



## RESEARCH ARTICLE

# NON-STEROIDAL ANTI-INFLAMMATORY DRUGS (NSAIDS) AS DONOR LIGANDS IN ORGANO-LANTHANIDE DERIVATIVES: SYNTHESIS, SPECTROSCOPIC ANALYSIS, THERMAL STABILITY, HIGH PERFORMANCE-LIQUID CHROMATOGRAPHIC STUDIES AND BIOLOGICAL SCREENING OF ORGANO- LANTHANIDE DERIVATIVES

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### ABSTRACT

Non-steroidal anti inflammatory drugs can be used as donor ligands for complexations of rare earth metals. Amoxicillin is non-steroidal, anti inflammatory drug and is used as extended-spectrum also penicillin and clavulanic acid act as  $\beta$ -lactamase inhibitor. The active components of drugs were detected at 210nm wavelength with the UV detector. Some new organo Erbium (III), Lanthanum (III) and Gadolinium (III) derivatives of non-steroidal anti inflammatory drugs were synthesized. These compounds were structurally characterized by elemental, molar conductivity, U.V visible and Fourier transform infra red analysis. Also high performance liquid chromatography and thermal gravimetric analysis shows the stability and presence of hydrated and coordinated water molecules by which enthalpies can be determined. The thermal degradation study shows the final product metal oxide. The compounds were also screened against different plant pathogens. The molar conductance values suggest the non electrolytic nature of metal complexes. Thermal behavior suggests their more ordered activated state in complex formation. Phenyl bonded silica HPLC column was used to separate metal-NSAIDs complexes. The aim of present study is to synthesize and characterized a number of organo lanthanide complexes with NSAIDs, based on the fact that newly synthesized compounds show significant activity against microbes. Their cytotoxicity data indicates their positive lethality.

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## INTRODUCTION

NSAIDs are used as anti diarrhoeal and anti-pyretics. Their effect is inhibition of prostaglandins which are produced by cyclo-oxygenase (Arayne *et al.*, 2006; Saria Shazad *et al.*, 2004). The reaction of organic reagents with metal ions depends on position of functional groups (Bajia *et al.*, 2012). Development of PR-HPLC method for the determination of cefpirome with the help of trace metals detected by UV at 265nm, 10mg was the detection limit of cefpirome. Drug complexes with metal ions were studied at 37°C. These studies drug ascertained medicinal amount in human body and in addition metal cation complexation. Human body's necessary metals present in the

form of chlorides like Mg (II), Mn (II), Fe(III), Co(II), Zn(II), Cd(II) etc. Comparative to the other group, carboxylic group of dehydrothiazine ring more potent to binding. This increases drug complexes with trace and essential elements (Arayne *et al.*, 2006). Formulation of spectroscopic technique for the finding of metal cation by chelating agent Dithiocarbamate with HPLC (Saria Shazad *et al.*, 2004). Metal salt reaction with Dithiocarbamate formed colored complexes that were extracted with methanol and separate by acetonitrile water as mobile phase. This method was affected by different parameters such as solvents, pH, types of column and mobile phase. Eluted sample passed through the UV detector then ICP-MS and their result help in determination and identification of complexes. This new developed method compared with other methods, result no difference was noted (Bajia *et al.*, 2012). Synthesis of stable zirconium (IV)-based metal that have best stability in water, chemicals and thermal and applied in fruit samples for

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8 plant growth regulators adsorbent for the dispersive solid phase extraction. To measure analyte fluorescence, combined high performance liquid chromatography for fluorescence detection (HPLC-FLD). This suggested method is verified to be simple, eco-friendly and low cost and viable to directly use as sorbent to extract analyte by changing conditions (Liu *et al.*, 2016). The combination of Electro spray ionization and mass spectrometry (ESI-MS) is utilized in a wide variety of fields to examine the manufacturing and stoichiometry including metals & organic ligands. ESI-MS is able to give direct knowledge about changes in specialty of metal: ligand ratio and pH identify metal oxidation state directly and also deals with its pH and allow insight into competitive interactions in ternary systems (Keith-Roach and Miranda, 2010). Both the instruments can produce changes in chemistry of solution and can affect the relative ion intensity of different metals. The use of HPLC-ESI-MS is also included, gives challenges of different types and fields of applications. Overall, there is need to get standard reporting to strengthen the applications of both techniques to metal-organic ligand complexes (Luther *et al.*, 2005). With increasing number of metal complexes in organic chemistry results in more demand to identify and to analyzed metals. Today most advance applications of high-performance liquid chromatography (HPLC) for the estimation an analysis of metal complexes brought. This concept use in various ways today (Wang and Lee, 1997). For analysis of metal complexes HPLC technique is used many times in past and still is in use. The different approaches involving ion-pair: Ion-pair, Ion-exchange, chelation separation mechanisms. New chemistry for elimination of interferents to special detections of metal ions like: Alkali and alkaline earths, heavy and transition metals, rare earths Multimodal or sometimes hyphenated techniques are employed for metal speciation like arsenic and chromium (Sarzanini, Corrado 1999). Aqueous solution of both mineral acids like hydrochloric acid and nitric acid were utilized for identification of structures of lanthanides and they were characterized by extended X-Ray absorption. It is indicated that lanthanides form strong complexes with nitrate but weak with chloride ions. It was analyzed that light lanthanides show Coordination number nine and heavy lanthanides exhibit the Coordination number eight (Yaita *et al.*, 1999). The compound 1,2,4-benzenetricarboxylate were investigated and confirm by X-ray diffraction analysis and IR spectroscopy. The fact that carboxylate groups of 1, 2, 4, benzenetricarboxylate were participated in chelation. The prepared chelated compounds were thermally analyzed by using TG-DTA. The compound showed stability up to 300°C but upon further heating it was dehydrated. The complexes without water were converted into oxides. The complete pathway of degradation was confirmed by combination of two techniques that were TG-FTIR (Zhang *et al.*, 2005). Photoluminescence process with metallic framework which was metallic in nature were prepared. They were isostructural in to each other and they also showed lanthanide contraction property. They attained the square-planar shape. With their photoluminescence process, they had many sizes of pore sizes with adsorption of by O<sub>2</sub> and N<sub>2</sub>. They also showed thermally stable property at 500-550°C (Ma *et al.*, 2009). Vanillin acid complexes with lanthanides and form co-ordination compounds and they were confirmed by many techniques for example, XRD pattern and IR spectra. Actually carboxylate group in Vanilic acid is responsible for

behavior of bidentate ligand. They were crystalline in nature. If they have water of crystallization attached with them, then upon heating they lose water and become oxides (Kula, 2005). Great number of complexes of transition metals like Ce and CO. Schiff base was used as ligand. The prepared compounds were characterized by magnetic measurements and molar conductivities. NMR and IR spectra gave changed pattern upon chelation. Thermal analysis revealed the method of degradation in detail (El-Wahab *et al.*, 2004). XRD pattern confirmed the complexes of three lanthanides i-e Lu, Er and Yb. A complex may be consisting of Ln with 8 C.N and present antiprismatic square shape. It can also have C.N 6 with octahedral shape. Two types of forces are involved that are hydrogen bonding and Vander waal forces. Six cyanide groups are arranged around iron. The given complex was verified by IR spectrophotometer or by thermal analysis (Mullica *et al.*, 2000). Mixing the salicylaldehyde and isatinmonohydrazone in exact ratio and formed by condensation reaction. These reactions worked out in microwave conditions. Number of techniques was employed for the characterization of metal complexes. U.V visible, far infrared, molar conductance, X-ray diffraction indicated the crystalline nature of compound. The thermal analysis was done at 40-800°C (Mohanan *et al.*, 2008)

## Experimental work

### Materials and reagents

All materials and solvents used in this study were pure and of analytical grade, Gadolinium chloride, Erbium chloride and lanthnium chloride. Ethanol, toluene were purchased from sigma-Aldrich (Germany). Melting points of ligands and complexes were noted by using Gallen Kemp melting apparatus (Germany) FTIR spectra was later or Perlcin Elmer (England) and Thermo FTIR Nicolet ISIO (USA)-Thermogravimetric analysis was performed on TGA instrument SDT Q600 T.A company, temperature maintained at the rate of 20<sup>o</sup> per minute. The elemental analysis of the complexes was carried on LECO Truspec micro Sr No. 4021 Model No. 200-200630- The analysis was carried out on the high pressure liquid chromatographic (HPLC) system was used of model HITACHI HPLC ELITE Lachrome series equipped with Binary gradient pumps with HITACHI L-2130, HITACHI Auto sampler series L-2200, Inertsil-ODS-3 column (150x4.6mm, 5um particle size) as stationary phase, HITACHI UV detector L-2400, Digital heated ultra sonic cleaner Supersonic X-3, Ultra filter (0.22um)

## Experimental work

### Sample solution of amoxicillin C16H19N3O5S

Amoxil 500mg capsule of Glaxosmith Kline Company was purchased from SHAMEEN PHARMACY. Capsule content was grinded to uniform size powder then weighed 100mg powder and dissolved into 100ml mobile phase in a 100ml volumetric flask. Then pipette out 1ml from 100ml solution and then further diluted 1ml solution by 4ml mobile phase. Completion of reactants was checked frequently by TLC test in acetonitrile: tetra chloride (1:1). By mixing equimolar

quantities of lanthanides chlorides in ethanol ligand in toluene. Mixture was heated with continuous stirring for 4-5 hours. The completion of reaction was checked by TLC techniques. After the completion of reaction the solvent was evaporated by rotary evaporator. Lanthanide complex was synthesized by shaking of equal amount of quantities of lanthanide chloride (3.54g,0.02moles) dissolved in flask containing ethanol and ligand dissolved in toluene. Ligand solution was randomly stirred and heated. Mixing of lanthanide salt and ligand solution was done and then continuously fluxed for 4-5 hours along with stirring. The success of reaction of the reaction was checked by TLC test. After the reaction, the solvent was removed by the rotary evaporator, washed with pet-ether. The peaks of Amoxicillin and Clavulanic acid have the significant response at single wavelength of 210 nm.

### Mass spectrometry

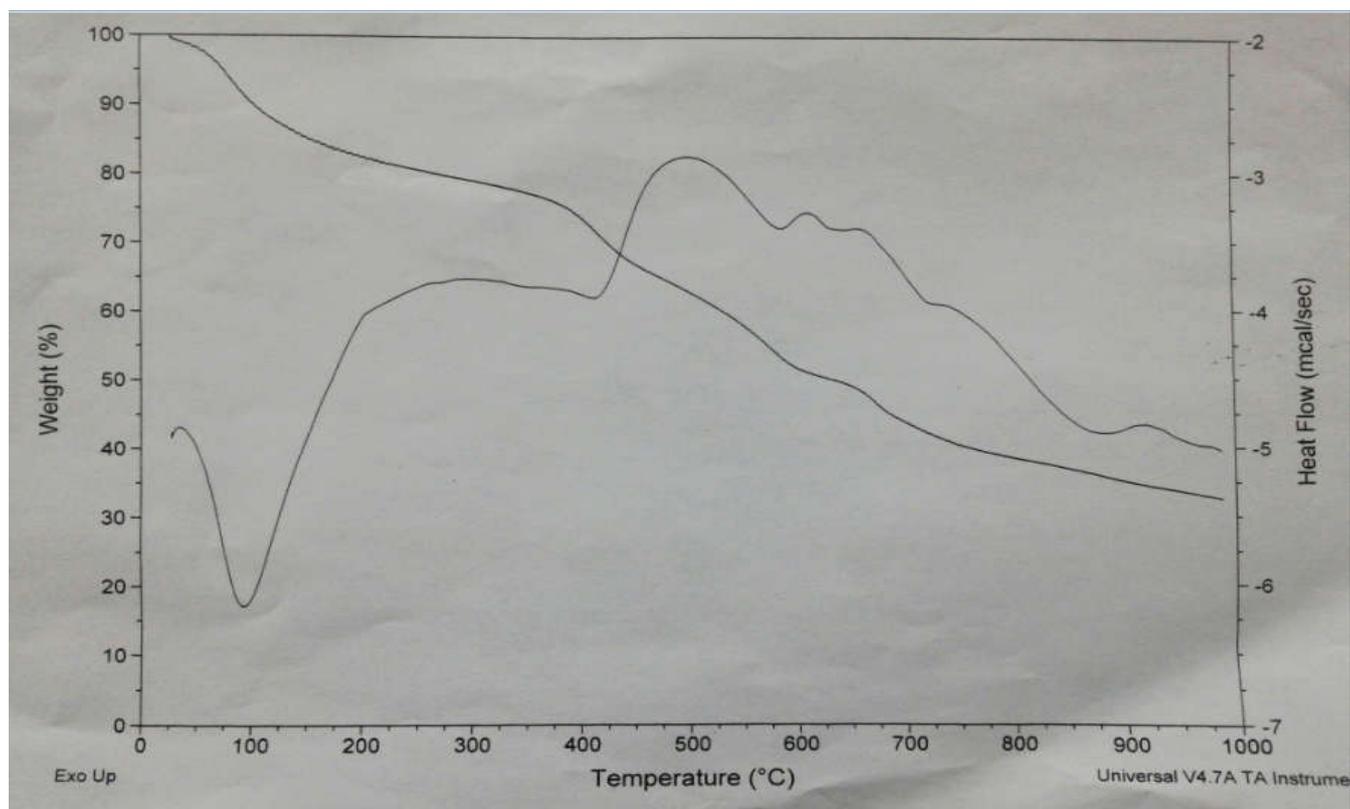
The molecular ion peak of Ligand was observed at 419 which is also a base peak. The molecular ion fragment was disintegrated by cleavage of OH group resulting the fragment peak at 398 the fragment pattern of molecules was observed by cleavage of nitrogen-ethylene bond. Two fragments were observed in the spectrum among these one was with molecular mass 348 and second was with 220. The second fragment with mass 220 after combining with nitrogen and resulted the peak at 234 in the spectrum. Isotopic peak for the molecule was observed at 369 with in intensity about 1% of the molecular ion peak.

**Table 1. Analytical and physical data of the metal complexes of NSAID, S ligand**

Ligand or complexes	Melting point °C	M:L	C%	H%	N%	S%
L	116	-	63.86	4.00	9.42	12.44
La-L	>350	1:1	56.34	6.00	9.34	4.35
Gd-L	>350	1:1	66.67	5.67	12.45	6.88
Er-L	>350	1:1	58.34	6.78	12.56	2.38

**Table 2. Deferential thermal analysis with exothermic peaks on Erbium complex**

Sample	Mass of the sample(Kg)	Exothermic peak	Peak Temp $T_p$ (K)	Peak width T (K)	Specific heat capacity	Enthalapy (H) (Kj)
ErL	24X 10 <sup>-6</sup>	1	350	120	394	9



**Figure 1. TGA of erbium complex**

### Thermogravimetric analysis

In the thermal analysis of rare earth complexes the heating rate was maintained at  $10^{\circ}\text{C per min}^{-1}$  and weight loss was measured up to temperature of  $1000^{\circ}\text{C}$  the residue are rare earth oxide. The weight loss was calculated within temperature range at which hydrated water molecules evaporate. The values are listed in table. The initial weight loss occurring in the temperature range is due to loss of two-three  $\text{H}_2\text{O}$  molecules from La-L, Gd-L and Er-L complexes. The TG-curves show decomposition of other anions and molecules followed by decomposition of other anions and molecules followed by decomposition of the organic part of complexes till a constant weight is observed where metal oxide residue is formed as final product. The second weight loss in complexes is due to loss of two ethanol molecules. Degradation of ligand was in the range ( $320\text{-}530^{\circ}\text{C}$ ). At  $530^{\circ}\text{C}$ , the complex completely converts into  $\text{Er}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{Gd}_2\text{O}_3$  and weight becomes stable. I have taken thermal gravimetric spectra of erbium and taken as standard for other lanthanides.

### FT-IR Spectrum

The IR spectra of Ligand L and its bimetallic complexes exhibited the bending vibrations due to  $\text{CH}=\text{N}$  group at  $1625$  and  $1609\text{ cm}^{-1}$ ,  $1625$  and  $1595\text{ cm}^{-1}$  and  $1633$  or  $1597\text{ cm}^{-1}$  for ligand L, La L, ErL and GdL respectively. Similarly the bending vibration of ligand L, LaL, ErL L and GdL for phenolic OH group were absorbed at  $1370$  or  $1198.8\text{ cm}^{-1}$ ,  $13866$  or  $1190.19$ ,  $1384.7$  or  $1200\text{ cm}^{-1}$  and  $1389.7$  or  $1190.3\text{ cm}^{-1}$  respectively.

### UV –Analysis

The electronic absorption spectra of free Schiff base L exhibit bands at  $210$  respectively due to transition in the whole molecule. The complex of Gd, La, Er show band in the range of  $320, 380, 360\text{ nm}$ . The disappearance and shifting which occurs in the bands of ligands is the evidence of complex formation.

**Table 3. Simultaneous differential thermal analysis with endothermic peaks on Erbium complex**

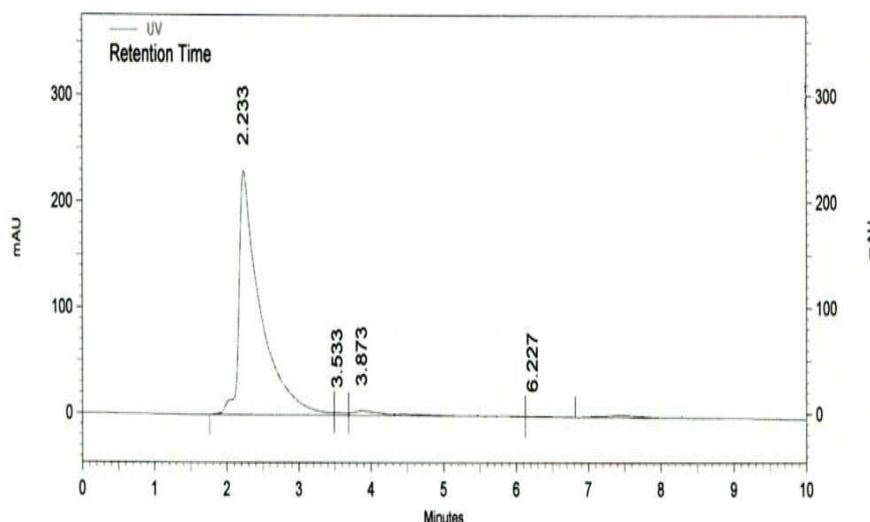
Sample	Mass of the sample	Peak nature	Peak temperature $T_p(\text{K})$	Peak width $T(\text{K})$	U (internal energy) $\text{PP JK}^{-1}$
ErL	$56.076 \times 10^{-6}$	Endothermic peak	449	491	6779
		Endothermic peak	928	370	5104

**Table 4. Calculation of entropy with themogravity analysis on Erbium complex**

Sample	Mass of the sample	Peak nature	Transition temperature $T_t(\text{k})$	Transition width $T(\text{K})$	Entropy ( $\mu\text{J/K}$ )
ErL	$57.0118 \times 10^{-6}$	Threshold	892	333	0.1

**Table 5. The conditions for the detection of the complexes varied mainly in the percent contents of the acetonitrile in the mobile phase based on water or buffer**

Compound	Retention time $T_R$ Min	Capacity factor $K'$	HPLC condition system
1	2.33	0.12	5
1a	15.29	3.32	5
1b	14.89	3.20	5
1c	10.85	2.06	2
1d	11.56	2.15	7



**Figure 2. Chromatogram of Amoxicil (amoxicillin trihydrate).  $R_T$  of amoxicillin= $2.233$  min at  $210\text{ nm}$**

## HPLC studies

The liquid RP-Chromatography studies were performed in order to determine the purity of the new synthetic products in comparison to the free ligand.

## Chromatogram of the ligands and products

**Column:** Inertsil-ODS-3 column (150x4.6mm, 5µm particle size)

**Mobile phase:** A: 95% buffer (sodium dihydrogen phosphate dihydrate 0.1N, pH= 5.0) B: 5% Methanol

**Detector:** UV-Detection of 210 nm

**Injection volume:** 20 µl

**Flow rate 1ml/min. Column Temp:** Ambient

## HPLC analysis of amoxicillin

The filter solution of amoxicillin was injected into the HPLC vial using disfilter. The vial is introduced into the HPLC auto sampler region. First of all the HPLC pressure of 63kgf/cm<sup>2</sup> was auto maintained then set the mobile phase conditions buffer: methanol 95:5 (v/v). Then set the maximum absorbance value at 210nm. Set the injection volume 20µl at run time of 10 minutes. Flow rate was set 1ml/min. The 20µl of amoxicillin (Amoxil) drug was injected in the HPLC injector part with the help of injection needle from the vial. Precaution was made that injecting solution of drug is free of any particular matter. Inertsil-ODS-3 (150x4.6mm, 5µm particle size) was used. The HPLC system given command of run after injecting sample. The retention time of drugs has been noted. The drug was eluted at the retention time of 2.233 min at wavelength 210nm with the area percent of 96.542. Total 4 peaks were observed at different retention times but our concerned peak was observed at 2.233 min retention time. The species other than Amoxicillin were observed at 3.533, 3.873 and 6.227 with area percent of 0.649, 2.477 and 0.330 respectively.

**Analyst:** System

**Sample ID:** Amoxil (Amoxicillin trihydrate)

## UV Results

The mixture of ligand and complex often revealed two peaks eluting closed to each other with similar retention times.

Name	Retention Time	Area	Area Percent	Integration Codes
	2.233	19134640	96.542	BV
	3.533	128749	0.649	VV
	3.873	490954	2.477	VB
	6.227	65577	0.330	BB
<b>Totals</b>		19819920	100.000	

## Biological assay

All the reported compounds were screened against fungal strains using tube diffusion method (Blank and Rewbell, 1965). The results of antifungal assay are given in table. It has been

reported that, within the given series lanthanide derivatives are more active against fungi (Molloy, 1989).

**Table 6. Antifungal activity for organo lanthanide complex**

Name of fungi	Percent inhibition			Reference drug
	1	2	3	
<i>Trichophyton longfusus</i>	57.8	42.1	89.4	Miconazole Ketocopnazole
<i>Candida albicans</i>	0	0	0	Miconazole Ketocopnazole
<i>Aspergillus flavus</i>	0	0	0	Amphotericin B Flucytosine
<i>Microsporum canis</i>	0	0	60	Miconazole Ketocopnazole
<i>Fusarium solani</i>	0	0	0	Miconazole
<i>Candida glabrata</i>	0	0	0	Miconazole

**Table 7. Antibacterial analysis of metal chelates**

Name of bacteria	Percent inhibition		
	GdL	ErL	LnL
<i>Escherichia coli</i>	10	10	10
<i>Bacillus subtilis</i>	-	10	17
<i>Chigella flexneri</i>	-	10	10
<i>Staphylococcus aureus</i>	10	10	12
<i>Pseudomonas aeruginosa</i>	11	12	11
<i>Salmonella typhi</i>	-	-	-

## Irritant activity of rare earth complexes

**Table 8. Fresh water fish lethality bioassay for lanthanide complexes**

Compound No.	Dose (µg/ml)	No. of fish	No. of survivors	LD <sub>50</sub> (µg/ml)
Gd-L	100	30	10	-
	10	30	10	
	1	30	10	
Er-L	100	30	10	-
	10	30	10	
	1	30	10	
Ln-L	100	30	30	-
	10	30	30	
	1	30	30	

## RESULTS AND DISCUSSION

In the present research work deals with the synthesis of rare earth metal complexes by using nonsteroidal anti inflammatory drug as ligand the purity of ligand was checked by using HPLC technique and by comparing the graph of metal chelates with free ligand complex formation was confirmed. Molar conductance measurement shows nonelectrolytic nature of complexes melting point data proves their high melting point as compared to amoxicillin which is used as ligand the stability of metal complex was confirmed by TGA analysis which show peaks at different temperatures with the absorption or evolution of heat also transition temperature indicates their high stability and low decomposition, enthalpy values from graph gives information about heat content in the tested compounds. FT-IR spectra show peaks which shifts towards higher frequency as compared to free ligand the bands appear at 1680-1665, 1625-1590, 1390-1370cm<sup>-1</sup> due to NH, C-C, O-H bonds shifted towards higher frequency. The broad band around 3600-3340cm<sup>-1</sup> is due to OH bond of water molecules

associated with complex formation. Elemental analysis confirms the presence of carbon, hydrogen and nitrogen which relates with the theoretical values the results of elemental analysis shows that all the prepared complexes have water or ethanol molecules co-ordinated to central metal atom and is not removed by static vacuum for three hours. This conclusion is also supported by the results of thermo gravimetric analysis which shows the removal of lattice and coordinated solvent molecules from the complexes under investigation. The biological screening of metal complexes were checked by using different plant pathogens and fungal activities shows some complexes show great and improved antibacterial and antifungal activities as compared to free ligand which is the most preferable object of this research work. The irritant activity is checked on fresh water fish which shows that lanthanum complex had shown neither lethal or chronic irritant activity by using NSAIDs as ligand in complexation.

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