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# Novel lanthanide(III) 4-methylbenzoylhydrazide complexes as precursors for lanthanide oxide nanophotocatalysts

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A series of metal complexes were prepared from separate reactions of lanthanide nitrate salts (La(III), Ce(III), Sm(III), Gd(III) and Ho(III)) with 4-methylbenzoylhydrazide. The structures of the complexes were confirmed by analytical studies, spectral measurements and thermal studies. Complexes were formed with different stoichiometries of 1 : 2 and 1 : 3 (M : L). The ligand chelates by the nitrogen and oxygen atoms of the amino and carbonyl groups of the hydrazide moiety in the neutral keto form. The coordination compounds were converted to metal oxide nanoparticles (MONPs) through solid state thermal decomposition as monocuclear source precursors. The obtained MONPs were investigated *via* XRD, TEM and UV-Vis spectra. As a representative, CeO<sub>2</sub> was utilized as a nanophotocatalyst to examine the photocatalytic activity of the MONPs for methylene blue (MB) photodegradation. CeO<sub>2</sub> showed high removal of MB dye by 90.1% after UV illumination for 220 min. The reported method provides a generalized and systematic method for the preparation of many metal oxide nanoparticles with manageable and reproducible features.

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## 1. Introduction

Hydrazide compounds contain terminal NH<sub>2</sub> groups and are precursors for numerous synthesized Schiff and azo compounds. Hydrazides and their derivatives have potential active sites; C=O, NH and NH<sub>2</sub> have the ability to coordinate with different metal ions.<sup>1</sup> Hydrazides and their derivative metal complexes have applications in biological fields as insecticidal, acaricidal, nematocidal, and antileishmanial agents and inhibit protease enzymes in some parasitic species and diamine oxidases.<sup>1</sup> Their lanthanide complexes have luminescent and magnetic properties; thus, they can be used in electroluminescent devices.<sup>2,3</sup> Also, due to their exhibited spectroscopic, magnetic, and chemical properties, these lanthanide complexes have many useful applications compared to other metal complexes. This is due to the fluxional nature of lanthanide(III) ion, which possesses high and variable coordination numbers as well as a lack of angular preference.<sup>4</sup> Hydrazide lanthanide complexes are an ongoing area of active research due to their good antioxidant activities and their biological activities, such as anticoagulation, antiallergic, antibacterial, anti-inflammatory and anticancer. Also, they have been used for treatment of burns.<sup>5-7</sup>

Metal oxide nanoparticles show a wide range of applications, including catalysis, sensing, optics, semiconductors, solar cells, batteries and biotechnology. Also, metal oxide nanoparticles have been used as nanophotocatalysts for the degradation of methylene blue and Safranin-O dyes.<sup>8-12</sup> The synthesis of metal oxide nanoparticles from their corresponding metal complexes is of great interest. This technique offers several unique advantages over other methods, including facility, reproducibility, short reaction times, short washing and drying durations, and production of inorganic nanomaterials with narrow size distributions.<sup>9</sup>

In this work, we aimed to synthesize lanthanide metal complexes of lanthanum(III), cerium(III), samarium(III), gadolinium(III), and holmium(III) with 4-methylbenzoylhydrazide ligand. Structural characterization of all the prepared compounds was performed based on elemental analysis, spectral methods (UV-Vis, IR, <sup>1</sup>H NMR, and mass spectroscopy), molar electrical conductivity, magnetic susceptibility and thermal analyses. Also, nano-metal oxides were prepared by thermal degradation of the metal complexes, and their applications in wastewater treatment were studied through photocatalytic degradation of methylene blue.

## 2. Experimental

### 2.1 Materials and methods

All chemicals were of analytical grade (BDH, Sigma or Aldrich) and were used as received without further purification.

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Elemental microanalysis (C, H, and N) was performed using a PerkinElmer-2400 elemental analyzer at Main Defense Chemical Laboratory. Infrared spectra were registered on a JASCO FTIR-6300 spectrophotometer in the range of 4000 to 400  $\text{cm}^{-1}$  to investigate the infrared spectral bands. The  $^1\text{H}$ -NMR spectra were recorded in  $\text{DMSO}-d_6$  on a Bruker NMR spectrometer at 600 MHz. Fast atom bombardment (FAB) mass spectra for the ligand and its  $\text{La(III)}$  and  $\text{Gd(III)}$  complexes were acquired using a spectrometer. The electronic absorption spectral bands were revealed in Nujol mulls using Varian Vary 5000 UV-Vis spectrophotometer. Molar conductance measurements of the complexes in  $10^{-3}$  M DMSO were performed using a Tacussel CD6N conductimeter. The magnetic susceptibility was measured at room temperature by a modified Gouy method using a Johnson Matthey magnetic susceptibility balance. A Shimadzu DAT/TG-50 thermal analyzer was used to conduct the thermogravimetric analysis (TG and DTG) under certain conditions (a heating rate of  $10^\circ\text{C min}^{-1}$  under nitrogen and oxygen atmosphere with a flowing rate of  $20\text{ ml min}^{-1}$  from room temperature to  $900^\circ\text{C}$  using platinum crucibles). Melting points were detected by a Stuart melting point apparatus. The X-ray diffraction (XRD) measurements for the MONPs were performed using an Bruker D8 Advance diffractometer with a copper target and nickel filter with  $\text{CuK}\alpha$  radiation ( $k = 0.154056\text{ nm}$ ). Measurements were performed in the  $2\theta$  range of  $20^\circ$  to  $80^\circ$ . The morphology of the  $\text{CeO}_2$  nanoparticles was obtained by transmission electron microscopy (TEM) with a JEOL JEM 1230 (JEOL Ltd., Japan) operating at 120 kV. The average particle size was determined statistically by manually counting 90 particles.

## 2.2 Synthesis of 4-methylbenzoylhydrazide ligand (HL)

The ligand was prepared as reported.<sup>13</sup> The reaction was performed by dissolving 4-toulic acid in ethanol in the presence of conc. sulfuric acid as a catalyst to yield the ester derivative. Then, an excess of hydrazine hydrate was added. The reaction mixture was refluxed for 4 h. The solid ligand was filtered, washed, and recrystallized from methanol to afford pale yellow

crystals which were finally dried under vacuum over anhydrous calcium chloride. The measured melting point was  $164^\circ\text{C}$ .

## 2.3 Synthesis of the lanthanide(III) complexes

The complexes were synthesized by adding an appropriate ethanolic solution of  $\text{M}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$  ( $\text{M} = \text{La(III)}, \text{Ce(III)}, \text{Sm(III)}, \text{Gd(III)}$  and  $\text{Ho(III)}$ ,  $n = 3$  to 6) to an ethanolic solution of ligand with a molar ratio of 1 : 3 ( $\text{M} : \text{L}$ ). The mixture was stirred for three hours at  $50^\circ\text{C}$ , then filtered, washed and completely dried under vacuum over anhydrous  $\text{CaCl}_2$ .

## 2.4 Preparation of metal oxide nanoparticles

In a typical procedure, certain amounts of  $\text{La(III)}$ ,  $\text{Ce(III)}$ ,  $\text{Sm(III)}$ ,  $\text{Gd(III)}$  and  $\text{Ho(III)}$  complexes were maintained inside a crucible and heated to  $600^\circ\text{C}$  under air in a muffle furnace for 60 minutes (heating rate:  $10^\circ\text{C min}^{-1}$ ). The thermal degradation of the coordinated precursors resulted in the formation of their analogue metal oxides. The produced oxides were cooled to room temperature and then collected for analysis.

## 2.5 Photocatalytic activity

The photodegradation test for methylene blue dye (model pollutant) was performed as follows:  $\text{CeO}_2$  nanoparticles (10 mg/100 ml) were dispersed in methylene blue aqueous solution (10 ppm) using a sonicator for 20 minutes in the dark to exclude the adsorption results. After that, the solution was irradiated with a UV lamp (6 W at a wavelength of 254 nm). Aliquots of 5.0 ml of the tested solution were collected each 20 min, centrifuged at 5000 rpm to monitor absorbance changes, then analyzed spectrophotometrically to detect the absorbance changes as a function of irradiation time.

# 3. Results and discussion

## 3.1 Analytical data

Table 1 presents the analytical data of the prepared lanthanide(III) nitrate complexes. The prepared complexes have the chemical formulas  $[\text{La}(\text{HL})_2(\text{NO}_3)_2] \cdot \text{NO}_3 \cdot \text{EtOH}$ ,  $[\text{Ce}(\text{HL})_3(\text{NO}_3)_2] \cdot$

**Table 1** Analytical data and molar conductance values of 4-methylbenzoylhydrazide (HL) and its metal complexes

No.	Compound	Colour, F. W.	Elemental analysis, F (cal.)%			Mp	$A^a$
			C	H	N		
1	$\text{HL}^1 \cdot 0.5\text{H}_2\text{O}$ , $\text{C}_8\text{H}_{11}\text{N}_2\text{O}_{1.5}$	Off-white, 159.19	60.67, (60.36)	6.42, (6.96)	17.64, 17.59	132	—
2	$[\text{La}(\text{HL})_2(\text{NO}_3)_3] \cdot \text{EtOH}$ , $\text{C}_{18}\text{H}_{26}\text{N}_7\text{O}_9\text{La}$	White, 623.35	34.49, (34.40)	3.67, (3.95)	15.05, (14.78)	222	42
3	$[\text{Ce}(\text{HL})_3(\text{NO}_3)_2] \cdot \text{NO}_3$ , $\text{C}_{24}\text{H}_{30}\text{N}_9\text{O}_{12}\text{Ce}$	White, 812.67	36.96, (37.11)	3.94, (3.89)	16.22, (16.23)	238	52
4	$[\text{Sm}(\text{HL})_3(\text{NO}_3)_2] \cdot \text{NO}_3 \cdot \text{H}_2\text{O}$ , $\text{C}_{24}\text{H}_{32}\text{N}_9\text{O}_{13}\text{Sm}$	White, 804.93	35.66, (35.81)	4.00, (4.01)	16.09, (15.67)	246	56
5	$[\text{Gd}(\text{HL})_3(\text{NO}_3)_2] \cdot \text{NO}_3 \cdot 0.5\text{H}_2\text{O}$ , $\text{C}_{24}\text{H}_{31}\text{N}_9\text{O}_{12.5}\text{Gd}$	White, 802.81	36.06, (35.91)	3.82, (3.89)	15.69, (15.75)	248	55
6	$[\text{Ho}(\text{HL})_3(\text{NO}_3)_2] \cdot \text{NO}_3 \cdot 0.5\text{EtOH}$ , $\text{C}_{25}\text{H}_{32}\text{N}_9\text{O}_{12.5}\text{Ho}$	White, 854.52	35.99, (35.13)	3.82, (3.77)	15.68, (14.75)	250	54

$a$  ( $\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ ).



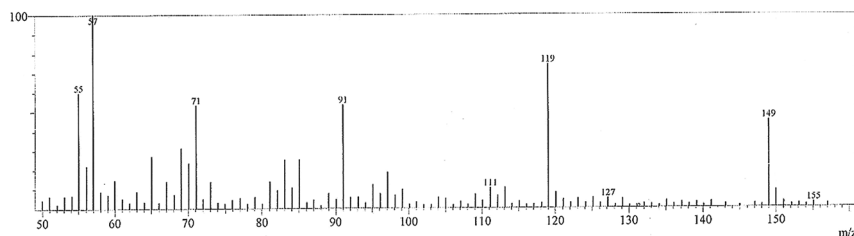


Fig. 1 FAB mass spectrum of the ligand.

$\text{NO}_3$ ,  $[\text{Sm}(\text{HL})_3(\text{NO}_3)_2] \cdot \text{NO}_3 \cdot \text{H}_2\text{O}$ ,  $[\text{Gd}(\text{HL})_3(\text{NO}_3)_2] \cdot \text{NO}_3 \cdot 0.5\text{H}_2\text{O}$  and  $[\text{Ho}(\text{HL})_3(\text{NO}_3)_2] \cdot \text{NO}_3 \cdot 0.5\text{EtOH}$ . The complexes are stable in air and non-hygroscopic. All the chelates showed solubility in polar and nonpolar solvents. The molar conductance values of the complexes were in the range of  $52$  to  $56 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , which demonstrates the uni-electrolytic properties of all the complexes.<sup>14</sup>

### 3.2 Spectral studies

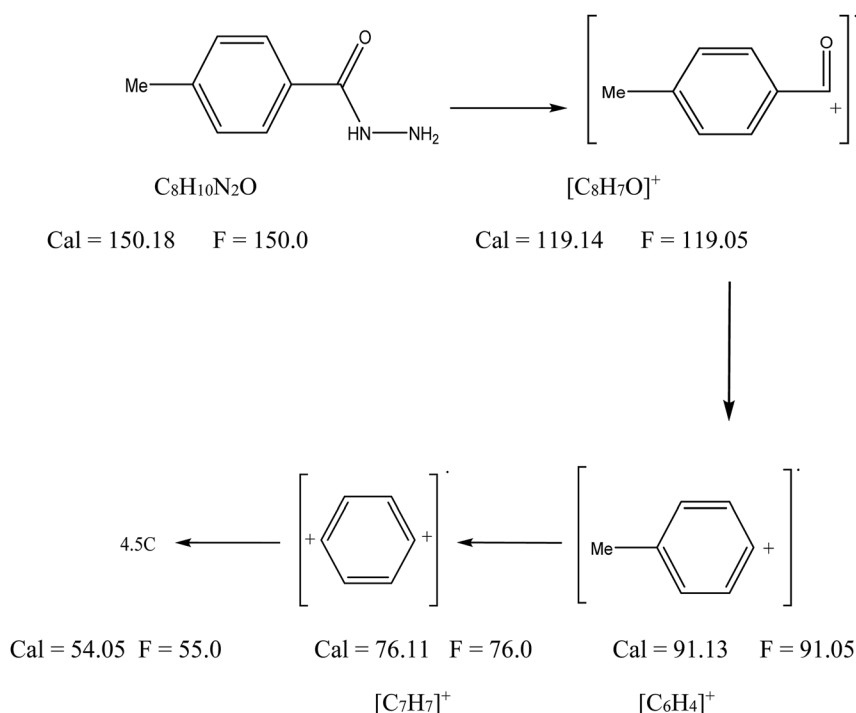
**3.2.1 Mass spectra.** The FAB mass spectra of the ligand is shown in Fig. 1. The FAB mass spectrum of the hydrazide ligand (Fig. 1) contains a molecular ion peak at  $m/z$  150.0 amu, which matches the theoretical molecular weight of the ligand without solvent. This proved its formation. Also, the spectrum exhibited other degradation peaks at 119, 91.05, 76, and 55 amu, which are assignable to  $[\text{C}_8\text{H}_7\text{O}]^+$ ,  $[\text{C}_7\text{H}_7]^+$ ,  $[\text{C}_6\text{H}_4]^+$  and  $4.5\text{C}$ , respectively; this is compatible with Scheme 1. The mass spectra of the La(III) and Gd(III) complexes are consistent with the formulae  $[\text{La}(\text{HL})_2(\text{NO}_3)_3] \cdot$

$\text{EtOH}$  and  $[\text{Gd}(\text{HL})_3(\text{NO}_3)_2] \cdot \text{NO}_3 \cdot 0.5\text{H}_2\text{O}$ , giving parent molecular ions at  $m/z$  623 and 803, respectively; this confirms the theoretical data.

**3.2.2  $^1\text{H-NMR}$ .** The  $^1\text{H-NMR}$  spectrum of the ligand (HL) and its lanthanum(III) complex are compiled in Table 2 and represented in Fig. 2. The spectrum of the ligand exhibits signals at  $\delta$ , ppm: 2.32 (3H, s,  $\text{CH}_3$ ), 4.52 (2H, s,  $\text{NH}_2$ ), 7.22 to 7.82 (4H, s, Ar-CH) and 9.69 (1H, s, NH).<sup>15,16</sup> In comparison, the spectrum of the La(III) complex shows signals at 2.92, 4.80, and 9.77 ppm, which are assigned to  $\text{CH}_3$ ,  $\text{NH}_2$ , and NH,

Table 2  $^1\text{H}$  NMR spectra of hydrazide ligand (HL) and its La(III) complex

(HL)	La(III) complex	Assignment
2.32	2.33–2.49	3H of 2( $\text{CH}_3$ )
4.52	4.80	2H of ( $\text{NH}_2$ )
7.22–7.82	7.23–7.72	H of (CH)
9.69	9.77	1H of (NH)



Scheme 1 Mass ion of the HL ligand and its fragmentation.



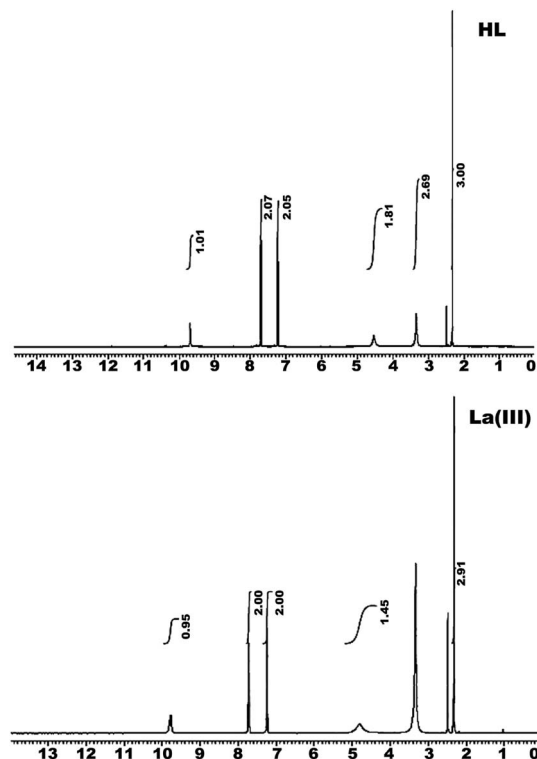


Fig. 2  $^1\text{H}$  NMR spectra of the hydrazide ligand (HL) and its La(III) complex.

respectively. The  $\text{NH}_2$  signal shifted downfield relative to the uncoordinated ligand, confirming its involvement in chelation. The absence of a signal at 12 to 14 ppm assigned to the enolic OH suggests that the ligand chelated with metal ion in its neutral keto structure.

**3.2.3 Infrared spectra of the ligand (HL) and its metal complexes.** The fundamental spectral bands and their assignments of the ligand and its metal complexes are tabulated in Table 3 and diagrammed in Fig. 3. The spectrum of the ligand contains strong bands at  $3306$ ,  $3222$ ,  $3027$ ,  $1616$ , and  $1503\text{ cm}^{-1}$ ;  $1042$  and  $922\text{ cm}^{-1}$ ; and  $787$ ,  $719$  and  $446\text{ cm}^{-1}$ , which can be assigned to  $\nu_{\text{asy}}(\text{NH}_2)$ ,  $\nu_{\text{sy}}(\text{NH}_2)$ ,  $\nu(\text{NH})$ ,  $\delta(\text{NH}_2)$ , and  $\delta(\text{NH})_{\text{amide}}$ ;  $\nu(\text{N-N})$ ,  $\gamma(\text{NH}_2)$ , and  $\gamma(\text{NH})_{\text{amide}}$ ; and  $\rho(\text{NH}_2)$ , respectively.<sup>16</sup> The carbonyl groups are assigned to strong bands located at  $1659$  and  $677\text{ cm}^{-1}$ ,  $633\text{ cm}^{-1}$  and  $522\text{ cm}^{-1}$ , attributed to  $\nu(\text{C=O})$ ,  $\delta(\text{C=O})$ , and  $\gamma(\text{C=O})$ , respectively. The spectrum of the ligand exhibits the presence of fundamental bands corresponding to NH and C=O ( $\nu$ ,  $\delta$ ,  $\gamma$ ) with the absence of  $\nu(\text{OH})$ ; this indicates that the ligand has a keto structure. The spectrum of the ligand shows additional fundamental bands at  $2920$  and  $2878\text{ cm}^{-1}$  due to the  $\nu(\text{CH})$  aromatic and methyl groups, respectively. Comparison of the spectral bands of the ligand with those of its metal complexes led to the following observations:  $\nu_{\text{asy}}$ ,  $\nu_{\text{sy}}$ , and  $\delta$  of the  $\text{NH}_2$  and  $\nu(\text{C=O})$  groups of the ligand undergo blue shifts at  $10$  to  $13\text{ cm}^{-1}$  upon complexation. However,  $\delta(\text{C=O})$  of the ligand at  $617\text{ cm}^{-1}$  disappeared, while the second one at  $633\text{ cm}^{-1}$  shifted to lower values by  $5$  to  $17\text{ cm}^{-1}$  upon complexation.

Table 3 Infrared spectral bands ( $\text{cm}^{-1}$ ) and their assignments for hydrazide ligand (HL) and its metal complexes<sup>a</sup>

No.	Compound	$\nu_{\text{as}}(\text{NH}_2)$	$\nu_{\text{sy}}(\text{NH}_2)$	$\gamma(\text{NH}_2)$	$\nu_{\text{amide}}(\text{NH})$	$\gamma(\text{NH})$	$\nu(\text{C=O})$	$\delta(\text{NH}_2)$	$\nu(\text{N-N})$	$\delta(\text{C=O})$ , $\gamma(\text{C=O})$	$\gamma(\text{C=O})$ , $\nu(\text{M-O})$	$\text{NO}_3^-$ band			
												Ionic	$\nu_4$	$\nu_1$	$\nu_1$
1	(HL)0.5H <sub>2</sub> O	3306(s)	3222(s), 787(w)	3027(s), 719(s)	1616(s)	1659(s)	1647(m)	1616(s)	1042(w), 992(s)	677(m), 633(s)	522	446(m)	1384	1466	1210
2	[La(HL) <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub> ]·EtOH	3295(m)	3216(m), 792(vw)	3060(vw), 778(w)	1603(m)	1647(m)	1648(m)	1603(m)	1034(vw), —	—, 6159(w)	516	—	1384	1464	1208
3	[Ce(HL) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ]·NO <sub>3</sub>	3295(b, m)	3210(w), 792(w)	3022(w), 778(w)	1605(m)	1648(m)	1648(m)	1603(sh)	1034(vw), —	613(w)	518	462(w)	1382	1465	1212
4	[Sm(HL) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ]·NO <sub>3</sub> ·H <sub>2</sub> O	3295(w)	3207(w), 792(vw)	—, 748(w)	1606(s)	1648(s)	1646(s)	1606(s)	1037(vw), —	—, 621(m)	528	463(w)	1383	1465	1212
5	[Gd(HL) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ]·NO <sub>3</sub> ·0.5H <sub>2</sub> O	3297(w)	3210(w), —	—, 748(w)	1606(s)	1649(s)	1649(s)	1606(w)	1038(vw), —	—, 630(m)	527	472(w)	1383	1465	1212
5	[Ho(HL) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ]·NO <sub>3</sub> ·0.5EtOH	3297(m)	3208(m), 794(vw)	—, 748(m)	1606(w)	1649(s)	1649(s)	1606(w)	1038(w)	—, 628(m)	528	463(w)	1383	1463	1210

<sup>a</sup> vw: very weak, w: weak, m: medium, s: strong, b: broad, sh: shoulder.



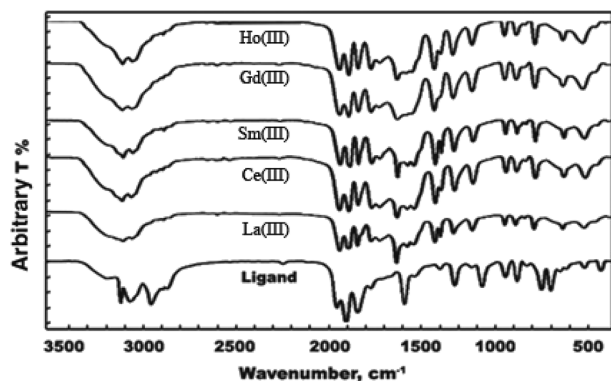


Fig. 3 IR spectra of the ligand and its metal complexes.

The above assignments indicate that the metal ions attach to the ligand *via* carbonyl oxygen and amino nitrogen atoms, leading to the construction of five-membered rings. The ligand

bands at 522 and 446  $\text{cm}^{-1}$  due to  $\gamma(\text{C}=\text{O})$  and  $\rho(\text{NH}_2)$  exhibit shifts in the ranges of 518 to 528 and 462 to 472  $\text{cm}^{-1}$  upon complexation, which are attributed to  $\nu(\text{M}-\text{O})$  and  $\nu(\text{M}-\text{N})$ , respectively.<sup>17</sup> The absorption bands appearing at around 1380 and 784  $\text{cm}^{-1}$  in the spectra of the investigated complexes are assigned to the ionic nitrate group.<sup>14</sup> The complexes exhibit absorption bands in the regions of 1463 to 1466  $\text{cm}^{-1}$  and 1208 to 1212  $\text{cm}^{-1}$ ; these are not observed in the spectrum of the ligand and can be assigned to  $\nu_4$  and  $\nu_1$ , respectively. This situation suggests that the nitrate ions are covalently bonded and are located in the coordination sphere; this indicates that the magnitude of separation  $\Delta\nu = \nu_1 - \nu_4$  is sufficiently greater than 200  $\text{cm}^{-1}$ , considering that the nitrate groups are covalently bonded to the metal ion in bidentate fashion. The data show that the lanthanide nitrate complexes contain both coordinated and ionic nitrate groups, which confirms the chemical formulae.

Table 4 Electronic absorption spectra and magnetic moment values of the ligand and its complexes

No.	Compound	Electronic spectral bands (nm)	Assignment	$\mu/\mu_B$
1	(HL)0.5H <sub>2</sub> O	296, 272, 240	N- $\pi^*$ , $\pi$ - $\pi^*$	—
2	[La(HL) <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub> ]·EtOH	308, 284, 242	n- $\pi^*$ , $\pi$ - $\pi^*$	Diam
3	[Ce(HL) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ]·NO <sub>3</sub>	297, 287, 242	n- $\pi^*$ , $\pi$ - $\pi^*$	3.09
4	[Sm(HL) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ]·NO <sub>3</sub> ·H <sub>2</sub> O	313, 284, 242	n- $\pi^*$ , $\pi$ - $\pi^*$	3.69
5	[Gd(HL) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ]·NO <sub>3</sub> ·0.5H <sub>2</sub> O	312, 284, 246	n- $\pi^*$ , $\pi$ - $\pi^*$	7.91
5	[Ho(HL) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ]·NO <sub>3</sub> ·0.5EtOH	312, 284, 242	n- $\pi^*$ , $\pi$ - $\pi^*$	10.78

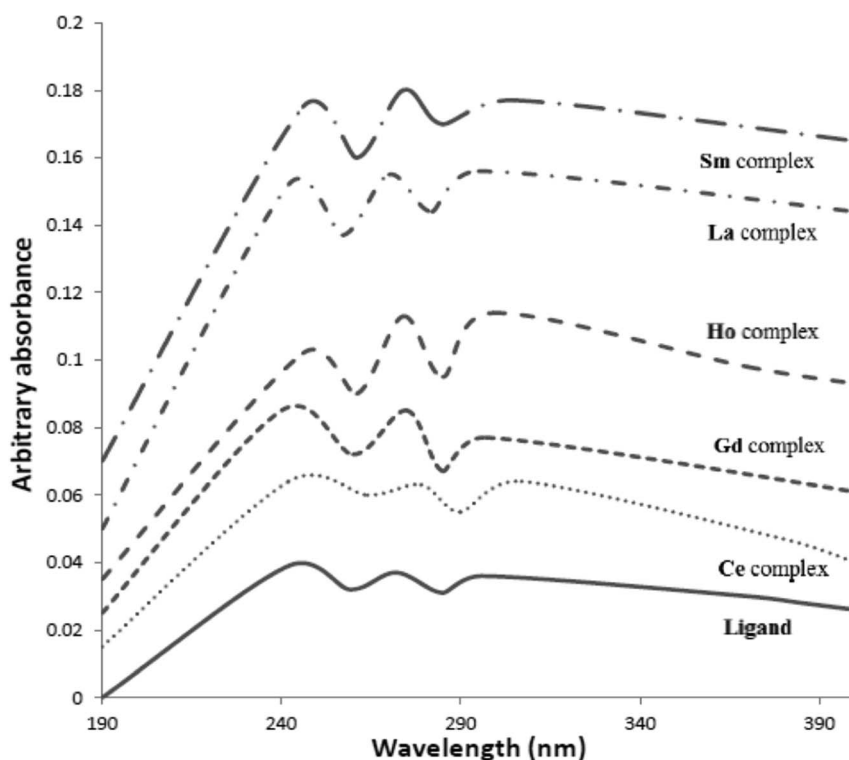


Fig. 4 Electronic absorption spectra of the ligand and its complexes.





Table 5 Thermal decomposition of the ligand and its metal complexes

No.	Compound	TG range (°C)	DTA peak (°C)	Mass loss% found (calcd.)	Assignment	TS (°C)
1	(HL)·0.5H <sub>2</sub> O	109–163		2.70 (2.83)	Loss of 0.25 mol of H <sub>2</sub> O <sup>a</sup>	163
		163–292		69.37 (70.14)	Ligand pyrolysis <sup>c</sup>	
		292–322		26.13 (24.52)	Complete ligand pyrolysis <sup>c</sup>	
2	[La(HL) <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub> ]·EtOH	30–228		7.39 (8.18)	Loss of 1 mol of EtOH <sup>b</sup>	228
		228–325	293	55.21 (55.90)	Loss of 1 mol of L + 2 mol of NO <sub>3</sub> <sup>−</sup> + 1 mol of NO <sub>2</sub> <sup>c</sup>	
		325–787	487	18.95 (17.73)	Complete ligand pyrolysis <sup>c</sup>	
		At 787		18.44 (18.91)	0.5La <sub>2</sub> O <sub>3</sub> <sup>d</sup>	
3	[Ce(HL) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ]·NO <sub>3</sub>	30–206		7.49 (7.63)	Loss of 1 mol of NO <sub>3</sub> <sup>−b</sup>	206
		206–250	231	63.80 (63.56)	Loss of 2 mol of L + 2 mol of NO <sub>3</sub> <sup>−c</sup>	
		250–466	387	7.06 (6.89)	Complete L pyrolysis <sup>c</sup>	
		At 466		20.65 (20.19)	0.5Ce <sub>2</sub> O <sub>3</sub> <sup>d</sup>	
4	[Sm(HL) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ]·NO <sub>3</sub> ·H <sub>2</sub> O	30–217		2.60 (2.24)	Loss of 1 mol of H <sub>2</sub> O <sup>a</sup>	217
		217–297	257	56.93 (58.43)	Loss of 2 mol of L + 2 mol of NO <sub>3</sub> <sup>−</sup> + 1 mol of NO <sub>2</sub> <sup>c</sup>	
		297–692	467	19.34 (17.92)	Complete ligand pyrolysis <sup>c</sup>	
		At 692		21.41 (21.67)	0.5Sm <sub>2</sub> O <sub>3</sub> <sup>d</sup>	
5	[Gd(HL) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ]·NO <sub>3</sub> ·0.5H <sub>2</sub> O	30–267		1.36 (1.12)	Loss of 0.5 mol of H <sub>2</sub> O <sup>a</sup>	267
		267–334	290	64.81 (65.07)	Loss of 2 mol of L + 1 mol of NO <sub>3</sub> <sup>−</sup> + 1 mol of NO <sub>2</sub>	
		334–893	453	11.55 (11.23)	Complete ligand pyrolysis <sup>c</sup>	
		At 893		22.41 (22.58)	0.5Gd <sub>2</sub> O <sub>3</sub> <sup>d</sup>	
6	[Ho(HL) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ]·NO <sub>3</sub> ·0.5EtOH	30–234		2.70 (2.81)	Loss of 0.5EtOH <sup>b</sup>	234
		234–300	174	64.42 (63.89)	Loss of 2 mol of L + 2 mol of NO <sub>3</sub> <sup>−</sup> + 1 mol of NO <sub>2</sub> <sup>c</sup>	
		300–575	264	11.01 (11.23)	Complete ligand pyrolysis <sup>c</sup>	
		At 575	452	22.11 (22.08)	0.5Ho <sub>2</sub> O <sub>3</sub> <sup>d</sup>	

<sup>a</sup> Dehydration. <sup>b</sup> Desolvation. <sup>c</sup> Decomposition. <sup>d</sup> Remain.

**3.2.4 Electronic absorption spectra.** The electronic spectral data of the hydrazide organic compound (HL) and its metal chelates in Nujol mulls are reported in Table 4 and demonstrated in Fig. 4. The electronic spectrum of the ligand displays spectral bands in the range of 272 to 240 nm and at 296 nm, assigned to the  $\pi$ – $\pi^*$  and  $n$ – $\pi^*$  electronic transitions of the entire conjugate system of the ligand, respectively. On the other hand, the electronic spectra of the metal chelates (1–5) display  $\pi$ – $\pi^*$  and  $n$ – $\pi^*$  transitions of the ligand, which are shifted to higher values upon complexation; this indicates that chelation was achieved. None of the spectra of the complexes showed bands in the visible region. This is probably due the fact that the  $f$ – $f$  bands are weak and obscured by the intense charge transfer bands.<sup>18,19</sup> The magnetic moments of the lanthanide(III) complexes indicate that only the La(III) complex is diamagnetic, and the other tripositive lanthanide ion complexes are paramagnetic.

**3.2.5 Thermal analysis of the metal complexes.** The thermograms (TG, DTA) gathered with thermoanalytical data and their assignments for each decomposition step to follow the decomposition pathways for the ligand and its metal complexes are given in Table 5 and Fig. 5. The TGA curve of the ligand shows thermal stability up to 109 °C followed by a small weight loss of 2.70% up to 163 °C, corresponding to the release of 0.25 mol of H<sub>2</sub>O. The pyrolytic process was achieved through two steps by TG weight losses of 69.37% and 26.13% and DTA peaks at  $T_{\max}$  = 180 °C and 292 °C, respectively. The DTA curve displays a sharp endothermic peak at 132 °C, which is assignable to the melting point of the compound and

corresponds with the measured value. The thermoanalytical data in Table 5 combined with the TG and DTA patterns of the La(III), Sm(III), Gd(III), and Ho(III) complexes show that these complexes decompose in a similar way, indicating that they are isothermal.

The TG curves showed weight losses in the temperature range of 30 °C to 234 °C due to removal of the solvents of crystallization. After that, the chelates decomposed in two consecutive stages. The first stage exhibited weight losses of 55.21%, 56.90%, 64.80% and 64.42% from 228 °C to 325 °C, 217 °C to 297 °C, 214 °C to 334 °C and 234 °C to 300 °C for La(III), Sm(III), Gd(III) and Ho(III), respectively. This process is associated with sharp exothermic DTA peaks at  $T_{\max}$  = 293 °C, 257 °C, 290 °C, and 264 °C, respectively; this signifies that the oxidative process of the ligand involves the release of two moles of organic ligand (one mole in the La(III) complex), two moles of NO<sub>3</sub> groups and one mole of NO<sub>2</sub> gas. The last ligand pyrolysis was characterized by TG weight losses of 18.93%, 19.34%, 11.55% and 11.01% up to 787 °C, 692 °C, 893 °C and 575 °C for the La(III), Sm(III), Gd(III) and Ho(III) complexes, respectively. The thermal decomposition process ended with the formation of 0.5 M<sub>2</sub>O<sub>3</sub> (M = La(III), Sm(III), Gd(III) and Ho(III)). However, the TG curves of the Ce(III) complex reveal a weight loss of 7.49% in the 30 °C to 206 °C range due to elimination of the ionic nitrate group. This step was followed by a TG weight loss of 63.8% up to 250 °C. This process was accompanied by two exothermic DTA peaks at  $T_{\max}$  = 231 °C to 253 °C, indicating the oxidation of the ligands with removal of two moles of the ligand and two



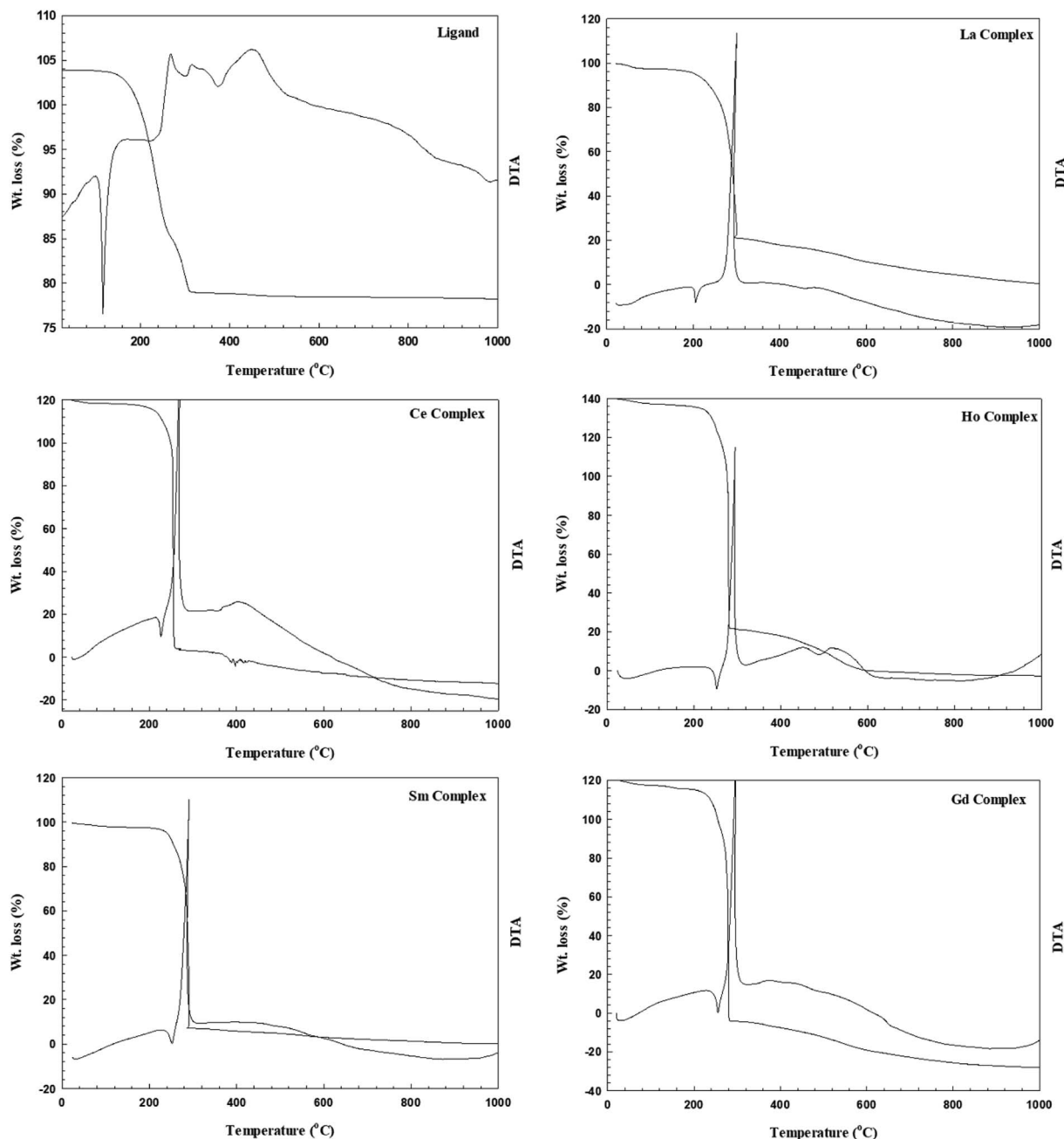


Fig. 5 Thermograms of the ligand and its metal complexes.

moles of the coordinated nitrate group. The last decomposition step exerted a TG weight loss of 6.89% in the 250 °C to 466 °C range due to complete ligand pyrolysis, and the metal reacts with atmospheric oxygen to produce  $0.5\text{Ce}_2\text{O}_3$  as a product. This process is associated with the exothermic DTA peak at  $T_{\text{max}} = 387$  °C.

### 3.3 Characterization of nanoparticles

In Fig. 6, the diffraction peaks for  $\text{CeO}_2$  at  $28.5^\circ$ ,  $33.0^\circ$ ,  $47.4^\circ$  and  $56.3^\circ$  can be indexed to the (111), (200), (220) and (311) planes of the face-centered cubic structure of  $\text{CeO}_2$  (JCPDS no. 81-0792). For the  $\text{La}_2\text{O}_3$  NPs, the peaks obtained at  $28.67^\circ$ ,

$31.21^\circ$ ,  $43.28^\circ$ ,  $47.86^\circ$ ,  $59.29^\circ$ ,  $64.97^\circ$  and  $70.12^\circ$  are indexed to the (002), (400), (125), (600), (127), (800) and (822) planes, respectively, and assigned as per JCPDS no. 65-3185.<sup>20</sup> For the  $\text{Sm}_2\text{O}_3$  NPs, the diffraction peaks located at  $28.2^\circ$ ,  $32.7^\circ$ ,  $38.6^\circ$ ,  $45.4^\circ$ , and  $54.3^\circ$  correspond to the (222), (400), (332), (521), and (541) planes of cubic  $\text{Sm}_2\text{O}_3$  (JCPDS no. 15-0813), respectively.<sup>21</sup> For the  $\text{Ho}_2\text{O}_3$  NPs, diffraction lines of cubic holmium oxide (JCPDS card 88-2163) were obtained.<sup>22</sup> For the  $\text{Gd}_2\text{O}_3$  NPs, the pattern was well-indexed with the cubic structure reported in the standard JCPDS card no. 43-1014.<sup>23</sup> No diffraction peaks of any impurity were observed, indicating the high purity of the final products. These results



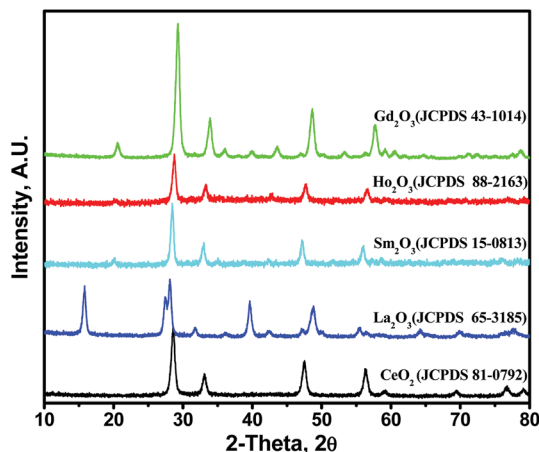


Fig. 6 X-ray diffraction patterns of the prepared lanthanide oxide nanoparticles.

suggest that the precursor samples crystallized into their analogous oxide nanoparticles at a heating temperature of 700 °C. The crystallite sizes for the lanthanide oxide NPs were calculated using the Debye–Scherrer equation:<sup>24</sup>

$$D = k\lambda/(\beta \cos \theta) \quad (1)$$

where  $k$  is a shape factor ( $k = 0.89$ ),  $\lambda$  is the wavelength of the radiation,  $\beta$  is the full width at half maximum (FWHM) and  $\theta$  is the angle corresponding to the most intense peak in the XRD pattern. The crystallite sizes were found to be 2.9 nm, 3.7 nm, 4.2 nm, 3.8 nm and 3.3 nm for the CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub>, Ho<sub>2</sub>O<sub>3</sub> and Gd<sub>2</sub>O<sub>3</sub> NPs, respectively.

The absorption spectra for the prepared lanthanide oxide nanoparticles were measured, as shown in Fig. 7. All the nanoparticles showed similar absorption behavior, with a strong absorption peak at ~240 to 250 nm, which is consistent with the literature. The band gap energy values for the lanthanide oxide nanoparticles were calculated using Tauc plots by applying the equation  $(\alpha h\nu)^{1/n} = A(h\nu - E_g)$ ,

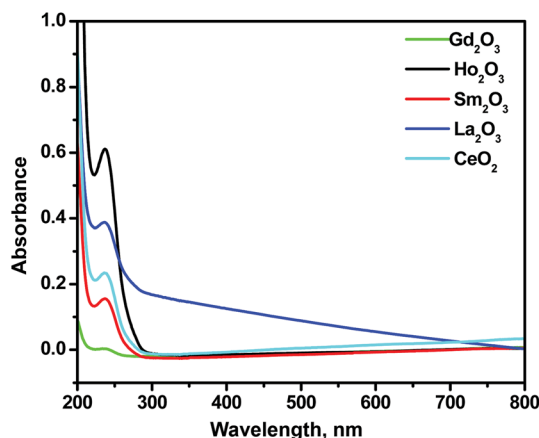


Fig. 7 UV-Vis absorption spectra of the prepared lanthanide oxide nanoparticles.

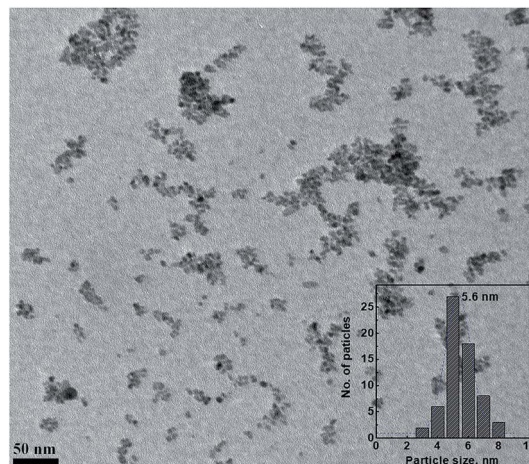


Fig. 8 TEM image of the CeO<sub>2</sub> nanoparticles. The inset is the size distribution for CeO<sub>2</sub> nanoparticles.

where  $h$  is Planck's constant,  $\nu$  is the photon frequency,  $\alpha$  is the absorption coefficient,  $E_g$  is the band gap, the exponent  $n$  denotes the nature of the electronic transition (direct or indirect), and  $A$  is a proportionality constant. The calculated values were found to be in the range of 4.64 to 4.85 eV. The increase of the band gap can be attributed to the quantum confinement effect, which led to decreased charge carrier recombination rates.<sup>20</sup> The sizes and morphologies of the CeO<sub>2</sub> nanoparticles were investigated by TEM. The TEM image of CeO<sub>2</sub> is shown in Fig. 8. From the figure, the nanoparticles can be found to be monodisperse and spherical, with an average particle size of 5.6 nm.

### 3.4 Photocatalytic activity

Because all the prepared NPs revealed the same absorption spectra and band gap energy values, in this work, the CeO<sub>2</sub> NPs were chosen for evaluation as a photocatalyst due to their smaller particle size relative to the other metal oxides. Photocatalytic degradation of MB dye using the CeO<sub>2</sub> NPs as a model photocatalyst was performed to evaluate their photocatalytic activity. Fig. 9 shows the photocatalytic activity of the CeO<sub>2</sub> NPs. The photo degradation efficiency was calculated to be 90.1%, as shown in Fig. 9B. Fig. 9C showed that the photodegradation reaction follows pseudo-first-order kinetics. The photodegradation rate constant for the photodegradation reaction was determined from the equation:

$$\ln(C_0/C) = kt \quad (2)$$

where  $C_0$  and  $C$  are the initial concentration and the concentration at time  $t$ , respectively, and  $k$  is the apparent first-order rate constant. The plot of  $\ln(C_0/C)$  versus time represents a straight line, as shown in Fig. 9C; the slope upon linear regression equals the apparent first-order rate constant  $k$ . The degradation rate obtained was 0.014 min<sup>-1</sup>. To evaluate the photostability of CeO<sub>2</sub>, four photodegradation experiments (reusability tests) under identical conditions were performed.





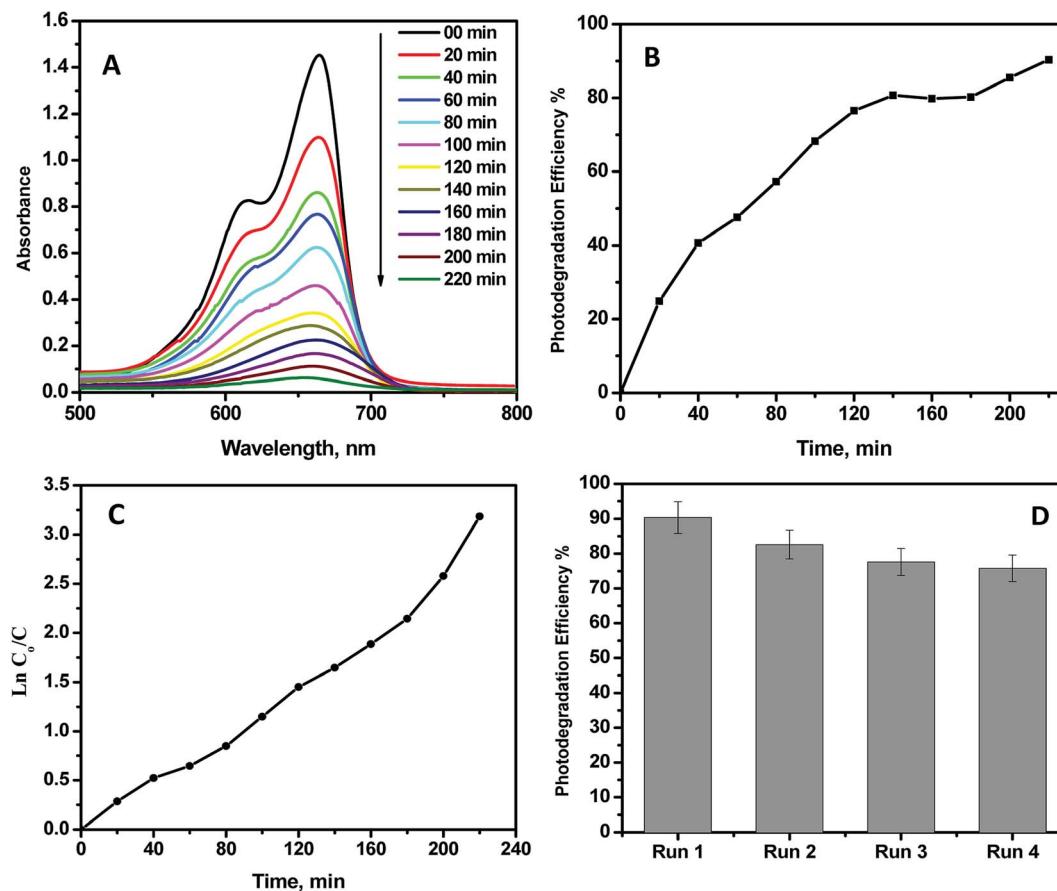


Fig. 9 (A) Methylene blue dye absorption spectra at different times upon irradiation with CeO<sub>2</sub>. (B) Evaluation of MB conversion efficiency upon irradiation. (C) Kinetics of MB photocatalytic degradation. (D) Reusability of CeO<sub>2</sub> nanoparticles.

From Fig. 9D, it can be noted that CeO<sub>2</sub> was almost completely stable and photoactive up to the 4<sup>th</sup> run, as its photocatalytic activity decreased by only 15% after the 4<sup>th</sup> run.

## 4. Conclusion

In this work, a series of metal complexes were prepared by separate reactions of lanthanide nitrate salts (La(III), Ce(III), Sm(III), Gd(III) and Ho(III)) with 4-methylbenzoylhydrazide. The structures of the complexes were confirmed by analytical studies, different spectral measurements and thermal studies. Complexes were formed with different stoichiometries of 1 : 2 and 1 : 3 (M : L). The coordination compounds were converted to metal oxide nanoparticles (MONPs) through solid state thermal decomposition as mononuclear source precursors. The obtained MONPs were investigated *via* XRD, TEM and UV-Vis spectral analyses. CeO<sub>2</sub> was utilized as a representative nanophotocatalyst to examine the photocatalytic activity of the MONPs in methylene blue (MB) photodegradation. The CeO<sub>2</sub> catalyst showed high MB removal of 90.1% after UV illumination for 220 min. The reported method provides a generalized and systematic method for the preparation of many nanoparticle metal oxides with manageable and reproducible features.

## Conflicts of interest

There are no conflicts to declare.

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