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Synthesis, structural characterization and pesticidal studies of lanthanide complexes with tridentate Schiff base ligands

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Tridentate Schiff base ligands 2-acetamido propanoic acid isonicotinoyl hydrazone (L^1H_2) and 2-acetamido acetic acid isonicotinoyl hydrazone (L^2H_2) and their Ln(III) metal complexes have been synthesized. Eight mononuclear lanthanide complexes of the type $[Ln(L^1)(L^1H)].3H_2O$ have been synthesized and characterized by elemental analysis (CHNO), magnetic susceptibility, electronic and spectral studies. Ligands and lanthanide complexes of the type $LnCl_3.6H_2O$ (where Ln = La, Pr, Nd and Sm) react in 2:1 stoichiometric ratio. Electronic spectra indicate that there is slight covalent character in the bonding between metal and ligand. Magnetic moment values show that all metal complexes are paramagnetic except the La(III) complexes. The effect of Ln(III) complexes with selected ligand(L^1H_2) have been tested for pesticidal activity on *Helicoverpa armigera* and *Spodoptera litura*. As compared to the ligand, the complexes are found to have increased pesticidal activity.

Keywords: Electronic studies, Spectral studies, Lanthanide(III) metal complexes, Magnetic susceptibility, Pesticidal activity, Tridentate Schiff base ligands

Infectious plants diseases due to harmful microbes are the leading cause of the destruction of many fruits, groundnuts and plants leave worldwide and in which major part is India[1,2]. Pests affect the crop yield and quality of fruits, thereby dropping its market worth that's why pesticidal resistance has become global anxiety. The clinical efficacy of many existing pesticides is being threatened by the emergence of multidrug-resistant pathogens. In view of the rapid development and also challenging demands it has become necessary to synthesized and screen newer compounds for pesticidal activity[3-6]. Such a study is highly useful to evaluate the possibilities of using metal complexes against microorganism. Study of the coordination chemistry of lanthanide metal ions with several categories of Schiff base ligands has been heightened by the recent developments in the arenas of bioinorganic chemistry and medical science[7-10]. In our present study, we select amino acid Schiff base complexes because of their physiological and pharmacological activities[11-13]. Studies of such transition metal ion complexes with Schiff bases have recently been published[14-16], although amino acid Schiff base ligands with lanthanide metal ions are less common.

In this context, our aim is to synthesised and characterization of new amino acid Schiff base ligands derived from isonicotinoyl hydrazones and their La (III), Pr(III), Nd(III) and Sm(III) complexes. The prepared ligands and metal complexes were characterized by elemental analysis, IR, ^1H NMR, magnetic susceptibility measurements and electronic spectra. Selected ligand 2-Acetamido propanoic acid isonicotinoyl hydrazone(L^1H_2) and its complexes were screened for their pesticidal activity.

Experimental Section

Materials and Methods

All Chemicals and reagents were used analytical grade, used without any extra purification. Hydrated lanthanide chlorides($LnCl_3.6H_2O$), isonicotinic acid hydrazide and 2-acetamido acetic acid purchased from Alfa-Aesar.

The lanthanide metal contents (La, Pr, Nd, and Sm) were calculated complexometrically using EDTA and Erichrome Black T as an indicator. The Kjeldahl technique was used to measure nitrogen, and the Micro-analytical Laboratory of the Department of Chemistry, Punjab University, Chandigarh, was used to estimate carbon and hydrogen in ligands as well as metal complexes. In KBr discs, IR spectra were collected using a Perkin-Elmer model 577 grating spectrophotometer in the range 4000-200 cm^{-1}. TMS was used as the internal standard for ^1H NMR spectra acquired on a Jeol-AL-300 FT NMR spectrometer in DMSO-d_6. At SAIF, IIT, Madras, Chennai, the electronic spectra were captured using a Varian-Cary/5E spectrophotometer. The Rast Camphor Method was used to estimate molecular weights. Magnetic susceptibility measurements were made at RT with the Faraday balance using $Hg[Co(NCS)_4]$ as calibrant. To test the homogeneity of the synthesized compounds, TLC was employed on silica gel-G using different solvents.

Preparation of the ligands

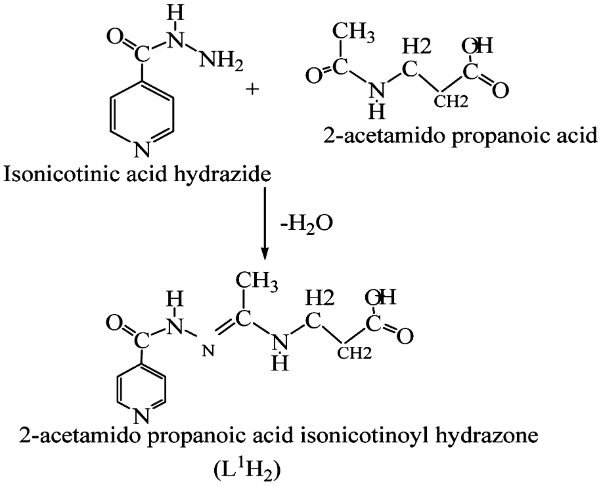
The isonicotinoyal hydrazones of 2-acetamido propanoic acid and 2-acetamido acetic acid were synthesized by the condensation reaction of isonicotinic acid hydrazide with 2-acetamido acetic acid and 2- acetamido propanoic acid in 1:1 molar ratio, respectively, in the medium of ethanol. The contents were refluxed for about 3.5-5 h. These were purified by recrystallization in the same solvent and dried. The synthetic route of the ligands is given in Scheme 1 and Scheme 2.

Synthesis of the sodium salt of the ligands

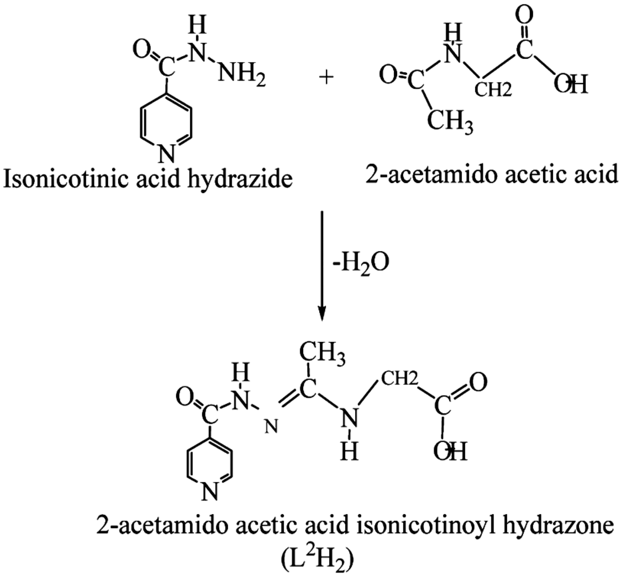
Sodium metal was taken corresponding to the ligand. Then, the ligand and sodium metal were both individually dissolved in a small quantity of methanol. Finally, a sodium salt of the ligand was made by dissolving these two solutions. In this procedure, methanol and sodium metal first interact to generate sodium methoxide. In the next step, this sodium methoxide combines with the ligand to create sodium salt of the specific ligand by exchanging an acidic proton from the enolic form of the ligand with the sodium metal. Although the reaction rate would be slower than it would be with sodium salt, we may still employ the ligand in this manner. It is simpler to remove chloride from metal chloride using sodium than with hydrogen.

Synthesis of the lanthanide(III) complexes

In a 1:2 molar ratio, the methanolic solution of the sodium salt of the ligand and the methanolic solution of the hydrated lanthanide chloride ($LnCl_3•6H_2O$) were combined. The mixture was then refluxed for 30-36 h. The excess solvent from the mother liquid was removed at reduced pressure, and the precipitate of NaCl that forms during the reaction was removed by filtering through the G-4 alkoxy funnel. The complexes were then dried under decreased pressure after being rinsed with a solution of methanol and petroleum ether(50:50). Cyclohexane was used to wash and recrystallize the resultant compounds. They were also subjected to a TLC homogeneity testing using silica gel-G. The molecular weight analysis has revealed that the complexes are monomeric. Table 1 provides analytical information and physical characteristics of the compounds. The systematic reaction for preparation of complexes is shown in Scheme 3.



Scheme 1 — Preparation of ligand 2-Acetamido propanoic acid isonicotinoyl hydrazone(L^1H_2)



Scheme 2 — Preparation of ligand 2-Acetamido acetic acid isonicotinoyl hydrazone(L^2H_2)

Table 1 — Analytical data and physical properties of the ligands and their complexes

Compd	Colour	m.p. (°C)	Found (Calcd) (%) C	H	N	Ln	M_{eff} (B.M.)	Mol. wt. Found (Calcd)
$(L^1H_2), C_{11}H_{14}N_4O_3$	Cream	110	52.68 (52.79)	5.51 (5.63)	21.74 (22.38)	–	–	228.35 (250.24)
$(L^1H_2), C_{10}H_{12}N_4O_3$	White	101	50.76 (50.84)	5.32 (5.48)	22.82 (23.71)	–	–	214.41 (236.21)
$La(L^1)(L^1H).3H_2O$	Light red	90	38.04 (38.27)	4.39 (4.52)	17.01 (16.22)	19.89 (20.11)	0.00	674.32 (690.435)
$Pr(L^1)(L^1H).3H_2O$	Brick red	105	37.98 (38.16)	4.38 (4.51)	17.10 (16.18)	19.56 (20.34)	3.60	668.85 (692.43)
$Nd(L^1)(L^1H).3H_2O$	Reddish brown	75	37.58 (37.97)	4.23 (4.49)	15.56 (16.10)	19.59 (20.73)	3.49	709.57 (695.77)
$Sm(L^1)(L^1H).3H_2O$	Dark yellow	80	37.24 (37.64)	4.28 (4.45)	14.85 (15.96)	21.16 (21.42)	1.50	688.02 (701.89)
$La(L^2)(L^2H).3H_2O$	Dark brown	100	36.12 (36.26)	4.02 (4.10)	16.71 (16.91)	20.10 (20.96)	0.00	637.32 (662.38)
$Pr(L^2)(L^2H).3H_2O$	Mud yellow	112	36.04 (36.15)	4.01 (4.09)	15.97 (16.86)	20.86 (21.20	3.69	638.95 (664.38)
$Nd(L^2)(L^2H).3H_2O$	Blackish brown	105	35.81 (35.97)	3.98 (4.07)	16.62 (16.78)	20.89 (21.60)	3.49	629.79 (667.72)
$Sm(L^2)(L^2H).3H_2O$	Brown	120	35.43 (35.64)	3.90 (4.03)	16.46 (16.62)	21.84 (22.31)	1.61	652.91 (673.84)

$$LnCl_3.6H_2O + 2\ LH_2 + 4\ Na \xrightarrow{MeOH} [Ln(L)(LH)].3H_2O + 3\ NaCl + 3H_2O$$

Where, Ln = La, Pr, Nd and Sm, $LH_2 = L^1H_2$ and L^2H_2

Scheme 3 — Synthetic scheme of the complexes

Pesticidal Activity

The pesticidal activity of one ligand L^1H_2 and its lanthanide(III) complexes has been conducted on *Helicoverpa armigera* and *Spodoptera litura pets*. The nature of damage caused by *Helicoverpa armigera* and *Spodoptera litura* was studied critically by observing infested plants of Chickpea (*Cicer arietinum*) and cotton plants, respectively. Their larvae were subjected to a bioactive experiment. The activity of the ligand and metal complexes was assessed using the larval death rate.

Materials and methods

Helicoverpa armigera and *Spodoptera litura* larvae were used in the experiment. Daily temperature and relative humidity measurements were taken in the laboratory.

Preparation of the solution

The solutions of different concentration(0.02%, 0.05% and 0.1%) of compounds were prepared by adding required quantity of compounds in methanol. Distilled water was taken as control.

Rearing technique of *Helicoverpa armigera* and *Spodoptera litura*

To raise the initial culture of *Helicoverpa armigera* and *Spodoptera litura* in laboratory large number of larvae were collected from the infested fields of chickpeas and cotton, respectively. Field collected larvae of both the pests were reared separately in round galvanised trays (35 cm x 11.5 cm) containing fresh tender leaves of chickpeas and cotton, respectively. The petiole of each leaf was warped with cotton wool and dipped in water to maintained turbidity of leaves. Every day sufficient amount of fresh leaves of chickpeas and cotton were provided to larvae of both the pest, respectively. After changing all the stages of life cycle of the pest, new generations of third stage larvae were used for experiment.

Bio-efficacy of the compounds

The laboratory trials included eleven treatments, each at three concentrations: 0.02%, 0.05%, and 0.1%. 2 mL of each concentration of the corresponding treatment's suspension was applied uniformly on chickpea and cotton leaves put in

Petridishes using Potter's tower (15 cm diameter). Petridishes with treated leaves were placed under a ceiling fan to allow the water on the leaves to evaporate. The treated leaves were put to glass jars when the water had completely evaporated (15cm height x 10 cm diameter). The third instar larvae of both pests were then introduced separately into each glass jar and allowed to feed on treated food materials for 24 hours. Three replications of each treatment were maintained. After 24 hours of treatment, fresh untreated chickpea and cotton leaves were delivered daily. The number of deaths was reported 72 hours following therapy. The mortality % was computed, and the resulting data was statistically analysed.

Statistical analysis

In terms of percentage mortality in larvae, the mortality of *Helicoverpa armigera* and *Spodoptera litura* larvae in proportion to the original population was calculated. The % data were then converted to an arcsine scale and statistically analysed using a Completely Randomized Design (CRD).

Results and Discussion

Magnetic studies

The magnetic moment values of the present complexes show that there is very little deviation of the μ_{eff} values from the Van-Vleck values, indicating that there is very little interaction of 4f electrons in metal-ligand bond formation, because the 4f electrons are so well screened that they are the least affected by external influences (Table 1). It is possible that the current ligand is insufficiently strong to impact the f electrons. Lanthanum compounds were discovered to be diamagnetic, as predicted, whilst the others were paramagnetic. Because of the low J-J separation, the thermal population of a higher energy level adjacent to the ground state resulted in a somewhat larger value in the instance of samarium complex.

Electronic spectra

The ligand's UV-Visible spectra has bands at 299 and 332 nm that correspond to n–π* electronic transitions. The spectra of the complexes were comparable to those of the corresponding aquo ions, with a modest shift of spectral bands to lower energy. Table 2 shows the nephelauxetic effect (β)[17], Sinha's covalency parameter (δ%)[18] (metal ligand covalency percentage), bonding parameter ($b^{1/2}$)[19], and covalency angular overlap parameter (η) for Pr(III) and Sm(III) complexes. Sinha's covalency parameter (δ %) indicates the degree of covalency and is calculated using the equation:

$$\delta\% = \frac{(1-\beta\text{avg})}{\beta\text{avg}} \qquad ...(1)$$

$$\text{where, } \beta\text{avg} = \nu(\text{complex}) / \nu\,(\text{metal ion})$$

The magnitude of the bonding parameters ($b^{1/2}$) suggests the degree of involvement of 4f orbitals in metal-ligand bonding and related to nephelauxetic ratio (β)by the equation,

$$\text{b}1/2 = [(1-\beta\text{avg})/2]1/2 \qquad ...(2)$$

Angular covalency is calculated by the following equation:

$$\eta = [(1-\beta avg)/\beta avg]1/2 \qquad ...(3)$$

An interesting finding is the strength of the f-f transitions. The strength of the regular f-f transitions does not alter significantly. The hypersensitive transitions, on the other hand, exhibit substantial fluctuations in intensity. The shape and strength of these transitions, according to Karraker[20], reveal the complex's geometry. The nephelauxetic ratio (β) is less than one in the present complexes, and positive values of $b^{1/2}$ and δ suggest minor covalent interaction between the metal and the ligand. Because to lanthanide contraction, the covalency drops from Pr(III) to Sm(III) complexes (Table 2). The current complexes have a coordination number of six, based

Table 2 — Electronic spectral data of Pr(III) and Sm(III) complexes

Compd	Assignment	ν_{max} of Ln^{+3} ion (cm^{-1})	ν_{max} of complexes(cm^{-1})	β	1-β	$b^{1/2}$	δ	η
$[Pr(L^1)(L^1H)].3H_2O$	$^3H_4{}^{-1}D_2$	16898	16698	0.9882	0.0118	0.0543	1.1971	0.0059
	$^{-3}P_0$	20798	20598	0.9904	0.0096	0.0490	0.9703	0.0048
	$^{-3}P_1$	21229	21029	0.9906	0.0094	0.0485	0.9509	0.0047
	$^{-3}P_2$	22397	22237	0.9928	0.0071	0.0422	0.7191	0.0036
$[Sm(L^2)(L^2H)].3H_2O$	$^6H_{5/2}{}^{-4}I_{13/2}$	21602	21442	0.9926	0.0074	0.0430	0.7455	0.0037
	$^{-4}F_{9/2}$	24901	24701	0.9920	0.0080	0.0448	0.8095	0.0040
	$^{-6}P_{5/2}$	24000	23800	0.9917	0.0083	0.0466	0.3480	0.0041

Table 3 — IR spectral data of ligands and their Lanthanide(III) complexes

Compd	ν(NH)	ν(C=O)	ν(COO$^-$)		ν(C=N)	ν(M→N)	ν(M→O)
			ν_{sym}	ν_{asym}			
L^1H_2	3240	1712	1425	1516	1632	–	–
L^2H_2	3300	1714	1428	1518	1635	–	–
$La(L^1)(L^1H).3H_2O$	–	1020	1389	1448	1620	539	604
$Pr(L^1)(L^1H).3H_2O$	–	1005	1394	1458	1623	540	612
$Nd(L^1)(L^1H).3H_2O$	–	1015	1396	1470	1625	550	615
$Sm(L^1)(L^1H).3H_2O$	–	1012	1392	1485	1622	545	610
$La(L^2)(L^2H).3H_2O$	–	1002	1389	1455	1624	550	608
$Pr(L^2)(L^2H).3H_2O$	–	1000	1390	1478	1620	543	615
$Nd(L^2)(L^2H).3H_2O$	–	1050	1393	1450	1625	548	605
$Sm(L^2)(L^2H).3H_2O$	–	1035	1394	1487	1624	550	616

on a comparison of their spectra to those of known compounds. All of the complexes' electronic spectra are obviously compatible with an octahedral geometry.

IR Spectra

In the spectra of the ligands the absorption bend at 3300-3240, 1635-1632 and 980-995 cm^{-1} have been attributed to ν(N-H), ν(C=N) and ν(N-N), respectively. The hydrazide ν(N-H) bands disappeared in the complexes indicating the absence of the >C=O group and loose of the NH proton *via* enolization. After enolization, new bands appeared. A sharp band at 1620 cm^{-1} was diagnostic of the >C=N-N=C< group indicating transformation of the carbonyl group to its enolic form through keto-enol or amide-imidol tautomerism and subsequent coordination of the enolic oxygen to metal after deprotonation.

The bands in the 3416-3429 cm^{-1} region in the spectra of the Schiff bases are ascribed to ν(OH) vibrations of carboxyl group. The disappearance of this band indicates deprotonation of the -OH of carboxyl group with involvement of the ‘O’ in bonding. The characteristic vibrations of the free ligands were shifted upon complex formation. A shift to a lower frequency, (relative to the free Schiff bases) of >C=N- stretching vibration in the complexes showed that coordination occurs through the nitrogen atoms of the azomethine group. The characteristic absorption peaks in the Ln(III) complex for ν(C=N) and ν C=O(hydrazoic) vibrations were at 1620-1625 and 1000-1050 cm^{-1} respectively, while these peaks of the ligands were at 1632-1635 and 1712-1714 cm^{-1}, respectively. These shifts demonstrated that the above groups had taken part in coordination to metal ions.

The high absorptions at 1516-1518 and 1425-1428 cm^{-1} in the IR spectra of the Schiff bases are due to the asymmetric and symmetric(COO$^-$) bands. The complexes' IR spectra revealed a significant band in the areas 1448-1487 and 1389-1396 cm^{-1}, which can be attributed to the carbonyl group. After complexation, this band moved to lower frequency values, showing that the 'O' atom of the band at 604-616 cm^{-1} is allocated to ν (M-O). These show that the carbonyl's 'O' has established a coordination bond with the lanthanide ion. Weak bands between 539-550 cm^{-1} are attributed to ν (M-N) band. These results demonstrate that the azomethine group's 'N' binds to the lanthanide ion. IR spectral data of the ligands and their metal complexes are shown in Table 3.

$$LnCl_3.6H_2O + 2\ LH_2 + 4\ Na \xrightarrow{MeOH} [Ln(L)(LH)].3H_2O + 3\ NaCl + 3H_2O$$

Where, Ln = La, Pr, Nd and Sm, $LH_2 = L^1H_2$ and L^2H_2

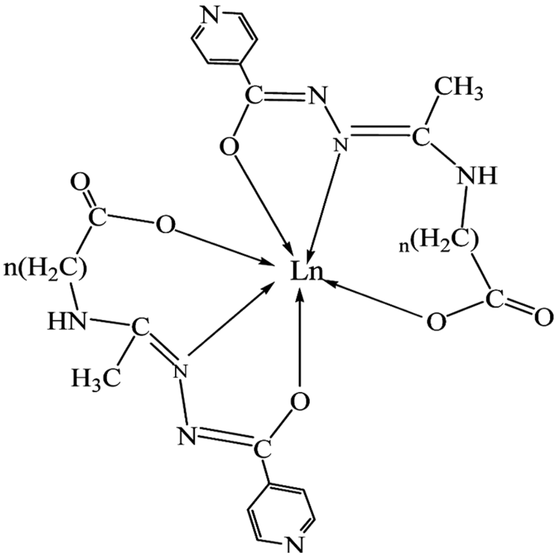
^{1}H NMR Spectra

The ^{1}H NMR spectra of the ligands show the expected signals due to the alanine –CH_3, alanine –CH, glycine –CH_2, glycine -NH at δ 2.59, 2.14, 2.30 and 9.13, respectively, remain unchanged in the spectra of the complexes. The signals due to OH of the carbonyl group and hydrazidic –NH were obtained at δ 10.92 and 9.34, disappeared in the spectra of the complexes suggesting coordination through these groups. The multiplet at δ 6.8-7.9 due to aromatic protons is unaffected in case of metal complexes.

On the basis of forgoing discussion of the following geometry has been proposed for the Ln(III) complexes (Fig. 1).

Where n=2 for $[Ln(L^1)(L^1H)].3H_2O$ and n=1 for $[Ln(L^2)(L^2H)].3H_2O$

Ln = La, Pr, Nd and Sm



Where n=2 for $[Ln(L^1)(L^1H)].3H_2O$ and n=1 for $[Ln(L^2)(L^2H)].3H_2O$
Ln = La, Pr, Nd and Sm

Fig. 1 — Proposed structure of Ln(III) complexes

Pesticidal effect of compounds

The effect of compounds against of *Helicoverpa armigera* and *Spodoptera litura* were evaluated under laboratory conditions (Fig. 2). The effect of the different concentrations on the larval mortality rate was examined at 72 hours after treatment. The results revealed that there was significant difference in percent mortality at different concentrations and it was noted that as concentration increases the larval mortality rate also increases. At 0.02% concentration the complexes gave 32.29-79.05 percent mortality rate, at 0.05% concentration the complexes gave 39.95-83.22 percent mortality rate and at 0.1% concentration the complexes gave 61.79-85.40 percent mortality rates and it was significantly superior over rest of the treatments. The ligands ranked second in effectiveness at these concentratios (0.02, 0.05 and 0.1%) with 27.98-36.10, 18.4-20.30 and 33.25-48.87 percent mortality, respectively. The treatment with distilled(control) gave no significant mortality of larvae of *Helicoverpa armigera* and *Spodoptera litura*, which leads to starvation in the developing larvae. All the complexes were found to be more active against both the pests used than the ligands themselves. Pesticidal effect of *Helicoverpa armigera* and *Spodoptera litura* are shown in Table 4 and Table 5.

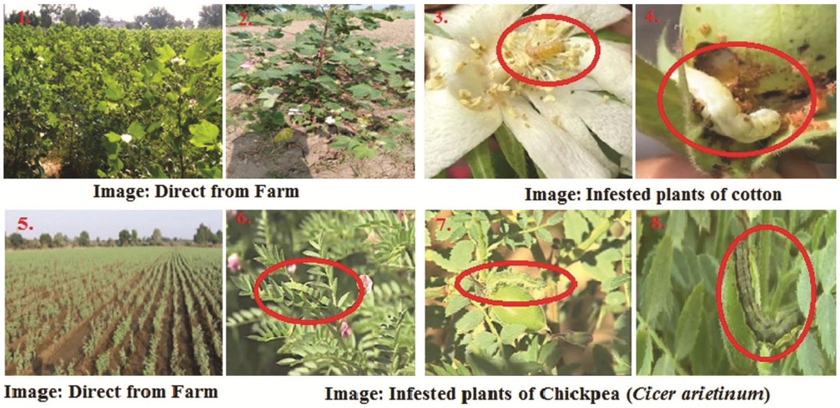


Image: Direct from Farm **Image: Infested plants of cotton**

Image: Direct from Farm **Image: Infested plants of Chickpea (*Cicer arietinum*)**

Fig. 2 — Images direct from cotton and Chickpea (*Cicer arietinum*) farm and showing larvae in round circle

Table 4 — Pesticidal effects of ligand L^1H_2 and their complexes against *Helicoverpa armigera* at 72 hrs after treatment

Treatment	% Solution		
	0.02	0.05	0.10
	*Mortality(%)	Mortality(%)	Mortality(%)
L^1H_2	**30.20(25.40)***	36.10(33.42)	48.87(56.73)
$La(L^1)(L^1H).3H_2O$	35.20(32.96)	43.06(46.62)	62.30(78.39)
$Pr(L^1)(L^1H).3H_2O$	79.05(96.39)	83.22(98.61)	85.30(99.33)
$Nd(L^1)(L^1H).3H_2O$	70.18(88.50)	82.86(98.85)	85.40(99.54)
$Sm(L^1)(L^1H).3H_2O$	71.88(90.86)	79.05(96.39)	82.46(97.99)
Control	4(2.50)	4(2.50)	4(2.50)
S.Em.± C.D. at 5%	1.20	1.42	1.12
	3.52	4.17	3.16

*Mean of three replications

**Figures outside the parentheses are Arcsine transformed values

***Figures in the parentheses are re-transformed values

Table 5 — Pesticidal effects of ligand L^1H_2 and their complexes against *Spodoptera litura* at 72 h after treatment

Treatment	% Solution		
	0.02	0.05	0.10
	*Mortality(%)	Mortality(%)	Mortality(%)
L^1H_2	**24.40(17.07)***	30.28(25.42)	35.10(33.06)
$La(L^1)(L^1H).3H_2O$	50.83(60.11)	63.95(80.69)	70.25(88.64)
$Pr(L^1)(L^1H).3H_2O$	76.05(94.19)	79.05(96.39)	85.30(99.33)
$Nd(L^1)(L^1H).3H_2O$	50.83(60.11)	64.90(82.12)	72.54(91.11)
$Sm(L^1)(L^1H).3H_2O$	64.79(82.00)	71.88(90.86)	82.46(97.99)
Control	4(2.50)	4(2.50)	4(2.50)
S.Em.±	1.82	1.83	2.17
C.D. at 5%	5.38	5.39	6.37

*Mean of three replications

**Figures outside the parentheses are Arcsine transformed values

***Figures in the parentheses are re-transformed values

Conclusion

The Schiff base ligands of isonicotinoyl hydrazones and their Ln(III) complexes have been synthesised. The analytical data show that the metal ligand stoichiometry is 1:2. The spectral data show that the ligands act as tridentate, coordinating through nitrogen and oxygen atom of isonicotinic acid hydrazide, oxygen atom of hydroxyl group of 2-acetamido propanoicacid and 2-acetamido acetic acid in respective ligand. The aforesaid results reveal that the Ln^{3+} ion is hexa-coordinated with two imine nitrogen atom and four oxygen atoms. Pesticidal studies of the complexes reveal that they show better activity when compared to that of the Schiff base ligand.

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