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Thermal study of δ-valerolactam complexes of lanthanoid perchlorates

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Abstract

The thermal behaviour of complexes with compositions $[LnL_8](ClO_4)_3$ (Ln = La–Ho) and $[LnL_7](ClO_4)_3$ (Ln = Er–Lu, Y and L = δ-valerolactam) has been investigated by applying TG, DTG and DSC techniques under various conditions.

INTRODUCTION

The thermogravimetric study of δ-valerolactam lanthanoid trifluoromethanesulphonate complexes was carried out by Vicentini et al. [1]. The thermal behaviour of hydrated lanthanide perchlorates has already been investigated by Cucinotta et al. [2].

In this paper we describe the thermoanalytical results obtained by employing TG, DTG and DSC techniques in the investigation of δ-valerolactam complexes of lanthanoid perchlorates with compositions $[LnL_8](ClO_4)_3$ for Ln = La–Ho and $[LnL_7](ClO_4)_3$, for Ln = Er–Lu, Y and L = δ-valerolactam.

The complexes were obtained by the reaction between the hydrated perchlorate salts and the organic ligand using triethylorthoformate (teof) as reaction medium. The compounds were characterized by microanalytical procedures, conductance measurements, IR spectra, electronic absorption spectrum (Nd^{3+}), fluorescence spectrum (Eu^{3+}), X-ray powder diffraction patterns and X-ray single crystal studies of the neodymium compound [3].

EXPERIMENTAL

TG, DTG and DSC analyses were carried out with a Mettler TA 4000 Thermal Analyser System connected to a TC 10 TA processor for results evaluation.

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TG and DTG curves were obtained using 2–5 mg of the powdered samples in a stainless steel crucible with a perforated cap, using dynamic nitrogen or air atmospheres at 30 ml min^{-1} gas flow and heating rates of 2, 5 or 10 K min^{-1}.

DSC curves were obtained using 2–5 mg of the powdered samples in aluminium crucibles with a perforated cap, under auto-generated atmosphere, dynamic nitrogen or air atmospheres at 30 ml min^{-1} gas flow and heating rates of 5 and/or 10 K min^{-1}. IR spectra were recorded on a Perkin-Elmer FTIR 1750 model, using KBr plates for the complexes and decomposition products.

The usual microanalytical procedures were employed to determine carbon, nitrogen and hydrogen contents of the decomposition products.

RESULTS AND DISCUSSION

The complexes are slightly hygroscopic crystalline solids. They behave as 1:3 electrolytes in acetonitrile and 1:2 in nitromethane. IR spectra show that the anion is not coordinated to the central ion and that the organic ligand is bonded through the oxygen [3].

Figures 1 and 2 present TG, DTG and DSC curves of the samarium and erbium compounds, respectively. It can be observed that both compounds are submitted simultaneously to melting and decomposition processes, since at the beginning of the melting a continuous mass loss is evident.

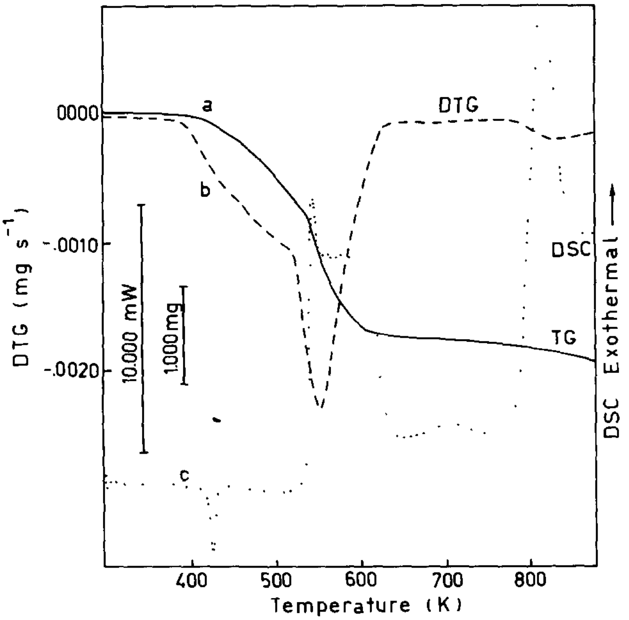

Fig. 1. TG, DTG and DSC curves of the samarium compound in dynamic air atmosphere.

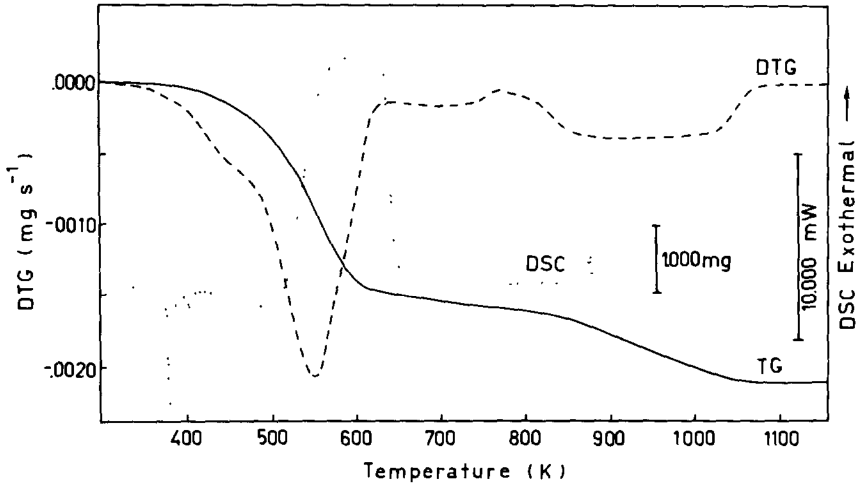

Fig. 2. TG, DTG and DSC curves of the erbium compound in dynamic nitrogen atmosphere.

DSC curves from octacoordinated compounds reveal only one endothermic peak attributed to melting and initial organic ligand liberation. In the case of heptacoordinated compounds, two or three endothermic peaks are found.

Small baseline changes appear after endotherms corresponding to the beginning of the thermal decomposition in the region of about 350–850 K. The curves show no characteristic plateaus of thermostable intermediate compound formation. This fact may be a result of the summation of both endothermic and exothermic events, and owing to their overlap no measurable effect is observed. For all compounds in the region between 525 and 650 K large amounts of heat are liberated corresponding to the thermal decomposition process; DSC curve peaks (Fig. 2) are consistent with this interpretation. The peaks seem to result from both perchlorate decomposition and remaining ligand pyrolysis and oxidation processes.

The black aspect of the residues at 623 K in the case of nitrogen atmosphere confirms the formation of elemental carbon. Microanalytical data show that the carbon content gradually decreases as the temperature increases.

Figure 3 illustrates the IR spectrum of the decomposition products of the erbium compound obtained at different temperatures. It indicates that up to 513 K all the perchlorate anions underwent decomposition, since the corresponding absorption bands ν_3 and ν_4 (1090 and 630 cm^{-1}) are absent. Concerning the organic ligand, the characteristic absorption bands are not observed at temperatures higher than 513 K.

DSC curves (Fig. 1), under dynamic air atmosphere, show a strong exothermic peak between 773 and 873 K which may be related to the

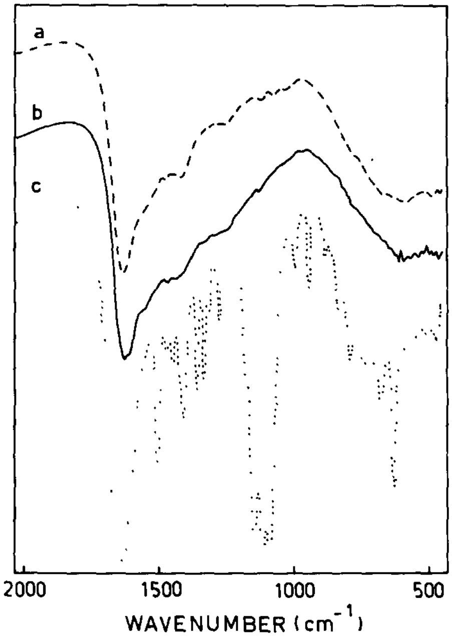

Fig. 3. IR spectra of the decomposition products of the erbium complex: curve a, 873 K; curve b, 623 K; and curve c, 523 K.

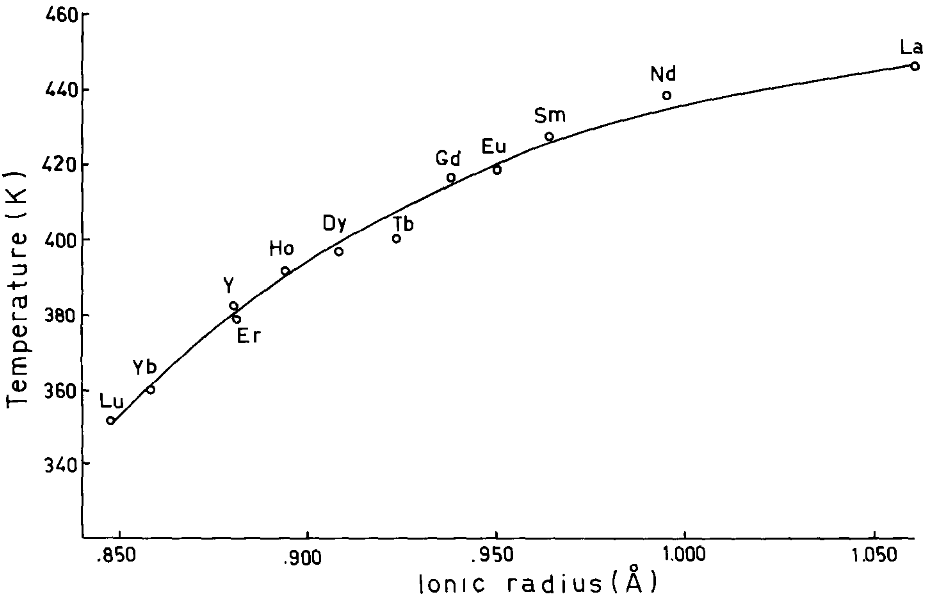

Fig. 4. Correlation between melting point and ionic radius.

conversion of carbon into volatile products, such as CO and CO_2. This is in agreement with the lowering of the carbon percentage of the thermal decomposition products and that under dynamic nitrogen atmosphere this exothermic peak is not observed.

The residue up to 973 K is thermostable and exhibits a similar colour to the respective hydrated Ln^{3+} ion. It can be easily dissolved in dilute nitric acid and the solution gives a positive chloride test ion.

Data from TG curves (Table 1) suggest that the final decomposition product is LnOCl under any atmosphere and it originates from the lanthanide perchlorate thermal decomposition. At the final temperature of 1198 K the lanthanide oxychlorides are stable [4].

Enthalpy data of the endothermic and exothermic processes obtained from DSC curves of some complexes are listed in Table 1. It is interesting to observe that the values corresponding to the endothermic peaks from

TABLE 1

TG and DSC data

Ln	DSC 1 peak (K)	ΔH (kJ mol^{-1})	DSC 2 peak (K)	ΔH (kJ mol^{-1})	DSC 3 peak (K)	ΔH (kJ mol^{-1})	LnOCl	
							Calc.	Obs.
La[a]	450	34.1	568	−2431	802	−1186	15.47	16.9
La[b]	446	39.4	590	−2423				
Nd[a]	437	59.7	582	−2461			15.84	16.9
Nd[b]	438	61.3	570	−2268				
Sm[a]	425	69.3	546	−2546	811	−1282	16.25	16.5
Sm[b]	427	99.8	563	−2356				
Eu[a]	400	40.4	523	−1891	770	−4861	16.36	17.1
Eu[b]	419	79.6	546	−2263				
Gd[a]	415	105	564	−2466			16.71	16.6
Gd[b]	416	112	562	−2328				
Tb[a]	400	50.7	562	−2536			16.82	17.7
Tb[b]	398	41.4	538	−1752				
Dy[a]	397	102	561	−2283	800	−3.147	17.06	16.4
Dy[b]	397	108	557	−2228				
Ho[a]	390	87.5	565	−2512			17.22	16.9
Ho[b]	391	94.1	577	−2355				
Er[a]	379	47.9	587	−1968	813	−3593	18.86	18.5
Er[b]	379	58.2	610	−2199				
Yb[a]	360	37.4	603	−2402	845	−2946	19.26	19.0
Yb[b]	359	30.4	572	−2374				
Lu[a]	351	16.1	553	−1833	836	−3998	19.40	19.0
	479	31.7						
Lu[b]	351	24.5	562	−2450				
Y[a]	406	19.7	589	−2135	806	−3239	12.92	12.7
Y[b]	381	35.3	560	−2341				

[a] Dynamic air atmosphere. [b] Dynamic nitrogen atmosphere.

the melting and decomposition processes decrease along the lanthanide series. Figure 4 presents the correlation between melting temperatures and average ionic radii. It is consistent with the decrease of the thermal stabilities of the complexes as the Ln^{3+} ionic radius decreases and it is probably related to the steric hindrance of the ligands. In the case of heavier lanthanides this behaviour becomes even more pronounced and in fact a coordination number decrease is observed.

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