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NEODYMIUM AND EUROPIUM COMPLEXES WITH AMIDES AND CYCLIC AMINOXIDES
Thermal behaviour and spectroscopic effects

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Abstract

Complexes of neodymium and europium with amides and aminoxides were synthesized and characterized by complexometric analyses with EDTA, CHN microanalytical procedures, IR absorption spectra, absorption spectra of neodymium complexes, emission spectrum of europium compounds at 77 K, thermogravimetric analyses in N_2 and differential scanning calorimetry (DSC) in N_2. Infrared spectroscopy results revealed that the nitrate molecules are bound to the central ions as bidentate. Thermogravimetric plots indicated that the decomposition of the complexes occurs in the range 363–1163 K and resulted in the formation of Ln_2O_3 residues.

Keywords: amides and cyclic aminoxides, europium, neodymium, thermal behaviour

Introduction

The elements neodymium and europium are some of the most interesting lanthanides, especially in the +3 oxidation state. Their compounds present several important properties and applications [1–4]. Neodymium and europium nitrate complexes with ε-caprolactam, 2-azacyclononanone, bis(pentamethylene)urea, 4-methylmorfoline-N-oxide and 2,2'-dithiobis(pyridine-N-oxide) have already been described [5–9]. Amides present nitrogen bonded to the carbonyl group improving the donor ability of oxygen [10, 11]. Amine-N-oxides have commercial importance as fungicides and preservatives, their biological activity being attributed to the presence of the N-oxide group adjacent to the carbon bearing a sulfur atom [12–14].

The thermal decomposition of rare earth complexes has also been studied [12, 15–17]. These complexes decompose at moderate temperatures, usually giving metallic oxides, pure metal particles and/or inorganic salts as final product. The composition of the final product depends on several variables such as the atmosphere (oxi-

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dizing, reducing or inert) and the organic ligands and metal center present. The purpose of this study is to evaluate the thermal decomposition of the complexes between neodymium and europium nitrates with 2-azacyclononanone, bis(pentamethylene)urea, 4-methylmorfoline-N-oxide and 2,2'-dithiobis(pyridine-N-oxide) using TG and DSC techniques. In addition, in this work we report a comparison between the spectroscopic properties of these compounds with the objective of verifying the influence of different ligands in the thermal decomposition behaviour.

Experimental

The compounds were prepared reacting rare earth nitrates and 2-azacyclononanone (molar ratio 1:3) (AZA), bis(pentamethylene)urea (ratio 1:3) (BPMU), 4-methylmorfoline-N-oxide (molar ratio 1:3) (MMNO) and 2,2'-dithiobis-(pyridine-N-oxide) (molar ratio 1:2) (DTPO) in ethanol. The compounds were dried under vacuum over anhydrous calcium chloride.

IR spectra were performed on a FT-IR Prospect MIDAC apparatus, using KBr pellets. The absorption spectra of the neodymium compounds were registered on a Zeiss DMR-10 spectrophotometer, using silicone mulls in a 0.5 cm cell.The emission spectrum of the europium compound was obtained at room temperature and at 77 K on a Hitachi Perkin Elmer MPF-4 spectrofluorimeter with 394 nm excitation.

Thermogravimetric curves were obtained on a Shimadzu TGA-50H instrument at a heating rate of 10 K min^{-1} in 50 $\text{cm}^3\ \text{min}^{-1}$ nitrogen flow rate. DSC curves were obtained using a Shimadzu DSC 50 instrument in nitrogen atmosphere, heating rate 10 K min^{-1} and gas flow 50 $\text{cm}^3\ \text{min}^{-1}$.

Results and discussion

The analytical results indicate the formulations: $Ln(NO_3)_3{\cdot}3AZA$ [6], $Ln(NO_3)_3{\cdot}3BPMU$ [7], $Ln(NO_3)_3{\cdot}3MMNO$ [8], $Ln(NO_3)_3{\cdot}2DTPO{\cdot}4H_2O$ [9] where *Ln*=Nd and Eu.

The D_{3h} symmetry of the free ion (NO_3^-) is lowered to C_{2v} or C_s when they behave as monodentate or bidentate bonded to a central ion or act as bridges. The number of bands increases in the infrared spectra due to the E species (ν_3 and ν_4) splitting and IR activation of a ν_2 band [18]. In all cases several coordination modes are possible. By applying such criteria ν_1/ν_4 and comparing with the data of [19] it is possible to conclude for the existence of bidentate nitrates in these complexes. The νCO of amides band displacement and that of νNO in amine-N-oxides suggest that the ligands are coordinated through the carbonyl oxygen for amides and through the NO group in amine-N-oxides (Table 1). The absorption spectrum of the neodymium complexes was registered for the $^4G_{5/2}$, $^2G_{7/2}\leftarrow{}^4I_{9/2}$ transitions. The values obtained (Table 2) indicated the essentially ionic character of the bonds between the ligands and the central ion. $Nd(NO_3)_3{\cdot}3MMNO$ presents a higher covalent character than the others. It reflects the inductive effect of the structure of this ligand in the interaction with the central atom. The emission spectrum at 77 K of the complexes shows that the $^5D_0\rightarrow{}^7F_j$ (j=0, 1, 2) transitions are presented as spectra by sharp emission lines in the spectral range from 560 to 720 nm. The $^5D_0\rightarrow{}^7F_0$ non-degenerate transition appears in all spectra, indicating that the europium ion is loaded in a low symmetry environment [1, 4]. Table 3 presents the data obtained for the complexes. The most frequent symmetry of these europium complexes is C_{3v}.

Table 1 Infrared data (cm^{-1}) for $Ln(NO_3)_3\cdot 3L$ (where L=AZA, BPMU, MMNO) and $Ln(NO_3)_3\cdot 2DTPO\cdot 4H_2O$ complexes

L	ν_1/ν_4		$\Delta\nu CO$		$\Delta\nu NO$	
	Nd	Eu	Nd	Eu	Nd	Eu
AZA	0.88	0.89	27	28	–	–
BPMU	0.87	0.86	27	24	–	–
MMNO	0.90	0.90	–	–	32	33
DTPO	0.87	0.89	–	–	42	35

Table 2 Spectroscopic parameters at room temperature for $Nd(NO_3)_3\cdot 3L$ (where L=AZA, BPMU, MMNO) and $Nd(NO_3)_3\cdot 2DTPO\cdot 4H_2O$ complexes

L	Parameters		
	β	$b^{1/2}$	δ
AZA	0.989	0.074	1.112
BPMU	0.992	0.063	0.806
MMNO	0.987	0.057	1.317
DTPO	0.991	0.067	0.908

The thermogravimetric curves (Fig. 1) show a mass loss corresponding to dehydration at temperatures between 363–393 K and several other steps between 393–823 K, due to the ligand and nitrate decomposition. Table 4 summarizes the thermogravimetric data.

The organic ligands loss, at ca. 393 K, occurs in the several consecutive reactions liberating several products, which depend on the ligand type, the structure and character of the bonds between ligands and central atom. The thermal decomposition process of the nitrate groups, at ca. 823 K, occurs in one step liberating nitrogen and dinitrogen oxides. The residue at ca. 1163 K corresponds essentially to Ln_2O_3. The process of the thermal decomposition of these complexes is very complex, but it can be schematically shown as:

$$Ln(NO_3)_3\cdot 3L \text{ or } Ln(NO_3)_3\cdot 2L'\cdot 4H_2O\rightarrow Ln(NO_3)_3+L''$$

$$L''\rightarrow L'''+L''''$$

$$Ln(NO_3)_3\rightarrow NO+NO_2+Ln_2O_3$$

Table 3 Data from $Eu(NO_3)_3 \cdot 3L$ complexes at 77 K (where L=AZA, BPMU, MMNO) and $Eu(NO_3)_3 \cdot 2DTPO \cdot 4H_2O$

L	Symmetry	Fluorescence	Peaks
AZA	C_{3v}	$^5D_0 \rightarrow {}^7F_0$	1
		$^5D_0 \rightarrow {}^7F_1$	3
		$^5D_0 \rightarrow {}^7F_2$	3
BPMU	C_{3v}	$^5D_0 \rightarrow {}^7F_0$	1
		$^5D_0 \rightarrow {}^7F_1$	3
		$^5D_0 \rightarrow {}^7F_2$	4
MMNO	C_{3v}	$^5D_0 \rightarrow {}^7F_0$	2
		$^5D_0 \rightarrow {}^7F_1$	several
		$^5D_0 \rightarrow {}^7F_2$	6+ 1week
DTPO	C_{2v}	$^5D_0 \rightarrow {}^7F_0$	1
		$^5D_0 \rightarrow {}^7F_1$	3
		$^5D_0 \rightarrow {}^7F_2$	5

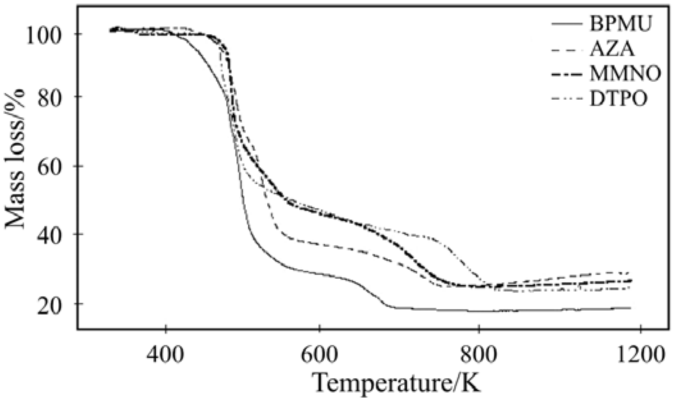

Fig. 1 Thermogravimetric curves of $Eu(NO_3)_3 \cdot 3L$ (where L=AZA, BPMU, MMNO) and $Eu(NO_3)_3 \cdot 2DTPO \cdot 4H_2O$ complexes recorded in dynamic N_2 atmosphere (50 $cm^3\ min^{-1}$) and heating rate of 10 K min^{-1}

where L=AZA, BPMU, MMNO, L'=DTPO and L'', L''', L''''=products of ligand decomposition.

Amides DSC curves present melting followed by decomposition and the aminoxides show only decomposition. Figure 2 shows the DSC curve obtained in N_2 atmosphere at 10 K min^{-1}.

Table 4 Summary of thermal decomposition of the $Ln(N_3)_3·3L$ complexes (where *L*=AZA, BPMU, MMNO) and $Ln(NO_3)_3·2DTPO·4H_2O$, in flowing N_2 (50 cm^3 min^{-1}) and heating rate of 10 K min^{-1} from TG measurements

L	Stage of decomposition							
	I–mass loss/%		II–mass loss/%		III–mass loss/%		IV–mass loss/%	
	Nd	Eu	Nd	Eu	Nd	Eu	Nd	Eu
AZA	56.7	55.9	6.4	6.3	12.3	13.6	23.5	24.6
BPMU	61.2	63.5	7.4	6.9	10.4	10.3	19.8	19.6
MMNO	48.1	52.1	27.5	23.7	–	–	25.1	24.6
DTPO	5.9	3.4	53.3	49.9	20.3	26.1	20.5	20.0

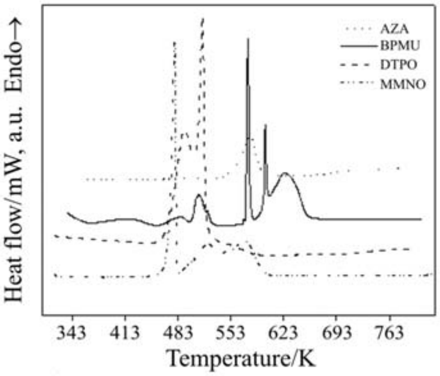

Fig. 2 DSC curves of $Eu(NO_3)_3·3L$ (where *L*=AZA, BPMU, MMNO) and $Eu(NO_3)_3·2DTPO·4H_2O$ complexes recorded in dynamic N_2 atmosphere (50 cm^3 min^{-1}) and heating rate of 10 K min^{-1}

Conclusions

The thermal decomposition of the lanthanide complexes with amides and aminoxides occurs in the 363–1163 K range. The proposed thermal decomposition process is very complex, but consists of consecutive reactions. The events are both endothermic and exothermic for all the amides and exothermic for the aminoxides. The covalent character decreases as a function of the inductive effect of the ligands interacting with the central atom:

$$Nd(NO_3)_3·3MMNO>Nd(NO_3)_3·3AZA>Nd(NO_3)_3·2DTPO·4H_2O>Nd(NO_3)_3·3BPMU$$

The most frequent symmetry of europium complexes is C_{3v}. The luminescence data recorded at 77 K shows a decrease in the europium $^5D_0\rightarrow{}^7F_2$ hypersensitive transition due to symmetry effects promoted by the ligands, as follows:

$$Eu(NO_3)_3·3AZA>Eu(NO_3)_3·2DTPO·4H_2O>Eu(NO_3)_3·3MMNO>Eu(NO_3)_3·3BPMU$$

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