



P-ISSN2349-8528
E-ISSN 2321-4902
IJCS 2016; 4(5): 17-25
© 2016 JEZS
Received: 04-07-2016
Accepted: 05-08-2016

Iram Khan
Department of Chemistry
University of Punjab, Lahore-
54590 Pakistan

Zaid Mahmood,
Department of Chemistry
University of Punjab, Lahore-
54590 Pakistan

Maham Naz
Department of Chemistry
University of Punjab, Lahore-
54590 Pakistan

Physiochemical and biochemical correlation between lanthanide and transition metal derivatives of 2- (bis-2-hydroxyphenylidene)- 1, 2-iminoethanne as ligand

Iram Khan, Zaid Mahmood and Maham Naz

Abstract

Present work aims to study the physiochemical and biochemical correlation between lanthanide and transition metal complexes conductivity, thermogravimetric, high performance liquid chromatographic analysis, XRD diffraction analysis and other spectroscopic analysis provide assistance to find the stability and separation of ions between metal chelates. Some new derivatives of organometallic and rare earth metals were synthesized by using amoxicillin as donor ligand. Conclusion obtained by the studies showed that lanthanide complexes were more stable as compared to transition complexes and effective against bacterial strains. Bacterial strains like *Xenorhabdus luminescens*, *Xanthomonas axonopodis* and *Acidovorax* tampons and Fungal strains like *Trichoderma* strains, *Alternaria alternata*, *Aspergillus flavus* strains were obtained from Agricultural department Laboratory from University of Punjab, Lahore. They were maintained on a slant on nutrient agar in MC- Cartney bottles. Synthesized compounds have a novel mode of action against destined targets. Once their effectiveness against biological targets can find then it can be modified to uncover potentially active new bioactive lanthanides compounds as compare to transition metal compounds.

Keywords: Synthetic compounds, ligand, dimethyl sulphoxide, TGA, HPLC, FTIR, antimicrobial activity

Introduction

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 cations 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 [1]. Formulation of spectroscopic technique for the finding of metal cations by chelating agent Dithiocarbamate with HPLC [2]. The herbal drugs used throughout the world have received greater attention in recent times because of their diversity of curing diseases safety and well tolerated remedies when compared with conventional medicines. Development of resistance against antibiotics has further emphasized the necessity of research for new therapeutically effective synthetic analogues and salvarsan for syphilis. He invented the term "Chemotherapy" and his research taught what he called. Paul Ehrlich discovered the curative properties of dye Try pan Red. When used against experimental trypanosomiasis "magic bullets" chemical that would be toxic to infectious microorganisms but harmless to human [3] Metal ions used therapeutic agents are known to accelerate drug action and their efficiency is enhanced upon coordination with metal ion [4]. Copper atom played structural and catalytic role in several proteins. It has been recognized as important co-factor in biological molecules either as structural template in protein folding or as a Lewis acid catalyst that can readily adopt 4, 5 or 6 coordination number. Physiochemical and spectral studies of Copper (II) complexes. The complexes have their own importance in pharmaceutical and medical fields [5]. Metal chelates formed by oximes due to their fascinating chemistry as well as anticancer activities By changing pH value and chemical potential of reaction mixture, hydrothermal synthesis of lanthanide might serve as way for biological agents, because of number of potential applications of lanthanide. hydroxide single-

Correspondence
Iram Khan
Department of Chemistry
University of Punjab, Lahore-
54590 Pakistan

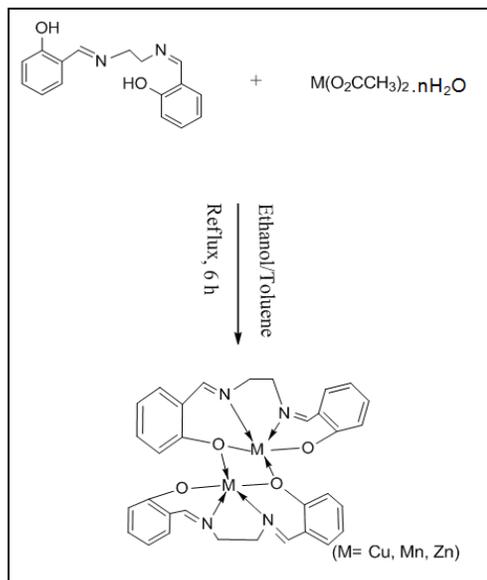
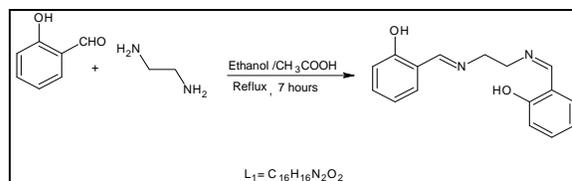
crystal has been generated the properties as well as dimensions of which can be further be exploited [6]. The coordination Chemistry of antibiotics and compounds with transition and [10]. metal ions help to determine models of binding in solid state and to investigate biological activities [7]. The biological activates of transition metal complexes are potent antibacterial and antioxidant agents [8]. Secondary metabolic contents were increased by cadmium chloride application and sampling time, while dry cell weight was reduced by cadmium chloride treatment [9]. It is a well-known hepatotoxic agent in liver tissues. It was examined that the inhibitory effect of the green tea on cadmium chloride induced antioxidant activity in liver [10] It was analyzed that phenolic content and DNA protecting in lamiaceae plants prevent carcinogenesis through scavenging CdCl [11]. Lanthanide metal-organic compounds had generated by action of lanthanide as metal ion and 1, 4-benzenedicarboxylic acid with triethylenetetramine in presence of solution of *N,N*-dimethylformamide (DMF), H₂O, in ethyl alcohol. X-ray diffraction explain them as complete similarity in structure. The formed complexes shows blue light, and shows a Tb³⁺ characteristic value of emission in the range of 450–650 nm [12]. Separation of complexes have been carried out by high performance liquid chromatography. The separation components were detected by spectroscopic techniques¹³. The electronic properties of trivalent lanthanide ions make them luminescent groups with much currently developing application in biotechnology. Lanthanides (Eu, Th, Dy) used for multiplexing. Er-YAG laser is used for surgical resurfacing. It has ablative properties with water as main chromophore. It was concluded that both proliferation and apoptosis occurred when the laser irradiated the skin [14]. The compounds which are employed as detoxification agents usually stable complexes of cadmium. Thiocarbazono ligands and their complexes have shown a wide range of pharmacological properties [15]. The complexes were tested by MTT reduction assay against two mouse tumor cell lines. The proliferation inhibitory effect of the complexes compared to that of the ligand proved their cytotoxic properties against both the tumor cell lines [16].

Materials and Methods.

Chemicals and solvents including Bromosuccinimide, nitro toluene, dimethyl amine, sodium bicarbonate, copper chloride and praseodymium chloride, Ethanol, Toluene were purchased from Sigma-Aldrich, Lab Scan and Acro Organics. FTIR spectra in the range 4000-250cm⁻¹ as KBr disk was recorded. The UV-Vis spectra was recorded on UV-530 spectrophotometer. Conductivity was measured on Wescan-212 conductometer in Dimethyl sulphoxide. Thermogravimetric analysis was performed on TGA instrument SDT Q600 T.A company, temperature maintained at the rate of 20° per minute. The elemental analysis of the complexes was carried on LECO Truspec micro Sr No. 4021 Model No. 630-200-200. The dimensions of the crystal were 0.30x0.25x0.10 and measurements were found by using 100(2k with the AXS SMART APX diffractometers using graphite λ (MoKα) Å° (0.71073). Unit cell parameter and orientation matrix were determined by least square calculations based on angles and 6651 reflections ranging from 1.332 to 27.916 deg. The formation was solved by direct method (SHELX 86 AND SHELX 93) 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).

Synthesis of 2- (bis-2-hydroxyphenylidene)-1, 2-iminoethane



Synthesis of 2- (bis-2-hydroxyphenylidene)- 1, 2-iminoethane takes place in two steps. salicylaldehyde (23.4 g, 0.1 moles) and ethylenediamine (6 g, 0.1 moles). in 250ml of carbon tetrachloride, nitrotoluene (0.5 mol), benzoyl peroxide (1.0g) were charged in a quick fit equipped with water condenser and reaction mixture was heated under reflux for 6-8 hours, then mixture was allowed to cool down and filtered off the regenerated material produce in the reaction flask was o-nitrobenzylbromide now add NaHCO₃ and water in quick fit flask equipped with water condenser. Dimethylamine was added to the reaction mixture drop wise, reflux the mixture for four hours then the mixture was allowed to cool and filter off the solid material the filtrate consisted of two layers the organic layer and upper orange layer. The orange layer on evaporation gave orange oily liquid which was soluble in almost all organic solvents and having highly pungent smell [17].

Reaction of ligand with metal chloride

2- (bis-2-hydroxyphenylidene)- 1, 2-iminoethane in ethanol was mixed with clear solution of metal acetate monohydrate chloride (2mole) in distilled water, the mixture was refluxed with continues stirring for three hours solid material settled which was filtered and washed with ethanol and hexane and The success of the reaction was checked by TLC test. After the reaction, the solvent was removed by the rotary evaporator, washed with pet- ether dried under vacuum to get solid product

Antimicrobial Activity

Disc diffusion method was used to test the antibacterial and antifungal activity. Different strains (bacterial and fungal strains) were engaged to check the antibacterial and antifungal activities. Different strains were used to test the antibacterial activity. The selected strains were *Acidovorax tampons*, *Xanthomonas axonopodis*, *Xenorhabdus luminescens*. The ligands and metal complexes were employed for antimicrobial activity by using Disc diffusion method. Nutrient agar was mixed in distilled water and dispersed homogeneously. Sterilization of the medium was carried out by means of autoclave at 121 °C for 20 min. Medium was treated with Inoculums before it was transferred to Petri plates. Hereafter, filter paper discs were placed parallel on growth medium which contains 100 µL of complexes and ligands, respectively. The incubation of Petri plates was taken for 24 hours at 37 °C for bacterial growth. The complexes and ligands that exhibited the antibacterial activities well, inhibited the growth of bacteria and formed clear zones. Zone reader was employed to measure the inhibition zones in millimeters. The standard drug used was Ciprofloxin [18]

Antifungal activity

Fungal strains were used to test the antifungal activity. The selected strains were and fungal strains *Trichoderma* spp, *Alternaria alternate* and *Aspergillus flavus*. The growth medium was synthesized, sterilized and then transferred to the Petri plates. Petri dishes were incubated for 48 hours at 28 °C for fungus growth. Filter paper discs were cited on growth medium for the growth of fungus. The complexes and ligands were applied up to 100 µL (micro liter) on each disc. Petri plates were then incubated. The complexes and ligands that exhibited the antifungal activities, inhibited the growth of fungus and clear zones were produced. The standard drug used in order to compare the antifungal potential of the complexes and ligands was Fluconazole [19].

Results and Discussion

The physical data of ligand and metal complexes is given in table 1. The CHNS analysis shows metal to ligand ratio 1:2 stoichiometry for metal complexes. The ligand and metal

complexes showed sharp melting point and most of them were soluble in suitable solvents as shown in Table 2. Both metal and rare earth metal complexes are soluble in DMSO, copper complex shows solubility in acetone where as lanthanide complex is insoluble in acetone.

Table 1: Physical Properties of Ligands and Metal complexes.

Sr #	Compound Nature	Mol Weight	Mol formula	Melting point
1	L ₁	268	C ₁₆ H ₁₆ O ₂ N ₂	116 °C
2	Pr(L ₁)	658	Cu ₂ (C ₁₆ H ₁₆ O ₂ N) ₂	>350 °C
4	Zn(L ₁)	562	Zn ₂ (C ₁₆ H ₁₆ O ₂ N) ₂	>350 °C

Table 2: Solubility of ligands and metal complexes

Sr #	Compd/Complex	Solubility of complexes			
		DMSO	DMF	Chloroform	Acetone
1	Ligand	+	+	+	+
2	Zn complex	Soluble	Slightly soluble	Insoluble	Partially soluble
3	Pr complex	Soluble	Insoluble	Insoluble	Insoluble

FTIR spectra

In order to clarify the manner of the ligand coordination to metal center, IR spectra in the range 4000-250cm⁻¹ was recorded and important bands for structural elucidation were confirmed. The spectrum of ligand shows the stretching vibrations in the range of 3000-2900cm⁻¹ which may be assigned due to N(CH₃)₂ which is again confirmed by the bands at 1530cm⁻¹ due to presence of nitro group in N-N Dimethylbenzylamine. The bands above 3400cm⁻¹ in the complexes may be assigned to methyl groups present on nitrogen. Lowering in frequencies in the range 1600-1300cm⁻¹ indicates the coordinate bond formation, spectrum of two complexes indicate a strong band in 2900-2600cm⁻¹ region due to formation of OH bond, it shows deprotonation and coordination of the carboxylate group with metals are formed. The vacant d orbital of Zn and Pr tends to give higher coordination number with ligands. The value found less than 500cm⁻¹ shows the chelation of metal with ligand.

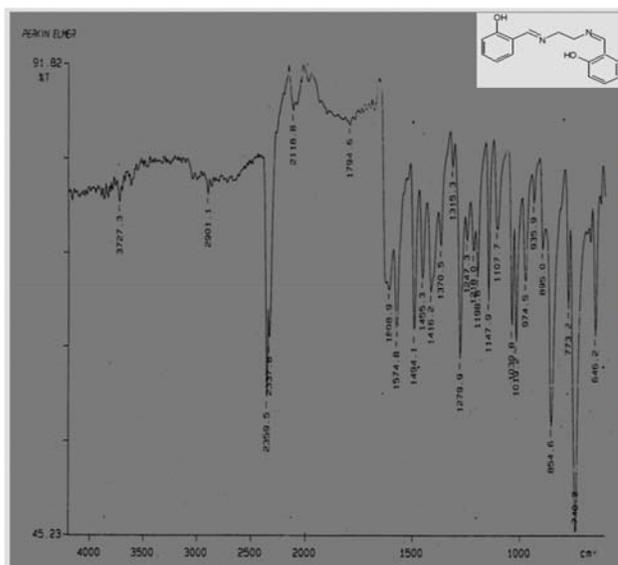


Fig 1

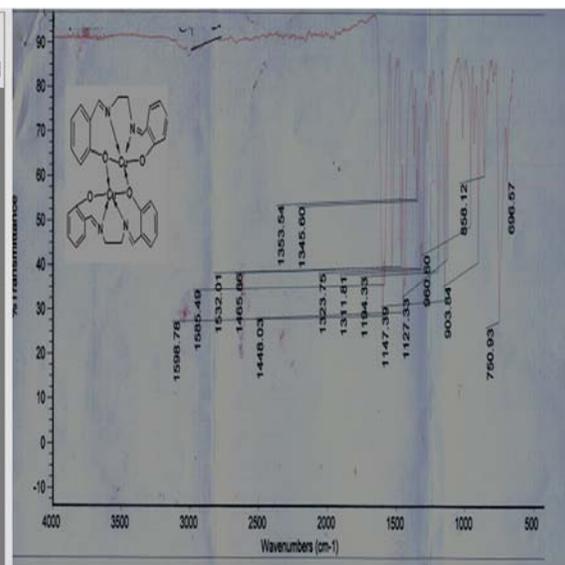


Fig 2

Spectroscopic Analysis

The U.V analysis was carried to find absorption λ_{max} of ligand and complexes. It was found that rare earth metal complex show absorption band at higher values as compared to organometallic complex. The absorption spectra towards maximum wavelength confirms the presence of complex formation.

Table 3: physico-analytical data of ligand and its metal complexes

Compound	Color	Conductivity	λ_{max}	Absorption	Yield
Ligand	Orange	-	225	2.647	23.53 %
zinc complex	Green	71	216,281	0.309,0.241	32.02 %
praseodymium complex	Brown	8	370,280	0.241,0.432	51.72 %

Conductivity Analysis

Conductivity measurements were performed on Wescan-212 conductometer in Dimethyl sulfoxide at room temperature [20]. The electric conductance measurement in DMSO shows electrolytic nature of zinc complex which is $71(\text{ohm}^{-1}\text{cm}^2\text{Mol}^{-1})$. Electric conductance measurement in case of praseodymium complex shows its non-electrolytic nature ($8 \text{ ohm}^{-1}\text{cm}^2\text{Mol}^{-1}$).

Elemental Analysis

The elemental analysis of the complexes was carried out by engaging complexes with elemental analyzer (LECO Truspec micro Sr No. 4021 Model No. 630-200-200). The results are presented in (Table 4). Sulphur is absent in ligands as well as in metal chelates. Rare earth metal complex shows greater content of carbon as compared to copper complex, which clarify the combustion of Praseodymium complex.

Table 4: Elemental analysis of complexes

Compound	Nitrogen	Hydrogen	Carbon
zinc complex	32.454	4.6786	12.5771
Praseodymium complex	15.9642	8.0323	63.8656

Thermogravimetric analysis

Thermal analysis performed on universal V4.7A instrument SDT Q600V20.9Build20. Thermal analysis shows greater stability of rare earth metal complex as compared to transition metal complex. Elimination of water in both complexes shows endothermic peaks with evolution of heat while formation of residue with complete decomposition of complex endothermic peaks were observed.

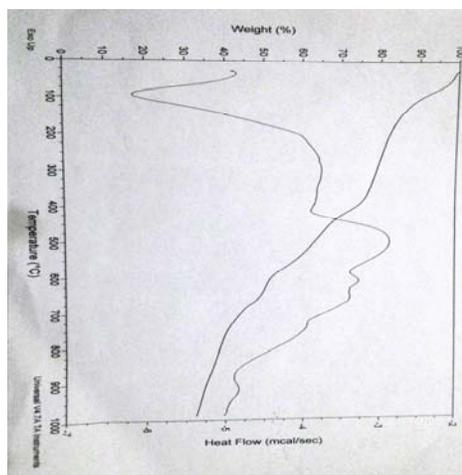


Fig 3: TGA spectra of zinc complex

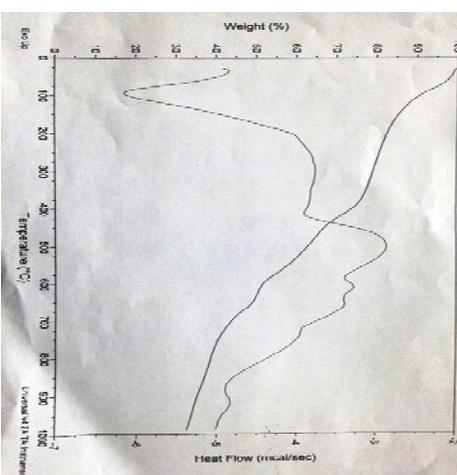


Fig 4: TGA spectra of praseodymium complex

Table 5. TGA analysis of complexes

Complexes	Temperature range	Mass Loss % Found(calcd)	Expected nature of decomposition	Peaks
zinc complex	130-160	23.92(23.80)	Elimination of water molecule	endo
	160-280		Partial decomposition of complex	exo
	290-320		Formation of residue	exo
Praseodymium complex	310-450	25.00(24.54)	Elimination of water molecule	endo
	450-565		Partial decomposition of complex	exo
	565-720		Complete decomposition of complex	exo

High performance liquid chromatographic analysis

- **Chromatographic Conditions**
- Column: Inertsil-ODS-3 column (150x4.6mm, 5um 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

The peaks of ligand have the significant response at single wavelength of 210 nm.

HPLC analysis of ligand

The filter solution of ligand 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^2

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 20 μ l at run time of 10 minutes. Flow rate was set 1ml/min. The 20 μ l of ligand 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, 5 μ m particle size) was used. The HPLC system given command of run after injecting sample. The retention time of ligand has been noted. The column used was Inertsil-ODS-3 (150x4.6mm, 5 μ m particle size) and flow rate was 1ml/min. The mobile phase consisted of buffer and methanol in the ratio of 95:5(v/v). The column was properly washed and calibrated under standard condition before run. The ligand 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 ligand were observed at 3.533, 3.873 and 6.227 with area percent of 0.649, 2.477 and 0.330 respectively.

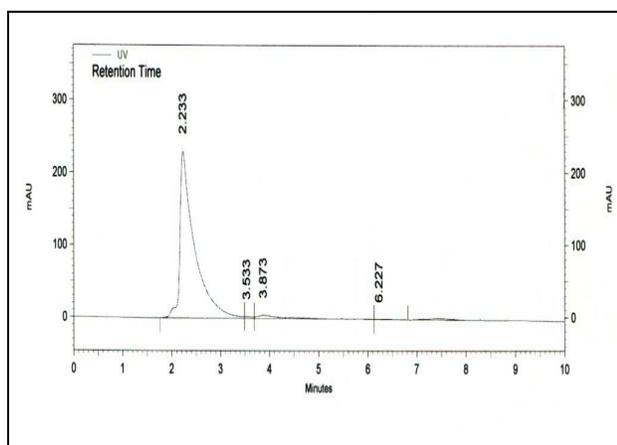


Fig 5: Chromatogram of ligand R_T of ligand=2.233 min at 210nm

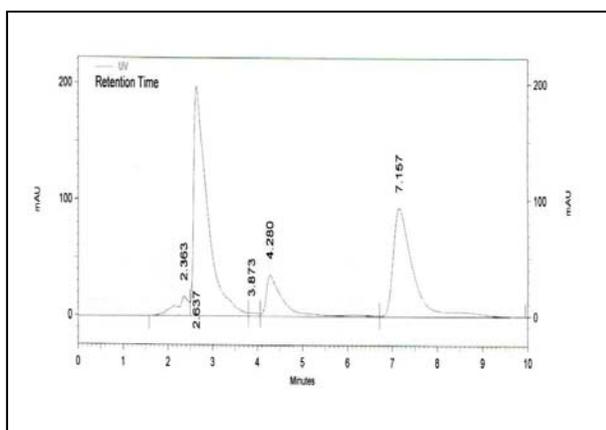


Fig 6: Chromatogram of ligand of batch (15TB24). R_T of ligand=2.637 min at 210nm

UV Results

Table 6: HPLC analysis of complexes

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

Sample ID: praseodymium complex (15TB24)

Vial: 191

UV Results

Table 7.

Name	Retention Time	Area	Area percent	Integration Codes
	2.363	763039	2.318	BV
	2.637	16868966	51.264	VV
	3.873	177521	0.539	VV
	4.280	3504887	10.651	VB
	7.157	11591473	35.226	BB
Totals		19819920	100.000	

X-ray Powder diffraction analysis

The structure of complexes of copper and praseodymium were elucidated x-ray diffraction technique.

X-Ray powder diffraction of praseodymium complex

The complexes obtained in powder form were gently grounded in an agate mortar then powder of each complex was deposited in sample holder equipped with silicon zero – background plate. The diffraction data were collected by scans in the 2θ range of $20^\circ - 80^\circ$ by using an advanced refractometer equipped with λ Source $CuK\alpha_1 = 1.54 \text{ \AA}$. PANalytical X PERT Pro Voltage = 40 KV current = 40 mA $\theta = 20^\circ - 80^\circ$. Standard peak search followed by visualizing the intensity we can find a size of crystallite, unit cell parameters and space groups.

2θ values of hexagonal shape zinc complex are (31.91), (34.529), (36.41), (47.75) and with hkl values (101), (002), (101), (102), respectively. The average crystalline size of zinc complex was calculated by Scherer formulae

$$\tau = \frac{K\lambda}{\beta \cos\theta}$$

τ is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size while K is constant of grain shape having constant value 0.94 and λ is the X-ray wavelength value 1.54 \AA and θ is the Bragg angle while β is the full width half maximum with peak breadth.

The shape of copper complex was hexagonal while the average crystalline size shown by Scherer formulae was 6.887562. This confirmed zinc complex.

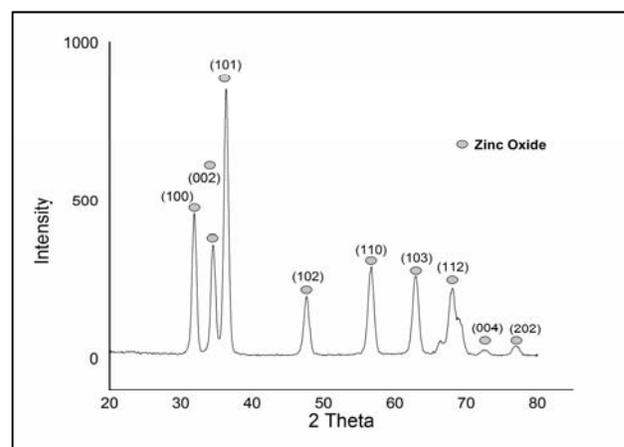


Fig 7: XRD -spectrum of ZnO nanoparticles praseodymium. Peak at 2θ reflected the presence of amorphous complex

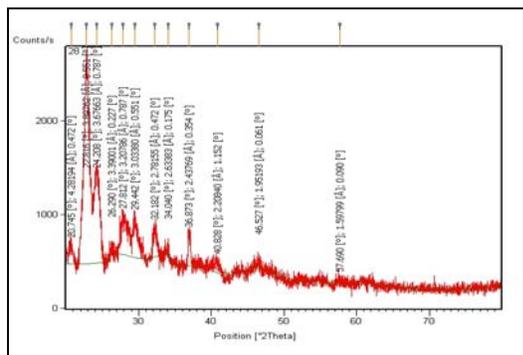


Fig 8: Refinement plot having maximum and minimum intense peaks showed the presence of respective metal

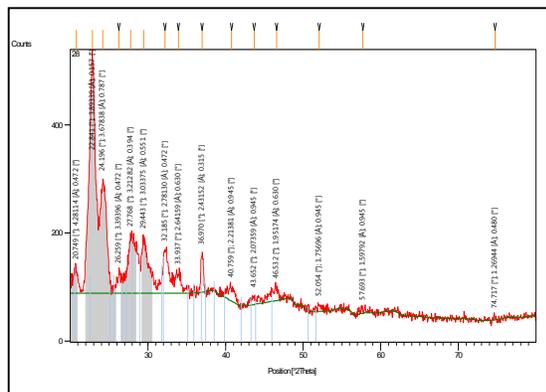


Fig 9: Data collection parameters of Pr-L

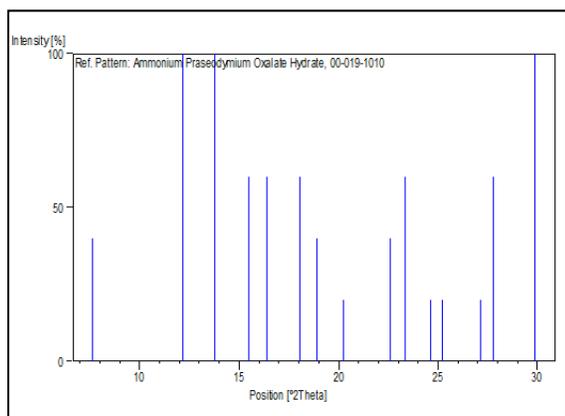


Fig 10: Stick pattern of praseodymium complex

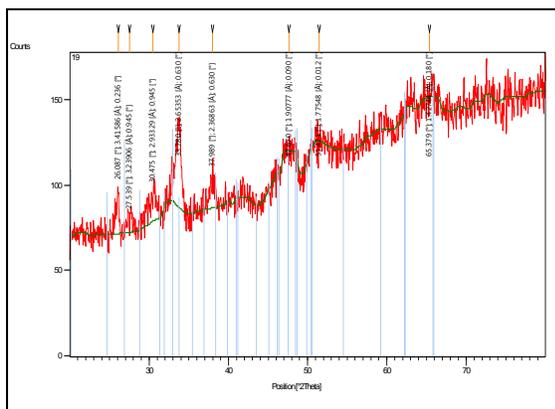


Fig 11: praseodymium Hydrate Hydrazine carbonate Mass spectrometric analysis of L₁

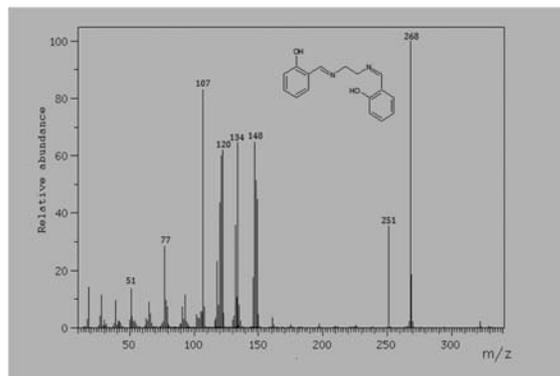


Fig 12: Mass spectrum of L₁ (a) Nuclear Magnetic Resonance Spectroscopic analysis of L₁

Molecular ion peak of L₁ was observed at 268 which is also a base peak. The molecular ion fragment was disintegrated by the cleavage of OH group resulting the fragment peak at 251. The fragment pattern of the molecules was observed by the cleavage of nitrogen – ethylene bond. Two fragments were observed in the spectrum. Among these one was with molecular mass 148 and the second was with 120. The second fragment with mass 120 after combining with nitrogen and resulted the peak at 134 in the spectrum. The second fragment after eliminating nitrogen resulted the fragment that observed at 106. Isotopic peak for the molecule was observed at 269 with intensity of about 1% of the molecular ion peak (Table 4.14). The results can be visualized from the spectrum

(i) ¹HNMR analyses of L₁

The singlet peak at 3.95 ppm was exhibited by protons of ethylene. Each aryl group has four protons in the molecule. Different environment of these protons was found (Table 4.15) with labeling from C₁----C₄. C₁, C₂, C₃ and C₄ protons showed doublet, triplet, triplet and doublet at 7.02, 7.52, 7.08, and 7.66 ppm, correspondingly. Imine protons showed singlet at 8.54ppm. Imine group have π electrons which were deshielded and showed high value. A singlet at 11.26 ppm is exhibited by phenolic protons which is probably due to the strong effect of deshielded oxygen atom. The results can be visualized from the spectrum.

Table 8: ¹HNMR data of ligand (L₁)

Position of Protons	Type of Peak	Value in ppm
C ₁	Doublet	7.02
C ₂	Triplet	7.08
C ₃	Triplet	7.52
C ₄	Doublet	7.66

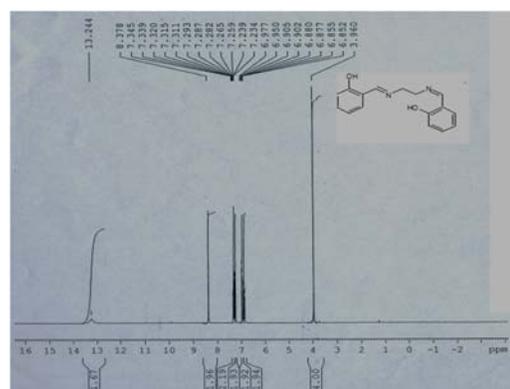


Fig 13: ¹H NMR spectrum of L₁

Antimicrobial bioassay

The antimicrobial activity was done by using disc diffusion method against different strains. Confirmed that lanthanide complex exhibit more bacterial and fungal activities than ligands. Also the synthesized compounds have a novel mode of action destined targets. Once their effectiveness against biological targets can find then it can be modified to uncover potentially active new bioactive lanthanides compounds as compare to transition metal compounds.

Antibacterial analysis Activity

The ligand and metal complexes were screened for antibacterial activity. The ligands and metal complexes were employed for antibacterial activity by using the grams well diffusion methods. Nutrient agar (LB media) 15g was mixed in distilled water and dispersed homogeneously. The medium was sterilized by means of autoclave for 1 hour at 121 °C. To each petri dish add a sterilized LB media. After the agar was

set 10% of suspension culture was added to each petri dish and spread thoroughly. After inoculation wells were scooped out with 7mm sterile cork borer and different concentrations of metal complexes in DMSO were added. Control was maintained in DMSO. The complexes and ligands that exhibited the antibacterial activities well, inhibited the growth of bacteria and formed clear zones. Zone reader was employed to measure the inhibition zones in mili meters.

The ligands and their complexes were engaged for activity against *Xanthomonas axonopodis*, *acidovorax* tampons, *Xenorhabdus luminescens*, using Ciprofloxin as positive control. The highest activity shown by Praseodymium complex was found against *Xenorhabdus luminescens* with zone 15.5± 0.577mm. The activity against *Xanthomonas axonopodis* and *Acidovorax* tampons were average with zones 11.25±0.54 and 12±0.154, respectively. All results are given in comparison with standard drug (Ciprofloxin) (Juneja *et al.*, 2013) which gave the zone 24.5±0.577 mm (Table 6)

Table 9: Antibacterial activity data of ligand and its metal complexes.

Sr#	Compounds	Tested Microorganism Diameter of Inhibition Zone		
		<i>Xanthomonas axonopodis</i>	<i>Acidovorax tampons</i>	<i>Xenorhabdus luminescens</i>
1	ligand	Nil	5.25±0.957	7± 0.816
3	Praseodymium complex	11.25±0.5	12±0.154	15.5±0.577
4	copper complex	12±0.154	8.5±0.577	13.5±1.732
5	Standard	23±2.061	24.5±0.577	23.5±0.816

Antifungal activity analysis

The ligand and metal complexes were tested for antifungal activities against different fungal strains. The synthesized complexes and ligands were tested for activity against various fungus strains (*Trichoderma* spp, *Alternaria alternate*, *Aspergillus flavus*) by using disc diffusion method. Fluconazole is used as standard drug. The highest activity was

found by Pr-complex against *A. alternata* with zone 12.5±1.732. The activity against *Aspergillus flavus* and against *Trichoderma* spp was average with zone 11±0.154 and 9.5±0.577, respectively. The results are in comparison with standard drug (Fluconazole) which gave the zone 24±0.816 (Table 7).

Table 10: Antifungal activity data of ligand and its metal complexes.

Sr#	Compounds	Tested Microorganism Diameter of Inhibition Zone		
		<i>Trichoderma</i> spp	<i>Aspergillus flavus</i>	<i>Alternaria alternate</i>
1	ligand	4.25±1.5	3.25±0.957	4±0.816
3	copper complex	7.25±0.957	9.5±1	9±0.816
4	Praseodymium complex	11±0.154	9.5±0.577	12.5±1.732
5	Standard	23.5±0.577	23.5±2.061	24±0.816

Discussion

The complexes obtained are in solid form, a comparative study of lanthanide complexes and transition complexes Shows that rare earth complexes have sharp melting points as compared to transition metal complexes as shown by physical data obtained which is also confirmed by thermal gravimetric analysis (TGA) of Zn(II) complex and Pr(III) complex. The removal of coordinated water from complexes under investigation is observed for transition as well as for Lanthanide complex. By examining the I.R spectra of the complexes as compared to free Ligand shows that bands located at 3380-3250, 1680-1665, 1625-1529 cm⁻¹ due to N-H, O-H and C-C band respectively shifted to lower frequency in case of Cu(II) complex but in case of Pr(III) complex it shift to higher frequency overtones are observed due to Fermi resonance effects. The disappearance of the bands at 1390-1370 and 1140-1120 cm⁻¹ due to -OH and C-OH groups is the indication of displacement of proton to metal ions on chelation. The spectra of both complexes show broad band at 3600-3300 cm⁻¹ due to -OH of water molecules in contact with complex formation and it is supported from TGA measurement two new bands observed at 400-800 and 350-380 cm⁻¹ which were not observed in spectra of free Ligands

is due to metal-ligand respectively. The transition observed in UV analysis in rare earth complex absorb at high wavelength as compare to transition complex. In order to elute in shorter time both complexes are subjected to HPLC analysis. Many chromatographic parameters such as peak, symmetry, number of theoretical plates and retention factor were considered specific was evaluated by comparing the chromatograph of each analyte regarding the appearance of eluting peaks with the same selected transition and retention times change at transition temperature of 728K which is indicated with sudden drop in TGA. Two inverted peaks are due to some changes such as interstitial formation or due to ion migration. The complexes are screened for antimicrobial and antifungal activities which shows that praseodymium complex show greater antibacterial effect as compared to copper maximum inhibition is shown by *Xenorhabdus luminescens* and medium is shown by *Acidovorax tampos*. Similarly *Alternaria alternate* was inhibited strongly by Praseodymium complex as compared to copper complex. The concentration factor upto about 250 and injection volume of 50 micro litre allow us to determine the quality of metal ion upto microgram per litre level in water.

Conclusion

By synthesizing the Metal chelates belong to transition metal that is zinc and praseodymium that belongs to lanthanides. These complexes were characterized by different physiochemical and spectroscopic techniques. The results are finalized by comparing the bioactivities of both complexes. Lanthanide complex was able to be more active compound having novel mode of action against particular strains of

bacteria. New bioactive compounds can be prepared to increase the potential against bacteria. The current antifungal drugs have limitations, they are effective against certain metal complexes. I have selected complexes against some strains of fungus to evaluate their bioactivities. Lanthanide complex display significant antifungal activity.

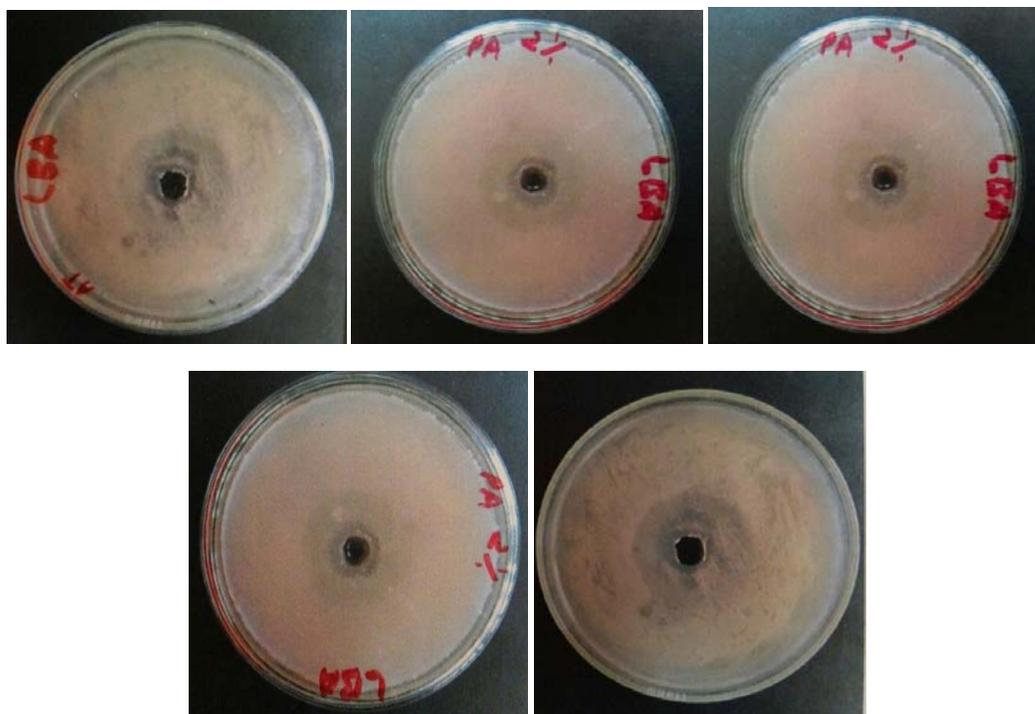


Fig 14: Minimum zone of inhibition for bacteria

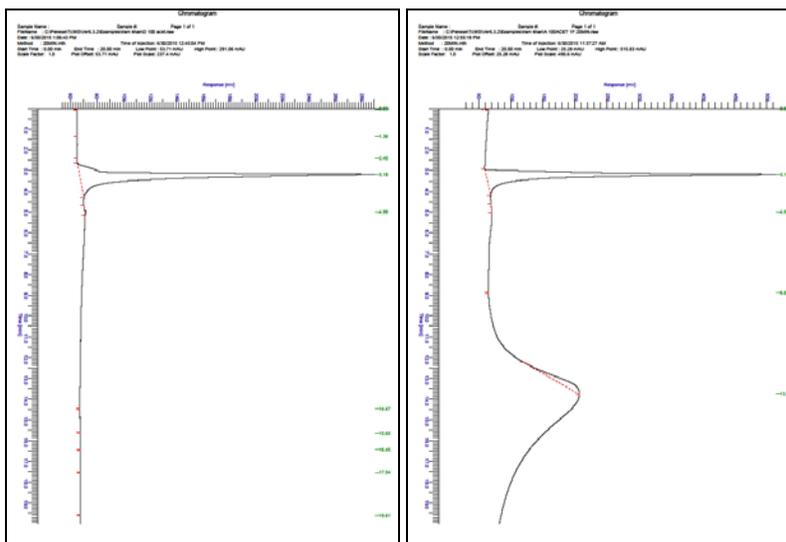


Fig 15: HPLC spectrum of ligand

Fig 16: FT-IR Spectrum of praseodymium complex

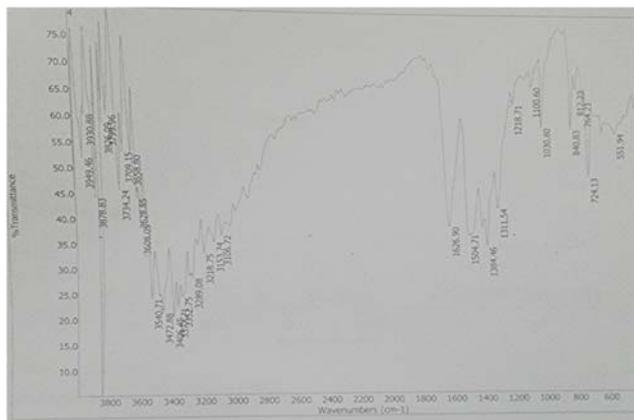


Fig 17: FT-IR Spectrum of zinc complex

Acknowledgments

I am grateful to Department of chemistry, University of Punjab, Lahore for providing me facilities for analysis of my complex also department of agriculture sciences in University of Punjab for providing me microorganisms for biological screening of metal complexes.

References

- Salami A, Ukavba TN, Lyiola NG, Agbola TO, Olowole FS, Olabye S. Gastroprotective properties of manganese chloride on acetic acid induced ulcer in Wistar rats. *J biomed research*. 2014; 17:109-117.
- Pan T, Wang W, Chia W, Fong L, Chen C, Huang C *et al*. Systematic evaluation of skin damage irradiated by an Erbium, YAG Laser: histopathologic analysis of proteomic profiles and cellular response *J derma sci*. 2010; 58:8-18.
- Alomar KA, lancreau A, Mustayeen K, Khan A, Bouet G. Synthesis, crystal structure, characterization of Zinc(II) Cadmium(II) complexes with 3_ thiophene aldehyde thiosemicarbazone-Biological activities of 3TTSCH and its complexes. *J Inorg Biochem* 2010; 104: 397-404.
- Ruber G, Bendorf K, Wellner A, Kircher B, Bergemann S, Gust R. Synthesis and biological activities of transition metal complexes based on acetylsalicylic acid as Neo-anti cancer agent. *J med. chem*. 2010; 53:6889-6898.
- Silva S, leite Q, Pava F. Co-ordinative versatility of a Schiff base containing thiophene: synthesis, characterization and biological activities of Zinc (II) and silver (I) complexes. *J poly*. 2013; 2:2316-2345.
- Abu-el Wafa, Samy M, EL-Behairy M, Issa R, Saleh A. Formation of Mn(II) anthranilic acid and anilide complexes. Structural elucidation by TGA, IR, electronic, EPR spectra and potentiometric studies. *J. chem soc of Pak*. 1988; 10:464-469.
- Wang X, Li Y. Synthesis and Characterization of Lanthanide Hydroxide Single-Crystal Nanowires. *Angewandte Chemie International Edition*, 2002; 41(24):4790-4793.
- Kumar K, Chandro S, Singh RP, Singh AK. Synthesis and electrochemical properties of different sizes of CuO nanoparticles *J med chem*. 1984; 14:185-189.
- Kuwar AS, Shimpi SR, Mahulikar PP, Bendre RS. Synthesis, characterization and antimicrobial activities of metal complexes of 2-formyl thymoloxime. *J Sci and Ind research*. 2004; 65:665-669.
- Sultana N, naz A, Saeed Aryan M. Synthesis, characterization, antibacterial, antifungal and immunomodulating activities of gatifloxacin_ metal complexes. *J of. Molr Str*. 2010; 969:17-24.
- Sheikh J, Juneja H, InjkV. Synthesis and *in vitro* biology of Co (II), Ni(II), Cu(II) and zinc (II) complexes of functionalized beta-diketone bearing energy buried potential antibacterial and antiviral O,O pharmacophoresites. *J Saud Chem Soc*. 2010; 17:269-276.
- Semacetin E, Babalik Z, Turk FH, Turk NG. The effects of cadmium chloride on metabolite production in *Vitis Vinifera* CV- cell suspension cultures. *Jbio Research*. 2014; 47:167-178.
- Wang X, Li Y. Synthesis and Characterization of Lanthanide Hydroxide Single-Crystal Nano wires. *Angewandte Chemie International Edition*. 2002; 41(24):4790-4793
- Lima L, Vasconcellos MC. Genotoxic cytotoxic effects of manganese chloride in cultured human lymphocytes treated in different phases of cell cycles. *J Toxicology in vitro science direct*. 2011; 2:391-394.
- Akbar j, Iqbal MS, Masih R. Kinetics and mechanism of thermal degradation of pentose and hexose based Carbohydrate polymers. *Malaysian Journal of. Analytical science*. 2012; 90:1386-1393.
- Daud JM, Alakil M. High performance liquid chromatographic separations of metal-Pyrollidine Dithiocarbamate complexes. *Jou Chem society of Pak* 2013; 7:113-120
- Pal R, Kumar V, Gupta AK. Synthesis, characterization and DNA cleavage study of dehydroacetic acid based tridentate Schiff's base and its metal complexes of first transition series *Journal of medicinal research*. 2014; 10:14-98.
- Sheikh J, Juneja H, Ingle V, Ali P. synthesis, spectra, thermal, potentiometric and antimicrobial studies of transition metal complexes of tridentate ligand. *J Saudi Chem Soc*. 2011; 17:269-276.
- Singh D, Kumar K, Dhiman K, Sharma J. Synthesis, characterization and antimicrobial activities of copper (II) complexes with N,N'-propanediyl-bis-benzene sulfonamide and N,N'-ethanediyl-bis-2-methyl benzene sulfonamide. *J enz inhib and medchem*. 2010; 25:21-28.
- Gujral RS, Hague SM. Simultaneous determination of potassium clavulanate and amoxicillin trihydrate in bulk, pharmaceutical formulations and in human urine samples by UV Spectrophotometry. *Int J Biomed Sci*. 2010; 6(4):335-43.