Research Article

Synthesis and Thermal Characterization of Lanthanide(III) Complexes with Mercaptosuccinic Acid and Hydrazine as Ligands

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Reaction of hydrazine and mercaptosuccinic acid with metal ions forms complexes with general formula $[\text{Ln}(\text{N}_2\text{H}_4)_2\{\text{CH}_2(\text{COO})\text{CH}(\text{SH})(\text{COO})\}_{1.5}] \cdot (\text{H}_2\text{O})$, where Ln = La(III), Pr(III), Nd(III), Sm(III), and Gd(III) at pH 5. The complexes have been characterized by elemental analysis, IR and UV-visible spectroscopic, thermal and X-ray diffraction studies. The IR data reveal that the acid moiety in the complexes is present as dianion due to the deprotonation of COOH groups by lanthanides in these complexes, leaving -SH group unionized and hydrazine as bidentate neutral ligand showing absorptions in the range of $945\text{--}948\text{ cm}^{-1}$. The thermoanalytical data evince that the complexes are stable up to 103°C and undergo complete decomposition in the range of $550\text{--}594^\circ\text{C}$ resulting in metal oxides. SEM images of La_2O_3 and Gd_2O_3 residues show their nano sized clusters suggesting that the complexes may be used as precursors for nano La_2O_3 and Gd_2O_3 , respectively. X-ray powder diffraction patterns show isomorphism among the complexes. The kinetic parameters of the decomposition of the complexes have been computed by Coats-Redfern equation.

1. Introduction

Mercaptosuccinic acid, as a ligand, has been of interest because of its versatility in coordinate modes due to two carboxylic acid and sulfhydryl groups. It is known to form complexes with divalent transition metal ions, Mn(II), Fe(II), Co(II), and Ni(II). It is reported that, in these complexes, S-H is ionised and coordinated in addition to coordination of one of the COOH groups [1]. Patil and Krishnan have reported that alkaline earth metals Mg, Sr, and Ba also form 1 : 1 complexes in which S-H group is not involved and two COOH groups involve in coordination. These complexes are found to form precipitates of metal mercaptosuccinates with aqueous solution of zinc and cadmium salts, leaving alkaline earth metal ions in solution and hence they can be used as antidote for Zn and Cd poisoning [2]. A potentiometric titration study indicates the formation of mercaptosuccinic acid complexes of Zn and Ni with and without the involvement of sulfhydryl group in coordination [3]. Another potentiometric study of chelates formed by La^{3+} , Ce^{3+} , Pr^{3+} , and Nd^{3+} with this acid

reveals that the chelates of acids containing -SH group are less stable than those with NH_2 or OH donor group [4].

A study on heterochelates of Zn^{2+} with nitrilotriacetic acid and mercapto acids system explains the stability of chelates due to two factors, π interaction in M-S bond and sigma bonding of M-S bond due to polarisation of sulfur [5]. A similar type of study on heterochelates of Ni and Zn containing this acid and dipyrityl supports the above factors. However, it concludes that the greater stability of M-S bond may be due to strengthening of M-S sigma bond and the contribution of M-S π interaction, its lower stability due to the presence of coligands.

In spite of these reports, there is no systematic study of synthesis of mercaptosuccinic acid complexes with lanthanides found in the literature. We have been studying carboxylate complexes of lanthanides and transition metals using hydrazine as coligand. There are numerous reports on metal hydrazine complexes of formic [6], acetic [7], propionic [8], glycolic [9], salicylic [10], tri- and tetracarboxylic [11, 12], and naphthoxy and hydroxy naphthoic

acid [13, 14] systems. In many complexes, hydrazine being a simple diamine acts as neutral monodentate, bidentate-bridged, and monodentate $N_2H_5^+$ cation in many complexes [15, 16]. With the interest of understanding the nature of interaction of lanthanides with carboxylic acid containing S-H group and hydrazine together, we performed this work. We have reported the synthesis of new lanthanide complexes using mercaptosuccinic acid and hydrazine as ligands and their characterization by IR and UV-visible spectroscopic methods, simultaneous TG-DTA analysis, powder X-ray diffraction method, and magnetic measurements. Since these complexes were found to yield metal oxides of nanosize on decomposition, SEM image reports of residual oxides have also been presented.

2. Experimental

2.1. Preparation of $[Ln(N_2H_4)_2\{CH_2(COO)CH(SH)(COO)\}_{1.5}] \cdot (H_2O)$, Where $Ln = La(III), Pr(III), Nd(III), Sm(III), \text{ and } Gd(III)$. These complexes were prepared by adding a ligand solution which was obtained by mixing an aqueous solution of mercaptosuccinic acid (0.3 g, 2 mmol in 60 mL of H_2O) and hydrazine hydrate (0.2 g, 4 mmol) to a metal nitrate solution which was prepared by dissolving metal oxide (e.g., La_2O_3 , 0.163 g, 0.5 mmol) in a minimum quantity of 1:1 conc. HNO_3 and evaporated to eliminate excess of acid and dissolved in distilled water at pH 5. A crystalline product formed from the turbid solution while heating over water bath at $80^\circ C$ for 1 h was filtered, washed with absolute alcohol followed by ether, and dried in a desiccator over anhydrous $CaCl_2$.

2.2. Experimental Techniques. The composition was fixed by chemical analysis. Hydrazine content was determined by titrating against standard KIO_3 (0.025 mol L^{-1}) [17]. Metal contents were determined by titrating with EDTA (0.01 mol L^{-1}) after decomposing the complexes with 1:1 nitric acid [17].

IR Spectra of the complexes in the region $4000\text{--}400 \text{ cm}^{-1}$ were recorded as KBr pellets using Perkin Elmer 597 spectrophotometer. Electronic reflectance spectra of Pr(III), Nd(III), Sm(III), and Gd(III) complexes were obtained using a Varian Cary 5000 recording spectrophotometer. The magnetic susceptibility of Pr(III) and Nd(III) complexes was measured using a vibrating sample magnetometer, VSM EG & G model 155 at room temperature. The X-ray powder diffraction patterns of the complexes were recorded using Philips X-ray diffractometer (model PW 1050/70) employing $Cu\text{-K}\alpha$ radiation with nickel filter. The simultaneous TG-DTA experiments were carried out using SDT Q600 V8.3 instrument and Stanton 781 simultaneous thermal analyzer. Thermal analyses were carried out in air at the heating rate of $10^\circ C/\text{min}$ using 5 to 10 mg of the samples. Platinum cups were employed as sample holders and alumina as reference. The temperature range was ambient to $800^\circ C$. The SEM images for the final products of La(III) and Gd(III) complexes

FIGURE 1: Comparison of IR spectrum of (a) $[La(N_2H_4)_2\{CH_2(COO)CH(SH)(COO)\}_{1.5}] \cdot (H_2O)$, (b) $[Pr(N_2H_4)_2\{CH_2(COO)CH(SH)(COO)\}_{1.5}] \cdot (H_2O)$, (c) $[Nd(N_2H_4)_2\{CH_2(COO)CH(SH)(COO)\}_{1.5}] \cdot (H_2O)$, (d) $[Sm(N_2H_4)_2\{CH_2(COO)CH(SH)(COO)\}_{1.5}] \cdot (H_2O)$, and (e) $[Gd(N_2H_4)_2\{CH_2(COO)CH(SH)(COO)\}_{1.5}] \cdot (H_2O)$.

were recorded using a Cambridge scanning electron microscope (JEOL model JSM-6390LV) with EDX attachment (JEOL model JED-2300).

3. Results and Discussion

3.1. IR Spectra. IR and analytical data of the complexes are listed in Table 1. In the IR spectra of the complexes, the broad bands in the region $3333\text{--}3355 \text{ cm}^{-1}$ are assigned to ν_{OH} vibrations of the associated water molecule. The ν_{SH} arising from sulfhydryl group which appears at 2565 cm^{-1} in the spectrum of pure acid was found to be shifted to lower frequencies, $2542\text{--}2555 \text{ cm}^{-1}$ in case of complexes [18] implying that mercapto group is not involved in the coordination. This observation agrees with the reported values found in the literature [2]. Further this peak appears strong, clear, and sharp for La, Pr, and Nd complexes and weak for Sm and Gd. The hydrazine complexes display a N-N stretching frequency in the range of $945\text{--}948 \text{ cm}^{-1}$ showing bidentate bridging nature in the complexes [19]. All the complexes show absorption in the range of $1531\text{--}1556 \text{ cm}^{-1}$ and $1309\text{--}1319 \text{ cm}^{-1}$ corresponding to ν_{COO} (asym) and ν_{COO} (sym), respectively, and their difference being greater than 200 cm^{-1} corroborates monodentate coordination of carboxylate group to the metal [20]. A comparison of IR spectra of lanthanide complexes is shown in Figure 1.

3.2. Thermal analysis. Thermal analysis data shown in Table 2 indicate that all complexes follow similar type of decomposition pattern confirming their similar formulation indirectly.

TABLE 1: Analytical and IR data.

Molecular formula of complexes	Colour	Yield %	D,pt/ °C	Carbon		Hydrogen		Nitrogen		Sulfur		Hydrazine	Metal	$\nu_{\text{O-H}}$ (H ₂ O)		$\nu_{\text{S-H}}$	$\nu_{\text{C=O}}$		$\nu_{\text{C=O}}$ asy-sym	$\nu_{\text{N-N}}$	ν_{NH}
				Fd. (cald.)	Fd. (cald.)	Fd. (cald.)	Fd. (cald.)	Fd. (cald.)	Fd. (cald.)	Fd. (cald.)	Fd. (cald.)			sym	Asym						
[La(N ₂ H ₄) ₂ {CH ₂ (COO) CH(SH)(COO)} _{1.5}].-(H ₂ O)	White	65	103	14.4 (14.5)	4.5 (4.6)	11.3 (11.1)	9.3 (9.4)	13.2 (13.3)	28.8 (28.9)	3346 (b)	2542 (m)	1319 (s)	1533 (s)	214 (m)	945 (m)	3346 (b)					
[Pr(N ₂ H ₄) ₂ {CH ₂ (COO) CH(SH)(COO)} _{1.5}].-(H ₂ O)	Light Green	65	95	14.5 (14.4)	4.5 (4.6)	11.5 (11.1)	9.3 (9.4)	13.1 (13.2)	29.1 (29.2)	3334 (b)	2543 (m)	1319 (s)	1531 (s)	212 (m)	945 (m)	3242 (b)					
[Nd(N ₂ H ₄) ₂ {CH ₂ (COO) CH(SH)(COO)} _{1.5}].-(H ₂ O)	Light violet	65	93	14.4 (14.3)	4.5 (4.6)	11.01 (11.0)	9.4 (9.3)	13.2 (13.1)	29.6 (29.7)	3355 (b)	2543 (m)	1319 (s)	1536 (s)	217 (m)	945 (m)	3355 (b)					
[Sm(N ₂ H ₄) ₂ {CH ₂ (COO) CH(SH)(COO)} _{1.5}].-(H ₂ O)	Dull white	60	95	14.2 (14.1)	4.4 (4.5)	11.7 (11.8)	9.1 (9.2)	13.1 (13.0)	30.4 (30.5)	3334 (b)	2553 (m)	1311 (s)	1556 (s)	245 (m)	948 (m)	3242 (b)					
[Gd(N ₂ H ₄) ₂ {CH ₂ (COO) CH(SH)(COO)} _{1.5}].-(H ₂ O)	Dull white	60	95	14.8 (14.9)	4.4 (4.5)	11.6 (11.7)	9.2 (9.1)	12.9 (12.8)	31.5 (31.6)	3333 (b)	2555 (m)	1309 (s)	1543 (s)	234 (m)	945 (m)	3248 (b)					

(s): sharp, (b): broad, and (m): medium.

(s): sharp, (b): broad, and (m): medium.

TABLE 2: Thermal analysis data.

Molecular formula of the complex	DTA peak temp (°C)	Temperature range (°C)	TG		Decomposition product
			Observed	Weight loss % Calculated	
$[\text{La}(\text{N}_2\text{H}_4)_2\{\text{CH}_2(\text{COO})\text{CH}(\text{SH})(\text{COO})\}_{1.5}] \cdot (\text{H}_2\text{O})$	103(+)	40–270	18.5	18.5	$\text{La}\{\text{CH}_2(\text{COO})\text{CH}(\text{SH})(\text{COO})\}_{1.5}$
	220(–)				
	311(–)	270–650	63.0	63.3	La_2O_3
	590(–)				
$[\text{Pr}(\text{N}_2\text{H}_4)_2\{\text{CH}_2(\text{COO})\text{CH}(\text{SH})(\text{COO})\}_{1.5}] \cdot (\text{H}_2\text{O})$	95(+)	40–290	18.3	18.4	$\text{Pr}\{\text{CH}_2(\text{COO})\text{CH}(\text{SH})(\text{COO})\}_{1.5}$
	280(–)				
	309(–)	290–650	59.9	61.7	Pr_6O_{11}
	563(–)				
$[\text{Nd}(\text{N}_2\text{H}_4)_2\{\text{CH}_2(\text{COO})\text{CH}(\text{SH})(\text{COO})\}_{1.5}] \cdot (\text{H}_2\text{O})$	93(+)	40–290	18.0	18.0	$\text{Nd}\{\text{CH}_2(\text{COO})\text{CH}(\text{SH})(\text{COO})\}_{1.5}$
	280(–)				
	311(–)	290–650	61.5	62.0	Nd_2O_3
	550(–)				
$[\text{Sm}(\text{N}_2\text{H}_4)_2\{\text{CH}_2(\text{COO})\text{CH}(\text{SH})(\text{COO})\}_{1.5}] \cdot (\text{H}_2\text{O})$	95(+)	40–300	17.9	18.0	$\text{Sm}\{\text{CH}_2(\text{COO})\text{CH}(\text{SH})(\text{COO})\}_{1.5}$
	290(–)				
	325(–)	300–650	58.9	61.6	Sm_2O_3
	572(–)				
$[\text{Gd}(\text{N}_2\text{H}_4)_2\{\text{CH}_2(\text{COO})\text{CH}(\text{SH})(\text{COO})\}_{1.5}] \cdot (\text{H}_2\text{O})$	95(+)	40–300	17.9	17.8	$\text{Gd}\{\text{CH}_2(\text{COO})\text{CH}(\text{SH})(\text{COO})\}_{1.5}$
	290(–)				
	323(–)	300–650	59.6	60.0	Gd_2O_3
	594(–)				

(+) endotherm and (–) exotherm.

TABLE 3: Energies (in cm^{-1}) of the bands of complexes.

Molecular formula of the complexes	Bands observed for complexes (bands of aquo complexes)	Assignments
$[\text{Pr}(\text{N}_2\text{H}_4)_2\{\text{CH}_2(\text{COO})\text{CH}(\text{SH})(\text{COO})\}_{1.5}] \cdot (\text{H}_2\text{O})$	20900 (21000) 22800 (23500)	$^3\text{P}_0$ $^3\text{P}_2$
$[\text{Nd}(\text{N}_2\text{H}_4)_2\{\text{CH}_2(\text{COO})\text{CH}(\text{SH})(\text{COO})\}_{1.5}] \cdot (\text{H}_2\text{O})$	17100 (17358) 18400 (19289)	$^4\text{G}_{5/2}$ $^4\text{G}_{7/2}$
$[\text{Sm}(\text{N}_2\text{H}_4)_2\{\text{CH}_2(\text{COO})\text{CH}(\text{SH})(\text{COO})\}_{1.5}] \cdot (\text{H}_2\text{O})$	17680 (18200) 18700 (19300)	$^4\text{G}_{5/2}$ $^4\text{F}_{3/2}$
$[\text{Gd}(\text{N}_2\text{H}_4)_2\{\text{CH}_2(\text{COO})\text{CH}(\text{SH})(\text{COO})\}_{1.5}] \cdot (\text{H}_2\text{O})$	32200 (32700)	$^6\text{P}_{7/2}$

FIGURE 2

TABLE 4: Kinetic parameters of the complexes.

Complex	Reaction	E in KJ/mole	A/min^{-1}	n	ΔS in KJ/Kelvin
$[\text{La}(\text{N}_2\text{H}_4)_2\{\text{CH}_2(\text{COO})\text{CH}(\text{SH})(\text{COO})\}_{1.5}] \cdot (\text{H}_2\text{O})$	Dehydration	55.8	4.8×10^6	3	0.029
	Decomposition	13.7	2.4×10^{11}	0.1	0.068
$[\text{Pr}(\text{N}_2\text{H}_4)_2\{\text{CH}_2(\text{COO})-\text{CH}(\text{SH})(\text{COO})\}_{1.5}] \cdot (\text{H}_2\text{O})$	Dehydration	15.0	1.0×10^9	3	0.049
	Decomposition	25.9	8.1×10^7	3	0.039
$[\text{Nd}(\text{N}_2\text{H}_4)_2\{\text{CH}_2(\text{COO})\text{CH}(\text{SH})(\text{COO})\}_{1.5}] \cdot (\text{H}_2\text{O})$	Dehydration	39.1	1.2×10^7	3	0.033
	Decomposition	143.6	1.2×10^{12}	3	0.074
$[\text{Sm}(\text{N}_2\text{H}_4)_2\{\text{CH}_2(\text{COO})\text{CH}(\text{SH})(\text{COO})\}_{1.5}] \cdot (\text{H}_2\text{O})$	Dehydration	18.2	7.4×10^7	3	0.039
	Decomposition	108.3	1.7×10^{10}	1.9	0.059
$[\text{Gd}(\text{N}_2\text{H}_4)_2\{\text{CH}_2(\text{COO})\text{CH}(\text{SH})(\text{COO})\}_{1.5}] \cdot (\text{H}_2\text{O})$	Dehydration	63.2	5.6×10^5	0.1	0.021
	Decomposition	54.9	1.5×10^6	3	0.025

FIGURE 3

FIGURE 4

FIGURE 5

TABLE 5: X-ray diffraction of metal complexes (D spacing in Å units and intensity (Cps) in parentheses).

[Ln(N ₂ H ₄) ₂ {CH ₂ (COO)CH(SH)(COO)} _{1.5}] · (H ₂ O)				
La	Pr	Nd	Sm	Gd
9.0	9.6	8.9	9.7	8.9
(9.8)	(9.1)	(9.8)	(9.2)	(9.8)
8.3	8.9	8.3	8.4	5.7
(10.5)	(9.8)	(10.5)	(10.4)	(15.5)
4.5	4.5	4.5	4.6	4.6
(19.5)	(19.6)	(19.4)	(19.1)	(19.1)
4.0	4.0	4.1	4.1	4.2
(21.9)	(21.8)	(21.5)	(21.6)	(21.1)
3.9	3.9	3.9	3.9	3.2
(22.5)	(22.5)	(22.6)	(22.6)	(21.9)
3.5	3.5	3.5	3.6	3.0
(24.7)	(24.8)	(24.7)	(24.5)	(29.5)
2.8	3.2	3.2	3.2	2.8
(30.9)	(27.2)	(27.2)	(27.5)	(30.9)

The thermograms (Figure 2) reveal that the complexes start losing water first and then hydrazine up to 290°C, showing endotherms in the range of 93°C to 105°C and broad exotherms in the range of 220–290°C, respectively. Dehydration happening around 100°C indicates that water present in the complexes is not coordinated. Endotherm and exotherm suppress each other by mutual exchange of heat resulting in display of weaker peaks. This is a commonly observed phenomenon in case of decompositions of hydrazine complexes eliminating water and hydrazine simultaneously [21]. Then a continuous decomposition of hydrazine complexes from 290 to 650°C corresponding to the decomposition of

the remaining compound in to oxide exhibiting exotherms at 309–325°C and 550–594°C. No stable intermediate could be identified. The oxide formation is confirmed by comparing the XRD pattern of the residues. XRD patterns of final residues of La(III) and Gd(III) complexes are shown as representative examples in Figures 3(a)-3(b) with JCPDS patterns. The scheme of decomposition reactions are shown in (1).

The scheme of decomposition reactions are as follows:

Ln = La(III), Pr(III), Nd(III), Sm(III) & Gd(III).

3.3. Scanning Electron Microscopy. The SEM images of the final products formed after the incineration of the complexes at their decomposition points, and sintering at the same temperature for about 3-4 hrs show that they are in nanoscale (40–50 nm). This fact is further substantiated by their XRD patterns using Scherrer's formula [22] $D = K\lambda/\beta \cos\theta$, where λ is the X-ray wavelength, β is the full width of height

FIGURE 6: Comparison of XRD pattern of (a) $[\text{La}(\text{N}_2\text{H}_4)_2\{\text{CH}_2(\text{COO})\text{CH}(\text{SH})(\text{COO})\}_{1.5}] \cdot (\text{H}_2\text{O})$, (b) $[\text{Pr}(\text{N}_2\text{H}_4)_2\{\text{CH}_2(\text{COO})\text{CH}(\text{SH})(\text{COO})\}_{1.5}] \cdot (\text{H}_2\text{O})$, (c) $[\text{Nd}(\text{N}_2\text{H}_4)_2\{\text{CH}_2(\text{COO})\text{CH}(\text{SH})(\text{COO})\}_{1.5}] \cdot (\text{H}_2\text{O})$, (d) $[\text{Sm}(\text{N}_2\text{H}_4)_2\{\text{CH}_2(\text{COO})\text{CH}(\text{SH})(\text{COO})\}_{1.5}] \cdot (\text{H}_2\text{O})$, and (e) $[\text{Gd}(\text{N}_2\text{H}_4)_2\{\text{CH}_2(\text{COO})\text{CH}(\text{SH})(\text{COO})\}_{1.5}] \cdot (\text{H}_2\text{O})$.

maximum (FWHM) of a diffraction peak, θ is the diffraction angle, and K is Scherrer's constant of the order of 0.89. The SEM images of final residue of La(III) and Gd(III) complexes are shown in Figures 4(a)-4(b) as representative examples. SEM image of La(III) and Gd(III) complexes residue show its nanosized clusters suggesting that the complexes may be used as a precursors for nanometal oxides [23].

3.4. UV-Visible Spectroscopy and Magnetic Susceptibility. The reflectance data of the UV-visible electronic spectra for Pr(III), Nd(III), Sm(III), and Gd(III) complexes are summarized in Table 3. While comparing the spectral data [24] of

complexes with those of aquo ion complexes, it is understood that all complexes show red shifts implying the complex formation. These magnetic moments from magnetic susceptibility measurements for Pr(III) and Nd(III) complexes are 4.10 and 3.40 BM, respectively. The variation of these values from that of free ions, 3.426 and 3.526, respectively, may be because of the influence of ligands on metal ions in complexes.

3.5. Kinetic Studies. Dehydration and decomposition kinetics of complexes were followed using TG. Their parameters have been computed using integral method developed by Coats and Redfern. The equation used for calculation of the E and A parameters is

$$\log \left[1 - \frac{(1 - \alpha)^{n-1}}{(1 - n) T^2} \right] = \log \frac{AR}{\varphi E} \left[1 - \frac{2RT}{E} \right] - \frac{E}{2.303RT}, \quad (2)$$

where α is the fraction reacted in time (t), T is temperature in K , A is the preexponential factor in min^{-1} , φ is the heating rate, E is the activation energy in KJ/mole , and R is the gas constant. Plotting Y versus $1/T$ gives a straight line; for a parameter, n , order of the reaction, where $Y = 1 - (1 - \alpha)^{n-1}/(1 - n)T^2$, the activation energy E was calculated from the slope and the A factor from the intercept [25]. Studies reveal that all the complexes follow the same mechanism of decomposition as inferred from their computed E values. The activation energies for dehydration of the complexes are found to be almost similar in the range of 15.0–63.2 KJ/mole . Activation energies of decomposition of anhydrous complexes are found to be varying from 13.7 to 143.6 KJ/mole . Table 4 shows the computed kinetic parameters for all the complexes, and the dehydration and decomposition kinetics for La(II) complex is shown in Figures 5(a)-5(b) as a representative example.

3.6. X-Ray Diffraction. The X-ray powder diffraction data of the complexes are summarized in Table 5. The X-ray powder diffraction data of the complexes with the formulation, $[\text{Ln}(\text{N}_2\text{H}_4)_2\{\text{CH}_2(\text{COO})\text{CH}(\text{SH})(\text{COO})\}_{1.5}] \cdot (\text{H}_2\text{O})$ where $\text{Ln} = \text{La(III), Pr(III), Nd(III)}$ show similarity among them, implying isomorphism. The XRD pattern of the complexes are shown in Figures 6(a)–6(e). Sm(III) and Gd(III) complexes could not be compared from their pattern showing widening of peaks with weak intensity. This may be because of the very small particle size.

4. Conclusion

The reaction of metal nitrate with mercaptosuccinic acid and hydrazine hydrate yields stable complexes of formula $[\text{Ln}(\text{N}_2\text{H}_4)_2\{\text{CH}_2(\text{COO})\text{CH}(\text{SH})(\text{COO})\}_{1.5}] \cdot (\text{H}_2\text{O})$, where $\text{Ln} = \text{La(III), Pr(III), Nd(III), Sm(III), and Gd(III)}$ at pH 5. Analytical data confirm their formulation. The IR spectroscopic data of complexes indicate the monodentate coordination of carboxylic acid with metals, noninvolvement of sulfhydryl group in coordination and bidentate bridging mode of hydrazine.

All the complexes may be isomorphous due to their similarity in their XRD patterns. The complexes undergo thermal decomposition to metal oxide particles of nanosize. This is because of the evolution of gases, N_2 , CO_2 , NO_2 , and SO_2 due to instantaneous oxidation of organic moiety and hydrazine in the complex in the temperature range 550–594°C. Powder XRD and SEM images results of residual oxides confirm the nanosize. Hence, it is suggested that the complexes may be used as precursors of nano La_2O_3 and Gd_2O_3 .

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