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RESEARCH ARTICLE

SYNTHESIS, SPECTRAL CHARACTERIZATION AND ANTIFUNGAL STUDIES ON LANTHANUM (III) AND PRASEODYMIUM (III) COMPLEXES WITH N₂O₂DIAZADIOXAMACROCYCLES

Priti Tripathi, Akhilesh Kumar Srivastava, Om Prakash Pandey and Soumitra Kumar Sengupta
Department of Chemistry, DDU Gorakhpur University, Gorakhpur 273009, India.

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Abstract

A novel series of N₂O₂diazadioxamacrocyclic complexes of type [Ln(mac)Cl₃] has been synthesized via the condensation reactions of a 3-(phenyl/substituted phenyl)-4-amino-5-hydrazino-1,2,4-triazoles with salicylaldehyde and 1,4-dibromobutane in the presence of lanthanum(III) chloride and praseodymium(III) chloride in ethanol. All the newly synthesized compounds were characterized by elemental analysis, electronic absorption, IR, ¹HNMR. The particle size of the complexes have been calculated from XRD spectral using Debye-Scherrer formula and these are found to be in 29-31 nm range. In order to evaluate the biological activity of Schiff bases and to assess the role of Ln(III) and Pr(III) metal on biological activity, the hydrazine triazole Schiff bases and their lanthanide complexes have been studied for in vitro antifungal activity against *Fusariumoxysporum*, *Curvularialunata* and *Colletotrichumfalcatum*.

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Introduction:-

The synthetic challenge, exceptional kinetics and the possible use as models for systems of biological interest has contributed to the prominence of the coordination chemistry of macrocycles¹⁻². The reactivity and biological importance of synthetic macrocyclic complexes, especially those of azamacrocycles, continue to promote interest in the design of new complexes³.

The reactions of a metal ion by a macrocyclic ligands and modification of the resulting complexes controlled to a large extent by a match between the size of a ligand hole and that of the metal ion⁴. There has been considerable activity concerned with the synthesis of cyclic systems, which also contain appended side chains incorporating additional donor functions⁵. Such products have been obtained both from structural modification of selected simple rings as well as via synthetic procedure design to produce the required macrocycle directly from non-cyclic precursors⁶. Many ligands of this category offer the prospect of inducing axial metal-ion coordination even for those cases where the pendant arms incorporate weak donor functions. The use of metals as templates in such reaction has led to the synthesis of metal complexes of macrocyclic ligands. Several macrocyclic complexes have been synthesized by the template condensation and this provides an opportunity to design and study the model biological systems to understand the chemical changes taking place in such cases⁷⁻⁸.

Macrocyclic ligands form stable complexes with lanthanides and actinides. Macrocyclic complexes of lanthanides are currently attracting much attention as pharmaceuticals, in radioimmunotherapy, radio immunography (γ-Scientigraphy), as contrast-enhancing agents in magnetic resonance imaging, as NMR shift reagents and relaxation

Corresponding Author:- Priti Tripathi

Address:- Department of Chemistry, DDU Gorakhpur University, Gorakhpur 273009, India.

agents for proteins and biological cations as fluorescent probes in fluoroimmunoassay. There is an emerging interest in the application of macrocyclic ligands as effective metal ion chelators and in the separation of lanthanides. One of the most tantalizing applications of lanthanide(III) macrocyclic complexes is the efficient catalytic cleavage of RNA. Dinuclearlanthanide(III) complexes are also important as novel tunable photonic devices and potential application in biomedical diagnostics and fluorescent imaging. They are also important in studying the molecular recognition processes which govern the lanthanide(III) cations pairing events. There is no report available on simultaneous study of synthesis, spectral and biological activity of newly synthesized this complexes so far. So that, in the present communication, authors were focused on simultaneous study of synthesis, spectral and biological activity of newly synthesized lanthanum(III) and praseodymium(III) complexes with N₂O₂diazioxamacrocycles

Experimental:

All the solvents and chemicals used were of reagent grade and used without further purification. Lanthanum(III) and praseodymium(III) chloride was procured from Aldrich Chemical Co., England. 3-(phenyl/ substituted phenyl)-4-amino-5-hydrazino-1,2,4-triazoles were prepared by a previously reported method⁹. The progress of the reaction, throughout the synthesis, was monitored by TLC. The physical measurements and analytical methods were the same as those described previously. Elemental analyses (C, H and N) were measured with a Perkin-Elmer 1400C analyzer. The lanthanum(III) and praseodymium(III) metal was estimated gravimetrically as oxide form. Infra-red spectra (4000-200cm⁻¹) of the ligands and complexes were recorded as KBr pellets on a Nicolet-5700 FTIR spectrophotometer. The room temperature magnetic susceptibilities were measured by Gouy's method using Hg[Co(NCS)₄] as calibrant. Electronic spectra of the complexes were recorded on Varian Cary-100 Bio UV-Vis spectrophotometer using DMSO as solvent. Conductance measurements were recorded in DMSO (10⁻³ M) using Elico conductivity bridge type CM-82, provided with a dip type conductivity cell fitted with Pt electrodes. The particle size of the complexes has been calculated by analysis of the X-ray diffraction pattern, obtained using an X-ray powdered diffractometer (RigakuGeigerflex) with Cu K α 1 (λ = 1.54060 Å) source.

Synthesis of Schiff bases derived from 3-(phenyl/ substituted phenyl)-4-amino-5-hydrazino-1,2,4-triazoles and salicylaldehyde:

A mixture of 3-(phenyl/ substituted phenyl)-4-amino-5-hydrazino-1,2,4-triazoles and salicylaldehyde in 1:2 molar ratio, respectively, was refluxed in ethanol (30mL) containing few drops hydrochloric acid for 5-6 h. Solvent was removed and the products, so obtained, were recrystallised from ethanol:ether mixture.

Synthesis of lanthanum(III) and praseodymium(III) macrocyclic complexes:

A mixture of appropriate Schiff base, derived from 3-(phenyl/ substituted phenyl)-4-amino-5-hydrazino-1,2,4-triazoles and salicylaldehyde (1mmol), 1,4-dibromobutane (1 mmol) and lanthanum(III) chloride and praseodymium(III) chloride (1 mmol) was refluxed in ethanol for 8-12 h. Reaction shown in Scheme 1. The compound separated in the form of crystals from the clear solution of the mixture was filtered, washed several times with cold ethanol and dried in vacuo.

The empirical formulae, color, percentage yield, elemental analyses values are listed. Synthesis of the macrocyclic complexes are schematically represented in the Table 1(a) and Table 1(b).

Steps used for fungicidal activityIn vitro antifungal activity:

All newly prepared Schiff bases and their complexes were screened for their activity against three fungal organisms *Colletotricumfalcatum*, *Fusariumoxysporum* and *Curvularialunataby* petridishes method [10]. Fungicidal activity of each compound was evaluated at three different concentrations, i.e., 10, 100 and 1000 ppm. For each compound 1% standard solution was prepared and 1 mL of the solution was diluted with 9 mL of the solvent (DMSO). Petridishes of equal diameter were sterilised at 180°C. Stock solutions of each compound were prepared for three concentration viz. 10, 100 and 1000 ppm. Solution of 1 mL of each concentration was poured in presterilisedpetridishes and 9 mL of agar medium was added immediately. Each dish was rotated on the table top in order to achieve through mixing of medium with the compound. After this, fungus and bacterial strain was inoculated in the dishes (diameter 5 mm). These set were then inoculated at 30 $\pm$ 2°C. The colony diameter of the test organism was measured with mm scale after 6 days. The percentage inhibition of the growth of the test organism was calculated by following formula.

$$\% \text{ inhibition} = 100(\text{Cd}-\text{Td})/\text{Cd}$$

Where Cd = Colony diameter of control

Td = Colony diameter of treated set

Each set was kept in triplicate.

Minimum inhibitory concentrations:

The minimum inhibitory concentrations (MICs) in 1000, 100 and 10 ppm were noted. To ensure that solvent had no effect on fungal growth, a control test was performed with test medium supplemented with DMSO at the same dilutions as used in the experiment. Fluconazole was used as a standard drug for antifungal activity.

Results And Discussion:-

A new series of diazadioxamacrocyclic lanthanum(III) and praseodymium(III) complexes have been prepared by the template synthesis of Schiff bases derived from 3-(phenyl/ substituted phenyl)-4-amino-5-hydrazino-1,2,4-triazoles and 1,4-dibromobutane in the presence of lanthanum(III) chloride and praseodymium(III) chloride in 1:1:1 M ratio. All the lanthanum(III) and praseodymium(III) complexes are brown to light yellow to orange colored polycrystalline solids and the elemental analyses data agree well with the proposed mononuclear macrocyclic framework. The complexes are stable in the atmosphere and are soluble in DMF, DMSO, acetone and nitrobenzene. Reaction is shown in Scheme 1.

Magnetic moment and electronic Spectra:

All the complexes in which lanthanum(III) acts as a metal are diamagnetic in nature which is in accord with the $5d^0 4f^0$ electronic configuration of lanthanum(III). The praseodymium(III) complexes have magnetic moments lie in the range of 3.50–3.60 μ_B . These values of magnetic moments show little deviation from Van Vleck¹¹ value and that of hydrated sulphate. This is probably due to very effective shielding of 4f electrons from external forces by the overlaying $5s^2$ and $5p^6$ shells. The f–f electronic bands of praseodymium(III) complexes are obscured by intense charge transfer bands. The complexes show broad bands at ca. 17200–17815, 20800–21200, 21700–22000 cm^{-1} and at ca. 22400–22600 cm^{-1} corresponding to the transitions from $^3H_4 \rightarrow ^1D_2$, 3P_6 , 3P_1 and 3P_2 energy levels, respectively. Nephelauxetic ratio (β), covalency parameter (δ) and bonding parameter ($b^{1/2}$) were calculated in Table 2, using standard procedures¹²⁻¹³ and were found to lie in the range 0.9883–0.9986, 0.3814–1.1838 and 0.0264–0.0765, respectively. These values suggest that the complexes are slightly covalent and 4f orbitals are very slightly involved in the bonding.

Infrared spectra:

The infrared spectral bands of the lanthanum(III) and praseodymium(III) macrocyclic complexes are presented in Table 3. The tentative assignments of the data for the compounds were made by comparing the spectra of similar systems¹⁴ reported in the literature. The acyclic ligands and their corresponding lanthanum(III) and praseodymium(III) macrocyclic complexes show band at ca. 3210 assigned to $\nu(\text{N-H})$. The strong characteristic peak for azomethine nitrogen appears in the 1640–1620 cm^{-1} region which shifts downward (ca. 15–20 cm^{-1}) in the complexes indicating¹⁵ a decrease in the bond order of $\text{C}=\text{N}$ due to the coordination of the azomethine nitrogens to lanthanum(III) and praseodymium(III). This has further been confirmed by the appearance of medium bands at ca. 380–410 cm^{-1} assignable to $\nu(\text{Ln-N})$.

The infrared spectra of the acyclic ligands show medium bands in the 3380–3410 cm^{-1} due to phenolic oxygens. This disappears in their corresponding lanthanum(III) and praseodymium(III) complexes indicating the coordination of phenolic oxygen atoms. The $\nu(\text{C-O})$ band of the ligands, which occurs at 1265–1280 cm^{-1} , shifted to 1278–1295 cm^{-1} in the complexes which further suggests the coordination of the phenolic oxygens with the lanthanide(III). The $\nu(\text{Ln-O})$ band appears at ca. 500 cm^{-1} . The two moderately strong bands appearing at ca. 710 and 880 cm^{-1} can be attributed to $\nu(\text{N-N})$ of the hydrazone residue and in plane deformation of triazole ring, respectively. Bands in the 300–320 cm^{-1} region are assignable to $\nu(\text{Ln-Cl})$.

¹H NMR Spectra:

The proton magnetic resonance spectra of lanthanum(III) complexes in Table 4 have been recorded in deuterated dimethylsulphoxide. A comparison of the spectra of ligands with complexes leads to the following conclusions:

1. The spectrum showed two singlet in the range of 8.25–8.42 ppm, assignable to the two imine protons ($-\text{CH}=\text{N}$, 2H).
2. Multiplet observed in the range of 7.20–7.65 ppm corresponding¹⁶ to aromatic protons.

3. The spectrum showed a multiplet in the range of 4.18-4.20 ppm, which may reasonably be assigned to (-CH₂-O; 4H) protons adjacent to oxygen.

X-ray diffraction study:

X-ray powder diffraction pattern of one representative complex [La(mac₄)Cl₃] is shown in Figure 1. The structural characterization of the complex was carried out from the analysis of X-ray powder diffraction (XRD) patterns obtained using an X-ray powder diffractometer (Bruker AXS D8 Advance) with CuKα₁ ($\lambda = 1.54056 \text{ \AA}$) source. The peaks in the XRD pattern clearly indicate the formation of nanocrystals. The crystallite sizes have been calculated using Debye-Scherrer formula¹⁷ given by, $D = 0.94 \lambda / \beta \cos \theta$, where D is the crystallite size, λ is the wavelength of X-ray used; β is the full width at half maximum (FWHM) and θ is the Bragg angle of diffraction. The average crystallite size of the complex was found to be 30.32 nm.

The indexing of the powder patterns for each complex was carried out using the program N-TREOR. The Miller indices (hkl) relate the peak positions or d-spacings to the lattice parameters by an equation specific to the crystal system. The initial unit cell (lattice) parameters were also determined by N-TREOR¹⁸. These unit cell parameters were refined from the regression analysis and the best crystal system and space group were assigned using CHEKCELL¹⁹ program. It was found that the complex reveals monoclinic crystal system with the most probable space group P2 / c. The lattice parameters and observed & calculated X-ray diffraction data for the complex has been shown in Table 5.

Antifungal activity:

Activities of the complexes in Table 6 reveal that the activity of the complexes is affected by the nature of substituent(s) and donor site of the ligands, this in relation to their membrane permeability, a key factor in determining their entry inside the cell. Activities of the complexes with respect to different fungi at different concentrations have been compared with standard drug fluconazole. All complexes show slightly higher activity as compared to free ligands to all fungi. Chelation reduces the polarity of central ion mainly because of partial sharing of its positive charge with donor groups and possible pi-electron delocalization within the whole chelating ring. The chelation increases the lipophilic nature of the central atom which favours its permeation through lipid layer of cell membrane²⁰. Furthermore, the mode of action of compounds may involve the formation of hydrogen bonds through the azomethine (C=N) group of complexes with the active centers of cell constituents resulting in the interference with normal cell process. Though, the complexes possess activity. It could hardly reach the effectiveness of the standard drug such as fluconazole. Some compounds are less effective, the variation in effectiveness depends on either on the impermeability of the cells of the microbes. The toxicity of compounds is directly proportional to the concentration. The most active complexes of this series against different fungi at 1000 ppm concentrations have also been compared and illustrated in Figure 2.

Table 1(a):-Reactions of lanthanum(III) and praseodymium(III) chloride with Schiff bases derived from 4-amino-3-(phenyl / substituted phenyl)-5-hydrazino-1,2,4-triazoles and salicylaldehyde with 1,4-dibromobutane.

Reactants	Molar ratio	Refluxing time (h)	Product	Color	Yield (%)	Decomp. temp (°C)
LaCl ₃ + SPH ₂ TH ₂ +Br(CH ₂) ₄ Br	1:1:1	12	[La(mac ₁)Cl ₃]	Brown	60	210
PrCl ₃ + SPH ₂ TH ₂ +Br(CH ₂) ₄ Br	1:1:1	10	[Pr(mac ₁)Cl ₃]	Light yellow	63	180
LaCl ₃ + SOCH ₂ TH ₂ +Br(CH ₂) ₄ Br	1:1:1	8	[La(mac ₂)Cl ₃]	Yellow	59	200
PrCl ₃ + SOCH ₂ TH ₂ +Br(CH ₂) ₄ Br	1:1:1	8	[Pr(mac ₂)Cl ₃]	Brown	58	260
LaCl ₃ + SPCH ₂ TH ₂ +Br(CH ₂) ₄ Br	1:1:1	9	[La(mac ₃)Cl ₃]	Light yellow	61	210
PrCl ₃ + SPCH ₂ TH ₂ +Br(CH ₂) ₄ Br	1:1:1	8	[Pr(mac ₃)Cl ₃]	Dark brown	60	210
LaCl ₃ + SNH ₂ TH ₂ +Br(CH ₂) ₄ Br	1:1:1	10	[La(mac ₄)Cl ₃]	Orange	63	180

PrCl ₃ + SNH ₂ TH ₂ +Br(CH ₂) ₄ Br	1:1:1	8	[Pr(mac ₄)Cl ₃]	Orange	59	200
LaCl ₃ + SMH ₂ TH ₂ +Br(CH ₂) ₄ Br	1:1:1	10	[La(mac ₅)Cl ₃]	Brown	63	260
PrCl ₃ + SMH ₂ TH ₂ +Br(CH ₂) ₄ Br	1:1:1	9	[Pr(mac ₅)Cl ₃]	Light yellow	63	220

Table 1(b):-Analytical data of lanthanum(III) and praseodymium(III) macrocyclic complexes with ligands derived from 4-amino-3-(phenyl / substituted phenyl)-5-hydrazino-1,2,4-triazoles and salicylaldehyde with 1,4-dibromobutane.

Complex	Molecular formula	Analyses (%)							
		Found						Calcd.	
		C	H	N	Ln Cl	C	H	N	Ln Cl
[La(mac ₁)Cl ₃]	C ₂₆ H ₂₄ N ₆ O ₂ Cl ₃ La	47.0	3.4	12.4	20.7 15.1	47.1	3.6	12.6	20.9 15.2
[Pr(mac ₁)Cl ₃]	C ₂₆ H ₂₄ N ₆ O ₂ Cl ₃ Pr	39.9	3.4	12.4	21.1 15.2	47.0	3.6	12.6	21.2 15.3
[La(mac ₂)Cl ₃]	C ₂₆ H ₂₃ N ₆ O ₂ Cl ₄ La	44.5	3.1	11.9	20.0 16.2	44.6	3.3	12.0	20.1 16.4
[Pr(mac ₂)Cl ₃]	C ₂₆ H ₂₃ N ₆ O ₂ Cl ₄ Pr	44.4	3.1	11.9	19.8 16.5	44.7	3.3	12.0	19.9 16.7
[La(mac ₃)Cl ₃]	C ₂₆ H ₂₃ N ₆ O ₂ Cl ₄ La	44.4	3.0	11.8	20.0 16.3	44.6	3.3	12.0	20.1 16.4
[Pr(mac ₃)Cl ₃]	C ₂₆ H ₂₃ N ₆ O ₂ Cl ₄ Pr	44.6	3.2	11.7	19.6 16.5	44.7	3.3	12.0	19.9 16.7
[La(mac ₄)Cl ₃]	C ₂₆ H ₂₃ N ₇ O ₄ Cl ₃ La	42.5	3.1	13.5	19.1 16.6	43.7	3.2	13.7	19.4 16.8
[Pr(mac ₄)Cl ₃]	C ₂₆ H ₂₃ N ₇ O ₄ Cl ₃ Pr	43.5	3.0	13.5	19.4 16.8	43.6	3.2	13.7	19.7 16.9
[La(mac ₅)Cl ₃]	C ₂₇ H ₂₆ N ₆ O ₂ Cl ₃ La	47.5	3.6	12.3	20.3 14.9	47.9	3.8	12.4	20.5 15.0
[Pr(mac ₅)Cl ₃]	C ₂₇ H ₂₆ N ₆ O ₂ Cl ₃ Pr	47.3	3.7	12.2	20.4 15.0	47.8	3.8	12.3	20.7 15.1

Table 2:-Electronic spectral parameters of praseodymium(III) complexes of macrocyclic ligands derived from 4-amino-3-(phenyl / substituted phenyl)-5-hydrazino-1,2,4-triazoles and salicylaldehyde with 1,4-dibromobutane.

Complex	Bands (cm ⁻¹)	Assignments	β	δ	$b^{1/2}$	μ_{eff}
[Pr(mac ₁)Cl ₃]	17472 21087 21957 22600	³ H ₄ → ¹ D ₂ ³ H ₄ → ³ P ₆ ³ H ₄ → ³ P ₁ ³ H ₄ → ³ P ₂	0.9883	1.1838	0.0765	3.55
[Pr(mac ₂)Cl ₃]	17352 21157 21822 22597	³ H ₄ → ¹ D ₂ ³ H ₄ → ³ P ₆ ³ H ₄ → ³ P ₁ ³ H ₄ → ³ P ₂	0.9886	1.1531	0.0755	3.60
[Pr(mac ₃)Cl ₃]	17728 21113 21743 22428	³ H ₄ → ¹ D ₂ ³ H ₄ → ³ P ₆ ³ H ₄ → ³ P ₁ ³ H ₄ → ³ P ₂	0.9896	1.0509	0.0721	3.65
	17200	³ H ₄ → ¹ D ₂				

[Pr(mac ₄)Cl ₃]	21898 21718 22513	³ H ₄ → ³ P ₆ ³ H ₄ → ³ P ₁ ³ H ₄ → ³ P ₂	0.9962	0.3814	0.0436	3.50
[Pr(mac ₅)Cl ₃]	17813 20998 21708 22498	³ H ₄ → ¹ D ₂ ³ H ₄ → ³ P ₆ ³ H ₄ → ³ P ₁ ³ H ₄ → ³ P ₂	0.9986	0.1402	0.0264	3.52

Table 3: Infrared spectral bands of Schiff bases derived from 4-amino-3-(phenyl / substituted phenyl)-5-hydrazino-1,2,4-triazoles and salicylaldehyde with 1,4-dibromobutane and their corresponding macrocyclic complexes of lanthanum(III) and praseodymium(III) complexes.

Ligand / Complexes	Data (cm ⁻¹)
SPH ₂ TH ₂	3380s, 3210s, 2980w, 2920w, 2480w (soln.), 1625s, 1580m, 1520s, 1500m, 1440w, 1320m, 1265w, 1060m, 940w, 820m, 710s
SOCH ₂ TH ₂	3410s, 3200s, 2980w, 2950w, 2460w (soln.), 1640s, 1575m, 1525s, 1505m, 1450w, 1280m, 1160w, 1120w, 1040m, 950w, 880s, 710w, 650w
SPCH ₂ TH ₂	3395s, 3210s, 2960w, 2485w (soln.), 1620s, 1570m, 1510s, 1500m, 1450w, 1270m, 1210w, 1150w, 1050m, 960w, 710s, 750w, 640w
SNH ₂ TH ₂	3405s, 3205s, 2970w, 2475w (soln.), 1630s, 1580m, 1530s, 1495m, 1300m, 1265w, 1150w, 1045m, 950w, 880s, 790m, 680w, 640w
SMH ₂ TH ₂	3410s, 3210s, 2860w, 2478w (soln.), 1635s, 1570m, 1528s, 1500m, 1460w, 1310m, 1270w, 1140w, 1055m, 950w, 810s, 740w, 670w
[La(mac ₁)Cl ₃]	3200s, 2980w, 2920w, 1620s, 1590m, 1500m, 1440w, 1155w, 1295w, 950w, 880s, 730w, 620m, 510m, 415m, 390m, 320w
[Pr(mac ₁)Cl ₃]	3215s, 2975w, 2915w, 1625s, 1585m, 1500m, 1440w, 1170w, 1280w, 980w, 940w, 710s, 600m, 500m, 430m, 410m, 320w
[La(mac ₂)Cl ₃]	3200s, 2980w, 2955w, 1630s, 1575m, 1505m, 1450w, 1285w, 1150w, 1120w, 960w, 880s, 745w, 650w, 610m, 515m, 425m, 380m, 315w
[Pr(mac ₂)Cl ₃]	32085s, 2985w, 2960w, 1620s, 1578m, 1500m, 1455w, 1278w, 1165w, 1120w, 960w, 710s, 640w, 615m, 500m, 428m, 390m, 320w
[La(mac ₃)Cl ₃]	3205s, 2950w, 2940w, 1610s, 1570m, 1500m, 1450w, 1280w, 1150w, 950w, 710s, 640w, 620m, 500m, 490m, 420m, 395m, 315w
[Pr(mac ₃)Cl ₃]	3200s, 2960w, 1615s, 1575m, 1510m, 1460w, 1290w, 1150w, 960w, 880s, 645w, 610m, 500m, 415m, 390m, 310w
[La(mac ₄)Cl ₃]	3215s, 2970w, 2920w, 1610s, 1580m, 1490m, 1290w, 1160w, 960w, 710s, 680w, 640w, 625m, 510m, 425m, 410m, 305w
[Pr(mac ₄)Cl ₃]	3218s, 2975w, 2940w, 1620s, 1580m, 1500m, 1450w, 1285w, 1150w, 965w, 880s, 685w, 618m, 515m, 428m, 385m, 310w
[La(mac ₅)Cl ₃]	3210s, 2970w, 2950w, 1620s, 1565m, 1500m, 1460w, 1290w, 1165w, 960w, 710s, 670w, 622m, 510m, 430m, 390m, 320w
[Pr(mac ₅)Cl ₃]	3215s, 2965w, 2940w, 1605s, 1568m, 1500m, 1450w, 1280w, 1220w, 1155w, 960w, 710s, 620m, 500m, 420m, 385m, 300w

Table 4: ¹H NMR data (δ scale, ppm of lanthanum(III) complexes with Schiff bases derived from 3-(phenyl / substituted phenyl)-4-amino-5-hydrazino-1,2,4-triazoles and salicylaldehyde with 1,4-dibromobutane.

Complex	Phenyl ring	-CH-N	-CH ₂ O
[La (mac ₁)Cl ₃]	7.20-7.50 m	8.28-8.42 s	4.15 s
[La(mac ₂)Cl ₃]	7.28-7.55 m	8.25-8.35 s	4.18 s

[La(mac ₃)Cl ₃]	7.30-7.60 m	8.30-8.40 s	4.20 s
[La(mac ₄)Cl ₃]	7.35-7.60 m	8.27-8.38 s	4.15 s
[La(mac ₅)Cl ₃]	7.38-7.65 m	8.31-8.42 s	4.18 s

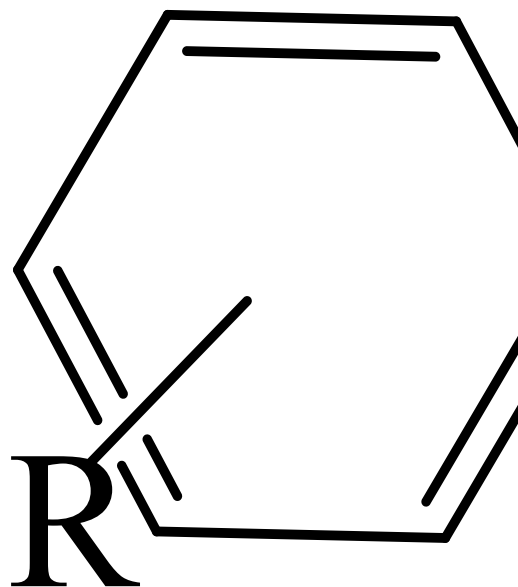
Table 5:-The unit cell parameters and observed & calculated X-Ray diffraction data data for [La(mac₄)Cl₃]complex.

a= 10.5230 Å°, b= 14.7738 Å°, c= 8.4075 Å°, β= 100.28°, cell vol.= 1286.06 Å°								
S. N.	d(obs)	D(calc)	Δ(d)	I/I _m x100	2 θ (obs)	2θ (calc)	Δ(2θ)	h k l
1	4.0089	4.0188	-0.0099	10.07	22.156	22.101	0.055	-2 1 2
2	3.5265	3.5204	0.0061	1.35	25.234	25.278	-0.044	1 1 2
3	3.3250	3.3215	0.0035	6.98	26.791	26.820	-0.029	-3 1 1
4	3.0207	3.0067	0.0140	1.67	29.548	29.689	-0.141	-2 0 4
5	2.9359	2.9407	-0.0048	2.81	30.422	30.371	0.051	3 1 1
6	2.8367	2.8413	-0.0046	100.0	31.513	31.461	0.052	-1 0 5
7	2.8262	2.8263	-0.0002	68.49	31.633	31.631	0.002	-3 0 3
8	2.3260	2.3267	-0.0007	3.28	38.679	38.667	0.012	-1 1 6
9	2.0156	2.0160	-0.0004	5.22	44.936	44.927	0.009	0 3 5
10	1.7986	1.7989	-0.0003	20.18	50.715	50.707	0.008	2 4 1
11	1.6445	1.6442	0.0003	9.39	55.863	55.872	-0.009	0 1 5
12	1.4251	1.4253	-0.0002	6.23	65.437	65.429	0.008	-3 4 7
13	1.3420	1.3420	-0.0000	2.43	70.059	70.058	0.001	4 7 3
14	1.2739	1.2739	-0.0000	6.02	74.412	74.410	0.002	4 2 5

Table 6:-Fungitoxic screening data of lanthanum(III) and praseodymium(III) derivatives with macrocyclic ligand derived from 4-amino-3-(phenyl / substituted phenyl)-5-hydrazino-1,2,4-triazoles and salicylaldehydewith 1,4-dibromobutane.

Compound	Fungicidal Inhibition (%)			Compound dose (ppm)					
	<i>Fusariumoxysporum</i>			<i>Curvularialunata</i>			<i>Colletotrichumfalcatum</i>		
	10	100	1000	10	100	1000	10	100	1000
[La(mac ₁)Cl ₃]	30.2	38.7	45.5	34.2	35.4	44.7	32.3	34.4	41.2
[Pr(mac ₁)Cl ₃]	34.2	35.6	42.4	32.8	39.5	42.6	32.5	35.6	44.0
[La(mac ₂)Cl ₃]	32.2	35.5	48.0	33.6	34.2	44.5	30.1	36.6	46.2
[Pr(mac ₂)Cl ₃]	30.6	36.8	40.4	34.6	38.6	42.4	34.8	35.8	45.0
[La(mac ₃)Cl ₃]	35.0	37.2	41.5	30.8	34.8	40.6	30.0	37.1	44.6
[Pr(mac ₃)Cl ₃]	32.8	36.7	46.6	31.8	35.2	45.5	35.2	36.8	47.4
[La(mac ₄)Cl ₃]	31.5	37.8	44.5	30.5	38.6	45.0	34.4	38.2	40.1
[Pr(mac ₄)Cl ₃]	32.5	38.3	46.2	33.2	35.6	43.4	32.8	39.0	41.0
[La(mac ₅)Cl ₃]	30.3	34.2	47.4	31.1	36.8	46.2	35.0	38.0	48.5

[Pr(mac ₅)Cl ₃]	30.5	36.4	46.0	30.8	37.2	43.0	32.2	37.4	42.4
Fluconazole	100	100	100	100	100	100	100	100	100



Scheme 1: Synthesis of macrocyclic complexes

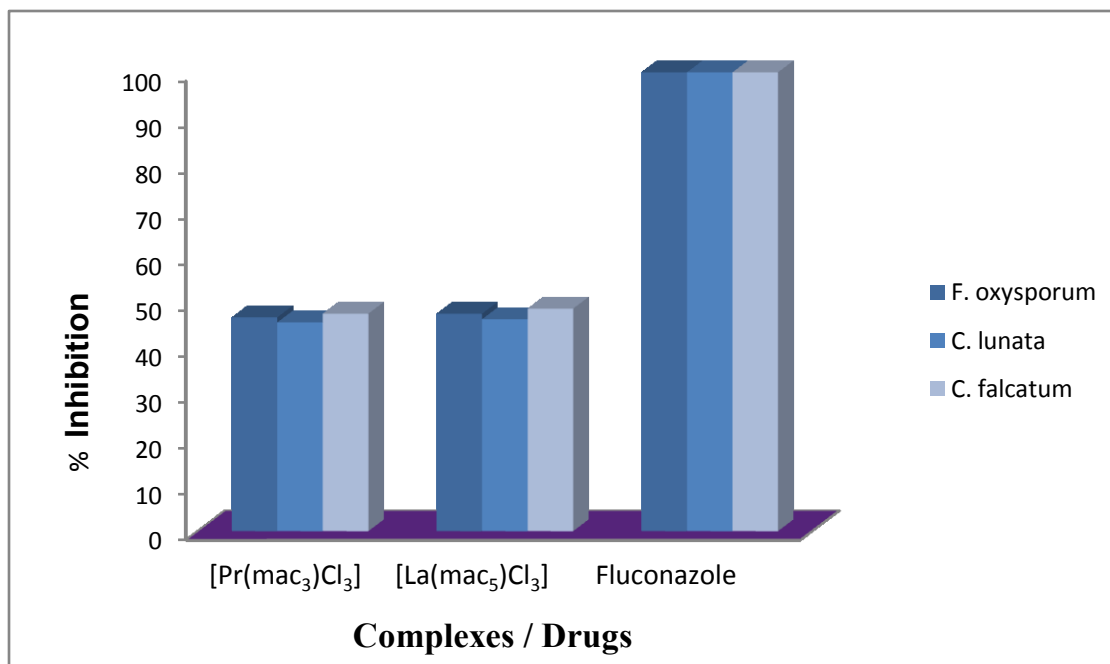


Fig1:- Inhibition percentage of synthesized compounds against fungus species.

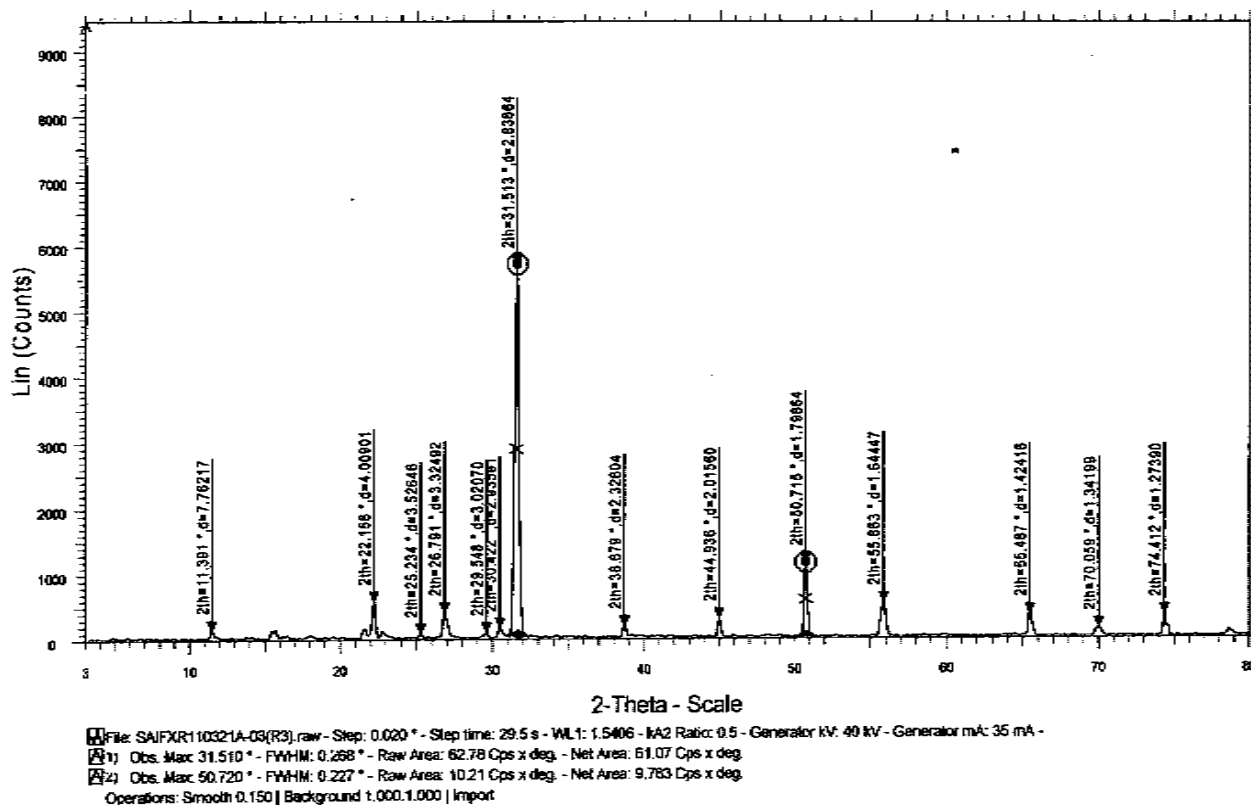


Fig 2:- XRD of [La(mac4)Cl₃] complex.

Conclusions:-

The N₂O₂ type Schiff bases, synthesized from 3-(phenyl/ substituted phenyl)-4-amino-5-hydrazino-1, 2, 4-triazoles and salicylaldehyde, and 1, 4-dibromobutane form stable complexes with lanthanum(III) and praseodymium(III) chloride. The ligands and respective complexes were characterized using spectral and analytical data, XRD spectra

shows that complexes are 29-31 nm in size. All complexes show slightly higher activity as compared to free ligands to all fungi.

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