

SYNTHESIS AND THERMAL DECOMPOSITION OF NEW COMPLEXES OF BIPYRIDINE ISOMERS WITH ZINC(II) AND CADMIUM(II) OXALATES

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Abstract

The new mixed ligand complexes with the formulae $Zn(2\text{-bipy})(ox)$, $Zn(4\text{-bipy})_{1.5}(ox)\cdot H_2O$, $Zn(2,4'\text{-bipy})_2(ox)\cdot 2H_2O$, $Cd(2\text{-bipy})(ox)\cdot 2H_2O$, $Cd(4\text{-bipy})_2(ox)$ and $Cd(2,4'\text{-bipy})(ox)\cdot 2H_2O$ (2-bipy, 4-bipy, 2,4'-bipy=2,2'-, 4,4'- and 2,4'-bipyridine, ox=oxalate) were prepared. The thermal decompositions of these compounds were studied by means of TG, DTG and DTA in air. During heating the complexes decompose *via* different intermediate products to ZnO and CdO. The Zn(II) complexes are thermally more stable than the corresponding Cd(II) complexes. The influence of nitrogen atom position in the bipyridine isomers and nature of central atom on the thermal behaviour of these complexes was discussed.

Keywords: bipyridine-oxalato complexes, cadmium(II), thermal decomposition, zinc(II)

Introduction

This paper is a continuation of the research on Zn(II), Cd(II) complexes with the bipyridine isomers [1]. The mixed bipyridine-oxalato complexes with Zn(II) and Cd(II) are unknown. Recently only several studies of synthesis and characterization of mixed 2,2'-bipyridine-oxalato complexes with Mn(II), Fe(II), Fe(III) and Cu(II) have been published [2–5].

The object of the present investigation was to obtain in pure form of the solid state of the mixed bipyridine-oxalato complexes of zinc(II) and cadmium(II) (bipyridine(bipy)=2,2'-bipyridine(2-bipy), 4,4'-bipyridine(4-bipy) or 2,4'-bipyridine(2,4'-bipy)) and to study their thermal decomposition in air atmosphere. It was interesting to examine the influence of the position of the nitrogen atoms in the bipyridine isomers and the nature of the central atom on thermal behaviour of the isolated complexes.

Experimental

Solutions for synthesis

Water solutions of oxalate complexes of Zn(II) and Cd(II): 4.3 mmol of $Zn(ox)\cdot 2H_2O$ ($ox=C_2O_4^{2-}$) in 70 cm³ of 0.4 M $K_2(ox)$ solution with 0.1 cm³ of 0.5 M $H_2(ox)$ solution;

4.3 mmol Cd(ox) in 100 cm³ of 1.0 M K₂(ox) solution with 0.1 cm³ of 0.5 M H₂(ox) solution. Solutions of bipyridine: 8.6 mmol of 2-bipy or 4-bipy in 10 cm³ of 96% v/v ethanol; 8.6 mmol of 2,4'-bipy in 10 cm³ water with 0.2 cm³ of 96% v/v ethanol. 2-Bipy, 4-bipy and 2,4'-bipy were obtained from Aldrich; other chemicals were p.a. products from POCh-Gliwice.

The mixed bipyridine-oxalato complexes of Zn(II) and Cd(II) were prepared by reacting solutions of oxalate complexes of these metals (*M*) with suitable isomers of bipyridine dissolved in ethanol or water. The resulting mixtures were heated to 80°C for ca 10 min. The precipitates were formed immediately. They were filtered off, washed with 40% v/v ethanol, then with ethanol and diethyl ether mixture (1:1). The products were dried in room temperature.

The apparatus, measuring conditions and analyses were the same as described in our previous papers [1, 6].

Results and discussion

The new mixed bipyridine-oxalato complexes of Zn(II) and Cd(II) with the empirical formulae Zn(2-bipy)(ox), Zn(4-bipy)_{1.5}(ox)·H₂O, Zn(2,4'-bipy)₂(ox)·2H₂O, Cd(2-bipy)(ox)·2H₂O, Cd(4-bipy)₂(ox) and Cd(2,4'-bipy)(ox)·2H₂O in the solid state were obtained. Chemical analysis confirmed the theoretical composition with 0.0±0.3%. All complexes are stable air in room temperature. The data for the TG, DTG and DTA curves of these compounds are given in Table 1. The decomposition products obtained during heating were established from thermoanalytical curves and confirmed by chemical analysis together with the X-ray diffraction pattern investigations. The thermal curves of bipyridine-oxalato complexes with Cd(II) are presented, as an example, in Fig. 1.

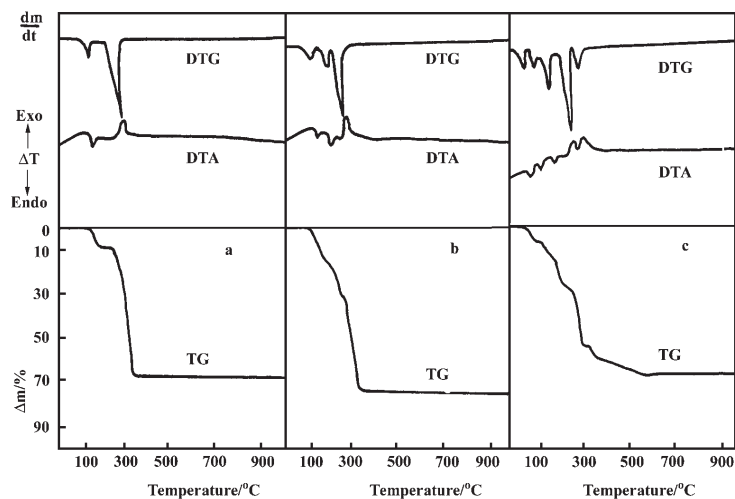


Fig. 1 Thermoanalytical curves of a – Cd(2-bipy)(ox)·2H₂O; b – Cd(4-bipy)₂(ox); c – Cd(2,4'-bipy)(ox)·2H₂O

Table 1 Thermal decomposition data for the mixed bipyridine-oxalato complexes with zinc(II) and cadmium(II) in air

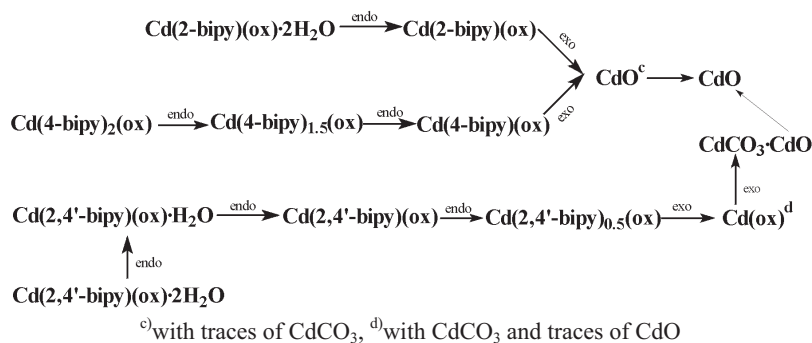
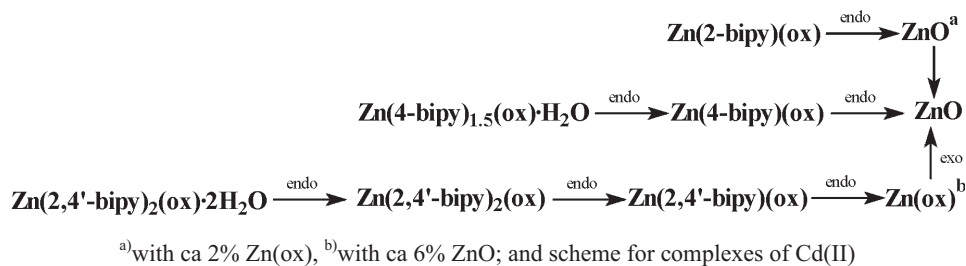
Complex	$T_{\text{range}}/$ °C	DTA _{peak} / °C	Mass loss/%		Intermediate and residue
			found	calcd.	
Zn(2-bipy)(ox)	310–410	380 endo	71.5	73.72	ZnO with ca 2% Zn(ox)
	>590		2.0		ZnO
Zn(4-bipy) _{1.5} (ox)H ₂ O	218–280	268 endo	23.0	23.69	Zn(4-bipy)(ox)
	310–410	360 endo	57.0	56.25	ZnO
Zn(2,4'-bipy) ₂ (ox)2H ₂ O	55–108	90 endo	7.0	7.18	Zn(2,4'-bipy) ₂ (ox)
	120–270	210 endo	30.5	31.12	Zn(2,4'-bipy)(ox)
	270–340	320 endo	37.5	31.12	Zn(ox) with ca 6% ZnO
Cd(2-bipy)(ox)2H ₂ O	340–590	560 exo	8.5	14.35	ZnO
	155–240	218 endo	9.5	9.18	Cd(2-bipy)(ox)
	280–380	365 exo	58.5	58.12	CdO with traces of CdCO ₃
Cd(4-bipy) ₂ (ox)	~600				CdO
	140–215	205 endo	14.5	15.23	Cd(4-bipy) _{1.5} (ox)
	215–295	285 endo	15.5	15.23	Cd(4-bipy)(ox)
	295–360	342 exo	43.5	44.50	CdO with traces of CdCO ₃
Cd(2,4'-bipy)(ox)2H ₂ O	~600				CdO
	65–125	118 endo	5.0	4.59	Cd(2,4'-bipy)(ox)H ₂ O
	130–170	165 endo	4.5	4.59	Cd(2,4'-bipy)(ox)
	170–242	238 endo	17.0	19.89	Cd(2,4'-bipy) _{0.5} (ox)
	242–345	330 exo	27.0		mixture of Cd(ox) with CdCO ₃ and traces of CdO
	345–400	370 exo	5.5	32.62	CdCO ₃ ·CdO
	~600		7.0	5.61	CdO

In the first stage of thermal decomposition of the hydrated bipyridine-oxalato complexes liberation of water takes place. The Zn(2,4'-bipy)₂(ox)2H₂O and Cd(2-bipy)(ox)2H₂O lose all water in one step. The Zn(4-bipy)_{1.5}(ox)H₂O is very stable, in temperature range 218–280°C 1 mol of H₂O and 0.5 mol of 4-bipy are eliminated. The complex Cd(2,4'-bipy)(ox)2H₂O undergoes dehydration in two stages. The hydrated 2,4'-bipyridine-oxalato complexes with Zn(II) and Cd(II) are very unstable and begin to lose water at 55–65°C. The endothermic effects connected with dehydration are observed for all hydrated bipyridine complexes.

The anhydrous transient bipyridine-oxalato complexes and prepared complex $\text{Cd}(4\text{-bipy})_2(\text{ox})$ decompose to give intermediate compounds of type $\text{M}(\text{bipy})(\text{ox})$. The complexes $\text{Zn}(2\text{-bipy})(\text{ox})$ and $\text{Zn}(4\text{-bipy})(\text{ox})$ transformed endothermically to ZnO (DTA peak at 380 and 360°C, respectively). The complexes $\text{Cd}(2\text{-bipy})(\text{ox})$ and $\text{Cd}(4\text{-bipy})(\text{ox})$ undergo decomposition to CdO via mixture of CdO with traces of CdCO_3 and the exothermic peaks are observed at 365 and 342°C. The pure CdO level begins at ca 600°C. The X-ray diffraction patterns indicate CdO in the decomposition product of $\text{Cd}(4\text{-bipy})_2(\text{ox})$ heated up to 600°C [7]. The intermediate compound $\text{Zn}(2,4'\text{-bipy})(\text{ox})$ eliminated 1 mol of 2,4'-bipy and gives ZnO with ca 6% ZnO . A constant mass for pure ZnO begins at 590°C (small exothermic peak at 560°C). However, complex $\text{Cd}(2,4'\text{-bipy})(\text{ox})$ deaminates in two stages. In the temperature range 242–345°C, the last portion of diamine is split off and decomposition of cadmium oxalate begins. During this decomposition a mixture of cadmium oxalate and carbonate with traces of oxide is formed. Then, latter mixture is converted into $\text{CdO}\cdot\text{CdCO}_3$ at 400°C. The DTA curve exhibits exothermic peaks at 330 and 370°C, associated with these processes. A plateau in the TG curve begins at 600°C, corresponding to the formation of pure CdO .

The thermal stabilities of hydrated bipyridine-oxalato complexes are as follows: $\text{Zn}(4\text{-bipy})_{1.5}(\text{ox})\cdot\text{H}_2\text{O} > \text{Zn}(2,4'\text{-bipy})_2(\text{ox})\cdot 2\text{H}_2\text{O}$ and $\text{Cd}(2\text{-bipy})(\text{ox})\cdot 2\text{H}_2\text{O} > \text{Cd}(2,4'\text{-bipy})(\text{ox})\cdot 2\text{H}_2\text{O}$. These sequences result from the temperature relating to the first decomposition process.

The influence of central atom and nature of bipyridine isomers on thermal decomposition of the studied complexes can be illustrated by scheme for the complexes of $\text{Zn}(\text{II})$



DTA curves show that the decompositions of Zn(2-bipy)(ox) and Zn(4-bipy)(ox) to ZnO are endothermic, whereas the decomposition of Zn(ox) (formed as intermediate of Zn(2,4'-bipy)(ox)) exhibits an exothermic peak. The exothermic effects also are presented on DTA curve for the step of total decomposition of all intermediate complexes of Cd(II).

On the basis of the literature data the change in character of the decomposition from endothermic to exothermic for oxalates is due to the autocatalytic oxidation of pyrolysis products in air [8]. Thus, endothermic effect connected with the decomposition of intermediate Zn(2,4'-bipy)(ox) or intermediate compounds of Cd(II) is probably masked by the exothermic nature of the reaction conversion of carbon monoxide to carbon dioxide catalysed by surface of solid decomposition products in air.

The isolated complexes Cd(2-bipy)(ox)·2H₂O, Cd(2,4'-bipy)(ox)·2H₂O and the intermediate compounds M(2-bipy)(ox), M(4-bipy)(ox), M(2,4'-bipy)(ox) (where: M(II)=Zn or Cd) are new example of complexes with ligand isomerism.

Conclusions

Generally, the Zn(II) complexes are thermally more stable than the corresponding Cd(II) complexes.

The temperature of decomposition of mixed bipyridine-oxalato complexes of these metals increases according to the type of bipyridine isomers in order:



This trend can be attributed to the molecular structure of these isomers. The bipyridine isomers favour mainly following types of coordination: 2-bipy is potential bidentate chelating ligand; 4-bipy act as bidentate bridging ligand; 2,4'-bipy can coordinate as monodentate ligand via the least hindered (4')N atom [9, 10]. The higher stability of 2-bipy and 4-bipy complexes than that of 2,4'-bipy complexes may be due to the strong ability of the five-ring forming and polymeric structures, respectively.

References

- 1 D. Czakis-Sulikowska, J. Radwańska-Doczekalska, M. Markiewicz, N. Pustelnik and B. Kuźnik, Polish J. Chem., 71 (1997) 513.
- 2 D. Degueon, G. Bernardinelli, J. P. Tuchagues and P. Castan, Inorg. Chem., 29 (1990) 3031.
- 3 S. Ducurtins, H. W. Smalle, P. Schneuwly, J. Ensling and P. Gutlich, J. Am. Chem. Soc., 116 (1994) 9521.
- 4 A. Gleizes, M. Julve, M. Verdaguer, J. A. Real, J. Faus and X. Solans, J. Chem. Soc. Dalton Trans., (1992) 3209.
- 5 P. Roman, C. Guzman-Miralles and A. Lague, *ibid.*, (1996) 3985.
- 6 D. Czakis-Sulikowska and A. Malinowska, J. Thermal Anal. Cal., 51 (1998) 575.
- 7 Powder Diffraction File. International Center of Diffraction. ICPDS-ICDD, 1990.

- 8 D. Dollimore, J. Thermal Anal., 11 (1977) 185; Thermochim. Acta, 117 (1987) 331 and references therein.
- 9 D. Czakis-Sulikowska, J. Radwańska-Doczekalska, B. Kuźnik and A. Malinowska, Transition Met. Chem., 20 (1995) 203.
- 10 I. S. Ahuja, Raghuvier Singh and C. L. Yadava, J. Mol. Struct., 74 (1981) 43.