Research Article

Hydrazine Complexes of Lanthanides with 3-Acetoxy- and 4-Acetoxybenzoic Acids: Spectroscopic, Thermal, and XRD Studies

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New bis-hydrazine lanthanide complexes with 3-acetoxybenzoic acid (3-abH) of formula, $[\text{Ln}(\text{3-ab})_3(\text{N}_2\text{H}_4)_2] \cdot x\text{H}_2\text{O}$ where Ln = La, Ce, Pr and Gd and $x = 0$; Ln = Nd and Sm and $x = 1$, and monohydrazine complexes of some trivalent lanthanides with 4-acetoxybenzoic acid (4-abH) of formula, $[\text{Ln}(\text{4-ab})_3(\text{N}_2\text{H}_4)] \cdot \text{H}_2\text{O}$ where Ln = La, Ce, Pr, Nd, Sm and Gd have been prepared in ethanolic medium and characterized by spectroscopic techniques (IR and UV reflectance), microelemental analysis, thermoanalytical technique, powder XRD, SEM-EDS studies, and magnetic susceptibility measurements. The IR spectra of both series show bidentate coordination of carboxylate ion with the metal by displaying, $\nu_{\text{C=O}}(\text{asym})$ in the range of 1587–1602 cm^{-1} and the $\nu_{\text{C=O}}(\text{sym})$ in the range of 1433–1410 cm^{-1} , with a separation of around 200 cm^{-1} . The ester C=O remains unaltered indicating the noninvolvement in coordination. All the complexes show $\nu_{\text{N-N}}$ absorption in the range of 929–962 cm^{-1} indicating the presence of hydrazine in a bridged bidentate fashion. The thermal data reveals that the hydrated compounds show endothermic dehydration followed by exothermic decomposition to leave their metal oxide as end products, and the anhydrous compounds undergo exothermic decomposition to form the respective metal oxide residues.

1. Introduction

Salicylic acid plays vital role in coordination chemistry due to its capacity for chelation. One of its acetyl derivatives, aspirin, has also been used in the preparation of complexes due to its therapeutic applications [1–3]. It has been used as an axial ligand for the preparation of tin porphyrin complexes [4]. The other two isomers of aspirin, namely, 3-acetoxybenzoic acid (3-abH) and 4-acetoxybenzoic acid (4-abH) have not been used for synthesis of complexes yet. In our laboratory, we have been synthesising metal carboxylate complexes using hydrazine as coligand [5–7]. When hydrazine is used as a coligand, it generally leads to the formation of polymeric complexes owing to its action as bridging ligand [8–11]. With the idea of preparing new hydrazine complexes, we selected the 3 and 4-acetoxybenzoic acids. In this paper, we have presented the preparation and the characterization of 3- and

4-acetoxybenzoic acid complexes of some lighter lanthanides with hydrazine as coligand by IR, uv-visible spectroscopic studies, thermoanalytical, XRD, SEM-EDX, and magnetic susceptibility measurement studies.

2. Experimental

The solvents were distilled prior to use, and double distilled water was used for the preparation and chemical analyses. The chemicals used were of AR grade. In all the reactions, 99.99% pure hydrazine hydrate was used as received.

2.1. Preparation of $[\text{Ln}(\text{3-ab})_3(\text{N}_2\text{H}_4)_2] \cdot x\text{H}_2\text{O}$ Where Ln = La, Ce, Pr, and Gd and $x = 0$; Ln = Nd and Sm and $x = 1$. Lanthanum oxide (0.325 g, 1 mmol) was dissolved in a minimum quantity of 1 : 1 HNO_3 , evaporated to eliminate excess of acid, and dissolved in 20 mL of ethanol. This

FIGURE 1: TG-DTA of $[\text{Pr}(3\text{-ab})_3(\text{N}_2\text{H}_4)_2]$. FIGURE 2: TG-DTA of $[\text{Sm}(3\text{-ab})_3(\text{N}_2\text{H}_4)_2] \cdot \text{H}_2\text{O}$.

was added slowly to a freshly prepared ethanolic solution (40 mL) of the ligand containing 3-abH (1.081 g, 6 mmol) and hydrazine hydrate (0.40 g, 8 mmol), stirring the reaction mixture at pH 3. Then the reaction mixture was kept over hot water bath for 1 h 30 min. A dull white, crystalline product obtained was washed with alcohol, ether, and air dried. A similar procedure was adopted for obtaining the other lanthanides with the molar ratio Metal : Acid : Base = 1 : 6 : 8.

2.2. Preparation of $[\text{Ln}(4\text{-ab})_3(\text{N}_2\text{H}_4)] \cdot \text{H}_2\text{O}$ Where $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}$ and Gd . These complexes were prepared using 4-abH, hydrazine hydrate and their respective lanthanum nitrates in alcohol medium at pH 3.5 by adopting similar procedure as mentioned above. The products obtained were washed with alcohol, ether and dried in air. All these complexes were prepared by using the molar ratio Metal : Acid : Base = 1 : 6 : 8.

2.3. Physico chemical Methods. The hydrazine content in all complexes was determined volumetrically using 0.025 M potassium iodate solution under Andrews' conditions [12]. The metal content was determined by EDTA complexometric titration [12] after decomposing a known weight of the sample with 1:1 HNO_3 . Magnetic measurements were carried out by the Gouy method using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as calibrant. The electronic spectra for solid-state complexes

FIGURE 3: TG-DTA of $[\text{Pr}(4\text{-ab})_3(\text{N}_2\text{H}_4)] \cdot \text{H}_2\text{O}$. FIGURE 4: TG-DTA of $[\text{Gd}(4\text{-ab})_3(\text{N}_2\text{H}_4)] \cdot \text{H}_2\text{O}$.

were obtained using a Varian, Cary 5000 recording spectrophotometer. Infrared spectra were recorded using KBR disc ($4000\text{--}400\text{ cm}^{-1}$) on a Shimadzu FTIR-8201 (PC) S spectrophotometer. The simultaneous TG-DTA studies were done on a Perkin Elmer Diamond TG/DTA analyzer, and the curves were obtained in static air using 5–10 mg of the samples at the heating rate of $10^\circ\text{C}/\text{min}$. The XRD patterns were recorded on a Bruker AXS D8 advance diffractometer with an X-ray source Cu, wavelength $1.5406\text{ \AA}$ using a Si (Li) PSD detector. The elemental analysis was carried out using a CHNS Elementar Vario EL III Elemental Analyzer. The SEM with EDX analysis was obtained using JEOL model JSM-6390 LV and JEOL model JED-2300 instrument.

3. Results and Discussion

All the complexes obtained were polycrystalline powders that are stable in air and insensitive to light. Lanthanum complex is sparingly soluble in water but other complexes were insoluble. They were also insoluble in organic solvents such as ethanol, ether, and benzene, but soluble in DMSO.

FIGURE 5: XRD patterns of lanthanide complexes of 3-abH. (a) $[\text{La}(\text{3-ab})_3(\text{N}_2\text{H}_4)_2]$. (b) $[\text{Ce}(\text{3-ab})_3(\text{N}_2\text{H}_4)_2]$. (c) $[\text{Pr}(\text{3-ab})_3(\text{N}_2\text{H}_4)_2]$. (d) $[\text{Nd}(\text{3-ab})_3(\text{N}_2\text{H}_4)_2] \cdot \text{H}_2\text{O}$. (e) $[\text{Sm}(\text{3-ab})_3(\text{N}_2\text{H}_4)_2] \cdot \text{H}_2\text{O}$. (f) $[\text{Gd}(\text{3-ab})_3(\text{N}_2\text{H}_4)_2]$.

The analytical data of the complexes is given in Table 1 and the values were consistent with the proposed formulae for them.

3.1. Electronic Spectra and Magnetic Susceptibility Measurements. The compounds were insoluble in water and organic solvents, and hence their electronic spectra were recorded for solid samples. The electronic spectral data and the assignments were summarized in Table 2. The levels assigned were $^3\text{F}_4 \rightarrow ^2\text{P}_2$ and $^4\text{I}_{15/2} \rightarrow ^2\text{F}_{3/2}$, $^2\text{D}_{3/2}$ for Nd and Pr complexes of 4-abH. Similarly the levels assigned for complexes of Nd and Pr of 3-abH were $^2\text{H}_{11/2} \rightarrow ^4\text{S}_{3/2}$ and $^2\text{H}_{11/2} \rightarrow ^3\text{F}_4$, respectively [13, 14]. The effective magnetic moment values, 3.43, 3.48 BM corresponding to Pr and 3.51, 3.56 BM for Nd complexes of 3-abH and 4-abH, respectively, are in good agreement with the values reported [15].

3.2. IR Spectra of Complexes. The IR data of the complexes and that of the respective acids are given in Table 3. The

spectrum of 3-abH acid shows absorptions at 1091 cm^{-1} , 1207 cm^{-1} , 1276 cm^{-1} due to $\nu_{\text{C-O ester}}$, 1761 cm^{-1} due to $\nu_{\text{C=O ester}}$, and 1676 cm^{-1} due to $\nu_{\text{C=O acid}}$.

Spectra of the complexes show broad spectrum $1246\text{--}1315\text{ cm}^{-1}$ and centered at 1315 cm^{-1} (La), 1277 cm^{-1} (Ce), 1300 cm^{-1} (Pr), 1303 cm^{-1} (Nd), 1300 cm^{-1} (Sm), and 1300 cm^{-1} (Gd) due to $\nu_{\text{C-O ester}}$. A medium sharp band observed at 1091 cm^{-1} for the acid is found at 1112 cm^{-1} for the complexes. These absorptions are found to shift in the same direction for all the complexes due to coordination [16].

Further, $\nu_{\text{C=O (asym)}}$ and $\nu_{\text{C=O (sym)}}$ are observed in the range of $1587\text{--}1602$ and $1433\text{--}1430\text{ cm}^{-1}$. The difference being less than 200 cm^{-1} may be because of their bidental coordination. The similar type of bidental coordination is found to occur in Cu aspirinate complexes [16–18]. The complexes show two sharp bands in the range of $1001\text{--}1005$ and $929\text{--}962\text{ cm}^{-1}$ raising ambiguity about the assignment of coordination mode of hydrazine [19]. Since lanthanides

FIGURE 6: XRD patterns of lanthanide complexes of 4-abH. (a) $[\text{La}(4\text{-ab})_3(\text{N}_2\text{H}_4)] \cdot \text{H}_2\text{O}$. (b) $[\text{Ce}(4\text{-ab})_3(\text{N}_2\text{H}_4)] \cdot \text{H}_2\text{O}$. (c) $[\text{Pr}(4\text{-ab})_3(\text{N}_2\text{H}_4)] \cdot \text{H}_2\text{O}$. (d) $[\text{Nd}(4\text{-ab})_3(\text{N}_2\text{H}_4)] \cdot \text{H}_2\text{O}$. (e) $[\text{Sm}(4\text{-ab})_3(\text{N}_2\text{H}_4)] \cdot \text{H}_2\text{O}$. (f) $[\text{Gd}(4\text{-ab})_3(\text{N}_2\text{H}_4)] \cdot \text{H}_2\text{O}$.

TABLE 1: Analytical data of 3-abH and 4-abH complexes.

Complexes	Analytical data (%)				
	Carbon Fd (calc.)	Hydrogen Fd (calc.)	Nitrogen Fd (calc.)	Hydrazine Fd (calc.)	Metal Fd (calc.)
$[\text{La}(3\text{-ab})_3(\text{N}_2\text{H}_4)_2]$	43.6 (43.8)	4.1 (3.9)	7.3 (7.6)	8.4 (8.6)	18.7 (18.8)
$[\text{Ce}(3\text{-ab})_3(\text{N}_2\text{H}_4)_2]$	44.0 (43.7)	4.0 (3.9)	7.4 (7.6)	8.5 (8.6)	18.7 (18.9)
$[\text{Pr}(3\text{-ab})_3(\text{N}_2\text{H}_4)_2]$	43.1 (43.6)	4.0 (3.9)	7.4 (7.5)	8.7 (8.6)	18.9 (19.0)
$[\text{Nd}(3\text{-ab})_3(\text{N}_2\text{H}_4)_2] \cdot \text{H}_2\text{O}$	42.3 (42.4)	4.0 (4.1)	7.3 (7.3)	8.3 (8.4)	18.9 (18.9)
$[\text{Sm}(3\text{-ab})_3(\text{N}_2\text{H}_4)_2] \cdot \text{H}_2\text{O}$	42.2 (42.1)	4.0 (4.1)	7.2 (7.3)	8.3 (8.3)	19.5 (19.5)
$[\text{Gd}(3\text{-ab})_3(\text{N}_2\text{H}_4)_2]$	43.0 (42.7)	3.7 (3.9)	7.3 (7.4)	8.5 (8.4)	20.7 (20.7)
$[\text{La}(4\text{-ab})_3(\text{N}_2\text{H}_4)] \cdot \text{H}_2\text{O}$	44.5 (44.6)	3.7 (3.8)	4.0 (3.9)	4.4 (4.4)	19.5 (19.1)
$[\text{Ce}(4\text{-ab})_3(\text{N}_2\text{H}_4)] \cdot \text{H}_2\text{O}$	44.5 (44.5)	3.6 (3.7)	3.8 (3.9)	4.4 (4.4)	19.2 (19.3)
$[\text{Pr}(4\text{-ab})_3(\text{N}_2\text{H}_4)] \cdot \text{H}_2\text{O}$	45.0 (44.5)	3.7 (3.7)	3.7 (3.8)	4.4 (4.4)	19.5 (19.4)
$[\text{Nd}(4\text{-ab})_3(\text{N}_2\text{H}_4)] \cdot \text{H}_2\text{O}$	44.0 (44.3)	3.6 (3.7)	3.7 (3.8)	4.4 (4.4)	19.6 (19.7)
$[\text{Sm}(4\text{-ab})_3(\text{N}_2\text{H}_4)] \cdot \text{H}_2\text{O}$	43.8 (43.9)	3.5 (3.7)	3.7 (3.8)	4.3 (4.3)	20.6 (20.4)
$[\text{Gd}(4\text{-ab})_3(\text{N}_2\text{H}_4)] \cdot \text{H}_2\text{O}$	43.1 (43.5)	4.1 (3.9)	3.9 (3.8)	4.3 (4.3)	21.4 (21.1)

FIGURE 7: SEM image of Gd_2O_3 -Obtained using $[Gd(3-ab)_3(N_2H_4)_2]$ and the corresponding SEM-EDX image of Gd_2O_3 Shown in Figure 8.

FIGURE 8: SEM-EDX image of Gd_2O_3 .

FIGURE 9: SEM image of Nd_2O_3 -Obtained using $[Nd(4-ab)_3(N_2H_4)] \cdot H_2O$ and the corresponding SEM-EDX image of Nd_2O_3 Shown in Figure 10.

FIGURE 10: SEM-EDX image of Nd_2O_3 .

TABLE 2: Electronic spectral data lanthanide complexes of 3-abH and 4-abH.

Acid	Complex	Absorption maximum (cm^{-1})	Assignment
3-abH	Nd^{+3}	15552	$^2H_{11/2}$,
		12063	$^3H_{9/2}$, $^4S_{3/2}$,
	Pr^{+3}	15552	$^2H_{11/2}$,
		9208	1G_4
4-abH	Nd^{+3}	7143	3F_3 , 3F_4
		20000	$^2F_{3/2}$, $^2D_{3/2}$
		17986	$^2G_{7/2}$
		15673	$^2H_{11/2}$
		13089	$^4F_{7/2}$,
	Pr^{+3}	12005	$^3H_{9/2}$, $^4S_{3/2}$
		6262	$^4I_{15/2}$, $^4I_{13/2}$,
		5714	
		23310	$^2P_{2}$,
		17953	1D_2
		9588	1G_4
		7215	3F_3 , 3F_4

preferably set in complexes with higher coordination number greater than eight, hydrazine molecules present in the complexes reported in this work should be of bridged bidentate mode [20].

Similar to 3-isomer acid, 4-isomer acid also shows peaks at 1126 cm^{-1} , 1225 cm^{-1} , and 1295 cm^{-1} due to $\nu_{C=O\text{ ester}}$. The peak observed at 1753 cm^{-1} is due to $\nu_{C=O\text{ ester}}$. The peak at 1680 cm^{-1} due to $\nu_{C=O\text{ acid}}$ is found. In the case of complexes, $\nu_{C=O\text{ ester}}$ is observed at 1157 cm^{-1} , 1285 cm^{-1} , 1326 cm^{-1} , 1285 cm^{-1} , 1159 cm^{-1} , and 1239 cm^{-1} for La, Ce, Pr, Nd, Sm and Gd complexes, respectively. Further $\nu_{C=O\text{ acid}}$ found at 1680 cm^{-1} is split into two $\nu_{C=O\text{ (asym)}}$ and $\nu_{C=O\text{ (sym)}}$ peaks displaying at 1600 cm^{-1} (La), 1598 cm^{-1} (Ce), 1601 cm^{-1} (Pr), 1601 cm^{-1} (Nd), 1599 cm^{-1} (Sm), 1600 cm^{-1} (Gd) and 1404 cm^{-1} (La), 1417 cm^{-1} (Ce), 1406 cm^{-1} (Pr), 1417 cm^{-1}

TABLE 3: IR data of lanthanide complexes of 3-abH and 4-abH (4-abH: 4-acetoxy benzoic acid, 3-abH: 3-acetoxy benzoic acid).

Acid	$\nu_{\text{C-O ester}}$ cm^{-1}	$\nu_{\text{C=O ester}}$ cm^{-1}	$\nu_{\text{C=O acid}}$ cm^{-1}	Complexes	$\nu_{\text{C=O asym}}$ cm^{-1}	$\nu_{\text{C=O sym}}$ cm^{-1}	$\nu_{\text{N-N}}$ cm^{-1}	$\nu_{\text{N-H}}$ cm^{-1}	$\nu_{\text{O-H}}$ cm^{-1}	$\nu_{\text{HOH bending}}$ cm^{-1}	$\nu_{\text{C-O ester}}$ cm^{-1}
3-abH	1091 m, 1207 s, 1276 s	1761 s	1676 s	[La(3-ab) ₃ (N ₂ H ₄) ₂]	1602 s	1433 m	937 s, 1001 s	3358 b	—	—	1315
				[Ce(3-ab) ₃ (N ₂ H ₄) ₂]	1599 s	1430 b	962 s, 1003 m	3273 b	—	—	1277
				[Pr(3-ab) ₃ (N ₂ H ₄) ₂]	1587 s	1410 b	929 s, 1003 b	3373 b	—	—	1300
				[Nd(3-ab) ₃ (N ₂ H ₄) ₂].H ₂ O	1595 s	1429 m	931 s, 1001 m	3277 b	3335 b	862 m	1303
				[Sm(3-ab) ₃ (N ₂ H ₄) ₂].H ₂ O	1589 s	1433 m	931 s, 1005 m	3300 b	3300 b	820 s	1300
				[Gd(3-ab) ₃ (N ₂ H ₄) ₂]	1593 s	1430 m	924 s, 1005 m	3268 b	—	—	1300
4-abH	1126 s, 1225 b, 1290 m	1753 s	1683 b	[La(4-ab) ₃ (N ₂ H ₄) ₂].H ₂ O	1600 m	1404 b	932 s	3330 b	3380 b	845 s	1157 m
				[Ce(4-ab) ₃ (N ₂ H ₄) ₂].H ₂ O	1598 s	1417 s	929 s	3200 m	3379 s	847 s	1285 s
				[Pr(4-ab) ₃ (N ₂ H ₄) ₂].H ₂ O	1601 s	1406 b	932 s	3276 b	3343 m	848 s	1326 s
				[Nd(4-ab) ₃ (N ₂ H ₄) ₂].H ₂ O	1601 m	1415 b	932 s	3294 b	3374 b	849 s	1285 m
				[Sm(4-ab) ₃ (N ₂ H ₄) ₂].H ₂ O	1599 s	1416 m	931 s	3391 b	3390 b	845 s	1159 s
				[Gd(4-ab) ₃ (N ₂ H ₄) ₂].H ₂ O	1600 s	1417 s	930 s	3364 b	3396 b	847 s	1239 m

s: sharp, m: medium, b: broad.

(Gd), 1415 cm^{-1} (Nd), and 1416 cm^{-1} (Sm). The difference $\Delta\nu$ being less than 200 cm^{-1} implies the bidental coordination. The sharp peaks observed in the range of 929–932 cm^{-1} are assigned to N–N stretching of hydrazine which is involved in bidental coordination with the metal ion.

In addition, the hydrated complexes show broadbands observed in the range of 3400 cm^{-1} corresponding to OH stretching and 862 cm^{-1} corresponding to OH bending of water molecules present in the lattice. This broadband extends up to 3030 cm^{-1} may be because of the merging of N–H stretching of hydrazine molecule with $\nu_{\text{O-H}}$ of water.

3.3. Thermal Data of Complexes. The thermal data of the complexes were given in Table 4.

3.3.1. Thermal Analysis of Lanthanides of 3-abH. The lanthanides of 3-abH show two steps of decomposition in their TG curve, namely, dehydrazination and decomposition to their corresponding metal oxides without forming intermediates. Among them, Sm and Nd complexes being hydrated show endothermic dehydration in the temperature range of 40–45°C showing the weight loss temperature of 30–100°C in the TG. All the complexes show exothermic dehydrazination between 180 and 197°C and undergo oxidative decomposition to form their corresponding metal oxides, displaying the exotherms in the range of 437–640°C in DTA.

The TG-DTA of [Pr(3-ab)₃(N₂H₄)₂], [Sm(3-ab)₃(N₂H₄)₂].H₂O, and [Pr(4-ab)₃(N₂H₄)₂].H₂O, [Sm(4-ab)₃(N₂H₄)₂].H₂O are shown in Figures 1, 2, 3, and 4 as representative examples.

The sequence of reactions proposed for the decompositions is:

where Ln = Sm and Nd

where Ln = Ln, Pr and Gd

where Ln = Ln, Pr and Gd

3.3.2. Thermal Analysis of Lanthanides of 4-abH. La, Pr, Nd, and Sm complexes with 4-abH show almost similar type of decomposition pattern in their thermograms. They undergo dehydration showing endotherms in the range of 50–71°C, dehydrazination showing exotherms in the range

TABLE 4: Thermal data of lanthanide complexes of 3-abH and 4-abH.

Complex	DTA Temp (°C)	Thermo gravimetry			Nature of the reaction
		Temp. Range (°C)	Weight Loss %		
			Obsd.	Calcd.	
[La(3-ab) ₃ (N ₂ H ₄) ₂]	180.0 (–)	60–120	8.5	8.6	Dehydrazination
	406.0 (–) s				
	510.0 (–) b	120–700	78.1	78.0	Decomposition to metal oxide
	640.0 (–)				
[Ce(3-ab) ₃ (N ₂ H ₄) ₂]	191.4 (–)	120–200			
	226.0 (–) d	200–280	8.5	8.6	Dehydrazination
	437.0 (–) s	280–600	76.5	76.7	Decomposition to metal oxide
[Pr(3-ab) ₃ (N ₂ H ₄) ₂]	190.0 (–) s	150–195	8.7	8.6	Dehydrazination
	200.0 (–)				
	289.0 (–)	195–700	77.0	77.0	Decomposition to metal oxide
	477.0 (–) s				
[Nd(3-ab) ₃ (N ₂ H ₄) ₂].H ₂ O	40.0 (+)	30–100	2.2	2.4	Dehydration
	197.4 (–) s	100–200	10.6	10.7	Dehydrazination
	248.6 (–) b	200–700	78.0	77.9	Decomposition to metal oxide
	474.3 (–) s				
[Sm(3-ab) ₃ (N ₂ H ₄) ₂].H ₂ O	45.0 (+)	30–100	2.4	2.3	Dehydration
	186.0 (–)	100–190	10.5	10.6	Dehydrazination
	240.0 (–) b	190–700	77.4	77.3	Formation of metal oxide
	480.0 (–) s				
[Gd(3-ab) ₃ (N ₂ H ₄) ₂]	186.0 (–)	160–210	8.5	8.4	Dehydrazination
	226.0 (–) d				
	320.0 (–)	210–700	76.2	76.1	Decomposition to metal oxide
	474.2 (–) s				
[La(4-ab) ₃ (N ₂ H ₄)]·H ₂ O	60.3 (+)	40–100	2.3	2.5	Dehydration
	166.0 (–)	100–180	6.9	6.9	Dehydrazination
	247.0 (–) s	180–265	62.1	62.0	Formation of metal carbonate
	323.0 (–)				
	475.1 (–)	265–700	77.2	77.6	Decomposition to metal oxide
[Ce(4-ab) ₃ (N ₂ H ₄)]·H ₂ O	543.0 (–) b				
	50.0 (+) b	80–190	2.3	2.5	Dehydration
	225.0 (–)				
	323.0 (–) s	190–700	76.1	76.3	Decomposition to metal oxide
	418.0 (–)				
[Pr(4-ab) ₃ (N ₂ H ₄)]·H ₂ O	490.0 (–) b				
	71.2 (+)	40–100	2.6	2.5	Dehydration
	167.0 (–)	100–175	7.0	6.9	Dehydrazination
	200.0 (–)	175–440(–)	61.5	61.4	Formation of metal carbonate
	275.0				
[Nd(4-ab) ₃ (N ₂ H ₄)]·H ₂ O	475.0 (–)	440–700	76.9	76.7	Decomposition to metal oxide
	541.8 (–) s				
	60.5 (+)	40–100	2.3	2.5	Dehydration
[Nd(4-ab) ₃ (N ₂ H ₄)]·H ₂ O	167.2 (–)	100–190	6.9	6.8	Dehydrazination
	205.0 (–)	190–700	77.2	77.0	Decomposition to metal oxide
	247.0 (–)				
	387.0 (–)				
	540.2 (–) s				

TABLE 4: Continued.

Complex	DTA Temp (°C)	Thermo gravimetry			Nature of the reaction
		Temp. Range (°C)	Weight Loss %		
			Obsd.	Calcd.	
[Sm(4-ab) ₃ (N ₂ H ₄)]·H ₂ O	62.4 (+)	40–150	2.5	2.4	Dehydration
	175.3 (–)	150–200	6.7	6.8	Dehydrazination
	213.2 (–)	200–700	76.3	76.4	Decomposition to metal oxide
	247.0 (–)				
	481.3 (+)				
	550.0 (–) b				
[Gd(4-ab) ₃ (N ₂ H ₄)]·H ₂ O	63.2 (+)	40–150	2.2	2.4	Dehydration
	178.0 (–)	150–700	75.7	75.5	Decomposition to metal oxide
	275.0 (–)				
	448.1 (–)				
	549.0 (–)				

(+) : endo, (–) : exo, s: singlet, d: doublet, b: broad.

TABLE 5: X-ray diffraction data of lanthanide complexes of 3-abH and 4-abH (D spacing in Å units and intensity in parentheses).

[Ln(3-ab) ₃ (N ₂ H ₄) ₂]·xH ₂ O					
where Ln: La, Ce, Pr and Gd and x = 0; Ln: Nd, and Sm, x = 1 and 3-abH: 3-acetoxy benzoic acid					
La	Ce	Pr	Nd	Sm	Gd
11.5531 (10.90)	9.9750 (15.40)	9.7115 (21.80)	9.7427 (24.70)	9.6352 (15.70)	9.6122 (10.00)
10.2367 (7.30)	9.5507 (25.00)				6.3314 (21.70)
6.5266 (14.50)	6.2677 (59.60)	6.3777 (43.60)	6.3563 (35.60)	6.3011 (21.40)	4.8156 (21.70)
5.3813 (4.00)	5.2698 (9.60)	5.3390 (5.50)	4.8651 (35.60)	4.8100 (31.40)	4.1634 (13.30)
5.1392 (4.50)	4.9985 (48.38)	5.0584 (20.00)	4.1932 (19.20)	4.1718 (31.40)	3.8362 (38.30)
4.6080 (38.20)	4.7902 (40.40)	4.8561 (40.00)	3.8369 (43.80)	3.8350 (42.90)	
4.1537 (10.90)	4.2796 (40.40)	4.1857 (25.50)	3.4426 (11.00)	3.5184 (12.90)	
3.7752 (3.40)	4.1427 (40.40)	3.8368 (52.73)	3.2630 (100.00)	3.2532 (100.00)	
3.5802 (21.80)	3.8030 (48.10)	3.5400 (25.50)	2.7969 (5.50)	2.4051 (10.00)	
3.3916 (34.50)	3.5070 (25.00)	3.3826 (14.50)	2.5720 (1.40)	2.2485 (7.10)	
3.1643 (34.50)	3.3427 (7.70)	3.2571 (100.00)			
2.9345 (16.40)	3.2274 (100.00)	3.0248 (10.90)			
2.2874 (12.70)	2.7711 (3.80)	2.4107 (14.50)			
[Ln(4-ab) ₃ (N ₂ H ₄)]·H ₂ O					
where Ln: La, Ce, Pr, Nd, Sm, and Gd, and 4-abH: 4-acetoxy benzoic acid					
La	Ce	Pr	Nd	Sm	Gd
10.3780 (52.10)		10.3974 (80.40)	10.2188 (29.40)	10.5230 (23.60)	10.3142 (21.70)
5.0111 (79.20)	5.0852 (25.83)	9.0799 (100.0)	8.8619 (33.00)	9.5067 (20.00)	9.5467 (36.70)
4.5658 (43.80)	4.5507 (24.49)	5.0283 (67.40)	6.5901 (13.70)	6.3442 (20.00)	5.0142 (45.00)
3.9225 (39.60)	3.6554 (100.0)	4.5186 (60.90)	5.5530 (15.70)	5.0280 (74.50)	4.5436 (28.30)
3.3174 (72.90)	3.3221 (42.61)	3.9491 (84.80)	4.9752 (25.50)	4.5902 (18.20)	3.9100 (23.30)
3.1956 (35.40)	3.0444 (14.16)	3.4136 (43.50)	3.5742 (100.00)	3.8450 (18.20)	3.4281 (25.00)
2.9905 (77.10)	2.9899 (83.93)	3.1655 (73.90)	3.2815 (17.60)	3.4495 (21.80)	3.3191 (50.00)
2.5716 (31.30)	2.5720 (3.25)	2.9805 (67.40)	3.1302 (15.70)	3.3172 (47.30)	2.9848 (60.00)
2.4191 (29.20)	2.4120 (9.26)	2.5601 (65.20)	2.9494 (19.60)	2.9754 (100.0)	2.6726 (23.30)
2.1659 (37.50)	2.1779 (3.96)	2.4124 (45.70)	2.5377 (13.73)	2.6822 (18.20)	2.4047 (25.00)
1.5059 (14.60)		2.1176 (41.30)	2.4634 (11.76)	2.4916 (34.50)	2.1502 (20.00)
12450 (18.80)	1.5775 (0.88)	1.5186 (32.60)		2.2736 (18.20)	
				1.5759 (29.10)	1.2850 (13.30)

of 166–175°C and oxidative decomposition showing many exotherms in the range of 213–550°C to metal oxide residue. La and Pr complexes show the formation of metal carbonate intermediate [21] before final decomposition to metal oxide, whereas the other two do not.

Ce and Gd complexes, though found to follow similar type of decomposition to form metal oxide residue, the TG traces are not clear to identify dehydrazination and the intermediate formation. The thermal degradation patterns are indicated by the following reactions:

where Ln = La, Ce, Pr, Nd, Sm and Gd

where Ln = La, Pr, Nd and Sm

where Ln = La and Pr

where Ln = Nd and Sm

3.4. X-Ray Diffraction Analysis. The powder XRD patterns along with their d spacings are given in Table 5. The comparison of XRD patterns of the lanthanide complexes is shown in Figures 5 and 6. The XRD patterns of lanthanides of 4-abH and 3-abH reveal that each set of complexes has similarity in their structures implying similar compositions.

3.5. SEM-EDX Studies. The complexes were calcined in muffle furnace at their decomposition temperature, heating subsequently at the same temperature, and analyzed for their morphology and particle size. The SEM-EDX images of residues obtained from $[\text{Gd}(3\text{-ab})_3(\text{N}_2\text{H}_4)_2]$ and $[\text{Nd}(4\text{-ab})_3(\text{N}_2\text{H}_4)] \cdot \text{H}_2\text{O}$ are shown in Figures 7, 8, 9, and 10. From the images, it is understood that the residues are micro-sized metal oxides with irregular shapes.

4. Conclusion

The isomeric acetoxybenzoic acids and hydrazine hydrate yield the complexes of formulae, $[\text{Ln}(3\text{-ab})_3(\text{N}_2\text{H}_4)_2] \cdot x\text{H}_2\text{O}$

where Ln = La, Ce, Pr and Gd and $x = 0$; Ln = Nd and Sm and $x = 1$ and $[\text{Ln}(4\text{-ab})_3(\text{N}_2\text{H}_4)] \cdot \text{H}_2\text{O}$ where Ln = La, Ce, Pr, Nd, Sm and Gd resulting from their reaction with the respective metal nitrates. The compositions of the complexes were confirmed by elemental data. The presence of hydrazine in bidentate bridging mode is inferred from their N–N stretching frequencies. The complexes of 3-abH release hydrazine exothermally in the temperature range 166–178°C whereas 4-abH complexes undergo exothermic dehydrazination at higher temperature range 180–197°C indicating that the two molecules of hydrazine are tightly held between the metal atoms in four directions. All the complexes of 3-abH undergo oxidative decomposition in the range of 437–477°C excepting for lanthanum, and the complexes of 4-abH in the range of 490–550°C. The lower-temperature decomposition of 3-abH complexes may be due to fuelling effect of two hydrazine molecules. The magnetic and electronic data indicate the presence of metal in the complexes. A comparable XRD data of complexes imply that they have similar type of structures. However, single crystal XRD can only confirm their structures. In our case since the complexes are insoluble in any solvent due to their polymeric nature, single crystals could not be prepared. SEM-EDX analysis indicated the oxides formation in microsize.

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