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Thermal behaviour of complex cation–complex anion type coordination compounds.
Part 7

N.D. Dragoe [a,]*, E. Segal [a] and Marius Andruh [b]

[a] *Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest, Bulevardul Carol I, Bucharest (Romania)*

[b] *Department of Inorganic Chemistry, Faculty of Chemistry, University of Bucharest, Str. Dumbrava Rosie 23, Bucharest (Romania)*

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Abstract

This paper deals with the thermal behaviour of $[Ni(phen)_3][ZnBr_4]$ and $[Ni(dipy)_3][ZnBr_4]2H_2O$, with special emphasis on the non-isothermal kinetics of the dehydration and of the migration of the ligand between the two coordination spheres.

INTRODUCTION

In a previous paper [1], the thermal behaviour of coordination compounds of complex cation–complex anion type was analysed [1]. The thermochromic properties of these compounds were assigned to the migration of the organic ligand between the two coordination spheres.

This paper reports a reversible thermochromic change due to a reversible migration exhibited by $[Ni(phen)_3][ZnBr_4]$, and an unusual thermal behaviour exhibited by $[Ni(dipy)_3][ZnBr_4]2H_2O$.

EXPERIMENTAL

The two coordination compounds were precipitated from methanolic solutions of $Ni(AA)_3Br_2$, AA being phen or dipy, on adding ice-cooled aqueous solutions of $ZnBr_2$ and HBr (HBr promotes the formation of the $ZnBr_4^{2-}$ anion). The coordination compounds $[Ni(phen)_3][ZnBr_4]$ (pale pink) and $[Ni(dipy)_3][ZnBr_4]2H_2O$ (deep pink) were filtered off, washed

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* Corresponding author.

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with methanol and dried over P_4O_{10}. Elemental chemical analyses gave results which confirmed the formulation of the two coordination compounds.

The diffuse reflectance spectra of the coordination compounds were recorded on a Carl Zeiss VSU-2 spectrophotometer with MgO as standard. The heating curves of the powdered samples were recorded in static air atmosphere in the temperature range 20–1000°C, using a MOM Budapest Q-1500 Paulik–Paulik–Erdey derivatograph with heating rate β in the range 2–10 K min^{-1}. In an attempt to confirm some thermal changes, DSC curves for heating rates in the range 1–20 K min^{-1} were recorded using a Du Pont 1090 thermal analyser.

A Philips PW 1140 X-ray diffractometer was used to achieve a rough initial characterisation of the crystalline structure of the coordination compounds. The powder diffractograms were recorded using copper Kα radiation. The crystallite mean size l was calculated for the most intense diffraction line using Scherrer's formula [2].

The values of the non-isothermal kinetic parameters were obtained using three methods: the Coats–Redfern [3], the Flynn–Wall for constant heating rate [4] and the Coats–Redfern modified by Urbanovici and Segal [5]. The experimental data were analysed using a computer program written in Basic language [6]. The same program was applied to regenerate the TG curve in (α, T°C) coordinates using the Coats–Redfern values of the non-isothermal kinetic parameters.

RESULTS AND DISCUSSION

Figure 1 shows the electronic spectrum of $[Ni(phen)_2][ZnBr_4]$. The bands $^3T_{1g}(P) \leftarrow {}^3A_{2g}$, $^3T_{1g} \leftarrow {}^3A_{2g}$, $^3T_{2g} \leftarrow {}^3A_{2g}$ and the spin-forbidden band

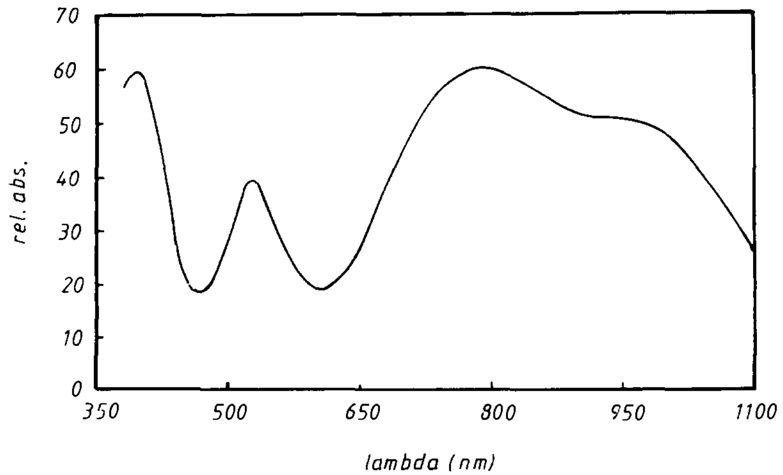

Fig. 1. Diffuse electronic spectrum of $[Ni(phen)_3][ZnBr_4]$.

TABLE 1

Interplanar distances, relative intensities and mean crystalite size for $[Ni(phen)_3][ZnBr_4]$

d (Å)	I/I_0	l (Å)	d (Å)	I/I_0	l (Å)
8.601	65		3.51	25	
7.033	100	345	3.44	15	
6.830	30		3.36	35	
6.342	22		3.32	15	
6.19	37		3.23	10	
5.88	22		3.14	20	
5.63	12		3.07	25	
5.49	11		2.95	13	
4.88	42		2.90	20	
4.64	20		2.81	10	
4.51	7		2.78	15	
4.37	12		2.717	10	
4.27	7		2.70	13	
4.101	60		2.68	10	
4.00	70		2.52	12	
3.74	55		2.49	10	
3.68	42		2.22	10	
3.58	7		2.154	15	
			1.95	18	
			1.82	10	
			1.79	10	

$^1E_g \leftarrow {}^3A_{2g}$, located at 390, 525, 810 and 880–900 nm, indicate an octahedral coordination. A similar spectrum was obtained for $[Ni(dipy)_3][ZnBr_4]$-$2H_2O$.

As shown by the X-ray diffractograms, both coordination compounds exhibit a crystalline state. The interplanar distance d, relative intensities I/I_0 and crystallite mean sizes for the most intense diffraction line l are listed in Tables 1 and 2.

Thermal behaviour of the coordination compound $[Ni(phen)_3][ZnBr_4]$

According to the recording derivatogram, this compound exhibits a fairly high thermal stability up to 350°C. The endothermic peak on the DTA curve located at 345°C for $\beta = 10\,K\,min^{-1}$ can be assigned to the migration of the ligand between the two coordination spheres. This change is accompanied by a change in colour from pale pink to pale green. An inspection of the DSC curves recorded at $10\,K\,min^{-1}$ and $5\,K\,min^{-1}$ (Fig. 2(a) and (b)) shows the reversibility of the migration. The double peak corresponding to the first heating and cooling (at $10\,K\,min^{-1}$) can probably

TABLE 2

Interplanar distances, relative intensities and mean crystalite size for $[Ni(dipy)_3][ZnBr_4]2H_2O$

d (Å)	I/I_0	l (Å)	d (Å)	I/I_0	l (Å)
7.65	3		3.25	5	
6.96	7		3.17	3	
6.60	22		3.14	3	
6.26	2		3.07	11	
5.88	25		3.00	20	
5.45	27		2.90	8	
5.21	35		2.828	3	
4.89	3		2.74	2	
4.74	9		2.700	4	
4.55	2		2.634	4	
4.38	100	430	2.57	8	
4.316	4		2.53	7	
4.14	7		2.44	2	
3.98	21		2.307	3	
3.88	19		2.132	3	
3.68	11		1.97	4	
3.5	5		1.79	4	
3.44	45				

be assigned to a two-stage mechanism of the migration. There is no peak splitting during the second heating, which may be a result of the difference in the dependence of the temperatures of the split peak on the heating rate.

The activation energy of the migration was calculated according to Reich's formula [7] as $E_8 = 42\ \mathrm{kcal\ mol^{-1}}$.

Thermal behaviour of the coordination compound $[Ni(dipy)_3][ZnBr_4]2H_2O$

From the derivatogram recorded at $2.5\ \mathrm{K\ min^{-1}}$, the first significant change is dehydration according to the equation

$$[Ni(dipy)_3][ZnBr_4]2H_2O(s) \xrightarrow{65°C} [Ni(dipy)_3][ZnBr_4](s) + 2H_2O(g) \qquad (1)$$

where 65°C corresponds to the maximum dehydration rate. This is the only change whose non-isothermal kinetic parameters could be determined, see Table 3. Table 3 shows a satisfactory agreement of the values obtained by the three applied methods. Figure 3 shows the regenerated TG curve in the coordinates (α, T°C) using the values of the non-isothermal kinetic parameters obtained from the Coats–Redfern method: the experimental points lie practically on the curve, thus indicating the correctness of the

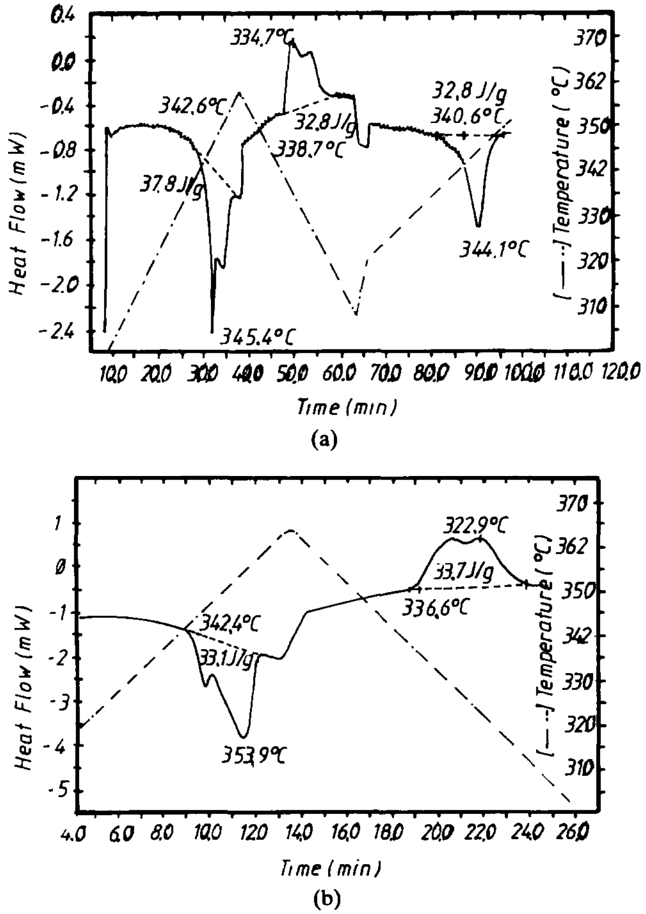

Fig. 2. DSC curves of $[Ni(phen)_3][ZnBr_4]$ recorded at (a) 10 K min^{-1} and (b) 5 K min^{-1}.

approximation used to calculate the values of the non-isothermal kinetic parameters.

The DTA curve recorded at 10 K min^{-1} shows an endothermic change located at 300–310°C which corresponds to the migration of the ligand accompanied by a change in colour from pink to green. The migration is

TABLE 3

Non-isothermal kinetic parameter values for reaction (1) at $\beta = 2.5$ K min^{-1}

	Coats–Redfern	Flynn–Wall	Mod. Coats–Redfern
n	2.5	2.5	2.4
E_a (kcal mol^{-1})	32.8	32.2	32.3
A (s^{-1})	1.15×10^{19}	7.0×10^{18}	7.2×10^{18}
Correl. coeff.	0.99990	0.99992	0.99984

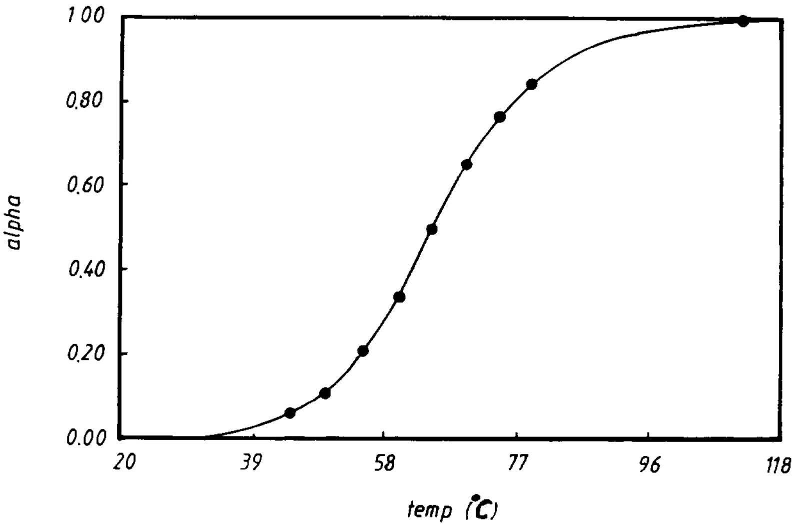

Fig. 3. The regenerated α, T curve for reaction (1) at $\beta = 2.5\ \mathrm{K\ min^{-1}}$ using the values of non-isothermal kinetic parameters obtained from the Coats–Redfern method.

followed by a many-stepped (kinetically insignificant) decomposition which ends at about 700°C.

CONCLUSIONS

An investigation of the thermal behaviour of two coordination compounds of complex cation–complex anion type showed that the thermochromic properties exhibited by the compounds are associated with the migration of the ligand between the two coordination spheres.

The activation energy of the migration for $[\mathrm{Ni(phen)_3}][\mathrm{ZnBr_4}]$ and the non-isothermal kinetic parameters of the dehydration of $[\mathrm{Ni(dipy)_3}]$-$[\mathrm{ZnBr_4}]2\mathrm{H_2O}$ were determined.

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