

THERMAL INVESTIGATION BY SIMULTANEOUS TG/DTG-DTA AND IR SPECTROSCOPY OF NEW LANTHANIDE COMPLEXES WITH SALICYLHYDROXAMIC ACID

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The reaction of a hydrated nitrate salt of lanthanide ($Ln=Pr, Nd, Gd, Dy, Er$) with the polyfunctional ligand salicylhydroxamic acid (H_3sha), in the presence of base, afforded solid compounds, insoluble in common organic solvents and in water. The new complexes characterized by means of elemental analyses (C, H, N, Ln), magnetic moment determinations and spectroscopic data (IR, MS). It is proposed that they are neutral, with a possible polymeric structure of the general type:



Their thermal decomposition was studied in nitrogen and/or oxygen atmosphere, between 25–1000°C by using simultaneous TG/DTG-DTA technique. The IR spectroscopy used to determine the intermediates and the final products. The intermediates at 180°C suggest the formation of N-hydroxylactam complex, which upon further heating gives a carbonaceous residue of Ln_2O_3 at 1000°C in nitrogen, while in oxygen the stable oxides are formed at 600°C.

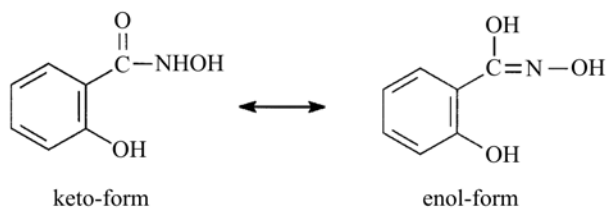
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Introduction

The increasing interest in the chemistry of lanthanide ions is due to their recent applications in therapeutic and diagnostic pharmaceutical [1, 2], in catalysis and laser technology [3, 4]. Their ability for high coordination number, results in the preparation of complexes with structural differences especially when polyfunctional ligands are used. Such ligands can be the hydroxamic acids which may act as bidentate, tridentate or tetradentate ligands in a number of coordination modes as mono- or dianions depending mostly on the metal involved, the pH of the reaction solution [5] and the stoichiometry of metal to ligand ratio. The knowledge of the biological and medical importance of hydroxamic acids is well recognized [6] and it has been proved that the active sites of some biological enzymes include the hydroxamic acids. In the chelates of simple hydroxamic acids the ligands behave as bidentate O,O' donors forming five-membered ring complexes.

However, in the chelates of salicylhydroxamic acid (2-OH hydroxamic acid, H_3sha , Scheme 1), the ligand contains a further coordination site adjacent to the hydroxamate group. So, the salicylhydroxamic acid may act as bidentate monoanion through the hydroxamic oxygens [7, 8] or in the same complex as bidentate monoanionic or dianionic ligands with bridg-

ing hydroxamate oxygen atoms [9] but not with the phenolic oxygen atom. When, however, the stoichiometric ratio M:L is 1:1, it may act as trianion, tetradentate forming a metallacrown polymer in which the metals take part in five- and six-membered chelating ring [10, 11]. Recently, there is an increasing research interest on the thermal properties of lanthanide complexes with ligands having O and N donor ability, studied by TG-DTA techniques [12, 13].



Scheme 1 Tautomeric configurations of the salicylhydroxamic acid

Survey in the literature revealed that no research has been done with lanthanide ions and salicylhydroxamic acid. Herein we report the synthesis, spectroscopic (IR, MS) and thermal studies (TG/DTG-DTA) of the reaction products of lanthanide nitrates and the ligand salicylhydroxamic acid.

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Experimental

Synthesis of the complexes



The hydrated nitrate salts of lanthanide ($\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, where $\text{Ln}=\text{Pr}$, Nd , Gd , Dy , Er) and the salicylhydroxamic acid ($\text{H}_3\text{sha}=\text{C}_7\text{H}_7\text{NO}_3$) were purchased from Aldrich.

To a MeOH-DMF solution (5:1) of lanthanide nitrate (0.65 mmol) was added dropwise a methanolic solution of deprotonated by NaOH, salicylhydroxamic acid (1.0 mmol). Immediately a solid product came out, filtrated and dried in air.

The compounds prepared are pale coloured, insoluble in common organic solvents and in water, indicative of polynuclear species, and are stable in air in the solid-state. Their physicochemical characteristics are listed in Table 1. The results of elemental analyses are consistent with metal-to-ligand ratio of 2:3, while the magnetic moments (μ_{eff}) are characteristics of trivalent lanthanide ions. Similar values have been observed with substituted benzoate complexes of lanthanides [14, 15].

Physical measurements

Stoichiometric analyses (C, H, N) were performed on a Perkin-Elmer 240B elemental analyzer. Metal content was determined by EDTA titration after decomposition with nitric acid, using as indicator xylenol orange and buffer hexamethylenetetramine [16].

Magnetic susceptibility measurements on powdered samples were performed at 25°C employing the Faraday method in instrument of Johnson Matthey, type MSB-MKI, calibrated against $\text{Hg}[\text{Co}(\text{SCN})_4]$.

Infrared spectra were recorded on a Perkin-Elmer FT-IR 1650 spectrometer, in the region 4000–200 cm^{-1} using KBr pellets. Mass spectra were run on a RMU-6L Hitachi Perkin-Elmer, double focusing mass spectrometer, model TS 250 Fision, using direct probe insertion for the samples, operating at 70 eV.

The simultaneous TG/DTG-DTA curves were obtained on a Setaram instrument, model SETSYS-1200. The samples were heated in platinum crucibles, in nitrogen and/or oxygen atmosphere, within the temperature range 25–1000°C. The heating rate was 10°C min^{-1} and the sample size ranged in mass from 10–15 mg. The stoichiometry of the residues checked with energy dispersive spectrometry (EDS) of JSM-840A type with analytical system Oxford ISIS-300.

Results and discussion

The reactions of the lanthanide nitrate with the polyfunctional ligand salicylhydroxamic acid (H_3sha) af-

forded immediately in good yield, insoluble solid compounds, very stable in air in solid-state, but extremely sensitive upon heating. For this reason, their thermal behaviour was studied by TG-DTA technique to explore their thermal stability and decomposition mode under controlled heating rate, as well as their fragmentation pattern with the aim of mass spectroscopy.

The characterization of their molecular structure was made by elemental analyses, magnetic moments and infrared spectroscopy. A representative IR spectrum for the Nd complex (compound 2) is given in Fig. 1.

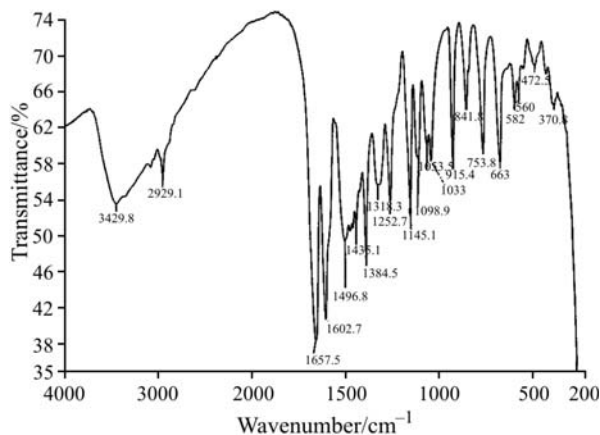


Fig. 1 IR spectrum of the Nd complex

It is deduced that the ligand may act in the same complex both as bidentate monoanion (H_2sha) and dianion (Hsha) through the oxygens O, O' of the hydroxamato group (CONHO^-), as well as from the N atom, possibly coordinated to a second lanthanide atom, while at least one phenolate hydroxyl is not deprotonated and coordinated [17]. (IR bands: 1603 cm^{-1} $\nu(\text{CO})$ carbonyl oxamato, 1590 cm^{-1} $\nu(\text{C}=\text{N})$, 3410 cm^{-1} $\nu(\text{OH})$ phenolate hydroxyl, ~ 478 $\text{Ln}-\text{N}$, ~ 378 $\text{Ln}-\text{O}$.)

Based on the above mentioned, the prepared compounds seem to be polymeric with possible structure of the type:



where $x=2, 3, 4, 5$ (Table 1). The existence of crystal water and coordinated DMF molecules is inferred from the bands at 3440 and 1657 cm^{-1} , respectively.

Mass spectra

Mass spectra were obtained for the salicylhydroxamic acid (Fig. 2a) and for its complex with praseodymium (Fig. 2b). In the mass spectrum of the ligand detected the molecular ion ($m/e=153$) and its fragments corresponding to the elimination of one hydroxylamine ($m/e=120$) and one CO molecule ($m/e=93$). A second

fragmentation process of the ligand gives the daughter ion, salicylic acid ($m/e=138$), from which the salicylaldehyde results ($m/e=122$) as the basic peak.

In the mass spectrum of the complex, neither the molecular ion nor those corresponding to the elimination of one ligand from the parent ions are detected. This was expected because of their high molecular mass (967) and thermal instability, which makes it difficult to give a complete fragmentation pattern.

The two mass spectra exhibit significant differences in their profiles. There are peaks beyond the molecular mass of the ligand at m/e 219, 249, 262, 276, 389, 482, 491, which cause evidence for the Pr-ligand bonds. More specifically, the fragments 249, 262 and 276 are assigned to intermediate fragments which contain the metal and one ligand molecule from which CO_2 , NH_2OH and H_2O have respectively been eliminated.

In the low mass-number region, the observed peaks correspond to the released DMF molecule ($m/e=73$, base peak) and some fragments of the coordinated ligand. The most prominent from these are CO_2 ($m/e=44$) benzaldehyde ($m/e=105$) and the ligand after the release of a water molecule ($m/e=135$).

Thermal behaviour

The new lanthanide(III) complexes (1–5) and the ligand H_3sha were subjected to TG-DTA analysis from ambient temperature up to 1000°C in nitrogen and oxygen atmospheres. The temperature ranges, the determined percentage mass losses and the thermal effects accompanying the decomposition are given in Tables 2 and 3, respectively. Representative thermal curves TG/DTG-DTA for the Pr and Dy complexes in nitrogen are depicted in Figs 3a and b, while in oxygen for the same complexes in Figs 4a and b, respectively.

For all the investigated compounds, the thermal decomposition mode in nitrogen seems to follow the same model. The anhydrous studied compounds, after

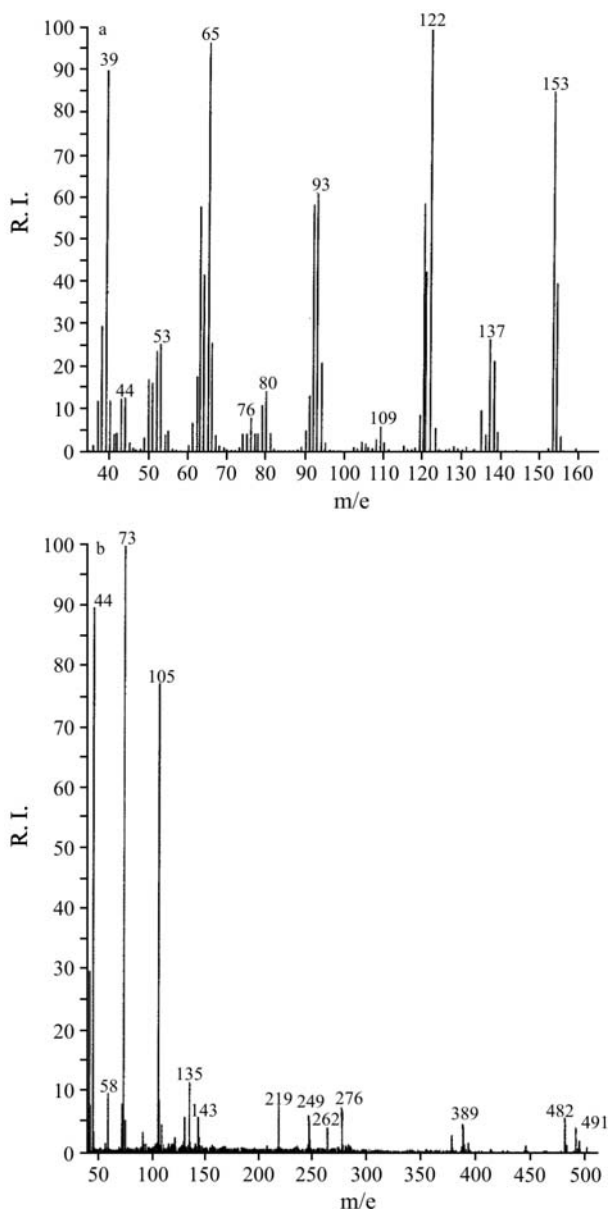


Fig. 2 Mass spectra of the a – ligand H_3sha and b – Pr complex

Table 1 Analytical, physical and magnetic data for the complexes $[\text{Ln}_2(\text{Hsha})_2(\text{H}_2\text{sha})(\text{DMF})_x(\text{CH}_3\text{O})(\text{H}_2\text{O})]_n \cdot 2\text{H}_2\text{O}$

Compound	Colour	Yield/%	C/%	N/%	H/%	Ln/%	$\mu_{\text{eff}}/\text{MB}$	
1	Pr $x=2$	green	72	34.2 (34.74) ^a	7.4 (7.24)	3.9 (4.00)	28.2 (29.14)	4.25
2	Nd $x=3$	pale violet	70	35.3 (35.56)	8.3 (8.03)	3.9 (4.00)	27.0 (27.57)	3.70
3	Gd $x=5$	brownish	62	35.9 (36.43)	9.6 (9.19)	4.7 (4.59)	25.3 (25.81)	8.94
4	Dy $x=4$	white	65	34.9 (35.32)	8.8 (8.4)	4.1 (4.2)	27.5 (28.13)	11.80
5	Er $x=2$	pink	75	32.4 (32.95)	7.1 (6.86)	3.4 (3.43)	32.0 (32.81)	10.82

^acalculated values in parenthesis

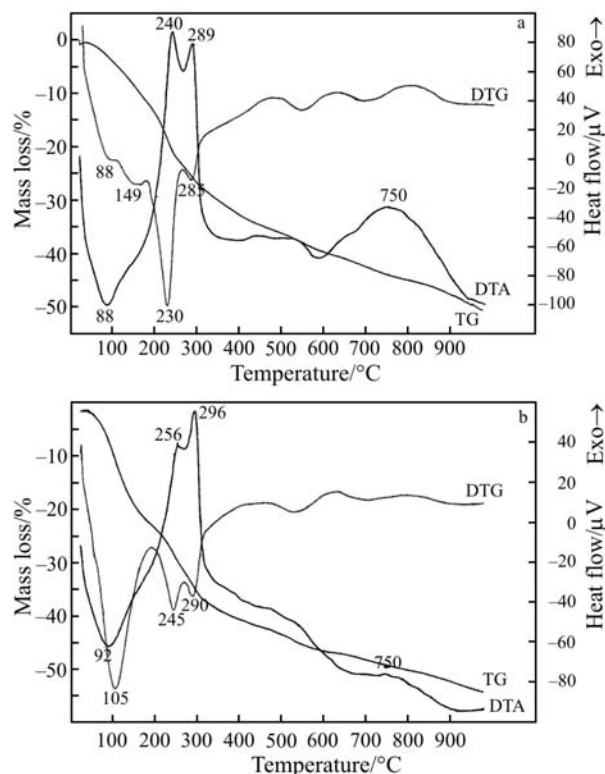


Fig. 3 Thermal curves TG/DTG-DTA for the a – Pr and b – Dy complexes in nitrogen

the elimination of the crystal water molecules at $\sim 90^\circ\text{C}$, decompose in several stages followed by several exothermic effects. The DTA curve shape indicates that no melting takes place before decomposition. The endotherm at $\sim 150^\circ\text{C}$, together with the mass loss, is evidence for the elimination of the coordinated water molecule.

Upon increasing the temperature, intramolecular transformations in the coordinated ligands take place, as it is deduced from the IR spectra of the intermediates at 180°C , where a new band at $\sim 1758\text{ cm}^{-1}$ appeared (Fig. 5a). This can be attributed to the stretching mode of a carbonyl group $\nu(\text{C}=\text{O})$ belonging to a four-membered ring, such as a lactam.

This transformation may take place by elimination of a water molecule from one coordinated ligand and a hydroxylamine from another one. This process is in accordance with the thermal decomposition of the ligand and their complexes with some transition metals mentioned previously [18]. Beyond 200°C , the continuous mass loss is due to successive elimination of the DMF molecules and simultaneous degradation of the derived N-hydroxylactam complex with DTG_{max} at 230 and 290°C , as it is inferred from the absence of the corresponding peaks in the IR spectra (1657 cm^{-1} due to DMF and 1758 cm^{-1} due to lactam) of the intermediates at 400°C (Fig. 5b).

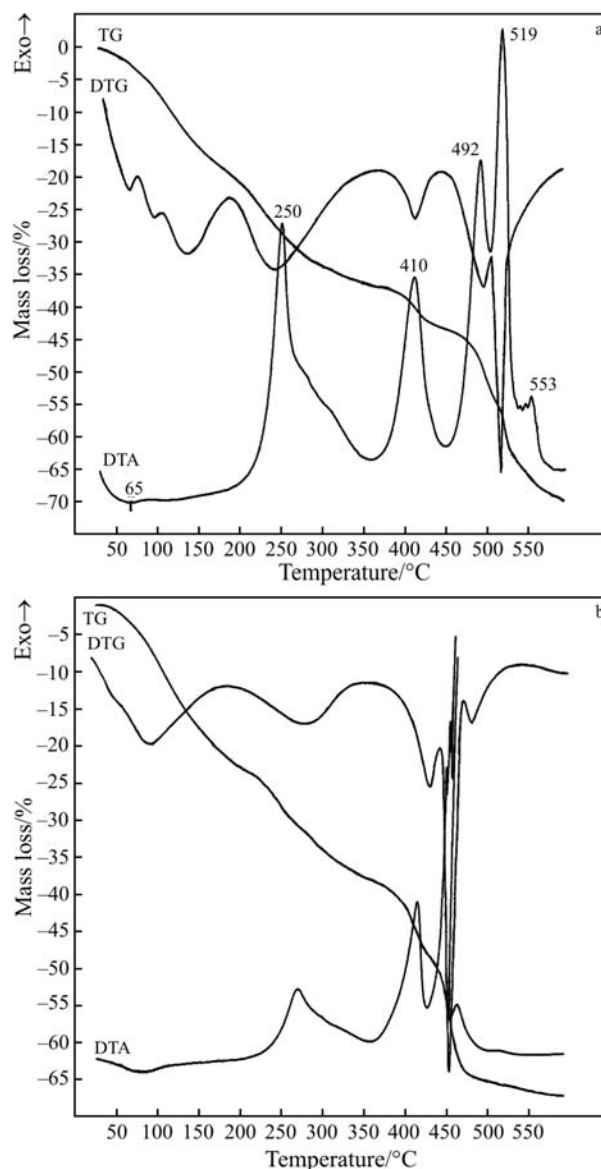


Fig. 4 Thermal curves TG/DTG-DTA for the a – Pr and b – Dy complexes in oxygen

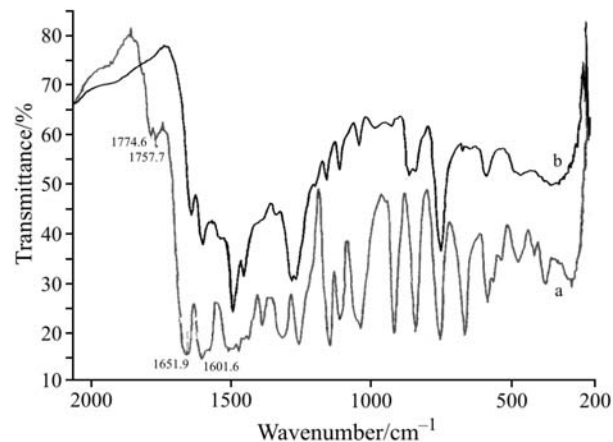


Fig. 5 Infrared spectra for the Pr complex: a – at 180°C and b – at 400°C

Table 2 Thermoanalytical results (TG/DTG-DTA) for the complexes $[\text{Ln}_2(\text{Hsha})_2(\text{H}_2\text{sha})(\text{DMF})_x(\text{CH}_3\text{O})(\text{H}_2\text{O})]_n \cdot 2\text{H}_2\text{O}$, in nitrogen

Compound	Stage	$T_{\text{range}}/^\circ\text{C}$	$\text{DTG}_{\text{max}}/^\circ\text{C}$	DTA	Mass loss/%	Evolved moiety formula	Mass calc./%
1	1	40–130	88	88 endo	6.9	$2\text{H}_2\text{O}+\text{CH}_3\text{OH}$	6.92
	2	130–180	149	150 endo	3.8	$2\text{H}_2\text{O}$	3.73
	3	180–320	230, 285	240, 289 exo	18.0	$2\text{DMF}+\text{NH}_2\text{OH}$	18.51
	4	320–600	570	570 exo	11.0	$\text{C}_7\text{H}_6\text{O}$	10.96
	5	600–980	–	750 exo	12.3	unknown	
	residue	>980			48.0	$\text{Pr}_6\text{O}_{11}+\text{C}$	35.23+x
2	1	45–130	74	74 endo	6.5	$2\text{H}_2\text{O}+\text{CH}_3\text{OH}$	6.40
	2	130–180	120	120 endo	3.4	$2\text{H}_2\text{O}$	3.44
	3	180–320	232, 290	245, 290 exo	24.0	$3\text{DMF}+\text{NH}_2\text{OH}$	24.05
	4	320–600	540	540 exo	10.1	$\text{C}_7\text{H}_6\text{O}$	10.13
	5	600–980	–	760 exo	9.0	unknown	
	residue	>980			47.0	$\text{Nd}_2\text{O}_3+\text{C}$	32.16+x
3	1	60–200	110	100 endo	8.4	$4\text{H}_2\text{O}+\text{CH}_3\text{OH}$	8.44
	2	200–320	237, 297	245, 297 exo	32.0	$5\text{DMF}+\text{NH}_2\text{OH}$	32.46
	3	320–600	–	534 exo	8.7	$\text{C}_7\text{H}_6\text{O}$	8.70
	4	600–980	–	750 exo	10.9	unknown	
	residue	>980			40.0	$\text{Gd}_2\text{O}_3+\text{C}$	29.75+x
4	1	50–200	105	92 endo	8.9	$2\text{H}_2\text{O}+\text{CH}_3\text{OH}$	8.90
	2	200–320	245, 290	256, 296 exo	28.0	$4\text{DMF}+\text{NH}_2\text{OH}$	28.14
	3	320–620	520	520 exo	9.2	$\text{C}_7\text{H}_6\text{O}$	9.18
	4	620–980	–	750 exo	7.0	unknown	
	residue	>980			47.0	$\text{Dy}_2\text{O}_3+\text{C}$	32.29+x
5	1	50–140	88	88 endo	6.5	$2\text{H}_2\text{O}+\text{CH}_3\text{OH}$	6.57
	2	140–180	130	140 endo	3.5	$2\text{H}_2\text{O}$	3.53
	3	180–310	245, 295	265, 295 exo	17.5	$2\text{DMF}+\text{NH}_2\text{OH}$	17.54
	4	310–600	520	530 exo	10.5	$\text{C}_7\text{H}_6\text{O}$	10.40
	5	600–980	–		9.0	unknown	
	residue	>980			53.0	$\text{Er}_2\text{O}_3+\text{C}$	37.46+x

Table 3 Thermoanalytical results (TG/DTG-DTA) for the complexes $[\text{Ln}_2(\text{Hsha})_2(\text{H}_2\text{sha})(\text{DMF})_x(\text{CH}_3\text{O})(\text{H}_2\text{O})]_n \cdot 2\text{H}_2\text{O}$, in oxygen

Compound	Stage	$T_{\text{range}}/^\circ\text{C}$	$\text{DTG}_{\text{max}}/^\circ\text{C}$	DTA	Mass loss/%	Evolved moiety formula	Mass calc./%
1	1	40–100	65, 90	65, 90 endo	6.9	$2\text{H}_2\text{O}+\text{CH}_3\text{OH}$	6.92
	2	100–180	130	250 exo	3.8	$2\text{H}_2\text{O}$	3.72
	3	180–320	240	410 exo	18.0	$2\text{DMF}+\text{NH}_2\text{OH}$	18.51
	4	320–450	410	490, 519 exo	11.0	$\text{C}_7\text{H}_6\text{O}$	10.96
	5	450–580	490, 520	and 553 exo	25.3	$\{2(\text{L}-\text{O})-\text{H}_2\text{O}\}$	25.26
	residue	>580			35.0	Pr_6O_{11}	35.23
2	1	45–120	70	70 endo	6.5	$2\text{H}_2\text{O}+\text{CH}_3\text{OH}$	6.40
	2	120–320	245	250 exo	26.0	$2\text{H}_2\text{O}+3\text{DMF}+\text{NH}_2\text{OH}$	27.45
	3	320–470	395	395 exo	10.0	$\text{C}_7\text{H}_6\text{O}$	10.13
	4	470–580	485	485 exo	22.0	$\{2(\text{L}-\text{O})-\text{H}_2\text{O}\}$	24.00
	residue	>580			35.5	Nd_2O_3	32.16
3	1	60–200	80, 110	80, 110 endo	8.5	$4\text{H}_2\text{O}+\text{CH}_3\text{OH}$	8.44
	2	200–320	240	265 exo	32.5	$5\text{DMF}+\text{NH}_2\text{OH}$	32.46
	3	320–420	390	388 exo	8.5	$\text{C}_7\text{H}_6\text{O}$	8.70
	4	420–600	480	485, 582 exo	21.50	$\{2(\text{L}-\text{O})-\text{H}_2\text{O}\}$	21.00
	residue	>600			29.00	Gd_2O_3	29.75
4	1	50–120	80	80 endo	7.5	$3\text{H}_2\text{O}+\text{CH}_3\text{OH}$	7.41
	2	120–350	275	275 exo	30.0	$4\text{DMF}+\text{NH}_2\text{OH}+\text{H}_2\text{O}$	29.70
	3	350–440	430	430 exo	9.5	$\text{C}_7\text{H}_6\text{O}$	9.18
	4	440–460	453	453, 470 exo	21.0	$\{2(\text{L}-\text{O})-\text{H}_2\text{O}\}$	22.16
	4a	460–560	470	and 525 exo			
residue	>580			32.0	Dy_2O_3	32.29	
5	1	50–130	110	90 endo	10.0	$4\text{H}_2\text{O}+\text{CH}_3\text{OH}$	10.36
	2	130–290	280	280 exo	18.0	$2\text{DMF}+\text{NH}_2\text{OH}$	17.54
	3	290–400	330	335 exo	10.5	$\text{C}_7\text{H}_6\text{O}$	10.40
	4	400–600	465	465, 560 exo	24.5	$\{2(\text{L}-\text{O})-\text{H}_2\text{O}\}$	24.64
	residue	>600			37.0	Er_2O_3	37.46

The intermediates at 400°C are thermally unstable and decompose further gradually until 1000°C, giving a total mass loss of about 50% of the complex. The residues at 1000°C for all the studied complexes are carbonaceous solids consisting of the lanthanide oxide Ln₂O₃ plus carbon in a ratio of 20% of the complex. Evidence for this arises from the IR peak at ~370 cm⁻¹, attributable to Ln–O bond and from EDS spectra. The formation of the oxide is accompanied by a broad exotherm on DTA curve at ~750°C in nitrogen, while in oxygen the stable oxides are formed until 600°C [12, 19, 20].

Based on the initial decomposition temperatures, the thermal stability of the complexes under investigation follows the series: Gd>Dy=Er>Nd>Pr.

Conclusions

The newly prepared salicylhydroxamate complexes of lanthanides are thermally very unstable both in nitrogen and in oxygen atmosphere. They decompose exothermally in several stages giving pure, stable lanthanide oxide at ~600°C in oxygen, while in nitrogen the residue at 1000°C is carbonaceous lanthanide oxide. It is proposed the thermal decomposition studies of this kind of complexes to be done in oxygen, in order to obtain desirable products.

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