Research Article

2,4-Dichlorophenoxyacetic Acid Derived Schiff Base and Its Lanthanide(III) Complexes: Synthesis, Characterization, Spectroscopic Studies, and Plant Growth Activity

Ganesh N. Naik,¹ Raghavendra P. Bakale,¹ Aishakhanam H. Pathan,¹ Shashikala G. Ligade,² Shreenivas A. Desai,³ and Kalagouda B. Gudasi¹

¹ Department of Chemistry, Karnatak University, Pavate Nagar, Karnataka, Dharwad 580003, India

² Department of Botany, Karnatak Science College, Karnataka, Dharwad 580001, India

³ Department of Genetics and Plant Breeding, University of Agricultural Sciences, Karnataka Dharwad, 580005, India

Correspondence should be addressed to Kalagouda B. Gudasi; kbgudasi@gmail.com

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2,4-Dichlorophenoxyacetic acid derived Schiff base (HL) and its lanthanide [La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Dy(III), Y(III)] complexes were synthesized and characterized by various spectroscopic (¹H, ¹³C, DEPT and 2D HMQC NMR, FT-IR, UV-Vis, and mass) techniques and other analytical methods. HL exhibits “E” and “Z” isomerism and was confirmed by variable temperature ¹H NMR studies. The spectral and analytical data reveals the bidentate coordination of HL to lanthanide(III) ion, through carboxylic acid group via deprotonation. Fluorescence spectrum of europium complex shows bands at 578, 592, and 612 nm assignable to ⁵D₀ → ⁷F₀, ⁵D₀ → ⁷F₁, and ⁵D₀ → ⁷F₂, respectively. Auxin activity of HL and lanthanum(III) complex on wheat seeds (*Triticum durum*) was measured at different concentrations. The percentage germination, root length, and shoot length were recorded. An enhancement in the plant growth activity of the ligand was observed on complexation and the best activity was observed at 10⁻⁶ M concentration.

1. Introduction

Rare earth elements are being used in agriculture as micronutrients and fertilizers [1–4]. These are found to have nitrogen fixing capacity, to enhance activity of hydrolytic enzymes, to promote seed germination, to strengthen photosynthetic rate, and to reduce water loss in plants [5, 6]. Recent experiments indicate that lanthanide salts could accelerate the seed germination, increases chlorophyll content, and improve root growth [7, 8]. These elements also found to have significant effect on the physiological and biochemical reactions in plant growth and development [9, 10]. The effect of lanthanide(III) complexes on the growth of plants has been an important topic in agricultural field. There are only few reports which explain the auxin effect of lanthanide complexes on plant growth [11, 12].

Indole-3 acetic acid, naphthalene acetic acid, and 2,4-dichlorophenoxyacetic acid are the well known plant growth regulating hormones, widely used in agricultural field [13, 14]. The derivatives of these hormones were also found to have plant growth regulating and other biological activities [13, 15, 16].

Literature survey reveals that chelation of lanthanide metal ions with plant growth promoting auxins synergistically increases the plant growth [12]. Keeping this in view, we have synthesized 2,4-dichlorophenoxy acetic acid derived Schiff base and its lanthanide(III) complexes and screened for their auxin activity on wheat seeds. The work is focused on the synthesis, characterization, spectroscopic investigation, thermal, fluorescent behavior, and plant growth promoting activity of a series of rare earth complexes of 2,4-dichlorophenoxy acetic acid derived Schiff base (HL).

2. Experimental

2.1. Instrumentation and Materials. Elemental analyses (C, H, and N) were performed using Leco Model TruSpec CHNS analyzer. The percentage of metal content was determined according to the literature procedure [17] with xylenol orange as the indicator and EDTA as the chelating agent. SHIMADZU LCMS 2010A spectrometer is used to know the mass. Molar conductivities in DMSO (10^{-3} M) at room temperature were measured using an Elico conductivity bridge having platinum electrode. Melting points were determined in an open capillary on a Gallenkamp melting point apparatus and are uncorrected. IR spectra were recorded in a KBr matrix using an Impact-410 Nicolet (USA) FT-IR spectrometer in $4000\text{--}400\text{ cm}^{-1}$ range. The ^1H , ^{13}C , DEPT, 2D HMQC NMR, and variable temperature ^1H NMR were recorded in DMSO- d_6 solvent on BRUKER AV-500 MHz High Resolution Multinuclear FT-NMR spectrometer using SiMe_4 as an internal standard at $\delta = 0$ ppm. Thermogravimetry (TG) and differential thermal analysis (DTA) were run in nitrogen atmosphere in a temperature range of 20°C to 1000°C at a heating rate of $10^\circ\text{C min}^{-1}$ using a Perkin-Elmer (Pyris Diamond) analyzer. UV-Visible spectra were recorded on a CARY 50 Bio UV-Visible spectrophotometer in $200\text{--}1100\text{ nm}$ range in DMSO solvent. Fluorescence spectrum was measured on F-7000 FL spectrophotometer. Plant growth activity was performed in a dual chamber seed germinator at 25°C temperature and $70 \pm 5\%$ humidity with proper illumination.

2,4-Dichlorophenoxyacetic acid and 2-formyl phenoxyacetic acid were obtained from Sigma Aldrich. Lanthanide(III) oxides were procured from Indian Rare Earths Ltd, India. Other chemicals were obtained from s.d. Fine Chemicals, India, and used as received. Solvents were purified by standard methods [18]. Lanthanide nitrates were prepared by dissolving the corresponding oxide (99.99%,) in 50% HNO_3 followed by evaporation of the excess acid. All the compounds were routinely checked by thin-layer chromatography (TLC) on aluminum-backed silica gel plates. The wheat seeds (*Triticum durum*) DWR-2006 were collected from University of Agricultural Sciences (UAS), Dharwad, India.

2.2. Synthesis

2.2.1. Synthesis of 2-([2-(2, 4-Dichloro-phenoxy)-Acetyl]-Hydrazonomethyl)-Phenoxy)-Acetic Acid (HL). A mixture of 2,4-dichlorophenoxyacetic acid (**1**) (12 g, 54.28 mmol) and concentrated H_2SO_4 (4 mL) in dry methanol (50 mL) was refluxed for 15 hrs to yield the 2,4-dichlorophenoxy acetic acid methyl ester (**2**). Product was separated and purified. To the methanolic solution of **2**, (8 g, 34.03 mmol), hydrazine hydrate (3 g, 44.08 mmol) was added slowly and stirred for 30 min. The 2,4-dichlorophenoxyacetic acid hydrazide separated (**3**) was filtered and washed with methanol. The hydrazide (**3**) (7 gm, 29.77 mmol) was stirred with 2-formyl phenoxy acetic acid (**4**) (5.36 g, 29.77 mmol) in THF (75 mL) for 30 min and the product formed was filtered and

washed thoroughly with THF to obtain 2-([2-(2,4-dichloro-phenoxy)-acetyl]-hydrazonomethyl)-phenoxy)-acetic acid (HL) (**5**). Yield: 90%, M.P: $233\text{--}235^\circ\text{C}$.

^1H NMR (DMSO- d_6 , ppm): 4.82, 4.90 (s, 2H, $\text{C}_2\text{H}/\text{C}_2'\text{H}$), 4.80, 5.31 (s, 2H, $\text{C}_{11}\text{H}/\text{C}_{11}'\text{H}$), 6.97, 7.01 (d, 1H, $J = 9.4\text{ Hz}$, $\text{C}_4\text{H}/\text{C}_4'\text{H}$), 7.03, 7.08 (d, 1H, $J = 6.4\text{ Hz}$, $\text{C}_{17}\text{H}/\text{C}_{17}'\text{H}$), 7.11, 7.17 (d, 1H, $J = 6.4\text{ Hz}$, $\text{C}_{16}\text{H}/\text{C}_{16}'\text{H}$), 7.32–7.41 (m, 2H, $\text{C}_{14}\text{H}/\text{C}_{14}'\text{H}$ and $\text{C}_5\text{H}/\text{C}_5'\text{H}$), 7.57, 7.61 (d, 1H, $J = 5\text{ Hz}$, $\text{C}_7\text{H}/\text{C}_7'\text{H}$), 7.83–7.90 (m, 1H, $\text{C}_6\text{H}/\text{C}_6'\text{H}$), 8.42, 8.65 (s, 1H, $\text{C}_9\text{H}/\text{C}_9'\text{H}$), 11.72, 11.80 (1H, $\text{NH}/\text{N}'\text{H}$), 13.16 (s, 1H, OH).

^{13}C NMR (DMSO- d_6 , ppm): 64.62, 64.75 (C_2/C_2'), 64.67, 66.91 ($\text{C}_{11}/\text{C}_{11}'$), 112.47, 112.84 (C_4/C_4'), 114.97, 115.12 ($\text{C}_{17}/\text{C}_{17}'$), 116.15, 117.13 (C_8/C_8'), 121.01, 121.03 ($\text{C}_{16}/\text{C}_{16}'$), 122.02, 122.20 ($\text{C}_{13}/\text{C}_{13}'$), 124.38, 124.94 (C_6/C_6'), 125.58, 125.77 ($\text{C}_{15}/\text{C}_{15}'$), 127.75, 127.96 (C_5/C_5'), 129.12, 129.30 (C_7/C_7'), 131.15, 131.44 ($\text{C}_{14}/\text{C}_{14}'$), 139.00, 143.00 (C_9/C_9'), 152.54, 152.73 ($\text{C}_{12}/\text{C}_{12}'$), 156.08, 156.20 (C_3/C_3'), 163.28, 168.12 ($\text{C}_{10}/\text{C}_{10}'$), 169.88, 169.94 (C_1/C_1').

2.2.2. General Procedure for the Synthesis of Lanthanide Complexes. The complexes were prepared by treating HL with freshly prepared lanthanide(III) nitrates in presence of triethyl amine according to literature procedure [19] with slight modifications. The mixture of HL (0.5 gm, 1.26 mmol) and triethyl amine (0.14 g, 1.38 mmol) was taken in THF (50 mL) and stirred till HL completely dissolves. To this solution, freshly prepared $\text{Ln}(\text{NO}_3)_3$ (0.42 mmol) ($\text{Ln} = \text{La}$, Pr, Nd, Sm, Eu, Gd, Dy, Y) was added slowly under stirring and was further refluxed for 2 hrs. Solvent was evaporated under reduced pressure. The solid obtained was washed with water and THF several times. The product was dried under vacuum. Yield: 60–70%.

^1H NMR of lanthanum(III) complex (DMSO- d_6 , ppm): 4.70 (s, 2H, C_2H), 5.28 (s, 2H, C_{11}H), 6.92 (d, 1H, $J = 9.2\text{ Hz}$, C_4H), 7.10 (d, 1H, $J = 6.3\text{ Hz}$, C_{16}H), 7.25 (d, 1H, $J = 6.3\text{ Hz}$, C_{17}H), 7.39 (m, 1H, C_5H), 7.40 (s, 1H, C_{14}H), 7.56 (d, 1H, $J = 9.2\text{ Hz}$, C_7H), 7.86–7.90 (m, 1H, C_6H), 8.41 (s, 1H, C_9H), 11.64 (1H, NH).

^{13}C NMR lanthanum(III) complex (DMSO- d_6 , ppm): 66.91 (C_{11}), 67.55 (C_2), 112.47 (C_4), 115.28 (C_{17}), 117.13 (C_8), 122.13 (C_{13}), 122.25 (C_{16}), 124.30 (C_{15}), 126.92 (C_6), 127.96 (C_5), 129.12 (C_7), 131.90 (C_{14}), 138.50 (C_9), 153.00 (C_{12}), 156.08, (C_3), 164.30 (C_{10}), 176.46 (C_1).

2.3. Protocol for the Plant Growth Activity on Wheat Seeds. DWR-2006 (*Triticum durum*), a local variety of wheat seeds developed at University of Agricultural Sciences, Dharwad, India, was selected to investigate the growth activities of the synthesized compounds. The solutions of HL, lanthanum(III) complex, $\text{La}(\text{NO}_3)_3$, and 2,4-dichlorophenoxyacetic acid were prepared by dissolving them in minimum quantity of DMSO ($\sim 1\text{ mL}$) and further diluted with distilled water to obtain the solutions of $1 \times 10^{-5}\text{ M}$, $1 \times 10^{-6}\text{ M}$ and, $1 \times 10^{-7}\text{ M}$ concentrations. Seed germination experiments were carried out according to the literature method [20] with slight modifications. Healthy wheat seeds were selected and

SCHEME 1: Synthetic route for the preparation of HL.

washed with distilled water before soaking in test solutions. Hundred seeds were soaked in test solutions of particular concentration for 3 minutes and then arranged on the moistened specially prepared germination paper placed on polythene sheet. One more moistened germination paper was placed over the seeds and loosely rolled. Each roll was labeled clearly and kept upright in the seed germinator and maintained at 25°C temperature and $70 \pm 5\%$ humidity, with proper illumination. The conditions were maintained for eight days. After eight days, percentage germination was calculated. Further, 10 seeds were randomly selected from each roll for root and shoot length measurements. The experiments were performed in triplicate.

2.3.1. Statistical Analysis. The results are evaluated with SPSS (Statistical Package for Social Science, Windows, version 17.0) packed program. One way ANOVA with Duncan statistical analysis with significance at $P < 0.05$ was used for data analysis.

3. Results and Discussions

The Schiff base (HL) was prepared as shown in Scheme 1. The structure of HL was confirmed by IR, NMR, and mass spectral analysis. All the complexes were obtained in moderate to good yields (60–70%) by reacting HL and lanthanide(III) nitrates in THF in 3 : 1 (ligand to metal) molar ratio. The complexes are soluble in DMSO and DMF. The analytical results given in Table 1 agree with the suggested formula of complexes. Elemental analysis, FT-IR, ^1H , ^{13}C , 2D HMQC NMR, TGA/DSC, and UV-Visible spectroscopy were

used to characterize the complexes. The elemental analyses indicate 3 : 1 (ligand to metal) stoichiometry. The lower molar conductance values of the complexes in DMSO at 10^{-3} M concentration suggest their nonelectrolytic nature and are given in Table 1.

3.1. IR Spectral Studies. The characteristic IR bands of HL and Ln(III) complexes are compiled in Table 2. In the IR spectrum of HL, the broad band observed at 3290 cm^{-1} was assigned to $\nu(\text{OH})$ group of carboxylic acid. The appearance of this frequency at a slightly lower wave number is due to the involvement of OH group in intermolecular hydrogen bonding with oxygen atom of amide $\nu(\text{C}=\text{O})$ functional group [21]. The HL shows a very strong absorption band at 1736 cm^{-1} assigned to the $\nu(\text{C}=\text{O})$ of the carboxylic acid. The bands at 1659 cm^{-1} and 1609 cm^{-1} were assigned to amide $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N})$, respectively.

The absence of band due to carboxylic OH group in the spectra of all lanthanide (III) complexes suggests the coordination to the metal ion via deprotonation. The band due to $\nu(\text{C}=\text{O})$ of carboxylic acid of HL was absent in all the lanthanide(III) complexes, indicating the participation of carbonyl oxygen in coordination to the metal ion [22–24]. Whereas the two new characteristic bands appeared on complexation in the ranges of $1590\text{--}1562\text{ cm}^{-1}$ and $1372\text{--}1346\text{ cm}^{-1}$ were assigned to asymmetric and symmetric stretching frequencies of carboxylate ion, respectively. The difference between $\nu_{\text{asy}}(\text{COO}^-)$ and $\nu_{\text{sy}}(\text{COO}^-)$ frequencies in all complexes were found to be less than the difference observed in the sodium salt of HL. This implies that carboxylic acid group of HL has coordinated to metal ion in

TABLE 1: Elemental analysis and molar conductivity measurements.

Compounds	Color	Calculated (found)*			M	Molar conductance**
		C	H	N		
HL	White	51.40 (51.42)	3.55 (3.56)	7.05 (6.98)	—	—
[La(L) ₃ ·2H ₂ O]	Yellow	44.82 (44.81)	3.39 (3.39)	6.15 (6.13)	10.16 (10.56)	5.2
[Pr(L) ₃ ·2H ₂ O]	Yellow	44.76 (44.75)	3.39 (3.40)	6.14 (6.13)	10.30 (10.35)	7.8
[Nd(L) ₃ ·3H ₂ O]	Light pink	44.17 (44.68)	3.27 (3.26)	6.06 (6.10)	10.40 (11.03)	6.3
[Sm(L) ₃ ·2H ₂ O]	Yellow	44.45 (44.42)	3.36 (3.37)	6.10 (6.11)	10.91 (11.12)	9.8
[Eu(L) ₃ ·2H ₂ O]	Yellow	44.40 (44.43)	3.36 (3.35)	6.09 (6.10)	11.01 (10.08)	7.1
[Gd(L) ₃ ·3H ₂ O]	Off white	43.76 (43.69)	3.24 (3.26)	6.00 (6.03)	11.23 (11.56)	4.6
[Dy(L) ₃ ·3H ₂ O]	Yellow	43.59 (43.55)	3.23 (3.22)	5.98 (6.05)	11.56 (12.05)	8.5
[Y(L) ₃ ·2H ₂ O]	Yellow	46.53 (46.31)	3.52 (3.53)	6.38 (6.39)	06.75 (06.86)	4.5

*The values in the parenthesis are calculated ones.

**Ohm⁻¹ cm² mol⁻¹.TABLE 2: FT-IR analysis of HL and [Ln(L)₃ · nH₂O].

Compounds	ν (OH)	ν (CO) (amide)	ν (CO) (carboxylic)	ν_{asy} (COO ⁻)	ν_{s} (COO ⁻)	Δn ($\nu_{\text{asy}} - \nu_{\text{s}}$)	ν (C=N)	ν (H ₂ O)
HL	3290	1659	1736	n.o*	n.o	n.o	1609	n.o
NaL	n.o	1692	n.o	1603	1377	226	1611	3460
[La(L) ₃ ·2H ₂ O]	n.o	1692	n.o	1590	1372	218	1609	3448
[Pr(L) ₃ ·2H ₂ O]	n.o	1690	n.o	1564	1348	216	1613	3450
[Nd(L) ₃ ·3H ₂ O]	n.o	1695	n.o	1574	1362	212	1612	3435
[Sm(L) ₃ ·2H ₂ O]	n.o	1689	n.o	1574	1358	216	1608	3448
[Eu(L) ₃ ·2H ₂ O]	n.o	1691	n.o	1581	1370	211	1610	3450
[Gd(L) ₃ ·3H ₂ O]	n.o	1692	n.o	1573	1355	218	1613	3421
[Dy(L) ₃ ·3H ₂ O]	n.o	1696	n.o	1562	1346	216	1608	3425
[Y(L) ₃ ·2H ₂ O]	n.o	1693	n.o	1581	1368	213	1613	3448

*n.o: not observed.

bidentate fashion via deprotonation as suggested by Deacon [22, 25–28].

A strong band at 1659 cm⁻¹ in the spectrum of uncoordinated ligand is assigned to amide ν (C=O) and has shifted to higher wave number in all complexes. This increase in frequency of amide ν (C=O) functional group may be due to the breaking of hydrogen bond present in HL on complexation. Azomethine nitrogen ν (C=N) has not suffered any change on complexation indicating its noninvolvement in coordination.

The presence of a broad band in the region 3460–3421 cm⁻¹ was attributed to the ν (O-H) of coordinated water molecules in all complexes [29]. This was further confirmed by the appearance of a weak nonligand band in the region 831–856 cm⁻¹, assignable to rocking mode of coordinated water molecule [30]. The presence of coordinated water molecules was further confirmed by thermal studies.

3.2. NMR Spectroscopy

3.2.1. NMR Spectral Studies of HL. The NMR spectrum of HL shows double set of signals for all the protons and carbons due to its existence in E and Z isomeric forms arising due

to the restricted rotation along the (–HC=N–) functional group. From the ¹H NMR data, the ratio of E and Z isomers was approximately found to be 70:30 with E isomer as the predominant one over Z isomer.

The isomeric structure of HL and its numbering are presented in Figure 1. The ¹H NMR spectrum is given in Figure 2. The detailed assignments for both the isomers are given in the experimental section. The singlet observed at 13.16 ppm was assigned to OH proton of carboxylic acid. Two singlets observed at 11.72 and 11.80 ppm were assigned to amide NH and NH' protons, respectively. The C11H and C11'H protons present adjacent to carbonyl functional group were observed at 4.80 and 5.31 ppm, respectively. The C2H and C2'H protons present adjacent to carboxylic functional group were observed at 4.82 and 4.90 ppm, respectively. The azomethine protons C9H and C9'H were observed at 8.42 and 8.65 ppm, respectively [31]. The aromatic protons were observed between 6.99–7.90 ppm.

¹H-NMR analysis is supported by the ¹³C and DEPT NMR spectral analysis for the confirmation of E and Z isomerism in HL. The ¹³C spectrum of HL is given in Figure 3 and its DEPT NMR is presented at Figure 4. DEPT NMR at 135° pulse assisted the assignment of ¹³C

FIGURE 1: Isomeric structures of HL.

FIGURE 2: ^1H NMR spectrum of HL. FIGURE 3: ^{13}C NMR spectrum of HL.

resonance. The primary and tertiary carbons phased up and secondary carbons phased down, while signals for quaternary carbons and other carbons with no attached protons found absent in DEPT NMR were observed at 169.88 and 169.94 ppm, respectively. These quaternary carbons were absent in DEPT-135 NMR spectrum. Carbon signals at

116.15, 117.13 (C8/C8'), 122.02, 122.20 (C13/C13'), 125.58, 125.77 (C15/C15'), 152.54, 152.73 (C12/C12'), 163.28, 168.12 (C10/C10'), 156.08, 156.20 (C3/C3'), and 169.88, 169.94 (C1/C1') were absent in DEPT-135 NMR spectrum which confirms their assignment for quaternary carbons. In ^{13}C NMR spectrum, the methyne carbons C9 and C9' were

FIGURE 4: DEPT NMR spectrum of HL.

FIGURE 5: 2D HMQC NMR spectrum of HL.

resonated at 139.00 and 143.00 ppm, respectively, and were phased up in the DEPT-135 NMR spectrum. The signals for CH carbons in DEPT NMR were observed at 112.47, 112.84 (C4/C4'), 114.97, 115.12 (C17/C17'), 121.01, 121.03 (C16/C16'), 124.38, 124.94 (C6/C6'), 127.75, 127.96 (C5/C5'), 129.12, 129.30 (C7/C7'), 131.15, 131.44 (C14/C14') and 139.00, 143.00 (C9/C9') phased up in spectrum are in accordance with ^{13}C NMR spectral assignments. The C11 and C11' carbons were observed at 64.67 and 66.91 ppm, respectively. The signals for C2 and C2' were observed at 64.62 and 64.75 ppm, respectively. The signals for methylene carbons C11, C11', C2, and C2' were phased down in the DEPT NMR spectrum. In ^{13}C NMR the resonances for aromatic carbons were observed in the range of 112.47–131.90 ppm.

All assignments were further studied by 2D HMQC NMR spectral analysis and the spectrum is given in Figure 5. The spectrum correlates the directly bonded ^1H and ^{13}C NMR resonances. The resonance observed in ^1H NMR spectrum

FIGURE 6: Variable temperature ^1H NMR spectra of HL.

at 13.16 ppm, 11.72, and 11.80 were assigned to OH, NH, and NH' protons, respectively, which are devoid of any attached carbon signals, and were confirmed in 2D HMQC NMR spectral analysis.

Isomeric Investigation of HL by Variable Temperature NMR. It is well known that, in case of E and Z isomers, as the temperature increases, interconversion of two isomers also increases due to the increase in rotation along C8-C9 bond and one of them will become predominant over the other isomer at higher temperature [32]. To study the interconversion phenomenon, variable temperature ^1H NMR analyses were undertaken [33] in the temperature range from 298 K to 363 K and the spectrum is given in Figure 6. At room temperature (298 K), the resonances for both E and Z isomers are well distinguishable. As the temperature is increased (308 K), the intensities of signals assigned to Z isomer have comparatively decreased. At 338 K, signals were reduced to more than half of their original intensity. It implies that increase in temperature causes the interconversion of two isomers. At 348 K, the signals observed at 8.65 ppm (C9'H), 7.61 ppm (C7'H), and 5.31 ppm (C11'H) for Z isomer have

FIGURE 7: ^1H NMR spectrum of $[\text{La}(\text{L})_3 \cdot 2\text{H}_2\text{O}]$. FIGURE 8: ^{13}C NMR spectrum of $[\text{La}(\text{L})_3 \cdot 2\text{H}_2\text{O}]$.

completely disappeared and at the same time, the remaining signals have also suffered a significant decrease in their intensities. At 363 K, almost a single set of signals was observed.

3.2.2. NMR Spectral Studies of Lanthanum(III) Complex. In the spectrum of the lanthanum(III) complex shown at Figure 7, only one set of signals was observed for each proton and carbon, indicating the presence of HL in only one form. The resonance at 13.16 ppm assigned to carboxylic acid proton in HL has completely disappeared in lanthanum(III) complex indicating the coordination of HL through carboxylic group via deprotonation [22]. The carboxylic acid coordination was supported by downfield shift of CH_2 protons adjacent to carboxylic acid. The C11H, C9H, and NH signals observed at 4.80, 8.42, and 11.72 ppm, respectively in the spectrum of HL have now been observed at 4.70, 8.41, and 11.64 ppm, respectively, in the NMR spectrum of lanthanum(III) complex. This observation confirms that the carbonyl oxygen and azomethine nitrogen were not involved in coordination. Significant changes were not observed in the chemical shift values of aromatic protons after complexation.

^{13}C NMR spectrum further supports the mode of coordination of HL. The spectrum is given in Figure 8. The carbonyl carbon C1 of carboxylic acid observed at 169.88 ppm in HL has shifted downfield to 176.46 ppm in the complex suggesting the involvement of carboxylic acid in coordination [22]. It was further supported by downfield shift of C2 carbon resonance from 64.62 ppm to 67.55 ppm on complexation. Small change was observed in the chemical shift values of carbonyl carbon C10 on complexation. This

FIGURE 9: DEPT NMR spectrum of $[\text{La}(\text{L})_3 \cdot 2\text{H}_2\text{O}]$. FIGURE 10: 2D HMQC spectrum of $[\text{La}(\text{L})_3 \cdot 2\text{H}_2\text{O}]$.

indicates breakdown of hydrogen bond after complexation [34].

The ^{13}C NMR spectral assignment was further confirmed by DEPT spectral analysis and is presented in Figure 9. The CH_2 carbons observed at 66.91 ppm assigned to C11 carbon and 67.55 ppm to C2 carbon were found phased down in the spectrum. The signals at 112.47 (C4), 115.28 (C17), 122.25 (C16), 126.92 (C6), 127.96 (C5), 129.12 (C7), 131.90 (C14), and 138.50 (C9) are due to CH carbons and were found phased up in the spectrum. The resonances at 117.13 (C8), 122.13 (C13), 124.30 (C15), 153.00 (C12), 156.08, (C3), 164.30 (C10), and 176.46 (C1) are the quaternary carbons, which were absent in DEPT spectrum.

The assignments were further studied by 2D HMQC NMR spectrum. The spectrum is given in Figure 10. The resonance observed at 11.64 ppm was devoid of any attached carbon signal confirming their assignment to NH proton.

TABLE 3: Thermal decomposition data of $[\text{Ln}(\text{L})_3 \cdot n\text{H}_2\text{O}]$.

Complex	Temperature range ($^{\circ}\text{C}$)	Weight loss in %		Molecule decomposed
		Found	Calculated	
$[\text{La}(\text{L})_3 \cdot 2\text{H}_2\text{O}]$	137.03–148.31	2.60	2.64	$2\text{H}_2\text{O}$
	378.71–488.46	87.38	87.35	3L
	488.46–1000	10.02	10.01	Residue
$[\text{Pr}(\text{L})_3 \cdot 2\text{H}_2\text{O}]$	152.03–173	2.66	2.64	$2\text{H}_2\text{O}$
	375.71–510.60	87.35	87.23	3L
	510.60–1000	9.99	10.13	Residue
$[\text{Nd}(\text{L})_3 \cdot 3\text{H}_2\text{O}]$	155.33–181.03	3.90	3.91	$3\text{H}_2\text{O}$
	376.71–485.32	86.13	86.03	3L
	485.32–1000	9.97	10.06	Residue
$[\text{Sm}(\text{L})_3 \cdot 2\text{H}_2\text{O}]$	142.03–170.02	2.59	2.62	$2\text{H}_2\text{O}$
	365.71–483.40	86.50	86.53	3L
	483.40–1000	10.91	10.85	Residue
$[\text{Eu}(\text{L})_3 \cdot 2\text{H}_2\text{O}]$	162.51–210.02	2.65	2.62	$2\text{H}_2\text{O}$
	370.71–484	86.40	86.46	3L
	484–1000	10.95	10.92	Residue
$[\text{Gd}(\text{L})_3 \cdot 3\text{H}_2\text{O}]$	168.20–203.72	3.82	3.86	$3\text{H}_2\text{O}$
	369–477	85.11	85.14	3L
	477–1000	11.07	11.10	Residue
$[\text{Dy}(\text{L})_3 \cdot 3\text{H}_2\text{O}]$	156.03–183.66	3.87	3.84	$3\text{H}_2\text{O}$
	386.01–495.48	84.72	84.68	3L
	495.48–1000	11.41	11.48	Residue
$[\text{Y}(\text{L})_3 \cdot 2\text{H}_2\text{O}]$	156–173	2.72	2.71	$2\text{H}_2\text{O}$
	374.07–488	89.55	89.59	3L
	488–1000	7.73	07.70	Residue

FIGURE 11: Thermogram of $[\text{La}(\text{L})_3 \cdot 2\text{H}_2\text{O}]$.

3.3. Thermal Analysis. The thermal stability data of Ln(III) complexes (where, Ln = La, Pr, Nd, Sm, Eu, Gd, Dy, Y) are compiled in Table 3. As a representative, the thermogram of La(III) complex is shown in Figure 11. Under nitrogen atmosphere, the complex undergoes a three-step decomposition.

The first weight loss found between 137.03°C to 210.02°C corresponds to the loss of coordinated water molecules. In La(III), Pr(III), Sm(III), Eu(III), and Y(III) complexes, the weight loss corresponds to two coordinated water molecules while in Nd(III), Gd(III), and Dy(III) complexes, the weight

FIGURE 12: Mass spectrum of HL.

FIGURE 13: ESI mass spectrum of $[La(L)_3 \cdot 2H_2O]$.

loss corresponds to three coordinated water molecules. The second weight loss between 365.71°C to 510.60°C is due to the loss of three ligand molecules in all complexes. Third step weight losses correspond to the formation of residue. The observed weight losses match with calculated values for the metal content [35].

3.4. ESI Mass Analysis. The ESI mass spectrum of HL is given in Figure 12. The molecular ion peak $m/z = 419$ corresponds to sodium adduct of HL. The mass spectra of complexes are in good agreement with the expected molecular weights. All the molecular weights are adducting with the proton. The representative spectrum of lanthanum complex is given in Figure 13. In the given mass spectrum of La(III) complex, the molecular ion peak $m/z = 1358$ due to $[M-H]^+$ ion.

3.5. Electronic Spectra. The electronic spectra of HL and its lanthanide(III) complexes were recorded in DMSO at room temperature. The two absorption maxima at 278 nm and 318 nm in the spectrum of HL were assigned to $\pi \rightarrow \pi^*$ transitions of carbonyl oxygen and azomethine ($-C=N-$) moiety. No significant changes were observed in these bands on complexation.

3.6. Emission Spectra. The emission spectrum of Eu(III) complex was recorded in the solid state in the range of 300–700 nm by selective excitation wavelength at 318 nm. The three emission peaks observed were at 578, 592, and 612 nm. The bands at 578, 592, and 612 nm were assigned to $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$, and $^5D_0 \rightarrow ^7F_2$, respectively. The intensity of 612 nm band was found to be more intense than other two bands [36, 37].

Ln = La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Dy(III), Y(III)

$n = 2$ for La(III), Pr(III), Sm(III), Eu(III), Y(III)

$n = 3$ for Nd(III), Gd(III), Dy(III)

FIGURE 14: Tentative structure of $[Ln(L)_3 \cdot nH_2O]$.

TABLE 4: Plant growth activity on wheat seeds.

Sl. no.	Treatments	Germination percentage	Root length (cm)	Shoot length (cm)
1×10^{-5} M				
1	Group 1**	100	18.60 ± 1.89 fghi	16.14 ± 0.56 bc*
2	Group 2	97.60	18.08 ± 1.95 ghi	16.03 ± 0.53 bc
3	Group 3	80.00	17.87 ± 2.88 hi	15.55 ± 1.67 c
4	Group 4	85.00	20.97 ± 2.37 cd	16.31 ± 1.48 bc
5	Group 5	76.00	16.82 ± 1.29 i	13.09 ± 1.91 e
6	Group 6	80.50	14.77 ± 0.92 j	13.56 ± 2.47 de
1×10^{-6} M				
1	Group 1	98.50	18.04 ± 0.92 ghi	16.55 ± 2.03 bc
2	Group 2	98.00	17.91 ± 2.63 hi	16.28 ± 1.63 c
3	Group 3	98.60	21.35 ± 1.30 c	17.06 ± 2.22 bc
4	Group 4	98.00	20.05 ± 2.14 cdefg	16.84 ± 2.15 bc
5	Group 5	100	25.70 ± 1.25 b	18.10 ± 2.23 b
6	Group 6	98.50	28.28 ± 0.99 a	20.06 ± 1.22 a
1×10^{-7} M				
1	Group 1	100	18.90 ± 2.51 efgh	15.98 ± 2.04 bc
2	Group 2	99.00	18.82 ± 3.08 efghi	16.17 ± 2.94 bc
3	Group 3	98.00	19.32 ± 0.73 defgh	15.27 ± 2.52 cd
4	Group 4	96.00	20.26 ± 2.37 cdef	16.92 ± 1.77 bc
5	Group 5	98.50	20.74 ± 1.83 cde	16.48 ± 3.17 bc
6	Group 6	98.00	21.78 ± 2.63 c	16.24 ± 1.13 bc

*Values are the mean of triplicates. Mean values followed by different letters are significantly different within a row or column at 5% probability level; that is, $\alpha = 0.05$ ($P < 0.05$) according to Duncan statistics.

**Group 1: water, Group 2: DMSO and water mixture, Group 3: 2,4-D, Group 4: lanthanum nitrate, Group 5: HL, Group 6: La (III) complex.

FIGURE 15: Comparison of shoot length Group 1 = Water, Group 2 = DMSO and Water mixture, Group 3 = 2,4-D, Group 4 = Lanthanum nitrate, Group 5 = HL, Group 6 = $\text{La}(\text{L})_3 \cdot 2\text{H}_2\text{O}$.

FIGURE 16: Comparison of root length. Group 1 = Water, Group 2 = DMSO and Water mixture, Group 3 = 2,4-D, Group 4 = Lanthanum nitrate, Group 5 = HL, Group 6 = $\text{La}(\text{L})_3 \cdot 2\text{H}_2\text{O}$.

From the spectral and analytical data, the general molecular formula for complexes is given as $[\text{Ln}(\text{L})_3 \cdot n\text{H}_2\text{O}]$. The tentative structure for the complexes is given in Figure 14.

3.7. Plant Growth Activity. The effect of HL and its $\text{La}(\text{III})$ complex at different concentrations in the growth of root and shoot of the germinated wheat seeds was analyzed with statistical analysis and data are compiled in Table 4. Among the three concentrations used, that is, 1×10^{-5} , 1×10^{-6} , and 1×10^{-7} M, the growth of root and shoot is more at 1×10^{-6} M concentration. The growth activity exhibited by HL (Group 5) and $\text{La}(\text{III})$ complex (Group 6) is compared with that of control (Group 1), solvent (Group 2), standard auxin (Group 3), and metal salt (Group 4). At 1×10^{-5} M concentration, the percentage germination is less, while it is good and almost equal at 1×10^{-6} and 1×10^{-7} M concentrations.

This indicates that, at 10^{-6} M concentration, both HL and $\text{La}(\text{III})$ complex have more growth promoting activity than the standard auxin used.

3.7.1. Shoot Length. At 1×10^{-5} M concentration, surprisingly Groups 5 and 6 have shown a decreased activity while at 1×10^{-7} M, a significant change was observed. But at 1×10^{-6} M, a significant enhancement in shoot length is observed on complexation (Group 6). The graph is given in Figure 15.

3.7.2. Root Length. At 1×10^{-5} M concentration, Group 4 has shown significant increase in root length compared to Groups 3, 5, and 6. At 1×10^{-6} M, Groups 5 and 6 have shown significant enhancement in root length compared to even Group 3 (the commercial auxin). When compared

among the Groups 5 and 6, the activity has enhanced on complexation (Group 6). A similar observation is made at 1×10^{-7} M concentration, but the extent of enhancement is less compared to that at 1×10^{-6} M. The comparative graph is given in Figure 16.

4. Conclusion

A series of lanthanide complexes were prepared by treating novel 2-{[2-(2, 4-dichloro-phenoxy)-acetyl]-hydrazonomethyl}-phenoxy)-acetic acid with lanthanide(III) nitrates. The structure of HL was confirmed by various spectroscopic techniques. NMR spectral data of HL reveal its existence in E and Z isomeric forms in solution at room temperature. The coordination mode of ligand is well established from elemental analysis, molar conductivity, IR, NMR, mass, electronic spectral, and thermal studies. The results confirm that ligand has coordinated in bidentate fashion through carboxylic acid group via deprotonation. Based on spectral and analytical results, tentative structure for complexes is given in Figure 14. The results obtained on plant growth activity indicate that germination percentage is more at 1×10^{-6} M and 1×10^{-7} M concentrations. When compared between the standard, HL and lanthanum(III) complex, an enhancement in the plant growth activity was observed on complexation and the best activity was observed at 10^{-6} M concentration.

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