# Synthesis, Characterization and Plant Growth Regularity Activity of Some Rare Earth Metal (III) Complexes Derived from Schiff base Ligand Containing the 1H-indole-2,3-dione Moiety

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**Abstract**

New complexes of La(III), Sm(III)and Yb(III) with bidentate Schiff base ligand, 5-nitro-3-(indolin-2-one)hydrazinecarbothioamide(LH) have been synthesized. Ln(III) chloride was reacted with these ligands in 1:3 molar ratios. The characterization and nature of bonding of these complexes were elucidated by the elemental analysis, melting point, molecular weight determinations, IR $^{1}H$ and $^{13}C$ NMR spectral studies. From elemental analysis, the complexes have been found to be in 1:3 (metal: ligand). The study results propose an octahedral geometry for Ln(III) complexes. Plant growth regulatory activity on Seeds of *Trigonellafoenum-graecum*(Methi) has been studied and results have been discussed. Studies show that the complexes are more potent than the ligand.

**Keywords:** Ln(III) complexes, Schiff base, IR and $^{1}H$ and $^{13}C$ NMR Spectral studies, Plant growth regulating activity, *Trigonellafoenum-graecum*(Methi).

**Introduction**

Rare earth elements have shown interesting plant growth effects on plants. These show positive or negative effects on plants depending on the dosage. In recent years, there is increasing interest in the application of these elements to crop plants, as it can affect the growth and development of these plants. Application of adequate amount of rare earth elements can promote the germination of seeds, roots and shoot development and also increase the plant biomass, and improve the quality of fruiting. These elements can improve the growth and development of plants when provided at an appropriate concentration. Studies originating from China showed that low amount of lanthanide metal elements including La, promote the growth of crops and can be used as fertilizers[1-2]. If the concentration exceeds the optimum level, they can inhibit plant growth and even cause mortality[3].Recently lanthanides Schiff base complexes have an important and remarkable area of research due to their simple synthesis, versatility and diverse range of applications[4-5].Literature survey showed that metal chelates with Schiff base ligands acting a significant role in the advancement of coordination chemistry[6-10]. Although several transition and main group metal complexes of Schiff bases have been reported, those have 1-H-indole-2,3-dione(isatin) moiety[11-14] but lanthanide complexes with this moiety have been less attention[15-16]. 1-H-indole-2,3-dione and its derivatives are gaining increasing importance in biological areas and it also acts as uncooked material for drug synthesis. It is evident from literature that Schiff base of isatin exhibit wide range of biomedical application like bactericidal, antifungal and anti-viral[17-18], anti-HIV[19], DNA cleavage[20], anti-oxidant [21], plant growth regulatory activity[22] and many more.

It is clear from the literature survey that the use of rare earth elements in agriculture to promote the growth of plants, so keeping this fact in mind decide to synthesize and characterize metal complexes of La(III),Sm(III) and Yb(III) with 5-nitro-3-(indolin-2-one) hydrazinecarbothioamide by conventional thermal method to evaluating their structure and bonding. Plant growth regulatory activity on Seeds of the

*Trigonellafoenum-graecum* (Methi) has been studied. The present experiment was conducted with a view to study the following:

1. Effect of compounds on germination of seeds, root, shoot length and Seed vigourindex(SVI).
2. Comparative effect of the complexes and ligand on the above mentioned factors and compared to the control i.e. water.

**Experimental**

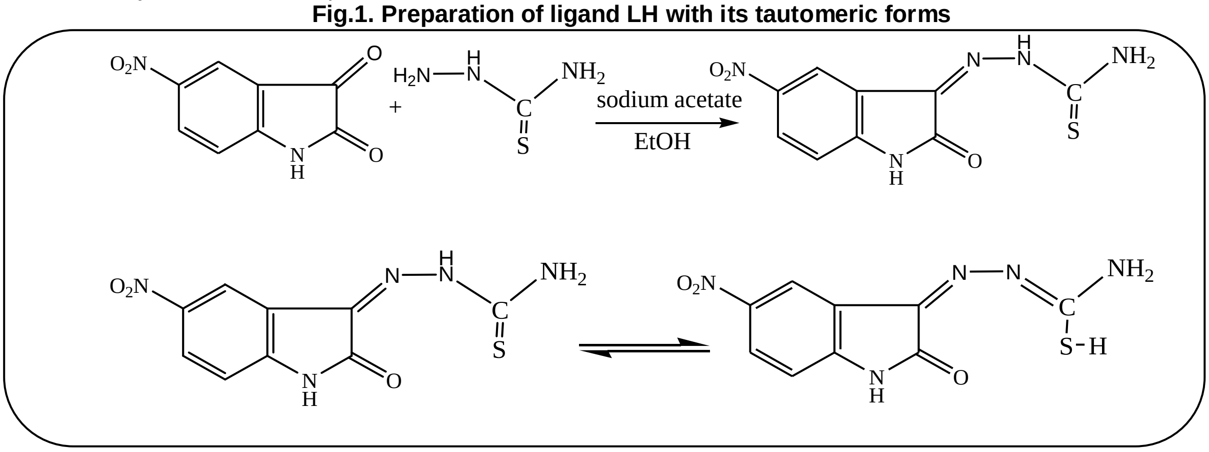
**Materials and Reagents**

The metal chlorides ($LnCl_3.6H_2O$) were obtained from Alfa aesar and used as such and solvents employed in this study were used after distillation. All the chemicals and solvents used were of analytical grade. All the solvents were dried and distilled before use. The metal contents were estimated complexometrically with EDTA using Erichrome Black T as an indicator. Molecular weight determinations were carried out by the Rast Camphor Method. Sulfur and nitrogen were estimated by the Messenger's and Kjeldahl's method, respectively. C and H analyses of the complexes, as well as the ligands, were performed at NFDD, Saurashtra University, Rajkot. Melting points were determined by using capillaries in an electrical melting point apparatus. Infrared (IR) spectra of the ligand and their complexes were recorded on a Nicolet Magna FTIR-550 spectrophotometer as KBr pellets. $^1$H and $^{13}$CNMR spectra were scanned on a 400MHz Advance III NMR, Spectrometer in DMSO-d6 using TMS as an internal standard at room temperature.

**Preparation of Schiff base ligand (LH)**

5-nitro-3-(indolin-2-one) was prepared by the literature method in the laboratory [23]. The corresponding ligand was prepared(Fig.1) by the condensation of 5-nitro-3-(indolin-2-one) with hydrazinethiosemicarbazide hydrochloride in the presence of sodium acetate in absolute alcohol, in the 1:1 molar ratio. The reaction mixture was refluxed over a water bath for 3–4 h and allowed to stand overnight. The products were recrystallized from the ethanol and dried in *vacuo*. Their physicochemical properties and analytical data of the ligands are given in Table 1.

**Fig.1. Preparation of ligand LH with its tautomeric forms**




**Synthesis of The Sodium Salt of the Ligand**

Sodium metal was taken corresponding to the ligand and both the Na metal and ligand was dissolved in the least amount of methanol independently. Finally, these two solutions had been dissolved to prepare sodium salt of the ligand. In this process, the sodium metal initially reacts with methanol and forms sodium methoxide. This sodium methoxide in the next step reacts with the ligand and replaces acidic proton from the enolic form of the ligand with the sodium metal and forms Na salt of the particular ligand.

**Synthesis of Complexes**

The ethanolic solution of a hydrated metal chloride, $LnCl_3.6H_2O$ was added to the ethanolic solution of sodium salt of the ligands LH in 1:3 molar ratio(s). Further, it was refluxed for ~16h. On cooling, the sodium chloride which formed in this reaction was filtered through the alkoxy funnel and the excess of solvent was removed under reduced pressure. The unfinished product was washed with ethanol for many times to remove unused metal chloride. The physical properties and analytical data of these complexes are summarized in Table 1. Suggested structure of the complexes is given in Figure 2

The reactions of hydrated lanthanide chlorides with monobasic bidentate ligands have been shown by the following general equation:-

$$LnCl_3.xH_2O + 3LNa \xrightarrow{MeOH} [Ln(L)_3].nH_2O + 3NaCl + (x\text{-}3)H_2O$$

Where, LNa is the sodium salt of the ligand, Ln = La, Sm and Yb, n=3 and x=6.

**Table 1:-The Physicochemical Properties and Analytical Data of the Ligands and Their Metal Complexes**

| Ligand | Colour/ State | M.P. (°C) | Analyses (%) Found/(Calcd.) | | | | | Mol.Wt. Found/ (Calcd.) |
|---|---|---|---|---|---|---|---|---|
| | | | C | H | N | S | La/Sm/Yb | |
| LH | Dark Yellow/ Solid | 247 | 40.63 (40.75) | 2.79 (2.65) | 26.32 (26.40) | 12.26 (12.08) | ----- | 264.54 (265.24) |
| $[La(L)_3].3H_2O$ | Dark Yellow/ Solid | 260-265(d) °C | 32.71 (32.90) | 2.35 (2.45) | 20.91 (21.31) | 9.51 (9.75) | 13.91 (14.09) | 983.88 (985.64) |
| $[Sm(L)_3].3H_2O$ | Dark Yellow/ Solid | 272-277(d) °C | 28.11 (32.52) | 1.19 (2.42) | 18.81 (21.07) | 7.41 (9.64) | 13.51 (15.07) | 996.18 (997.10) |
| $[Yb(L)_3].3H_2O$ | Dark Yellow/ solid | 274-279(d) °C | 26.71 (31.79) | 1.87 (2.38) | 17.81 (20.60) | 6.71 (9.43) | 10.91 (16.96) | 1015.18 (1019.78) |

**Plant Growth Regulating Activity (Towel Paper Method)**

Lanthanide elements on crop and medicinal plants widely used to promote the growth of plants is well known [24-25]. Keeping this fact in view, the ligand(LH) and La(III) ,Sm(III) and Yb(III) complexes were used to carry out the germination study on *Trigonellafoenum-graecum*(Methi). The germination method was followed by the literature method[26]. Percent germination and normal seedlings were recorded on the 6th days. Seeds which possess the ability to develop into healthy plants considered as a normal and healthy seedling. In the second experiment, the seeds were treated with physiologically active concentration of the plant growth regulators solution for 6 h at room temperature and drying them to the original moisture level by a hot air circulating oven. Later on, uniform size seeds were positioned on Whatman No. 1 filter paper lying in the glass Petri plates. Each Petri plate has 50 seeds placed atequidistance. The filter papers were moistened with fresh solutions of required concentrations. The concentrations of the plant growth regulators used were 5, 10, and 25 ppm. Compounds were tested with the seeds of plant and their growth was studied in comparison to water as a control.

Total germination percentage is calculated by the following formula:-

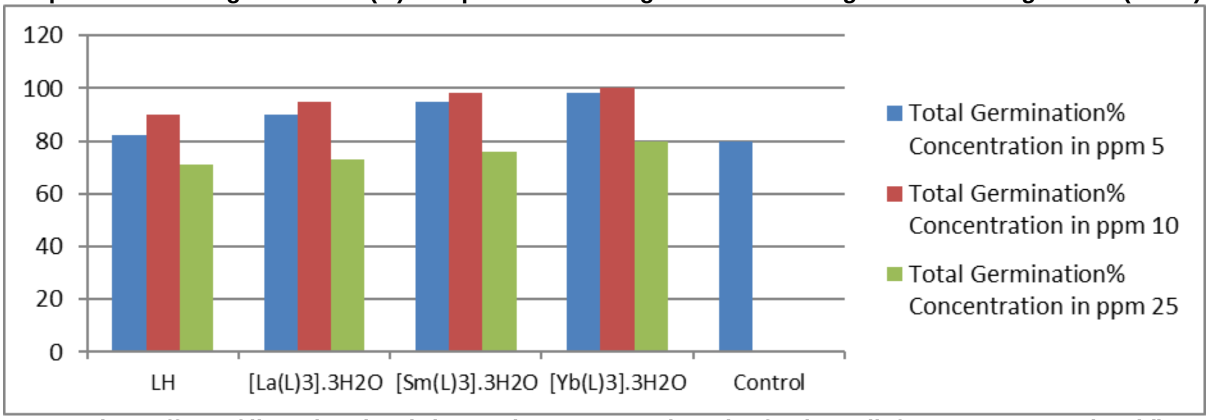
Total Germination% = [No. of seeds germinated/Total seeds] x100

Vigor index was determined by using the following equations:-

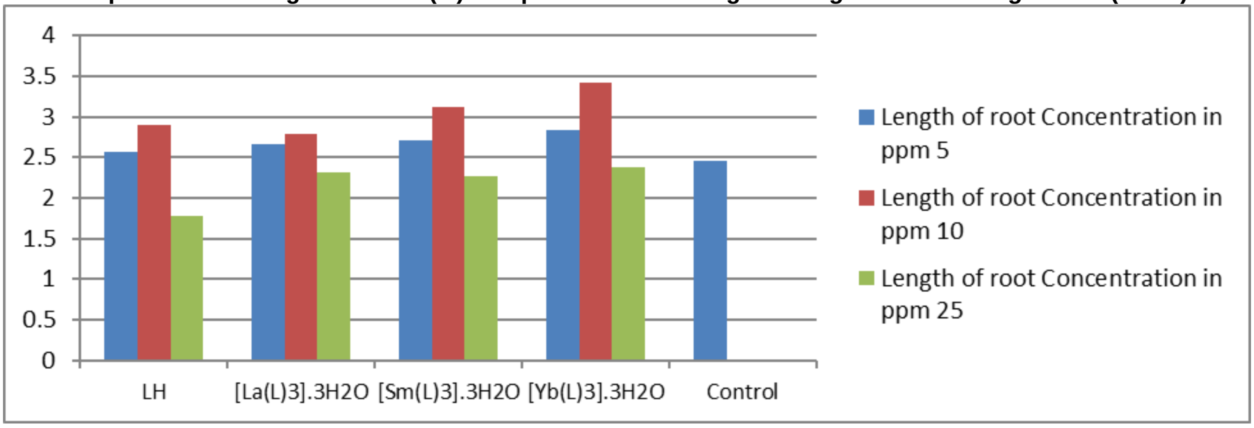
Seed Vigourindex(SVI) = [% germination] x [root length + shoot length]

The results of plant growth parameters such as percentage of germination, shoot length, root length, seed vigor index for *Trigonellafoenum-graecum*(Methi) are reported in Graph no. 1 to 4

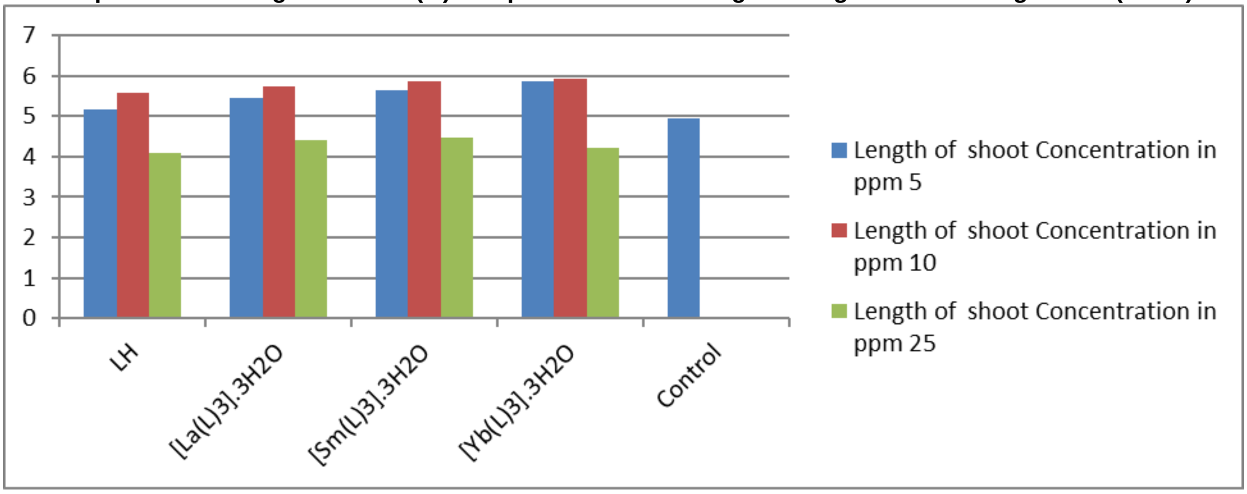
**Graph 1–Effect of ligand and Ln(III) complexes on seed germination of *Trigonellafoenum-graceum*(Methi)**



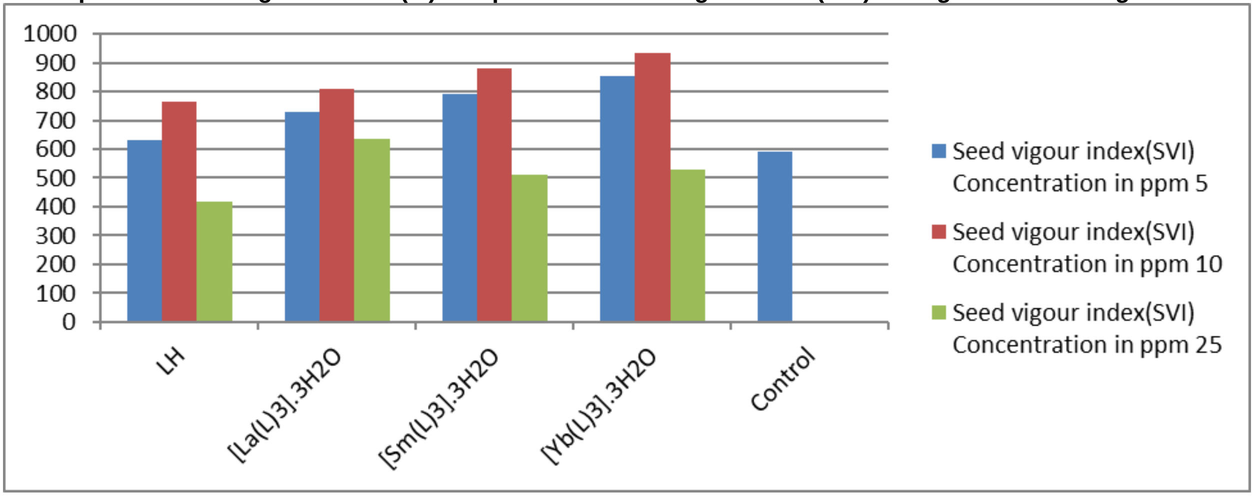

**Graph 2–Effect of ligand and Ln(III) complexes on root length of *Trigonellafoenum-graceum*(Methi)**



**Graph 3–Effect of ligand and Ln(III) complexes on shoot length of *Trigonellafoenum-graceum*(Methi)**




**Graph4 - Effect of ligand and Ln(III) complexes on Seed vigour index(SVI) of *Trigonellafoenum-graceum***




**Result and Discussion**

***IR spectra***

The IR spectra of the free ligand LH display two sharp bands at 3440 and 3320–3325 $cm^{-1}$ due to $v_{asym}$ and $v_{sym}$ vibrations of the $-NH_2$ group, respectively, which remain at almost the same positions in the spectra of the complexes, suggesting that the $-NH_2$ group is not involved in chelation. The broad band in the region 3240–3286 $cm^{-1}$ due to *v*(NH) vibrations, is absent from the spectra of the $[Ln(L)_3].3H_2O$ complexes, indicating the deprotonation of this group on coordination with the metal atom. The spectra of the ligands and complexes exhibit a strong band at 3170-3180 $cm^{-1}$ which is assigned to *v*(NH) of the indole ring of the 1-H indole-(2,3-dione) moiety. This band remains almost unchanged in the spectra of the metal complexes indicating that 1-H indole-(2,3-dione) ring –NH does not take part in complexation. The band at 1615-1625 $cm^{-1}$ in the spectra of the free ligands due to *v*(>C=N), is shifted to a lower wave number(10–20$cm^{-1}$) in the complexes, suggesting coordination through the azomethine nitrogen atom. The bands at 1020-1035 $cm^{-1}$ due to >C=S and shifted towards lower frequency in the complexes, indicating coordination of sulphur and oxygen to the metal atom, respectively. The appearance of the non-ligand bands further support the bonding of the ligands to the metals through the nitrogen, sulphur atoms. The coordination through the azomethine nitrogen atoms and the thiolosulphur is further substantiated by the appearance of new bands in the regions 461-474 $cm^{-1}$ and 401-428 $cm^{-1}$ in the lanthanide complexes due to *v*(Ln←N) and *v*(Ln←S)frequencies, respectively.

***$^{1}H$ NMR and $^{13}C$ NMR Spectra***

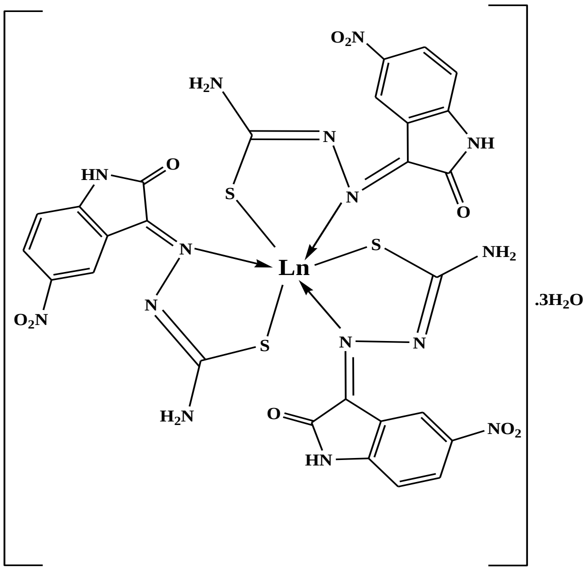
The $^{1}H$ NMRspectra of free ligand show the broad signal of –NH protons signals at $\delta$ 11.31 ppm, this peak disappear in the spectra of the complexes which indicate the deprotonation during the formation of complex. Indole ring proton show a broad signal at $\delta$11.96 ppm and this band remains almost unchanged in the spectra of the metal complexes, indicating that 1-H indole-(2,3-dione) ring –NH does not take part in coordination. The free ligand shows a multiplet at $\delta$ 6.76-8.26 ppm for the aromatic protons. Signal of the ammino group remain almost at the same position which indicate the non-involvement of this group in coordination. In $^{13}C$ NMR spectrum of ligand, signal observed at $\delta$ 167.85 ppm due to >C=S group which shifted to higher value(*$\delta$ 172.43 ppm)* in the spectra of complex which indicate the formation of coordinate bond of sulphur atom to the lanthanide metal atom. The aromatic carbon signals are observed in the range *δ* 120.31–149.97 ppm. Thus, the 1H and 13C NMR spectra, confirms the monobasic bidentate nature of the ligand, which has already been suggested by the IR spectral studies, discussed above.$^{1}$H and $^{13}$C NMR spectral data of the ligand and their La(III) complexes were listed in table 2.

**Table 2 $^{1}$H and$^{13}$C NMR (δ, ppm) spectral data of the ligands and their La(III) complexes**

| $^{1}$H NMR | | | | | $^{13}$C NMR | | |
|---|---|---|---|---|---|---|---|
| **Compounds** | **-$NH_2$** | **-NH (bs)** | **-NH(ring) (bs)** | **Aromatic protons(m)** | **(C=S/C-S)** | **(>C=N)** | **Aromatic carbon** |
| LH | 3.47 | 11.31 | 11.96 | 6.76-8.26 | 167.85 | 156.24 | 142.12,124.19,128.93, 127.16, 127.91, 123.03 |
| [La(L)].3$H_2O$ | 3.46 | - | 11.98 | 6.78-8.36 | 172.43 | 166.45 | 142.58,124.39,129.49, 127.89, 128.85, 123.64 |

On the basis of physicochemical and spectral data the proposed structure of the complexes is shown in figure 2.

**Fig. 2 Proposed structure of [Ln(L)$_3$].3$H_2O$ complexes where Ln = La, Sm and Yb**




**Plant Growth Activity**

The result of the plant growth study showed that lanthanide metal complexes are more potent than the ligand and control. All metal treatments affected the development and growth of roots, the shoot lengths of *Trigonellafoenum-graceum*were significantly increased as compared to control treatment (Graph 1 to 4). In the case of ligand and metal complexes, the shoots and root length increases when concentration increases from 5ppm to 10ppm, however further increase in concentrations(25ppm) caused a failure of seed germination and also inhibit shoot and root length. Reduction in shoot and root lengths could be due to excess accumulation of metal salts in the cell wall, which reduce the metabolic activities and limits the cell wall elasticity[27]. Also results indicate that ligand and metal complexes concentration induce more positive growth on shoot than the roots.

**Conclusion**

The bonding of ligand to metal was confirmed by the analytical, IR, NMR spectral studies. From the present investigation it has been observed that Schiff base ligand was monobasic bidentate towards La(III), Sm(III) and Yb(III). Analytical and physicochemical studies reveal that the octahedral geometry was assigned for all complexes. This paper extended the plant growth regulatory activity on *Trigonellafoenum-graceum*(methi) plant and outcomes shows that metal complexes have higher plant growth activity than the ligand and further the lower concentration of lanthanides metal Schiff base complexes is beneficial to promote plant growth instead of higher concentration.

**Endnotes**

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