Journal of Thermal Analysis and Calorimetry, Vol. 90 (2007) 2, 557–564

SYNTHESIS AND CHARACTERIZATION OF NEW METAL(II) COMPLEXES WITH FORMATES AND SOME NITROGEN DONOR LIGANDS

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New mixed-ligands complexes with empirical formulae: M(2,4'-*bpy*)$_2$L$_2$·H$_2$O (*M*(II)=Zn, Cd), Zn(2-*bpy*)$_3$L$_2$·4H$_2$O, Cd(2-*bpy*)$_2$L$_2$·3H$_2$O, M(phen)L$_2$·2H$_2$O (where *M*(II)=Mn, Ni, Zn, Cd; 2,4'-*bpy*=2,4'-bipyridine, 2-*bpy*=2,2'-bipyridine, *phen*=1,10-phenanthroline, *L*=HCOO$^-$) were prepared in pure solid state. They were characterized by chemical, thermal and X-ray powder diffraction analysis, IR spectroscopy, molar conductance in MeOH, DMF and DMSO. Examinations of OCO$^-$ absorption bands suggest versatile coordination behaviour of obtained complexes. The 2,4'-*bpy* acts as monodentate ligand; 2-*bpy* and *phen* as chelating ligands. Thermal studies were performed in static air atmosphere. When the temperature raised the dehydration processes started. The final decomposition products, namely MO (Ni, Zn, Cd) and Mn$_3$O$_4$, were identified by X-ray diffraction.

Keywords: *bipyridine isomers, IR spectra, mixed-ligands complexes, thermal decomposition, 1,10-phenanthroline, X-ray diffraction*

Introduction

Considerable attention has been devoted in recent years to the study of mixed-ligands complexes of metal(II) containing nitrogen donor ligands (among others bipyridine isomers, 1,10-phenanthroline) with biologically active carboxylates [1–7]. They are interest both chemical and biological point of view. The research of these types of complexes are motivated by their potential applications (i.e. separation materials, catalysis precursors, potential models of the catalyse enzymes [4, 8–13]) and their interesting structures [14–16]. Very little is known on mixed-ligands compounds with bipyridine isomers or 1,10-phenanthroline and formates (*L*). The complexes Cu(2-*bpy*)$_2$ (HCOO$_2$·H$_2$O and[Cu(2-bpy)$_2$(HCOO)]ClO$_4$ were prepared by Hathaway *et al.* [17] and [Cu(2-bpy)$_2$(HCOO)]BF$_4$·0.5H$_2$O was studied by Fitzgerald *et al.* [18]. The mixed-ligands complexes of Mn(II), Co(II), Ni(II) and Cu(II) with 4,4'-bipyridine (4-*bpy*) and formates have been prepared as five hydrates or anhydrous forms [19, 20]. Their structural and magnetic properties were studied. However, thermal behaviour data of these complexes were not published. We have recently reported of 4,4'-bipyridine-formato complexes of *M*(II) ions (*M*(II)=Mn, Co, Ni, Cu, Zn, Cd) and 2,2'-bipyridine or 2,4'-bipyridine-formato complexes of Mn(II), Co(II), Ni(II) and Cu(II) [21, 22]. In these papers were examined physico-chemical properties and thermal decomposition of these complexes in static air atmosphere. The single-crystal X-ray diffraction method of copper(II) compound with 1,10-phenanthroline and formates exhibited the dimeric structure with formate bridges [23].

Continuing our interest on mixed-ligands complexes, we reported the synthesis of new metal(II) complexes of bipyridine-formato (bipyridine=2-*bpy* or 2,4'-*bpy*; *M*(II)=Zn, Cd) and 1,10-phenanthroline-formato (*M*(II)=Mn, Ni, Zn, Cd). They have been characterized by elemental analysis, IR spectroscopy, molar conductivity, X-ray powder diffraction measurements. Additionally, for nickel(II) complex electronic spectrum and effective magnetic moment (in room temperature) was examined. Also the results of thermal decomposition of obtained compounds are described below.

Experimental

Materials

2,4'-Bipyridine (*m.p.*=61°C), 2,2-bipyridine (*m.p.*= =72°C), dimethylsulfoxide (DMSO), formic acid were obtained from Aldrich; 1,10-phenanthroline·H$_2$O from POCh Gliwice, methanol (MeOH) anhydroscan and dimethylformamide (DMF) from Lab-Scan and Chempur, respectively; hydroxylamine (50% water solution) from Fluka; other chemicals

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1388–6150/$20.00

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were p.a. products of POCh-Gliwice. Water solutions of metal(II) formates were prepared by adding 2 mol L^{-1} formic acid to freshly precipitated metal(II) carbonates in ca. stoichiometric quantities.

Complex synthesis

The mixed-ligand complexes with 2,4'-bipyridine or 2,2'-bipyridine and formates were prepared by methods described earlier [22]. 1,10-Phenanthroline-formato compounds were synthesized by reaction of freshly obtained solutions of appropriate metal(II) formates with solutions of 1,10-phenanthroline. A solution 5 mmol of *phen* in 15.6 mL of 96% *v*/*v* ethanol was added to solution of metal(II) formates (5 mmol in 14.4 mL water). In case of nickel(II) complex, 6 mmol of *phen* dissolved in 27.1 mL of 96% *v*/*v* ethanol was mixed with 3 mmol of nickel(II) formate in 12 mL of water. The mixtures were heated up to 70°C. During several days the compounds were crystallized. The products were washed with 40% *v*/*v* ethanol and then with ethanol and diethyl ether mixture (1:1). All compounds were dried in open air and analysed. C, N, H was determined by elementary analysis with V_2O_5 as oxidizing agent (Carlo-Erba instrument), contents of M(II) in mineralized samples by complexometric titration with EDTA.

Methods

Conductivity measurements were performed on OK-102/1 conductometer with OK 0902 electrode at 25±0.5°C. The molar conductivity (Λ_M) of the complexes was measured for $1.0\cdot10^{-3}$ mol L^{-1} solutions in MeOH, DMF and DMSO. IR spectra were recorded on FTIR-8501 Shimadzu spectrophotometer over the range 4000–400 cm^{-1} using KBr pellets. VIS spectra (only for nickel(II) complex) were obtained in Nujol mull on M-40 SPECORD over the range 29500–11000 cm^{-1}. The magnetic susceptibility of Ni(II) complexes was measured on magnetic balance (Sherwood Scientific MSB MK 1) using $Co[Hg(SCN)_4]$ as a calibrant. Experimental magnetic susceptibility was corrected by diamagnetism data [24].

The thermal decomposition was studied by means of Q-1500 derivatograph. The samples of 100 mg were heated in ceramic crucible in static air atmosphere. α-Al_2O_3 was used as standard material. All thermal investigations were carried out to the temperature range 20–1000°C at heating rate of 10°C min^{-1}. From TG curves the solid intermediate products of decomposition were determined. In sinters (prepared during the heating sample of complex up to temperatures definite from TG curves) the presence of carbonates were analyzed. The obtained final solid thermal decomposition products of complexes were identified by the X-ray diffraction patterns using a D-5000 diffractometer with a nickel- filtered CuK_α radiation. The curves were recorded in the range of 2θ angles 2–80°.

Results and discussion

The new fine-crystalline complexes with the empirical formulae $Zn(2,4'\text{-bpy})_2L_2\cdot H_2O$ (**I**), $Cd(2,4'\text{-bpy})_2L_2\cdot H_2O$ (**II**), $Zn(2\text{-bpy})_3L_2\cdot 4H_2O$ (**III**), $Cd(2\text{-bpy})_2L_2\cdot 3H_2O$ (**IV**), $Mn(phen)L_2\cdot 2H_2O$ (**V**), Ni(*phen*)$L_2\cdot 2H_2O$ (**VI**), $Zn(phen)L_2\cdot 2H_2O$ (**VII**), $Cd(phen)L_2\cdot H_2O$ (**VIII**) were isolated. All the compounds are stable at room temperature (expect complex of Mn(II)). The X-ray diffraction patterns of $Zn(2,4'\text{-bpy})_2L_2\cdot H_2O$ and $Cd(2,4'\text{-bpy})_2L_2\cdot H_2O$ indicate that they are isostructural. The molar conductivity for all complexes in MeOH, (**V**)–(**VIII**) in DMF and (**V**) in DMSO exhibited a behaviour intermediate between those of non-electrolytes and 1:1 electrolytes. The compounds (**I**)–(**IV**) in DMF and all except (**V**) in DMSO are non-electrolytes (Table 1) [25].

The ligand field-spectrum for $Ni(phen)L_2\cdot 2H_2O$ in solid state was recorded. It exhibits three bands at 24940, 16460 and 11620 cm^{-1} which may be attributed to transitions ${}^3A_{2g}\rightarrow{}^3T_{1g}(P)$, ${}^3A_{2g}\rightarrow{}^3T_{1g}(F)$ and ${}^3A_{2g}\rightarrow{}^1E_g$, respectively. The room temperature effective magnetic moment of $Ni(phen)L_2\cdot 2H_2O$ is equal 3.36 B.M. Above observations are in accordance with distorted octahedral geometry around nickel(II) [26, 27].

Infrared spectra

IR spectra of all obtained complexes were investigated. As result of the formation of complexes with metal(II) ions, the IR spectra of 2-*bpy* and 2,4'-*bpy* undergo changes. They were found to be similar to those obtained for other complexes of d^n metals [14, 22, 28–30]. Spectrum of 2,4'-*bpy* (unsymmetrical isomer of *bpy*) changes only, following complexation [28], in the region of vibration modes of the 4-substituted (4-*sub*) pyridine. The stretching vibration of 4-*sub* pyridine ν_{CC}, ν_{CN}, $\nu_{CC_{\text{inter ring}}}$ (1595 cm^{-1} for free ligand [31]) was shifted to higher value in the spectrum of the complex (**II**) by about 15 cm^{-1}. The characteristic ring breathing vibration of 4-*sub* pyridine (band as a shoulder at 990 cm^{-1} in unbonded 2,4'-*bpy* [31]) is observed in spectra of the complexes (**I**) and (**II**) at 1016.4 and 1012.6 cm^{-1}, respectively. Also the band (assigned as ring stretching mode for 4-*sub* pyridine) at 1405 cm^{-1} in free 2,4'-*bpy* is displaced for complexes by ca. 10 cm^{-1} toward higher frequencies. From these observations and literature data [14, 28, 32] it is possible to state, that

Table 1 Analytical data, molar conductivity Λ_M (Ω^{-1} cm^2 mol^{-1}) in MeOH, DMF and DMSO c=1·10^{-3} mol L^{-1} at 25°C

No.	Complex	Analysis: found (calculated)/%				Λ_M		
		M	C	N	H	MeOH	DMF	DMSO
(I)	$Zn(2,4'\text{-bpy})_2L_2\cdot H_2O$ (white)	13.64 (13.46)	54.01 (54.34)	11.43 (11.53)	4.11 (4.15)	53.0	10.2	9.2
(II)	$Cd(2,4'\text{-bpy})_2L_2\cdot H_2O$ (white)	21.20 (21.09)	49.23 (49.09)	10.51 (10.42)	3.77 (3.78)	47.5	9.8	16.5
(III)	$Zn(2\text{-bpy})_3L_2\cdot 4H_2O$ (white)	12.00 (12.07)	55.10 (55.12)	9.08 (9.15)	4.96 (4.92)	74.7	10.1	12.3
(IV)	$Cd(2\text{-bpy})_2L_2\cdot 3H_2O$ (white)	19.76 (19.78)	46.38 (46.45)	9.82 (9.85)	4.19 (4.25)	69.7	11.4	17.7
(V)	$Mn(phen)L_2\cdot 2H_2O$ (yellow)	15.35 (15.21)	45.99 (46.55)	7.71 (7.77)	3.29 (3.35)	74.7	28.3$^{a)}$	19.4
(VI)	$Ni(phen)L_2\cdot 2H_2O$ (green)	16.08 (16.50)	46.12 (46.07)	7.65 (7.67)	3.36 (3.31)	74.7	37.6	16.6
(VII)	$Zn(phen)L_2\cdot 2H_2O$ (white)	17.70 (17.59)	45.01 (45.24)	7.23 (7.54)	3.19 (3.25)	67.7	24.2	8.8
(VIII)	$Cd(phen)L_2\cdot H_2O$ (white)	28.40 (28.15)	41.76 (41.97)	6.88 (6.99)	1.49 (1.51)	64.6	20.2	9.2

$^{a)}$ 6.0·10^{-4} mol L^{-1}

2,4'-*bpy* coordinated via least hindered 4'(N) atom as monodentate ligand.

In spectra of $Zn(2\text{-bpy})_3L_2\cdot 4H_2O$ and $Cd(2\text{-bpy})_2L_2\cdot 3H_2O$ complexes the bands attributed to ring stretching vibrations ν_{CC}, ν_{CN}, $\nu_{CC_{\text{inter ring}}}$ and ring breathing mode (in unbonded ligand at 1599 and 991 cm^{-1}, respectively [29]) are moved towards higher frequencies in comparison to free 2-*bpy*; these bands occurred at 1596.9 and 1018.3 cm^{-1} (for Zn(II)) and 1603.1 and 1012.6 (for Cd(II)), respectively. The band γ_{CH} out-of-plane deformation modes are observed at higher waven numbers (781.1, 763.8 for (**III**) and 769.5 cm^{-1} for (**IV**)) in comparison to unbonded N-donor ligand (753 cm^{-1}). Also weak satellite of this band at 738 cm^{-1} gains intensity and is strongly moved away from the parent peak. These observations suggested that 2-*bpy* is coordinated to metal ions [29, 30, 33].

The spectrum of free 1,10-phenanthroline [30] undergoes modification on coordination to metal(II) [1, 30]. Similar results have been obtained for IR spectra of investigated complexes with 1,10-phenanthroline and formates. The principal IR spectra bands of *phen* in isolated compounds are collected in Table 2. There occur changes of complexes spectra in the ranges ca. 1615–1423 and ca. 795–730 cm^{-1}. The bands at 1615 and 1423 cm^{-1} (attributed to $\nu_{(CN,CC)}$ vibrations of free *phen*) [30] appear for complexes between 1596.9–1591.2 and 1429.2–1427.2 cm^{-1}. Presence of strong band at 1519.8–1515.9 cm^{-1} (1505 cm^{-1} for free *phen*) is associated with carbocyclic ring vibrations. There are observed also absorption bands (γ_{CH}) in the range 794.6–783.0 and 731.0–727.1 cm^{-1} (in free *phen* at 767 and 734 cm^{-1}).

The IR spectra of investigated complexes (**II–VII**) show bands arising from asymmetric $\nu_{as(OCO)}$

Table 2 Principal IR bands for 1,10-phenanthroline in free ligand and their complexes/cm^{-1}

	Compound	$\nu_{CN,\,CC}$	ν_{CC}*	$\nu_{CN,\,CC}$	γ_{CH}
	phen [30]	1615	1505	1423	767 734
(V)	$Mn(phen)L_2\cdot 2H_2O$	1595.0	1515.9	1427.2	788.8 731.0
(VI)	$Ni(phen)L_2\cdot 2H_2O$	1593.1	1515.9	1427.2	794.6 727.1
(VII)	$Zn(phen)L_2\cdot 2H_2O$	1596.9	1519.8	1429.2	792.7 729.0
(VIII)	$Cd(phen)L_2\cdot 2H_2O$	1591.2	1515.9	1427.2	783.0 730.0

* associated with carbocyclic ring vibrations

and symmetric $\nu_{s(OCO)}$ vibrations of OCO groups in the ranges 1631.7–1604.7 and 1375.9–1348.1 cm^{-1}, respectively (Table 3). However, the analysis of these regions of spectrum, in the case of **I** and **VIII** compounds does not permit an interpretation of the nature of the metal(II)-formate bonds; $\nu_{as(OCO)}$ (from Zn(2,4'-bpy)$_2$L$_2$·H$_2$O) and $\nu_{s(OCO)}$ (from Cd(phen)L$_2$·H$_2$O) overlaid by 2,4'-bpy frequencies and the absorption $\pi_{CH}+\rho_{r(OCO)}$, respectively. The frequencies of asymmetric ($\nu_{as(OCO)}$) and symmetric ($\nu_{s(OCO)}$) carboxylate vibrations in the IR spectra, and the magnitude of separation $\Delta\nu=\nu_{as(OCO)}-\nu_{s(OCO)}$, are often used as spectroscopic criterions to determine the mode of carboxylate binding [34–39]. Values of $\Delta\nu$ between $\nu_{as(OCO)}$ and $\nu_{s(OCO)}$ for **II**, **III** and **IV** are higher than those for sodium formate ($\Delta\nu_{NaHCOO}=$ $=240$ cm^{-1} [38]). Thus, we state that carboxylate groups in these complexes are probably monodentate.

The $\Delta\nu$ values of formates for M(phen)L$_2$·2H$_2$O are equal 233.3 (Mn), 228.8 (Ni) and 235.3 cm^{-1} (Zn). It suggests, that carboxylate groups in 1,10-phenanthroline complexes of Mn(II), Ni(II) and Zn(II) behave as bidentate chelate ligands. Full interpretation of mode of coordination between metal(II)-carboxylates in obtained compounds would be possible after the determination of crystal structure. The presence of water molecules in isolated complexes is shown by a strong and broad band in the region 3400–3200 cm^{-1}.

Thermal studies

The thermal decomposition data are collected in Table 4. Thermoanalytical curves of Zn(2-bpy)$_3$L$_2$·4H$_2$O and Zn(2,4'-bpy)$_2$L$_2$·H$_2$O (Fig. 1) and Mn(phen)L$_2$·2H$_2$O and Ni(phen)L$_2$·2H$_2$O (Fig. 2) are presented as examples. All the compounds decompose progressively. Thermal decomposition started by dehydration process and is accompanied by endothermic effect. The compounds lose molecules of water in one step. The complexes with 2,4'-*bpy* are thermally more stable than 2-*bpy* compounds. The complexes (**I**) and (**II**) begin to decompose at 200 and 130°C, respectively. Zn(2-bpy)$_3$L$_2$·4H$_2$O and Cd(2-bpy)$_2$L$_2$·3H$_2$O are stable up to 90 and 70°C. When the temperature increases the intermediate anhydrous complexes Zn(2,4'-bpy)$_2$L$_2$ (310–510°) and Zn(2-bpy)$_3$L$_2$ (205–520°C) convert to ZnO with residue of organic fragments. The TG curves show rapid mass loss. Next, the combustion of the remaining organic prod-

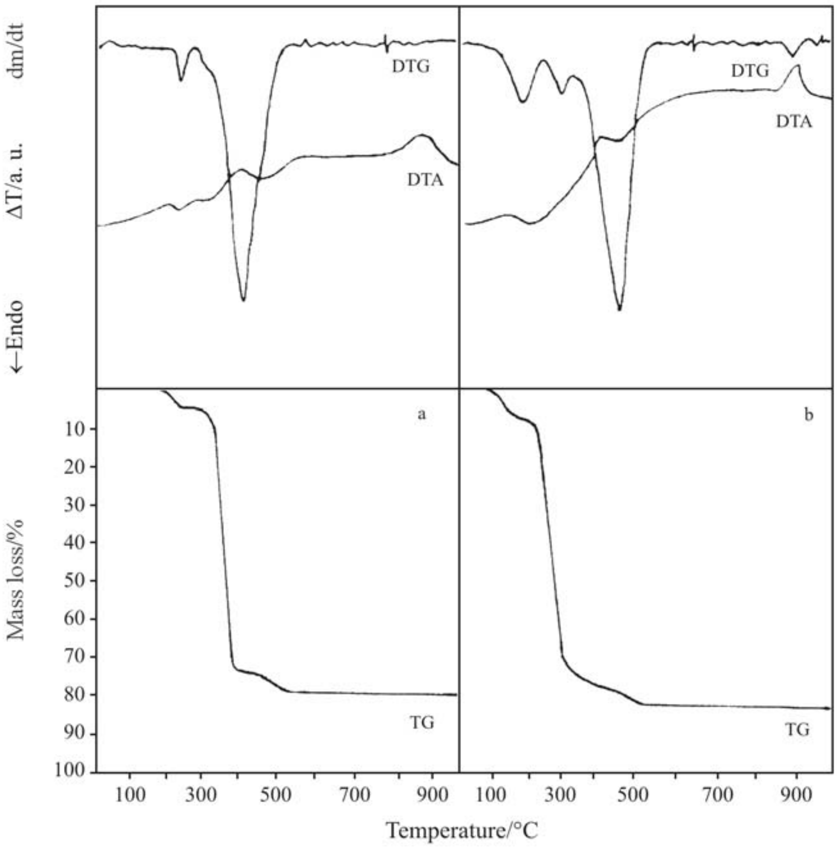

Fig. 1 Thermoanalytical curves for a – Zn(2,4'-bpy)$_2$(HCOO)$_2$·H$_2$O and b – Zn(2-bpy)$_3$(HCOO)$_2$·4H$_2$O (mass sample 100 mg)

Table 3 Principal IR bands for OCO groups in free ligand and obtained complexes/cm^{-1}

	Compound	$\nu_{as(OCO)}$	$\nu_{s(OCO)}$	$\pi_{CH}+\rho_{r(OCO)}$	$\Delta\nu=\nu_{as}-\nu_{s}$
	HCOONa [40]	1597	1357	1389	240
	2,4'-bipyridine-formato complexes				
(I)	Zn(2,4'-bpy)$_2$L$_2$·H$_2$O		1373.2	1390.0	*
(II)	Cd(2,4'-bpy)$_2$L$_2$·H$_2$O	1631.7	1370.0	1385.0	261.7
	2,2-bipyridine-formato complexes				
(III)	Zn(2-bpy)$_3$L$_2$·4H$_2$O	1631.7	1348.1	1384.8	283.6
(IV)	Cd(2-bpy)$_2$L$_2$·3H$_2$O	1631.7	1352.0	1380.9	279.7
	1, 10-phenanthroline-formato complexes				
(V)	Mn(phen)L$_2$·2H$_2$O	1608.5	1375.2	1388.7	233.3
(VI)	Ni(phen)L$_2$·2H$_2$O	1604.7	1375.9	1380.9	228.8
(VII)	Zn(phen)L$_2$·2H$_2$O	1610.5	1375.2	1390.6	235.3
(VIII)	Cd(phen)L$_2$·2H$_2$O	1631.7			*

* the nature of the M-formate bonds does not interpreted

ucts takes place and pure ZnO is formed. The strong and broad exothermic peaks originating from oxidation of organic residues are observed (Table 4). In the range 320–570°C the intermediate product Cd(2,4'-bpy)$_2$L$_2$ begins to decompose and formation mixture of CdCO$_3$ with CdO occurs. A constant mass level for CdO begins at 760°C. The appropriate endothermic peaks on DTA are at 410 and 540°C. The anhydrous compound (**IV**) lose one mol of 2-*bpy* between 160–380°C. The decomposition of intermediate Cd(2-bpy)L$_2$ to CdCO$_3$ takes place at 380–480°C. In higher temperature (~760°C) pure CdO is observed. The DTA curve shows endothermic peaks at 360 and 440°C.

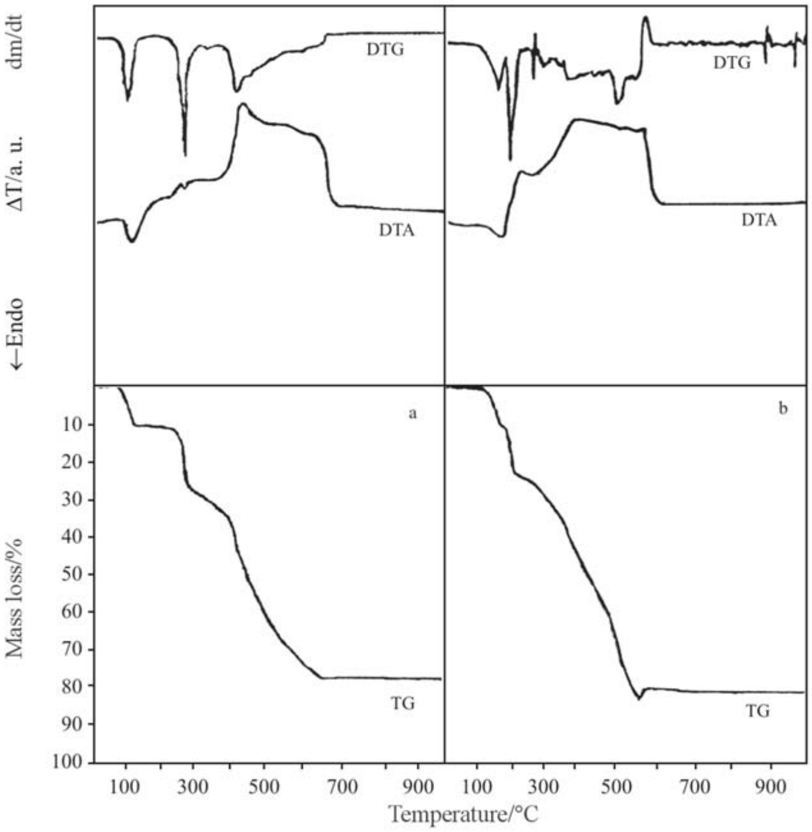

Fig. 2 Thermoanalytical curves for a – Mn(phen)(HCOO)$_2$·2H$_2$O and b – Ni(phen)(HCOO)$_2$·2H$_2$O (mass sample 100 mg)

Table 4 Thermal decomposition data of obtained complexes in air; mass sample 100 mg

No.	Complex	Ranges of decomposition/°C	DTA peaks/°C	Mass loss/% found	Mass loss/% calc.	Intermediate and final solid products
(I)	$Zn(2,4'\text{-}bpy)_2L_2\cdot H_2O$	200–240	230 endo	4.0	3.71	$Zn(2,4'\text{-}bpy)_2L_2$
		310–510	395 exo			ZnO+organic fragments[a]
		510–920	850 exo br	75.0	75.54	ZnO
(II)	$Cd(2,4'\text{-}bpy)_2L_2\cdot H_2O$	130–220	205 endo	3.5	3.38	$Cd(2,4'\text{-}bpy)_2L_2$
		320–570	410, 540 endo	69.5	–	mixture of $CdCO_3$ and CdO[a]
		>760	900 exo	3.0	72.52	CdO
(III)	$Zn(2\text{-}bpy)_3L_2\cdot 4H_2O$	90–200	170 endo	10.5	10.53	$Zn(2\text{-}bpy)_3L_2$
		205–520	400 exo			ZnO + organic fragments[a]
		520–920	900 exo	71.0	70.96	ZnO
(IV)	$Cd(2\text{-}bpy)_2L_2\cdot 3H_2O$	70–150	140 endo	9.0	9.50	$Cd(2\text{-}bpy)_2L_2$
		160–380	360 endo	27.0	27.45	$Cd(2\text{-}bpy)L_2$
		380–480	440 endo	33.0	32.73	$CdCO_3$
		480–760	770 exo	8.0	7.74	CdO
(V)	$Mn(phen)L_2\cdot 2H_2O$	80–120	110 endo	10.0	9.98	$Mn(phen)L_2$
		230–380	260 endo	24.0	24.94	$Mn(phen)_{0.5}L_2$
		380–660	440–630 exo	43.5	43.97	Mn_3O_4
(VI)	$Ni(phen)L_2\cdot 2H_2O$	100–180	160 endo	10.0	9.87	$Ni(phen)L_2$
		180–250	220 endo	12.0	12.35	$Ni(phen)_{0.75}L_2$
		250–560	400–560 exo	58.0	–	NiO with traces of Ni
		>570		+2.0	57.31	NiO
(VII)	$Zn(phen)L_2\cdot 2H_2O$	90–125	100 endo	10.0	9.69	$Zn(phen)L_2$
		180–335	200 endo	25.0	24.24	$Zn(phen)_{0.5}L_2$
		335–630	525 exo br	43.0	43.17	ZnO
(VIII)	$Cd(phen)L_2\cdot H_2O$	110–190	120 endo	4.0	4.49	$Cd(phen)L_2$
		190–370	250 endo	38.0	–	mixture of $CdCO_3$ and CdO[a]
		370–770	680 exo br	25.0	63.01	CdO

br – broad

[a] – quantitative composition does not investigated

During heating, the $Mn(phen)L_2\cdot 2H_2O$ (**V**), $Ni(phen)L_2\cdot 2H_2O$ (**VI**) and $Zn(phen)L_2\cdot 2H_2O$ (**VII**) complexes lose molecules of water in the ranges 80–120 (**V**), 100–180 (**VI**) and 90–125°C (**VII**). After that, elimination of 1,10-phenanthroline begins and the intermediate products: $Mn(phen)_{0.5}L_2$ (230–380°C), $Ni(phen)_{0.75}L_2$ (180–250°C) and $Zn(phen)_{0.5}L_2$ (180–335°C) were formed. On DTA curve endothermic effects at 260 (**V**), 220 (**VI**) and 200°C (**VII**) exist. Between 380–660 (**V**) and 335–630°C (**VII**) the Mn_3O_4 and ZnO occur, respectively. Further heating $Ni(phen)_{0.75}L_2$ causes decomposition to mixture NiO with trace of Ni. X-ray diffraction patterns indicate that NiO with Ni are presented in the sinter of complex (**VI**) heated up to 560°C. A plateau for NiO in the TG curve being obtained above 570°C. Thermal decomposition of $Cd(phen)L_2\cdot H_2O$ is started at 110°C. First is dehydration process with endothermic effect on DTA curve at 120°C. With increasing of temperature (190–370°C) mixture of $CdCO_3$ and CdO exists. The final solid product of decomposition is CdO accompanied by broad exothermic effect at 680°C. The lines for all final products corresponded to those reported in Powder Diffraction File [41].

Conclusions

In this paper we described in solid state mixed-ligands metal(II) complexes with N-donors (2-*bpy*, 2,4'-*bpy* or *phen*) and formates. On basis of our previous papers [21, 22], the literature data [19, 20] and present studies stated, that metal(II) complexes with bipyridine isomers or *phen* and formates formed compounds of the principally following empirical formulae: $M(2\text{-}bpy)_2L_2\cdot nH_2O$

(Co, Cu [22], Cd), $M(2\text{-bpy})_3L_2\cdot nH_2O$ (Ni [22], Zn), $M(2,4'\text{-bpy})_2L_2\cdot nH_2O$ (Mn, Co, Ni, Cu [22], Zn, Cd) and $M(4\text{-bpy})L_2\cdot nH_2O$ (Mn, Co, Ni, Cu [19–21]). They were prepared as solid state with various degree of hydration or in anhydrous form [21]. The IR spectroscopy confirms, that the metal ions are bonded to N-donor ligands. The carboxylate groups have versatile the mode of coordination to metal(II). These groups in the obtained complexes with 2-*bpy* or 2,4'-*bpy* are bonded as monodentate (or 'pseudomonodentate') ligands [22], whereas bidentate chelating or bridging formates exist in the major 4,4'-bipyridine complexes [19–21]. The mode of metal-carboxylate coordination probably depends on the nitrogen atoms position in the bipyridine isomers [14, 32, 33]. The carboxylate groups in 1,10-phenanthroline-formato complexes of Mn(II), Ni(II) and Zn(II) behave as bidentate chelating ligands.

The investigated mixed-ligands metals(II) complexes with N-donors and formates are more stable than the major formate dihydrates of M(II) [42]. Thermal decomposition of obtained complexes started with the release of water molecules. The pyrolysis of transition anhydrous complexes is multistage and yields oxides as final products. Among obtained complexes the most stable are 2,4'-bipyridine-formato (initial temperature of decomposition of $Zn(2,4'\text{-bpy})_2L_2\cdot H_2O$ is 200°C) and some 4,4'-bipyridine-formato compounds [21]. The phenathroline-formato complexes are somewhat more stable than compounds with 2,2-bipyridine.

Additionally, in this paper we stated, that the complexes of $Zn(2,4'\text{-bpy})_2L_2\cdot H_2O$ and $Cd(2,4'\text{-bpy})_2L_2\cdot H_2O$ are isostructural. The magnetic moment and the ligand field spectrum of complex $Ni(phen)L_2\cdot 2H_2O$ is characteristic of octahedral environment around Ni(II).

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Received: October 19, 2006
Accepted: January 4, 2007
OnlineFirst: April 29, 2007

DOI: 10.1007/s10973-006-7980-9