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Synthesis and Characterization of New d^n Metal Complexes with 4,4′-Bipyridine and Formates

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New mixed-ligand complexes of the stoichiometric formulae: $Mn(4\text{-}bpy)_2(HCOO)_2 \cdot 2H_2O$, $Co(4\text{-}bpy)(HCOO)_2 \cdot H_2O$, $Ni(4\text{-}bpy)(HCOO)_2 \cdot 4H_2O$, $Cu(4\text{-}bpy)(HCOO)_2 \cdot H_2O$, $Zn_2(4\text{-}bpy)_3(HCOO)_4$ and $Cd(4\text{-}bpy)(HCOO)_2$ (where 4-bpy = 4,4′-bipyridine) have been isolated in pure state. The IR and VIS spectra (for compounds of Co(II), Ni(II), Cu(II)), molar conductivity measurements and other physical properties of these compounds are discussed. Thermal behaviour of all compounds was studied by means of DTA, DTG, TG techniques under static conditions in air. The resultant final products were the metal oxide in all cases. A coupled TG-MS system was used to analysis of princpal volatile thermal decomposition (or fragmentation) products of Co(II) and Ni(II) complexes. The principal volatile mass fragments correspond to: C^+, OH^+, H_2O^+, NO^+, CO_2^+ and other.

Key words: 4,4′-bipyridine-formato complexes, IR, VIS, TG-MS data, thermal decomposition

Transition metal complexes with N donor ligands and carboxylates are interesting objects of biological studies [1]. Very little is known on mixed ligand complexes of d^n metal with N-donors and formates. Hathaway *et al.* [2] prepared complexes with empirical formulae: $Cu(2\text{-}bpy)_2(HCOO)_2 \cdot 4H_2O$ and $[Cu(2\text{-}bpy)_2(HCOO)]ClO_4$ (where 2-bpy = 2,2′-bipyridine). These compounds have been characterized by electronic, ESR, and IR spectra. Also the complex $[Cu(2\text{-}bpy)_2(HCOO)_2]BF_4 \cdot 0.5H_2O$ was described [3]. Thermal decomposition of $cis[Co(2\text{-}bpy)_2(HCOO)_2]NO_3$ and $cis[Co(o\text{-}phen)_2(HCOO)_2]NO_3$ (where o-phen = 1,10-phenanthroline) was carried out by Brini *et al.* [4]. The crystal structure of $[Cu(HCOO)(o\text{-}phen)H_2O]_2(NO_3)_2 \cdot 4H_2O$ was determined [5]. Coordination compounds of M(II) ions with 4,4′-bipyridine (4-bpy) and formates were not yet described. This paper presents the synthesis and properties of new 4,4′-bipyridine-formato complexes of M(II) ions (M(II) = Mn, Co, Ni, Cu, Zn and Cd). They were characterized by chemical and elemental analyses, IR, and VIS spectra (for compounds of Co(II), Ni(II), Cu(II)), molar conductivity measurements and thermal decompostion in air.

EXPERIMENTAL

The apparatus and measuring conditions were the same as described in [6,7]. Solutions of $M(HCOO)_2$ (M(II) = Mn, Co, Ni, Cu, Zn and Cd) were prepared by the method published in publication [6]. HCOOH p.a. were obtained from Aldrich; other chemicals were the same as those described earlier [6,7].

The analyses of the solid decomposition products were performed using TG and DTG curves, and supported by X-ray diffractograms. A coupled TG-MS system (derivatograph TG/DTA-SETSYS-16/18, mass spectrometer ThermoStar from Balzers) was used to analysis of the principal volatile thermal decomposition (or fragmentation) products of the investigated compounds. Ion currents were monitored *vs* temperature in the range 20–600°C. Dynamic measurements were carried out in air atmosphere; heating rate 10°C min^{-1}.

4,4′-Bipyridine-formato complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) were prepared by methods, described earlier [6,7]. The theoretical compositions were confirmed by analysis inside 0.2÷0.5%.

RESULTS AND DISCUSSION

The new mixed complexes with the empirical formulae $Mn(4\text{-}bpy)_2(HCOO)_2\cdot 2H_2O$, $Co(4\text{-}bpy)(HCOO)_2\cdot H_2O$, $Ni(4\text{-}bpy)(HCOO)_2\cdot 4H_2O$, $Cu(4\text{-}bpy)(HCOO)_2\cdot H_2O$, $Zn_2(4\text{-}bpy)_3(HCOO)_4$ and $Cd(4\text{-}bpy)(HCOO)_2$ were obtained. All complexes are stable in air. The solubilities of these compounds in water (at 21°C) are of the order $1\cdot 10^{-3}$ mol L^{-1}. The molar conductance (Λ_M) of methanol solutions ($1\cdot 10^{-3}$ mol L^{-1} at 25°C) of complexes $Mn(4\text{-}bpy)_2(HCOO)_2\cdot 2H_2O$, $Ni(4\text{-}bpy)(HCOO)_2\cdot 4H_2O$ and $Zn_2(4\text{-}bpy)_3(HCOO)_4$ is in the range 58–69 Ω^{-1} cm^2 mol^{-1} being intermediate between those of non- and 1:1 electrolytes [8]. They dissociate in a limited degree in methanol. Compounds of Co(II), Cu(II) and Cd(II) are sparingly soluble in methanol.

Electronic and IR spectra: The electronic spectrum of the complex $Co(4\text{-}bpy)(HCOO)_2\cdot H_2O$ shows band at 19800 cm^{-1} ascribed to the transition $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ and shoulder at 21500 cm^{-1}. The $Ni(4\text{-}bpy)(HCOO)_2\cdot 4H_2O$ exhibits only one spin allowed band at 15750 cm^{-1} ($^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$). The ligand field spectra of these complexes are characteristic of distorted octahedral environment around Co(II) and Ni(II) [9]. In the case of $Cu(4\text{-}bpy)(HCOO)_2\cdot H_2O$ very broad band at 13800 cm^{-1} is observed and the stereochemistry of the copper(II) ion environment in this compound is difficult to determination.

As a result of the formation of complexes with investigated metal ions, the IR spectrum of 4-bpy changes. The characteristic ring breathing mode appearing at 988 cm^{-1} [10] in free ligand is observed in these compounds in the range 1008.5–1018.5 cm^{-1}. The ring vibration stretching mode $\nu(CC)$, $\nu(CN)$, $\nu(CC)_{\text{inter ring}}$ (A_1 symmetry) and $\nu(CC)$, $\nu(CN)$ (B_1 symmetry) [10] are shifted by *ca* 5–20 cm^{-1} towards higher frequencies in comparison to unbonded 4-bpy [11]. These observations suggest that 4-bpy is coordinated to metal ions [13]. The IR spectra of isolated complexes show asymmetric $\nu_{as}(OCO)$ and symmetric $\nu_s(OCO)$ vibrations of OCO groups in the ranges 1560.3–1631.7 cm^{-1} and 1336.6–1400.2 cm^{-1}, respectively (Table 1). On the grounds of spectroscopic criteria [14–16] and our previous study [6] it is possible to state, that in the case of Mn(II), Co(II) and Zn(II) complexes formate groups are bonded as bidentate chelating ligands (the values of $\Delta\nu = \nu_{as} - \nu_s$ of these complexes are smaller than those for sodium salt $\Delta\nu$(HCOONa) [17]), whereas unidentate formate groups exist in Cu(4-bpy)$(HCOO)_2 \cdot H_2O$ ($\Delta\nu > \Delta\nu$(HCOONa) (Table 1). The ν_s absorption of Mn(II) and Zn(II) complexes and the ν_{as} absorption of Co(II) and Cu(II) complexes are splitted. It suggests, that non-completely equivalent bonds between these metals and carboxylate groups of the formate ligand are formed. In the case of Cd(4-bpy)$(HCOO)_2$ two clearly resolved bands ν_{as} are observed ($\Delta\nu < \Delta\nu$(HCOONa) and $\Delta\nu > \Delta\nu$(HCOONa)). It states, that probably compound of Cd(II) contains both bidentate chelating, as well, unidentate formate ligands. The frequencies ν_{as}(OCO) from Ni(4-bpy)$(HCOO)_2 \cdot 4H_2O$ are superimposed on 4-bpy vibrations. Thus, it is difficult to discuss the nature of the metal-formate bonds. Hydrated complexes exhibit a broad band in the water stretching region (3400–3500 cm^{-1}).

Table 1. Principal bands (cm^{-1}) for carboxylate group in complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with 4-bpy and formates.

Compound	ν_{as}(OCO)	ν_s(OCO)	$\Delta\nu$
HCOONa [17]	1597	1357	140
Mn(4-bpy)$_2$$(HCOO)_2 \cdot 2H_2O$	1577.7 s	1400.2 m	175.5
		1392.5 s	185.2
		1352.0 s	225.7
Co(4-bpy)$(HCOO)_2 \cdot H_2O$	1569.9 vs	1350.1 vs	219.8
	1564.2 vs		214.1
Ni(4-bpy)$(HCOO)_2 \cdot 4H_2O$	*	1365.5 vs	*
Cu(4-bpy)$(HCOO)_2 \cdot H_2O$	1629.7 s	1336.6 vs	293.1
	1589.2 s		252.6
Zn_2(4-bpy)$_3$$(HCOO)_4$	1577.7 s	1398.3 vs	179.4
		1390.6 vs	187.1
		1352.0 vs	225.7
Cd(4-bpy)$(HCOO)_2$	1631.7 vs	1350.1 vs	281.6
	1560.3 vs		210.2

* – overlaid by 4-bpy absorption; $\Delta\nu = \nu_{as}$(OCO) – ν_s(OCO); v, s, m, w – very, strong, medium.

Thermal analyses: The results of the thermal decomposition are given in Table 2. According to X-ray analyses of the final products of decomposition, in the case of all complexes, the oxides MO (M(II) = Co, Ni, Cu, Zn, Cd) and Mn_3O_4 are formed. Co(4-bpy)$(HCOO)_2 \cdot H_2O$, Zn_2(4-bpy)$_3$$(HCOO)_4$ and Cd(4-bpy)$(HCOO)_2$ decomposed in similar way. Most thermally stable is Co(4-bpy)$(HCOO)_2 \cdot H_2O$. It starts to decompose at 170°C. The diffraction pattern of the sinter heated up to 320°C indicates the presence of Co_3O_4 with traces of Co. Above 330°C only diffraction lines characteristic of Co_3O_4 were detected. Next, the process of decomposition of Co_3O_4 takes place. Over 900°C, formation of CoO begins. Complexes of Zn(II) and Cd(II) in the temperature ranges 60–290°C and 140–300°C decompose directly to ZnO (with 3% organic fragments) and CdO, respectively. The X-ray diffraction patterns indicate that only CdO is present in the sinter of $Cd(4\text{-bpy})(HCOO)_2$ heated up to 300°C. According to Douval [18], $Cd(HCOO)_2$ also is converted into CdO at 300°C. A constant mass level for pure ZnO began at 450°C. The exothermic peak in the DTA curve at 440°C is associated with combustion of the remaining carbonization products. $Ni(4\text{-bpy})(HCOO)_2\cdot4H_2O$ starts to lose water between 80–153°C. In the range 153–260°C forms NiO with 4% organic fragments and traces of Ni. A constant mass level for pure NiO begins at 460°C. $Mn(4\text{-bpy})_2(HCOO)_2\cdot2H_2O$ and $Cu(4\text{-bpy})(HCOO)_2\cdot H_2O$ decompose progressively. In the first step of decomposition complex of Mn(II) loses all water molecules (60–110°C). For $Cu(4\text{-bpy})(HCOO)_2\cdot H_2O$ dehydration process is connected with 0.5 mol of 4-bpy elimination (60–180°C). On increasing temperature, complex of Mn(II) deaminates and at 340°C formation of $Mn(HCOO)_2$ occurs. Next, this salt was oxidized to Mn_2O_3. Above 900°C the final product Mn_3O_4 is formed. The temperature of formation of Mn_3O_4 from Mn_2O_3 is similar to that reported in the literature [19]. Intermediate compound $Cu(4\text{-bpy})_{0.5}(HCOO)_2$ decomposes *via* $CuCO_3$ to CuO. A plateau for CuO in the TG curve being obtained at 455°C. The temperature of decomposition of 4,4′-bipyridine-formates complexes increase in sequence: Mn(II) ≈ Cu(II) ≈ Zn(II) < Ni(II) < Cd(II) < Co(II). Peaks from DTA curves of investigated compounds are given in Table 2.

Table 2. Thermal decomposition data for complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with 4-bpy and formates in air; mass sample 100 mg.

Complex	Ranges of decomposition/°C	DTA peak/°C	Mass loss %		Intermediate and final solid products
			found	(calcd.)	
$Mn(4\text{-bpy})_2(HCOO)_2\cdot2H_2O$	60–110	80 endo	6.0	(7.30)	$Mn(4\text{-bpy})_2(HCOO)_2$
	140–340	265, 320 endo	64.0	(64.50)	$Mn(HCOO)_{2*}$
	340–370	370 exo	12.0	(13.83)	Mn_2O_3
	> 900		0.5	(0.54)	Mn_3O_4
$Co(4\text{-bpy})(HCOO)_2\cdot H_2O$	170–320	315 endo	75.0	(74.16)	Co_3O_4 + *ca* 1% of Co
	320–330	330 exo			Co_3O_4 pure
	> 900	940 endo	1.5	(1.66)	CoO
$Ni(4\text{-bpy})(HCOO)_2\cdot4H_2O$	80–153	135 endo	20.0	(19.11)	$Ni(4\text{-bpy})(HCOO)_2$
	153–260	255 exo	57.0	(61.07)	Ni + 4% organic fragments + traces of Ni
	260–460	315 endo 370 exo	4.0		pure NiO
$Cu(4\text{-bpy})(HCOO)_2\cdot H_2O$	60–180	160 endo	29.0	(29.32)	$Cu(4\text{-bpy})_{0.5}(HCOO)_2$
	180–290	280 endo	33.0	(32.99)	$CuCO_3$

Table 2 (continuation)

	290–455	360 exo	12.0	(13.43)	CuO
Zn_2(4-bpy)$_3$(HCOO)$_4$	60–290	240, 280 endo	76.0	(79.12)	ZnO + 3% organic fragments
	290–450	440 exo	3.0		pure ZnO
Cd(4-bpy)(HCOO)$_2$	140–300	220 endo 300 exo	65.0	(64.20)	CdO

*by projecting minimum of DTG curve on TG curve

Mass spectrometric thermal analysis: Thermogravimetry coupled with mass spectroscopy (TG-MS) system was used only to characterization of complexes Co(4-bpy)(HCOO)$_2 \cdot H_2O$ and Ni(4-bpy)(HCOO)$_2 \cdot 4H_2O$ in air atmosphere (with samples of mass 5.69 mg and 5.58 mg respectively). Generally, many signals of ion currents are observed in the range *ca* 120–420°C for Co(II) complex and *ca* 140–280, 300–380°C in the case of Ni(II) compound. Figures 1 and 2 present the ion current for *m/z* detected in the mass spectrometer *vs* time for investigated compounds. TG-MS data for some ions current are presented, as an example, in Figure 3. The first peak of ion current for H_2O^+ (*m/z* = 18) occurs at around 151°C in the case of Ni(II) complex. This coincides with elimination of coordination (or crystalline) water. For complex of Co(II) the corresponding MS maximum for coordination water appeared at 185°C. Next, the H_2O^+ was produced during decomposition of organic ligands; MS-peaks at 251°C and 325°C (for Ni) and at 326°C (for Co). The first maximum of ion current in the elimination of CO_2^+ and its isotopes (*m/z* = 45; 46) occurs in the case Ni(4-bpy)(HCOO)$_2 \cdot 4H_2O$ at 249°C and second at 320°C. For Co(4-bpy)(HCOO)$_2 \cdot H_2O$

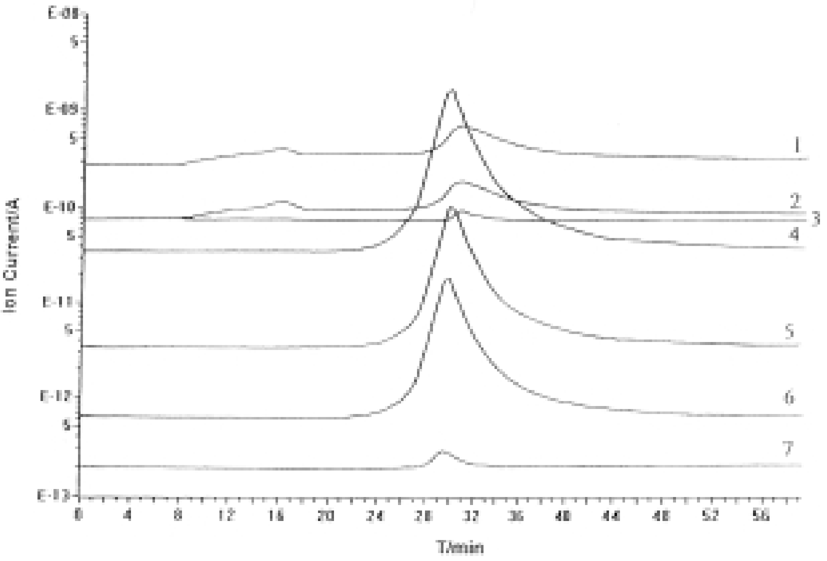

Figure 1. Ion current detected in the mass spectrometer *vs* time for complex Co(4-bpy)(HCOO)$_2 \cdot H_2O$; heating rate 10°C min^{-1}; mass sample 5.69 mg; *m/z*: 1–18 (H_2O^+); 2–17 (OH^+); 3–30 (probably NO^+); 4–44 (CO_2^+); 5–45 and 6–46 (isotopes of CO_2^+); 7–12 (C^+).

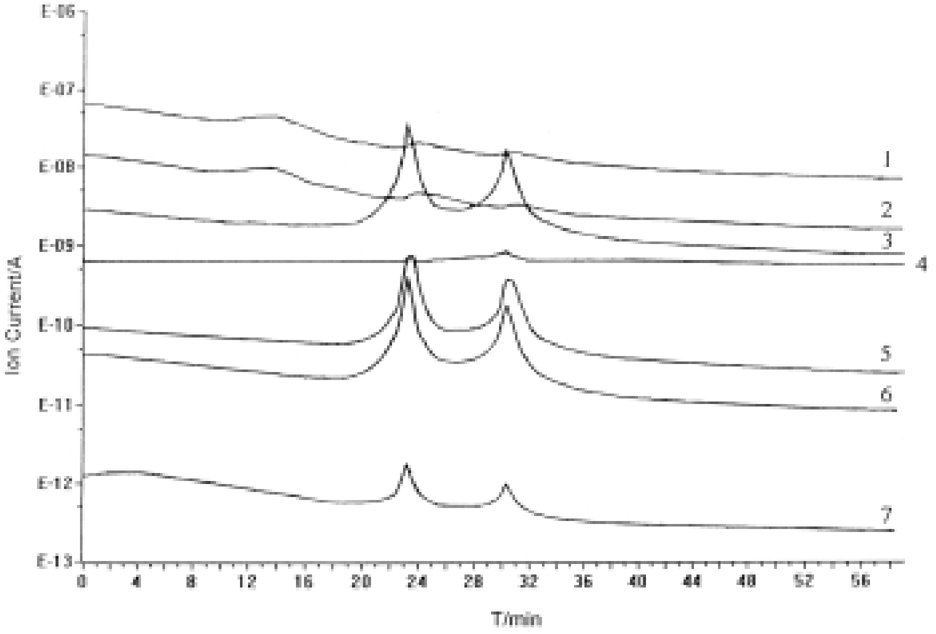

Figure 2. Ion current detected in the mass spectrometer *vs* time for complex Ni(4-bpy)$(HCOO)_2 \cdot 4H_2O$; heating rate 10°C min^{-1}; mass sample 5.58 mg; *m/z*: 1–18 (H_2O^+); 2–17 (OH^+); 3–30 (probably NO^+); 4–44 (CO_2^+); 5–45 and 6–46 (isotopes of CO_2^+); 7–12 (C^+).

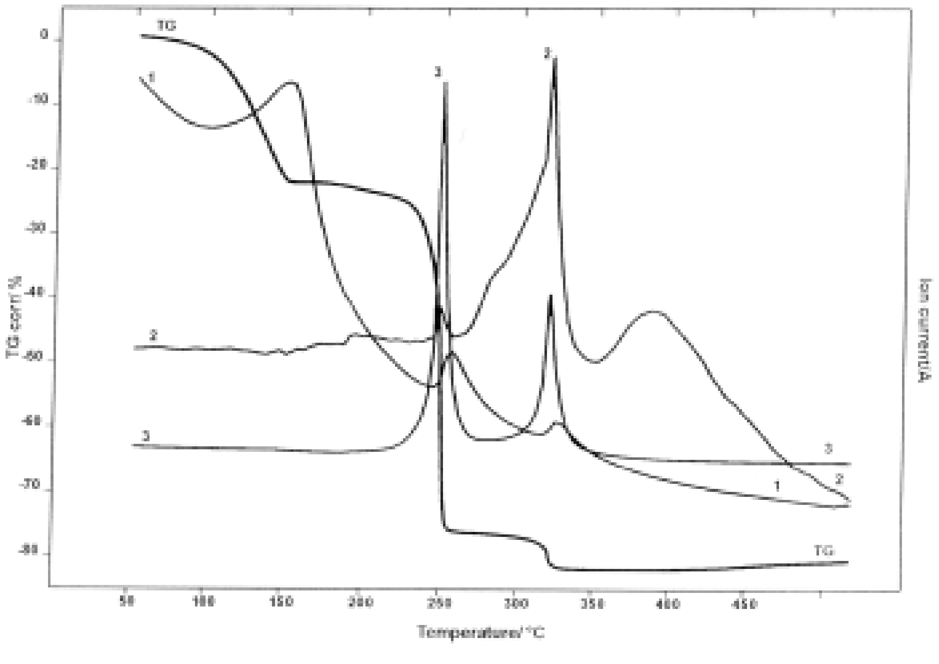

Figure 3. TG curve and ion current for Ni(4-bpy)$(HCOO)_2 \cdot 4H_2O$ detected by the MS in air atmosphere; mass sample 5.58 mg; heating rate 10°C min^{-1}; *m/z*: 1–18; 2–30; 3–44 with a sensitivity of ion current: E–10, E–10, E–08 A, respectively.

the ion signal intensites CO_2^+ occur in region *ca* 250–360°C. Maximum rates of forming for *m/z* = 30 (probably NO^+) at 325°C (Co) and 260, 330°C (Ni) are observed. Also peaks for fragments with *m/z* = 12 (C^+) and 17 (OH^+) of investigated complexes were detected.

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