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Complexes of Zinc(II) and Cadmium(II) with Bipyridine Isomers and Monohalogenoacetates

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Previously, the preparation, properties and thermal decompostion of some bipyridine (2-bpy = 2,2′-bipyridine, 4-bpy = 4,4′-bipyridine or 2,4′-bpy = 2,4′-bipyridine) complexes of metals containing inorganic ligands, acetates or oxalates have been described [1–3]. Data concerning bipyridine complexes of Zn(II) and Cd(II) were also published by other autors [4,5]. Recently, mixed ligand complexes of Zn(II) and Cd(II) with 4-bpy [3] or 2-bpy [6] and trichloroacetates were obtained and investigated. It is interesting to examine the influence of other halogeno substituted acetates on properties of mixed ligand bipyridine complexes of title metals(II). Now, complexes of Zn(II) and Cd(II) with 4,4′-bipyridine or 2,4′-bipyridine and monobromoacetates or monochloroacetates in the solid state were prepared and their physico-chemical properties and thermal decomposition in air were described. Water solutions of Zn(II) and Cd(II) monobromoacetates or monochloroacetaes were prepared by dissolving freshly precipitated metal(II) carbonates in 20 cm^3 of 2 M suitable monohalogenoacetic acid in *ca* equimolar ratio. Other materials were the same as described in [1,7]. The thermal stability of the prepared complexes was investigated by TG, DTA, DTG techniques as previously [3]. In this paper, a coupled TG-MS system was used for detection of some volatile pyrolysis products of complex $Zn(4\text{-}bpy)(ClCH_2COO)_2 \cdot 2H_2O$: derivatograph TG/DTA-SETSYS-16/18, mass spectrometer ThermoSTART from Balzers, crucible Pt 100 μl (with sample of 8.52 mg). All the thermal investigations were carried out in air. IR spectra were recorded on FTIR-8501 Shimadzu spectrometer as KBr pellets (4000–400 cm^{-1}). The devices and experimental conditions were given earlier [1,7]. 4-Bpy complexes of Zn(II) and Cd(II) were prepared by mixing 12.8 mmol of 4-bpy in 96% v/v ethanol (31.3 cm^3) with the solution of 4.3 mmol metal monohalogenoacetates in 8.7 cm^3 of water. 2,4′-Bpy complexes of Zn(II) and Cd(II) were obtained by adding 12.8 mmol of 2,4′-bpy in 14.8 cm^3 of water with 0.2 cm^3 96% v/v ethanol to suitable solution of monohalogenoacetates (4.3 mmol in 15 cm^3 of water). In both cases reacting mixtures were stirred at room temperature. Precipitations of the products occurred immediately. They were collected by filtration, washed with 40% v/v ethanol (or water for 2,4′-bpy complexes) and then with ethanol and diethyl ether mixture (1:1) and dried at room temperature. The metal analyses in mineralized samples of these complexes were carried out by complexometric method. The contents of C, H and N were determined by elemental analysis with V_2O_5 as oxidizing agent. The theoretical composition was confirmed by analysis in limits 0.05÷0.5%. Six new complexes with the empirical formulae: $Zn(4\text{-}bpy)(BrCH_2COO)_2{\cdot}H_2O$ (**1**), $Zn(4\text{-}bpy)(ClCH_2COO)_2{\cdot}2H_2O$ (**2**), $Cd(4\text{-}bpy)(BrCH_2COO)_2{\cdot}H_2O$ (**3**), $Cd(4\text{-}bpy)(ClCH_2COO)_2{\cdot}H_2O$ (**4**), $Cd(2,4'\text{-}bpy)_2(BrCH_2COO)_2{\cdot}2H_2O$ (**5**), $Cd(2,4'\text{-}bpy)_2(ClCH_2COO)_2{\cdot}2H_2O$ (**6**) in the solid state were synthesized. Zn(II) complexes with 2,4’-bpy and monobromoacetates or monochloroacetates were obtained as $Zn(2,4'\text{-}bpy)_2Br_2$ and $Zn(2,4'\text{-}bpy)_2Cl_2$, respectively. The same complexes were prepared by the direct reaction of 2,4′-bpy with suitable halides of Zn(II) and were described in [1]. All the obtained complexes were white. After three months their white colour transformed to clearly beige. The molar conductivities (Λ_M) in methanol solution ($1{\cdot}10^{-3}$ mol dm^{-3} at 25°C) for complexes $Zn(4\text{-}bpy)(BrCH_2COO)_2{\cdot}H_2O$, $Cd(4\text{-}bpy)(ClCH_2COO)_2{\cdot}H_2O$, $Cd(2,4'\text{-}bpy)_2(BrCH_2COO)_2{\cdot}2H_2O$ and $Cd(2,4'\text{-}bpy)_2(ClCH_2COO)_2{\cdot}2H_2O$ were: 61.1; 49.5; 42.9 and 48.5 Ω^{-1} cm^2 mol^{-1}, respectively. Thus, they behave as non-electrolytes [8]. The compounds $Zn(4\text{-}bpy)(ClCH_2COO)_2{\cdot}2H_2O$ and $Cd(4\text{-}bpy)(BrCH_2COO)_2{\cdot}H_2O$ are practically insoluble in anhydrous methanol. The presence of water in all complexes is shown by strong and broad bands in region 3300–3500 cm^{-1}. Some important IR bands of 4-bpy (I–III) and 2,4′-bpy (IV–VII) and their complexes together with possible assignments described in [9] are given in Table 1.

Table 1. Principal IR bands (cm^{-1}) for 4-bpy or 2,4′-bpy and bipyridine–monohalogenoacetato complexes (**1**÷**6**).

No	Assignment of bands [9]	4,4′-Bipyridine–halogenoacetato complexes				
		4-bpy [10]	(**1**)	(**2**)	(**3**)	(**4**)
I	C–C, C–N, C–C$_{i.r.}$ str.	1588 vs	1610 vs	1608 vs	1605 vs	1604 vs
II	C–N, C–C str.	1530 vs	1541 m	1541 m	1533 m	1539 w
III	ring “breathing”	988 vs	1012 m	1009 vs	1007 vs	1007 m

		2,4′-Bipyridine–halogenoacetato complexes		
		2,4′-bpy [10]	(**5**)	(**6**)
IV	C–C, C–N, C–C$_{i.r.}$ str. (4-sub)	1595 s	1608 vs	1610 vs
V	C–C, C–N, C–C$_{i.r.}$ str. (2-sub)	1586 s	1589 vs	1589 vs
VI	H bend. + ring str. (4-sub)	1405 m	1416 s	1416 s
VII	ring “breathing”: (4-sub)	990 sh	1011 vs	1013 s

i. r. – inter-ring; vs, m, w, sh – very strong, medium, weak, shoulder.

In spectra of Zn(II) and Cd(II) 4-bpy complexes the bands assigned as ring stretching modes: I (A_1 symmetry), II (B_1 symmetry) and ring “breathing” modes are observed in the ranges 1604–1610, 1533–1541 and 1007–1012 cm^{-1}, respectively. These bands are shifted towards higher frequencies in comparison to free 4-bpy [10], what indicates that this ligand is coordinated to metal ions [3,7]. Due to formation of complexes with Cd(II), the IR spectrum of 2,4′-bpy undergoes a change only in the region of vibration modes for 4-substituted pyridine (4-sub). The bands IV and VI assigned as ring stretching modes for (4-sub) pyridine appear at 1595 and 1405 cm^{-1} for free ligand [10] and are displaced for complexes by *ca* 10–15 cm^{-1} towards higher frequencies. The ring "breathing" frequencies for (4-sub) pyridine (bands VII as shoulder in free 2,4′-bpy at 990 cm^{-1}) are observed at 1011 and 1013 cm^{-1} in complexes as very strong bands. At the same time, the position of bands V for (2-sub) pyridine does not much change in spectra of compounds investigated. Thus, it is possible to assume that 2,4′-bpy coordinates *via* the least hindered (4′) N atom as a monodentate ligand [11–13]. In IR spectra the absorption bands corresponding to symmetric vibrations $\nu_s(OCO)$ of OCO groups appear in the range 1373–1429 cm^{-1} (in monobromoacetato complexes) and 1394–1404 cm^{-1} (for monochloroacetato complexes). The bands of asymmetric vibrations $\nu_{as}(OCO)$ for complexes (**1**), (**5**) and (**6**) occur at 1578, 1632 and 1640 cm^{-1}, respectively. In the spectra of complexes (**2**), (**3**) and (**4**) the bands of $\nu_{as}(OCO)$ are masked by the absorption of 4-bpy. For complexes $Zn(4\text{-}bpy)(BrCH_2COO)_2{\cdot}H_2O$, $Cd(2,4'\text{-}bpy)_2(BrCH_2COO)_2{\cdot}2H_2O$ and $Cd(2,4'\text{-}bpy)_2(ClCH_2COO)_2{\cdot}2H_2O$ the values of separation between $\nu_{as}(OCO)$ and $\nu_s(OCO)$ frequencies $\Delta\nu = \nu_{as}(OCO) - \nu_s(OCO)$ are equal to 154, 259 and 246 cm^{-1}, respectively. In comparison with suitable sodium salts ($BrCH_2COONa$ $\Delta\nu = 181$ cm^{-1}, $ClCH_2COONa$ $\Delta\nu = 185$ cm^{-1} [14]), the values of $\Delta\nu$ for 2,4′-bpy complexes of Cd(II) are higher, whereas for $Zn(4\text{-}bpy)(BrCH_2COO)_2{\cdot}H_2O$ $\Delta\nu$ is smaller. On the basis of the Nakamoto criterion [15] and other papers [16–20], the carboxylate groups in complexes (**5**) and (**6**) are monodentate. In the case of $Zn(4\text{-}bpy)(BrCH_2COO)_2{\cdot}H_2O$ the carboxylate groups are bonding as chelating ligands. Probably non-completely equivalent bonds between Zn(II) and carboxylate groups of the monobromoacetate ligand are formed (the band $\nu_s(OCO)$ is splitted into two) [21]. The results of the thermal decomposition for the complexes were established from thermoanalytical curves (TG, DTA, DTA) and chemical analysis. MS data for $Zn(4\text{-}bpy)(ClCH_2COO)_2{\cdot}2H_2O$ were also applied to confirm the presence of H_2O and CO_2 (and its isotopes) in gaseous products of decomposition. The thermoanalytical data are given in Table 2. The TG and DTG curves of all complexes show a few gradual overlapping stages of the decomposition. The thermal curves exhibit a sufficiently clearly defined dehydration process. The complexes (**2**), (**3**), (**4**), (**5**) and (**6**) are stable up to 60–90°C and then lose water molecules in one step with formation of anhydrous compounds. The dehydration process of $Zn(4\text{-}bpy)(BrCH_2COO)_2{\cdot}H_2O$ is connected with a partial decomposition of the organic ligand between 90–200°C. The mass loss observed on the TG curves corresponds to the formation of $Zn(4\text{-}bpy)Br(BrCH_2COO)$. The dehydration processes are accompanied by small endothermic effects. In the case of complex $Zn(4\text{-}bpy)(ClCH_2COO)_2{\cdot}2H_2O$ (TG-MS measurements Figure 1) the first maximum of ion current for $m/z = 18$ occurs at around 85°C, which coincides with elimination of crystalline water. The thermal decomposition of all anhydrous products occurs in one step. MS data for $Zn(4\text{-}bpy)(ClCH_2COO)_2{\cdot}2H_2O$ suggested that in gaseous pyrolysis products dominates the molecular ion CO_2^+ ($m/z = 44$) probably from the decomposition of carboxylate groups. As it follows from Figure 1, the first maximum for CO_2^+ at

170°C corresponds perfectly to the second mass loss. Further MS peaks for H_2O appeared at 220° and 400°C. In the range 480–530°C and at 620°C were observed the next maxima of ion current for CO_2^+. All peaks are connected with the total decomposition of ligands and the burning of organic residues. MS measurement presents traces of CH_2O^+ (or NO^+ $m/z = 30$), CH_3Cl^+ ($m/z = 50$), $CH_2Cl_2^+$ ($m/z = 84$) and other fragments with $m/z = 78, 79$ in gaseous products of decomposition. At the end of thermal decomposition of all investigated complexes a release and gradual volatilization of appropriate metal(II) halides take place. The total mass loss is observed between 760–780°C, only for $Zn(4\text{-bpy})(ClCH_2COO)_2{\cdot}2H_2O$ at 700°C *ca* 4% ZnO is found. DTA curves exhibited several exo- and endoeffects. The obtained results are in agreement with the thermal behaviour of other mixed ligand complexes of Zn(II) and Cd(II) containing nitrogen donors and halogenocarboxylates [1,3,22–24].

Table 2. Thermal decomposition for complexes of Zn(II) and Cd(II) with 4-bpy or 2,4′-bpy and monohalogenoacetates in air (mass sample 100 mg).

No	Complex	Temp. range/°C	DTA peak /°C	Mass loss for dehydration obs. (calcd) %
(**1**)	$Zn(4\text{-bpy})(BrCH_2COO)_2{\cdot}H_2O$	90–200	90 endo	14.5 (14.75) [a]
		200–760 [b]	310, 520 exo br	
(**2**)	$Zn(4\text{-bpy})(ClCH_2COO)_2{\cdot}2H_2O$	75–100	95 endo	8.5 (8.10)
		135–700 [b]	160, 430, 665 exo	
		> 700 [c]		
(**3**)	$Cd(4\text{-bpy})(BrCH_2COO)_2{\cdot}H_2O$	90–150		3.0 (3.20)
		150–760 [b]	200, 350, 480 exo	
			505 exo	
(**4**)	$Cd(4\text{-bpy})(ClCH_2COO)_2{\cdot}H_2O$	60–120		3.5 (3.80)
		135–770 [b]	165, 275, 350 exo	
			480, 540 exo	
			760 endo	
(**5**)	$Cd(2,4'\text{-bpy})_2(BrCH_2COO)_2{\cdot}2H_2O$	90–140	115 endo	5.0 (4.89)
		140–780 [b]	275 exo, 400 endo	
			540 exo	
(**6**)	$Cd(2,4'\text{-bpy})_2(ClCH_2COO)_2{\cdot}2H_2O$	70–120	100 endo	5.0 (5.56)
		120–780 [b]	130 exo, 430 endo,	
			490 exo, 600 endo	

[a] Forms $Zn(4\text{-bpy})Br(BrCH_2COO)$; [b] decomposition of organic ligands and gradual volatilization of appropriate metal(II) halides; [c] forms *ca* 4% ZnO.

Generally, bipyridine–monobromoacetato complexes of Zn(II) or Cd(II) are thermally more stable than corresponding bipyridine–monochloroacetato complexes. Thermal stability for two types of compounds: $Cd(4\text{-bpy})L_2{\cdot}H_2O$ and $Cd(2,4'\text{-bpy})_2L_2{\cdot}2H_2O$ (where: $L = CH_3COO^-, BrCH_2COO^-, ClCH_2COO^-, Cl_3CCOO^-$) increases in the following sequences: $ClCH_2COO^- < BrCH_2COO^- < Cl_3CCOO^-$ [3] and $ClCH_2COO^- < CH_3COO^-$ [1] $< BrCH_2COO^-$, respectively. The decomposition temperature of complexes $M(4\text{-bpy})(ClCH_2COO)_2{\cdot}nH_2O$ increases in dependence on the nature of the central atoms in the following sequence: Cd(II) < Zn(II) < Cu(II) ~ Mn(II) < Co(II) ~ Ni(II) (for Mn(II), Co(II), Ni(II) and Cu(II) with [7]).

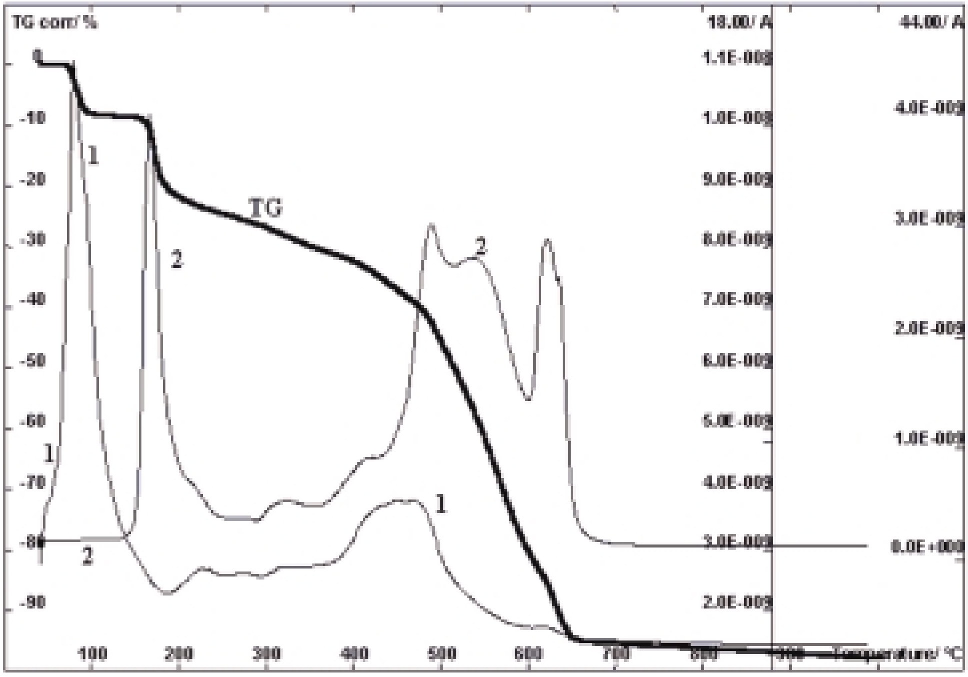

Figure 1. TG of $Zn(4\text{-}bpy)(ClCH_2COO)_2\cdot 2H_2O$ and signal of ion current for mass fragments; curves: 1 – H_2O^+, 2 – CO_2^+ (mass sample of 8.52 mg).

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