INVESTIGATIONS ON REACTIVITY OF COPPER(II) AMINO ACID COMPLEXES, DINUCLEAR METAL COMPLEXES OF ROBSON TYPE LIGANDS AND THEIR REDUCED ANALOGUES

A THESIS
SUBMITTED FOR THE AWARD OF THE DEGREE OF

DOCTOR OF PHILOSOPHY
IN
CHEMISTRY

BY
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MARCH 1994

to my

beloved parents *

CONTENTS

CERTIFICATE

Certified that the work contained in this thesis entitled, **"Investigations on reactivity of copper(II) amino acid complexes, dinuclear metal complexes of Robson type ligands and their reduced analogues"**, has been carried out by **Chepuri Ramakishan Rao**, under my supervision and the same has not been submitted elsewhere for a degree.

DEAN

SCHOOL OF CHEMISTRY

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STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the school of chemistry, University of Hyderabad, Hyderabad, under the supervision of Professor P.S. Zacharias.

In keeping with the general practice of reporting scientific observations, due acknowledgements have been made wherever the work described is based on the findings of other investigators. Any omission which might have occurred by oversight or error is regretted.

Chepuri Ramakishan Rao

21-10-04

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Chepuri Ramakishan Rao

Abbreviations

acac	acetyl acetonate anion
ala	alaninato anion
CV	cyclic voltammetry
DMF	dimethyl formamide
DMSO	dimethyl sulfoxide
DTBC	di-t-butyl catechol
DTBQ	di-t-butyl quinone
dab	diamino butane
Et	Ethyl
en	ethylene diamine
gly	glycinato anion
HMDE	hanging mercury drop electrode
Me	Methyl
Pr	Propyl
SCE	saturated calomel electrode
ser	serinato anion
salen	N,N'-ethylenebis(salicylaldimine)
thr	threoninato anion

PREFACE

The work presented in this thesis consists of six chapters. The first chapter reviews condensation reactions of bis(amino acidato)copper(II) complexes with formaldehyde and acetaldehyde under various experimental conditions. Condensation reactions of many bis(amino acidato)copper(II) complexes with formaldehyde and acetaldehyde are known where the chirality of the α-aminoacidato ligands influenced the reaction process. For example condensation of $Cu(L\text{-ser})_2$ and $Cu(L\text{-thr})_2$ with formaldehyde at pH 4.5 yield optically active compounds 11 and 12, while in presence of ammonia at pH 4.5 and 8.5, $Cu(L\text{-ser})_2$ gives the products 13 and 3. The reaction of $Cu(DL\text{-ser})_2$ and $Cu(DL\text{-thr})_2$ with formaldehyde at pH 4.5 yield the products 8 and 10. These reactions suggest differential reactivity pattern for DL- and L- amino acids when coordinated to copper(II) ion.

The first chapter also reviews structural, magnetic, redox and catalytic properties of transition metal complexes of Robson type ligands. Dinuclear transition metal complexes obtained from ligands which can coordinate to two metal ions in close proximity exhibit interesting structural, magnetic, electrochemical and catalytic properties. One such system is derived from 2+2 condensation of 2,6-diformyl-4-methylphenol and 1,3-diaminopropane (15) and its reduced analogue (22), obtained by $NaBH_4$ reduction.

Chapter II deals with experimental details of the synthesis of ligands, their metal complexes and various techniques employed in the investigation.

Chapter III deals with condensation reactions of copper(II) complexes

of DL- and L- forms of alanine, serine and threonine with aliphatic aldehydes. $Cu(DL\text{-}ala)_2$ reacts with formaldehyde and ammonia at pH 5-6 to give a new complex 36, while at pH 8.5 it gives the known product 6. Reaction of $Cu(L\text{-}ala)_2$ with formaldehyde and ammonia at pH 8.5 is known to yield an optically active isomer of 5. This reaction also yields product 6 at very basic pH (>10), but is optically inactive. Similarly $Cu(DL\text{-}ser)_2$ and $Cu(DL\text{-}thr)_2$ undergo condensation reactions with aliphatic aldehydes (RCHO) such as acetaldehyde, propionaldehyde to yield oxazolidine group containing products 38-49. The corresponding D- and L- amino acidato copper(II) complexes do not undergo condensation reactions under the same experimental conditions.

Crystal structures of the products obtained from reactions of $Cu(DL\text{-}ser)_2$ and $Cu(DL\text{-}thr)_2$ with formaldehyde, 8 and 10 are determined. Both complexes crystallizes in triclinic space group $P\bar{1}$. The asymmetric unit cell of complex 8 consists of two crystallographically independent complex molecules and three water molecules of solvation which involve in hydrogen bonding with free carboxylic oxygens. One of the complex molecules (molecule A) exists as a dimer, whereas the other molecule exists as monomer.The asymmetric unit cell of complex 10 consists of one complex molecule and one water molecule. This complex molecule also exists as dimer as a result of mutual long axial interaction between carboxylic oxygens and coppers of two neighbouring molecules.

Chapter IV discusses the synthesis, structural, magnetic and catalytic properties of dinuclear copper(II), nickel(II), cobalt(II/III), iron(III) and manganese(II) complexes of ligands H_2L^1-H_2L^3. These complexes are characterized by C, H, N elemental, IR, UV-VIS spectral and magnetic data. The copper(II), cobalt(II) and manganese(II) complexes are square pyramidal. The nickel(II) complexes are square planar. A cobalt(III) complex is obtained from ligand H_2L^1

instead of expected cobalt(II) complex. Similarly iron(III) complexes are obtained from the ligands H_2L^1-H_2L^3. Catalytic property of copper(II), nickel(II) and cobalt(II/III) complexes in the oxidation reaction of 3,5-di-t-butylcatechol by molecular oxygen is examined. The cobalt(III) complex exhibits highest catalytic activity among the group. The copper(II) complexes exhibit two nearly reversible redox couples at two different potentials.

Chapter V deals with synthesis of dinuclear copper(II), nickel(II), cobalt(II/III), iron(III) and manganese(II) complexes of the tetraaminodiphenol ligands H_2L^4-H_2L^6. The copper(II) and nickel(II) complexes of the ligand H_2L^5 are known, whereas the cobalt(II), iron(III) and manganese(II) complexes are synthesized for the first time. The copper(II), cobalt(II), iron(III) and manganese(II) complexes are square pyramidal. Nickel(II) complex of H_2L^4 is square planar while complexes of ligands H_2L^5 and H_2L^6 are distorted octahedral. The ligand H_2L^4 yields a cobalt(III) complex. Similarly iron(III) complexes are obtained from these ligands. Catalytic activity of the copper(II), nickel(II) and cobalt(II/III) complexes is examined for the oxidation reaction of 3,5-di-t-butylcatechol to quinone. The cobalt(III) complex exhibits highest catalytic activity. Copper(II) complexes exhibit two nearly reversible redox couples at two different potentials.

Chapter VI deals with synthesis, characterization and catalytic properties of dinuclear copper(II), nickel(II) and cobalt(II) complexes of ligand L^7. These complexes possess a near tetrahedral structure. This chapter also deals with results of our efforts to synthesize dinuclear lanthanum(III), neodymium(III), samarium(III) and europium(III) complexes from the ligands H_2L^8-H_2L^{10}. Analytical data show that these complexes are mononuclear.

CHAPTER - I

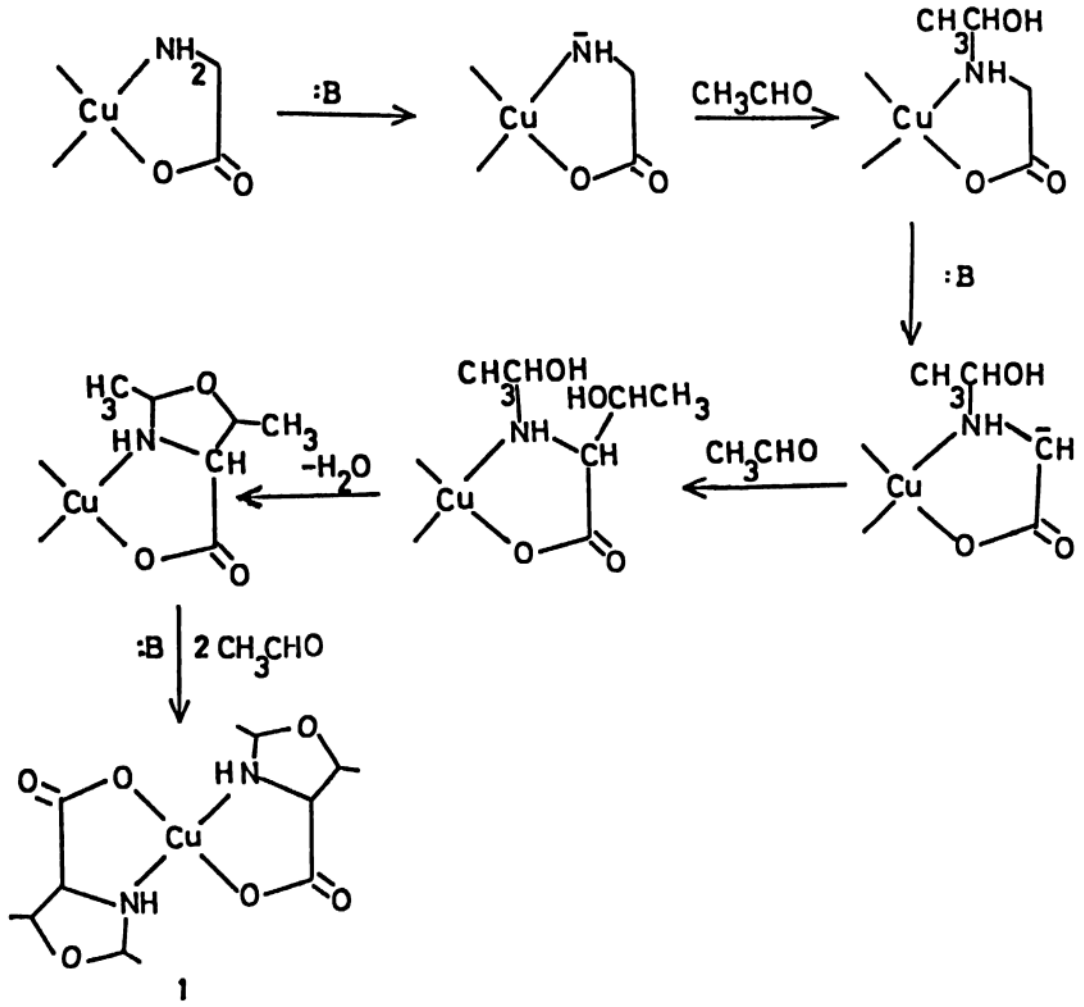
INTRODUCTION

1.1.0 Reactions of metal coordinated α-amino acids

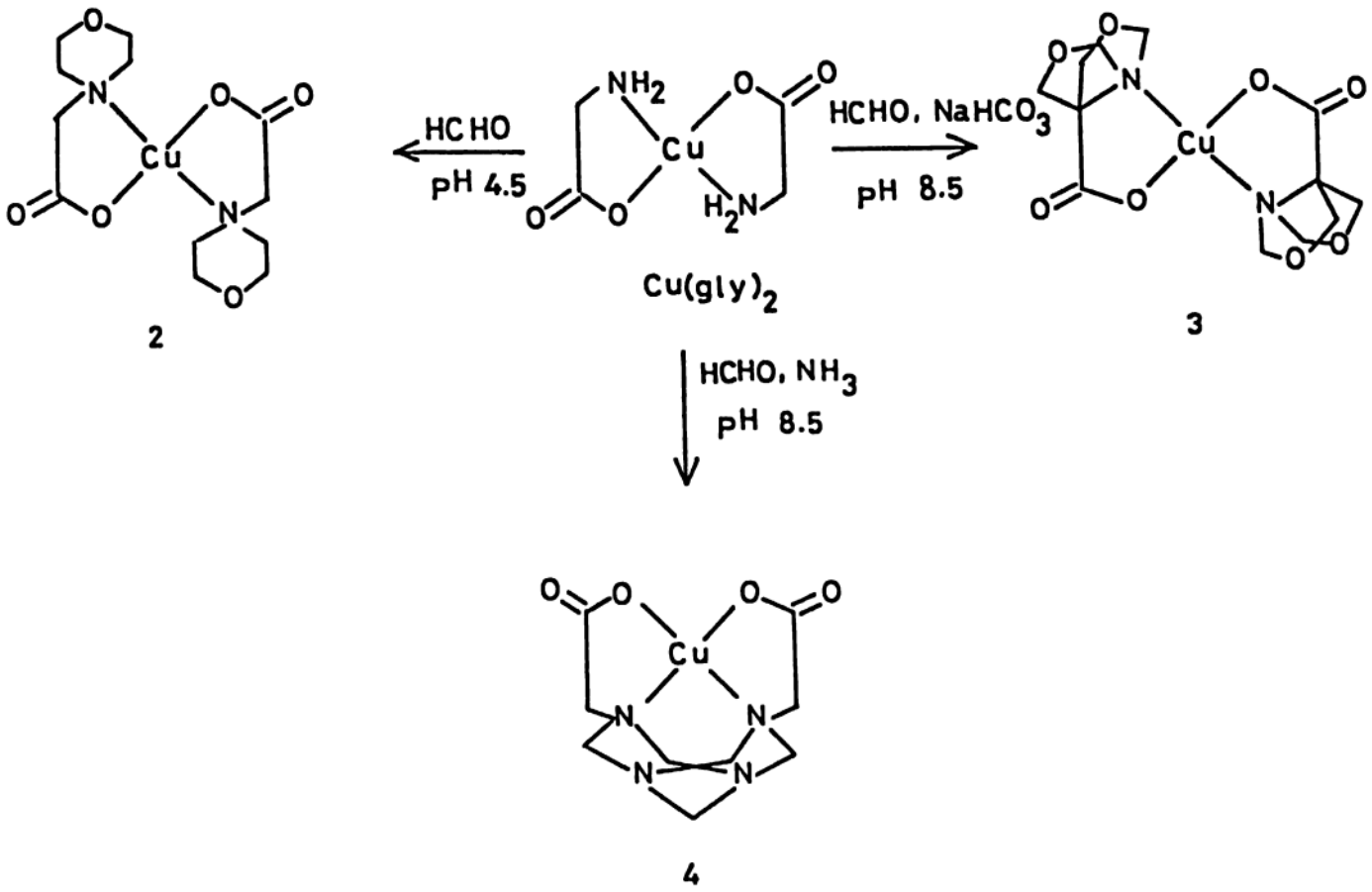
Complexation of copper(II) by amino acids and reactions of these complexes with aldehydes have been studied in detail.[1-25] Bidentate α-amino acids coordinate to copper(II) through amino nitrogen and carboxylic oxygen atoms which results in the increase of nucleophilic reactivity of the α-carbon atom through bond polarization.[26,27] Product formation in reactions of aldehydes with bis(α-amino acidato) metal complexes is dependent on the nature of the α-amino acids and the pH of the reaction medium.[18,20,28-31] Copper(II) assisted synthesis of DL-threonine from glycine is the first such reaction reported.[11] Acetaldehyde reacts with $Cu(gly)_2$ under mild conditions to yield DL-threonine in 40% yield. The reaction mechanism is similar to aldol condensation and is shown in Scheme 1.1.

Complex 1, bis(2,5-dimethyloxazolidine-4-carboxylato)copper(II) dihydrate, on treatment with H_2S releases DL-threonine. $Cu(gly)_2$ when reacted with formaldehyde at different pHs yields variety of products. The structures of these products and reaction conditions are given in Scheme 1.2.

It is evident from the structures of these products (Scheme 1.2) that amino protons in $Cu(gly)_2$ are activated more than α-methylene group to form product 2, [bis(N-1,3-dioxa-5-azacyclohexyl)acidato]copper(II)[32] at pH 4.5. When the pH is 8.5, both amino protons and α-carbon protons are activated to give the product[20] 3, bis(dihydro-1H,3H,5H-oxazolo[3,4-C]-oxazole-7a-carboxylato)copper(II). However at the same pH in presence of ammonia, product 4, [3N,7N-1,3,5,7-tetraazabicyclo(3.3.1)nonyl)diacetato]copper(II), is formed.[29] Though this reaction is carried out at pH 8.5, the α-carbon protons do not involve in the condensation. Also the two trans glycine units in $Cu(gly)_2$ have



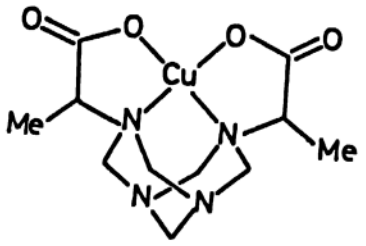
Scheme 1.1 Mechanism for the condensation reaction between $Cu(gly)_2$ and acetaldehyde.



Scheme 1.2 Product formation in the reaction between $Cu(gly)_2$ and formaldehyde at various pH conditions.

undergone cis arrangement.[33] $Ni(gly)_2$ is also known to form similar products under the same experimental conditions.[29]

Investigations on similar condensation reactions of L-alanine, DL-alanine, L-serine and DL-serine were carried out.[31,34] $Cu(L\text{-}ala)_2$ on reaction with formaldehyde in presence of ammonia at pH 8.5 yields product 5, [(2S,8S)-3N,7N-(1,3,5,7-tetraazabicyclo[3.3.1]nonyl)dipropionato]copper(II), similar to 4. Under the same experimental conditions $Cu(DL\text{-}ala)_2$ yields 6, bis(4-methyloxazolidine-4'-carboxylato)copper(II) dihydrate. This reveals different reactivity pattern for the two forms of alanine when coordinated to copper(II) ion.



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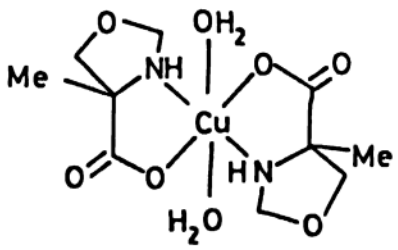

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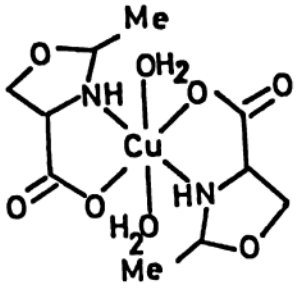
Recently it has been reported that $Cu(DL\text{-}ser)_2$ when reacted with acetaldehyde[35] at pH 4.5 yielded 7, bis(2-methyloxazolidine-4-carboxylato)-copper(II) dihydrate and with formaldehyde product 8, N,N'-1,3-(2-oxapropane-diyl)bis(oxazolidine-4-carboxylato)copper(II) monohydrate. $Cu(DL\text{-}thr)_2$ with formaldehyde at pH 8.5 gave 9, bis(5-methyloxazolidine-4-carboxylato)copper(II) dihydrate, and at pH 4.5 gave 10, N,N'-1,3-(2-oxapropanediyl)bis(5-methyl-oxazolidine-4-carboxylato)copper(II) monohydrate. The four products thus obtained were characterized by spectral and analytical data.



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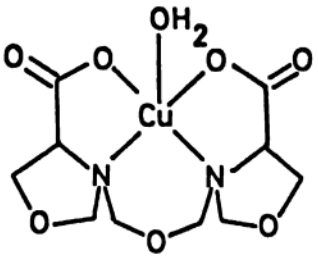

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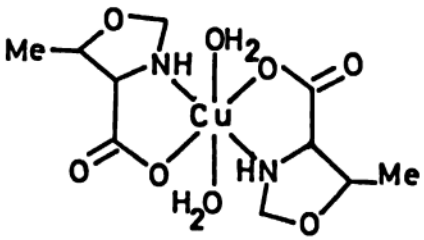

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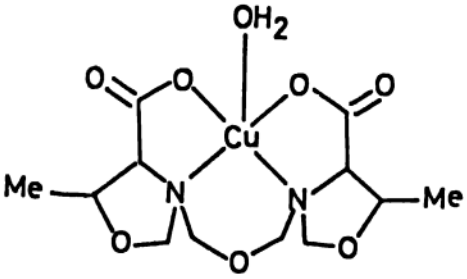

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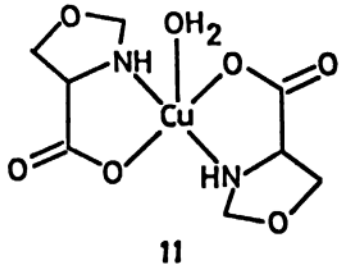
The complexes 8 and 10 are bridged complexes as the two coordinating nitrogen atoms are bridged by a dimethyleneether group. They exhibit considerable electronic and e.s.r spectral differences compared to the unbridged complexes 7 and 9. A red shift in the absorption band maxima is observed for the unbridged complexes. These complexes (7 and 9) exhibit four-line e.s.r spectra which changes on lowering the pH. In contrast the bridged complexes show unchanged e.s.r spectra on lowering the pH. Both types of complexes have similar electrochemical behavior.

Condensation of optically active $[Co(en)_2(gly)]^{+2}$ with acetaldehyde was shown to form optically active threonine stereoselectively with low yield.[14] It was also shown that the optical yield can be improved by careful control of the reaction conditions.[36] Using Λ-(+)-$[Co(en)_2(gly)]^{+2}$ it has been shown that the

preferred isomeric product had the 2S configuration both for threonine (2S.3R) and allo threonine (2S.3S), while use of Λ-(-)-[Co(en)$_2$(gly)]$^{+2}$ was found to yield 2R-threonine preferentially. In general, such stereoselective reactions are less facile for the copper(II) complexes due to their labile nature.[22] Investigations were carried out to see whether copper(II) complexes of optically active serine and threonine show stereospecificity in their condensation reactions.[37] Condensations of Cu(L-ser)$_2$ and Cu(L-thr)$_2$ with formaldehyde at pH 4.5 yield optically active compounds 11, bis[L-(oxazolidine-4-carboxylato)]copper(II) monohydrate and 12, bis[L-(N-hydroxymethyl-5-methyloxazolidine-4-carboxylato)]copper(II) dihydrate respectively. Condensation of Cu(L-ser)$_2$ with formaldehyde in presence of ammonia at pH 4.5 and 8.5 yield the products 13, [3N,7N-(1,3,5,7-tetraazabicyclo[3.3.1]nonyl-(dihydroxymethyl)acetato]copper(II) and 3. CD spectra of complexes 11 and 12 revealed positive Cotton effect which is opposite to that of their parent copper(II) complexes *viz.*, Cu(L-ser)$_2$ and Cu(L-thr)$_2$. This was attributed to the generation of new asymmetric centre at the nitrogen atoms. Under the same experimental conditions Cu(D-ser)$_2$ and Cu(D-thr)$_2$ give similar products which



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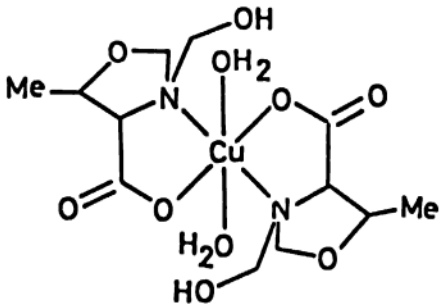

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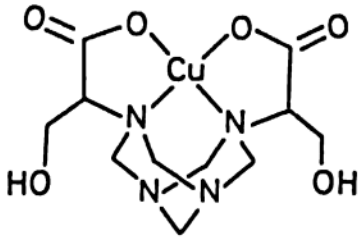
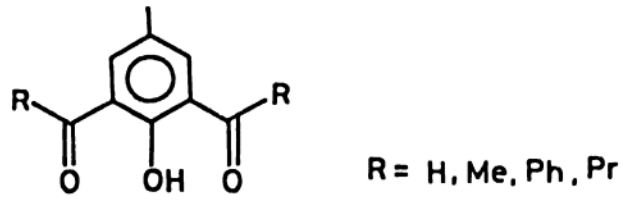


13

are optical isomers of 11 and 12. Since $Cu(DL\text{-}ser)_2$ or $Cu(DL\text{-}thr)_2$ gave products 8 and 10 which are different from 11 and 12, the reactions of $Cu(L\text{-}ser)_2$ and $Cu(L\text{-}thr)_2$ with formaldehyde are stereospecific and a mechanism has been suggested.[37]

1.2 Structure and properties of dinuclear complexes

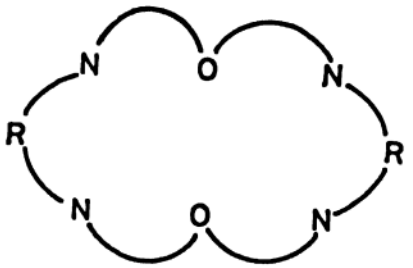
The term 'binucleating ligand', introduced by Robson in 1970, refers to ligand which is capable of securing two metal ions. Since then there has been continuous increase in the synthesis and characterization of such ligands and their complexes.[38,39] One of the promising applications of these systems was their capability for binding and activating small molecules such as oxygen, carbon monoxide, carbon dioxide or bonds like C-H, for the subsequent formation of organic substrates.[40-43] Compartmental ligands contain adjacent sites in which the central donor atoms provide a bridge when complexed to a metal ion. These ligands are predominantly Schiff bases or their reduced compounds. A large number of such ligands have been obtained from substituted phenols, thio phenols, 1,3,5-triketones, β-keto phenols and keto acids. One of the extensively studied ligands is derived from 2,6-disubstituted-p-cresols, 14.



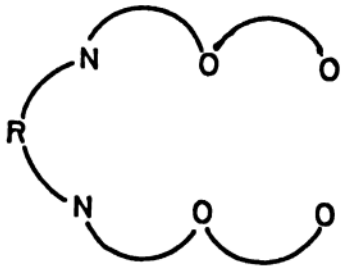
14

Four types of ligands (A, B, C, D) can be obtained when 2,6-di-substituted-4-methylphenol (14) is condensed with an amine. Type A are macrocycles and are obtained by 2+2 condensation with diamines. Type B and C are

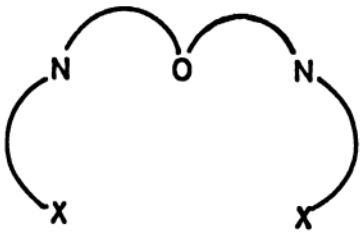
obtained when the condensation is 2+1 and 1+1 respectively. Type D are polypodal ligands.



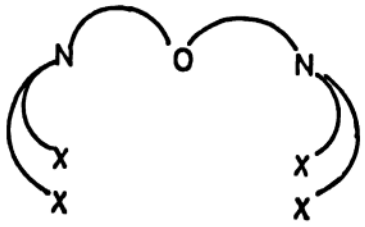
A



B



C

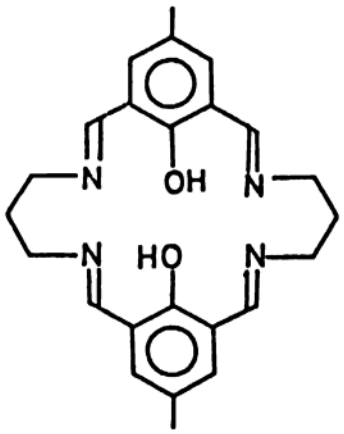


D

Macrocyclic dicopper(II) complexes derived from 2,6-diformyl (diacetyl)-4-methylphenol are numerous and dominate the chemistry of dinuclear transition metal complexes. In general metal complexes of these ligands are strongly antiferromagnetically coupled similar to the dinuclear metal sites in some biological systems.[45,46]

Robson synthesized Zn(II), Cu(II), Ni(II), Co(II), Fe(II) and Mn(II) dinuclear complexes of macrocycle (15) derived from the condensation of 2,6-diformyl-4-methylphenol with 1,3-diaminopropane. On the basis of magnetic and spectral evidence the complexes were assigned dinuclear structures as shown in 15a, in which the cations have approximately square pyramidal environment. These structural features have been confirmed in the case of copper(II) and cobalt(II) complexes by X-ray crystallographic analysis.[46,47] In both cases

metal ion is coordinated in square pyramidal fashion with one halide ion in axial position as shown in 15a. The cobalt(II) ion is further out of the ligand N_2O_2 plane than copper(II) ion. Variable temperature magnetic studies on these complexes suggested antiferromagnetic exchange interaction between the metal ions which decreases in the series Cu(II), Ni(II), Co(II) and become ferromagnetic interaction with Mn(II) complex. This was attributed to the number of unpaired electrons, increased metal-ligand plane distance from Cu(II) to Mn(II) and exchange path ways.



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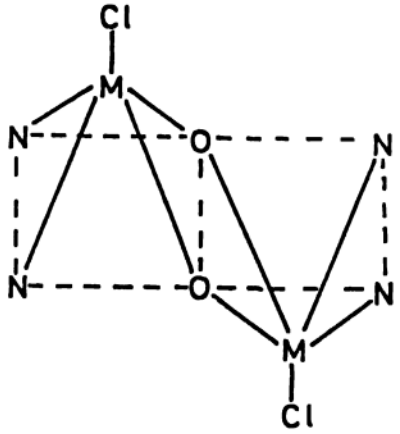


15a

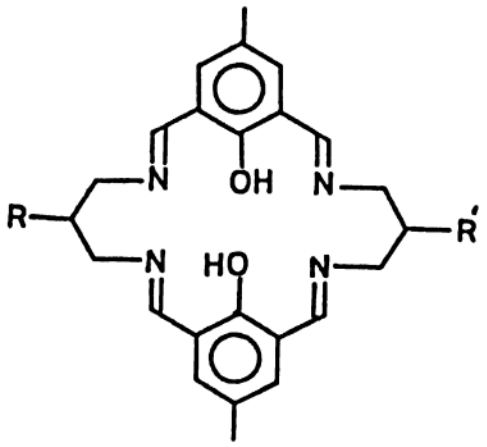
When the axially bound halide ions in these complexes (15) are replaced by four molecules of bases like pyridine, imidazole and 1-methyl imidazole, the geometry around metal centres changes to octahedral in which an improvement in the overlap between the metal centres can be expected. As a consequence of this, the antiferromagnetic exchange interaction increases marginally.[48] This is possibly because the increased ligand field splitting in the six coordinated complex attenuated the antiferromagnetic interaction.

Hetero dinuclear complexes of ligand 15 are also known.[49] Gagne *et al* have prepared Cu(II)-Mn(II), Cu(II)-Fe(II) and Cu(II)-Co(II) complexes. The

magnetic moments are less than the spin only values and have both metals in square pyramidal environment.

Structurally and magnetically interesting polynuclear manganese(II) complexes were synthesized and their magnetic, e.p.r properties were studied.[50] Ligands L^1 and L^2 of 16 gives two types of complexes $[Mn_2L^1(MeCO_2)]ClO_4$ and $[Mn_2L^2](ClO_4)_2$. The effective magnetic moments decrease with lowering of temperature in both the cases. Based on these studies and X-ray powder diffraction pattern, the second complex is suggested to be an assembly of two dinuclear units with alcoholic oxygen interacting with Mn(II) atoms of two units resulting in tetra nuclear complex as shown in 16a. Crystal structure of the first complex shows that the dinuclear units are bridged by acetate ions to afford infinite chains as shown in 16b. The dinuclear nickel(II) and manganese(II) complexes of ligand L^3 are known. Crystal structures of the complexes $[(Mn_2L^3(CH_3COO)_2].2H_2O$ and $[Ni_2L^3(H_2O)_2Cl_2]$ are solved. The alcohol groups of the ligand do not coordinate to the metal ion. The acetate ion coordinates to manganese atom in a bidentate fashion as shown 16c. The nickel complex possesses an octahedral geometry as shown in 16d.

Okawa and Kida[51] prepared mono and dinuclear copper(II) and nickel(II) complexes using 2,6-diformyl-4-methylphenol, ethylenediamine and propylenediamine, 17a, 17b, 17c. Their structures were elucidated on the basis of spectral and magnetic data. All mono nuclear and dinuclear nickel(II) complexes have planar configuration around the metal atoms. The planarity is slightly distorted for mono nuclear copper(II) complexes of 1,3-diaminopropane as evident from increased magnetic moment and red shift of the electronic absorption bands. Dinuclear copper(II) complexes have square pyramidal geometries.

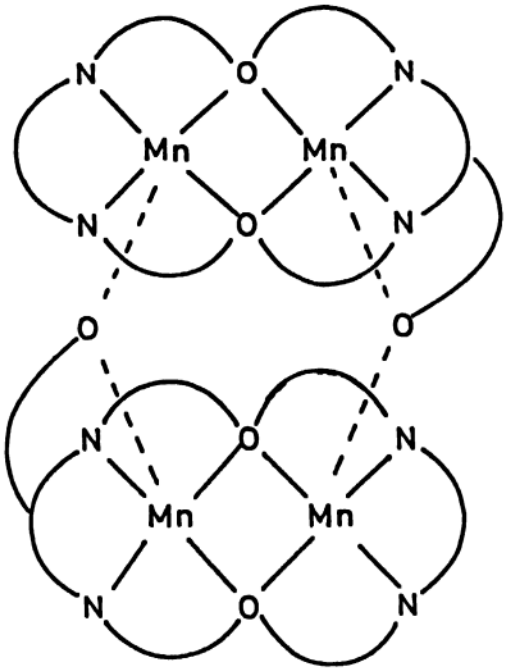


H_2L^1 : R = H , R' = OH

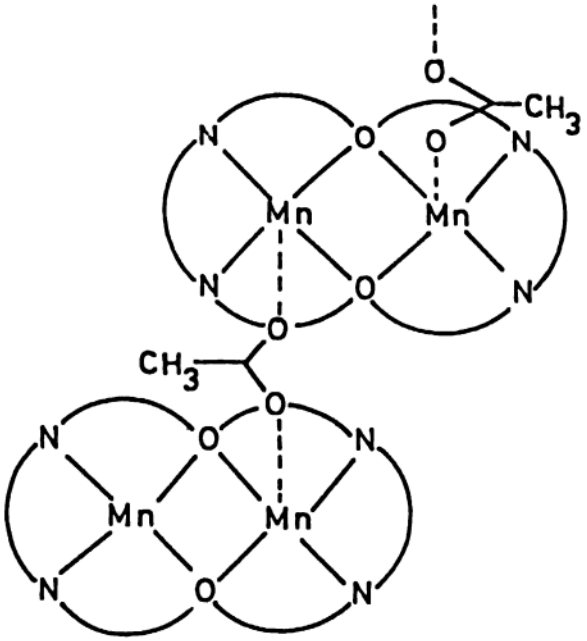
H_2L^2 : R = H , R' = O^-

H_2L^3 : R = R' = OH

16



16a



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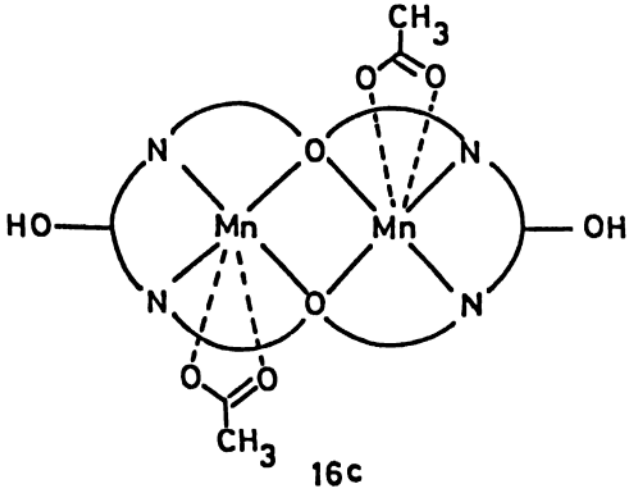
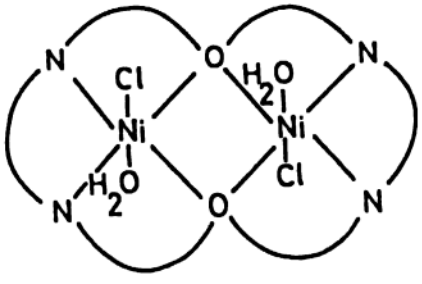
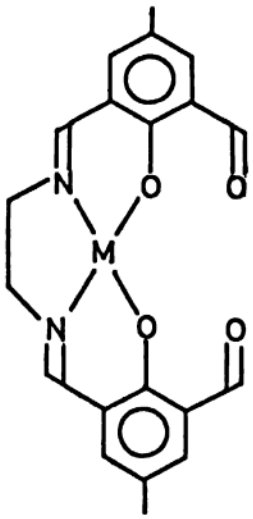


16c

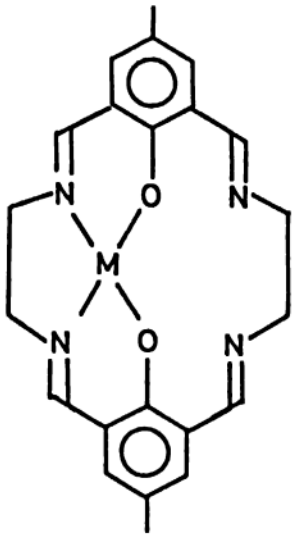


16d

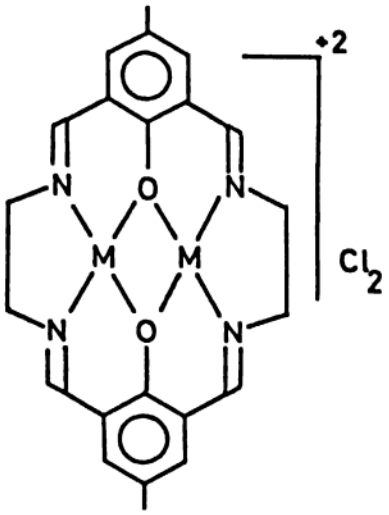
Homo and hetero dinuclear Ni(II), Co(II) and Mn(II) complexes, 18 derived from[52] 2,6-diacetyl-4-methylphenol were investigated. The homo dinuclear



17a

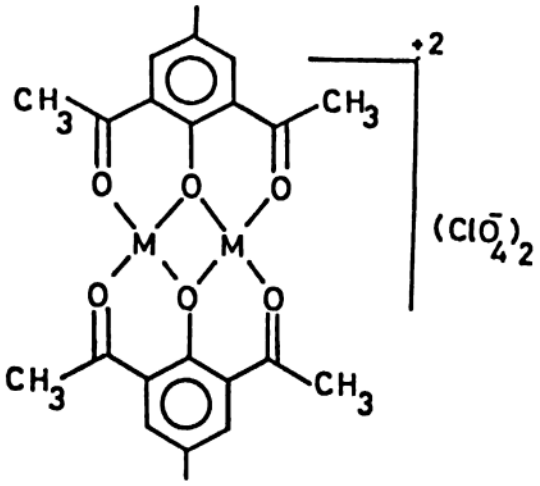


17b



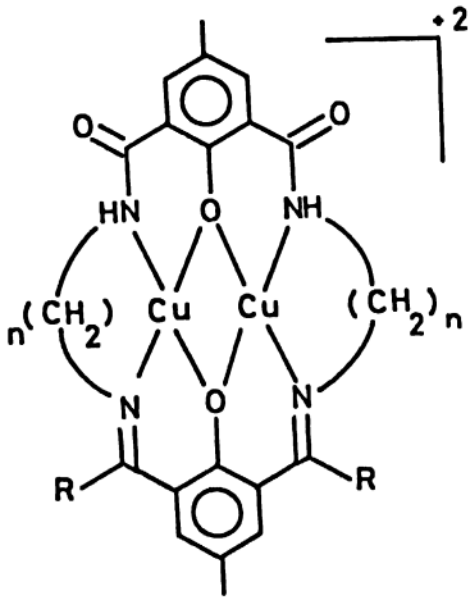
17c

complexes are high spin and are square pyramidal with antiferromagnetic exchange interactions. For the hetero dinuclear complexes, Cu(II)-Ni(II), Cu(II)-Co(II) and Cu(II)-Mn(II), the observed magnetic moments are less than the expected spin only values and have both metal ions in square pyramidal environment.



18

Nag and Okawa studied structural and magnetic properties of macrocyclic aza-amido dinuclear copper(II) complexes obtained from 2,6-diformyl(dibenzoyl)-4-methylphenol and 2,6-dicarboxylato-4-methylphenol[53,54] (19). Room temperature magnetic moment of 19a indicated strong spin coupling between the copper centres. Crystal structures are reported for 19b and 19c. The two copper centres in 19b have square planar N_2O_2 donor sets with two phenoxide oxygen atoms bridging the copper centres. Complex 19c has its two copper(II) centres distorted from square pyramidal geometry involving an N_2O_2 in plane donor set with two phenoxide oxygen bridges. The fifth coordination is from amide oxygen from neighboring molecule. Strong antiferromagnetic exchange is seen in these complexes.



19a, R = H, n = 2

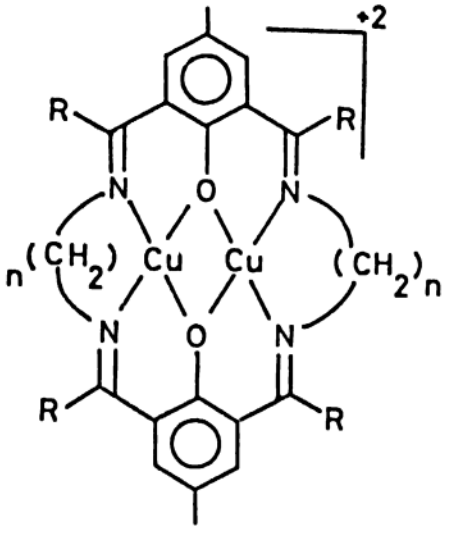
19b, R = Pr, n = 2

19c, R = Ph, n = 3

19

Structural, magnetic and electrochemical studies[55,71] were performed on macrocyclic dicopper(II) complexes of ligands shown in 20. These ligands have chelating rings of varying sizes, i.e, 5, 6 and 7. Copper complex 20a contains two different molecules in the unit cell, one molecule has pseudo octahedral

copper centres and the second molecule has square pyramidal centres. Both 20a and 20b exhibit comparable antiferromagnetic exchange, $-2J = 850\ cm^{-1}$ and 857 cm^{-1} respectively. Complex 20c has reduced Cu-O-Cu bridge angle and is less strongly coupled, $-2J = 689\ cm^{-1}$. It was found that the chelating ring size affects $E_{1/2}$ values of one electron reduction of these complexes. Complex 20a upon constant potential electrolysis in acetonitrile at -0.7 V results in corresponding mixed valent Cu(II)-Cu(I) complex.[56,57] It was shown that this complex forms an adduct with carbon monoxide. Solution e.p.r spectra of the mixed valence complex shows seven line pattern at room temperature in both dichloromethane and acetonitrile. This indicates that the odd electron is delocalized between the copper centres. Complex 20b behaves similarly. In contrast, one electron reduced mixed valent complexes of 20d and 20e show four line spectra.



20a, R = H, n = 3

20b, R = H, n = 4

20c, R = Me, n = 2

20d, R = Me, n = 3

20e, R = n-Pr, n = 3

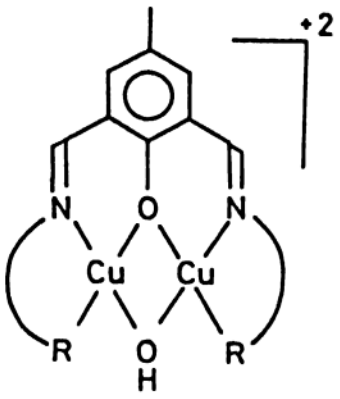
20f, R = Ph, n = 3

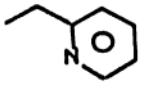
20

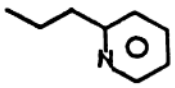
Several complexes of various metals were synthesized from 2,6-diformyl-4-methylphenol with 2-aminophenol,[58,59,60] aminothiophenols,[61] aminoacids,[62,63] dialkylalkanediamines,[64-66] 2-aminoalkylpyridines,[67-69]

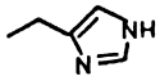
histamine,[67,68] thiosemicarbazide[69] and diamines.[66,70,71]

By condensation of 2,6-diformyl-4-methylphenol with primary amines (R), followed by the addition of $Cu(BF_4)_2.6H_2O$, complexes shown in 21 have been prepared.[67,68] In these complexes each copper is five coordinated. The fifth coordination is provided by water molecule for one copper and oxygen of hydroxide bridge of an adjacent molecule for the other copper.[73]



21a, R= 

21b, R= 

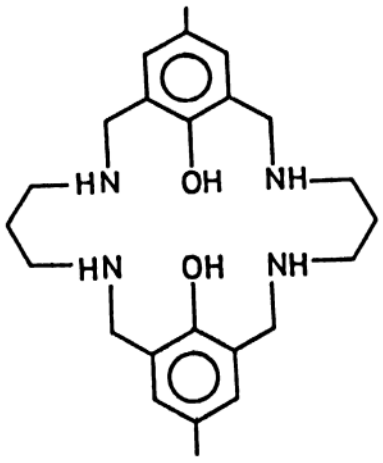
21c, R= 

21

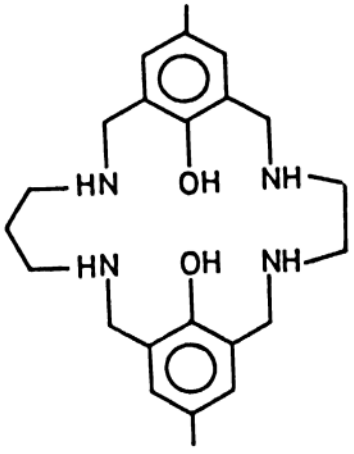
Many dinuclear Mn(II), Fe(II) and mixed valence Mn(II)-Mn(III), Fe(II)-Fe(III) complexes of ligands 21 are known.[74-79] Mixed valence Mn(II)-Mn(III) complex of 21a was synthesized and characterized.[80] The Mn atoms are bridged by two bidentate acetate ions and are in pseudo octahedral geometry. Magnetic susceptibility data for this complex is consistent with isotropic magnetic exchange between high spin Mn(II) and Mn(III) ions. Dinuclear Fe(II) and mixed valence Fe(II)-Fe(III) complexes of this ligand are also known.[77] These complexes are high spin and the metal centres are bridged by carboxylato oxygens.

A new type of macrocyclic ligand 22 and its Cu(II), Ni(II) complexes

were synthesized.[82,83,84] The ligand 22 is more flexible compared to its analogue 15, which has four azomethine functionalities. This ligand forms copper(II) complexes of the type $[Cu_2L(ClO_4)_2]$, $[Cu_2L](ClO_4)_2$ and $[Cu_2L(H_2O)_2](ClO_4)_2$ where two perchlorate molecules bridge the two copper centres and give a near octahedral structure to the first complex while they are out side the coordination sphere in the second complex and hence square planar. The third one has square pyramidal centres with water molecule occupying the apical position. Variable temperature magnetic studies showed strong antiferromagnetic exchange interaction of the order 824 cm^{-1} and 827 cm^{-1} respectively for the first two complexes. Crystal structure of the complex $[Ni_2L(CH_3OH)_2](ClO)_4$ showed that Ni(II) ions are in pseudo octahedral environment. Room temperature magnetic moment indicates spin exchange interactions. These complexes exhibit oxidation-reduction processes involving +1 to +3 oxidation states. Copper(II) and nickel(II) complexes of the ligand 23 are known.[85,86] This ligand forms a mixed spin state (S = 0 and 1) dinickel complex in which one nickel atom is hexa coordinate and possesses an octahedral geometry. The other nickel atom is coordinated in a square planar fashion by the N_2O_2 site.[86]



22



23

1.3 Electrochemical properties

Electrochemical investigations on Cu(II) amino acidato complexes have shown that electrochemical reduction of these complexes proceed via Cu(I) intermediate species.[9] Cyclic voltammetric profiles of these complexes constitute two redox couples, one corresponding to close reversible Cu(II)/Cu(I) process at -0.25 V vs S.C.E. and another at -0.01 V corresponding to Cu(II)(aq)/Cu(0)(Hg). The electrode mechanism involves the following steps. First Cu(II) gets reduced to Cu(I) some of which is oxidized to Cu(II) giving the redox couple at -0.25 V. Some Cu(I) species produced undergoes disproportionation/chemical decomposition to Cu(0). This undergoes two electron oxidation to Cu(II) and again gets reduced to Cu(0) giving a couple at less negative potential. These steps can be represented as

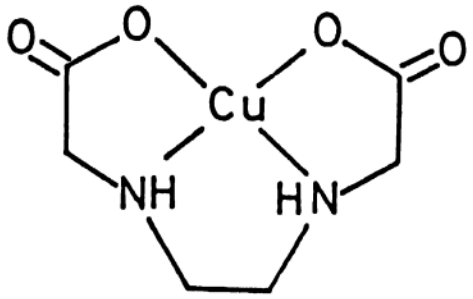
$$\mathrm{Cu(II)} \underset{}{\overset{1e}{\rightleftharpoons}} \mathrm{Cu(I)}$$

$$\mathrm{2Cu(I)} \xrightarrow{\text{disproportionation}} \mathrm{Cu(0)(Hg) + Cu(II)(aq)}$$

$$\mathrm{Cu(0)(Hg)} \overset{2e}{\rightleftharpoons} \mathrm{Cu(II)(aq)}$$

As the Cu(I) species is stable only in tetrahedral or pseudo-tetrahedral environments, the reversibility and the redox potential of Cu(II)/Cu(I) process depend on the ability of the ligand to stabilize Cu(I) state. It has been shown that more the planarity of the copper(II), more negative is the Cu(II)/Cu(I) reduction potential, less stable is the Cu(I) intermediate species and less reversible is the redox processes.[35] Compound 4 and 5 prepared from the condensation of formaldehyde with $Cu(gly)_2$ and $Cu(L\text{-}ala)_2$ were shown to have different cyclic voltammetric behavior. Due to their bridged structure, they undergo irreversible one electron reduction at -0.51 V in contrast to $Cu(gly)_2$ or $Cu(L\text{-}ala)_2$ complexes. Complex 24 has

different cyclic voltammetric behavior. In addition to the couple at +0.01 V which is common for copper(II) amino acid complexes, it gives two overlapping couples at -0.27 V and -0.38 V vs S.C.E. It was suggested that an inter molecular interaction believed to exist in this complex is responsible for the two couples. The two interacting copper(II) centres are reduced to Cu(I) sequentially.[32]



24

There are very large number of reports on the redox properties of dinuclear copper(II) complexes. Two types of electron transfer mechanisms are reported. i) Two electron transfer at the same potential similar to biological copper and ii) one electron transfer at two different potentials. There are very few examples[85,86] on the first type electron transfer compared to many reports of second type. Most of the dinuclear complexes derived from 2,6-diformyl-4-methylphenol which were discussed in section 1.2 fall under the second category.

The redox properties of Cu(II), Ni(II), Co(II), Fe(II) and Mn(II) complexes prepared from 2,6-diformyl-4-methylphenol and 1,3-diamino propane (15) were studied.[49] The dicopper(II) complex undergoes, one electron reductions at ca. -0.925 V and -1.31 V vs ferrocene/ferrocenium^{+} couple in DMF. The other dinuclear complexes give two couples involving M(III)/M(II) process at *ca.* -0.05

V, +0.065 V for Mn(II); -0.02 V, +0.24 V for Fe(II); +0.01 V, +0.24 V for Co(II) complexes in methanol. Nickel(II) complex in water has these couples at *ca.* +0.08 V and +0.425 V.

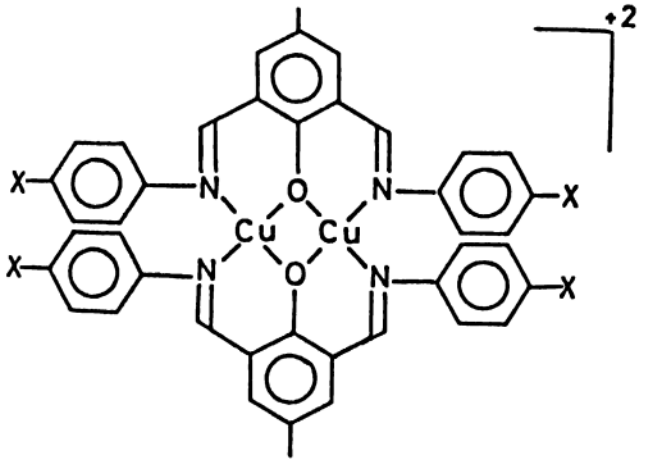
Mandal *et al* have studied the electrochemistry of dicopper(II) complexes which have chelate rings of varying sizes (20). These complexes undergo one electron reductions at two different potentials producing Cu(II)-Cu(I) and Cu(I)-Cu(I) species. A comparison of $E_{1/2}$ for the first electron reductions (Table 1.1) shows that most thermodynamically favoured process occurs for 20b, which can be rationalized in terms of added molecular flexibility associated with the butylene bridge which enhance the stability of the copper(I) centre. The second one electron reduction step for this system also occurs at the most positive potential for the group. The first one electron reduction potentials for 20a and 20c are same indicating that changing the chelate ring size from five to six does not promote the formation of

Table 1.1 Electrochemical data of copper(II) complexes.

R	Compound	Ring size	First electron reduction potential $E^1_{1/2}$ (V)	Second electron reduction potential $E^2_{1/2}$ (V)
H	20a	six	-0.41	-0.89
H	20b	seven	-0.30	-0.76
Me	20c	five	-0.41	-1.115
Me	20d	six	-0.46	-1.04
n-Pr	20e	six	-0.45	-1.00

Cu(II)-Cu(I) intermediate. Electronic effects associated with methyl and propyl groups of the ring do not appear to influence the first electron reduction process very much, but differences in $E_{1/2}$ values for the second reduction (versus that of 20a) indicate possible electronic influence. Replacement of 4-methyl substituent by CF_3 in 20a and 20b has been shown to increase $E_{1/2}$ for one electron reduction steps in DMF by 0.14 to 0.19 V, clearly indicating the transmission of electron withdrawing effect to the copper(II) centres.[87]

Electrochemical properties of mono and dinuclear copper(II) complexes 25 and 26 were investigated.[88] The dicopper(II) complexes of the type 25 undergo one electron reductions near 0.0 V and -0.3 V to -0.4 V vs SCE reversibly or quasi-reversibly in DMF at a glassy carbon electrode. Though complexes 26 behaved similarly, a considerable shift in the second electron reduction potential (which is near -0.73 V to -0.78 V) is observed for these complexes.



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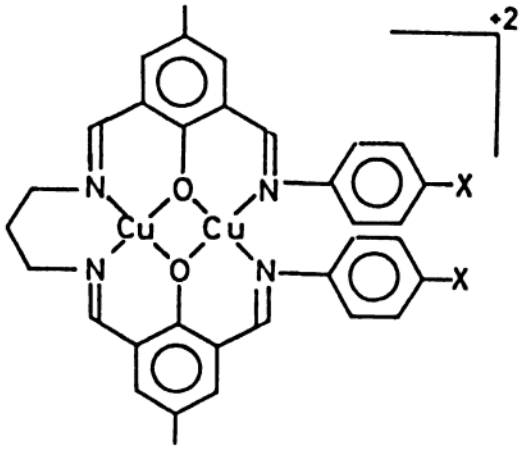
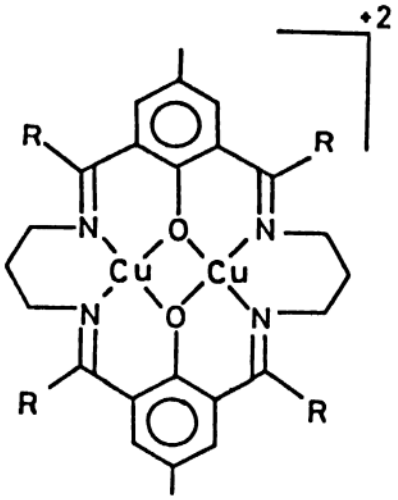


26

Electrochemical properties of two series of macrocyclic dicopper(II) complexes 27 and 28 (where R is varied among H, Me, Ph, n-Pr) were studied[89] in acetonitrile and dichloromethane solvents. It was shown that the first electron

reduction potential (E^1) values of 27 remain unchanged and show no substitution effect, where as the E^2 (second electron reduction potential) values show some dependence on the nature of the peripheral substituents which is sequel to the difference in electron releasing power of the substituents. It was also shown that the first electron transfer for 28 type complexes occur at more negative potential than for the first type. This was attributed to the strong donor property of amino nitrogens.



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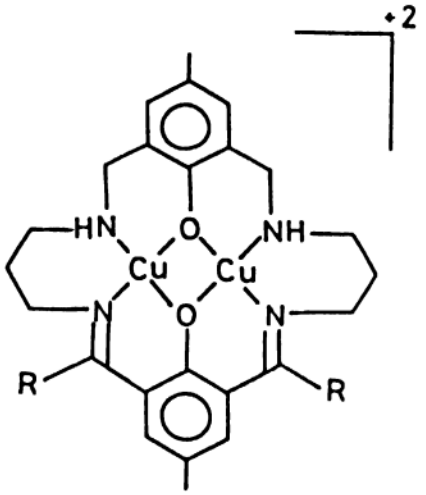


28

Electrochemistry of mixed valence Mn(II)-Mn(III) and Fe(II)-Fe(III) complexes obtained from the ligand 2,6-diformyl-4-methylphenol and 2-methylaminopyridine, 21a, is reported.[71,80,81] The Mn(II)-Mn(III) mixed valence complex exhibits two quasi reversible redox waves at *ca.* +0.47 V and +1.02 V vs SCE in acetonitrile at glassy carbon electrode. The two sets of redox waves correspond to two stepwise electron transfer processes, Mn(II,III)/Mn(II,II) and Mn(III,III)/Mn(II,III) processes respectively. The mixed valence Fe(II)-Fe(III) complex exhibits two redox couples at *ca.* +0.68 V and -0.03 V vs SCE. The constant potential coulometry revealed that these redox

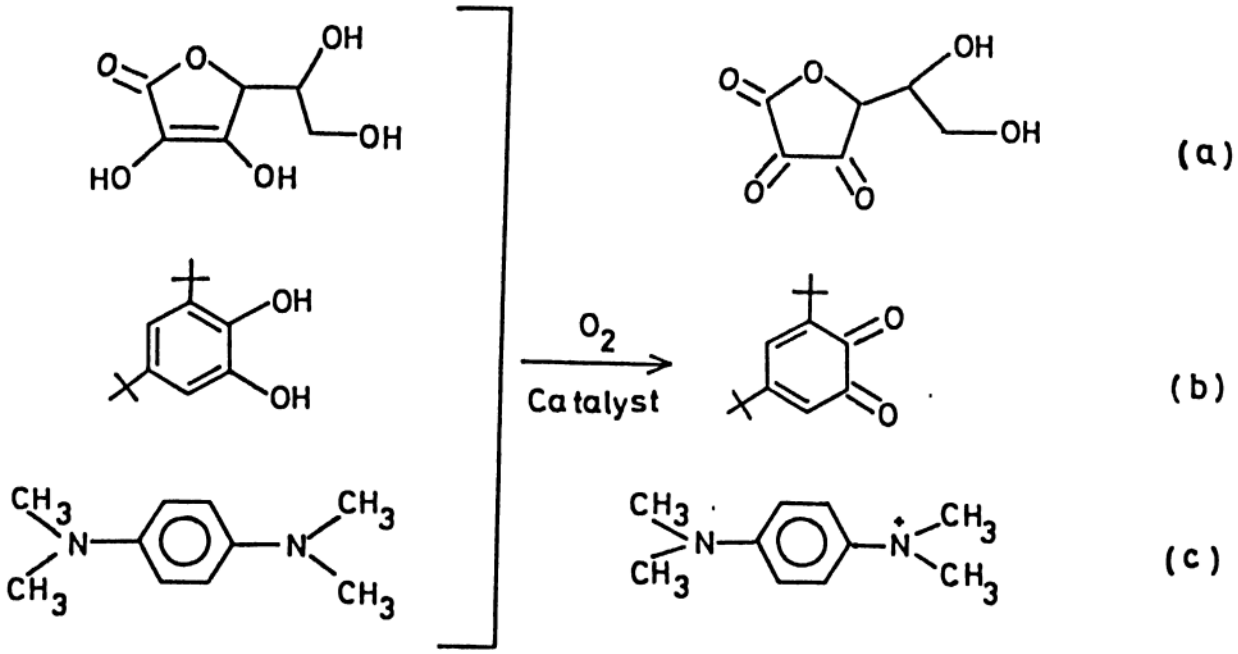
couples correspond to one electron redox reaction corresponding to Fe(III,III)/Fe(II,III) and Fe(II,III)/Fe(II,II) processes respectively.

The dinuclear copper(II), nickel(II) complexes of 22 undergo two one electron reductions and oxidations.[82,83] The dicopper complex shows two redox couples at *ca.* -0.76 V and -0.90 V vs SCE, which correspond to Cu(II)-Cu(I) and Cu(I)-Cu(I) species. It also undergoes one electron oxidation at *ca.* +1.21 V and +1.41 V which involve Cu(II)-Cu(III) and Cu(III)-Cu(III) intermediate species. Similar behavior was found for the dinickel complex giving Ni(II)-Ni(I) and Ni(I)-Ni(I) species at *ca.* -1.32 V and -1.65 V. The formation of Ni(II)-Ni(I) species was confirmed by coulometry. Oxidations involving Ni(II)-Ni(III) and Ni(III)-Ni(III) species occur at *ca.* +0.94 V and +1.08 V.

1.4 Catalytic properties of metal complexes

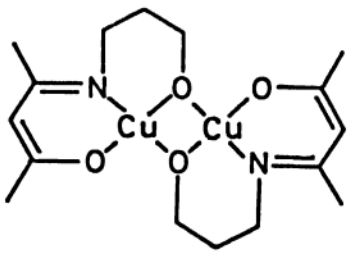
Catalytic activity of many mono and dinuclear copper(II), nikel(II) and cobalt(II) complexes was investigated in oxidizing ascorbic acid, 3,5-di-t-butylcatechol (3,5-DTBC) and N,N,N,'N'-tetramethyl-p-phenylene diamine (TMPD) by molecular oxygen to form the products according to the Scheme 1.3.

Dinuclear copper(II) complexes obtained from variety of ligands with appropriate Cu-Cu distance (3.0-3.5 A^0) were checked for their catalytic activity for the oxidation of TMPD by molecular oxygen.[90] The results revealed that some dinuclear complexes with equivalent coordination sites 29, exhibited high catalytic activities whereas other dinuclear complexes 30, and planar mononuclear complexes like $Cu(acac)_2$ have little or practically no catalytic activity. The low catalytic activity of 30 was attributed to long Cu-Cu distance. Complexes with inequivalent coordination sites (like N_2O_2 and O_4) were



Scheme 1.3 Oxidation products of a) ascorbic acid b) 3,5-DTBC c) TMPD.

shown to be poor catalysts. Complexes with more positive reduction potentials exhibited high catalytic activity.



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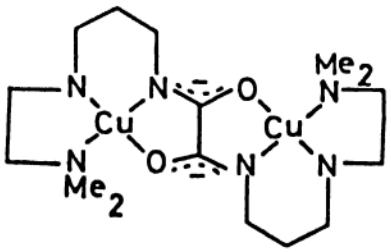
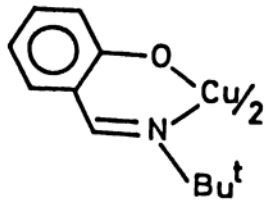


30

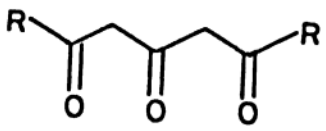
The electron transfer reactions between various copper(II) complexes, ascorbic acid and 3,5-di-t-butylcatechol were investigated.[91] Mononuclear copper(II) complexes with distorted tetrahedral structures 31 and trigonal bipyramidal structure like $[Cu(bpy)_2Cl]^+$ were readily reduced to copper(I) complexes by ascorbic acid where as mono nuclear planar copper(II) complexes like $Cu(acac)_2$ and Cu(salen) did not undergo reductions. The d-d band at 16000

cm^{-1} for these compounds disappeared upon the addition of ascorbic acid under nitrogen atmosphere and appeared again when the solution was exposed to air. These complexes were found to be good catalysts for the oxidation of 3,5-DTBC where as square planar complexes $Cu(acac)_2$ and Cu(salen) have very little activity.

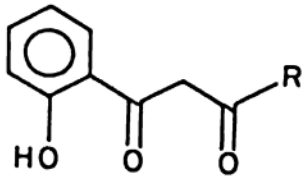


31

Catalytic activity for the oxidation of 3,5-DTBC by some mono and dinuclear copper(II) complexes **32** and **33** were compared.[92] The ability of dinuclear complexes decreased in the order Cu(aap) > Cu(bap) > $Cu(daa)_2$ > $Cu(baa)_2$. The dinuclear complexes showed enhanced activity over its mononuclear analogues. The dicobalt(II) complexes show low catalytic activity.



32



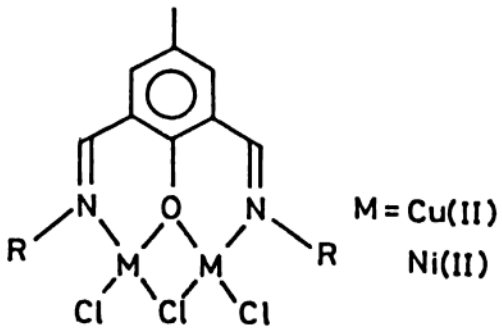
R = Me, aap
R = Ph, baap

33

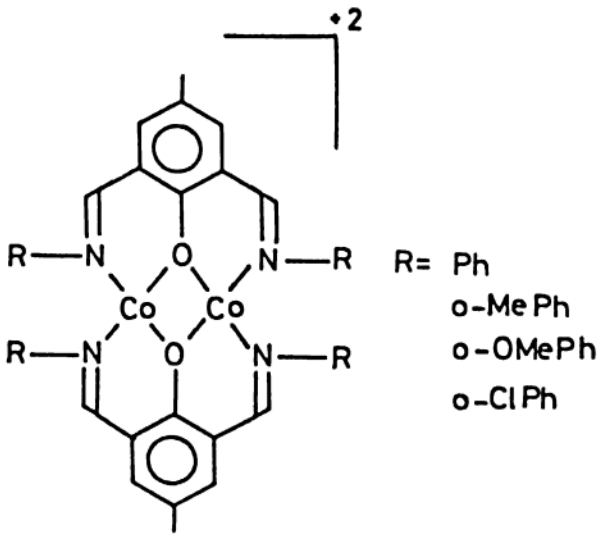
Catalytic oxidation of substituted diphenols by copper(II) complexes derived from 2,6-diformyl-4-methylphenol and aminoacids in presence of appropriate copper(II) salts gave several products such as oligomers, polymers

besides the desired quinone.[93,94]

Recently catalytic activity of dinuclear copper(II), nickel(II) and cobalt(II) complexes 34 and 35 for the oxidation of 3,5-DTBC has been reported.[95,96] The conversion of catechol to quinone was complete in about 90 minutes for the copper(II) complexes. The copper(II) complex with R = O-ClC_6H_4 substituent showed maximum catalytic activity in the group. The electron transfer reaction between ascorbic acid and these complexes were investigated. It was shown that these complexes can be easily reduced to copper(I) species. The nickel(II) and cobalt(II) complexes were found to be less active than copper(II) complexes.



34



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1.5 Scope of the present investigation

It is clear from the discussion in section 1.1 that some reactions of

copper(II) amino acid complexes with aldehydes are stereospecific and are influenced by the chirality of the α-amino acidato ligands.[31,34,35,37] For example $Cu(L\text{-ala})_2$ with formaldehyde and ammonia at pH 8.5 gives complex 5, while $Cu(DL\text{-ala})_2$ gives 6. Similarly $Cu(L\text{-ser})_2$ and $Cu(DL\text{-ser})_2$ react with formaldehyde at pH 4.5 to give products 7 and 8 respectively. However the role of chirality in these reactions has not been studied in detail. Therefore it seemed appropriate to investigate these reactions more thoroughly to understand the role of chirality. The reactions of copper(II) complexes of L and DL forms of serine and threonine are known with only formaldehyde and acetaldehyde and there are no reports on the reactions of these complexes with other aliphatic aldehydes. In view of this , we have proposed to examine the reactions of copper(II) complexes of DL and L forms of alanine under various experimental conditions with formaldehyde and ammonia, serine, threonine with aldehydes such as propionaldehyde, n- and iso-butyraldehydes, caproaldehyde and n-veleraldehyde.

It was previously reported[35] from our group that $Cu(DL\text{-ser})_2$ and $Cu(DL\text{-thr})_2$ reacts with formaldehyde at pH 4.5 to give the products 8 and 10 containing dimethylene ether groups. Structures of these complexes were deduced from only IR and analytical data. To establish their structures unambiguously, crystal structures of these complexes were solved by X-ray method. The structures are found to be as predicted from spectral and other data.

Many macrocyclic dinuclear copper(II) complexes derived from 2,6-diformyl-4-methylphenol are known and are studied for their structural, magnetic and redox properties. In contrast very few reports are available on other transition metal complexes, in particular iron and manganese and to some extent nickel and cobalt. The dinuclear Cu(II), Ni(II), Co(II), Mn(II) and

Fe(II) complexes of macrocycle 15 are known and are investigated. Macrocyclic copper(II) complexes using 1,2-diaminoethane and 1,4-diaminobutane are synthesized in which the size of the macrocycles are different. There are no reports on Co(II), Mn(II) and Fe(II) complexes of these macrocycles. Hence these metal complexes are synthesized with varying the size of the macrocycles using amines of the type NH_2-$(CH_2)_n$-NH_2. Their structure, magnetic and redox properties are investigated.

Another macrocycle 22 is obtained from 15 by reducing the azomethine linkages to -CH-NH-. Complexes with this reduced ligands are synthesized and investigated to identify the differences in their magnetic and electrochemical properties.

1.6.0 References

1. M. Voelterer, G. Sokolowski, V. Weber and V. Weser, *Eur. J. Biochem.*, 1975, 58, 159; J.K. Beattie, D.J. Fenson and H.C. Freeman, *J. Am. Chem. Soc.*, 1976, 98, 500.
2. B.A. Goodman, D.B. McPhail and K.J. Powell, *J. Chem. Soc., Dalton Trans*, 1981, 822.
3. J.M. Tsugaris and R.B. Martin, *J. Am. Chem. Soc.*, 1970, 92, 4255; T.P.A. Cruck and B. Sarkar, *Can. J. Chem.*, 1973, 51, 3549, 3563.
4. H.A. Kuska and M T. Rogers, *J. Chem. Phys.*, 1965, 43, 1744; H. Yokoi amd T. Isobe, *Bull. Chem. Soc. Jpn.*, 1969, 42, 2085.
5. H. Yokoi, M. Sai and T. Isobe, *ibid.*, 1972, 42, 3488.
6. H. Yokoi, M. sai, T. Isobe and S. Ohsawa, *ibid.*, 1972, 42, 2189.
7. H.C. Allen Jr, M.I. Andrioli and J.W. Becker, *J. Chem. Phys.*, 972, 56, 997.
8. G. Thomas and P.S. Zacharias, *Polyhedron*, 1984, 3, 861.
9. G. Thomas and P.S. Zacharias, *ibid.*, 1985, 4, 811.
10. P.S. Zacharias, T. Sreenivas and J.M. Elizabathe, *ibid.*, 1986, 5, 1383
11. M. Sato, K. Okawa and S. Akbori, *Bull. Chem. Soc. Jpn.*, 1957, 30, 937.
12. S. Akbori, T.T. Octani, R. Marshall, M. Wintiz and J.P. Greenstein, *Arch. Biochem. Biophys.*, 1959, 83, 1.
13. Y. Ikutani, T. Okuda, M. Sato and S. Akbori, *Bull. Chem. Soc. Jpn.*, 1959, 32, 203.
14. M. Murukami and K. Takahashi, *ibid.*, 1957, 32, 308.
15. T.T. Octani and M. Wintiz, *Arch. Biochem. Biphys.*, 1966, 90, 254.
16. F. Basalo and R.G. Pearson, 'Mechanism of Inorganic Reactions', Wiley, Newyork, 1967, p.633.
17. Y. Ichikuwa, S. Maeda, T. Okamato, Y. Araki and Y. Ishido, *J. Am. Chem. Soc.*, 1970, 92, 5514.

18. J.P. Aune, P. Maldonado, G. Larcheres and M. Pierrot, *J. Chem. Soc., Chem. Commun.*, 1970, 1351.

19. T. Ichikawa, S. Maeda, T. Okamato, Y. Araki and Y. Ishido, *Bull. Chem. Soc. Jpn.*, 1971, 44, 2779.

20. S.B. Teo and S.G. Teoh, *Inorg. Chim. Acta.*, 1980, 44, L269.

21. R.D. Gillard, S.H. Laurie, D.C. Price, D.A. Phipps and C.F. Weick, *J. Chem. Soc., Dalton Trans.*, 1974, 1385.

22. R.J. Geue, M.R. Snow, J. Springborg, A.J. Herlet, A.M. Sargeson and D. Taylor, *J. Chem. Soc., Chem. Commun.*, 1976, 285.

23. M.J. O'Connor, J.F. Smith and S.B. Teo, *Aust. J. Chem.*, 1976, 29, 375.

24. K. Noda, M. Bessho, T. Karto and N. Izumiya, *Bull. Chem. Soc. Jpn.*, 1970, 43, 1834.

25. M. Fujikova, Y. Nakao and A. Nakahara, *J. Inog. Nucl. Chem.*, 1977, 39, 1805.

26. A.E. Martell, 'Metal ions in Biological Systems', Ed., H. Sigel, Dekker, Newyork, 1973, vol. 2, p.208; E.N. Safanova and V.M. Belikov, *Russ. Chem. Rev.*, 1974, 43, 745.

27. A. Pasini and L. Casella, *J. Inorg. Nucl. Chem.*, 1974, 36, 2133; R.D. Gillard, P. O'Brien, P.R. Norman and D.A. Phipps, *J. Chem. Soc., Dalton Trans.*, 1977, 1988; D.A. Phipps, *J. Mol. Catal.*, 1974, 5, 81.

28. J.R. Brush, R.J. Magee, M.J. O'Conner and S.B. Teo, *J. Am. Chem. Soc.*. 1973, 95, 2034.

29. S.B. Teo, S.G. Teoh and M.R. Snow, *Inorg. Chim. Acta*, 1984, 85, L1.

30. S.B. Teo and S.G. Teoh, *Inorg. Chim. Acta*, 1984, 91, L17.

31. S.B. Teo, S.G. Teoh and M.R. Snow, *Inorg. Chim. Acta*, 1985, 107, 211.

32. N. Arulsamy, K. Rajeshwar and P.S. Zacharias, *Polyhedron*, 1992, 11, 1837

33. H.C. Freeman and J.M. Guss, *Acta. Crystallogr.*, 1968, B24, L23.

34. S.B. Teo, C.H. Ng and E.R.T. Tiekink, *Inorg. Chim. Acta*, 1989, 163, 129.

35. N. Arulsamy, B. Srinivas and P.S. Zacharias, *Transition Met. Chem.*, 1990, 15, 309.

36. J.C. Dabrowiak and D.W. Cooke, *Inorg. Chem.*, 1975, 14, 1305.

37. N. Arulsamy, Chepuri R.K. Rao and P.S. Zacharias, *Transition Met. Chem.*, 1991, 16, 606.

38. R. Robson, *Inorg. Nucl. Chem. Lett.*, 1970, 6, 125.

39. R. Robson, *Aust. J. Chem.*, 1970, 23, 2217.

40. D.E. Fenton, U. Casellato, P.A. Vigato and M. Vidali, *Inorg. Chim. Acta*, 1984, 95, 187.

41. D.E. Fenton, U. Casellato, P.A. Vigato and M. Vidali, *ibid.*, 1982, 62, 57.

42. U. Casellato, D.E. Fenton and M.R. Vidali, *Coord. Chem. Rev.*, 1979, 8, 199.

43. S.E. Groh, *Isr. J. chem.*, 1976, 15, 277.

44. E.I. Soloman, D.M. Dooley, R. Wang, H.B. Gray, M. Cerdonio, F. Magno and G.L. Romain, *J. Am. Chem. Soc.*, 1976, 98, 1029.

45. N. Makino, P. McMahill, H.S. Mason and T.H. Moss, *J. Bio. Chem.*, 1974, 249, 6062.

46. B.F. Hoskins and G.A. Williams, *Aust. J. Chem.*, 1975, 2607.

47. B.F. Hoskins, N.J. McLeod and H. Schaap, *Aust. J. Chem.*, 1976, 29, 515.

48. C.L. Spiro, S.L. Lambert, T.J. Smith, E.N. Duesler, R.R. Gagne and D.N. Hendrickson, *Inorg. Chem.*, 1981, 20, 1229.

49. R.R. Gagne, C.L. Spiro, T.J. Smith, C.A. Hamann, W.R. Thies and A.K. Shiemke, *J. Am. Chem. Soc.*, 1981, 103, 4073.

50. D. Luneau, J.M. Savariault, P. Cassoux and J.P. Tuchagues, *J. Chem. Soc., Dalton Trans.*, 1988, 1225.

51. H. Okawa and S. Kida, *Bull. Chem. Soc. Jpn.*, 1972, 45, 1759.

52. B. Adhikary, A.K. Biswas, K. Nag, P. Zanello and A. Cinquantini, *Polyhedron*, 1987, 6, 897.

53. H. Okawa, M. Honda and S. Kida, *Chem. Lett.*, 1972, 1027.

54. S.K. Mandal, L.K. Thompson, M.J. Newlands, A.K. Biswas, B. Adhikary, K. Nag, E.J. Gabe and F.L. Lee, *Can. J. Chem.*, 1989, 67, 662.

55. S.K. Mandal, L.K. Thompson, M.J. Newlands and E.J. Gabe, *Inorg. Chem.*, 1989, 28, 3707.

56. R.R. Gagne, C.A. Koval and T.J. Smith, *J. Am. Chem. Soc.*, 1977, 99, 8367.

57. R.R. Gagne, C.A. Koval and T.J. Smith, *ibid.*, 1979, 4571.

58. R. Robson, *Inorg. Nucl. Chem. Lett.*, 1970, 6, 125.

59. R. Robson, *Aust. J. Chem.*, 1970, 23, 2217.

60. H. Okawa, I. Ando and S. Kida, *Bull. Chem. Soc. Jpn.*, 1974, 47, 3041.

61. W.D. McFadyen and R. Robson, *J. Coord. Chem.*, 1976, 5, 49.

62. H. Okawa and S. Kida, *Bull. Chem. Soc. Jpn.*, 1974, 14, 1172.

63. H. Okawa, S. Kida, Y. Muto and T. Tokii, *ibid.*, 1972, 45, 2480.

64. H. Okawa, T. Tokii, Y. Nonako, Y. Muto and S. Kida, *ibid.*, 1973, 46, 1462.

65. T. Ichinose, Y. Nishida, H. Okawa and S. Kida, *ibid.*, 1974, 47, 3045.

66. R.R. Gagne and R. Robson, *Inorg. Chem..*, 1974, 13, 1301.

67. R.R. Gagne, R.P. Creh and J.A. Dodge, *J. Am. Chem. Soc.*, 1979, 101, 6917.

68. J.J. Grzybowski, F.H. Merrel and F.L. Urbach, *Inorg. Chem.*, 1978, 17, 3078.

69. J.R. Majeste, C.L. Klein and E.D. Stevens, *Acta. Crystallogr., Sect C,* 1983, 39, 52.

70. B.F. Hopkins, R. Robson and H.A. Schoap, *Inorg. Nucl. Chem. Lett.*, 1975, 8, 21.

71. S.K. Mandal and K. Nag, *J. Chem. Soc., Dalton Trans.*, 1984, 2429.

73 R.R. Gagne, M.W. McCool and R.E. Marsh, *Acta. Crystallogr., Sect B,* 1986, 36, 2420.

74. H. Sakiyama, H. Tamaki, M. Kodera, N. Matsumoto and H. Okawa, *J. Chem. Soc., Dalton Trans.*, 1993, 591.

75. N.H. Pilkington and R. Robson, *Aust. J. Chem.*, 1970, 23, 2225.

76. R.N. Buchanan, K.J. Oberhausen and J.F. Richardson, *Inorg. Chem.*, 1988, 27, 971.

77. M. Suzuki, A. Vehara, H. Oshio, K. Endo, M. Yanaga, S. Kida and K. Saito, *Bull. Chem. Soc. Jpn.*, 1987, 60, 3547.

78. A.S. Borovik and Lawrence Que, Jr., *J. Am. Chem. Soc.*, 1988, 110, 2345.

79. M.S. Masuta, R.J. Web, K.J. Oberhauser, J.F. Richardson, R.M. Buchanan and D.N. Hendrickson, *J. Am. Chem. Soc.*, 1989, 111, 2745.

80. M. Suzuki, S. Murata, A. Vehara and S. Kida, *Chem. Lett.*, 1987, 281.

81. Y. Maeda, Y. Tanigawa, S. Hayami and Y. Takashima, *Chem. Lett.*, 1992, 591.

82. S.K. Mandal, L.K. Thompson, K. Nag, J.P. Charland and E.J. Gabe, *Inorg. Chem.*, 1987, 26, 1391.

83. S.K. Mandal, L.K. Thompson, K. Nag, J.P. Charland and E.J. Gabe, *Can. J. Chem.*, 1987. 65, 2815.

84. K. Nag and R.P. Das, *Inorg. Chem.*, 1991, 30, 2831.

85. D.E. Fenton, R.R. Schroeder and R.L. Lintvedt, *J. Am. Chem. Soc.*, 1978, 100, 1431.

86. S.K. Mandal and K. Nag, *J. Chem. Soc., Dalton Trans.*, 1983, 2429.

87. P. Lacroix, O. Kahn, F. Theobald, J. Leroy and C. Wakselman, *Inorg. Chim. Acta*, 1988, 142, 129.

88. B. Adhikary, S.K. Mandal and K. Nag, *J. Chem. Soc., Dalton Trans.*, 1988, 935.

89. S.K. Mandal, B. Adhikary and K. Nag, *J. Chem. Soc., Dalton Trans.*, 1986, 1175.

90. Y. Nishida, N. Oishi, H. Kumarato and S. Kida, *Inorg. Chim. Acta*, 1982, 57, 753.

91. N. Oishi, Y. Nishida, K. Ida and S. Kida, *Bull. Chem. Soc. Jpn.*, 1980, 53, 2847.

92. U. Casellato, S. Tamburini, P.A. Vigato, A. Destefani, M. Vidali and D.E. Fenton, *Inorg. Chim. Acta.*, 1983, 69, 45.

93. K. Moore and G.S. Vigee, *Inorg. Chim. Acta*, 1982, 66, 125.

94. D. Bolus and G.S. Vigee, *Ibid.*, 1982, 67, 19.

95. B. Srinivas, N. Arulsamy and P.S. Zacharias, *Polyhedron*, 1991, 10, 731.

96. B. Srinivas and P.S. Zacharias, *Transition Met. Chem.*, 1991, 16, 521.

CHAPTER - II

SYNTHESIS OF LIGANDS, METAL COMPLEXES AND METHODS OF MEASUREMENTS

2.1.0 Chemicals

L-alanine, DL-alanine, L-serine, DL-serine, L-threonine, DL- threonine, formaldehyde(40% W/V), propionaldehyde, n- and iso-butyraldehyde, valeraldehyde and n-caproaldehyde (Sisco and Fluka), p.toluene-4-sulfonylchloride (Fluka), sodium dichromate (SD) were used as supplied. All amines 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane and 1,6-diaminohexane were distilled prior to use. The solvents, methanol, ethanol, chloroform were purified by standard methods.[1-4] Spectroscopic grade N,N'-dimethylformamide (DMF), acetonitrile (SD fine chemicals) were used for spectral and electrochemical studies. These solvents were purified by stirring over CaH_2 followed by vacuum distillation at low temperatures and stored over molecular sieves. Iron(II) perchlorate hexahydrate was prepared by slow action of perchloric acid with iron(II) sulphide lumps. Other metal(II) perchlorates were prepared by treating perchloric acid with respective carbonates. Manganese(II) perchlorate hexahydrate was purchased from Fluka.

2.2.0 Preparation of tetraethylammonium perchlorate (TEAP)

A warm solution of sodium perchlorate monohydrate (13.0 g, 0.1 mol) in water (200 cm^3) was added to a solution of tetraethylammonium bromide (21 g, 0.1 mol) while stirring. The reaction mixture was concentrated and cooled. The resulting white crystalline product was recrystallized several times from water and dried over P_2O_5. Yield is 90% before recrystallization.

Tetrabutylammonuim perchlorate(TBAP) is prepared in a similar way.

Caution : All perchlorates are explosive prone and have to be handled with care.

2.3.0 Preparation of copper(II) amino acid complexes

2.3.1.0 Reactions of $Cu(L\text{-}ala)_2$ and $Cu(DL\text{-}ala)_2.H_2O$ with formaldehyde and ammonia

Bis(α-amino acidato)copper(II) complexes, *viz.*, $Cu(L\text{-}ala)_2$, $Cu(DL\text{-}ala)_2.H_2O$, $Cu(L\text{-}ser)_2$, $Cu(D\text{-}ser)_2$, $Cu(DL\text{-}ser)_2$, $Cu(L\text{-}thr)_2.H_2O$, $Cu(D\text{-}thr)_2$, and $Cu(DL\text{-}thr)_2$ were prepared by known procedure.[5]

2.3.1.1 Preparation of [(2R,8S)-3N,7N-(1,3,5,7-tetraazabicyclo[3.3.1]-nonyl)dipropionato]copper(II) (36)

To an aqueous solution (25 cm^3) of $Cu(DL\text{-}ala)_2.H_2O$ (1.25 g, 5 mmol) was added formaldehyde solution (10 cm^3, 37% w/v) and ammonia (5 cm^3, 25% w/v). The reaction mixture was stirred well and the pH was adjusted to 6 by addition of hydrochloric acid. The solution was filtered and the filtrate was allowed to stand at room temperature for about seven days. The blue microcrystalline product was separated by filtration, washed with little amount of ethanol, diethylether and dried in vacuum at 50°C for 12 h.

2.3.1.2 Preparation of bis[(R,S)-4-Methyloxazolidine-4 -carboxylato] copper(II) dihydrate (6)[6]

Similar reaction procedure used for the preparation of 36 is used except that the pH is adjusted to 8.5 by the addition of ammonia solution. The deep blue crystals that formed after seven days were filtered, washed successively with cold distilled water, ethanol and acetone and were finally

dried under reduced pressure at 50^0C for 12 h.

2.3.1.3 Preparation of bis[(S)-4-Methyloxazolidine-4-carboxylato] copper(II) dihydrate (37)

To an aqueous solution (25 cm^3) of $Cu(L\text{-}ala)_2$ (1.11 g, 5 mmol) was added formaldehyde (10 cm^3, 37% w/v). The reaction mixture was stirred well, adjusted to pH 10 by addition of ammonia (25% w/v) and filtered. The filtrate was allowed to stand at room temperature for about seven days. The volume of the reaction mixture was reduced to one fourth on water bath and cooled. The blue product deposited was filtered, washed with little amount of ethanol and diethylether and dried in vacuum at 50^0C for 12 h.

This product is identified to be optically inactive bis[(R,S)-4-methyl-oxazolidine-4'-carboxylato]copper(II) dihydrate, 6.

2.3.1.4 Preparation of [(2S,8S)-3N,7N-(1,3,5,7-tetraazabicyclo[3.3.1]di-propionato]copper(II) (5)[7]

Procedure similar to that used for the preparation of 37 is followed. The pH of the reaction mixture was adjusted to 8.5 by the slow addition of ammonia solution and filtered. After seven days, the dark blue solution was reduced to 15 ml. Blue needle shaped crystals were filtered, washed with ethanol and acetone and dried under reduced pressure at 50^0C for 12 h.

2.3.2.0 Reactions of copper(II) complexes of D, L and DL forms of serine and threonine with aliphatic aldehydes

The reactions of $Cu(L\text{-}ser)_2$, $Cu(DL\text{-}ser)_2$, $Cu(L\text{-}thr)_2$, $Cu(DL\text{-}thr)_2$ with aliphatic aldehydes propionaldehyde, n- and iso-butyraldehyde, valeraldehyde and n-caproaldehyde were carried out by the following general procedure. *It must be noted that D and L forms of serine and threonine with these aldehydes did not yield any products.*

In a typical reaction, to an aqueous solution (25 cm^3) of $Cu(DL\text{-}ser)_2$ (1.35 g, 5 mmol) was added propionaldehyde (1 cm^3, 13.9 mmol). The reaction mixture was stirred well and allowed to stand at room temperature for six hours. Blue crystalline product 38 formed was filtered, washed with acetone, diethylether and dried in vacuum at 50^0C for 12 h.

Reactions of $Cu(DL\text{-}ser)_2$ with other aldehydes, *viz.*, n- and iso-butyraldehyde, valeraldehyde and n-caproaldehyde yielded the products 39-43. Reaction of these aldehydes with $Cu(DL\text{-}thr)_2$ yielded the products 44-49.

2.3.2.1 Preparation of aqua[N,N'-(2-oxapropanediyl)bis(oxazolidine-4-carboxylato)]copper(II) dihydrate (8)[8]

To an aqueous solution (50 ml) of $Cu(DL\text{-}ser)_2$ (1.35 g, 5 mmol) excess formaldehyde (15 ml, 40% w/v) was added and the reaction mixture was stirred and filtered. The filtrate (pH 4.5) was allowed to stand at room temperature for seven days. Blue crystals suitable for X-ray analysis were obtained.

2.3.2.2 Preparation of [N,N'-(2-oxapropanediyl)bis(5-Methyloxazolidine-4-carboxylato)]copper(II) monohydrate (10)[8]

This complex was prepared from $Cu(DL\text{-}thr)_2$ by the method described for

the complex 8. The product was deep blue coloured and crystalline.

2.4.0 Synthesis of ligands

2,6-Diformyl-4-methylphenol was prepared according to the procedure given by Gagne *et al*[9] and is preferred over that reported by Ulmann and Britner.[10] The ligands H_2L^1-H_2L^3 and H_2L^8-H_2L^{10} are not isolated and prepared according to the procedure given by Pilkington and Robson[11] in presence of metal salts. The ligands H_2L^4- H_2L^6 are prepared by the procedure reported by Mandal *et al.*[12] Preparation of these ligands involves condensation of 2,6-diformyl -4-methylphenol and an appropriate α,ω-diamine in presence of template ion Mg^{+2} or Pb^{+2} followed by reduction with $NaBH_4$.

2.4.1 Synthesis of 2,6-diformyl-4-methylphenol

p-Cresol (21.6 g) was added to a solution of NaOH (10 g) in 40 ml of water. Following full development of gold colour, 37% formaldehyde (43 g) was added. The mixture was stirred for 20 minutes and kept overnight. The yellow granular 2,6-dimethylol-4-methylphenol was filtered and washed with saturated sodium chloride solution (2 X 40 ml).

The above product was transferred to 1L round bottom flask fitted to an overhead stirrer. Water (130 ml) and 13 ml of 33% NaOH solution were added. The mixture was stirred for 0.5 h, p-toluene-4-sulfonylchloride (49.4 g) dissolved in toluene (52 ml) was added and the solution was allowed to stir for 20 h. The mixture was cooled in ice-water bath and toluene (20, 30, 10 ml) was added in 20 minute intervals. The white tosylated derivative was collected by vacuum filtration, washed with toluene (40 ml) and dried under vacuum for 12 h.

The dry tosylated derivative was taken in 500 ml three-neck round bottom flask equipped with overhead reflux condenser and 125 ml addition funnel. Acetic acid (14 mol/1 mol of tosylated derivative) and sodium dichromate (1 mol/mol of tosylated phenol) were used for the oxidation as follows. One fourth of acetic acid was added to the tosylated phenol and the mixture was heated to reflux with stirring. The remaining acetic acid was added to the sodium dichromate and heated to dissolve on water bath. This solution was added dropwise with stirring to the tosylated phenol over 35 minutes after which the solution is allowed to cool slowly to ambient temperature. The dark green crystalline solid formed was filtered and washed with ice-cold water until a pale green solid was obtained.

The dry tosylated dialdehyde (28 g) was added slowly to con.H_2SO_4 (90 ml) while stirring for 1 h. The beaker was placed in an ice bath and ice-water slurry was added to the acid solution until the volume reached 400 ml. The precipitate was collected by filtration and washed with little amount of water. The crude product was recrystallized from toluene to obtain pure yellow crystalline product of 2,6-diformyl-4-methylphenol (9 g, 28% yield) which melts at 131^{0}C.

^{1}H NMR ($CDCl_3$, δ): 2.4 (s, 3H, Me), 7.8 (s, 2H, Ar), 10.2 (s, 2H, aldehyde)
11.4 (s, 1H, phenolic).

The macrocyclic ligands H_2L^1-H_2L^3 and H_2L^8-H_2L^{10} are not isolated and synthesis of metal complexes is discussed in sections 2.5.0 and 2.5.6.0.

2.4.2 Preparation of macrocyclic ligand H_2L^4

To a boiling methanol solution (50 ml) of 2,6-diformyl-4-methyl phenol (4.9 g, 30 mmol) was added a hot methanol solution (20 ml) of $Mg(NO_3)_2.6H_2O$ (7.79 g, 30 mmol) and 1,2-diaminoethane (1.8 g, 30 mmol). The mixture was refluxed for 8 h during which time a yellow crystalline compound deposited. The product was filtered, washed with methanol and air dried. The magnesium complex (8.1 g) was finely ground to powder and suspended in methanol (150 ml). To this stirred suspension was added an aqueous solution (10 ml) of $NaBH_4$ (5 g) in small portions over a period of 1 h. During this period all the material went into the solution and colourless solution was obtained. After additional stirring for 1 h, the solution was filtered, diluted with water (400 ml) and acidified with HCl (6 M) to make clear solution. To this solution was added the disodium salt of EDTA (10 g) dissolved in mixture of water (15 ml) and ammonia (25 ml) with stirring. The solution was adjusted to pH *ca.*10 by adding ammonia and the solution was extracted with chloroform (2 X100 ml). The chloroform extract after treating with anhydrous Na_2SO_4 was evaporated to dryness. The product H_2L^4 was recrystallized from methanol (yield 16%) which melts at 210-211^{0}C.

IR (Nujol, cm^{-1}): 3520 [m, ν(OH)], 3250 [m, ν(NH)], 1605 [m, δ(NH)], 1250 [m, ν(CO)].

^{1}H NMR ($CDCl_3$, δ): 2.2 (s, 6H, Me), 2.80 (s, 8H, CH_2CH_2), 3.76 (s, 8H, ArCH), 4.02 (br.s, 6H, NH, OH), 6.73 (s, 4H, Ar)

2.4.3 Preparation of macrocyclic ligand H_2L^5

To a boiling methanol solution (50 ml) of 2,6-diformyl-4-methylphenol (4.9 g, 30 mmol) was added a mixture of $Pb(OAc)_2$ $3H_2O$ (5.7 g, 15 mmol) and $Pb(NO_3)_2$ (5 g, 15 mmol) dissolved in hot DMF (20 ml) and 1,3-diaminopropane (2.2 g, 30 mmol) diluted with methanol (20 ml) at one time . The resulting mixture

was refluxed for 8 h during which time an orange-yellow crystalline product deposited. This was filtered, washed with methanol and chloroform and finally air dried. This complex (9 g) was pulverized and suspended in methanol (120 ml). Sodium borohydride (3.5 g) dissolved in water (10 ml) was added to this suspension with stirring over a period of 30 minutes. Stirring was continued for 2 h, after which the solution was filtered to remove any undissolved material. The filtrate was diluted with water (350 ml) and acidified with cold dilute H_2SO_4 (8 M). Lead sulphate precipitated was filtered and was washed with cold water. The combined filtrate was treated with ammonia in an ice bath until the solution reached pH *ca.*10. This was then extracted with chloroform (2 x100 ml). The chloroform layer was treated with Na_2SO_4, filtered and evaporated to dryness. This on extraction with pet ether (80-100 ^{0}C) and slow evaporation gave a colourless crystalline product H_2L^5 (2.1 g, 30% yield) which melts at 125 ^{0}C.

IR (nujol, cm^{-1}): 3540 [m, ν(OH)], 3260 [m, ν(NH)], 1605 [m, δ(NH)], 1250 [m, ν(CO)]

^{1}H NMR ($CDCl_3$, δ): 1.86 (q, 4H, $CH_2CH_2CH_2$), 2.18 (s, 6H, Me), 2.58 (t, 8H, $CH_2CH_2CH_2$), 3.83 (s, 8H, Ar-CH_2), 5.1 (br, 6H, NH, OH), 6.74 (s, 4H, Ph).

2.4.4 Preparation of macrocyclic ligand H_2L^6

Similar procedure that employed for the preparation of macrocycle H_2L^4 was followed. Yield of the product is 12%.

M.P. 178-179^{0}C

IR (KBr) 3450 [br, ν(OH)], 3270 [m, ν(NH)], 1610 [m, δ(NH)],

1260 [m, ν(CO)].

^{1}H NMR ($CDCl_3$, δ) 1.56 (m, 8H, $CH_2CH_2CH_2CH_2$), 2.21 (s, 6H, Me), 2.61 (t, 8H, $CH_2CH_2CH_2CH_2$), 3.81 (s, 8H, Ar-CH_2), 4.71 (br s, 6H, NH, OH), 6.73 (s, 4H, Ph).

2.4.5. Preparation of ligand L^7

The ligand L^7 is obtained by reacting the diamine, 3,3'-dimethyl-4,4'-diaminodiphenyl and pyridine-2-aldehyde in 1:2 molar ratio. In a typical reaction, 20 mmol of the diamine was dissolved in absolute ethanol (50 ml) and 40 mmol of freshly distilled pyridine-2-aldehyde was added in absolute ethanol (20 ml) and the mixture was refluxed for 3-4h. The resulting yellow solids were filtered and washed with alcohol to get analytically pure compound.

Structures of these ligands are shown in Fig.2.1.

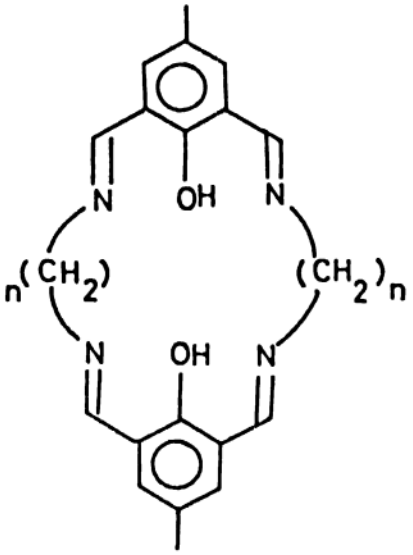
2.5.0 Synthesis of metal complexes

2.5.1 Synthesis of copper(II) complexes

All complexes derived from ligands H_2L^1-H_2L^3 are prepared by the same procedure adopted by Robson *et al*[11] and complexes derived from ligands H_2L^4-H_2L^6 are prepared by the procedure given by Mandal and Nag.[13,14]

2.5.1.1 Preparation of $Cu_2[L^1$-$L^3](ClO_4)_2$ complexes (50-52)

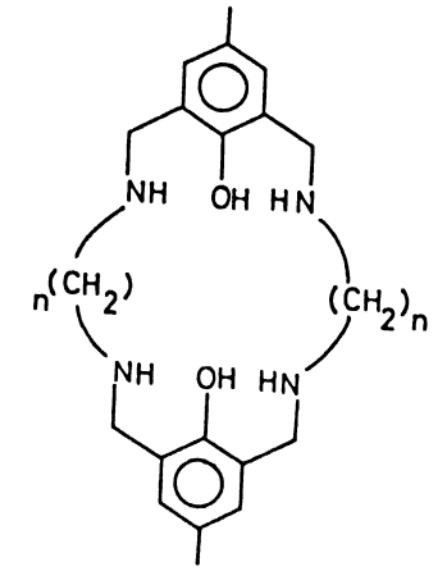
1,2-diaminoethane (0.180 g, 3 mmol) dissolved in methanol (10 ml) was added to a solution of copper perchlorate (0.74 g, 2 mmol) in methanol (25 ml). 2,6-diformyl-4-methylphenol (0.328 g, 2 mmol) in methanol (25 ml) was added



n = 2, H_2L^1

n = 4, H_2L^2

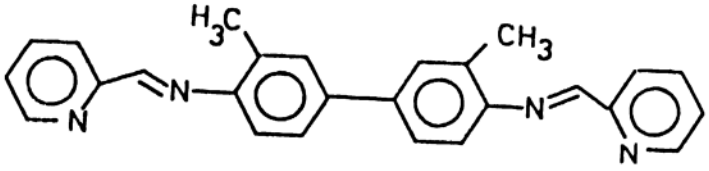
n = 6, H_2L^3



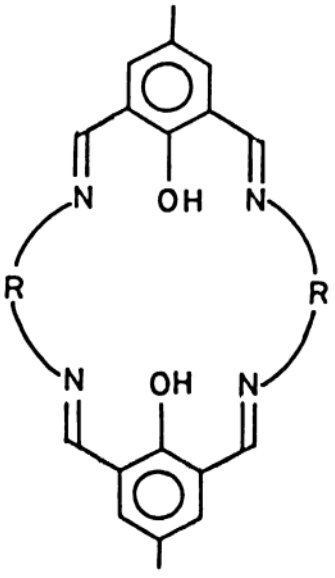
n = 2, H_2L^4

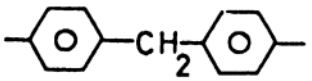
n = 3, H_2L^5

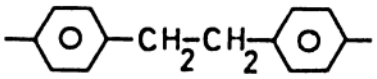
n = 4, H_2L^6

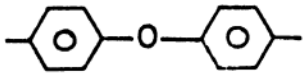


L^7



H_2L^8 R = 

H_2L^9 R = 

H_2L^{10} R = 

$H_2L^8 - H_2L^{10}$

Fig.2.1 Structures of the ligands.

while hot and the resulting mixture was refluxed for 7 h with stirring. The green precipitate $[Cu_2L^1(ClO_4)_2]$, 50 was filtered and washed with water. This was recrystallized from 1:1 methanol and water mixture.

The complexes $Cu_2L^2(ClO_4)_2$ and $Cu_2L^3(ClO_4)_2$, 51 and 52 were prepared by similar methods.

2.5.1.2 Preparation of $Cu_2[L^4\text{-}L^6](ClO_4)_2$ complexes (53-55)

To the ligand H_2L^5 (0.41 g, 1 mmol) dissolved in methanol (10 ml) was added an aqueous (10 ml) solution of NaOH (0.08 g, 2 mmol). $Cu(ClO_4)_2.6H_2O$ (0.74 g, 2 mmol) dissolved in water (10 ml) was added and the resulting mixture was refluxed for 3 h. The deep green crystals, 54 formed when cooled to room temperature were filtered and recrystallized from methanol.

A similar procedure was adopted for the preparation of complexes, 53 and 55, derived from the ligands H_2L^4 and H_2L^6. The resulting green products were recrystallized from methanol.

2.5.1.3 Preparation of $Cu_2L^7_2(ClO_4)_4$ complex (56)

To a suspension of ligand L^7 (0.362g, 1mmol) in ethanol (15 ml), an ethanolic solution (10 ml) of copper(II) perchlorate (0.370g, 1mmol) was added and refluxed for 3h. The resulting dark brown solid (56) was filtered washed with alcohol and dried under vacuum for 4h.

2.5.2.0 Preparation of nickel(II) complexes

2.5.2.1 Preparation of $Ni_2[L^1\text{-}L^3](ClO_4)_2$ complexes (57-59)

The nickel(II) complexes, $Ni_2L^1(ClO_4)_2$, 57 and $Ni_2L^3(ClO_4)_2$, 59 were prepared by methods similar to the corresponding copper(II) complexes. These complexes are orange or yellow in colour. The complex $Ni_2L^2(ClO_4)_2$, 58 was prepared according to the scheme 2.1.

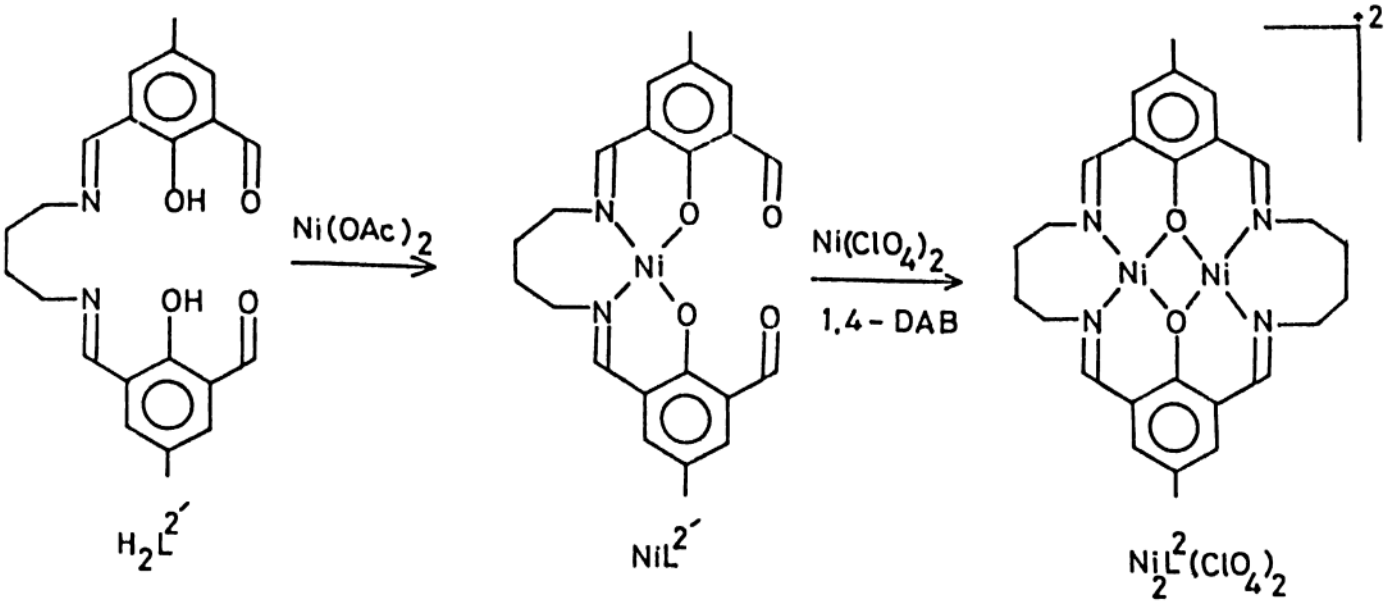
To the preformed ligand $H_2L^{2'}$ (0.4 g, 1 mmol) obtained by the condensation of 2,6-diformyl-4-methylphenol and 1,4-diaminobutane (2:1), in hot ethanol (5 ml) was added $Ni(OAc)_2$ (0.194 g, 1 mmol) in water (5 ml). The resulting green colour solution was evaporated to get mononickel(II) complex, $Ni(L^{2'})$. To this monocomplex in methanol (5 ml) was added $Ni(ClO_4)_2.6H_2O$ (0.310 g, 0.85 mmol) and 1,4- diaminobutane (0.075 g, 0.85 mmol) and refluxed for 3 h. The solids obtained after the removal of solvent were recrystallized from water-methanol mixture to get the green product, $Ni_2L^2(ClO_4)_2$.

2.5.2.2 Preparation of $Ni_2[L^4\text{-}L^6](ClO_4)_2$ complexes (60-62)

The complexes are prepared by the same procedure[14] as described for the preparation of the known complex, $Ni_2L^5(ClO_4)_2$, 61.

To the methanol solution (15 ml) of the ligand H_2L^5 (0.41 g, 1 mmol), $Ni(ClO_4)_2.6H_2O$ (0.731 g, 2 mmol) and triethylamine (0.3 ml, 98%) were added and refluxed for 1 h. The resulting wine red solution on concentration over $CaCl_2$ afforded pink crystalline compound, $Ni_2L^5(ClO_4)_2$. This was filtered and recrystallized from methanol by diffusion of diethylether.

The complexes derived from H_2L^4, 60 and H_2L^6, 62 were pink and green respectively and were recrystallized from methanol and diethylether.



Scheme 2.1 Synthetic route for the preparation of the complex $Ni_2L^2(ClO_4)_2$.

2.5.2.3 Preparation of $Ni_2L^7_2(ClO_4)_4$ complex (63)

The complex is prepared by the same procedure as described for the preparation of the corresponding copper(II) complex.

2.5.3.0 Preparation of cobalt(II) complexes

2.5.3.1 Preparation of $Co_2[L^1\text{-}L^3](ClO_4)_2$ complexes (64-66)

To 1,2-diaminoethane (0.180 g, 3 mmol) dissolved in dry methanol (10 ml), under dry nitrogen atmosphere, was added a solution of $Co(ClO_4)_2.6H_2O$ (0.732 g, 2 mmol) in methanol (10 ml), followed by 2,6-diformyl-4-methylphenol (0.328 g, 2 mmol) in methanol (15 ml) and was refluxed for 3 h. The black product $Co_2L^1(ClO_4)_2$, 64 obtained after the concentration of the reaction mixture was filtered, washed with diethylether and dried under vacuum at room temperature.

The complexes $Co_2L^2(ClO_4)_2$, 65 and $Co_2L^3(ClO_4)_2$, 66 were also prepared as described above and are brown in colour.

2.5.3.2 Preparation of $Co_2[L^4\text{-}L^6](ClO_4)_2$ complexes (67-69)

To the ligand H_2L^4 (0.384 g, 1 mmol) in dry methanol (15 ml) under dry oxygen free nitrogen was added methanol solution (10 ml) of $Co(ClO_4)_2.6H_2O$ (0.732 g, 2 mmol) followed by triethyl amine (0.3 ml, 98%) and was refluxed for 3 h. The resulting black product $Co_2L^4(ClO_4)_2$, 67, on concentration of the reaction mixture was filtered and washed with diethylether. This was recrystallized from methanol by diffusion of diethylether.

$Co_2L^5(ClO_4)_2$, 68 and $Co_2L^6(ClO_4)_2$, 69 were prepared and recrystallized by adopting the above procedure and were brown in colour.

2.5.3.3 Preparation of $Co_2L_2^7(ClO_4)_4$ complex (70)

The complex is prepared by the same procedure as described for the preparation of the corresponding copper(II) complex.

2.5.4.0 Preparation of iron(III) complexes

2.5.4.1 Preparation of $Fe_2[L^1\text{-}L^3](ClO_4)_4$ complexes (71-73)

These complexes are prepared by methods similar to that described for the corresponding $Co_2[L^1\text{-}L^3](ClO_4)_2$ complexes and are brown in colour.

2.5.4.2 Preparation of $Fe_2[L^4\text{-}L^6](ClO_4)_4$ complexes (74-76)

These complexes are prepared according to the procedures described for the preparation of corresponding $Co_2[L^4\text{-}L^6](ClO_4)_2$ complexes and are brown in colour.

2.5.5.0 Preparation of manganese(II) complexes

2.5.5.1 Preparation of $Mn_2[L^1\text{-}L^3](ClO_4)_2$ complexes (77-79)

These complexes are prepared by methods similar to that described for the $Co_2[L^1\text{-}L^3](ClO_4)_2$ complexes. Ihe complexes $Mn_2[L^1\text{-}L^2](ClO_4)_2$, 77 and 78 are brown and $Mn_2L^3(ClO_4)_2$, 79, is orange.

2.5.5.2 Preparation of $Mn_2[L^4\text{-}L^6](ClO_4)_2$ complexes (80-82)

These complexes are prepared by methods similar to that described for $Co_2[L^4\text{-}L^6](ClO_4)_2$ complexes and are brown in colour.

2.5.6.0 Preparation of lanthanide(III) complexes

To a methanolic solution (25 ml) of 2,6-diformyl-4-methylphenol (0.164 g, 1 mmol), was added sodium hydroxide (0.040 g, 1 mmol) and was stirred for 5 minutes. Lanthanum(III) nitrate (0.325 g, 1 mmol) was added to this and refluxed for 15 minutes. 4,4'-diaminodiphenylmethane (0.198 g, 1 mmol) was added and the refluxion was continued for 7h. The resulting orange red microcrystalline product (83) was filtered, washed with hot methanol, diethylether and air dried.

Similar reactions of 4,4'-diaminodiphenylethane and 4,4'-diaminodiphenylether with 2,6-diformyl-4-methylphenol in presence of lanthanum(III) nitrate gave complexes 84 and 85.

Complexes $Nd[L^8\text{-}L^{10}](NO_3)$, 86-88, $Sm[L^8\text{-}L^{10}](NO_3)$, 89-91 and $Eu[L^8\text{-}L^{10}](NO_3)$, 92-94 were prepared similarly.

2.6.0 Physical measurements

The C, H and N elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. Metal estimations were done on an inductively coupled plasma spectrometer (Labtem, Australia). Conductivity measurements were done on a CM-82T Elico conductivity meter at 25^0C in DMF at solution concentration of ca. 0.001 mole-dm^{-3}. Infrared spectra were recorded on a Perkin-Elmer 1310

spectrometer in the region 4000-600 cm^{-1} as KBr pellets. Electronic spectra were recorded on Perkin-Elmer Lamda 3B UV/VIS and Cary 17D spectrophotometer. The CD spectra were recorded on JASCO J20 instrument in the wavelength region 700-400 nm. ^1H NMR spectra were recorded on JEOL JEL 980B JNM-FX--100 FT NMR spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. Mossbauer spectra were recorded by employing a constant acceleration Eliscint drive in conjunction with multichannel analyzer (Promeda). The data were recorded in 512 channels with a mirror image spectrum simultaneously acquired. Magnetic susceptibility measurements were carried out by Faraday technique on CAHN research magnetic susceptibility system equipped with model 4600 adjustable gap electromagnet and CAHN 1000 electrobalance. $Hg[Co(SCN)_4]$ was used as standard. The resultant susceptibilities were corrected for diamagnetism. A JEOL FE-3X ESR spectrometer was used for recording the electron spin resonance spectra. Cyclic voltammograms were recorded on PAR elctrochemistry system consisting of model 174A polarographic analyzer, model 175 universal programmer and RE 0074 X-Y recorder. Model 374 three electrode cell system consisting of Metrohm E410 Hanging Mercury Drop Electrode(HMDE), BAS MF2013 Platinum or Glassycarbon electrode as working electrodes, PAR model 9331 saturated calomel electrode(S.C.E) as reference electrode and Pt-wire as auxiliary electrode were used. The experiments were carried out for 0.001 M solutions of the complexes under nitrogen atmosphere using sodium perchlorate monohydrate, tetraethyl or tetrabutyl ammonium perchlorates (TEAP or TBAP, 0.1 M) as supporting electrolytes at room temperature.

Catalysis experiments were carried out on Shimadzu UV 200S double beam spectrophotometer. These experiments were carried out in methanol using 3,5-di-t-butylcatechol (3,5-DTBC) as substrate by the following general procedure.

A methanol solution of 3,5-DTBC (0.001 M) and the respective copper(II), nickel(II) or cobalt(II) complexes (0.02 X 10^{-3}M) in 10 ml standard flask was kept under nitrogen. 3,5-di-t-butylquinone (3,5-DTBQ) has a characteristic absorbance band at 400 nm (ε/ $mol^{-1}dm^3$ cm^{-1}= 1900 in methanol[15]) and was taken as measure of quinone formation. Absorbance was measured at regular intervals immediately after exposing the solution to air.

X-Ray structural analyses were performed at room temperature on Nicolet R3m/V diffractometer equipped with molybdenum tube ($\lambda(k\alpha_1)$ = 0.70926 Å; $\lambda(k\alpha_2)$= 0.71354 Å) and a graphite monochromator. Cell constants were determined by least square fits to the scattering parameters of 50 independent reflections.The intensity data were collected in the 2θ range of 4-45 and 4-50^0 respectively for the complexes 8 and 10. The intensity of three standard reflections, measured after every 100, showed no significant decay. The crystal data were corrected for Lorentzian polarization effects and absorption. The structures were solved by direct methods or Patterson technique and refined by least square technique. The programs used were from the SHELXTL system.[16] The weighting schemes w = $[\sigma^2(F) + 0.0005\ F^2]^{-1}$ and w = $[\sigma^2(F) + 0.0004\ F^2]^{-1}$, respectively for 8 and 10, gave satisfactory analyses. All non-hydrogen atoms were refined anisotropically.

2.7.0 References

1. D.R. Burfield and R.H. Smithers, *J. Org. Chem.*, 1978, 43, 39966.
2. A.I. Vogel, 'Text book of practical organic chemistry', ELBS and Longman, 4th ed., 1978, 264.
3. J.A. Riddick and W.B. Burger, 'Organic solvents', Ed. A. Weissberger, 3, Wiley Interscience, Newyork, 1970.
4. D.D. Derrin, W.L.F. Armarego, D.R. Perrin, 'Purification of Laboratory chemicals', Pergamon press, London, 1966.
5. H.C. Freeman, M.J. Healy and M.L. Suddin, *J. Biol. Chem.*, 1977, 252, 8840.
6. S.B. Teo, S.G. Teoh and M.R. Snow, *Inorg. Chim. Acta*, 1985, 107, 211.
7. S.B. Teo CH Ng and E.R.T. Tiekink , *ibid.*, 1989, 163, 129.
8. N. Arulsamy, B. Srinivas and P.S. Zacharias, *Transition Met. Chem.*, 1990, 15, 309.
9. R.R. Gagne, C.L. Spiro, T.J. Smith, C.A. Hamann, W.R. Thies and A.K. Shiemke, *J. Am. Chem. Soc.*, 1981, 103, 4073.
10. F. Ulman and K. Brittner, *Chem. Ber.*, 1909, 42, 2539.
11. N.H. Pilkington and R. Robson, *Aust. J. Chem.*, 1970, 23, 2225.
12. S.K. Mandal and K. Nag, *J. Org. Chem.*, 1986, 51, 3900.
13. S.K. Mandal, L.K. Thompson, K. Nag and J.P. Charland, *Inorg. Chem.*, 1987, 26, 1391.
14. R.P. Das and K. Nag, *ibid.*, 1991, 30, 2831.
15. W. Flaig, Th. Ploetz and A. Kullmer, *Z. Naturforsch Teil B.*, 1955, 10, 668.
16. G.M. Sheldrick, 'SHELXTL-PLUS crystallographic system', Version 2; Nicolet XRD Corp.; Madisan, WI, 1987.

CHAPTER - III

DIFFERENTIAL REACTIVITY OF DL- AND L- COPPER(II) AMINO ACID COMPLEXES WITH ALDEHYDES

3.1.0 Abstract

Condensation reactions of copper(II) complexes of DL and L forms of alanine, serine and threonine with aliphatic aldehydes formaldehyde, propionaldehyde, n-butyraldehyde, iso-butyraldehyde, n-valeraldehyde, iso-valeraldehyde and n-caproaldehyde are investigated. $Cu(DL\text{-}ala)_2$ reacts with formaldehyde and ammonia at pH 5-6 to give a new complex, [(2R,8S)-3N,7N-(1,3,5,7-tetraazabicyclo[3.3.1]nonyl)dipropionato]copper(II) **36**, while at pH 8.5 it gives the known product **6**, bis[(R,S)-(4-methyloxazolidine-4-carboxylato)]-copper(II) dihydrate. $Cu(L\text{-}ala)_2$ reacts with formaldehyde and ammonia at pH >10 to yield the known complex **6**, instead of the expected product bis[(S)-4-methyloxazolidine-4'-carboxylato]copper(II) dihydrate **37**, while at pH 6-8.5 it gives the reported complex [(2S,8S)-3N,7N-(1,3,5,7-tetraazabicyclo-[3.3.1]nonyl)dipropionato]copper(II), **5**. Copper(II) complexes of DL-serine and DL-threonine readily undergo condensations with aliphatic aldehydes to give oxazolidine group containing products whereas the corresponding D- and L-amino acidato copper(II) complexes are unreactive towards these condensation reactions. These products are characterized by IR, electronic spectral data, elemental analyses and cyclic voltammetry. Crystal structures of the complexes aqua[N,N'-(2-oxapropanediyl)bis(oxazolidine-4-carboxylato)]copper(II) sesqui-hydrate, **8**, obtained from $Cu(DL\text{-}ser)_2$ with formaldehyde at pH 4.5 and [N,N'-(2-oxapropanediyl)bis(5-methyloxazolidine-4-carboxylato]copper(II) mono-hydrate, **10**, obtained from $Cu(DL\text{-}thr)_2$ with formaldehyde are determined.

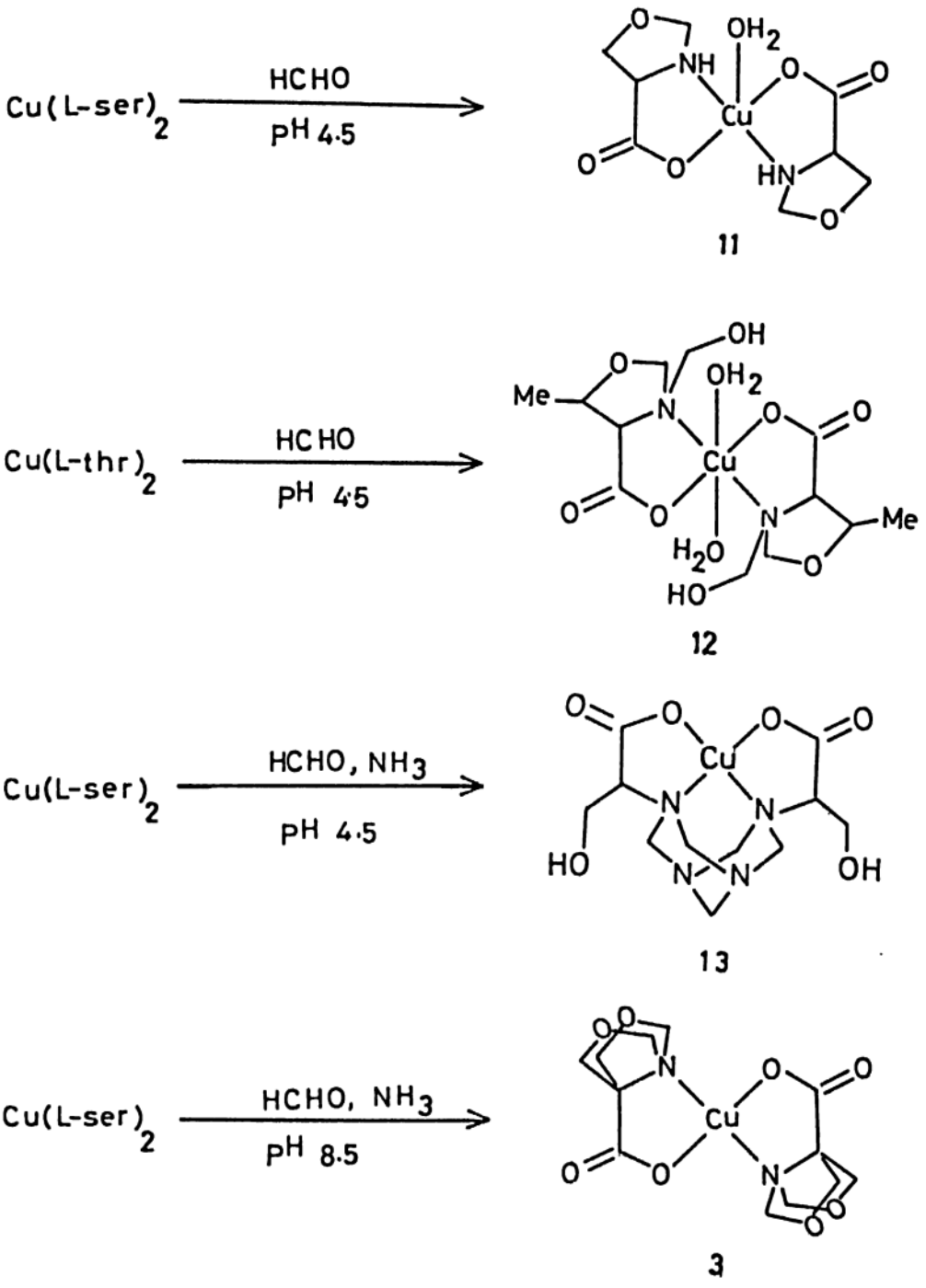
Part of this work has appeared in *J. Chem. Soc, Dalton Trans.*, 1993, 3581

Complex 8 crystallizes in triclinic space group $P\bar{1}$, a=10.802(2), b=11.039(2), c=13.460(3) Å, $\alpha=75.14(3)^0$, $\beta=69.57(3)^0$, $\gamma=87.53(3)^0$, Z=4. Complex 10 also crystallizes in triclinic space group $P\bar{1}$, a=7.388(2), b=10.017(2). c=11.485(2) Å, $\alpha=115.27(3)^0$, $\beta=101.89(3)^0$, $\gamma=91.79(3)^0$, Z=2. Results of the condensation reactions reveal differential reactivity for DL- and L- amino acids when coordinated to copper(II) ion.

3.2.0 Introduction

Various transition metal ions such as copper(II) are known to activate the amino acidato ligand units through bond polarization[1-4] enhancing the reactivity of the complex molecules. Reactions of copper(II) complexes of various amino acids are briefly presented in chapter 1. In some cases chirality of the α-amino acidato ligands influence the reaction process.[5-8] It is known that condensation of $Cu(L\text{-ser})_2$ and $Cu(L\text{-thr})_2$ with formaldehyde[8] at pH 4.5 yield optically active compounds containing oxazolidine ring namely bis[L-(oxazolidine-4-carboxylato)]copper(II) monohydrate 11, and bis[L-(N-hydroxymethyl-5-methyloxazolidine-4-carboxylato)]copper(II) dihydrate, 12 respectively. $Cu(D\text{-ser})_2$ and $Cu(D\text{-thr})_2$ were also reported[8] to give similar products which were identified to be the optical isomers of 11 and 12. Condensation of $Cu(L\text{-ser})_2$ with formaldehyde and ammonia at pH 4.5 yields pentamethylenediaza group containing product, [3N,7N-(1,3,5,7-tetraazabicyclo-[3.3.1]nonyl)di(hydroxymethyl)acetato]copper(II), 13, whereas condensation of $Cu(L\text{-ser})_2$ with formaldehyde and ammonia at pH 8.5 yield oxazolidine ring containing product[8], bis[(dihydro-1H,3H,5H-oxazolo[3,4-C]oxazole-7a-carboxy-lato)]copper(II), 3 (Scheme 3.1).

These reactions suggest differential reactivity pattern for DL- and L-amino acids when coordinated to copper(II) ion. Therefore it seemed appropriate to investigate this type of reactions in detail to understand the reactivity pattern of optically active bis(α-amino acidato)copper(II) complexes. For this purpose reactions of copper(II) complexes of DL and L forms of alanine, serine and threonine under various experimental conditions with formaldehyde and other aliphatic aldehydes are investigated. Our results are presented and discussed in subsequent sections.



Scheme 3.1 Products obtained in the reactions between $Cu(L\text{-}ser)_2$ and $Cu(L\text{-}thr)_2$ with formaldehyde.

3.3.0 Experimental

3.3.1 Preparation of the complexes

The preparative details of the complexes are given in section 2.2 of chapter 2.

3.3.2 Physical measurements

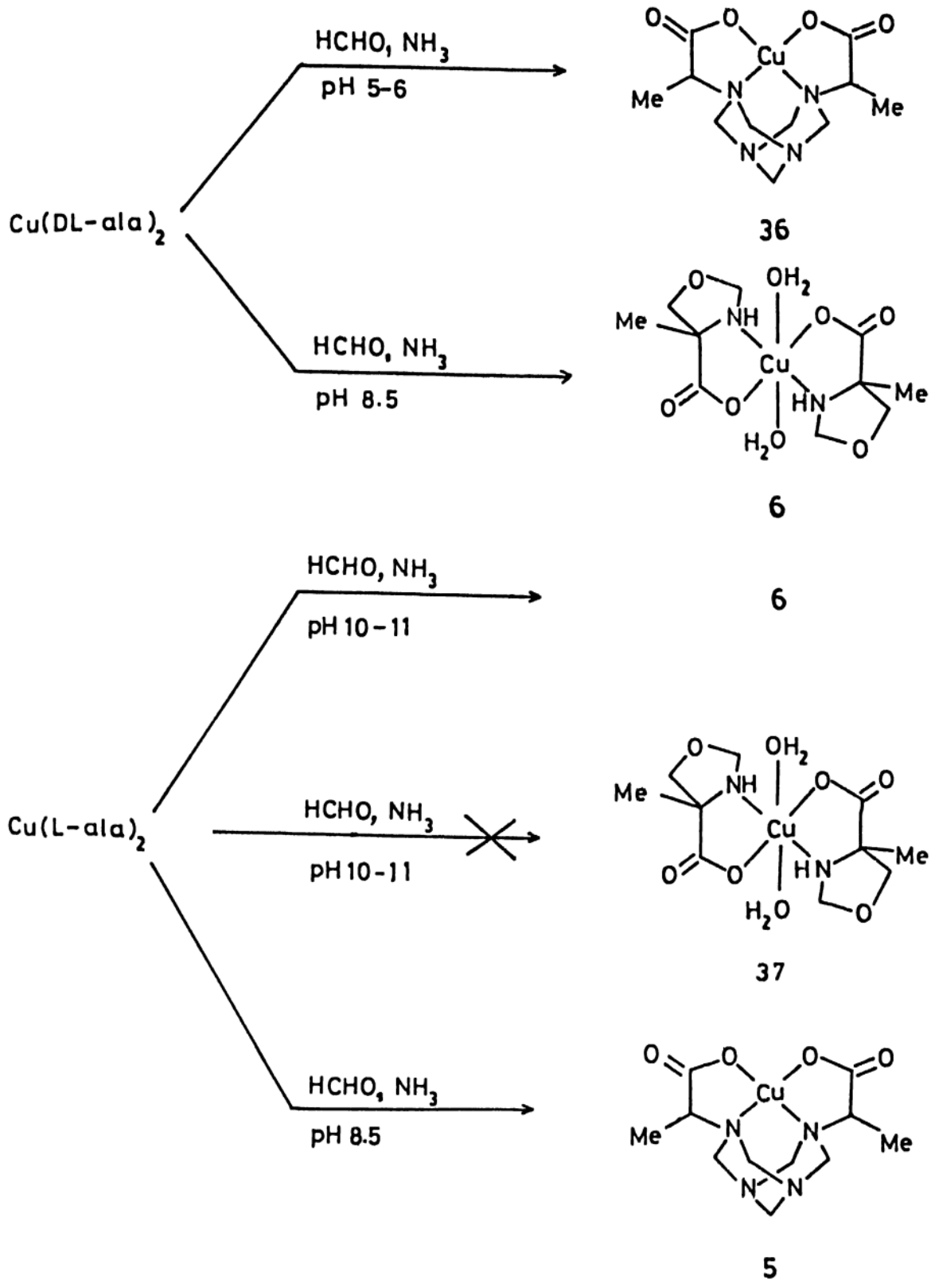
These are briefly described in section 2.6 of chapter 2.

3.4.0 Results and discussion

3.4.1 Reactions of $Cu(DL\text{-}ala)_2$ and $Cu(L\text{-}ala)_2$ with formaldehyde and ammonia

Complexes $Cu(DL\text{-}ala)_2$ and $Cu(L\text{-}ala)_2$ are prepared by known procedure.[11] Condensation of $Cu(DL\text{-}ala)_2$ and $Cu(L\text{-}ala)_2$ with formaldehyde and ammonia at different pH conditions gives complexes 36, 6 and 5. These conditions are schematically presented in Scheme 3.2. All the complexes are characterized by analytical and spectral methods. Analytical and IR data of the complexes are collected in Table 3.1.

It is known in the literature that condensation of $Cu(DL\text{-}ala)_2$ with formaldehyde and ammonia at pH 8.5 yields the complex[5] bis[(R,S)-4-methyloxazolidine-4'-carboxylato]copper(II) dihydrate, 6. The IR spectrum of this complex exhibits a set of three closely spaced bands in the region, 1200-1080 cm^{-1} characteristic of oxazolidine group and two absorption bands at ca. 3200 and 3500 cm^{-1} characteristic of -NH- and -OH of coordinated water groups respectively. Under similar experimental conditions, $Cu(L\text{-}ala)_2$ is known to form a different product,[6] [(2S,8S)-3N,7N-(1,3,5,7-tetraazabicyclo-



Scheme 3.2 Reaction conditions for the preparation of complexes 5, 6 and 36.

Table 3.1 Analytical and IR data of the complexes 5, 6 and 36.

complex	Analysis % found (calculated)			IR bands (cm^{-1})	
	C	H	N	oxazolidine	-NH-
5	39.5 (39.6)	5.3 (5.4)	16.9 (16.8)	-	-
$6.2H_2O$	33.3 (33.4)	5.5 (5.6)	7.8 (7.8)	1100,1140,1160	3250
36	39.4 (39.6)	5.3 (5.4)	16.9 (16.8)	-	-

[3.3.1]nonyl)dipropionato]copper(II), 5. Crystal structure of this complex is determined and the structure is shown to be 5. In this reaction the α-carbon atoms of $Cu(L\text{-}ala)_2$ are unaffected by formaldehyde condensation, instead the condensation involves the amino nitrogens of the alaninato ligand units with the formation of pentamethylenediaza unit, which bridges, the two chelated alanine ligands. The two alanine units in the resultant complex are *cis* with respect to each other implying the conversion of *trans* to *cis* arrangement of ligands during the condensation process. Similar conversion of *trans* disposed ligands units to *cis* arrangement is known only in few such reactions.[9,12,13,14]

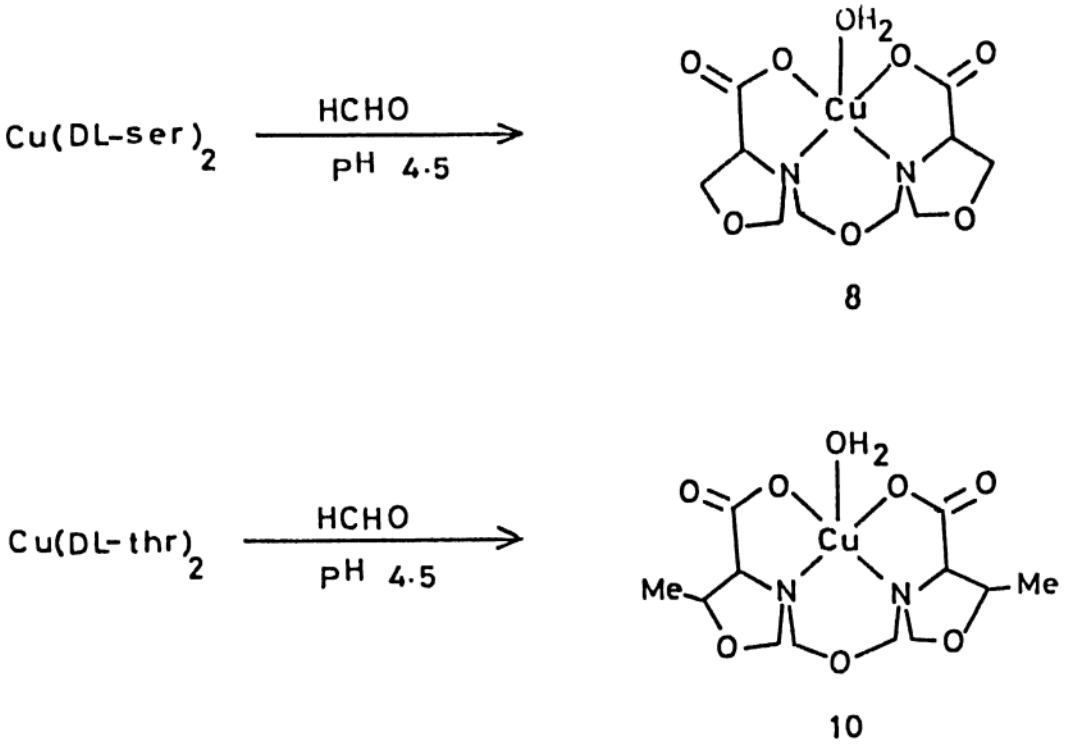
Similar condensation reactions were also carried out with copper(II) complexes of DL- and L- alanines as shown in Scheme 3.2. Reaction of $Cu(DL\text{-}ala)_2$ with formaldehyde and ammonia in the pH range 5-6 yielded a new pentamethylenediaza group containing product [(2R,8S)-3N,7N-(1,3,5,7-tetraazabicyclo[3.3.1]nonyl)dipropionato] copper(II), 36. The IR spectrum of this complex does not exhibit three closely spaced absorption bands in the region 1200-1080 cm^{-1} indicating the absence of oxazolidine group. Similarly no bands at *ca.* 3200 and 3500 cm^{-1} are observed revealing the absence of -NH- and -OH groups. The spectrum is identical to that of 5, the well characterized pentamethylenediaza group containing product which is obtained from the condensation of $Cu(L\text{-}ala)_2$ with formaldehyde and ammonia,[6] indicating that the product 36 is an optically active form of 5.

Reaction of $Cu(L\text{-}ala)_2$ with formaldehyde and ammonia in the higher pH range, 10-11, yielded a dark blue crystalline complex which is characterized to be the known optically inactive complex, bis[(R,S)-(4-methyloxazolidine-4-carboxylato)]copper(II) dihydrate, 6, which could also be obtained from the known condensation reaction[5] of $Cu(DL\text{-}ala)_2$ with formaldehyde and ammonia at pH 8.0. The identity of the product was established by comparison of the unit cell

dimensions and space group of the product with those of the reported complex 6, and also by the absence of circular dichroism band. Formation of the optically inactive complex 6 in the reaction against the formation of the expected optically active product, bis[(S)-4-methyloxazolidine-4'-carboxylato]copper(II) dihydrate, **37**, reveals that during the deprotonation of the α-methylene groups of the alaninato ligands, racemization also occurred resulting in the loss of optical activity.

3.4.2 Reactions of $Cu(DL\text{-}ser)_2$ and $Cu(DL\text{-}thr)_2$ with formaldehyde

Reactions of $Cu(DL\text{-}ser)_2$ and $Cu(DL\text{-}thr)_2$ with formaldehyde yielded the known[7] products aqua[N,N'-1,3-(2-oxapropanediyl)bis(oxazolidine-4-carboxylato)]copper(II) sesquihydrate, **8** and [N,N'-1,3-(2-oxapropanediyl)bis(5-methyl-



8 **10**

Scheme 3.3 Reaction conditions for the preparation of complexes **8** and **10**.

oxazolidine-4-carboxylato)]copper(II) monohydrate, 10 according to the Scheme 3.3. Structures of the complexes are deduced from the IR and analytical data which are collected in Table 3.2. The IR spectrum of these complexes show bands due to the oxazolidine and -OH groups and show no bands due to -NH- stretchings. To establish these structural assignments unambiguously, the complexes are also characterized by three dimensional X-ray crystallographic data.

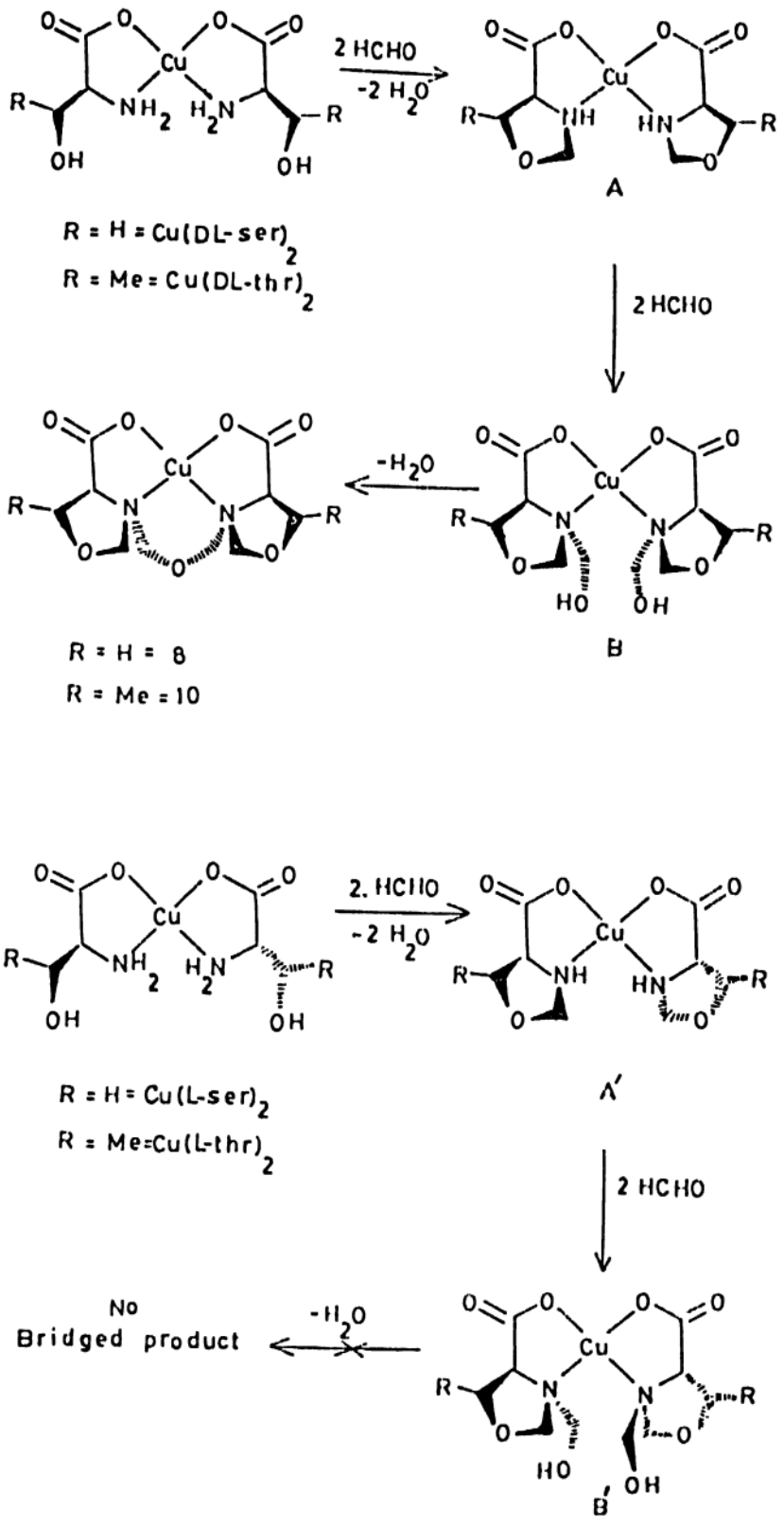
Reactions of $Cu(L\text{-}ser)_2$ and $Cu(L\text{-}thr)_2$ with formaldehyde at pH 4.5 yield complexes 11 and 12 (Scheme 3.1) respectively which are different from the complexes obtained from reactions of $Cu(DL\text{-}ser)_2$ and $Cu(DL\text{-}thr)_2$, *viz.*, 8 and 10. Complexes 8 and 10 have dimethyleneether group bridging the two amino acid ligand units which is absent in complexes 11 and 12. A mechanism has been proposed to explain formation of different products in these reactions[8] and is shown in Scheme 3.4. Initial condensation in both cases lead to the formation of oxazolidine ring containing intermediate (A) or (A') which depending upon the stereochemistry of the amino acid ligand units, forms different products on further condensation. Intermediate (B') [$Cu(L\text{-}ser)_2$ or $Cu(L\text{-}thr)_2$ reactions] has the two N-hydroxymethyl groups disposed above and below the CuN_2O_2 plane contrary to (B) [$Cu(DL\text{-}ser)_2$ or $Cu(DL\text{-}thr)_2$ reactions] and prevent further condensation of the two N-hydroxy methyl groups. Hence dimethyleneether bridged products are not formed in the reactions of $Cu(L\text{-}ser)_2$ and $Cu(L\text{-}thr)_2$ with formaldehyde.

3.4.2.1 Crystal and molecular structure of [N,N'-(2-oxapropanediyl)-bis(oxazolidine-4-carboxylato)]copper(II) sesquihydrate (8)

The gross structure assigned to the complex 8 is found to be correct when its crystal structure is determined from X-ray diffraction data. The crystallographic data are presented in Table 3.3.

Table 3.2 Analytical and IR data of the complexes 8 and 10.

complex	Analysis % found(calculated)			IR bands (cm^{-1})	
	C	H	N	oxazolidine	-NH-
8.1.5H_2O	31.20 (31.35)	5.10 (5.01)	7.20 (7.31)	1120, 1140, 1170	-
10.1H_2O	35.70 (37.82)	5.38 (5.52)	7.10 (7.00)	1120, 1150, 1180	-



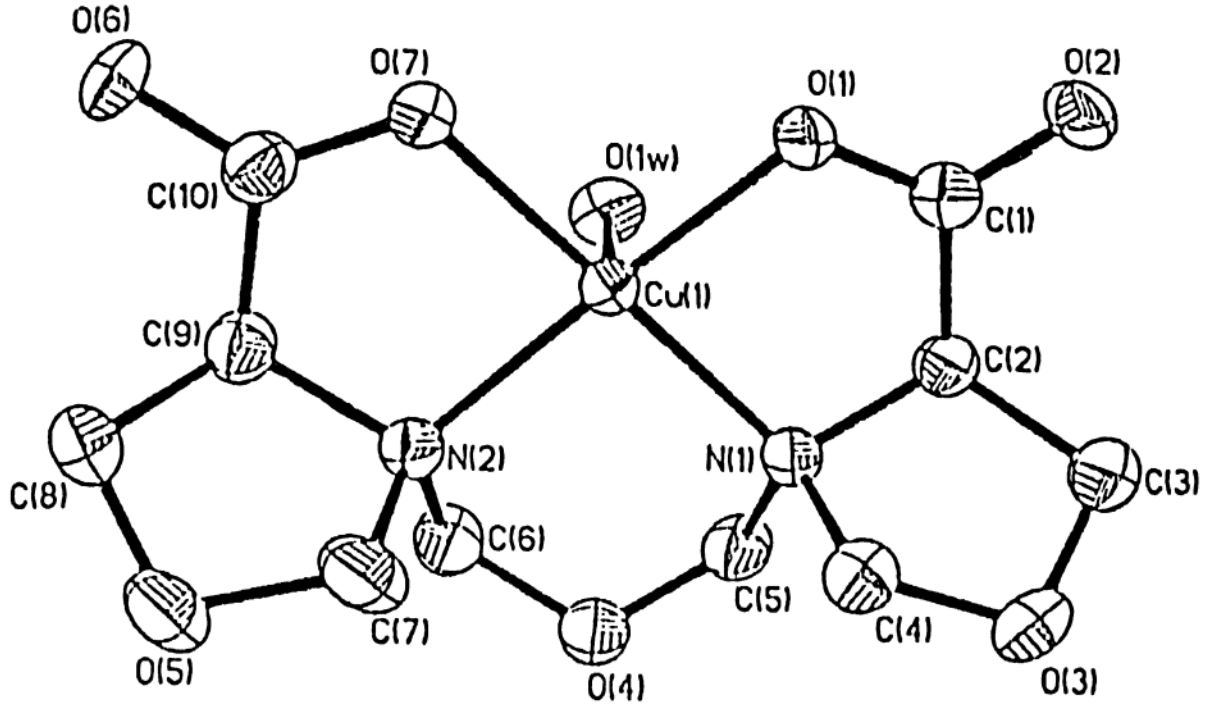
Scheme 3.4 Mechanism for the formation of different products from $Cu(L\text{-ser})_2$, $Cu(L\text{-thr})_2$ and $Cu(DL\text{-ser})_2$, $Cu(DL\text{-thr})_2$ with formaldehyde.

Table 3.3 Crystallographic data of the complexes 8 and 10.

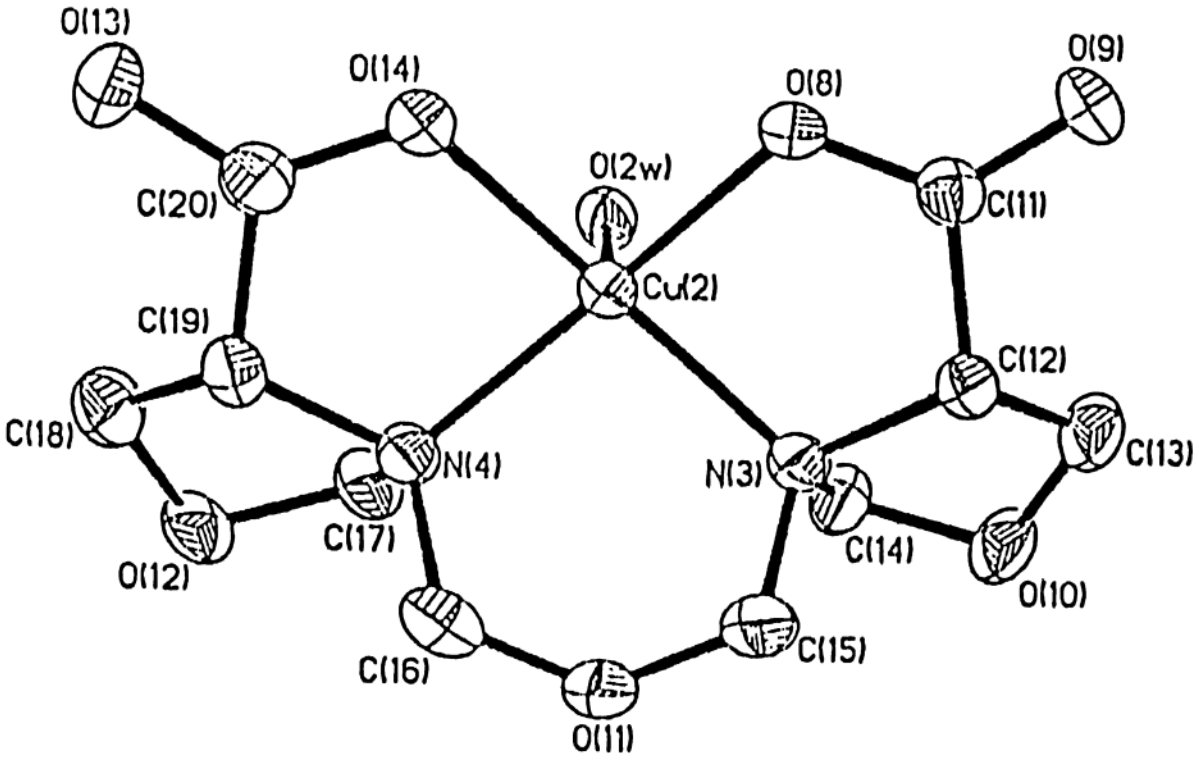
Complex	8	10
Formula	$C_{10}H_{19}CuN_2O_{9.5}$	$C_{12}H_{22}CuN_2O_9$
M	382.8	401.9
Crystal system	Triclinic	Triclinic
Space group	PĪ	PĪ
a/Å	10.802(2)	7.388(2)
b/Å	11.039(2)	10.017(2)
c/Å	13.460(3)	11.485(2)
α/°	75.14(3)	115.27(3)
β/°	69.57(3)	101.89(3)
γ/°	87.53(3)	91.79(3)
U/Å^3	1451.8(5)	745.3(3)
D_c/g cm^{-3}	1.628	1.791
μ/cm^{-1}	15.44	15.20
F(0 0 0)	732	418
Crystal size/mm^{-1}	0.08 x 0.22 x 0.22	0.08 x 0.10 x 0.22
2θ limits/°	4-45	4-50
Temperature/K	295	295
Reflections measured	4035	2855
Unique reflections	3792	2631
Observed reflections	2771	1911
Weighting scheme	$[\sigma^2(F) + 0.0005F^2]^{-1}$	$[\sigma^2(F) + 0.0004F^2]^{-1}$
Parameters refined	406	208
R	0.0375	0.0327
wR	0.0472	0.0383
Goodness of fit	1.47	1.12

The asymmetric unit consists of two crystallographically independent complex molecules and three water molecules of solvation. One of the complex molecules (molecule A) exists as a dimer as a result of mutual long axial interaction between carboxylic oxygens and coppers of the two neighboring molecules whereas the other molecule (molecule B) exists as a monomer. Views of both molecules with their atom numbering scheme are shown in Fig.3.1. The dimeric association in molecule A is shown in Fig.3.2. Non-hydrogen atom coordinates are listed in Table 3.4 along with equivalent isotropic displacement coefficients. Bond lengths and angles are listed in Table 3.5.

In molecule A, the coordination polyhedron around each copper atom is tetragonally elongated octahedral geometry. The four equitorial ligands being two nitrogens and two carboxylic oxygens of the tetradentate ligand while the axial sites are occupied by a water molecule and a carboxylic oxygen that is equitorial to the other copper centre in the dimer. The Cu-O bond distances associated with the bridging carboxylic oxygens differ considerably, the axial distance being 2.879 Å and the equitorial distance being 1.939(4) Å. The Cu...Cu separation is 3.931 Å and the bond angle involving the coordinated water molecule, copper and the bridging carboxylic oxygen is 167.22^{0}. The other Cu-N and $Cu-O_{carboxyl}$ bond distances are normal, in the range 1.925(4)-2.030(4) Å and are comparable to those of molecule B (Table 3.5) whereas the $Cu-O_{aqua}$ bond distances of 2.495(4) Å is considerably longer than that of molecule B (2.218 Å), which may be due to the dimeric nature of molecule A. Similar dimeric-type structures have also been reported for 2,2'-bipyridine(Phthalato)copper(II) dihydrate and (2,7-diacetyl-3,6-dimethylnaphthalene-1,8-diolato)ethylenediamine-copper(II).[15,16] The long axial Cu-O distances are 2.58 and 2.848 Å for the two complexes respectively. In molecule B, geometry about copper is roughly tetragonal pyramidal with the base plane formed by the two nitrogens and two carboxylic oxygens of the ligand and the fifth site (apical) being occupied by a



A



B

Fig.3.1 View of molecules A and B of complex 8.

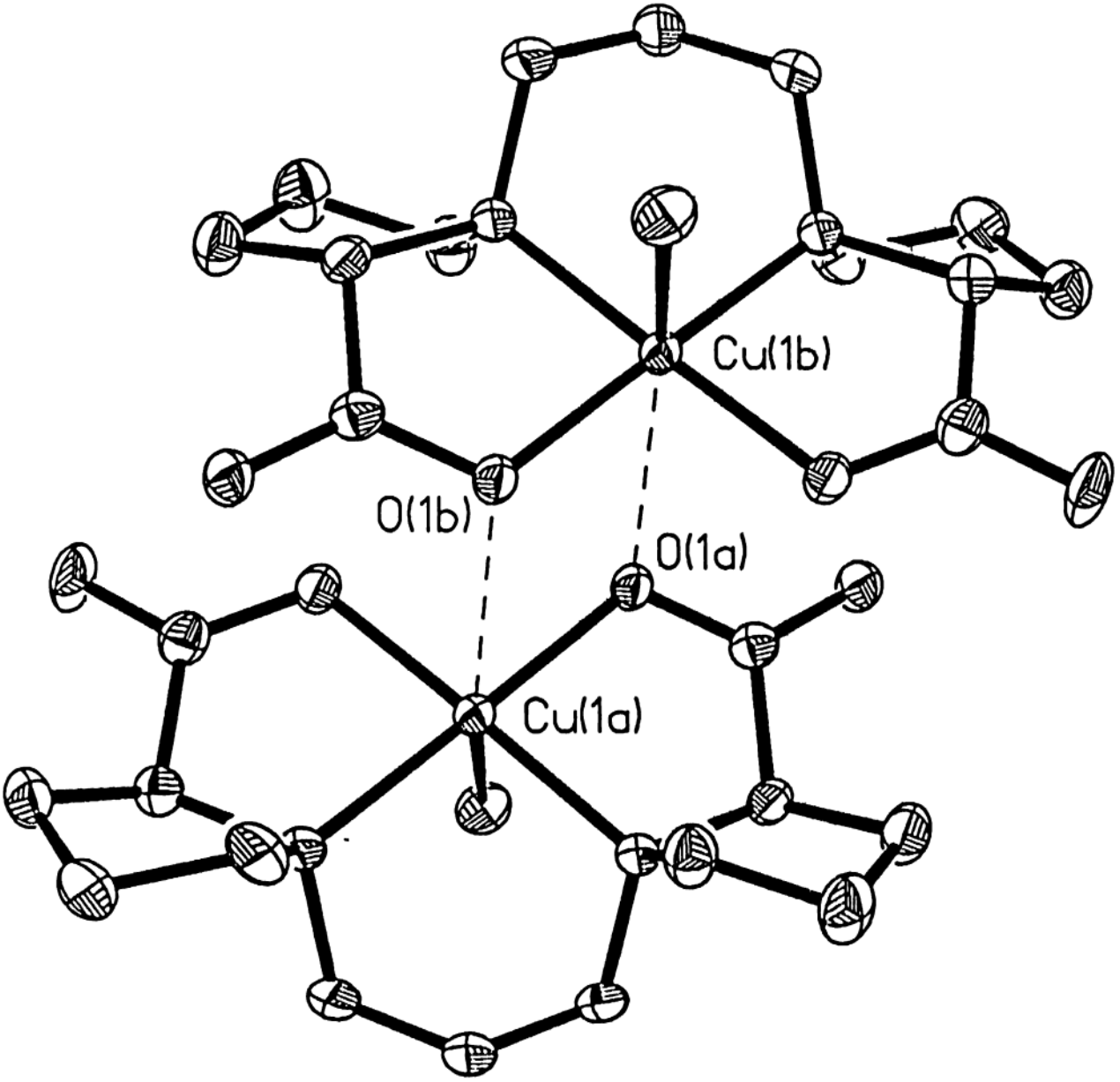


Fig.3.2 The dimeric association of molecule A of the complex 8.

Table 3.4 Atomic coordinates and equivalent isotropic displacement coefficients of the complex 8.

	x	y	z	U(eq)
Cu(1)	1561(1)	13(1)	3691(1)	29(1)
O(1)	-58(3)	908(3)	4007(3)	33(2)
O(7)	755(4)	-1500(3)	3674(3)	35(2)
N(1)	2438(4)	1608(4)	3630(4)	30(2)
N(2)	3241(4)	-938(4)	3484(4)	31(2)
O(1W)	1905(4)	811(3)	1699(3)	44(2)
C(1)	108(6)	2093(5)	3823(4)	32(2)
C(2)	1511(5)	2626(5)	3477(5)	33(2)
C(3)	1655(6)	3508(6)	4154(6)	51(3)
C(4)	2584(6)	1676(5)	4670(5)	45(3)
C(5)	3743(5)	1906(5)	2722(5)	40(3)
C(6)	4383(6)	-145(5)	2585(5)	40(3)
C(7)	3614(6)	-1450(6)	4473(5)	46(3)
C(8)	3587(6)	-3150(5)	3851(6)	50(3)
C(9)	3007(6)	-2101(5)	3176(5)	38(3)
C(10)	1546(6)	-2358(5)	3431(5)	38(3)
O(2)	-793(4)	2828(3)	3906(3)	42(2)
O(3)	2646(4)	2978(4)	4592(4)	57(2)
O(4)	4604(4)	936(4)	2879(3)	47(2)
O(5)	4326(4)	-2524(4)	4280(4)	51(2)
O(6)	1233(5)	-3386(4)	3371(4)	58(2)
Cu(2)	765(1)	4122(1)	8352(1)	29(1)
O(8)	-307(3)	5491(3)	8776(3)	35(2)
O(14)	-818(3)	3007(3)	8924(3)	37(2)

Table 3.4 continued...

N(3)	2333(4)	5233(4)	8153(3)	30(2)
N(4)	1770(4)	2531(4)	8282(3)	29(2)
O(2W)	813(4)	4655(3)	6634(3)	35(2)
C(11)	319(5)	6451(5)	8766(4)	31(2)
C(12)	1786(5)	6344(5)	8592(5)	34(2)
C(13)	2645(6)	7484(6)	7735(6)	52(3)
C(14)	3192(6)	5835(5)	6999(5)	37(3)
C(15)	3167(6)	4536(5)	8768(5)	40(3)
C(16)	2746(6)	2424(5)	8860(5)	39(3)
C(17)	2431(6)	2362(5)	7150(5)	38(3)
C(18)	1211(6)	581(6)	8023(5)	48(3)
C(19)	779(5)	1435(5)	8816(5)	34(2)
C(20)	-633(6)	1842(5)	9044(5)	34(3)
O(9)	-179(4)	7444(4)	8914(3)	47(2)
O(10)	3735(4)	6946(4)	7043(3)	48(2)
O(11)	3644(4)	3470(3)	8393(3)	39(2)
O(12)	2503(4)	1049(3)	7309(3)	41(2)
O(13)	-1516(4)	1012(4)	9329(3)	48(2)
O(3W)	6984(11)	4563(10)	8615(9)	194(7)
O(4W)	5286(19)	3643(13)	133(14)	362(17)
O(5W)	5722(6)	1276(7)	9777(5)	119(4)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 3.5 Bond lengths and bond angles of the complex 8.

Bond lengths (Å)

Cu(1)-O(1)	1.939 (4)	Cu(1)-O(7)	1.925 (4)
Cu(1)-N(1)	2.006 (5)	Cu(1)-N(2)	2.026 (4)
Cu(1)-O(1W)	2.495 (4)	O(1)-C(1)	1.276 (7)
O(7)-C(10)	1.275 (7)	N(1)-C(2)	1.495 (7)
N(1)-C(4)	1.483 (9)	N(1)-C(5)	1.490 (6)
N(2)-C(6)	1.503 (6)	N(2)-C(7)	1.491 (9)
N(2)-C(9)	1.503 (8)	C(1)-C(2)	1.518 (8)
C(1)-O(2)	1.234 (7)	C(2)-C(3)	1.540 (11)
C(3)-O(3)	1.430 (9)	C(4)-O(3)	1.417 (8)
C(5)-O(4)	1.411 (7)	C(6)-O(4)	1.403 (8)
C(7)-O(5)	1.417 (8)	C(8)-C(9)	1.534 (9)
C(8)-O(5)	1.422 (10)	C(9)-C(10)	1.516 (9)
C(10)-O(6)	1.229 (8)	Cu(2)-O(8)	1.944 (4)
Cu(2)-O(14)	1.951 (4)	Cu(2)-N(3)	2.034 (5)
Cu(2)-N(4)	2.030 (4)	Cu(2)-O(2W)	2.218 (4)
O(8)-C(11)	1.276 (7)	O(14)-C(20)	1.270 (7)
N(3)-C(12)	1.506 (7)	N(3)-C(14)	1.495 (6)
N(3)-C(15)	1.490 (8)	N(4)-C(16)	1.499 (9)
N(4)-C(17)	1.498 (7)	N(4)-C(19)	1.502 (6)
C(11)-C(12)	1.522 (8)	C(11)-O(9)	1.231 (7)
C(12)-C(13)	1.544 (7)	C(13)-O(10)	1.436 (7)
C(14)-O(10)	1.406 (8)	C(15)-O(11)	1.405 (8)
C(16)-O(11)	1.403 (7)	C(17)-O(12)	1.413 (7)
C(18)-C(19)	1.542 (9)	C(18)-O(12)	1.418 (7)
C(19)-C(20)	1.519 (8)	C(20)-O(13)	1.239 (7)

Table 3.5 continued...

Bond angles (°)

O(1)-Cu(1)-O(7)	95.4(2)	O(1)-Cu(1)-N(1)	85.3(2)
O(7)-Cu(1)-N(1)	177.3(2)	O(1)-Cu(1)-N(2)	175.5(2)
O(7)-Cu(1)-N(2)	85.8(2)	N(1)-Cu(1)-N(2)	93.6(2)
O(1)-Cu(1)-O(1W)	88.4(1)	O(7)-Cu(1)-O(1W)	88.1(2)
N(1)-Cu(1)-O(1W)	89.3(2)	N(2)-Cu(1)-O(1W)	96.0(2)
Cu(1)-O(1)-C(1)	114.9(3)	Cu(1)-O(7)-C(10)	115.5(4)
Cu(1)-N(1)-C(2)	106.7(4)	Cu(1)-N(1)-C(4)	115.3(3)
C(2)-N(1)-C(4)	102.0(5)	Cu(1)-N(1)-C(5)	112.2(4)
C(2)-N(1)-C(5)	110.5(4)	C(4)-N(1)-C(5)	109.6(5)
Cu(1)-N(2)-C(6)	110.1(3)	Cu(1)-N(2)-C(7)	117.1(3)
C(6)-N(2)-C(7)	109.4(5)	Cu(1)-N(2)-C(9)	106.8(4)
C(6)-N(2)-C(9)	110.2(4)	C(7)-N(2)-C(9)	102.8(4)
O(1)-C(1)-C(2)	117.5(5)	O(1)-C(1)-O(2)	124.4(5)
C(2)-C(1)-O(2)	118.2(5)	N(1)-C(2)-C(1)	111.3(4)
N(1)-C(2)-C(3)	105.0(5)	C(1)-C(2)-C(3)	113.4(5)
C(2)-C(3)-O(3)	104.7(5)	N(1)-C(4)-O(3)	104.4(5)
N(1)-C(5)-O(4)	109.8(4)	N(2)-C(6)-O(4)	110.0(5)
N(2)-C(7)-O(5)	105.1(5)	C(9)-C(8)-O(5)	105.2(5)
N(2)-C(9)-C(8)	104.7(6)	N(2)-C(9)-C(10)	111.2(5)
C(8)-C(9)-C(10)	112.0(4)	O(7)-C(10)-C(9)	118.3(6)
O(7)-C(10)-O(6)	125.6(6)	C(9)-C(10)-O(6)	116.0(5)
C(3)-O(3)-C(4)	106.0(6)	C(5)-O(4)-C(6)	114.9(5)
C(7)-O(5)-C(8)	104.7(5)	O(8)-Cu(2)-O(14)	90.4(2)
O(8)-Cu(2)-N(3)	85.5(2)	O(14)-Cu(2)-N(3)	165.9(2)
O(8)-Cu(2)-N(4)	167.0(2)	O(14)-Cu(2)-N(4)	85.1(2)
N(3)-Cu(2)-N(4)	95.9(2)	O(8)-Cu(2)-O(2W)	95.1(2)

Table 3.5 continued...

O(14)-Cu(2)-O(2W)	95.3(2)	N(3)-Cu(2)-O(2W)	98.5(2)
N(4)-Cu(2)-O(2W)	97.5(2)	Cu(2)-O(8)-C(11)	116.1(3)
Cu(2)-O(14)-C(20)	116.4(3)	Cu(2)-N(3)-C(12)	107.3(3)
Cu(2)-N(3)-C(14)	116.6(4)	C(12)-N(3)-C(14)	102.7(4)
Cu(2)-N(3)-C(15)	110.7(3)	C(12)-N(3)-C(15)	109.8(5)
C(14)-N(3)-C(15)	109.3(4)	Cu(2)-N(4)-C(16)	111.4(4)
Cu(2)-N(4)-C(17)	114.8(3)	C(16)-N(4)-C(17)	110.4(4)
Cu(2)-N(4)-C(19)	107.8(3)	C(16)-N(4)-C(19)	109.9(4)
C(17)-N(4)-C(19)	102.2(4)	O(8)-C(11)-C(12)	117.3(5)
O(8)-C(11)-O(9)	125.0(5)	C(12)-C(11)-O(9)	117.6(5)
N(3)-C(12)-C(11)	111.8(5)	N(3)-C(12)-C(13)	104.6(4)
C(11)-C(12)-C(13)	113.0(5)	C(12)-C(13)-O(10)	104.6(4)
N(3)-C(14)-O(10)	105.3(5)	N(3)-C(15)-O(11)	110.4(6)
N(4)-C(16)-O(11)	110.2(4)	N(4)-C(17)-O(12)	104.3(4)
C(19)-C(18)-O(12)	104.8(5)	N(4)-C(19)-C(18)	104.2(4)
N(4)-C(19)-C(20)	112.1(4)	C(18)-C(19)-C(20)	114.5(6)
O(14)-C(20)-C(19)	117.5(5)	O(14)-C(20)-O(13)	125.0(5)
C(19)-C(20)-O(13)	117.4(5)	C(13)-O(10)-C(14)	104.7(4)
C(15)-O(11)-C(16)	114.3(4)	C(17)-O(12)-C(18)	103.5(4)

water molecule. The four basal atoms are nearly coplanar, with no atom deviating from the least-squares plane by more than 0.0106 Å. The copper sits 0.2292 Å above this plane, towards the apical water molecule as is expected for this geometry.[17-20] The Cu-N and Cu-$O_{carboxyl}$ bond distances are in the range 1.944(4)-2.034(5) Å and are comparable to those of related complexes[10,21] 1 and 3 obtained from the reactions of $Cu(gly)_2$ with acetaldehyde at pH 11 and $Cu(L\text{-}ser)_2$ with excess formaldehyde at pH 8-9.

The geometry of the tetradentate ligand is similar in both the molecules. The oxazolidine rings are disposed *trans* to the dimethyleneether linkage. However the coordination of the water molecule is different for the two molecules. In molecule A, water is disposed *anti* to the oxazolidine rings whereas in molecule B, it is disposed *syn* to the oxazolidine rings. The six membered chelate ring involving the dimethyleneether linkage adopts a chair conformation in both the molecules. The solvate water molecules in the crystal are involved in extensive hydrogen bonding with the free carboxylic oxygens of both molecules.

3.4.2.2 Crystal and molecular structure of [N,N'-1,3-(2-oxapropanediyl)-bis(4-methyloxazolidine-4-carboxylato)]copper(II) monohydrate (10)

Structure of this complex proposed from the IR and analytical data is found to be correct. Crystallographic data are collected in Table 3.3. The non-hydrogen atom coordinates are listed in Table 3.6 along with isotropic displacement coefficients. The bond lengths and angles are listed in Table 3.7.

The asymmetric unit consists of one complex molecule and a water molecule. This complex molecule also exists as a dimer as a result of mutual long axial interaction between carboxylic oxygens and coppers of two neighboring

Table 3.6 Atomic coordinates and equivalent isotropic displacement coefficients of the complex 10.

	x	y	z	U(eq)
Cu(1)	1924(1)	3916(1)	4901(1)	22(1)
O(1)	3510(1)	5802(1)	5789(1)	24(1)
O(7)	249(1)	4500(1)	3696(1)	25(1)
N(1)	3712(1)	3323(1)	6138(1)	24(1)
N(2)	547(1)	1859(1)	3742(1)	23(1)
C(1)	5032(1)	5884(1)	6591(1)	24(1)
C(2)	5355(1)	4527(1)	6854(1)	25(1)
C(3)	5668(1)	4884(1)	8333(1)	33(1)
C(4)	3035(1)	3239(1)	7253(1)	31(1)
C(5)	7664(1)	5075(1)	9045(1)	55(1)
C(6)	4352(1)	1869(1)	5366(1)	31(1)
C(7)	1796(1)	673(1)	3491(1)	30(1)
C(8)	-1047(1)	1500(1)	4214(1)	33(1)
C(9)	-2321(1)	832(1)	2028(1)	34(1)
C(10)	-426(1)	1828(1)	2453(1)	25(1)
C(11)	-635(1)	3399(1)	2594(1)	25(1)
C(12)	-2610(1)	-554(1)	733(1)	59(1)
O(2)	6270(1)	6948(1)	7141(1)	39(1)
O(3)	4648(1)	3599(1)	8289(1)	36(1)
O(4)	2816(1)	736(1)	4702(1)	32(1)
O(5)	-2268(1)	383(1)	3080(1)	41(1)
O(6)	-1617(1)	3530(1)	1661(1)	37(1)
O(1W)	7201(1)	1655(1)	8964(1)	94(1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 3.7 Bond lengths and bond angles of the complex 10.

Bond lengths (Å)

Cu(1)-O(1)	1.925 (2)	Cu(1)-O(7)	1.955 (3)
Cu(1)-N(1)	2.028 (3)	Cu(1)-N(2)	2.005 (3)
O(1)-C(1)	1.274 (4)	O(7)-C(11)	1.291 (3)
N(1)-C(2)	1.501 (4)	N(1)-C(4)	1.500 (6)
N(1)-C(6)	1.498 (5)	N(2)-C(7)	1.494 (5)
N(2)-C(8)	1.487 (6)	N(2)-C(10)	1.493 (5)
C(1)-C(2)	1.528 (6)	C(1)-O(2)	1.224 (4)
C(2)-C(3)	1.542 (6)	C(3)-C(5)	1.494 (6)
C(3)-O(3)	1.448 (6)	C(4)-O(3)	1.410 (4)
C(6)-O(4)	1.408 (4)	C(7)-O(4)	1.413 (5)
C(8)-O(5)	1.404 (4)	C(9)-C(10)	1.553 (5)
C(9)-C(12)	1.507 (5)	C(9)-O(5)	1.452 (6)
C(10)-C(11)	1.528 (6)	C(11)-O(6)	1.224 (5)

Bond angles (^{o})

O(1)-Cu(1)-O(7)	93.8(1)	O(1)-Cu(1)-N(1)	85.4(1)
O(7)-Cu(1)-N(1)	178.7(1)	O(1)-Cu(1)-N(2)	169.9(1)
O(7)-Cu(1)-N(2)	85.3(1)	N(1)-Cu(1)-N(2)	95.2(1)
Cu(1)-O(1)-C(1)	116.8(3)	Cu(1)-O(7)-C(11)	114.3(3)
Cu(1)-N(1)-C(2)	107.7(3)	Cu(1)-N(1)-C(4)	116.9(2)
C(2)-N(1)-C(4)	102.8(3)	Cu(1)-N(1)-C(6)	110.4(2)
C(2)-N(1)-C(6)	109.9(3)	C(4)-N(1)-C(6)	108.8(3)
Cu(1)-N(2)-C(7)	113.2(2)	Cu(1)-N(2)-C(8)	113.6(2)
C(7)-N(2)-C(8)	110.9(3)	Cu(1)-N(2)-C(10)	107.3(2)
C(7)-N(2)-C(10)	109.4(3)	C(8)-N(2)-C(10)	101.8(3)

Table 3.7 continued...

O(1)-C(1)-C(2)	117.2(3)	O(1)-C(1)-O(2)	125.1(4)
C(2)-C(1)-O(2)	117.7(3)	N(1)-C(2)-C(1)	111.8(3)
N(1)-C(2)-C(3)	105.6(3)	C(1)-C(2)-C(3)	113.2(3)
C(2)-C(3)-C(5)	114.7(4)	C(2)-C(3)-O(3)	103.0(3)
C(5)-C(3)-O(3)	109.9(4)	N(1)-C(4)-O(3)	105.3(3)
N(1)-C(6)-O(4)	110.0(3)	N(2)-C(7)-O(4)	110.5(3)
N(2)-C(8)-O(5)	105.3(3)	C(10)-C(9)-C(12)	114.5(4)
C(10)-C(9)-O(5)	104.3(3)	C(12)-C(9)-O(5)	108.3(4)
N(2)-C(10)-C(9)	105.0(4)	N(2)-C(10)-C(11)	111.4(2)
C(9)-C(10)-C(11)	113.4(3)	O(7)-C(11)-C(10)	117.3(3)
O(7)-C(11)-O(6)	124.6(4)	C(10)-C(11)-O(6)	118.1(3)
C(3)-O(3)-C(4)	104.4(3)	C(6)-O(4)-C(7)	114.3(3)
C(8)-O(5)-C(9)	105.8(3)		

molecules. View of the complex molecule with atom numbering scheme is shown in Fig.3.3.

The geometry about the copper is roughly tetragonal pyramidal, the four equitorial ligands being two nitrogens and two carboxylic oxygens of the tetradentate ligand. The apical site is occupied by a carboxylic oxygen that is equitorial to the other copper centre in the dimer. The Cu-O bond distances associated with the bridging carboxylic oxygens differ considerably, the axial distance being 2.595 Å and the equitorial distance being 1.955(3) Å. The Cu...Cu separation is 3.617 Å which is considerably shorter than the separation of 3.931 Å in molecule A of complex 8. The Cu-N bond distances of 2.028(3) Å and 2.005(3) Å and Cu-O_{aqua} bond distances of 1.925(2) Å and 1.955(3) Å are normal and are comparable to the those of 8 and related complexes 1 and 3. The geometry of the ligand is similar to that of the ligand in complex 8. The two oxazolidine rings are disposed *anti* to the dimethyleneether linkage and the six membered chelate ring involving the dimethyleneether linkage adopts a chair conformation.

3.4.3 Cyclic voltammetric data

Structural similarity of the complex 36 with the known complex 5 is also investigated by cyclic voltammetry technique. The new complex 36 exhibits similar cyclic voltammetric behavior[7] as that of 5, further supporting the structure proposed. The CV profile is characterized by an irreversible reduction peak at -0.51 V vs SCE and a reversible two-electron redox couple at +0.01 V which appears only from the second scan. Cyclic voltammograms for the complexes are shown in Fig.3.4.

Considerable data are available on the cyclic voltammetric behavior of copper(II) amino acid complexes, and their condensation products with

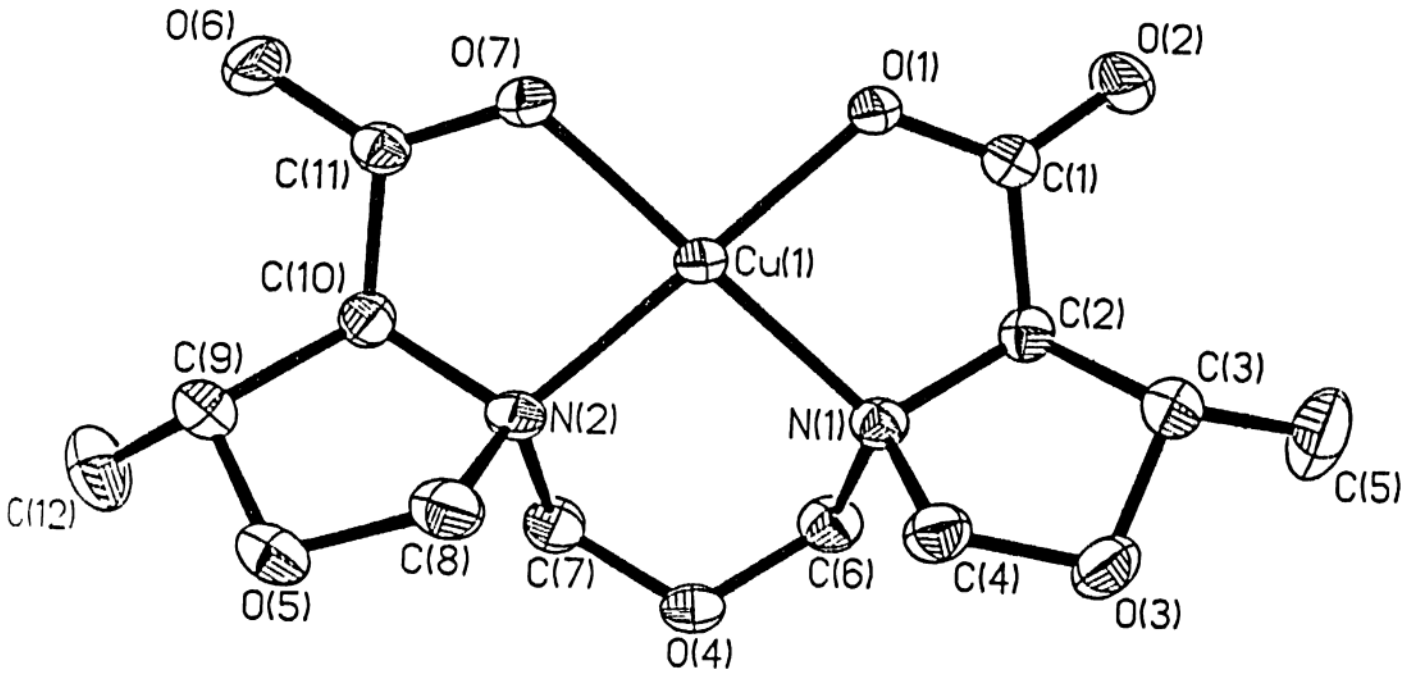


Fig.3.3 View of complex molecule of 10.

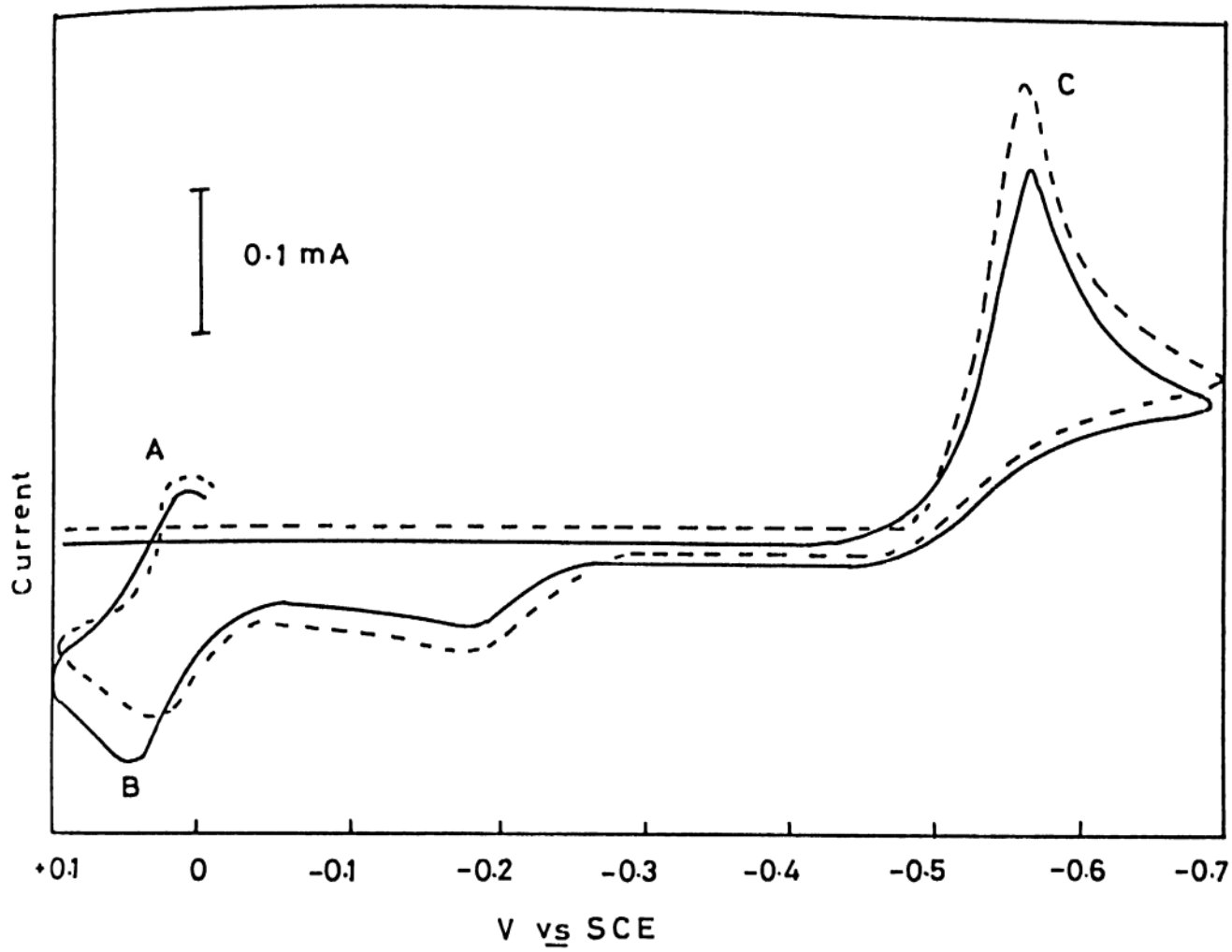


Fig.3.4 CV profiles of the complexes 5 (—) and 36 (---). The scan rate is 100 mv/sec.

aldehydes.[7,8,22-24] In many such systems two reversible redox couples, C-D and A-B are observed. After extensive analysis of the CV data, a three step electrode mechanism has been proposed for their CV behavior.[22-24] By comparison, complexes 36 and 5 have similar CV behavior.

Electrochemical reduction of these complexes leads to the formation of the corresponding Cu(I) species. A fraction of the Cu(I) species undergoes chemical decomposition/disproportionation generating Cu(0) at HMDE. The Cu(0) species produced undergoes two electron oxidation to Cu(II)(aq) during the reverse scan which subsequently gets reduced at less negative potential during the second scan. These steps can be represented by equations 1-3 (ligands are omitted).

$$Cu(II) \underset{}{\overset{1\ e}{\rightleftharpoons}} Cu(I) \qquad (1)$$

$$2Cu(I) \xrightarrow{\text{disproportionation}} Cu(0)(Hg) + Cu(II)(aq) \qquad (2)$$

$$Cu(0)(Hg) \overset{2e}{\rightleftharpoons} Cu(II)(aq) \qquad (3)$$

Step (1) generates the reduction peak C while (2) and (3) are responsible for A-B couple. The absence of peak A in the first scan and its appearance from the second scan onwards show that Cu(II)(aq) has to be electrochemically generated. The electrode sequence shown above explains this observation.

3.4.4 Electronic and CD spectral data

Electronic spectra for the complexes 36, 6 and 5 have been obtained in aqueous media. The data are collected in Table 3.8. The spectra are shown in Fig.3.5. Since the complexes 36, 6 and 5 are obtained from DL and L forms of alaninato copper(II) complexes, it is reasonable to expect that they are optical

Table 3.8 Electronic and CD spectral data of the complexes 5, 6 and 36.

complex	Electronic spectra[a] $\lambda_{max}(\varepsilon)$ nm ($LM^{-1}cm^{-1}$)	CD spectra[a] $\lambda_{max}(\Delta\varepsilon)$ nm ($LM^{-1}\ cm^{-1}$)
5	612(178)	600(-0.225)
6	615(154)	-
36	612(179)	-

a: measured in water

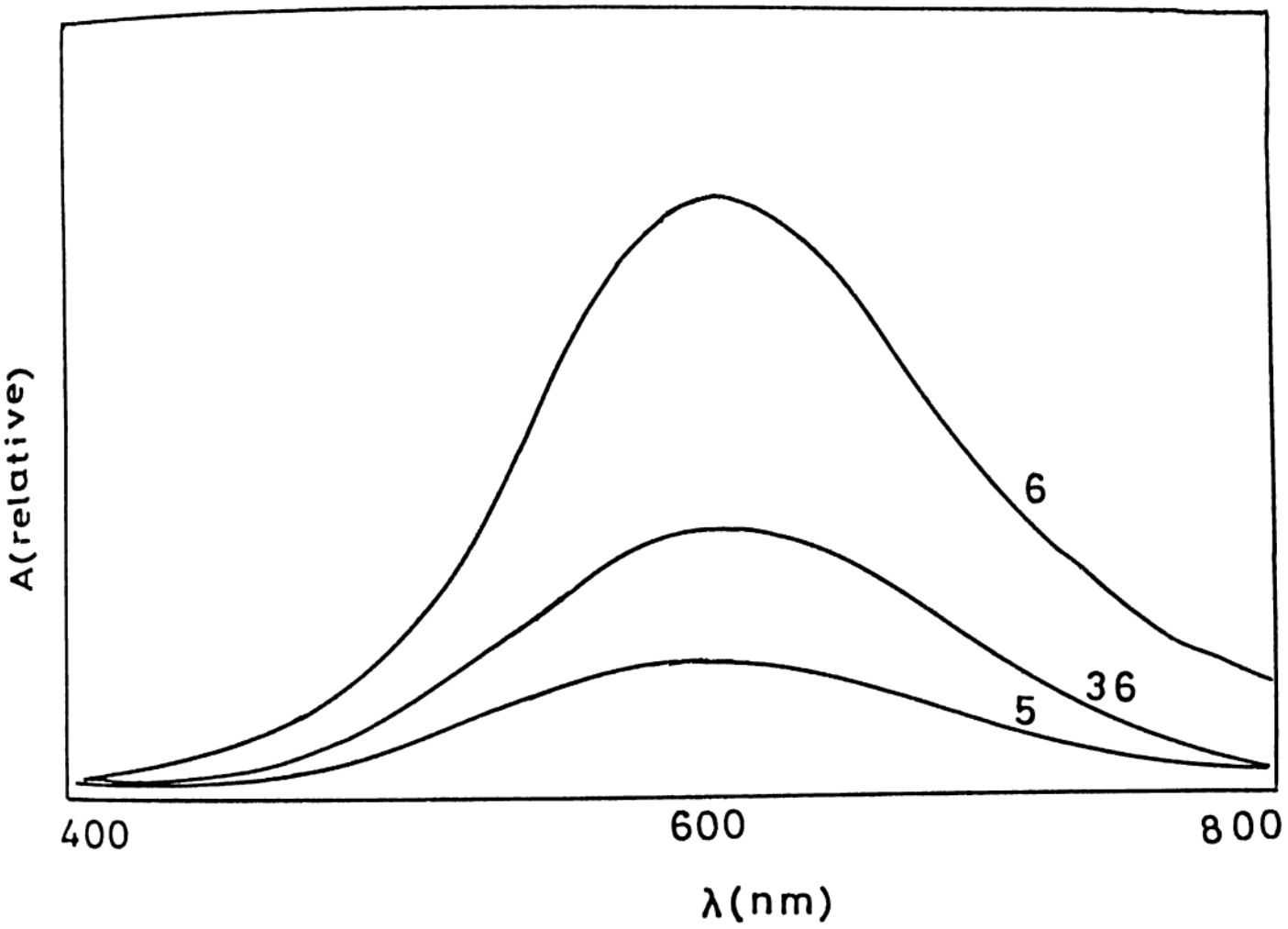


Fig.3.5 Electronic spectra of the complexes 5, 6 and 36 in water.

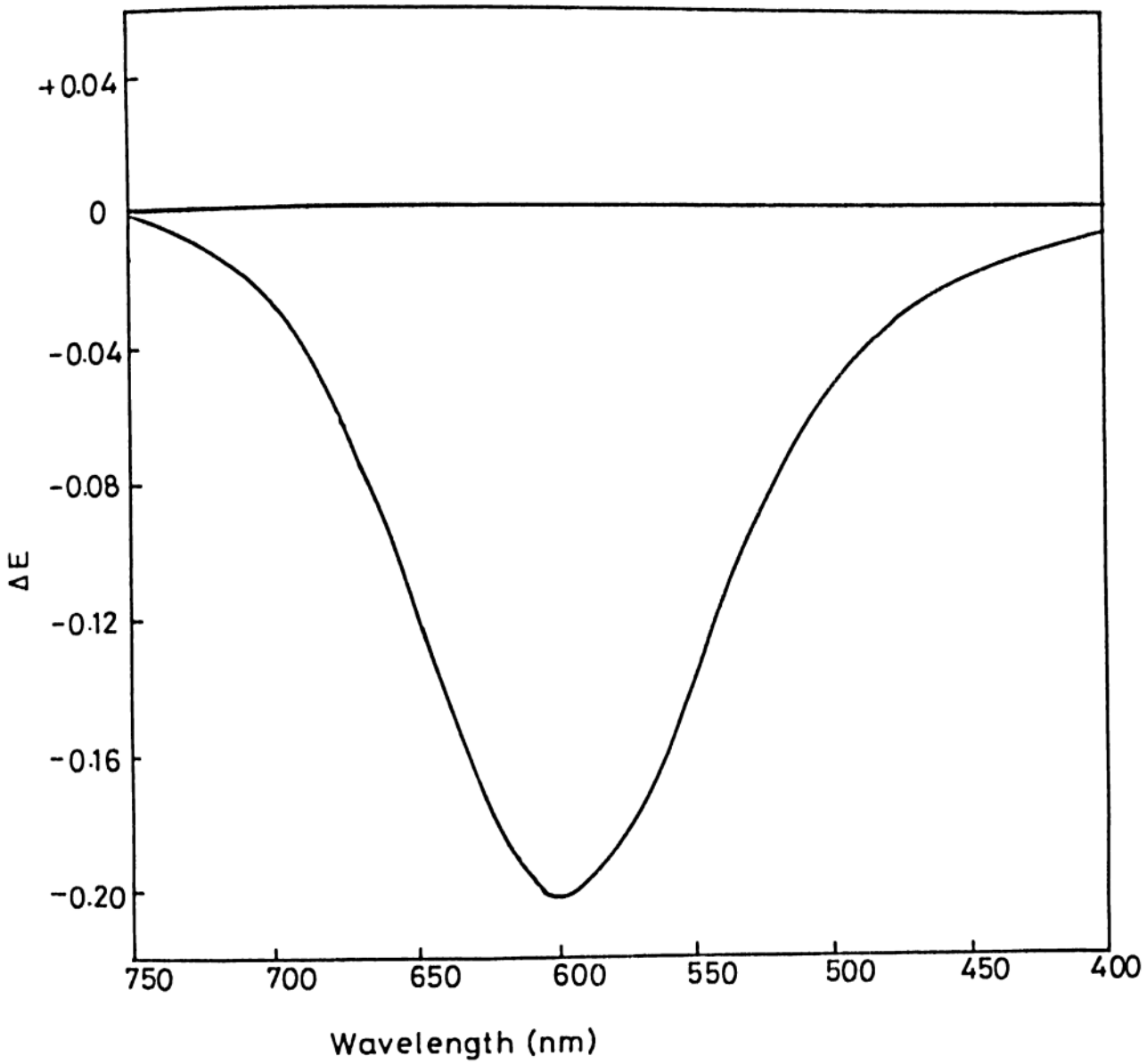


Fig.3.6 CD spectra of the complex 5 in water.

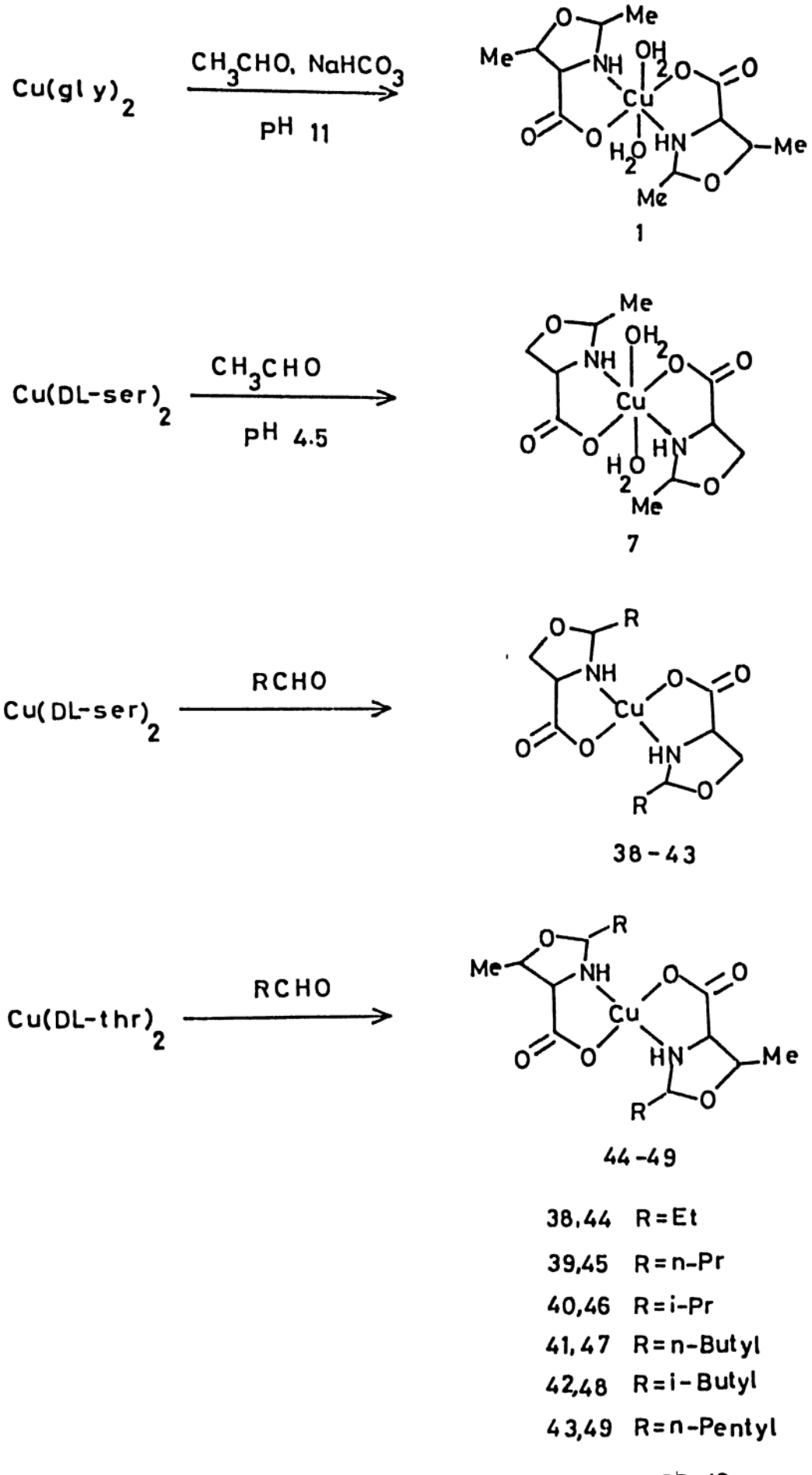
isomers. Hence CD spectral data are collected for the complexes and the data are collected in Table 3.8. The spectrum is shown for complex 5 in Fig.3.6. The complex obtained from $Cu(L\text{-}ala)_2$, 5 exhibits negative cotton effect similar to the parent $Cu(L\text{-}ala)_2$[25] complex with $\Delta\varepsilon$ value -0.225. The product obtained from the reaction of $Cu(L\text{-}ala)_2$ with formaldehyde and ammonia at pH 10, 37, did not exhibit any CD band indicating the loss of optical activity during the condensation process. Complexes obtained from $Cu(DL\text{-}ala)_2$, 36 and 6 do not have any CD spectral bands as expected.

3.4.5 Reactions of $Cu(DL\text{-}ser)_2$ and $Cu(DL\text{-}thr)_2$ with higher aldehydes

Reactions of $Cu(gly)_2$ and $Cu(DL\text{-}ser)_2$ with acetaldehyde are known[7,10] in which the resulting products 1 and 7 contain oxazolidine groups (Scheme 3.5). As the condensation reactions of copper(II) amino acids with other higher aldehydes are not investigated, reactions of copper(II) complexes of D, L and DL forms of serine and threonine with propionaldehyde, n- and iso- butyraldehydes, valeraldehydeds and n-caproaldehyde are investigated. $Cu(DL\text{-}ser)_2$ and $Cu(DL\text{-}thr)_2$ complexes readily undergo condensation reactions with these aldehydes and give products 38-43 and 44-49 respectively. The complexes are prepared at neutral pHs according to the Scheme 3.5. The analytical and IR data are collected in Table 3.9. The structures of the new complexes 38-49 are deduced from the following data.

i) All the complexes 38-49 show the three closely spaced IR bands in the region, 1200-1080 cm^{-1} characteristic of oxazolidine rings and a sharp band at 3250 cm^{-1} indicative of the presence of -NH- groups.

ii) All the complexes except 47-49 show IR bands at *ca.* 3500 cm^{-1} suggesting water coordination.



Scheme 3.5 Synthetic route for the preparation complexes 38-49.

Table 3.9 Analytical and spectral data of the complexes 38-49.

complex	Analysis % found (calculated)			IR bands (cm^{-1})	
	C	H	N	oxazolidine	-NH-
$38.2H_2O$	36.8 (37.2)	5.9 (6.2)	6.7 (7.2)	1100, 1140, 1160	3250
$39.2H_2O$	39.6 (40.4)	6.4 (6.8)	6.6 (6.7)	1100, 1140, 1160	3250
$40.2H_2O$	39.6 (40.4)	6.4 (6.8)	6.6 (6.7)	1100, 1140, 1160	3250
$41.2H_2O$	43.2 (43.5)	6.3 (6.8)	6.4 (6.3)	1100, 1140, 1160	3250
$42.2H_2O$	43.3 (43.5)	6.3 (6.8)	6.4 (6.3)	1100, 1140, 1160	3250
$43.2H_2O$	45.4 (45.9)	6.9 (7.3)	6.2 (6.0)	1100, 1140, 1180	3250
$44.H_2O$	41.9 (42.3)	6.2 (6.6)	6.6 (7.0)	1100, 1140, 1170	3200
$45.H_2O$	45.2 (45.1)	6.8 (7.1)	6.5 (6.6)	1100, 1140, 1190	3250
$46.2H_2O$	43.2 (43.3)	7.2 (7.3)	5.9 (6.3)	1120, 1140, 1190	3250

Table 3.9 continued...

complex	Analysis %[a] found (calculated)			IR bands (cm^{-1})	
	C	H	N	oxazolidine	-NH-
47	49.3 (49.5)	7.6 (7.3)	6.5 (6.4)	1100, 1140, 1170	3250
48	49.4 (49.50	7.2 (7.3)	6.4 (6.4)	1110, 1140, 1180	3250
49	51.8 (51.7)	8.0 (7.8)	6.4 (6.0)	1120, 1140, 1170	3250

iii) Similar bands i) and ii) are observed for the known products **7** and **1** obtained from the condensation of $Cu(DL\text{-}ser)_2$ and $Cu(gly)_2$ with acetaldehyde. Thus structures similar to **7** and **1** are assigned for these complexes.

iv) The electronic absorption spectral and esr spectral data (Table 3.10) are comparable to those of the other well characterized condensation products, **3**, **4**, **5**, **6**, **11**, **36**.

v) Analytical data collected in Table 3.9 is commensurate with the proposed structures.

The sharp IR bands of these complexes at *ca.* 3200 cm^{-1} arising from -NH- groups rules out the formation of the ether bridged products similar to **8** and **10**. The absence of further condensation is due to the steric effects of alkyl substituents on the oxazolidine ring which could disallow the *trans* to *cis* arrangement of the ligand units essential for the formation of the bridged products.

The D and L serine or threonine complexes do not undergo reactions in presence of higher aldehydes under similar conditions. This further confirms the differential reactivity behavior of DL- and L- amino acidato copper(II) complexes.

Table 3.10 Electronic and e.p.r spectral data of the complexes 38-49.

complex	$\lambda_{max}(\varepsilon)^a$ nm (let/mol)	e.p.r A_{iso}	g_{iso}(G)
38	624(60)	2.145	80
39	623(75)	2.146	80
40	623(72)	2.148	80
41	622(44)	2.145	80
42	622(45)	2.143	80
43	607(63)[b]	2.145	90
44	623(62)	2.150	80
45	617(66)	2.142	85
46	623(63)	2.140	80
47	626(46)	2.143	82
48	615(68)[b]	2.141	81
49	607(81)[b]	2.135	90

a: measured in water; b: measured in methanol

3.5.0 References

1. A.E. Martell, 'Metal ions in Biological systems', Ed., H. Sigel, Dekker, New York, 1973, 2, p.208.
2. A. Pasini and L. Casella, *J. Inorg. Nucl. Chem.*, 1974, 36, 2133.
3. D.A. Phipps, *J. Mol. Catal.*, 1974, 7, 81.
4. R.D. Gillard, P. O'Brien, P.R. Norman and D.A. Phipps, *J. Chem. Soc., Dalton Trans.*, 1977, 1988.
5. S.B. Teo, S.G. Teoh and M.R. Snow, *Inorg. Chim. Acta*, 1985, 107, 211.
6. S.B. Teo, C.H. Ng and E.R.T. Tiekink, *ibid.*, 1989, 163, 129.
7. N. Arulsamy, B. Srinivas and P.S. Zacharias, *Transition Met. Chem.*, 1990, 15, 309.
8 N. Arulsamy, Ch. R.K. Rao and P.S. Zacharias, *ibid.*, 1991, 16, 606.
9. S.B. Teo, S.G. Teoh and M.R. Snow, *Inorg. Chim. Acta*, 1984, L1.
10. J.P. Aune, D. Maldonado, G. Larchers and M. Pierrot, *J. Chem. Soc., Chem. Commun.*, 1970, 1351.
11. H.C. Freeman, M.J. Healy and M.L. Suddin, *J. Biol. Chem.*, 1977, 252, 8840.
12. A. Dijkstra, *Acta. Crystallogr.*, 1966, 20, 588.
13. K. Tomita, *Bull. Chem. Soc. Jpn.*, 1961, 34, 297.
14. N. Arulsamy, B. Srinivas and P.S. Zacharias, *Transition Met. Chem.*, 1991, 16, 645.
15. B. Prelesnick, R. Herek, D. Stajakovik and D. Poleti, *Mantash. Chem.*, 1986, 17, 47.
16. B.F. Hoskins, C.J. McKenzie and R. Robson, *J. Chem. Soc., Dalton Trans.*, 1992, 3083.
17. V.F. Duckworth and N.C. Stephensen, *Acta Crystallogr.*, 1969, B 26, 1795.
18. P. Singh, D.Y. Jeter, W.E. Hatfield and D.J. Hodgson, *Inorg. Chem.*, 1972, 11, 1657.
19 D.W. Phelps, W.H. Goodman and D.J. Hodgson, *ibid.*, 1976, 22, 2266.

20. S.M. Morehouse, A. Polychronopoulson and G.J.B. Williams, *ibid.*, 1980, 19, 3558.

21. J.R. Brush, R.J. Magee, M.J. O'Connor, S.B. Teo and M.R. Snow, *J. Am. Chem. Soc.*, 1973, 95, 2034.

22. G. Thomas and P.S. Zacharias, *Polyhedron*, 1984, 3, 861.

23. G. Thomas and P.S. Zacharias, *ibid.*, 1985, 4, 811.

24. P.S. Zacharias, T. Sreenivas and J.M. Elizabathe, *ibid.*, 1986, 5, 1383.

25. T. Yasui, *Bull. Chem. Soc. Jpn.*, 1965, 38, 1746.

CHAPTER - IV

DINUCLEAR METAL COMPLEXES OF ROBSON TYPE LIGANDS: SYNTHESIS, SPECTRAL, MAGNETIC, ELECTROCHEMICAL AND CATALYTIC RESULTS

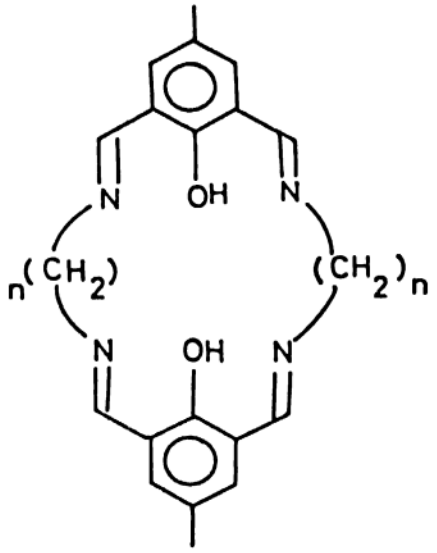
4.1.0 Abstract

Ligands H_2L^1-H_2L^3 and copper(II), nickel(II), cobalt(II), manganese(II) complexes of these ligands are synthesized. These complexes are characterized by C, H, N elemental, IR, UV-Vis spectral and magnetic measurements. Attempts to synthesize iron(II) complexes of the above ligands resulted in corresponding iron(III) complexes. A cobalt(III) complex is obtained from ligand H_2L^1 instead of expected cobalt(II) complex. Many of the copper(II), cobalt(II) and manganese(II) complexes have square pyramidal geometry, while nickel(II) complexes are square planar. Copper(II) complexes have two nearly reversible redox couples at two different potentials. Of the various copper(II), nickel(II) and cobalt(II/III) complexes, only the cobalt(III) complex exhibited catalytic activity in the oxidation of 3,5-di-t-butylcatechol by molecular oxygen.

4.2.0 Introduction

Dinuclear complexes with two metal ions in close proximity show interesting magnetic, catalytic and electron transfer properties. Efforts to synthesize ligands capable of generating such dinuclear complexes have resulted in large number of dinucleating ligands.[1-3] One such ligand system is derived from 2,6-diformyl-4-methylphenol with various mono or diamines. Pilkington and Robson first reported the template synthesis of a dinucleating macrocycle obtained from 2+2 condensation of 2,6-diformyl-4-methylphenol and 1,3-diaminopropane (15). Similar macrocycles (called Robson type ligands) have been used for studies on homo- and hetero- dinuclear and mixed valence complexes. Mostly ethylene and propylene diamines were used in the synthesis of these ligands. Structural and chemical characteristics of these type of complexes are briefly reviewed in the first chapter. The copper(II) and nickel(II) complexes have been investigated in greater detail compared to other 3d metal complexes. Effect of chelate ring size on structural, magnetic and elecrochemical properties of only copper(II) complexes have been studied.[5]

Ligands H_2L^1-H_2L^3, shown by general structure in Fig.4.1 have increasing chelate ring size. To investigate the influence of chelate ring size on spectral, magnetic, catalytic properties, copper(II), nickel(II), cobalt(II), iron(III) and manganese(II) complexes of these ligands are synthesized, characterized and investigated. Structural, magnetic and catalytic properties of these complexes are presented.



n = 2 , H_2L^1

n = 4 , H_2L^2

n = 6 , H_2L^3

Fig.4.1 General strucure of the ligands.

4.3.0 Results and discussion

4.3.1 Copper(II) complexes

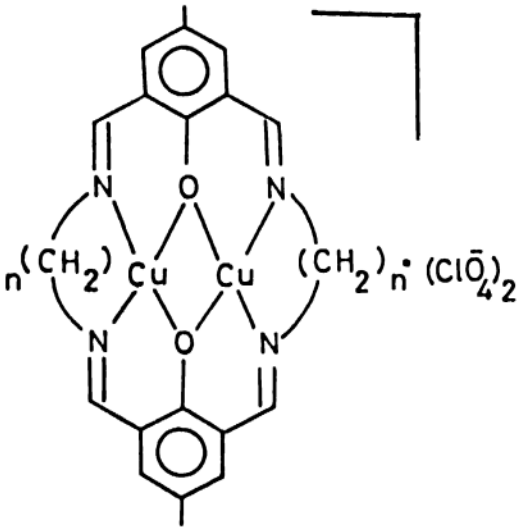
Copper(II) complexes of the ligands H_2L^1-H_2L^3, 50-52 are prepared in situ by template condensation of 2,6-diformyl-4-methylphenol with appropriate diamines viz., 1,2-diaminoethane (50), 1,4-diaminobutane (51) and 1,6-diaminohexane (52) in presence of copper(II) perchlorate in 1:1:1 ratio in methanol.[4] Preparative details are given section 2.5.1.1. The complex 50 is reported in literature as the chloride salt[6] while complex 51 is known as perchlorate salt.[5] Complex 50 is recrystallized from 50% aqueous methanol, while complex 51 is recrystallized from water. Since complex 52 is soluble only in DMF, it is thoroughly washed with hot methanol to get pure compound. The purity of these complexes is checked by C, H, N elemental analysis and the data are collected in Table 4.1. The general structure of the complexes is shown in Fig.4.2(a).

IR spectra of these complexes are recorded as KBr pellets in the range 4000-600 cm^{-1}. The positions of the prominent peaks and their assignments based on comparison to the related complexes[4] are presented in Table 4.1. Conversion of the aldehyde groups into schiff base derivatives is indicated by the absence of aldehyde C=O stretching band at 1680 cm^{-1} and appearance of a strong band at 1640 cm^{-1} assignable to C=N group. The complexes 50 and 52 exhibit a broad band at ca. 3450 cm^{-1} originating from ν_{OH} of water present. The complex 51 does not show any band in this region. IR spectra show ν_3 and ν_4 vibrations of perchlorate ion at 1100 cm^{-1} and 630 cm^{-1} respectively. The band at 1100 cm^{-1} for these complexes is broad indicating possible coordination of perchlorate ion in the solid state.[7] The conductivity measurements in DMF (Table 4.1) show that the complexes are 1:2 electrolytes.[8]

Table 4.1 Analytical, spectral and other data of copper(II) complexes.

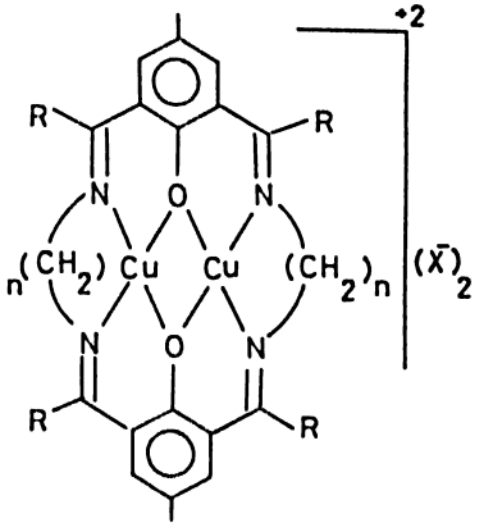
complex	analysis[a]% C	H	N	IR(cm^{-1}) C=N	ClO_4^-	λ^b_{max}(ε) nm ($M^{-1}cm^{-1}$)	μ^c_{eff}/ atom BM	Λ^b_M S cm^2/ mole
50.H_2O	37.00 (36.80)	3.45 (3.42)	7.80 (7.79)	1630	1100 630	545(264) 395(2610)	1.10	177
51	41.40 (41.22)	4.12 (3.96)	7.42 (7.39)	1620	1100 630	770(160) 640 400sh	0.77	175
52.2H_2O	42.51 (42.42)	5.00 (4.95)	6.80 (6.60)	1630	1080 630	670(171) 420(2760)	1.34	175

a: values in parentheses are calculated; b: measured in DMF; c: measured at 298^0K



(a)

50, n = 2
51, n = 4
52, n = 6



(b)

17c : R = H, n = 2, X = Cl^-
20a; R = H, n = 3, X = Cl^-, ClO_4^-
20c ; R = Me, n = 2, X = BF_4^-
20d; R = Me, n = 3, X = ClO_4^-
20e; R = n-Pr, n = 3, X = ClO_4^-
20f; R = Ph, n = 3, X = ClO_4^-

Fig.4.2 Structure of copper(II) complexes a) new complexes b) known complexes.

Magnetic measurements have been carried out for these complexes at room temperature. The μ_{eff}/metal for these complexes are 1.10, 0.77 and 1.34 BM respectively (Table 4.1). The reported magnetic moment of the known complex 51 is 0.46 BM.[5] Experimental difficulty of measuring the susceptibilities of weakly paramagnetic, spin coupled systems led to variations in μ_{eff} values reported by various groups. For example, the complex 20a [Fig.4.2(b)] is reported to exhibit μ_{eff} values of 0.47,[5] 0.6[9] and 0.74[10] BM at room temperature by various groups. The μ_{eff} values of the present complexes are less than spin only value expected for one unpaired electron and indicate antiferromagnetic interactions between the copper(II) centres. Antiferromagnetic interaction has already been established[5] in complex 51.

Magnetic studies[5] on five (20c), six (20a) and seven (51) membered chelate ring complexes showed that no significant changes in antiferromagnetic interaction are observed when the ring size is increased from six to seven (-2J = 850 and 857 cm^{-1}), but five membered chelate ring complex showed lower antiferromagnetic interaction (-2J = 689 cm^{-1}). This was attributed to smaller phenoxide bridge angle (Cu--O--Cu) in complex 20c compared to the complex 20a. However, enough data are not available to generalize the degree of antiferromagnetic interactions in terms of planarity and the angle of phenoxide bridges.

Electronic spectra

The electronic spectra of the complexes are recorded in DMF solvent. The spectra are shown in Fig.4.3 and the data are collected in Table 4.1. The complexes exhibit high intensity band in the range 360-420 nm in the UV region and another one in the visible region. The high intensity band in the UV region can be due to a combination of intra ligand π ---> π^* transition of C=N and

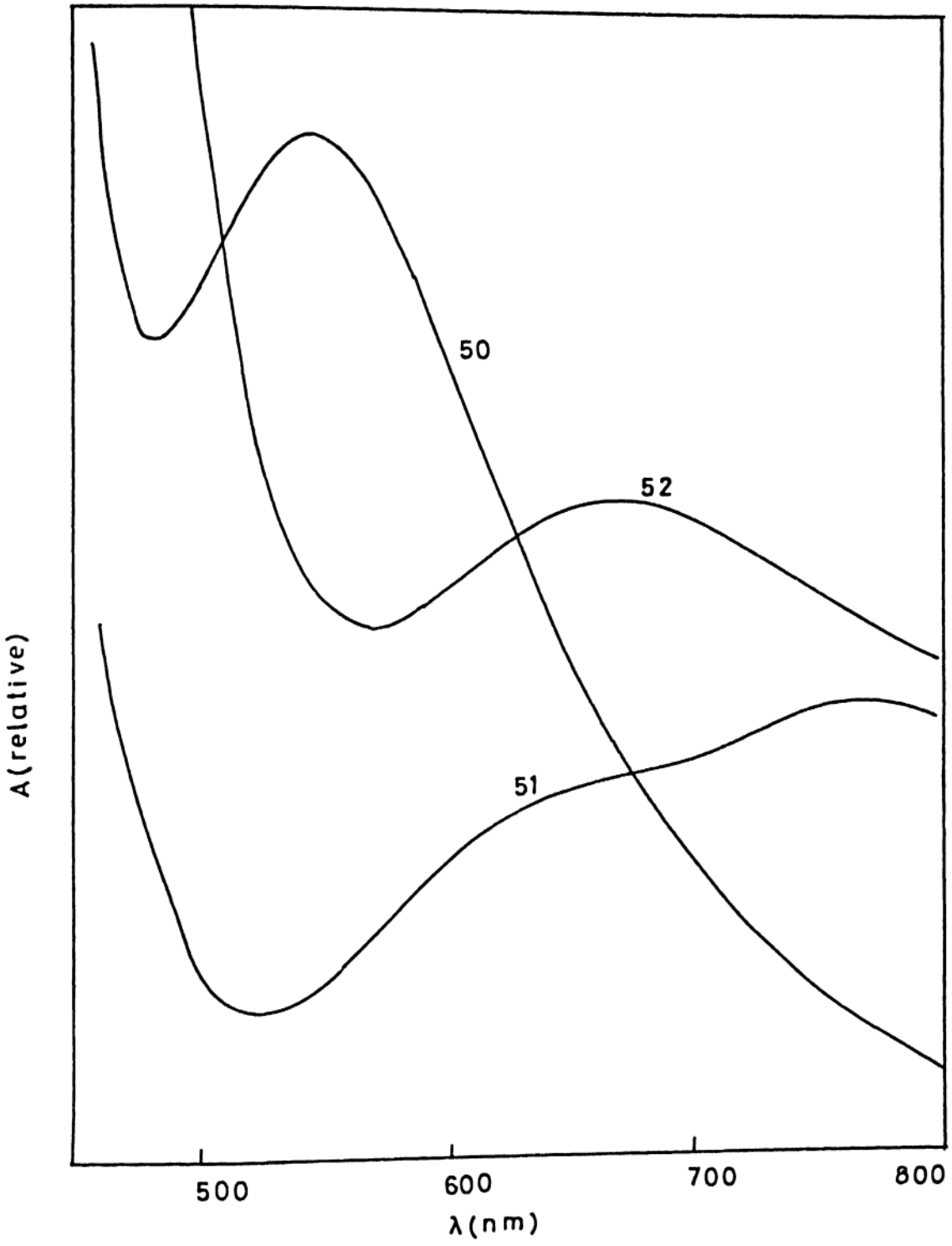


Fig.4.3 Electronic spectra of copper(II) complexes.

ligand to metal charge transfer transitions.[11] The charge transfer may be from p orbital of coordinated phenolic oxygen to the vacant d orbitals of copper(II). Similar charge transfer bands have been observed in several oxo bridged copper(II) complexes.[12-16]

Many dinuclear copper(II) complexes analogous to 50-52 are known[4-6,11,17-19] and are shown in Fig.4.2(b). Complex 17c which has a square pyramidal geometry and exhibits one ligand field band at 574 nm both in solid and in solution. This geometry results from axial interaction of one chloride ion each to copper centre in a trans fashion.[6] Similarly complex 20c showed band at 530 nm and is also square pyramidal with two water molecules coordinating with the two copper(II) ions as shown by X-ray crystal structure.[17] By comparison the new complex 50 which has ligand field band at 545 can be of square pyramidal geometry like 17c and 20c. This geometry is achieved by the coordination of one perchlorate group each to the copper(II) atoms in a trans axial fashion in the solid state. IR spectrum of this complex indicates coordinated perchlorate groups. X-ray structure of complex 51 shows that the copper(II) centres are coordinated axially by two perchlorate groups in a bidentate fashion giving a distorted octahedral structure in the solid state.[5] The electronic spectrum of the complex 51 in DMF solution shows two overlapping bands at *ca.* 770 nm and at 640. The complex 52 has band at 670 nm which lies in between the band positions of square pyramidal complex 50 and octahedral complex 51. IR spectrum of this complex shows coordinated perchlorate group and analytical data indicate the presence of two water molecules. The red shift of the absorption band of 52 with respect to 50 and blue shift with respect to 51 may arise because of the weak coordination of water molecule to each copper centre thereby providing an octahedral geometry wherein one of the axial positions is occupied by loosely coordinated water molecule and the other axial position is held by perchlorate group. The conductivity experiments show that

these complexes are 1:2 electrolytes. The two coordinated perchlorate groups of the complexes have been replaced by solvent DMF molecules in solution.

Electrochemistry

Redox properties of complexes 50 and 51 have been investigated by cyclic voltammetric technique in DMSO solvent using glassy carbon electrode. Complex 52 gave only ill defined peaks. Cyclic voltammograms are shown in Fig.4.4. The complexes undergo stepwise reductions at two different potentials.This is similar to the behavior observed for related complexes,[10] 20a, 20d-20f. The two redox couples are seen at *ca.* -0.49, -1.07 V for complex 50 and at *ca.* -0.34, -0.76 V for 51 with reference to SCE. A comparison of the first one electron reduction potential for the two complexes indicate that the electron transfer is more facile in complex 51. Ligand flexibility associated with the butylene bridge may be responsible for this. Such effect has been noticed previously.[5] The ΔE_p values of the two redox couples are, 120, 80 mv for complex 50 and 80, 120 mv for complex 51. These values show that redox couples involve nearly reversible one electron processes. Therefore the mechanism involves Cu(II)-Cu(II) ---> Cu(I)-Cu(II) and Cu(I)-Cu(II) ---> Cu(I)-Cu(I) stepwise reductions. The stability of the mixed valence Cu(I)-Cu(II) complex intermediate is expressed by the conproportionation constant[10], K_{con}, for the equilibrium

$$[Cu(II)\text{-}Cu(II)] + [Cu(I)\text{-}Cu(I)] \underset{}{\overset{K_{con}}{\rightleftharpoons}} 2[Cu(I)\text{-}Cu(II)]$$

and is given by $K_{con} = \exp(nF(\Delta E)/RT)$ where $\Delta E = E^1_{1/2} - E^2_{1/2}$. The larger the separation between the potentials of the couple (ΔE), the greater the stability of mixed valence species with respect to conproportionation. The K_{con} values

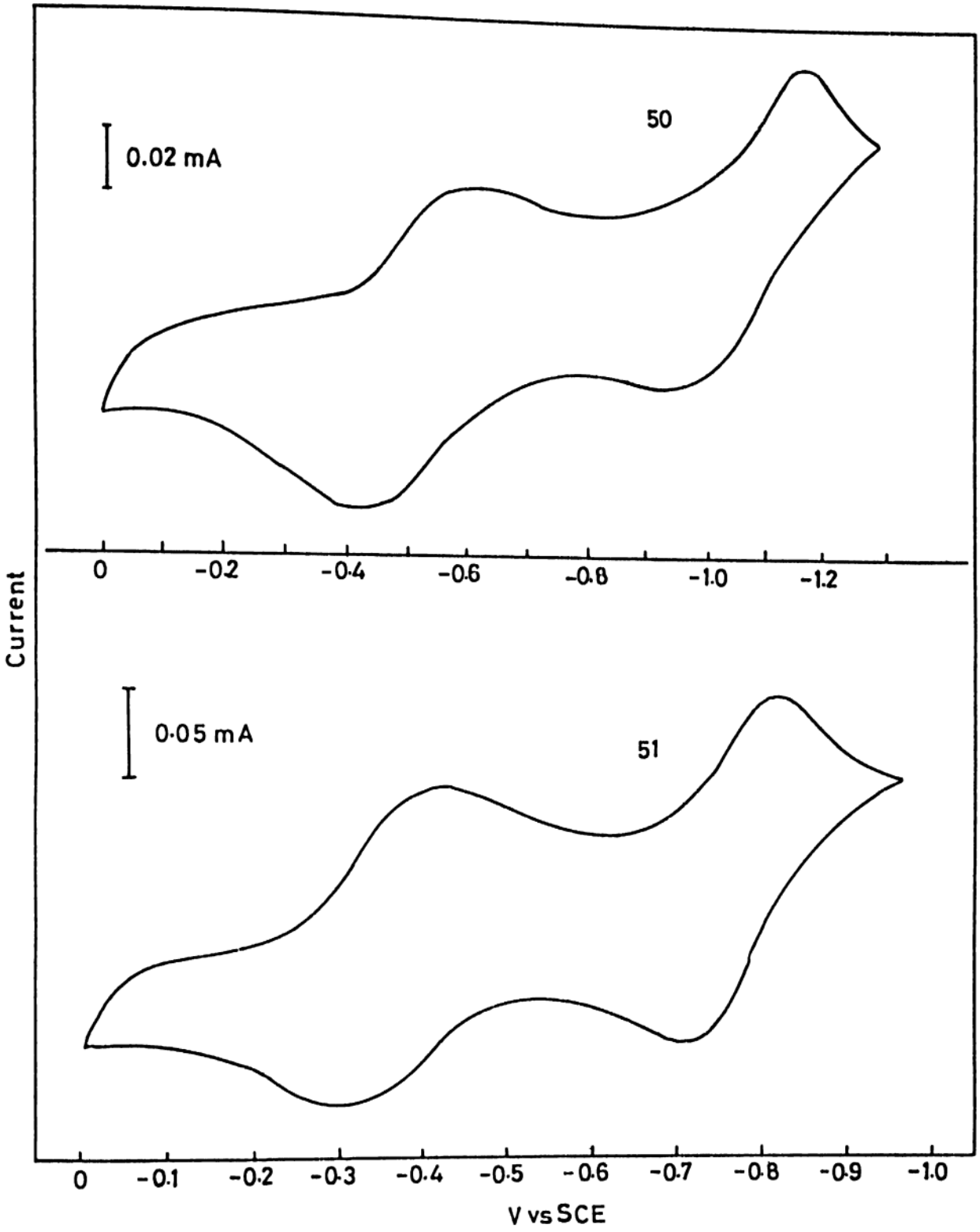


Fig.4.4 CV profiles of copper(II) complexes. The scan rate is 100 mv/sec.

have been estimated for the complexes 50 and 51. The higher value of K_{con}(6.5 x 10^9) for 50 compared compared to 51 (1.3 x 10^7) indicate that the intermediate species, Cu(II)-Cu(I) is more stable for complex 50. The electrochemical data are given in Table 4.2.

4.3.2 Nickel(II) complexes

The nickel(II) complexes 57 and 59 are obtained as orange or yellow solids by template condensation of 2,6-diformyl-4-methylphenol with 1,2-diaminoethane and 1,6-diaminohexane in presence of nickel(II) perchlorate in methanol.[4] When the same procedure is used for the preparation of complex 58, only the mono nickel complex resulted. Therefore complex 58 is prepared by adopting procedure similar to the one given by Gagne *et al* for the preparation of heterodinuclear complexes.[19] This is shown in Scheme 2.1. The ligand $H_2L^{2'}$ on reaction with nickel(II) acetate gave the mono nickel complex, $NiL^{2'}$. Subsequent addition of nickel(II) perchlorate followed by 1,4-diaminobutane yielded the green complex 58. This was recrystallized from water-methanol mixture. Preparative details of these complexes are given in section 2.5.2.1. The analytical data of the complexes are collected in Table 4.3 and general structure of the complexes is shown in Fig.4.5.

IR spectral data of the complexes are collected in Table 4.3. Broad bands are observed at 3400 cm^{-1} for the complexes indicative of lattice water.[5] All the complexes show intense bands at *ca.* 1640 cm^{-1} due to C=N groups of the ligands. The ν_3 absorption of perchlorate group at *ca.* 1100 cm^{-1} is seen as sharp band, while ν_4 absorption is seen at 630 cm^{-1}. The conductivity experiments on these complexes are carried out in DMF solvent. The data are collected in Table 4.3. The complexes behave as 1:2 electrolytes.[8]

Table 4.2 Electrochemical data of copper(II) complexes.

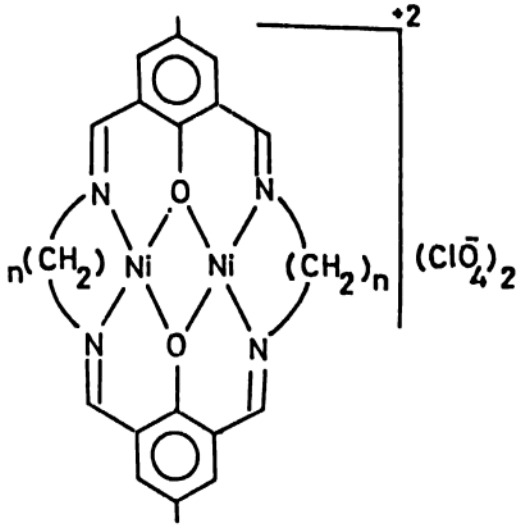
complex	Cu(II)-Cu(II)/ Cu(II)-Cu(I) $E^1_{1/2}(V)^a$	ΔE_p(mv)	Cu(II)-Cu(I)/ Cu(I)-Cu(I) $E^2_{1/2}(V)^a$	ΔE_p(mv)	K_{con}
50	-0.49	120	-1.07	80	6.5×10^9
51	-0.34	80	-0.76	120	1.3×10^7

a: potential (V) vs S.C.E.

Table 4.3 Analytical, spectral and conductivity data of nickel(II) complexes.

complex	analysis(%)[a] C	H	N	IR (cm^{-1}) C=N	ClO_4^-	λ^b_{max}(ε) nm($M^{-1}cm^{-1}$)	Λ^b_M S cm^2/ mole
57.H_2O	38.00	3.42	8.31	1640	1100	470sh	147
	(37.26)	(3.38)	(7.90)		630	410(5700)	
						390(4575)	
58.H_2O	40.28	4.24	7.50	1640	1100	570(144)	135
	(40.08)	(4.18)	(7.32)		630	405sh	
						400sh	
59.MeOH	44.90	5.10	6.82	1640	1100	c	c
	(44.58)	(5.03)	(6.71)		630		

a: values in parentheses are calculated; b: measured in DMF; c: insoluble



(a)

57 , n = 2

58 , n = 4

59 , n = 6

Fig.4.5 General structure of nickel(II) complexes.

All the complexes are diamagnetic which suggests square planar geometry.

Electronic spectra

The electronic spectra of the complexes 57 and 58 are measured in DMF solvent and the complex 59 is insoluble. The visible spectra are shown in Fig.4.6 and the spectral data are collected in Table 4.3. The complexes show two high intensity bands in the range 360-410 nm in UV region and one band in the range 470-570 nm in the visible region.

Nickel(II) ion with d^8 electronic configuration has tendency to form four coordinate diamagnetic planar complexes, especially with stronger ligands or where steric hindrance restricts high coordination number. Such complexes exhibit single d-d band in the range 400-550 nm and often orange, yellow or red. The only one d-d band observed in the diamagnetic square planar nickel(II) complexes is assigned to $^1A_1(F)\text{--->}^1B_1$ transition.[21,22]

The two high intensity bands at *ca.* 370 and 400 nm of the complexes 57 and 58 in the UV region can be interpreted as intra ligand $\pi\text{--->}\pi^*$ transition of azomethine group and charge transfer from ligand to metal, similar to the copper(II) complexes. It is worthy to mention that nickel(II) complex analogous to 57 with chloride as anion, $Ni_2L^1Cl_2.3H_2O$, is also planar with similar electronic spectrum.[6] Similarly all the N,N'-polymethylenebis(salicylaldimine)nickel(II) complexes retain planar structure when n is varied from 2 to 5, and are diamagnetic.[21]

4.3.3 Cobalt(II/III) complexes

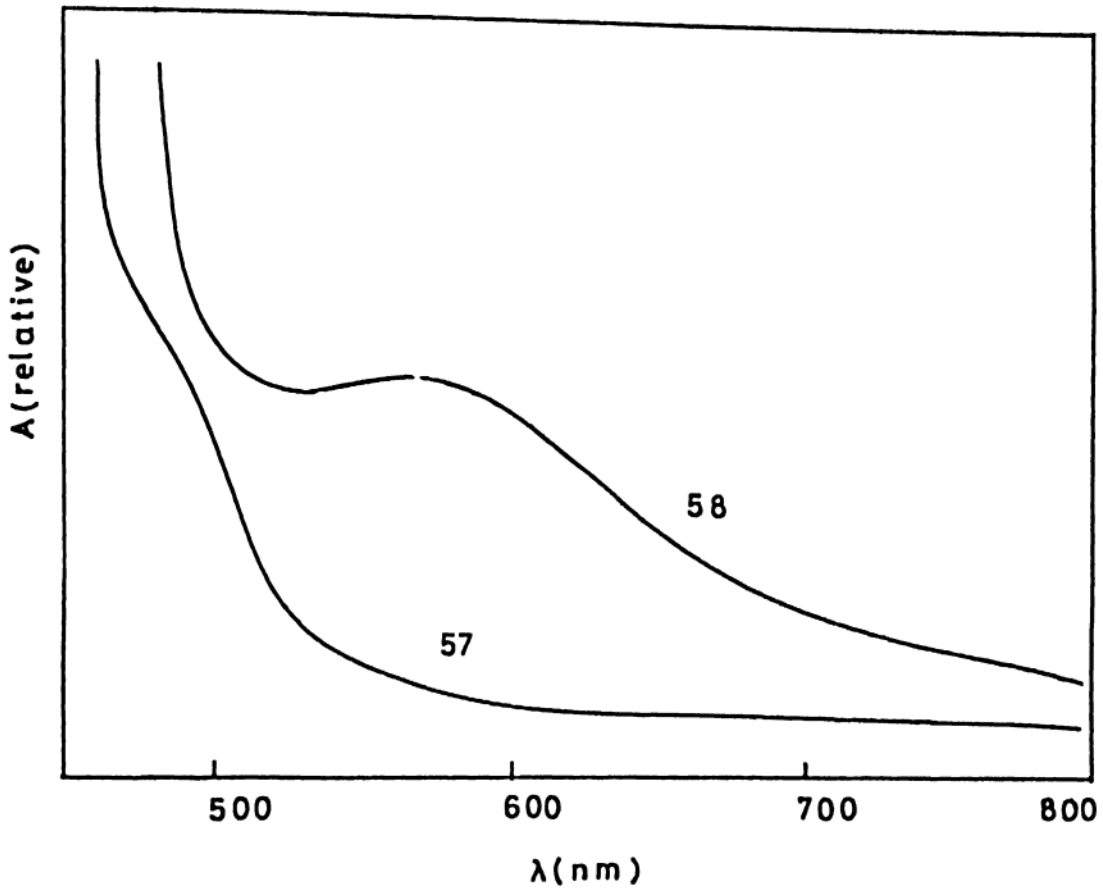
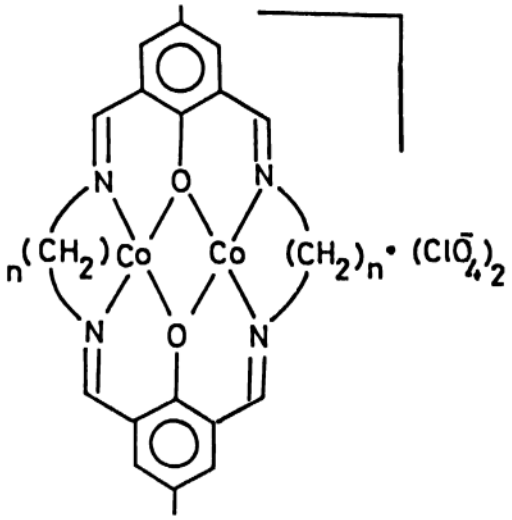


Fig.4.6 Electronic spectra of nickel(II) complexes.

The cobalt complex 64 is obtained as black cobalt(III) complex, while other two cobalt(II) complexes are stable and are brown in colour. Complexes 64 and 65 are recrystallized from their methanol solutions by the diffusion of diethyleher. The compound 66 is washed several times with hot methanol to get analytically pure sample. Preparative details are given in section 2.5.3.1. The general structure of the complexes is shown in Fig.4.7.

IR spectra of these complexes, recorded as KBr discs, indicate the presence of water, as ν_{OH} absorption is seen as broad band at *ca.* 3400 cm^{-1}. The analytical data collected in Table 4.4 suggest that two water molecules are present in the complexes. Sharp and intense bands are seen at 1640 cm^{-1} and are assigned to C=N groups. The broad bands at *ca.* 1100 cm^{-1} for the complexes are assignable to ν_3 modes of perchlorate group. The ν_4 absorption is seen at 630 cm^{-1} as sharp bands. The IR spectral data of the complexes are collected in Table 4.4.

The observed μ_{eff} values for the cobalt(II) complexes are generally diagnostic of coordination geometry around the metal ion. The low spin cobalt(II) square planar complexes can be readily identified from the observed μ_{eff} values which fall in the range 2.1-2.9 BM, arising from one unpaired electron with added orbital contribution.[23-25] Tetrahedral and high spin octahedral cobalt(II) complexes though possess three unpaired electrons, can be distinguished from the deviation of μ_{eff} from the spin only value. The magnetic moments of tetrahedral cobalt(II) complexes with an orbitally non degenerate ground term are increased above the spin only value via contribution from higher orbitally degenerate term and occur in the range 4.2-4.7 BM. Octahedral cobalt(II), maintains a large contribution due to $^4T_{1g}$ ground term and exhibits μ_{eff} in the range 4.8-5.6 BM.[23-25] For the high spin five coordinate complexes the range is 4.5-4.8 BM. The magnetic moment expected for the high spin



65, n= 4

66, n=6

Fig.4.7 General structure of cobalt(II) complexes.

Table 4.4 Analytical, spectral and other data of cobalt(II/III) complexes.

complex	analysis(%)[a] C	H	N	IR (cm^{-1}) C=N	ClO_4^-	λ^b_{max}(ε) nm($M^{-1}cm^{-1}$)	μ^c_{eff}/ atom BM	Λ^b_M S cm^2/ mole
64.$2H_2O$	28.90 (28.51)	3.00 (2.80)	6.25 (6.05)	1640	1100 630	405(7900)	d	185
65.$2H_2O$	41.00 (39.84)	4.51 (4.34)	7.25 (7.15)	1640	1100 630	410(3289)	4.67	176
66.$2H_2O$	43.10 (42.90)	5.01 (5.00)	6.72 (6.67)	1630	1090 630	410(2760)	4.62	180

a: values in parentheses are calculated; b: measured in DMF; c: measured at 298^0K; d: diamagnetic

cobalt(III) ion in an octahedral ligand field is about 5.8 BM.[26] However the majority of the cobalt(III) complexes are of the low spin type and are diamagnetic.[26]

Room temperature magnetic moments for the present complexes are collected in Table 4.4. The cobalt(III) complex 64 is diamagnetic and presumably six coordinated. The μ_{eff} values of 65 and 66 fall in the range expected for pseudo tetrahedral or five coordinate geometries. For complexes 65 and 66 tetrahedral arrangement may not be favoured due to the dinuclear nature of these complexes. An analogous dicobalt(II) complex [n = 3, Fig.4.7], as chloride salt[4], possesses a square pyramidal geometry with μ_{eff} value of 4.61 BM. The μ_{eff} values of the complexes 65 and 66 are 4.67 and 4.62 respectively. Square pyramidal geometry appears to be reasonable for these complexes with two perchlorate groups coordinating to the two cobalt(II) ions.[4,28] The conductivity experiments in DMF solvent show that these complexes are 1:2 electrolytes[8] (Table 4.4). This indicates that the perchlorate groups are replaced by solvent DMF molecules in solution.

Electronic spectra

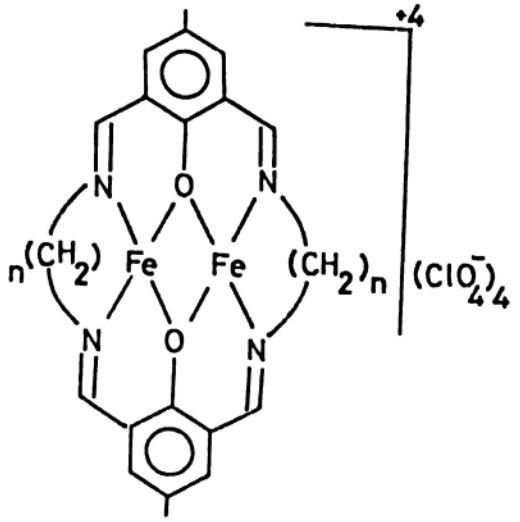
The electronic spectra of these complexes are recorded in DMF and the data are collected in Table 4.4. The complexes show one high intensity band at *ca.* 400 nm in the UV region and no bands are observed in the visible region. Because of this high intense UV bands tailing into the visible region, the d-d bands might have been masked. Dinuclear cobalt(II) systems are reported where d-d bands are masked by such high intensity UV bands.[29,30] Therefore electronic spectra in visible region have not been effective to differentiate between square pyramidal or octahedral geometry of the complexes.

4.3.4 Iron(III) complexes

Though iron complexes are prepared under nitrogen with iron(II) perchlorate, the final products obtained are iron(III) complexes. Experimental details for the preparation of these complexes 71-73 are given in section 2.5.4.1. The complex 71 is recrystallized from methanol by diffusion of diethylether. The complexes 72 and 73 are not soluble in any organic solvent. Elemental analysis showed that the complexes are dinuclear as shown in Fig.4.8, similar to other M^{+2} metal ion complexes discussed earlier.

IR spectra showed sharp and intense bands at *ca.* 1630 cm^{-1} originating from azomethine group. The ν_3 absorptions of perchlorate ions at *ca.* 1100 cm^{-1} are sharp and indicate ionic nature. The ν_4 absorption is seen as sharp band at 620 cm^{-1}. All complexes exhibit broad band centred at 3400 cm^{-1} due to coordinated water or methanol. Analytical data presented in Table 4.5 show that two methanol molecules are present in the complexes. The conductivity experiments on complex 71 show that it is a 1:2 electolyte.[8]

The room temperature magnetic moment values for these complexes are collected in Table 4.5. The observed μ_{eff} values are in the range 5.8 to 5.9 BM. The high spin iron(III) complexes either in octahedral or square-pyramidal environments exhibit magnetic moment close to the spin only value of 5.92 BM. While it is difficult to differentiate between these two geometries form μ_{eff} values alone, square-pyramidal geometry is favoured for the following reasons. As the perchlorate groups are ionic, as shown by the IR spectra and the presence of two methanol molecules are indicated from analytical data, coordination of two methanol molecules to the two iron centres would give a square pyramidal structure. Iron(III)-Schiff base complexes[31-33] derived from salicylaldehyde are known in literature which are square-pyramidal and exhibit μ_{eff} value of 5.8 BM.



71, n = 2
72, n = 4
73, n = 6

Fig.4.8 General structure of iron(III) complexes.

Table 4.5. Analytical, spectral and other data of iron(III) complexes.

complex	analysis(%)[a] C	H	N	IR (cm^{-1}) C=N	ClO_4^-	λ^b_{max}(ε) nm($M^{-1}cm^{-1}$)	μ^c_{eff}/ atom BM	Mossbauer[d] data δ mm/sec	ΔE_q
71.2MeOH	30.60 (30.40)	3.28 (3.17)	6.20 (5.91)	1630	1080 620	520sh 380(6000)	5.83	0.556	0.925
72.2MeOH	34.00 (33.48)	3.91 (3.79)	5.70 (5.58)	1630	1100 630	e	5.86	0.556	0.921
73.2MeOH	36.21 (36.17)	4.90 (4.83)	5.31 (5.28)	1630	1100 630	e	5.92	0.556	1.050

a: values in parentheses are calculated; b: measured in DMF; c: measured at room temperature; d: measured at RT relative to SNP (Subtract 0.16 to convert to relative to iron foil); e: insoluble

Mossbauer spectra

Mossbauer spectroscopy is used as a probe to identify the oxidation state of iron complexes. Mossbauer experiments have been carried on the present complexes at room temperature. The data are collected in Table 4.5, and the spectra of the complexes are shown in Fig.4.9. At room temperature δ varies +1.0 to +1.6 mm/sec for high spin iron(II) complexes whereas it is +0.45 to +0.75 mm/sec for for high spin iron(III) complexes. For the low spin complexes δ varies 0.0 to 0.3 mm/sec, relative to sodium nitropruside.[34] These complexes exhibit δ value of 0.556 mm/sec and ΔE_q of 0.9 to 1.1 mm/sec which are indicative of iron in +3 oxidation state.

Electronic spectra

The Fe^{+3} ion has a d^5 configuration. The present complexes are high spin (S= 5/2) as shown by magnetic moment values. Because of the orbital singlet nature of the high spin Fe^{+3}, there are no exited states of the same spin multiplicity and all d-d transitions are therefore spin forbidden as well as Laporte forbidden.[34] Complex 71 shows a shoulder at 520 nm with high intensity (ε = 2000) in DMF solvent. This band appears to be a charge transfer transition from $p\pi$ orbitals of bridging phenolic oxygen to the half filled $d\pi^*$ orbitals of the iron(III) ions. Similar charge transfer bands have been observed for many known iron(III)-phenolate complexes.[35-37]

4.3.5 Manganese(II) complexes

Condensation of 2,6-diformyl-4-methylphenol with diamines, viz., 1,2-diaminoethane, 1,4-diaminobutane and 1,6-diaminohexane in presence of

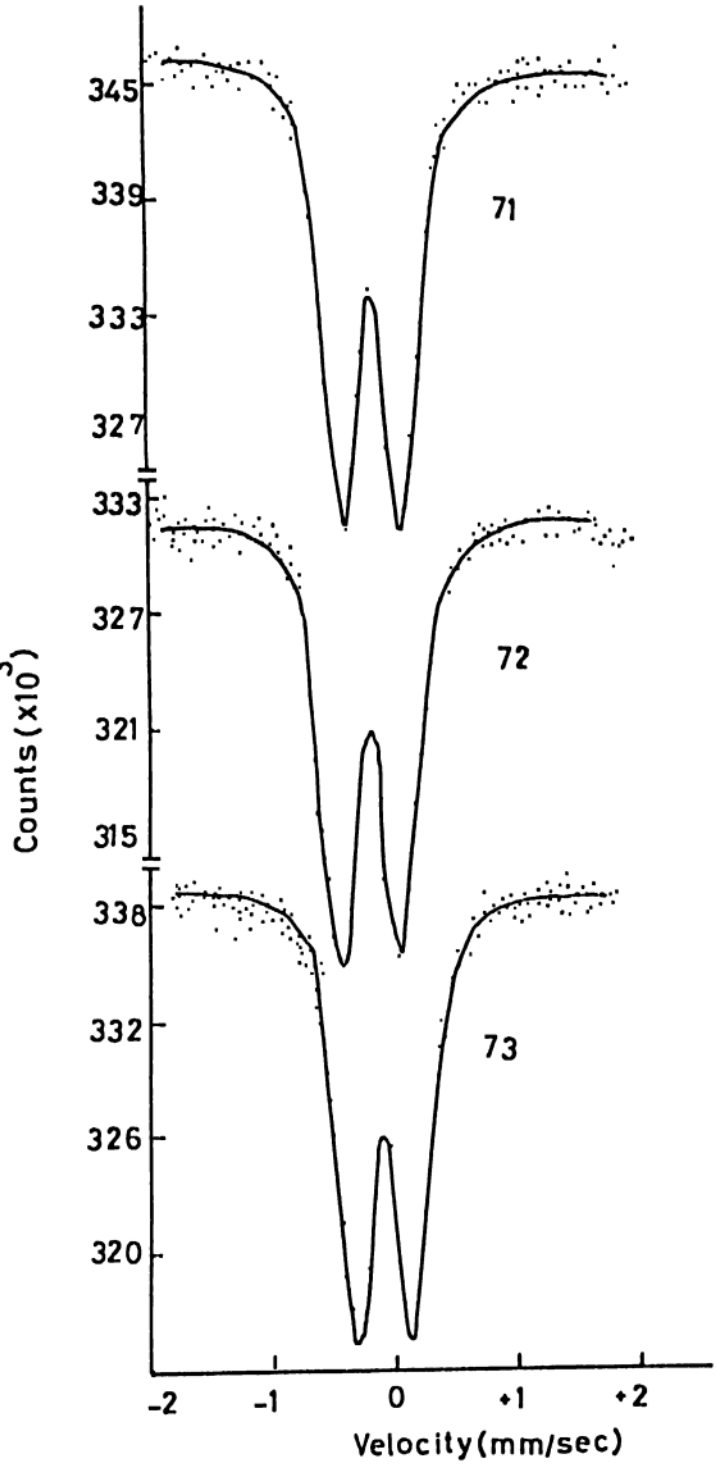


Fig.4.9 Mossbauer spectra of iron(III) complexes.

manganese(II) perchlorate, as template ion yielded the brown (77, 78) and orange (79) complexes. Experimental details for the preparation of these complexes are given in section 2.5.5.1. The complexes are washed several times with hot methanol to get analytically pure compounds. The general structure of the complexes is shown in Fig.4.10.

IR spectra of the complexes recorded as KBr discs, showed a broad band in the region *ca.* 3400 cm^{-1} indicating coordinated methanol or water molecules. Analytical data in Table 4.6 show that two methanol molecules are present in the complexes. The C=N groups of the ligands showed intense band at *ca.* 1640 cm^{-1}. The ν_3 absorption of perchlorate group is seen as sharp band at 1100 cm^{-1} for the complexes and is indicative of ionic perchlorate. The ν_4 absorption is seen at 630 cm^{-1}. The coductivity experiments (Table 4.6) on these complexes in DMF solvent show that these are 1:2 electrolyte.[8]

Magnetic measurements on these complexes at room temperature show μ_{eff} value close to 5.9 BM and are very much comparable with the moments exhibited by dimanganese(II) complexes of similar ligands.[4,38] The magnetic moments are collected in Table 4.6.

Electronic spectra

The electronic spectra of these complexes are recorded in DMF solvent. The data are collected in Table 4.6. The complexes show one band at *ca.* 400 nm which can be assigned to charge transfer bands, based on their high ε values. Similar high intensity band are observed in this range for dimanganese(II) systems derived from analogous ligands.[38] The complexes do not give any band in visible region, which indicate high spin nature of the complexes. However the complex 79 exhibited a weak shoulder at *ca.* 590 nm and this may be due to

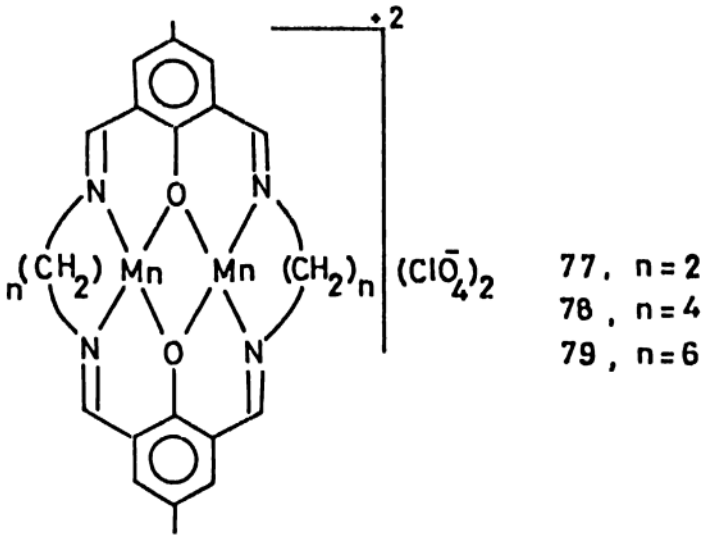


Fig.4.10 General structure of manganese(II) complexes.

Table 4.6. Analytical, spectral and other data of manganese(II) complexes.

complex	analysis(%)[a] C	H	N	IR (cm^{-1}) C=N	ClO_4^-	λ^b_{max}(ε) nm($M^{-1}cm^{-1}$)	μ^c_{eff}/ atom BM	Λ^b_M S cm^2/ mole
77.2MeOH	39.00 (38.55)	4.12 (4.01)	7.60 (7.49)	1630	1100 620	410(2790)	5.66	171
78.2MeOH	42.00 (41.84)	4.82 (4.73)	7.20 (6.97)	1640	1100 630	390(2440)	5.59	162
79.2MeOH	44.81 (44.50)	5.35 (5.34)	6.76 (6.50)	1640	1100 630	400(6600)	5.71	174

a: values in parentheses are calculated; b: measured in DMF; c: measured at room temperature

manganese(III) impurities. Generally manganese(III) complexes show an absorption at 20000 cm^{-1} attributable to $^5E_g \rightarrow {}^5T_{2g}$ transition.

While it is difficult to predict the geometry of these complexes from magnetic moment values and electronic spectra, possible geometry can be predicted from a consideration of all experimental evidences. Presence of two methanol molecules per complex provide possibility of square pyramidal geometry by the coordination of one methanol molecule each to the manganese ions in trans axial fashion. This situation compares well with the geometry of the other metal complexes discussed earlier.

4.4.0 Catalysis

Many mono and dinuclear copper(II), nickel(II) and cobalt(II) complexes act as good catalysts for the oxidation reaction of 3,5-di-t-butylcatechol to its quinone form. The catalytic activity of the copper, 50-52, nickel, 57-59 and cobalt 64-66 complexes for the above reaction by molecular oxygen in methanol has been examined. Experimental procedure for the measurements is given in section 2.6. The amount of 3,5-di-t-butylquinone (3,5-DTBQ) formed is calculated by measuring the absorbance of its characteristic band at 400 nm.[41] Catalytic activity is checked for 50:1 molar ratio of catechol to the complex, except for the cobalt(III) complex 64 for which it is 100:1. The results are summarized in Table 4.7.

The experiments on the copper(II) complexes show that complex 52 converts 17.5% of quinone to catechol in 24 h. Complex 50 catalyzes only 7.7% and complex 51 is not responsive to the reaction. The nickel(II) complexes 57 and 58 behaved in a similar way by catalyzing nearly 7%. Since the nickel(II) complex 59 is not soluble, its activity is not examined. The cobalt(III)

Table 4.7 Time vs absorbance (% of conversion of 3,5-DTBC) of 3,5-DTBQ data of catalytic experiments for the copper(II), nickel(II) and cobalt(II/III) complexes.

	absorbance of 3,5-DTBQ (% of conversion)					
complex	0.5h	1h	3h	8h	20h	24h
50	0.105 (5.5)	0.105 (5.5)	0.110 (5.8)	0.120 (6.4)	0.132 (7.0)	0.145 (7.7)
52	0.115 (6.1)	0.125 (6.6)	0.150 (7.9)	0.190 (10.1)	0.290 (15.4)	0.330 (17.5)
57	0.090 (4.7)	0.090 (4.7)	0.090 (4.7)	0.090 (4.7)	0.130 (6.9)	0.145 (7.7)
58	0.080 (4.2)	0.080 (4.2)	0.090 (4.7)	0.100 (5.3)	0.130 (6.9)	0.135 (7.2)
65	0.095 (5.0)	0.100 (5.3)	0.125 (6.6)	0.150 (7.9)	0.250 (13.2)	0.295 (15.6)
66	0.080 (4.2)	0.080 (4.2)	0.100 (5.3)	0.120 (6.4)	0.200 (10.6)	0.220 (11.6)
	5 mts	0.5h	1h	2h	3h	24h
64	0.435 (23)	1.485 (78.8)	1.53 (81.3)	1.71 (90.8)	1.83 (97)	1.83 (97)

complex 64 has shown highest catalytic activity by converting 97% in 3h for 100:1 ratio, compared to the other complexes with 50:1 ratio. The time dependent growth of 3,5-DTBQ catalyzed by this complex is shown in Fig.4.11.

Catalytic activity of dinuclear complexes is influenced by several factors such as geometry, redox potential and antiferromagnetic interaction. Dinuclear complexes exhibit catalytic activity even if they have planar geometry, while mononuclear complexes of planar geometry are catalytically inactive. The more positive the reduction potential, higher will be the activity.[42] Dinuclear systems with larger antiferromagnetic interactions are more efficient catalysts.[42] However the copper complex of high antiferromagnetic interaction ($-2J = 857\ cm^{-1}$)[5] is not catalytically active in the oxidation reaction. Mechanism of the catalytic process is suggested to involve a weak 1:1 adduct between the the complex and substrates.[43,44] These results show that cobalt(III) complex is the most efficient catalyst.

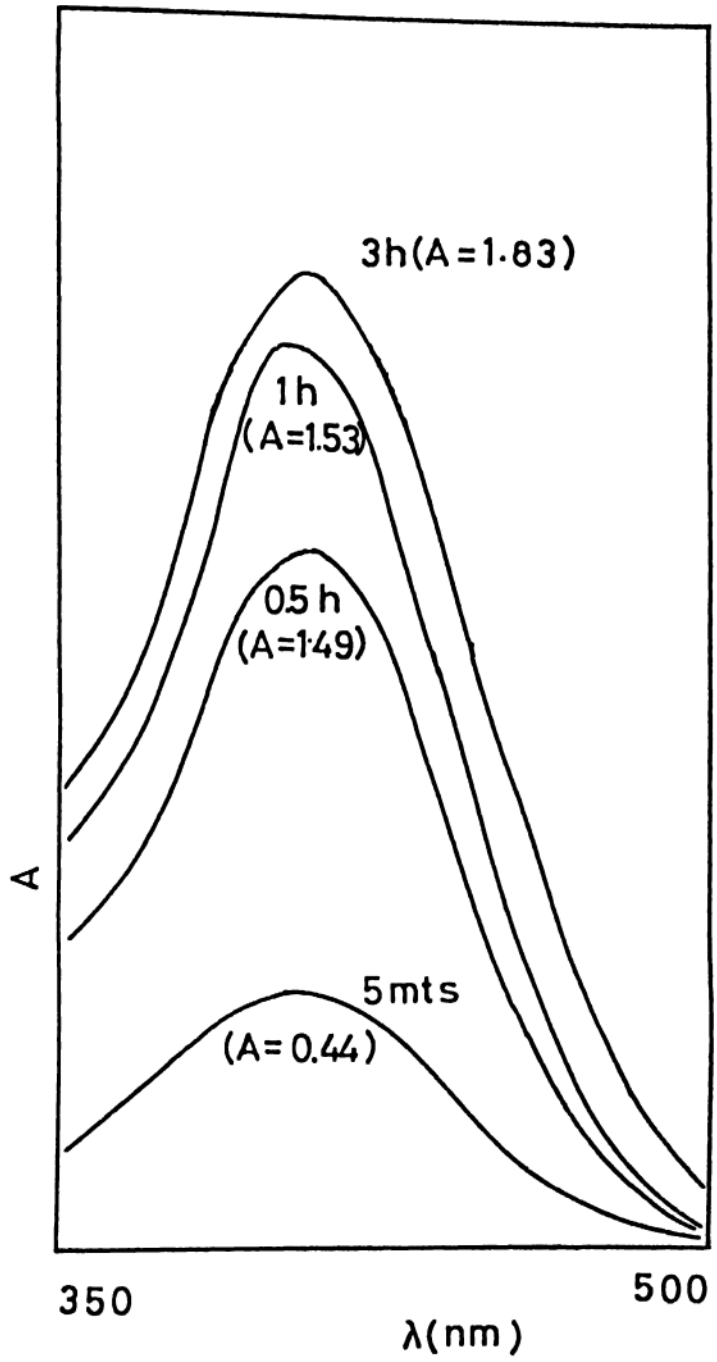


Fig.4.11 Time dependent growth of 3,5-DTBQ catalyzed by cobalt(III) complex 64.

4.5.0 References

1. U. Casellato, P.A. Vigato and M. Vidali, *Coord. Chem. Rev.*, 1977, 23, 31
2. P. Zanello, S. Tamburini, P.A. Vigato and G.A. Mazzochin, *Coord. Chem. Rev.*, 1987, 77, 165.
3. P.A. Vigato, S. Tamburini and D.E. Fenten, *ibid.*, 1990, 106, 25.
4. N.H. Pilkington and R. Robson, *Aust. J. Chem.*, 1970, 23, 2225.
5. S.K. Mandal, L.K. Thompson, M.J. Newlands and E.J. Gabe, *Inorg. Chem.*, 1989, 28, 3707.
6. H. Okawa and S. Kida, *Bull. Chem. Soc. Jpn.*, 1972, 45, 1759.
7. K. Nakamato, "Infrared Spectra of Inorganic and Coordination Compounds, 3rd ed.; Wiley ; New York 1978.
8. W.J. Geary, *Coord. Chem. Rev.*, 1971, 7, 81.
9. R.R. Gagne, C.A. Koval, T.J. Smith and M.C. Cimolino, *J. Am. Chem. Soc.*, 1979, 101, 4571.
10. S.K. Mandal and K. Nag, *J. Chem. Soc., Dalton Trans.*, 1983, 2429.
11. B. Adhikary, S.K. Mandal and K. Nag, *ibid.*, 1988, 935.
12. J.J. Grzybowski, R.H. Merrell and F.L. Urbach, *Inorg. Chem.*, 1978, 17, 3078.
13. J.J. Grzybowski, R.H. Merrell and F.L. Urbach, *ibid.*, 1980, 19, 2604.
14. Y. Nishida and S. Kida, *J. Inorg. Nucl. Chem.*, 1976, 38, 451.
15. Y. Nishida, Y. Numata and S. Kida, *Inorg. Chem. Acta*, 1974, 11, 189.
16. H. Okawa, M. Tadokora, Y. Aratake, M. Ohba, K. Shindo, M. Mitsumi, M. Koikawa, M. Tomono and D.E. Fenton, *J. Chem. Soc., Dalton Trans.*, 1993, 253.
17. W. Daniel Carlisle, D.E. Fenton, P.B. Roberts, U. Casellato, P.A. Vigato and R. Graziani, *Transition Met. Chem.*, 1986, 11, 292.
18. S.K. Mandal, B. Adhikari and K. Nag, *J. Chem. Soc., Dalton Trans.*, 1986, 1175.

1175.

19. R.R. Gagne, C.L. Spiro, T.J. Smith, C.A. Hamann, W.R. Thies and A.K. Shiemke, *J. Am. Chem. Soc.*, 1981, 103, 4073.

20. A.B.P. Lever, 'Inorganic Electronic Spectroscopy', Elsvier, Amsterdam, 1968, p534.

21. R.H. Holm, *J. Am. Chem. Soc.*, 1960, 82, 5632.

22. G. Maki, *J. Chem. Phys.*, 1958, 29, 1129.

23. M. Hariharan and F.L. Urbach, *Inorg. Chem.*, 1969, 8, 556.

24. B.N. Figgis and R.S. Nyholm, *J. Chem. Soc.*, 1959, 338.

25. S. Yamada, *Coord. Chem. Rev.*, 1966, 1, 415.

26. B.N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, 6, Interscience, 1964.

27. H. Weigold and B.O. West, *J. Chem. Soc., A*, 1967, 1310.

28. L. Sacconi, *Pure appl. Chem.*, 1968, 17, 95.

29. W.D. Mc Fadyen, R. Robson and H. Schaap, *Inorg. Chem.*, 1972, 11, 1777.

30. B. Srinivas and P.S. Zacharias, *Transition Met. Chem.*, 1991, 16, 521.

31. G.M. Bancrofit, A.G. Maddock and R.P. Randle, *J. Chem. Soc., A*, 1968, 2939.

32. J.A. Bertrand, J.L. Breece, A.R. Kalyanaraman, G.J. Long and W.A. Becker, *J. Am. Chem. SOc.*, 1970, 92, 5233.

33. J.M. Elizabathe and P.S. Zacharias, *Indian J. Chem.*, 1985, 24A, 936.

34. "Coprehensive Coordination Chemistry", 4, Ed. Geofrey Wilkinson, Pergamon, 1987.

35. M. Suziki, A. Uehara, H. Oshio, K. Endo, M. Yanaga, S. Kida and K. Saito, *Bull. Chem. Soc. Jpn.*, 1987, 60, 3547.

36. A.W. Aniscough, A.M. Brodie, J.E. Plowman, K.L. Brown, A.W. Addision and A.R. Gainford, *Inorg. Chem.*, 1980, 19, 3655.

37. J.W. Pyrz, A.L. Roe, L.J. Stern and L. Que Jr., *J. Am. Chem. Soc.*, 1985, 107, 614.

38. A.J. Downard, Vickie McKee and S.K. Tandons, *Inorg. Chim. Acta*, 1990, 173, 181.

39. B.C. Sharma and C.C. Patel, *Indian J. Chem.*, 1970, 8, 94.

40. B.C. Sharma and C.C. Patel, *ibid.*, 1970, 8, 747.

41. W. Flaig, Th. Poetz and A. Kullmer, *Z. Natur fesch, Tiel B*, 1955, 10, 668.

42. B. Srinivas, N. Arulsamy and P.S. Zacharias, *Polyhedron*, 1991, 10, 731.

43. Y. Nishida, N. Oishi, H. Kuramato and S. Kida, *Inorg. Chim. Acta*, 1980, 46, L69.

44. J.J. Grazbowski, P.H. Merrell and F.L. Urbach, *Inorg. Chem.*, 1978, 17, 3078.

CHAPTER - V

DINUCLEAR METAL COMPLEXES OF TETRAAMINODIPHENOL LIGANDS: SYNTHESIS, SPECTRAL, MAGNETIC, ELECTROCHEMICAL AND CATALYTIC RESULTS

5.1.0 Abstract

Copper(II), nickel(II), cobalt(II) and manganese(II) complexes of ligands H_2L^4-H_2L^6 are synthesized and characterized by C, H, N elemental, IR, UV-Vis spectral and magnetic measurements. Attempts to synthesize iron(II) complexes of the above ligands resulted in iron(III) complexes. Similarly a colbalt(III) complex is obtained from ligand H_2L^4. The copper(II), cobalt(II) and manganese(II) complexes are square pyramidal. Nickel(II) complex of ligand H_2L^4 is square planar while other nickel complexes possess distorted octahedral structure. Only one copper(II) complex (53) and cobalt(III) complex (67) are catalytically active in the oxidation of 3,5-di-t-butylcatechol by molecular oxygen. Copper(II) complexes have two quasi-reversible redox couples.

5.2.0 Introduction

Macrocyclic dinuclear complexes have been investigated in the recent past because of their ability to mimic the active sites of some metalloenzymes[1], to find appropriate systems for binding and activating small molecules[2] and to study the influence of two metal centres on the electronic, magnetic and redox properties.[2-4] Macrocyclic complexes are thermodynamically stabilized and kinetically retarded towards metal dissociation or substitution relative to complexes of the corresponding non-cyclic ligands[5] (macrocyclic effect). In addition they influence the physiochemical properties and reactivities of the metal complexes.[6]

Recently an analogue of Robson type ligand (15) with fully saturated azomethine linkages (22) was prepared and its dinuclear copper(II), nickel(II) complexes are investigated electrochemically and structurally.[7,8,9] It has been suggested that the saturation of azomethine linkages has significant effect on stereochemistry and redox properties of these complexes. The copper(II) and nickel(II) complexes of the ligand (23) are also known in which the metal atoms possess different geometries owing to different ring sizes of the two coordinating sites.[10,11]

Since structural, spectral, magnetic and other properties of copper(II), nickel(II), cobalt(III), iron(III) and manganese(II) complexes of macrocyclic ligands H_2L^1-H_2L^3 were investigated and reported in the previous chapter, it appeared to be a logical extension to investigate the metal complexes of the reduced ligands (H_2L^4, H_2L^6) to probe the effect of saturation on various properties of these complexes. H_2L^5 corresponds to the reduced ligand from diaminopropane bridged macrocycle (15). Results of these investigations form the subject material for this chapter.

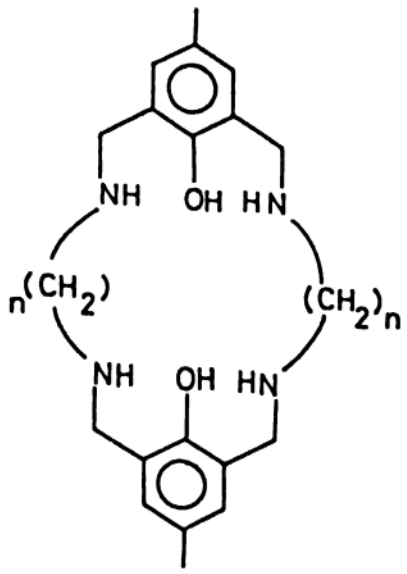
5.3.0 Results and Discussion

5.3.1 Synthesis of Ligands

Macrocyclic tetraaminodiphenol ligands H_2L^4, H_2L^5 and H_2L^6 are synthesized by adopting reported procedure.[12] The experimental details of syntheses are given in section 2.4.2. These ligands are white crystalline compounds and are obtained in low yields. The general structure of the ligands are shown in Fig.5.1. These ligands are characterized by analytical, IR and NMR techniques. IR spectra of the these compounds do not show band at 1640 cm^{-1} of C=N functionality indicating complete reduction of these groups to -NH-CH_2-. In addition they show sharp band at *ca.* 3200 cm^{-1} and 1600 cm^{-1} assignable to υ_{NH} and δ_{NH} modes of secondary amine -NH- of the ligand. Weak and broad band at *ca.* 3500 cm^{-1} can be assigned to υ_{OH} mode of phenol. NMR spectra of the ligands shown in Fig.5.2-5.4 confirm the formation of tetraaminodiphenol macrocycles. The electronic absorption spectra of these ligands in DMF show two absorptions at *ca.* 289 nm and 265 nm in the UV region. The $\pi \text{---} > \pi^*$ transition of azomethine (C=N) group expected at *ca.* 340 nm is absent. The electronic spectra of the ligands are shown in Fig.5.5.

5.3.2 Copper(II) complexes

Preparative details of copper(II) complexes (53-55) of the ligands H_2L^4-H_2L^6 are given in section 2.5.1.2. These complexes are prepared by reaction of ligands with $Cu(ClO_4)_2.6H_2O$ in presence of NaOH in methanol.[7] The products are green in colour and are recrystallized from methanol. The purity of the complexes is checked by C, H, N elemental analysis and the analytical data are collected in Table 5.1. Complex 54 is known in literature.[7,8] The general structure of the complexes are shown in Fig.5.6(a).



n= 2 , H_2L^4

n= 3 , H_2L^5

n= 4 , H_2L^6

Fig.5.1 The structure of tetraaminodiphenol ligands.

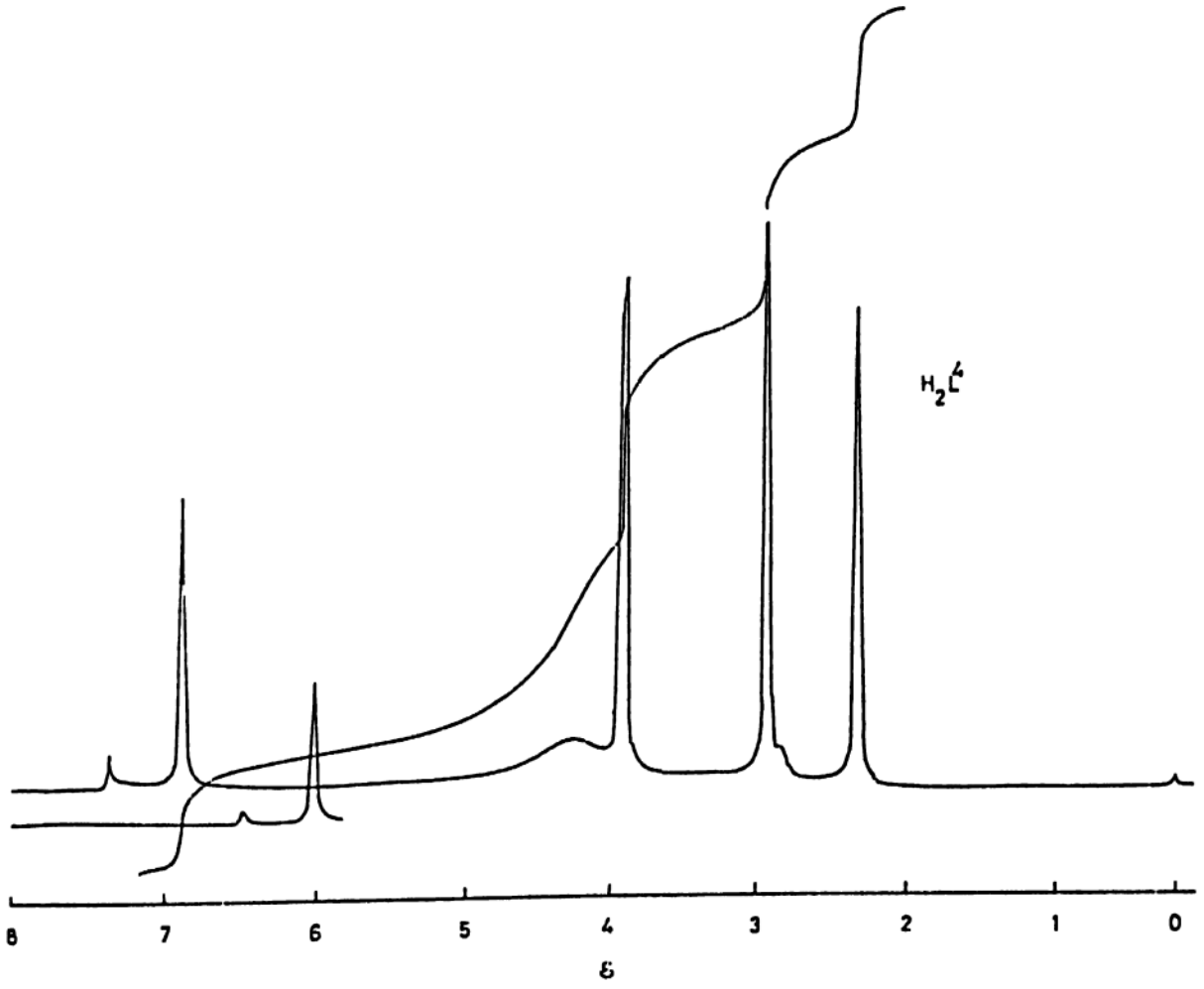


Fig.5.2 ^1H NMR spectrum of ligand H_2L^4.

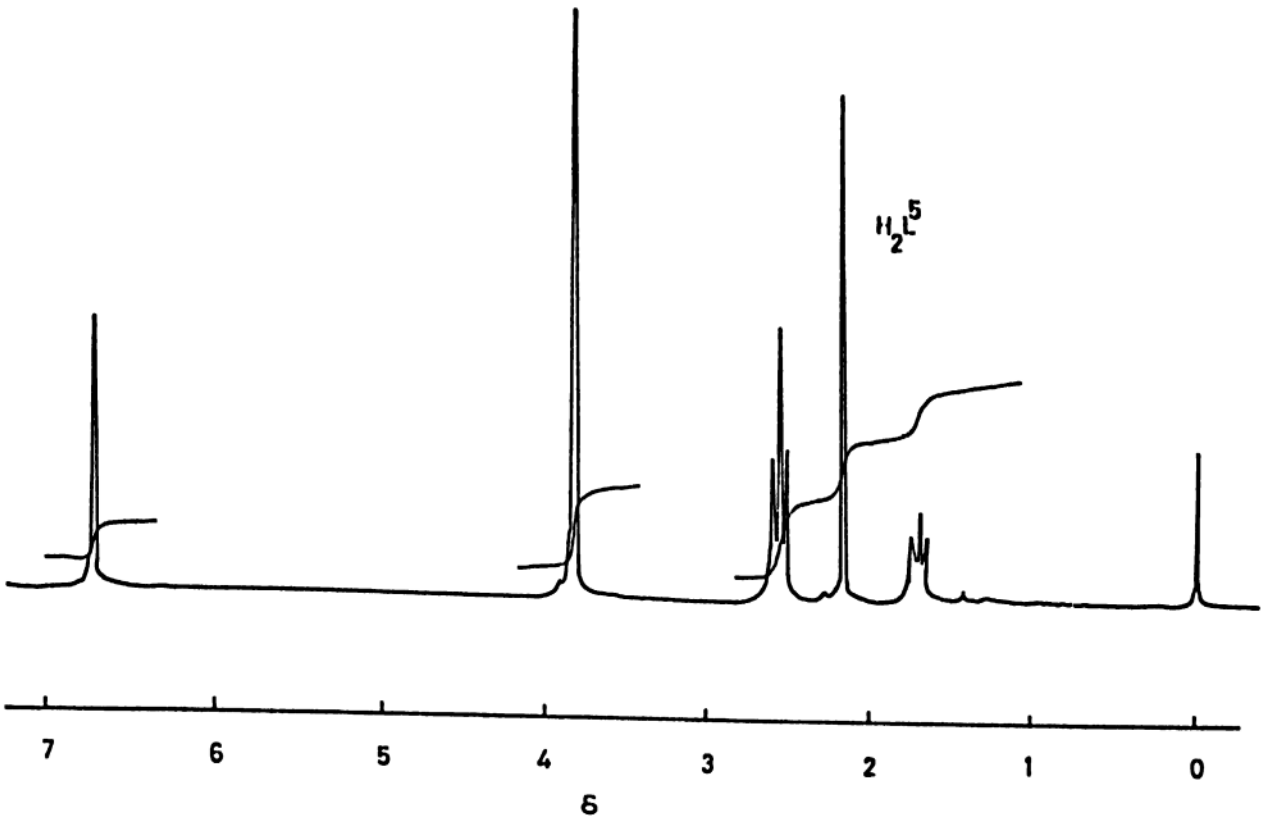


Fig.5.3 ^1H NMR spectrum of ligand H_2L^5.

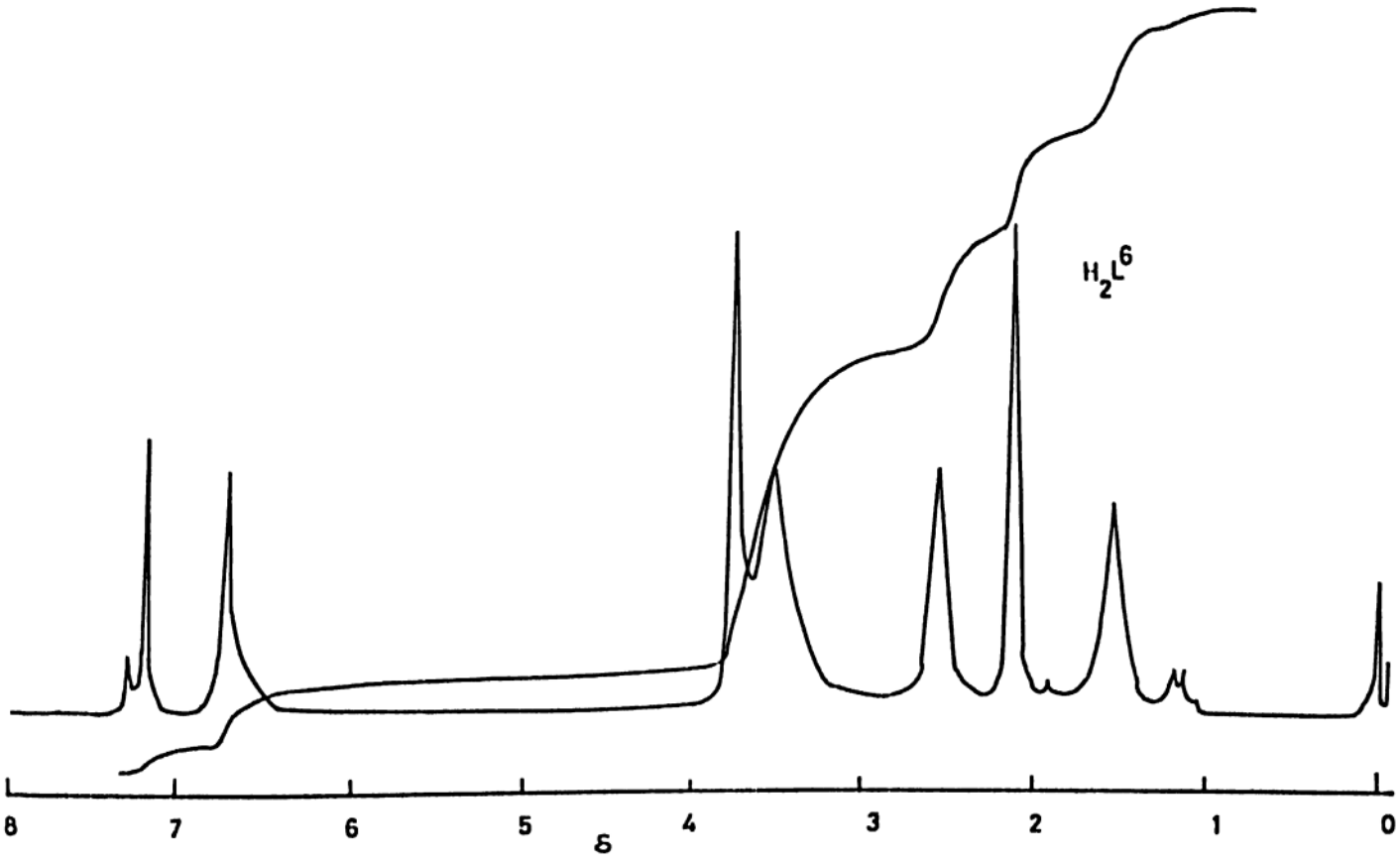


Fig.5.4 ^1H NMR spectrum of ligand H_2L^6.

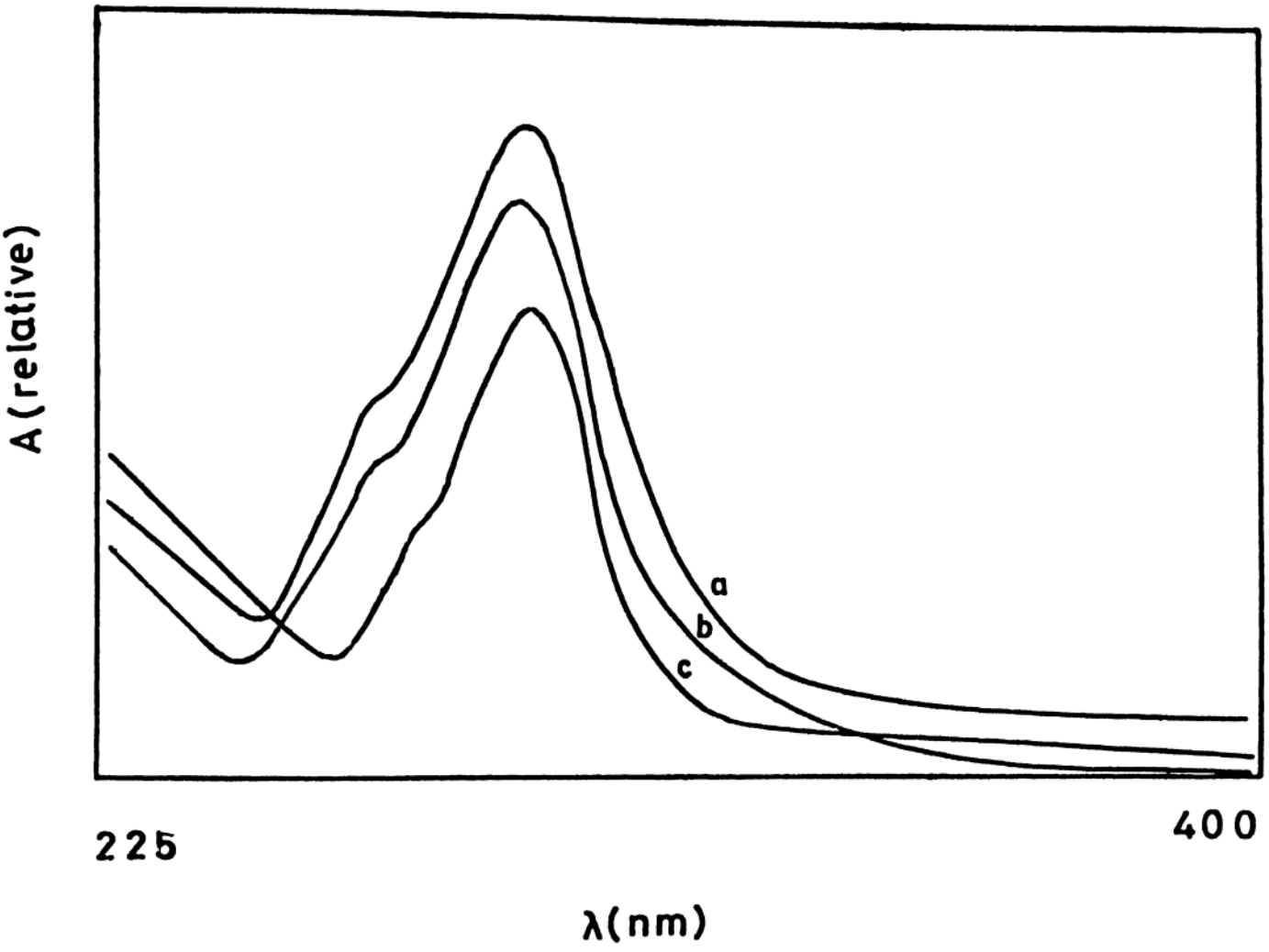
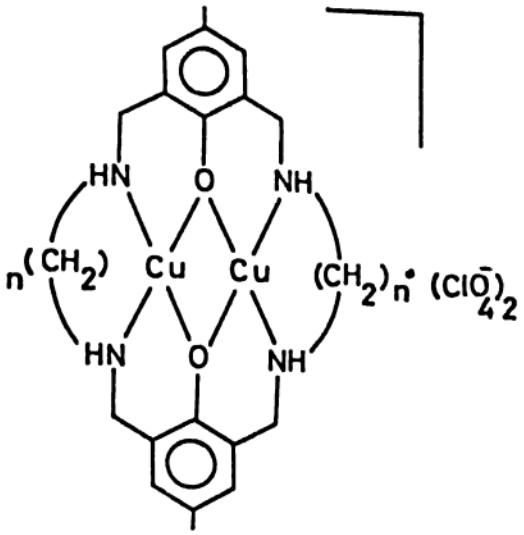


Fig.5.5 Electronic spectra of ligands a) H_2L^4 b)H_2L^5 c) H_2L^6.

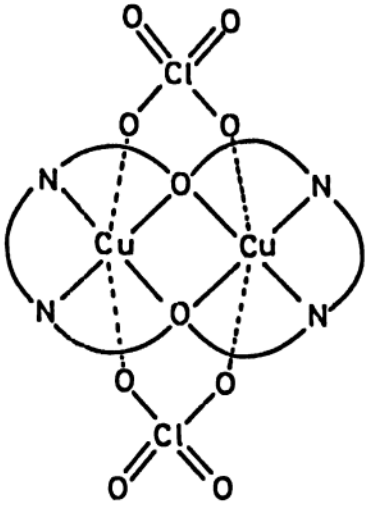
Table 5.1 Analytical, spectral and other data of copper(II) complexes.

complex	analysis(%)[a]			IR (cm^{-1})		λ^{b}_{max}(c)	μ^{c}_{eff}/	Λ^{d}_{M}
	C	H	N	-NH-	ClO_4^-	nm ($M^{-1}cm^{-1}$)	atom(BM)	S cm^2/ mole
53.$2H_2O$	35.52	4.72	7.52	3200	1100	610sh	1.10	220
	(35.49)	(4.60)	(7.52)	1600	630	340(4800)		
54.$2H_2O$	37.30	4.97	7.15	3200	1100	590(270)	0.80	225
	(37.25)	(4.92)	(7.25)	1600	620	340(2550)		
55.$2H_2O$	39.01	5.14	7.03	3250	1100	580(192)	1.07	222
	(38.95)	(5.24)	(6.99)	1600	620	340(2760)		

a: values in parentheses are calculated; b: measured in DMF; c: measured at room temperature; d: measured in acetonitrile

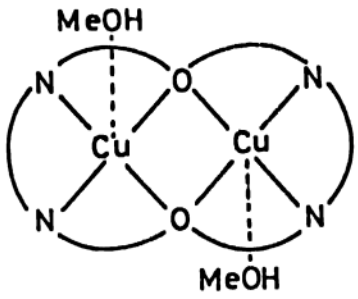


(a)



(b)

53, n = 2
54, n = 3
55, n = 4



(c)

Fig.5.6 Structure of copper(II) complexes.

IR spectra of the complexes exhibit moderately strong bands at *ca.* 3500 cm^{-1} assignable to υ_{OH} mode of water. The C, H, N analytical data suggests two such water molecules for each of the complex. The υ_{NH} and δ_{NH} absorptions originating from the ligands are seen at *ca.* 3200 cm^{-1} and 1600 cm^{-1} respectively. The υ_3 absorption of the perchlorate ion appears as a broad band around 1100 cm^{-1} indicating its coordination to the copper centres.[13] The υ_4 absorption is seen at 620 cm^{-1}. Important IR data are collected in Table 5.1.

Room temperature magnetic moment values for the complexes are collected in Table 5.1. They fall in the range 0.8-1.1 BM and are less than the spin only value of 1.73 BM. This suggests that antiferromagnetic interaction is present in the complexes.

Electronic spectra

The ligand H_2L^5 is reported to form copper(II) complexes of composition $[Cu_2L^5(ClO_4)_2]$,[7] $[Cu_2L^5(CH_3OH)_2](ClO_4)_2$,[8] $[Cu_2L^5(H_2O)_2](ClO_4)_2$.[8] The former complex is blue and has electronic absorption bands at 580 nm and 340 nm both in solid and solution phases. The magnetic moment of this complex is 0.58 BM. The crystal structure of this complex shows two copper(II) centres in a distorted octahedral geometry with two perchlorate units coordinated in a bidentate fashion as shown in Fig.5.6(b). On the other hand the X-ray structure of the second complex $[Cu_2L^5(CH_3OH)_2](ClO_4)_2$ shows two copper centres to be of square pyramidal geometry with one methanol molecule each coordinating to copper centres as shown in Fig.5.6(c). The third complex $[Cu_2L^5(H_2O)_2](ClO_4)_2$ is also square pyramidal with coordination of water molecules and has electronic bands at 574 nm and 344 nm. This complex is green in colour and has magnetic moment of 0.5 BM.[8]

The present complexes 53-55 are green in colour and exhibit d-d bands in the range 580-610 nm. The exact position of the electronic bands are given in Table 5.1 and the spectra are shown in Fig.5.7. Since IR spectra indicate perchlorate coordination, these complexes are suggested to possess a square pyramidal structure with axial coordination of perchlorate ions to the copper(II) centres. The conductivity experiments on these complexes show that these are 1:2 electrolytes and indicate replacement of perchlorate groups in solution by solvent acetonitrile molecules. All complexes show an intense band in the UV region at *ca.* 340 nm and is assigned to charge transfer band from the bridging phenolic oxygen to vacant d orbital of the copper(II) ions. This type of ligand to metal charge transfer bands have been observed for analogous copper(II) complexes.[10]

Electrochemistry

Complexes 53-55 have been investigated by cyclic voltammetry in DMSO using glassy carbon electrode. The complex $[Cu_2L^5(ClO_4)_2]$ is reported to exhibit two one electron oxidation steps ($E_{1/2}$ = 1.21, 1.41 V) to form Cu(III)-Cu(III) species and two one electron reduction steps ($E_{1/2}$ = -0.76, -0.90 V) to form Cu(I)-Cu(I) species.[7] The present complexes behaved in a similar way. The CV profiles of the complexes are shown in Fig.5.8 and data are collected in Table 5.2. These complexes undergo stepwise one electron reductions and generate Cu(II)-Cu(I) and Cu(I)-Cu(I) intermediate species. The $E^1_{/2}$ and $E^2_{1/2}$ values for the complexes are -0.59 V , -1.15 V for 53 ; -0.71 , -1.62 V for 54 and -0.5 V, -0.95 V for 55 with reference to SCE. Comparison of $E^1_{1/2}$ values for the complexes show that the first electron addition is facile for the complex 55. This trend is also observed for the copper(II) complexes 50 and 51 (chapter IV, unreduced forms of 53 and 55) and also known in

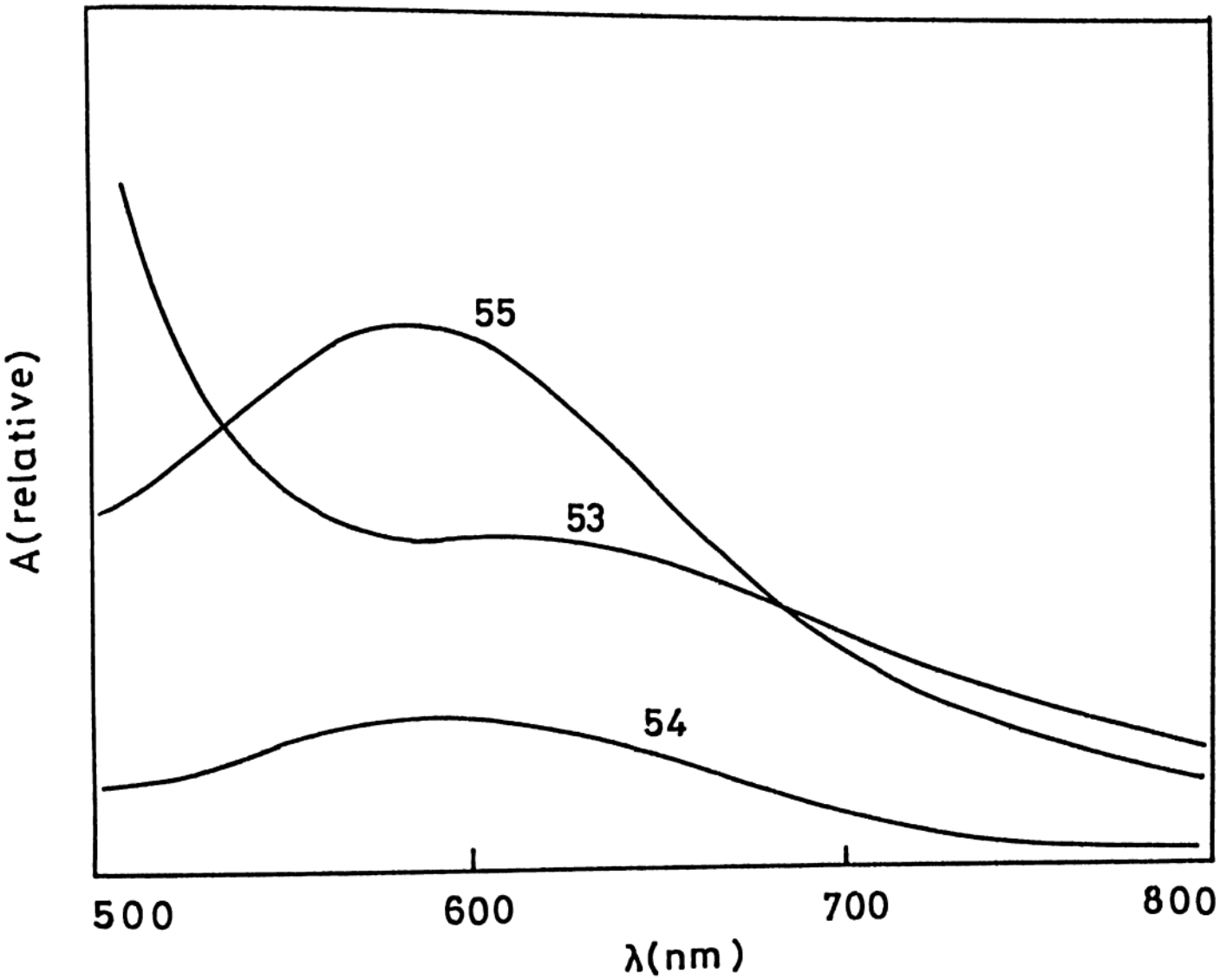


Fig.5.7 Electronic spectra of copper(II) complexes.

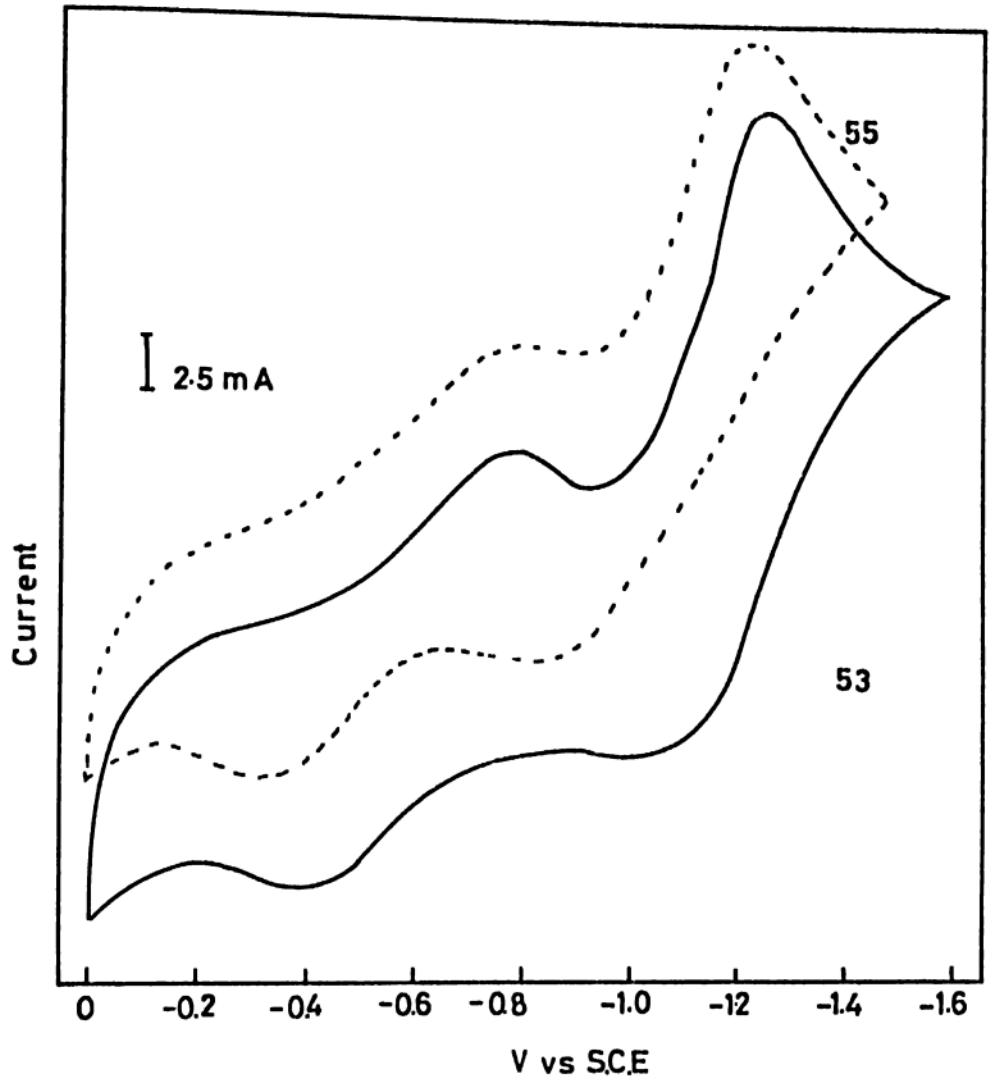


Fig.5.8 CV profiles of copper(II) complexes. The scan rate is 100 mv/sec.

Table 5.2 Electrochemical data of copper(II) complexes.

complex	Cu(II)-Cu(II)/ Cu(II)-Cu(I) $E^1_{1/2}$(V)[a]	ΔE_p(mv)	Cu(II)-Cu(I)/ Cu(I)-Cu(I) $E^2_{1/2}$(V)[a]	ΔE_p(mv)	K_{con}
53	-0.59	380	-1.15	200	2.96×10^9
54	-0.71	120	-1.06	100	8.3×10^5
55	-0.50	380	-0.95	200	4.09×10^7

a: potential (V) vs S.C.E.

literature.[14] The $E^{1}_{1/2}$ values of the complexes 50 and 51 are -0.49 V and -0.34 V respectively. Comparison of $E^{1}_{1/2}$ values shows a negative shift for the complexes 53 and 55. This indicates that Cu(I) states are destabilised when the ligands are saturated. This may result from the ability of the unsaturated macrocycle to accept electrons from copper(I) through the antibonding orbital of C=N linkages whereas the saturated macrocycle act solely as electron donor.[10] This effect has been observed previously.[7,10]

5.3.3 Nickel(II) complexes

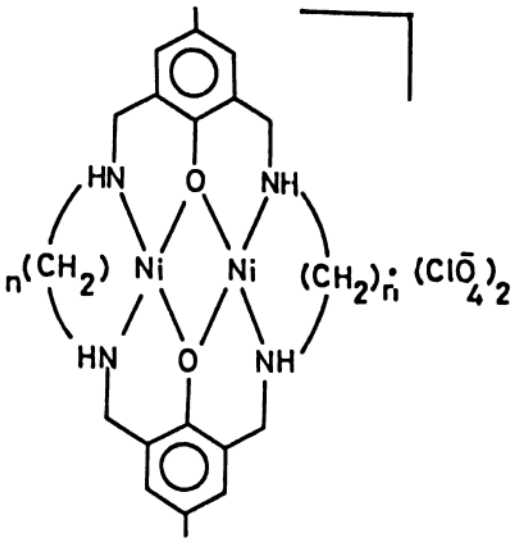
The new complexes 60 and 62 and the known complex 61 are obtained when the respective ligands are refluxed with $Ni(ClO_4)_2.6H_2O$ in presence of triethylamine.[9] Preparative details of these complexes are given in section 2.5.2.2. Complexes 60 and 61 are pink and the complex 62 is green in colour. These complexes are recrystallized from their methanol solutions by diffusion of diethylether. The purity of the complexes is checked by C, H, N elemental analysis. The data are collected in Table 5.3. The general structure of the complexes is shown in Fig.5.9.

IR spectra of these complexes are recorded in the range of 4000-600 cm^{-1} as KBr discs. The spectra of the complexes 61 and 62 exhibit broad band centred at 3400 cm^{-1} and indicates the presence of water or methanol. The C, H, N analytical data show two and three methanol molecules are respectively present in these complexes. The υ_3 absorption band of the complexes 61 and 62 at 1100 cm^{-1} are broad and indicate coordination to the metal centres. The υ_4 absorption is seen at 620 cm^{-1}. The υ_{NH} and δ_{NH} of the -NH- group are seen at *ca.* 3200 cm^{-1} and 1600 cm^{-1} respectively for all the complexes. IR data of the complexes are collected in Table 5.3. Conductivity experiments on these

Table 5.3 Analytical and spectral and other data of nickel(II) complexes.

complex	analysis(%)[a]			IR (cm^{-1})		λ^{b}_{max}(c)	μ^{c}_{eff}/	Λ^{d}_{M}
	C	H	N	-NH-	ClO_4^-	nm ($M^{-1}cm^{-1}$)	atom BM	S cm^2/ mole
60	37.90	4.50	8.12	3150	1100	1040(24)	1.65	225
	(37.80)	(4.29)	(8.09)	1600	620	482(98)		
						340(361)		
61.2MeOH	37.93	6.09	7.10	3250	1100	840(14)	3.10	230
	(38.20)	(6.20)	(7.00)	1610	620	776(9)		
						496(110)		
						360(390)		
62.2MeOH	41.50	5.72	6.80	3250	1100	885(15)	3.31	230
	(41.10)	(5.62)	(6.84)	1600	620	770(12)		
						486(17)		
						360sh		

a: values in parentheses are calculated; b: measured in DMF; c: measured at 298^0K; d: measured in acetonitrile



(a)

60, n = 2

61, n = 3

62, n = 4

Fig.5.9 General structure of nickel(II) complexes.

complexes show that these are 1:2 electrolytes.[17]

Room temperature magnetic moment values for the complexes are collected in Table 5.3. The μ_{eff} values for the complexes 61 and 62 are in the range 3.1-3.3 BM and fall in the range usually observed for octahedral nickel(II) complexes and are comparable to related systems.[9,11,15] The complex 60 is also paramagnetic, but with reduced μ_{eff} value of 1.65 BM.

Electronic spectra

Electronic spectra of the complexes are measured in DMF and the data are collected in Table 5.3. Spectra of these complexes are shown in Fig. 5.10. The known complex 61 $[Ni_2L^5(CH_3OH)_2(ClO_4)_2]$ with distorted octahedral geometry exhibits electronic bands at 1160, 810, 750, 495, 375 nm. These bands are assigned to transitions from $^3B_{1g}$ to ^3E_g, $^3B_{2g}$, $^3A_{2g}$, ^3E_g, $^3A_{2g}$ and/or $^3E_g(P)$ in a tetragonally distorted octahedral field.[9] Complex 62 exhibit bands at 885, 770, 486 and 360 nm similar to complex 61. Thus this complex should also have teragonally distorted octahedral structure. This geometry is achieved by coordination of both methanol and perchlorate ions to each of the nickel centre. However, complex 60 exhibits an electronic spectrum with bands at 1040 and 482 nm in DMF in visible region, different from that of 61 and 62. It is established that[11] squeezing the macrocycle H_2L^5 by replacing one of the diaminopropane lateral chain (-NH-$(CH_2)_3$-NH-) with diaminoethane chain (-NH-$(CH_2)_2$-NH-), i.e, the ligand 23, generated a dinickel complex with one octahedral and one square planar nickel centres. Since complex 60 has only diaminoethane as bridging unit on both the sides, two square planar nickel(II) centres can be expected for this complex. However, the complex is paramagnetic with low μ_{eff} value (1.65 BM per nickel) at room temperature contrary to the

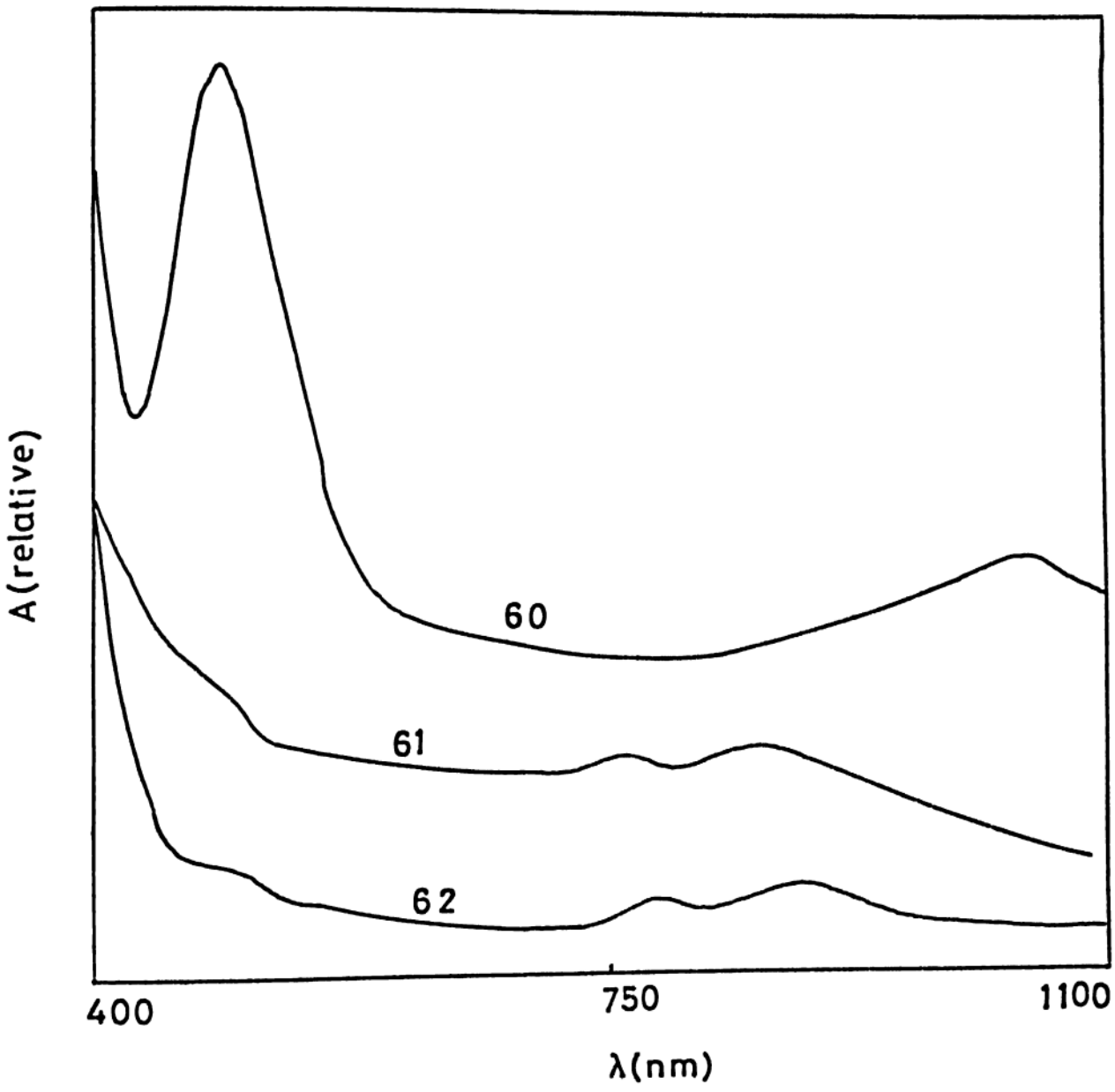


Fig.5.10 Electronic spectra of nickel(II) complexes.

diamagnetism expected for square planar complexes. This may arise due to possible interaction of nickel atoms with oxygens of other molecules in the solid state. Similar type of interactions are reported in N,N'-polymethylenebis(salcilaldimino)nickel(II) complexes with μ_{eff} value of 1.6 BM and electronic bands at 600 and 1000 nm.[16] This complex behaves as 1:2 electrolyte in acetonitrile.[17]

5.3.4 Cobalt(II/III) complexes

Syntheses of cobalt(II) complexes 67-69 from the ligands H_2L^4-H_2L^6 are given in section 2.5.3.2. Complex 67 is highly unstable and is obtained as black cobalt(III) complex, while the other complexes are stable and are brown in colour. These complexes are recrystallized from their methanol solutions by slow diffusion of diethylether. The purity of the compounds is checked by C, H, N elemental analysis which are collected in Table 5.4. General structure of the complexes is shown in Fig.5.11.

IR spectra of the complexes are indicative of presence of methanol or water. Broad bands with moderate intensity are observed at *ca.* 3450 cm^{-1} due to υ_{OH} of water or methanol present. The υ_3 perchlorate absorption at 1100 cm^{-1} is broad and indicates its coordination to the metal centres. The υ_4 absorption is seen at 630 cm^{-1}. These complexes also exhibit bands originating from the ligands. The bands at *ca.* 3200 cm^{-1} and 1600 cm^{-1} are assigned to υ_{NH} and δ_{NH} of the -NH- groups of the ligands. IR spectral data are collected in Table 5.4. Conductivity experiments on these complexes in acetonitrile show that these are 1:2 electrolytes.[17]

Room temperature magnetic moments are collected in Table 5.4. The

Table 5.4 Analytical, spectral and other data of cobalt(II/III) complexes.

complex	analysis(%)[a] C	H	N	IR (cm^{-1}) -NH-	ClO_4^-	λ_{max}^{b}(ε) nm ($M^{-1}cm^{-1}$)	μ_{eff}^{c}/ atom(BM)	Λ_M^{d} S cm^2/ mole
67.2MeOH	30.01	4.04	6.00	3200	1100	600(540)	e	220
	(29.94)	(3.95)	(5.92)	1600	630	400(2625)		
68.$3H_2O$	36.75	5.10	7.20	3200	1100	600sh	4.71	230
	(36.87)	(5.12)	(7.17)	1620	620	360(3096)		
69.2MeOH	41.12	5.70	7.00	3150	1100	370(1670)	4.81	225
	(41.02)	(5.62)	(6.83)	1620	620			

a: values in parentheses are calculated; b: measured in DMF; c: measured at 298^0K; d: measured in acetonitrile; e: diamagnetic

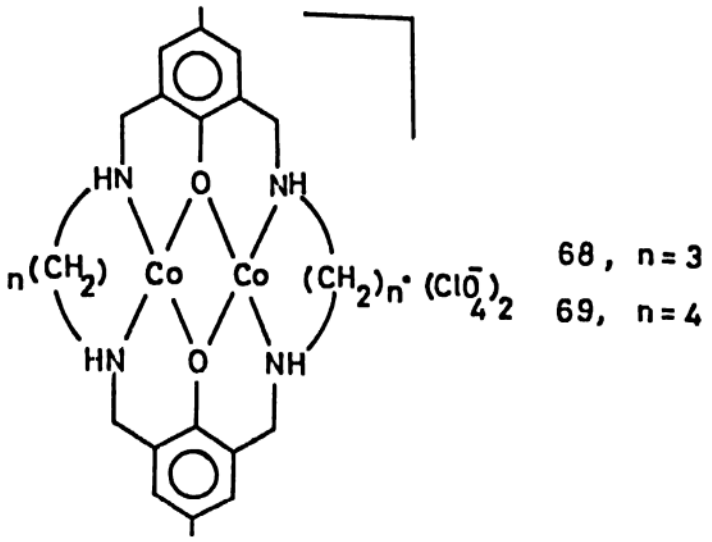


Fig.5.11 General structure of cobalt(II) complexes.

cobalt(III) complex 67 is diamagnetic.[18] The other complexes 68 and 69 exhibit μ_{eff} values in the range 4.7-4.8 BM per metal atom. The magnetic moment for high spin five coordinate cobalt(II) complexes falls in the range 4.5-4.8 BM. Square pyramidal geometry with two perchlorate groups coordinating to each of the cobalt(II) ion is a distinct possibility.[19]

Electronic spectra

The electronic spectra of the complexes are recorded in DMF and the data are collected in Table 5.4. The spectra are shown in Fig.5.12. All complexes exhibit high intensity charge transfer band below 400 nm. The cobalt(III) complex 67 shows one band at 600 nm assignable to $^1A_{1g}$--->^1E_g transition, expected for low spin six coordinated cobalt(III) complexes.[20] The complex 68 exhibit a shoulder at *ca.* 600 nm and may be due to cobalt(III) impurities. The complex 69 does not show any such band in the visible region.

5.3.5 Iron(III) complexes

Experimental details for the preparation of these complexes 74-76 from the ligands H_2L^4-H_2L^6 are given in section 2.5.4.2. Though these complexes are prepared under nitrogen with iron(II) perchlorate, the final products obtained are iron(III) complexes. These complexes are dark brown and are obtained in good yields. These complexes are recrystallized by diffusion technique. Purity of these complexes is checked by C, H, N analysis and the analytical data are collected in Table 5.5. Structure of the complexes is shown in Fig.5.13.

IR spectra of the complexes indicate the presence of water or methanol. Broad bands with moderate intensity are observed at *ca.* 3400 cm^{-1}

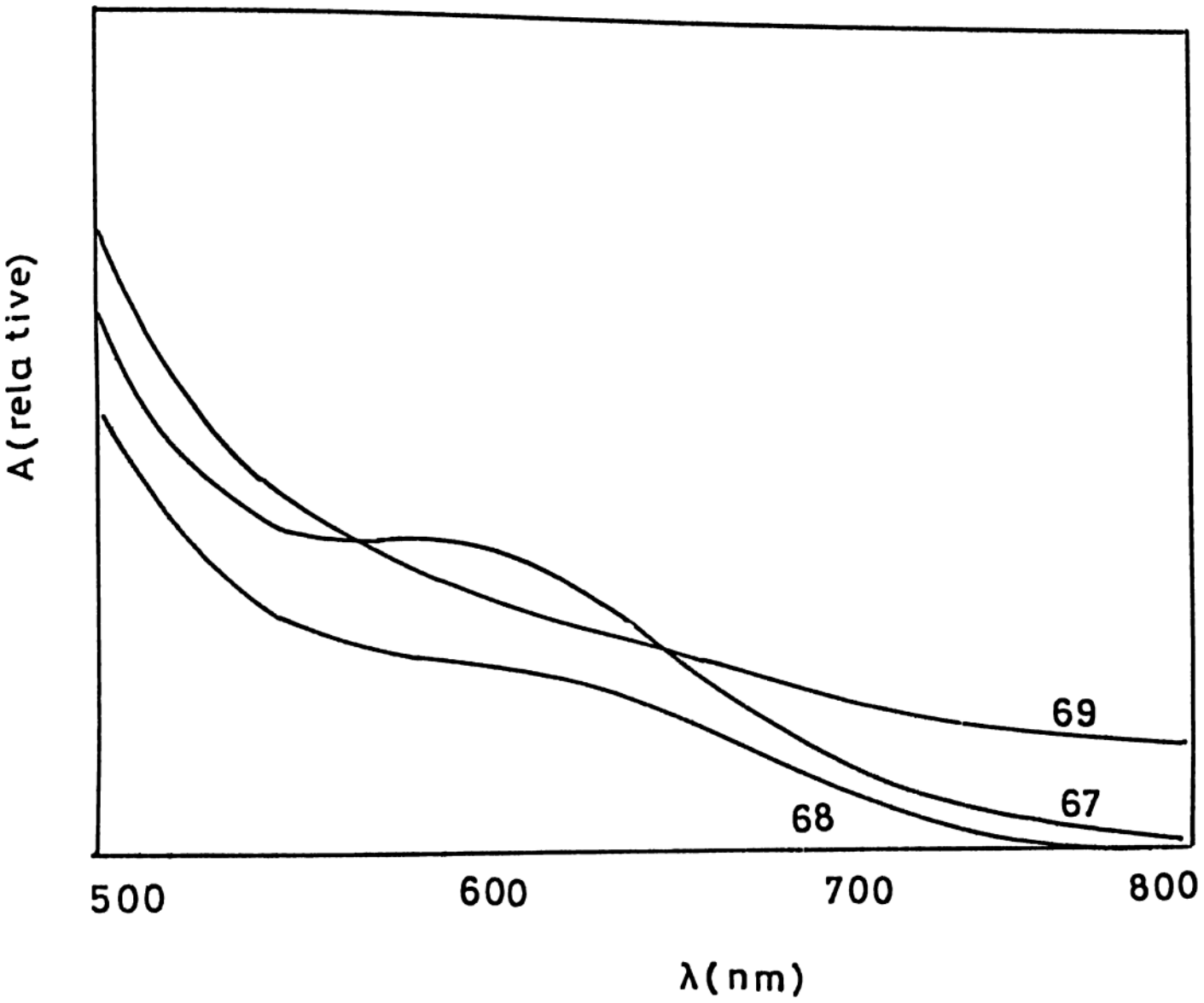


Fig.5.12 Electronic spectra of cobalt(II/III) complexes.

Table 5.5 Analytical, spectral and other data of iron(III) complexes.

complex	analysis(%)[a]			IR (cm^{-1})		λ^{b}_{max}(ε) nm ($M^{-1}cm^{-1}$)	μ^{c}_{eff}/ atom BM	Mossbauer[d] data		Λ^{e}_{M} S cm^2/ mole
	C	H	N	-NH-	ClO_4^-			δ mm/sec	ΔE_q	
74.2MeOH	30.00	4.01	5.91	3250	1100	520(3106)	5.79	0.457	0.831	240
	(30.14)	(3.97)	(5.86)	1620	630	326(3565)				
75.2MeOH	31.84	4.32	5.60	3200	1100	530(2138)	5.83	0.556	0.765	249
	(31.72)	(4.27)	(5.69)	1620	630	330sh				
76.2MeOH	33.19	4.64	5.60	3250	1080	514sh	5.86	0.556	0.960	260
	(33.21)	(4.55)	(5.54)	1600	620	380(1073)				

a: values in parentheses are calculated; b: measured in DMF; c: measured at 298^0K; d: measured at 298^0K relative to S.N.P; e: measured in acetonitrile

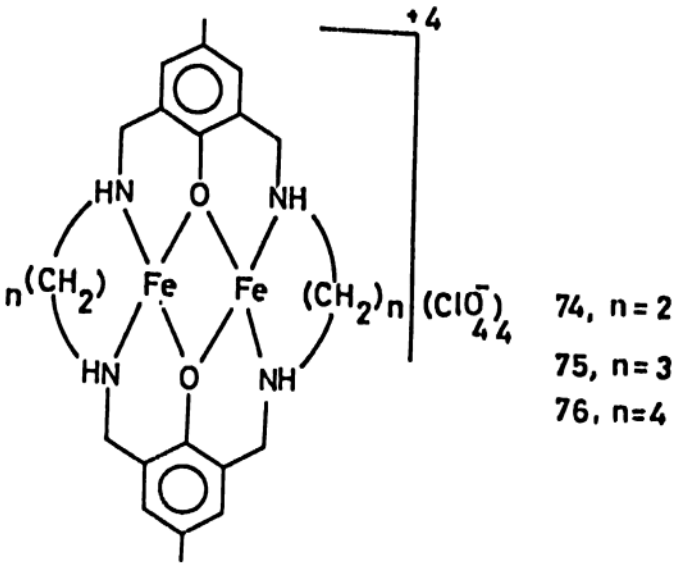


Fig.5.13 General structure of iron(III) complexes.

assignable to υ_{OH} mode of water or methanol. Analytical data show that the two methanol molecules are present in each of the complex. The υ_3 absorption of the perchlorate ion is sharp and indicate ionic nature. The υ_4 absorption is seen at 620 cm^{-1}. The υ_{NH} and δ_{NH} of ligand -NH- groups are observed at *ca.* 3200 cm^{-1} and 1600 cm^{-1} for the complexes. The exact position of the bands are collected in Table 5.5. Conductivity experiments on these complexes in acetonitrile show that these are 1:2 electrolytes.[17]

Room temperature magnetic moments of the complexes are collected in Table 5.5. These complexes exhibit μ_{eff}/atom in the range 5.8-5.9 BM. The high spin iron(III) complexes exhibit magnetic moments close to the spin only value of 5.92 BM. The magnetic moments of the complexes are close to the expected value.

Mossbauer spectra

Mossbauer spectral data of these complexes are collected in Table 5.5 and the spectra are shown in Fig.5.14. All these complexes exhibit one quadrupole split doublet. The observed isomer shift (δ) and quadrupole splitting (ΔE_q) for these complexes are in the range 0.46-0.56 mm/sec and 0.8-1.0 mm/sec respectively with respect to sodium nitropruside. This suggests that the iron is in +3 oxidation state.[21]

Electronic spectra

Electronic spectra of these complexes are recorded in DMF solvent and the data are collected in Table 5.5. These complexes exhibit only one band at *ca.* 520 nm in the visible region. The high ε value of these bands (2000-3000

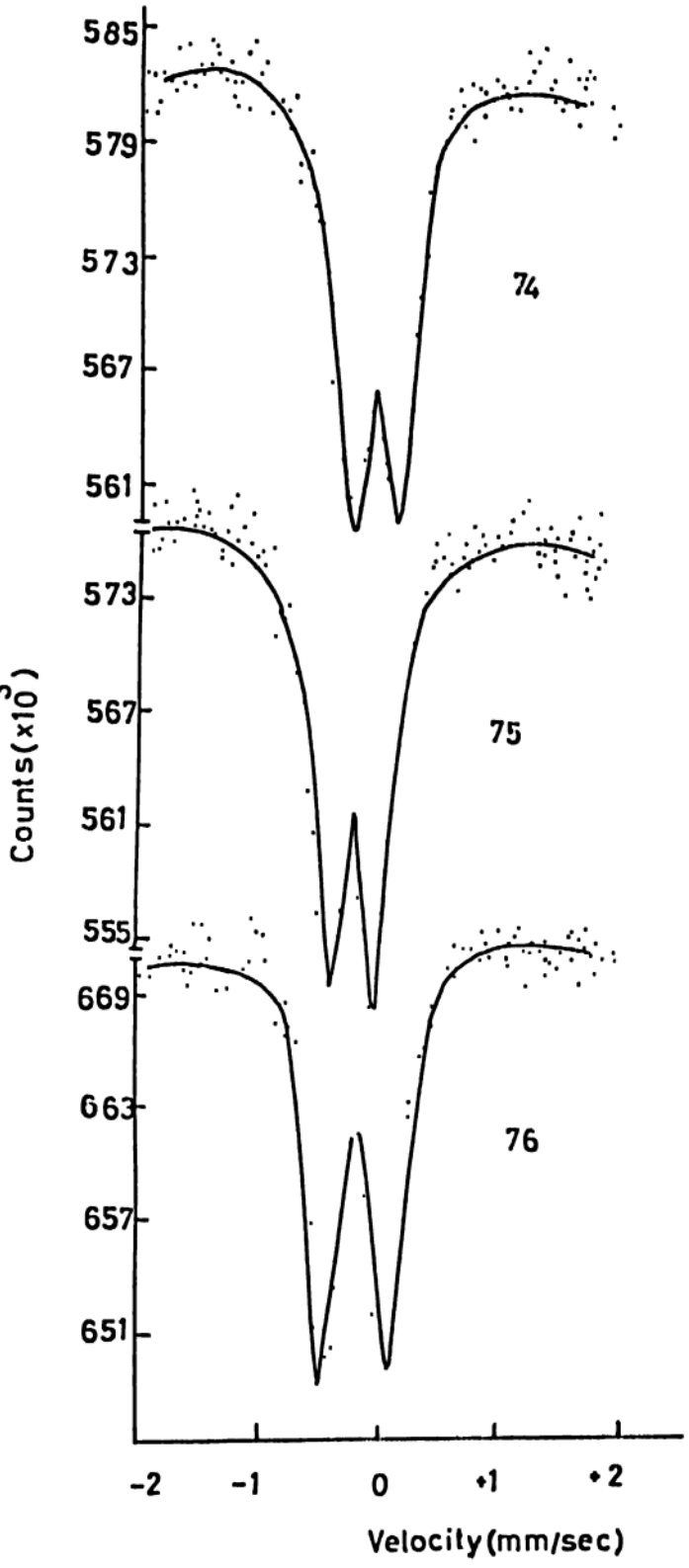


Fig.5.14 Mossbauer spectra of iron(III) complexes.

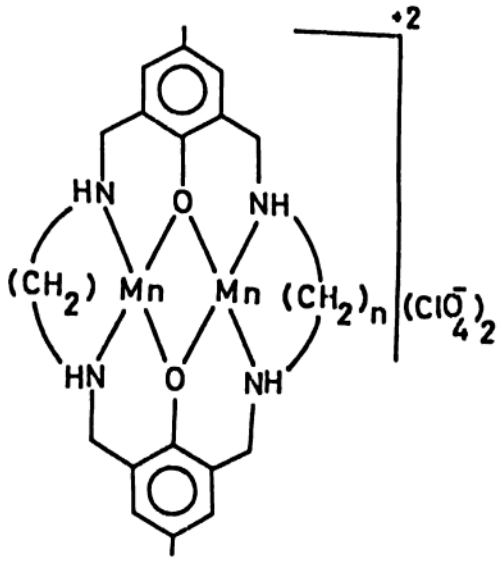
lit/mole/cm) suggests that these are charge transfer bands. The charge transfer is from $p\pi$ orbital of bridging phenolate group to half filled $d\pi^*$ orbitals of the iron(III). Similar charge transfer bands have been observed for iron(III)-phenolate complexes.[22-24]

5.3.6 Manganese(II) complexes

Experimental details for the preparation of manganese complexes, 80-82 are given in section 2.5.5.2. These complexes are obtained as brown amorphous powders when the ligands are refluxed in methanol with $Mn(ClO_4)_2.6H_2O$ in presence of triethylamine. Recrystallization from methanol by diffusion of diethylether gave analytically pure samples. The general structure of the complexes is shown in Fig.5.15.

IR spectra of the complexes showed broad band centred at 3500 cm^{-1} indicate presence of water or methanol. The analytical data collected in Table 5.6 show that two methanol molecules are present in the complexes. The spectra are indicative of uncoordinated perchlorate ions as sharp bands are observed at 1100 cm^{-1}(υ_3 absorption). The υ_4 absorption is seen at 630 cm^{-1}. These spectra show bands due to υ_{NH} and δ_{NH} modes of -NH- group of ligands at 3200 cm^{-1} and at 1600 cm^{-1} respectively. The IR data of the complexes are summarized in Table 5.6. The conductivity experiments show that the complexes are 1:2 electrolytes in acetonitrile.[17]

Room temperature magnetic moments of the complexes are collected in Table 5.6. The observed μ_{eff} values are in the range 5.6-5.7 BM per Mn atom. These values are close to the spin-only value of 5.9 BM and are comparable to the related dimanganese(II) complexes.[19,25] The complexes are assigned square



80, n = 2
81, n = 3
82, n = 4

Fig.5.15 General structure of manganese(II) complexes.

Table 5.6 Analytical, spectral and other data of manganese(II) complexes.

complex	analysis(%)[a] C	H	N	IR (cm^{-1}) -NH-	ClO_4^-	λ^b_{max}(c) nm ($M^{-1}cm^{-1}$)	μ^c_{eff}/ atom(BM)	Λ^d_M S cm^2/ mole
80.2MeOH	38.40	4.91	7.53	3250	1100	650sh	5.6	240
	(38.15)	(5.03)	(7.42)	1620	630			
81.2MeOH	40.01	5.44	7.26	3200	1100	670sh	5.7	230
	(39.84)	(5.36)	(7.15)	1600	630	380(6000)		
82.2MeOH	41.71	5.91	7.01	3200	1100	560sh[e]	5.63	e
	(41.43)	(5.67)	(6.91)	1600	630	470		
						380		

a: values in parentheses are calculated; b: measured in DMF; c: measured at 298^0K; measured in acetonitrile; e: partially soluble

pyramidal structure with coordination of methanol molecules to each of the manganese(II) ions.

Electronic spectra

Electronic spectra of the complexes are recorded in DMF solvent and the data are collected Table 5.6. In manganese(II) high spin complexes the d-d transitions are forbidden by spin selection rule and rarely these bands are observed. However the complexes show weak shoulder in the range 560-670 nm possibly from manganese(III) impurities. Usually the spin-free manganese(III) complexes in an octahedral field give one d-d transition assignable to ^5E_g ---> $^5T_{2g}$ around 20000 cm^{-1}. When the symmetry is lowered, the band shifts to higher wave length.[26]

5.4.0 Catalysis

Catalytic activity of copper(II), 53-55, nickel(II), 60-62, cobalt(II), 68, 69 and cobalt(III), 67 complexes for the conversion of 3,5-DTBC to quinone (3,5-DTBQ) is measured in methanol. Detailed procedure for these measurements is given in section 2.6.0. 3,5-DTBQ has an absorption at 400 nm whose growth is monitored during the experiments. Catalytic activity is checked for 50:1 molar ratio of 3,5-DTBC to the complex solutions, except for complex 67 for which it is 100:1. The results are summarized in Table 5.7. These experiments show that complex 53 is more active than the other copper(II) complexes. The complex 53 converts 55% of 3,5-DTBC to quinone in 6h and nearly 94% in 24h. The other copper(II) complexes 54 and 55 are found to be less efficient. The nickel(II) complexes 60-62 are poor catalysts for this oxidation reaction. The cobalt(III) complex 67 is found to be an effective catalyst for the oxidation. This complex

Table 5.7 Time vs absorbance (% of DTBC conversion) of 3,5-DTBQ in the catalytic experiments for the copper(II), nickel(II) and cobalt(II/III) complexes.

	absorbance of 3,5-DTBQ (% of conversion)							
complex	1h	2h	3h	4h	5h	6h	23h	24h
53	0.390 (21)	0.610 (32)	0.760 (40)	0.870 (46)	0.990 (52)	1.05 (55)	1.75 (92.7)	1.76 (93.7)
54	0.088 (4.6)	0.108 (5.7)	0.127 (6.7)	0.163 (8.6)	0.195 (10.3)	0.205 (10.8)	0.510 (27)	0.510 (27)
55	0.070 (5.1)	0.124 (6.5)	0.157 (8.3)	0.237 (12.5)	0.258 (13.7)	0.260 (13.8)	0.702 (37)	0.702 (37)
	1h	2h	5h	7h	9h	11h	13h	24h
60	0.060 (3.2)	0.100 (5.3)	0.150 (7.9)	0.180 (9.5)	0.210 (11.2)	0.240 (12.7)	0.280 (14.9)	0.430 (22.8)
61	0.030 (1.5)	0.040 (2.1)	0.080 (4.2)	0.090 (4.8)	0.110 (5.8)	0.130 (6.9)	0.150 (7.9)	0.250 (13.3)
62	0.020 (1.0)	0.030 (1.5)	0.040 (2.1)	0.050 (2.7)	0.060 (3.2)	0.070 (3.7)	0.080 (4.3)	0.140 (7.4)
	10mts	20mts	40mts	50mts	1h	1.10h	1.20h	1.30h
67	0.227 (12)	0.384 (20)	0.647 (34)	0.812 (43)	0.936 (50)	1.04 (55)	1.14 (60)	1.21 (64)

Table 5.7 continued...

1.4h	2h	3h	4h	5h	6h
1.295	1.390	1.540	1.650	1.720	1.796
(68.7)	(74.0)	(84.7)	(87.7)	(91.5)	(95)

	1h	2h	5h	6h	8h	9h	22h	23h	24h
68	0.060	0.100	0.200	0.220	0.300	0.340	0.740	0.760	0.78
	(3.18)	(5.3)	(10.6)	(11.7)	(15.9)	(18.1)	(39.3)	(40.4)	(41.4)
69	0.324	0.452	0.636	0.769	0.888	0.945	1.502	1.535	1.534
	(16.7)	(23.9)	(33.8)	(40.8)	(47.2)	(50)	(79.8)	(81.3)	(81.3)

converts 95% of 3,5-DTBC to quinone within 6h. The other cobalt(II) complexes are less effective. Fig.5.16 and 5.17 show the time dependent growth of 3,5-DTBQ catalyzed by copper(II) complex 53 and cobalt(III) complex 67. These results show some general trend in the catalytic properties. Catalytic efficiency of the complexes is in the order cobalt(III) > cobalt(II) > copper(II) > nickel(II). Of these, complexes of ligand H_2L^4 , where the bridging unit is ethylenediamine are more effective than other complexes.

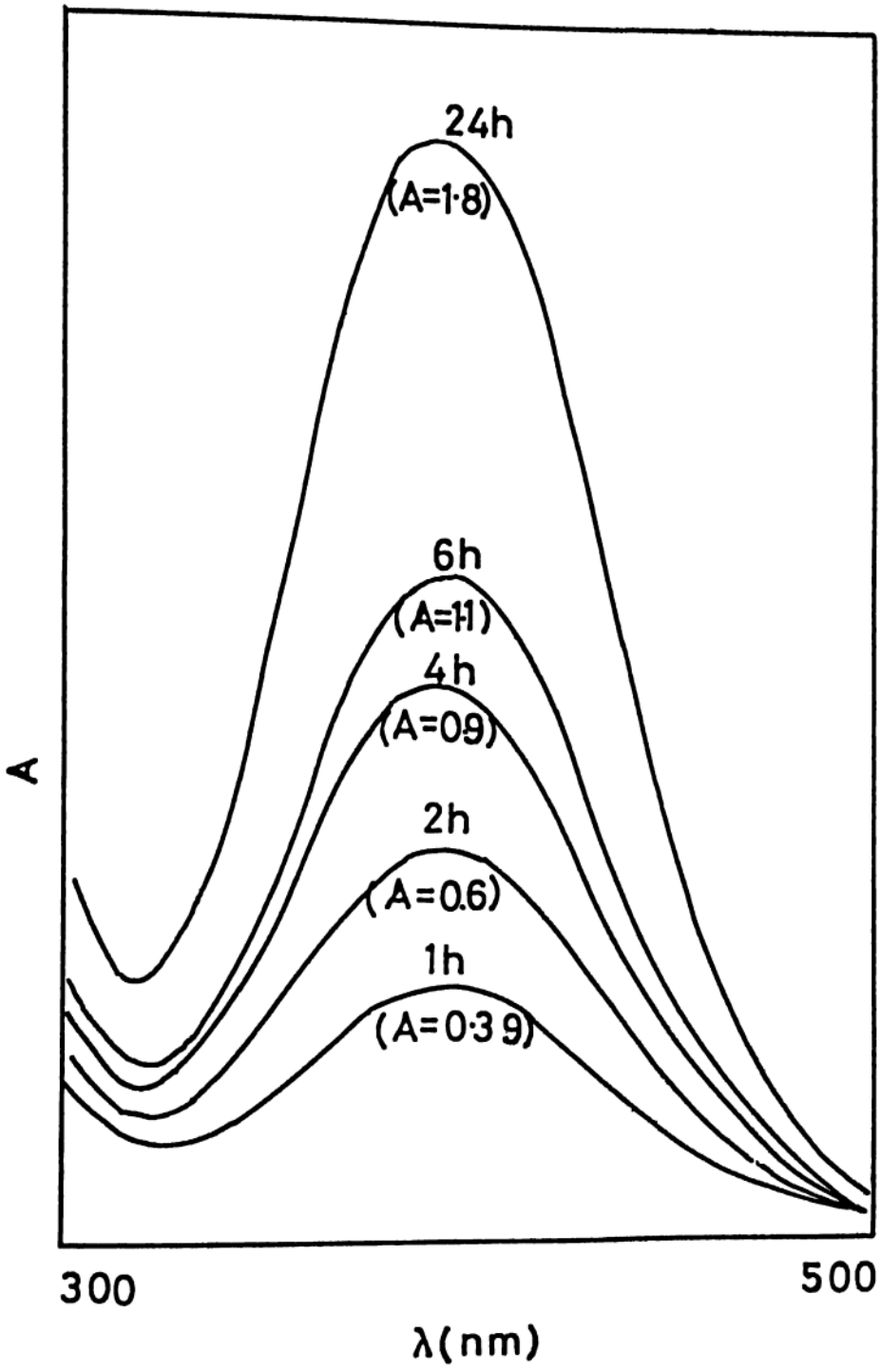


Fig.5.16 Time dependent growth of 3,5-DTBQ catalyzed by copper(II) complex 53.

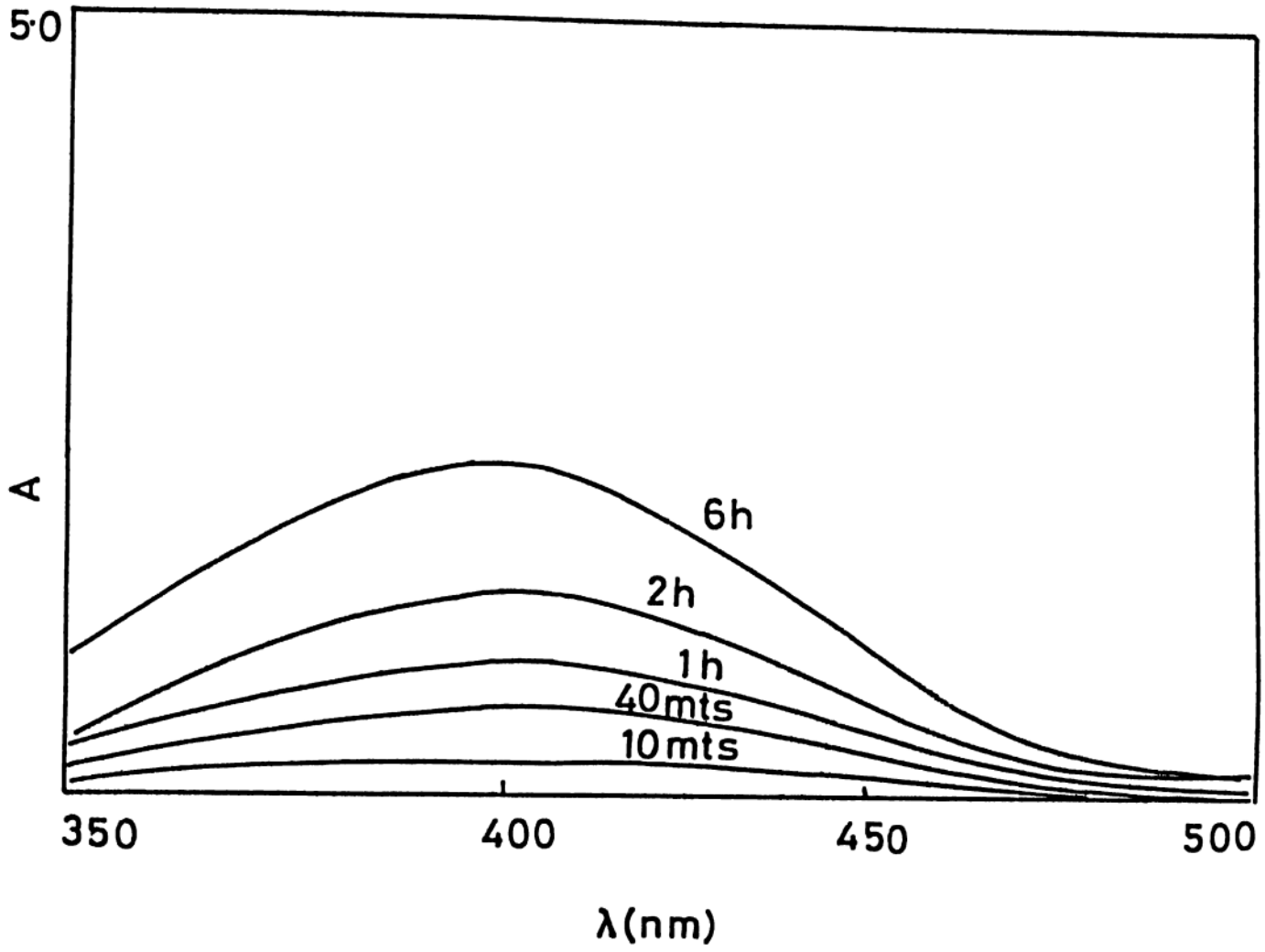


Fig.5.17 Time dependent growth of 3,5-DTBQ catalyzed by cobalt(III) complex 67.

5.5.0 References

1. P.K. Conghlin, S.J. Lippard, *J. Am. Chem. Soc.*, 1984, 106, 2328; Y. Angus, R. Louis, J.P. Gisselbrecht and R. Weiss, *ibid.*, 1984, 106, 93.
2. J.M. Lehn, *Pure and Appl. Chem.*, 1980, 52, 2441; S.M. Nelson, *ibid.*, 1980, 52, 2441; D.E. Fenton, V. Casellato, P.A. Vigato and M. Vidali, *Inorg. Chim. Acta*, 1982, 62, 57.
3. S.E. Groh, *Isr. J. Chem.*, 1976, 15, 277.
4. P. Zanello, S. Tamburini, P.A. Vigato and G.A. Mazzocchin, *Coord. Chem. Rev.*, 1987, 77, 165.
5. D.K. Cabbines and D.W. Margerum, *J. Am. Chem. Soc.*, 1969, 91, 6450; J.D. Lamb, R.M. Izzat, J.J. Christensen and D.J. Eatough, "Coordination chemistry of macrocyclic compounds", ed. G.A. Nelson, Plenum, New York, 1979, p145.
6. J.F. Endicott and B. Durham, "Coordination chemistry of macrocyclic compounds", ed. G.A. Nelson, Plenum, New York, 1979, p343.
7. S.K. Mandal, L.K. Thompson, K. Nag and J.P. Charland, *Inorg. Chem.*, 1987, 26, 1391.
8. S.K. Mandal, L.K. Thampson, K. Nag, J.P. Charland and E.J. Gabe, *Can. J. Chem.*, 1987, 65, 2815.
9. R.P. Das and K. Nag, *Inorg. Chem.*, 1991, 30, 2831.
10. H. Okawa, M. Tadokoro, Y. Aratake, M. Ohba, K.Shindo, M. Mitsumi, M. Koikawa, M. Tomono and D.E. Fenton, *J. Chem. Soc., Dalton Trans.*, 1993, 253.
11. K.K. Nanda, R.P. Das, K.V. Subramanian, P. Paul and K. Nag, *J. Chem. Soc. Dalton Trans.*, 1993, 2515.
12. S.K. Mandal and K. Nag, *J. Org. Chem.*, 1986, 51, 3900.
13. K. Nakamoto, "Infrared spectra of Inorganic and coordination compounds",

3rd Ed., Wiley, New York, 1978.

14. S.K. Mandal, L.K. Thompson, M.J. Newlands and E.J. Gabe, *Inorg. Chem.*, 1989, 28, 3707.

15. R.P. Das, K.K. Nanda, K.V. Subramanian, P.Paul, and K. Nag, *J. Chem. Soc. Dalton Trans.*, 1992, 1253.

16. W.C. Hoyt and G.W. Everett, Jr, *Inorg. Chem.*, 1969, 8, 2013.

17. W.J. Geary, *Coord. Chem. Rev.*, 1971, 7, 81.

18. B.N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, 6, Interscience, 1964.

19. N.H. Pilkington and R. Robson, *Aust. J. Chem.*, 1970, 23, 2225 and references therein.

20. M. Mahapatra, V. Chakravorty and K.C. Dash, *Polyhedron*, 1989, 8, 1509 and references therein.

21. "Comprehensive coordination chemistry", Ed. G. Wilkinson, Pergamon, 1987.

22. M. Suzuki, A. Uehera, H. Oishio, K. Endo, M. Yanaga, S. Kida and K. Saito, *Bull. Chem. Soc. Jpn.*, 1987, 60, 3547.

23. E.W. Aniscough, A.M. Brodie, J.E. Plowman, K.L. Brown, A.W. Addison and A.R. Gainford, *Inorg. Chem.*, 1980, 19, 3655.

24. J.W. Pyrz, A.L. Roe, L.J. Stern and L. Que, Jr, *J. Am. Chem. Soc.*, 1985, 107, 614.

25. A.J. Doward, V. McKee and S.K. Tandon, *Inorg. Chim. Acta*, 1990, 173, 181; H. Sakiyama, K. Tokuyama, Y. Matsumara and H. Okawa, *J. Chem. Soc., Dalton Trans*, 1993, 2329.

26. B.C. Sharma and C.C. Patel, *Ind. J. Chem.*, 1970, 8, 94, 747 and references therein.

CHAPTER - VI

SOME DINUCLEAR COPPER(II), NICKEL(II), COBALT(II) COMPLEXES AND MONONUCLEAR LANTHANIDE COMPLEXES

6.1.0 Abstract

Reaction of the ligand L^7, derived from the condensation of pyridine-2-aldehyde with 3,3'-dimethyl-4,4'-diaminodiphenyl with metal perchlorates in the ratio 1:1 yielded dinuclear copper(II), nickel(II) and cobalt(II) complexes. Spectral, magnetic and catalytic properties of these complexes are presented and discussed.

This chapter also describes the syntheses of some dinuclear lanthanide complexes obtained from ligands (H_2L^8-H_2L^{10}) of 2,6-diformyl-4-methylphenol and diamines 4,4'-diaminodiphenylmethane (H_2L^8) or 4,4'-diaminodiphenylethane (H_2L^9) and 4,4'-diaminodiphenylether (H_2L^{10}). Condensation reactions of 2,6-diformyl-4-methylphenol with the above amines in presence of La^{+3}, Nd^{+3}, Sm^{+3} and Eu^{+3} yielded only mono nuclear complexes. These complexes are characterized by C, H, N elemental analysis and IR spectral data.

Part of the work presented here will appear in *Polyhedron*, 1994, 13, 0000

6.2.0 Dinuclear Copper(II), Nickel(II) and Cobalt(II) complexes

6.2.1 Introduction

Although a large number of bridged dinuclear systems are known, only few biphenyl bridged systems are known.[1,2] One such system is obtained from bis[3,3'-dimethoxy-4,4'-bis(3-methyltriazene-3-oxide)biphenyl)] and copper-copper distance in its dicopper complex is nearly 12 A^0. The geometry at the copper(II) centres is distorted square planar with D_{2d} point group.[3] The torsional angle between the two phenyl planes in each biphenyl bridge is ~ 26^0 which results in an inclination of 70^0 between the coordination planes of the two copper centres. Dinuclear complexes where metal-metal separation is more than 3-4 A^0 are magnetically non interacting unless spin is delocalized through bridging units. Dinuclear complexes of biphenyl bridged ligand systems will behave more like mono nuclear complexes since spin delocalization is limited. Since the expected geometry at the copper(II) centre is distorted from square planar in this type of ligand systems, these complexes can be catalytically active for the oxidation of two electron donors such as 3,5-DTBC or ascorbic acid.

Therefore few dinuclear complexes of Schiff base ligand from 3,3'-dimethyl-4,4'-diaminobiphenyl and pyridine-2-aldehyde are synthesized and investigated. The ligand is designated as L^7.

6.2.2 Results and discussion

These complexes of ligand L^7 are characterized by C, H, N analytical, IR and electronic absorption spectral data and which are collected in Table 6.1. The structure of the complexes is shown in Fig.6.1. IR spectra of the complexes

Table 6.1 Analytical, spectral and magnetic data of the copper(II), nickel(II) and cobalt(II) complexes.

complex	analysis[a] %			IR (cm^{-1})		λ^{b}_{max}(ε)	μ^{c}_{eff}
	C	H	N	C=N	ClO_4^{-1}	nm (M^{-1} cm^{-1})	BM
56	47.26 (47.83)	3.61 (3.40)	8.72 (8.60)	1630	1100 625	740sh 370(6000)	2.02
63	48.51 (48.18)	3.57 (3.42)	8.80 (8.65)	1630	1100 625	580(270) 530sh 350(36750)	2.94
70	49.02 (48.61)	3.21 (3.42)	8.54 (8.64)	1630	1100 625	670(313) 606(285) 597(287) 360(14500)	4.07

a: values in parentheses are calculated; b: measured in DMF; c: measured at room temperature.

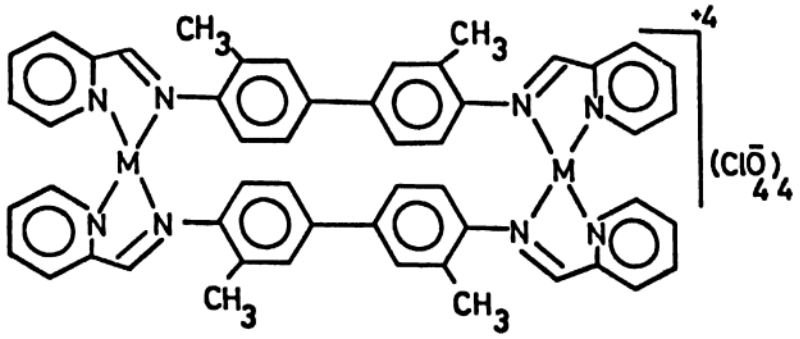


Fig.6.1 General structure of copper(II), nickel(II) and cobalt(II) complexes.

showed bands at 1630 cm^{-1} due to $\nu_{C=N}$ of azomethane groups. The ν_3 absorption of perchlorate ion at 1100 cm^{-1} is sharp. The ν_4 absorption is seen at 625 cm^{-1}. The analytical data support the assigned structure of the complexes.

Electronic spectra and magnetic moments

Magnetic moment values per metal (Table 6.1) at room temperature are close to the corresponding mono nuclear complexes implying the absence of antiferromagnetic interactions between the metal ions. The μ_{eff} value of copper(II) complex is 2.02 BM. The electronic absorption spectrum shows only one band at 740 nm for this complex. Monomeric complexes of pyridine-2-aldemines are essentially planar[4] with electronic bands at 530 and 409 nm and geometry was shown to be sensitive to the nature of substitution 'R'on the azomethine nitrogen. When R is changed from n-propyl to t-butyl, absorption band showed a red shift of *ca.* 3000 cm^{-1}, due to distortion towards tetrahedral geometry. For pseudo tetrahedral pyrrole-2-aldemine complexes the band is observed at 645 nm.[5] Since the R group is replaced by bulkier biphenyl moiety in the present complex, tetrahedral distortion is expected to be more and hence a larger red shift of the absorption band. This is indeed observed. For analogous biphenyl bridged dinuclear complexes with distorted planar geometry, the d-d band is at 900 nm.[1]

The dinuclear nickel(II) complex has μ_{eff} value of 2.94 BM and is comparable to the value of monomeric pseudo tetrahedral complexes of pyrrole-2-aldemine and salicylaldimine complexes.[5] Planar nickel(II) complexes are diamagnetic. Nickel(II) in tetrahedral geometry shows bands at 910 nm and another with splitting in region 830-550 nm. For the present nickel(II) complex, a band at 580 nm was observed besides a shoulder at 1000 nm indicating

the pseudo tetrahedral geometry.

The dinuclear cobalt(II) complex has μ_{eff} per atom of 4.07 BM. Although μ_{eff} values of high spin octahedral and tetrahedral complexes overlap considerably, tetrahedral complexes have generally low μ_{eff} often in the range 4.2-4.5 BM, while octahedral complexes have the value around 4.8 BM. The magnetic moment of present cobalt(II) complex is close to tetrahedral complexes. Pseudo tetrahedral cobalt(II) complexes have a visible band whose component lie in the range 470-625 nm. The other transitions are generally in the IR region.[5-7] The present cobalt(II) complex give bands at 670, 606 and 597 nm suggestive of pseudo tetrahedral geometry.

Catalysis

These complexes are examined for catalytic activity in the oxidation of 3,5-DTBC by molecular oxygen to the quinone, DTBQ. Since the dinuclear complexes non planar geometry, magnetically non interacting which in turn makes them like mono nuclear complexes. Formation of DTBQ is monitored by measuring the growth of absorption band at 400 nm.[8] Fig.6.2 shows the comparison of catalytic activity of these complexes. Cobalt(II) complex show marginal activity even after 24h. Copper(II) complex converts nearly 60% of 3,5-DTBC, while for nickel(II) complex it is 25% after 24h. The order of catalytic efficiency for the complexes is Cu(II) > Ni(II) > Co(II).

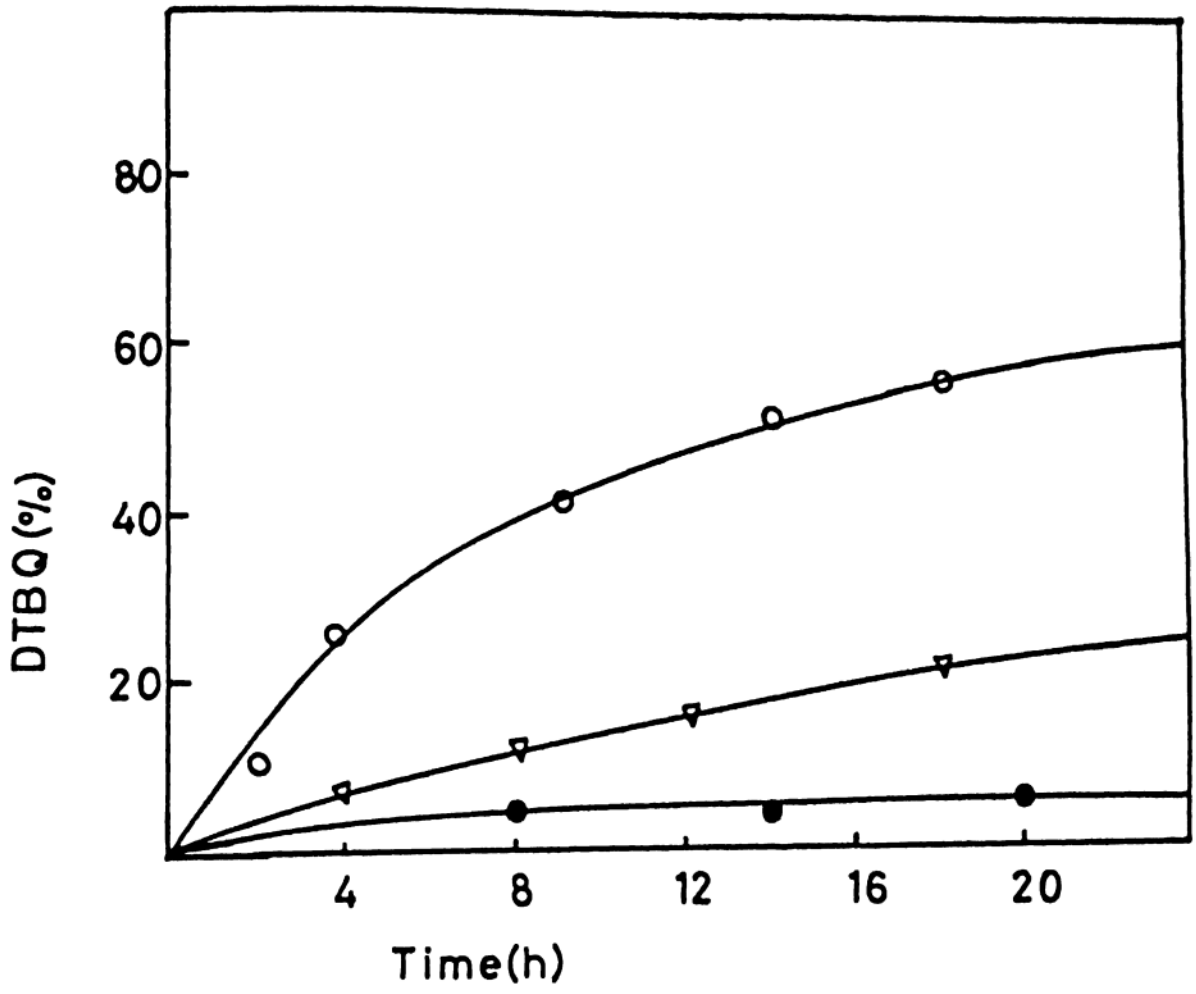


Fig.6.2 Comparison of catalytic activity of copper(II) (o), nickel(II) (∇) and cobalt(II) (●) complexes.

6.3.0 Mononuclear Lanthanide complexes

6.3.1 Introduction

Facile generation of macrocyclic Schiff bases in presence of alkaline earth metal cations led to the use of lanthanide cations also as template agents. Many lanthanide complexes of Schiff bases derived from salicylaldehyde, 2,6-diformyl(diacetyl)pyridine and 2,6-diformyl-4-chlorophenol have been synthesized and studied.[9] Macrocyclic complexes obtained from 2,6-diformyl(diacetyl)pyridines and phenols with short chain diamines are mononuclear.[10-13] However dinuclear complexes were obtained by 2+2 condensation of 2,6-diformyl-4-methyl(chloro)phenol with long chain diamines like triethylenetetraamine in presence of lanthanide ions.[14,15] Dinuclear lanthanide complexes of Schiff base macrocycles, Robson type ligands, discussed in chapter IV and V are rare. It appeared appropriate to investigate the possible formation of dinuclear lanthanide complexes by increasing the chain length of bridging diamine groups in Robson type macrocyclic systems. These results are presented and discussed.

6.3.2 Results and discussion

Preparative details of lanthanide complexes are given section 2.5.6.0. The complexes are red or orange in colour. The preformed ligands H_2L^8-H_2L^{10} are not reactive with the metal ions, even at high dilutions and resulted in poor yields of the complexes. Hence these complexes are prepared insitu in presence of metal ions as template agents.

Analytical and IR spectral data of the complexes are collected in Table 6.2. Analytical data of the complexes are in agreement with the general $Ln(L)NO_3$

Table 6.2 Analytical and IR data of Lanthanide complexes.

complex	analysis[a] %			IR (cm^{-1})	
	C	H	N	C=N	NO_3^{-1}
83	62.11 (62.04)	3.95 (3.99)	8.39 (8.22)	1630	1460, 1260, 1020, 830
84	61.45 (61.54)	4.58 (4.46)	8.01 (7.80)	1630	1450, 1260, 990, 820
85	60.00 (59.00)	3.96 (3.51)	8.18 (8.19)	1630	1450, 1260, 990, 820
86.$3H_2O$	58.12 (58.00)	4.12 (4.39)	7.45 (7.69)	1630	1450, 1260, 1020, 820
87	62.77 (62.43)	4.65 (4.31)	8.21 (7.91)	1630	1450, 1260, 1020, 820
88	59.00 (58.59)	3.61 (3.49)	8.41 (8.14)	1630	1450, 1260, 1030, 830
89	61.51 (61.15)	4.11 (3.93)	8.38 (8.11)	1630	1460, 1260, 990, 820
90.$3H_2O$	58.40 (58.44)	4.40 (4.65)	7.60 (7.41)	1630	1450, 1270, 1020, 820
91	58.35 (58.17)	3.63 (3.46)	8.31 (8.07)	1630	1450, 1250, 1050, 840

Table 6.2. continued...

complex	analysis[a] %			IR (cm^{-1})	
	C	H	N	C=N	NO_3^{-1}
92	61.35 (61.12)	4.21 (3.96)	8.14 (8.10)	1640	1450, 1260, 1020, 820
93	62.10 (61.75)	4.38 (4.25)	7.61 (7.83)	1630	1450, 1260, 1030, 820
94	58.25 (58.06)	3.63 (3.45)	7.83 (8.06)	1630	1450, 1250, 1040, 840

a: values in parentheses are calculated

composition, where Ln = lanthanide ion and L = H_2L^8-H_2L^{10}. IR spectra of the complexes exhibit a band at 1630 cm^{-1} due to $\nu_{C=N}$ of azomethine group. The spectra show bands due to coordinated nitrate ion which gave bands[13] at ca. 1450, 1260, 1050 and 820 cm^{-1}. The proposed structure of the complexes based on analytical and IR data is shown in Fig.6.3. The four azomethine groups and two phenolic oxygens coordinate to the metal ions along with one nitrate ion to give seven coordinate complexes. While 3d group metal ions are known to form dinuclear complexes, formation of mononuclear complexes of lanthanide ions is attributed to the large ionic radii of these elements.

The poor solubility of these complexes in all solvents prevented any further investigation.

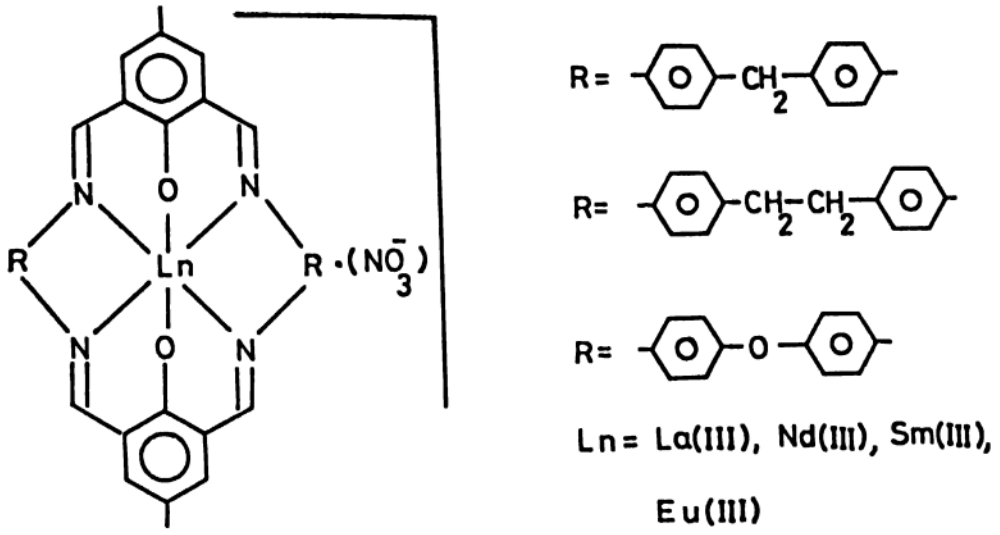


Fig.6.3 General structure of lanthanide complexes.

6.4.0 References

1. P.S. Zacharias and A. Ramachandraiah, *Polyhedron*, 1985, 4, 1013.
2. J.M. Elizabathe and P.S. Zacharias, *Indian J. Chem.*, 1985, 24A, 936.
3. D.J. Hodgson, *Inorg. Chim. Acta*, 1983, 75, 225.
4. F.P. Dwyer and D.D. Mellor, "Chealating agents and metal chelates", Academic press, New York, 1964.
5. R.H. Holm, A. Chakravorthy and L.J. Theriot, *Inorg. Chem.*, 1966, 5, 625.
6. J. Ferguson, *J. Chem. Phys.*, 1960, 32, 528.
7. A.B.P. Lever and S.M. Nelson, *J. Chem. Soc., A*, 1966, 859.
8. W. Flaig, Th. Ploetz and A. Kuller, *Z. Natur forsch, Teil B*, 1955, 10, 668.
9. P.A. Vigato and D.E. Fenton, *Inorg. Chim. Acta*, 1987, 139, 39 and references therein
10. W.R. Paryzek, *ibid.*, 1981, 52, 261.
11. J.D.J. Baker-Dicks, C.J. Gray, F.A. Hart, M.B. Hursthouse and B.C. Schoop, *J. Chem. Soc., Chem. Comm.*, 1979, 774.
12. W.R. Paryzek, *Inorg. Chim. Acta*, 1980, 45, L147.
13. P. Guerrieno, U. Casellato, S. Tamburini, P.A. Vigato and R. Graziani, *ibid.*, 1987, 129, 127.
14. I.A. Kahwa, J. Selbin, Thomas C.Y. Hsieh and R.A. Laine, *ibid.*, 1986, 118, 179.
15. E. Bullita, U. Casellato, P. Guerrioro and P.A. Vigato, *ibid.*, 1987, 139, 59.

SUMMARY

$Cu(DL\text{-}ala)_2$ reacts with formaldehyde and ammonia, at pH 5-6 to give complex 36, while $Cu(L\text{-}ala)_2$ reacts with formaldehyde and ammonia at pH 8.5 to give complex 5. Both these complexes are bridged by pentamethylenediaza group. These reactions involve only the deprotonation of the amino groups. Structure of the complex 6, which can be obtained from the condensation of $Cu(DL\text{-}ala)_2$ and $Cu(L\text{-}ala)_2$ with formaldehyde and ammonia at pH 8.5 and 10 respectively, reveals that these reactions involve deprotonation of both amino and α-methylene groups. These pH dependent reactions reveal that the α-methylene groups of $Cu(DL\text{-}ala)_2$ are more readily deprotonated than those of $Cu(L\text{-}ala)_2$.

The crystal structures of the complexes 8 and 10, obtained from the condensation of $Cu(DL\text{-}ser)_2$ and $Cu(DL\text{-}thr)_2$ respectively, with formaldehyde at pH 4.5, establish the formation of oxazolidine bridged condensation products as proposed by us previously. The copper(II) complexes of DL-serine and DL-threonine undergo condensation with aliphatic aldehydes such as acetaldehyde, propionaldehyde and yield oxazolidine containing products (38-49). Under the same experimental conditions, the copper(II) complexes of L or D-serine and threonine do not undergo similar condensation reactions.

Copper(II) complexes 50, 52, obtained from the Robson type ligands H_2L^1, H_2L^3 and the complexes 53-55, obtained from the reduced ligands H_2L^4-H_2L^6 are square pyramidal. No significant differences are observed in structure when the chelate ring size is varied for both the type of ligands. The first one electron reduction potentials ($E^1_{1/2}$) for the complexes of the saturated ligands (H_2L^4-H_2L^6), 53-55, are shifted to more negative potentials.

Nickel(II) complexes 57-59, obtained from the ligands H_2L^1-H_2L^3 are square planar. Increase of chelate ring does not effect the structure of the

complexes. Chelate ring size and saturation of azomethine groups of the ligands (H_2L^4-H_2L^6) influence the structure of the complexes. The complex of H_2L^4 is square planar (60), while complexes of H_2L^5 and H_2L^6 (61 and 62) are of octahedral geometry.

Both unsaturated and saturated ligands, H_2L^1 and H_2L^4, yielded only cobalt(III) complexes (64 and 67). Increase of chelate ring in these ligands stabilizes the +2 state as is evident from the isolation of stable cobalt(II) complexes (65, 66, 68, 69).

Similarly neither saturation nor ring size could stabilize the iron(II) complexes of H_2L^1-H_2L^6. Only iron(III) complexes are obtained in all cases.

Both types of ligands yielded stable, square pyramidal manganese(II) complexes.

Catalytic experiments showed that cobalt(III) complexes are good catalysts for the oxidation of 3,5-DTBC to 3,5-DTBQ.

Dinuclear complexes of L^7 ligand are magnetically non interacting and are not efficient catalysts.

The lanthanide complexes obtained from the ligands H_2L^8-H_2L^{10} are mono nuclear and seven coordinate.

PUBLICATIONS

1. Stereospecific reactions of copper(II) complexes of serine and threonine with formaldehyde

   N. Arulsamy, Chepuri R.K Rao and P.S. Zacharias

   Transition Metal Chemistry, 1991, 16, 606

2. Differential reactivity pattern for the condensation reactions of copper(II) complexes of DL- and L- amino acids

   Chepuri R.K Rao, N. Arulsamy, P.S. Zacharias and D.J. Hodgson

   J. Chem. Soc., Dalton Trans., 1993, 3581

3. Catalytic oxidation of two electron donors by dinuclear copperr(II), nickel(II) and cobalt(II) complexes and epoxidation of olefins using iron(III) complexes

   Chepuri R.K Rao, H. Aneetha, B. Srinivas, A. Ramachandraiah and P.S. Zacharias

   Polyhedron, 1994, 13, 0000 (in press)

4. Transition metal complexes of Robson type ligands and their reduced analogues: synthesis, spectral, magnetic, electrochemical and catalytic investigations

   Chepuri R.K Rao and P.S. Zacharias

   Manuscript under preparation