Thermochimica Acta, 161 (1990) 259–266
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL BEHAVIOUR OF COMPLEX CATION–COMPLEX ANION-TYPE COORDINATION COMPOUNDS. PART II

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(Received 19 September 1989)

ABSTRACT

This paper deals with the synthesis, thermal stability and non-isothermal kinetics of the decomposition of two coordination compounds $[Cu(phen)_3][ZnCl_4]\cdot 2H_2O$ and $[Cu(dipy)_3][ZnCl_4]\cdot 2H_2O$.

INTRODUCTION

Although known from the last century, thermochromism has recently been reconsidered as it seems to present a new field of research in coordination chemistry [1]. As shown in a previous paper [2] such thermochromic phenomena are related to the migration of ligand molecules between two coordination spheres. To determine whether or not the reported thermochromic phenomena exhibit a certain degree of generality for compounds with similar structures, our investigation was extended to other coordination compounds of the complex cation–complex anion type, namely $[Cu(phen)_3][ZnCl_4]\cdot 2H_2O$ and $[Cu(dipy)_3][ZnCl_4]\cdot 2H_2O$. This paper presents the results of our study concerning their thermal stability and non-isothermal decomposition kinetics.

0040-6031/90/$03.50

EXPERIMENTAL

The two compounds were synthesised by adding the stoichiometric amount of the ligand to a solution of $CuCl_2 \cdot 2H_2O$ in ethanol, to give soluble $[CuL_3]Cl_2$. The coordination compounds were precipitated by treating this solution with a solution of $ZnCl_2$ acidulated with hydrochloric acid. The precipitates, blue for $[Cu(dipy)_3][ZnCl_4] \cdot 2H_2O$ and green-blue for $[Cu(phen)_3][ZnCl_4] \cdot 2H_2O$, were filtered, washed with ethanol and vacuum dried over P_2O_5. Because of some slight colour change over time exhibited by $[Cu(phen)_3][ZnCl_4] \cdot 2H_2O$, filtration was performed immediately after precipitation.

The thermogravimetric (TG), derivative thermogravimetric (DTG) differential thermal analysis (DTA) and temperature T curves were recorded in air in the range 20–700 °C at various heating rates, between 2.5 K min^{-1} and 10 K min^{-1}, using a MOM Budapest Q-1500 D derivatograph, of a Paulik–Paulik–Erdey type.

The crystalline states of the powdered compounds were determined using a Philips PW 1140 X-ray diffractometer using Cr $K\alpha$ radiation. Scherrer's formula was applied to calculate the crystallite sizes [3].

The EPR spectra of the investigated compounds, as well as of their intermediates, were recorded on an ART-5 spectrograph in the X-frequency band. The spectral parameters were evaluated with respect to Mn^{2+} as a standard.

RESULTS AND DISCUSSION

In order to evaluate the non-isothermal kinetic parameters, the Coats–Redfern [4] and Flynn–Wall methods for constant heating rate [5] and the Coats–Redfern method modified by Urbanovici and Segal [6] were applied. The data were automatically processed using two programs written in BASIC by Coseac and Segal [7,8]. To regenerate the TG curve in α, t °C coordinates, a program written in BASIC by Coseac and Segal [9] was used.

The X-ray diffractograms showed that both investigated compounds are in an amorphous state.

The thermal decomposition of the compound $[Cu(phen)_3][ZnCl_4] \cdot 2H_2O$

According to the derivatogram recorded at 4.96 K min^{-1}, the significant thermal phenomena exhibited by this compound are:

(a) the dehydration

$$[Cu(phen)_3][ZnCl_4] \cdot 2H_2O(s) \xrightarrow{52\,^\circ C} [Cu(phen)_3][ZnCl_4](s) + 2H_2O(g) \quad (I)$$

which occurs with maximum rate at 52 °C. (The temperatures of maximum

TABLE 1

Interplanar distances *d*, relative intensities of the diffraction lines and crystallite mean sizes (*l*) of $[Cu(phen)_3][ZnCl_4]\cdot 2H_2O$

d (Å)	Relative intensities	*l* (Å)
3.91	69	
3.74	100	248
3.42	80.5	

reaction rates will be noted in the following above the arrows as an indication of the reaction temperature.)

(b) The crystallisation of the compound, as shown by an exothermic peak on the DTA curve at 210 ° C, and confirmed by X-ray diffractograms recorded at temperatures slightly lower and slightly higher than 210 ° C, (Table 1).

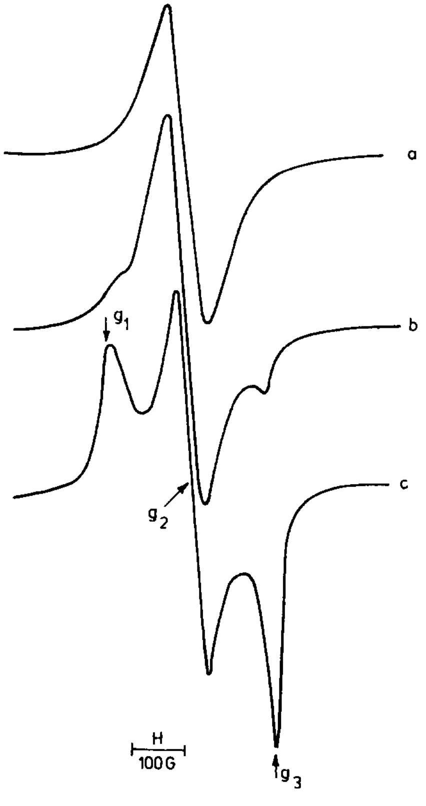

Fig. 1. The EPR spectra of phenanthroline complexes: a, before heating and heated at 100 ° C; b, heated at 210 ° C; and c, heated at 250 ° C.

TABLE 2

EPR parameters

Initial compound	Heating temp. (°C)	$g_{\perp}$	$g_{\parallel}$	g_2	$g_{\perp}$	g_3
$[Cu(phen)_3][ZnCl_4]\cdot 2H_2O$	20			2.123		
	210	2.233		2.123		2.018
	250	2.228		2.133		2.031
$[Cu(dipy)_3][ZnCl_4]\cdot 2H_2O$	20			2.116		
	120		2.179		2.118	
	170					
	215		2.241		2.060	
	250					

(c) The weak endothermic effects without weight change in the 200–250 ° C range, due to ligand migration, according to the equation

$$\underset{\text{green}}{[Cu(phen)_3]\,[ZnCl_4](s)} \rightarrow \underset{\text{light green}}{[Cu(phen)_2Cl_2](s)} + [Zn(phen)Cl_2](s) \qquad \text{(II)}$$

which has been enhanced by using the reaction product at 250 ° C as a reference [10]. At higher temperatures, the ligand is lost and oxidative degradation occurs, the decomposition being complete at ~ 700 ° C.

Figure 1 and Table 2 show the EPR spectral data of samples heated at various temperatures. The EPR spectrum recorded at room temperature exhibits an isotropic line (Fig. 1a), the averaging of the anisotropy observed at 77 K [11] and deriving from a fluxional behaviour [12]. A slight rhombic distortion is exhibited by the sample heated at 210 ° C (Fig. 1b), a distortion which becomes stronger for the sample heated at 250 ° C (Fig. 1c) and probably derives from $[Cu(phen)_2Cl_2]$. We consider this result as a confirmation of the migration according to eqn. (II).

The only kinetically workable reaction was the dehydration (I). Table 3 lists the values of the non-isothermal kinetic parameters of the dehydration for $\beta = 1.31$ K min^{-1} in the framework of the 'reaction order' model. A satisfactory agreement between the values of the non-isothermal kinetic parameters (reaction order n, pre-exponential factor A and activation energy E) obtained with the three applied methods can be seen.

TABLE 3

Non-isothermal kinetic parameters values for reaction (I) at $\beta = 1.31$ K min^{-1}

Method	n	A (s^{-1})	E (kcal mol^{-1})	r [a]
Coats–Redfern	2	7.70×10^{11}	21.4	−0.99483
Flynn–Wall	1.9	2.92×10^{11}	20.7	−0.99496
Modified Coats–Redfern	1.9	3.30×10^{11}	20.8	−0.99479

[a] r is the correlation coefficient of the linear regression.

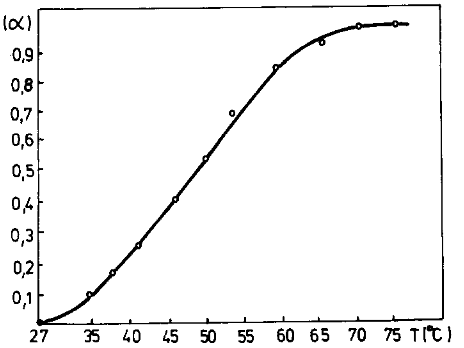

Fig. 2. Regenerated ($\alpha, t\,^\circ$C) for reaction (I) at $\beta = 4.96$ K min^{-1}: ———, calculated curve; o, experimental points.

Figure 2 shows the TG curve regenerated in the coordinates (α, $t\,^\circ$C) for reaction (1), using the experimental Coats–Redfern non-isothermal kinetic parameters. The experimental points lie on practically the same curve, thus indicating the correctness of the Coats–Redfern approximation, even reduced at its first term.

The thermal decomposition of the coordination compound $[Cu(dipy)_3][ZnCl_4] \cdot 2H_2O$

The derivatogram recorded at $\beta = 5.14$ K min^{-1} shows the following significant phenomena which occur in the temperature range 20–1000 °C:

(i) dehydration in two steps according to the chemical equations

$$[\mathrm{Cu(dipy)_3}][\mathrm{ZnCl_4}] \cdot 2\mathrm{H_2O(s)} \xrightarrow{78\,^\circ\mathrm{C}} [\mathrm{Cu(dipy)_3}][\mathrm{ZnCl_4}] \cdot \tfrac{1}{2}\mathrm{H_2O(s)} + \tfrac{3}{2}\mathrm{H_2O(g)} \qquad \text{(III)}$$

$$[\mathrm{Cu(dipy)_3}][\mathrm{ZnCl_4}] \cdot \tfrac{1}{2}\mathrm{H_2O(s)} \xrightarrow{165\,^\circ\mathrm{C}} [\mathrm{Cu(dipy)_3}][\mathrm{ZnCl_4}]\mathrm{(s)} + \tfrac{1}{2}\mathrm{H_2O(g)} \qquad \text{(IV)}$$

(ii) migration of the ligand

$$\underset{\text{blue}}{[\mathrm{Cu(dipy)_3}]\,[\mathrm{ZnCl_4}]\mathrm{(s)}} \xrightarrow{198\,^\circ\mathrm{C}} \underset{\text{green}}{[\mathrm{Cu(dipy)_2Cl_2}]} + [\mathrm{Zn(dipy)Cl_2}]\mathrm{(s)} \qquad \text{(V)}$$

(iii) the first decomposition step of the resultant mixture

$$[\mathrm{Cu(dipy)_2Cl_2}]\mathrm{(s)} + [\mathrm{Zn(dipy)Cl_2}]\mathrm{(s)} \xrightarrow{235\,^\circ\mathrm{C}} [\mathrm{Cu(dipy)_2Cl_2}]\mathrm{(s)} + \mathrm{Zn(dipy)_{0.5}Cl_2(s)} + 0.5\mathrm{dipy(g)} \qquad \text{(VI)}$$

At higher temperatures, the loss of the ligand molecules continues until 650 °C, the temperature corresponding to the completion of the decomposition.

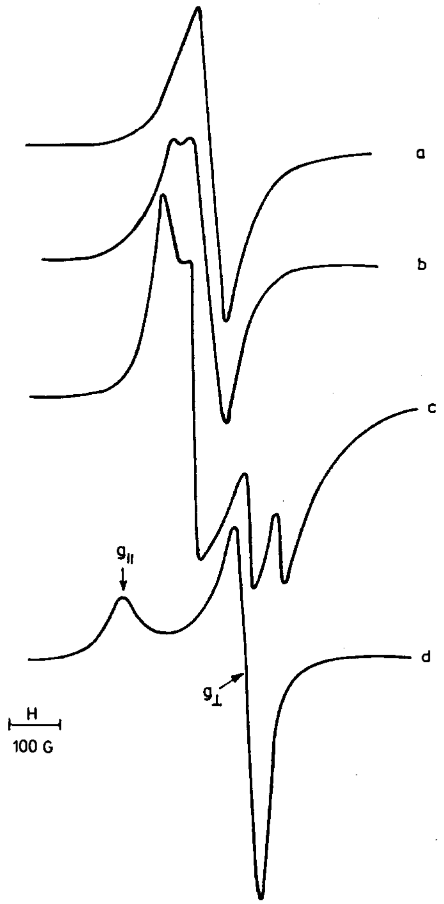

Fig. 3. The EPR spectra of dipyridyl complexes isolated at: a, 20 °C, before heating; b, 120 °C; c, 130 °C; and d, 170, 225 °C and 250 °C.

The occurrence of the migration (V) as well as of reaction (VI) is confirmed by the EPR spectra given in Fig. 3. The EPR spectrum of the sample heated at 120 °C * exhibits an axial distortion which can be assigned to a relaxation of the lattice after the dehydration (Fig. 3b and Table 2). The sample heated at 130 °C (Fig. 3c) is characterised by a complex EPR spectrum resulting from the superposition of the spectra of the reactant and product of reaction (V). The spectrum characteristic for the product, that of $[Cu(dipy)_2Cl_2]$, is recorded for the sample heated at 140 °C (Fig. 3d). This spectrum corresponds to a strongly axially-distorted octahedral ($g_{\parallel} > g_{\perp}$, as shown in Table 2), specific for $[Cu(dipy)_2Cl_2]$. Taking into account the fact that this last spectrum preserves its form at 250 °C, it follows that the loss of the ligand in reaction (VI) is due to the decomposition of $[Zn(dipy)Cl_2]$.

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* The heated samples were obtained in the derivatograph by stopping heating at the given temperatures.

TABLE 4

Non-isothermal kinetic parameters values for reactions (III) and (VI) at $\beta = 1.29$ K min^{-1}

Reaction	Method	n	A (s^{-1})	E (kcal mol^{-1})	r
(III)	Coats–Redfern	1.1	4.30×10^{12}	22.5	−0.99832
	Flynn–Wall	1.1	5.15×10^{12}	22.6	−0.99863
	Modified Coats–Redfern	1.1	6.90×10^{12}	22.8	−0.99802
(VI)	Coats–Redfern	0	6.3×10^{9}	28.6	−0.99903
	Flynn–Wall	0	10.1×10^{9}	28.9	−0.99913
	Modified Coats–Redfern	0	10.2×10^{9}	28.9	−0.99929
(VI) [a]	Coats–Redfern	0.4	2.88×10^{9}	28.1	−0.99858
	Flynn–Wall	0.3	2.76×10^{9}	27.9	−0.99861
	Modified Coats–Redfern	0.3	1.83×10^{9}	27.6	−0.99833

[a] For a compound previously heated at 130 ° C.

For the decomposition kinetics, the values of the non-isothermal kinetic parameters for reactions (III) and (VI) at $\beta = 1.29$ K min^{-1} are listed in Table 4. There is a quite good agreement between the values of the non-isothermal kinetic parameters obtained using the three applied methods. The slight increase in the reaction order from 0 to 0.3–0.4 is perhaps due to a change in the decomposition regime from a diffusional one to a combined diffusional and kinetic one [13].

CONCLUSIONS

(1) The investigation concerned two coordination compounds with Cu^{II} of the complex cation–complex anion type.

(2) The thermochromic properties of the investigated compounds, similar to those exhibited by the analogous coordination compounds of Co^{II} and Ni^{II}, are due to the migration of the ligands between the two coordination spheres.

(3) The values of the non-isothermal kinetic parameters of some decomposition reactions calculated by three methods are in satisfactory agreement.

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