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THE EFFECT OF Er(III) ON THE THERMAL BEHAVIOR OF AZO (–N=N–) AND AZOMETHINIC (–CH=N–) CHROMOPHORES[*]

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This paper reports the investigation of the thermal stability of a series of new complexes with azo and azomethinic chromophores of the type $[Er(HL)_2(H_2O)_2](HO)$; ((**B**) H_2L: *o,o*'-dihydroxy-azobenzene (**A**); (**D**) H_2L: N-(2-hydroxy-1-naphthalidene)aminophenol (**C**); (**F**) H_2L: N-(2-hydroxy-1-naphthalidene)anthranilic acid (**E**)). The complexes thermal behaviour steps were investigated and comparatively presented with those of corresponding ligand. The thermal transformations are complex processes according to TG and DTG curves including phenol elimination, oxidative condensation and thermolysis processes. The final product of complexes decomposition is Er_2O_3.

Keywords: *azo-derivatives, azomethinic derivatives, Er(III) complex, thermal stability*

Introduction

In the last years the complexes having non-linear optic properties became of a great interest because such compounds could be used in optic devices. Moreover, this kind of compounds can be incorporated in a polymeric matrix in order to improve their properties. The azo-derivatives allow the achievement of coloured layers of optics application such as filters, transformers of solar energy, non-linear optics and laser environments [1–3].

Thermal characterization of some azo-derivatives [4] as well as of complexes bearing this kind of ligands [5–8] has been attracting the attention in the last years. Also there are some reports concerning the thermal behaviour of complexes with azomethine derivatives [9, 10]. In previous papers [11–13] we have reported data about the thermal behaviour of some azo- respectively azomethinic derivatives and their complexes.

From a scientific and practical point of view, it is important to investigate the thermal behaviour of the chromophor systems such as azo- and azomethinic ones in order to evidence the influence of the metallic ions before complexes incorporation in a polymeric matrix. In our paper, the thermal behaviour of Er(III) complexes and organic ligands was comparatively discussed in order to evidence the influence of the metallic ion on the azo- or azomethinic derivatives stability.

The results presented here concern the decomposition steps and the analysis of intermediates and final residues.

Experimental

The compounds (**B**), (**D**) and (**F**) have been synthesized and characterised by chemical analysis, electronic IR and emission spectra [14]. The thermal decomposition curves were recorded using a MOM Hungary, Paulik–Paulik–Erdey derivatograph type in the temperature range 20–1000°C at heating rates of 10 K min^{-1}.

The chemical analysis and IR spectral data were used to confirm the nature of the intermediates and also the final products.

IR spectra were recorded in KBr pellets with a FTIR-BIORAD 135 spectrometer.

Results and discussion

In order to obtain new complexes with azo- and azomethinic derivatives as ligands we studied the reactions of the $Er(OH)_3$ with the organic compounds as it is shown in Scheme 1.

The formulae of the obtained complexes are of the general type $[Er(HL)_2(H_2O)_2](OH)$ ((**B**) H_2L: *o,o*'-dihydroxy-azobenzene (**A**); (**D**) H_2L: N-(2-hydroxy-1-naphthalidene)aminophenol (**C**); (**F**) H_2L: N-(2-hydroxy-1-naphthalidene)anthranilic acid (**E**)). It was evidenced that these compounds exhibit excellent fluorescent properties and may be incorporated in polyvinyl acetate (PVA) and poly(methyl) methacrylate (PMMA) [14]. The excitation wavelengths are in the 300–380 nm range while for the emission phenomenon

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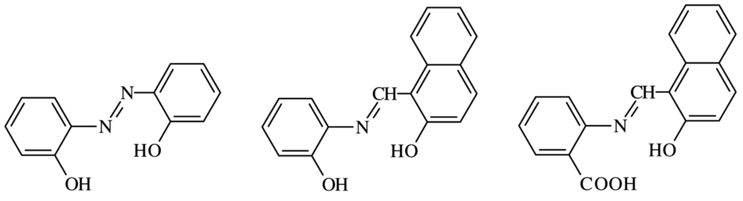


H_2L^1 H_2L^2 H_2L^3

Scheme 1

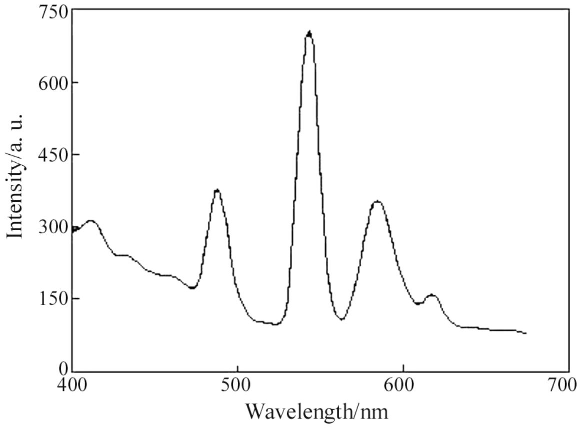


Fig. 1 Emission spectrum of $[Er(HL^1)_2(H_2O)_2](OH)$ (**B**)

these are in the 400–450 nm range. In Fig. 1 is shown the emission spectrum of complex (**B**).

Considering that the thermal behaviour and the thermal stability is a very important condition in order to obtain good materials possessing non-linear optic properties we studied these solid compounds from this point of view:

H_2L^1 or $C_{12}H_{10}N_2O_2$ (**A**)

$[Er(HL^1)_2(H_2O)_2](OH)$ or $ErC_{24}H_{23}N_4O_7$ (**B**)

H_2L^2 or $C_{17}H_{13}NO_2$ (**C**)

$[Er(HL^2)_2(H_2O)_2](OH)$ or $ErC_{34}H_{29}N_2O_7$ (**D**)

H_2L^3 or $C_{18}H_{13}NO_3$ (**E**)

$[Er(HL^3)_2(H_2O)_2](OH)$ or $ErC_{36}H_{29}N_2O_9$ (**F**)

The results concerning the organic ligands and their Er(III) complexes decomposition are comparatively presented below. Table 1 summarises the thermogravimetric data.

*Thermal decomposition of $C_{12}H_{10}N_2O_2$ **(A)** and $ErC_{24}H_{23}N_4O_7$ **(B)***

TG, DTG and DTA curves corresponding to the *o*,*o*'-dihydroxy-azobenzene (**A**) heating in the 20–1000°C temperature range are presented in Fig. 2.

The first decomposition step occurred in the temperature range 180–310°C (the maximum rate corresponds to the 250°C temperature) and it has been accompanied by a weak endothermic effect. This step corresponds to the C_{arom}–N bond cleavage, leading to the gaseous phenol formation (boiling point 182°C).

Table 1 Thermoanalytical data of the compounds (**A**)–(**F**) (the mass loss, Δm, was calculated related to the corresponding residue)

Compound	Step	Thermal effect	Temperature interval/°C	Δm_{exp}/%	Δm_{calc}/%
H_2L^1 (**A**)	1	endo	180–310	43.84	43.93
	2	exo	310–760	56.17	56.07
$[Er(HL^1)_2(H_2O)_2](OH)$ (**B**)	1	endo	140–310	34.21	34.67
	2	exo	340–570	35.32	35.76
		residue Er_2O_3		30.47	29.57
H_2L^2 (**C**)	1	endo	210–280	35.65	35.74
	2	exo	280–750	64.42	64.26
$[Er(HL^2)_2(H_2O)_2](OH)$ (**D**)	1	endo+exo	180–380	16.81	17.47
	2	exo	390–480	12.33	12.63
	3	exo	480–660	44.84	44.22
		residue Er_2O_3		26.02	25.68
H_2L^3 (**E**)	1	endo	250–290	42.25	41.92
	2	exo	290–760	57.73	58.08
$[Er(HL^3)_2(H_2O)_2](OH)$ (**F**)	1	endo+exo	180–390	19.69	19.75
	2	exo	390–690	55.75	56.37
		residue Er_2O_3		24.56	23.88

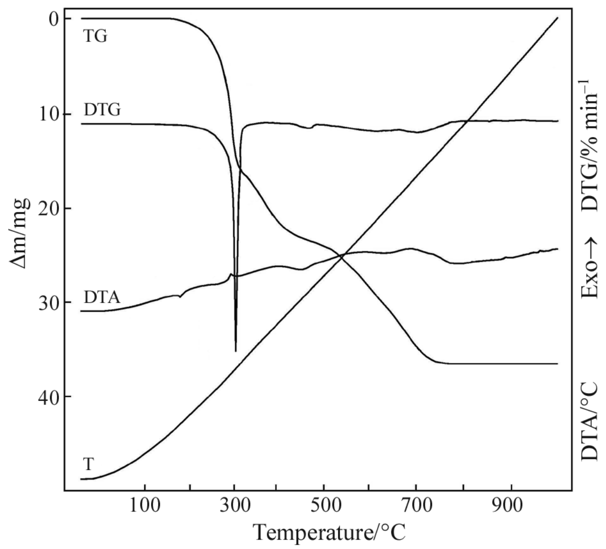
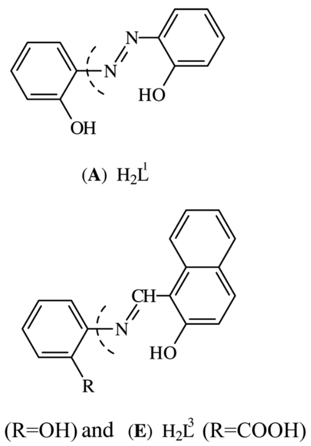


Fig. 2 The TG, DTG and DTA curves of organic compounds H_2L^1 (sample mass: 36.5 mg)



(**A**) H_2L^1

(**C**) H_2L^2 (R=OH) and (**E**) H_2L^3 (R=COOH)

Scheme 2

The rest of the organic component undergoes a cyclisation reaction leading to 1,2,3-benzoxadiazole as it is shown in Scheme 2.

The chemical elemental analysis was used in order to confirm the composition of the solid residue (found: C, 61.44; H, 3.12; N, 23.22%; requires for $C_6H_4N_2O$: C, 60.00; H, 3.33; N, 23.33%). In the IR spectrum of this reaction product (Fig. 3b) the bands at 3440 (ν_{OH}) and 1261 cm^{-1} (ν_{OH}) disappear while a new band appears at 870 cm^{-1} ($\nu_{N\text{–}O}$) [15]. The band at 1471 cm^{-1} ($\nu_{N=N}$) in the *o,o*'-dihydroxy-azobenzene spectrum (Fig. 3a) is slightly shifted to lower wavelengths.

The second decomposition step is accompanied by a strong exothermal effect and it corresponds to the oxidative degradation of the 1,2,3-benzoxadiazole. This step is not a single process (according to DTG and DTA curves) but consists of at least two processes.

TG, DTG and DTA curves recorded for complex (**B**) are shown in Fig. 4.

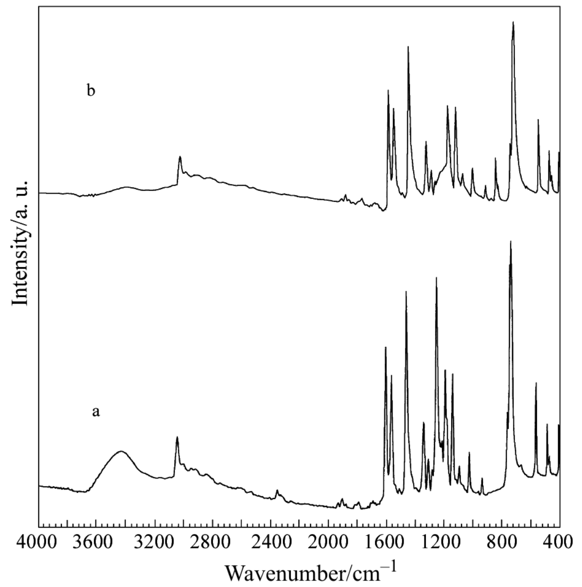


Fig. 3 The IR spectra of the ligand **A** – a and the intermediate at 300°C resulted from thermal degradation – b

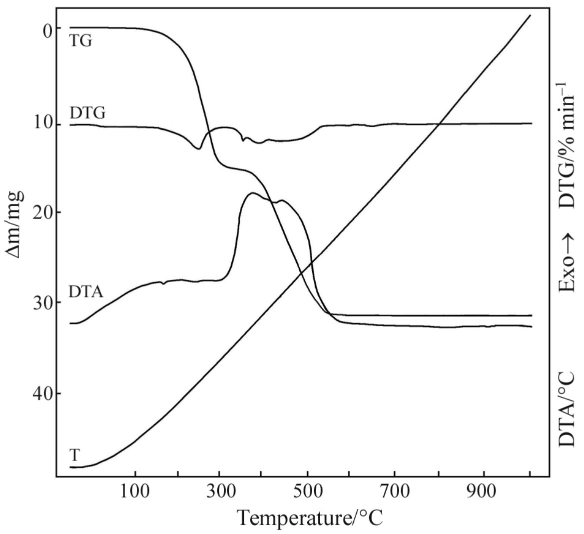


Fig. 4 The TG, DTG and DTA curves of $[Er(HL^1)_2(H_2O)_2](OH)$ (sample mass: 45.3 mg)

The complex decomposition occurs also in two steps, the first one weak endothermic corresponds to simultaneously water and phenol elimination. These processes end at 290°C and the second step occurs within 340–570°C and it corresponds to the oxidative degradation of the organic part resulted after phenol elimination. This step is strong exothermic and consists of at least two processes (according to DTG and DTA curves). The final product of these transformations is Er_2O_3.

*Thermal decomposition of $C_{17}H_{13}NO_2$ **(C)** and $ErC_{34}H_{29}N_2O_7$ **(D)***

The TG and DTG curves indicate that the thermal decomposition of (**C**) occurs through two steps.

The first decomposition step was performed in 115–230°C temperature range and it is almost similar with the one observed for compound (**A**). This step also assumes the phenol elimination. The cyclisation of the remaining part leads to 1,2-naphtoxazole (Scheme 2). The nature of this intermediate was established by chemical elemental analysis and IR spectrum which exhibits the characteristic vibration band $\nu_{N–O}$ at 870 cm^{-1}.

The reaction (C.2) occurs in several processes that are difficult to separate; all exhibit an exothermal effect.

As for the complex (**D**) the DTA, TG and DTG profiles show three steps, first one corresponds again to simultaneously water and phenol elimination. These processes are accompanied by a weak endothermic and weak exothermal effect, respectively. The mass loss registered for the second step corresponds also to phenol loss but the effect that accompanies this transformation is strong exothermal one. The last step can be associated with the oxidative degradation of the remaining organic fragment leading to Er_2O_3. A strong exothermal effect is registered for this step that consists of at least two processes (according to DTG and DTA curves).

The final decomposition temperature of the complex is almost with 100°C lower than the ligand's corresponding one.

*Thermal decomposition of $C_{18}H_{13}NO_3$ **(E)** and $ErC_{36}H_{29}N_2O_9$ **(F)***

Despite the fact that compound (**E**) differs from (**C**) only by a carboxylic group, the decomposition steps are different.

According to the heating curves, thermal decomposition occurs in two steps difficult to separate. The registered mass loss of 42.25% corresponds to benzoic acid elimination, process accompanied by a weak endothermic effect. It follows immediately the second step that consists of at least three processes. Regarding the compound (**E**), the decomposition and melting processes are starting and finishing at higher temperatures comparing with compound (**C**)**,** probably as a result of a higher molecular mass.

Two decomposition steps can be evidenced also for the corresponding complex (**F**).

The first step corresponds to a complex process in which occur the cleavage of C–N bond, the formation of diazole ring and also the volatilisation of water and benzoic acid (the benzoic acid can be eliminated as it is or its oxidative degradation may occur, its boiling temperature being 249°C). The DTA curve indicates two processes one endo and one weak exothermic, respectively.

Next step, which is accompanied by a strong exothermic effect, corresponds to the oxidative degradation of the rest of the organic component. This step occurs in several processes that are difficult to separate; all exhibit an exothermal effect. The final product of the thermal decomposition is Er_2O_3. In the case of compound (**F**), both steps are finished at higher temperatures than those corresponding for the compound (**D**), a**s** a consequence of the higher molecular mass.

Conclusions

Azo- and azomethinic derivatives have various and interesting applications as allowing the achievement of coloured layers of optics application such as filters transformers of solar energy, laser environments and non-linear optics.

The main decomposition steps of three azo- and azomethinic derivatives and their Er(III) complexes have been evidenced. In order to confirm the nature of some of the intermediate the IR spectra and chemical analysis were used.

For the first decomposition steps of ligands, which occur with the phenol or benzoic acid elimination, a high difference between the temperature ranges were observed. Complexes suffer the same product elimination with ligands but the difference is the water simultaneously elimination.

In the case of all complexes, the oxidative degradation of ligands occurs at lower temperatures in comparison with free ones. For compounds with similar structures, the decomposition temperatures are as higher as the molecular masses are growing.

This could be determined by the fact that the erbium ion acts as catalyst in thermal decomposition of the complex compound.

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