SYNTHESIS AND CHARACTERIZATION OF COORDINATION COMPLEXES OF SOME TRANSITION METAL ELEMENTS WITH ELECTRON RICH LIGANDS

A THESIS
Submitted in Partial fulfillment of the requirement for the degree of
DOCTOR OF PHILOSOPHY in CHEMISTRY
by
MD. ARSHAD HUSSAIN KHAN
Enrollment No. 1050106793

Under the Supervision of
DR. ABDUL BASHAR

Department of Chemistry
Singhania University
Pacheribari, Jhunjhunu (Raj.), India
Year of Submission: 2014

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भारतीय गैर न्यायिक

भारत

बीस रुपये

Rs. 20

रु.20

INDIA NON JUDICIAL

BEFORE THE NOTARY :::::GOALPARA.

Arshad Hussain Khan

AFFIDAVIT

I, Arshad Hussain Khan, S/o Ahmed Hussain Khan, aged about 42 years, by religion-Islam, by profession-Lecturer Goalpara College, a resident of Goalpara Town, ward No.15, P.O. Boladmari, P.S.& Dist. Goalpara, Assam, do hereby solemnl affirm and declare as follows :

1. That I am the citizen of India by birth and permane residing of the aforesaid locality.

2. That my name has been enrolled in the voter list, [illegible] Goalpara Town, [illegible] No.30 (pyndo 5140) House No.447, under [illegible] in the District of Goalpara [illegible]

3. That the name of my father has been [illegible]

Identified by me.
Advocate
13/11/14

13.11.14

4. That the name of my father has been enrolled and written in various documents/voter list as Ahmed Khan and Ahmed Hussain Khan.But he is one and same person.

5. That I am doing Ph.D.in Chemistry Department under Singhani University and accordingly my name has been enrolled vide Enrollment No.1050106793.

6. That being the name of my father has been enrolled in the voter list ,1966 and my name also been enrolled in the voter list in the year of 2013.So I am the citizen of India by birth.

7. That this affidavit is a piece of document for the purpose of that I am the citizen of India by birth and further be used if that the name of my father is Ahmed Khan and Ahmed Hussain Khan is the same and one person and shall be submitted to the authority concerned whenever required it.

All the statements made in this affidavit are true to the best of my knowledge and belief.

Identified by me,

13/11/14

Advocate,Goalpara,

Arshad Hussain Khan

Deponent

Sworn before me by the deponent
being identified by Mr.Aynal Hoque,
Advocate,Goalpara on 13/11/14.

13.11.14

NOTARY

Acknowledgement

By the grace of Almighty, the most merciful and benevolent One, I could complete this prestigious and challenging research work.

The first person I would like to thank is **Dr. Abdul Bashar**, *my supervisor, mentor and guide. I express my wholehearted gratitude to him for his benevolent guidance, sympathetic behavior, keen interest and devotion throughout this work.*

I am greatly indebted to **Dr. Athar Adil Hashmi**, *Associate Professor, Department of Chemistry, Jamia Millia Islamia University, New Delhi, for his continous support, valuable suggestions and providing research facilities therein.*

I am very thankful to the authority, Jamia Millia Islamia University, New Delhi, for giving me the opportunity to proceed with my research work there.

I express my sincere thanks to **Urvashi Singh, Mohammad Maqbool Dar**, *Research Scholars, Department of Chemistry, Jamia Millia Islamia University, New Delhi and other* **Research Fellows** *for their kind help and intellectual support.*

I am also thankful to **Mr. Susanta Kumar Roy**, *Research Scholar, Department of Chemistry, Gauhati University, Assam, for his personal help and intellectual support.*

I would express my sincere thanks to **Dr. Dharmeswar Barman**, *Assistant Professor, Department of Botany, Goalpara College, Goalpara, Assam and* **Mr. Sabbir Ansary**, *Research Scholar, Department of Life Science, Jamia Millia Islamia University, New Delhi for their help in conducting the antimicrobial studies of the newly synthesized compounds.*

Finally, I would also like to express my gratitude to my **parents and brothers** *for their encouragements and interest in my academic persuit.*

Date: 20-11-2014

Arshad Hussain Khan

CERTIFICATE BY THE SUPERVISOR

(At the time of approval of Title/ Synopsis)

Certified that :

1. I am willing to guide the research work of Shri/ Km./ Smt. **Arshad Hussain Khan** on the above subject if he/ she is registered for Ph. D.
2. To the best of my knowledge the subject selected have not been studied and is not being studied so far in any university.
3. The subject is of sufficient scope to keep the candidate engaged for two years.
4. The subject will lead to a valuable contribution to the society. I have seen and approved the outline and bibliography, etc submitted by the candidate.
5. Necessary facilities are available for the above research work.
6. I have **1 (one)** research candidate registered under my supervision and the serial number of this candidate whose application being forwarded for registration is **1 (Enroll. No. 1050106793).**

Sl No.	**Name of Scholar**	**Enrollment No.**
1.	**Md. Arshad Hussain Khan**	**1050106793**

A. Bashar
20/11/14
Signature of the Supervisor with date

(with seal)

Associate Professor,
Deptt. of Chemistry,
B.P. Chaliha College,Nagarbera
Kamrup,Assam,(INDIA)

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Date : 20-11-2014

Certificate

Date : ....

Certified that the work embodied in this thesis entitled *"Synthesis and Characterization of Coordination Complexes of Some Transition Metal Elements with Electron Rich Ligands"* is the result of the original research work of *Mr. Arshad Hussain Khan,* carried out under my supervision. The work is suitable for the award *of Ph. D. Degree in Chemistry from Singhania University, Jhunjhunu, Rajasthan, INDIA.*

A. Bashar

(Dr. Abdul Bashar)

Supervisor
Ref. No. : SU/R &D/ 2011/ 481

Associate Professor,
Deptt. of Chemistry
B. Chaliha College, Nagarbera
Kamrup, Assam (INDIA)

SINGHANIA UNIVERSITY

(Established U/S 2(f) of UGC Act. 1956)
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Ph.: 01593-271299/300, Fax: 01593-271003
website: www.singhaniauniversity.co.in

Ref. No.: SU/R&D/2011/481

Dated: 2/7/2

OFFICE – ORDER

We are hereby directed to approve Dr. Abdul Bashar, as a Research Supervisor of the University for Chemistry.

Authorised Signatory
SINGHANIA UNIVERSITY
Pacheri Bari. Distt Jhunjhunu
Rajasthan

Copy To:

1. University Office, Singhania University , Pacheri Bari.
2. Dr. Abdul Bashar.

SINGHANIA UNIVERSITY, PACHERI BARI (JHUNJHUNU)

(CERTIFICATE BY SCHOLAR)

This is to certify that the thesis titled **Synthesis and Characterization of Coordination Complexes of Some Transition Metal Elements with Electron Rich Ligands**

and submitted by **Md. Arshad Hussain Khan** under the supervision of **Dr Abdul Bashar** Enrollment No. **1050106793** for award of Ph. D. Degree of the university carried out during the period of **2010** to **2014** embodies my original work and has not formed the basis for the award of any degree, diploma associateship, fellowship, titles in this or any other University or other similar Institution of higher learning.

Signature in full: Arshad Hussain Khan

Name in block letters: **MD. ARSHAD HUSSAIN KHAN**

Enrollment No. : **1050106793**

Date: **20-11-2014**

SINGHANIA UNIVERSITY

Pacheri Bari, (Jhunjhunu) - Raj.-333515
(Established under section 2(f) of the UGC Act 1956)
Phone No. 01593-271299/300/005, Fax No.: 01593-271003

Ref. No.: SU/SOR/2012/Duplicate-079 Dated: July 26, 2012

To
Md. Arshad Husain Khan

Subject: Provisional Registration for Ph.D. Degree

Dear Student,

You are provisionally registered for Ph.D. in Chemistry with Singhania University for session 2010 - 2011 and shall be governed by the academic regulations of the University.

Registration / Enrollment No: 1050106793

Date of Registration: 30/11/2010

As per the regulations for the Ph.D. degree, the candidate shall be required to complete course work within six months from the date of registration.

Authorized Signatory

Singhania University

Copy to:

1. Registrar Office, Singhania University, Pacheri Bari
2. Dean Research

SINGHANIA UNIVERSITY
Pacheri Bari, (Jhunjhunu) - Raj.-333515
(Established under section 2(f) of the UGC Act 1956)
Phone No. 01593-271299/300/005, Fax No.: 01593-271003

Ref. No.: SU/SOR/2011/Duplicate-3485

Dated: 25-07-2012

To
Dr. Abdul Bashar

Subject: Registration for Ph.D. Degree

Dear Sir/Madam,

This is in reference to the proposal submitted by Md. Arshad Hussain Khan regarding registration for Ph.D. degree. We are pleased to inform you that the said candidate has been registered for Ph.D. degree with the University and shall be governed by the rules and regulations of the University.

Thesis Topic:-"Synthesis and Characterization of Co-Ordination Complexes of Some Transition Metal Elements with Electron Rich Ligands"

Registration / Enrollment No.: 1050106793

Dean, Research

Copy to:

1. Registrar Office
2. Md. Arshad Hussain Khan

OUTLINE OF PROPOSED RESEARCH WORK

1) Name of Scholar : MD. ARSHAD HUSSAIN KHAN

2) Title of the Research Work :

SYNTHESIS AND CHARACTERIZATION OF COORDINATION COMPLEXES OF SOME TRANSITION METAL ELEMENTS WITH ELECTRON RICH LIGANDS.

3)Location :

(i) Synthesis and Characterization of the metal complexes were carried out in Jamia Millia Islamia University, New Delhi-110025, INDIA

(ii) The antimicrobial activity of newly synthesized coordination complexes were also screened in Jamia Millia Islamia University, New Delhi.

4) Introduction :

The existence of coordination compounds were proved in the nineteenth century. The modern study of coordination compounds began with Alfred Warner[1], the first inorganic Chemist who was awarded the Nobel Prize in 1913.

Transition metal elements have strong tendency to form coordination complexes. During formation of coordination compounds, the properties of both metal and ligand are altered. Since transition metals have usual tendency to expand their coordination number, hence it is interesting field of Chemistry to synthesize transition metal complexes

5) Importance of proposed Research Work :

The newly synthesized complexes have interesting bonding and antimicrobial activity against certain bacteria like Salmonella typhi and Klebsiella pneumonie and fungi.

6) Review of work already done on the subject :

A number of Review of Literature is made in Chapter-1 of the thesis.

7) Hypothesis/ Objective :

a) To synthesize some of the transition metal complexes.

b) To characterize the synthesized transition metal complexes.

c) To study the antimicrobial activity of the synthesized transition metal complexes.

8) Methodology :

Coordination complexes of some transition metal elements with electron rich ligands were synthesized. The synthesized complexes were characterized by elemental analysis, molar conductance, FTIR, UV-visible spectral methods. The complexes were screened for antimicrobial activity against bacteria Salmonella typhi and Klebsiella pneumonie and fungi.

9) Chapter-wise details of Proposed Research :

Chapter-1 of the thesis reports the Introduction and Review of Literature already done on the subject.

Chapter-2 discusses the synthesis, characterization and antimicrobial activity of some Schiff base metal complexes. Schiff base are named after Hugo Schiff, describe the condensation between an aldehyde and an amine[2]. Schiff bases are versatile ligands that are an important class of ligands that coordinate with metal ions via azomethine (-CH=N-) nitrogen and have been studied extensively[3].

Diethanolamine and acetylacetone complexes with Co(II) and Fe(III) have been discussed in Chapter-3. Ethanolamines commonly known as aminoalcohols were prepared in 1860 by Wurtz from ethylene chlorohydrins and aquous ammonia. Ethanolamines are a class of organic molecules containing amino and alcohol group[4]. Acetylacetone co-exist in keto form and enol form in solution. The metal acetylacetonate complexes can be used as phase precursor in alkoxo synthesis of esters and finds considerable attention[5].

In Chapter-4, the synthesis of Cu(II) and Ni(II) complexes derived from diethanolamine and nitro ligands have been discussed.

Finally, Chapter-5 discusses the synthesis and characterization of Zn(II) complex derived from diethanolamine and thiocyanate ligands.

10) Bibliography (Updated):

1) J. A. Huheey et. al., *Inorganic Chemistry,* **2011**, Chapter-14.

2) S. Kalaivani et. al., *International Journal of Applied Biology and Pharmaceutical Technology,* **2012**, 3, 1, 219-223.

3) A. Prakash et. al., *International Journal of Chem. Tech. Research,* **2011**, 3, 4, 1891-1896.

4) T. Esker et. al., *Ethanolamines, CHE Report,* **1999.**

5) Y. Abe et. al., *J. Non- Cryst. Sol.* **1990,** 21, 121.

Arshad Hussain Khan
20/11/2014
Signature of the Candidate with date

A. Bashar
20/11/14
Signature of Supervisor with date & Seal

Associate Professor,
Deptt. of Chemistry,
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Kamrup,Assam,(INDIA)

PUBLICATION

1. "Synthesis, Characterization and Antimicrobial Activity of Schiff Base Metal Complexes," **Arshad Hussain Khan**, Abdul Bashar, Urvashi Singh, Mohammad Maqbool Dar and Athar Adil Hashmi, "*Journal of Applicable Chemistry*," 2014, vol. 3, No. 4, page 1538- 1542.

2. "Synthesis, Characterization and Antimicrobial Activity of Transition Metal Complexes with Diethanolamine and Acetylacetone" **Arshad Hussain Khan**, Abdul Bashar, Urvashi Singh, Mohammad Maqbool Dar and Athar Adil Hashmi, "*Journal of Applicable Chemistry*," 2014, vol 3, No. 5, page 1907- 1912.

3. "Synthesis, Characterization and Antimicrobial Activity of Metal Complexes with Diethanolamine and Nitro Ligands." **Arshad Hussain Khan**, Abdul Bashar, Urvashi Singh, Mohammad Maqbool Dar and Athar Adil Hashmi, "*European Academic Research*", **2014**, vol. II, issue 8, page 10714-10724.

4. "Synthesis, Characterization and Antimicrobial Activity of Metal Complex with Diethanolamine and Thiocyanate Ligands."

"*International Journal of Advanced Scientific and Technical Research. (IJAST)*," (Accepted)

CONTENTS

CHAPTER 3

Synthesis, Characterization and Antimicrobial Activity of Transition Metal Complexes with Diethanolamine and Acetylacetone.

CHAPTER 4

Synthesis, Characterization and Antimicrobial Activity of Metal Complexes with Diethanolamine and Nitro Ligands.

CHAPTER 5

Synthesis, Characterization and Antimicrobial Activity of Metal Complex with Diethanolamine and Thiocyanate Ligands.

CHAPTER 1

CHAPTER-1

GENERAL INTRODUCTION:

Coordination compounds were identified in the nineteenth century. The modern study of coordination compounds began with Alfred Warner[1], the first inorganic Chemist to be awarded the Nobel Prize in Chemistry in 1913.

The elements arising from the filling of the 3d, 4d and 5d subshells and located in the periodic table following the alkaline earth metals, are commonly referred to as transition elements or d-block elements. They are also called transition metals and make up 56 of the 103 elements. These transition metals are classified into d-block metals, which consist of 3d elements from Sc to Cu, 4d elements from Y to Ag and 5d elements from Hf to Au and f- block metals which consist of lanthanoid elements from La to Lu and actinoid elements from Ac to Lr.

However, a transition element is defined as one that has an incomplete d-orbital in either the neutral atom or its ions. Thus the Group 12 elements (Zn, Cd and Hg) are members of the d- block but they are not transition elements.

Transition metals differ from main group metals in several key properties. One of the more interesting aspects of transition metals is their ability to form coordination compounds. Coordination compounds are formed between a metal ion and a molecule with one or more unshared electron pairs, called the ligands. Anions as well as neutral molecules may act as ligands.

Some methods of verifying the presence of complex ions include studying the chemical behavior of the complex. This can be achived by observing the colour of the compound, solubility, absorption spectrum, magnetic properties etc. The properties of the complex compounds are separate from the properties of the individual atoms. By forming coordination compounds, the properties of both metal and ligand are altered.

The metal atom acts as an electron pair acceptor (Lewis acid) while the ligands act as electron pair donor (Lewis base). The nature of the bond between metal and ligand is stronger than intermolecular forces because they form directional bonds between the metal ion and ligands, but are weaker than covalent and ionic bonds.

The transition metal elements have strong tendency to form coordination complexes. In transition metal elements, d and f-orbitals are far inside to be influenced by the ligands. Therefore in some cases, it is difficult for them to be involved in co-ordination. However, a large number of coordination compounds have been synthesized, characterized and their bio-chemical activities have been studied widely.

Transition metals have inherent tendency to expand their coordination number around them by using d- or f- orbitals. Therefore, it is a very interesting field of Chemistry to synthesize complexes of transition metals with various electron rich ligands. In many cases, water molecule is coordinated with these metals and hence strong coordinating ligands are necessary for the synthesis of new coordination complexes.

Organic ligands containing significantly different donor functionalities (-N, -P, -O, -S ,) find increasing Interest in coordination Chemistry.

The research being conducted in the design of new metal-ligand combination is vast and varied.

REVIEW OF LITERATURE :

Yakubreddy Naini, Tarab J. Ahmed, Gilles K. Kouassi, S. Ananda, and Netkal M. Made Gowda[2] in one of their paper reported the synthesis of chlorpromazine complexes of transition metal ions Zn(II), Cd(II) and Hg(II). They determined the molecular formula of the newly synthesized complexes to be $[ZnBr(C_{17}H_{19}ClN_2S.HCl)_2]Br$, $[CdBr(C_{17}H_{19}ClN_2S.HCl)_2]Br.H_2O$, $[Cd(C_{17}H_{19}ClN_2S.HCl)_2]I_2$ and $[HgBr(C_{17}H_{19}ClN_2S.HBr)_2]Br.2H_2O$ where the ligand chlorpromazine = $C_{17}H_{19}ClN_2S$ having the following structure

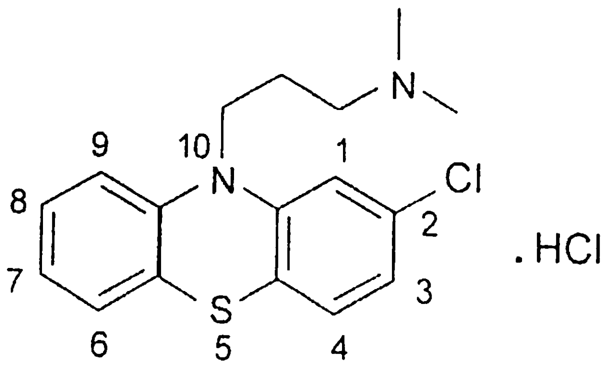


Fig. 1 : Molecular structure of chlorpromazine hydrochloride

They measured the molar conductances for the complexes in DMF and acetonitrile solutions and concluded that all the complexes to behave as 1:1 electrolyte except CdI_2 complex which had 1:2 ionic ratio.They found that the N-alkyl amino phenothiazine derivatives including chlorpromazine were biologically active heterocyclic compounds.

They characterized the complexes by elemental analysis, molar conductivity, magnetic susceptibility, IR, UV-visible and ^{1}H NMR spectral methods. They also proposed square pyramidal environment around each metal centre with an sp^{3}d hybridization for five coordinated complexes while for four coordinated complex a tetrahedral environment had been suggested.

Aref A.M. Aly, Mohmoud A. Ghanddour, Majed S. Al-Fakeh[3] synthesized a series of coordination complexes of transition metal ions Co(II), Ni(II) and Cu(II) with 1,4 benzenedicarboxylate (BDC) of azoles such as 2-amino-benzothiazole (ABZ), 2-amino thiazole (AZ) and 2-amino 4-methyl thiazole (AMTZ). They proposed the following structure of the ligands.

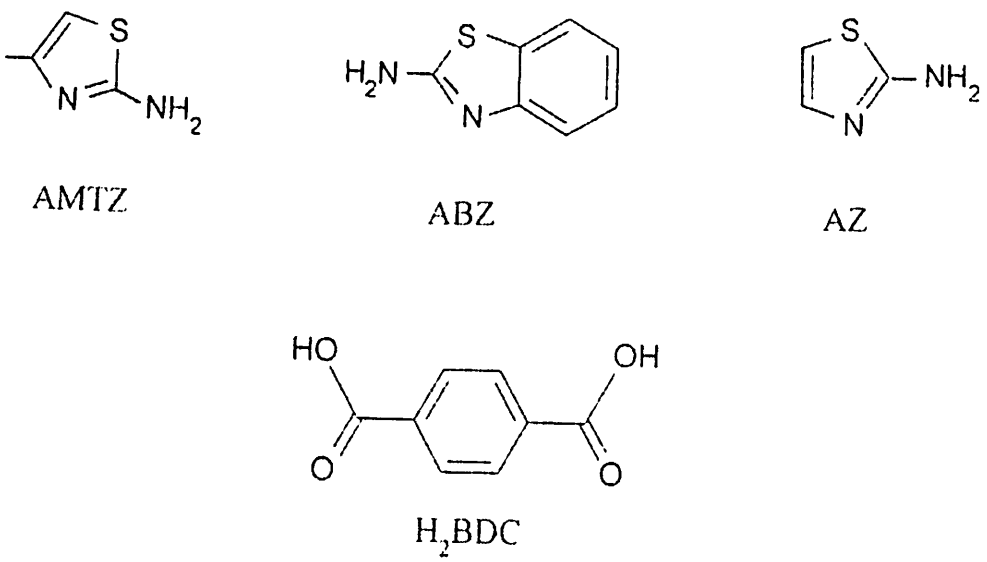


Fig. 2 : Structure of the ligands

They studied the 1,4-benzenedicarboxylic acid and its metal complexes because of their chemical and biological activities. They characterized the complexes by elemental analysis, molar conductance, thermal analysis, X-ray diffraction, scanning electron microscopy, magnetic measurements, IR and electronic spectral studies. They calculated the kinetic parameters using Coats-Redfern and Horowitz-Metzger equations.

Reghad Haddad, Emad Yousuf and Ahmed Ahmed[4] prepared a series of co-ordination compounds of Ni(II), Cu(II), Zn(II), Cd(II) and Sn(II) metals with 4-amino 5(pyridyl) 4H-1,2 triazole-3 thiol ligands in alcoholic medium. They reported the triazoles as bidentate ligands which coordinate to the metal ions through sulphur and amine group. They characterized the complexes by micro elemental analysis, magnetic susceptibility, conductivity measurements, FTIR, UV-visible and ^1H and ^{13}C NMR spectroscopic studies. From the spectral data they suggested tetrahedral geometry for the newly synthesized complexes except Cu(II) complex which exhibited a square structure.

Mahendra Yadav [5] synthesised Mn(II), Fe(II), Ni(II) and Cu(II) complexes of N-benzyl N$'$ 2- thiophenethiocarbohydrazide (H_2 BTTH) ligands. He characterized the complexes by elemental analysis, magnetic susceptibility measurements, IR, NMR spectral studies. He determined the composition of the complexes as $[Mn(H\ BTTH)_2]$, $[Ni(BTTH)(H_2O)]$, $[Cu(BTTH)]$ and $[Fe(H\ BTTH)_2\ EtOH]$. He reported that the substituted thiosemicarbazides, thiosemicarbazones and dithiocarbazates to have remarkable antineoplastic activity against a variety of tumors in addition to their antibacterial and antifungal activities of the complexes against several bacteria like Staphylococcus aureus, Escherichia coli and Pseudomonas aeruginosa and fungi Candida albicans.

Prem Mohan Mishra, Manoj Kumar Jha, Ram Subhag Choudhury and Chandan Kumar[6] reported the synthesis of complexes of divalent transition metals Co(II), Ni(II) and Cu(II) with ligands 2-hydroxy 4-nitro acetophenone thiosemicarbazone. They prepared the ligands by dissolving 2- hydroxyl 4- nitro acetophenone in methanol treated with semicarbazide hydrochloride solution in water. They synthesized the complexes by treating metal chlorides with the ligand. They characterized the complexes on the basis of elemental analysis, magnetic studies, electrical conductances, IR and electronic spectral methods. They reported that the thiosemicarbazones to posses considerable medicinal applications such as anti T. B.

and Leprosy antiviral, antitumor, anticancer and biological properties. They proposed octahedral geometry for Co(II) and Ni(II) complexes while square planner geometry for Cu(II) complex with the following structure.

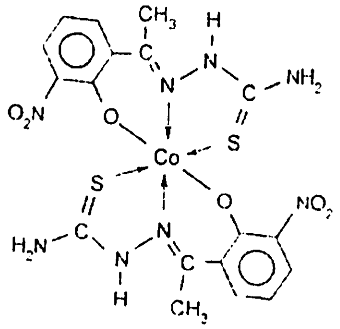


Fig. 3 : Bis - (2 - hydroxy - 4-nitro acetophenone thio semicarbazone) Co (II)

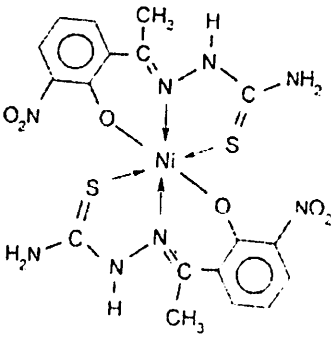


Fig. 4 : Bis - (2 - hydroxy - 4-nitro acetophenone thio semicarbazone) Ni (II)

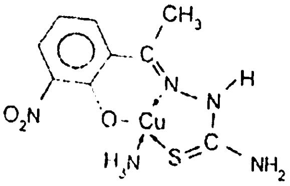


Fig. 5 Mono amine-2-hydroxy-4-nitro acetophenone thio semicarbazone Cu (II)

R. K. Mohapatra, M. Dash. S.B.Patjoshi and D. C. Dash[7] synthesized a series of coordination complexes of Cu(II), Co(II), Ni(II) and Zn(II) with benzothiazolyl -2-hydrazones of salicylidene acetone and salicylidene acetophenone such as 2(salicylidene acetone 2′ imino) amino benzothiazole (HSAB) and 2(salicylidene acetophenone-2′-imino) amino benzothiazole (HSPB). They prepared the ligands by condensing respective aldehydes and ketones such as salicylidene acetone and salicylidene acetophenone with 2- hydrazinobenzo- thiazole.

These complexes were characterized on the basis of elemental analysis. molar conductivity, thermal analysis, magnetic moment, IR and electronic spectral studies. They proposed tridentate chelation of ligands with azomethine nitrogen. ring sulphur and oxygen atom.

Dharmpal Singh, Krishan Kumar, Ramesh Kumar and Jitender Singh[8] reported the template synthesis of complexes of transition metals Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with tetradentate macro- cyclic ligands of the type $[M(C_{28}H_{24}N_4)X_2]$ where M=divalent metal ion, $X=Cl^-$, NO_3^-, CH_3COO^- and $C_{28}H_{24}N_4$ = tetradentate macrocyclic ligand. They synthesized the complexes by template condensation of 1,8-diamino naphthalene and diacetyl in presence of divalent metal salts in methanolic medium. They characterized the complexes by elemental analysis, conductance and magnetic measurements, IR, UV-visible, NMR and MS spectroscopy. They also reported that the complexes were non-electrolytes due to their low value of molar conductance. Based on the spectral data, they proposed a distorted octahedral geometry for all the newly synthesized complexes. Some synthetic macrocyclic complexes such as Cu- complex had been investigated for accelerating the photodegradation of hazardeous pollutants. They tested all the macrocyclic complexes for their antibacterial activities against some pathogenic bacterial strain like Bacillus cereus, Salmonella typhi, Escherichia coli and Staphylococcus aureus.

Zhen Su, Liyuan Zhang, Liyuan Chai, Haiying Wang, Wanting Yu, Ting Wang and Jianxiong Yang[9] synthesized high yield of poly (m-phenylenediamine) hollow nanostructures by oxidation of assisted diethanolamine with a high specific surface area. The diethanolamine concentration has a significant influence on poly m-phenylenediamine morphology. They found that the nanostructures showed an excellent Ag^+ adsorption ability.

Weiqing Song, Qinghuan Song and Chengxun Wu[10] synthesized novel hyperbranched polyamides from diethanolamine and maleic anhydride with ethylene glycol as core monomer. They found no gelation in the melt polymerization when diethanolamine and maleic anhydride were used in equimolar quantity and the products obtained were soluble in water and organic solvents. It was suggested that the hyperbranched polyesteramides were formed via a mechanism of a combination of esterification and addition reactions. The addition of a hydroxyl group to the –C=C- in maleic anhydride unit resulted in the formation of CH methane group. They also examined the rheological properties of the polymers in aquous solutions. They characterized the polymers by IR and NMR spectroscopies as well as GPC.

D. K. Singh and Vijay Kumar[11] synthesized Zirconium(IV) diethanolamine complex as new chelating ion exchanger. Zirconium (IV) diethanolamine samples were prepared by mixing Zirconium oxychloride and diethanolamine.These were characterized by usual methods and studied the sorption of eight heavy metal ions at different P^H (1-6). They found that the sorption capacity of Zirconium (IV) diethanolamine sample ($ZDEA_5$) for Cu^{+2} and Hg^{+2} to be 1.2 and 0.7 m mol/g respectively. They studied the effect of P^H on sorption and revealed that the capacity of sorption generally decreases with decrease in P^H.

Zafar A. Siddiqi et.al.[12] prepared homo-dinuclear complexes $[M(dea)_2(H_2O)_4]$ of diethanolamine with Cobalt, Nickel, Copper and Iron metal ions. Different spectral methods were applied to characterize the complexes.

P. Balaramesh, A. A. Jabbar and P. Venkatesh[13] studied the structure and properties of Platinum(II) complexes of ethylenediamine and diethanolamine dithiocarbamates. They found that the dithiocarbamate complexes to be very stable and highly soluble in water due to the presence of hydrophilic moiety in their structure. They reported that these dithiocarbamates chelated with almost all metal ions in the Periodic Table and found numerous applications on biological, agricultural, electronics, stabilizing agents and had been used as metal complexing agents for several decades. The complexes were characterized by elemental analysis, IR and electronic spectral analysis.

Mahmoud Najim Al. Jibouri [14] synthesized a series of metal complexes of Cr(III), Fe(III), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) ions with 4-[Z-(4-hydroxy 6-methyl-2-oxo -2H-pyran-3-yl]-1-methyl-2-phenyl 1.2-dihydro 3H-pyrazol-3-one (HL). He prepared the ligand by azo coupling of diazotized 4-amino antipyrene with 4-hydroxy 6-methyl 2-pyranone. He characterized the free ligands and its metal complexes on the basis of elemental analysis, FTIR, UV-visible and ^{1}H NMR spectroscopy. From ^{1}H NMR and FTIR spectroscopy, he suggested that the keto- enol tautomer azo ligand was a mixture of E and Z isomers. He studied the chelating properties of the new azo ligands towards the metal ions. He revealed from spectral data that the nitrogen and oxygen atoms atoms of –N=N-, C=O and -OH groups participated in bonding with metal ions. From the study of NMR, IR and UV-visible spectra, he elucidated an octahedral structure for all the metal complexes except Zn(II) complex which has the tetrahedral structure. He also proposed the following structures for the complexes.

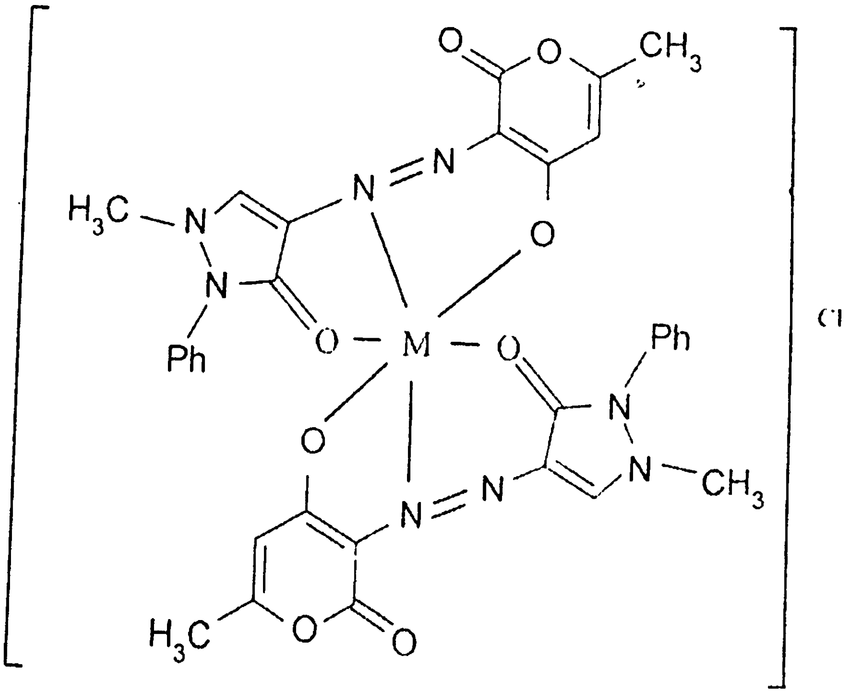


Fig. 6 : Proposed octahedral structure of Cr(III) and Fe(III) complexes of 4-[Z-(4-heydroxy-6-methyl-2-oxo-2H-pyran-3yl]-1-methyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one (HL) ligand, (if M = Mn, Co, Ni, or Cu(II),there is no Cl in the outer sphere ..

Sabita Shrestha and Sudha Maharjan[15] synthesized copper complex of salicyldehyde benzyl hydrazone. They studied the complex by different analytical procedures, IR and electronic spectral studies.

Omar Hamad Shaheb Al. Obaidi and Abdalhady R. H. Al. Hiti[16] synthesized macrocyclic complexes of Cu(II), Ni(II) and Co(II) by template reaction of urea or thiourea with malonic acid and metal(II) chloride. They characterized the complexes by conductivity measurements, melting points, FTIR, UV-visible spectral methods. They tested the complexes for their antibacterial activities against Staphylococcus aureus and Escherichia coli.

T. Peter Amaladhas and S. Sheeba Thavamoni[17] synthesized metal complexes of Copper, Nickel and Vanadium with ascorbic acid ligand encapsulated in the super cages of fly ash based Zeolite. They characterized the complexes by usual analytical techniques, FTIR, Atomic Absorption spectroscopy, UV-visible spectroscopy. They established the catalytic activity of these complexes towards the liquid phase hydroxylation of phenol with hydrogen peroxide.

Kalpana, Randhir Singh, Baljinder Singh and Avneesh Kumar[18] synthesized Tetraaza macrocyclic complexes of transition metals Ni(II), Cu(II), Fe(III) and Mn(II) using template synthesis. They performed the structural identification of these complexes using analytical techniques, IR, UV-visible spectroscopy. They also screened the complexes for anti- bacterial activities against Gram positive bacteria Bacillus subtilis and Staphylococcus aureus.

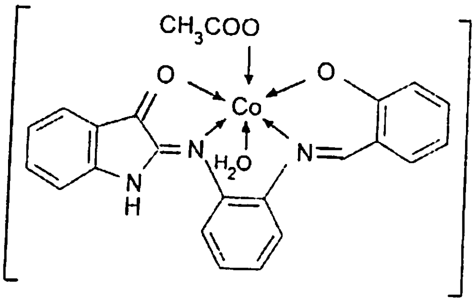
Khurram Shoaib, Wajed Rahman, Bakhtiar Mohammad and Saqib Ali [19] synthesized Copper, Nickel, Cobalt, Zinc and Manganese metal complexes of Nitrogen, Oxygen donor ligands. They characterized the ligands and the metal complexes on the basis of physical properties, elemental analysis, magnetic susceptibility, FTIR, UV-visible and ^{1}H and ^{13}C NMR spectral methods. They also made a study about the antibacterial property of these complexes.

Ahmed Majeed, Emad Yousif and Yang Farina[20] synthesized Fe(III), Rh(III), Pd(II), Pt(IV) and Au(III) complexes with thioacetic acid benzothiazole ligands. They characterized the complexes by elemental analysis, magnetic susceptibility, conductivity measurements, FTIR, UV-visible, ^{1}H NMR, ^{13}C NMR spectral methods.

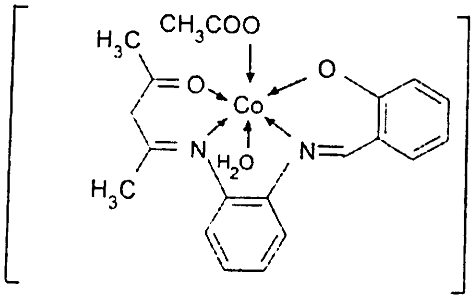
Ni(II), Cu(II), Co(II), Fe(II), Mn(II) and Zn(II) metal complexes with N,N′-bis [2-hydroxy acetophenone] ethylenediamine and bis[4-methoxy benzylidene] ethylenediamine ligands were synthesized by Y.J. Thakor, S. G. Patel and K. N. Patel[21]. They characterized the complexes by elemental analysis, magnetic measurements, thermo-gravimetric analysis, IR, and UV-visible spectral methods. They also tested the biocidal activity of the complexes.

Alka Choudhury et. al.[22] synthesized Fe(III), Co(II) and Cu(II) metal complexes with camphor derivatives. They characterized the complexes by elemental analysis, molar conductance measurements, thermogravimetric analysis, IR, electronic and mass spectroscopic studies. They also observed the anti-oxidant activity of the complexes.

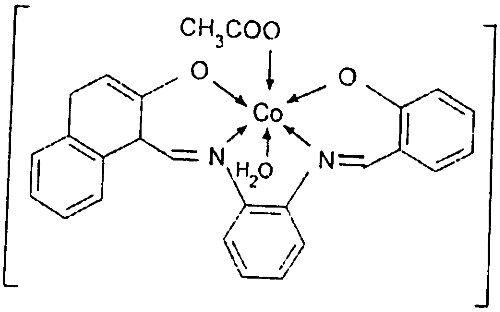
A.Nagajothi , A.Kiruthika, S.Chitra and K. Parameswari[23] in one of their paper reported the synthesis of tetradentate N_2O_2 type complexes of Co(II) by the condensation of o-phenylenediamine, salicyldehyde and isatin 2-hydroxy naphthaldehyde/ acetylacetone. They prepared Schiff base ligands L_1/ L_2/L_3 by mixing an alcoholic solution of o-phenylene- diamine with isatin/ acetylacetone/ 2-hydroxyl naphthaldehyde and salicyldehyde. The metal complexes were synthesized by adding the prepared Schiff base ligands L_1/ L_2/ L_3 to an ethanolic solution of metal acetate (Cobalt acetate). They characterized the complexes by elemental analysis, molar conductance, magnetic susceptibility, IR, UV- visible spectral data and thermal analysis. From the spectral datas, they proposed an octahedral geometry for all the complexes with probable structures as follows.



$[Co(L_1)(H_2O)(OAc)]$



$[Co(L_2)(H_2O)(OAc)]$



$[Co(L_3)(H_2O)(OAc)]$

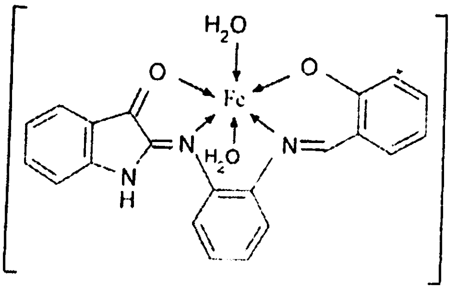
Fig. 7 : Structure of the complexes

They found low value of molar conductance for the complexes indicating the complexes were non-electrolytic in nature. The metal complexes had been tested for their antibacterial activity on Gram positive bacteria Staphylococcus aureus and Gram negative bacteria Escherchia coli and fungal stain Candida albicans. They investigated the interaction of double stranded DNA and DNA binding agents and monitored the DNA cleavage activities of Schiff base and their metal complexes by agarose gel electrophoresis method in presence of H_2O_2.

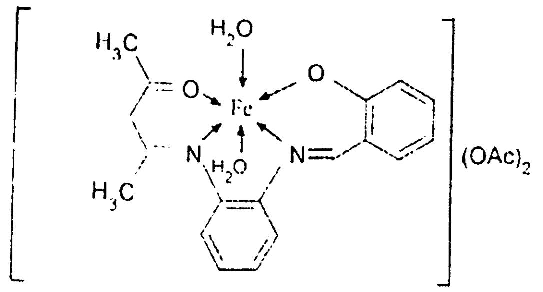
Sandeep Kumar and Nitin Kumar[24] synthesized eleven complexes of Cu(II), Cd(II), Co(II), Zn(II) and Hg(II) with acetyl acetone thiosemicarbazone and Cl, NO_3, CH_3COO, SO_4 ligands. They characterized the complexes by molar conductance, magnetic susceptibility measurements, IR, UV- visible spectroscopy. They had screened all the complexes for their antibacterial activity against Gram positive bacteria Staphylococcus aureus, Staphylococcus epidermis and Gram negative bacteria Escherichia coli and Pseudomous aeruginosa and found that some complexes exhibited appreciable activity.

Akram A. Mohammed[25] synthesized few new co-ordination compounds of Cobalt(II), Nickel(II) and Copper(II) with some Schiff bases derived from acetyl acetone and p-amino phenol or p-amino benzoic acid. He characterized all the complexes by molar conductance, magnetic susceptibility, IR, UV- visible spectral methods. From the spectral data and magnetic properties he suggested square planar geometry for all the complexes.

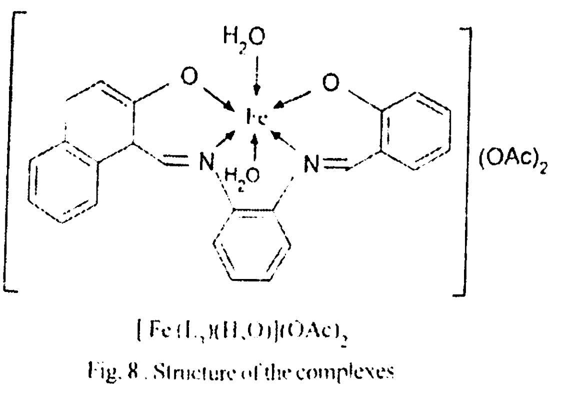
A.Nagajothi, A. Kiruthika, S. Chitra and K. Parameswari[26] in one of their paper reported the synthesis of Fe(III) complexes with Schiff base ligands obtained by the condensation of o-phenylenediamine, salicyldehyde and isatin / 2-hydroxy naphthyldehyde/acetylacetone. They prepared Schiff base ligands L_1/ L_2/ L_3 by mixing an alcoholic solution of o- phenylenediamine with isatin/ acetylacetone/ 2-hydroxyl naphthaldehyde and salicyldehyde. The metal complexes were synthesized by adding the Schiff base ligand L_1/ L_2/ L_3 to an ethanolic solution of metal acetate (Ferric acetate). They proposed the following structures for the complexes.



$[Fe(L_1)(H_2O)](OAc)_2$



$[Fe(L_2)(H_2O)](OAc)_2$



$[Fe(L_3)(H_2O)](OAc)_2$

Fig. 8 . Structure of the complexes

They characterized the complexes by elemental analysis, molar conductance, magnetic susceptibility, IR, UV-visible spectral data and thermal analysis. On the basis of molar conductances, they concluded that the complexes were electrolytic in nature. From the spectral data they proposed octahedral geometry for the complexes. The metal complexes had been screened for antibacterial activity against two pathogenic bacteria one Gram positive Staphylococcus aureus and one Gram negative Escherichia coli and fungal strain Candida albicans.

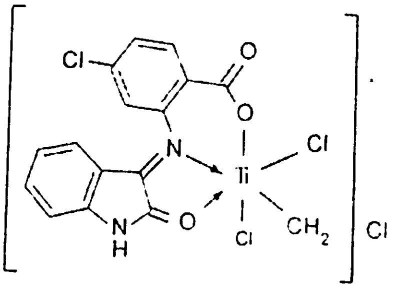
Eid A. Abdalrazaq, Omar M. Al-Ramadane and Khansa S. Al-Numa[27] synthesized Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes with acetylacetonimine and acetylacetanilidimine Schiff base ligands. They prepared new tetradentate dianion Schiff base ligands by the condensation of hydrazine with acetylacetone or acetylacetanilide. They characterized the ligands and their dinuclear metal complexes by CHN elemental analysis, molar conductivity, magnetic susceptibility, FT-IR, UV-visible spectral methods.

Zakiyeeh Khoshkhan and Mehdi Salehi[28] synthesized sub- micron alumina powders by the condensation of aluminium complexes of acetylacetone and salicyldehyde. They characterized the complexes by FTIR and FESEM techniques. From FESEM images they concluded that the synthesized materials had porous structures.

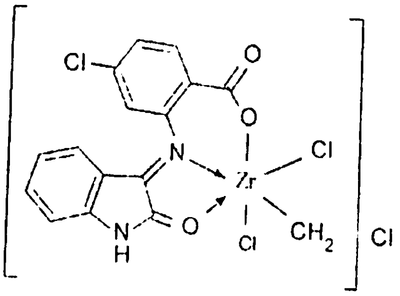
Anis Chandra Pandey, Richa Kothari and Brajraj Sharma[29] synthesized metal complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with a Schiff base derived from 2- pyridyl carboxyldehyde and o-phenylenediamine. They characterized the complexes by chemical analysis, conductometric and magnetic data and spectroscopic methods. They studied the antibacterial activities of the ligands and complexes against Gram positive bacteria Staphylococcus aureus and Bacillus subtilis and Gram negative bacteria Salmonella typhi and Escherichia coli.

R. K. Mohapatra, U. K. Mishra, S. K. Mishra, A. Mohapatra and D. C. Dash[30] synthesized a series of co-ordination complexes of transition metal ions Cu(II), Co(II), Ni(II) and Zn(II) with some hydrazone derivatives containing benzidazole moiety such as 2-(o-anisylidene 2-imino) amino benzimidazole and 2-(furfurylidene imino) amino ligands. They found that the complexes were highly coloured and insoluble in water and common organic solvents, but soluble in highly co-ordinated solvents like dioxane, DMSO and DMF. They characterized the complexes on the basis of elemental analysis, molar conductivity, magnetic moments, IR, electronic and NMR spectral studies. They screened all these Schiff bases and their metal complexes for their antibacterial activities against Bacillus subtilis, Bacillus stearothermophilus, Escherichia coli and Salmonela typhi and antifungal activities against Aspergillus niger and Aspergillus flavus.

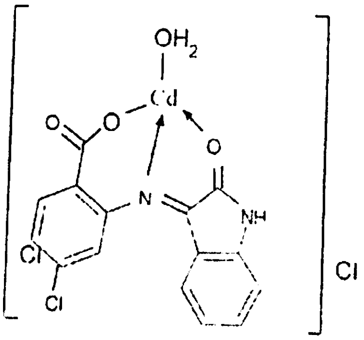
Suraj B. Ade, M. N. Deshpande and J. H. Deshmukh[31] synthesized a new Schiff base ligand (ACBAI) by refluxing 2-amino 4-chloro benzoic acid and Isatin (1H- indol 2,3- dione) in ethanol. They prepared the coordination complexes from chlorides of transition metal ions Ti(IV), Zr(IV) and Cd(II) with the newly synthesized Schiff base ligands. They reported that Isatin, a synthetically versatile substrate, could be used for the synthesis of a large variety of heterocyclic compounds. They characterized the complexes by elemental analysis, molar conductance, magnetic moments, thermogravimetric studies, IR, NMR spectral methods. Following the above results, they suggested that the ligand to act as uninegative tridentate in nature containing tertiary nitrogen, ketonic carbonyl and carboxyl group. On the basis of elemental analysis and spectral studies, they assigned six and four coordinated geometry to the complexes having the following structure.



Dichloro-[4-Chloro-2(2-oxo-1,2-dihydro-indol-3-ylidene amono)-benzoic acid](ACBAI) aquo Ti (IV) Chloride complex



Dichloro-[4-Chloro-2(2-oxo-1,2-dihydro-indol-3-ylidene amono)-benzoic acid](ACBAI) aquo Zr (IV) Chloride complex



Dichloro-[4-Chloro-2(2-oxo-1,2-dihydro-indol-3-ylidene amono)-benzoic acid](ACBAI) aquo Cd (II) Chloride complex

Fig. 9

Gajendra Kumar, Shoma Devi and Rajeev Johari[32] in one their paper reported the synthesis of M (III) Schiff base complexes of the type [HLMX$_2$] where M = Cr (III), Mn (III), Fe (III) and X = Cl, CH$_3$COO. They prepared the Schiff base ligand by condensation of acetylacetone and thiocarbohydrazide in ethanolic medium by the following reaction scheme.

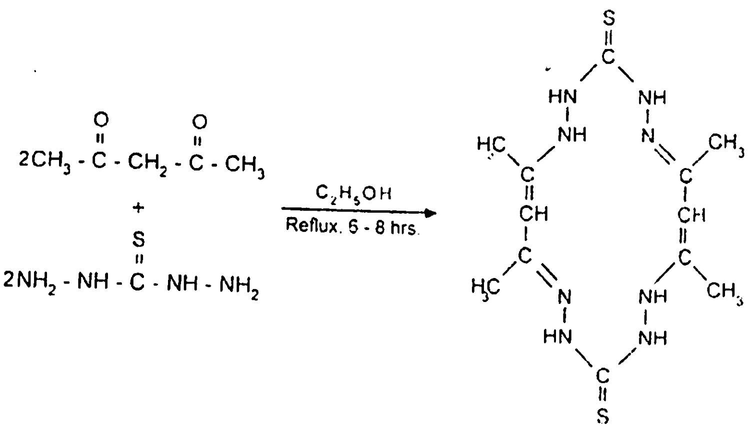
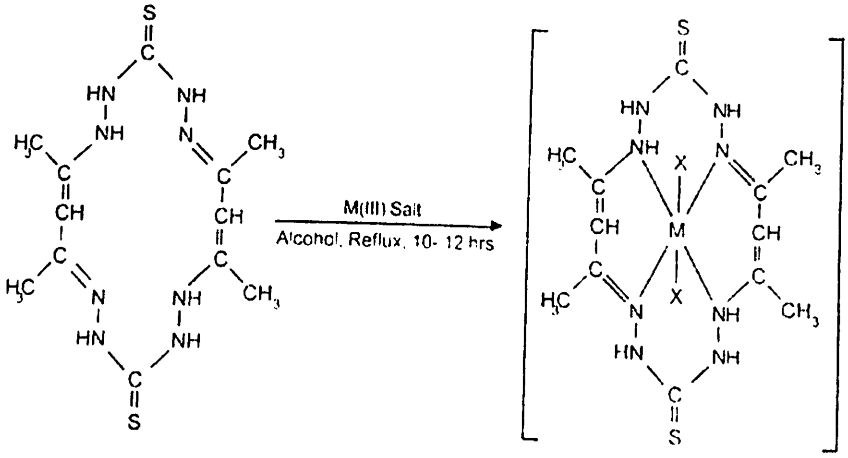


Fig. 10 : Synthesis of Schiff's base macrocyclic ligand



Where M = Cr(III), Mn(III), Fe(III)
$X = Cl^-, CH_3COO^-$

Fig. 11 : Synthesis of novel macrocyclic Schiff's base complexes

They synthesized Cr (III), Mn (III) and Fe (III) macrocyclic complexes by refluxing trivalent metal salt with macrocyclic Schiff base ligand in methanol by the above reaction scheme.

They characterized the complexes with the help of elemental analysis, conductance measurements, magnetic measurements, IR, ^1H NMR, ^{13}C NMR, UV-visible, GCMS spectroscopic techniques. From analytical data they concluded the presence of one metal ion per ligand molecule and suggested a mononuclear structure of the complexes. They proposed an octahedral geometry for the newly synthesized complexes from spectral studies.

Yang Qu, H. L. Zhu, J. L. You and M. Y. Tan[33] synthesized pentan 2,4 dione complexes with Nickel (II) and Cobalt (III) having molecular formula as $[Ni(acac)_2]$ $0.5CH_3OH$ (1) and $[Co(acac)_2\ NO_3]\ 2.H_2O$ (2) respectively where acac = pentan 2,4 dione. They characterized the complexes by single X-ray analysis. They reported that complex (1) crystallized in monoclinic space group with one dimensional chain like structure while complex (2) crystallized in triclinic space group showing a three dimensional network structure.

K. Mazid, R. Mustaq and S. Ahmad[34] reported the synthesis of coordination complexes of Cu (II) ion with aminoalcohols, Ni (II) and Co (II) theophyllinate complexes with monoethanolamine, Co (II), Ni (II), Cu (II) and Zn(II) thiocyanate complexes with diethanolamine and triethanolamine. They made thermal, magnetic and FTIR studies of the complexes for their characterization and structure elucidation. They discussed the coordination behavior of aminoalcohols with transition metals.

Complexation of metal thiocyanate complexes with diethanolamine and triethanolamine :

A.Karadag, V. T. Yilmaz and C. Theone[35] reported the synthesis, spectra and thermal reactivity of novel Co(II), Ni(II), Cu(II) and Zn(II) thiocyanate complexes with diethanolamine (dea) and triethanolamine (tea) with single crystal structure of bis(μ-diethanolaminato) bis(isothiocyanato) dicopper(II) complex $[Cu_2(dea)_2(NCS)_2]$ in the year 2001. They characterized the complexes by various spectroscopic techniques and found that Co(II) and Cu(II) complexes of diethanolamine were dimeric and other complexes of diethanolamine were mononuclear. They concluded that the dimeric structures of these complexes were also evidenced from thermal analysis and single crystal X-ray analysis.

Complexation of Co(II) and Ni(II) theophyllinate complexes with monoethanolamine :

Thermal, magnetic, and FTIR study of Co(II) and Ni(II) theophyllinato complexes of monoethanolamine were studied in 1998 by J. Madarazs[36] and his co-workers. They synthesized two theophyllinato complexes of Co(II) and Ni(II) with formula $[Co(th)_2(ea)_2]$ and $[Ni(th)_2(ea)_2]$ respectively containing monoethanolamine ligands. They got structural information from comprehensive FTIR spectroscopy, powder XRD, magnetic and thermal studies of those mixed ligand complexes.

On the basis of FTIR, XRD and thermal analysis, they concluded that the two bidentate ethanolamine ligands to support octahedral inner coordination sphere. From magnetic study they found that both the complexes were paramagnetic.

Complexation of amino alcohols with cupric ion.

The complexes of monoethanolamine, diethanolamine and triethanolamine with copper have been studied by potentiometric, conductometric and spectrophotometric methods by C. W. Davies and B. N. Patel[37] in 1968. The Cu: ligand ratio in case of monoethanolamine and diethanolamine was found to be 1:1 and 1:2 respectively, but only 1:1 for triethanolamine The cupric salts react with monoethanolamine, diethanolamine and triethanolamine to form non-conducting complex. The hydroxyl group of all the three ethanolamines when co-ordinated to copper show markedly acid properties and form uncharged complex. The uncharged complex formed can not react further in case of mono- ethanolamine, whereas in case of diethanolamine and triethanolamine, they react further to form an anion by losing further hydrogen. The complex formation of Cu(II) with monoethanolamine and diethanolamine in the aquous solution has been studied by means of ESR spectroscopy. using ESR titration method by R. Tauler and E. Casassas[38] in1986.

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CHAPTER 2

CHAPTER 2

SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF SCHIFF BASE METAL COMPLEXES.

INTRODUCTION :

Schiff bases, named after Hugo Schiff, are formed when a primary amine reacts with an aldehyde or a ketone under specific conditions. Structurally a Schiff base (also knownas imine or azomethine) is a nitrogen analogue of an aldehyde or ketone in which the carbonyl group (>C=O) has been replaced by an azomethine or imine group. Schiff bases are some of the most widely used organic compounds. Imine or azomethine groups are present in various natural, natural- derived and non natural compounds. The first preparation of imines was reported in the 19th century by Schiff (1864). Since then a variety of methods for the synthesis of imine have been described. The classical synthesis reported by Schiff involves the condensation of a carbonyl compound with an amine under azotropic distillation. Molecular sieves are then used to completely remove water formed in the system. Chakraborty et. al. proposed the use of substances that function as Lewis acid (or Bronsted- Lowry acid) to activate the carbonyl group of aldehydes, catalyse the nucleophillic attack by amines and dehydrate the system[1].

Schiff bases are versatile ligands that are an important class of ligands that coordinate with metal ions via azomethine (-CH=N-) nitrogen and have been studied extensively. The azomethine linkage is essential for biological activity and several azomethines were reported to possess wide range of biological activities, including antibacterial, antifungal, antimalarial, anti-inflamatory, antiviral, antipyretic, anticancer and diuretic activities[2].

Schiff bases are generally bi, tri or tetradentate ligands capable of forming very stable coordination compounds with transition metal ions. Schiff base reactions are useful in making carbon- nitrogen bonds in organic synthesis. Schiff bases appear to be an important intermediate in various enzymatic reactions[3].

A large number of Schiff bases and their coordination compounds have been extensively studied for their important properties e.g. their ability to bind reversibly with oxygen, catalytic activity in hydrogenation of olefin , transfer of an amino group and complexing ability towards some toxic metals[4].

Schiff base derived from aromatic aldehydes or their metal coordination compounds catalyze reactions like oxygenation, hydrolysis, electroreduction and decomposition[5].

Schiff bases and their transition metal complexes have gained remarkable importance because of their applications in biological, biochemical, analytical, antimicrobial system, antibacterial, antifungal, anticancer activities. The chemotherapeutic Schiff bases attracted the attention of biochemists[6].

Schiff bases have been playing an important part in the development of Co-ordination Chemistry. Schiff base metal complexes have been studied extensively because of their attractive physical and chemical properties and their wide range of applications in numerous scientific areas. They play an important role in both synthetic and structural research because of their preparative accessibility and structural diversity[7].

MATERIALS AND METHODS :

All chemicals used were of analytical grade (AR) reagents and of the highest purity available.They included ferric chloride anhydrous (fisher scientific), cobalt(II) chloride hexahydrate (RANKEM), cupric(II) chloride dihydrate (fisher scientific), ethylenediamine (MERCK), succinic acid (s.d.finechem Ltd.) and formaldehyde (MERCK).

Elemental analyses were performed using an elemental analyser. The conductance of the complexes were measured on a conductometer at 25^0 C. The IR spectra were recorded in a spectrometer (4000-400 cm^{-1}).

The UV –VIS electronic spectra (200-800 nm) were recorded using double beam spectrophotometer. The geometries of the metal complexes were evaluated using the molecular calculation.

Template synthesis of Schiff base metal complexes :

An ethanolic solution of MX_n (0.00105 moles, $CoCl_2 . 6H_2O$ = 0.25g, $FeCl_3$ = 0.17g, $CuCl_2 . 2H_2O$ = 0.179g) M = Co(II), Fe(III) and Cu(II) is added slowly to an ethanolic solution of ethylenediamine (2 × 0.00105 moles = 0.15ml) with constant stirring. The mixture is refluxed for one hour at 80^0 C. Then an ethanolic solution of succinic acid (0.00105 moles = 0.124g) is added dropwise and the mixture is refluxed for about 6 hours at 80^0 C. Finally, an ethanolic solution of formaldehyde (2 × 0.00105 moles = 0.15ml) is added dropwise and the reaction mixture is refluxed for about 3 hours at 80^0 C. The mixture is then filtered, washed with ethanol and dried the residue.

schem-1

The synthetic route of the Schiff base metal complexes

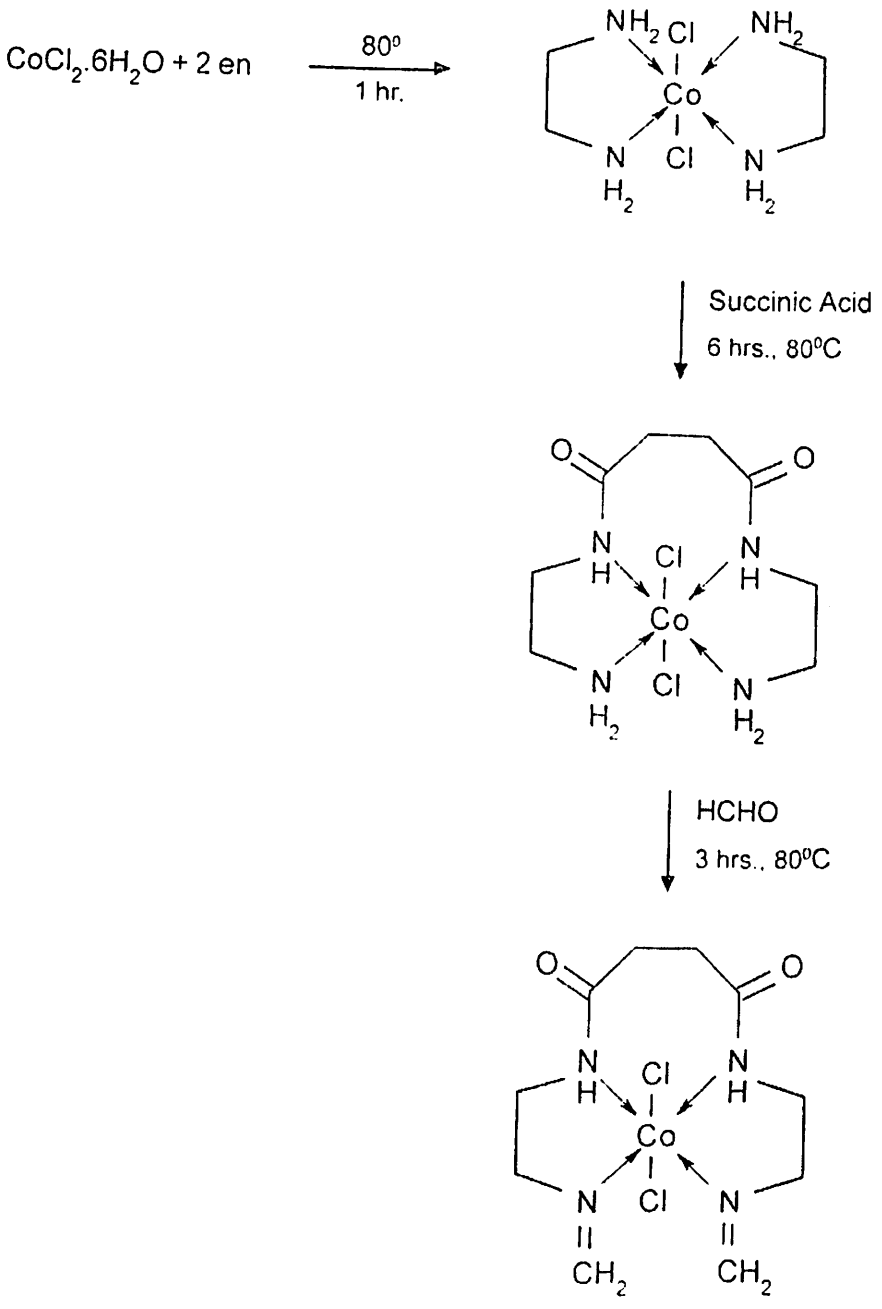


Fig. : Synthetic reaction of Co-complex

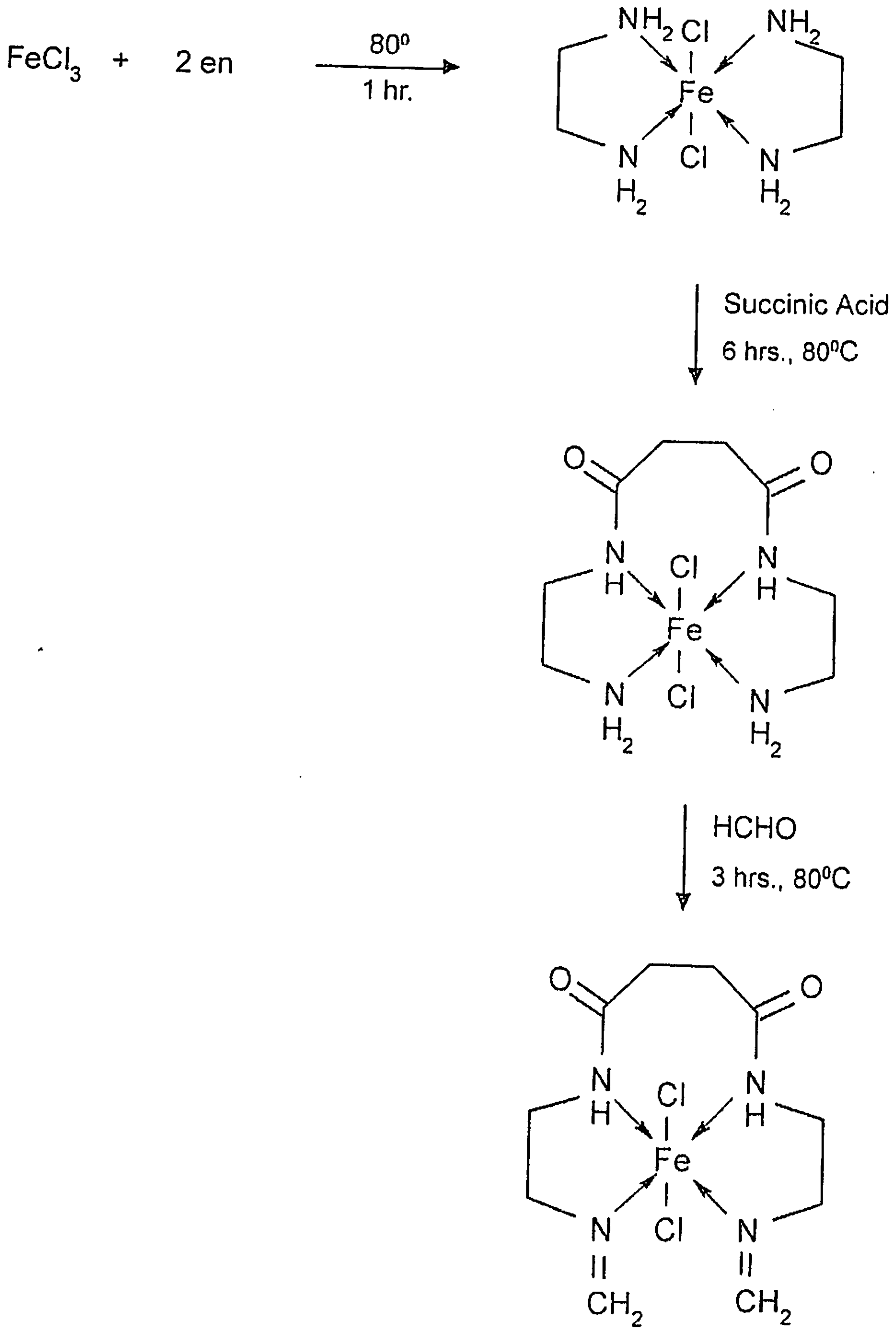


Fig. : Synthetic reaction of Fe-complex

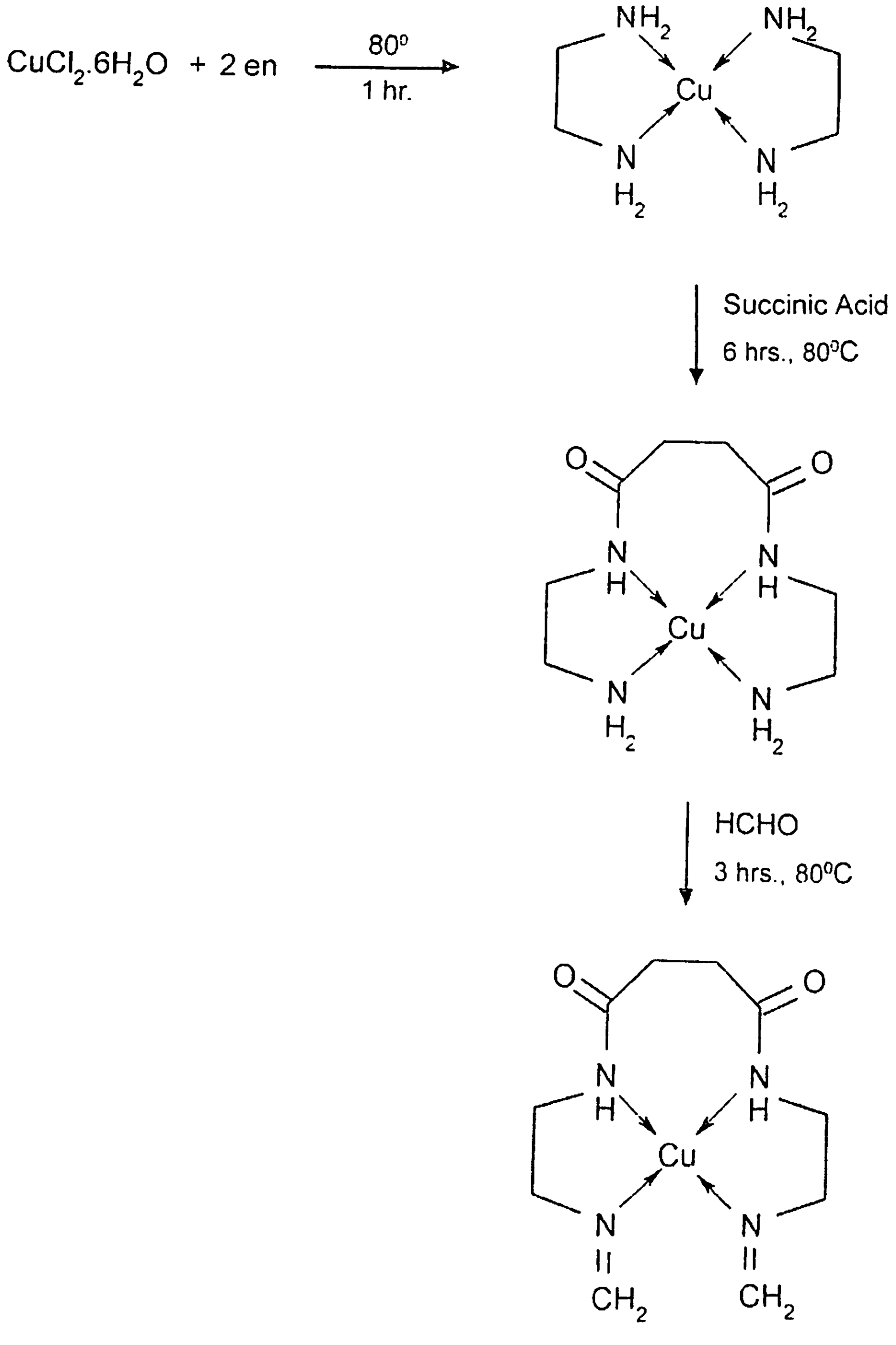


Fig. : Synthetic reaction of Cu-complex

The IUPAC name of the Schiff base ligand is

N^1, N^4 – bis (2-(methylene amino) ethyl) succinamide.

RESULTS AND DISCUSSION :

Physical properties:

The pink coloured Cobalt complex is amorphous solid compound with molecular weight 356.0 g/mol. as confirmed by elemental analysis and molecular weight determination. The complex has a melting point of 292^0 C. The solubility of the complex is tested in different solvents and it is found that the complex is soluble in water and DMSO, partially soluble in methanol but insoluble in ethanol, acetone, hexane, dichloromethane, benzene, chlorlobenzene, ethyl acetate and chloroform.

The Iron complex is yellow coloured amorphous solid compound with molecular weight 353.0g/mol. as confirmed by elemental analysis and molecular weight determination. The complex has a melting point of 282 deg. Celcius. The solubility of complex is tested in different solvents and it is found that the complex is soluble in acetic acid and DMSO but insoluble in water, methanol, ethanol, acetone, hexane, dichloromethane, benzene, chlorobenzene, ethylacetate, carbontetrachloride and chloroform.

The blue coloured Copper complex is amorphous solid compound with molecular weight 289.5 g/mol. as confirmed by elemental analysis and molecular weight determination. The complex has a melting point of 172^0 C. The complex is soluble in water, methanol and DMSO but insoluble in ethanol, hexane, acetone, dichloromethane, benzene, chlorobenzene, ethylacetate and chloroform.

Elemental analysis and molar conductance:

The analytical data and physical properties of the complexes are presented in the following table. The data are inconsistent with the calculated results from the empirical formula of each compound.

Table 1 : Elemental analysis, specific conductivity and melting point of the complexes.

Complex	Emperical Formula	Mol. Wt., g/mol	Elemental Analysis Found (Calculated) %			Specific Conductance mS/cm	Melting Point in ^{0}C
			C	H	N		
Co- complex	$C_{10}H_{18}O_2N_4CoCl_2$	356	32.36 (33.71)	4.81 (5.056)	14.94 (15.73)	0.30	292
Fe- complex	$C_{10}H_{18}O_2N_4FeCl_2$	353	32.42 (33.99)	4.91 (5.14)	24.31 (25.86)	0.18	282
Cu- complex	$C_{10}H_{18}O_2N_4Cu$	289.5	39.07 (41.45)	5.85 (6.22)	18.42 (19.34)	0.36	172

Conductance of Cobalt complex :

For conductometric study. a milimolar solution is taken for conductivity which is prepared by dissolving 0.0036 g of the complex in 10 ml of double distilled water. Specific conductance of the above Co-complex solution is found to be 0.30 mS/cm at 25 degree Celcius.

Conductance of Copper complex :

1 milimolar solution of the complex is prepared by dissolving 0.0029 g of the complex in 10 ml of double distilled water and the resulting solution is taken for conductivity. Specific conductance of the above solution of Cu-complex is found to be as 0.36 mS/cm at 25 deg.C

Conductance of Iron complex :

A milimolar solution of the complex is prepared by dissolving 0.0036 g. of the complex in 1ml DMSO and diluted to 10ml with double distilled water. Specific conductance of the solution of Fe-complex is found to be 0.18mS/cm at 25^0 C.

The above conductance values indicate that the complexes are electrolytes [8].

IR- Spectra :

The infrared (IR) spectra were taken on a thermo nicolet NEXUS IR spectrometer in the wavenumber range 400 – 4000 cm^{-1} at a resolution of 4 cm^{-1}. The samples were prepared in the form of pellets together with KBr.

The significant IR bands for the complexes are complied and presented in table-2. The IR spectrum of the complexes, a sharp band observed at 1616 cm^{-1} is assigned to the v (C=N) mode of the azomethine group. This shifts to lower wave number 1606- 1609 cm^{-1} in all the complexes suggesting the coordination of the azomethine nitrogen to the metal centres. A strong band observed at 1640-1690 cm^{-1} is assigned to v (C=O, amide) of the ligand.

Table-2 : IR spectral data (in cm^{-1}) for the metal complexes :

Complex	V(C=O)	V (C=N)	V (M-N)	V (C-N)	V(N-H)
Co-complex	1640-1690	1600-1620	457-464	1080-1360	3100-3500
Fe- complex	1640-1690	1600-1620	457-464	1080-1360	3100-3500
Cu-complex	1640-1690	1600-1620	457-464	1080-1360	3100-3500

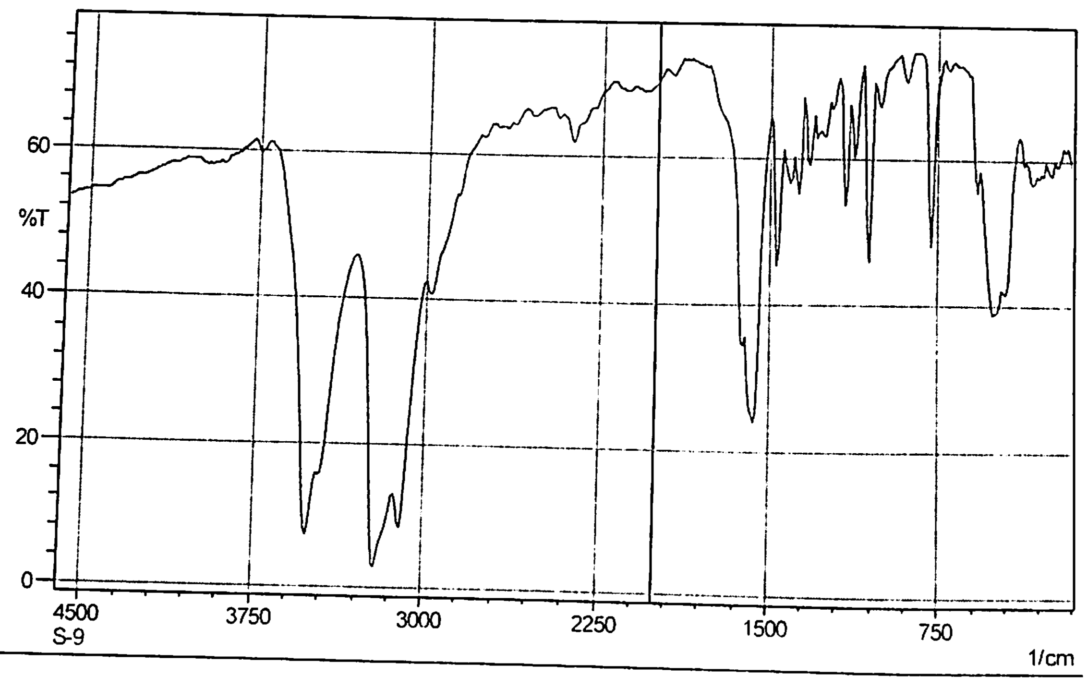


Fig: IR-spectra of Fe-complex.

UV-VIS Electronic spectra :

The UV – visible absorption spectra were taken at room temperature on a UV -1800 spectrophotometer (SHIMADZU CORPORATION) with a variable wavelength between 190 -700 nm using a glass cuvette with 0.5 cm optical path.

The UV-VIS spectral data of the complexes are presented in Table3. The electronic absorption spectra of the complexes of Cobalt and Copper were recorded in double distilled water while that of Fe-complex was recorded in DMSO in the range 200-700 nm. For the complex of Cobalt, absorption peak was found at 478 nm and 413 nm and for the complex of iron absorption peak was found at 644.5 nm, 463.0 nm, 446.5 nm, 363.5 nm and209.0 nm. For the complex of Copper absorption peak was found at 236.4 nm and 213.0 nm.

Table : 3 Electronic spectral data for the complexes :

Complex	Absorbance(nm)	Assignment	Geometry
Co-complex	478	Octahedral	Octahedral
do-	413	n-pi *	-do-
Fe- complex	463	Octahedral	Octahedral
-do-	446	n-pi *	-do-
-do-	341	Pi-pi *	-do-
Cu-complex	236.4	Square planar	Square planar
-do-	213.0	Pi-pi*	-do-

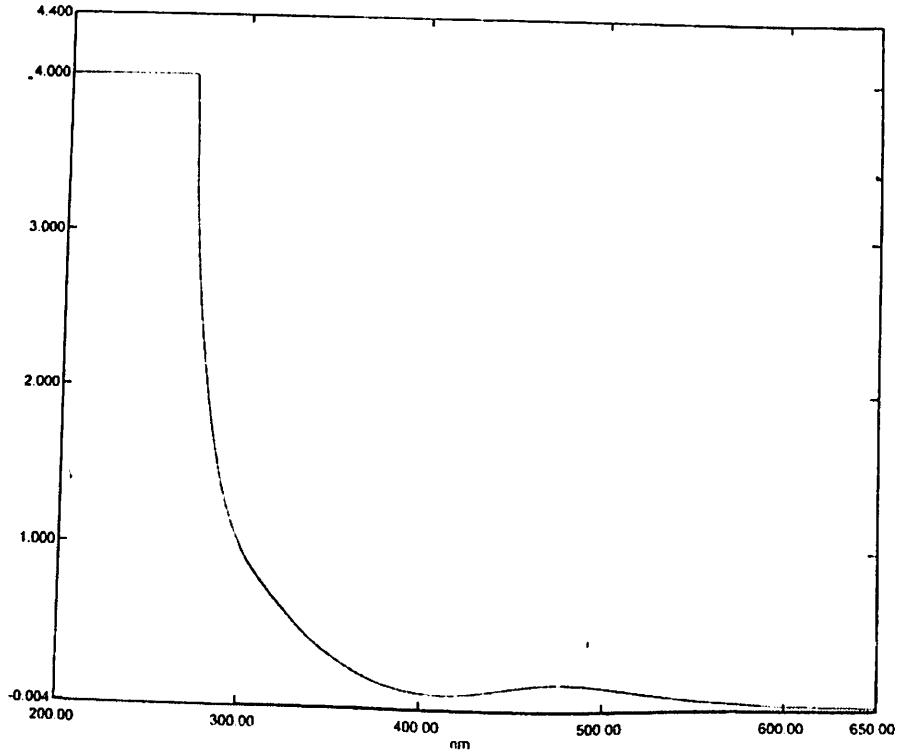


Fig: UV-VIS-Spectrum of Co-complex.

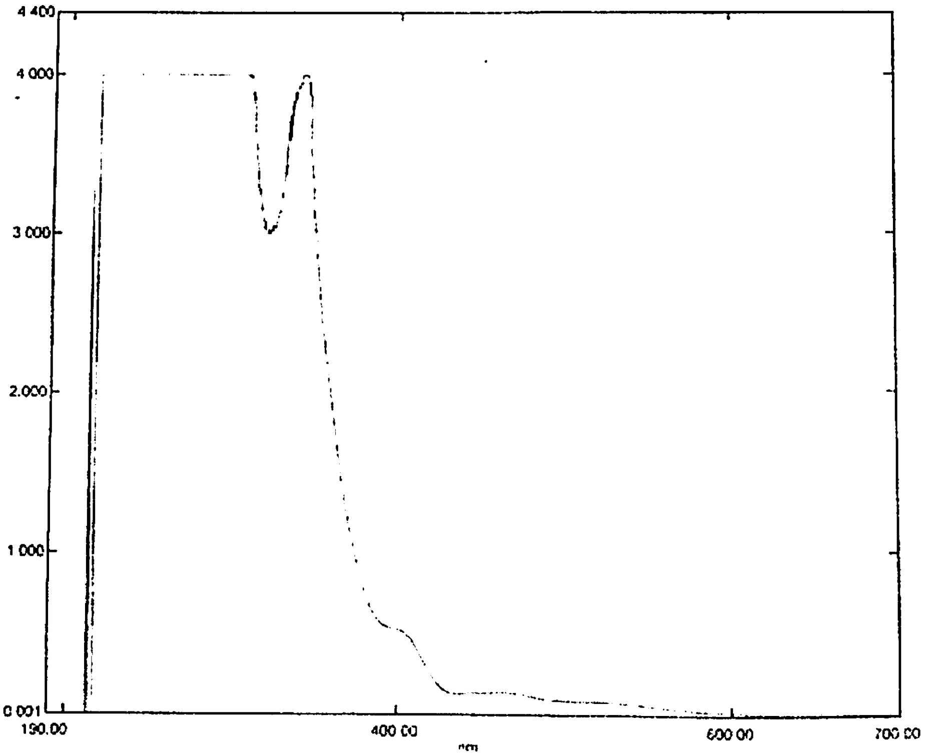


Fig: UV-VIS- Spectrum of Fe-complex.

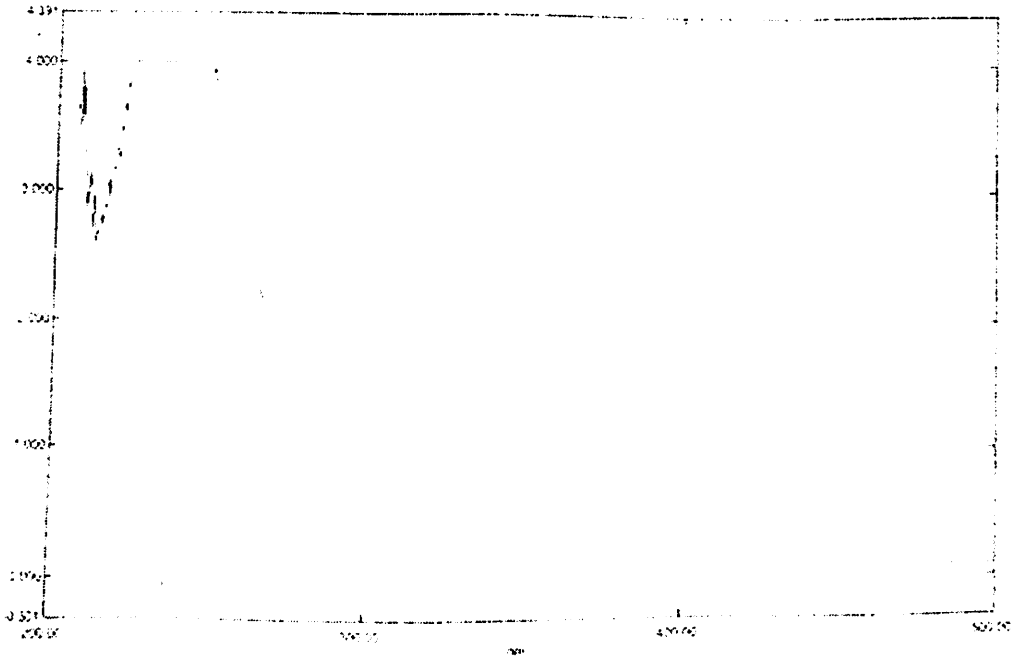
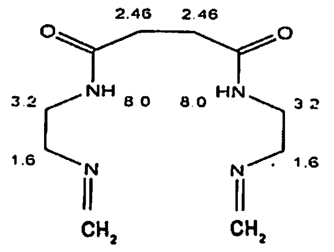


Fig: UV-VIS- Spectrum of Cu-complex.

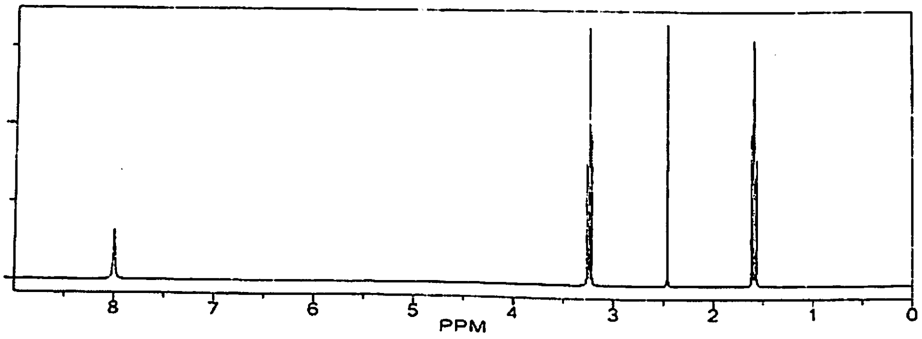
NMR spectrum of the ligand:

NMR spectrum of the ligand:

ChemNMR H-1 Estimation



Estimation Quality: blue = good, magenta = medium, red = rough



```
Protocol of the H-1 NMR Prediction:

Node       Shift     Base + Inc.    Comment (ppm rel. to TMS)

 NH        8.0          8.00        sec. amide
 CH2       2.46         1.37        methylene
                        0.85        1 alpha -C(=O)N
                        0.24        1 beta -C(=O)N
 CH2       2.46         1.37        methylene
                        0.85        1 alpha -C(=O)N
                        0.24        1 beta -C(=O)N
 NH        8.0          8.00        sec. amide
 CH2       3.2          1.37        methylene
                        1.87        1 alpha -NC(=O)-C
                         ?          1 unknown beta substituent(s)
                                    -> 1 increment(s) not found
 CH2       3.2          1.37        methylene
                        1.87        1 alpha -NC(=O)-C
                         ?          1 unknown beta substituent(s)
                                    -> 1 increment(s) not found
 CH2       1.6          1.37        methylene
                         ?          1 unknown alpha substituent(s)
                        0.22        1 beta -NC(=O)-C
                                    -> 1 increment(s) not found
 CH2       1.6          1.37        methylene
                         ?          1 unknown alpha substituent(s)
                        0.22        1 beta -NC(=O)-C
                                    -> 1 increment(s) not found
 CH2       —            —           no substructure found
 CH2       —            —           no substructure found
```

APPLICATIONS:

Antimicrobial Studies :

An antimicrobial is a substance that kills or inhibits the growth of micro-organism such as bacteria, fungi or protozoans. The discovery of antimicrobials like penicillins, by Alexander Fleming and tetracyclines pave the way for better health of millions around the world.

The antimicrobial activities of Schiff base derived from furylglyoxal and p-toluidene were studied by S. Kumar et. al.[4]. They found that the tridentate Shiff base and their metal complexes exhibit antibacterial activities against Escherichia coli, Staphylococcus aureus and Bacillus subtilis.

Shiff base and their metal complexes formed between furan or furylglycoxal with various amines exhibit antifungal activities against Helminthosporium gramineum, Syncephalostrum racemosus and Collectotricum capsisi. A series of 1-(5-substituted-2-oxoindolin-3-ylidene) 4-(substituted-pyridine-2-yl) thiosemicarbazide derivatives were synthesized by M.V. Anandhi et. al.[2]. The compounds were tested for antibacterial and antifungal activity against Becillus subtilis, Staphylococcus aureus, Escherichia coli, Pseudomonas aeruginosa, Candida albicans and Aspergillus niger.

The antimicrobial activity of Shiff bases derived from indoline 2,3-dione and 2-amino benzoic acid and their tin complexes were observed by A. Prakash and D. Adhikari[1] and found to exhibit antibacterial activity against Staphylococcus aureus. They noticed that the Co(II), Ni(II) and Cu(II) complexes with Schiff base 3-3$'$ thiodipropionic acid bis (4-amino-5-ethylimino 2,3 dimethyl 1-phenyl 3-pyrazoline) show antifungal activity against Alternaria brassicea, Aspergillus nigar and Fusarium oxysprum.

Rajeev Johari et. al.[9] synthesised Schiff basecomplexes of Cu(II), Ni(II), Fe(II) and Zn(II) Schiff base complexes prepared from salicylaldehyde and o-amino benzoic acid. The free Shiff base and its complexes had been tested for their antibacterial activity against Pseudomonas aeruginosa, Proteus vulgaris, Proteus mirabilis, Klebsiella pneumonia and Staphylococcus aureus.

Fe(III)complexes with Schiff base ligands derived by the condensation of o-phenylenediamine, salicylaldehyde and isatin/ 2- hydroxyl Naphthaldehyde/ acetylacetone were synthesized by A.Nagajothi and his co-workers[10]. The complexes were screened for antimicrobial activities against the bacteria Staphylococcus aureus, Escherichia coli and fungi Candida albicans .

The in vitro biological screening effects of the investigated compounds were tested against the bacteria. Klebsiella pneumonie and Salmonella typhi and fungi in Mueller Hinton Agar media.

Mueller Hinton Agar media is a microbiological growth medium that is commonly used for antibiotic susceptibility testing. It is also used to isolate and maintain Neisseria and Moraxella species.

It typically contains (w/v)

(1) 30.0 % beef infusion

(2) 1.75% casein hydrolysate

(3) 0.15 % starch

(4) 1.7 % agar

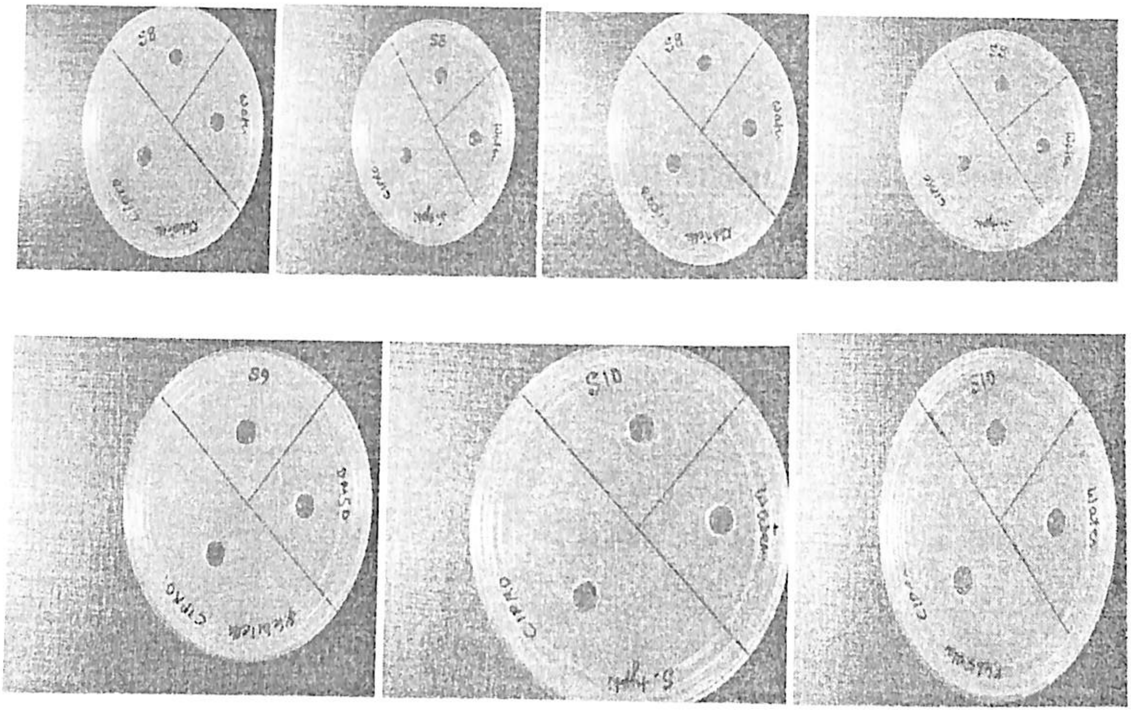
p^H is adjusted to neutral at 25^0 C

Five percent sheep blood and nicotinamide adenine dinucleotide may also be added when susceptibility testing is done on Streptococus species. This type is also commonly used for susceptibility testing done on Campylobacter.

It has few properties that make it excellent for antibiotic use. First of all, it is a non – selective, non – differential medium. This means that almost all organism plated on here will grow. Additionally it contains starch. Starch is known to absorb toxins released from bacteria, so that they cannot interfere with antibiotic. Secondly, it is a loose agar. This allows for better diffusion of the antibiotic than most other plates. A better diffusion leads to a truer zone of inhibition.

To prepare stock solutions. 2 mg of the complexes were dissolved in 1ml distilled water while 2 mg of the compound of Fe-complex was dissolved in 1ml DMSO. Serial dilution of the compounds were prepared in sterile distilled water to determine the minimum inhibitory concentration (MIC). Different dilution of the stock solution were applied on the 10mm diameter sterile disc. The discs were placed in an incubator for 3 days. Antibacterial and antifungal potential of the complexes were assessed in terms of zone of inhibition of bacterial and fungal growth in figures 1-3.

The minimum inhibitory concentration (MIC) were calculated as the highest dilution showing complete inhibition of the tested bacterial and fungal stains and are reported in table 4-7.



S-8=Co complex, S-9=Fe complex, S-10=Cu-complex.

Fig: Disk diffusion assay showing zones of inhibition in the presence of the compounds.

Table-4: Determination of MIC for antibacterial and antifungal activity of the Fe-complex

Micro-organism	2.0mg /ml	1.7mg/ ml	1.5 mg /ml	1.2mg /ml	1.0mg /ml	0.7mg /ml	0.5mg /ml	0.1 mg /mg
S. typhi	-	-	-	-	-	+	+	+
K. pneu-monie	-	-	-	-	-	+	+	+
Fungi	-	-	-	-	-	+	+	+

Table-5: Determination of MIC for antibacterial and antifungal activity of the Co-complex

Micro-organism	2.0mg /ml	1.7mg /ml	1.5mg /ml	1.2mg /ml	1.0mg /ml	0.7mg /ml	0.5mg /ml	0.1mg /ml
S. typhi	-	-	-	-	+	+	+	+
K. pneumonie	-	-	-	-	+	+	+	+
Fungi	-	-	-	-	+	+	+	+

Table-6: Determination of MIC for antibacterial and antifungal activity of the Cu-complex

Micro-organism	2.0mg /ml	1.7mg /ml	1.5mg /ml	1.2mg /ml	1.0mg /ml	0.7mg /ml	0.5mg /ml	0.1mg /ml
S. typhi	-	-	-	-	-	+	+	+
K.pneumonie	-	-	-	-	-	+	+	+
Fungi	-	-	-	-	-	+	+	+

Table-7: Antibacterial and antifungal activity of the complexes: MIC values

Micro-organism	Complex	MIC value
Bacteria	Fe-complex	1.0mg/ml
Fungi	do	1.0mg/ml
Bacteria	Co-complex	1.2mg/ml
Fungi	do	1.2mg/ml
Bacteria	Cu-complex	1.0mg/ml
Fungi	do	1.0mg/ml

The complexes were effective against both bacteria and fungi. It is evident from the table- 7 that the MIC values[10] for the complexes of Fe- and Cu- were 1.0mg/ml while that of Co-complex was 1.2mg/ml.

CONCLUSION :

In this chapter, we have reported the synthesis of Co(II), Fe(III) and Cu(II) metal complexes of Schiff base derived from ethylenediamine, succinic acid and formaldehyde. The complexes were characterized by spectral methods and analytical data. Based on these an octahedral geometry has been assigned for Co(II) and Fe(III) complexes while Cu(II) complex has square planar geometry . The antimicrobial studies carried out with the complexes confirm that they are good antibacterial and antifungal agents with their MIC values.

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(10)A.Nagajothi et .al., *Research J.of Chem. Sciences*, **2013**, 3, 2, 35-43.

CHAPTER 3

CHAPTER-3

SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF TRANSITION METAL COMPLEXES WITH DIETHANOLAMINE AND ACETYLACETONE

INTRODUCTION:

Ethanolamines commonly known as aminoalcohols were prepared in 1860 by Wurtz from ethylene chlorohydrins and aquous ammonia. Ethanolamines are a class of organic molecules containing amino and alcohol groups. The amino group may be primary (monoethanolamine, mea), secondary (diethanolamine, dea) or tertiary (triethanolamine, tea) and display reactivity of the corresponding amines. It was the end of 19th century that ethanolamine mixture was separated into its mono-, di- and tri- ethanolamine components was achived by fractional distillation. Ethanolamines are primary alcohols and, therefore, reactions are typical of primary alcohols. Because of their basic nitrogen atom and hydroxyl group, the chemical properties resemble those of both amines and alcohols. Monoethanolamine is the strongest of these bases. The bifunctional nature of ethanolamines enables them to serve as a variety of commercial applications such as corrosion inhibitors, surfactants, gas purification and herbicides[1].

Ethanolamines are also versatile ligands in which nitrogen and oxygen act as donor atoms, that readily form coordination compounds with almost all metal ions and their transition metal complexes were synthesized[2, 3].

In some cases, ethanolamines lose their ethanolic hydrogen being as ethanolaminate anions, which also behave as ligands similar to ethanolamines and ethanolaminate derivatives of a number of metals have been reported recently [4-7].

Diethanolamine, dea, is an example of tridentate ligand and is a common substances used in the chemical and pharmaceutical industries as an intermediate for the production of detergents, solubilizers, cosmetics, drugs, textile finishing agents and as an absorbent for acidic gases, (Sutton,1963).

Diethanolamine is widely used in the preparation of diethanolamides and diethanolamie salts of long fatty acids that are formulated into soaps and surfactants used in liquid laundry, dishwashing detergents, cosmetics, shampoos and hair conditioners. Diethanolamine is also used in the production of lubricants in the textile industries, in industrial gas purification to remove acid gases, as an emulsifier and dispersing agent in preparation of agricultural chemicals.

The complexation of ethanolamines with various transition metals have been studied since eighteen century. The Coordination Chemistry of amino alcohols with metal ions deserves further study because they play important role in nature, for example in hormones and in amino sugars.

The interaction of metal ion with naturally occurring organic chelating moieties has drawn the attention of research for inorganic and bio-inorganic chemists. The Chemistry of mixed ligands or ternary complexes has recently attracted the attention of researchers because such complexes have important structural diversities as well as biological applications.

Ternary complexes containing amino alcohols or their derivatives as primary ligand and N-donor heterocyclic ligands like pyridine, phenanthroline, bipyridine and their substituted analogues as auxiliary ligand have been considered useful models for several mono and poly metallic enzymes or biosites. The flexible amino alcohols like monoethanolamine, diethanolamine and triethanolamine are among the potential agents capable to produce different kinds of polynuclear complexes.

Acetylacetone is a ß-diketone (1, 3 diketone) in which two ketones are separated only by one carbon. The ß -ketone is stable as a conjugated enol rather than alpha-diketone due to the delocalization which makes the counterion more stable and less likely to regain the proton.

The keto form [$CH_3COCH_2COCH_3$] and enol form [$CH_3COCH=C(OH)CH_3$] co-exist in solution. This keto-enol tautomerism results in the tautomeric migration of a hydrogen atom from an adjacent carbon atom to a carbonyl group of a keto compound to produce the enol form of the compound. Although the enolate form of acetylacetone anion is most commonly found in coordination complexes, other possibilities are also known. Acetylacetonate is an example of a bidentate ligand. Metal acetylacetonate complexes which can be used as phase precursors in alkoxo synthesis of esters finds considerable attention[8-11].

Diketone derivatives find versatile applications in making biomolecules, agrochemicals, dyes, pigments, pharmaceuticals and stabilizers for PVC and Polyester.

The d-transition metal beta – diketone compounds were used extensively as starting materials in the early days of metallocene chemistry. Currently complexes containing the pentandianato ligand have been the focus of much investigation as electroluminescent materials presumably due to their ease of preparation, high stability and high volatility in comparision to other chelate complexes[12].

MATERIALS AND METHODS :

The chemicals used were of analytical grade (AR) reagents and of high purity available. They included ferric chloride anhydrous (fisher scientific), cobalt(II) chloride hexahydrate (RANKEM), diethanolamine (MERCK) and acetylacetone (MERCK). Elemental analysis were performed using an elemental analyser. The measurement of conductance of the complexes were measured using a conductometer at 30 deg. Celcius. The IR spectra were recorded in a spectrometer (4000-400cm^{-1}). The UV-VIS electronic spectra (200-800nm) were performed using a double beam spectrophotometer. The geometries of the metal complexes were determined using the molecular calculations.

Synthesis of the metal complexes:

An ethanolic solution of MX_n (0.005 moles. $CoCl_2 . 6H_2O$ = 1.19g, $FeCl_3$ = 0.811g), where M=Co and Fe, n=2 or 3, is added slowly to an ethanolic solution of diethanolamine (0.005moles = 0.83ml) with constant stirring. The mixture is refluxed for 6 hours at 60^0 C. Then an ethanolic solution of acetylacetone (0.005 moles = 0.52ml) is added dropwise and the mixture is refluxed for 3 hours at 60^0 C. The mixture is then filtered, washed with ethanol and dried.

Scheme 1

The synthetic route of the metal complexes:

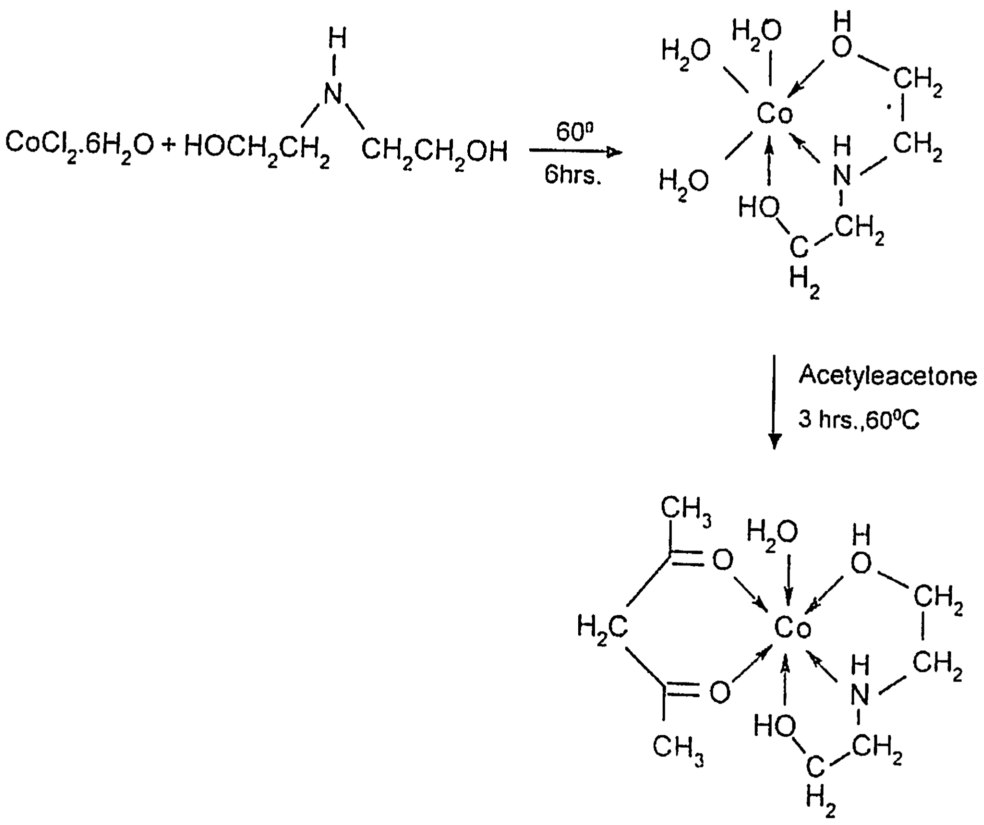


Fig. 1: Synthetic reaction of Co-complex

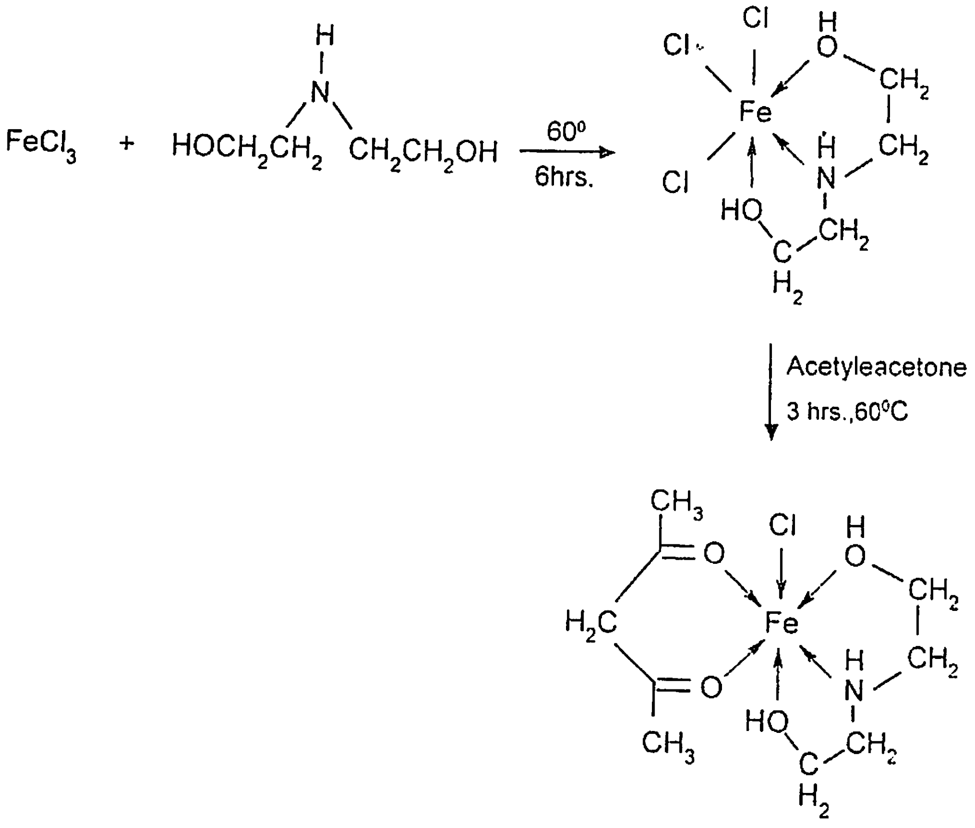


Fig. 2 : Synthetic reaction of Fe-complex

RESULTS AND DISCUSSION :

Physical properties:

The Cobalt complex is pink coloured amorphous solid with molecular weight 282.2 g/mol as confirmed by elemental analysis and molecular weight determination. The complex has a melting point of 315^0 C. The complex is tested for its solubility in different solvents and it is found that the complex is soluble in water on heating, methanol, ethanol, acetone and DMSO but insoluble in hexane, benzene, chlorobenzene, dichloromethane, ethyl acetate and chloroform.

The Iron complex is brown coloured amorphous solid with molecular weight 279.1 g/mol as confirmed by usual procedure. The complex has a melting point of 186^0 C. The solubility of the complex is carried out in different solvents and it is found that the complex is soluble in water, methanol, ethanol, acetone, dichloromethane, benzene, chlorobenzene, ethylacetate and DMSO but insoluble in hexane.

Elemental analysis and molecular conductance :

The metal complex of iron is soluble in water and the complex of cobalt is soluble in hot water and ethanol. The analytical data and physical properties of the complexes are presented in the following table. The data are consistent with the calculated results from the empirical formula of each compound.

Table 1: Elemental analysis, specific conductance and melting points of the complexes.

Complex	Emperical formula	Mol. Wt. g/mol	Elemental Analysis Found (Calculated)% C	H	N	Specific Conductance mS/cm	Melting Point in ^{0}C
Co-complex	$C_9H_{21}O_5NCo$	282.2	36.38 (38.3)	7.21 (7.50)	4.761 (4.96)	O.14	315
Fe – complex	$C_9H_{21}O_5NFe$	279.1	36.88 (38.7)	7.27 (7.52)	4.82 (5.02)	O.26	186

Conductance of Cobalt complex :

A milimolar solution of the complex is prepared by dissolving 0.0028 g. of the salt in 1ml ethanol and diluting the solution to 10 ml with double distiled water. The conductance of Co-complex is found to be 0.14 mS/cm at 30^0 C.

Conductance of Iron complex:

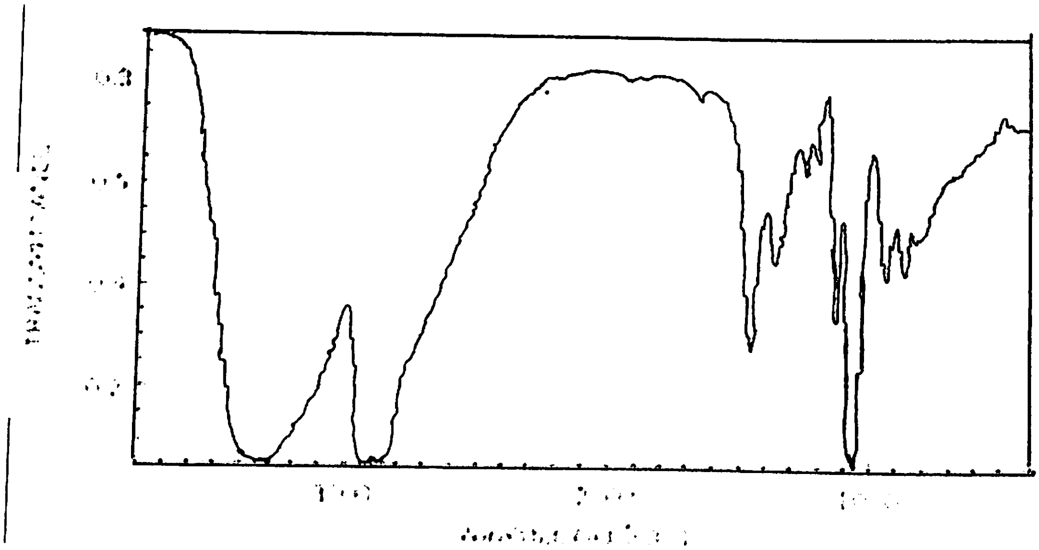
A one milimolar solution is taken for conductometric study. The solution is prepared by dissolving 0.0029 g of the complex in 10 ml of double distilled water. The conductance of Fe-complex is found to be 0.26 mS/cm at 30^0 C

The above conductance values indicate that both the complexes are electrolytes[13].

IR Spectra : -

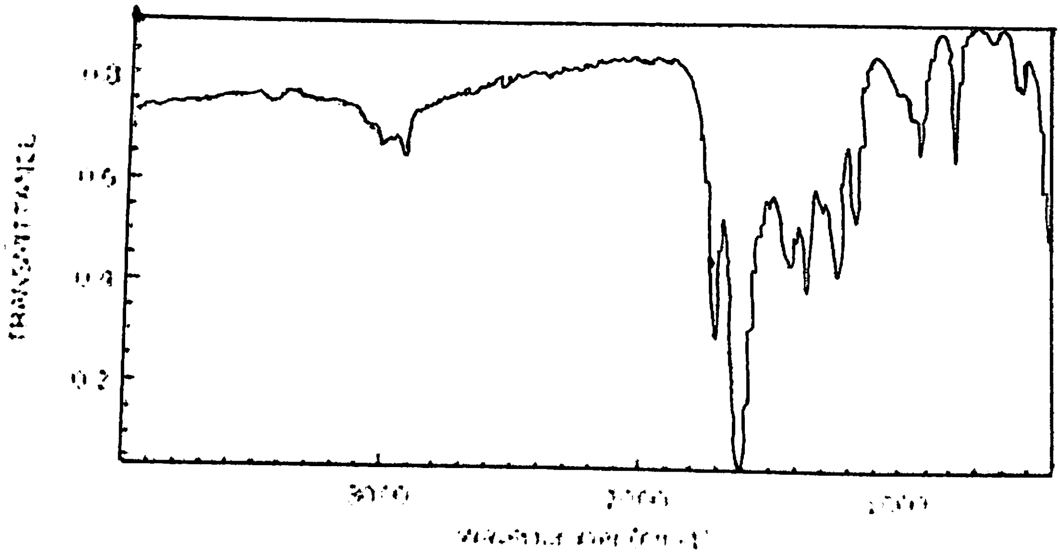
In performing the infrared (IR) spectra, it was collected on a thermo nicolet NEXUS IR spectrometer in the wavenumber range 400 – 4000 cm^{-1} at a resolution of 4 cm^{-1}. The samples were prepared in the form of pellets together with KBr.

The infrared spectrum of the ligand diethanolamine is as show below.



The organic molecule 2,4-pentandione (also called acetylacetone and abbreviated acacH) exists in the equilibrium of two tautomeric forms although the enolate form of acetylacetone is far the most commonly found in coordination complexes. A useful method for assigning the exact mode of bonding in metal acetylacetonate complexes is based on infrared spectroscopy. The frequency of the stretching vibration of the C-O bond gives the strength and, therefore, the nature of that bond. Simple ketonic species eg , acetone, generally exhibit v (C=O) at around 1700 cm^{-1} , whereas ethers show v (C=O) at approximately 1300 cm^{-1}.

The infrared spectrum of the ligand acetylacetone is as given below.



The significant IR bands for the complexes are complied and presented in table-2. The IR spectrum of the complexes, a sharp band observed at 1700 cm^{-1} is assigned to the v (C=O, carbonyl) mode. This shifts to a lower wave number suggesting the coordination of the carbonyl oxygen to the metal centre.

A strong sharp band observed at 3400 cm^{-1} is assigned to v (>N-H) of the ligand.

Table-2 : Infrared spectral data (in cm^{-1}) for the metal complexes :

Complex	V(C=O)	V(M-N)	V(C-N)	V(>N-H)	V(C-O)	V(M-O)
Co-complex	1700	457-464	1600	3400	1100	537-555
Fe-complex	1700	457-464	1600	3400	1100	537-555

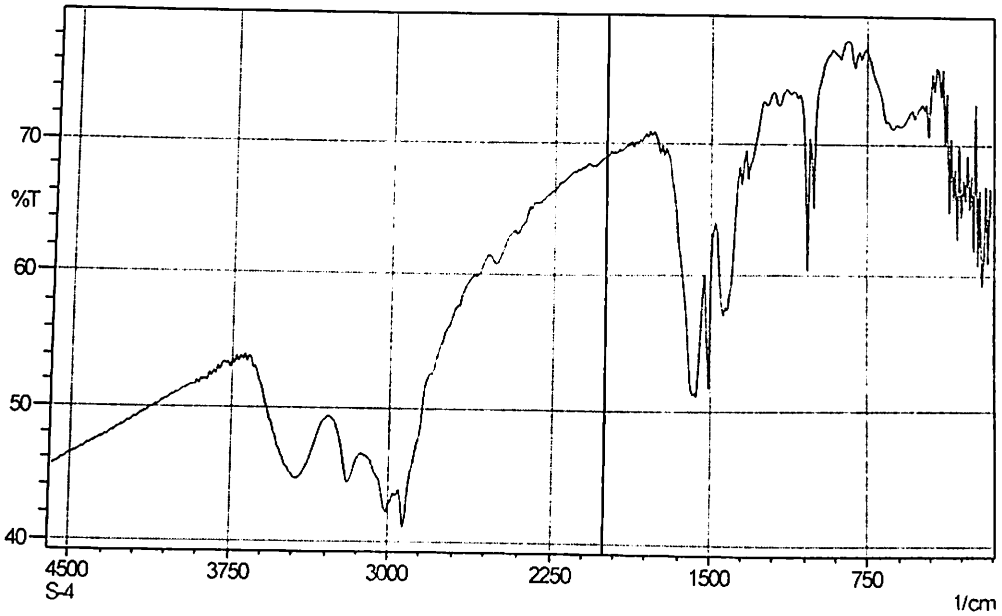


Fig 2: IR Spectrum of Fe –complex.

UV-VIS Electronic spectra :

For the UV – visible absorption spectra were taken at room temperature on a UV -1800 spectrophotometer of the brand SHIMADZU CORPORATION with a variable wavelength between 190 -700 nm using a glass cuvette with 0.5 cm optical path is employed.

The UV-VIS spectral data of the complexes are presented in table-3. The electronic absorption spectra of the Co- complex is made in ethanol and then diluting with double distilled water while the Fe- complex is soluble in double distilled water in the range 200-700 nm.

For the Co- complex, absorption peak was found at 270.2 nm, 213.8 nm and 209.2 nm and for the Fe-complex, absorption peak was found at 378.0 nm, 330.0 nm, 281.5 nm, 442.5 nm, 356.0 nm, 300.5nm and 239.5 nm.

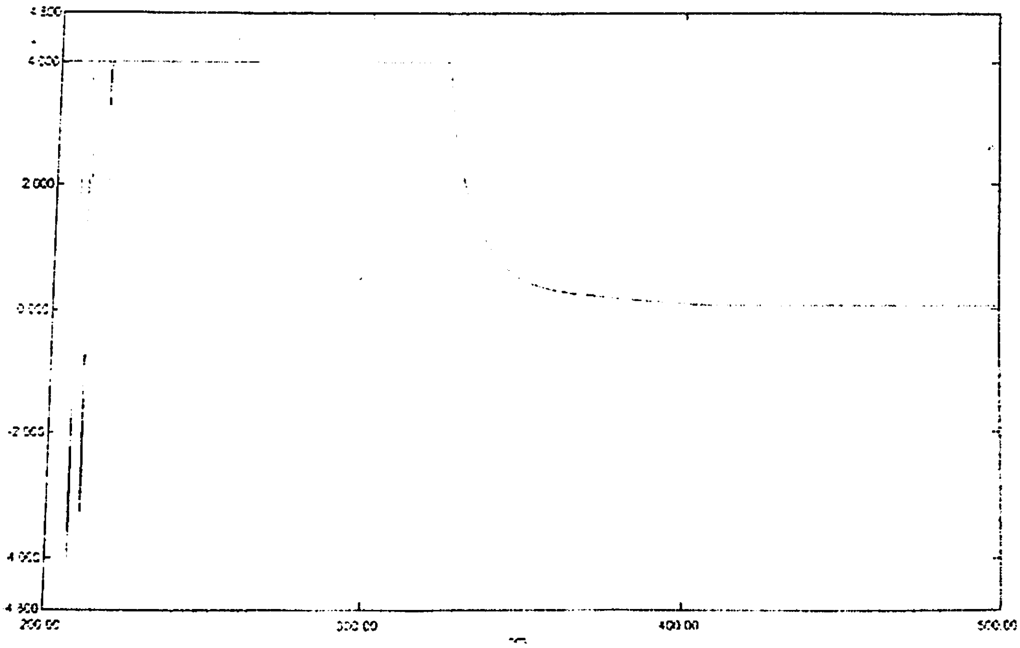


Fig 3: UV-VIS Spectrum of Co-complex.

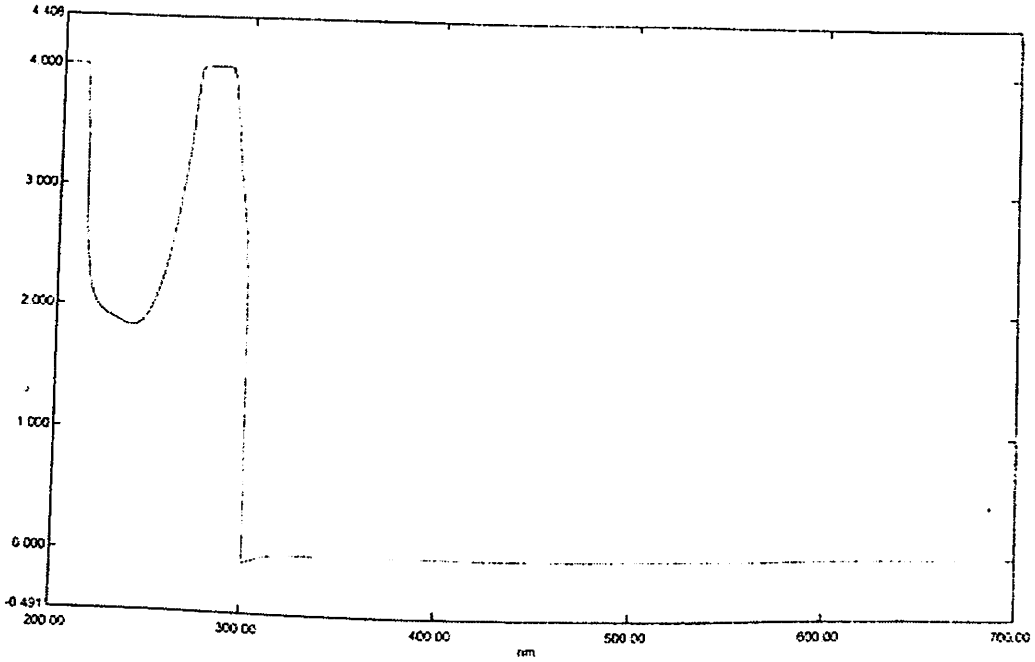


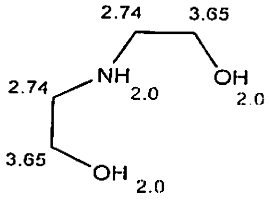
Fig 4: UV-VIS Spectrum of Fe-Complex.

Table-3 : Electronic spectral data for the metal complexes :

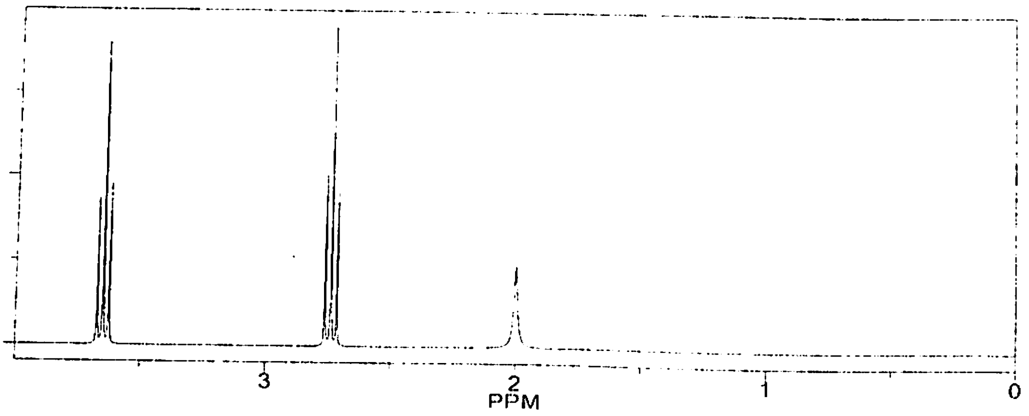
Complex	Absorbance (nm)	Assignment	Geometry
Co-complex	270.2	Octahedral	Octahedral
-do-	213.8	Pi-pi*	-do-
-do-	209.2	Pi-pi*	-do-
Fe-complex	378.0	Octahedral	Octahedral
-do-	330.0	n-pi*	-do-
-do-	281.5	Pi-pi*	-do-

NMR spectrum of the ligand diethanolamine:

ChemNMR H-1 Estimation



Estimation Quality: blue = good, magenta = medium, red = rough



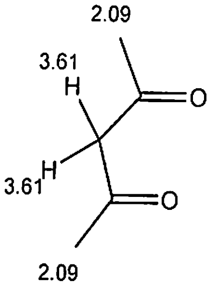
```
Protocol of the H-1 NMR Prediction:

Node       Shift     Base + Inc.    Comment (ppm rel. to TMS)

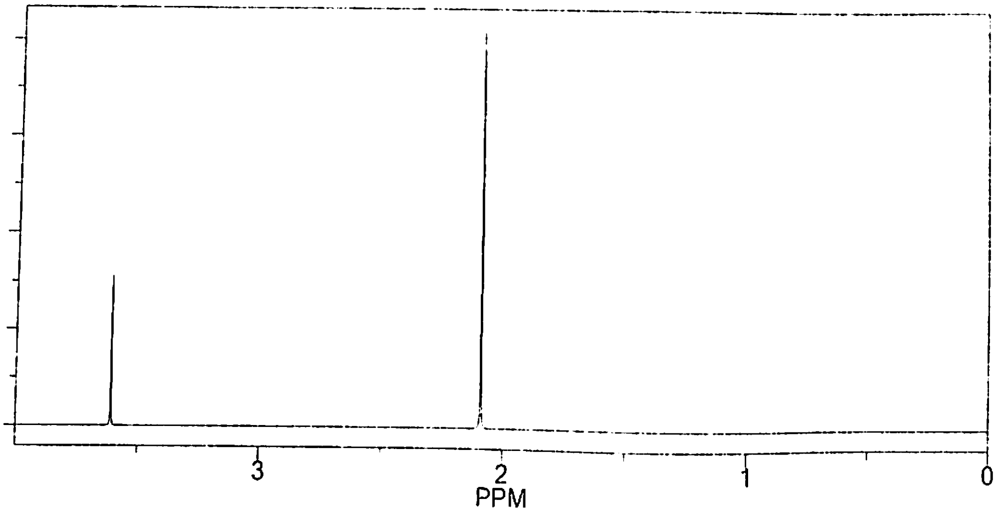
CH2         2.74        1.37        methylene
                        1.22        1 alpha -N-C
                        0.15        1 beta -O
CH2         3.65        1.37        methylene
                        2.20        1 alpha -O
                        0.08        1 beta -N-C
OH          2.0         2.00        alcohol
NH          2.0         2.00        amine
CH2         2.74        1.37        methylene
                        1.22        1 alpha -N-C
                        0.15        1 beta -O
CH2         3.65        1.37        methylene
                        2.20        1 alpha -O
                        0.08        1 beta -N-C
OH          2.0         2.00        alcohol
```

NMR spectrum of the ligand acetylacetone :

ChemNMR H-1 Estimation



Estimation Quality: blue = good, magenta = medium, red = rough



Protocol of the H-1 NMR Prediction:

Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH3	2.09	0.86	methyl
		1.23	1 alpha -C(=O)C
CH3	2.09	0.86	methyl
		1.23	1 alpha -C(=O)C
H	3.61	1.37	methylene
		2.24	2 alpha -C(=O)-C
H	3.61	1.37	methylene
		2.24	2 alpha -C(=O)-C

APPLICATIONS:

Antimicrobial activity :

An antimicrobial substance can kill or inhibit the growth of micro-organism such as bacteria, fungi or protozoans. The discovery of antimicrobials like penicillins. by Alexender Fleming and tetracyclines was a land mark for better health for millions around the world.

The in-vitro biological screening effects of investigated compounds were tested against the bacteria Salmonella typhi and Klebsiella pneumonie and fungi in Mueller Hinton Agar medium.

Mueller Hinton Agar media is a microbiological growth media that is commonly used for the antibiotic susceptibility testing by the disk diffusion method.

Mueller Hinton Agar media is based on formula recommended by Mueller and Hinton for the primary isolation of Neissieria species with the following composition.

Formula/ litre

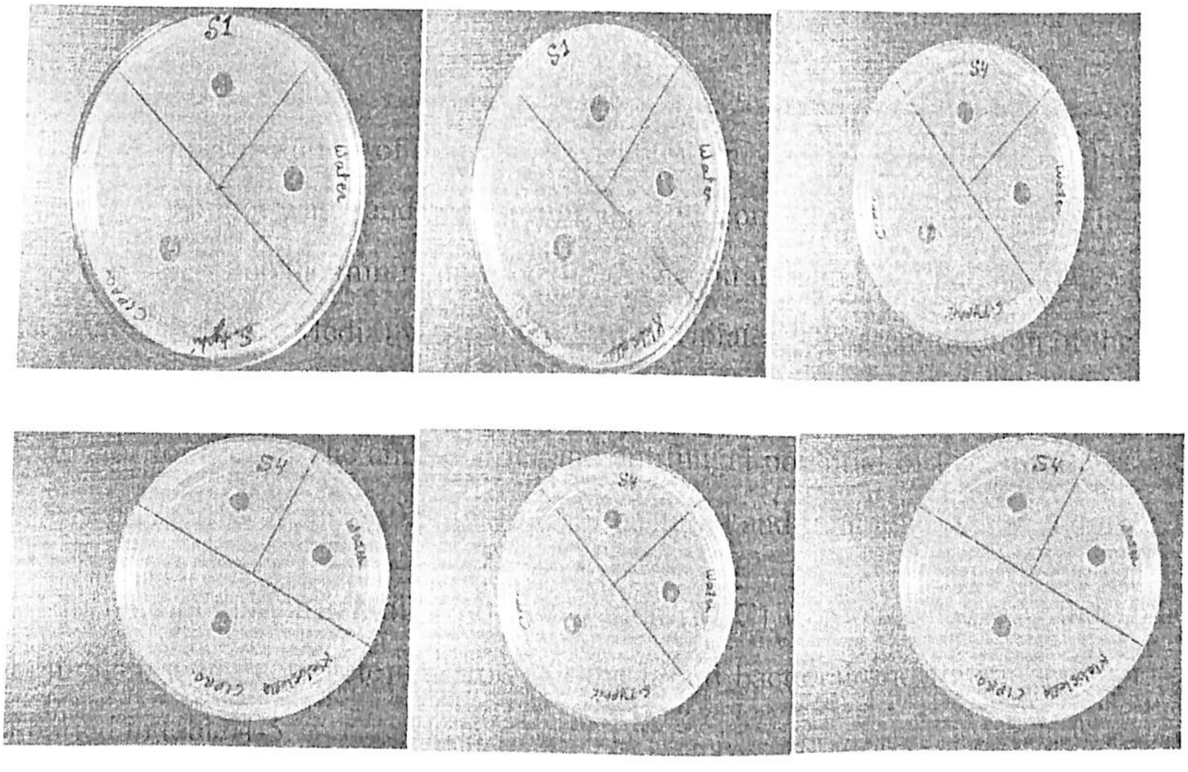
1) Beef extract : 2.0 g
2) Acid hydrolysate of casein : 17.5 g
3) Starch : 1.5 g
4) Agar : 17.0 g

Final p^H is 7.3 at 25 ^{0}C

Its antibiotic use has given the complex a new dimension of interest. Firstly, it is a non – selective, non – differential medium. This means that almost all organism plated on here will grow. Additionally it contains starch, which is known to absorb toxins released from bacteria. so that they can not interfere with antibiotic. Secondly, it is a loose agar. This allows for better diffusion of the antibiotic than most other plates. A better diffusion leads to a truer zone of inhibition.

A stock solution of 2mg/ml concentration were prepared by dissolving the compounds in hot water and serial dilution of the compounds were prepared in sterile water to determine the minimum inhibition concentration (MIC). The nutrient Mueller Hinton media (MH Media) was poured into petriplates. Different dilution of the stock solution were applied on the 10 mm diameter sterile disc. The discs were placed in an incubator for 3 days.The antibacterial and antifungal potential of the complexes were assessed in terms of zone of inhibition[14] of bacterial and fungal growth in figure -5.

The minimum inhibitory concentration (MIC) were calculated as the highest dilution showing complete inhibition of the tested bacterial and fungal stain and are reported in table 4-5.



S-1 = Co –complex, S-4 = Fe –complex.

Fig 5: Disk diffusion assay showing zones of inhibition in the presence of compounds.

Table-4: Determination of MIC for antibacterial and antifungal activity of the Co-complex.

Micro-organism	2.0 mg/ml	1.7mg/ml	1.5 mg/ml	1.2 mg/ml	1.0 mg/ml	0.7mg/ml	0.5mg/ml	0.1mg/ml
S. typhi	-	-	-	+	+	+	+	+
K. pneumonie	-	-	-	-	+	+	+	+
Fungi	-	-	-	-	+	+	+	+

Table-5 : Determination of MIC values for antibacterial and antifungal activity of the Fe-complex.

Micro-organism	2.0mg /ml	1.7mg /ml	1.5mg /ml	1.2mg /ml	1.0mg /ml	0.7mg /ml	0.5mg /ml	0.1mg /ml
S. typhi	-	-	-	+	+	+	+	+
K. pneumonie	-	-	-	-	+	+	+	+
Fungi	-	-	-	-	+	+	+	+

The Co-complex is effective against both bacteria and fungi. It is evident from the table-4, that the MIC- value for Co-complex against bacteria S. typhi is 1.5mg/ml while for bacteria K. pneumonie MIC value is1.2mg/ml. The Co-complex is antifungal at MIC- value of 1.2mg/ml.

The Fe-complex is effective against both bacteria and fungi. It is evident from the table-5, that the MIC –value for Fe-complex against bacteria S. typhi is 1.5mg/ml while for bacteria K. pneumonie MIC-value is 1.2 mg/ml. The complex is antifungal at MIC-value of 1.2mg/ml.

CONCLUSION :

In this chapter, we have reported the synthesis of Co(II) and Fe(III) metal complexes with diethanolamine and acetylacetone. The complexes were charactrrized by spectral methods and analytical data. Based on these an octahedral geometry has been assigned for both the complexes. The antimicrobial studies carried out with the complexes with their MIC values, which confirm that they act as antibacterial and antifungal agents.

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CHAPTER 4

CHAPTER-4

SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF METAL COMPLEXES WITH DIETHANOLAMINE AND NITRO LIGANDS.

INTRODUCTION :

Ethanolamines are a class of organic compounds containing amine and alcohol groups. The reaction of ethylene oxide with aquous ammonia first produces ethanolamine.

$C_2H_4O + NH_3 = H_2NCH_2CH_2OH$

Which reacts with a second and third equivalent of ethylene oxide to give diethanolamine and triethanolamine.

$C_2H_4O + H_2NCH_2CH_2OH = HN(CH_2CH_2OH)_2$

$C_2H_4O + HN(CH_2CH_2OH)_2 = N(CH_2CH_2OH)_3$

Diethanolamine is a tridentate ligand and readily forms co-ordination complexes with almost all metal ions and behave as nitrogen and oxygen donor ligands and their transition metal complexes were synthesised [1, 2].

In some cases, diethanolamine loses its ethanolic hydrogen being as diethanolaminate anion, which also behave as a ligand similar to diethanolamine and diethanolaminate derivatives of metals have been reported [3-6].

There are some alkanolamine solutions like monoethanolamine(mea), diethanolamine(dea), methyldiethanolamine(mdea) etc, which had been used for carbon dioxide removal. The amine based absorption process has been used for 60 years for the removal of carbon dioxide from natural gas[7].

Diethanolamine is used in the production of diethanolamides, which are common ingrediants in cosmetics and shampoos added to confer a creamy texture and foaming action. Diethanolamine is also a common material used in the chemical and pharmaceutical industries as an intermediates for the production of detergents, drugs, textile finishing agents and as an absorbent for acidic gases.

Nitrite being a strong ligand never acts as a non –coordinating or ionic ligand in coordination compounds. It can bond through the nitrogen to give nitro complexes or through one of the oxygen to give the less common nitrito species. It can also act as a bridging ligand bonding through the nitrogen and one of the oxygens [8].

MATERIALS AND METHODS :

All chemicals used were of analytical grade (AR) reagents and of the highest purity available. They included cupric chloride dehydrate (fisher scientific), nickel chloride hexahydrate (Qualigens fine chemicals), diethanolamine (MERCK) and sodium nitrite (s.d.fine chem.ltd.)

The elemental analysis were performed using an elemental analyser. The measurement of conductance of the complexes were measured using a conductometer at 30^0 C. The IR spectra were recorded in a spectrometer (4000-400 cm^{-1}). The UV-VIS electronic spectra 200-800 nm were taken using a double beam spectrophotometer. The geometries of the metal complexes were determined using molecular calculations.

Synthesis of the metal complexes :

An ethanolic solution of MX_2 (0.005 moles. $CuCl_2.2H_2O$ = 0.835g. $NiCl_2.6H_2O$ = 1.188g) M=Cu and Ni. is added slowly to an ethanolic Solution of diethanolamime (0.005 mole=0.83ml) with constant stirring. The mixture is refluxed for 5 hours at 60^0 C. Then an aqueous solution of sodium nitrite (0.005 mol=0.345g) is added drop wise and the mixture is refluxed for 2 hours at 60^0 C. The mixture is filtered, washed with ethanol and it was dried.

The synthetic route of the metal complexes were outlined in scheme 1:

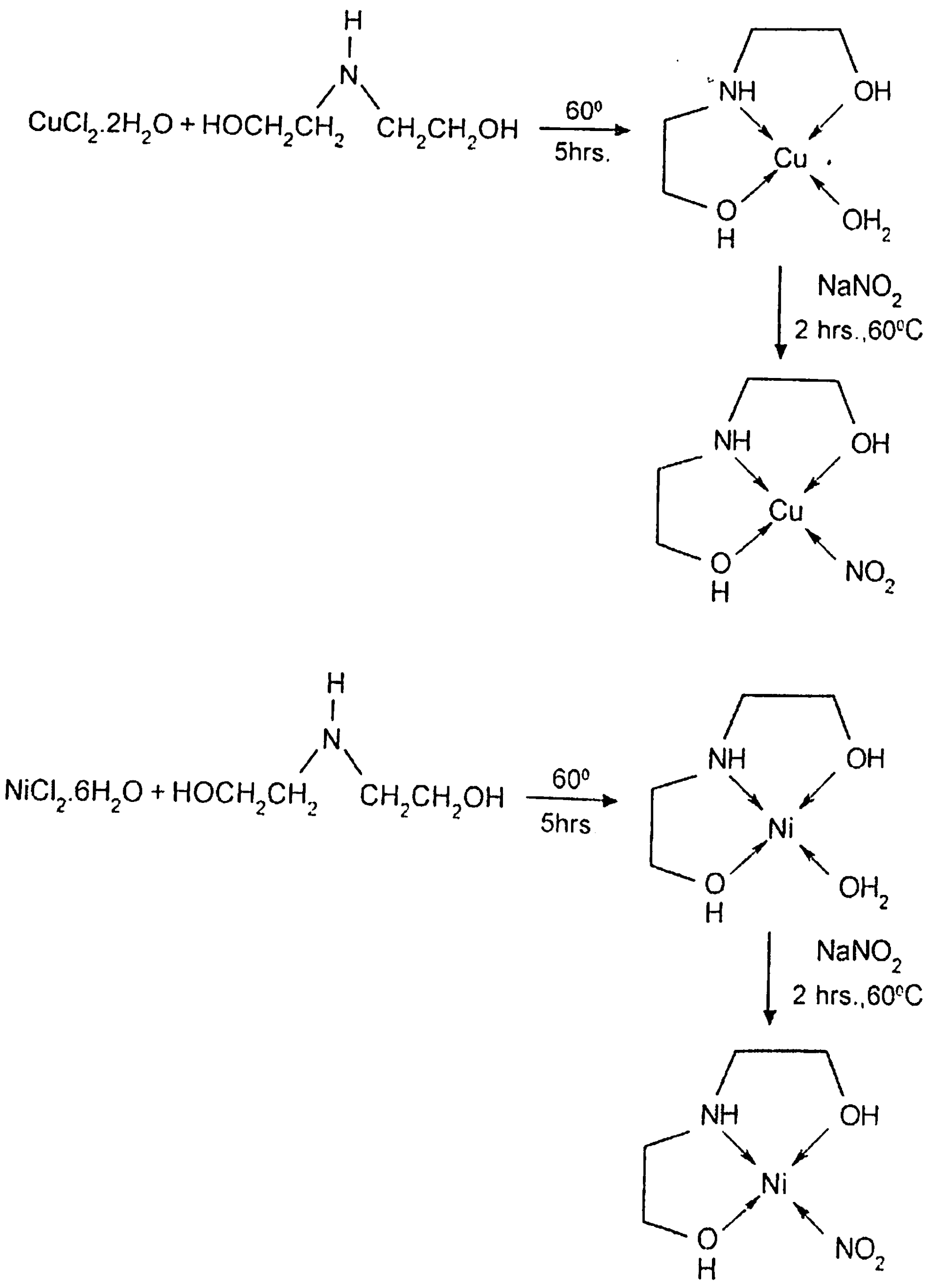


Fig. : Reactions for the synthesis of Cu and Ni complexes

RESULTS AND DISCUSSION :

Physical properties:

Cu-complex:

It is blue coloured amorphous solid with molecular weight 214.6 g/mol. The melting point of the complex is above 300^0 C. However, the complex changes to pink coloured at 178^0 C and dark pink on increasing temperature. It is found that the complex is soluble in acetic acid and DMSO but insoluble in water, methanol, ethanol, hexane, acetone, dichloromethane, benzene, chlorobenzene, ethylacetate, diethylether, chloroform and DMF.

Ni-complex:

It is green coloured amorphous solid compound having molecular weight 209.8 g/mol having melting point above 300^0 C. Solubility of the complex is tested in different solvents and the complex is soluble in acetic acid and DMSO but insoluble in water, methanol, ethanol, hexane, acetone, dichloromethane, benzene, chlorobenzene, carbon tetrachloride, ethylacetate and chloroform.

Elemental analysis and molecular conductance :

The analytical data and physical properties of the complexes are presented in the following table -1. The data are consistent with the calculated results from the empirical formula of each compound.

Table1: Elemental analysis. specific conductance and melting points of the complexes.

Complex	**Emperical Foumula**	**Mol. Wt. g/mol**	**Elemental Analysis Found (Calculated) %**			**Specific Conductance mS/cm**	**Melting Point in ^{0}C**
			C	H	N		
Cu-complex	$C_4H_{11}O_4N_2$ Cu	214.64	20.81 (22.1)	4.86 (5.167)	12.27 (13.1)	0.03	>300
Ni-complex	$C_4H_{11}O_4N_2$ Ni	209.84	21.73 (22.87)	5.02 (5.284)	12.67 (13.34)	0.02	>300

Conductance of Cu-complex :

A milimolar solution of the complex is prepared by dissolving 0.0022 g. of the complex in 1ml DMSO and diluted to 10ml with double distilled water. The conductance of Cu-complex is found to be 0.03 mS/cm at 30^0 C.

Conductance of Ni-complex :

1 milimolar solution of the complex is prepared by dissolving 0.0021g. of the complex in 1ml DMSO and diluted with 9 ml double distilled water. The conductance of Ni-complex is found to be 0.02 Ms/cm at 30^0 C.

The low conductance values indicates that the above complexes are non electrolytes [9].

IR Spectra :

The infra red (IR) spectra were collected on a thermo nicolet NEXUS IR spectrometer at a resolution of 4 cm^{-1} as has been described in chapter 2.

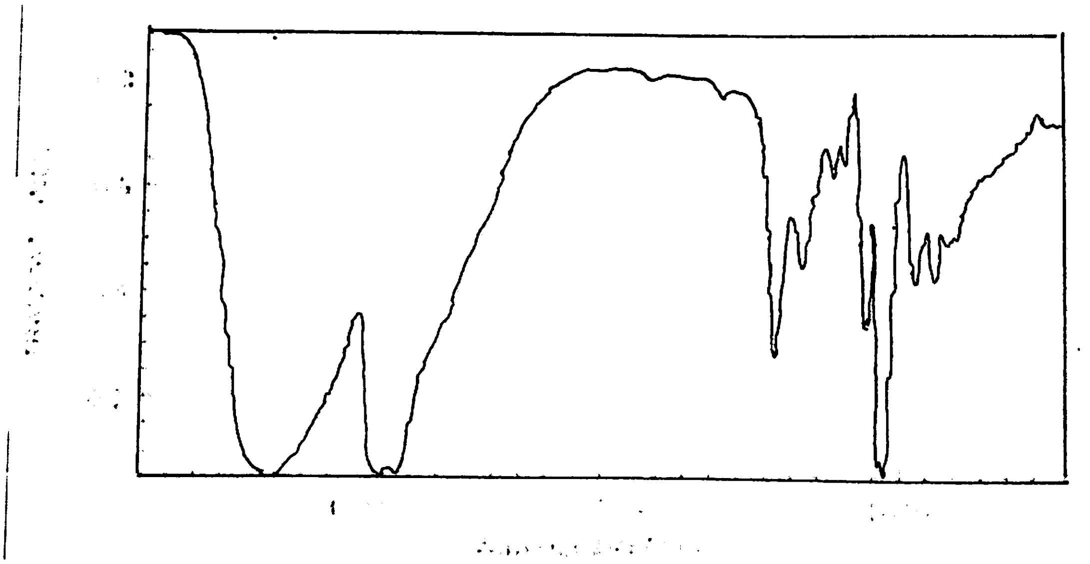


Fig : The infrared spectrum of the ligand diethanolamine.

The significant IR bands for the complexes are complied and presented in table -2 . The IR spectrum of the complexes, a sharp band observed at 1600 cm^{-1} is assigned to the v (C-N) mode. This shifts to a lower wavenumber suggesting the co-ordination of the nitrogen to the metal centre. A strong sharp band observed at 3400cm^{-1} is assigned to v (>N-H) of the ligand.

Table : 2, IR spectral data for the metal complexes:

Complex	V(M-N)	V(C-N)	V(C-O)	V(>N-H)	V(M-O)
Cu-complex	457-464	1600	1100	3400	537-555
Ni- complex	457-464	1600	1100	3400	537-555

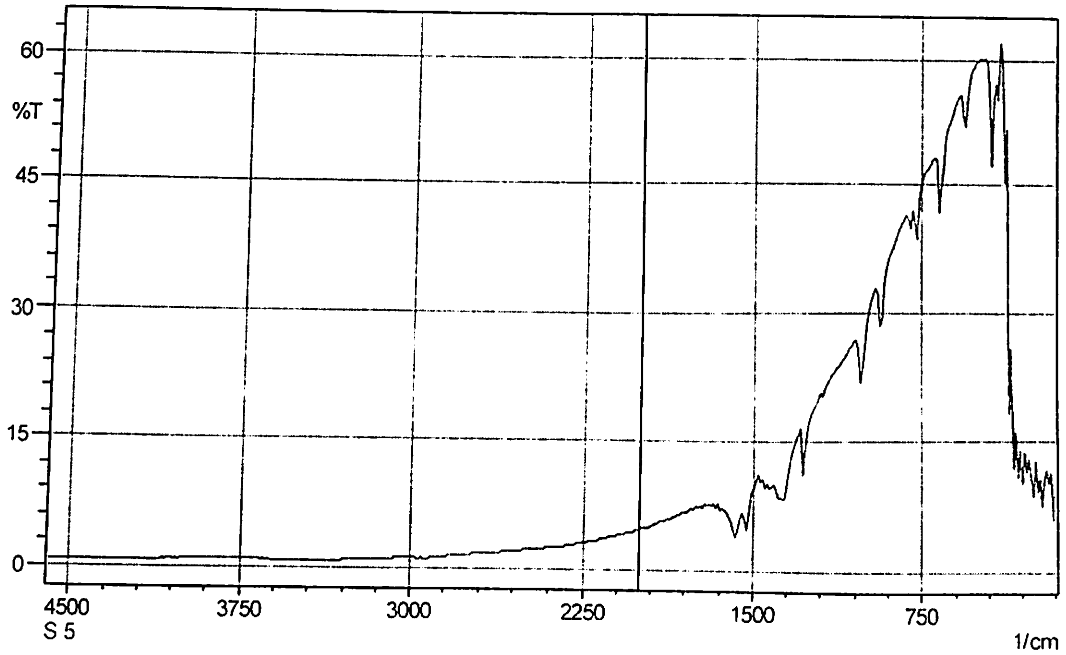


Fig: IR spectrum of Ni- complex.

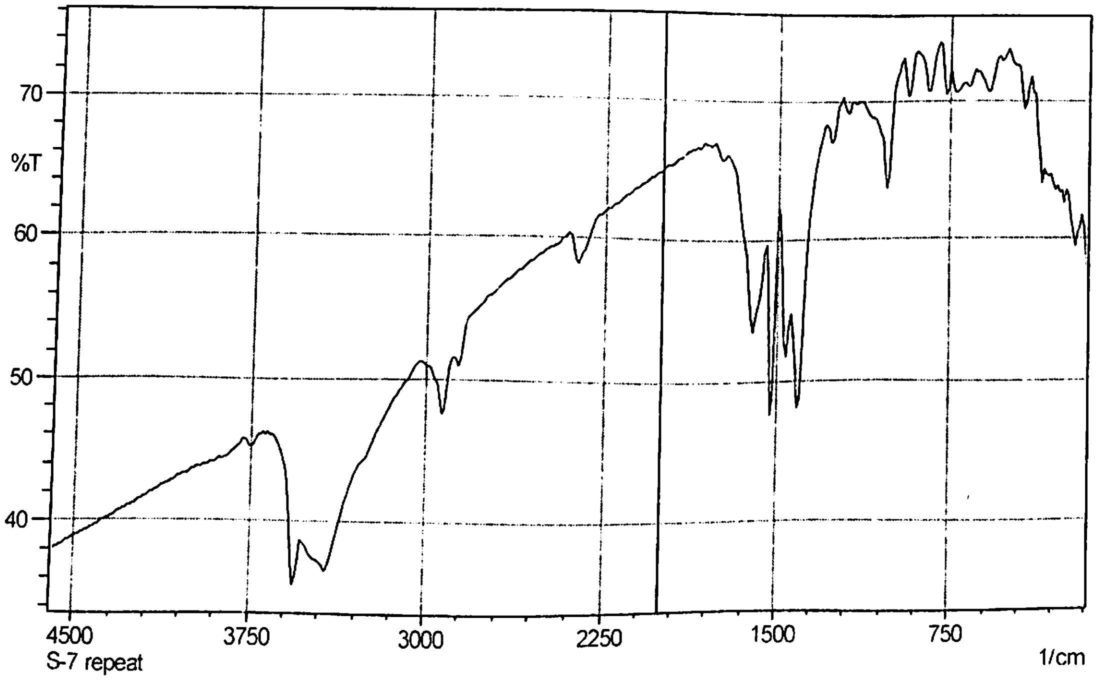


Fig: IR spectrum of Cu-complex.

UV-VIS spectra :

The UV – visible absorption spectra were taken at room temperature on a UV -1800 spectrophotometer (SHIMADZU CORPORATION) with a variable wavelength between 190 -700 nm using a glass cuvette with 0.5 cm optical path.

The UV-VIS spectral data of the complexes are presented in Table-3. The electronic absorption spectra of both the complexes of Copper and Nickel was made in DMSO and then diluting the solution with double distilled water in the range 190-700 nm. For the Cu-complex, absorption peak was found at 248.5 nm, 228.0 nm and 199.0 nm. And for the Ni-complex, absorption peak was found at 283.5 nm and 232.5 nm.

Table -3: Electronic spectral data for the metal complexes.

Complex	Absorbance (nm)	Assignment	Geometry
Cu- complex	248.5	Square planar	Square planar
-do-	228.0	Pi-pi*	-do-
-do-	199.0	Pi-pi*	-do-
Ni- complex	283.5	Square planar	Square planar
-do-	232.5	Pi-pi*	-do-

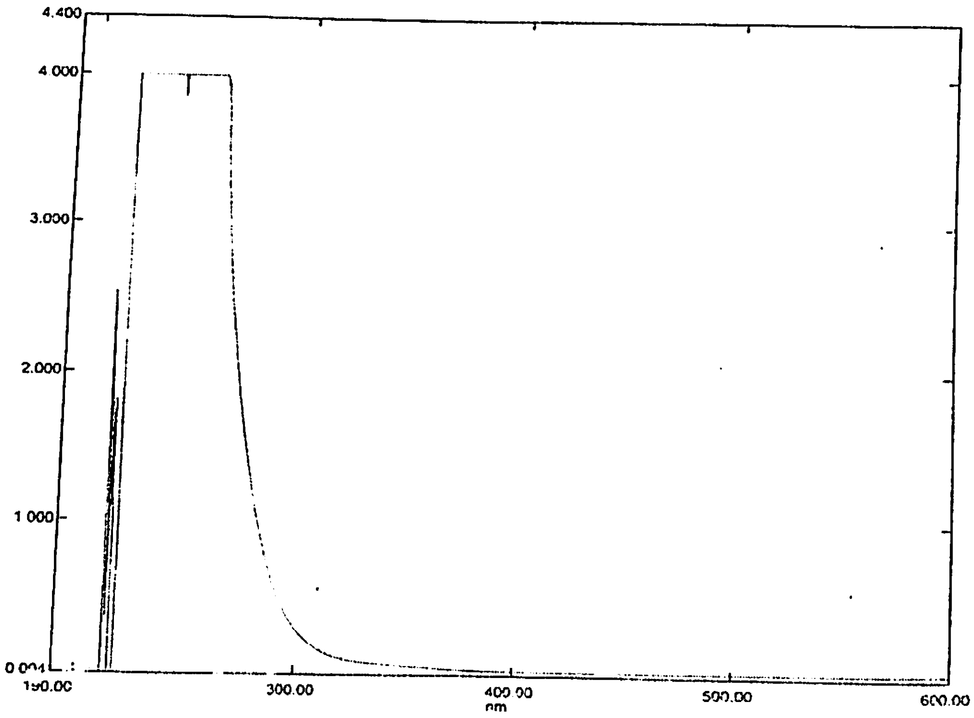


Fig: UV-VIS-Spectrum of Cu-complex.

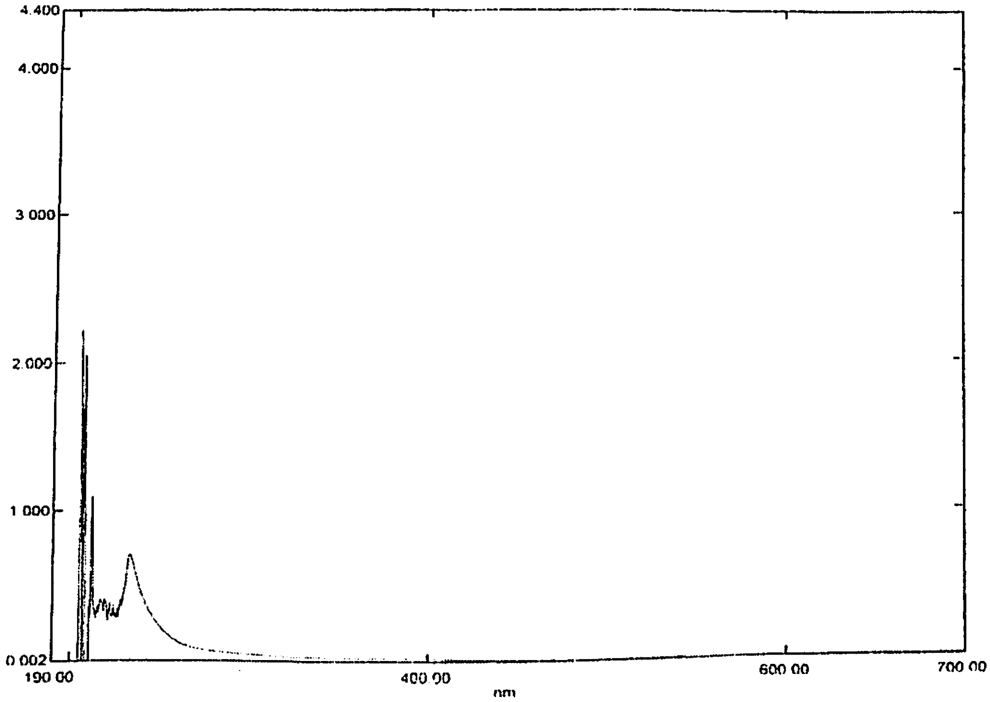
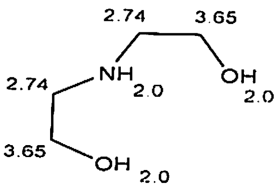


Fig: UV-VIS-Spectrum of Ni-complex.

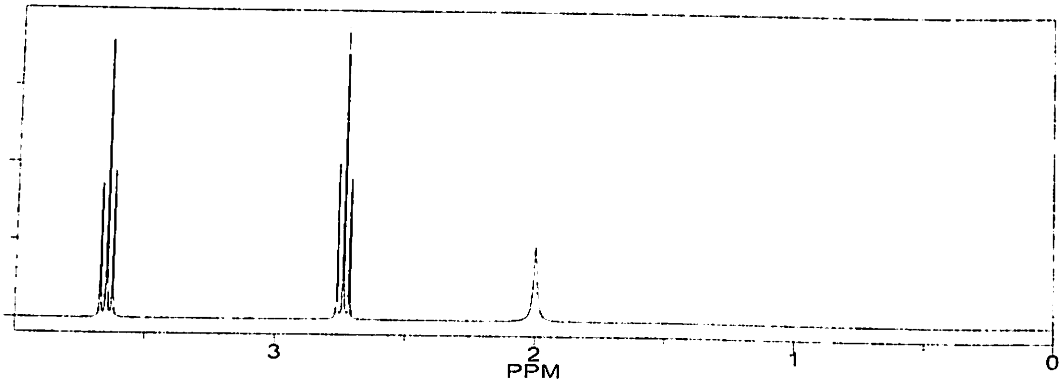
NMR spectra:

NMR spectra of diethanolamine ligand :

ChemNMR H-1 Estimation



Estimation Quality: blue = good, magenta = medium, red = rough



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Protocol of the H-1 NMR Prediction:

Node      Shift     Base + Inc.    Comment (ppm rel. to TMS)

 CH2       2.74         1.37       methylene
                        1.22       1 alpha -N-C
                        0.15       1 beta -O
 CH2       3.65         1.37       methylene
                        2.20       1 alpha -O
                        0.08       1 beta -N-C
  OH       2.0          2.00       alcohol
  NH       2.0          2.00       amine
 CH2       2.74         1.37       methylene
                        1.22       1 alpha -N-C
                        0.15       1 beta -O
 CH2       3.65         1.37       methylene
                        2.20       1 alpha -O
                        0.08       1 beta -N-C
  OH       2.0          2.00       alcohol
```

NMR spectra of the Nickel – complex:

In the spectrum graph report, three signals given by the complex in proton (^{1}H)NMR were observed. At 3.757 ppm the signal is corresponding to proton (^{1}H) attached to the secondary nitrogen atom. At 3.133 ppm, the signal is corresponding to two protons (^{1}H) near to the hydroxyl group. The signal corresponding to 2.162 ppm is due to two protons (^{1}H) near to the secondary nitrogen atom.

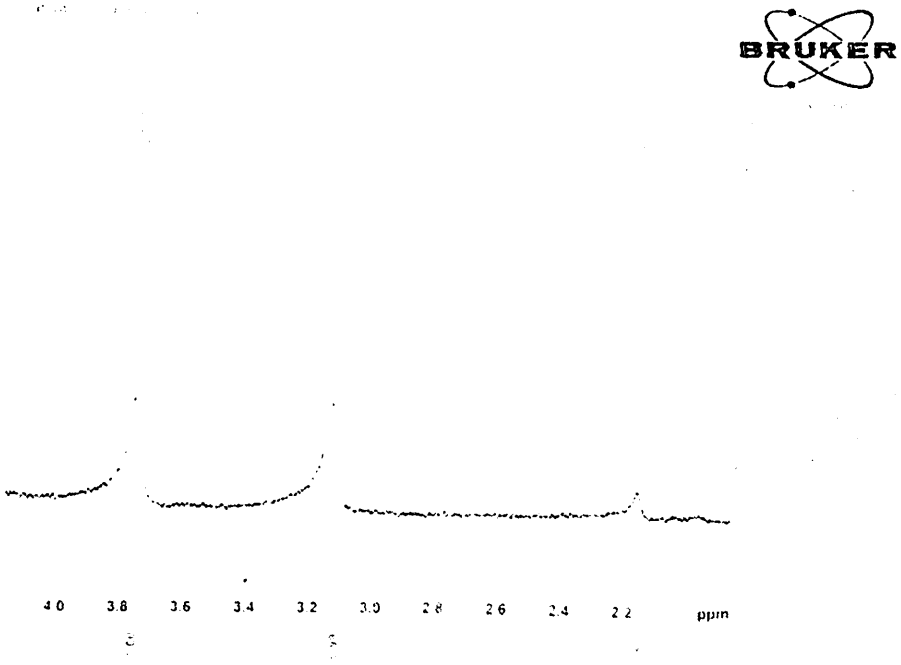


Fig: NMR-Spectrum of Ni-complex.

APPLICATIONS:

Antimicrobial activity :

The growth of micro-organisms like bacteria, fungi or protozoans are destroyed or inhibited by certain substances known as antimicrobials.

In Mueller Hinton Agar medium, the in vitro biological screening effects of the investigated compounds were tested against the bacteria Salmonella typhi and Klebsiella pneumonie and fungi.

A microbiological growth medium, Mueller Hinton Agar media, is commonly used for antibiotic susceptibility testing. The isolation and maintainance of Neisseria and Moraxella species can also be done in Mueller Hinton Agar media.

It typically contains (w/v)

I) 30.0 % beef infusion

II) 1.75% casein hydrolysate

III) 0.15 % starch

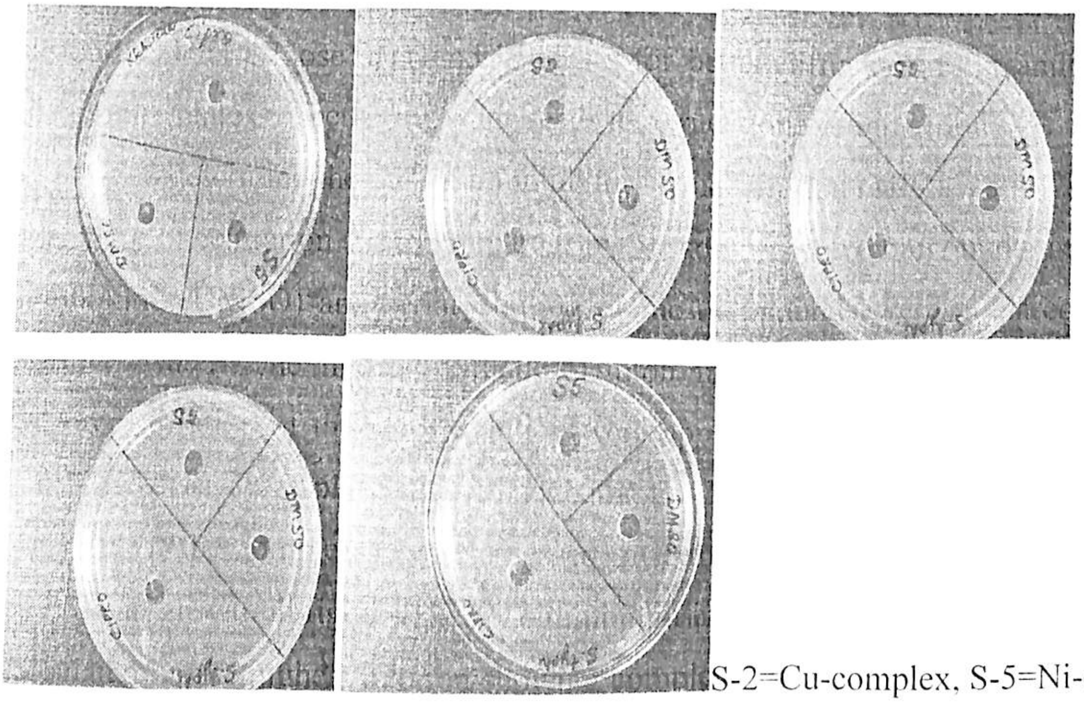
IV) 1.7 % agar

p^H is adjusted to neutral at 25^0 C

In susceptibility testing on Streptococus and Campylobacter species. 5% sheep blood and nicotinamide adenine dinucleotide may also be added.

Few properties of Mueller Hinton Agar media that make it excellent for antibiotic use. Firstly, it is a non – selective, non – differential medium. This means that almost all organism plated on here will grow. Moreover it contains starch which is absorbs toxins released from bacteria, so that they can not interfere with antibiotic. Secondly, it is a loose agar and it allows for better diffusion of the antibiotic than most other plates. A better diffusion leads to a truer zone of inhibition.

To determine the minimum inhibitory concentration (MIC), a stock solution of 2mg/ml concentration were prepared by dissolving the compounds in dimethyl sulphoxide (DMSO) and serial dilution of the compounds were prepared in sterile distilled water. The nutrient Mueller Hinton media was poured into petriplates. Different dilution of the stock solution were applied on the 10mm diameters sterile disc. The discs were placed in an incubator for 3 days. Antibacterial and antifungal potential of the complexes were assessed in terms of zone of inhibition of bacterial and fungal growth in figures 1, 2. The minimum inhibitory concerntration (MIC) were calculated on the highest dilution showing complete of the tested bacterial and fungal stain and we reported in table 1, 2.



S-2=Cu-complex, S-5=Ni-complex

Fig: Disk diffusion assay showng zones of inhibition in presence of the compounds.

Table-4: Determination of MIC for antibacterial and antifungal activities of the complex : Cu-complex.

Micro-organism	2.0mg /ml	1.7mg/ml	1.5mg/ml	1.2mg/ml	1.0mg/ ml	0.7mg/ml	0.5mg/ml	0.1mg/ml
S. typhi	-	-	-	+	+	+	+	+
K. pneumonie	-	-	-	+	+	+	+	+
Fungi	-	-	-	+	+	+	+	+

Table-5: Determination of MIC for antibacterial and antifungal activity of the complex : Ni- complex.

Micro-organism	2.0mg /ml	1.7mg /ml	1.5mg /ml	1.2mg /ml	1.0 mg/ml	0.7mg /ml	0.5mg /ml	0.1mg /ml
S. typhi	-	-	-	-	+	+	+	+
K. pneumonie	-	-	-	-	+	+	+	+
Fungi	-	-	-	-	+	+	+	+

Table -6: Antibacterial and antifungal activity of the complexes : MIC value.

Micro-organism	**Complex**	**MIC value**
Bacteria	Cu- complex	1.5mg/ml
Fungi	Cu- complex	1.5mg/ml
Bacteria	Ni -- complex	1.2mg/ml
Fungi	Ni- complex	1.2mg/ml

The complexes were effective against both bacteria and fungi. It is evident from the table - 6 that MIC values[10] for the Cu-complex was 1.5mg/ml for both bacteria and fungi while that of Ni-complex was 1.2mg/ml.

CONCLUSION :

In this chapter, the synthesis of Cu(II) and Ni(II) metal complexes with diethanolamine and nitro ligands have been discussed. Various spectral methods and analytical techniques have been employed to characterize the complexes. Based on these, a square planar geometry has been assigned for both the complexes. The antimicrobial studies carried out with the complexes confirms that they are antibacterial and antifungal agents with their MIC values.

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CHAPTER 5

CHAPTER-5

SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF METAL COMPLEX WITH DIETHANOLAMINE AND THIOCYANATE LIGANDS

INTRODUCTION :

Ethanolamines are products obtained from the reaction between ethylene oxide and ammonia. Depending on the number of ethylene oxide moles. they are called monoeethanolamine (mea). diethanolamine (dea), and triethanolamine (tea).

$H_2NCH_2CH_2OH$, $HN(CH_2CH_2OH)_2$. $N(CH_2CH_2OH)_3$

mea dea tea

Ethanolamines are a class of organic molecules containing amino and alcohol groups. The bifunctional nature of ethanolamines, enables them to serve as a commercial applications such as surfactants. inhibitors, gas purification and herbicides[1].

Ethanolamines are versatile ligands that readily form coordination compounds with almost all metal ions and behave as nitrogen and oxygen donor atoms of the ligands[2,3]. Their transition metal complexes were synthesized.

Diethanolamine is an example of tridentate ligand. In some cases, ethanolamines lose their ethanolic hydrogen being as ethanolaminate anions. which also behave as ligands similar to ethanolamines. Ethanolaminate derivatives of a number of metals have been reported[4-7]. Diethanolamine is a common substance used in the chemical and pharmaceutical industries as an intermediate for the production of detergents. solubilizers, cosmetics, drugs, textile finishing agents and as an absorbent for acidic gases.

Thiocyanates ions show several toxic effects towards vertebrates. For example, potassium thiocyanate accelerates the production of large DNA fragments, as well as the induction of trace amounts of inter nucleosomal DNA cleavage in human peripheral blood polymorphonuclear leukocytes[8].

The thiocyanate ions are released to the aquatic environments as a results of the treatment of cyanide-bearing wastes from the precious metal mining activity and it has been demonstrated that juvenite rainbow trouts were less tolerant than alevine [9].

The linear thiocyanate group can be present in compounds as an anion or as a ligand, a monodentate ligand coordinated to sulphur or nitrogen. The great coordination ability of the thiocyanate group and a great variety of its bonding modes are responsible for the existence of relatively great number of coordination compounds in liquid or solid state in which this group occurs.

Thiocyanate complexes with the formula of $[\ M(NCS)_2\ L_4]$, where L is a monodentate nitrogen donor ligand are known to act as host to include organic guest molecules with appropriate sizes and were used in the separation of aromatic compounds[10].

MATERIALS AND METHODS:

All chemicals used were of analytical grade (AR) reagents and of the highest purity available. They included Zinc chloride (Qualigens fine chemicals), diethanolamine (MERCK), and potassium thiocyanate (MERCK).

Elemental analyses were performed using an elemental analyser. The measurement of conductance of the complex was carried out on a conductometer at 30^0 C. The IR spectra was recorded in Spectrometer (4000-400 cm^{-1}). The UV –VIS electronic spectra (200-800 nm) was recorded using a double beam spectrophotometer. The geometry of the complex has evaluated using molecular calculations.

Synthesis of the Zn (II) Complex :

An ethanolic solution of $ZnCl_2$ (0.005 mole=0.68 g) is added slowly to an ethanolic solution of diethanolamine (0.005 mole =0.83ml) with constant stirring. The mixture is refluxed for 5 hours at 60^0 C. To this solution, an aquous solution of potassium thiocyanate (0.005 mole =0.485 g) is added dropwise and the mixture is refluxed for 2 hours. The mixture is filtered, washed with ethanol and dried the residue. The filtrate is crystalised by slow evaporation of the solvent.

The synthetic route of the metal complex is presented in scheme- 1

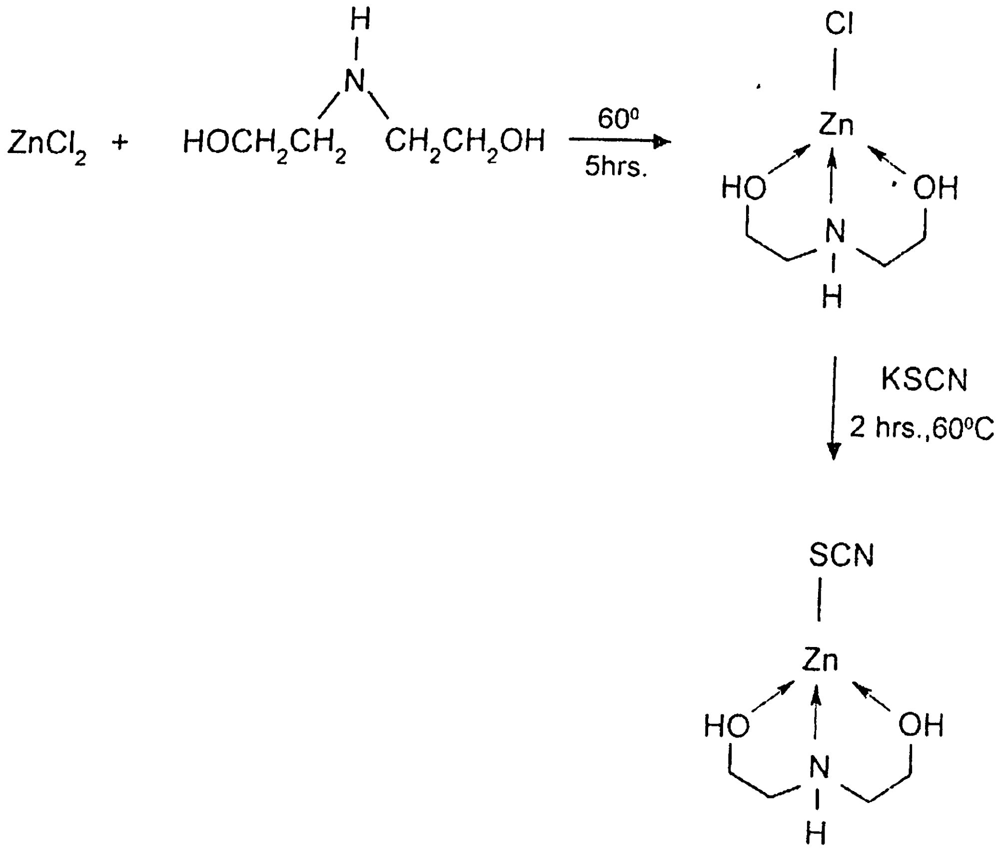


Fig. : Synthetic Reaction of Zn-complex

RESULTS AND DISCUSSION :

Physical properties:

The Zinc complex is colourless crystalline solid compound with molecular weight 282.5 g/mol having melting point 250^0 C. It is found that the complex is soluble in water, methanol, ethanol and DMSO but insoluble in acetone, hexane, dichloromethane, ethylacetate and chloroform.

Elemental analysis and molar conductance :

The metal complex is soluble in water. The analytical data and physical properties of the complex are presented in the following table. The data are consistent with the calculated results from the empirical formula of the compound.

Table1: Elemental analysis, specific conductance and melting point of the complex

Complex	Emperical Formula	Mol. Wt. g/mol	Elemental Analysis Found (Calculated)%				Specific Conductance mS/cm	Melting Point in °C
			C	H	N	S		
Zn-complex	$C_5H_{11}O_2N_2S$ Zn	228.5	25.21 (26.3)	4.62 (4.85)	11.76 (123.)	13.31 (14.0)	1.28	250

Conductance of Zn -complex

For conductometric study, one milimolar solution of the complex was prepared by dissolving 0.0029 g of the complex in 10 ml of double distilled water. The conductace of Zn-complex is found to be 1.28 mS/cm at 30^0 C

The above conductance value indicates that the complex is an electrolyte[11].

IR spectra:

To collect infrared (IR) spectra, a thermo nicolet NEXUS IR spectrometer in the wavenumber range 400 – 4000 cm^{-1} at a resolution of 4 cm^{-1} was used. The samples were prepared in the form of pellets with KBr.

Fig : The infrared spectrum of the ligand diethanolamine.

The significant IR bands for the complex is complied and presented in table - 2. The IR spectrum of the complex, a sharp band observed at 1600 cm^{-1} is assigned to the v (C-N) mode. This shifts to a lower wavenumber suggesting the co-ordination of the nitrogen to the metal centre.

A strong sharp band observed at 3400 cm-1 is assigned to v (>N-H) of the ligand.

Table-2 : IR spectral data for the metal complex .

COMPLEX	V(M-N)	V(C-N)	V(C-O)	V(>N-H)	V(M-O)
Zn-complex	457-464	1600	1100	3400	537-555

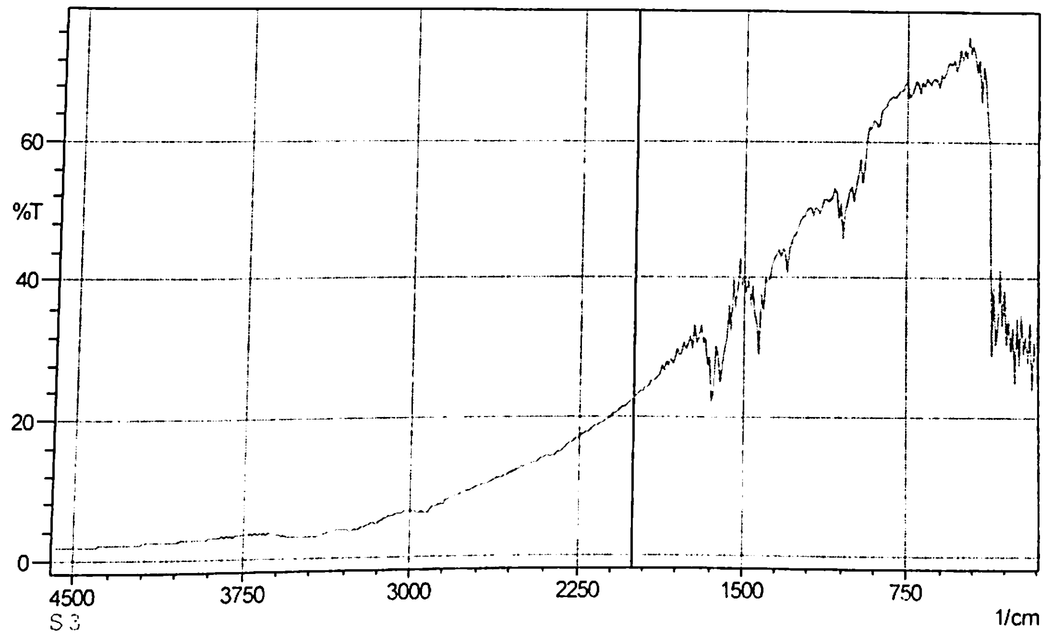


Fig: IR spectrum of Zn-complex.

UV-VIS, Electronic spectra:

A UV-1800 spectrophotometer (SHIMADZU CORPORATION) with a variable wavelength between 190 -700 nm using a glass cuvette with 0.5 cm optical path was used to perform UV-visible absorption spectra.

The UV-VIS spectral data of the complex is presented in table-3. The electronic absorption spectra of the complex was made in double distilled water in the range of 190-500 nm. For the complex absorption peak was found at 216.2nm and 200.8 nm.

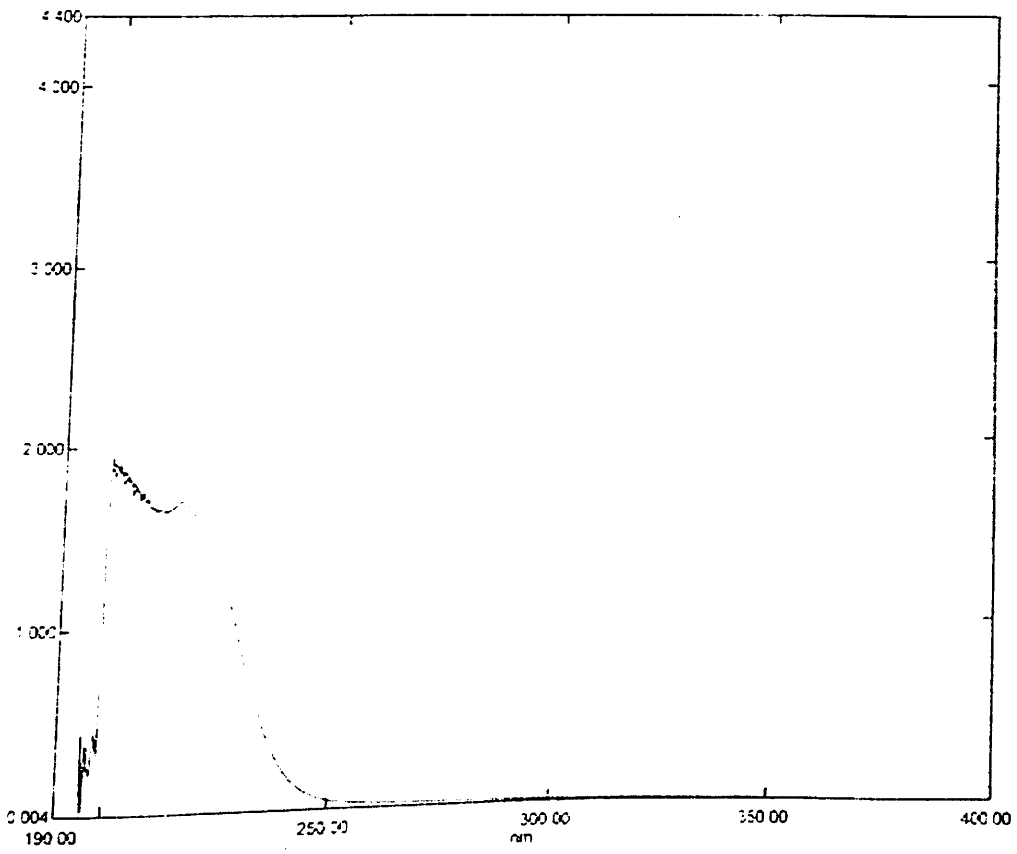


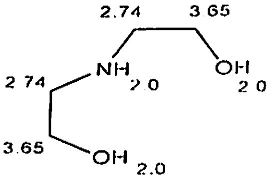
Fig: UV-VIS-Spectrum of Zn-Complex.

Table-3 : Electronic spectral data for the metal complex .

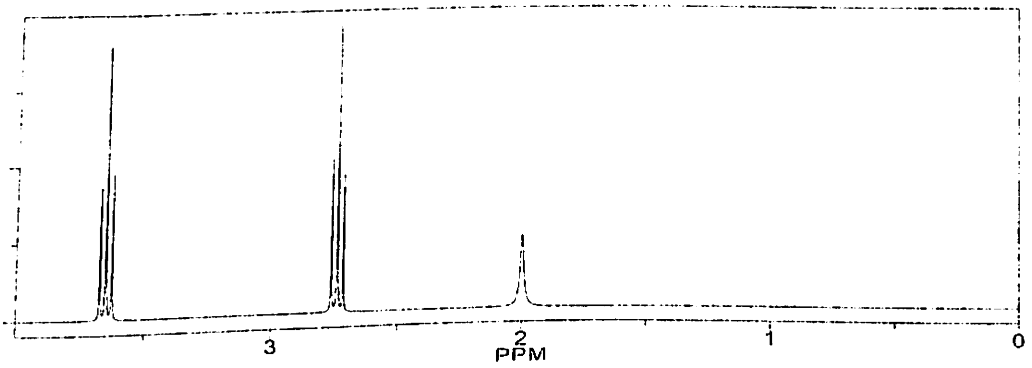
Complex	Absorbance(nm)	Assignment	Geometry
Zn-Complex	216.2	Tetrahedral	Tetrahedral
-do-	200.8	Pi-pi*	-do-

NMR spectrum of diethanolamine ligand:

ChemNMR H-1 Estimation



Estimation Quality: blue = good, magenta = medium, red = rough



Protocol of the H-1 NMR Prediction:

Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH2	2.74	1.37	methylene
		1.22	1 alpha -N-C
		0.15	1 beta -O
CH2	3.65	1.37	methylene
		2.20	1 alpha -O
		0.08	1 beta -N-C
OH	2.0	2.00	alcohol
NH	2.0	2.00	amine
CH2	2.74	1.37	methylene
		1.22	1 alpha -N-C
		0.15	1 beta -O
CH2	3.65	1.37	methylene
		2.20	1 alpha -O
		0.08	1 beta -N-C
OH	2.0	2.00	alcohol

APPLICATIONS

Antimicrobial activity :

An antimicrobial is a substance that kills or inhibits the growth of micro-organism such as bacteria. fungi or protozoans.

The in vitro biological screening effects of the investigated compound was tested against the bacteria Salmonella typhi and Klebsiella pneumonie and fungi in Mueller Hinton Agar medium.

Mueller Hinton Agar media is one of the best medium for microbiological growth that is commonly used for antibiotic susceptibility testing. It is also used to isolate and maintain Neisseria and Moraxella species.

It typically contains (w/v)

I) 30.0 % beef infusion

II) 1.75% casein hydrolysate

III) 0.15 % starch

IV) 1,7 % agar

Final p^{H} is 7.3 at 25^{0} C

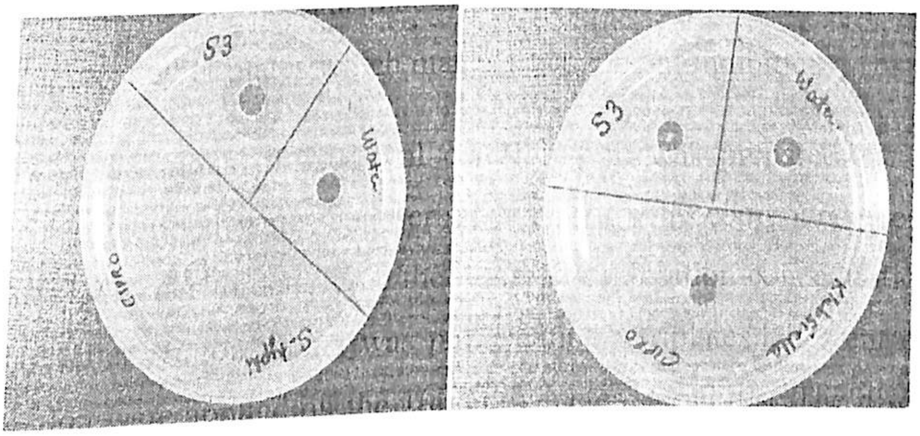
Nicotinamide adenine dinucleotide and 5% sheep blood may also be added when susceptibility testing is done on Camphylobactor and Streptococus species.

Mueller Hinton Agar media is an excellent medium for antibiotic use due to some of its properties.

1. It is a non- selective, non- differential medium which means that almost all plated on here will grow.
2. It contains starch which is known to absorb toxins released from bacteria, so that they can not interfere with antibiotic.
3. This is a loose agar that allows for better diffusion of the antibiotic than most other plates which makes truer zone of inhibition.

Stock solutions of 2.0 g/ml concentration was prepared by dissolving the compound in distilled water and serial dilution of the compound were prepared in sterile distilled water to determine the minimum inhibition concentration (MIC). The nutrient Mueller Hinton media was poured into petriplates.Different dilution of the stock solution were applied on the 10mm diameter sterial disc.The discs were placed in an incubator for 3 days. Antibacterial and antifungal potential of the complex were assessed in terms of zone of inhibition of bacterial and fungal growth in figure1.

The minimum inhibitory concentration (MIC)were calculated as the highest dilution showing complete inhibition of the tested bacterial and fungal stain and are reported in table-1.



S-3=Zn-complex

Fig: Disk diffusion assay showing zones of inhibition in presence of the compound.

Table-4:Determination of MIC for antibacterial and antifungal activity of the complex Zn- complex.

Micro-organism	2.0mg/ml	1.7mg/ml	1.5mg/ml	1.2mg/ml	1.0 mg/ml	0.7 mg/ml	0.5mg/ml	0.1mg/ml
S. typhi	-	-	-	+	+	+	+	+
K. pneu-monie	-	-	-	-	+	+	+	+
Fungi	-	-	-	-	+	+	+	+

The Zn-complex is effective against both bacteria and fungi. It is evident from the table-4 that the MIC –value for this complex against bacteria S. typhi is 1.5mg/ml while for bacteria K. pneumonie it is 1.2mg/ml. The complex is antifungal at MIC-value 1.2mg/ml.

The complex was effective against both bacteria and fungi.It is evident from the table that the MIC value[12] for the complex was 1.5mg/ml.

CONCLUSION:

We have reported the synthesis of Zn(II) metal complex with diethanolamine and thiocyanate ligands in this chapter. The complex was characterized by spectral methods and analytical data. Analysing these, a tetrahedral geometry has been assigned for the complex. The antimicrobial studies carried out with the complex confirm that it is antibacterial and antifungal agent with the MIC values.

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ABSTRACT

ABSTRACT:

In Chapter 1, we have reported a brief introduction and review of literature on Coordination compounds. Coordination compounds were identified in the nineteenth century. The modern study of coordination compounds began with Alfred Warner[1], the first inorganic Chemist to be awarded the Nobel Prize in Chemistry in 1913.

The transition metal elements have strong tendency to form coordination complexes. During formation of coordination compounds, the properties of both metal and ligand are altered. The metal atom acts as electron pair acceptor (Lewis acid) while the ligands act as electron pair donor (Lewis base). The bond between metal and ligand is stronger than intermolecular forces because they form directional bonds between the metal ion and ligands, but are weaker than covalent and ionic bonds.

In transition metal elements, d and f-orbitals are far inside to be influenced by the ligands. Therefore in some cases, it is difficult for them to be involved in coordination. However, a large number of coordination compounds have been synthesized, characterized and their bio-chemical activities have been studied widely.

Transition metals have inherent tendency to expand their coordination number around them by using d- or f- orbitals. Therefore, it is a very interesting field of Chemistry to synthesize complexes of transition metals with various electron rich ligands. In many cases, water molecule is coordinated with these metals and hence strong coordinating ligands are necessary for the synthesis of new coordination complexes.

Organic ligands containing significantly different electron rich donor functionalities (-N, -P, -O , -S .) find increasing Interest in coordination Chemistry.

In Chapter-2 of the thesis, we have reported the synthesis of the Schiff base complexes of Co(II), Fe(III) and Cu(II) from ethylenediamine, succinic acid and formaldehyde.

A Schiff base named after Hugo Schiff, is a compound with a functional group that contains a carbon – nitrogen double bond with the nitrogen atom connected to an alkyl or aryl group. Schiff bases in a broad sense have the general formula $R^1R^2C=NR^3$ where R is an organic side chain, R^1, R^2 and R^3 may be same or different. Actually these are imines. In this definition. Schiff base is synonymous with azomethine. Schiff bases are some of the most widely used organic compounds.

Schiff bases are versatile ligands which are synthesized from the condensation of aliphatic or aromatic primary amines with carbonyl compounds. Schiff base ligands coordinate with metal ions via azomethine (-CH=N-) nitrogen and have been studied extensively[2].

Schiff bases are generally bi, tri or tetra-dentate ligands capable of forming stable coordination compounds with transition metals. In organic synthesis, Schiff base reactions are usefull in the formation of carbon- nitrogen bonds. Schiff bases appear to be important intermediate in a large number of enzymatic reactions[3].

Schiff bases and their transition metal complexes have gained remarkable importance because of their broad range of applications in biological, biochemical, analytical, antimicrobial activities. The chemotherapeutic Schiff bases have attracted the attention of biochemists[4].

The Schiff base complexes so synthesized are characterized by elemental analysis, melting point determination, conductance measurements and various spectral methods. Based on these an octahedral geometry has been assigned for Co(II) and Fe(III) complexes while Cu(II) complex has square planar geometry. The complexes have been screened for antimicrobial activities against bacteria Salmonella typhi and Klebsiella pneumonie and fungi.

The probable structures of the complexes are given below.

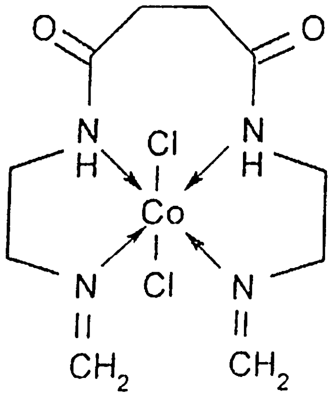

Fig 1. Proposed octahedral structure of Cobalt-complex.

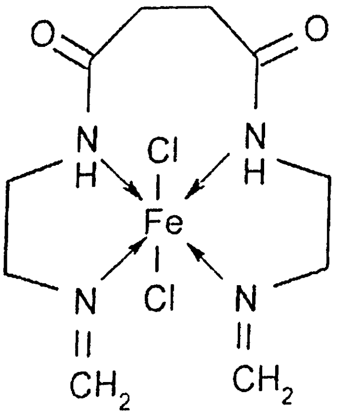

Fig 2. Proposed octahedral structure of Iron- complex.

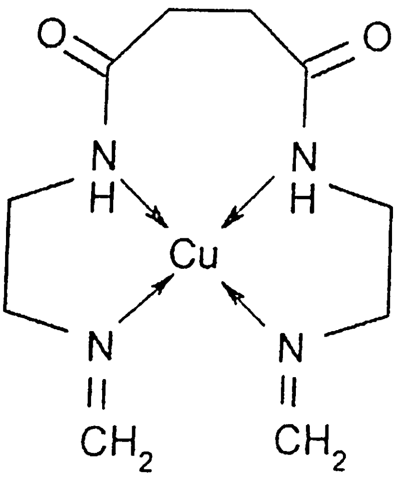

Fig 3. Proposed square planar structure of Copper – complex.

In Chapter 3, the synthesis of Co(II) and Fe(III) complexes derived from diethanolamine and acetylacetone has been discussed.

Diethanolamine is an organic ligand containing an amino group and two alcohol groups. The amino group in diethanolamine is secondary one and having primary alcohols groups. The bifunctional nature of diethanolamine enables it to serve as a variety of commercial applications such as corrosion, inhibitors, surfactants, gas purifier and herbicides[5]. Diethanolamie is a versatile ligand that readily form coordination compounds with almost all transition metal ions.

Acetylacetone is a 1, 3-diketone in which two ketones are separated by only one carbon atom. Acetylacetone is an example of bidentate ligand. Diketone derivatives find versatile applications in the synthesis of biomolecules, agrochemicals, dyes, pigments, pharmaceuticals and stabilizers for PVC and polyesters.

The transition metal complexes so synthesized are characterized by elemental analysis, melting point determination, conductance measurements and various spectral methods.

Based on these, an octahedral geometry has been assigned for both the complexes. The complexes have been tested for antimicrobial activities against bacteria Salmonella typhi and Klebsiella pneumonie and fungi. The probable structures of the complexes are given below.

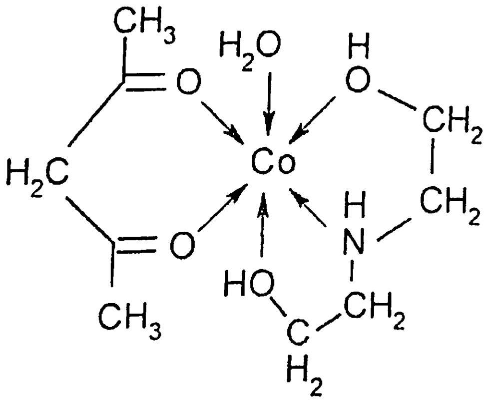

Fig 4. Proposed octahedral structure of Cobalt – complex.

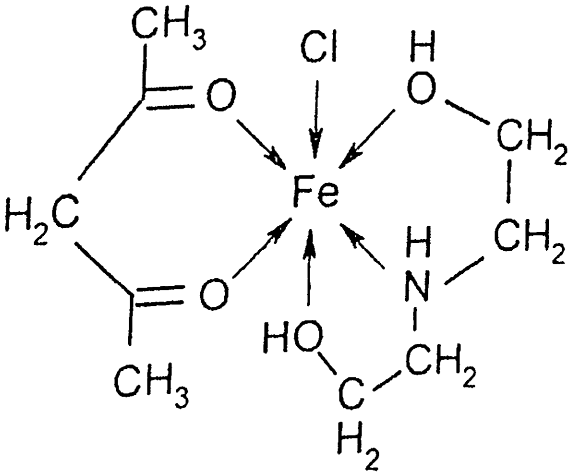

Fig 5. Proposed octahedral structure of Iron-complex.

In Chapter 4, the synthesis of Cu(II) and Ni(II) complexes derived from diethanolamine and nitro ligands has been discussed.

The reaction of ethylene oxide with aquous ammonia first produces ethanolamine which reacts with a second equivalent of ethylene oxide to give diethanolamine. Diethanolamine is a tridentate ligand and readily forms co-ordination complexes with almost all transition metal ions and behave as nitrogen and oxygen donor ligands and their transition metal complexes were synthesized[6].

Nitro ligand being a strong ligand never acts as a non coordinating ligand in Coordination Chemistry. It can bond through the nitrogen to give nitro complexes or through one of the oxygen to give the less common nitrito species[7].

The transition metal complexes so synthesized are characterized by elemental analysis, melting point determination, conductance measurements and various spectral methods. Based on these studies a square planar geometry has been assigned for both the complexes. The complexes have been screened for antimicrobial activities against bacteria Salmonella typhi and Klebsiella pneumonie and fungi.

The probable structures of the two complexes are given below.

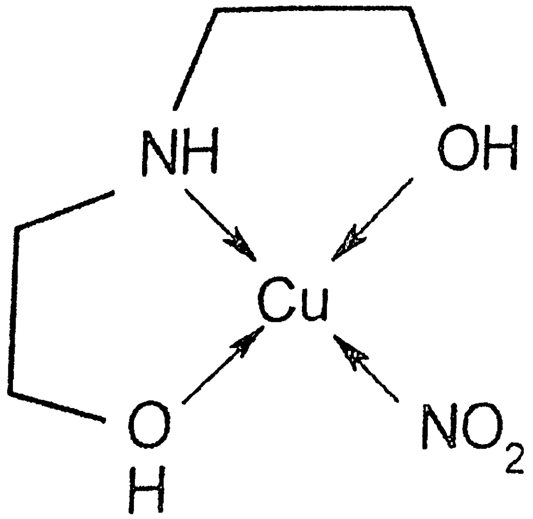

Fig 6. Proposed square planar structure of Copper complex.

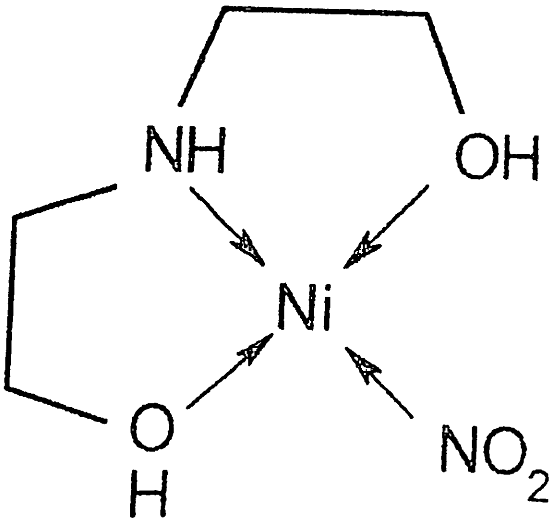

Fig 7. Proposed square planar structure of Nickel-complex.

Finally in Chapter 5 discussions of the synthesis of Zn(II) complex derived from diethanolamine and thiocyanate ligands have been done.

Diethanolamine is an example of tridentate ligand. In some cases, ethanolamines lose their ethanolic hydrogen to give ethanolaminate anion, a ligand similar to respective ethanolamines. Ethanolaminate derivatives of a number of metals have been reported[8].

Thiocyanate ions show several toxic effects towards vertebrates. The thiocyanate ions are released to the aquatic environments during the treatment of cyanide bearing wastes from the precious metal mining activity[9].

The Zinc metal complex so synthesized is characterized by elemental analysis, melting point determination, conductance measurements and various spectral methods. Based on these, a tetrahedral geometry has been assigned for the complex. The complex has been tested for antimicrobial activities against bacteria Salmonella typhi and Klebsiella pneumonie and fungi.

The probable structure of the complex is given below.

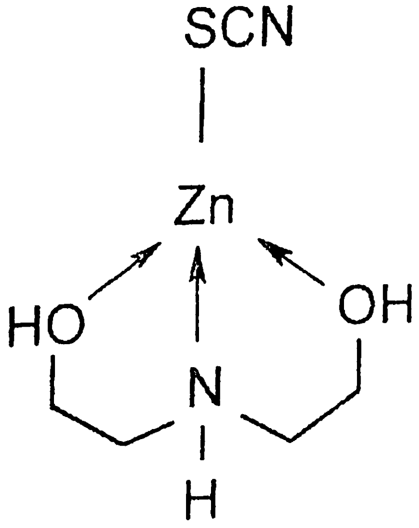

Fig 8. Proposed tetrahedral structure of Zinc – complex.

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Synthesis, Characterization And Antimicrobial Activity of Schiff Base Metal Complexes

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ABSTRACT

Co(II), Fe(III) and Cu (II) metal complexes of Schiff base derived from ethylenediamine, succinic acid and formaldehyde. The newly synthesized Schiff base complexes were characterized by elemental analysis, Melting point, conductivity, IR and UV-VIS spectral methods. The complexes have been tested for their antimicrobial activity against bacteria and fungi. The anti- microbial activity was determined in Mueller Hinton media (M H Media).

Keywords: Schiff base complex synthesis, characterization, antimicrobial activity.

INTRODUCTION

Schiff bases are versatile ligands that are synthesized from the condensation of primary amines with carbonyl groups. Schiff bases are an important class of ligands that co-ordinate with metal ions via azomethine (-CH=N-) nitrogen and have been studied extensively. The azomethine linkage is essential for biological activity and several azomethines were reported to possess antibacterial, antifungal, anticancer and diuretic activities [1]. Schiff bases are generally bi,tri or tetradentate ligands capable of forming very stable co-ordination compounds with transition metal ions. Schiff base reactions are useful in making carbon- nitrogen bonds in organic synthesis. Schiff bases appear to be an important intermediate in various enzymatic reactions [2].

A large number of Schiff bases and their coordination compounds have been extensively studied for their important properties e.g. their ability to bind reversibly with oxygen, catalytic activity in hydrogenation of olefin , transfer of an amino group and complexing ability towards some toxic metals [3]. Schiff base derived from aromatic aldehydes or their metal coordination compounds catalyze reactions like oxygenation, hydrolysis, electroreduction and decomposition [4]. Schiff bases have also been shown to exhibit a broad range of biological activities, including antifungal, antibacterial, antimalarial, antiproliferative, anti-inflammatory, antiviral, and antipyretic properties [5,6]. Imine or azomethine groups are present in various natural, natural-derived, and non-natural compounds. The imine group present in such compounds has been shown to be critical to their biological activities [7-9].The chemotherapeutic Schiff bases are attracted the attention of biochemists [10].

MATERIALS AND METHODS

All chemicals used were of analytical grade (AR) reagents and of the highest purity available. They included ferric chloride anhydrous (fisher scientific), cobalt(II) chloride hexahydrate (RANKEM), cupric(II) chloride dihydrate (fisher scientific), ethylenediamine(MERCK), succinic acid (Sd.Fine. chem ltd.) and formaldehyde (MERCK).

Elemental analyses were performed using an elemental analyser. The conductance of the complexes was measured on a Conductometer at 25^{0}C. The IR spectra were recorded in a spectrometer (4000-400 cm^{-1}). The UV -VIS electronic spectra (200-800 nm) were recorded using double beam spectrophotometer. The geometries of the metal complexes were evaluated using the molecular calculation.

Template synthesis of Schiff base metal complexes: An ethanolic solution of MXn (0.00105 mols) [M=Co(II),Fe(III) and Cu(II)] is added slowly to an ethanolic solution of ethylenediamine (0.0021 mols) with constant stirring. The mixture is refluxed for one hour at 80^{0}C. Then an ethanolic solution of succinic acid (0.00105 mols) is added drop wise and the mixture is refluxed for about 6 hours at 80^{0}C. Finally an ethanolic solution of formaldehyde (0.0021 mols) is added drop wise and the reaction mixture is refluxed for about 3 h at 80^{0}C.The mixture is then filtered, washed with ethanol and dried the residue.

RESULTS AND DISCUSSION

Elemental analysis and molar conductance: The metal complexes CoSAF and CuSAF are soluble in water while FeSAF is insoluble in water but soluble in DMSO. The analytical data and physical properties of the complexes are presented in the table 1. The data are consistent with the calculated results from the empirical formula of each compound.

Table1: Elemental analysis, specific conductivity and melting points of the complexes.

Compounds	Emperical formula	mol.wt., g/mol	Elemental analysis found(calculated)% C	H	N	Specific conductance mS/cm	Melting point ^{0}C
Co-complex	$C_{10}H_{18}O_2N_4CoCl_2$	356	32.36 (33.71)	4.81 (5.056)	14.94 (15.73)	0.30	292
Fe- complex	$C_{10}H_{18}O_2N_4FeCl_2$	353	32.42 (33.99)	4.91 (5.14)	24.31 (25.86)	0.18	282
Cu- complex	$C_{10}H_{18}O_2N_4Cu$	289.5	39.07 (41.45)	5.85 (6.22)	18.42 (19.34)	0.36	171

Specific conductance of Co-complex=0.30mS cm^{-1} at 25^{0}C, Specific conductance of Fe-complex =0.18mS cm^{-1} at 25^{0}C, Specific conductance of Cu-complex=0.36mS cm^{-1} at 25^{0}C. The above conductance values indicates that the complexes are electrolytes [11]

IR Spectra: The significant IR bands for the complexes are complied and presented in table 2. The IR spectrum of the complexes, a sharp band observed at 1616 cm^{-1} is assigned to the (C=N) mode of the azomethine group. This shifts to lower wave number 1606- 1609 cm^{-1} in all the complexes suggesting the co-ordination of the azomethine nitrogen to the metal centers. A strong band observed at 1640-1690 cm^{-1} is assigned to (C=O, amide) of the ligand.

Table 2. FT-IR spectral data for the metal complexes

Componds	V(C=O), cm^{-1}	V(C=N), cm^{-1}	V(M-N), cm^{-1}	V(C-N), cm^{-1}	V(N-H), cm^{-1}
Co-complex	1640-1690	1600-1620	457-464	1080-1360	3100-3500
Fe- complex	1640-1690	1600-1620	457-464	1080-1360	3100-3500
Cu- complex	1640-1690	1600-1620	457-464	1080-1360	3100-3500

UV-Vis Electronic spectra: The UV-VIS spectral data of the complexes are presented in table3. The electronic absorption spectra of the complexes of Cobalt and Copper were recorded in double distilled water while that of Fe-complex was recorded in DMSO in the range 200-700 nm. For the complex of Cobalt absorption peak was found at 478 nm and 413 nm and for the complex of iron absorption peak was found at 644.5 nm, 463.0 nm, 446.5 nm, 363.5 nm and209.0 nm. For the complex of Copper absorption peak was found at 236.4 nm and 213.0 nm.

APPLICATIONS

Antimicrobial Studies: The free Schiff base and its complexes had been tested for their antibacterial activity against Pseudomonas aeruginosa, Proteus vulgaris, Proteus mirabilis, Klebsiella pneumonia and Staphylococcus aureus. Fe(III)complexes with Schiff base ligands derived by the condensation of o-phenylenediamine, salicylaldehyde and isatin/2-hydroxyl naphthaldehyde/acetylacetone were synthesized by A.Nagajothi and his co-workers [12].The complexes were screened for antimicrobial activities against the bacteria Staphylococcus aureus, Escherichia coli and fungi Candida albicans. The in vitro biological screening effects of the investigated compounds were tested against the bacteria, Klebsiella pneumonia and salmonella typhi and fungi. Stock solutions of 2 mg of the complexes were dissolved in 1ml distilled water while 2 mg of the compound Fe-complex was dissolved in1ml DMSO. Serial dilution of the compounds were prepared in sterile distilled water to determine the minimum inhibitory concentration (MIC) .Different dilution of the stock solution were applied on the 10mm diameter sterile disc .The discs were placed on a incubator for 3 days .Antibacterial and antifungal potential of the complexes were assessed in terms of zone of inhibition of bacterial and fungal growth in figures 1-3.

The minimum inhibitory concentration (MIC)were calculated as the highest dilution showing complete inhibition of the tested bacterial and fungal strains and are reported in Table 4-7. The complexes were effective against both bacteria and fungi. It is evident from the table 7 that the MIC values for the complexes of Fe- and Cu- were 1.0mg ml^{-1} while that of Co-complex was 1.2mg ml^{-1} [12].

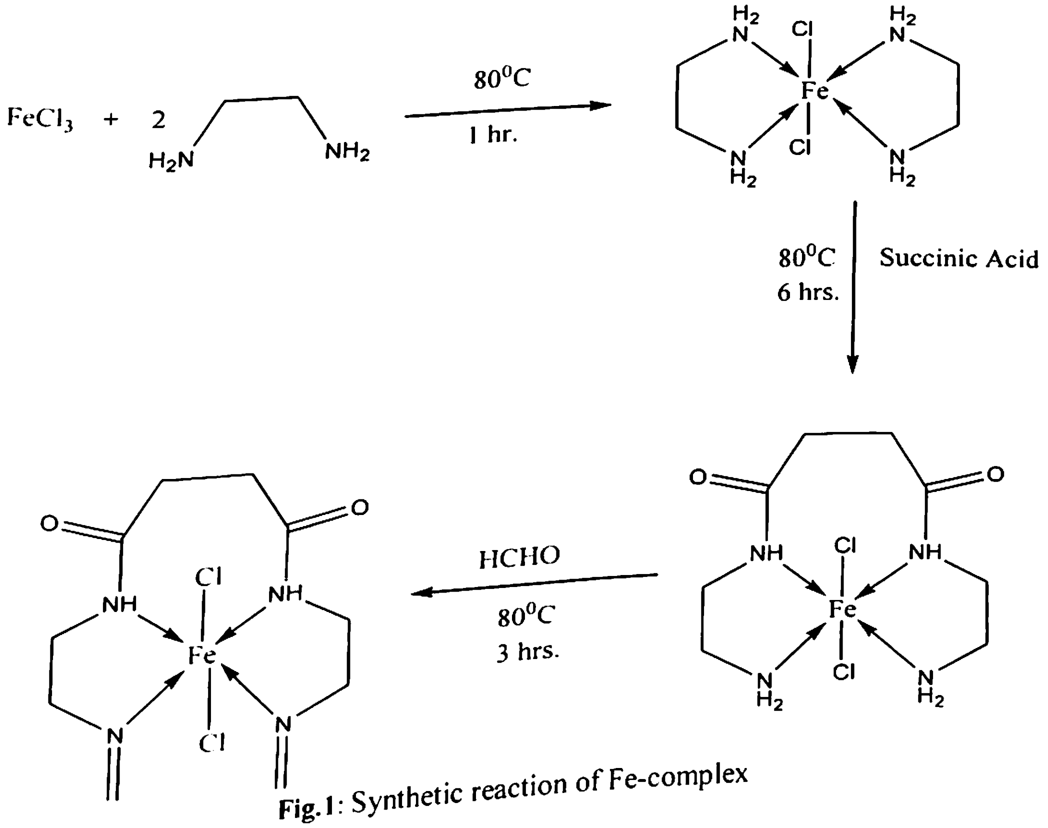

Fig.1: Synthetic reaction of Fe-complex

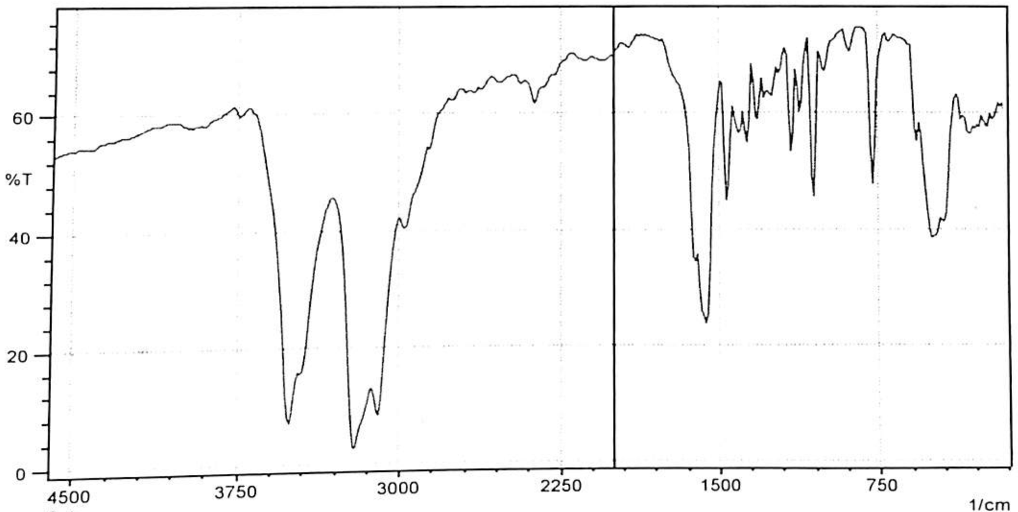

Fig.2: FT-IR spectra of metal complex

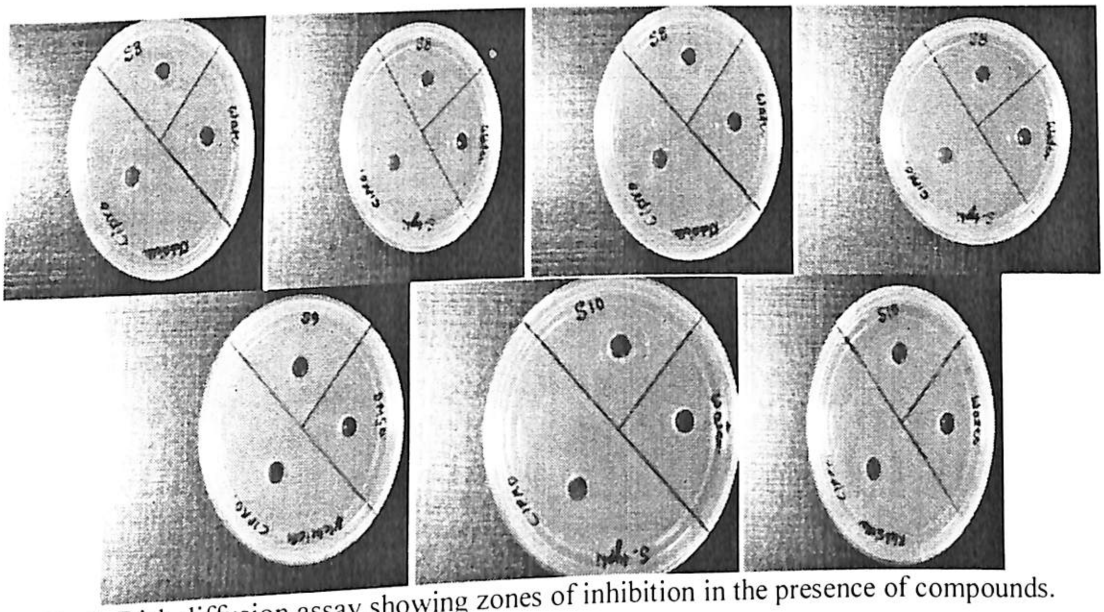

Fig.3: Disk diffusion assay showing zones of inhibition in the presence of compounds.

Table 4: Determination of MIC for antibacterial and antifungal activity of the Fe-complex

Micro-organism	2.0 mg/ml	1.7 mg/ml	1.5 mg/ml	1.2 mg/ml	1.0 mg/ml	0.7 mg/ml	0.5 mg/ml	0.1 mg/mg
S. typhi	-	-	-	-	-	+	+	+
K. pneu- monie	-	-	-	-	-	+	+	+
Fungi	-	-	-	-	-	+	+	+

Table-5: Determination of MIC for antibacterial and antifungal activity of the Co-complex

Micro-organism	2.0 mg/ml	1.7 mg/ml	1.5 mg/ml	1.2 mg/ml	1.0 mg/ml	0.7 mg/ml	0.5 mg/ml	0.1 mg/ml
S. typhi	-	-	-	-	+	+	+	+
K. pneu- monie	-	-	-	-	+	+	+	+
Fungi	-	-	-	-	+	+	+	+

Table 6: Determination of MIC for antibacterial and antifungal activity of the Cu-complex

Micro-organism	2.0 mg/ml	1.7 mg/ml	1.5 mg/ml	1.2 mg/ml	1.0 mg/ml	0.7 mg/ml	0.5 mg/ml	0.1 mg/ml
S. typhi	-	-	-	-	-	+	+	+
K. pneu-monie	-	-	-	-	-	+	+	+
Fungi	-	-	-	-	-	+	+	+

Table 7: Antibacterial and antifungal activity of the complexes: MIC values

Micro-organism	Complex	MIC value
Bacteria	Fe-complex	1.0mg/ml
Fungi	Do	1.0mg/ml
Bacteria	Co-complex	1.2mg/ml
Fungi	Do	1.2mg/ml
Bacteria	Cu-complex	1.0mg/ml
Fungi	Do	1.0mg/ml

CONCLUSIONS

In this paper, we have reported the synthesis of Co(II), Fe(III) and Cu(II) metal complexes of Schiff base derived from ethylenediamine, succinic acid and formaldehyde .The complexes were characterized by spectral methods and analytical data . Based on these an octahedral geometry has been assigned for Co(II) and Fe(III) complexes while Cu(II) complex has square planner geometry . The antimicrobial studies carried out with the complexes confirm that they are good antibacterial and antifungal agents with their MIC values.

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Synthesis, Characterization and Antimicrobial Activity of Transition Metal Complexes with Diethanolamine and Acetylacetone

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ABSTRACT

Diethanolamine and acetylacetone are versatile ligands that readily form co-ordination compounds with almost all transition metal ions. Co(II) and Fe(III) metal complexes derived from diethanolamine and acetyl-acetone have been prepared. The newly synthesized compounds have been confirmed on the basis of elemental analysis, melting points, conductivity, IR, UV-VIS spectral methods .The metal complexes have been screened for their antibacterial and antifungal activity in Mueller Hinton Media.

Keywords: synthesis, characterization, antibacterial and antifungal activity.

INTRODUCTION

Ethanolamines are a class of organic molecules containing amino and alcohol groups. The amino group may be primary (monoethanolamine, mea), secondary(diethanolamine, dea) or tertiary (triethanolamine, tea) and display reactivity of the corresponding amines. Ethanolamines are primary alcohols and therefore, reactions are typical of primary alcohols. The bifunctional nature of ethanolamines enables them to serve as a variety of commercial applications such as corrosion inhibitors, surfactants, gas purification and herbicides [1].

Ethanolamines are also versatile ligands that readily form co-ordination compounds with almost all metal ions and behave as nitrogen and oxygen donor ligands and their transition metal complexes were synthesized[2,3]. In some cases, ethanolamines lose their ethanolic hydrogen being as ethanolaminate anions, which also behave as ligands similar to ethanolamines and ethanolaminate derivatives of a number of metals have been reported recently [4-7].

Diethanolamine, dea, is an example of tridentate ligand and is a common substances used in the chemical and pharmaceutical industries as an intermediate for the production of detergents, solubilizers, cosmetics, drugs, textile finishing agents and as an absorbent for acidic gases.(Sutton,1963).

Acetylacetone is a beta-diketone (1, 3 diketone) in which two ketones are separated only by one carbon. The beta-ketone is stable as a conjugated enol rather than alpha-diketone due to the delocalization which makes the counter-ion more stable and less likely to regain the proton.The keto form[$CH_3COCH_2COCH_3$]

and enol form[$CH_3COCH=C(OH)CH_3$] co-exist in solution. This keto-enol tautomerism results in the tautomeric migration of a hydrogen atom from an adjacent carbon atom to a carbonyl group of a keto compound to produce the enol form of the compound. Although the enolate form of acetylacetone anion is most commonly found in co-ordination complexes, other possibilities are also known. Acetylacetonate is an example of a bidentate ligand.Metal acetylacetonate complexes which can be used as phase precursors in alkoxo synthesis of esters finds considerable attention[8-11]. Diketone derivatives find versatile applications in making biomolecules, agrochemicals, dyes, pigments, pharmaceuticals and stabilizers for PVC and Polyester.

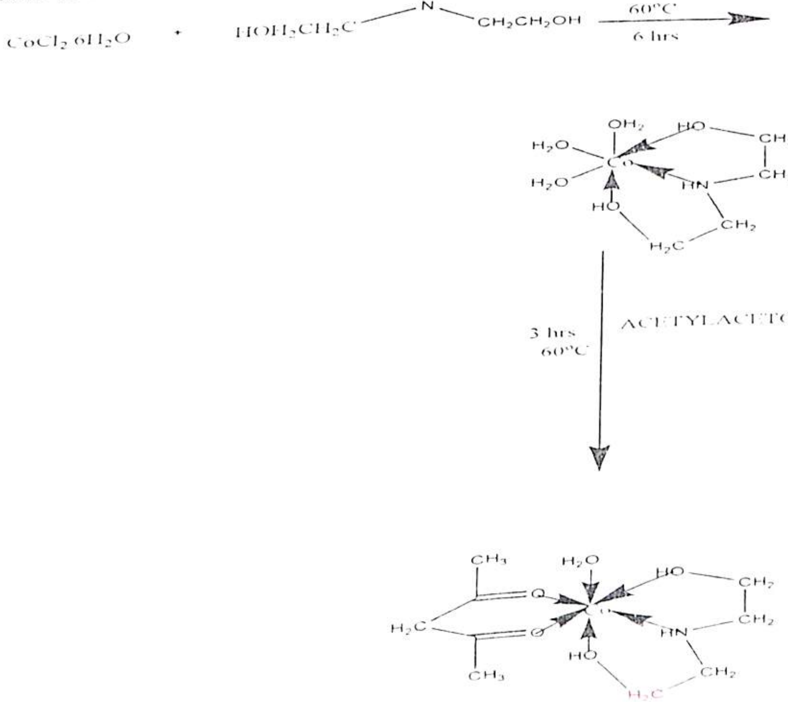
MATERIALS AND METHODS

All chemicals used were of analytical grade (AR) reagents and of highest purity available .They included ferric chloride anhydrous(fisher scientific), cobalt(II)chloride hexahydrate (RANKEM), diethanolamine (MERCK) and acetylacetone (MERCK). Elemental analysis was performed using an elemental analyser. The measurement of conductance of the complexes were measured using a conductometer at 30° C .The IR spectra were recorded in a spectrometer (4000-400cm-1). The UV-VIS electronic spectra (200-800nm) were performed using double beam spectrophotometer.The geometries of the metal complexes was determined using the molecular calculations.

Synthesis of the metal complexes: An ethanolic solution of MX_n(0.005 mols) M=Co and Fe, is added slowly to an to an ethanolic solution of diethanolamine (0.005mols) with constant stirring. The mixture is refluxed for 6 h at 60°C. Then an ethanolic solution of acetylacetone (0.005 mols) is added drop wise and the mixture is refluxed for 3 h at 60°C. The mixture is then filtered, washed with ethanol and dried the residue.

RESULTS AND DISCUSSION

The synthetic route of the metal complexes were depicted in scheme 1 .



Scheme 1 Synthetic reaction of Co-complex.

Elemental analysis and molecular conductance: The metal complex of iron is soluble in water and the complex of cobalt is soluble in hot water and ethanol. The analytical data and physical properties of the complexes are presented in table 1. The data are consistent with the calculated results from the empirical formula of each compound.

Table 1: Elemental analysis, specific conductance and melting points of the complexes.

COMPLEX	*EMPERICAL*	MOLE WT g/mol	ELEMENTAL ANALYSIS FOUND(CALCULATED)%			*SPECIFIC* CONDUCTANCE mS/cm	*MELTING* POINT 0C
			C	H	N		
Co-complex	$C_9H_{21}O_5NCo$	282.2	36.38 (38.27)	7.21 (7.50)	4.761 (4.961)	0.14	315
Fe – complex	$C_9H_{21}O_5NFe$	279.1	36.88 (38.70)	7.27 (7.52)	4.82 (5.02)	0.26	186

Conductance of Fe-complex: A 1mM solution is taken for conductivity.

Conductance of Co-Complex : Co-Complex is prepared by dissolving 0.0028g. of the salt in 1mL ethanol and diluting the solution to 10 mL with double distilled water. The conductance Fe-complex=0.26 mS cm^{-1} at 30^0 C. The conductance of Co-complex=0.14 mS cm^{-1} at 30^0 C. The above conductance values indicate that the complexes are electrolytes [12].

IR spectra: The significant IR bands for the complexes are complied and presented in table2. The IR spectrum of the complexes (Fig.1), a sharp band observed at 1700 cm^{-1} is assigned to the v (C=O, carbonyl) mode. This shifts to a lower wave number suggesting the co-ordination of the carbonyl oxygen to the metal centre. A strong sharp band observed at 3400 cm^{-1} is assigned to v (>N-H) of the ligand.

Table 2. IR spectral data for the metal complexes

Complex	V(C=O)	V(M-N)	V(C-N)	V(>N-H)	V(C-O)	V(M-O)
Co-complex	1700	457-464	1600	3400	1100	537-555
Fe-complex	1700	457-464	1600	3400	1100	537-555

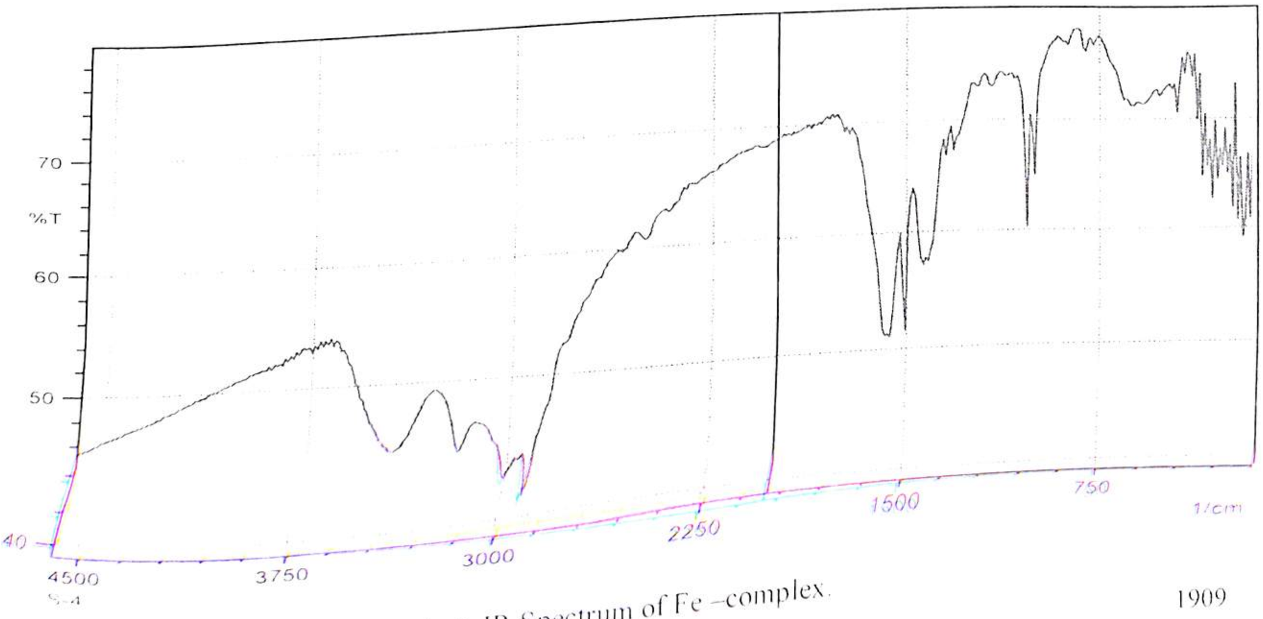


Fig 1. IR Spectrum of Fe –complex.

UV-VIS-Electronic spectra: The UV-VIS spectral data of the complexes are presented in table 3. The electronic absorption spectra of the Co- complex is made in ethanol and then diluting with double distilled water while the Fe- complex is soluble in double distilled water in the range 200-700 nm. For the Co-complex, absorption peak was found at 270.2 nm, 213.8 nm and 209.2 nm (Fig. 2) and for the Fe-complex, absorption peak was found at 378.0 nm, 330.0 nm, 281.5 nm, 442.5 nm, 356.0 nm, 300.5nm and 239.5 nm (Fig.3).

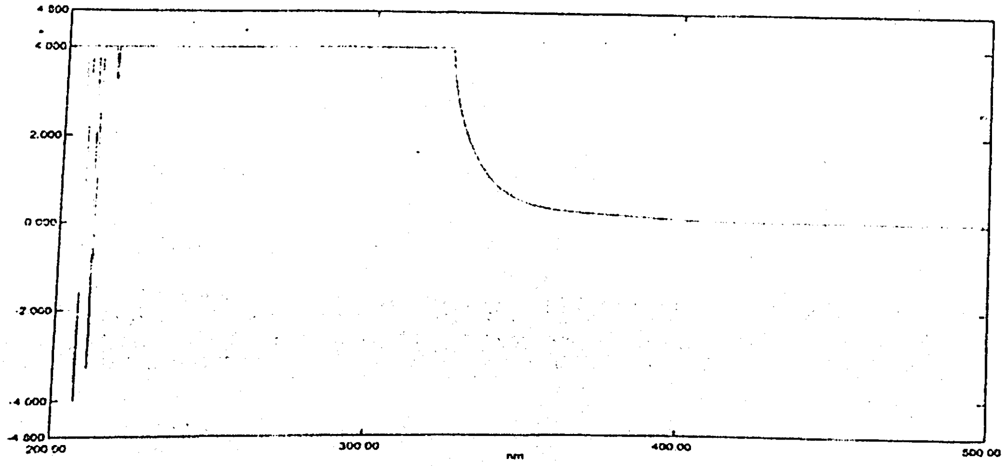


Fig 2: UV-VIS-Spectrum of Co-complex.

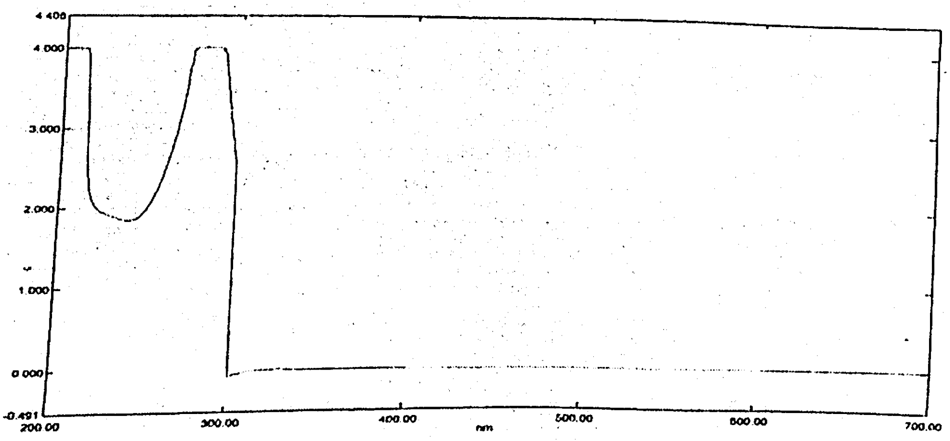


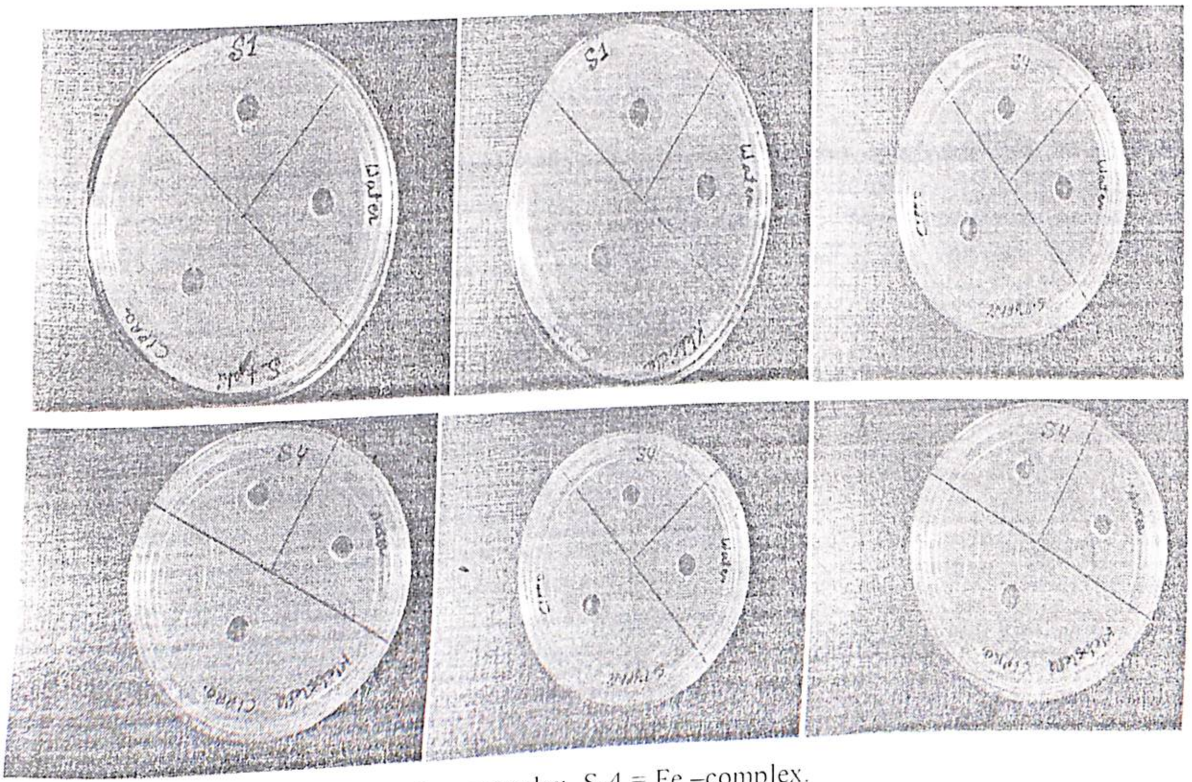
Fig 3: UV-VIS-Spectrum of Fe-Complex.

Table -3 Electronic spectral data for the metal complexes

COMPLEX	Absorbance (nm)	Assignment	Geometry
Co-complex	270.2	Octahedral	Octahedral
-do-	213.8	Pi-pi*	-do-
-do-	209.2	Pi-pi*	-do-
Fe-complex	378.0	Octahedral	Octahedral
-do-	330.0	n-pi*	-do-
-do-	281.5	Pi-pi*	-do-

APPLICATIONS

Antimicrobial activity: An antimicrobial is a substance that kills or inhibits the growth of micro-organism such as bacteria, fungi or protozoans. The discovery of antimicrobials like penicillin's by Alexender Fleming and tetracyclines paved the way for better health for millions around the world. The in-vitro biological screening effects of investigated compounds were tested against the bacteria Salmonella typhi and Klebsiella pneumonie and fungi. Stock solution of 2mg/ml concentration were prepared by dissolving the compounds in hot water and serial dilution of the compounds were prepared in sterile water to determine the minimum inhibition concentration (MIC). The nutrient Mueller Hinton media (MH Media) was poured into petriplates. Different dilution of the stock solution was applied on the 10 mm diameter sterile disc. The discs were placed in incubator for 3 days. The antibacterial and antifungal potential of the complexes were assessed in terms of zone of inhibition (12) of bacterial and fungal growth in figures 4. The minimum inhibitory concentration(MIC) were calculated as the highest dilution showing complete inhibition of the tested bacterial and fungal strain and are reported in table 4-5.



S-1 = Co –complex, S-4 = Fe –complex.

Fig 5: Disk diffusion assay showing zones of inhibition in the presence of compounds.

Table 4: Determination of MIC for antibacterial and antifungal activity of the Co-complex.

Micro-organism	2.0 mg/ml	1.7mg/ml	1.5 mg/ml	1.2 mg/ml	1.0 mg/ml	0.7mg/ml	0.5mg/ml	0.1mg/ml
S. typhi	-	-	-	+	+	+	+	+
K. pneumo-nie	-	-	-	-	+	+	+	+
Fungi	-	-	-	-	+	+	+	+

Table-5: Determination of MIC values for antibacterial and antifungal activity of the Fe-complex.

Micro-organism	2.0mg /ml	1.7mg /ml	1.5mg /ml	1.2mg /ml	1.0mg /ml	0.7mg /ml	0.5mg /ml	0.1mg /ml
S. typhi	-	-	-	+	+	+	+	+
K pneu- monie	-	-	-	-	+	+	+	+
Fungi	-	-	-	-	+	+	+	+

The Co-complex is effective against both bacteria and fungi. It is evident from the table-4, that the MIC-value for Co-complex against bacteria S. typhi is 1.5mg mL^{-1} while for bacteria K. pneumonie MIC value is 1.2mg m L^{-1}.

The Co-complex is antifungal at MIC- value of 1.2mg m L^{-1}.The Fe-complex is effective against both bacteria and fungi. It is evident from the table-5, that the MIC –value for Fe-complex against bacteria S. typhi is 1.5mg m L^{-1} while for bacteria K. pneumonie MIC-value is 1.2 mg m L^{-1}. The complex is antifungal at MIC-value of 1.2mg m L^{-1}.

CONCLUSIONS

In this paper, we have reported the synthesis of Co(II) and Fe(III) metal complexes with diethanolamine and acetylacetone. The complexes were charactrrized by spectral methods and analytical data. Based on these an octahedral geometry has been assigned for both the complexes. The antimicrobial studies carried out with the complexes confirms that they are antibacterial and antifungal agents with their MIC values.

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Table-5: Determination of MIC values for antibacterial and antifungal activity of the Fe-complex.

Micro-organism	2.0mg /ml	1.7mg /ml	1.5mg /ml	1.2mg /ml	1.0mg /ml	0.7mg /ml	0.5mg /ml	0.1mg /ml
S. typhi	-	-	-	+	+	+	+	+
K. pneu- monie	-	-	-	-	+	+	+	+
Fungi	-	-	-	-	+	+	+	+

The Co-complex is effective against both bacteria and fungi. It is evident from the table-4, that the MIC-value for Co-complex against bacteria S. typhi is 1.5mg mL^{-1} while for bacteria K. pneumonie MIC value is 1.2mg m L^{-1}.

The Co-complex is antifungal at MIC- value of 1.2mg m L^{-1}.The Fe-complex is effective against both bacteria and fungi. It is evident from the table-5, that the MIC –value for Fe-complex against bacteria S. typhi is 1.5mg m L^{-1} while for bacteria K. pneumonie MIC-value is 1.2 mg m L^{-1}. The complex is antifungal at MIC-value of 1.2mg m L^{-1}.

CONCLUSIONS

In this paper, we have reported the synthesis of Co(II) and Fe(III) metal complexes with diethanolamine and acetylacetone. The complexes were charactrrized by spectral methods and analytical data. Based on these an octahedral geometry has been assigned for both the complexes. The antimicrobial studies carried out with the complexes confirms that they are antibacterial and antifungal agents with their MIC values.

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Synthesis, Characterization and Antimicrobial Activity of Metal Complexes with Diethanolamine and Nitro Ligands

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Abstract:

Cu(II) and Ni(II) metal complexes derived from diethanolamine and nitro ligands have been prepared. The newly synthesized compounds have been confirmed on the basis of elemental analysis, melting points, conductivity, IR, UV-VIS and NMR(1H) spectral methods .The metal complexes have been tested for their antimicrobial activity in Mueller Hinton Media, (MH Media) .

Key words: Synthesis, characterization, antibacterial and antifungal activity.

Introduction:

Ethanolamines are a class of organic compounds containing *amine and alcohol groups.*

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The reaction of ethylene oxide with aqueous ammonia first produces ethanolamine.

$$C_2H_4O + NH_3\ (H_2NCH_2CH_2OH)$$

Which reacts with a second and third equivalent of ethylene oxide to give diethanolamine and triethanolamine.

$$C_2H_4O + H_2NCH_2CH_2OH = HN(CH_2CH_2OH)_2$$

$$C_2H_4O + HN(CH_2CH_2OH) = N(CH_2CH_2PH)_3$$

Diethanolamine is a tridentate ligand and readily forms co-ordination complexes with almost all metal ions and behave as nitrogen and oxygen donor ligands and their transition metal complexes were synthesised (1,2)

In some cases, diethanolamine loses its ethanolic hydrogen being as diethanolaminate anion, which also behave as a ligand similar to diethanolamine and diethanolaminate derivatives of metals have been reported (3-6.).

Diethanolamine is used in the production of diethanolamides , which are common ingrediants in cosmetics and shampoos added to confer a creamy texture and foaming action . Diethanolamine is also a common material used in the chemical and pharmaceutical industries as an intermediates for the production of detergents,drugs,textile finishing agents and as an absorbent for acidic gases.(Sutton,1963)

Nitrite being a strong ligand never acts as a non – coordinating or ionic ligand in co-ordination compounds. It can bond through the nitrogen to give nitro complexes or through one of the oxygen to give the less common nitrito species. It can also act as a bridging ligand bonding through the nitrogen and one of the oxygens (7).

Materials and Methods:

All chemicals used were of analytical grade (AR) reagents and of the highest purity available. They included cupric chloride dihydrate (fisher scientific), nickel chloride hexahydrate

(Qualigens fine chemicals), diethanolamine (MERCK) and sodium nitrite (s.d.fine chem.ltd.)

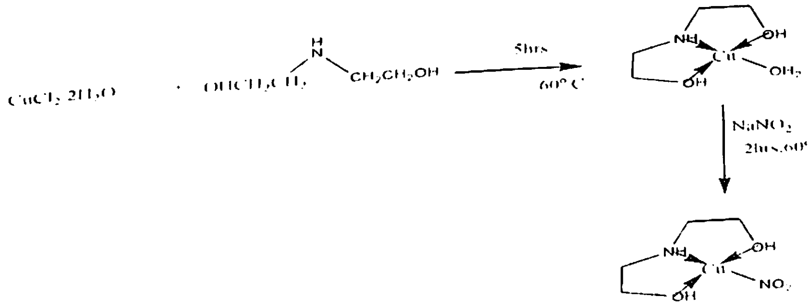
The elemental analysis was performed using an elemental analyser. The measurement of conductance of the complexes were measured using a conductometer at 30 deg. Celcius. The IR spectra were recorded in a spectrometer (4000-400 cm-1). The UV-VIS electronic spectra (200-800nm) were performed using a double beam spectrophotometer .The geometries of the metal complexes were determined using molecular calculations.

Synthesis of the metal complexes:

An ethanolic solution of MX_2 (0.005 moles,) M=Cu and Ni, is added slowly to an ethanolic Solution of diethanolamime (0.005 mole,) with constant stirring. The mixture is refluxed for 5 hours at 60 deg. Celsius. Then an aqueous solution of sodium nitrite (0.005 mol) is added drop wise and the mixture is refluxed for 2 hours at 60 deg. Celsius. The mixture is filtered, washed with ethanol and dried the residue.

Result and Discussion:

The synthetic route of the metal complexes were outlined in scheme 1:



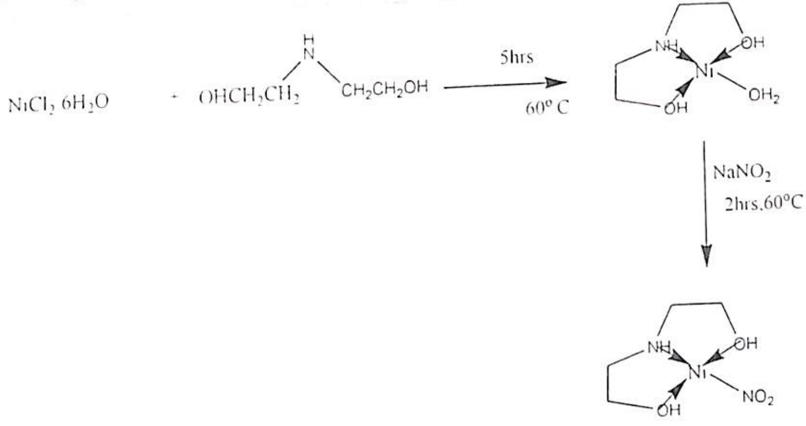


Fig 1: Reactions for the synthesis of Cu and Ni complexes.

Elemental analysis and molecular conductance:

The metal complexes are insoluble in water but soluble in DMSO. The analytical data and physical properties of the complexes are presented in the following table. The data are consistent with the calculated results from the empirical formula of each compound.

Table1: Elemental analysis, specific conductance and melting points of the complexes.

Complex	Emperical formula	Mol.wt g/mol	Elemental analysis found(calculated)%			Specific conductance mS/cm (30deg.C)	Melting point Deg C
			C	H	N		
Cu-complex	$C_4H_{11}O_4N_2Cu$	214.64	20.81 (22.36)	4.86 (5.167)	12.27 (13.05)	0.03	>300
Ni-complex	$C_4H_{11}O_4N_2Ni$	209.84	21.73 (22.87)	5.02 (5.284)	12.67 (13.34)	0.02	>300

Conductance of Cu-complex: A milimolar solution of the complex is prepared by dissolving 0.0022 g. of the complex in 1ml DMSO and diluted to 10ml with double distilled water.

Conductance of Ni-complex: 1milimolar solution of the complex is prepared by dissolving 0.0021g. of the complex in 1ml DMSO and diluted to 10ml with double distilled water.

Conductance of Cu-complex =0.03 mS/cm at 30 deg. C

Conductance of Ni –complex =0.02 mS/cm at 30 deg. C

The low conductance values indicates that the above complexes are non electrolytes.(8)

IR spectra:

The significant IR bands for the complexes are compiled and presented in table-2. The IR spectrum of the complexes, a sharp band observed at 1600 cm^{-1} is assigned to the υ(C-N) mode. This shifts to a lower wavenumber suggesting the co-ordination of the nitrogen to the metal centre. A strong sharp band observed at 3400cm^{-1} is assigned to υ (>N-H) of the ligand.

Table: 2 IR spectral data for the metal complexes:

COMPLEX	υ(M-N)	υ (C-N)	υ (C-O)	υ (>N-H)	υ (M-O)
Cu-complex	457-464	1600	1100	3400	537-555
Ni- complex	457-464	1600	1100	3400	537-555

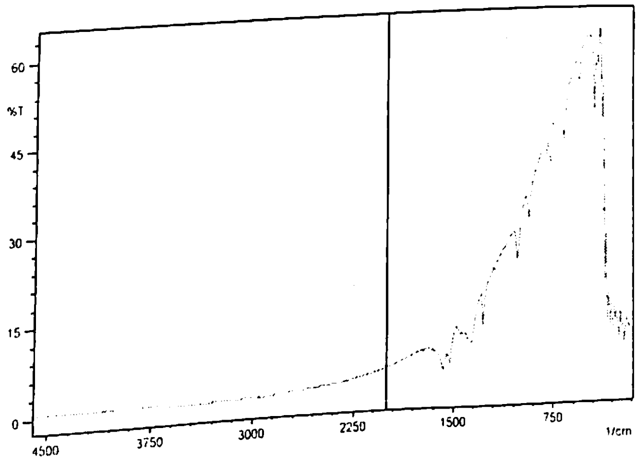


Fig 2: IR spectrum of Ni- complex.

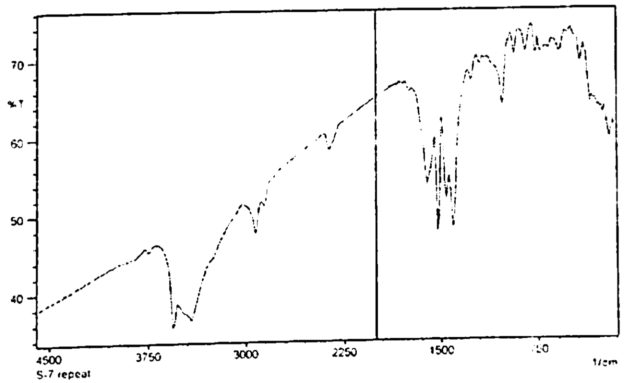


Fig 3: IR spectrum of Cu -complex.

UV-VIS spectra:

The UV-VIS spectral data of the complexes are presented in Table-3. The electronic absorption spectra of both the complexes of Copper and Nickel was made in DMSO and then diluting the solution with double distilled water in the range 190- 700 cm^{-1} . For the Cu-complex, absorption peak was found at 248.5 nm, 228.0 nm and 199.0 nm. And for the Ni-complex, absorption peak was found at 283.5 nm and 232.5 nm.

Table -3: Electronic spectral data for the metal complexes.

COMPLEX	Absorbance (nm)	Assignment	Geometry
Cu- complex	248.5	Squre planner	Squre planner
-do-	228.0	π- π *	-do-
-do-	199.0	π - π *	-do-
Ni- complex	283.5	Squre planner	Squre planner
-do-	232.5	π - π *	-do-

Fig 4:UV-VIS-Spectrum of Cu-complex.

Fig 5: UV-VIS-Spectrum of Ni-complex.

NMR spectra:

Here NMR spectra of Ni-complex is discussed. In the spectrum graph report we found three signals given by the complex in proton (H-1) NMR.

At 3.757 ppm the signal is corresponding to proton (H-1) attached to the secondary nitrogen atom. At 3.133 ppm, the signal is corresponding to two protons (H-1) near to the hydroxyl group. The signal corresponding to 2.162 ppm is due to two protons (H-1) near to the secondary nitrogen atom.

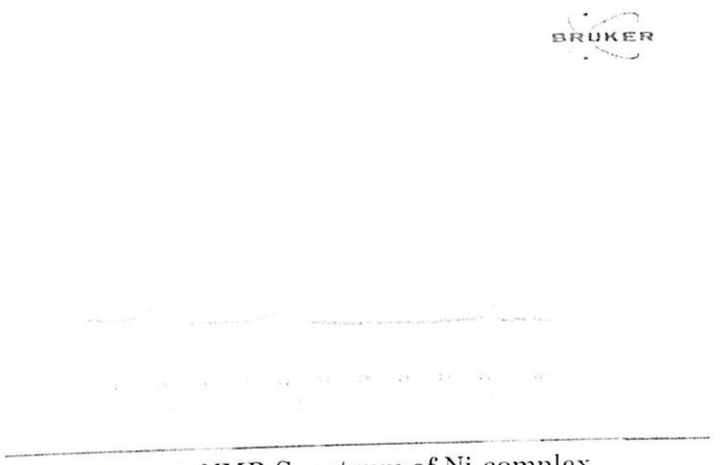
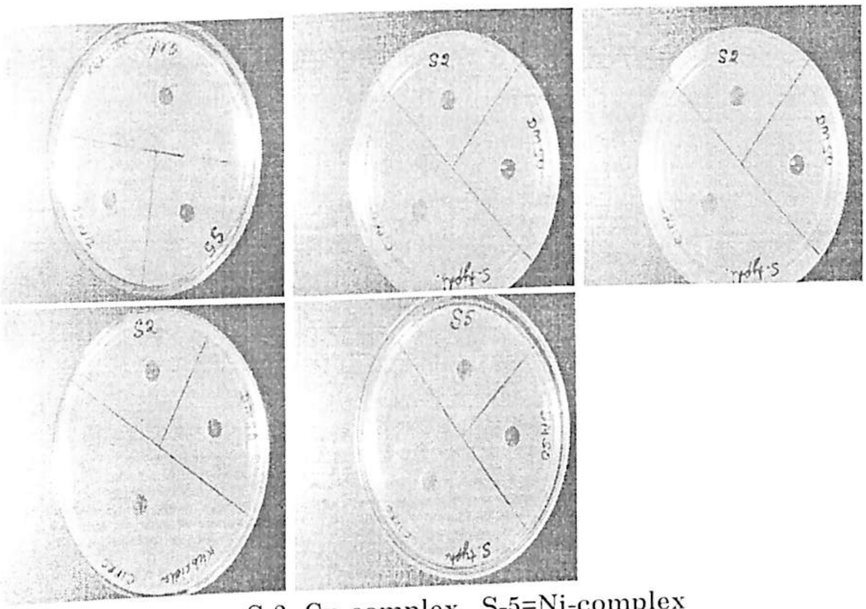


Fig 6: NMR-Spectrum of Ni-complex.

Applications:

Antimicrobial activity: An antimicrobial is a substance that kills or inhibits the growth of micro-organism such as bacteria, fungi or protozoans. The discovery of antimicrobials like penicillins by Alexender Fleming and tetracyclines paved the way for better health for millions around the world.

The in vitro biological screening effects of the investigated compounds were tested against the bacteria Salmonella typhi and Klebsiella pneumonie and fungi. Stock solution of 2mg/ml concentration were prepared by dissolving the compounds in dimethyl sulphoxide (DMSO) and serial dilution of the compounds were prepared in sterile distilled water to determine the minimum inhibition concentration (MIC).The nutrient Mueller Hinton media was poured into petriplatis. Different dilution of the stock solutions were applied on the 10mm diametis staile disc. The discs were placed in an incubator for 3 days. Antibacterial and antifungal potential of the complexes were assessed in terms of zone of inhibition of bacterial and fungal growth in figures 1,2. The minimum inhibitory concerntration (MIC) were calculated on the highest dilution showing complete of the tested bacterial and gungal strain and we reported in table 4,5.



S-2=Cu-complex, S-5=Ni-complex

Fig 6: Disk diffusion assay showing zones of inhibition in the presence of compounds

Table-4: Determination of MIC for antibacterial and antifungal activities of the complex Cu-complex.

Micro-organism	2.0 m g/mi	1.7mg/ml	1.5mg/ml	1.2 m g/ml	1.0 m g/ml	0.7 m g/ml	0.5 m g/ml	0.1 m g/ml
S. typhi	-	-	-	+	+	+	+	+
K. pneu-monie	-	-	-	+	+	+	+	+
Fungi	-	-	-	+	+	+	+	+

Table-5: Determination of MIC for antibacterial and antifungal activity of the complex Ni- complex.

Micro-organism	2.0mg /ml	1.7 m g/ml	1.5mg /ml	1.2mg /ml	1.0 m g/ml	0.7mg /ml	0.5mg /ml	0.1mg /ml
S. typhi	-	-	-	-	+	+	+	+
K. pneu-monie	-	-	-	-	+	+	+	+
Fungi	-	-	-	-	+	+	+	+

Table -6: Antibacterial and antifungal activity of the complexes : MIC value.

Micro-organism	Complex	MIC value
Bacteria	Cu- complex	1.5mg/ml
Fungi	Cu- complex	1.5mg/ml
Bacteria	Ni – complex	1.2mg/ml
Fungi	Ni- complex	1.2mg/ml

The complexes were effective against both bacteria and fungi. It is evident from the table - 6 that MIC values (9) for the Cu-complex was 1.5mg/ml for both bacteria and fungi while that of Ni-complex was 1.2mg/ml.

Conclusion:

In this paper, we have reported the synthesis of Cu(II) and Ni(II) metal complexes with diethanolamine and nitro ligands. The complexes were characterized by spectral methods and analytical data. Based on these, a square planner geometry has been assigned for both the complexes. The antimicrobial studies carried out with the complexes confirms that they are antibacterial and antifungal agents with their MIC values.

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Manuscript Acceptance Letter

TITLE: "SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF METAL COMPLEX WITH DIETHANOLAMINE AND THIOCYANATE LIGANDS"

Edition: (ISSUE 4, Vol.5) October 2014

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We are pleased to inform you that your manuscript is accepted for publication in next edition of IJAST. Your paper is peer reviewed by our expert panel and they found

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Abstract:	Good
Introduction	Satisfactory , more references can be added
Methodology:	Good,
Results:	Satisfactory,
How well is the paper integrated with current research :	good
Over all évaluation on the manuscrit:	Satisfactory
Bibliography/References:	more references can be added
Others:	NA
Figures:	More figure can be added
Tables:	More figure can be added

SECTION II - Please rate the following: ***(1 = Excellent) (2 = Good) (3 = Fair) (4 = poor)***

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