Complexes of Zn(II) and Cd(II) with Bipyridine Isomers and Chloroacetates

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Metal complexes with carboxylates and N-donors play an essential role in biological systems. Some of these compounds have pharmaceutical effects. Furthermore, Zn(II) complexes can be used as model compounds to study of properties of the active site of metalloenzymes [1–3]. Recently, mixed ligand complexes of Zn(II) and Cd(II) with 4,4′-bipyridine (4-bpy) and monobromo-, monochloro- or trichloroacetates, Cd(II) complexes with 2,4′-bipyridine (2,4′-bpy) and monobromo- or monochloroacetates were obtained and investigated in our laboratory [4,5]. The coordination compounds of Zn(II) with 2,2′-bipyridine (2-bpy) or 4-bpy and trichloro- or trifluoroacetates were described in other papers [3,6]. Now, we present the results of synthesis, molar conductivity and IR spectra of new complexes of Zn(II) and Cd(II) with three isomers of bipyridine (2-bpy, 4-bpy and 2,4′-bpy) and dichloroacetates (dca) and 2-bpy complexes of these metals with trichloroacetates (tca). The thermal decomposition was investigated in static air atmosphere in the temperature range 20–1000°C. Molar conductivity (Λ_M) was measured using $1 \cdot 10^{-3}$ mol L^{-1} solutions in methanol (MeOH), dimethylformamide (DMF) and dimethylsulfoxide (DMSO) at 25°C. Other experimental conditions, the apparatus and materials were the same as those described earlier [4,5,7]. Solutions of Zn(II) and Cd(II) dichloro- or trichloroacetates were obtained by dissolving freshly precipitated metal(II) carbonates in 2 mol L^{-1} suitable chloroacetic acid in *ca* stoichiometric quantities. 2-Bpy complexes of Zn(II) and Cd(II) were prepared by adding a solution of 2-bpy (12.8 mmol in 31 mL of 96% v/v ethanol) to freshly obtained solutions of appropriate metal(II) dichloro- or trichloroacetates (6.4 mmol in 9 mL of water). The product was collected, washed with 40% v/v ethanol and then with ethanol and diethyl ether mixture (1:1). The remaining complexes were obtained by reacting of dichloroacetates of Zn(II) and Cd(II) with 4-bpy or 2,4′-bpy in accordance with previously published procedure [5]. All complexes were dried in open air. The complexes were analysed: C, N, H by elemental analysis with V_2O_5 as oxidizing agent; metals in mineralized sample were determined complexometrically. The theoretical composition was confirmed by analysis in limits $0.05 \div 0.5\%$. New complexes of empirical formulae: Zn(2-bpy)(dca)$_2$·2H$_2$O (**1**), Zn(4-bpy)(dca)$_2$·2H$_2$O (**2**), Zn(2,4′-bpy)$_2$(dca)$_2$·H$_2$O (**3**), Zn(2-bpy)$_2$(tca)$_2$·2H$_2$O (**4**), Cd(2-bpy)$_2$(dca)$_2$·H$_2$O (**5**), Cd(4-bpy)(dca)$_2$·H$_2$O

(**6**), Cd(2,4′-bpy)$_2$(dca)$_2$·2H$_2$O (**7**) and Cd(2-bpy)$_2$(tca)$_2$·H$_2$O (**8**) in solid state were isolated. The molar conductivity for investigated complexes in DMF solutions is in the range 4–35 Ω^{-1} cm^2 mol^{-1}. Thus, they behave as non-electrolytes. Conductivity data suggest that the complexes in methanol solutions (Λ_M in the range 70–103 Ω^{-1} cm^2 mol^{-1}) show behaviour between those of non-electrolytes and 1:1 electrolytes (complexes **1–3**, **6**, **7**) or 1:1 electrolytes (complexes **4**, **5**, **8**). However, in DMSO solutions (Λ_M in the range 13–47 Ω^{-1} cm^2 mol^{-1}) the complexes indicate probably 1:1 electrolytic properties (except complexes **4** and **8**, which are non-electrolytes in this solvent) [8]. Higher than anticipated values of Λ_M are usually due to the displacement of halogenoacetatates ligands by solvent molecules [4,5,7]. In Table 1 some relevant IR absorption bands of 2-bpy, 4-bpy and 2,4′-bpy in complexes together with possible assignments described in [9,10] are reported. All above bands in the spectra of complexes are shifted towards higher frequencies in comparison to unbonded bipyridine isomers, what indicates that these N-donors are coordinated to metal(II) [4,5].
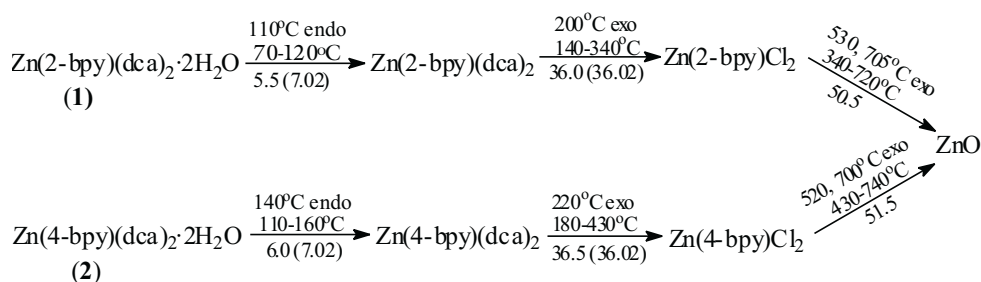
Table 1. Principal IR bands (cm^{-1}) for bipyridine and OCO group in obtained complexes (dca = dichloroacetates, tca = trichloroacetates).

Complex	Assignment					
	ν(CC), ν(CN), ν(CC)$_{i.r.}$ [a]	ν(CN), ν(CC) [b]	Ring "breathing"	ν_{as}(OCO)	ν_s(OCO)	$\Delta\nu = \nu_{as} - \nu_s$
Zn(2-bpy)(dca)$_2$·2H$_2$O	1608.5	1575.7	1026.1	1651.0	1371.2	279.8
				1625.9	1357.8	268.1
Zn(2-bpy)$_2$(tca)$_2$·2H$_2$O	1606.6	1577.7	1022.2	1678.0	1330.8	347.2
				1662.5	1319.2	343.3
Cd(2-bpy)$_2$(dca)$_2$·H$_2$O	1593.1	1575.7	1012.6	1656.0	1373.2	282.8
				1652.0	1359.7	292.3
				1627.8	1344.3	283.5
Cd(2-bpy)$_2$(tca)$_2$·H$_2$O	1595.0	1577.7	1014.5	1695.3	1342.2	353.1
				1683.7	1321.1	362.6
Zn(4-bpy)(dca)$_2$·2H$_2$O	1608.5	1539.1	1008.1	1645.2	1402.2	243.0
					1388.7	285.0
Cd(4-bpy)(dca)$_2$·H$_2$O	1616.0	1533.3	1008.1	*	1379.0	–
Zn(2,4′-bpy)$_2$(dca)$_2$·H$_2$O [c]	1620.1	1552.6	1026.1	1660.6	1380.9	279.7
				1643.2	1388.7	285.4
Cd(2,4′-bpy)$_2$(dca)$_2$·2H$_2$O [c]	1612.4	1552.6	1018.3	1629.7	1377.1	252.6

i.r. – inter ring, [a] A_1 symmetry, [b] B_1 symmetry, [c] only for 4-substituted pyridine, * overlaid by 4-bpy absorption
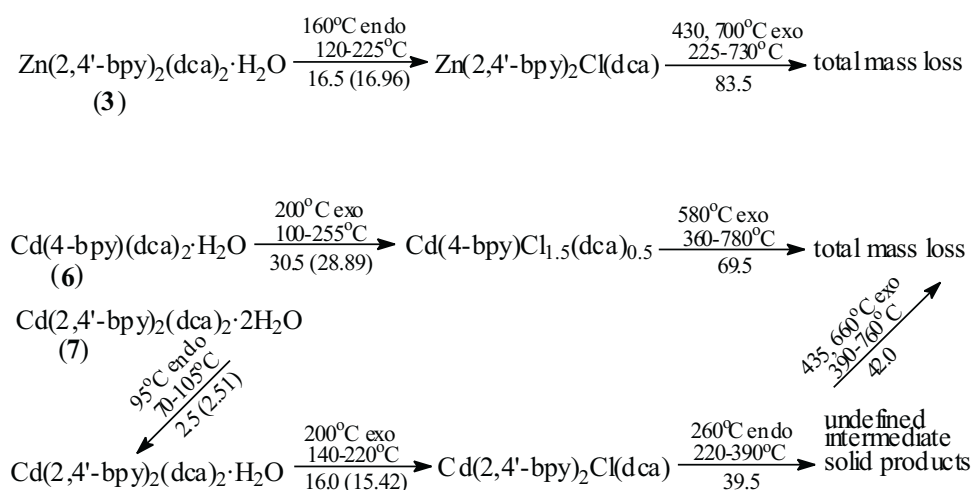
In 2-bpy complexes the bands characteristic for out-of- plane mode of the C–H group at 763.8–776.6 and 734.8–736.8 cm^{-1} are shifted when compared to free 2-bpy (753 and 738 cm^{-1}). These IR data suggest that they are *cis*-2,2′-bipyridine chelates [11].

Due to formation of complexes with metal ions, IR spectrum of 2,4′-bpy undergoes a change only in the region of the ring vibration modes of 4-substituted pyridine. These observations permit to presume that 2,4′-bpy coordinates *via* the least hindered (4′) N atom as a monodentate ligand [5,12,13]. The IR spectra of complexes exhibit absorption of the dichloro- or trichloroacetato ligands. Principal bands corresponding to asymmetric (ν_{as}) and symmetric (ν_s) stretching frequencies of OCO groups are also listed in Table 1. Generally, increase $\nu_{as}(OCO)$ and decrease $\nu_s(OCO)$ frequencies relative to values for sodium salts is observed. The values of separation $\Delta\nu = \nu_{as}(OCO) - \nu_a(OCO)$ of dichloro- or trichloroacetate groups are in the range 253–292 and 347–363 cm^{-1}, respectively. They are higher than the values for suitable sodium salts (CCl$_2$HCOONa $\Delta\nu$ = 241 cm^{-1}; CCl$_3$COONa $\Delta\nu$ = 324 cm^{-1} [14]). On the basis of the spectroscopic criterium [15] and other IR data [16–19], the carboxylate groups of dichloro- and trichloroacetates are monodentate, only in complex Zn(4-bpy)(dca)$_2$·2H$_2$O the group OCO acts as monodentate and probably strong intermolecular hydrogen bonds exist (one value of $\Delta\nu$ is almost the same as for sodium salt). The nature of cadmium−dichloroacetate bonds in Cd(4-bpy)(dca)$_2$·H$_2$O is not discussed, because the band of $\nu_{as}(OCO)$ is masked by the absorption of 4-bpy. The splitting of $\nu_{as}(OCO)$ and $\nu_a(OCO)$ bands is observed for all investigated zinc(II) compounds and 2-bpy complexes of Cd(II). It is probably due to formation of non-completely equivalent bonds between metal(II) and carboxylate groups [20]. The strong and broad bands occur in the range *ca* 3400–3500 cm^{-1} confirm the presence of water in all the complexes. The synthesized complexes are stable at room temperature. The thermal decomposition of complexes was investigated by TG, DTA, DTG techniques in air. The solid intermediate products of pyrolysis were determined from TG curves and confirmed by recording the IR spectra of sinters. The IR spectra of sinters (prepared during the heating of complexes up to an appropriate temperature determined from the TG curves) show the existance of bipyridine and carboxylate groups of dichloroacetates bands for compounds M(bpy)$_n$Cl$_m$(dca)$_{2-m}$ or only bands of bipyridine in M(bpy)$_n$Cl$_2$. In sinters presence of anion Cl$^-$ was stated. At the end of thermal decompostion of all complexes, on increase of the temperature a continuous loss in mass is observed as a result of the gradual volatilization of ZnCl$_2$ or CdCl$_2$. Final decompostion of complexes **3**, **6** and **7** ends with a total mass loss. For remaining complexes only *ca* 6% corresponding metal oxide (ZnO or CdO) is formed as a final product. Similar effects were stated for other mixed ligand complexes of Zn(II) and Cd(II) with N-donor and halogenocarboxylate [4,5,21,22]. The processes of pyrolysis of investigated complexes are accompanied by several exo- and endothermic effects in the DTA curves (they are given on Schemes below). The complexes Zn(2-bpy)(dca)$_2$·2H$_2$O, Zn(4-bpy)(dca)$_2$·2H$_2$O and Cd(2,4′-bpy)$_2$(dca)$_2$·2H$_2$O are stable up to 70–110°C and then lose water with the formation of anhydrous Zn(II) compounds and Cd(2,4′-bpy)$_2$(dca)$_2$·H$_2$O. Next, anhydrous complexes **1** and **2** decompose to intermediate product Zn(bpy)Cl$_2$.

$$\text{Zn(2-bpy)(dca)}_2\cdot 2\text{H}_2\text{O} \xrightarrow[\substack{5.5\,(7.02)}]{\substack{110^\circ\text{C endo}\\70\text{-}120^\circ\text{C}}} \text{Zn(2-bpy)(dca)}_2 \xrightarrow[\substack{36.0\,(36.02)}]{\substack{200^\circ\text{C exo}\\140\text{-}340^\circ\text{C}}} \text{Zn(2-bpy)Cl}_2 \xrightarrow[\substack{50.5}]{\substack{530,\,705^\circ\text{C exo}\\340\text{-}720^\circ\text{C}}}$$

(1)

$$\text{ZnO}$$

$$\text{Zn(4-bpy)(dca)}_2\cdot 2\text{H}_2\text{O} \xrightarrow[\substack{6.0\,(7.02)}]{\substack{140^\circ\text{C endo}\\110\text{-}160^\circ\text{C}}} \text{Zn(4-bpy)(dca)}_2 \xrightarrow[\substack{36.5\,(36.02)}]{\substack{220^\circ\text{C exo}\\180\text{-}430^\circ\text{C}}} \text{Zn(4-bpy)Cl}_2 \xrightarrow[\substack{51.5}]{\substack{520,\,700^\circ\text{C exo}\\430\text{-}740^\circ\text{C}}}$$
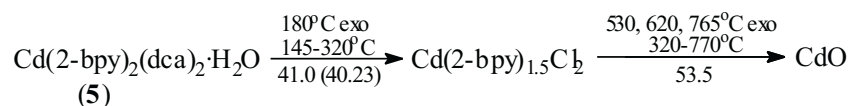
(2)

On all schemes are shown below the arrows the mass loss (%) found (without brackets) and those calculated (in brackets). Above the arrows there are given ranges of decomposition and peaks from DTA (°C).
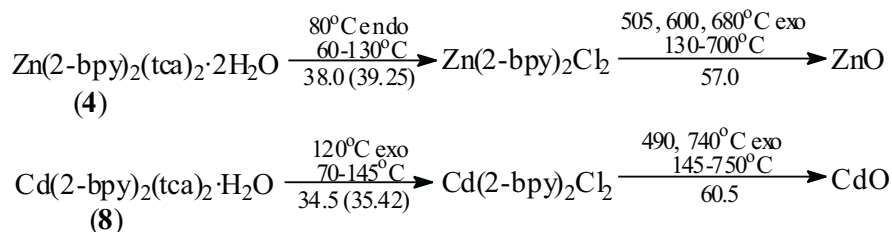
The dehydration of complexes $\text{Zn(2,4'-bpy)}_2(\text{dca})_2\cdot\text{H}_2\text{O}$, $\text{Cd(4-bpy)(dca)}_2\cdot\text{H}_2\text{O}$ and transitional compound $\text{Cd(2,4'-bpy)}_2(\text{dca})_2\cdot\text{H}_2\text{O}$ (in the range 120–255°C) is connected with partial pyrolysis of dichloroacetates and the formation of $\text{Zn(2,4'-bpy)}_2\text{Cl(dca)}$, $\text{Cd(4-bpy)Cl}_{1.5}(\text{dca})_{0.5}$ and $\text{Cd(2,4'-bpy)}_2\text{Cl(dca)}$, respectively.

$$\text{Zn(2,4'-bpy)}_2(\text{dca})_2\cdot\text{H}_2\text{O} \xrightarrow[\substack{16.5\,(16.96)}]{\substack{160^\circ\text{C endo}\\120\text{-}225^\circ\text{C}}} \text{Zn(2,4'-bpy)}_2\text{Cl(dca)} \xrightarrow[\substack{83.5}]{\substack{430,\,700^\circ\text{C exo}\\225\text{-}730^\circ\text{C}}} \text{total mass loss}$$

(3)

$$\text{Cd(4-bpy)(dca)}_2\cdot\text{H}_2\text{O} \xrightarrow[\substack{305\,(28.89)}]{\substack{200^\circ\text{C exo}\\100\text{-}255^\circ\text{C}}} \text{Cd(4-bpy)Cl}_{1.5}(\text{dca})_{0.5} \xrightarrow[\substack{69.5}]{\substack{580^\circ\text{C exo}\\360\text{-}780^\circ\text{C}}} \text{total mass loss}$$

(6)

$$\text{Cd(2,4'-bpy)}_2(\text{dca})_2\cdot 2\text{H}_2\text{O}$$

(7)

$$\xrightarrow[\substack{2.5\,(2.51)}]{\substack{95^\circ\text{C endo}\\70\text{-}105^\circ\text{C}}}$$

$$\text{Cd(2,4'-bpy)}_2(\text{dca})_2\cdot\text{H}_2\text{O} \xrightarrow[\substack{16.0\,(15.42)}]{\substack{200^\circ\text{C exo}\\140\text{-}220^\circ\text{C}}} \text{Cd(2,4'-bpy)}_2\text{Cl(dca)} \xrightarrow[\substack{39.5}]{\substack{260^\circ\text{C endo}\\220\text{-}390^\circ\text{C}}} \substack{\text{undefined}\\\text{intermediate}\\\text{solid products}}$$

$$\xrightarrow[\substack{42.0}]{\substack{435,\,660^\circ\text{C exo}\\390\text{-}760^\circ\text{C}}}$$

In the case of $\text{Cd(2-bpy)}_2(\text{dca})_2\cdot\text{H}_2\text{O}$ the first step of decomposition is characterized by a sudden mass loss between 145–320°C. At that time the dehydration, total pyrolysis of dichloroacetates and partial elimination of 2-bpy take place, and $\text{Cd(2-bpy)}_{1.5}\text{Cl}_2$ is formed.

$$\text{Cd(2-bpy)}_2(\text{dca})_2\cdot\text{H}_2\text{O} \xrightarrow[\substack{41.0\,(40.23)}]{\substack{180^\circ\text{C exo}\\145\text{-}320^\circ\text{C}}} \text{Cd(2-bpy)}_{1.5}\text{Cl}_2 \xrightarrow[\substack{53.5}]{\substack{530,\,620,\,765^\circ\text{C exo}\\320\text{-}770^\circ\text{C}}} \text{CdO}$$

(5)

Dehydration process of complexes $Zn(2\text{-bpy})_2(tca)_2 \cdot 2H_2O$ and $Cd(2\text{-bpy})_2(tca)_2 \cdot$ $\cdot H_2O$ (60–145°C) is associated with complete decomposition of trichloroacetates and compounds of the type $M(2\text{-bpy})_2Cl_2$ are formed as intermediate products.

$$Zn(2\text{-bpy})_2(tca)_2 \cdot 2H_2O \xrightarrow[\substack{60\text{-}130^o C \\ 38.0\,(39.25)}]{80^o C\ endo} Zn(2\text{-bpy})_2Cl_2 \xrightarrow[\substack{130\text{-}700^o C \\ 57.0}]{505,\,600,\,680^o C\ exo} ZnO$$

$$\textbf{(4)}$$

$$Cd(2\text{-bpy})_2(tca)_2 \cdot H_2O \xrightarrow[\substack{70\text{-}145^o C \\ 34.5\,(35.42)}]{120^o C\ exo} Cd(2\text{-bpy})_2Cl_2 \xrightarrow[\substack{145\text{-}750^o C \\ 60.5}]{490,\,740^o C\ exo} CdO$$

$$\textbf{(8)}$$

The bipyridine–dichloroacetato complexes of Zn(II) or Cd(II) are thermally more stable than corresponding bipyridine–trichloroacetato complexes. The $Cd(2\text{-bpy})_2(dca)_2 \cdot H_2O$ is the most stable compound of all studied complexes. During the thermal decomposition of bipyridine–dichloroacetato complexes of other metals(II) (Mn, Co, Ni), the formation of intermediate compounds of the type $M(bpy)_nCl_m(dca)_{2\text{-}m}$ and $M(bpy)_nCl_2$ was also stated [7]. The prepared complexes $Zn(2\text{-bpy})(dca)_2 \cdot 2H_2O$, $Zn(4\text{-bpy})(dca)_2 \cdot 2H_2O$ and anhydrous compounds $Zn(2\text{-bpy})(dca)_2$, $Zn(4\text{-bpy})(dca)_2$ are new examples of complexes with ligand isomerism.

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