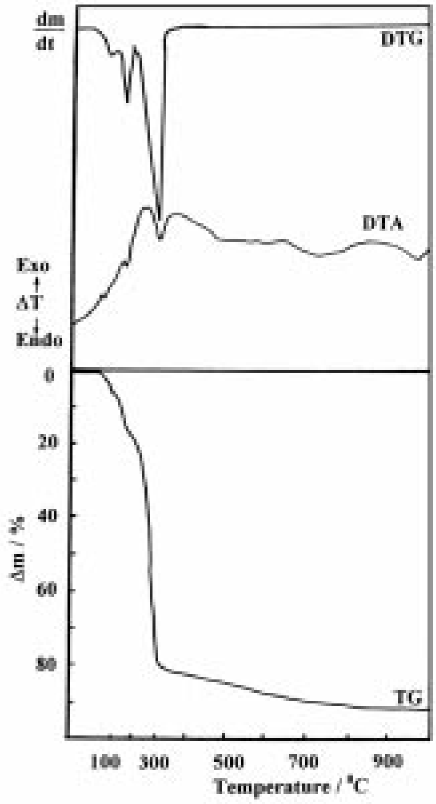

Fig. 1 Thermoanalytical curves of $Zn(4\text{-}bpy)_2(CCl_3COO)_2\cdot 2H_2O$; mass sample of 100 mg

In contrast to the Ni(II) complex, anhydrous $Zn(4\text{-}bpy)_2(CCl_3COO)_2$ decomposed to ZnO *via* undefined products (formed during the thermal decomposition process) and $ZnCl_2$ (Fig. 1). The mass loss is very rapid; the TG curve show only one bending at 180°C. The pure $ZnCl_2$ we identified at 300°C (found 18.5%; calcd. 18.45%). Further mass loss is due to the partial volatilization of $ZnCl_2$ and ZnO is formed. The calculated mass loss for conversion of $ZnCl_2$ into ZnO is 7.43, whereas the recorded loss is 10.0%. These transformations are accompanied by several exo- and endoeffects. Following Scheme is proposed for decomposition process of $Zn(4\text{-}bpy)_2(CCl_3COO)_2\cdot 2H_2O$ complex:

$$Zn(4\text{-}bpy)_2(CCl_3COO)_2\cdot 2H_2O \xrightarrow[5.0\ (4.88)]{\overset{70\ \text{endo}}{65-95^\circ\text{C}}} Zn(4\text{-}bpy)_2(CCl_3COO)_2 \xrightarrow[13.5]{\overset{160\ \text{endo}}{100-180^\circ\text{C}}}$$

$$\text{intermediate solid products} \xrightarrow[64.5]{\overset{272\,\text{exo},\,300\ \text{endo}}{180-300^\circ\text{C}}} ZnCl_2 \xrightarrow[10.0\ (7.43)]{>300^\circ\text{C}} \text{process of partial} \tag{3}$$

$$\text{volatilization of } ZnCl_2 \text{ and formation of ZnO.}$$

Mass spectrometric thermal analysis

In this paper, a coupled TG-MS system was used to analyse of volatile fragments evolved during the dynamic thermal decomposition of Mn(4-bpy)$(CCl_3COO)_2 \cdot H_2O$ and Ni$(4\text{-bpy})_2(CCl_3COO)_2 \cdot 2H_2O$ in air atmosphere. Data for some decomposition products (ion current for *m/z* detected in the mass spectrometry *vs*. temperature) are presented in Figs 2 and 3. In these figures the profiles for MS are not presented,

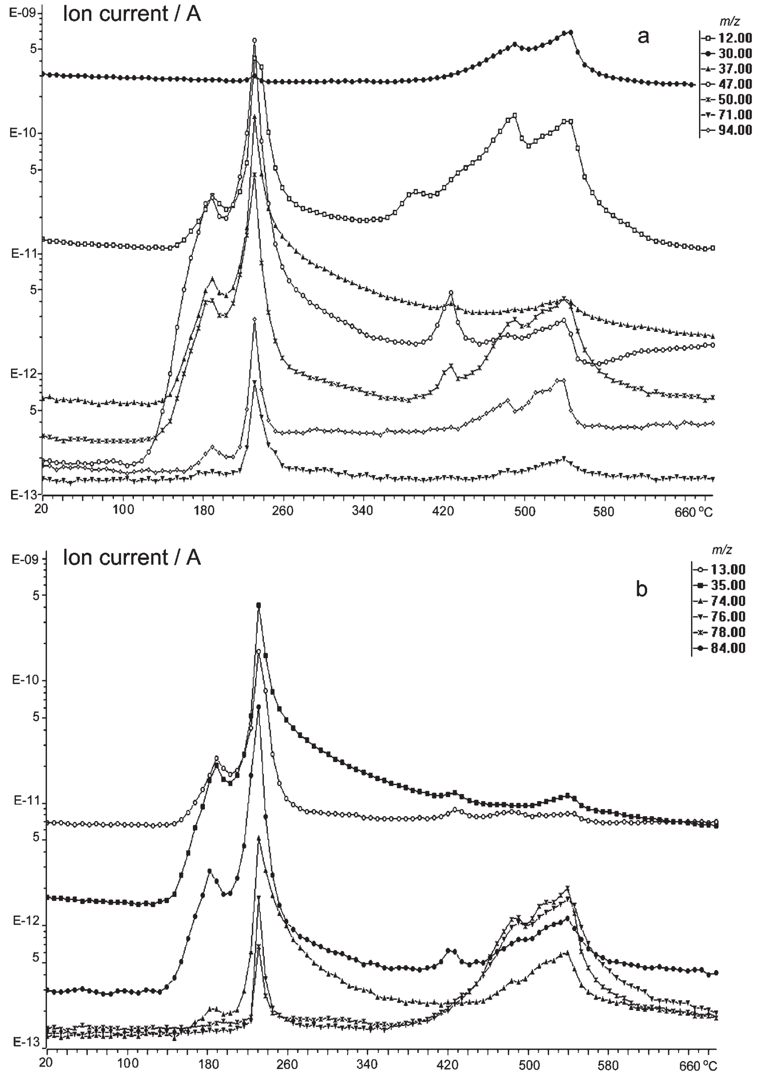

Fig. 2 Ion current for *m/z* detected in the mass spectrometry *vs*. temperature (not present the profiles, which curves are given in Fig. 4). Complex Mn(4-bpy)$(CCl_3COO)_2 \cdot H_2O$, mass sample 8.73 mg

which curves are given in Figs 4 and 5, where TG-MS data are listed. Obtained results show that many ion signals intensities are observed.

Major maxima of ion current appear at ca.: 190, 230, 490 and 540°C for Mn(II) compound. The mass spectra measured at low temperatures (MS peaks 190–230°C) suggested that material volatilized contains the several substances, corresponding

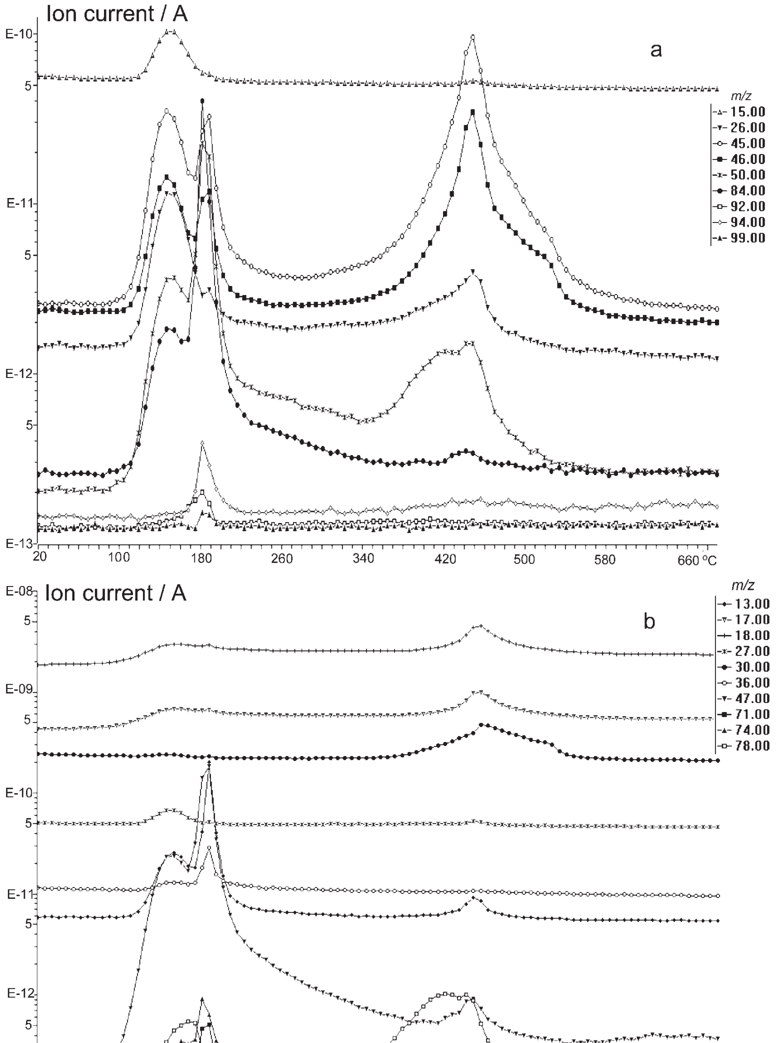

Fig. 3 Ion current for *m/z* detected in the mass spectrometry *vs*. temperature (not present the profiles, which curves are given in Fig. 5). Complex Ni(4-bpy)$_2$(CCl$_3$COO)$_2$· 2H$_2$O, mass sample 5.18 mg

perfectly to the first sudden mass loss represented by TG curve. In gases molecular ions CO_2^+ (m/z=44), formed probably by decomposition of carboxylate groups dominate. The profiles observed for CO_2^+ and its isotopes are similar, only relative intensities of ion currents (m/z=45, 46) are low. In this region of temperatures, ion signals were detected for: H_2O^+, OH^+, C^+, Cl^+, HCl^+, Cl_2^+, NO^+, $N_2O_3^+$, $C_2H_2^+$, CCl^+ (m/z=18, 17, 12, 35, 37, 36, 70, 74, 30, 76, 26, 47, respectively) and traces of other ion signals. At higher temperatures (MS peaks at 490 and 540°C) the presence of the greater part

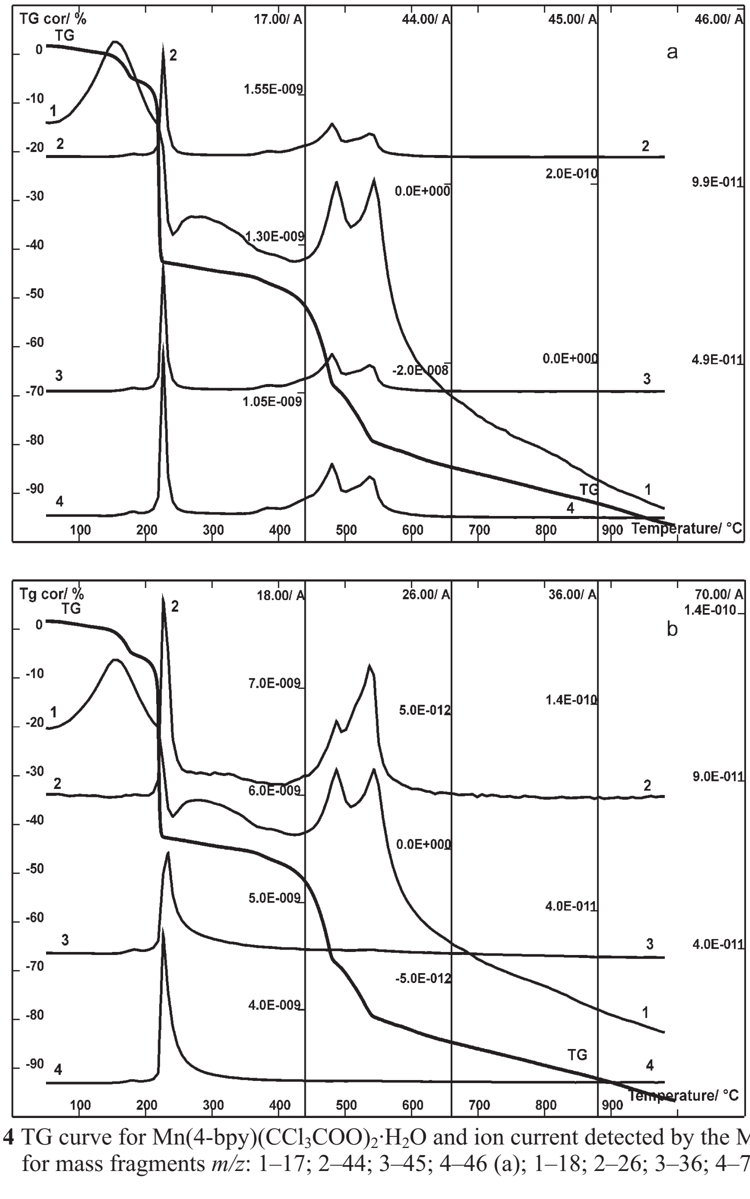

Fig. 4 TG curve for $Mn(4\text{-}bpy)(CCl_3COO)_2{\cdot}H_2O$ and ion current detected by the MS for mass fragments m/z: 1–17; 2–44; 3–45; 4–46 (a); 1–18; 2–26; 3–36; 4–70 (b)

of the same ion signals was also shown; for example, the MS peaks of CO_2^+ appeared additionally at 482 and 538°C. Maximum rates of forming of NO^+ (*m/z*=30) at 482°C, $N_2O_3^+$ at 488 and 540°C are observed. The very low intensity of ion current occurs for *m/z*=78 (probably 4-bpy radical). In air atmosphere CO was not detected. Apparent in these temperature ranges MS peaks for Mn(II) complex corresponded to total pyroly-

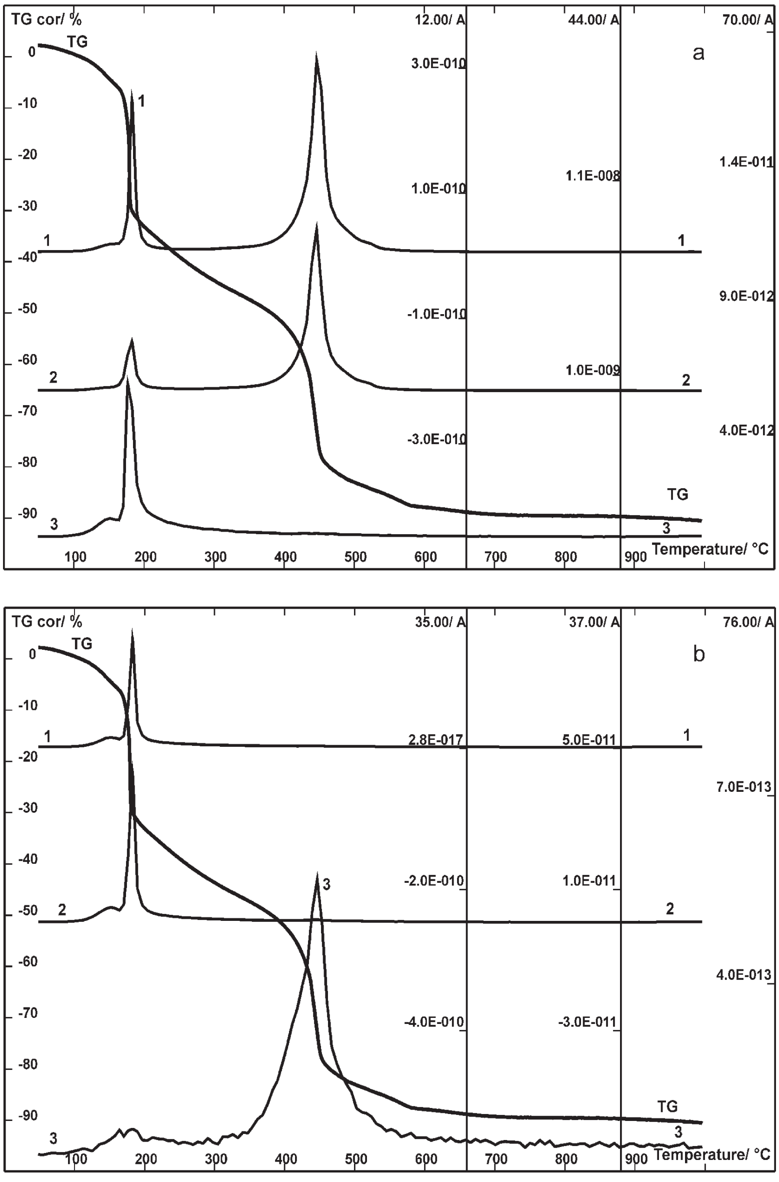

Fig. 5 TG curve for $Ni(4\text{-bpy})_2(CCl_3COO)_2\cdot 2H_2O$ and ion current detected by the MS for mass fragments *m/z*: 1–12; 2–44; 3–70 (a); 1–35; 2–37; 3-76 (b)

sis of organic ligands. Correlation of some decomposition gaseous products observed by MS with TG curve is presented in Fig. 4.

The total amount and relative abundance of volatile substances produced during pyrolysis of Ni(II) complex are very similar to those of detected for Mn(II) complex. In the case of Ni(II) complex many maxima of signals take place at ca.: 150, 185 and 450°C. In contrast to the $Mn(4\text{-bpy})(CCl_3COO)_2\cdot H_2O$ maxima for ion currents are shifted by ca.: 40–45°C to lower temperatures and not observed MS peaks at ca. 540°C for $Ni(4\text{-bpy})_2(CCl_3COO)_2\cdot 2H_2O$. Figure 3 shows that the corresponding MS peak for coordination water appeared at 154°C, and for H_2O produced during decomposition of organic ligand at 452°C. Very strong peaks CO_2^+ ($m/z=44$) were present at 182 and 448°C; HCl^+ at 155, 183°C and Cl_2^+ at 151, 178°C. TG coupled with MS data for some decomposition products are shown in Fig. 5.

The gaseous products decomposition of $Zn(4\text{-bpy})_2(CCl_3COO)_2\cdot 2H_2O$ were not investigated.

Conclusions

Three new mixed-ligand complexes of general formulae $M(4\text{-bpy})_2(CCl_3COO)_2\cdot 2H_2O$ (M(II)=Ni, Zn) and $Mn(4\text{-bpy})(CCl_3COO)_2\cdot H_2O$ were prepared as small-crystalline compounds. It can be stated that 4-bpy is coordinated to metal(II). The values of $\Delta\nu=\nu_{as(OCO)}-\nu_{s(OCO)}$ for Mn(II) and Zn(II) complexes correspond to the chelating character of carboxylate groups. However, on the basis of the IR and conductance measurements, we conclude that nonequivalent bonds between these metals(II) and carboxylate groups of trichloroacetate ligand are formed. The thermal decomposition of all obtained hydrated compounds begins with the release of water, bonded as coordination water.

From previous studies for the $Co(4\text{-bpy})_2(CCl_3COO)_2\cdot 2H_2O$, $Cu(4\text{-bpy})_2(CCl_3COO)_2\cdot H_2O$ and $Cd(4\text{-bpy})(CCl_3COO)_2\cdot H_2O$ [18] and data presented in this paper, the thermal stability of complexes increases as following:

$$\underset{\text{ca. 60–65°C}}{\text{Co(II)}\approx\text{Ni(II)}\approx\text{Cu(II)}\approx\text{Zn(II)}}<\underset{100°\text{C}}{\text{Cd(II)}}<\underset{120°\text{C}}{\text{Mn(II)}}$$

Co(II), Cu(II), Mn(II), Zn(II) and Cd(II) complexes decompose *via* intermediate products and MCl_2 to oxides; formation of $NiCl_2$ is not observed. The temperature of oxide formation increase in the order: Cu(II)<Ni(II)<Mn(II)<Co(II) (except for ZnO and CdO, where partial volatilization of MCl_2 was noticed).

The volatile substances produced during pyrolysis of Mn(II), Co(II), Ni(II) and Cu(II) complexes with 4-bpy and trichloroacetates are similar. The molecular ions CO_2^+, H_2O^+, HCl^+, Cl_2^+, NO^+, $N_2O_3^+$, mass fragments with m/z=12, 17, 26, 50, 47, 78 and others were observed.

* * *

We thank Dr. G. Wrzeszcz for the magnetic measurements.

References

1 J. Radwańska-Doczekalska, D. Czakis-Sulikowka and M. Markiewicz, J. Thermal Anal., 48 (1997) 865.

2 D. Czakis-Sulikowska, J. Radwańska-Doczekalska, M. Markiewicz, N. Pustelnik and B. Kuźnik, Polish J. Chem., 71 (1997) 513.

3 D. Czakis-Sulikowska, A. Malinowska and J. Radwańska-Doczekalska, ibid., 74 (2000) 607.

4 D. Czakis-Sulikowska and J. Kałużna-Czaplińska, ibid., 72 (1998) 2218; ibid., 74 (2000) 131; J. Therm. Anal. Cal., 58 (1999) 51; ibid., 62 (2000) 821.

5 D. Czakis-Sulikowska, J. Radwańska-Doczekalska and M. Markiewicz, J. Therm. Anal. Cal., 60 (2000) 145.

6 D. Czakis-Sulikowska, A. Malinowska and M. Markiewicz ibid., 60 (2000) 151.

7 J. T. Bartczak, D. Czakis-Sulikowska and J. Kałużna, J. Coord. Chem., 46 (1998) 193.

8 I. S. Ahuja, Radhuvir Singh and C. L. Yadava, J. Mol. Struct., 74 (1981) 143; Indian J. Chem., 20A (1981) 1127 and references therein.

9 B. H. Ye, X. M. Chen, F. Xue, L. N. Jiand and T. C. W. Mak, Inorg. Chim. Acta, 299 (2000) 1.

10 Chin-Wing Chan, Chi-Ming Che and Shu-Ming Pen, Polyhedron, 12 (1993) 2169.

11 S. Sen, S. Mitra, P. Kundu, M. K. Saha, C. Krüger and J. Bruckmann, Polyhedron, 16 (1997) 2475.

12 S. G. Shova, L. G. Turyatke, G. V. Novitsky, M. D. Mazus and A. P. Gulya, Koord. Khim., 22 (1996) 517.

13 M. F. Obier, M. Dartiquenave and Y. Dartiquenave, Bull. Soc. Chim., (1971) 2520.

14 M. D. Juddo, B. A. Plunkett and M. I. Pope, J. Thermal Anal., 9 (1976) 83.

15 D. C. K. Lin and J. B. Westmore, Canad. J. Chem., 51 (1973) 2999.

16 V. Zeleňák, K. Györyova and J. Simon, J. Thermal Anal., 46 (1996) 573.

17 D. Czakis-Sulikowska, A. Czylkowska and J. Radwańska-Doczekalska, J. Therm. Anal. Cal., 63 (2001) 387.

18 D. Czakis-Sulikowska, A. Czylkowska and A. Malinowska, ibid., (in press).

19 D. Czakis-Sulikowska, J. Radwańska-Doczekalska, B. Kuźnik and A. Malinowska, Transition Met. Chem., 21 (1996) 19.

20 W. I. Geary, Coord. Chem., 7 (1971) 81.

21 Saiyid Aftab Ahmad Zaidi, Shahjahan and Khwaja Salahuddin Siddiqui, Transition Met. Chem., 18 (1993) 51.

22 E. Spinner, J. Chem. Soc., (1964) 4217.

23 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York 1997.

24 W. Brzyska and W. Ożga, J. Therm. Anal. Cal., 61 (2000) 135 and references therein.

25 W. Ferenc and B. Bocian, ibid., 60 (2000) 131.

26 S. C. Mojumdar, M. Melnik and M. Valko, Polish J. Chem., 73 (1999) 457.

27 W. Ferenc, B. Bocian and M. Chudziak, J. Therm. Anal. Cal., 58 (1999) 639.

28 W. Brzyska, Z. Rzączyńska and A. Kula, Monatsh. Chem., 120 (1989) 211.

29 A. B. P. Lever, Inorganic Electronic Specroscopy, Elsevier, Amsterdam 1984.