

THERMAL CHARACTERIZATION OF NEW COMPLEXES OF Zn(II) AND Cd(II) WITH SOME BIPYRIDINE ISOMERS AND PROPIONATES

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New mixed ligand complexes of the following stoichiometric formulae: $M(2\text{-bpy})_2(\text{RCOO})_2 \cdot n\text{H}_2\text{O}$, $M(4\text{-bpy})(\text{RCOO})_2 \cdot \text{H}_2\text{O}$ and $M(2,4'\text{-bpy})_2(\text{RCOO})_2 \cdot \text{H}_2\text{O}$ (where $M(\text{II}) = \text{Zn}, \text{Cd}$; 2-bpy=2,2'-bipyridine, 4-bpy=4,4'-bipyridine, 2,4'-bpy=2,4'-bipyridine; $R = \text{C}_2\text{H}_5$; $n = 2$ or 4) were prepared in pure solid-state. These complexes were characterized by chemical and elemental analysis, IR and conductivity studies.

Thermal behaviour of compounds was studied by means of DTA, DTG, TG techniques under static conditions in air. The final products of pyrolysis of Cd(II) and Zn(II) compounds were metal oxides MO. A coupled TG/MS system was used to analyse of principal volatile products of thermal decomposition or fragmentation of $\text{Zn}(4\text{-bpy})(\text{RCOO})_2 \cdot \text{H}_2\text{O}$ under dynamic air and argon atmosphere. The principal species correspond to: C^+ , CH^+ , CH_3^+ , C_2H_2^+ , HCN^+ , C_2H_5^+ or CHO^+ , CH_2O^+ or NO^+ , CO_2^+ , $^{13}\text{C}^{16}\text{O}^+$ and $^{12}\text{C}^{16}\text{O}^{18}\text{O}^+$ and others; additionally CO^+ in argon atmosphere.

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

Introduction

Transition metal complexes with carboxylates are a subject of considerable interest [1–6]. Małecka *et al.* [1] described the synthesis and thermal behaviour of some cadmium(II) carboxylates [1, 2, 4]. The thermal decomposition of $\text{Zn}(\text{C}_2\text{H}_5\text{COO})_2 \cdot \text{H}_2\text{O}$ was also studied [6].

The work presented here is a continuation of our earlier investigations on transition metal complexes with bipyridine and carboxylates. Mixed ligand complexes of Zn(II) containing N-donor ligands and COO groups are especially attractive due to their important role in biological systems [7–9]. For example: $\text{Zn}(\text{C}_2\text{H}_5\text{COO})_2(\text{imidazole})_2$ was applied as a model compound in the studies of active metal ion sites of metalloenzymes [10]. On the other hand cadmium(II) complexes are inhibitors of different biological processes [7]. The crystal structure of $[\text{Cd}(\text{CH}_3\text{CH}_2\text{COO})_2\text{phen}]_2 \cdot 2\text{CH}_3\text{CH}_2\text{COOH}$ (where phen=1,10-phenanthroline) was determined [11]. The compound was characterized by thermal behaviour and other physical properties. Mikurija *et al.* reported the preparation and X-ray researches of the chain structures of $[\text{Cu}_2(4\text{-bpy})(\text{C}_2\text{H}_5\text{COO})_4]_n$ and $[\text{Cu}_2(4\text{-bpy})(\text{C}_2\text{H}_5\text{COO})(\text{OCH}_3)_2(\text{CH}_3\text{OH})_2]_n \cdot 2n \cdot \text{CH}_3\text{OH}$ (where 4-bpy=4,4'-bipyridine) [12]. Also the complex of Cu(II) with 2,4'-bipyridine (2,4'-bpy) and propionates was synthesized, characterized by thermal analysis, IR and electronic spectroscopy and X-ray

crystallography [13]. Thermal decomposition of *cis* $[\text{Co}(2\text{-bpy})(\text{C}_2\text{H}_5\text{COO})_2]\text{NO}_3$ (where 2-bpy=2,2'-bipyridine) was carried out [14]. Thus, also investigations of coordination compounds of Zn(II) and Cd(II) with N-donors and propionates are of significant interest. In our previous report we described the preparation and characterization of 4,4'-bipyridine–propionato complexes of Mn(II), Co(II), Ni(II) and Cu(II) [15]. This paper includes the results of the synthesis, molar conductivity and thermal properties of mixed ligand complexes of Zn(II) and Cd(II) with bipyridine isomers (2-bpy, 4-bpy and 2,4'-bpy) and propionates in the solid state.

Experimental

Materials

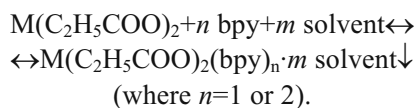
Water solutions of zinc(II) and cadmium(II) propionates were obtained by adding 40 mL 3 M propionic acid to freshly precipitated metal carbonates in *ca* equimolar ratio. Other chemicals used in this work were the same as those described in [15–17] and from POCh-Gliwice.

Synthesis of the complexes and analysis

Preparation of mixed metal(II) bipyridine-propionato complexes: zinc(II) and cadmium(II) compounds with bipyridine and propionates was prepared as result of the reaction of metal(II) propionates with bpy (where

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bpy=2-bpy, 4-bpy or 2,4'-bpy) in *ca* 75% *v/v* ethanol for 2-bpy or 4-bpy and in water solution for 2,4'-bpy. A solution of 12.0 mmol of 2-bpy or 4-bpy in 23.3 mL of 96% *v/v* ethanol was added to 6.7 mL $M(C_2H_5COO)_2$ ($M(II)=Zn, Cd$) water solutions (6.0 mmol). 2,4'-bpy (8.0 mmol) dissolved in 14.8 mL water (containing 0.2 mL 96% *v/v* ethanol) was mixed with 4.0 mmol of $M(C_2H_5COO)_2$ ($M(II)=Zn, Cd$) in 15.0 mL of water. The obtained products were washed with 40% *v/v* ethanol (or water for 2,4'-bpy complexes) and then with ethanol and diethyl ether mixture (1:1). All compounds were dried in open air and analysed. The equation for synthesis of complexes is:



The contents of metal(II) in obtained complexes and solutions of zinc(II) or cadmium(II) propionates were determined complexometrically; C, H and N by elemental analysis with V_2O_5 as an oxidizing agent. The assumed composition was confirmed by analysis (maximal deviations 0.05–0.5%).

Physical measurements

Thermal decomposition was investigated on Q-500 derivatograph using Al_2O_3 as a standard. The samples of 100 mg were heated in ceramic crucible in static air atmosphere. A coupled TG/MS system was used to analyse principal volatile products of thermal decomposition or fragmentation for a complex of Zn(II) with 4-bpy and propionates. Dynamic measurements were carried out in air or argon atmosphere (at flow rate of $1 \text{ L}^3 \text{ h}^{-1}$). Data were recorded with commercial software (Derivatograph TG/DTA-SETYS-16/18, coupled to a Mass-Spectrometer QMS-422 model Thermo Star

from Balcers); platinum crucible, sample 8.36 mg; an ion source temperature of *ca* 150°C (70 eV electron impact ionisation). All thermal investigations were carried out in the range of temperature 20–1000°C, at a heating rate, $10^\circ\text{C min}^{-1}$. The *m/z* values are given based on ^1H , ^{12}C , ^{14}N and ^{16}O (additionally ^{13}C and ^{18}O in the case of CO_2). Molar conductivities (Λ_M) of the studied complexes were measured [16] using $1.0 \cdot 10^{-3} \text{ mol L}^{-1}$ solutions in MeOH, DMF and DMS. The apparatus and other experimental conditions were described in previous papers [16, 17].

Results and discussion

The new small-crystalline compounds with empirical formulae $Zn(2\text{-bpy})_2(\text{RCOO})_2 \cdot 2\text{H}_2\text{O}$ (**I**), $Cd(2\text{-bpy})_2(\text{RCOO})_2 \cdot 4\text{H}_2\text{O}$ (**II**), $Zn(4\text{-bpy})(\text{RCOO})_2 \cdot \text{H}_2\text{O}$ (**III**), $Cd(4\text{-bpy})(\text{RCOO})_2 \cdot \text{H}_2\text{O}$ (**IV**), $Zn(2,4'\text{-bpy})_2(\text{RCOO})_2 \cdot \text{H}_2\text{O}$ (**V**) and $Cd(2,4'\text{-bpy})_2(\text{RCOO})_2 \cdot \text{H}_2\text{O}$ (**VI**) (where $R=C_2H_5$) were isolated. The observed molar conductivities values in MeOH, DMF and DMSO are given in Table 1. Low values of molar conductivity Λ_M ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) for all the obtained compounds in DMSO solutions (Λ_M in the range 1.1–2.4) and complex (**III**) in DMF ($\Lambda_M=1.6$) point out that complexes are non-electrolytes in these solutions. The molar conductivity data of all the complexes in MeOH (Λ_M in the range 25.1–65.1) and compounds (**I**), (**II**) and (**IV**)–(**VI**) in DMF (Λ_M in the range 17.7–50.6) probably show behaviour intermediate between those of non-electrolytes and 1:1 electrolytes. They dissociate in a limited degree in the solutions used [18].

Table 1 Analytical data, molar conductivity $\Lambda_M(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$ in MeOH, DMF and DMSO $c=1 \cdot 10^{-3} \text{ mol L}^{-1}$ at 25°C , ($R=C_2H_5$)

No.	Complex	Analysis: found (calculated)/%				Λ_M		
		M	C	N	H	MeOH	DMF	DMSO
I	$Zn(2\text{-bpy})_2(\text{RCOO})_2 \cdot 2\text{H}_2\text{O}$	11.94 (11.67)	55.98 (55.77)	10.25 (10.01)	5.32 (5.40)	65.1	35.1	1.8
II	$Cd(2\text{-bpy})_2(\text{RCOO})_2 \cdot 4\text{H}_2\text{O}$	16.49 (17.48)	48.89 (48.57)	8.11 (8.71)	5.25 (5.33)	49.4	39.5	2.4
III	$Zn(4\text{-bpy})(\text{RCOO})_2 \cdot \text{H}_2\text{O}$	17.22 (16.85)	50.05 (49.82)	7.16 (7.26)	5.00 (5.23)	30.5	1.6	1.2
IV	$Cd(4\text{-bpy})(\text{RCOO})_2 \cdot \text{H}_2\text{O}$	25.74 (25.97)	44.63 (44.41)	6.27 (6.47)	4.59 (4.66)	25.4	17.7	2.3
V	$Zn(2,4'\text{-bpy})_2(\text{RCOO})_2 \cdot \text{H}_2\text{O}$	12.24 (12.06)	58.01 (57.63)	10.31 (10.34)	5.15 (5.21)	29.7	50.6	1.1
VI	$Cd(2,4'\text{-bpy})_2(\text{RCOO})_2 \cdot \text{H}_2\text{O}$	19.09 (19.08)	53.46 (53.03)	9.43 (9.51)	4.70 (4.79)	25.1	37.8	2.3

Table 2 Principal IR bands [cm^{-1}] for complexes, bipyridine isomers and COO group of propionates

Complex	$\nu_{(\text{CC,CN,CC}_{\text{ir}})}$ (A ₁)	$\nu_{(\text{CN,CN})}$ (B ₁)	Ring breathing	$\nu_{\text{as}(\text{OCO})}$	$\nu_{\text{s}(\text{OCO})}$	$\Delta\nu_{\text{OCO}}$
2-bpy [19]	1579	1553	993			
I Zn(2-bpy) ₂ (RCOO) ₂ ·2H ₂ O	1598.0	1562.2	1020.0	1578.0	1444.6	133.4
II Cd(2-bpy) ₂ (RCOO) ₂ ·4H ₂ O	1590.0	1563.2	1010.6	1580.0	1436.9	143.1
4-bpy [20]	1588	1530	988			
III Zn(4-bpy)(RCOO) ₂ ·H ₂ O	1605.6	1542.0	1004.8 a)	1560.0	1440.0	120.0
IV Cd(4-bpy)(RCOO) ₂ ·H ₂ O	1602.7	1535.2	1006.8 a)	1566.1	*	–
2,4'-bpy (4-sub) [20]	1595	1405	990 sh			
V Zn(2,4'-bpy) ₂ (RCOO) ₂ ·H ₂ O	1610.5	1415.7	1019 a)	1585.4	1436.9	148.5
VI Cd(2,4'-bpy) ₂ (RCOO) ₂ ·H ₂ O	1609.5	1416.6	1011.6 a)	*	1440.0	–
RCOONa [26]	–	–	–	1558	1416	142

$R=\text{C}_2\text{H}_5$, $\Delta\nu_{\text{OCO}}=\nu_{\text{as}(\text{OCO})}-\nu_{\text{s}(\text{OCO})}$, a) – partly superimposed on the CH₃ wagging vibration of propionate groups, * – nature of the M-propionate bond does not interpreted

IR spectra

Water vibrations

The presence of water in all complexes is shown by the appearance of a broad band in the stretching vibrations region (3400–3300 cm^{-1}) followed by a shoulder at ca 1630 cm^{-1} assignable to water deformation frequencies.

2-bpy, 4-bpy and 2,4'-bpy vibrations

The most significant IR bands of these bipyridine isomers and their complexes together with possible assignments described in [19, 20] are given in Table 2. The characteristic bands attributed to the ring stretching vibrations $\nu_{(\text{CC,CN,CC}_{\text{ir}})}$, (A₁ symmetry) $\nu_{(\text{CN,CN})}$ (B₁ symmetry) and ring 'breathing' modes are shifted to higher frequencies in comparison with unbonded ligands. However, the ring 'breathing' vibration is partially obscured by the wagging vibration of the CH₃ group of propionates. These changes provide evidence for coordination of N-donors to Zn(II) and Cd(II) [21–23]. The strong band appears at 753 cm^{-1} (associated with $\gamma_{\text{C-H}}$ out of the plane deformation mode for free 2-Bpy) shifts by ca 15 cm^{-1} towards higher frequencies, also weak satellite of this band (at 735 cm^{-1}) gains intensity and is strongly split away from parent peak. Thus, it can be concluded that (**I**) and (**II**) are 2,2'-bipyridine chelates [21, 22]. Upon the coordination with Zn(II) and Cd(II) the IR spectrum of unbonded 2,4'-bpy changes in the region of the vibrations $\nu_{(\text{CC,CN,CC}_{\text{ir}})}$, $\nu_{(\text{CN,CN})}$ and ring 'breathing' 4-substituted pyridine (4-sub). These observations and literature

data [23–25] prove the coordination through the least hindered 4'N atom of 2,4'-bpy.

Propionates vibrations

For all the investigated compounds the most fundamental vibrations for carboxylates groups asymmetric ($\nu_{\text{as}(\text{OCO})}$) and symmetric ($\nu_{\text{s}(\text{OCO})}$) stretching modes were observed (Table 2). The spectrum of ionic sodium propionate shows $\nu_{\text{as}(\text{OCO})}$ and $\nu_{\text{s}(\text{OCO})}$ bands at 1558 and 1416 cm^{-1} , respectively [26]. The bands of $\nu_{\text{as}(\text{OCO})}$ and $\nu_{\text{s}(\text{OCO})}$ in the IR spectra of (**II**) and (**V**) complexes shift to higher vibrations relatively to those in ionic salt. The separations values $\Delta\nu=\nu_{\text{as}(\text{OCO})}-\nu_{\text{s}(\text{OCO})}$ for (**II**) and (**V**) are almost the same in comparison with the corresponding value for NaRCOO. Due to the spectroscopic criteria and literature data [27–32] the carboxylate groups in these complexes are probably of bidentate bridging ligands. In the case of (**I**) and (**III**) values $\Delta\nu$ decrease to about 133.4 and 120.0 cm^{-1} , respectively, indicating of bidentate chelate coordination of propionate groups in these compounds. The superposition of bands due to $\nu_{\text{s}(\text{OCO})}$ and 4-bpy (for Cd(4-bpy)(RCOO)₂·H₂O) as well as $\nu_{\text{as}(\text{OCO})}$ and 2,4'-bpy (for Cd(2,4'-bpy)₂(RCOO)₂·H₂O) respectively are observed. Thus, the interpretation of the coordination mode of Cd-propionates is difficult to discuss.

Thermal properties of compounds

The thermoanalytical data are presented in Table 3. The results of thermal, chemical and X-ray analyses

Table 3 Thermal decomposition of complexes in air (R=C₂H₅, sample mass 100 mg)

No.	Complex	Ranges of decomp./°C	DTA peak/°C	Mass loss/%		Intermediate and final solid products
				found	calc.	
I	Zn(2-bpy) ₂ (RCOO) ₂ ·2H ₂ O	60–120	75 endo	3.0	3.22	Zn(2-bpy) ₂ (RCOO) ₂ ·H ₂ O
		120–265	120 endo sh 210 exo br	38.5	38.08	Zn(2-bpy) _{0.75} (RCOO) ₂ ^{a)}
		265–375	320 endo sh	42.0		ZnO with organic residue
		375–480	385, 440 exo	2.0	44.16	pure ZnO
II	Cd(2-bpy) ₂ (RCOO) ₂ ·4H ₂ O	60–130	75 endo	2.5	2.80	Cd(2-bpy) ₂ (RCOO) ₂ ·3H ₂ O
		130–220	200 endo sh	20.0	20.05	Cd(2-bpy) _{1.5} (RCOO) ₂ ^{a)}
		220–380	315 endo, 360 exo	56.5		CdO with organic residue
		380–520	440 exo sh	2.5	57.17	pure CdO
III	Zn(4-bpy)(RCOO) ₂ ·H ₂ O	65–120	110 endo	4.5	4.65	Zn(4-bpy)(RCOO) ₂
		150–250	250 endo	11.0	10.12	Zn(4-bpy) _{0.75} (RCOO) ₂ ^{a)}
		250–370	295 endo	61.0		ZnO with organic residue
		370–495	400 exo	3.0	64.11	pure ZnO
IV	Cd(4-bpy)(RCOO) ₂ ·H ₂ O	110–150	145 endo	4.0	4.16	Cd(4-bpy)(RCOO) ₂
		210–350	300, 320 endo, 310 exo	63.0		CdO with organic residue
		350–515	360 exo	3.0	66.17	pure CdO
V	Zn(2,4'-bpy) ₂ (RCOO) ₂ ·H ₂ O	60–160	60 endo	3.0	3.32	Zn(2,4'-bpy) ₂ (RCOO) ₂
		160–350	240 exo br, 300 endo br	80.0		ZnO with organic residue
		350–490	385, 480 exo	2.0	81.92	pure ZnO
VI	Cd(2,4'-bpy) ₂ (RCOO) ₂ ·H ₂ O	80–110	105 endo	3.0	3.06	Cd(2,4'-bpy) ₂ (RCOO) ₂
		150–360	160, 310 endo	73.5		CdO with organic residue
		360–500	450 exo sh	2.5	75.14	pure CdO

^{a)}by projecting minimum of DTA curve on TG curve; br – broad; sh – shoulder

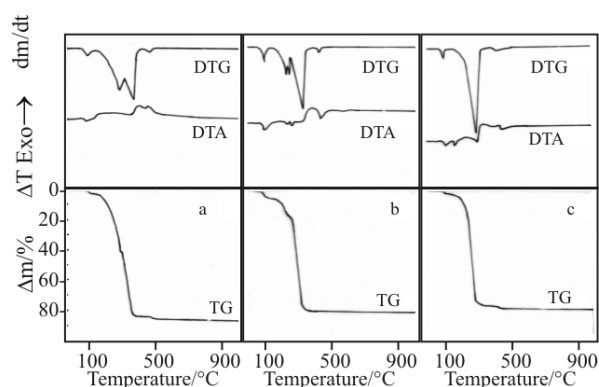


Fig. 1 Thermoanalytical curves of
 a – Zn(2-bpy)(C₂H₅COO)₂·2H₂O;
 b – Zn(4-bpy)(C₂H₅COO)₂·H₂O;
 c – Cd(2,4'-bpy)₂(C₂H₅COO)₂·H₂O in air, heating rate 10°C min⁻¹, mass sample 100 mg

make it possible to postulate the decomposition products of solid complexes. The thermal profiles (TG, DTA and DTG) of some complexes are given in Fig. 1. The complexes (I)–(III) and (V)–(VI) are stable up to about 60–80°C, whereas (IV) to 110°C, where

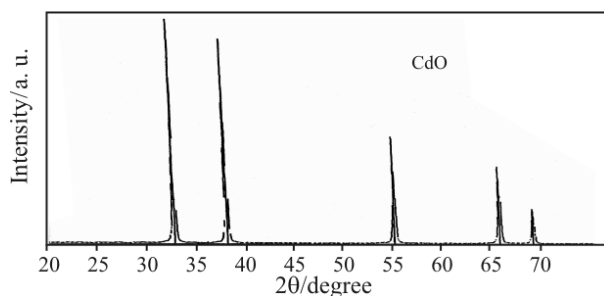


Fig. 2 X-ray diffraction pattern of decomposition of complex Cd(4-bpy)(C₂H₅COO)₂·H₂O heated up 550°C

dehydration takes place. The dehydration occurs in one endothermic step for (III)–(VI); in two endothermic steps for (I) and (II). In the case of (I), (II) and (V) compounds, decomposition of organic ligands occurs immediately after dehydration. The final stage of dehydration for (I) and (II) complexes is connected with partial elimination of 2-bpy. Thermal decompositions of anhydrous complexes (III), (IV) and (VI) begin at 150, 210 and 150°C, respectively. For the obtained complexes the deamination overlaps

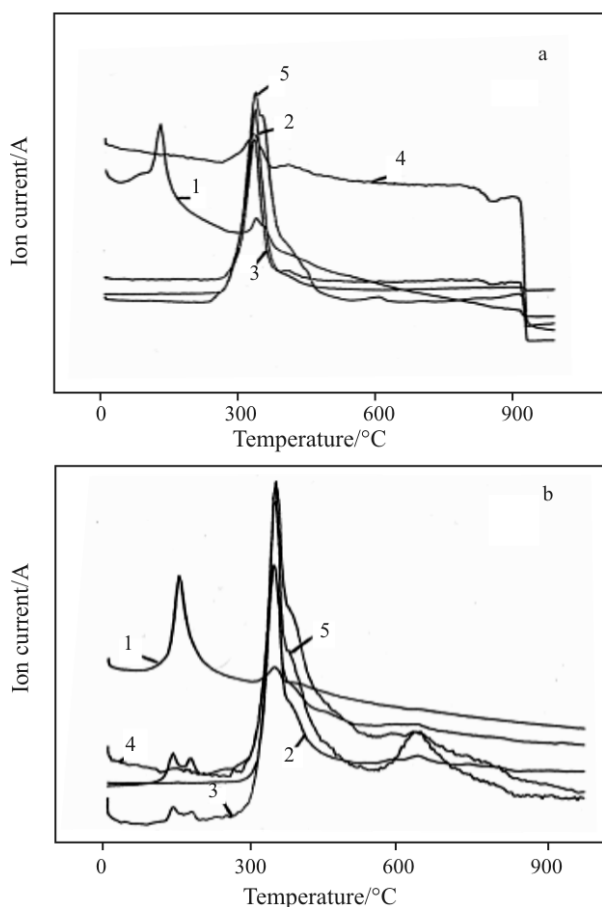


Fig. 3 Ion current detected by the MS for complex $\text{Zn}(4\text{-bpy})(\text{C}_2\text{H}_5\text{COO})_2\cdot\text{H}_2\text{O}$; a – in air, mass sample 7.62 mg; $m/z=1\text{-}18$; 2-26; 3-27; 4-30; 5-44 with sensitivity of: E-09, E-11, E-12, E-11, E-10 A, respectively; b – in argon; mass sample 8.36 mg; $m/z=1\text{-}18$; 2-27; 3-28; 4-30; 5-44 with sensitivity of: E-09, E-12, E-10, E-12, E-12 A, respectively; heating rate $10^\circ\text{C min}^{-1}$

the process of full decomposition of propionates. The products of this stage of pyrolysis are suitable metal oxides with *ca* 2% organic residue. The separate steps of bpy elimination are not clearly observed. According to the DTG curves, bpy is lost stepwise only for (I)–(III) complexes. Final solid products of the thermal decomposition of (I)–(VI) complexes are pure ZnO or CdO. They were identified on the basis of powder diffractograms [33] and analysis of TG curves. Figure 2 shows as an example the diffraction pattern of $\text{Cd}(4\text{-bpy})(\text{RCOO})_2\cdot\text{H}_2\text{O}$ heated up to 550°C . The DTA curves exhibit several exothermic peaks, which are associated with oxidation of organic fragments (Table 3).

Mass spectrometer was used for the characterization of principal volatile products evaluated during thermal decomposition and fragmentation processes only for the $\text{Zn}(4\text{-bpy})(\text{RCOO})_2\cdot\text{H}_2\text{O}$ complex in the dynamic air or argon atmosphere. The m/z values are

given for ^1H , ^{12}C , ^{14}N and ^{16}O (additionally ^{13}C and ^{18}O in the case of CO_2^+). MS data for the complex detected several profiles of ion current. The first peaks of ion current for H_2O^+ and OH^+ ($m/z=18$ and 17) appeared at 110°C in air and 125°C in argon. They correspond to the elimination of crystalline water (the first step of mass loss is observed in TG curve) (Fig. 3). The peaks of ions H_2O^+ and OH^+ appear also at *ca* 300°C (in air) and 320°C (in argon) as a consequence of oxidation of organic ligands. Major maxima of signals are observed in the temperature range $300\text{--}330$ and $310\text{--}370^\circ\text{C}$ in air and argon, respectively. The MS peaks of ions with $m/z=12, 13, 15, 26, 27, 29, 30, 44, 45, 46$ (C^+ , CH^+ , CH_3^+ , C_2H_2^+ , HCN^+ , C_2H_3^+ or CHO^+ , CH_2O^+ or NO^+ , CO_2^+ , $^{13}\text{C}^{16}\text{O}_2^+$ and $^{12}\text{C}^{16}\text{O}^{18}\text{O}^+$) were monitored. Additionally, in argon the elimination of molecular ion CO^+ is observed. The peaks of CO^+ or N_2^+ ($m/z=28$) appear at 320°C (strong) and 630°C (small). The maxima of ion signals coincide with the sudden mass loss occurring on TG curve (Fig. 1b). In gaseous products the molecular ion CO_2^+ and additionally CO^+ (in argon) formed by total pyrolysis of organic ligands dominate. Figure 3 shows some profiles of ion current detected in mass spectrometer for $\text{Zn}(4\text{-bpy})(\text{RCOO})_2\cdot\text{H}_2\text{O}$ in air (Fig. 3a) and in argon (Fig. 3b).

Conclusions

In this paper new mixed-ligand complexes: $\text{Zn}(2\text{-bpy})_2(\text{RCOO})_2\cdot 2\text{H}_2\text{O}$, $\text{Cd}(2\text{-bpy})_2(\text{RCOO})_2\cdot 4\text{H}_2\text{O}$, $\text{M}(4\text{-bpy})(\text{RCOO})_2\cdot\text{H}_2\text{O}$ and $\text{M}(2,4'\text{-bpy})_2(\text{RCOO})_2\cdot\text{H}_2\text{O}$ ($M(\text{II})=\text{Zn}, \text{Cd}$) were prepared and studied. Previously we described complexes of empirical formulae $\text{M}(4\text{-bpy})(\text{RCOO})_2\cdot 2\text{H}_2\text{O}$, where $M(\text{II})=\text{Mn}, \text{Co}$ and Ni [15]. As it was shown in IR data presented above, bipyridine and propionates coordinated to metal(II) ions. The compounds $\text{M}(2\text{-bpy})_2(\text{RCOO})_2\cdot n\text{H}_2\text{O}$ are *cis-bis* 2,2'-bipyridine chelates [21, 22]. 2,4'-Bpy coordinates via the least hindered nitrogen atom N(4') in complexes (V) and (VI). All the complexes are small crystalline solids and air stable. The thermal decomposition of the hydrated complexes begins with the release of water. During heating complexes (III)–(VI) lose water molecules in one stage. Anhydrous mixed ligand complex of Cd(II) with 4-bpy and propionates is most stable. The decomposition of $\text{Cd}(4\text{-bpy})(\text{RCOO})_2$ begins above 210°C . The complexes (I) and (II) lose water in two stages. Thermoanalytical data of bipyridino-propionate complexes of Zn(II) and Cd(II) indicate that several decomposition processes of these compounds are very weakly separated. Previously we described similar observations for some *d*-metal bipyridino-lactate or propionate complexes [15, 34]. Thermal decomposition of obtained complexes in air is multistage and yields pure ZnO and CdO as final products.

Generally, the MS detected during pyrolysis of complexes of type $M(4\text{-bpy})(\text{C}_2\text{H}_3\text{COO})_2 \cdot n\text{H}_2\text{O}$ (where $M(\text{II}) = \text{Mn, Co, Ni}$ [15] and Zn) are very similar. The maxima of ion current are associated with the decrease in mass sample observed on TG curve. The ion currents corresponding to C^+ , CH^+ , CH_3^+ , C_2H_2^+ , HCN^+ , C_2H_5^+ or CHO^+ , CH_2O^+ or NO^+ , CO_2^+ , $^{13}\text{C}^{16}\text{O}_2^+$ and $^{12}\text{C}^{16}\text{O}^{18}\text{O}^+$ ($m/z = 12, 13, 15, 26, 27, 29, 30, 44, 45$ and 46 , respectively) were detected.

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