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Studies on Some Transition Metal Complexes with LIX:84

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STUDIES ON SOME TRANSITION METAL COMPLEXES WITH LIX84

A Dissertation

Submitted to The University of Rajshahi in Partial Fulfilment of The Requirements for The Degree of Master of Philosophy in Chemistry

By

MD. RUSTOM ALI

B.Sc. (HONS) M.Sc.

RAJSHAHI
2007

PHYSICAL RESEARCH
LABORATORIES
DEPARTMENT OF CHEMISTRY
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Declaration

I hereby declare that the entire work now submitted as a thesis to the Department of Chemistry, University of Rajshahi, towards the fulfillment for the degree of Master of Philosophy is the result of my won investigation and was carried out under the supervision of Prof Dr. Md. Shamsul Islam, Department of Chemistry, University of Rajshahi, Rajshahi. The thesis has not been submitted elsewhere for any other degree.

(Prof. Dr. M. Shamsul Islam)
Supervisor

Rustom Ali.
(Rustom Ali)
M. Phil. Fellow

Department of chemistry
University of Rajshahi

Declaration Certificate

This is to certify that Mr. M. Rustom Ali, M.Sc. the M.Phil research fellow of the Department of Chemistry, Rajshahi University carried out his research work under my supervision in the research laboratories in the same department for his Dissertation submitted for the Degree of Master of Philosophy. This research involving the study of complexing behaviour of the three metal ions with the extractant LIX84, other physical and microbiological properties is an original work for the extension of knowledge in the fields of solvent extraction and organometallic Chemistry.During the progress of his research, he gave a successful seminar on his thesis material and passed the assigned theoretical courses successfully in this department.

(Prof. Dr. M.Shamsul Islam)
Supervisor

DEDICATED TO
MY
BELOVED PARENTS

PART-I

CHAPTER – 1

GENERAL INTRODUCTION

Page
ACKNOWLEDGEMENT I

ABSTRACT II

LIST OF TABLES III
LIST OF FIGURES IV

LIST OF ABBREVIATIONS V

CHAPTER-1

GENERAL INTRODUCTION

1.1 Transition Metal Chelates and their Stability 2

1.2 Solubilities of Metal Chelates 6

1.3 Electrolytic Properties of Complexes 8

1.4 Magnetic Properties of Transition Metal Complexes 8

1.5 IR Spectral Data of Complex Compounds 11

1.6 UV-VIS Spectra of Complex Compounds 12

1.7 LIX 84 as Extractant/Ligand 14

CHAPTER-2

LITERATURE REVIEWS

2.1 Literature Reviews 17

2.2 Scope of the Present Investigation 25

CHAPTER-3

PRESENT AIM AND PREPARATION

Page

3.1 Aim of the Present Investigation: 28

3.2 Preparation of the Complexes 28

CHAPTER-4

EXPERIMENTAL TECHNIQUES

4.1 Weighing 33

4.2 Melting Point Measurements 33

4.3 Conductivity Measurements 33

4.4 Magnetic Measurements 34

4.5 Infrared Spectra 35

4.6 Electronic Spectra 35

4.7 Determination of Molecular Weight 37

CHAPTER-5

RESULTS AND DISCUSSION

5.1 Molecular Weight 39

5.2 Molar Conductances 39

5.3 Magnetic Moments 39

5.4 Percent Solubilities 41

5.5 Infrared Spectra 41

5.6 Electronic Spectra 42

LIST OF STRUCTURE OF COMPLEXES

Page

i) $[(ZrO)_2(L)_4(H_2O)_2]$ 44

ii) [Ag(L)] 45

iii) $[Cd(L)_2.HL]$ 46

LIST OF TABLES

Table-1: Color, yield, decomposition temperature and molar conductance of the complexes. 47

Table-2: Data for solubility of the complexes. 48

Table-3: Percentage (%) determination of the solubility of complexes in various organic solvents (gdm^{-3}). 49

Table-4: Detailed magnetic data of the complexes (T=303K). 50

Table-5: Observed frequencies and assignments for LIX84. 51

Table-6: Infrared Absorption Maxima in cm^{-1} of LIX-84 and M-LIX84 complexes. 52

Table-7: Electronic spectral data of the prepared complexes with assignment. 53

Table-8: Electronic spectral data of LIX84 54

Table-9: Electronic spectral data of the prepared complex $[(ZrO)_2(L)_4(H_2O)_2]$ 55

Table-10: Electronic spectral data of the prepared complex [Ag(L)] 56

Table-11: Electronic spectral data of the prepared complex $[Cd(L)_2.HL]$ 57

LIST OF FIGURES

Page

Fig. 1. Infrared spectrum of LIX 84 in KBr cell. 57

Fig. 2. Infrared spectrum of $[(ZrO)_2(L)_4(H_2O)_2]$ in KBr cell. 58

Fig. 3. Infrared spectrum of $[Ag(L)]$ in KBr cell 59

Fig. 4. Infrared spectrum of $[Cd(L)_2.HL]$ in KBr cell 60

Fig. 5. Electronic spectrum of LIX 84 (in cychlohexane). 61

Fig. 6. Electronic spectrum of $[(ZrO)_2(L)_4(H_2O)_2]$ (in cychlohexane). 62

Fig. 7. Electronic spectrum of $[Ag(L)]$ (in cychlohexane). 63

Fig. 8. Electronic spectrum of $[Cd(L)_2.HL]$ (in cychlohexane). 64

REFERENCES 66-69

APPENDIX 98-100

LIST OF ABBREVIATIONS

1.	cm	Centimeter
2.	cm^{-1}	Per centimeter
3.	Fig.	Figure
4.	i.e.	That is
5.	K	Degree Kelvin
6.	m.p.	Melting point
7.	mL	Milliliter
8.	No.	Number
9.	nm	Nanometer
10.	%	Per cent
11.	^	Conductance
12.	λ	Wave length
13.	χ_g	Mass susceptibility
14.	χ_m	Molar susceptibility
15.	g	Gramme
16.	uv	Utra-violet
17.	IR	Infrared
18.	v	Absorption maximum frequency

PART-II

CHAPTER-6

ANTIBACTERIAL ACTIVITY TESTING

LIST OF TABLES

Table 6.1: Complexes abbreviation for antibacterial activity. 77

Table 6.2: Antibacterial activity of the complexes 1, 2, 3 and ligand 2-roxy-5-nonyl acetophenone, oxime against *Escherichia coli.* 78

Table 6.3: Antibacterial activity of the complexes 1, 2, 3 and ligand 2-hydroxy-5-nonylacetophenone against *Shigella dyscnteriae.* 79

Table 6.4: Antibacterial activity of the complexes 1, 2, 3 and ligand 2-hydroxy-5-nonylacetophenone against *Pseudomonas aeruginosa.* 80

Table 6.5: Antibacterial activity of the complexes 1, 2, 3 and ligand 2-hydroxy-5- nonylacetophenone against. *Bacillus subtilis* 81

Table 6.6: Antibacterial activity of the complexes 1, 2, 3 and ligand 2-hydroxy-5- against nonylacetophenone *Sarcina lutea.* 82

Table 6.7: Antibacterial activity of the complexes 1, 2, 3 and ligand 2-hydroxy-5- nonylacetophenone against *Staphylococcus aureus.* 83

LIST OF FIGURES

Fig-6.1 Photographic representation of zone of inhibition of the complexes 1, 2, 3 and the standard compound kanamycin against *Escherichia coli.* 84

Fig-6.2 Photographic representation of zone of inhibition of the complexes 1, 2, 3 and the standard compound kanamycin against *Shigella dysenteriae.* 85

Fig-6.3 Photographic representation of zone of inhibition of the complexes 1, 2, 3 and the standard compound kanamycin against *Pseudomonas aeruginosa.* 86

Fig-6.4 Photographic representation of zone of inhibition of the complexes 1, 2, 3 and the standard compound kanamycin against *Bacillus subtilis.* 87

Fig-6.5 Photographic representation of zone of inhibition of the complexes 1, 2, 3 and the standard compound kanamycin against *Sarcina lutea.* 88

Fig-6.6 Photographic representation of zone of inhibition of the complexes 1, 2, 3 and the standard compound kanamycin against *Staphylococcus aureus.* 89

ABSTRACT

The research work presented in this thesis deals with the preparation and characterization of some new complexes of the second transition metal ions (Zr^{4+}, Ag^{+} and Cd^{2+}) with the new solvent extraction reagent, LIX84 (i.e.2-hydroxy-5- nonylacetophenone oxime) as a ligand. For their synthesis, the prepared aqueous solutions of the metal chlorides (for Cd (II), nitrate) are allowed to react with an n-hexane solution of LIX84 (containing KOH) in different ratios. The prepared complexes have been characterized by conductivity and magnetic measurements, infrared spectra and electronic spectral studies. Their percent solubilities in various organic solvents and decomposition temperatures have been measured. The molecular weight of the complexes have also been determined by the cryoscopic method.

The prepared complexes have compositions;

1. $[(ZrO)_2(L)_4(H_2O)_2]$ **2.** $[Ag(L)]$ **3.** $[Cd(L)_2HL]$

where, L denotes a LIX84 anion.

The complex **1** is assumed octahedral and the complex 2 is linear but the complex **3** has tetrahedral structure based on experimental data. IR spectra of the complexes **1**,**2** and **3** indicate coordination of the ligand to the metal ion through its N and O atoms. In these complexes LIX84 acts as a uninegative bidentate ligand. From magnetic measurements, the complex **1** is found to be binuclear paramagnetic, whereas complexes **2** and **3** are diamagnetic. All the complexes are found to be insoluble in polar solvents viz, water, ethanol and acetone; but sparingly soluble in other organic solvents. Measured values of the molecular weights and magnetic moments for the complexes indicate that **1** is binuclear compound. Moreover, all the complexes have been observed to behave as non-electrolytes in DMSO or cyclohexane. Probable structures for the complexes have been suggested.

Further, the microbiological study of LIX84 and its Zr, Ag, Cd, complexes has been carried out. Studies of the antibacterial activity of the prepared complexes showed them to behave as good inhibitors on myeclial growth against selected standard and the ligand has been studied for six pathogenia bacteria viz.,

1. *Escherichira coli* (Gram negative)
2. *Shgiella desenteria* (Gram negative)
3. *Pesudomonus areuginosa* (Gram negative)
4. *Bacillus subtilis* (Gram positive)
5. *Sarcina lutea* (Gram positive)
6. *Staphylococcus aureus* (Gram positive)

and also investigated the minimum inhibitory concentration of the complexes 2 and 3. All the results obtained is compared with the standard compound, Kanamycine.

The results of this investigation reveal that the complexes are more or less active compared to the ligand (2-hyroxy-5-nonylacetophenone oxime).

Among the complexes, complexes 2 and 3 show the excellent result.

GENERAL INTRODUCTION

INTRODUCTION:

Transition metals are those elements, which usually have partly, field d or f-shells in any of their commonly occurring oxidation states[1]. Because of their variable valence, they form a large number of complexes with various types of ligands with a few exceptions. These compounds are colored in one if not all oxidation states, and at least a few of them are paramagnetic.

However, a few transition metal complexes with 2-hydroxy-5-nonylacetophenone oxime (LIX 84) are reported[2].

This compound has recently been introduced as a solvent extraction reagent by Hinkle Corporation, U.S.A. Being a 2- hydroxy-5-nonylaceto phenone it is expected that LIX 84 may form water insoluble complexes with various metal cations in slightly acidic solutions under controlled pH conditions. This reagent has been used in hydrometallurgy for the extraction a few very useful metals viz. copper from aqueous ammonia solutions using the method of solvent extraction (SX). But the chemistry of the extraction processes as well as the elucidation of the structures of the extracted complexes has not yet been studied. Complexing behaviour of LIX 84 with other useful metal ions are lacking.

Some first transition metal complexes of LIX 54 have been prepared and characterized , but these await publication. However, studies with heavier transition metals are also lacking therefore, the preparation and studies on isolated complexes of LIX 84 with such metals appear interesting from those points of view. The preparation and characterization of some complexes of Ag (I), Cd (II), Zr (IV) with LIX 84 have been presented in this dissertation, the reagent acting as a uninegative bidentate ligand. The knowledge acquired will be helpful for different metal extraction processes with LIX 84 using the solvent extraction method.

1.1 TRANSITION METAL CHELATES AND THEIR STABILIY:

A metal complex may be defined as a compound containing a central metal ion (cation) to which are attached oppositely charged ions or neutral molecules whose number usually exceeds the number corresponding to the oxidation number of the metal ion. The ions or neutral molecules which are attached (coordinated) to the central metal ion are called ligands.

Transition metal ions form stable chelate complexes with high molecular ligands containing more than one containing more than one coordinating centers, Nitrogen-sulpher, nitrogen-oxygen-sulpher or phosphorous-oxygen donor ligands are known to form very important complexes with transition metals. Such metal chelates are formed when metal cations (Lewis acids) react with large chelating anions (Lewis base). Usually, the chelating ligands destroy the hydration sphere of the metal ions in their aqueous solution forming a stable molecular species.

Most of organic ligands being weak acids of long carbon chains (>6C) are generally soluble in organic solvents. Usually, they contain at least two coordinating functional groups on either sides of 2 or 3 atoms. One group of the chelating molecule is an acidic OH. NH or SH each containing at least one electronegative atom O, N or S having basic character that possesses lone pair of electrons. The other is one uncharged basic functional group or atom capable of coordinating by its donor properties to the metal. Such chelating ligands function as bases by loss of a proton from the acidic group for an equivalent of metal, and thus produce reactive anionic ligands the chelating reagents remaining as almost undissociated neutral molecules (without solvation or coordination) in solution in an inert (non polar) organic solvent having no donor atoms capable of coordination to metal ions. In principle they do not undergo dissociation or association itself or with the metal chelates in the organic phase; but they dissociate ionically in the aqueous phase or at the interface of the two phases. Equilibrium studies have much contribution to the understanding of the various factors that influence metal complex formation in aqueous solutions.

The factors affecting the formation and stability of metal chelates include[3].

i) **The basic strength of the chelating agent:** the higher the basicity of the chelating group (higher pKa value), the greater is the stability of the metal chelate formed. Nevertheless, a more acidic chelating agent with a lower pKa value, will be more useful for the extraction of metals from acidic aqueous solutions.

ii) **The electronegativity of the bonding atoms of the basic group in the chelating agent:** atoms of lower electronegativity (increasing acidity of the group) tend to form stronger covalent bonds and there by increase the stability of metal chelates. For example, nitrogen and sulpher, have better donor properties than oxygen, as their electronegativity increases in that order.

iii) **Size and number of chelate rings formed;** from Bayer strain theory, five or six membered rings are most stable (minimum strain). All other factors being equal, a five membered ring chelate will be somewhat more stable than its six membered ring analog. Apart from any intrinsic advantage of ring formation, chelate stability also increases with the number of fings that are formed possibly owing to increasing number of say, water mole cules that are displaced from that metal coordination sphere by one molecule of the polyfunctional reagent.

iv) **The metal ion characteristics such as acidity i.e., ionic potential (i.e., charge/ionic, radius ratio) or charge^2/ionic ratio, electronegativity, coordination number and coordinating ability;** as the ration increases the stability of the metal complex usually rises, provided the metal ion has available bonding or bitals for the electron pairs it accepts. The nature of the orbitals affects both the bond strength and the stereochemical arrangement of the complex[4]. Moreover, complexes of the more electronegative metals (e.g. Zr,Ag,Cd) tend to be more stable.

v) **Resonance and steric effects:** the stability of the chelate structure is enhanced by contribution of resonance structures of the chelate ring[5.] But the stability decreases because of steric hindrance to chelate formation caused by the bulky substitution groups[6]; this hindrance is, however, at a minimum in tetrahedral grouping of the reagent molecules about the metal ion.

The majority of coordination compounds contain nitrogen, oxygen, sulpher or a halogen as the bonding atom. Some metals which prefer oxygen over nitrogen are Mg (II), Ca (II), Si(II), Sn(II), U (VI),Fe(III) are Be (II). Some of which prefer nitrogen donors over those of oxygen are Cu(I), Cu(II) ,Ag(I) Cd(II), Hg(II), V(II) Co(III) and Ni(II), Cr(III), Fe(II), Pt(IV), Zn(II) , Zr (IV), V) seem to coordinate equally well either with oxygen or nitrogen Except for Cu(I), Ag(I) Au(I) and Hg(II), oxygen donors are clearly superior to those of sulpher. With certain large ions of low charge (eg) Cu(I) Ag(I) Hg(I) the maximum stability occurs with sulpher containing ligands. However d^8 or d^{10} ions have little enderncy to become positively charged and are therefore, able to ccept electrons from ligands Such ions are, Hg(II), Ag(I), Pd(II) and Pt(II) which form more stable complexes with ligands of high polarizability, and the order is P>S>N>0.

Generaly donor atoms which gave large ligand field spliting from their strongest complexes with metal ions are particularly sensitive to ligand field stabilization whereas donor atoms producing small ligand fields tend to form relatively more stable complexes with cations which are insensitive to ligand field stabilization. Moreover, the difference in instability between complexes which produce small and large ligand fields will be mich greater for metal ions which are particularly sensitive to ligand field stabilization than those which are not. Metal chelates with least basic i.e. weakest donors dimerize to the greatest extent[7].

1.2 SOLUBILITY OF METAL CHELATES:

Metal chelates, being essentially neutral covalent compound, are far less soluble in water than in organic solvent (dilute). Rendering the chelate molecule larger and bulker, and more hydrophobic, its coordination properties can be altered. Factors causing low affinity of the metal chelate to aqueous are zero of low charge, large sizw, non polar nature, absence of electronegative atom at the surface and a highly ordered water structure, which also cause a high affinity for the organic phase neutral nonhydrated metal chelates are usually formed by many polyvalent metal cations whose coordination number is twice the charge; but some bivalent ions (Cd^{2+}, Zr^{4+}) having a coordination number higher than four may retain one or more water molecules in their first coordination sphere[8].

The chelates of heavy metals are in many cases soluble in organic solvents. Some of them, however, are soluble in highly polar solvents, e.g. alcohol and carbon terta chlorice ($CC1_4$), while others are soluble only in typically non polar solvents e.g. CH_2C1_2 or C_6H_6. Therefore, systematic compariso of the effects of various solvents on their structures of electronic polarity so that they can even serve as appfoximate indicators of solvent polarity.The solutions thus obtained sometimes exhibit a marvellous variety of colours according to the change in solvent states can often be carried out only over a limited range of solvent several different kinds of spectral charges are involved in these colour changes and those observed for the Cd(II) chelates are quite different from the Zr(II) chelates.

The nature of a solvent may also influence the reactivity of chemical compounds. The different reactivity of a solute X in two solvents, **1** and **2** may be characterized by standard free energy of transfer, $\Delta G^{tr.}$; and with its help the equilibrium constants of many reactions. e.g., A+B $\leftrightarrows$C in the solvents, **1** and **2** may be calculated.

$$-RT\ln K_1/K_2 = \Delta G^{tr.}(C) - \Delta G^{tr}(A) - \Delta G^{tr}(B)$$

Systematic investigations[9-12]. using various non-aqueous solvents have led to the conclusion that this ΔG^{tr} is almost exclusively determined by short range solute-solvent interactions. In order to express these short range interactions recourse has been taken to empirical solvent parameters such as Gutmann's donor and acceptor numbers (DN & AN), Kosower's Z, Zimoroth- Reichardt's E_T values etc.

Sone and Fukuda[13] have studied the electronic spectra of the solutions of some complexes, wach of which is soluble in a good number of solvents. They found that the colours of the solutions and the ν_{max} of the d-d bands are highly sensitive to changes in solvent polarity. For instance, mixed Cu(II)chelate with tetramethylethylenediamine and aacetylacetonate ion has a bluish or violet colour in aqueous solution. The colour becomes more and more reddish with the decrease in solvent polarity expressed in DN; and in solvents with very lox DN values, it is nearly red. On the other hand, in solvents of increasing polarity (high DN values) the complex assumes inereasingly bluish colour and in (CCl_4) it is blue. The parameter, donor number (DN) describes the nucleophilic behaviour and the acceptor number (AN) clectrophilic behaviour of the solvent.

Sone and Fukuda[13] who worked with square planar complexes argue that in solvents of increasing polarity, the complexes are ionized and the solvent molecules enter into the coordination sphere. Theoriginal square planar structure gradually tends towards the octahedral form and as a result, the d-d transition shifts towards higher wave lengths, that is lower v_{mas} values.

1.3 ELECTROLYTIC PROPERTIES OF COMPLEXES:

Conductance measurements can also be used to give useful information about the total number of ions (Complex, simple or both) yielded by a complex in solution and charge type on each ion.Electrolytic or non-electrolytic nature of the complex can be inferred from the experimental conductance data. Conductance values wall ascertain both the type and nature of electrolytes[14,15].

The state of the anionic species i.e., whether the anions are in bridge, inside or out side the coordination sphere, can also be predicted from the conductance which may thus help to determine the structures of the coordination complexes.

1.4 MAGNETIC PROPERTIES OF TRANSITION METAL COMPLEXES:

The fundamental magnetic properties (either paramagnetism or diamagnetism) of coordination compounds or complexes are used on the basis of measurements of their magnetic susceptibilities. From the experimental data, different possible electronic configurations can be assigned to them, which may give the clear information as well as stereochemistry of the complexes and even nature of bonding present there in[16,1].

Generally transition metal compounds show two types of magnetic properties, viz., paramagnetism and diamagnetism. A substance which is paramagnetic is attracted into a magnetic field with a force propotional to the field strength times the field gradient. Paramagnetism of a substance consisting of atoms, ions or molecules is generally caused by the presence of unpaired electrons. The greater the number of unpaired electrons, The greater will be the paramagnetism shown by the substance. The substance having no field than that in vacuum is called a diamagnetic substance and the property due to which it shows this behaviour is called diamagnetism.

Paramagnetic substances are characterized by the positive values of their magnetic susceptibilities. A paramagnetic substance increases the flux due to the applied field. Diamagnetic substances when brought under the influence of magnetic field, a repelled. These substances are characterized by negative values of magnetic susceptibilities. The diamagnetic character is an intrinsic phenomena, but the magnitude of the diamagnetic effect is small.

The ions of the first transition series starting with scandium (Sc^{3+}) ion and ending with zinc(Zn^{2+}) ion, second transition series starting with yttrium (Y^{3+}) ion and ending with cadmium (Cd^{2+}) ion, and the third transition series starting with lanthanum (La^{3+}) ion and ending with mercury (Hg^{+2}) ion have progressively zero to ten electrons in the 3d, 4d and 5d orbitals respectively. Their compounds may show paramagnetism or diamagnetism depending upon their oxidation states i.e., the presence of odd or even number of electrons in the ligand/crystal field. The greater the erystal field, the greater is the tendency of the electrons to be come paired up. If the crystal field is not so sufficient then the Hund's rule of maximum multiplicity is obeyed.

Hund's rule states that electrons tend to go separate orbitals with parallel spins provided the situation is energetically reasonable. The configuration with maximum number of unpaired electrons is of the high spin type and with minimum number of unparied electrons, the low spin type. For example Fe^{2+} which is d^6 system in presence of octahedral field of high spin type shows paramagnetism corresponding to two unpaired electrons. But in presence of square planar field, it becomes low spin type and diamagnetic[16].

The magnetism of second and third row electrons compared to that of the first row, is of much greater frequency with which diamagnetic occurs, and the paramagnetic moments are usually much lower. This is partly due to the fact that the complexes are invariably of the spin paired type[15], The Ag^+ is of course, diamagnetic[17]. The possible divalence of silver and of gold in $Cs_2\ Ag\ AuCl_6$ and in $Cs_2\ Au_2\ Cl_6$ respectively has been examined by Elliot[18]. Both the compounds are diamagnetic. Zirconium and halfnium apparently form no appreciable paramagnetic compounds. The useful valence of four is diamagnetic. The mercurous ion is diamagnetic because it always forms a double ion. Hg^{+2}. The mercury ion has no unpaired electrons and is diamagnetic[17].

Generally transition metal Compounds are coloured. The Colour and magnetic properties of transition metals are related to the presence of unpaired electrons in the system. Colour is not only due to upaired electrons but also due to other factors as well as electron transitions in presence of litght. Magnetic moments are extensively used to the study of complex compounds. From the evaluated magnetic moment, one can find out the number of unpaired electrons present in the system and thus gets an idea of its possible configuration and hence the structure.

1.5 IR SPECTRAL DATA OF COMPLEX COMPOUND:

All organic and inorganic species (except homonuclear diatomic molecules) absorb infrared radiation. IR spectroscopy has wide use in inorganic chemistry mainly coordination chemistry and proved to be a rich and convenient source of information concerning to the characteristic functional groups as well as structure and bonding. The condition of a reaction can be characterized from the initial IR and the product IR spectra. The field of vibrational spectroscopy of coordination chemistry has been expanded by a variety of research technich leading to many new and interesting result[19]. It is be coming more and more popular with ever increasing rapidly day by day. Therefore, the great utility of the vibrational spectroscopy in deducing structural and bonding information is noteworthy.

Since every different type of bond has a different natural frequency of vibration, and since the same type of bond in two different compounds is in a slightly different environment, no tow molecules of different structure will have exactly the same infrared absorption pattern or infrared spectrum. The presence or absence of a particular functional group in a molecule or the type of coordination in a compound can be assigned. IR spectrum can be used for compounds as finger prints can be used for human beings.

Penland et al[20] first studied the infrared spectra or urea complexes to determine whether coordination occurs through nitrogen or oxygen. If coordination occurs through nitrogen, an increase of the $\nu(C=0)$ stretching frequency with a decrease in the v(N-H) stretching frequency results. On the other hand, if oxygen atom participates in coordination, a decrease in the v(C=0) stretching frequency results without any appreciable change on the v(N-H) stretching frequency[21-22]. The metal nitrogen stretching frequencies usually lie in the range 480-310 cm^{-1} [23-24]. The bands at 400-200 cm^{-1} are attributed due to v(M-C1) stretching frequency[19]. Thus IR spectroscopy offers a variety of information about the complex compounds.

1.6 UV- VIS. SPECTRA OF COMPLEX COMPOUND:

The ultraviolet and visible spectroscopy is a simplex but powerful tool, which gives information on the geometries of complex molecules. In a typical electronic transition by metal complexes, the observed spectrum, in general, consists of a series of crystal field bands which are in the visible region and depends on the donor atom of the ligand and on the metal ion.

The crystal field transitions are of two types. One is the intens spin-allowed transition and another is the lower intensity spin-forbidden transitions, which appear as shoulders on the spin allowed transition. The ultraviolet spectrum is complicated and consists of electronic transitions between the ligands and the metal (charge transfer) and also transitions within the ligand itself which are usually $\pi-\pi^{*}, n-\pi^{*}$ otransitions. The bands in the electronic spectra represent` different vibration transitions according to the electronic charge in rotational energy superposde on the electronic and vibrational changes.

The ions of the transition metals give rise to a great rangeof colours which vary in hue and intensity from compound to compound and with oxidation state. This has long been known to be one of their more characteristic features. These colours arise from the absorption of the visible spectrum by the ions and their associated ligand group. The electronic dipole mechanism is the only of importance for the absorption fo light by the complex ions. when radiation of frequency equivalent to the energy separation between two levels specified by the functions Ψ_1 and Ψ_2 is applied this mechanism may be absorbe. The intensity of a band is best measured in terms of a quantity known as the ossillaror strength f; f is the area under the band when extinction co-efficient, ε, is plotted against frequency v.

If the terms of transition metal complexes correspond to a single energy level that absorption bands in their spectra should be exceedingly narrow. It has been that 10 Dq depends upon the metal-ligand separation in a bery critical manner. The energy differences between the highest and lowest states of a term (The overall multiplet width) is some simple multiple of the spin orbital coupling coupling is very large, the fine structure has been observed in solutions of their complexes.

The intense bands that are exhibited by the ligand around 345 nm and 303 nm are due to $n\text{-}\pi^*$ and $n\text{-}\pi^*$respectively[25]. For example. electronic spectra of all complexes show three bands about 400 nm, 290nm and 300 nm which may be assigned to the transitions respectively-

$${}^4T_{2g}(P) \longrightarrow {}^4T_{2g}(F)$$

$${}^4T_{1g}(P) \longrightarrow {}^4T_{1g}(F)$$

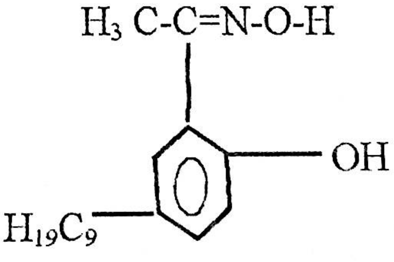
characteristic of octahedral geometry [26,27]. By this way, UV-VIS spectroscopy plays an important part in the detection and structure determination of complex compounds.

However, there are many other technique such as Dipole moment, X-ray diffraction, NMR (nuclear magnetic resonance), ESR (electron spin resonance) etc. which also furnish Valuable information on the structure of the complex compounds.

1.7 LIX-84 AS EXTRACTANT/LIGAND:

The high molecular weight hydroxyl amines and their suitable derivatives, which are being widely used as solvent extracting reagents all over the world in hydrometallurgy are known as LIX reagents. However, various α or β-hydroxy oximes (or phenolic oximes) and their derivatives βdiketones and quinoline sulphonamides are included in this class of metal extractants.

Although the popular LIX reagemts are β-hydroxy oxime but LIX 84 is a 2-hydroxy-5- nonylacetophonone oxime. It is a low viscosity (sp.gravity O.90) water insoluble 2-hydroxy –5-nonylacetophenone oxime having a molecular weight of 277 with the structure given below.



LIX-84 is a hydrogen ion donor and hence it forms a uninegative ion which acts as a l igand informing the complexes with metal ions. Like other chelating metal extractants, it operates on a similar hydrogen ion cycle as,

$[nRH]_{org}+[M^{n+}]_{aq} \rightleftharpoons [R_nM]_{org} +[nH^{+]}]_{aq}$ lacking in one- α -hydrogen, the LIX 84 complexes of transition metals are not expected to undergo polymerisation in the solid state. The 1:3 dicarbonyl compound, LIX 84 can be synthesized condensation (aldehydes or ketones).

Although LIX 84 has been used as an extractant for copper (II) from aqueous ammoniacal solutions but on report on the structure of its extracted complex with Cu (II) or any other metal ion is available.

Some observed extraction properties [28] of LIX 84 are outlined below.

(I) LIX 84 can be used neat without further kerosene dilution and still exhibit excellent phase separation properties. Phase separation is very rapid even at 100% concentrations.

(II) It does not load any free ammonia nor a copper-ammmine complex.

(III) LIX 84 has improved selectivity for Zr (IV) over Ag (I) and Cd (II).

(IV) It can be stripped of its complex with an aqueous solution having very low acid concentration and for this only one stripping stage is necessary.

(V) Extraction kinetics of LIX84 are very rapid (10 min) giving almost complete extraction. Moreover, LIX 84 has been found to be completely miscible in kerosene, ethanol and other usual organic and inorganic solvents except methanol. Its metal complexes are insoluble in ethanol and water.

CHAPTER – 2

LITERATURE REVIEWS

2.1 LITERATURE REVIEWS:

The survey of literature reveals that very little work have been done on the LIX® 84 reagent. However, much work of extraction and isolation of the extracted complexes of the transition metal ions has been made with other chelating LIX. reagents, their mixtures and the kelex reagents have been published The following summarizes the main reports on the use of LIX 84 reagent and other LIX reagents for different metal ions.

Law, Henrey H., Tierney, vicki[29], studied, "Direct recycling of copper from etching to platting. "In the manufacture of printed circuit boards, the copper dissolved during etching can be used to replace the Cu needed for plating using a liq. ion-exchange agent LIX 84 Extraction and stripping studies demonstrated the feasibility. The quality of the etching was not affected by the presence of the ion-exchange agent Good-quality deposits were plated from the stripping solution with a current efficiency of 100%

M.S. Islam and M.A.Salam [30] have prepared and characterized some complexes of first transition metal ions, Ti(III), V(II), Cr(III), Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Cu(II), Cu(I) and Zn(II) with LIX 54 (phenyl alkyl beta-diketone). Their characterization has been made by elemental analyses; conductivity and magnetic measurements, infrared and electronic spectral studies. The solubilities of the prepared complexes are investigated in various organic solvents. The decomposition temperatures are also measured. All these data have not yet been published

By the survey of existing literature it is evident that this reagent is related to the various types of the treatment of liver diseases. It can be used as a dental artifact. Being an ingredient of a composition of sintered porcelain product, LIX 84 may be also used as a dental material also LIX 84 reagent seems to be used in diabetes mellitus, and tumor growth stimulation. It is related to the transdermal pharmaceuticals to promote absorption. This reagent could be used for the prevention of treatment of gastritis.

The LIX 84 reagent has brain uptake property. So it acts as an agent of blood brain barrier. β-Adrenergic blockade restores glucose's anti ketogenic activity after exercise in carbohydrate- depleted athletes. Early T cell differentiated chronic mycloyed leukemia blast crisis with rearrangement of the break point cluster region but not of the T cell receptor B-chain genes.

This LIX 84 reagent may have industrial importance, too. There is a correlation between the oximes sensory and gas- chromatographic measurements on grape fruit juice volatiles. It' may have relation with stored –croude-oil sludge components identified. LIX 84 reagent can be used for some chromatographic investigation. It may act as an organic Pollutant. Oxime may have in cretaceous black shales. It also has some bio degradation in waste water treatment, The LIX 84 reagent acts as dental linear contg, It has also air pollutants effect. The transition metal complexes of LIX 84 reagent have some special type of physical and chemical properties. Some have coffee roasted aroma, some of them have cooked beef aroma; marasmius oreades fresh and dried mushroom aroma, pharmaceutical transdermal gels can be prepared by the metal complexes of the reagent. Most of the LIX84 complexes of transition metal elements may be used as corrosion inhibitors. These possess an excellent antirust and antifoaming properties. Cobait (II) loads and strips very quickly but cobalt (III) does not load on LIX84[31, 32] for the extraction of copper from ammonia leach solutions. LIX 64 N and other extractants with similar organic structures, have certain disadvantage[33,]

(a) They are limited in copper loading capacity such that high organic to aqueous flow ratios are required with large solvent extraction plants and associated capital investment costs:

(b) Some reagents will co-extract up to one mole of NH_3 per mole of copper which results in excessive loaded organic washing problem and subsequent wash effluent treatment, or disposal; and

(c) Other cheating extractants loads H_2SO_4 in the stripping circuit which would also demand another washing stage. However, LIX84 does not include the disadvantages cited above, but does offer the following positive advantages;

(I) LIX84 can be used neat without further kerosene dilution and still exhibit excellent phase separation properties. Phase separation is very rapid even at 100% concentrations.

(II) Used neat, LIX84 can extract up to 40gdm-^{3}cu from an aqueous solution containing 30gdm^{-3}NH3 thus eliminating or reducing the need for aqueous recycles in the extraction circuit.

(III) LIX84 does not load any free ammonia, nor a copper-ammine complex.

(IV) LIX84 has improved selectivity for copper over Cd and Zr.

(V) LIX84 can stripped with as 25 gdm$_{-3}$ H_2SO_4. At greater acid strengths, 80 or 100 gdm^{-3} H_2SO_4 only one stripping stage is necessary.

(VI) Extraction kinetics in very rapid rapid and sssentially complete extraction is obtained in 60 second (90%).

Thus LIX84 is a relatively weak copper extractnt which will load up to (4.75-4.80/ICu) Cu and can be used with no further dilution. Because it is a weak copper extractant, LIX84 can be striped with an aqueous solution whose equilibrium acid concentration is low but whose equilibrium copper concentration is high. LIX84 has been reported to be completely miscible in the solvents, acetone, toluene, isopropyl alcohol, ethanol (absolute), isodecanal, methylene chloride, cyclohexane, hexane and Kermac 470B (highly purified kerosene) to the extent 25 w/v% However, it is almost insoluble in methanol.

D.P. Graddon and E.C. Watton have reported some adducts of copper (II) β-diketone chelates with heterocyclic bases[33]. Equilibrium constants have been determined at room temperature for the 1:1 -addition of heterocyclic bases to copper (II) β-diketone chelates in three solvents, Irrespective of changes in the other two variables, the stability of the adducts increases in the order:

(a) 2:6: diethyl-pyridine<2:methyl-pyridine<4: methl-pyridine.

(b) acetylacetonate<benzoylacetonate<ethyl-acetoacetate.

(c) chloroform<acetone<benzene.

Variations of stability of the adducts due to changing bases are attributed in part to changes in donor power and in part to steric effects. Variations from one copper compound to another are related to the residual positive on the copper atoms of the chelates and solvent affects are thought to be due mainly to changes in the salvation energies of the bases.

The addition compounds have been isolated by crystallization of the β-diketonates from pyridine or 4-methyl pyridine. Infrared and vesible region absorption spectra of five-co-rodinated structure for all of these compounds, indicative the formation of 1:2 adducts of bis (ethyl acetoacetato) copper (II) having the additional molecule of heterocylic bade free in the crystal lattice. The magnetic properties of these adducts are normal,the moment of the copper atom be 1.81-1.85 β.M

P.A.O' Hara, M.P.Bohrer [34] worked on supported liquid membranes for copper transport. A carrier medicated liquid membrane process to printed wiring board shop as studied. Cu is transported from the alk. etching solution to the acid plation bath through a membrane consisting of a solution of a β-diketone in kerosene. A cu flux of 3.2 $\mu g/cm^2$ was obrtained with a 50% solution β-diketone (LIX 54-100) supported by a thin (25 µ m) microporous polypropylene film. The effect of process variables inclding aq. stirring rate, reactant concentrations and membrane thickness indicates that diffusion of the Cu carrier complex across the membrane is the permeation rate-controlling process at sufficiently high stirring rates and Cu feed concentration. The equilibrium distribution relation between the feed solution and the membrane is nonlinear for carrier concentrations>40%. Independent measurements using. well-characterized, track etched membranes qual. verified the inverse relation between concn. and diffusivety of the Cu-carrier complex, but are not accurate enough to quart. support the simple membrane diffusion model. The selectivity of the membrane for Cu is > 100 with respect to Ni, Zn and Sn..

The preparation and characterization of several complexes of first transition metal ions (V,Cr, Mn,Co, Ni and Zn) with LIX 34 was made by M.S. Islam and M.A. Islam[30]. They characterized the prepared complexes by comductivity, soluvility, infrared spectra, electronic spectroscopic studies and elemental analysis.

M.S.Islam et al[37] have prepared and characterized several new complexes of Cu(II), Zr(IV), Ag(I), Cd(II) and Hg(II) with-8 Alkyl sulfonamido-quinoline (LIX 34; Abbreviated as HL) and bis –(2,4,4-trimethylpentyl) phosphonic acid (cyanes 272; HL). Their characterizatioon was made by elemental analysis, conductivity and magnetic measurements, infrared spectra and electronic studies. The solubilities of the complexes in various. solvent and decomposition temperatures have also been measured. The stereochemistry of the complexes has been discussed on the basis of the experimental data.

The extraction of Cr (VI) from its aqueous acidic sulfate solution by Cyanex-272 in kerosene has been investigated[38] as a function of the aqueous phase acidity, extract ant concentration and temperatures: spectrophotometric technique was employed for the estimation of Cr (VI). The extraction ratio increases with increasing concentration of the extractant, aqueous phase acidity and temperatures. Chromium(VI) extraction by cyanex-272 is moderately slow requiring about 30 attain equilibrium cyanex-272 forms a 1:1 solvated complex with the metal ion in its dilute solution. From temperature dependence data, the apparent enthalpy change for the extraction reaction has been calculated to be AH=23.65 Kj) mol^{-1}The probable composition of the complex of Cr(VI) with Cyanex-272 at high loading has also been suggested from IR spectra, chromium(VI) - phosphorus ratio and molecular weight data. The mechanism of extraction at high loading is different from that at low loading.

The distribution of Ni (II) between benzene solutions of LIX 34 its aqueous acidic sulphate as well as ammoniacal sulphate solutions has been in estimated as a function of the extractable metal ion, sulphate acetate hydrogon ion and ammonia concentration. of the aqueous phase, extractant concentration,temperature and the nature of the diluents[29] ratio has been found to increase with increasing concentrtion of the extractant, acetate and temperature of extraction, and with decreasing acidity and sulphate concentration. Nickel extraction has been found to be quantitative in ammoniacal sulphate medium but very poor in acidic sulphate medium. LIX 34 forms a 1:1 complex with the metal ion[19]in its dilute solution. From the temperature dependence data, the apparent enthalpy change for the extraction reaction has been calculated to be $\Delta H=3.43$kj mol^{-1}. The extraction of NI(II) depends on the nature of the diluent.s Toluene may be used as diluent in place of benzene.

The solvent extractive separation of Co (II) from Ni (II) in acidic sulphate-acetate medium with 8-alkarylsulphonamidoquinoline (LI<34) has been investigated spectrophotometrically [40]. The effects of operating variable such as contact time, temperature, concentrations of LIX34, metal ions; and anions (SO_4=, Ac) on the extraction and separation behaviors have been studied. Experimental data suggest that the separation of Co(II) from Ni(II)-is possible with short contact times of 2 minutes under setected condition.

The probable structures of the metal chalets of Co(II), Ni(II) and Cu(II) with 8-alkarylsulfonamido-quinoline (LIX34 or HR) have been suggested by the sulphur-metal atom ratio (S/M), nitrogen-metal atom ratio (N/M), molecular weight, magnetic moment and infrared spectral data of the complexes[41]. As per data both Ni(II) and Cu(II) form 1:2 solid octahedral cheaters; but Co(II) may form semi-solid solvated square planar as well as octahedral complex.

The partition of Co(II) between its aqueous acidic sulphate-acetate solutions of LIX 34 in benzene has been investigated as function of the extractable metal ion, H^+; sulphate, acetate concentrations of the aqueous phase, extractant concentration, temperature and the nature of the diluents[41]. The extraction ratio incerases with increasing of the extractant, acetate and temperature and with. decreasing acidity and sulphate concentration. Cobalt (II) extraction has been found to be quantitative and moderately fast[42]. A spectrophotometric technique was employed for the estimation of Co(II). LIX 34 form a 1:1 complex with the metal ion in its dilute solution. From the temperature dependene data, the apparent enthalpy change for the extraction reaction has been calculated to be the extraction of Co(II) depends on the nature of the diluent. n-hexane may be used as diluent in place of benzene.

Some studies on complexes with chelatiing agents other than LIX reagent are mentioned below. the synthesis and characterization of some metal chelates of Ti(III), V(II), Mn(II), Fe(III), Co(II), Ni(II) and Zn(II) with bis 1,4,4-trimethyl-pentyl) phosphinic acid are reported by M.S Islam and M.K.H Talukdar[43]. They characterized the complexes by elemental analysis, conductivity and magnetic measurements and infrared and electronic spectral studies. The solubilities of the complexes in various solvents are also measured.

2.2 SCOPE OF THE PRESENT INVESTIGATION:

Complexes of transition metals with different known legends are of great importance, because many of them are efficient stoichiometric and catalytic reagents. These complexes have been extensively used in the therapeutic, analytical, biological and industrial fields and in co-ordination chemistry. As such, it is essential to develop new chelating agents for both therapeutic and analytical usages, and to understand the roles of transition metal ions in various properties extraction reagents [44,45], by solvent extraction method are of recent interest. These complexes (usually) cheaters) displaying distinctive co-ordination chemistry[46] and characteristic physical properties, may have industrial as well as biological significance. But complexes of heavier transition metals are rare. The extraction of common metals viz. Zr (IV), Ag (I) Cd (II), with various reagents has been studied frequently and their separation, especially from waste materials, low grade ores and sea nodule. The chemistry and mechanism of their extraction also has been the subjects of intense research. However, no report on such studies on complexes of lighter and heavier transition metal ions with the new extracting reagent LIX84 is available.

The transition metal complexes with legends are interesting from theoretical standpoint to broaden the present state of knowledge. With the rapid advancement of science and technology, the easily available sources of the useful transition metal ions are going to be exhausted and so substitute sources for them will be sought for, as is now the case of cobalt. As a result, the now un important ores (with too much contaminants) will certainly become increasingly important, for which usual methods of extraction do not work. Therefore, the study of completing properties of first transition series of metal ions with LIX84 will be of much value for extracting the metal ions from the sea nodules, low grade ores and the metal wastes employing the solvent extraction method economically.

Under the circumstances, it is thought appropriate, in view of the various importances of the transition metal complexes, to investigate complexing behaviour of LIX84 as a uninegative bidentate ligand. As such a programme is, undertaken to synthesize several new complexes of LIX84 with both lighter and heaviour transition metal ions, and characterize them by some physical methods of chemical analysis in order to get information about their compositions and structures as well as some other physical properties. The derived will be helpful for solvent extraction of these metal ions.

CHAPTER – 3

PRESENT AIM
AND
PREPARATION

3.1 AIM OF THE PRESENT INVESTIGATION:

The main aim or objective of this investigation is the preparation of some new second and third transition metal ions complexes with LIX84 acting as a ligand, their characterization based on some physical measurements and also solution behaviour. The Zr (IV), Ag (I) and Cd (II) ions are selected for their greater stabilities than their other oxidation states.The prepared complexes are proposed to be characterized on the basis of determination of molecular weight, IR and electronic spectra, magnetic and conductance measurements along with the melting point measurement.

Since LIX84 is a chelating extractant, the solubility of the chelate that is formed in different solvents in an important factor in the efficiency of solvent extraction.The study of the solubilities and electronic spectral of the prepared complexes in different solvents is also proposed to be made in order to throw further light on the structure of the complexes in solution.

The cadmium is in reletively low abundance in Nature (of the order of 10^{-6} of the earth's crust from Cd), but has long been known because it is easily obtained from it's ores.

Cadmium minerals are scare,but as a result of its chemical similarity to zinc occurs by isomophous replacement in almost all zinc ores. This element directly reacts with halogens and with nonmetals sush as S,Se and Pb and it Cadmium forms many alloys,s such as has being of technial importance.The oxide (CdO) is formed on burning the metals in air or by pyrolysis of the carbonate or nitrates;thus of oxide smokes can be obtained by combustion of the alkyls,those of cadmium being excendingly toxic.

Aquous solutions of cadmium halides appear, superficially to be in completely dissociated, that is, to be weak electrolytes. The formation constants for halides and other ligands(oxime) differ widely and the main feature is that they are many orders of magnitude smaller than those for Hg^{2+}.The cadmium ones are most *stable and the ion*[$CdCl_5$] $^{3-}$ *can also be formed* Cd^{2+} *is bound more strongly to Cl,S and oxime ligands.Cadmium* ^{113}Cd *nmr has provided* useful biological systems but shifts are very sensitive to concentration and counter ions.

Again, silver and gold are widely distributed in nature.They occurs as metals and also in numerous sulfides ores usually accompanined by sulfides of Fe,Cu,Ni etc. The main sources are Africa and the USSR.Silver also occur as horn silver(AgCl). After floaing or other concentration processes, the crucial chemical steps are cyanide loaching and zinc precipitation.

Silver is normally puriffied by electrolysis. It is a white,yellow metal and malleable metal with the highest known electrical and thermal conductivity.

However it is chemically less reactive than copper, except towared sulfur and hydrogen sulfide which rapidly blacken silver surfaces silver atoms that does not aggregate but are trappein a macrocyclic poly- nitrogen ligand are obtained by photochemicals or electrochemical reductions of the Ag^+ complex. There is a great variety of silver complexes which exist in solution or in the solid state.Since the most stable Ag^+complexes have the linear structure $L\text{-}Ag\text{-}L^+$, chelating ligands cannot form such simple ions, hence tend to give polynuclear complex ions. Slver chloride can be obtained as rather tough sheets that are transparent over much of the infrared region and have been used for cell materials. Moreover, silver chloride and bromide are light sensitively studied because of their importance in photography.

On the other hand, zirconium occurs widely over the earth's crust but is not as very concentrated deposit.The major minerals are baddeleyite, a form of

ZrO_2,and zircon ($ZrSiO_4$).The chemical similarity, of zirconium and hafinium are well examplified in their geochemistry for hafinium is found in nature in all zirconium minerals in the range of fractions of a percent of the zirconium content. Separation of the two elements are extremely difficult ,even more so than for adjacent lanthanides, but it can now be acoomplished in salts factory by ion-exchange or solvent extraction fractonation methods.

However, zirconium metal is hard and corrosion resistant, resembling stanless steel in appearance. It will burn in air at high temperatures, reacting with a anumber of compounds called"Zirconates" may be made by combining oxides, hydroxides,nitrates,oxime and so on, of other metals with similar zirconium compounds and firing the mixtures at 1000 to 2500 ^{0c}.These,like their titanium analogue,are mixed metal oxides;there are no discrete zrconate ions known.

Adition of hydroxide to zirconium(iv) solutions causes the precipitation of white gelatineous $ZrO_2.nH_2O$, where the content is variable; no true hydroxide exists. On strong heating,this hydrated oxide gives hard, white, insoluble ZrO_2.This has an extreamly high melting point (2700^{0}C).exceptional resitance to attack by both acids and alkalis,and good macanical properties;it is used for crucibles and furnace cores.Zrconium dioxide in its monoclinic(bad deleyite)form.

Aquous chemistry of zirconium aqua ions of low and medium valence state are not in general well defined or important for any of the heavier transition element. In Bangladesh zirconium is available in the soil of Cox's Bazar, the study for elemantal analys, quality and quantity of zirconium will provide to investigate zirconium metal in the soil of Cox's Bazar.

Therefore, this study of complaxing(extracting) beahaviour of three above mentioned three metals Ag, Cd and Zr will be helpful for their solvent extraction.

3.2 PREPARATION OF THE COMPLEXES:

(I). Preparation of $[(ZrO)_2(L)_4(H_2O)_2]$ complex:

LIX84 (2.84g;0.015 mol) was dissolved in n – haxane (40mL) in a beaker and KOH (O.56g; O.O1 mol) was dissolved in water (20mL) in another beaker. These two solutions were mixed together in a 250mL beaker. The mixture was stirred, heated on a water-bath for two tours and the resulting solution allowed to stand at room temperature for several hours.

A solution of Zr $(NO_3)_4$. $6H_2O$ (2.236g; 0.005 mol) in water (50 mL) was then added slowly to the above solution of the ligand. The resulting immiscble mixture was stirred well with the help of a magnetic stirrer and warmed on the water-bath. The deep coppy colour precipitate appeared was filtered off, washed several times with alcohol and water, and finally dried in vacuo over anhydrous $CaCl_2$.

(II). Preparation of [Ag(L)] complex:

An aquos solution (20mL) of KOH (0.28g; 0.005 mol) was added solution (30 ml) of LIX84 (1.23g, 0.005mol) in n-hexane in a 250 mL beakr. The mixture was stirred well and heated on a water-bath for 2 hours to reduce it to half its values. This solution was then allowed to stand at room temperature for several hours. In another beaker silver nitrate (o.849g; o0oo5 mol) was dissolved in distilled water (40mL) by heat and was added to the above solution. This resulting immiscible mixture was stirred and the black precipitate found was collected by filtration, washed several times with alcohol and water. and finally dried in vacuo over anhydrous $CaCl_2$.

(III). Preparation of $[Cd(L)_2.HL]$ complex:

A solution of KOH (0.56g; 0.015 mol) in was n-hexane solvent (40mL) into a 250 mL beaker. This mixture was stirred and heated on a water-bath for one hour. It was then allowed to stand at room temperature for several hours and to this was added a solution of $CdCl_2.2\frac{1}{2}H_2O$ (1.0066g; 0.005 mol) in water (30mL). The resulting mixture was immiscible and stirred well with a glass rod at room temperature. The white precipitates formed was filtered off, washed well with ethanol, and distilled water (to remove KCl). The product was air dried and finally dehydrated in a vacuo desicator over anhydrous $CaCl_2$.

CHAPTER – 4

EXPERIMENTAL TECHNIQUES

EXPERIMENTAL TECHNIQUES

4.1 WEIGHING:

The weighing operation was performed with the help of a METTLER TOLEDO AB204 electronic balance.

4.2 MELTING POINT MEASUREMENT:

The melting or decomposition temperatures of all the prepared metal-LIX84 complexes were observed with an AZ 6312 model Electrothermal Melting Point apparatus. It was, however, not possible to measure the melting points beyond 360^0C.

4.3 CONDUCTIVITY MEASUREMENTS:

The conductivity cell was cleansed several times with distilled water, rinsed with acetone and finally allowed to dry in air.

The conductance measurements of 10^{-3} M solution of the complexes in benzene (C_6H_6) or (C_6H_{12}) were made at room temperature using a type CG 857 No. 71798 SCHOT GERATE GmbH Germany digital conductivity meter and a dip-type cell with platinized electrodes. The cell was calibrated using .001N potassium chloride solution at the experimental temperature.

The molar conductivities were (Λ) calculated using following equation;

$\Lambda = 1000/c \times$ cell constant × experimental conductivity...........(i) where, c is the concentration of complex solution in the mol dm^{-3}. The experimental conductivity was obtained by subtracting the conductance of) C_6H_6) or (C_6H_{12}) from that of solution of solution of each complex in (C_6H_6) or (C_6H_{12})

4.4 MAGNETIC MEASUREMENTS:

Magnetic susceptibilities of the solid complexes were measured with the help of the SHER WOOD SCLENTIFIC Magnetic Susceptibitity Balance (Gouy method). The balance was calibrated using $HgCo(SCN)_4$ and the calibration was checked using a sealed off sample of $MnCl_2$ solution calculation of the corresponding mass susceptibilities were done using the equation [47].

$$\chi_g = 2.08.l.\ (R\text{-}R_0)/10^9.\ m\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(ii)}$$

where,

m=mass of sample in grammes

l = length of the sample in centimeters

R = observed reading for tube plus sample

and Ro = observed reading for the empty tube.

The calibration constant (C_B), 2.086 was evaluated using the relations[47], $C=C_B/10^9$ and $C_B=C_{tube}/(R\text{-}Ro)$ where C is the constant of proportionality related to the calibration constant of the balance. Then effective magnetic moments (spin only values, μ_{eff}) were calculated and the number of unpaired electrons (n) in the metal ions of the following relation[47]. μ_{eff} / number of metal ions in a molecule of the complexes = $\sqrt{n(n+2)}$

Experimental Procedure:

(I) The zero knob of the magnetic susceptibility balance was turned until numerical display showed zero (ooo) and calibration sample, HgCo $(SCN)_4$ was inserted into sample holder. It was then allowed to settle to give the numerical display[48].

(II) Reading was recorded and calibration constant C_B was calculated from the equation,

$C_B = C_{tube}/(R-Ro)$..(iii)

Operation of the balance:

(a) The range knob was turned to the display reads (ooo). The zero was adjusted on each side.

(b) The zero knob was adjusted until the display reads (ooo). The zero was adjusted on each side.

(c) An empty tube of known weight was placed into the tube guide and the reading Ro was taken

(d) The sample was packed, and the sample mass in grammes and the sample length, l in cm were noted. the packed sample tube was placed into the tube guide and the reading R was taken. From the data, χ_g was calculated.

4.5 INFRARED SPECTRA:

The IR spectra of all the solid metal-LIX84 complexes were run on a FTIR Shimadzu Japan Model No-8400 FOURIER TRANSFORM INFRARED SPECTROPHOTOMETER (as KBr pellets) in the range 400 to 4000 cm^{-1}. However, the spectrum of liquid LIX84 was obtained directly as thin film in the same range of frequency[49-51]. Another set of IR spectra were not also run on an infrared spectrophotometer,

Procedure: A requisite amount of complex was put in a mortar and thoroughly powdered with potassium bromide. This mixture was then transferred in a mini disc holder, and a KBr disc was made by hand press. This was then mounted in the sample cavity of the spectrophotometer[52] and its spectrum was taken. On the other hand, one drop of LIX84 (liquid) was placed into a rectangular cell made of NaCl its IR spectrum was then taken directly as thin film. From the spectra of complexes important vibration band frequencies of different groups were found out[19].

4.6 ELECTRONIC SPECTRA:

Electronic spectra of the complexes were run on a Lambda-19 UV/VIS/NIR spectrohotometer (PERK) NELMERAMERICA NO. All the spectra were taken for dilute solutions of the complexes in yclohexane in the wave length of 200 to 800 nm. The electronic spectra of LIX84 was also taken and it was compared with those of the complexes in order to find out the possible d-d transitions and charged transfer bands[53-55].

4.7 DETERMINATION OF MOLECULAR WEIGHT:

The cryoscopic method using a Beckmann apparatus has been used for determination of the molecular weights of the extracted complexes of Zr(IV), Ag (I) and Cd(II) with LIX84. This method gives more or less accurate when the molecular weight is small but discrepancies arise when the molecular weight is high. The accuracy obtainable with the Beckmann apparatus in stated to be methine approximately 5% of the molecular weight. The mojor source of error in the determination is the problem of super cooling of sample solution Pure solvents have little tendency to super cool, but their solutions are affected to a much larger extent; for this reason, the differential between freezing tube and cooling bath of the apparatus should be maintained at 1.5^0 to 1.0° for precies work.The determination of molecular weight by observation of the depression of the freezing point induced in a pure solvent by a known amount of the substance under investigation is based on the following equation; $M = k_f \frac{1000w}{G\Delta T_f}$

where,

K_f = molar depression constant for solvent=5.12 for Benzene.

ΔT_f= experimentally observed depression of the freezing point of the solvent.

w = weight of the added solute taken in g.

G = weight of the solvent taken in g.and

M = molecular weight of the solute.

The Beckmann apparatus of (Arther H. Thomas company, philadel phia, U.S.A) was used for determination of the molecular weight of samples (i.e.M.-LIX84 chelates). by the freezing point depression of the solent benzene. For this, benzene was previously dehydrated with an hydrous. CaO and then distilled. The apparatus was at firs calibrated by determining the molecular weight of pure naphthalene (several times) using the same solvent, and the percentage of error was found to be **2** approximately.

In operation, a weighed amount of benzene was introduced. into the inner tube and the side neck was stopped. It was then cooled near to its freezing point (5.5°C) by ice-water mixture placed in the cooling bath. To this nearly freezing solvent, a Beckmann thermometer was inserted so that the lower part of the thermometer read on the middle of the scale of the thermometer. This was adjusted by trial, each time by taking. out the thermometer. Transferring the mercury from the bottom to the top or vice versa by the application of heat or cooling by the freezing mixture.

Once the temperature on the Beckmann thermometer was fixed and the freezing point of the solvent was recorded, the thermometer was removed from the solvent tube and kept immersing in a beaker containing the freezing mixture. A weighed quantity of solute (M-LIX84) complex was introduced carefully into the inner freezing tube and allowed to dissolve in benzene The freezing point of the solution was determined with continuous vigorous stirring (avoiding super cooling) by the associated stirrer using the pre-set Beckmann thermometer. The difference of the two readings gave the depression of the freezing point for the given amount of the solute-solvent system. The experiment was repeated for each solute several times taking different amounts of the complexes. The molecular weights were then calculated by using the above formula.

CHAPTER – 5

RESULTS
AND
DISCUSSION

RESULTS AND DISCUSSION

The transition metal complexes of Zr (IV), Ag (I) and Cd (II) with the ligand LIX84 have been synthesized as described previously. These complexes are characterized on the basis of conductance, magnetic measurements, infrared, molecular weight and electronic spectral studies and their other physical properties such as per cent of solubilities.

5.1 Molecular weight:

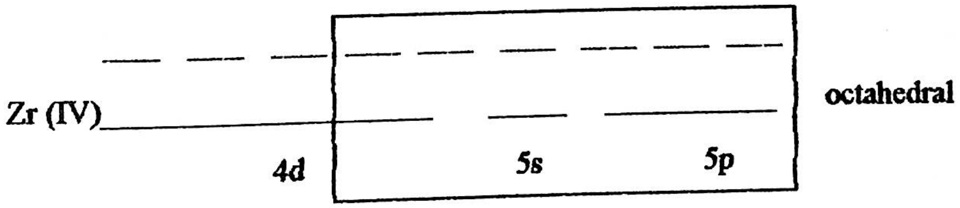
The molecular weight of the prepared complexes were determined by using cryoscopic method. Benzene was used as the solvent. The values obtained for the compounds have been used to determine the molar susceptibility and molar conductance values.These are shown in Table-4.

5.2 Molar Conductance:

The molar conductance data of the prepared transition metal-LIX 84 complexes along with that of the solvents are given in Table-1. These measured electrical conductances of 10^{-3} M solutions indicate that the complexes **1**, **2** and **3** do not behave as 1:1 electrolytes in DMSO or cyclohexane. The zero conductance values for all the prepared complexes **1**, **2** and **3** show that they are non-electrolytes. However, it was not possible to measure the conductance values of the complexes in DMSO or cyclohexane as they were found insoluble in DMSO.

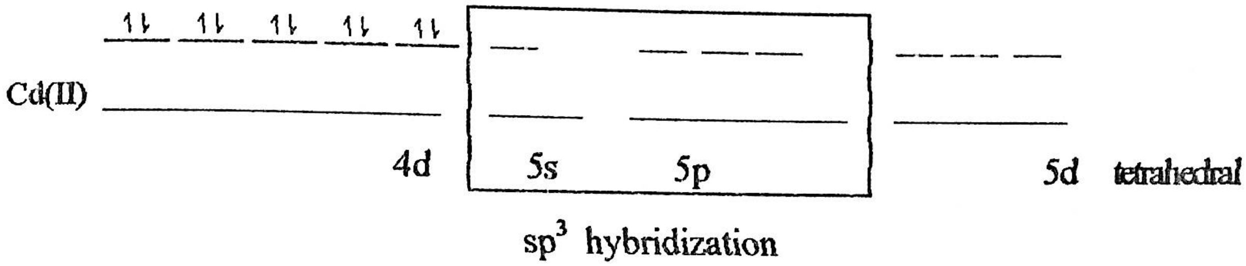
5.3 Magnetic Moments:

Molar susceptibilities of all the transition metal-LIX84 complexes were measured as stated as stated before and the data is shown in Table-4, which also contains the calculated magnetic moments (spin only values) and the number of unpaired electron per metal atom. It is found that the complexes No. **2** and **3** are diamagnetic. The diamagnetism is supported by its measured small negative magnetic susceptibility values and also observed repulsion by the applied magnetic field. Complex **1** is found to be paramagnetic in nature having μ_{eff} value 5.30 B.M respectively. The complex **1** appears to be paramagnetic with four unpaired electrons but it may be a binuclear compound having Zr atoms with four unpaired electrons in their inner orbital configuration with high spin states respectively. Using the magnetic data, the stereochemistry of the complexes may be suggested as follows. The Zr (IV) ion $4d^{10}$ electrons. But as the magnetic moment measurement of the complex **1** indicates the presence of four unpaired electrons for each Zr atom, it is suggested that this six coordinated paramagnetic Zr-LIX84 complex is octahedral with 4 $d^2 5s5p^3$ hybridization as depicted below.



d^2sp^3 hybridization

The two coordinate silver complex **2** is also diamagnetic with Ag (I) ion having d^{10} configuration and therefore its structure is probably linear with 5s5p hybridization. Finally, the Cd (II) ion has $4d^{10}$ configuration and hence the four-coordinated outerorbital diamagnetic cadmium complex **3** will be octahedral with $5s5p^35d^2$hyridization. This hybridization may be represented by the following schematic diagram.



5.4 Per cent solubilities:

The solubilities of the prepared transition metal complexes with LIX 84 were examined in different solvents[56-57]. Their solubility and percent solubility data are presented in table 2 and 3 respectively. The complexes are found to be insoluble in polar solvents, water, ethanol, acetone and sparingly soluble in other organic solvents. `

5.5 Infrared spectra:

Frequencies for LIX 84 are observed and M-LIX 84 Complexes are listed in the following **Table- (5-6)**. The infrared spectrum of LIX84 shows Vibrational bands for-OH free (3379.1-3350 cm^{-1}),C-H streching (2968.6 cm^{-1}), >C=N....... streching –CH_2-bending aromatic, C=C streching (1461.9 cm^{-1}), N - O – bending band at (1373.2-13.65 cm^{-1}). Medium absorption near (1022.2 cm^{-1}) is caused by wagging of the group – CH_3. for the interpretation of various absorption band found, the IR spectrum of all the metal-LIX84 complexes have been compared with that of LIX84.

The presence of water molecule in coordination sphere[58] is indicated by the very absorption band around 3583.5 –3382.9 cm^{-1} in the IR spectrum of the complex **1**.

Again the IR spectrum of complexes **1** exhibits characteristic band at 3382.9 cm^{-1}, (intra hydrozen) inside the coordination sphere. The IR spectrum of complex **1** shows an indication band at 1000-1072.3 cm^{-1},which indicate of-OH bridging[19] with metal to metal ions. However, the complexes have also bands in 1203.5 – 1257.5 cm^{-1} shifted towards lower frequencies. This is also an indication of oxygen atom of – OH group with the metal atom.

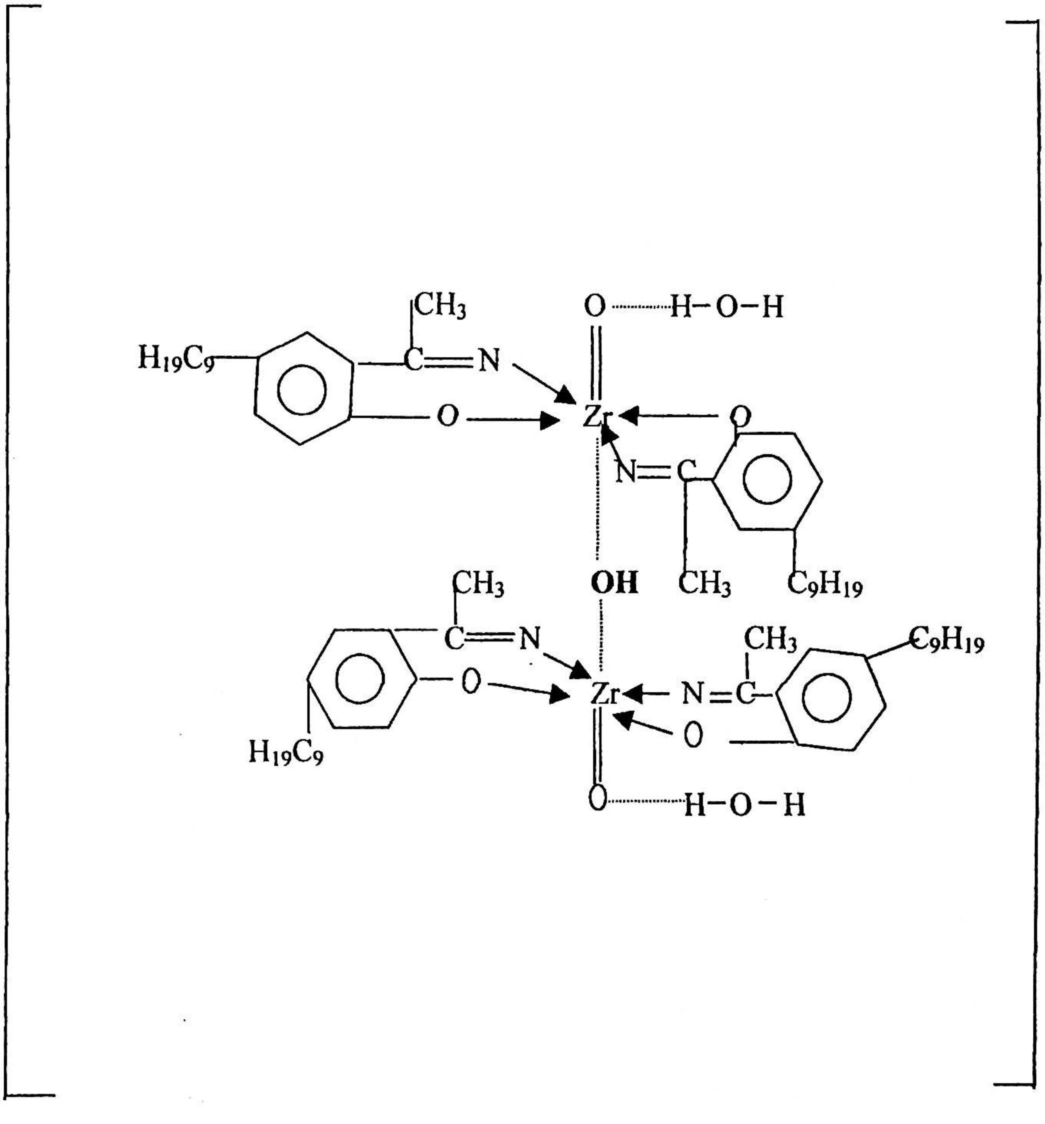
Moreover (M-O) band[19] at 640.3 – 412.7 cm^{-1} is indicative of M-O band formation in all the complexes. All complexes show $^{\vee}$ (M-N) band at 412.7 - 447.5 cm^{-1} which indicates the metal – nitrogen coordination band formation.

5.6 ELECTRONIC SPECTRA :

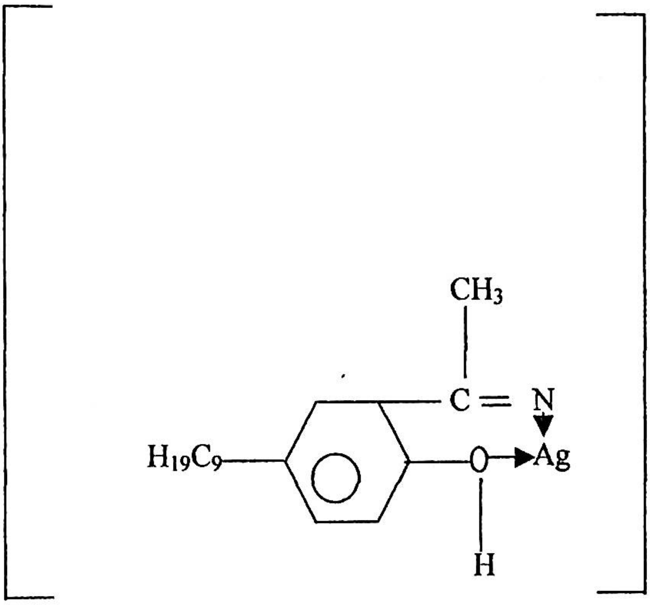
Information on probable geometries of the prepared matel-LIX84 Complexes may be obtained from their electronic spectra and that of LIX84. These spectra are shown in **Fig. (5-8)**. The selected UV/VIS absorption band maximum are given in **Table-(7-11)**. The absorption spectrum of 2-hydroxy-5-nonyl acetophenone oxime (i.e.LIX84) shows two bands at 251 nm and 350 nm which areas singed respectively[51] to the n → π* transition of C-O and >N-O groups in cyclohaxane solvent. All the complexes have only one absorption maximum within 300-600 nm in their spectra of their solution in cyclohaxane. However, the absorption band maximum of the octahedral

Cadmium (II) Complex at about 300 nm (300-450 nm) may be assigned to the n → π^* transition of >N-O group.

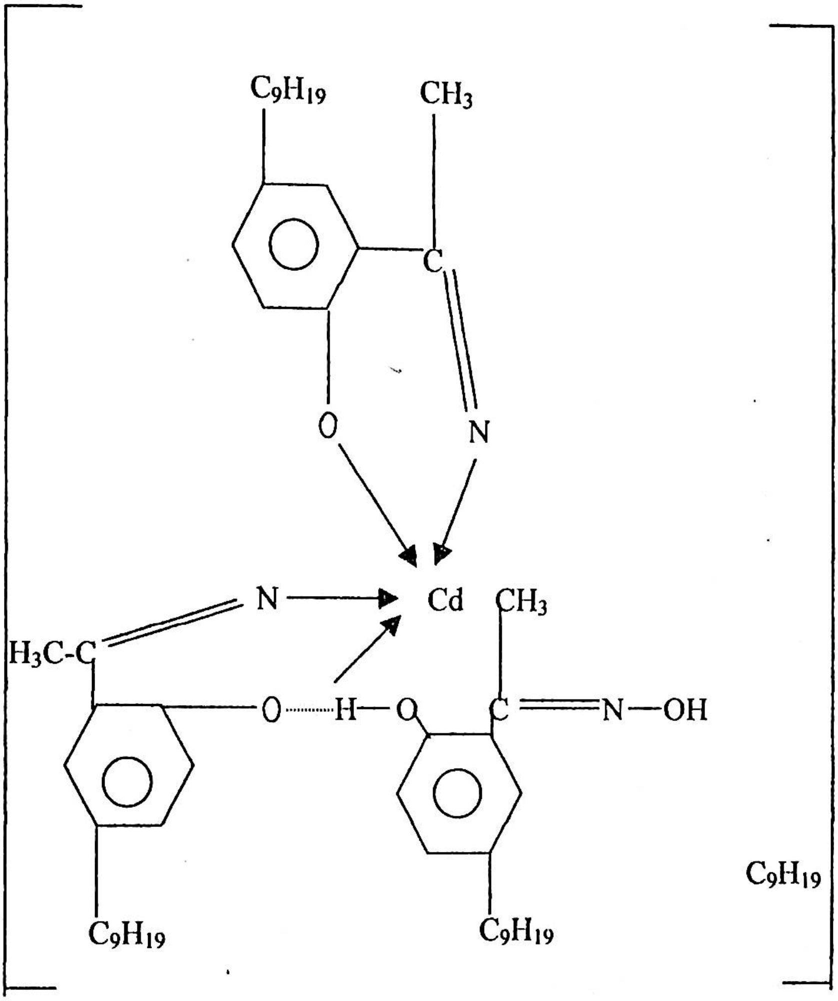
The absorption band of octahedral binuclear Zirconium complex of LIX84 in the higher wavelength i.e. at about 400 nm (300-500 nm may be due to d-d transition assignable to 4 A_{2g} (F) ← $4T_{1g}$. The complex 2 **exhibit** only the charge transfer bands[51] because of the d^{10} configuration. In This spin-paired complex, charge transfer bands may obscure the ligand field bands and hence it does not show d-d transition[51].



$[(ZrO)_2(L)_4(H_2O)_2]$, Octahedral



[Ag(L)] , Linear



[Cd(L)$_2$.HL], Tetrahedral

Table-1

Colour, yield, decomposition temperature and molar conductance of the complexes:

No	Compound	Colour	Yield	Decompose Tem (^{0}C)	Molar conductance $ohm^{-1}cm^{2}mol^{-1}$
1	$[(ZrO)_2(L)_4(H_2O)_2]$	Coffee	2.50	230	O
2	$[Ag(L)]$	Black	1.50	200	O
3	$[Cd(L)_2.HL]$	White	3.69	280	O

Table-2

Data for solubility of the complexes:

CompNo.	Complexes	DMSO	DMF	$C_2H_2Cl_2$	C_6H_6	CCl_4	C_2H_5OH	$CHCl_3$	C_6H_{12}	H_2O	CH_3COCH_3	$C_6H_5CH_3$
1	$[(ZrO)_2(L)_4(H_2O)_2]$	×	×	×	✓	×	×	×	✓	×	×	×
2	$[Ag(L)]$	×	×	×	✓	×	×	×	✓	×	×	×
3	$[Cd(L)_2.HL]$	×	×	×	✓	×	×	×	✓	×	×	×
Ligand LIX 84	$C_{17}H_{27}NO_2$	×	×	×	✓	×	×	×	✓	×	×	×

× = Insoluble, ✓ =Soluble

Table-3

Determination percentage (%) of the solubility of complexes in various organic solvents (gdm^{-3}):

Compound	DMSO	DMF	$C_3H_5CH_3$	C_6H_{12}	$CHCl_3$	CH_2Cl_2
$[(ZrO)_2(L)_4(H_2O)_2]$	-	-	3.35	4.65	4.60	3.75
$[Ag(L)]$	-	-	3.8	3.65	3.00	2.85
$[Cd(L)_2.HL]$	-	-	6.00	6.50	4.55	3.50

-,means insoluble.

Table-4

Detailed magnetic data of the complexes (T=303K):

Complexes and Extractant	Length of the sample (l) in cm	Mass weight of the complex, in (m) g	Susceptibility of the empty tube, R_o	Susceptibility of the sample with tube, R	Mass Susceptibility, $\chi_g \times 10^{-6}$ in C.G.S *unit*	Molecular weight M	Molar Susceptibility, $\chi_M \times 10^{-3}$ in *C.G.S unit*	Dia-magnetic correction, 10^{-6} in *C.G.S unit*	$^{corr}\chi_M \times 10^{-3}$ in *C.G.S unit*	μ_{eff} in B.M
$[(ZrO)_2(L)_4(H_2O)_2]$	3.2	.109	-48	+240	17.637	1277.44	22.53	-51238	11.321	5.30 (para)
[Ag(L)]	2.9	.058	-47	-62	-1.564	512	-.8002	-193.63	-.9938	-1.55 (diam)
$[Cd(L)_2HL]$	2.90	.044	-50	-64	-1.924	941.24	-1.8109	-512.38	-1.30	-1.78 (diam)
$C_{17}H_{27}NO_2$										

Table-5

Observed frequencies and assignments for LIX84

Reported wave numbers [45,53,58] for IR absoption of functional groups, cm^{-1}	Wave numbers for IR absorption of LIX84 in this study, cm^{-1}	Postulated assignments
3350 (m)	3379.1 (m)	-OH free
2960-2953 (ms)	2958.6-2927.7 (ms)	C-H stretching (symmetic)
1615 (w)	1620.4 (w)	>C=N-stretching
1450 (m)	1496.7 (m)	C=C stretching (aromatic-CH_2-)
1405 (w)	1461.0 (w)	C-H bending
1280 (mb)	1288.4 (mb)	C-H stretching in plane
1250 (w)	1257.5 (w)	N-O-bending
1230 (w)	1238.2 (w)	-O-H aromatic
1050 (w)	1076.2 (w)	-CH_3 wagging
970 (m)	948.9 (m)	C-H out of plane bending
720(m)	767.6 (m)	C-H bending aromatic
690 (s)	640.3 (s)	C-H bending (out of plane bend)

L = LIX84 = $C_{17}H_{27}NO_2$, b = broad, s = strong, m = medium, v = very, sh = shoulder, w = weak.

Table – 7

Electronic spectral data of the prepared complexes with assignment.

No.	Compounds	Observed spectral band maxima in, nm	Significant spectral bands,cm^{-1}
	LIX84	251, 350	21711, 30275
1	$[(ZrO)_2(L)_4(H_2O)_2]$	400	34601
2	[Ag(L)]	290	25085
3	$[Cd(L)_2.HL]$	300	25950

L = 2-hydroxy-5-nonylacetophenone oxime, anion.

Table – 8
Electronic spectral data of LIX 84

Spectrum: SCAN095(LIX84)
Comment:
No. of data points: 61
Data interval: -10.0
Abscissa units: nm
Ordinate units: %T

Abscissa	Ordinate
200	169.06
210	160.45
220	166.7
230	151.99
240	120.25
250	137.27
260	97.578
270	92.843
280	20.441
290	0.1797
300	0.0534
310	0.0146
320	0.0149
330	0.0028
340	0
350	0.0203
360	2.5025
370	25.752
380	68.845
390	101.14
400	121.72
410	136.84
420	146.95
430	152.42
440	155.43
450	156.86
460	157.48
470	158.38
480	159.49
490	159.56
500	160.04
510	161.3
520	162.02
530	162.2
540	162.24
550	162.08
560	161.81
570	161.6
580	161.39
590	161.2
600	160.92
610	160.64
620	160.43
630	160.32
640	159.87
650	159.38
660	159.36
670	159.02
680	158.6
690	158.32
700	157.97
710	157.23
720	156.67
730	156.54
740	156.12
750	155.24
760	154.53
770	154.88
780	155.14
790	155.04
800	154.74

Table – 9

Electronic spectral data of the prepared complex $[(ZrO)_2(L)_4(H_2O)_2]$

Spectrum: SCAN094 (Zr-LIX84)
Comment:
No.of data points: 61
Data interval: -10
Abscissa units: nm
Ordinate units: %T

Abscissa	Ordinate				
200	59.157	410	0.331	610	27.878
210	57.148	420	0.6047	620	32.751
220	64.26	430	0.9187	630	38.029
230	48.012	440	1.2569	640	43.618
240	49.971	450	1.6472	650	49.405
250	44.619	460	1.9987	660	55.345
260	29.516	470	2.3331	670	61.166
270	32.684	480	2.6736	680	66.653
280	9.6905	490	3.0708	690	71.871
290	0.1162	500	3.5547	700	76.643
300	0.0409	510	4.1301	710	80.905
310	0.0059	520	4.9042	720	84.706
320	0.017	530	5.8962	730	88.451
330	0	540	7.1536	740	91.666
340	0	550	8.7677	750	94.131
350	0	560	10.734	760	96.802
360	-0.01	570	13.187	770	99.741
370	-0.029	580	16.083	780	102.49
380	0.0082	590	19.513	790	104.66
390	0.0267	600	23.416	800	106.38
400	0.1261				

Table – 10

Electronic spectral data of the prepared complex [Ag (L)]

Spectrum: SCAN091 (Ag-LIX84)
Comment:
No. of data points: 61
Data interval: -10
Abscissa units: nm
Ordinate units: %T

Abscissa	Ordinate				
200	63.893	400	1.6444	600	38.849
210	63.941	410	2.481	610	40.372
220	56.001	420	3.6237	620	41.954
230	64.43	430	4.9472	630	43.506
240	49.224	440	6.3704	640	44.977
250	45.402	450	8.0018	650	46.619
260	39.055	460	9.769	660	48.436
270	32.163	470	11.588	670	50.235
280	8.6222	480	13.56	680	51.881
290	0.0439	490	16.057	690	53.359
300	0.0178	500	18.24	700	54.755
310	0.0104	510	19.913	710	55.94
320	-0.002	520	22.516	720	56.891
330	0.0018	530	25.288	730	57.968
340	0.0006	540	27.388	740	58.797
350	0	550	29.38	750	59.222
360	0.0321	560	31.508	760	59.698
370	0.186	570	33.704	770	60.674
380	0.5111	580	35.646	780	61.9
390	0.9863	590	37.343	790	63.086
				800	64.029

Table – 11

Electronic spectral data of the prepared complex $[Cd(L)_2.HL]$

Spectrum: SCAN093 (Cd-LIX84)

Comment:

No. of data points: 61

Data interval: -10

Abscissa units: nm

Ordinate units: %T

Abscissa	Ordinate				
200	111.52	400	0.2048	610	77.107
210	110.28	410	0.3921	620	82.074
220	90.829	420	0.7474	630	86.835
230	77.085	430	1.2594	640	91.259
240	74.975	440	2.0641	650	95.405
250	69.01	450	3.286	660	99.423
260	48.861	460	5.073	670	103.29
270	50.74	470	7.4507	680	106.99
280	13.942	480	10.218	690	110.35
290	0.1536	490	13.63	700	113.74
300	0.0391	500	17.618	710	116.33
310	0.0136	510	21.566	720	119
320	-0.002	520	25.302	730	121.79
330	0.0038	530	31.124	740	124.04
340	0.0014	540	36.134	750	125.7
350	-0.004	550	41.238	760	127.58
360	0.0037	560	46.947	770	129.91
370	-0.03	570	53.305	780	131.89
380	0.0312	580	59.676	790	133.59
390	0.0927	590	65.839	800	134.98
		600	71.674		

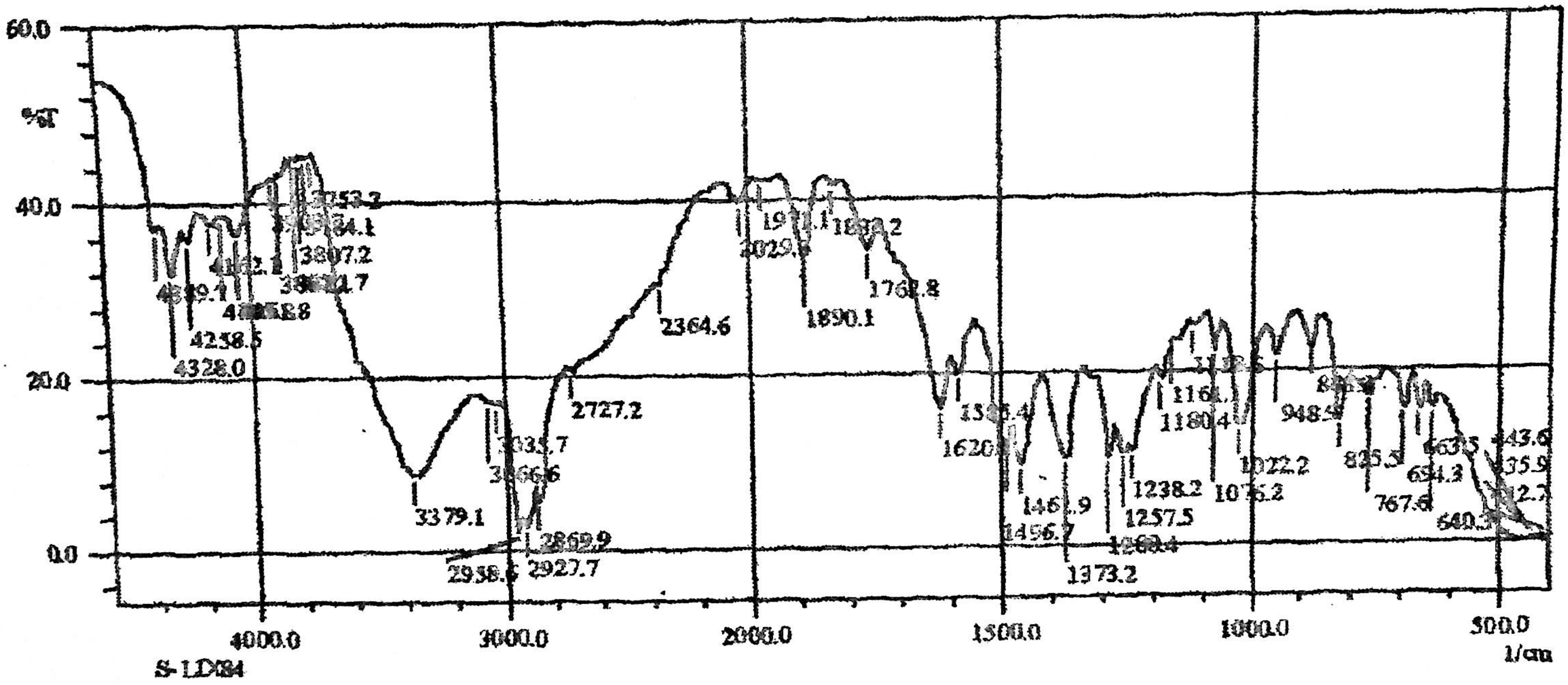


Fig. 1 : Infrared spectrum of LIX84 in KBr cell.

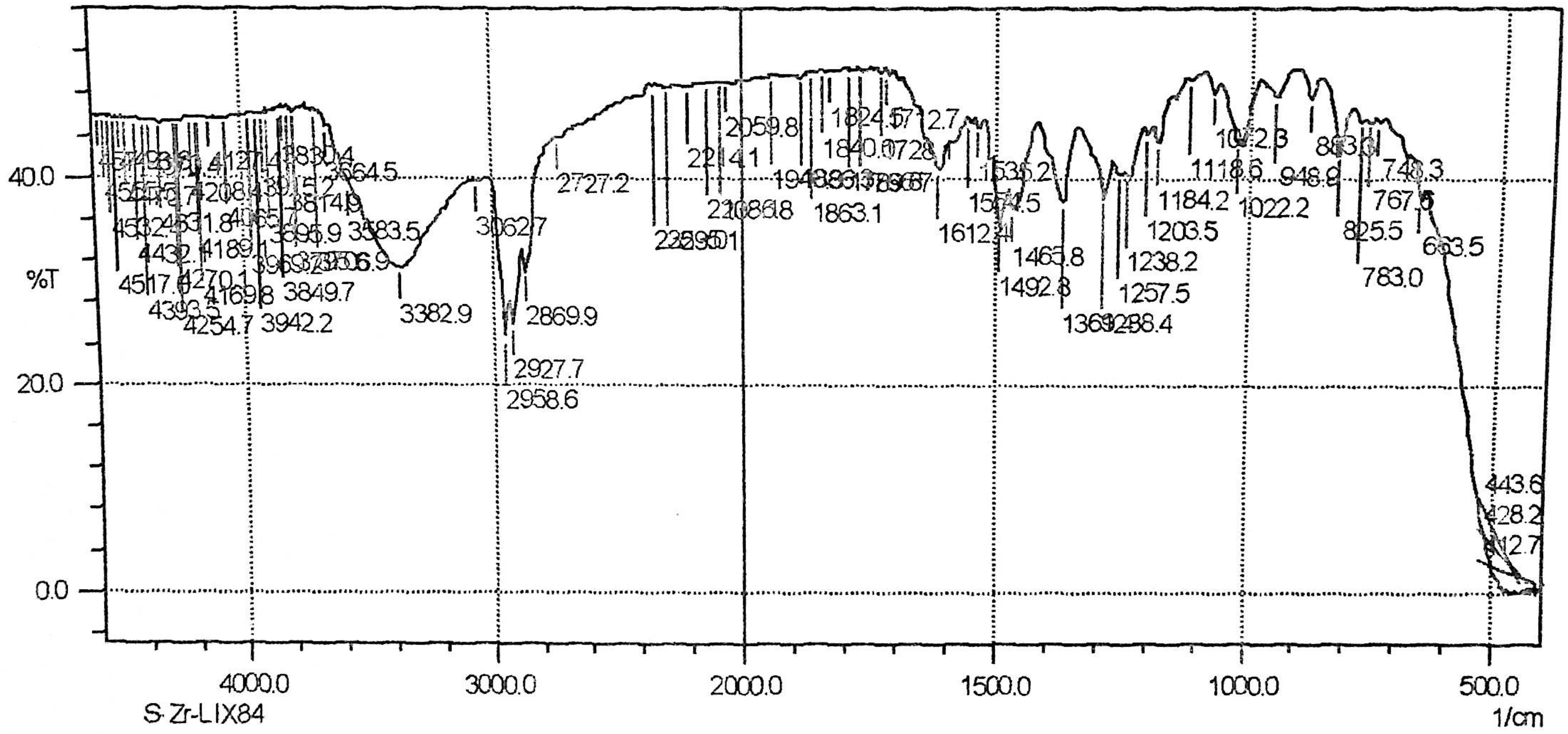


Fig. 2 : Infrared spectrum of $[(ZrO)_2(L)_4(H_2O)_2]$ in KBr cell.

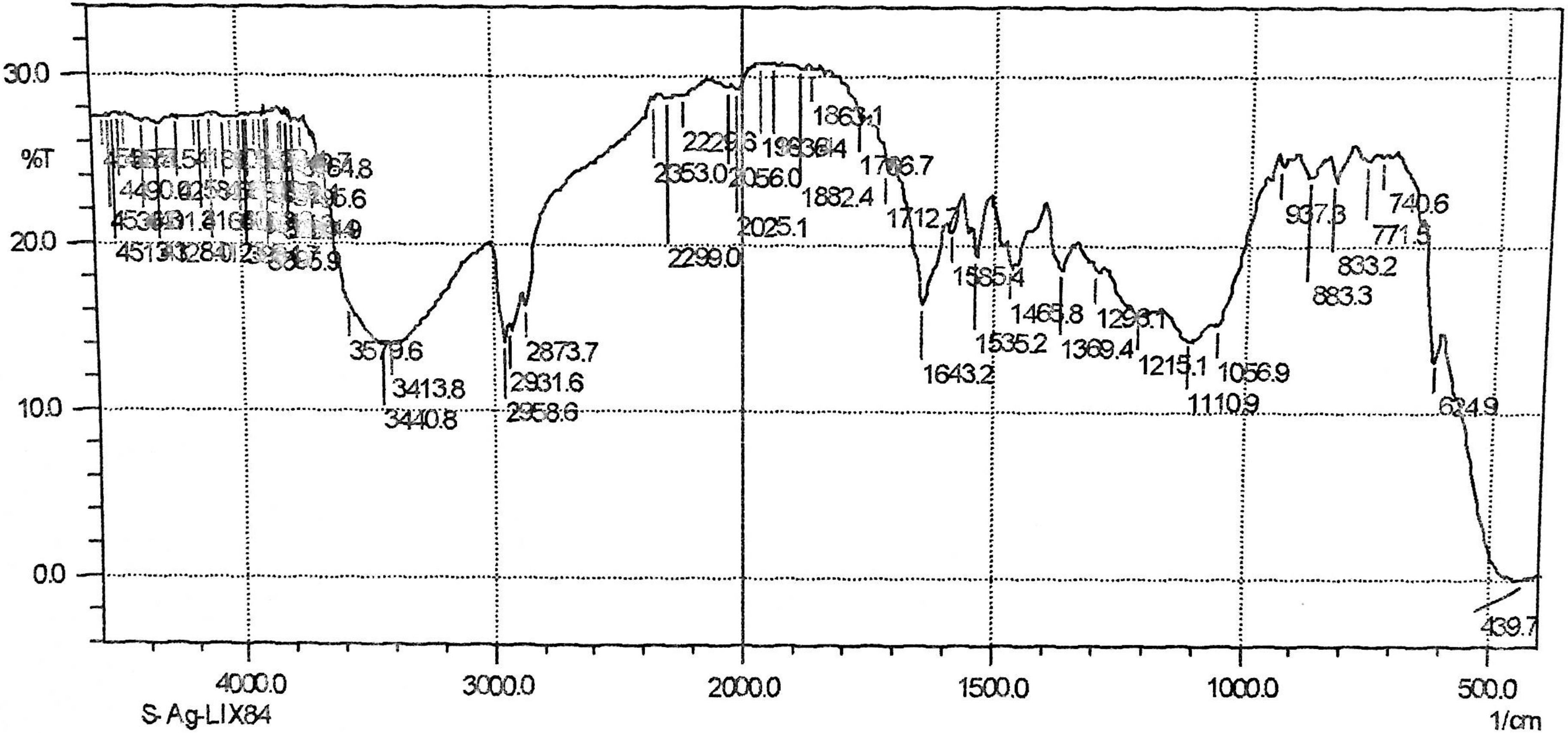


Fig. 3 : Infrared spectrum of [Ag (L)] in KBr cell.

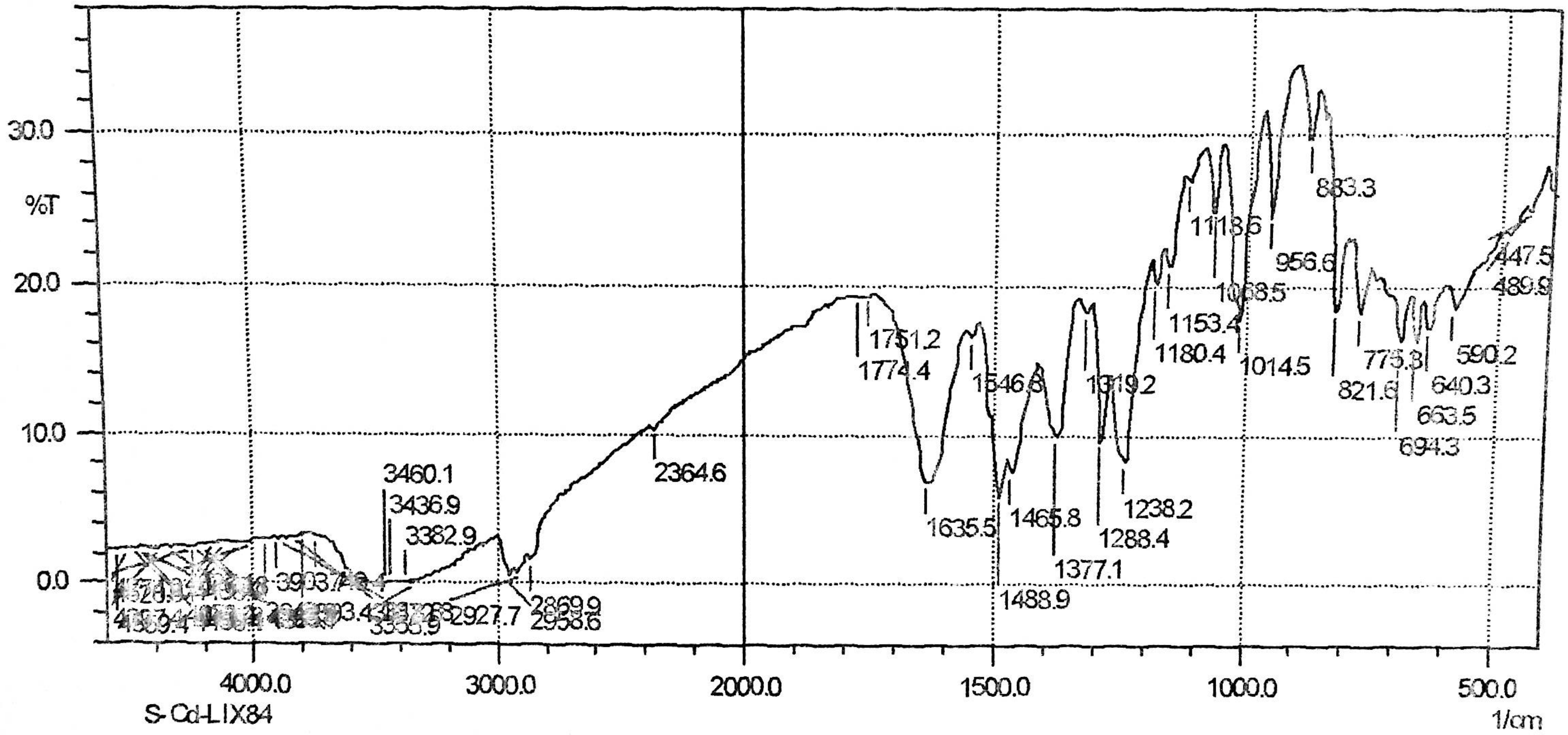


Fig. 4 : Infrared spectrum of $[Cd(L)_2.HL]$ in KBr cell.

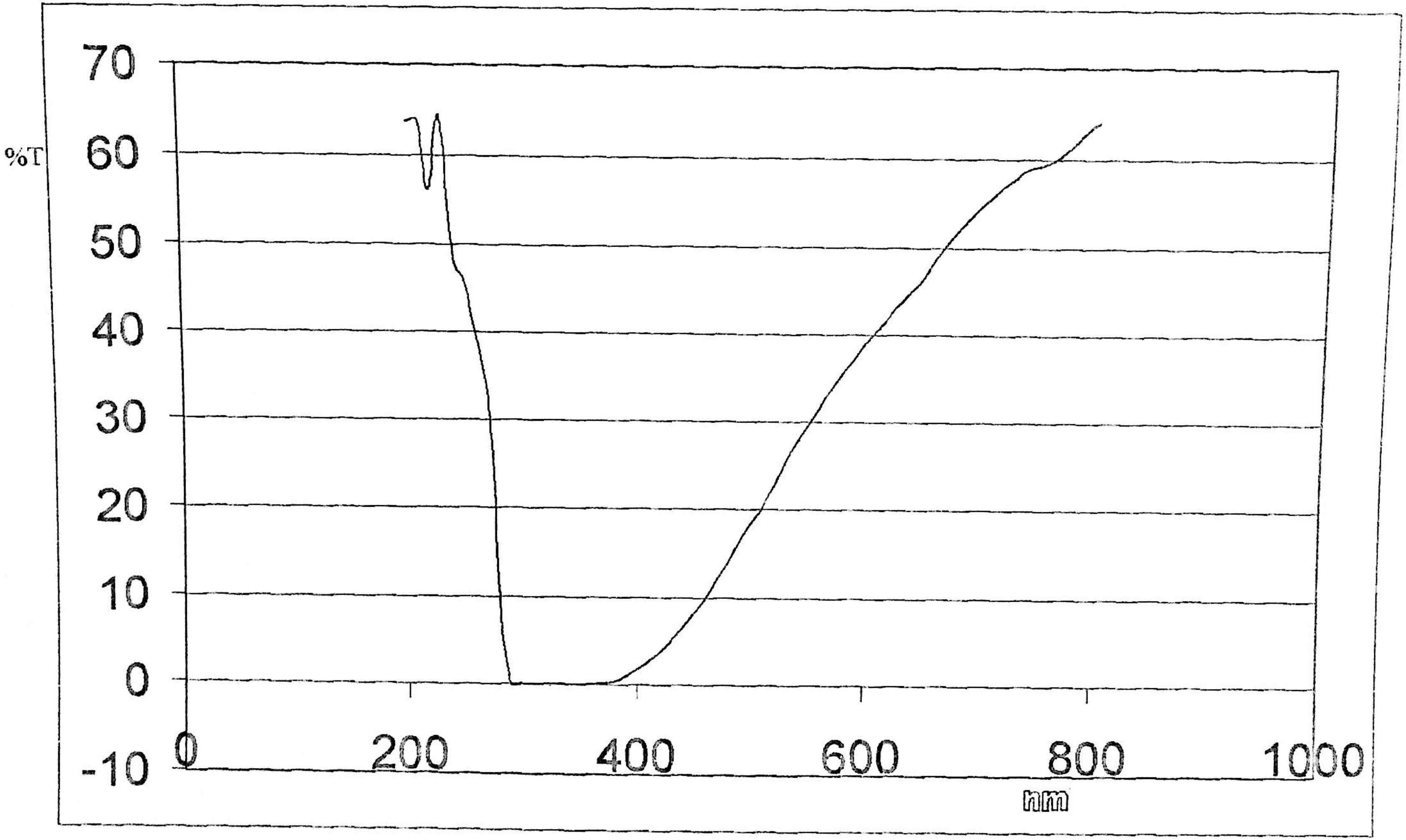


Fig. 5 : Electronic spectrum of LIX 84 (in cyclohexane)

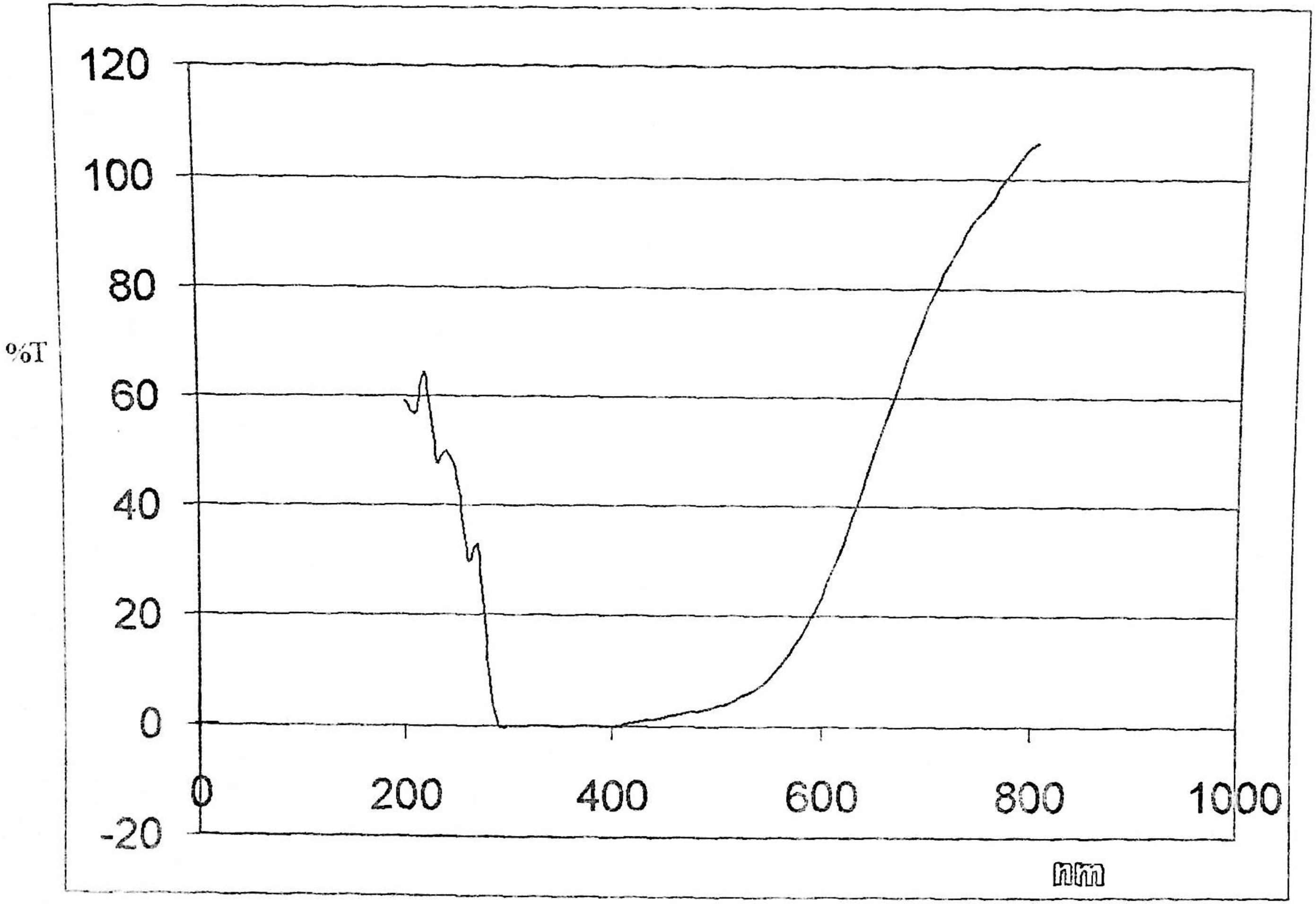


Fig. 6 : Electronic spectrum of $[(ZrO)_2(L)_4(H_2O)_2]$ (in cychlohexane)

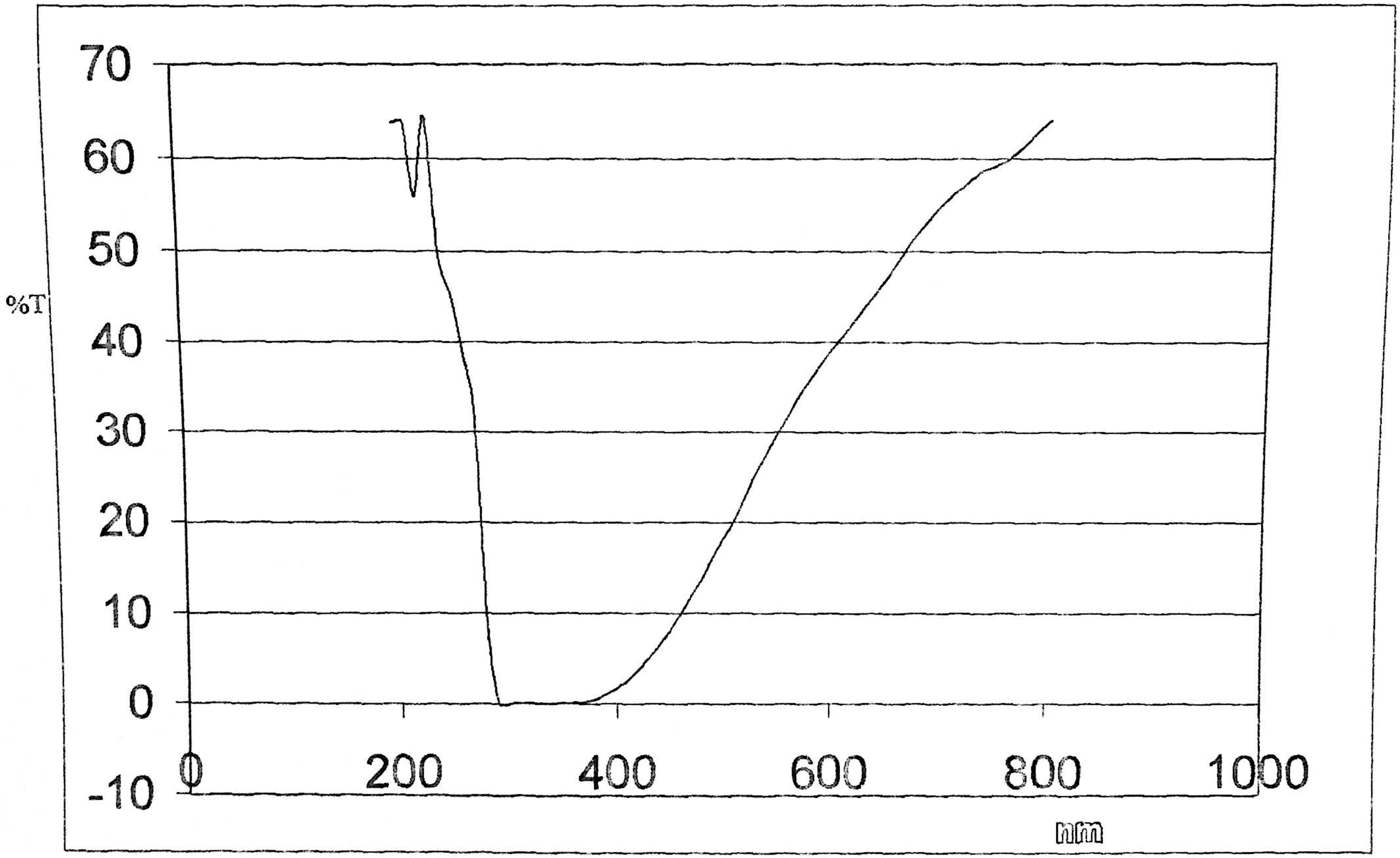


Fig. 7 : Electronic spectrum of [Ag(L)] (in cychlohexane)

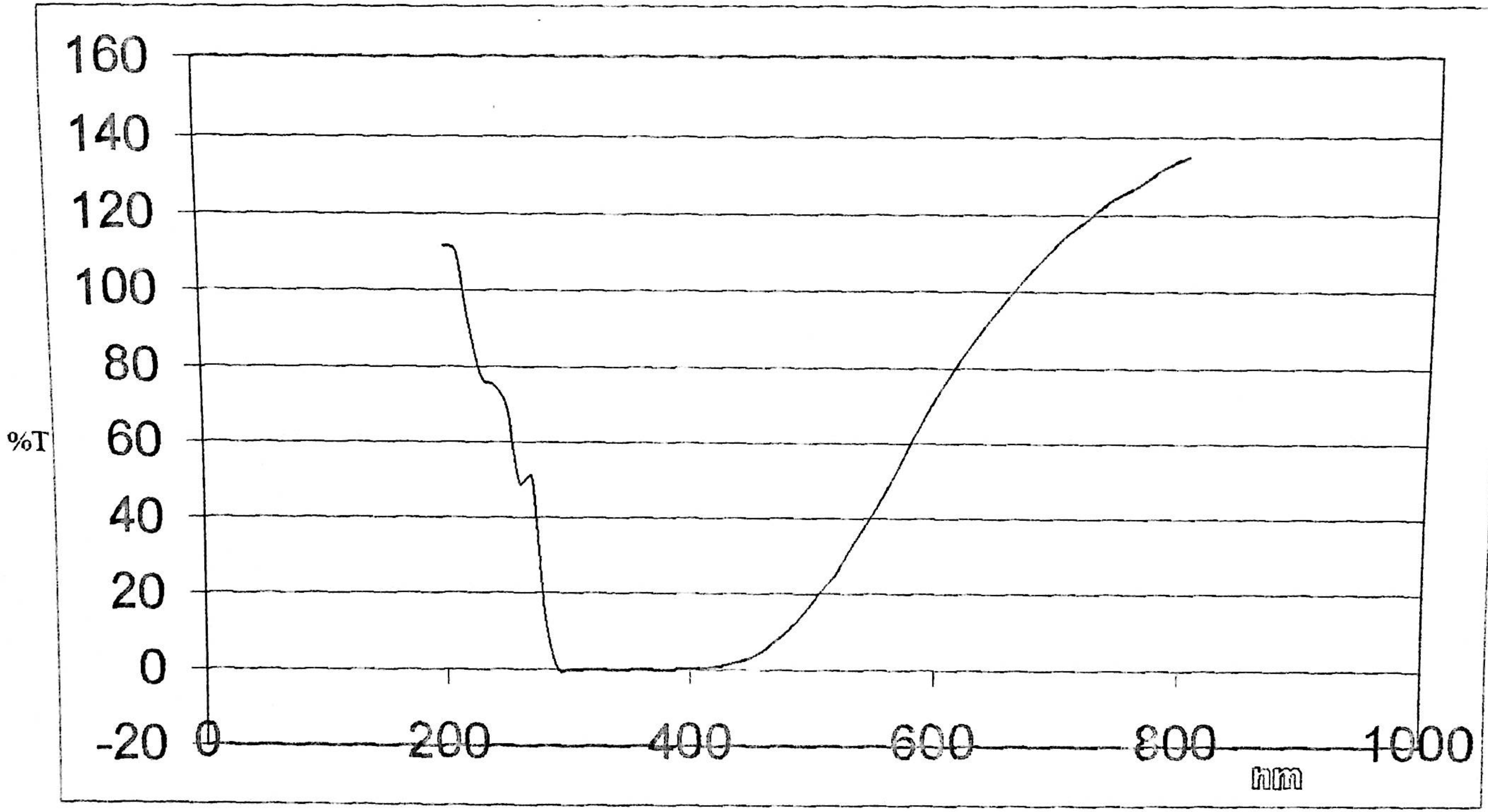


Fig. 8 : Electronic spectrum of $[Cd(L)_2.HL]$ (in cychlohexane)

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PART-II

CHAPTER-6

ANTIBACTERIAL ACTIVITY TESTING

ANTIBACTERIAL ACTIVITY TESTING

6.1 INTRODUCTION AND PRINCIPLE:

Any chemical or biological agent that either destroys or inhibits the growth of microorganisms is called antimicrobial agent.

The susceptibility of microorganism to antimicrobial agent can be determined in vitro by number of methods. The disc diffusion technique [1.2] is widely acceptable for preliminary investigation of materials which are suspected to posses antimicrobial properties. Diffusion procedure, as normally used is essentially a qualitative test which allocates organism of the susceptible intermediate (moderately susceptible) or resistant categories.

In the disc diffusion technique, dried filter paper discs containing known amount of test materials are placed on agar plates seeded with test organisms. These are kept at low temperature (4°C) for 4 hours.

Initially the dried discs absorb water from the surrounding test medium and the drug is dissolved. The drug migrates through the adjacent test medium by concentration gradient of the drug according to physical law that governs diffusion of molecules through an agar gel[3]. As a result, there is a gradual change of drug concentration in the agar surrounding each disc. Then the plates are incubated in an incubator at 37°C for 16 hours.

As the antibiotic diffusion progresses, microbial multiplication also proceeds. After an initial lag phase, a logarithmic growth phase is imitated, at that moment bacterial multiplication proceeds more rapidly than the drug can diffuse, and the bacterial cells which are not inhibited by the anti microbial agents will continue to multiply until a lawn of growth can be visualized. No growth will appear in the area where drug is present in inhibitory concentration.

Centrally, the more susceptible the test organism, the larger is the circular zone of inhibition. Antimicrobial activities of the test samples are expressed by measuring the zone of inhibition observed around the area. The diameter of the inhibition is usually measured to understand the extent of inhibition in different concentrations.

The size of the inhibitory zones depends principally on the following factors.

a. Intrinsic antimicrobial sensitivity of the test sample.
b. Growth rate of the test microorganism.
c. Diffusion rate of the drug which is related to its water solubility.
d. Number of concentration of the freshly seeded test organisms.
e. Amount of the test sample on disc.
f. Thickness of the test medium in the petridishes.
g. Thickness of the filter paper disc.

6.2 APPARATUS AND REAGENTS :

a. Micropipette
b. Autoclave
c. Incubator
d. Refrigerator
e. Filter paper disc
f. Petridishes
g. Inoculating loop
h. Sterile cotton
i. Sterile forceps
j. Spirit Lamp
k. Laminar air flow unit
l. Nutrient agar

6.3 METHOD:

The test organisms are all human pathogenic. For this reason all steps of the work were done with high precaution and aseptic condition which are mentioned below. All steps of the work were carried out at Microbiology Laboratory, Pharmacy Department, Rajshahi University.

6.4 TEST ORGANISMS:

The following human pathogenic bacteria have been studied:

Sl.No.	Gram Negative
1	Shigella dysenteriae
2	*Escherichia coli*
3	*Pseudomonas aeruginosa*
	Gram Positive
4	Bacilhis subtilis
5	*Sarcina lutea*
6	*Staphylococcus aureus*

6.5 CULTURE MEDIA:

Nutrient agar medium was used as culture media. The formulation of Nutrient agar media (DIFCO) is as follows:

Nutrient Agar (mast Diagnostics)

Formulation	Grams/liter
Peptone A	6.0
Yeast extract	2.0
Beef extract	1.0
Sodium Chloride	5.0
Agar A	14.0
Distilled water q.s. to 1000 ml	

28 grams of powder was weighed, dispersed in one litre of distilled water, allowed to soak for 10 minutes, swirled to mix and then sterilized by

autoclaving for 15 minutes at 121°C, and then the medium was cooled to 40-45°C and mixed well, then poured into plates.

6.6 PREPARATION OF FRESH CULTURE:

The liquid culture is called broth culture. The culture media without agar powder per liter:

Formulation	Grams/litre
Bacto-tryptone	10.0g
bacto-yeast extract	5.0g
NaCl	10.0g

Adjusted pH to 7.5 with sodium hydroxide.

Tryptone, NaCl and yeast extract of calculated amount were taken in a conical flask and distilled water was added (volume should be less than 1 litre). The contents were put on a water bath to make a clear solution. The pH of the solution was then adjusted to 7.5 using NaOH or HCl as necessary. Distilled water was added sufficiently to make the final volume (1 litre). Again the total volume was heated on a water bath to obtain a clear solution. The conical flask was plugged with cotton and then autoclaved at 1 atm pressure for 15 minutes at 121°C.

50 ml of both medium was transferred in a conical flask. The test microorganisms of pure culture were streaked on the mutrient both media with the help of sterile loop in an aseptic condition and incubated at 37°C for 24 hours. The both cultures thus obtained was considered as fresh culture. Fresh culture of this type was always used throughout the sensitivity testing.

6.7 PREPARATION OF PLATES:

Solid media in petridishes are often called 'plates'. The medium was poured into sterile petridishes in an aseptic condition on a level horizontal surface so as to give a uniform depth of approximately 4 mm. Then the medium had been allowed to cool at room temperature in order to solidify the medium.

6.8 PREPARATION OF DISCS :

A. Sample disc

1. Solutions of the compounds were prepared in respective solvents so that 20 μL contained 200 μg of the compounds.
2. Filter paper discs were taken in petridish and sterilized by oven at 110°C for 1 hour.
3. 20 μL of the solutions were placed on the discs with the help of a micropipette, thus discs containing 200 μg compounds were prepared.
4. These discs were then air dried.

B. Standard dics

Ready made Kanamycin K-30 discs containing 30 μg/disc of antibiotic Kanamycin were used as standard disc.

6.9 PLACEMENT OF THE DISCS AND INCUBATION :

The solidified agar plates were seeded with the 200 μL of fresh culture with the help of a micropipette and spread the microorganisms with the help of a sterile spreader in an aseptic condition.

The prepared discs of samples were placed gently on the freshly seeded solidified agar plates with a sterile forceps. Standard discs and control discs were also placed on the test to compare the effect of the test sample and to nullify the effect of solvent, respectively.

The plates were then kept in a refrigerator at 4°C for 4 hours in order that the materials had sufficient time to diffuse to a considered area of the plates. After this, the plates were incubated at 37°C for 16 hours.

6.10 CALCULATION OF THE ZONE OF INHIBITION:

After incubation, the diameter of the zone of inhibitions were observed and measured in mm by a transparent scale. Results obtained from these are listed in Tables (6.2-6.7).

6.11 RESULTS OF THE ANTIBACTERIAL ACTIVITY OF THE COMPLEXES 1, 2, 3 AND LIGALD AGAINST THE SIX PATHOGENIC BACTERIA (viz. *Escherichia Coil, Shiella Dysenteries, Pseudomonas aeruginosa, Bacillus Subtilis. Sarcina lutea AND Staphylococcus aureus).*

Table 6.1: Complexes abbreviation for antibacterial activity.

Complexes No	Complexes	Labelled
1	$[(ZrO)_2(L)_4(H_2O)_2]$	A
2	$[Ag(L)]$	B
3	$[Cd(L)_2.HL]$	C
Ligand	2-hybroxy-5-nonyl - acetophenone oxime =L	

Table 6.2: Antibacterial activity of the complexes **1, 2, 3** and ligand 2-hybroxy-5-nonyl acetophenone, oxime against *Escherichia coli.*

Complex No	Complexes	*Zone of inhibition of mycelia* growth (in mm)	
		200 $\mu g/disc$	30 $\mu g/disc$
1	$[(ZrO)_2(L)_4(H_2O)_2]$		
2	$[Ag(L)]$	24	
3	$[Cd(L)_2.HL]$	19	
Ligand	2-hybroxy-5-nonyl-acetophenone, oxime =L	9	
	Control disc	Nil	
	Standard disc		20

Where,

Kanamycin was used as standard compound labeled as K.

Control disc contains solvent only.

Table 6.3: Antibacterial activity of the complexes **1, 2, 3** and ligand 2-hydroxy-5-nonylacetophenone against *Shigella dyscnteriae.*

Complex No.	Complexes	Zone of ingibition of mycelia growth (in mm)	
		200 $\mu g / disc$	30 $\mu g / disc$
1	$[(ZrO)_2(L)_4(H_2O)_2]$	7	
2	$[Ag(L)]$	23	
3	$[Cd(L)_2.HL]$	25	
Ligand	2-hybroxy-5-nonyl - acetophenone, oxime =L	8	
	Control disc	Nil	
	Standard disc		18

Table 6.4: Antibacterial activity of the complexes **1**, **2**, **3** and ligand 2-hydroxy-5-nonylacetophenone against *Pseudomonas aeruginosa.*

Complex No.	Complexes	Zone of inhibition of mycelia growth (in mm)	
		200 μg/disc	30 μg/disc
1	$[(ZrO)_2(L)_4(H_2O)_2]$		
2	$[Ag(L)]$	19	
3	$[Cd(L)_2.HL]$	22	
Ligand	2-hybroxy-5-nonyl - acetophenone, oxime =L	8	
	Control disc	Nil	
	Standard disc		21

Table 6.5: Antibacterial activity of the complexes **1, 2, 3** and ligand 2-hydroxy-5- nonylacetophenone against. *Bacillus subtilis.*

Complex No.	Complexe	Zone of inhibition of mycelia growth (in mm)	
		200 μ g/disc	30 μ g/disc
1	$[(ZrO)_2(L)_4(H_2O)_2]$	7	
2	$[Ag(L)]$	23	
3	$[Cd(L)_2.HL]$	17	
Ligand	2-hybroxy-5-nonyl - acetophenone, oxime =L	9	
	Control disc	Nil	
	Standard disc		20

Table 6.6: Antibacterial activity of the complexes **1, 2, 3** and ligand 2-hydroxy-5- nonylacetophenone against *Sarcina lutea.*

Complex No.	Complexes	Zone of inhibition of mycelia growth (in mm)	
		200 µg/disc	30 µg/disc
1	$[(ZrO)_2(L)_4(H_2O)_2]$		
2	$[Ag(L)]$	21	
3	$[Cd(L)_2.HL]$	18	
Ligand	2-hybroxy-5-nonyl - acetophenone, oxime =L	9	
	Control disc	Nil	
	Standard disc		22

Table 6.7: Antibacterial activity of the complexes **1**, **2**, **3** and ligand 2-hydroxy-5- nonylacetophenone against *Staphylococcus aureus.*

Complex No.	Complexes	Zone of inhibition of mycelia growth (in mm)	
		200 μg/disc	30 μg/disc
1	$[(ZrO)_2(L)_4(H_2O)_2]$	8	
2	$[Ag(L)]$	16	
3	$[Cd(L)_2.HL]$	21	
Ligand	2-hybroxy-5-nonyl - acetophenone, oxime =L	8	
	Control disc	Nil	
	Standard disc		20

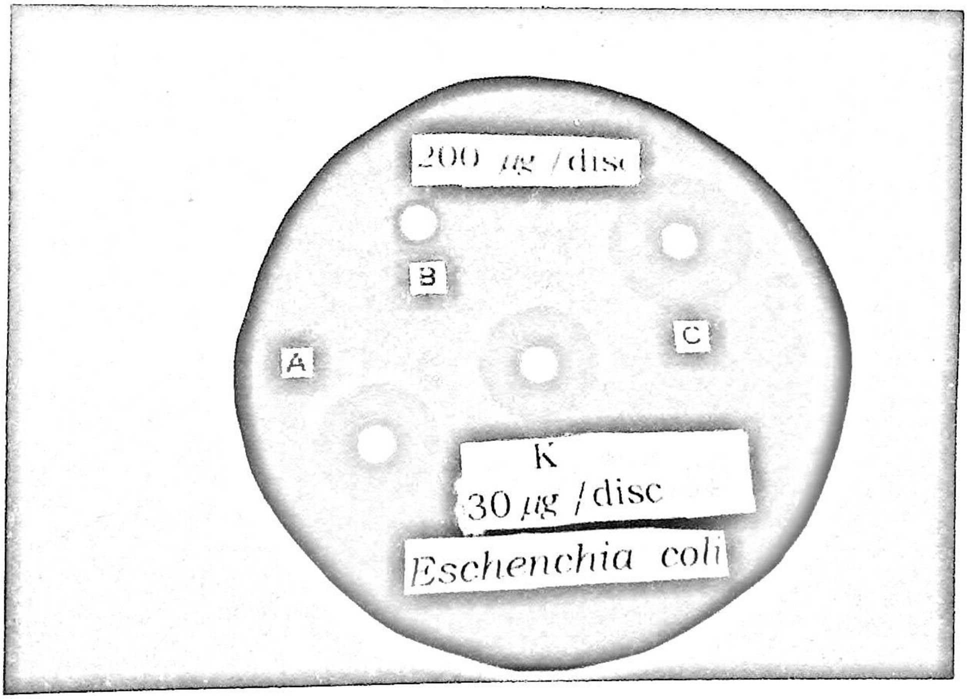

Fig-6.1 Photographic representation of zone of inhibition of the complexes **1, 2, 3** and the standard compound kanamycin against *Escherichia coli.*

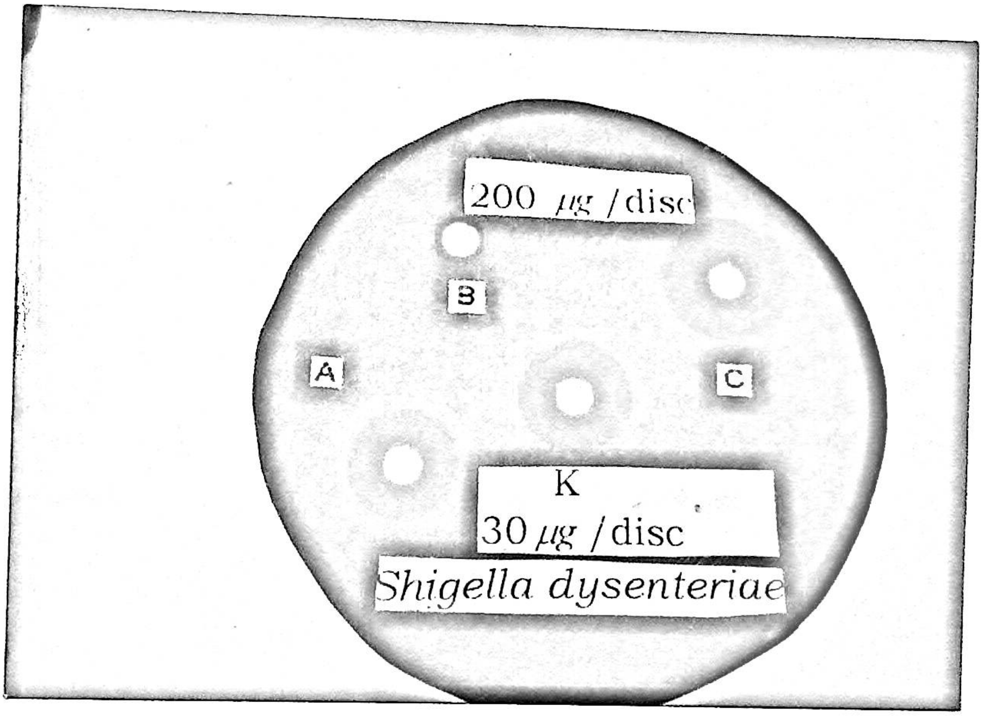

Fig-6.2 Photographic representation of zone of inhibition of thecomplexes 1, 2, 3 and the standard compound kanamycin against *Shigella dysenteriae.*

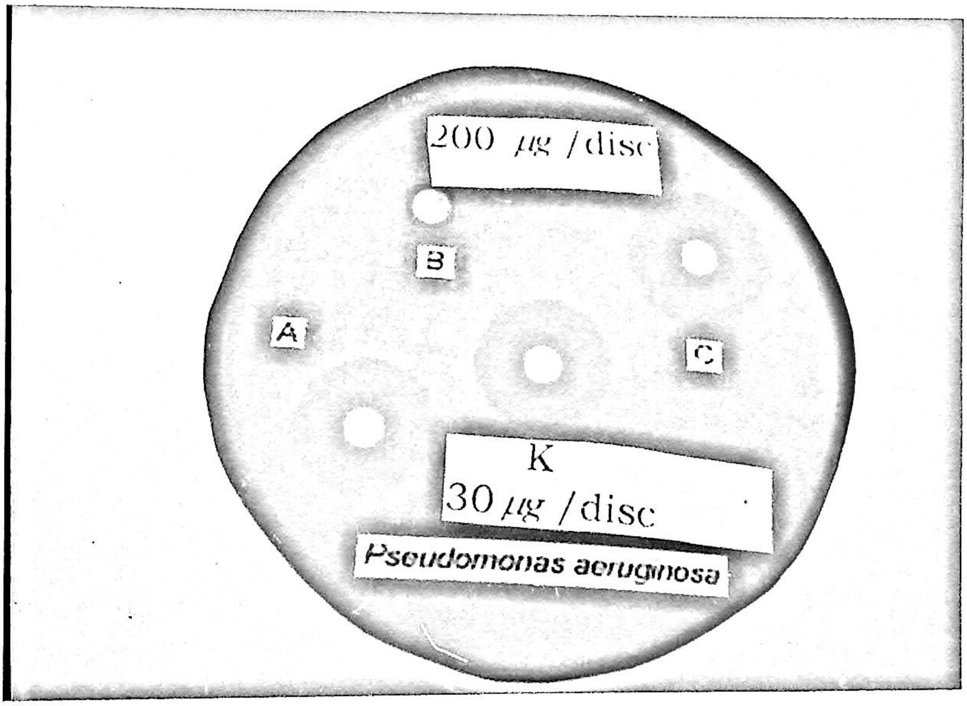

Fig-6.3 Photographic representation of zone of inhibition of the complexes **1, 2, 3** and the standard compound kanamycin against *Pseudomonas aeruginosa.*

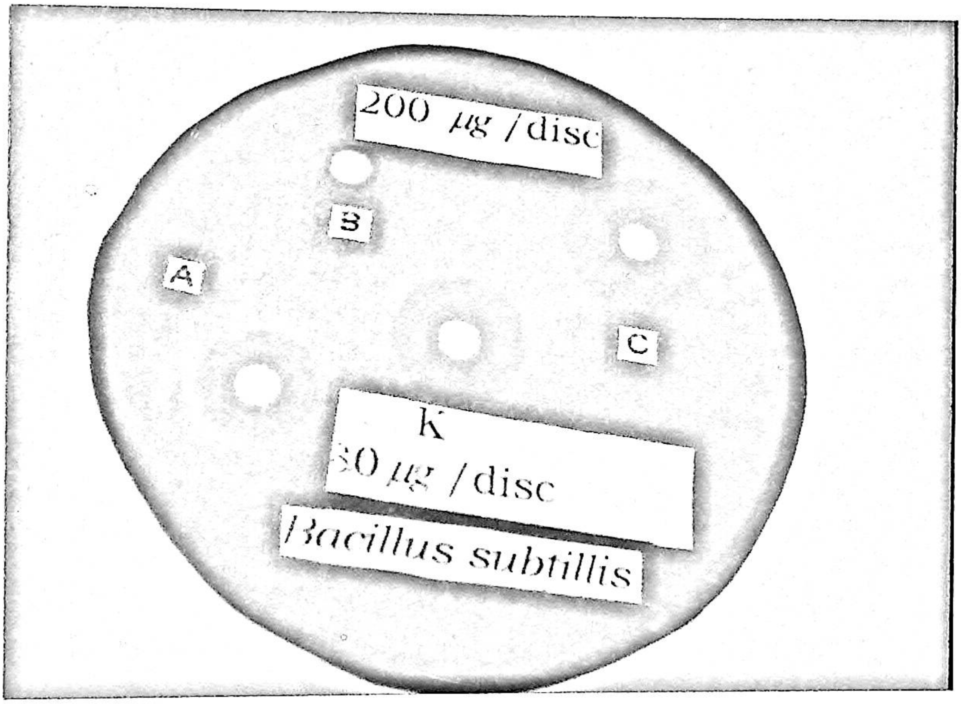

Fig-6.4 Photographic representation of zone of inhibition of the complexes **1, 2, 3** and the standard compound kanamycin against *Bacillus subtilis.*

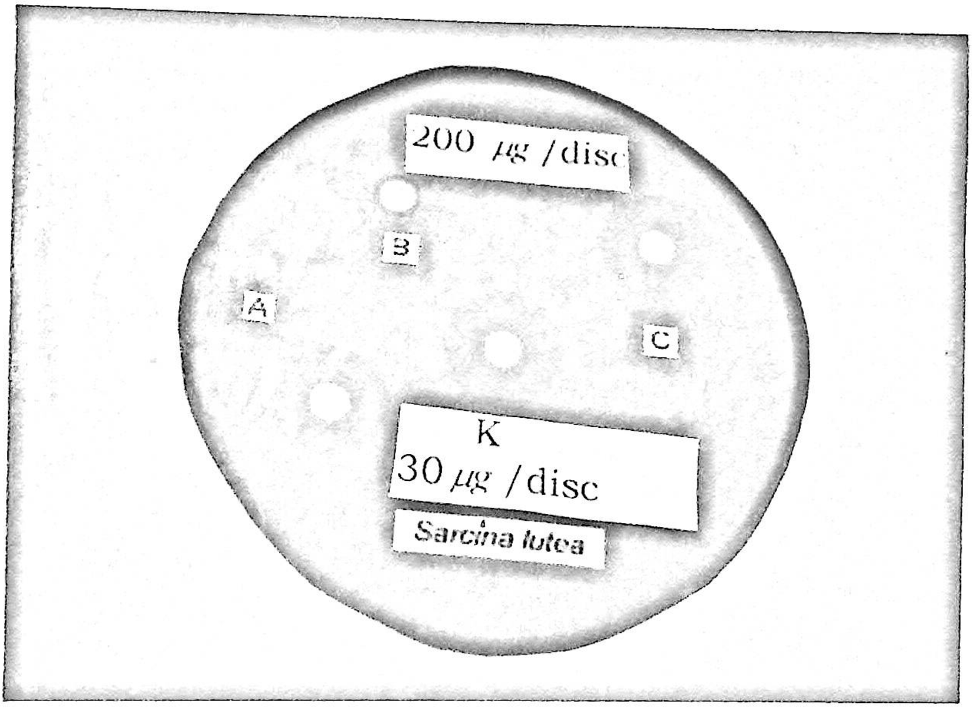

Fig-6.5 Photographic representation of zone of inhibition of the complexes **1, 2, 3** and the standard compound kanamycin against *Sarcina lutea.*

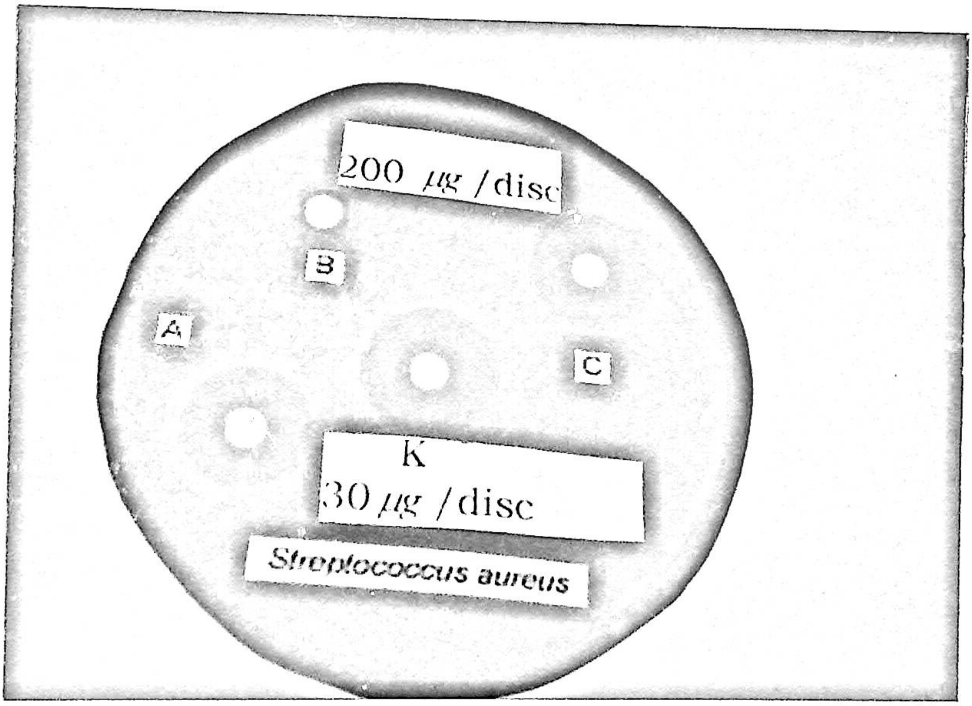

Fig-6.6 Photographic representation of zone of inhibition of the complexes **1, 2, 3** and the standard compound kanamycin against *Staphylococcus aureus.*

6.12 DISCUSSION :

It has been observed that some drugs (Ligands) increase the *activity when administered as metal complexes or their metal chelates*[4]. The antibacterial activity of the metal compsexes **1, 2, 3** and the ligand (2-hybroxy-5-nonyl acetophenone) are studied against with six pathogenic bacteria viz.

1. *Shigella. dysenteriae*
2. *Escherchia coli*
3. *Pscudomonas aeraginosa.*
4. *Bacillus subtilis.*
5. *Sarcina lutea.*
6. *Staphylococcus aureus.*

And the results are given in table (6.2-6.7). It is seen that the complex **2** and **3** showed the most activities above six pathogenic bacteria as shown in Table (6.2-6.7).

The Complex **2** showed the best activity against E. Coli and less activity against Staphylococcus aureus. The complexe **1** did not show activities against the six pathogenic bacteria.

All the results are compared with the standard compound, Kanamycin as seen in the Table (6.2-6.7). The ligand (oxime) did not show any activities against the above six pathogenic bacteria.

From the above discussion it is concluded that the complexe **2** and **3** showed good activities against the six pathogenic bacteria as compared to the stardard compound, Kanamycin. It is evident that the metal ion plays the key role to show good activities, because the ligand did not show any activity.

6.13 DETERMINATION OF MINIMUM INHIBITORY CONCENTRATIONS (MIC) OF COMPLEXES.

6.13.1 Introduction.

The lowest concentration of antimicrobial agent required to inhibit the growth of the organism in vitro is referred to as the minimum inhibitory concentration (MIC). There are two methods for determining this value:

i) Serial dilution technique or turbidimetric assay[5,6].

ii) Paper disc technique or agar diffusion assay[5].

Here, "serial dilution technique"[5,6] was followed using nutrient broth medium. The MIC values of Complexes were determined against the following six test organisms:

Gram Negative	Gram Positive
Shigella dysenteriae	*Bacilhs subtilis*
Escherichia coli	*Sarcina lutea*
Pseudomonas aeruginosa	*Staphylococcus aureus*

6.13.2 Preparation of sample solution

2.048 mg of the test compound was taken in a vial. 2 mL of methanol was added the vial to dissolve the compound. Thus solutions with a concentration or i. 024 mg/mL were obtained.

6.13.3 Preparation of incolum

Over night cultures of the test bacteria grown at 37.5°C in nutrient broth medium was diluted in sterile nutrient broth medium in such a *manner so that suspension contain about* 3.5×10^6 *cell/mL. This* suspension was sued as the inoculum.

6.13.4 Procedure.

i) 12 test tubes were taken, nine of which were marked (1-9) and rest three were assigned as C_M (nutrient broth medium), C_s (nutrient broth medium +compound) C_i [nutrient broth medium+ inoculum (organism)].

ii) 1 ml of nutrient broth medium was poured to each of the 12 test tubes.

iii) These test tubes were cotton plugged and sterilized in a autoclave for 15 minutes at 121°C temperature and 1 atm. pressure.

iv) After cooling, 1 mL of the sample solution was added to the 1st tube, mixed well and them 1 mL of this content was transferred to the second test tube.

v) The content of the 2nd test tube was mixed well and again 1 mL of this mixture was transferred to the 3rd tube. This process of serial dilution was continued up to the 9th test tube.

vi) 10 μL of properly diluted inoculum was added to each of the nine test tubes and mixed well.

vii) To the control test tube, C_s, 1 mL of the sample solution was added; mixed well and 1mL of this mixed content was discarded. This is to check the oleayyity of the medium in persence of diluted diluted solution of the compound.

viii) 10 µLof the incolumns was added to the control test tube $C_{i,}$ to observe the growth of the organism in the medium used.

ix) The control test tube C_{m}, containing medium only was used to confirm the sterility of the medium.

x) All the test tubes were incubated at 37.5°C for MIC is the lowest drug concentration at which there in no growth.

6.14 RESULT OF THE MINIMUM INHIBITORY CONCENTRATION OF THE COMPLEXE [Ag(L)] 2 AND [Cd(L)$_2$.HL] 3 AGAINST THE SIX PATHOGENIC BACTERIA VIZ:

1. *Escherchia coli.*
2. *Shigella dysenteriae.*
3. *Pscudomonas aeraginosa.*
4. *Bacillus subtills.*
5. *Sarcina lutea.*
6. *Staphylococcus aureus.*

Table 5.8: Minimum inhibitory concentration of complexes *[Ag(L)]* 2 againest six pathogenic bacteria.

Test tube No.	Nutrient both medium added (mL)	Diluted solution of complex (µg/mL)	Inoculums added(µL)	Bacterial Growth observation against					
				E. coli	*S.dysenteriae*	*P.aeruginosa*	*B.subtilis*	*Sarcina lutea*	*S.aureus*
1	1	512	10	-ve	-ve	-ve	-ve	-ve	-ve
2	1	256	10	-ve	-ve	-ve	-ve	-ve	+ve
3	1	128	10	-ve	-ve	-ve	-ve	-ve	+ve
4	1	64	10	-ve	+ve	+ve	+ve	+ve	+ve
5	1	32	10	+ve	+ve	+ve	+ve	+ve	+ve
6	1	16	10	+ve	+ve	+ve	+ve	+ve	+ve
7	1	8	10	+ve	+ve	+ve	+ve	+ve	+ve
8	1	4	10	+ve	+ve	+ve	+ve	+ve	+ve
9	1	2	10	+ve	+ve	+ve	+ve	+ve	+ve
Cs	1	512	10	-ve	-ve	-ve	-ve	-ve	-ve
Ci	1	0	10	+ve	+ve	+ve	+ve	+ve	+ve
Cm	1	0	10	-ve	-ve	-ve	-ve	-ve	-ve

Where, +ve = Growth and -ve = Not growth

Table 5.8: Minimum inhibitory concentration of complex *[Cd(L)$_2$.HL]* **3** against six pathogenic bacteria.

Test tube No.	Nutrient both medium added (mL)	Diluted solution of complex (µg/mL)	Inoculums added(µL)	Bacterial Growth observation against					
				E. coli	*S.dysenteriae*	*P.aeruginosa*	*B.subtilis*	*Sarcina lutea*	*S.aureus*
1	1	512	10	-ve	-ve	-ve	-ve	-ve	-ve
2	1	256	10	-ve	-ve	-ve	-ve	-ve	+ve
3	1	128	10	-ve	-ve	-ve	-ve	-ve	+ve
4	1	64	10	-ve	+ve	+ve	+ve	+ve	+ve
5	1	32	10	+ve	+ve	+ve	+ve	+ve	+ve
6	1	16	10	+ve	+ve	+ve	+ve	+ve	+ve
7	1	8	10	+ve	+ve	+ve	+ve	+ve	+ve
8	1	4	10	+ve	+ve	+ve	+ve	+ve	+ve
9	1	2	10	+ve	+ve	+ve	+ve	+ve	+ve
Cs	1	512	10	-ve	-ve	-ve	-ve	-ve	-ve
Ci	1	0	10	+ve	+ve	+ve	+ve	+ve	+ve
Cm	1	0	10	-ve	-ve	-ve	-ve	-ve	-ve

Where, +ve = Growth and -ve = Not growth

6.15 DISCUSSION:

The minimum inhibitory comcentration (MIC) of the determined against six pathogenic bacteria viz.

1. *Escherchia coli.*
2. *Shigella dysenteriae.*
3. *Pseudomonas aeraginosa.*
4. *Bacillus subtilis.*
5. *Sarcina lutea.*
6. *Staphylococcus aureus* by serial dilution technique. The results are shown in

Table. 6.10: MIC of the complexes [Ag(L)] 2 and [Cd$(L)_2$.HL] 3

Test organisms	MIC ($\mu g/ml$)	
	Complex 2	Complex 3
Escherichia coli.	64	64
S. dysenteries	128	128
Pseudomonas	128	128
Bacillus subtilis	128	128
Staphylococcus aureus	256	256
Sarcina lutea	256	256

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APPENDIX

A) Hydrometallurgy:

The processes involved in the production of pure metals from ores(i.e., the natural minerals in metals or their compounds occur in the earth) are known as Metallurgy. It involves some chemical and mechanical steps. The process in which the metals present in the ore is made to go into aqueous solution due to some chemical changes and the metal is then separated by suitable means e.g. fractional crystallization, precipitation, ion-exchange or solvent extraction, is called Hydrometallurgy. Hydrometallurgy is concerned usually with the processing (large and small scale) of low grade metalliferous bodies; the primary purpose being the extraction of the metal in a suitable form in aqueous solution for further processing. At presen, hydrometallurgical operations have become of worldwide interest over the long known pyrometallurgical processes mainly for the following reasons: i) Very low grade ores, and the burden of required antipollution equipments have proven the pyrometallurgical processes uneconomical; ii) Environmental pollution has encouraged the treatment of metallurgical wastes by hydrometallurgical means; iii) Increased cost of raw materials and their diminishing supply encourage the reprocessing of scrap; hydrometallurgy has made an impact on the isolation of metals of metals of complex mixtures in solution; iv) Hydrometallurgy can handle the purification problem of the leach solution which is complecated by the presence of more than one metal in single solution.

The methods have been tried on a commercial scale are mainly (a) solvent extraction (liquid-liquid) and (b) ion - exchange of the two, the solvent extraction method has now become a method of major importance, because of high cost of ion - exchange matters, very low output or capacity 4me g^{-1}, fixed low rate (very low process) and also very low selectivity of the ion exchange process as contrast to solvent extraction. Obviously, solvent extractant enjoys a favoured position among other exising powerful separating techniques because of its case, simplicity, selectivity, apeed and wide scope. It is applicable to both trace and macro levels of metal concentrations and gives high purity of the products. The cost of production is also low. Thus where fractional crystallization, precipitation and other usual techiques are tedious and gives high purity of the products. The cost of production is also low. Thus where fractional crystallization, precipitation and other usual techniques are tedious and costly, the solvent extraction process is very simple and cheap. The process (SX) is now well established in hydrometallurgy using more efficient and selective extractants developed, with full-scale plants with newly devised low-cost contactng devices. As a matter of face, a great variety of metals are now being treated hydrometallurgically, and extracted using the solvent extraction method.

During the last three decads solvent extraction finds increasing opplication in the extraction of the common metals (viz, coppir, Nickel, Cobalt and the like). A number of reports has of far been published. Most of these investions; but only a few of them are related to the kinetics of the processes. The chemical engineering principles underlying the techique of multistage counter-curent extraction are well understood and it is now possible to desing a full scale plant from simple distribution measurements. Moreover, the development of low cost new contacting devices has extended the applicability of the technique.

B) SOLVENT EXTRACTION(SX)

In hydrometallurgy, the solvent extraction method is a chemical process which involves the mass transfer of complex species of a metal ion across the boundary between two practically immiscible phases on agitation of which one is an inert is an inert organic solvent containing the extracting reagent (i.e. the extractant), and the other, an aqueous feed material. The extractant reacts with the distribuent by processes such as solvation, chelation, ion - pairing ion - exchange etc., to extract the metal species from the aqueous phase. The extractant and the diluent together act as an efficient extracting solvent; the latter modifies the extratant properties of the farmer.

As a physical method of purification and separation, the extraction using a suitable solvent(organic) of renerally organic matters has long been familiar to especially the organic[56] as well as analytical chemists. But there has been interest in solvent extraction in the field inorganic chemistry during the girst three decades of this century; although the extractability of several inorganic compoubds into organic solvents was early established. The extraction of uranyl nitrate from aqueous solution by ether[57], for example, was discovered in 1842.

Now a days, solvent extraction is not only used for the separation and production of rare earths but also finds increasing application in the extraction of commoner metals, especially from their low grade ores. Besides it has not extensive applications (laboratory and industrial) in the analytical field[58] for the separation and purification of metals.