CONDENSATION REACTIONS OF COPPER(II) AMINO ACID COMPLEXES AND INVESTIGATIONS ON THEIR PRODUCTS AND RELATED SYSTEMS

A THES IS

SUBMITTED FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

By

N. ARULSAMY

SCHOOL OF CHEMISTRY

UNIVERSITY OF HYDERABAD

HYDERABAD-500 134.

INDIA

DECEMBER 1990

TO

MY PARENTS

CONTENTS

STATEMENT i

CERTIFICATE ii

ACKNOWLEDGEMENTS iii

PREFACE iv

I **INTRODUCTION**

1.1 Biochemical activity of copper 1

1.2 Copper(II)-α-amino acid complexes 2

1.3 Condensation reactions of Cu(II)-amino acid complexes 5

1.4 Copper(II) alicyclic-α-amino acid complexes 11

1.5 Copper(II) complexes of amino acid Schiff bases 11

1.6 Scope of the present investigation 17

1.7 References 20

II **EXPERIMENTAL**

2.1 Chemicals 29

2.2 Preparation of complexes 30

2.3 Physical measurements 36

2.4 References 40

III **CONDENSATION PRODUCTS OF COPPER(II)-α-AMINO ACID COMPLEXES**

3.1 Abstract 41

3.2 Introduction 42

3.3 Experimental 43

3.4 Results and discussion 43

3.5 Conclusions 70

3.6 References 71

IV **STEREOSPECIFIC REACTIONS OF COPPER(II) COMPLEXES OF SERINE AND THREONINE WITH FORMALDEHYDE**

4.1 Abstract 74

4.2 Introduction 75

4.3 Experimental 76

4.4 Results and discussion 76

4.5 Conclusions 89

4.6 References 90

V **COPPER(II)-ALICYCLIC-α-AMINO ACIDATO COMPLEXES AND EFFECT OF ADDITION OF N-DONOR LIGANDS ON THE SPECTRAL AND ELECTRO-CHEMICAL PROPERTIES OF COPPER(II) COMPLEXES**

5.1 Abstract 91

5.2 Introduction 92

5.3 Experimental 93

5.4 Bis(alicyclic-α-amino acidato)copper(II) complexes 95

5.5 Effect of N-donor ligands 105

5.6 Conclusions 115

5.7 References 116

VI **COPPER(II)-N-SALICYLIDENE-AMINO ACIDATO COMPLEXES AND THEIR IMIDAZOLE, PYRAZOLE AND PYRIDINE ADDUCTS**

6.1 Abstract 118

6.2 Introduction 119

6.3 Experimental 120

6.4 Results and discussion 121

6.5 Conclusions 141

6.6 References 142

PUBLICATIONS 144

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 acknowledgement has been made wherever the work described is on the findings of other investigators.

N. Arulsamy

N. ARULSAMY

CERTIFICATE

Certified that the work contained in this thesis entitled, **'CONDENSATION REACTIONS OF COPPER(II)-AMINO ACID COMPLEXES AND INVESTIGATIONS ON THEIR PRODUCTS AND RELATED SYSTEMS'**, has been carried out by Mr. N. Arulsamy under my supervision and the same has not been submitted elsewhere for a degree.

P.S. Zacharias

Hyderabad
November, 1990

P.S. ZACHARIAS
(THESIS SUPERVISOR)

K d Sen

DEAN
SCHOOL OF CHEMISTRY

ACKNOWLEDGEMENTS

With profound respect, I wish to express my deep sense of gratitude to **Professor P.S. Zacharias** for his invaluable guidance and constant encouragement throughout the course of this work.

I am grateful to Professor K.D. Sen, Dean, School of Chemistry for providing all facilities to carry out my work. I wish to thank Dr. M.V. Rajasekharan for helpful discussions. All the faculty members have been helpful, I thank them all.

I take this opportunity to thank Drs. J. Mary Elizabathe, T.G. Narendra Babu and B. Venkateswara Rao for their encouragement and counsel. I extend my heartfelt thanks to my lab-mates, Messers. Md. Athar Masood, B. Srinivas, Ch. Ramakishan Rao and P. Shiva Prakash for having extended their unstinted cooperation. I also thank my dear friends, Bharatam V. Prasad, C. Satheesan Babu, C. Balagopala Krishna, A. Devasagaya Raj, G. Geeta, Y. Suseela, N. Venkatalakshmi, A. Chandrasekhar Reddy, G. Narahari Sastry, P. Balaya, D. Palaniappan and S. Ravi who made my stay here an enjoyable and memorable one.

All the non-teaching staff of the School have been extremely helpful, I thank them all. Messers. V. Bhaskara Rao, K.R.B.V. Prasad and Mrs. G. Vijayalakshmi are a few to mention. I also thank the CIL staff for their assistance in recording various spectra.

Financial assistance from the **UGC** and **CSIR**, New Delhi is gratefully acknowledged.

Finally, I wish to express my profound gratitude to my parents, brothers and sisters for their love and constant encouragement throughout the course of my academic career.

N. ARULSAMY

PREFACE

The Cu(II)-α-amino acid complexes have received tremendous interest due to their biochemical importance. Most of the investigations concern the synthesis and spectral properties of these complexes. Recent investigations focus on their reactivity in the hope of finding simple models of reactivity of some biological systems which contain metal. The enhanced reactivity of the metal coordinated-α-amino acid complexes has also been exploited for the synthesis of various products. The chemical reactions of $Cu(gly)_2$ and $Cu(ala)_2$ are well documented while the Cu(II) complexes of rest of the amino acids have received only less attention. The present investigation deals with the reactions of Cu(II) complexes of L-serine, DL-serine, L-threonine, DL-threonine and ß-alanine with formaldehyde and acetaldehyde under various experimental conditions. New products obtained have been characterized by spectral and analytical methods. The reactions have been found to be stereospecific in some cases. The new products synthesized together with a few known condensation products obtained from $Cu(gly)_2$, $Cu(DL\text{-}ala)_2$ and $Cu(L\text{-}ala)_2$ have been investigated in aqueous media by electronic and ESR spectral methods to determine the order of tetrahedral distortion. Redox behaviour of the complexes has been examined by cyclic and differential pulse voltammetric methods and an analogy between tetrahedral distortion and reversibility of the Cu(II)/Cu(I) process achieved. Similar studies on the Cu(II) complexes of biologically active alicyclic-α-amino acids such as 1-aminocyclopropane-1-carboxylic acid, 1-aminocyclopentane-1-carboxylic acid <u>etc.</u>

reveal that they exhibit similar redox behaviour as the Cu(II) complexes of simple α-amino acids. Change in planar covalency of (N-salicylidene-amino acidato)copper(II) complexes on adduct formation with imidazole, pyrazole and pyridine has also been investigated.

The first chapter briefly reviews the known chemistry of the Cu(II) complexes of α-amino acids and N-salicylidene-amino acid Schiff bases. Cyclic voltammetric investigation on a few Cu(II) complexes of α-amino acids and closely related systems has shown that these complexes undergo close to reversible one-electron Cu(II)/Cu(I) redox process. Generally, reversibility of the Cu(II)/Cu(I) redox process depends on the geometry of the complexes since Cu(I) species are stable in tetrahedral or pseudo-tetrahedral geometry. To study the influence of change in geometry on their redox behaviour, it was decided to synthesize and investigate Cu(II) complexes of different degrees of tetrahedral distortion. Since condensation reactions of Cu(II)-amino acids with various aldehydes have been used to synthesize various complexes, available data on these reactions are outlined. This chapter also presents scope of the present investigation.

In Chapter II experimental procedures pertaining to the synthesis of various Cu(II) complexes are presented. The condensation products and (ethene-bridged-α-amino acidato)copper(II) complexes were prepared by known general procedures. The new complexes were characterized by various spectral and analytical methods. The Cu(II) complexes of a few alicyclic-α-amino acids, viz., 1-aminocyclopropane-1-carboxylic acid, 1-aminocyclobutane-

1-carboxylic acid, 1-aminocyclopentane-1-carboxylic acid, 1-aminocyclohexane-1-carboxylic acid and 1-aminocycloheptane-1-carboxylic acid have been prepared by known methods. The Cu(II) complexes of N-salicylidene-amino acid Schiff bases derived from salicylaldehyde and amino acids viz., glycine, L-alanine, L-serine, L-threonine and ß-alanine and their imidazole, pyrazole and pyridine adducts were prepared by general procedures. Some of the adducts are new and were characterized by spectral and analytical methods. This chapter also describes various techniques employed in the investigation.

Chapter III describes structural elucidation for the new complexes and spectral and electrochemical properties of the condensation products. The complexes are classified as (i) unbridged, those which have CuL_2 composition and (ii) bridged, those which have CuL composition, their amino acid units being bridged by an ethene, dimethyleneether or pentamethylenediaza group. At dissolution pH the complexes exhibit the d-d transition at ca. 620 nm and ESR parameters $g_{iso} \simeq 2.120$ and $A_{iso} \simeq 70$ G commensurate with tetragonally distorted geometry. On the basis of the d-d band position and ESR data the order of increasing planarity is obtained. The unbridged complexes on lowering pH exhibit shift of the d-d band to higher wavelengths (720 nm) and change in ESR parameters, increase in g_{iso} (to 2.150) and decrease in A_{iso} (to 55 G), indicating formation of protonated species such as $[CuL]^+$. For the unbridged complexes formation of such protonated species could not be detected by the spectral studies.

Cyclic voltammograms of the unbridged complexes are constituted of two redox couples C,D and A,B. The major observations made are: (i) during the first cathodic scan a reduction peak (C) at ca. -0.25 V versus SCE appears and on reverse scan an oxidation peak (D) at ca. -0.19 V appears along with another oxidation peak (B) at 0.03 V (ii) from the second scan onwards a new reduction peak (A) at -0.01 V appears (iii) when the scan is reversed before the appearance of peak C the A-B peaks do not appear (iv) if the potential is held at a potential well past the peak C potential and scanned back heights of A-B peaks increase while no change is observed for the C-D peaks (v) peak separation values for the C-D couple (ΔE_p (C-D)) are ca. 60 mV and $-i_c/i_a$ values ca. 1. Based on these experimental observations an electrode mechanism is suggested to explain the redox behaviour of these complexes. For these complexes the Cu(II)/Cu(I) process is reversible and the Cu(I) intermediate species is stable in cyclic voltammetric time scale. The observation of peaks A-B indicates that the Cu(I) species undergoes partial decomposition/disproportionation also. The bridged complexes having ethylene or dimethyleneether bridging unit also exhibit similar electrochemical behaviour as that of the unbridged complexes while the complexes having rigid pentamethylenediaza bridging unit exhibit absence of peak D and shift of peak C to more negative potentials (ca. -0.52 V). This is explained to arise from the more planar geometry of the complexes and the rigid ligand system. One of the complexes, (N,N'-1,2-ethandiyl)bis(glycinato)copper(II), exhibits appearance of another redox couple (C',D') at a more negative potential (-0.39 V) along with the A-B and C-D couples, which is attributed

to presence of weak intermolecular interaction between the Cu(II) centres.

In Chapter IV stereospecificity exhibited by some of the reactions of the Cu(II)-α-amino acids is discussed. It is known that Cu(II) complexes of L-alanine and DL-alanine undergo condensation reaction with formaldehyde in the presence of ammonia yielding different products. Our investigations show that the Cu(II) complexes of L-serine, DL-serine, L-threonine and DL-threonine undergo stereospecific reactions with formaldehyde and acetaldehyde. Reaction of Cu(II) complex of ß-alanine with formaldehyde and ammonia is also included. The new products obtained have been characterized by IR, CD and analytical methods.

As a natural extension of the investigation on the Cu(II) complexes of α-amino acids, the redox behaviour of Cu(II) complexes of some alicyclic-α-amino acids is also studied. The results are presented and discussed in Chapter V. Biosynthesis of plant growth hormone, ethylene, has been shown to proceed through 1-aminocyclopropane-1-carboxylic acid, where copper plays an important role. A few other alicyclic-α-amino acids are also shown to be biologically active. While preparation and some spectral data are reported for the Cu(II) complexes of these alicyclic-α-amino acids, their redox behaviour has not been investigated. Our investigation shows that their redox behaviour is similar to that of Cu(II) complexes of α-amino acids such as glycine, L-alanine etc. The Cu(I) species involved in the redox process is stable in cyclic voltammetric time scale. Chapter V also describes various studies on the interaction of these Cu(II)

complexes and some of the condensation products discussed in Chapter III with different N-donor ligands. Spectral and electrochemical data of the complexes in the presence of ammonia reveal characteristic changes of axial coordination of ammonia for all the complexes except for the pentamethylenediaza group containing complexes. Addition of other N-donor ligands, *viz.*, imidazole, pyrazole and pyridine does not effect any such changes.

In Chapter VI spectral and electrochemical investigations on some (N-salicylidene-amino acidato)copper(II) complexes, Cu(sal-aa)(H_2O), where aa = glycine, L-alanine, L-serine, L-threonine or ß-alanine and their imidazole, pyrazole and pyridine adducts, Cu(sal-aa)L, are presented and discussed. Electronic spectra reveal a shift of 10-20 nm of d-d transition band towards lower wavelengths for the adducts and ESR data obtained at 120 K exhibit decrease in $g_{\parallel}$ and $A_{\parallel}$ values suggesting increased planar covalency on adduct formation. Cyclic voltammetric studies clearly demonstrate the structural differences between the Cu(sal-aa)(H_2O) complexes and the adducts. The parent complexes exhibit reversible Cu(II)/Cu(I) redox process similar to the unbridged condensation products at a slightly more negative potential (-0.36 V) while the imidazole and pyrazole adducts exhibit irreversible Cu(II)/Cu(I) process, irreversibility of the redox process arising from the more planar geometry of these adducts. However, the pyridine adducts exhibit reversible Cu(II)/Cu(I) redox process which is attributed to the higher π-acceptor ability of pyridine. At lower pHs formation of protonated species is evident from CV profiles obtained for the parent complexes and the adducts.

CHAPTER I

INTRODUCTION

1.1 Biochemical activity of copper

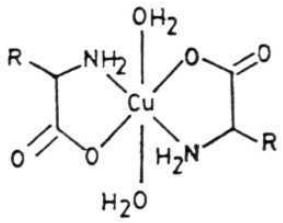
The general involvement of copper in biological systems is well documented.[1-9] Role of copper(II) ions in the biological systems was recognized in an early stage because of the isolation of copper proteins. The function of copper in biological systems is primarily associated with the reduction of oxygen to water with the transfer of oxygen to a substrate. More positive Cu(II)/Cu(I) redox potentials at neutral pH indicating a more effective stabilization of Cu(I) vs. Cu(II), characteristic visible absorption spectra and ESR behaviour differentiate biological copper species from the copper(II) complexes of synthetic origin.[10] The challenge to develop model systems has generated much activity in this field[11-14] and these studies have yielded copper(II) complexes with very interesting properties.[14] Often

it has been found that the spectral properties of the complexes are reflected in their redox behaviour, i.e. the spectral and redox properties are interrelated.[15]

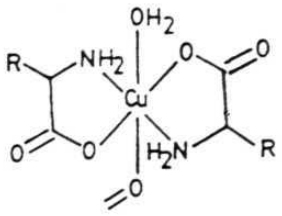
The low molecular weight Cu(II)-α-amino acidato complexes are considered to be biologically active since they have been found to involve in the transport of Cu(II) ions between blood and tissues[16]. Several ternary histidine Cu(II) complexes have been detected in human serum along with $Cu(L\text{-}his)_2$.[17] These observations acted as catalysts for the investigation of the properties of Cu(II)-α-amino acids and their derivatives. The chemistry of Cu(II) complexes of α-amino acids has developed not only from the inorganic point of view but also because of possible biological interest.

1.2 Copper(II)-α-amino acid complexes

Bidentate α-amino acids coordinate to Cu(II) through the amino nitrogen and the carboxylic oxygen donor atoms. Depending upon the pH of the medium, they form mainly two types of complexes, $[CuL]^+$ in the pH range 4.5-5.8 and CuL_2 in the pH range 6.2-7.5.[18-20] At neutral pH the complexes have square-planar arrangement of the donor atoms around the metal ion with the metal ion slightly disposed towards the axial positions. Few complexes have two water molecules occupying the axial coordination sites (I) and few have one water molecule and one carboxylic oxygen of neighbouring complex molecule at their axial positions (II). The nature of the donor oxygen atoms at the apical positions has been found to have little effect on the properties of the complexes.[21]



I



II

1.2.1 Spectral properties

Bis(α-amino acidato)copper(II) complexes exhibit the d-d transition in their electronic spectra at ca. 620 nm in aqueous media at neutral pH. The absorption band is weak with ε_{max} value in the range 50-100 $M^{-1}cm^{-1}$. On lowering pH, the d-d band shifts to higher wavelengths (ca. 720 nm) and has been ascribed to formation of protonated species such as $[CuL_2H]^+$, $[CuL]^+$, $[CuLH]^{2+}$ etc.,[18] where LH = α-amino acid. The Cu(II)-α-amino acid complexes have also been studied by CD spectroscopy[21-23] and are shown to exhibit two CD extrema, one in the 590-620 nm region and another at ca. 700 nm. Many Cu(II)-L-amino acidato complexes exhibit positive CD band at 700 nm (I) and a negative CD band in the 620-590 nm region (II); the Cu(II) complexes of imino acids L-proline and L-hydroxy proline exhibit opposite Cotton effect i.e. negative sign for the band I and positive sign for the band II. This has been attributed to the second asymmetric centre, imino nitrogen, produced in the ligand as a result of chelation.[23] In addition to these two CD extrema, another extrema has also been observed at ca. 730 nm. The assignment of the three possible transitions is in the following order of increasing energy:

$$B_{1g} \longrightarrow A_{1g} < B_{1g} \longrightarrow B_{2g} < B_{1g} \longrightarrow E_g$$

A great deal of literature is available on the ESR data of the Cu(II)-α-amino acid complexes.[19,25-32] Many workers have studied the ESR spectra as dilute powders,[28] glasses, and frozen solutions.[25-27] The nitrogen superhyperfine splitting is useful to establish the number of nitrogen atoms coordinated to the Cu(II) ion. Recently, it has also been shown that mono and bis-(α-amino acidato)copper(II) complexes can be readily distinguished on the basis of their g and hyperfine A values.[19] The X-band and K-band ESR spectra of the trans-planar Cu(II) complexes of α-amino acids, in polycrystalline state at room temperature, found to exhibit a variety of ESR line-shapes. However, the frozen glassy spectra are similar and represent typical axial spectra and have been fitted with $d_{x^2-y^2}$ ground state. The ESR parameters indicate a normal tetragonal geometry for the complexes.[25] ESR spectroscopy has also been used to investigate the change in copper-ligand bond strength; for example, decrease of g values characterizes elongation of axial band and shortening of the planar Cu-O bond.[32] Correlation among the g values, the d-d band energies, bonding parameter and geometrical configuration of the coordinating atoms for several Cu(II)-α-amino acid complexes has been obtained.[25-32]

1.2.2 Electrochemical properties

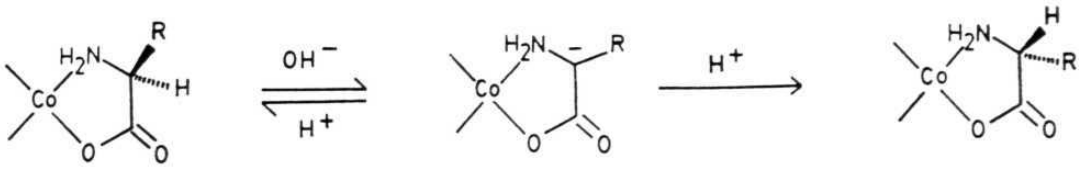
In comparison to the bulk of spectral investigations reported so far, the Cu(II) complexes of α-amino acids have received only less attention with respect to their redox properties.[33] Electrochemical reduction of these complexes leads to the formation of the corresponding Cu(I) species. A fraction of the Cu(I) species

could be reoxidized to Cu(II)-complex electrochemically while another fraction undergoes chemical decomposition/disproportionation generating Cu(0) at the hanging mercury drop electrode. The Cu(0) species produced undergoes two-electron oxidation to Cu(II)(aq) during the reverse scan which subsequently gets reduced at a less negative potential during the second scan. Thus the CV profile is constituted of two redox couples, one corresponding to the close to reversible Cu(II)/Cu(I) process at ca. -0.25 V vs. SCE and another at -0.01 V corresponding to Cu(II)(aq)/Cu(0)(Hg) process. Controlled potential coulometry (CPC) experiments over mercury pool towards the determination of number of electrons involved in the redox process have been unsuccessful. The CPC experiments yield coulombs which correspond to n = 2. This value does not agree with the other experimental evidences given for the involvement of Cu(I) species in the redox process. The apparent discrepancy arises because of the reason that under the continuous influence of cathodic potential the Cu(I) species generated by the first electron-transfer undergoes chemical decomposition/disproportionation to Cu(0)(Hg). Hence the overall process involves two electrons.

1.3 Condensation reactions of Cu(II)-amino acid complexes

Coordination of α-amino acids to metal ions increases the nucleophilic reactivity at the α-carbon atom through bond polarization by the metal ion.[34,35] The most obvious illustration of this effect is that, most (not all) metal ions increase the rate of racemization of α-amino acids. For example,

with Co(III) complexes, it has been demonstrated by NMR spectroscopy that the rate of racemization is similar to H-D exchange rate at the α-carbon atom (equation 1.1).



(1.1)

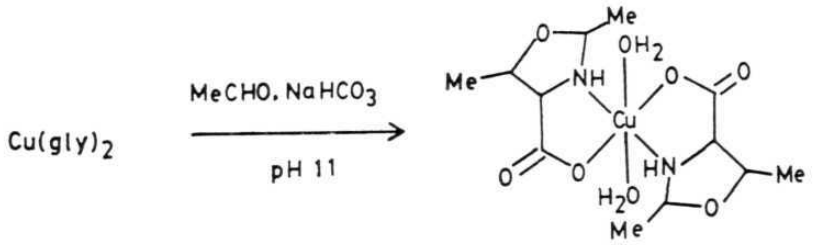
Co(III), Cr(III), Cu(II), Pd(II) and Pt(II) ions accelerate the racemization rates of α-amino acids. The mechanism is not always as simple as that outlined above (equation 1.1). This effect could also be considered as a simple model of the action of metal ions in some biological transformations of amino acids.[36]

During the last three decades a great deal of literature has appeared concerning the reactions of metal coordinated α-amino acids[37-49] or small peptides[50,51] with various aldehydes. In these reactions generally the simple bis(α-amino acidato)metal complexes are used. Reactions of chiral cobalt(III) complexes such as Λ-(+)$[Co(en)_2(gly)]^{2+}$ have been found to yield high asymmetric products with low overall yield.[52,53] The use of an α-amino acid-Schiff base metal complex instead of bis(α-amino acidato)metal complexes seems to increase the nucleophilicity at the amino acid α-carbon atom and prevents N-alkylation.[45,54-56]

The metal assisted synthesis of DL-threonine from glycine was one of the first such reactions reported three decades ago.[37] The reaction which is base catalyzed, proceeds under far milder conditions than for free glycine. Similar metal assisted reac-

tions are also known for ligands such as amino alcohols and amino thioethers.[57,58] A few metal-assisted condensation reactions of α-amino acids are discussed below.

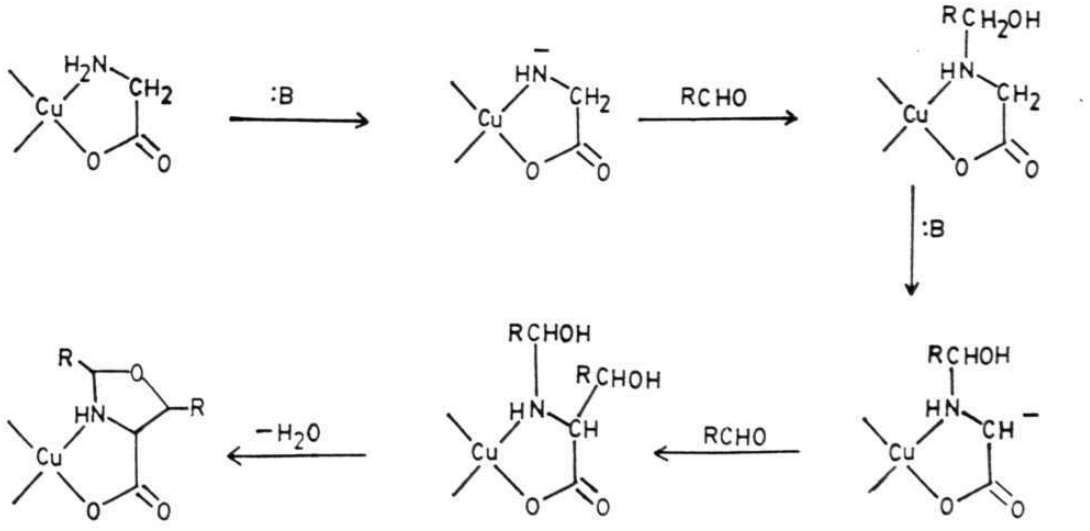
The reaction of $Cu(gly)_2$ with acetaldehyde under basic conditions (sodium bicarbonate, pH 11) yields, bis(2,5-dimethyloxazolidine-4-carboxylato)copper(II) dihydrate, **1** (equation 1.2).[44]



(1.2)

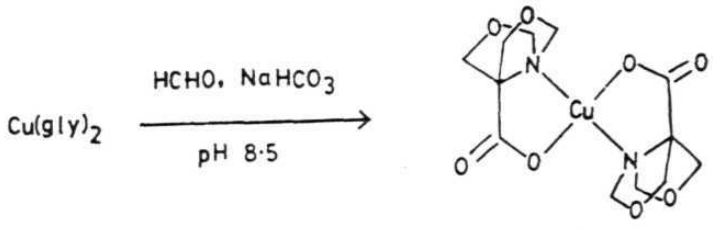
1

The complex on decomposition in an acid medium by H_2S releases DL-threonine in the aqueous solution, copper being recovered in the form of insoluble CuS. Comparative studies show that formaldehyde is unable to form serine from its reaction with $Cu(gly)_2$, in the conditions in which acetaldehyde gives DL-threonine, in <u>ca.</u> 40% yield.[45] The reaction is similar to aldol condensation and has been explained by the mechanism shown in Scheme 1.1.



Scheme 1.1

Condensation of $Cu(gly)_2$ with formaldehyde in presence of sodium bicarbonate at pH 8.5 yields bis(dihydro-1H,3H,5H-oxazolo[3,4-c]-oxazole-7a-carboxylato)copper(II), **2**.[46] The reaction has been suggested to follow the same mechanism (Scheme 1.1). However after the formation of the expected product, bis(oxazolidine-4-carboxylato)copper(II) (equation 1.3) further condensation takes place (which is absent in the case of acetaldehyde condensation probably due to steric hindrance) resulting the formation of complex **2** (equation 1.3).[46]



2

(1.3)

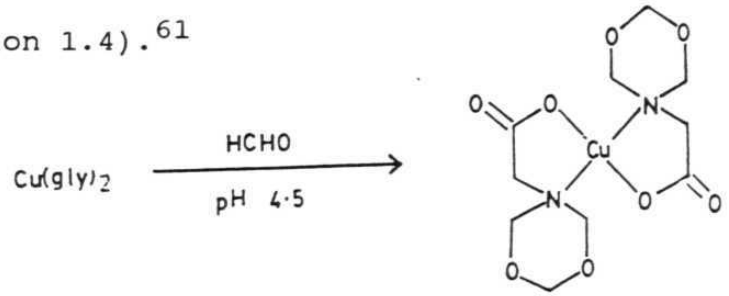
Condensation between aldehydes and α-amino acids in the absence of metal ions, with the acid and amino groups protected is known to occur very slowly, since the beginning of this century. The coordination not only protects the groups but also activates the α-methylene group that, in basic conditions, most easily forms carbanions as is seen in equations 1.2 and 1.3. This activation has been related to the charge of the complex species. For example, the condensation between the metal coordinated glycine and acetaldehyde has been shown[59] to follow the decreasing order of reactivity:

$[Co(en)_2(gly)]^{2+} > Co(gly)_3 > [Co(gly)_2(C_2O_4)]^-$

The reactivity order also changes with various metal ions as shown below:

$Cu(gly)_2 > Co(gly)_3 > Ni(gly)_2 > Zn(gly)_2$

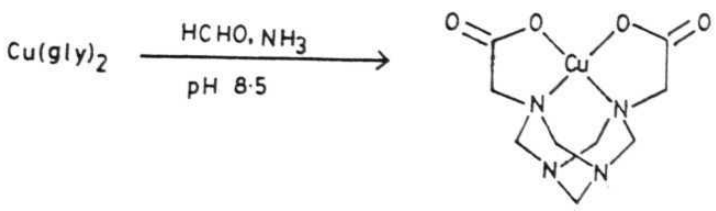
Activation of the amino protons more than the α-methylene group of metal coordinated glycine has been established recently.[60] Condensation of $Cu(gly)_2$ with formaldehyde at acidic pH (4.5) has been reported to yield, [bis(N-1,3-dioxa-5-azacyclohexyl)acetato]zinc(II).[60] Co(II), Ni(II) and Cu(II) complexes of glycine also undergo similar condensation reaction with formaldehyde at pH 4.5 yielding the corresponding metal complexes (equation 1.4).[61]



(1.4)

3

Another reaction of $Ni(gly)_2$ is also known, where the amino group alone reacts with formaldehyde even at a basic condition (pH 8.5) in presence of ammonia.[62] The product has been identified to be [3N,7N-(1,3,5,7-tetraazabicyclo[3.3.1]-nonyl diacetato)]nickel(II). It has also been shown that under the same experimental conditions $Cu(gly)_2$ also undergoes similar condensation reaction forming the corresponding Cu(II) complex, **4** as shown in equation 1.5.

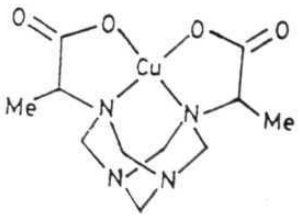


(1.5)

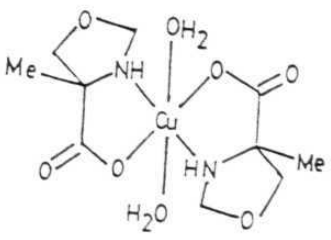
4

This reaction is interesting due to two important factors: (i) the non-involvement of α-methylene group in the condensation, though the reaction was carried out at pH 8.5 (ii) the two glycine units in the resultant complex (as explained for the nickel complex[62]) are <u>cis</u> to each other implying that they must have undergone conversion from the initial <u>trans</u> $Ni(gly)_2$.[63]

It is clear from the foregoing discussion that most of these reactions involve various transition metal complexes of glycine. This is due to the fact that mostly these reactions have been carried out in order to develop simple methods to synthesize substituted α-amino acids preferably in an optically active form, from glycine. The investigations on similar condensation reactions of Cu(II) complexes of the other α-amino acids are also significant, for these reactions seem to exhibit stereospecificity. So far, only α-alanine has been investigated in this respect.[64,65] It has been reported that, $Cu(L\text{-ala})_2$ undergoes condensation reaction with formaldehyde at pH 8.5 in presence of ammonia, to yield [3N,7N-(1,3,5,7-tetraazabicyclo-[3.3.1]nonyl)-dipropionato]copper(II), **5**, while $Cu(DL\text{-ala})_2$ under the same experimental conditions yields, bis(4-methyloxazo-lidine-4'-carboxylato)-copper(II) dihydrate, **6**.



5



6

It may be noted that formation of **5** is similar to the condensation reaction of $Cu(gly)_2$ with formaldehyde and ammonia at pH 8.5 (equation 1.5). Very little is known about the condensation reactions of most of the remaining α-amino acidato metal complexes. A few of the condensation products have been characterized by X-ray crystallography and their geometry established. However, no further investigations such as electronic spectra, ESR and electrochemical data in aqueous solution are reported.

1.4 Copper(II) alicyclic-α-amino acid complexes

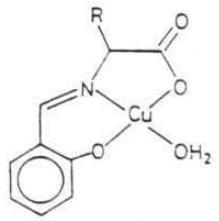
Copper(II) complexes of alicyclic-α-amino acids such as, 1-aminocyclopropane-1-carboxylic acid, 1-aminocyclobutane-1-carboxylic acid etc. have been found to be complexes of uniformly varying geometry;[66] the change in geometry from complex to complex arising from the increasing ring size at the α-carbon of the amino acid units. Recent investigations[27,32] on bis(1-aminocyclopentane-1-carboxylato)copper(II) and a few other trans bis (α-amino acidato) complexes reveal that the substitutions at the α-carbon have definite effect on the geometry and hence the properties of the complexes. These complexes are shown to be aquated in solution with two water molecules in the axial sites. Electronic spectral and ESR data are comparable to the Cu(II)-α-amino acid complexes.

1.5 Copper(II) complexes of amino acid Schiff bases

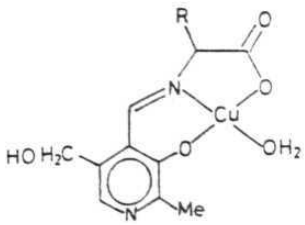
1.5.1 Reactivity

Condensation of glycine has been recognized to be the best way to synthesize ß-hydroxy-α-amino acids. However, this reaction

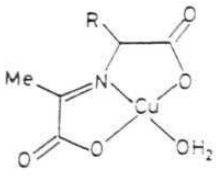
is not facile due to the low acidity of the methylene group. The use of transition metal complexes of Schiff bases derived from glycine and salicylaldehyde or pyruvic acid[42,53,54] instead of free glycine or bis(glycinato)metal complexes improves the yields and widens the scope of the reaction. The Schiff base complexes in many instances[67,68] undergo condensation reactions yielding optically active products with high enantiomeric excess (ee). For example, threonylglycine[68] and threonine[69-72] could be synthesized with an ee of 95% by condensation of Cu(II) complexes of chiral Schiff bases of glycylglycine and glycine respectively with acetaldehyde. Optically pure α-alkyl-α-amino acids could also be prepared <u>via</u> alkylation of Ni(II) complexes of Schiff bases derived from DL-alanine and (S)-2-N-(N'-benzylprolyl)amino benzaldehyde.[72] The transition metal complexes of Schiff bases of α-amino acids and salicylaldehyde (III), pyridoxal (IV), pyruvic acid (V), and (1R)-3-(hydroxymethylene)camphor (VI) are important from the bioinorgonic point of view, since the complexes have been shown to be good model systems for the catalytic intermediates in the reactions of pyridoxal phosphate with α-amino acids.[73-77]



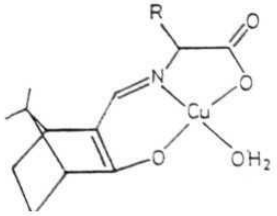
III



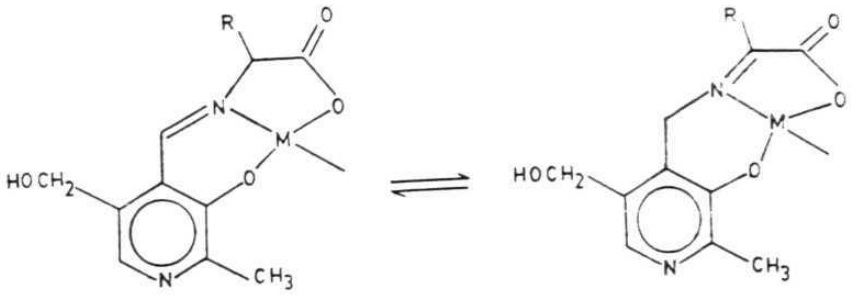
IV



V



The Schiff base complex IV exhibits tautomerism as shown by the equation 1.6.



(1.6)

Both transamination and racemization require loss of a proton attached to the α-carbon of the amino acid, which must be very reactive in these structures.[73] In fact, this property has been exploited to synthesize various ß-hydroxy-α-amino acids.[67-72]

1.5.2 Spectral and redox properties

Several Cu(II) complexes of α-amino acid Schiff bases have been characterized by X-ray crystallography.[78-82] The X-ray analysis revealed that the complexes coordinate via phenolic oxygen, one carboxylic oxygen and the imino nitrogen with a water molecule completing near square-planar geometry of Cu(II) ion.

Many of the model studies of the metal complexes of α-amino acid Schiff bases have been upon the spectroscopic and mechanistic properties of the complexes. Recently, enhancement of reactivity of α-methylene group has been related to its correct stereochemical positioning within the molecule.[83-86] Due to the importance of stereochemical factors that control the correct positioning of the groups to be labilized, considerable attention has been paid to the stereochemistry of the model

systems, which mimic the biological reaction types.[82,86-89] Detailed conformational studies on the Cu(II) complexes are available in literature and are briefly discussed here along with the UV-Vis and ESR spectral data.

The UV absorption spectra of Cu(sal-aa)(H_2O) complexes, where sal-aa = N-salicylidene-α-amino acidato anion, exhibit an intense band at ca. 375 nm and has been attributed to $\pi \rightarrow \pi^*$ transition originating mainly within the azomethine chromophore. The intense bands occurring at still higher energies, viz., 270 and 225 nm, have been assigned to be associated with benzene ring $\pi \rightarrow \pi^*$ transitions. Shoulders were observed in the spectra of most of the chelates.[86] The UV spectra of Cu(pyv-aa)(H_2O) complexes, where pyv-aa = N-pyruvylidene-α-amino acidato anion, are found to exhibit only a broad band centered near 220 nm, with badly resolved shoulders on its low energy side. The UV spectral data are available for few other Cu(II)-Schiff base complexes also.[86-89]

For Cu(sal-aa)(H_2O) complexes the d-d transitions were observed in the wavelength region 680-600 nm in solution, which has been ascribed to the square-planar or weakly distorted tetragonal geometry.[89-96] The d-d band was shifted significantly to higher energy regions whenever the α-amino acid unit had a third donor group (e.g. histidine), which can interact axially.[89,96]

CD spectra are more informative than the electronic spectra. Several Cu(II) and Zn(II) complexes of Schiff bases of aldehydes

such as salicylaldehyde, pyridoxal, pyruvic acid *etc.* and α-amino acids have been investigated by CD spectroscopy recently.[86,89,97] In general the complexes derived from salicylaldehyde and pyridoxal in methanol exhibit three CD extrema at 360, 270 and 230 nm corresponding to the maxima of the electronic absorption. Similarity in the CD spectra of various Schiff base complexes has been interpreted to be due to common conformation adopted by the coordinated ligands.[98] The Cotton effect associated with the azomethine and the high energy benzenoid band are related to the sign of visible band observed between 680 and 600 nm. This is always consignate with the azomethine band and dissignate with the 230 nm band. The visible CD spectra of Cu(II) complexes of L-amino acid Schiff bases in methanol or pyridine exhibit two or three resolved bands attributable to d-d transitions, similar to the simple Cu(II)-α-amino acidato complexes,[20,98-102] at a wavelength higher than 700 nm (positive), 680-600 nm (negative) and at a wavelength lower than 600 nm (positive). In several instances the band at the lower energy side of 700 nm was absent and has been explained to occur at lower energy beyond the instrumental range (800 nm), or more likely, be buried under the more intense oppositely signed band in the 680-600 nm region.[86] The Cu(II) complexes derived from pyruvylidene Schiff bases show significant dissimilarities to those of the salicylidene and pyridoxylidene series. CD spectral data available in literature[89,98] reveal that histidine containing complexes exhibit a striking tendency to bind Cu(II). For example, the CD spectra of Cu(pyv-L-his) in water displays dominant Cotton effects of opposite sign pattern of that of Cu(pyv-L-aa)

complexes, where the amino acid is with non polar side chain. The unique behaviour of Cu(pyv-L-his) has been inferred to be due to the interaction of the imidazole group with the central Cu(II) ion, leading to change in conformation.[89]

ESR data of the Cu(II) complexes of these Schiff bases are also available in literature.[86,88,89,94,96,103,104] The frozen glassy ESR spectra in aqueous methanol for most of these complexes could be fitted for $g_{\parallel} > g_{\perp} > 2.0$, showing the pattern typical for tetragonal symmetry.[86,89,96] The general characteristics of the spectra are as follows: (i) the frozen glassy ESR spectra of the complexes in methanol or water are axial with an extra high field absorption (ii) the ESR parameters show solvent dependence, indicative of coordination of donor molecules to the metal centres; the $g_{\parallel}$ and $g_{\perp}$ values obtained from pyridine solutions are smaller and $A_{\parallel}$ values larger (iii) in several instances the spectra exhibit superhyperfine interaction with the ligand (nitrogen) nuclei, which gives useful information of the number of nitrogen atoms involved in the donor set (iv) in some cases complex pattern of lines results from superposition of copper hyperfine and ligand superhyperfine splittings.

Using the ESR and CD data, molecular orbital coefficients, α, β_1 and β, which characterize the planar σ and π bonding and the out-of-plane π-bonding, respectively have been calculated for these Cu(II) complexes. The magnitudes of molecular orbital coefficients enable one to refine the stereochemical description of these Cu(II) complexes in terms of donor sets, ligand field symmetry and bonding character.

The (N-salicylidene-amino acidato)copper(II) complexes have a water molecule at the fourth equatorial site as has been mentioned already. Recently[105] it has been shown that, the change in ESR parameters g_{iso}, A_{iso}, $g_{\parallel}$ and $A_{\parallel}$ observed for the Cu(sal-aa)(H_2O) complexes in presence of pyridine is due to the formation of pyridine adducts. Though the metal complexes of amino acid-Schiff bases have been extensively studied, no detailed work on their redox properties is reported so far.

1.6 Scope of the present investigation

Electrochemical investigations on Cu(II)-amino acidato complexes have shown that electroreduction of these complexes proceeds <u>via</u> Cu(I) intermediate complex species. In general, reversibility of the Cu(II)/Cu(I) process depends on the stability of the intermediate Cu(I) species. The Cu(I) species is stable only in tetrahedral or pseudo-tetrahedral environments. To investigate the effect of structural variation on the reversibility of the Cu(II)/Cu(I) redox process, it was planned to synthesize Cu(II) complexes of varying geometry. It is known that $Cu(gly)_2$ undergoes condensation reactions with formaldehyde and acetaldehyde under various experimental conditions yielding products with the same CuN_2O_2 chromophore. However the products possess different degrees of tetragonal distortion. Towards synthesizing more number of such complexes similar condensation reactions of Cu(II) complexes of a few other amino acids are carried out. In this way it became possible to synthesize a variety of structurally different complexes. They are characterized and their electrochemical behaviour examined.

During the course of our investigation on the condensation reactions, it has been observed that some of these reactions are stereospecific. Similar behaviour has been reported only for Cu(II) complexes of L-alanine and DL-alanine previously.[61,65] In the present investigation condensation reactions of Cu(II) complexes of L-serine, DL-serine, L-threonine and DL-threonine with formaldehyde and acetaldehyde are included. CD spectroscopy has been used to follow the reactions.

While the Cu(II) complexes of α-amino acids such as glycine, alanine etc., have been investigated extensively only limited data is available on the Cu(II) complexes of alicyclic-α-amino acids. As a part of our investigation on the redox properties of Cu(II) complexes of α-amino acids and related systems it became a natural extension to study the spectral and electrochemical properties of the Cu(II) complexes of some alicyclic-α-amino acids.

The Cu(II) complexes of N-salicylidene-α-amino acids have been the subject of various spectral investigations because of their usefulness as model systems to study the enzymatic reactions of pyridoxal phosphate and their ability to catalyze transamination and racemization. However, their redox behaviour has not yet been reported. In conformity with our research plan, it appeared logical to investigate the redox behaviour of these complexes. For this purpose, Cu(II) complexes of Schiff bases of number of amino acids have been prepared and their redox characteristics examined. It is known that these complexes form

adducts with N-donor bases such as imidazole, pyrazole and pyridine.[105,106] The adducts show differences in their electronic and ESR parameters revealing change in geometry, nature of coordination etc. from their parent complexes. We also planned to investigate the adducts electrochemically in order to elucidate their redox mechanism and more fully understand the structural changes accompanying adduct formation.

1.7 References

1. K.E. Joester, G. Jung, U. Weber and U. Weser, FEBS Lett. 1972, **25**, 25.
2. R. Malkin, 'Inorganic Biochemistry' Ed., G.E. Eicchorn, Elsevier, Amsterdam, 1973, Vol. 2.
3. L.E. Bennett, Progr. Inorg. Chem. 1973, **18**, 1.
4. R. Lontie and L. Vanquickenborne, 'Metal Ions in Biological Systems' Ed., H. Sigel, Marcel Dekker, New York, 1974, Vol. 3; Chap. 6.
5. J. Weinstein and B.M. Bielski, J. Am. Chem. Soc. 1980, **102**, 4916; B. Reinhammar and B.G. Malmstrom, 'Metals in Biology' Ed., H. Sigel, Wiely, New York, 1981, Vol. 6, p. 109.
6. E.I. Solomon, K.W. Penfield and D.E. Wilcox, Struct. Bonding (Berlin) 1983, **53**, 1.
7. T.E. Adman, 'Topics in Molecular and Structural Bilogy. Metalloproteins' Ed., P.M. Harrison, Macmillan, New York, 1985, Vol. 6, p. 1; E.W. Ainscough, A.G. Bingham, A.M. Brodie, W.R. Ellis, H.B. Gray, T.M. Loehr, J.E. Plowman, G.E. Norris and E.N. Baker, Biochemistry 1987, **26**, 71.
8. 'Copper Coordination Chemistry: Biochemical and Inorganic Perspectives' Eds., K.D. Karlin and J. Zubieta, Adenine Press, New York, 1983; 'Biological and Inorganic Copper Chemistry' Eds., K.D. Karlin and J. Zubieta, Adenine Press, New York, 1986.
9. R. Osterberg, Coord. Chem. Rev. 1976, **18**, 125; K. Seff, Acc. Chem. Res. 1976, **9**, 121; H.S. Lee and K. Seff, J. Phys. Chem. 1981, **85**, 397; H.S. Lee, W.V. Cruz and K. Seff, J. Phys. Chem. 1982, **86**, 3562.

10. J.A. Fee, Struct. Bonding (Berlin) 1975, **21**, 1 and reference therein.

11. A.W. Addison and E. Sinn, Inorg. Chem. 1989, **22**, 1225; O.P. Anderson, C.M. Perkin and K.K. Britto, ibid. 1983, **22**, 1267 and reference therein.

12. E. John, P.K. Bharadwaj, J.A. Potenza and H.J. Schugar, ibid. 1986, **25**, 3065; P.K. Bharadwaj, J.A. Potenza and H.J. Schugar, J. Am. Chem. Soc. 1986, **108**, 1351.

13. W. Maret, A.K. Shiemke, W.D. Wheeler, T.M. Loehr, J. Saunders-Loehr, ibid. 1986, **108**, 6351.

14. J. Reedijk, W.L. Driessen and J. van Riju, 'Biological and Inorganic Copper Chemistry' Eds., K.D. Karlin and J. Zubieta, Adenine Press, New York, 1986, Vol. 22.

15. H. Yokoi and A.W. Addison, Inorg. Chem. 1977, **16**, 1341.

16. S.-J. Lau and B. Sarkar, J. Biol. Chem. 1971, **246**, 5938; P.M. May, P.W. Linder and D.R. Williams, J. Chem. Soc. Dalton Trans. 1977, 588.

17. B. Sarkar and T.P.A. Kruck, 'Biochemistryl of Copper' Eds., J. Peisach, P. Aisen and W.E. Blumberg, Academic Press, New York, 1966, p. 183; H. Beinert, Coord. Chem. Rev. 1980, **33**, 55.

18. M. Voelter, G. Sokolowski, U. Weber and U. Weser, Eur. J. Biochem. 1975, **58**, 159; J.K. Beattie, D.J. Fensom and H.C. Freeman, J. Am. Chem. Soc. 1976, **98**, 500.

19. B.A. Goodman, D.B. McPhail and K.J. Powell, J. Chem. Soc. Dalton Trans. 1981, 822.

20. J.M. Tsugaris and R.B. Martin, J. Am. Chem. Soc. 1970, **92**,

4255; T.P.A. Kruck and B. Sarkar, Can. J. Chem. 1973, **51**, 3549, 3563.

21. H.C. Freeman, Adv. Protein Chem. 1967, **22**, 257.
22. W. Camerman, J.K. Fawcett, T.P.A. Kruck, B. Sarkar and A. Camerman, J. Am. Chem. Soc. 1978, **100**, 2690.
23. T. Yasui, Bull. Chem. Soc. Jpn. 1965, **38**, 1746; T. Yasui, Y. Hidaka and Y. Shimura, J. Am. Chem. Soc. 1965, **87**, 2762.
24. D.R. Williams, J. Chem. Soc. Dalton Trans. 1972, 790.
25. H.A. Kuska and M.T. Rogers, J. Chem. Phys. 1965, **43**, 1744; H. Yokoi and T. Isobe, Bull. Chem. Soc. Jpn. 1969, **42**, 2085.
26. H. Yokoi, M. Sai, T. Isobe, ibid. 1972, **45**, 3488.
27. H. Yokoi, M. Sai, T. Isobe and S. Ohsawa, ibid. 1972, **45**, 2189.
28. H.C. Allen, Jr., M.I. Mandrioli and J.W. Becker, J. Chem. Phys. 1972, **56**, 997.
29. M. Fujimoto and Y. Tomkiewicz, ibid. 1972, **56**, 749.
30. H. Yokoi, Bull Chem. Soc. Jpn. 1974, **47**, 639.
31. B.N. Misra and S.D. Sharma, J. Chem. Phys. 1975, **63**, 5322; B.N. Misra, S.D. Sharma and S.K. Gupta, J. Magn. Reson. 1974, **16**, 193.
32. M.A. Hitchman, L. Kwan, L.M. Engelhardt and A. White, J. Chem. Soc. Dalton Trans. 1987, 457.
33. G. Thomas and P.S. Zacharias, Polyhdron 1985, **4**, 811.
34. A.E. Martell, 'Metal Ions in Biological Systems' Ed., H. Sigel, Dekker, New York, 1973, Vol. 2, p. 208; E.N. Safonova and V.M. Belikov, Russ. Chem. Rev. 1974, **43**, 745.
35. A. Pasini and L. Casella, J. Inorg. Nucl. Chem. 1974, **36**, 2133; D.A. Phipps, J. Mol. Catal. 1974, **5**, 81; R.D. Gillard,

P. O'Brien, P.R. Norman and D.A. Phipps, J. Chem. Soc. Dalton Trans. 1977, 1988.

36. R.H. Holm, 'Inorganic Biochemistry' Ed., G.L. Eicchorn, Elsevier, New York, 1973, Vol. 2, p. 1137; D.L. Leussing, 'Metal Ions in Biological systems' Ed., H. Sigel, Dekker, New York, 1976, Vol. 5, p. 2; J.T. Wrobleski and G.J. Long, Inorg. Chem. 1977, **16**, 2752.
37. M. Sato, K. Okawa and S. Akabori, Bull. Chem. Soc. Jpn. 1957, **30**, 937.
38. S. Akabori, T.T. Otani, R. Marshall, M. Winitz and J.P. Greenstein, Arch. Biochem. Biphys. 1959, **83**, 1.
39. Y. Ikutani, T. Okuda, M. Sato and S. Akabori, Bull. Chem. Soc. Jpn. 1959, **32**, 203.
40. M. Murakami and K. Takahashi, ibid. 1959, **32**, 308.
41. T.T. Otani and M. Winitz, Arch. Biochem. Biphys. 1966, **90**, 254.
42. F. Basolo and R.G. Pearson, 'Mechanisms of Inorganic Reactions' Wiley, New York, 1967, p. 633.
43. Y. Ichikawa, S. Maeda, Y. Araki and Y. Ishido, J. Am. Chem. Soc. 1970, **92**, 5514.
44. J.P. Aune, P. Maldonado, G. Larcheres and M. Pierrot, J. Chem. Soc. Chem. Commun. 1970, 1351.
45. T. Ichikawa, S. Maeda, T. Okamoto, Y. Araki and Y. Ishido, Bull. Chem. Soc. Jpn. 1971, **44**, 2779.
46. S.B. Teo and S. G. Teoh, Inorg. Chim. Acta 1980, **44**, L269.
47. R.D. Gillard, S.H. Laurie, D.C. Price, D.A. Phipps and C.F. Weick, J. Chem. Soc. Dalton Trans. 1974, 1385.

48. R.J. Geue, M.R. Snow, J. Springborg, A.J. Herlt, A.M. Sargeson and D. Taylor, J. Chem. Soc. Chem. Commun. 1976, 285.

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

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

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

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

53. D.A. Phipps, Inorg. Chim. Acta 1978, **27**, L103.

54. T. Ichikawa, T. Okamoto, S. Maeda, S. Ohdan, Y. Araki and Y. Ishido, Tetrahedron Lett. 1971, **1**, 79.

55. S. Ohdan, T. Okamoto, S. Maeda, T. Ichikawa, Y. Araki and Y. Ishido, Bull. Chem. Soc. Jpn. 1973, **46**, 981.

56. S. Ohdan, T. Ichikawa, Y. Araki and Y. Ishido, ibid. 1974, **47**, 1295; Y. Ikutani, T. Okuda and S. Akabori, ibid. 1960, **33**, 582; M. Murakami and K. Takahashi, ibid. 1959, **32**, 308.

57. G.A. Lawrance, T.M. Manning and M.A. O'Leary, Polyhedron 1988, **8**, 1263.

58. P. Comba, G.A. Lawrance, M. Rossignoli, B.W. Skelton and A.H. White, Aust. J. Chem. 1988, **41**, 773.

59. D.A. Buckingham, L.G. Marzilli and A.M. Sargeson J. Am. Chem. Soc. 1967, **89**, 5133.

60. S.B. Teo, S.G. Teoh, J.R. Rodgers and M.R. Snow, J. Chem. Soc. Chem. Commun. 1982, 141.

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

62. S.B. Teo, S.G. Teoh and M.R. Snow, ibid. 1984, **85**, L1.

63. H.C. Freeman and J.M. Guss, Acta Crystallogr. 1968, **B24**, L33; H.C. Freeman, J.M. Guss and R.L. Sinclair, J. Chem. Soc. Chem. Comm. 1968, 485.

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

65. S.B. Teo, C.-H. Ng and E.R.T. Tiekink, ibid. 1989, **163**, 129.

66. D.P. Graddon and L. Munday, Chem. Ind. 1959, 122; D.P. Graddon and L. Munday, J. Inorg. Nucl. Chem. 1961, **23**, 231; D.P. Graddon and L. Munday, ibid. 1963, **25**, 215.

67. K. Harada and J. Oh-hashi, J. Org. Chem. 1967, **32**, 1103.

68. Yu. N. Belekon, I.E. Zel'tzer, N.H. Loim, V.A. Tsiryapkin, G.G. Aleksandrov, D.N. Kursanov, Z.N. Parnes, Yu. T. Struchkov and V.M. Belekov, Tetrahedron Lett. 1980, **36**, 1089.

69. Yu. N. Belekon, I.E. Zel'tzer, M.G. Ryzhov, M.B. Saporovskaya, V.I. Bakhmutov and V.M. Belikov, J. Chem. Soc. Chem. Commun. 1982, 180.

70. Yu. N. Belokon, I.E. Zel'tzer, V.I. Bakhmutov, M.B. Saporovskaya, M.G. Ryzhov, A.I. Yanovsky, Yu. T. Struchkov and V.M. Belikov, J. Am. Chem. Soc. 1983, **105**, 2010.

71. Yu. N. Belokon, N.I. Chernoglazova, C.A. Kochetkov, N.S. Garbalinskaya and V.M. Belikov, J. Chem. Soc. Chem. Commun. 1985, 171.

72. Yu. N. Belokon, A.G. Bulychev, S.V. Vitt, Y.T. Struchkov, A.S. Batsanov, T.V. Timofeeva, V.A. Tsyryapkin, M.G. Ryzhov, L.A. Lysova, V.I. Bakhmutov and V.M. Belikov, J. Am. Chem. Soc. 1985, **107**, 4252.

73. D.E. Metzler, M. Ikawa and E.E. Snell, ibid. 1954, **76**, 648.

74. R.D. Gillard and R. Wootton, J. Chem. Soc. B 1970, 364.

75. H.R. Mohler and E.H. Corders, 'Biological Chemistry' Harper and Row, New York, 1971, p. 393.

76. 'Pyridoxal Catalysis: Enzymes and Model Systems' Eds., E.E. Snell, A.E. Braunstein, E.S. Severin and Y.M. Torchinsky, Interscience, New York, 1968.

77. T. Ueki, T. Ashida, Y. Sasada and M. Kakudo, Acta Crystallogr. Sect B. 1968, **24**, 1361.

78. A. Toni, H. Tamura-Kogayashi, K. Ogawa and T. Watanake, Z. Kristallogr. 1971, **24**, 1361.

79. K. Korhonen and R. Hamalainen, Acta Crystallogr. Sect. B 1981, **37**, 829.

80. T. Ueki, T. Ashida, Y. Sasada and M. Kakudo, Acta Crystallogr. Sect B. 1969, **25**, 328.

81. R. Hamalainen, V. Turpeinen, M. Ahlegren and M. Rantala, Acta Chem. Scand. Ser.A 1978, **32**, 549.

82. L. Casella, M. Gullotti, A. Pasini, G. Ciani, M. Manassero, and A. Sironi, Inorg. Chim. Acta 1978, **26**, L1.

83. M.D. Tsai, S.R. Byrn, C. Chang, H.G. Floss and H.J.R. Weintrab, Biochemistry 1978, **17**, 3177.

84. M.D. Tsai, H.J.R. Weintraub, S.R. Byrn, C. Chang and H.G. Floss, ibid. 1978, **17**, 3153.

85. J.R. Fischer and E.H. Abbott, J. Am. Chem. Soc. 1979, **101**, 2781.

86. L. Casella, M. Gullotti, A. Pasini, A. Rockenbauer, Inorg. Chem. 1979, **18**, 2825.

87. L. Casella, M. Gullotti, A. Pasini, M. Visca, Inorg. Chim. Acta 1976, **19**, L9.

88. L. Casella and M. Gullotti, Inorg. Chem. 1981, **20**, 1306.

89. L. Casella, M. Gullotti and G. Pacchioni, J. Am. Chem. Soc. 1982, **104**, 2386.

90. L. Sacconi, M. Ciampolini, F. Maggio and F.P. Cavasino, J. Inorg. Nucl. Chem. 1961, **19**, 73.

91. L. Sacconi and M. Ciampolini, J. Chem. Soc. 1964, 276.

92. M.J. O'Connor, R.E. Ernst, J.E. Schoenborn and R.H. Holm, J. Am. Chem. Soc. 1968, **90**, 1744.

93. R.J. Dudley, R.J. Fereday, B.J. Hathaway and P.G. Hodgson, J. Chem. Soc. Dalton Trans. 1972, 1341.

94. L.A. Zyzyck, H. Frummer and J.F. Villa, Inorg. Nucl. Chem. 1975, **37**, 1653.

95. S.-T. Chow, D.M. Johns, C.A. McAuliffe and D. Machin, J. Inorg. Chim. Acta 1977, **22**, 1.

96. M.R. Wagner and F.A. Walker, Inorg. Chem. 1983, **22**, 3021.

97. L. Casella and M. Gullotti, J. Am. Chem. Soc. 1981, **103**, 6338.

98. C.J. Hawkins and C.L. Wong, Aus. J. Chem. 1970, **23**, 2237.

99. R.D. Gillard and S.H. Laurie, J. Chem. Soc. Dalton Trans. 1970, 59.

100. B.C. Verma and Y.P. Myer, Bioinorg. Chem. 1972, **1**, 141.

101. E.W. Wilson, Jr., M.H. Kasperian and R.B. Martin, J. Am. Chem. Soc. 1970, **92**, 5365.

102. S. Bunel, M. Rodriguez, A. Urbina and C.A. Bunton, J. Inorg. Nucl. Chem. 1981, **43**, 190.

103. G.O. Carlisle, A. Syamal, K.K. Ganguli and L.J. Theriot, J. Inorg. Nucl. Chem. 1972, **34**, 2761.

104. J.F. Villa and L.A. Zyzyck, Spectrosc. Lett. 1972, **5**, 371.

105. J. Jezierska, Polyhedron 1987, **6**, 1669.

106. G. Plesch, C. Friebel, O. Svajlenova and J. Kratsmar-Smogrovic, Inorg. Chim. Acta 1987, **129**, 81.

CHAPTER II

EXPERIMENTAL

2.1 Chemicals

Glycine, L-alanine, L-serine, D-serine, DL-serine, L-threonine, D-threonine, DL-threonine, ß-alanine, formaldehyde (40% W/V), salicylaldehyde, imidazole (Sisco), pyrazole, N,N'-1,2-ethanediylbisglycine and 1-aminocyclopropane-1-carboxylic acid (Fluka) were used as supplied. Fresh acetaldehyde obtained from depolymerisation[1] of the commercially available paraldehyde (Ranbaxy) was used for the reactions. Pyridine (Sisco) was distilled prior to use. Spectroscopic grade methanol (Ranbaxy) was employed for spectral measurements.

2.2 Preparation of complexes

2.2.1 Bis(α-amino acidato)copper(II)

The Cu(II) complexes, viz., $Cu(gly)_2.H_2O$, $Cu(L\text{-}ala)_2$, $Cu(DL\text{-}ala)_2.H_2O$, $Cu(L\text{-}ser)_2.H_2O$, $Cu(D\text{-}ser)_2.H_2O$, $Cu(DL\text{-}ser)_2$, $Cu(L\text{-}thr)_2.H_2O$, $Cu(D\text{-}thr)_2.H_2O$, $Cu(DL\text{-}thr)_2$ and $Cu(ß\text{-}ala)_2.2H_2O$ were prepared by employing a known general procedure.[2] The alicyclic-α-amino acids, 1-aminocyclobutane-1-carboxylic acid, 1-aminocyclopentane-1-carboxylic acid, 1-aminocyclohexane-1-carboxylic acid and 1-aminocycloheptane-1-carboxylic acid were prepared from the corresponding alicyclic ketones[3] and their Cu(II) complexes were prepared by the same general procedure.[2]

2.2.2 Bis(2,5-dimethyloxazolidine-4-carboxylato)copper(II) dihydrate (**1**)[4]

To an aqueous solution of glycine (0.75 g, 10 mM) was added $CuCO_3.Cu(OH)_2$ (0.55 g, 2.5 mM) along with freshly cracked acetaldehyde[1] (5 ml). The pH was adjusted to 11 by addition of sodium bicarbonate. The reaction mixture was stirred well and filtered. The filtrate was kept at room temperature for 7 days. The blue crystalline product formed was filtered, washed successively with distilled water, ethyl alcohol and diethyl ether and dried at 50 °C under reduced pressure for 12 h.

2.2.3 Bis(dihydro-1H,3H,5H-oxazolo[3,4-c]oxazole-7a-carboxylato) copper(II) (**2**)[5]

A reaction mixture (30 ml) of $Cu(gly)_2.H_2O$ (1.2 g, 5 mM) and formaldehyde (20 ml, 40% W/V) was stirred well and adjusted to pH 8.5 by the addition of sodium bicarbonate. The reaction mixture was filtered and the filtrate kept at room temperature for 7

days. The blue crystalline product deposited was treated as described for the complex **1**.

The complex **2** can also be prepared by another reported method[6] from $Cu(L\text{-}ser)_2.H_2O$.

2.2.4 Bis[N-(1,3-dioxa-5-aza-cyclohexyl)acetato]copper(II) (**3**)[7]

A reaction mixture (30 ml) consisting of $Cu(gly)_2.H_2O$ (1.2 g, 15 mM) and formaldehyde (10 ml, 40% W/V) was stirred and its pH adjusted to 4.5 by dilution with distilled water. The reaction mixture was then filtered and the filtrate was allowed to stand for 3 days at room temperature. The blue crystalline product formed was treated as described for the complex **1**.

2.2.5 [3N,7N-(1,3,5,7-tetraazabicyclo[3.3.1]nonyl)diacetato] copper(II) (**4**)

This complex was prepared by a procedure reported for the preparation of the corresponding Ni(II) complex.[8]

To an aqueous solution (60 ml) of $Cu(gly)_2.H_2O$ (1.2 g, 5mM) was added formaldehyde (10 ml, 40% W/V) and the pH of the reaction mixture was adjusted to 8.5 by the addition of ammonium hydroxide solution. After filtration, the filtrate was allowed to stand for 7 days and the blue microcrystalline product deposited was filtered and treated as described for the complex **1**.

2.2.6 [3N,7N-(1,3,5,7-tetraazabicyclo[3.3.1]nonyl)di-2-propionato]copper(II) (**5**)[9]

To an aqueous solution (50 ml) of $Cu(L\text{-}ala)_2$ (1.2 g, 5 mM) was added formaldehyde (15 mM, 40% W/V) and the pH of the

reaction mixture was adjusted to 8.5 by the slow addition of ammonium hydroxide solution. After filtration the filtrate was allowed to stand at room temperature for 7 days. The dark blue solution was evaporated on a boiling water bath to 20 ml and cooled. Blue needle shaped crystals obtained were filtered, washed with ethanol and acetone and dried under reduced pressure at 50 °C for 12 h.

2.2.7 Bis(4-methyloxazolidine-4-carboxylato)copper(II) dihydrate (**6**)[10]

To an aqueous solution of $Cu(DL\text{-}ala)_2.H_2O$ (1.2 g, 5 mM) was added formaldehyde (15 ml, 40% W/V) and stirred. The pH was adjusted to 8.5 by the addition of concentrated ammonium hydroxide. The reaction mixture was allowed to stand for 7 days at room temperature hence deep blue crystals appeared. These were filtered, washed successively with cold distilled water, ethanol and acetone and were finally dried under reduced pressure at 50 °C for 12 h.

2.2.8 [N,N'-1,3-(2-oxapropanediyl)bis(oxazolidine-4-carboxylato] copper(II) (**7**)

To an aqueous solution (50 ml) of $Cu(DL\text{-}ser)_2$ (1.35 g, 5 mM) excess formaldehyde (15 ml, 40% W/V) was added and the reaction mixture was stirred and filtered. The filtrate (pH *ca.* 4.5) was allowed to stand at room temperature for 7 days. The blue microcrystalline product was filtered, washed successively with distilled water, ethanol and diethyl ether and finally dried under reduced pressure at 50 °C for 12 h.

2.2.9 [N,N'-1,3-(2-oxapropanediyl)bis(5-methyloxazolidine-4-carboxylato)] copper(II) monohydrate (**8**)

The complex (**8**) was prepared from $Cu(DL\text{-}thr)_2$ by the method described for the complex, **7**. The product was deep blue coloured and crystalline.

2.2.10 Bis(2-methyloxazolidine-4-carboxylato)copper(II) dihydrate (**9**)

To an aqueous solution (50 ml) of $Cu(DL\text{-}ser)_2$ was added freshly cracked acetaldehyde[1] (5 ml), the reaction mixture was stirred well and allowed to stand. The blue crystalline product deposited within 6 h was filtered and treated as described for the complex **7**.

$Cu(DL\text{-}thr)_2$ under the same experimental conditions yielded the complex **1**.

2.2.11 Bis(5-methyloxazolidine-4-carboxylato)copper(II) dihydrate (**10**)

To an aqueous solution (50 ml) of $Cu(DL\text{-}thr)_2$ (1.50 g, 5 mM) was added formaldehyde (10 ml, 40% W/V). The pH of the reaction mixture was adjusted 8.5 by the addition of sodium bicarbonate and filtered. The filtrate was allowed to stand at room temperature for 2 days. The blue crystalline product obtained was treated as described for the complex **7**. Use of concentrated ammonium hydroxide instead of sodium bicarbonate also yielded the same product.

$Cu(DL\text{-}ser)_2$ under the same experimental conditions yielded the complex **2**.

2.2.11 Copper(II) complexes of ethene-bridged-α-amino acids

The Cu(II) complexes of ethene-bridged amino acids, glycine (**11**), L-alanine[11] (**12**) and L-isoleucine[11] (**13**) were prepared by the following general procedure.

To the appropriate ethene-bridged amino acid (5 mM) in 50 ml water was added excess basic copper carbonate. The reaction mixture was heated for 30 min on a boiling water bath and filtered to remove unreacted copper carbonate. The resultant blue solution was evaporated to one third of its volume on a boiling water bath. Blue crystalline product formed after cooling was filtered and dried at 50 °C under reduced pressure.

2.2.12 Bis[L-(oxazolidine-4-carboxylato)]copper(II) monohydrate (**14**)

To an aqueous solution (30 ml) of $Cu(L\text{-}ser)_2.H_2O$ (1.35 g, 5 mM) was added formaldehyde (10 ml, 40% W/V), stirred well and the reaction mixture was filtered. The filtrate (pH was about 4.5) was allowed to stand for 7 days. The dark blue product deposited was filtered, washed successively with cold distilled water ethanol and diethyl ether and dried under reduced pressure at 50 °C for 12 h.

2.2.13 Bis[L-(N-2-hydroxymethyl-4-methyloxazolidine-4-carboxylato)copper(II) dihydrate **15**

The complex **15** was prepared by the same procedure described for **14** from $Cu(L\text{-}thr)_2.H_2O$. The product was washed with little amount of cold distilled water and acetone and dried under reduced pressure at 50 °C for 12 h.

The Cu(II) complexes of D-serine and D-threonine also undergo similar reaction yielding the corresponding D-products.

2.2.14 [3N,7N-(1,3,5,7-Tetraazabicyclo[3.3.1]nonyl)di-3-propionato] copper(II) **16**

To an aqueous solution (50 mL) of Cu(ß-ala)$_2$.2H$_2$O (1.4 g, 5 mM) was added formaldehyde (10 ml, 40% W/V) and the pH was adjusted to 8.5 by the addition of concentrated ammonium hydroxide. The reaction mixture was allowed to stand at room temperature for 7 days. The dark blue crystalline product formed was filtered, washed successively with ethanol and diethyl ether and dried at 50 °C under reduced pressure for 12 h.

The complexes **7-10** and **14-16** are new. Analytical data for all the complexes are collected in Table 2.1. Details of structural elucidation of the new complexes (**7-10** and **14-16**) are presented in Chapters III and IV.

2.2.15 (N-salicylidene-amino acidato)copper(II) complexes [Cu(sal-aa)(H$_2$O)]

The Cu(II) complexes of N-salicylidene-amino acid ligands derived from salicylaldehyde and various amino acids viz., glycine [Cu(sal-gly)(H2O)], L-alanine [Cu(sal-ala)(H$_2$O)], L-serine [Cu(sal-ser)(H$_2$O)], L-threonine (sal-thr)(H$_2$O)] and ß-alanine [Cu(sal-ß-ala)(H$_2$O) were prepared according to a general method.[12]

In a typical preparation, a solution of salicylaldehyde (0.61 g, 5 mM) in ethanol (30 ml) was added to the appropriate

amino acid (5 mM) in water (15 ml) followed by aqueous NaOH (10 mM) and the reaction mixture was stirred for 24 h. The resulting precipitate was removed by filtration, recrystallized from water and dried under reduced pressure at 50 °C for 12 h.

2.2.16 Adducts of Cu(sal-aa)(H_2O) complexes

The imidazole, pyrazole and pyridine adducts of the Cu(sal-aa)(H_2O) complexes were prepared by a known general procedure.[13] A solution of Cu(sal-aa)(H_2O) (5 mM) in 3:1, ethanol:H_2O (150 ml) was heated up to boiling and the ligand (10 mM) was added. The solution was filtered and allowed to cool. Dark green product separated was removed and recrystallized from methanol.

Analytical data for the Cu(sal-aa)(H_2O) complexes and the imidazole [Cu(sal-aa)(im)], pyrazole [Cu(sal-aa)(pz)] and pyridine [Cu(sal-aa)(py)] adducts are collected in Table 2.2.

2.3 Physical measurements

2.3.1 Spectroscopic studies

The C, H and N elemental analyses were performed on a Perkin Elmer 240C Elemental Analyzer. Infrared spectra were recorded on a Perkin-Elmer 297 Spectrometer in the region 4000-600 cm^{-1} as KBr pellets. Solution electronic spectral measurements were carried out using either a Shimadzu 200S double beam Spectro-photometer or a Perkin-Elmer Lambda 3B UV/VIS Spectro-photometer. The CD spectra were recorded on a JASCO J20 instrument in the wavelength region 700-400 nm. ESR spectra were recorded in the solution and frozen-glassy states on a JEOL FE-3X Spectrometer using DPPH as the internal standard. Quartz tubes were used for

Table 2.1. Analytical data for the complexes **1-16.**

Complex	Found(Calcd.) %			
	C	H	N	Cu
1	37.2(37.2)	6.1(6.2)	7.2(7.2)	16.5(16.4)
2	37.5(37.9)	4.1(4.2)	7.5(7.4)	16.5(16.7)
3	33.6(33.8)	4.5(4.5)	8.0(7.9)	17.6(17.9)
4	34.9(35.2)	4.7(4.6)	18.3(18.1)	20.5(20.7)
5	39.4(39.6)	5.5(5.4)	16.9(16.8)	18.7(19.0)
6	33.4(33.4)	5.4(5.6)	7.8(7.8)	17.5(17.7)
7	35.2(35.6)	4.2(4.2)	8.2(8.3)	18.7(18.8)
8	37.5(37.6)	5.2(5.2)	7.3(7.3)	16.5(16.6)
9	33.4(33.4)	5.4(5.6)	7.7(7.8)	17.6(17.7)
10	34.0(33.4)	5.5(5.6)	8.0(7.8)	17.5(17.7)
11	23.2(23.3)	5.7(5.9)	10.4(10.5)	20.3(20.5)
12	36.2(36.2)	5.4(5.3)	10.6(10.5)	23.8(23.9)
13	39.8(39.8)	8.3(8.4)	7.8(7.7)	17.4(17.6)
14	30.5(30.6)	4.7(4.5)	8.7(8.9)	19.8(20.2)
15	34.3(34.3)	5.7(5.8)	6.8(6.7)	15.0(15.1)
16	39.4(39.6)	5.4(5.4)	16.6(16.8)	18.7(19.1)

Table 2.2. Analytical data for Cu(sal-aa)(H_2O) complexes and their (im), (pz) and (py) adducts.

Complex	Found (Calcd.)%			
	C	H	N	Cu
Cu(sal-gly)$1\frac{1}{2}H_2O$	40.3(40.4)	3.7(3.8)	5.3 (5.2)	23.6(23.7)
Cu(sal-gly)im	46.8(46.7)	3.7(3.6)	13.5(13.6)	20.4(20.6)
Cu(sal-gly)pzH_2O	44.2(44.1)	4.05(4.0)	12.8(12.9)	19.3(19.5)
Cu(sal-gly)py	52.5(52.6)	3.8(3.8)	8.8 (8.8)	19.7(19.9)
Cu(sal-ala)$2H_2O$	41.3(41.3)	4.6(4.5)	4.9 (4.8)	21.7(21.9)
Cu(sal-ala)im	48.4(48.4)	4.1(4.1)	13.2(13.0)	19.5(19.7)
Cu(sal-ala)pz	48.3(48.4)	4.2(4.1)	13.2(13.0)	19.1(19.7)
Cu(sal-ala)py	54.1(54.0)	4.2(4.2)	8.4 (8.4)	19.7(19.0)
Cu(sal-ser)$2H_2O$	39.2(39.1)	4.3(4.3)	4.4 (4.6)	20.7(20.7)
Cu(sal-ser)im	45.8(46.1)	4.0(3.9)	14.5(14.4)	19.0(18.8)
Cu(sal-ser)pz	46.1(46.1)	3.9(3.9)	12.3(12.4)	18.9(18.8)
Cu(sal-ser)py	51.5(51.5)	4.0(4.0)	7.9 (8.0)	18.2(18.1)
Cu(sal-thr)$2H_2O$	41.1(41.2)	4.8(4.7)	4.4 (4.4)	19.7(19.8)
Cu(sal-thr)im	47.6(47.7)	4.3(4.3)	12.0(11.9)	18.1(18.0)
Cu(sal-thr)pz	47.7(47.6)	4.3(4.3)	11.9(11.9)	18.0(18.0)
Cu(sal-thr)py	52.8(52.8)	4.5(4.4)	7.8 (7.7)	17.4(17.5)
Cu(sal-ß-ala)H_2O	44.1(44.0)	4.1(4.0)	5.2 (5.1)	23.1(23.3)
Cu(sal-ß-ala)im	48.3(48.4)	4.2(4.1)	12.9(13.0)	19.4(19.7)
Cu(sal-ß-ala)pz	48.3(48.4)	4.0(4.0)	13.1(13.0)	19.6(19.7)
Cu(sal-ß-ala)py	54.1(54.0)	4.3(4.2)	8.4 (8.4)	19.0(19.0)

frozen solutions, while a quartz water solution cell was employed to collect room temperature spectra. JEOL NM 7700 Temperature Controller was used for low temperature measurements. Solutions of 0.005 M concentration of the Cu(II) complexes (in 95:5, water:methanol mixture) were used to record frozen-glassy ESR spectra.

2.3.2 Measurement of pH

The pH of the solutions was measured using an EC Model pH 5651 digital pH meter.

2.3.3 Electrochemical experiments

Cyclic and differential pulse voltammetric experiments were carried out using a Princeton Applied Research 370 Electrochemistry System, consisting of Model 174 Polarographic Analyzer, Model 175 Universal Programmer, RE 0074 XY Recorder and a 374 three-electrode cell system. Metrohm E410 Hanging Mercury Drop Electrode (HMDE) was used as the working electrode along with a Pt-wire auxiliary electrode and a PAR Model 9331 saturated calomel reference electrode (SCE). The experiments were carried out for 0.001 M solution of the complexes under nitrogen atmosphere using sodium perchlorate (0.1 M) as the supporting electrolyte. For pH adjustment dilute solution of perchloric acid or sodium hydroxide were used.

2.4 References

1. A.I. Vogel, 'Textbook of Practical Organic Chemistry' Longman, 4th Edition, 1978, Chap. 3, p. 417.
2. H.C. Freeman, M.J. Healy and M.L. Sudden, J. Biol. Chem. 1977, **252**, 8840.
3. R. Zand, O.Z. Sellinger, R. Water and R. Harris, J. Neurochem. 1974, **23**, 1201.
4. J.P. Aune, P. Maldonado, G. Larcheres and M. Pierrot, J. Chem. Soc. Chem. Commun. **1970**, 1351.
5. S.B. Teo and S.G. Teoh, Inorg. Chim. Acta 1980, **44**, L269.
6. J.R. Bush, R.J. Magee, M.J. O'Connor, S.B. Teo, R.J. Geue and M.R. Snow, J. Am. Chem. Soc. 1973, **95**, 2034.
7. S.B. Teo and S.G. Teoh, Inorg. Chim. Acta 1984, **91**, L17.
8. S.B. Teo, S.G. Teoh and M.R. Snow, ibid. 1985, **85**, L1.
9. S.B. Teo, C.-H. Ng and E.R.T. Tiekink, ibid. 1989, **163**, 129.
10. S.B. Teo, S.G. Teoh and M.R. Snow, ibid. 1985, **107**, 211.
11. B.M. Katz, V.I. Stenberg, Polyhedron 1985 **4**, 2031.
12. M.R. Wagner and F.A. Walker, Inorg. Chem. 1983, **22**, 3021.
13. G. Plesch, C. Friebel, O. Svajlemova and Kratsmar-Smogrovic Inorg. Chim. Acta 1987, **129**, 81.

CHAPTER III

CONDENSATION PRODUCTS OF COPPER(II)-α-AMINO ACID COMPLEXES

2.1 Abstract

Condensation reactions of Cu(II) complexes of DL-serine and DL-threonine with aliphatic aldehydes such as formaldehyde and acetaldehyde are investigated. The products obtained are characterized by spectral and analytical data. The new complexes together with a few known condensation products of Cu(II)-α-amino acid complexes are studied by electronic spectral, ESR, cyclic voltammetric and differential pulse voltammetric techniques in aqueous media at various pH conditions. Spectral data indicate tetrahedral distortion in the complexes as the ligand system varies. Electrochemical data reveal involvement of Cu(I) intermediate species in their redox process. A general conclusion, more the planarity of the system, more negative is the

Cu(II)/Cu(I) reduction potential, less stable is the Cu(I) intermediate species and less reversible is the redox process, has been achieved. Flexibility of the ligand system also influences considerably reversibility of the redox process as evidenced by the irreversible Cu(II)/Cu(I) reduction observed for two of the complexes, which contain rigid pentamethylenediaza group bridging the two amino acid units. Another complex, (N,N'-1,2-ethanediyl)bis(glycinato)copper(II), exhibits a unique redox behaviour, which is attributed to weak intermolecular interaction present between the metal centres in aqueous solution.

Spectral data at low pHs categorize the complexes into two groups viz., unbridged and bridged. The unbridged complexes exhibit formation of various protonated species at low pHs, $[CuL]^+$ (where L = ligand anion) being the dominant species. For the bridged complexes, species formation could not be detected by the spectral techniques. Electrochemical data at low pHs reveal that only the bis complex species undergo close to reversible Cu(II)/Cu(I) redox process. Bridged complexes show shift of Cu(II)/Cu(I) redox potential towards less negative potentials on lowering pH, which is related to protonation leading to change in ligand CFSE.

3.2 INTRODUCTION

In recent years, extensive studies have been carried out on the condensation reactions of bis(α-amino acidato)copper(II) complexes with formaldehyde and acetaldehyde as briefly discussed in Chapter I. Most of these investigations are on $Cu(gly)_2$ or $Cu(\alpha\text{-ala})_2$ while the complexes of several other amino acids have

received only scant attention.[1-6] In this respect, we have investigated the condensation reactions of Cu(II) complexes of DL-serine and DL-threonine with formaldehyde and acetaldehyde at various experimental conditions.

The new products together with some known condensation products are having the same CuN_2O_2 chromophore, however their geometry may vary since the complexes are having different substituents at the α-carbon and/or amino nitrogen atoms. It is known that tetrahedral distortion and electron donor properties are the important factors which influence redox properties of Cu(II) complexes.[7-10] Therefore, redox properties of the condensation products were investigated to see if any correlation between geometry and redox properties exists. Though precise estimation of geometry or the tetrahedral distortion of the complexes in solution is not facile, reasonable estimation can be obtained from their solution electronic absorption and ESR spectral data.[11-14] Hence, electronic and ESR spectral techniques have been used to gain an insight into the geometry of the complexes in aqueous media. Similar investigations have received considerable interest in recent years towards the understanding of the 'unique' spectral and redox properties of the type I or 'blue' Cu(II) sites in metallo-proteins.[15-20]

3.3 EXPERIMENTAL

3.3.1 Preparation of complexes

The complexes, bis(2,5-dimethyloxazolidine-4-carboxylato)-copper(II) dihydrate (**1**), bis(dihydro-1H,3H,5H-oxazolo[3,4-c]oxa-

zole-7a-carboxylato)copper(II) (**2**), bis[N-(1,3-dioxa-5-azacyclohexyl)acetato]copper(II) (**3**), [3N,7N-(1,3,5,7-tetraazabicyclo[3.3.1]nonyl)diacetato]copper(II) (**4**), [3N,7N-(1,3,5,7-tetraazabicyclo[3.3.1]nonyl)di-2-propionato]copper(II) (**5**), bis(4-methyloxazolidine-4'-carboxylato)copper(II) dihydrate (**6**), [N,N'-1,3-(2-oxapropanediyl)bis(oxazolidine-4-carboxylato]copper(II) (**7**), [N,N'-1,3-(2-oxapropanediyl)bis(5-methyloxazolidine-4-carboxylato] copper(II) monohydrate (**8**), bis(5-methyloxazolidine-4-carboxylato)copper(II) dihydrate (**9**), bis(2-methyloxazolidine-4-carboxylato)copper(II) dihydrate (**10**), [(N,N'-ethanediyl)bis(glycinato)copper(II) tetrahydrate (**11**), [(N,N'-ethanediyl)bis(L-alaninato)copper(II) (**12**), [(N,N'-ethanediyl)bis(L-isoleucinato)copper(II) dihydrate (**13**) were prepared as described in Section 2.2.

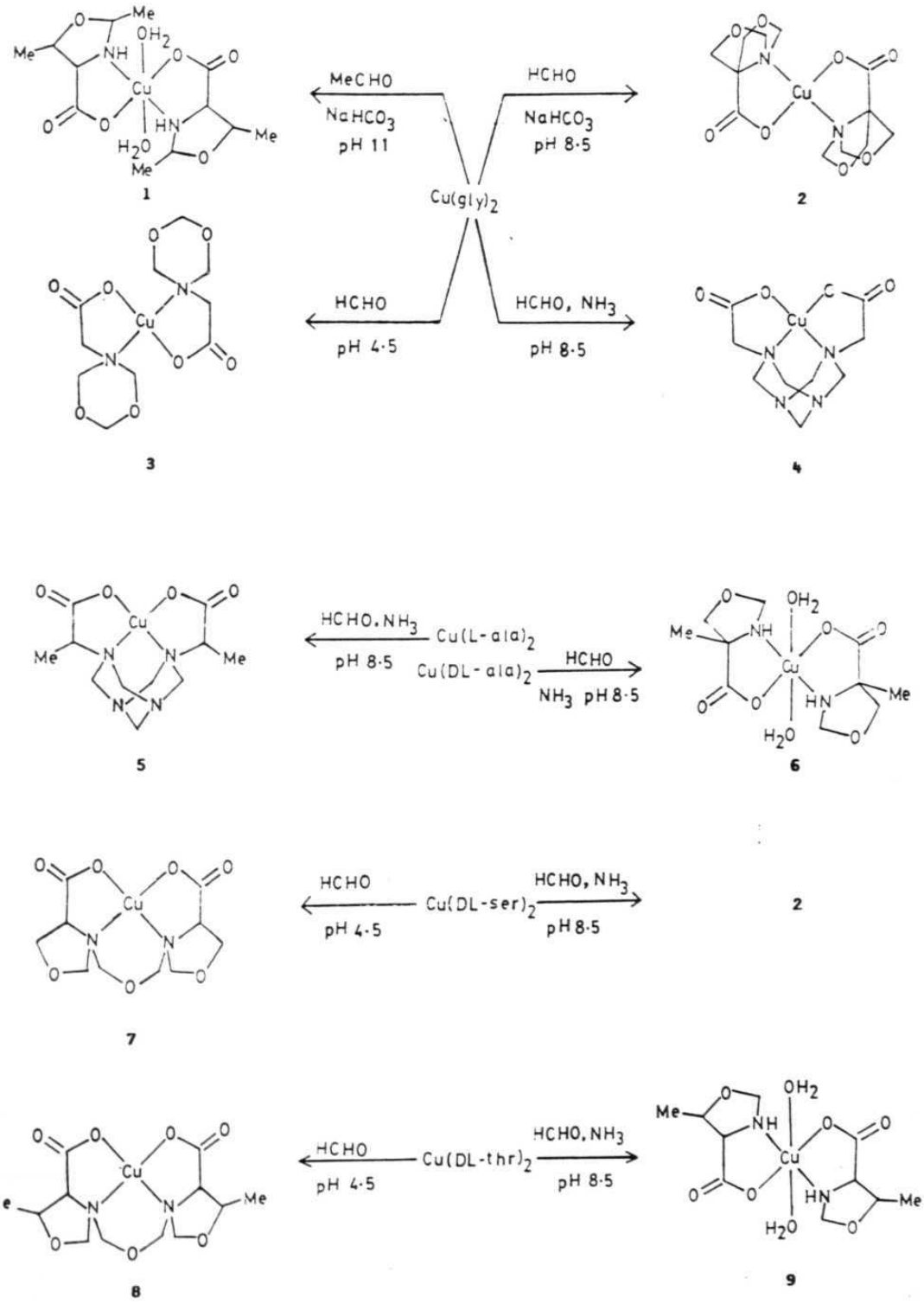
3.3.2 Physical measurements

The general techniques employed are briefly discussed in Section 2.3.

3.4 Results and discussion

3.4.1 Structure of the complexes

Analytical data of the complexes are given in Table 2.1. The known complexes **1-6** and **11-13** were prepared according to the reported procedures (Section 2.2). Their purity was checked by analytical data and IR spectra. The new complexes **7-9** were prepared as described in Section 2.2. Various reactions leading to the formation of complexes **1-10** and the structures of **11-13** are shown in Figure 3.1. The structures of the new complexes were deduced from the following data:


MeCHO
NaHCO3
pH 11
HCHO
NaHCO3
pH 8·5
Cu(gly)2
HCHO
pH 4·5
HCHO, NH3
pH 8·5
1
2
3
4
HCHO, NH3
pH 8·5
Cu(L-ala)2
Cu(DL-ala)2
HCHO
NH3 pH 8·5
5
6
HCHO
pH 4·5
Cu(DL-ser)2
HCHO, NH3
pH 8·5
2
7
HCHO
pH 4·5
Cu(DL-thr)2
HCHO, NH3
pH 8·5
8
9

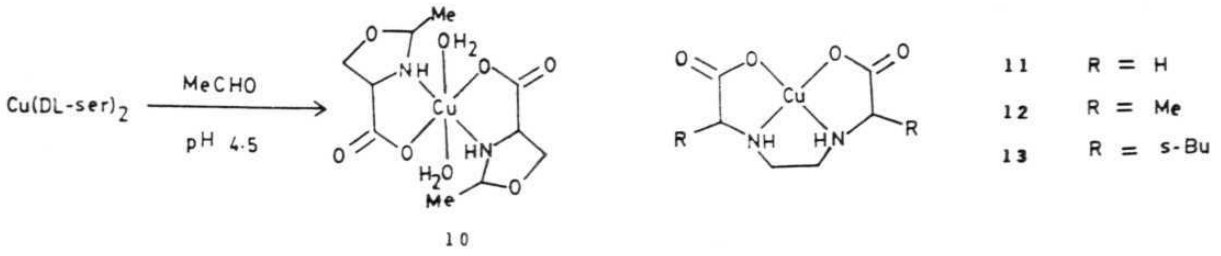


Figure 3.1. Reactions leading to the formation of complexes **1-10** and structures of complexes **11-13.**

(i) a closely spaced set of three IR bands is observed in the region 1200-1080 cm^{-1} for the complexes **7-10**, which is characteristic of oxazolidine ring system;

(ii) complex **7** does not show IR bands above 3100 cm^{-1} indicating the absence of both -OH and >NH groups;

(iii) complex **8** shows presence of an IR band at 3500 cm^{-1}, indicating the presence of -OH group;

(iv) complexes **9** and **10** show presence of both -OH and >NH groups since the characteristic bands are present;

(v) the complexes obtained from $Cu(DL\text{-}ser)_2$, **7**, **10** and the complexes obtained from $Cu(DL\text{-}thr)_2$, **8** and **9**, on decomposition by treatment of H_2S in acid media yield the parent amino acids (copper being separated as insoluble CuS), implying that the condensation has not taken place at the α-carbon atom.

Relevant IR data are presented in Table 3.1. Analytical data collected in Table 2.1 further support the structures proposed.

Table 3.1. IR data for the complexes **7-10**.

Complex	Bands	Assignment
7	1180, 1135, 1080 (t)	oxazolidine ring
8	1150, 1120, 1090 (t); 3580, 3440	oxazolidine ring; OH and >NH groups
9	1125, 1100, 1080 (t); 3440, 3200	oxazolidine ring; OH and >NH groups
10	1180, 1160, 1120 (t); 3500, 3200	Oxazolidine ring; OH and >NH groups

t = three closely spaced bands.

Based on their structural features, the complexes are categorized into two groups:

(i) unbridged complexes, those which are having their nitrogens unbridged and having the composition CuL_2 (**1-3**, **6**, **9** and **10**);

(ii) bridged complexes, those which are having their nitrogens bridged by a pentamethylenediaza group (**4** and **5**), dimethyleneether group (**7** and **8**) or ethene group (**11-13**) and having CuL composition.

3.4.2 Electronic and ESR spectral data

The condensation products **1-10** and the Cu(II) complexes of ethene-bridged-α-amino acids, **11-13** can be expected to possess geometry of varying tetrahedral distortion since they are substituted differently. Electronic and ESR spectral data were collected in order to find out, the order by which the complexes

vary in their tetrahedral distortion. The data were also collected at lower pHs to follow protonation and subsequent formation of different protonated species.

The unbridged complexes at neutral pH exhibit the d-d transition in the wavelength region 635-620 nm. The pentamethylenetetraaza-bridged complexes (**4** and **5**) exhibit the d-d band at 610 nm while the ethene-bridged complexes (**11-13**) exhibit the band in the higher wavelength region 670-640 nm. The dimethyleneether-bridged complexes (**7** and **8**) exhibit the d-d band similar to the unbridged complexes in the wavelength region 635-620 nm.

For all complexes ESR spectra were recorded in aqueous media at room temperature at neutral and lower pHs. At neutral pH, the complexes exhibit the normal four-line profiles. The spectra shows poorly resolved superhyperfine splitting of coordinated nitrogens. ESR parameters for all complexes are collected in Table 3.2. It could be seen from the data that, g_{iso} and A_{iso} values for all the unbridged complexes are ca. 2.120 and ca. 70 G respectively and do not vary considerably from complex to complex. The pentamethylenediaza-bridged complexes **4** and **5** show the lowest g_{iso} value, 2.101 and the highest A_{iso} value 75 G; the ethene-bridged complexes exhibit g_{iso} values ca. 2.115 and A_{iso} ca. 73 G while the dimethyleneether-bridged complexes exhibit g_{iso} and A_{iso} values similar to the unbridged complexes.

It is generally accepted that the g values decrease and A values increase as the planar ligand field becomes stronger[22-24] and this is accompanied by a blue shift of the d-d absorption

bands.[25] On the basis of the λ_{max} values and the ESR parameters, the complexes appear to have the following order of increasing tetrahedral distortion:

4,5 < 11-13 < 1-3, 6-10

At low pHs, the electronic spectral behaviour exhibited by the complexes is distinct for the unbridged and bridged complexes. The unbridged complexes exhibit a gradual shift of λ_{max} values towards low energy region (red shift). These complexes exhibit the d-d band at 720 nm at pH 4; on further decrease of pH decomplexation occurs resulting disappearance of the d-d band.

The red shift of the d-d band observed for the unbridged complexes at lower pHs parallels the behaviour exhibited by bis(α-amino acidato)copper(II) complexes,[26] which is explained to arise from the formation of various protonated species, $[CuL_2H]^+$, $[CuL]^+$, $[CuLH]^{2+}$ etc. where LH = α-amino acid. At lower pHs $[CuL]^+$ has been shown to be the most predominant species. The bridged complexes do not exhibit any shift in their d-d band position on lowering pH indicating that the protonation does not effect any change in geometry. Electronic spectra of representative complexes at various pHs are shown in Figure 3.2 and the data collected in Table 3.2.

ESR spectra of the complexes in aqueous media at various pHs also differentiate the unbridged and bridged complexes. The bridged complexes exhibit normal four-line (2I+1) pattern,

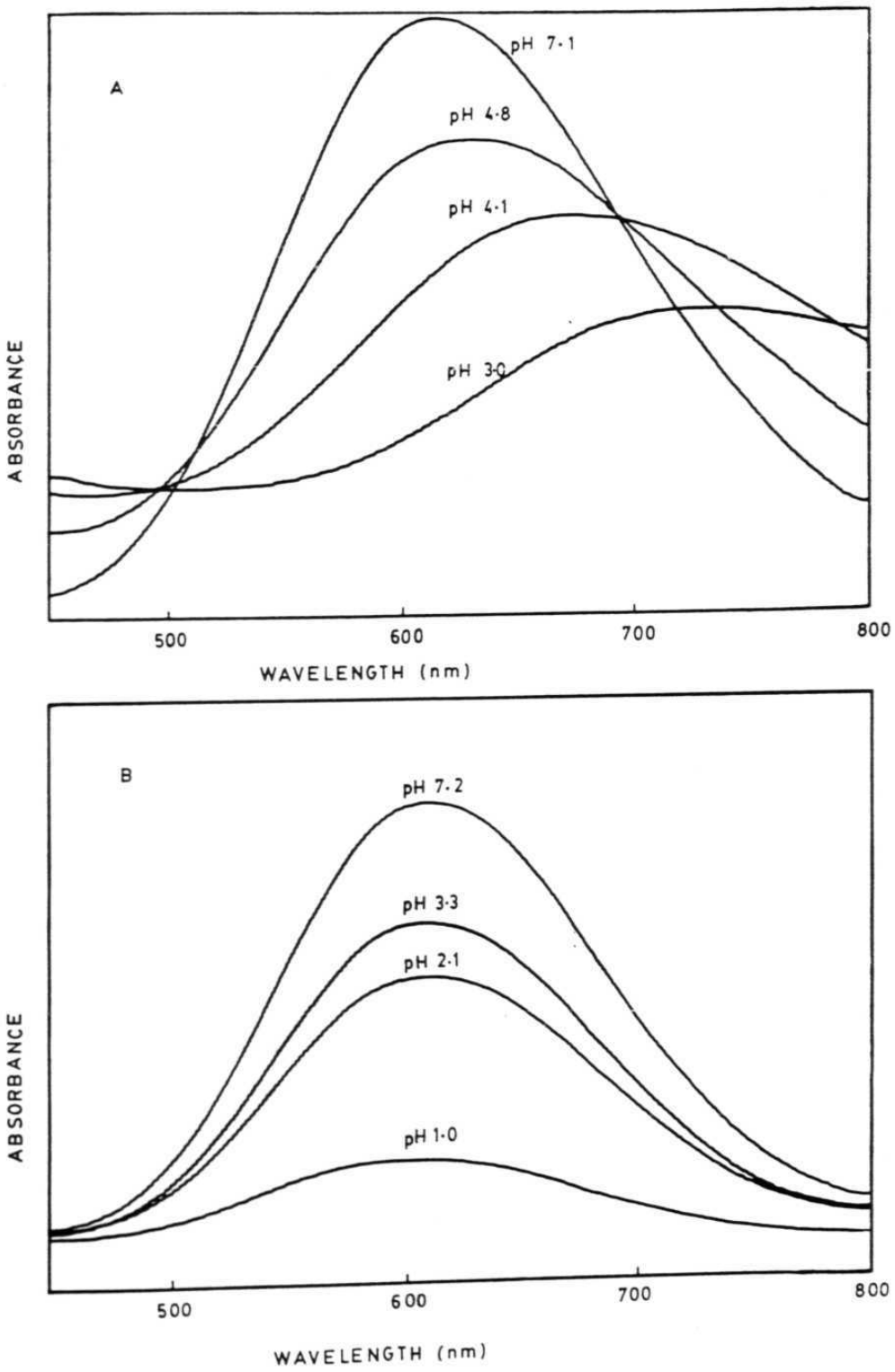


Figure 3.2. Electronic spectra of an unbridged complex, **1**, (A) and a bridged complex, **4**, (B) in aqueous media at various pHs.

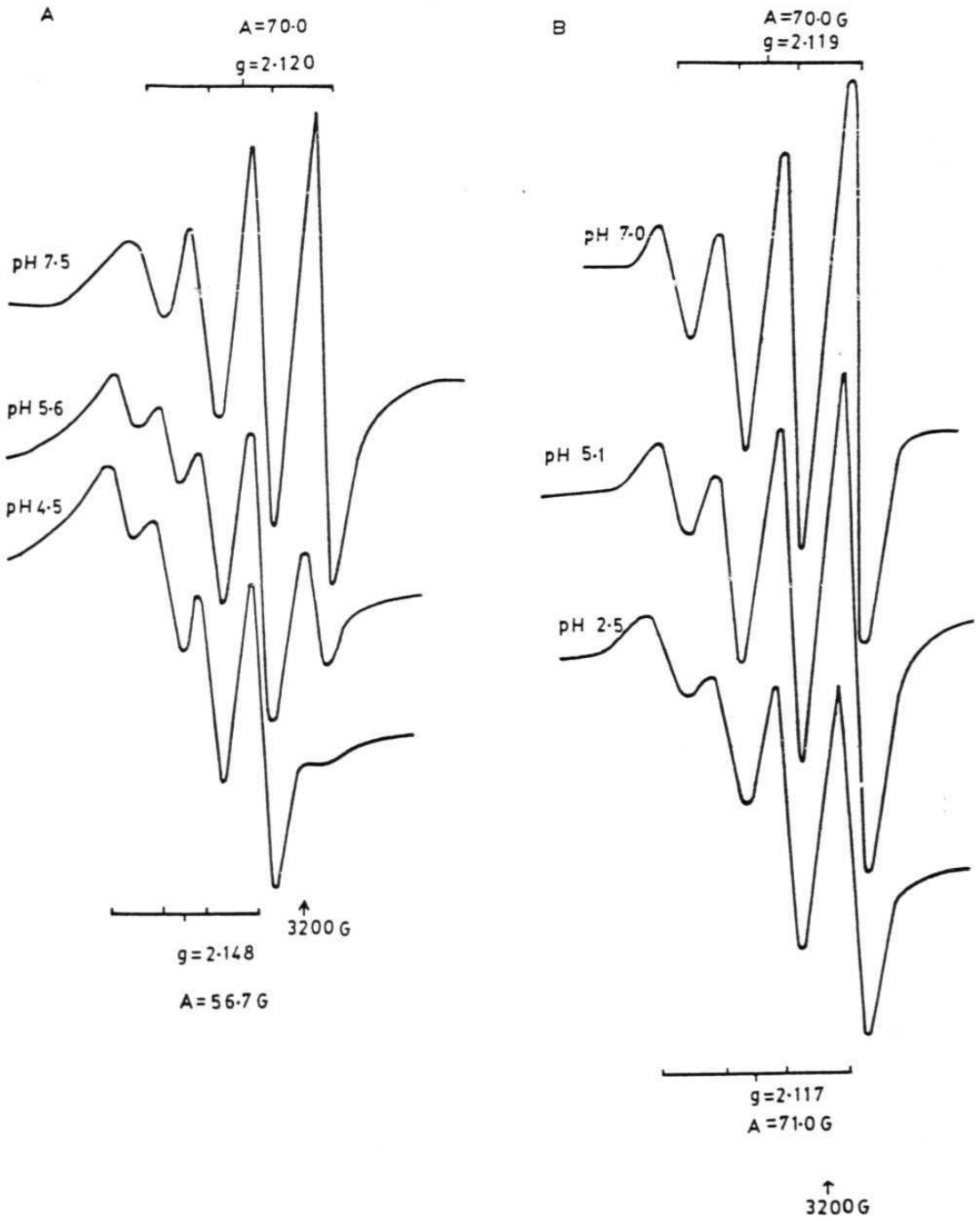


Figure 3.3. ESR spectra of an unbridged complex, **2**, (A) and a bridged complex, **8**, (B) in aqueous media at various pHs.

Table 3.2. Electronic and ESR data of the complexes 1-13 at various pHs.

Complex	pH	λ_{max} (nm)	g_{iso}	A_{iso} (G)	Complex	pH	λ_{max} (nm)	g_{iso}	A_{iso} (G)
1	7.1	625	2.121	69.3	8	7.0	635	2.119	70.0
	5.9	650	2.153	56.7		5.9	635	2.121	71.0
	4.8	710	2.153	56.7		5.1	635	2.119	72.0
	4.1	720	2.150	56.7		2.0	b	a	a
2	7.5	630	2.120	70.0	9	7.5	620	2.119	70.0
	6.0	660	2.123	70.0		5.9	670	2.125	73.0
	5.6	710	2.142	53.3		4.9	710	2.154	54.0
	4.5	720	2.148	5.67		4.2	720	2.146	55.0
3	7.3	635	2.120	65.0	10	7.0	620	2.120	69.3
	5.5	690	2.148	56.7		6.1	670	2.118	70.0
	4.4	720	2,151	56.7		4.7	710	2.156	52.0
	3.9	720	a	a		4.1	720	2.150	56.6
4	7.2	615	2.101	73.3	11	7.0	670	2.120	66.7
	5.6	615	2.101	75.0		5.5	670	2.120	66.7
	2.1	615	2.101	75.0		4.1	670	2.120	66.7
	1.2	615	2.101	75.0		2.5	b	a	a
5	7.0	610	2.114	75.0	12	7.0	640	2.118	73.8
	5.0	610	2.113	75.0		5.3	640	2.118	73.3
	3.5	610	2.113	75.0		3.8	640	2.118	73.3
	1.4	610	2.113	75.0		2.5	b	a	a
6	7.5	620	2.114	71.0	13	7.1	645	2.114	73.7
	6.0	650	2,151	56.7		5.3	640	2.118	73.8
	5.0	710	2.144	56.0		3.7	645	2.113	76.6
	4.3	710	2.152	5.83		2.3	b	a	a
7	7.1	635	2.120	67.7					
	4.7	635	2.123	70.0					
	3.7	635	2.123	71.0					
	2.0	b	a	a					

[a]Four-line ESR profile absent; [b]the d-d band absent.

commensurate with Cu(II) complexes; in the pH range 6-5, a five-line pattern is obtained, at still lower pHs (< 5) a four-line pattern with change in g_{iso} and A_{iso} values appears. The change of g_{iso} and A_{iso} values, from 2.120 and 70 G respectively at neutral pH to 2.150 and 55 G at pH < 5, suggests formation of different species at low pHs. The appearance of five-line pattern in the pH range 6-5 is due to the of presence of both protonated and neutral species. Similar ESR spectral changes have been observed for bis(α-amino acidato)copper(II) complexes also and were attributed to formation of $[CuL]^+$ species at lower pHs.

The bridged complexes do not exhibit change in g_{iso} and A_{iso} values on lowering pH, indicating absence of change in geometry accompanying the pH lowering. Besides, the complexes are more stable towards decomplexation than the unbridged complexes as evidenced by the observation of four-line ESR pattern at a pH, as low as 2. Electronic spectra also exhibit the d-d band at low pHs (ca. up to pH 2.0). These observations reveal that the bridged complexes are more stable towards protonation followed by decomplexation in comparison to the unbridged complexes. The enhanced stability is attributable to the additional chelation present in the bridged complexes. Representative ESR spectra of the two types of complexes at various pHs are shown in Figure 3.3 and data collected in Table 2.2.

3.4.3 Electrochemical data

CV and DPV data were collected for the analytically pure complexes in aqueous media at the dissolution pH (ca. 7.0). Experimental procedure is given in Section 2.3. CV and DPV pro-

files of all complexes except those of **4**, **5** and **11** were similar as shown in Figure 3.4. The experimental observations made for the complexes complexes **1-3**, **6-10**, **12** and **13** can be summarized as follows:

(i) only one reduction peak (C) appears in the first forward scan, the peak potential varies for each complex and the value is in the range -0.25 to -0.33 V;

(ii) during the reverse scan an anodic peak (D) in the potential range -0.18 to -0.26 V and another oxidation peak at ca. 0.03 V appear;

(iii) a new cathodic peak (A) appears from the second scan onwards at -0.01 V;

(iv) the C-D peaks form a redox couple with a peak separation value, ΔE_p,(C,D) of ca. 60-70 mV and the A-B peaks form another redox couple with ΔE_p,(A,B) value ca. 30-40 mV;

(v) A-B redox couple does not appear, if the scan is reversed before the appearance of peak C (at -0.20 V);

(vi) holding the potential well past the peak C for one min and scanning back, heights of A-B peaks increase considerably while the effect on C-D peaks is marginal;

(vii) the peak potential values do not vary considerably at various scan rates.

The peak C which appears from the first scan onwards can be due to either the one-electron Cu(II) $\overset{1e}{\rightleftharpoons}$ Cu(I) process or the two-electron Cu(II) $\overset{2e}{\rightleftharpoons}$ Cu(0) process. If it is due to the one-electron reduction, the oxidation peak D, which appears on reversing the scan, with ΔE_p,(C,D) value ca. 60 mV can be explained to

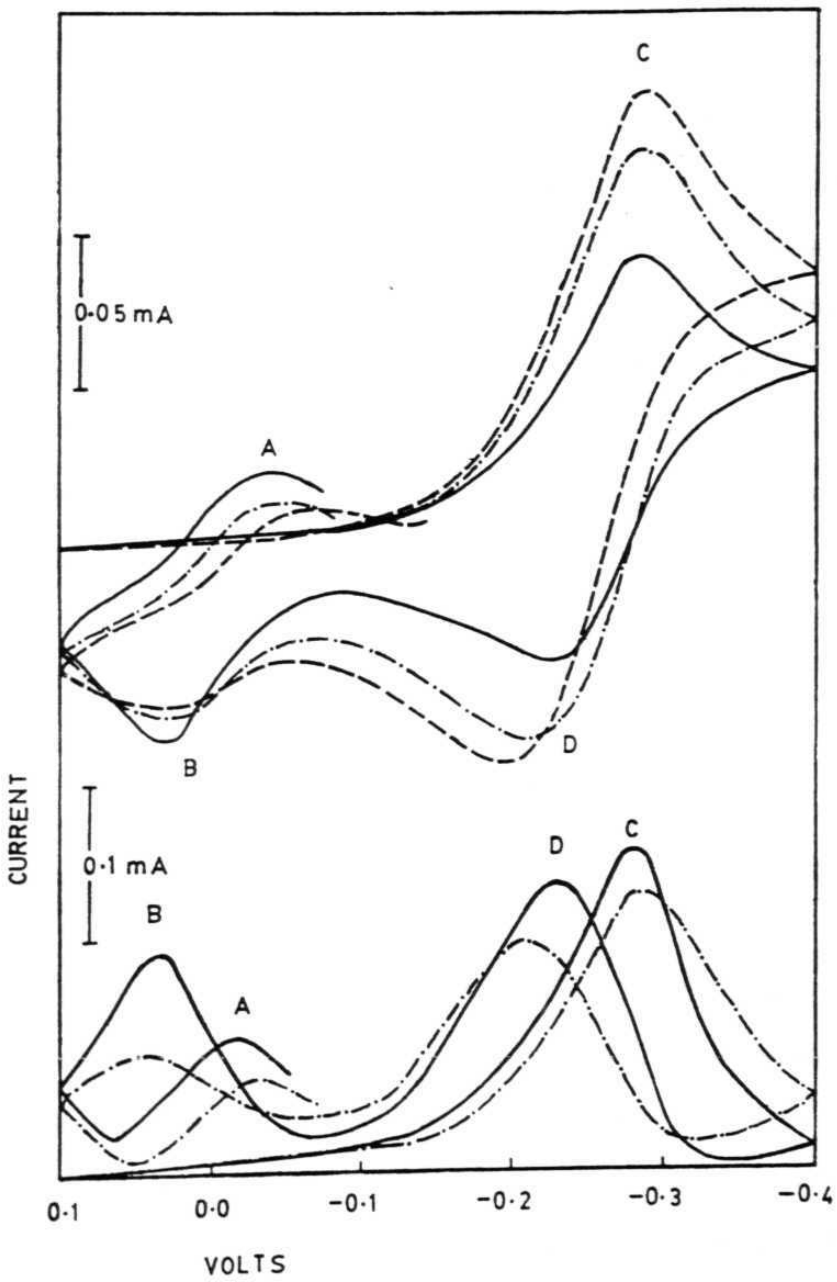


Figure 3.4. CV and DPV profiles of the complex **3** at various scan rates: 0.010 V/s (——); 0.020 V/s (—·—); 0.050 V/s (---).

arise from the corresponding oxidation i.e. the electrochemical process should involve Cu(I) intermediate species. The observation of A-B redox couple having ΔE_p value ca. 30 mV indicates clearly that this is not a one-electron process and can be a two-electron process. The potential at which the process occurs (ca. +0.01 V) is comparable to the Cu(II)/Cu(0) potential of free Cu(II) ions in aqueous media. Therefore, the A-B peaks must be due to Cu(II)(aq)/Cu(0)(Hg) redox couple, which necessitates the presence of Cu(0)(Hg). As it could be seen from the observations presented above, the complexes do not show the A-B peaks if the potential scan is reversed at -0.20 V, i.e. before the appearance of peak C which shows that the electrochemically produced Cu(I) species undergoes partial decomposition before getting oxidized to Cu(II) complex species on the reverse scan into Cu(II)(aq) ions and Cu(0)(Hg). Based on these arguments, the electrochemical processes can be presented as follows:

$$Cu(II) \underset{}{\overset{1e}{\rightleftharpoons}} Cu(I) \qquad (3.1)$$

$$2Cu(I) \xrightarrow{\text{Chemical reaction}} Cu(II)(aq) + Cu(0)(Hg) \qquad (3.2)$$

$$Cu(0)(Hg) \overset{2e}{\rightleftharpoons} Cu(II)(aq) \qquad (3.3)$$

The ΔE_p value is close to 60 mV and $-i_c/i_a$ ca. 1 (Table 3.3) for the C-D peaks supporting the mechanism. Similar electrochemical behaviour has been observed for the parent bis(α-amino acidato)-copper(II) complexes and a few Cu(II)-dipeptide complexes.[27,28] The complexes **4** and **5** exhibit different cyclic voltammetric behaviour, the major observations are as follows:

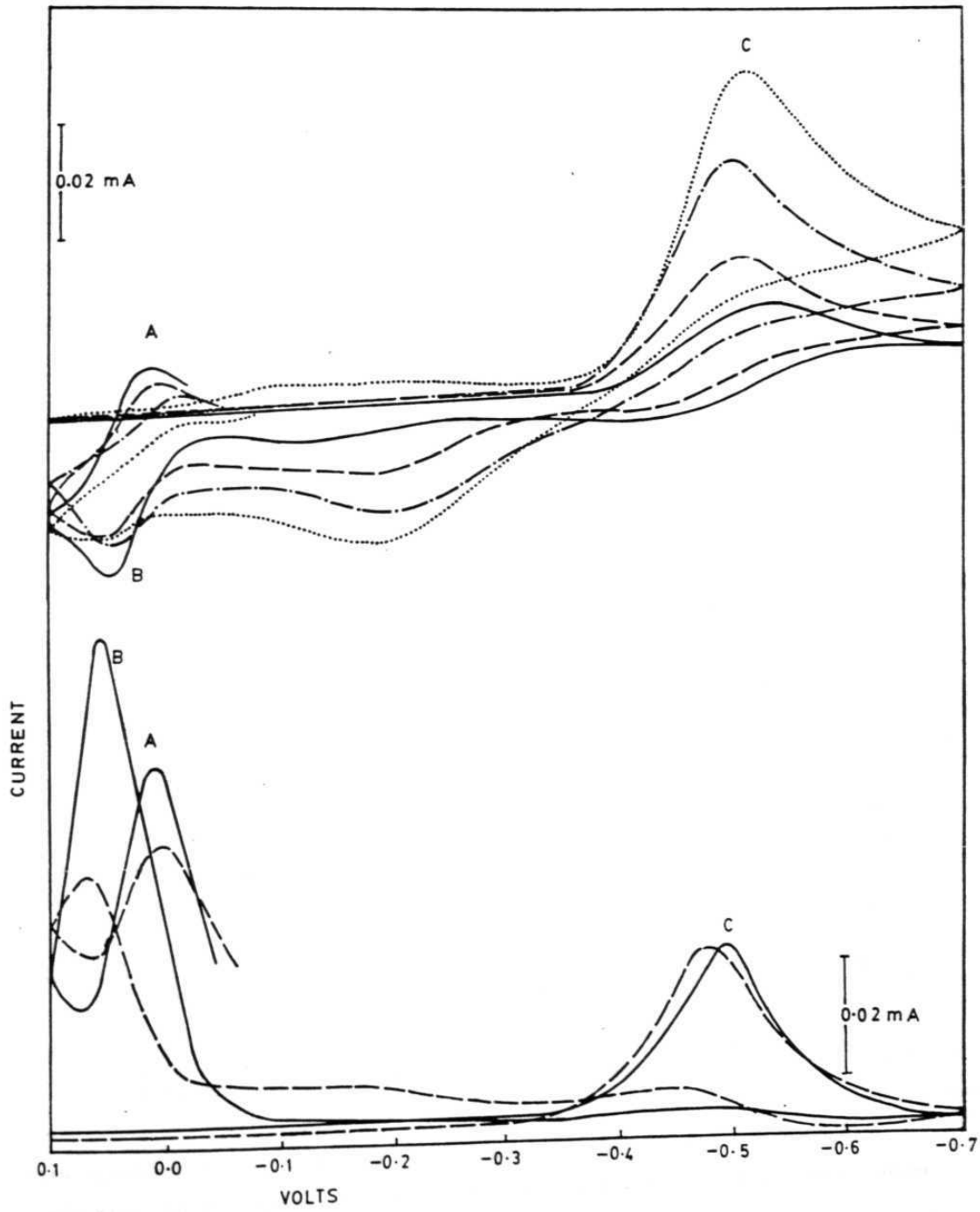


Figure 3.5. CV and DPV profiles of the complex **4** at various scan rates: 0.010 V/s (——); 0.020 V/s (---); 0.050 V/s (—·—); 0.100 V/s (·····).

Table 3.3. Cyclic voltammetric data of the complexes 1-13 at the dissolution pH in aqueous media at different scan rates.

Complex	Scan rate (V/s)	E_p(V)				ΔE_p(C,D) (V)	$E_{\frac{1}{2}}$(C,D) (V)	$-i_c/i_a$ (C,D)
		A[a]	B	C	D			
1	0.01	-0.03	0.02	-0.27	-0.21	0.06	-0.240	1.00
	0.02	-0.04	0.03	-0.27	-0.21	0.06	-0.240	1.00
	0.05	-0.05	0.03	-0.28	-0.19	0.09	-0.235	1.04
2	0.01	-0.02	0.04	-0.26	-0.20	0.06	-0.230	1.00
	0.02	-0.02	0.04	-0.26	-0.20	0.06	-0.230	1.00
	0.05	-0.02	0.06	-0.26	-0.18	0.18	-0.220	1.06
3	0.01	-0.03	0.03	-0.29	-0.23	0.06	-0.260	0.93
	0.02	-0.03	0.03	-0.29	-0.22	0.07	-0.255	0.96
	0.05	-0.03	0.03	-0.30	-0.21	0.09	-0.255	0.96
4	0.01	0.01	0.04	-0.51	b	--	--	--
	0.02	0.01	0.04	-0.51	b	--	--	--
	0.05	-0.01	0.04	-0.50	b	--	--	
5	0.01	-0.01	0.02	-0.53	b	--	--	
	0.02	-0.01	0.02	-0.53	b	--	--	
	0.05	-0.01	0.02	-0.53	b	--	--	
6	0.01	-0.01	0.03	-0.27	-0.21	0.06	-0.240	1.07
	0.02	-0.02	0.02	-0.27	-0.21	0.06	-0.240	1.03
	0.05	-0.02	0.02	-0.27	-0.20	0.07	-0.235	1.03
7	0.01	-0.02	0.03	-0.28	-0.22	0.06	-0.250	1.00
	0.02	-0.04	0.03	-0.28	-0.22	0.06	-0.250	1.06
	0.05	-0.04	0.03	-0.29	-0.21	0.08	-0.250	1.04
8	0.01	-0.03	0.03	-0.25	-0.19	0.06	-0.220	1.00
	0.02	-0.02	0.03	-0.26	-0.19	0.07	-0.225	1.05
	0.05	-0.02	0.03	-0.26	-0.17	0.09	-0.235	1.00
9	0.01	-0.01	0.03	-0.25	-0.19	0.06	-0.220	1.00
	0.02	-0.02	0.03	-0.26	-0.19	0.07	-0.225	1.05
	0.05	-0.02	0.03	-0.26	-0.17	0.09	-0.235	1.00
10	0.01	-0.04	0.02	-0.27	-0.21	0.06	-0.240	1.00
	0.02	-0.04	0.02	-0.28	-0.20	0.08	-0.240	1.00
	0.05	-0.05	0.02	-0.28	-0.19	0.09	-0.235	1.03
11	0.01	-0.02	0.05	-0.30 (-0.41)	-0.24 (-0.35)	0.06 (0.06)	-0.270 (-0.330)	0.96 (1.00)
	0.02	-0.02	0.05	-0.30 (-0.41)	-0.23 (-0.35)	0.07 (0.06)	-0.265 (-0.330)	0.92 (1.00)
	0.05	-0.02	0.06	-0.30 (-0.41)	-0.23 (-0.35)	0.07 (0.06)	-0.265 (-0.330)	1.00 (1.00)
12	0.01	0.00	0.04	-0.34	-0.29	0.05	-0.315	1.00
	0.02	0.00	0.05	-0.34	-0.28	0.06	-0.310	1.00
	0.05	-0.02	0.05	-0.35	-0.27	0.08	-0.310	1.00
13	0.01	0.00	0.03	-0.33	-0.27	0.06	-0.300	1.00
	0.02	-0.03	0.04	-0.34	-0.26	0.08	-0.290	1.00
	0.05	-0.03	0.04	-0.34	-0.25	0.09	-0.295	0.96

[a]Peak appears only in the second and subsequent scans; [b]peak not observed.

Values given in parentheses for the complex 11 correspond to the C' and D' peaks.

(i) during the first forward scan a reduction peak (C) appears at a more negative potential (-0.51 V for the complex **4** and -0.53 V for the complex **5**);

(ii) on the reverse scan, the corresponding oxidation peak (D) does not appear, however the two-electron oxidation peak, B appears;

(iii) from the second scan onwards a new reduction peak A appears forming a reversible two-electron redox couple (A-B) similar to the rest of the complexes;

(iv) on reversing the scan before the appearance of peak C the A-B peaks do not appear;

(v) if the potential is held at a potential well past peak C and scanned back, the heights of A-B peaks increase considerably.

Cyclic voltammetric profiles of complex **4** are shown in Figure 3.5. The CV profiles and the observations given above reveal that these complexes undergo irreversible one-electron reduction dissimilar to the complexes discussed before. However, the redox behaviour of these complexes could be explained by the same electrode mechanism except that the first step (equation 3.1) is irreversible implying that the Cu(I) intermediate species is very unstable.

The complex **11** exhibits a unique cyclic voltammetric behaviour. Two overlapping reduction peaks C and C′ appear for this complex at -0.30 and -0.41 V during the first forward scan and two oxidation peaks D′ and D appear at -0.35 and -0.24 V on the reverse scan. The observation of another oxidation peak (B)

at +0.03 V and a new reduction peak (A) at -0.01 V from the second scan onwards is similar to the other complexes of this investigation, which exhibit reversible Cu(II)/Cu(I) redox process. The appearance of the two overlapping redox couples C-D and C'-D' requires special mention. CV profile of the complex is shown in Figure 3.6.

A survey of literature on the redox properties of Cu(II) complexes reveals that, no mono nuclear Cu(II) complex is reported to exhibit similar redox behaviour. However, a wealth of binuclear Cu(II) complexes have been found to exhibit such a redox behaviour,[29-33] where the Cu(II) nuclei undergo sequential one-electron reduction at two different potentials involving a Cu(I)-Cu(II) intermediate species. In several instances the involvement of Cu(I)-Cu(II) species has been convincingly established.[29,31] It could also be noticed from the literature survey that mainly weakly interacting binuclear Cu(II) complexes exhibit the sequential one-electron reduction process,[7,29,31] while the strongly coupled systems show single two-electron reduction also.[38]

Since the complex **11** is mono nuclear, if the 'unique' redox behaviour is due to interaction of two Cu(II) nuclei, it can be only possible through intermolecular interaction. Interestingly, the complex has been recently suggested to possess weak intermolecular interaction on the basis of its inability to quench superoxide[34] while few other ethene-bridged-α-amino acidato-copper(II) complexes have been found to quench superoxide. The 'unique' redox behaviour of the complex can be

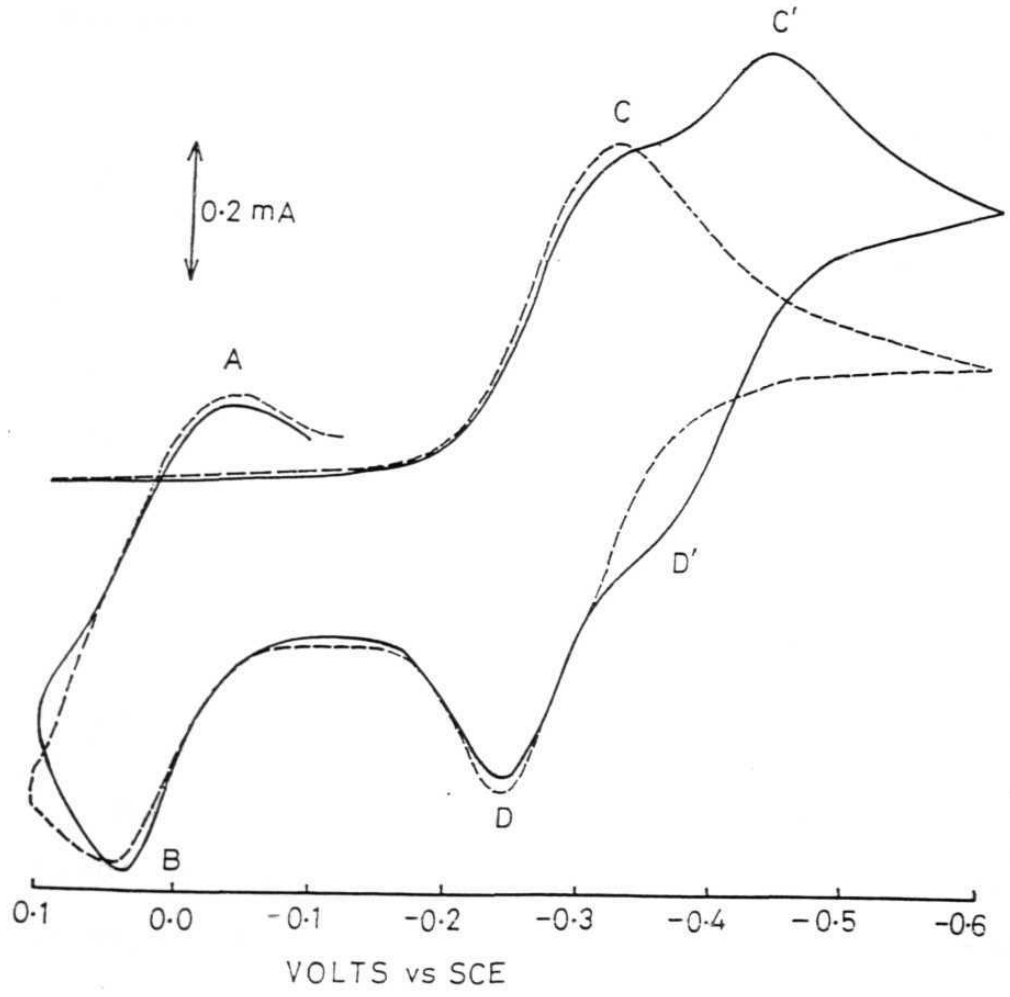


Figure 3.6. CV profiles of the complex **11** at the scan rate 0.050 V/s in aqueous media at pH 7.2 in the absence of ammonia (——) and in the presence of ammonia (---).

explained on the basis of weak intermolecular interaction of the metal atoms. To establish the validity of this conclusion, the following experiment was carried out:

Cyclic voltammogram was recorded for this complex in presence of ammonia (1:2, complex to ammonia ratio, at pH 7.0). It was expected that ammonia being a good donor might enter the apical coordination sites, thereby breaking the dimeric nature of the complex.

CV profile in the presence of ammonia exhibits only C-D and A-B couples as expected as shown in Figure 3.6. The redox couple C′-D′ does not appear. The following electrode mechanism is proposed to explain the redox behaviour of the complex (similar to the mechanism of the intramolecuarly coupled Cu(II) dinuclear complexes):

$$Cu(II)....Cu(II) \overset{1e}{\rightleftharpoons} Cu(I)....Cu(II) \qquad (3.4)$$

$$Cu(I)....Cu(II) \overset{1e}{\rightleftharpoons} Cu(I)....Cu(I) \qquad (3.5)$$

$$Cu(I)....Cu(I) \xrightarrow{\text{Chemical reaction}} Cu(II)(aq) + Cu(0)(Hg) \qquad (3.6)$$

$$Cu(0)(Hg) \overset{2e}{\rightleftharpoons} Cu(II)(aq) \qquad (3.3)$$

The equations 3.4, 3.5 and 3.3 explain the redox couples C-D, C′-D′ and A-B respectively. The equation 3.6 is a chemical reaction so it does not appear in the cyclic voltammogram.

As it could be seen from the Table 3.3, the Cu(II)/Cu(I) redox potential, $E_{\frac{1}{2}}$ (C,D) varies for each complex. For the unbridged complexes the value is in the range -0.23 to -0.25 V; for the complexes **7** and **8** which have a three-membered dimethylene-ether group bridging the nitrogens also exhibit $E_{\frac{1}{2}}$ (C,D) value

in the same range. The complexes **11-13** which have a comparatively short two-membered ethene group bridging the nitrogens, exhibit the value in the potential range -0.27 to -0.31 V while the complexes **4** and **5** which have a rigid pentamethylenediaza bridging group exhibit irreversible Cu(II)/Cu(I) reduction at the potentials -0.51 and -0.53 V respectively. The data can be presented in the following order of decreasing potential value:

Unbridged complexes, dimethyleneether bridged complexes > ethene-bridged complexes > > pentamethylenediaza bridged complexes.

Reversibility of the Cu(II)/Cu(I) process depends on the stability of the Cu(I) intermediate species, and the species is known to be stabilized by tetrahedral or pseudo-tetrahedral environment around the metal ion. All the complexes are of the same CuN_2O_2 chromophore and nature of the coordinating groups does not vary much for these complexes. Therefore, the main factors which can influence the redox properties are the geometry of the complexes and flexibility of the ligand systems.[7-10] When the redox properties of the unbridged and bridged complexes are compared, it is obvious that the unbridged complexes can easily undergo distortion towards tetrahedral geometry in order to stabilize the Cu(I) intermediate species. The observation that the complexes with three-membered bridges exhibit $E_{\frac{1}{2}}$ (C,D) values similar to the unbridged complexes while the complexes with 2-membered bridges exhibit more negative $E_{\frac{1}{2}}$ (C,D) values for the Cu(II)/Cu(I) process shows that shortening of the bridging group restricts the distortion. The complexes **4** and **5** are shown to be

the most planar from the electronic spectral and ESR data. Higher planarity of the complexes explains the irreversibility of the Cu(II)/Cu(I) reduction process exhibited by these complexes. The inflexibility of the pentamethylenediaza bridging group may also be another reason.

The investigation on the present set of complexes demonstrates that the geometry of the complexes (as revealed from the λ_{max} values and ESR parameters) is reflected in their redox behaviour. More the planarity of the complexes, more negative is the Cu(II)/Cu(I) reduction potential, less stable is the Cu(I) intermediate species and less reversible is the redox process.

On lowering pH, two different types of electronic and ESR spectral behaviour have been observed for the complexes. The unbridged complexes produce various protonated species at lower pHs and $[CuL]^+$ species has been found to be predominant species at pH 4.5 whereas the bridged complexes do not exhibit any shift in λ_{max} value, so as to ascribe to any species formation. Therefore, it is useful to investigate the low pH cyclic voltammetric behaviour of all complexes.

The unbridged complexes exhibit the following changes on lowering pH: i) no considerable shift in both C-D and A-B couples observed; ii) the heights of peaks C and D decrease while that of A-B peaks increase; iii) peak A starts appearing from the first scan onwards; iv) at decomplexation pH (ca. 4) only the A-B peaks appear. The bridged complexes also exhibit decrease in peak heights of the C-D couple and increase in the peak heights

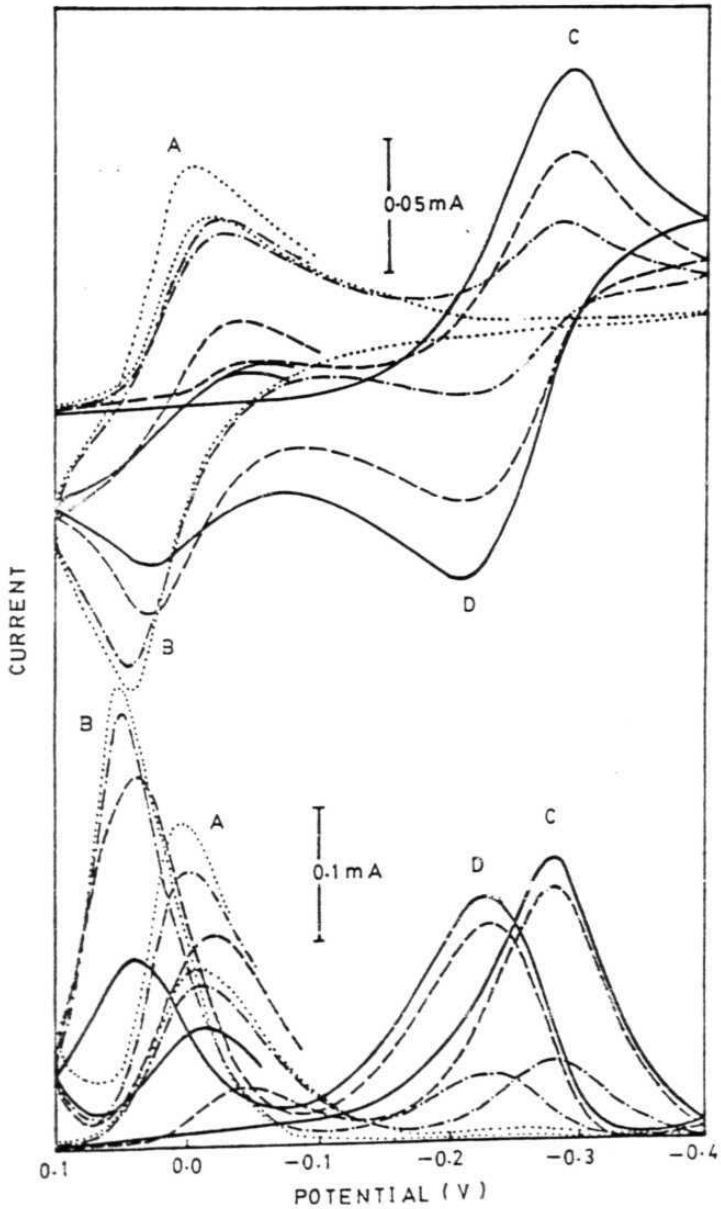


Figure 3.7. CV and DPV profiles of an unbridged complex, **3**, at scan rates 0.050 and 0.010 V/s respectively at various pHs: pH 7.3 (——); pH 5.5 (---); pH 4.4 (—·—·); pH 3.9 (·····).

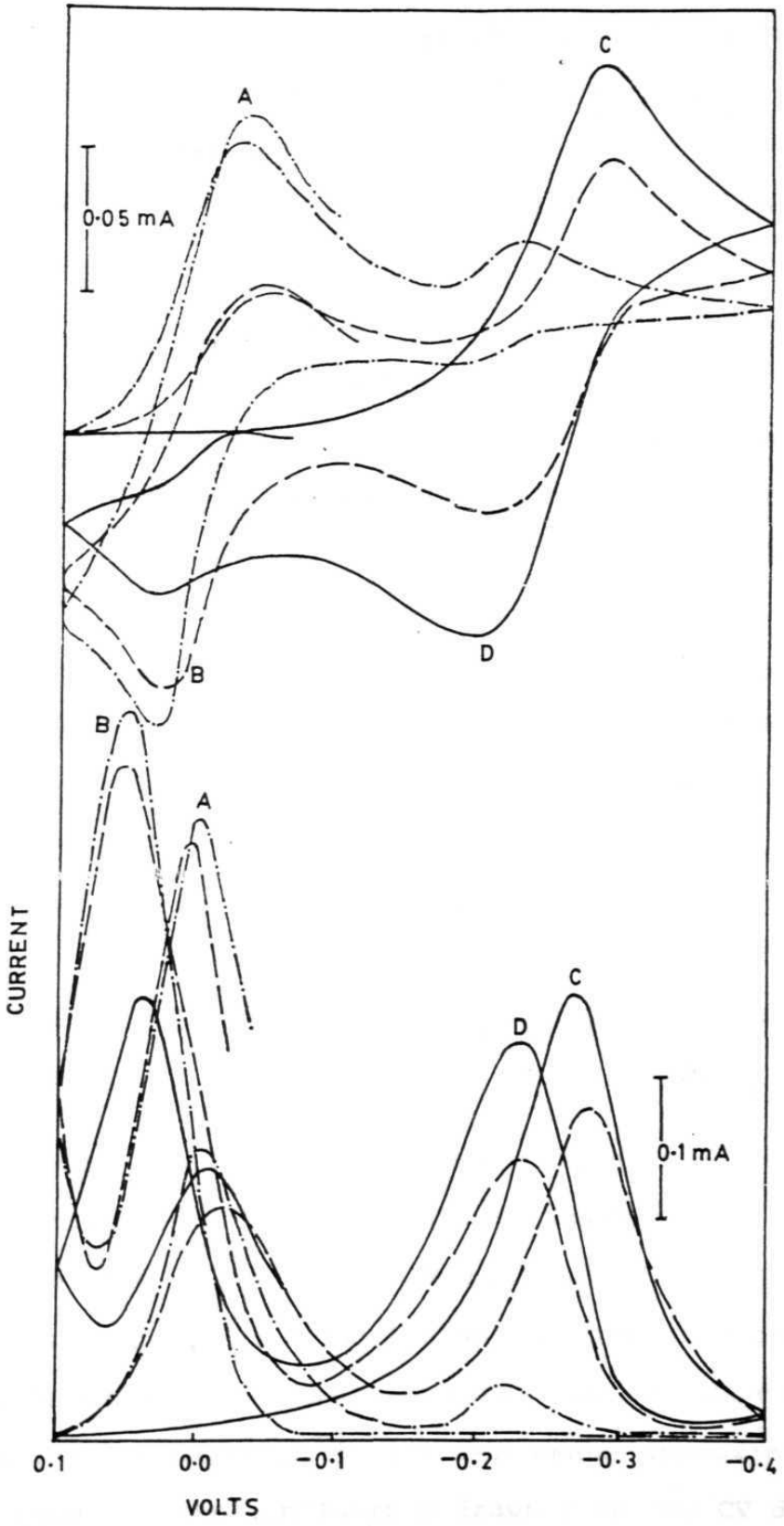


Figure 3.8. CV and DPV profiles of a bridged complex, **7**, at scan rates 0.010 and 0.050 V/s respectively at various pHs: pH 7.1 (——); pH 4.7 (---); pH 3.7 (—·—·).

of A-B couple. However, the complexes exhibit gradual shift of Cu(II))/Cu(I) redox potential towards less negative values. The complexes do not decompose until very low pH (ca. 2 for the complexes **7**, **8** and **11-13** and ca. 1 for the complexes **4** and **5**). Representative CV profiles for the unbridged and bridged complexes at various pHs are shown in Figures 3.7 and 3.8 respectively. CV data for all the complexes given in Table 3.4. The observations on the unbridged complexes reveal that only the bis complex species undergoes Cu(II)/Cu(I) redox process; the $[CuL]^+$ species undergo Cu(II)/Cu(0) redox process. For the bridged complexes though no electronic and ESR spectral changes could be detected at low pHs, the complexes do get protonated. The protonated species does not show change in geometry however the nature of ligands is affected, probably the protonation weakens the strength of ligand-metal bonds, effecting lowering of CFSE of the ligands and hence shift of Cu(II)/Cu(I) redox potential towards less negative values as is observed. Observations (iii) and (iv) indicate that at pH < 4, decomplexation occurs with the formation of Cu(II)(aq) ions. For the bridged complexes decomplexation occurs at pH < 2.

DPV data were obtained for all the complexes at the same experimental conditions as those of the CV experiments. The DPV data corroborate the CV results. Representative profiles are shown in Figures 3.4, 3.5, 3.7 and 3.8 and the DPV data presented in Table 3.5. The n value (number of electrons) calculated from the $W_{\frac{1}{2}}$ values (half peak-width[35]) for C-D peaks approximates to one, further supporting the conclusions drawn from the CV data.

Table 3.4. Cyclic voltammetric data of the complexes 1-13 at various pHs in aqueous media at the scan rate 20 mV/s.

Complex	pH	E_p(V)				i_p(μA)			
		A[a]	B	C	D	A[a]	B	C	D
1	7.1	-0.04	0.03	-0.27	-0.21	16	16	42	42
	5.9	-0.02	0.03	-0.27	-0.21	46	28	32	32
	4.8	-0.02	0.04	-0.26	-0.20	70	50	18	22
	4.1	-0.02	0.04	b	b	100	110	--	--
2	7.5	-0.02	0.04	-0.26	-0.20	24	24	40	40
	6.0	-0.03	0.04	-0.26	-0.19	32	34	34	34
	5.6	-0.03	0.04	-0.25	-0.19	50	54	22	20
	4.5	-0.02	0.05	b	b	120	120	--	--
3	7.3	-0.03	0.03	-0.29	-0.22	35	35	120	125
	5.5	-0.04	0.03	-0.29	-0.22	90	90	80	80
	4.4	-0.03	0.04	-0.29	-0.22	160	160	35	35
	3.9	-0.03	0.05	b	b	260	240	--	--
4	7.2	0.01	0.05	-0.51	b	14	12	24	--
	5.6	0.00	0.05	-0.46	b	24	20	30	--
	2.1	0.00	0.04	-0.26	b	40	36	18	--
	1.2	-0.02	0.03	-0.12	b	46	40	10	--
5	7.0	-0.01	0.02	-0.62	b	8	8	26	--
	5.0	-0.01	0.02	-0.54	b	14	18	24	--
	3.5	-0.01	0.02	-0.34	b	26	30	20	--
	1.4	-0.01	0.02	-0.18	b	42	44	12	--
6	7.5	-0.02	0.02	-0.27	-0.21	22	10	62	60
	6.0	-0.02	0.04	-0.26	-0.21	50	56	30	30
	5.0	-0.01	0.05	-0.25	-0.20	72	90	10	14
	4.3	0.00	0.05	b	b	110	110	--	--
7	7.1	-0.04	0.03	-0.28	-0.22	25	24	72	62
	4.7	-0.02	0.04	-0.28	-0.22	90	85	90	90
	3.7	-0.01	0.05	-0.21	b	150	165	25	--
	2.0	0.00	0.04	b	b	220	200	--	--
8	7.0	-0.03	0.03	-0.25	-0.19	12	12	30	30
	5.9	-0.03	0.03	-0.25	-0.19	22	24	28	28
	5.1	-0.03	0.04	-0.24	-0.18	40	42	18	20
	4.0	-0.3	0.04	b	b	84	96	--	--
9	7.5	-0.02	0.03	-0.26	-0.19	16	18	42	44
	5.9	-0.02	0.04	-0.24	-0.19	66	66	14	26
	4.9	-0.02	0.04	-0.23	-0.17	82	94	10	20
	4.2	-0.03	0.05	b	b	100	120	--	--
10	7.0	-0.04	0.02	-0.28	-0.20	44	24	40	40
	6.1	-0.04	0.03	-0.27	-0.20	44	32	38	38
	4.7	-0.04	0.04	-0.27	-0.21	52	64	18	22
	4.1	-0.03	0.04	b	b	120	126	--	--
11	7.0	0.00	0.05	-0.30 (-0.41)	-0.23 (-0.34)	24	40	24 (24)	26 (24)
	5.5	0.01	0.06	-0.29 (-0.40)	-0.23 (-0.33)	34	50	20 (18)	16 (18)
	4.1	0.01	0.06	-0.28 (-0.39)	-0.21 (-0.33)	50	62	16 (14)	10 (14)
	2.6	0.00	0.06	b	b	65	110	--	--

12	7.0	0.00	0.05	-0.34	-0.28	16	18	36	36
	5.3	0.00	0.05	-0.34	-0.28	16	18	36	36
	3.8	-0.04	0.03	-0.15	b	20	32	24	--
	2.5	-0.03	0.04	b	b	34	40	--	--
13	7.1	-0.03	0.04	-0.33	-0.26	6	8	36	36
	4.4	-0.02	0.04	-0.32	-0.26	14	22	16	14
	3.7	-0.02	0.04	-0.12	b	32	48	10	--
	2.3	-0.05	0.05	b	b	50	48	--	--

[a]Peak appeared from the second scan onwards; [b]peak absent.

Values given in parentheses for the complex 11 correspond to the C' and D' peaks.

Table 3.5. Differential pulse voltammetric data of the complexes 1-13 in aqueous media at various pHs at the scan rate 0.010 V/s.

Complex	pH	E_p(V)				$W_{\frac{1}{2}}$(mV)		n[a]	
		A[b]	B	C	D	C	D	C	D
1	7.3	-0.03	0.03	-0.27	-0.21	95	100	0.95	0.95
	5.9	-0.04	0.03	-0.27	-0.21	95	90	1.00	1.00
	4.1	-0.03	0.04	c	c	--	--	--	--
2	7.5	-0.03	0.04	-0.25	-0.20	100	100	0.90	0.90
	6.0	-0.03	0.04	-0.25	-0.19	100	100	0.90	0.90
	4.5	-0.04	0.04	c	c	--	--	--	--
3	7.3	-0.03	0.03	-0.29	-0.23	100	100	0.90	0.90
	5.5	-0.03	0.03	-0.29	-0.22	95	95	0.95	0.95
	3.9	-0.02	0.04	c	c	--	--	--	--
4	7.2	-0.03	0.04	-0.50	c	130	--	0.70	--
	5.6	-0.03	0.05	-0.45	c	95	--	0.95	--
	1.2	-0.03	0.03	-0.11	c	95	--	0.95	--
5	7.0	-0.01	0.02	-0.53	c	130	--	0.70	--
	5.0	-0.01	0.02	-0.42	c	95	--	0.95	--
	1.4	-0.01	0.02	-0.16	c	95	--	0.95	--
6	7.5	-0.02	0.03	-0.27	-0.21	90	95	1.00	0.95
	6.0	-0.02	0.04	-0.26	-0.21	90	90	1.00	1.00
	4.3	0.00	0.05	c	c	--	--	--	--
7	7.1	-0.03	0.03	-0.28	-0.22	90	95	1.00	0.95
	4.6	-0.03	0.03	-0.28	-0.22	90	95	1.00	0.95
	2.0	0.00	0.03	c	c	--	--	--	--
8	7.0	-0.03	0.03	-0.24	-0.17	110	110	0.82	0.90
	5.9	-0.03	0.03	-0.24	-0.17	100	100	0.90	0.90
	4.0	-0.04	0.04	c	c	--	--	--	--
9	7.5	-0.03	0.04	-0.25	-0.19	120	110	0.75	0.82
	5.9	-0.03	0.05	-0.25	-0.19	90	110	1.00	0.82
	4.2	-0.03	0.05	c	c	--	--	--	--
10	7.0	-0.02	0.03	-0.27	-0.21	110	110	0.82	0.82
	6.1	-0.03	0.03	-0.27	-0.21	95	100	0.95	0.90
	4.1	-0.03	0.03	c	c	--	--	--	--

Table. 3.5 (Contd.)

11	7.0	-0.02	0.04	-0.30 (-0.41)	-0.25 (-0.36)	100 (100)	100 (100)	0.90 (0.90)	0.90 (0.90)
	5.5	-0.03	0.06	-0.29 (-0.40)	-0.24 (-0.35)	90 (95)	90 (90)	1.00 (0.95)	1.00 (1.00)
	2.6	-0.03	0.05	c	c	--	--	--	--
12	7.0	-0.03	0.04	-0.34	-0.29	100	110	0.90	0.82
	5.3	-0.02	0.04	-0.34	-0.28	90	90	1.00	1.00
	2.5	-0.03	0.04	c	c	--	--	--	--
13	7.1	-0.03	0.04	-0.33	-0.27	95	100	0.95	0.90
	4.4	-0.03	0.04	-0.32	-0.26	95	100	0.95	0.90
	2.3	-0.03	0.06	c	c	--	--	--	--

[a] $W_{\frac{1}{2}} = 90.4/n$; [b] peak appeared from the second scan onwards; [c] peak absent.

3.5 Conclusions

The Cu(II) complexes of DL-serine and DL-threonine undergo condensation reaction with formaldehyde and acetaldehyde yielding products containing oxazolidine rings. Electronic and ESR spectral investigation on these new products together with some known products reveal variation of geometry for the complexes. At low pHs formation of $[CuL]^+$ is evident for the unbridged complexes while formation of such protonated species does not exhibit any spectral changes for the bridged complexes. This difference arises from the greater stability of chelates. Except for the doubly bridged complexes and one complex with weak intermolecular interaction all complexes exhibit similar redox behaviour. The electrochemical behaviour is commensurate with a three-step electrode mechanism. The Cu(II)/Cu(I) reduction potential of the complexes follows the order unbridged complexes > bridged complexes > doubly bridged complexes. The electrochemical irreversibility of the doubly bridged complexes arises from the instability of the electrochemically generated Cu(I) species in more planar geometry. The unique redox behaviour exhibited by an intermolecularly interacting complex is explained on the basis of a different electrode mechanism involving a Cu(II)-Cu(I) intermediate species.

3.6 References

1. J.P. Aune, P. Maldonado, G. Larcheres and M. Pierrot, J.Chem. Soc. Chem. Commun., 1970, 1351.
2. J.R. Brush, R. Magee, M.J. O'Connor, S.B. Teo, R.J. Geue and M.R. Snow, J. Am. Chem. Soc. 1973, **95**, 2034.
3. S.B. Teo and S.G. Teoh and M.R. Snow, Inorg. Chim. Acta 1984, **91**, L17.
4. S.B. Teo, S.G. Teoh and M.R. Snow, ibid. 1984, **85**, L1.
5. S.B. Teo, S.G. Teoh and M.R. Snow, ibid. 1985, **107**, 211.
6. S.B. Teo, C.-H. Ng and E.R.T. Tiekink, ibid. 1989, **163**, 129.
7. G.S. Patterson and R.H. Holm, Bioinorg. Chem. 1975, **4**, 257.
8. H. Yokoi A.W. Addison, Inorg. Chem. 1977, **16**, 1341.
9. U. Sakaguchi and A.W. Addison, J. Chem. Soc. Dalton Trans. 1979, 600.
10. R.D. Beremen, J.R. Dorfman, J. Bordner, D.P. Rillema, P. McCarthy and D. Shields, J. Inorg. Bioinorg. Chem. 1982, **16**, 47.
11. Y. Murakami, Y. Matsuda and K. Sakata, Inorg. Chem. 1971, **10**, 1734.
12. H. Yokoi, Bull. Chem. Soc. Jpn. 1974, **47**, 3037.
13. F.G. Herring, D.J. Patmore and A. Storr, J. Chem. Soc. Dalton Trans. 1975, 711.
14. R.C. Rosenberg, C.A. Root, P.K. Bernstein and H.B. Gray, J. Am. Chem. Soc. 1975, **97**, 2092.
15. J.A. Fee, Struct. Bonding (Berlin) 1975, **23**, 1.
16. A.S. Brill, 'Transition Metals in Biochemistry', Springer-Verlag, New York, 1977, Chap. 3.
17. R. Osterberg, Coord. Chem. Rev. 1974, **12**, 309.

18. H. Beinert, ibid. 1977, **15**, 119.

19. R. Malkin and B.G. Malmstrom, Adv. Enzymol. Relat. Areas Mol. Biol. 1970, **33**, 177.

20. R. Malkin, 'Inorg. Biochemistry', Ed., G.L. Eichhorn, Elsevier, Amsterdam, 1975, Vol. 2, p. 689.

21. E.D. Bergmann, Chem. Rev. 1953, **53**, 309; F. Bergel and M.A. Peutherer, J. Chem. Soc. 1964, 3965; Z. Badr, R. Bonnet, W. Klyne, R.J. Swan and J. Wood, J. Chem. Soc. (C) 1966, 2047.

22. B.R. McGarvey, 'Transition Metal Chemistry', Ed., R.L. Carlin Marcel Dekker, New York, 1967, Vol. 3, p. 89.

23. S. Antosik, A.M.D. Brown, A.A. McConnel and A.L. Porte, J. Chem. Soc. (A) 1969, 545.

24. H. Yokoi, M. Sai and T. Isobe, Bull. Chem. Soc. Jpn. 1969, **42**, 2232; ibid. 1970, **43**, 1078.

25. R.L. Belford, M. Calvin and G. Belford, J. Chem. Phys. 1957, **26**, 1165.

26. J.K. Beattie, D.J. Fensom and H.C. Freemen, J. Am. Chem. Soc. 1976, **98**, 500.

27. G. Thomas and P.S. Zacharias, Polyhedron 1984, **3**, 861; ibid. 1985, **4**, 811.

28. G. Thomas and P.S. Zacharias, Transition Met. Chem. 1984, **9**, 377.

29. A.W. Addison, J. Inorg. Chem. Nucl. Lett. 1979, **12**, 899; L.J. Wilson and D.N. Hendrickson, Inorg. Chem. 1978, **17**, 1834.

30. R.R. Gagne, C.A. Koval, T.J.Smith and M.C. Cimoline, J. Am. Chem. Soc. 1979, **101**, 4571; R.R. Gagne, C.A. Hamann, W.R. Thies and A.K. Shiemke, ibid. 1981, **103**, 4073.

31. R.C. Long and D.N. Hendrickson, ibid. 1983, **105**, 1513.

32. S.K. Mandal, B. Adhikari and K. Nag, J. Chem. Soc. Dalton Trans. 1986, 1175; S.K. Mandal, L.K. Thompson, M.J. Newlands and E.J. Gabe, Inorg. Chem. 1989, **28**, 3707; A.M. Bond, M. Haga, I.S. Creece, R. Robson and J.C. Wilson, ibid. 1989, **28**, 559.

33. D.E. Fenton and R.L. Lintvedt, J. Am. Chem. Soc. 1978, **100**, 6367.

34. B.M. Katz and V.I. Stenberg, Polyhedron 1985, **4**, 2031.

35. A.J. Bard and L.R. Faulkner, 'Electrochemical Methods, Fundementals and Applications', Wiley, New York, 1980, p.190.

CHAPTER IV

STEREOSPECIFIC REACTIONS OF COPPER(II) COMPLEXES OF SERINE AND THREONINE WITH FORMALDEHYDE

4.1 Abstract

Condensation reactions of $Cu(L\text{-ser})_2$ and $Cu(L\text{-thr})_2$ with formaldehyde at pH 4.5 yield two new optically active products, namely, bis[L-(oxazolidine-4-carboxylato)]copper(II) monohydrate, **14** and bis[L-(N-hydroxymethyl-5-methyloxazolidine-4-carboxylato)] copper(II) dihydrate, **15**, respectively. $Cu(D\text{-ser})_2$ and $Cu(D\text{-thr})_2$ also undergo similar reactions. The new products are different from the products obtained from $Cu(DL\text{-ser})_2$ and $Cu(DL\text{-thr})_2$. A mechanism has been suggested to explain the stereospecificity of these reactions. Condensation reaction of $Cu(\beta\text{-ala})_2$ with formaldehyde and ammonia at pH 8.5 yields a new product, [3N,7N-(1,3,5,7-tetraazabicyclo[3.3.1]nonyl)di-3-propionato]copper(II),

16. The ESR spectral data reveal similar geometry for all the new complexes, **14-16**, while CV and DPV data indicate distinct irreversible Cu(II)/Cu(I) reduction process for the complex **16**, which has been attributed to rigidity of the pentamethylenediaza-bridged ligand system.

4.2 Introduction

Synthesis of optically inactive, racemic mixture of threonine by the metal assisted reaction of glycine with acetaldehyde was first reported by Akabori.[1] Shortly afterwards, the condensation of optically active $[Co(en)_2(gly)]^{2+}$ with acetaldehyde was shown to form optically active threonine streoselectively with low overall yield.[2] It was also shown that the optical yield can be improved by careful control of the reaction condition.[3] 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 allothreonine (2S.3S) while use of Λ-(-)-$[Co(en)_2(gly)]^{2+}$ was found to yield 2R-threonine preferentially. The mechanism of the reaction is generally accepted to involve a carbanion intermediate, formed by the base catalyzed removal of the methylene proton. This has been directly supported by proton NMR observations[4] of H-D exchange of glycinate-methylene protons in alkaline D_2O and by comparison of the rate of exchange and ligand racemization in complexes of L-alanine and L-valine.[5] To explain the stereoselectivity of the reactions of Λ-(+)-$[Co(en)_2(gly)]^{2+}$ and Λ-(-)-$[Co(en)_2(gly)]^{2+}$ with acetaldehyde, intrinsic difference in the reactivities of the two pro-chiral glycinate-methylene hydrogens was suggested.[6] In general such stereoselec-

tive reactions are less facile for the Cu(II) complexes due to their labile nature.[7] However the Cu(II) complexes of optically inactive DL-alanine and optically active L-alanine undergo condensation reaction with formaldehyde and ammonia to yield different products.[8,9] In order to understand the mechanism of the condensation reaction and to check if the Cu(II) complexes of serine and threonine show any such stereospecificity, their reactions with formaldehyde and acetaldehyde have been investigated. Condensation reaction of an optically inactive complex, $Cu(\beta\text{-ala})_2$, is also included in the investigation.

The products obtained have been characterized and their electronic spectral, ESR and redox properties investigated. The results obtained are presented and discussed in the following sections.

4.3 Experimental

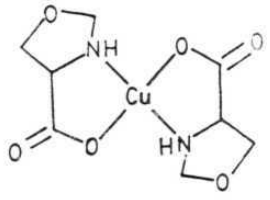
Various reactions of $Cu(L\text{-ser})_2$ and $Cu(L\text{-thr})_2$ were carried out as described in Section 2.2. General techniques employed to characterize and study the products are presented in Section 2.3.

4.4 Results and discussion

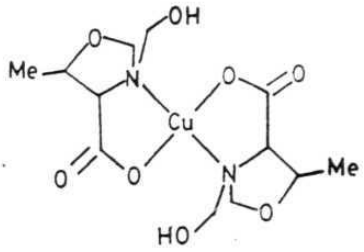
4.4.1 Reactions

The reactions of $Cu(L\text{-ser})_2$ and $Cu(L\text{-thr})_2$ with formaldehyde at pH 4.5 yield two new complexes **14** and **15** respectively. IR spectra of these complexes exhibit a set of three closely spaced bands in the 1200-1080 cm^{-1} region characteristic of oxazolidine rings. The complex **14** exhibits bands at 3500 and 3250 cm^{-1} indicating the presence of -OH and >NH groups; the complex **15** does

not exhibit the band at 3250 cm^{-1} showing the absence of >NH group. These complexes on decomposition in acid medium by treatment of H_2S yield the parent L-amino acids. These data together with the analytical data (Table 2.2) support the following structures for the complexes:



14

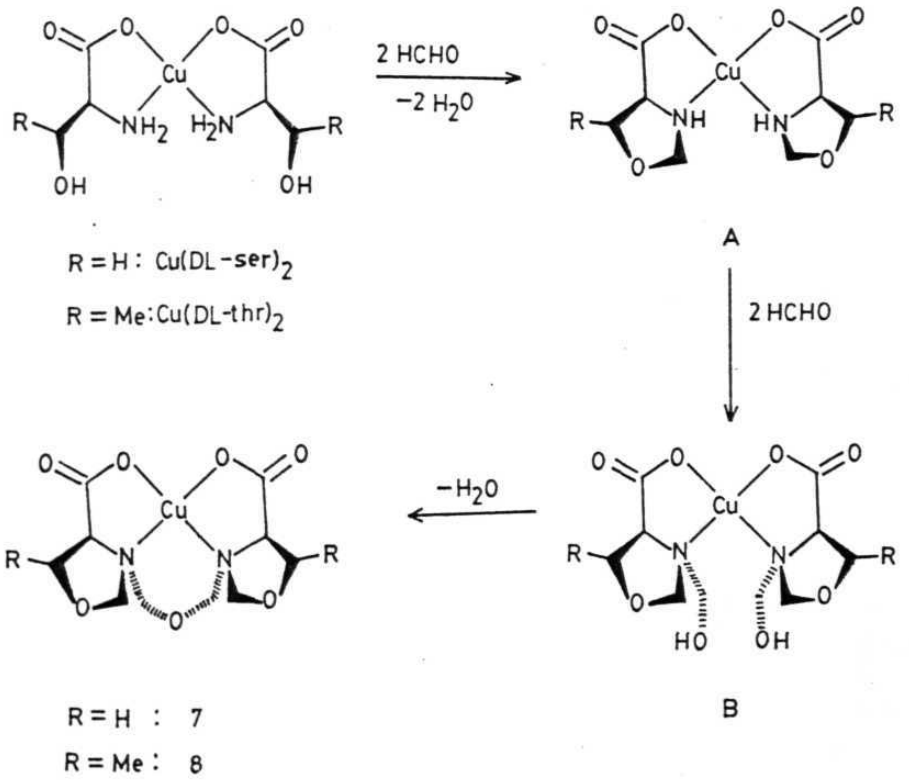


15

Under the same experimental conditions Cu(D-ser)$_2$ and Cu(D-thr)$_2$ react with formaldehyde yielding products which show similar IR spectra and analytical data as those of **14** and **15** respectively; electronic and ESR spectral data and electrochemical properties are also similar. The products exhibit difference only in their optical activity as could be seen from their CD spectra, showing that the products are optical isomers **14** and **15**.

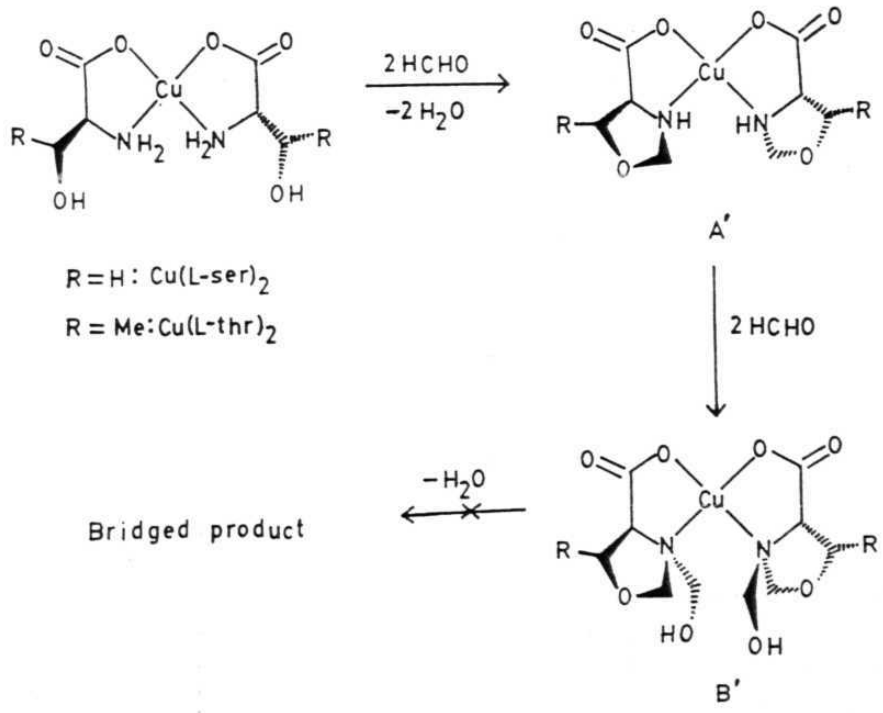
As it has been already described in Chapter III, Cu(DL-ser)$_2$ and Cu(DL-thr)$_2$ under similar experimental conditions yield the products **7** and **8** respectively, which are different from the products obtained from Cu(L-ser)$_2$ and Cu(L-thr)$_2$ (**14** and **15**). The complexes **7** and **8** have a dimethyleneether group bridging the two amino acid ligand units. Hence, it becomes necessary to discuss the probable mechanism involved in these reactions. Initial con-

densation in both cases seems to be formation of oxazolidine ring containing intermediate, A or A', which depending on the stereochemistry of the ligands forms different products on further condensation. For the formation of bridged products, <u>cis</u> geometry is essential. Mechanism for the reaction of $Cu(DL\text{-}ser)_2$ and $Cu(DL\text{-}thr)_2$ with formaldehyde can be given as shown in Scheme 4.1.



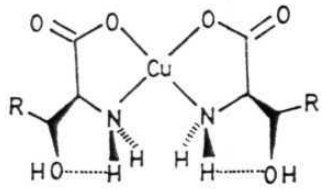
Scheme 4.1

Similarly the reaction of $Cu(L\text{-}ser)_2$ and $Cu(L\text{-}thr)_2$ also can be explained be the mechanism given in Scheme 4.2. The intermediate B′ (Scheme 4.2) has the two N-hydroxymethyl groups, disposed above and below the CuN_2O_2 plane dissimilar to B disallowing condensation of the two N-hydroxymethyl groups and hence bridged products are not formed in the reactions of $Cu(L\text{-}ser)_2$ and $Cu(L\text{-}thr)_2$ with formaldehyde. Presence of N-hydroxymethyl group in complex **14** supports this mechanism. However, in the case of $Cu(L\text{-}ser)_2$ after the formation of product A′ further condensation does not take place.



Scheme 4.2

$Cu(DL\text{-}ser)_2$ and $Cu(DL\text{-}thr)_2$ readily undergo condensation reaction with acetaldehyde at neutral pH forming products **10** and **1** respectively, while $Cu(L\text{-}ser)_2$ and $Cu(L\text{-}thr)_2$ do not react with acetaldehyde under the same experimental conditions. The difference in reactivity can be explained to arise from the difference in acidity of amino protons. For example, it has been shown that in chiral $[Co(en)_2(N\text{-benzylgly})]^{2+}$ the two methylene hydrogens of N-benzylglycine occupy diastereoisomeric positions, with one hydrogen undergoing H-D exchange more readily than the other.[12] A similar selective labilization of the amino protons favouring the condensation of acetaldehyde with bis(DL-amino acidato)copper(II) complexes can be suggested to explain their reactivity towards condensation with acetaldehyde as shown below:



R = H : $Cu(DL\text{-}ser)_2$
R = Me : $Cu(DL\text{-}thr)_2$

The labilization can be due to weak H-bonding between the hydroxy group of the $\alpha\text{-}CH_2OH$ or $\alpha\text{-}CH(CH_3)OH$ groups and one of the amino protons, which seems to be unfavourable in the case of $Cu(L\text{-}ser)_2$ and $Cu(L\text{-}thr)_2$. Irrespective of the absence of such labilization of one of the amino protons formaldehyde reacts

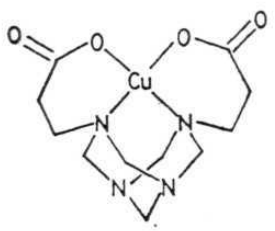
with $Cu(L\text{-}ser)_2$ and $Cu(L\text{-}thr)_2$ yielding products **14** and **15**, which can be attributed to higher reactivity of formaldehyde in comparison to acetaldehyde. The higher reactivity of formaldehyde is evident from the observation that at an acidic pH, 4.5, formaldehyde undergoes condensation with $Cu(gly)_2$ while similar reaction is not facile for acetaldehyde.[13]

These reactions demonstrate that besides the labile nature of Cu(II) complexes, coordination of Cu(II) to L and DL forms of serine and threonine stereospecifically activates the amino protons. Investigation on the reactions of Ni(II) and Zn(II) complexes of these amino acids reveals that they also react similar to the Cu(II) complexes yielding the corresponding Ni(II) and Zn(II) complexes.

It is known that $Cu(gly)_2$ and $Cu(L\text{-}ala)_2$ undergo condensation reaction with formaldehyde and ammonia yielding the pentamethylenediaza group containing products **4** and **5** respectively (Chapter III). Similar reactions have been carried out with Cu(II) complexes of L-serine, DL-serine, L-threonine and DL-threonine under similar experimental conditions but none of the reactions yields pentamethylenediaza-bridged products. These reactions yield, oxazolidine containing products, namely, **2** from the reactions of $Cu(L\text{-}ser)_2$ and $Cu(DL\text{-}ser)_2$ and **15** and **9** respectively, from $Cu(L\text{-}thr)_2$ and $Cu(DL\text{-}thr)_2$ revealing involvement $\alpha\text{-}CH_2OH$ or $\alpha\text{-}CH(CH_3)OH$ group which precludes the formation of pentamethylenediaza-bridged products.

Condensation reaction of optically inactive $Cu(\beta\text{-}ala)_2$ with

formaldehyde and ammonia at pH 8.5 has also been investigated. The reaction yields blue crystalline product, which is identified as the pentamethylenediaza-bridged complex, [3N,7N-(1,3,5,7-tetra-aza-bicyclo[3.3.1]nonyl)di-3-propionato]copper(II) (**16**).



16

The structure has been deduced on the basis of the following experimental data:

(i) the IR spectrum of the complex exhibits no characteristic bands of -OH and >NH groups;

(ii) the d-d band of the complex does not shift to higher wavelengths on lowering pH, indicating bridged structure for the complex;

(iii) on decomplexation by treatment of H_2S in acidic medium, the parent amino acid, ß-alanine, is obtained showing the non-involvement of the methylene groups in the condensation reaction;

(iv) in the presence of bases other than ammonia, such as sodium bicarbonate, sodium hydroxide etc. the same product could not be obtained.

The reaction is analogous to the reactions of $Cu(gly)_2$ and $Cu(L\text{-}ala)_2$ with formaldehyde and ammonia yielding similar penta-methylenediaza-bridged complexes, **4** and **5**. Analytical data (Table 2.2) conclusively supports the proposed structure.

4.4.2 CD spectral data

The complexes **14-16** are soluble in water; **15** is more soluble in ethanol. The complexes **14** and **15** are optically active while the complex **16** is optically inactive. CD spectra were recorded for the products obtained from $Cu(D\text{-ser})_2$ and $Cu(D\text{-thr})_2$ also. The CD spectra of **14** and **15** in aqueous media in the d-d transition region reveal positive Cotton effect, which is opposite to that of their parent Cu(II) complexes, namely $Cu(L\text{-ser})_2$ and $Cu(L\text{-thr})_2$. Inversion of the Cotton effect usually arises due to change in absolute configuration of the products. However, the observation that both **14** and **15** on decomplexation yield the parent α-amino acids, rules out substitution at the α-carbon atom, which may effect a change in the absolute configuration of the amino acid unit of the products. The only other possibility is creation of a new asymmetric centre during condensation. It could be seen from the structures of the complexes that the new asymmetric centre is the nitrogen atom. The CD spectral behaviour of these new complexes is similar to that of $Cu(L\text{-pro})_2$, where on complexation, creation of new asymmetric centre, nitrogen, has been suggested, to explain the CD spectral behaviour.[14] Similar explanation is relevant in the present case also. Therefore, the CD spectra of the complexes **14** and **15** are supportive of the structures proposed. In addition the complex, **14**, has been previously suggested to be an intermediate in the basic condensation reaction of $Cu(L\text{-ser})_2$ with formaldehyde, though more details are not available.[10] The CD spectra of $Cu(L\text{-thr})_2$ and the complex **15** are shown in Figure 4.1 and the data for both the complexes are

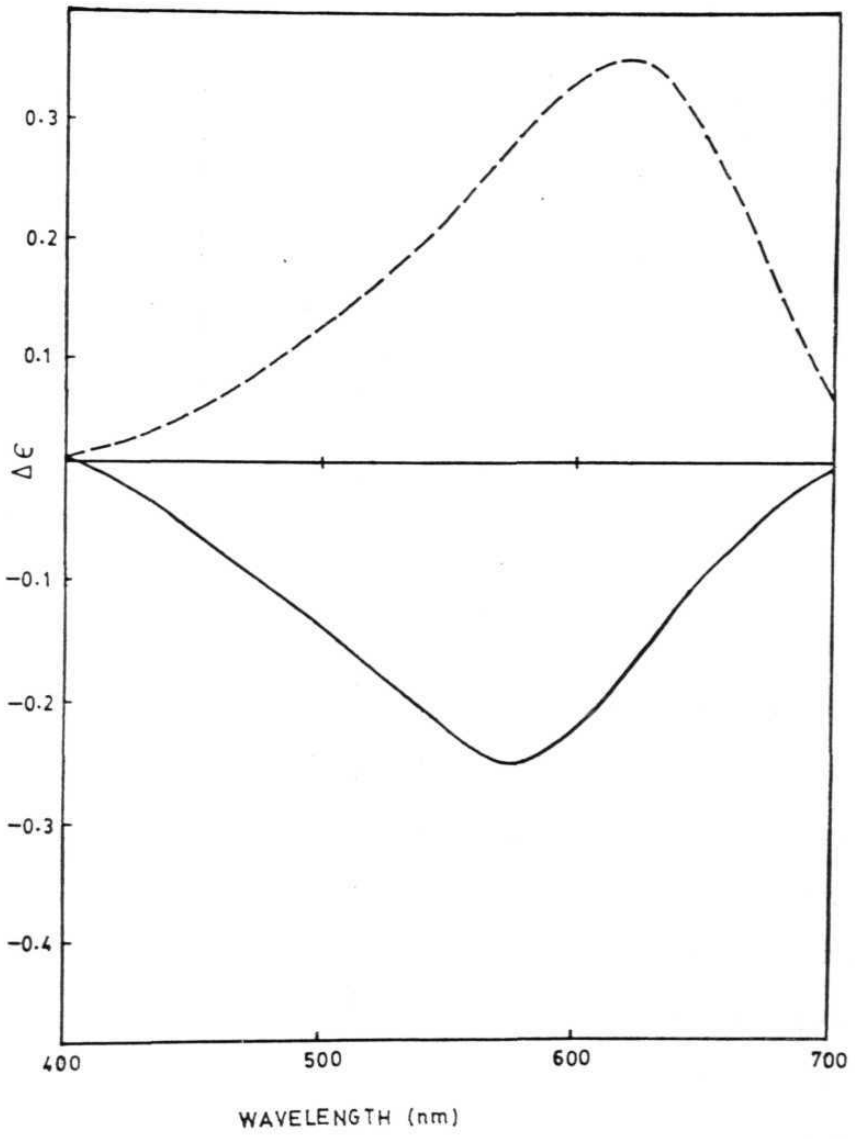


Figure 4.1. CD spectra of $Cu(L\text{-}thr)_2$ (——) and the complex, **15**, (---) in aqueous medium.

Table 4.1. Electronic, CD and ESR spectral data for the complexes 14-16 in aqueous media.

Complex	Electronic spectra $\lambda_{max}(\epsilon_{max})$ nm ($M^{-1}cm^{-1}$)	CD spectra $\lambda_{max}(\Delta\epsilon)$ nm ($M^{-1}cm^{-1}$)	ESR spectra[a] g_{iso}	A_{iso} (G)	$g_{\parallel}$	$A_{\parallel}$ (G)
14	630 (55)	630 (+0.097)	2.127	67	2.274	162
15	625 (67)	620 (+0.355)	2.127	67	2.273	167
16	660 (116)	...	2.125	72	2.262	165

[a]ESR parameters g_{iso} and A_{iso} were obtained from the room temperature spectra of the complexes in aqueous media and the $g_{\parallel}$ and $A_{\parallel}$ from frozen glassy spectra of the complexes in 95:5, water:methanol mixture at 120 K.

4.4.3 Electronic and ESR spectra

The d-d transition for the complexes **14** and **15** in water occurs at ca. 620 and 630 nm respectively, while for the complex **16** the band is observed at a relatively higher wavelength, 660 nm. The shift of the d-d band towards higher wavelength suggests presence of more tetrahedrally distorted geometry for the complex **16**. This is the direct result of increased chelate ring-size. However, ESR data (Table 4.1) does not reveal considerable change in the magnetic parameters for this complex. All the complexes in aqueous media exhibit the normal four-line ESR profile, with g_{iso} = 2.125 to 2.128 and A_{iso} = 67 to 72 G. Frozen glassy ESR spectra obtained at 120 K are axial with $g_{\parallel} > g_{\perp} > 2.0$, typical of square-planar or tetragonal Cu(II) complexes having $d_{x^2-y^2}$ ground state. Since the complexes possess the same CuN_2O_2 chromophore and the ESR parameters $g_{\parallel}$, $A_{\parallel}$, g_{iso} and A_{iso} do not show

significant change for any of the complexes, the complexes are suggested to possess similar geometry in aqueous solution.

4.4.3 Electrochemical data

The complexes **14-16** were examined by CV and DPV techniques in aqueous media. The complexes **14** and **15** exhibit similar CV behaviour as that of the unbridged complexes, **1-3**, **6**, **9** and **10** (Chapter III) while **17** resembles the pentamethylenediaza-bridged complexes, **4** and **5**. The major observations can be outlined as follows: (i) the complexes **14** and **15** exhibit a close to reversible redox couple (C,D) at -0.17 V with peak separation values (ΔE_p) 60 mV from the first forward scan onwards; a new redox couple (A,B) appears at ca. -0.01 V from the second scan onwards; (ii) the complex **16** exhibits a reduction peak C at -0.42 V in the first forward scan, the corresponding oxidation peak D is not observed. However from the second scan onwards the A-B redox couple appears at -0.01 V. CV profiles of the complexes **15** and **16** are shown in Figure 4.2 and the data collected in Table 4.2. Since CV behaviour of these complexes is similar to that of the complexes **1-13** (Chapter III), the same electrode-mechanism (equations 3.1-3.3) can explain the redox behaviour of present set of complexes.

The complexes **14** and **15** exhibit reversible Cu(II)/Cu(I) redox process and **16** exhibits irreversible Cu(II)/Cu(I) reduction. The irreversibility exhibited by **16** requires additional explanation. Reversibility of the Cu(II)/Cu(I) process depends on the stability of the electrochemically generated Cu(I) species. It is well known that Cu(I) species are more stable in

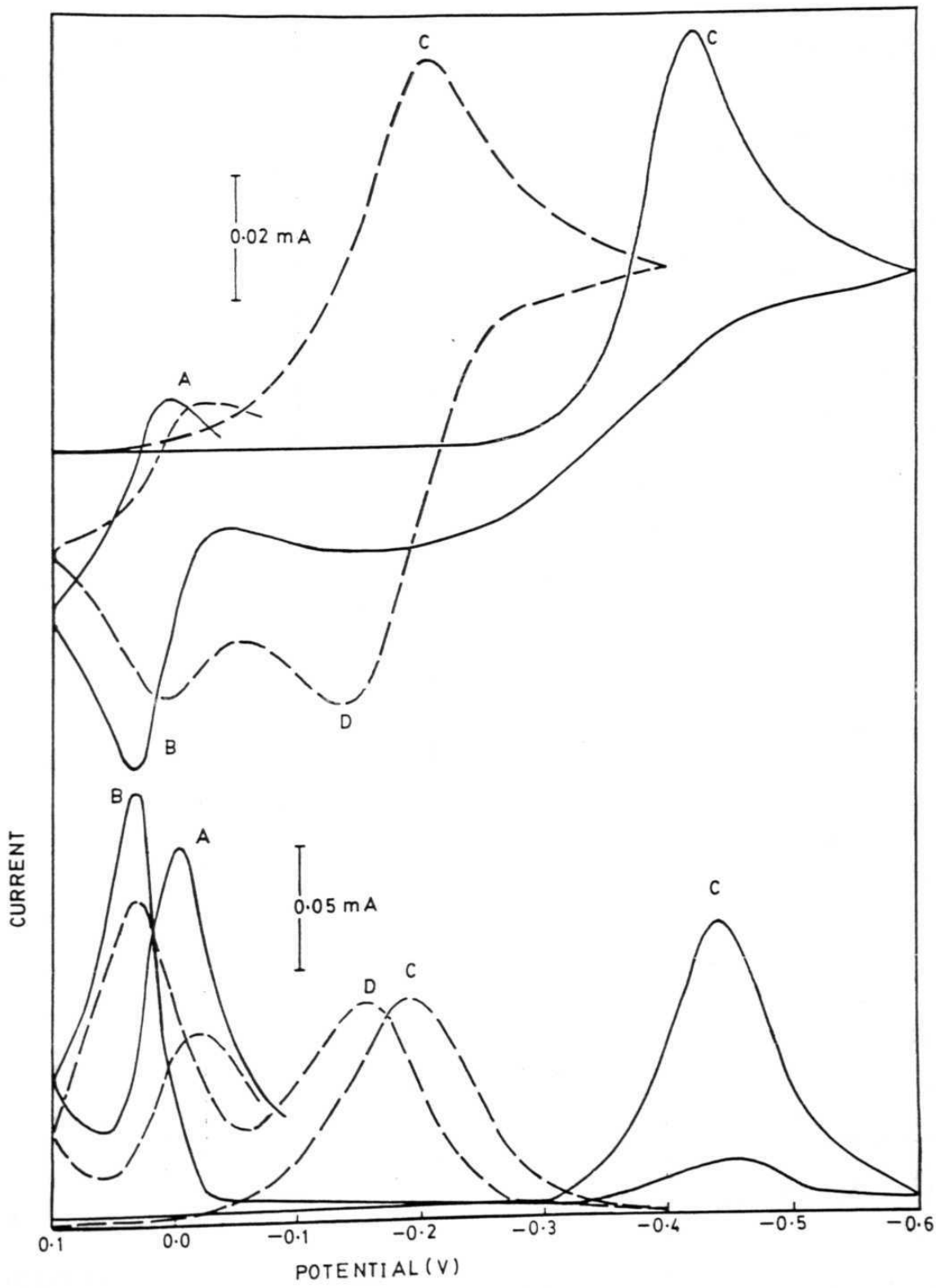


Figure 4.2. CV and DPV profiles of the complexes **15** (——) and **16** (---) in aqueous media at scan rates 0.050 V/s (CV) and 0.010 V/s (DPV).

Table 4.2. CV data for the complexes **14-16** in aqueous media at various scan rates at dissolution pH.

Complex	Scan rate	E_p (V)				ΔE_p(C,D) (V)	$E_{1/2}$(C,D) (V)
		A[a]	B	C	D		
14	0.01	-0.03	0.02	-0.19	-0.13	0.060	-0.160
	0.02	-0.02	0.02	-0.19	-0.13	0.060	-0.160
	0.05	-0.02	0.02	-0.19	-0.12	0.070	-0.165
	0.10	-0.02	0.02	-0.19	-0.12	0.070	-0.165
15	0.01	-0.02	0.02	-0.21	-0.15	0.060	-0.180
	0.02	-0.02	0.02	-0.21	-0.15	0.060	-0.180
	0.05	-0.02	0.02	-0.21	-0.14	0.060	-0.175
	0.10	-0.02	0.02	-0.21	-0.14	0.080	-0.170
16	0.01	0.00	0.03	-0.43	b	--	--
	0.02	0.00	0.03	-0.43	b	--	--
	0.05	0.00	0.03	-0.42	b	--	--
	0.10	0.00	0.03	-0.42	b	--	--

[a]Peak appeared from the second scan onwards; [b]peak absent.

Table 4.3. DPV data of the complexes **14-16** in aqueous media at 0.010 V/s.

Complex	E_p (V)				n[a]	
	A[b]	B	C	D	C	D
14	-0.02	0.02	-0.19	-0.13	1.00	0.95
15	-0.02	0.02	-0.20	-0.14	0.95	0.90
16	-0.01	0.02	-0.43	c	1.13	--

[a]$n = 90.4/W_{1/2}$; [b]peak appeared from the second scan onwards; [c]peak absent.

tetrahedral or pseudotetrahedral geometries.[15,16] The observation of irreversible Cu(II)/Cu(I) reduction process for **16**, which does not have a more planar geometry (ESR data) than the complexes **14** and **15** if not more tetrahedrally distorted geometry as suggested by the high λ_{max} value, reveals that another factor associated with the complex **17** influencing its redox behaviour. The significant difference in the structure is the rigid pentamethylenediaza bridging group present in this complex. This indicates that flexibility of the ligand system to undergo geometrical distortion towards the required tetrahedral geometry is another requirement for reversibility of Cu(II)/Cu(I) redox process.[17]

DPV profiles were also recorded for the complexes under the same experimental conditions as those of CV experiments. Representative profiles are shown in Figure 4.2 and the DPV data collected in Table 4.3. The n value (number of electrons) calculated from the DPV profiles for the C,D peaks is ca. 1 supporting the conclusions drawn from the CV data.

4.5 Conclusion

Products obtained from the reactions of Cu(II) complexes L-serine, DL-serine, L-threonine and DL-threonine with formaldehyde are illustrative of the difference in reactivity between the Cu(II)-L-amino acidato complexes and Cu(II)-DL-amino acidato complexes. Electrochemical irreversibility of Cu(II)/Cu(I) redox process exhibited by the pentamethylenediaza-bridged product obtained from the condensation of $Cu(\beta\text{-ala})_2$ with formaldehyde and ammonia reveals the influence of ligand rigidity on the reversibility of Cu(II)/Cu(I) redox process.

4.6 References

1. Y. Ikutani, T. Okuda, M. Sato and S. Akabori, Bull. Chem. Soc. Jpn. 1959, **32**, 203.
2. M. Murakami and K. Takahashi, ibid. 1959, **32**, 308.
3. J.C. Dabrowiak and D.W. Cooke, Inorg. Chem. 1975, **14**, 1305.
4. D.H. Busch and D.H. Williams, J. Am. Chem. Soc. 1965, **87**, 4644.
5. D.A. Buckingham, L.G. Marzilli and A.M. Sargeson, ibid. 1967, **89**, 5133.
6. D.A. Phipps, Inorg. Chim. Acta 1978, **27**, L103.
7. R.J. Geue, M.R. Snow, J. Springborg, A.J. Herlt, A.M.Sargeson and D. Taylor, J. Chem. Soc. Chem. Comm. 1976, 285.
8. S.B. Teo, S.G. Teoh and M.R. Snow, Inorg. Chim. Acta 1985, **107**, 211.
9. S.B. Teo, C.-H. Ng and E.R.T. Tiekink, ibid. 1989, **163**, 129.
10. J.R. Brush, R.J. Magee, J. O'Connor, S.B. Teo, R.J. Geue and M.R. Snow, J. Am. Chem. Soc. 1973, **95**, 2034.
11. S.B. Teo and S.G. Teoh, Inorg. Chim. Acta 1980, **44**, L269.
12. B.T. Golding, G.J. Gainsford, A.J. Herlt and A.M. Sargeson, Angew. Chem. Internat. Ed. Engl. 1975, **14**, 495.
13. S.B. Teo and S.G. Teoh, Inorg. Chim. Acta 1984, **91**, L17.
14. C.J. Hawkins, 'Absolute Configuration of Metal Complexes', Wiley-Interscience, New York, 1971.
15. R.D. Bereman, J.R. Dorfman, J. Bordner, P.D. Rillema, P. McCarthy and G.D. Shields, J. Inorg. Biochem. 1982, **16**, 47.
16. H. Yokoi and A.W. Addison, Inorg. Chem. 1977, **16**, 1341.
17. U. Sakaguchi and A.W. Addison, J. Chem. Soc. Dalton Trans. 1979, 600.

CHAPTER V

COPPER(II)-ALICYCLIC-α-AMINO ACIDATO COMPLEXES AND EFFECT OF ADDITION OF N-DONOR LIGANDS ON THE SPECTRAL AND ELECTROCHEMICAL PROPERTIES OF COPPER(II) COMPLEXES

5.1 Abstract

Cu(II) complexes of a few alicyclic-α-amino acids are investigated by electronic spectral, ESR and electrochemical methods. The complexes possess tetragonally distorted octahedral geometry with two molecules of water occupying the axial coordination sites in aqueous media. A reversible Cu(II)/Cu(I) redox couple at ca. -0.25 V has been observed and the overall redox behaviour is similar to that of the Cu(II) complexes of simple α-amino acids. The complexes form protonated species such as $[CuL]^+$ at low pHs. Electrochemical data obtained at low pHs discussed in terms of various protonated species present.

Spectral and electrochemical properties of the bis(alicyclic-α-amino acidato)copper(II) complexes and the condensation products discussed in Chapter III in the presence of N-donor ligands such as ammonia, imidazole etc. are examined. Frozen glassy ESR spectra reveal replacement of the axial water molecules by ammonia while no spectral changes could be observed for the addition of imidazole, pyrazole and pyridine indicating absence of replacement of the axial water molecules by these ligands. Steric effect has been suggested to explain this observation. CV and DPV data show that the replacement of the axially coordinating water molecules by ammonia effects shift of the Cu(II)/Cu(I) redox couple towards less negative potentials. The complexes, **4** and **5**, having more planar geometry and rigid ligand system do not exhibit any change in their redox behaviour in the presence of ammonia.

5.2 Introduction

Alicyclic-α-amino acids, such as 1-aminocyclopropane-1-carboxylic acid, 1-aminocyclopentane-1-carboxylic acid are naturally occurring and are shown to be biologically active.[1-3] For example, biosynthesis of ethylene in apple tissues, from methionine proceeds via 1-aminocyclopropane-1-carboxylic acid, where a copper enzyme was found to play major role.[2] This has generated considerable interest in this field. To develop a model for the biological process of conversion of 1-aminocyclopropane-1-carboxylic acid into ethylene, many investigations have been carried out.[4-6] These studies reveal the intermediacy of reduced copper in the process.[1,6] In this respect the redox properties of Cu(II)

complexes become important. While preparation and spectral behaviour of some of the bis(alicyclic-α-amino acidato)copper(II) complexes are reported,[7-9] their redox characteristics are yet to be investigated. In this chapter, results obtained on the redox properties of a few bis(alicyclic-α-amino acidato)copper(II) complexes are presented and discussed. Species formation at low pHs, has been studied by electronic and ESR spectral techniques.

These Cu(II) complexes are known to exist as hexa coordinated with two H_2O molecules occupying the axial sites in aqueous media. Some of the condensation products described in Chapter III also exhibit similar behaviour. The axial coordination seems to be weak since some of them crystallize as anhydrates. Therefore, it may be possible to replace the weakly coordinating water molecules by N-donor ligands such as, ammonia, imidazole, pyrazole and pyridine which in turn might lead to considerable change in spectral and redox properties.[15-23] ESR spectral and the CV and DPV electrochemical data were collected for the complexes in the presence of various N-donor ligands and the results obtained are discussed.

5.3 Experimental

5.3.1 Preparation of complexes

The complexes, bis(1-aminocyclopropane-1-carboxylato)copper(II) monohydrate (**17**), bis(1-aminocyclobutane-1-carboxylato)copper(II) (**18**), bis(1-aminocyclopentane-1-carboxylato)copper(II) (**19**), bis(1-aminocyclohexane-1-carboxylato)copper(II) monohydrate (**20**), and bis(1-aminocycloheptane-1-carboxylato)copper(II) (**21**) were prepared as described in Section 2.2.

The condensation products, **1-10** were also included in the investigation and were prepared as described in Section 2.2.

5.3.2 Physical measurements

Electronic absorption and ESR spectra were recorded for the complexes in aqueous media at room temperature as described in Section 2.3. Frozen glassy ESR spectra were recorded for the complexes in the absence and presence of ammonia on a JEOL FE-3X ESR spectrometer using JEOL NM-7700 Temperature controller at 120 K. For obtaining good glass, 95:5, water:methanol solutions of the complexes were used. The electrochemical experiments were performed in the presence of various N-donor ligands at neutral pH by the procedure described in Section 2.3.

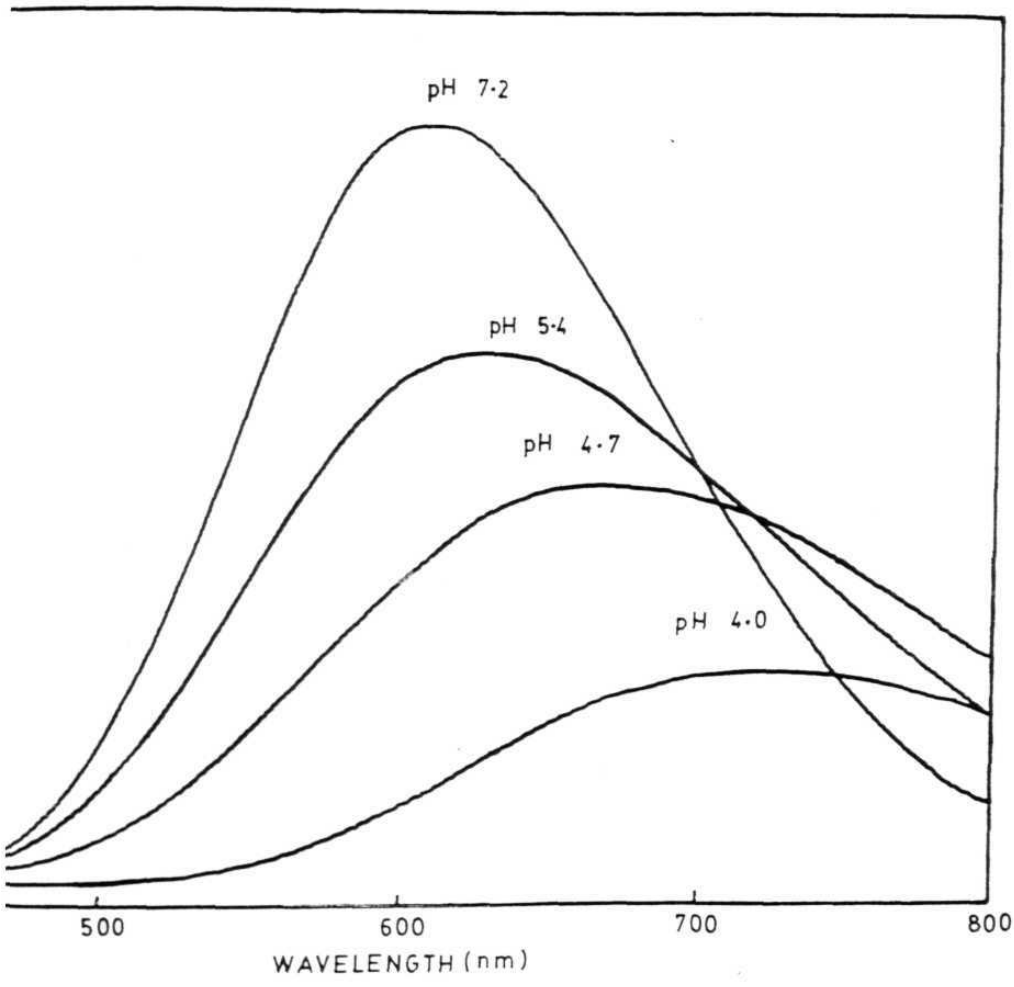
Solutions of various complex to N-donor ligand ratio were obtained by the following method: For example, a 1:1 complex to N-donor ligand solution was obtained by mixing equal volumes of 2 x 10^{-3} M solutions of the complex and the N-donor ligand. By increasing the concentration of the N-donor ligand solution to 4 x 10^{-3} and 6 x 10^{-3} *etc.*, the complex : N-donor ratio was varied. The solutions were basic after the addition of the ligands and were adjusted to neutral pH (7-7.5) by the addition of micro-litres of $HClO_4$ or NaOH solutions for a meaningful comparison of the data with the data obtained for the complexes at dissolution pH (7-7.5) in the absence of these ligands.

5.4 Bis(alicyclic-α-amino acidato)copper(II) complexes

Purity of the complexes was checked by elemental analyses and IR spectra. The complexes were blue coloured and soluble in water and methanol. The spectral and electrochemical data were collected in aqueous media.

5.4.1 Spectral data

The electronic spectra of the complexes, **17-21**, recorded in aqueous media at the dissolution pH (7-7.5) exhibit an absorption band corresponding to the d-d transition in the wavelength region 620-605 nm. The λ_{max} values are in the order **17** > **18** > **19**, **20** > **21**. Although variation of the values (Table 5.1) from complex to complex is very small it reflects the increasing tetragonal distortion due to increasing ring size.[7,8] At lower pHs the d-d band shifts to higher wavelengths (red shift) as shown in Figure 5.1. Similar shift in the d-d band position on lowering pH, exhibited by simple Cu(II)-α-amino acidato complexes has been attributed to formation of species such as $[CuHL_2]^+$, $[CuL]^+$, $[CuHL]^{2+}$ *etc.* (where L = amino acidato anion).[10] The stability constants of these complexes and related species also support the formation of various protonated species at lower pHs.[11] Recently, it has been shown by ESR studies that $[CuL]^+$ is the most predominant species in the pH range 5-4 for some Cu(II)-α-amino acidato complexes.[12] The present set of complexes also exhibits pH dependent ESR spectral behaviour. At neutral pH, the normal four-line pattern with g_{iso} = 2.110 and A_{iso} = 70 G is obtained indicating the presence of CuL_2 species. In the pH range 6-4.5 the spectra exhibit a five-line pattern, arising from the presence of $[CuL]^+$ species



5.1. Electronic spectra of the complex **19** in aqueous media at various pHs.

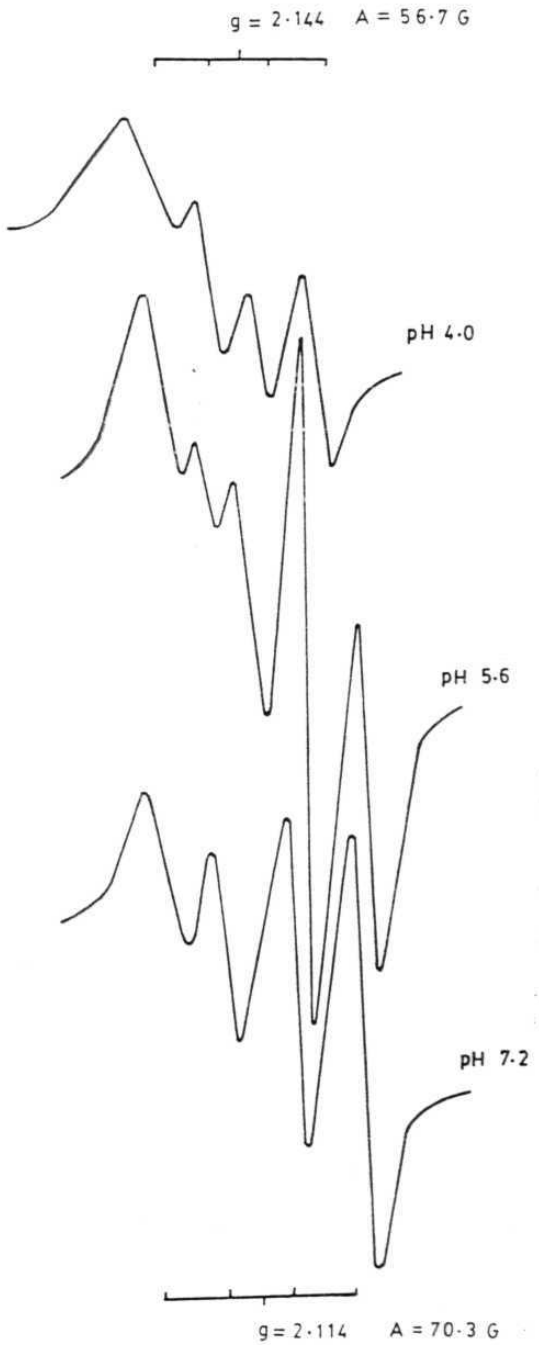


Figure 5.2. ESR spectra of the complex **17** in aqueous media at various pHs.

along with the CuL_2 species. On further lowering of pH to 4, the high-field peak of the five-line pattern disappears and a four-line pattern with g_{iso} = 2.140 and A_{iso} = 55 G, characteristic of $[CuL]^+$ species appears. The disappearance of the high-field component of the five-line pattern at this pH indicates absence of the CuL_2 species. ESR profiles for a representative complex at various pHs are shown in Figure 5.2 and the data presented in Table 5.1. The spectral behaviour of the complexes at lower pHs is similar to that of the unbridged condensation products described in Chapter III, for which formation of $[CuL]^+$ species at low pHs has been found to occur.

5.4.2 Electrochemical data

The CV and DPV data were collected for all the complexes in aqueous media. Representative CV and DPV profiles are shown in Figure 5.3. The major experimental observations can be summarized as follows: (i) only one cathodic peak (C) is observed in the first forward scan (ii) during the reverse scan an anodic peak (D) in the potential range -0.19 to -0.22 V and another anodic peak (B) at -0.01 V are observed (iii) a new cathodic peak (A) at -0.03 V appears from the second scan onwards (iv) a substantial decrease in the current function value of A and B is observed with increasing scan rates (v) peaks A and B do not appear if the scan is reversed at *ca.* -0.15 V *i.e.* before the appearance of peak C (vi) holding the potential well past peak C for a few min and scanning back, peak heights of A and B increase considerably, while the effect on the C-D peaks is only marginal (vii) the peak separation value for the C,D peaks (ΔE_p C,D) is about 60 mV

Table 5.1. Electronic and ESR spectral data for the complexes, **17-21** in aqueous media.

Complex	pH	$\lambda_{max}(\epsilon_{max})$ nm (M^{-1} cm^{-1})	g_{iso}	A_{iso} (G)
17	7.2	620 (50)	2.114	70.3
	6.6	620	2.116	71.0
	5.6	630	2.144	56.7
	5.0	650	2.144	56.7
	4.0	680	2.144	56.7
18	7.2	615 (70)	2.115	66.7
	6.5	630	2.115	66.0
	6.0	680	2.144	55.0
	5.1	720	2.143	58.0
	4.5	a	2.144	58.0
19	7.2	610 (65)	2.112	70.0
	6.2	625	2.139	55.3
	5.4	670	2.137	56.7
	4.7	710	2.139	56.7
	4.0	a	b	b
20	7.2	610 (75)	2.110	70.0
	6.5	615	2.141	56.7
	5.6	640	2.138	58.3
	4.7	690	2.139	60.0
	3.8	a	b	b
21	7.2	605 (80)	2.110	71.0
	6.5	630	2.142	53.0
	5.7	670	2.135	57.0
	5.0	690	2.135	56.7
	3.9	a	b	b

[a]Broad peak, could not be measured precisely; [b]ESR lines absent

and the ratio of peak currents ($-i_c/i_a$ C,D) about 1. The CV data for the complexes at various scan rates are given in Table 5.2.

Careful consideration of the above observations and a comparison with the data obtained for the unbridged complexes, discussed in Chapter III reveal that the same electrode mechanism (equations 3.1 to 3.3) can explain the redox behaviour of the present set of complexes also.

$$Cu(II) \xrightleftharpoons{1e} Cu(I)$$

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

$$Cu(0)(Hg) \xrightleftharpoons{2e} Cu(II)(aq)$$

The CV behaviour of the present set of complexes resembles that of Cu(II)-α-amino acidato complexes.[13] Both the systems exhibit considerable stability for the electrochemically generated Cu(I) species and the consequent electrochemical reversibility of the Cu(II)/Cu(I) redox process. The potential range at which the process occurs does not differ much confirming similarity in electrode mechanism.

CV profiles of the complexes also have been recorded for the complexes at lower pHs and the following changes observed: (i) heights of the peaks C and D gradually decrease and the peaks disappear at pH ca. 4 (ii) peak A begins to appear in the first scan itself at pHs < 6 (iii) peaks A and B increase in height as the heights of C and D decrease on further lowering of pH. These changes are reversible when the pH is adjusted back to 7.0, the initial pH. These changes are shown for a representative complex in Figure 5.4 and the data are collected in Table 5.3.

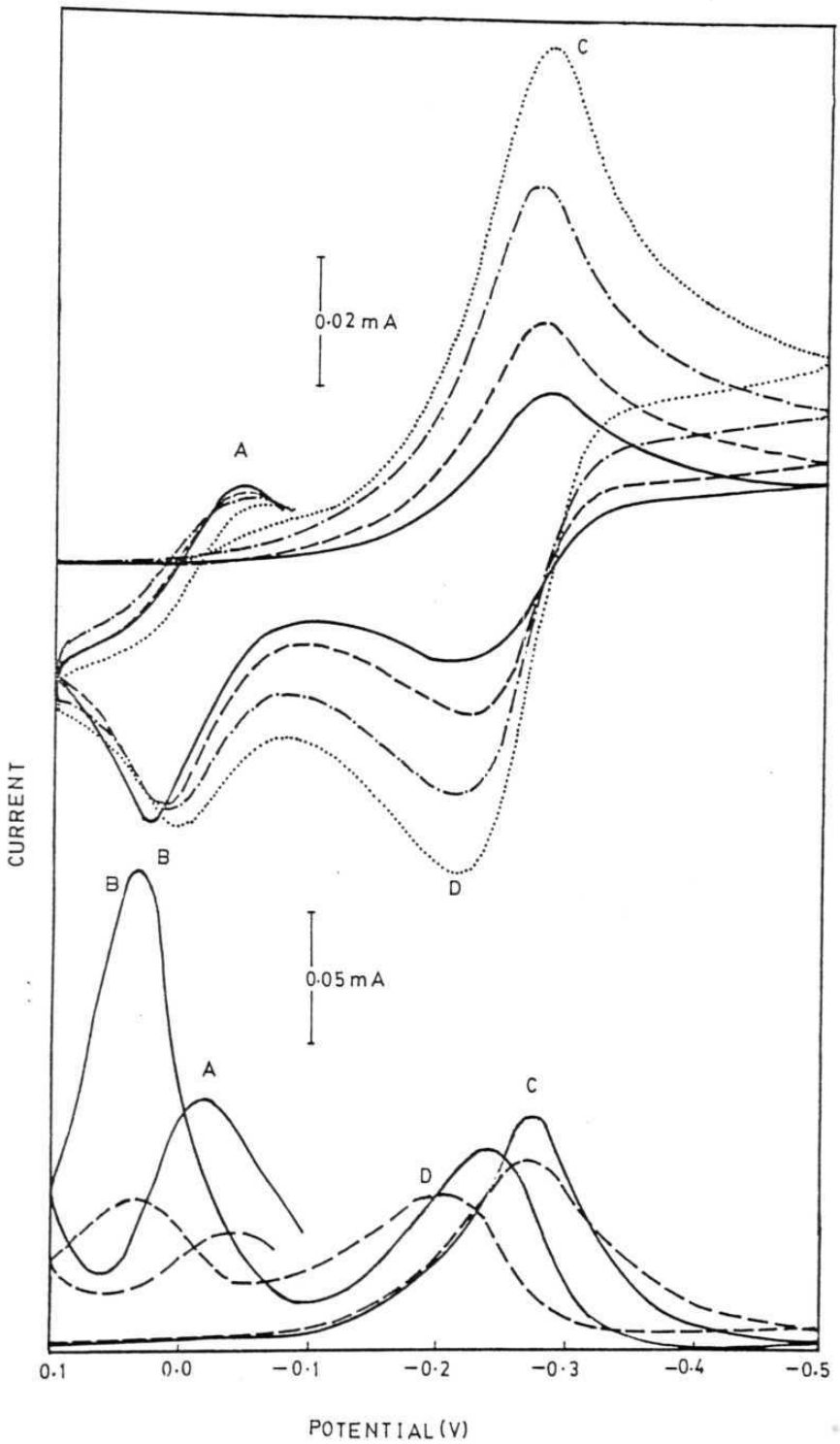


Figure 5.3. CV and DPV profiles of the complex **18** in aqueous media at various scan rates: 0.010 V/s (——), 0.020 V/s (----), 0.050 V/s (—·—·—) and 0.100 V/s (·····).

Table 5.2. CV data for the complexes, 17-21 in aqueous media at dissolution pH at different scan rates.

Complex	Scan rate (V/s)	E_p (V)				ΔE_p(C,D) (V)	$-i_c/i_a$
		A[a]	B	C	D		
17	0.01	-0.08	-0.03	-0.27	-0.21	0.06	0.87
	0.02	-0.08	-0.03	-0.27	-0.21	0.06	0.78
	0.05	b	b	-0.27	-0.20	0.07	0.91
	0.08	b	b	-0.27	-0.20	0.07	0.95
	0.10	b	b	-0.27	-0.20	0.07	0.94
18	0.01	-0.05	0.01	-0.28	-0.22	0.06	1.00
	0.02	-0.05	0.01	-0.28	-0.22	0.06	1.00
	0.05	-0.05	0.01	-0.28	-0.22	0.06	1.00
	0.08	-0.05	0.01	-0.28	-0.22	0.06	1.06
	0.10	-0.05	0.01	-0.28	-0.21	0.07	1.12
19	0.01	-0.03	0.02	-0.28	-0.22	0.06	1.00
	0.02	-0.05	0.02	-0.28	-0.22	0.06	1.00
	0.05	-0.06	0.02	-0.28	-0.21	0.07	0.96
	0.08	-0.06	0.03	-0.29	-0.21	0.08	0.93
	0.10	-0.06	0.03	-0.29	-0.21	0.08	1.03
20	0.01	-0.03	0.03	-0.28	-0.22	0.06	1.00
	0.02	-0.02	0.03	-0.28	-0.22	0.06	1.00
	0.05	-0.03	0.03	-0.28	-0.22	0.06	1.05
	0.08	-0.03	0.03	-0.29	-0.22	0.07	1.05
	0.10	-0.03	0.03	-0.29	-0.22	0.07	1.05
21	0.01	-0.03	0.03	-0.25	-0.19	0.06	1.00
	0.02	-0.03	0.03	-0.26	-0.20	0.06	1.00
	0.05	-0.03	0.01	-0.27	-0.20	0.07	1.00
	0.08	-0.03	0.01	-0.27	-0.20	0.07	1.05
	0.10	-0.03	0.01	-0.27	-0.20	0.07	1.05

[a]Peak observed from the second scan onwards. [b]Peak absent.

Table 5.3. CV data of the complexes **17-21** in aqueous media at different pHs at scan rate 0.020 V/s.

Complex	pH	E_p (V)				ΔE_p	$E_{\frac{1}{2}}$	$-i_c/i_a$
		A[a]	B	C	D	(C,D) (V)	(C,D) (V)	(C,D)
17	7.2	-0.08	-0.03	-0.27	-0.21	0.06	-0.24	0.87
	6.6	-0.08	-0.02	-0.27	-0.21	0.06	-0.24	0.93
	5.6	-0.08	-0.02	-0.27	-0.21	0.06	-0.24	0.92
	5.0	-0.07	-0.01	-0.27	-0.21	0.06	-0.24	0.92
	4.0	-0.06	-0.00	-0.26	-0.20	0.06	-0.23	0.83
18	7.2	-0.05	0.01	-0.28	-0.22	0.06	-0.25	1.00
	6.5	-0.05	0.03	-0.27	-0.21	0.06	-0.24	1.00
	6.0	-0.03	0.03	-0.27	-0.21	0.06	-0.24	1.00
	5.1	-0.02	0.03	-0.27	-0.21	0.06	-0.24	0.86
	4.5	-0.02	0.04	b	b	--	--	--
19	7.2	-0.03	0.02	-0.28	-0.22	0.06	-0.25	1.00
	6.5	-0.04	0.03	-0.28	-0.22	0.06	-0.25	1.00
	5.4	-0.04	0.03	-0.27	-0.21	0.06	-0.24	0.93
	4.7	-0.03	0.03	-0.27	-0.21	0.06	-0.24	0.86
	4.0	-0.01	0.04	b	b	--	--	--
20	7.2	-0.03	0.03	-0.28	-0.22	0.06	-0.25	1.00
	6.5	-0.03	0.03	-0.28	-0.22	0.06	-0.25	1.09
	5.6	-0.03	0.04	-0.28	-0.22	0.06	-0.25	1.09
	4.7	-0.04	0.04	-0.27	-0.21	0.06	-0.24	0.83
	3.7	-0.01	0.04	b	b	--	--	--
21	7.2	-0.03	0.03	-0.25	-0.19	0.06	-0.22	1.00
	6.5	-0.03	0.03	-0.25	-0.19	0.06	-0.22	1.00
	5.7	-0.02	0.03	-0.25	-0.19	0.06	-0.22	1.00
	5.0	-0.01	0.04	-0.25	-0.19	0.06	-0.22	1.00
	3.9	-0.01	0.04	b	b	--	--	--

[a]Peak observed from the second scan. [b]Peak absent.

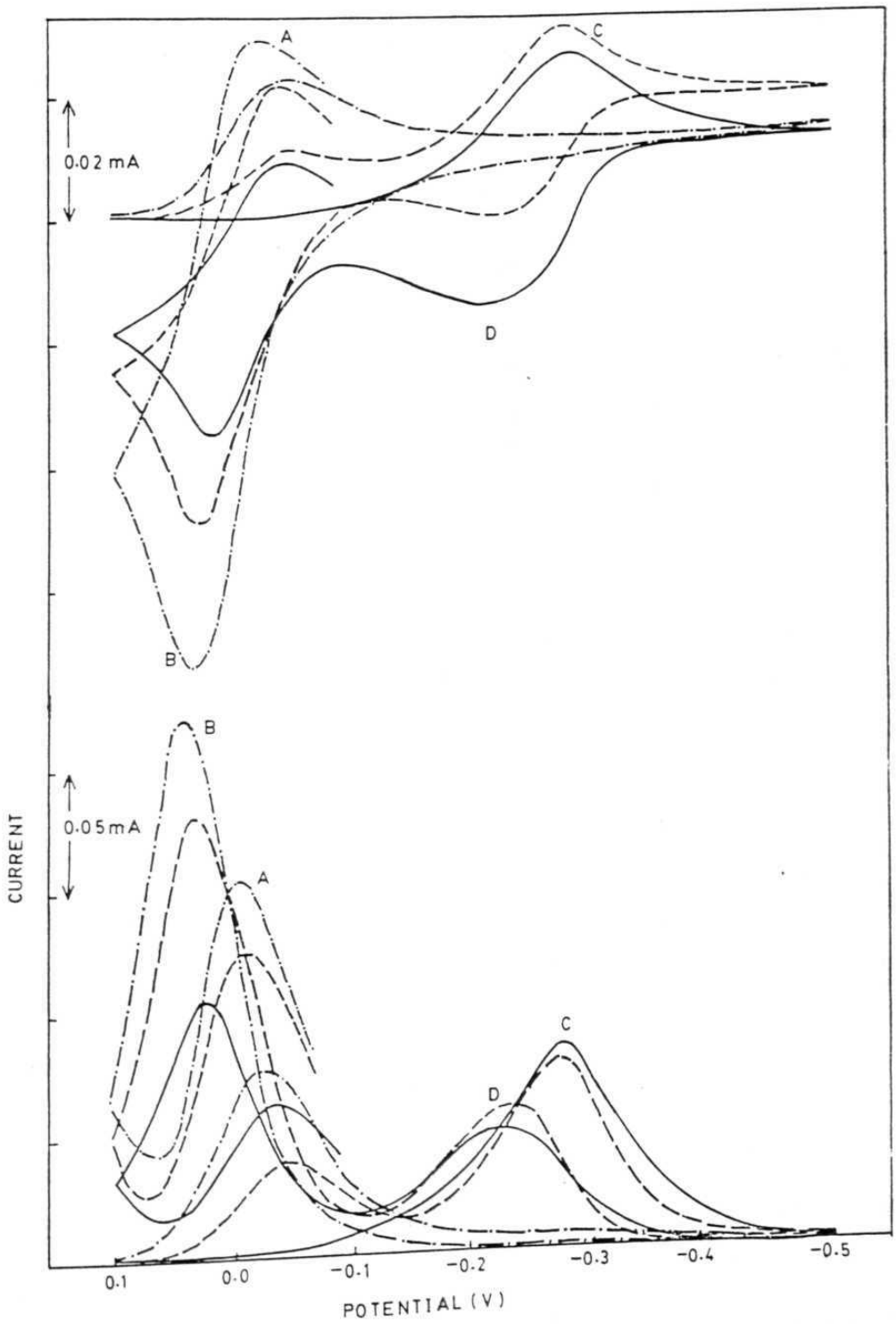


Figure 5.4. CV and DPV profiles of the complex **18** at various pHs: pH 7.2 (——), pH 6.0 (----) and pH 4.5 (—·—·—).

These observations together with the spectral data show that at the dissolution pH, CuL_2 is the major species. The CuL_2 species undergo reversible one-electron redox process as described above. At pH 4, CuL_2 species does not exist and the protonated species, $[CuL]^+$ being the dominant species undergoes redox process similar to simple Cu(II)(aq) ions. The redox process of the $[CuL]^+$ does not involve the Cu(I) intermediate species.

DPV profiles were recorded for all the complexes at various pHs. Representative DPV profiles are shown in Figure 5.3. The DPV profiles at the dissolution pH exhibit the two redox couples, C,D and A,B and the change in the DPV profiles at low pHs as could be seen from Figure 5.4 are similar to that observed in the CV profiles. The DPV data obtained for the complexes at various pH conditions are collected in Table 5.4. The n value (number of electrons) calculated from the $W_{\frac{1}{2}}$ values[14] for the C,D peaks approximate to one indicating one-electron redox process, which further supports the electrode mechanism suggested.

5.5 Effect of N-donor ligands

The Cu(II) complexes described in this Chapter (**17-21**) and the complexes described in Chapter III (**1-10**) were investigated in the presence of various N-donor ligands, namely, ammonia, imidazole, pyrazole and pyridine. In the presence of the ligands other than ammonia no change in the spectral and electrochemical properties of the complexes could be noticed. Results obtained in the presence of ammonia are presented and discussed in the subsequent sections.

Table 5.4. DPV data of the complexes **17-20** in aqueous media at various pHs at scan rate 0.010 V/s.

Complex	pH	E_p (V)				$W_{\frac{1}{2}}$ (mV)		n[c]	
		A[a]	B	C	D	C	D	C	D
17	7.2	-0.06	-0.01	-0.26	-0.20	100	100	0.904	0.904
	6.6	-0.07	-0.01	-0.26	-0.21	100	100	0.904	0.904
	5.6	-0.07	0.01	-0.26	-0.21	90	100	1.004	0.904
	5.0	-0.06	0.00	-0.26	-0.20	90	90	1.004	1.004
	4.0	-0.05	0.00	-0.25	-0.20	90	90	1.004	1.004
18	7.2	-0.02	0.02	-0.27	-0.23	90	100	1.004	0.904
	6.5	-0.02	0.04	-0.27	-0.23	90	90	1.004	1.004
	6.0	-0.01	0.04	-0.27	-0.23	90	90	1.004	1.004
	5.1	-0.01	0.04	-0.27	-0.23	90	90	1.004	1.004
	4.5	-0.01	0.05	b	b	---	---	---	---
19	7.2	-0.02	0.02	-0.27	-0.22	100	100	0.904	0.904
	6.2	-0.02	0.05	-0.27	-0.21	90	90	1.004	1.004
	5.4	-0.02	0.06	-0.27	-0.21	90	90	1.004	1.004
	4.7	-0.01	0.04	-0.27	-0.21	90	90	1.004	1.004
	4.0	-0.01	0.05	b	b	---	---	---	---
20	7.2	-0.02	0.03	-0.28	-0.23	100	100	0.904	0.904
	6.5	-0.01	0.03	-0.28	-0.23	100	100	0.904	0.904
	5.6	-0.02	0.04	-0.28	-0.22	110	110	0.820	0.820
	4.7	-0.02	0.04	-0.28	-0.22	100	100	0.904	0.904
	3.8	-0.01	0.04	b	b	---	---	---	---
21	7.2	-0.01	0.05	-0.25	-0.20	100	100	0.904	0.904
	6.5	-0.01	0.04	-0.25	-0.20	90	100	1.004	0.904
	5.7	-0.01	0.04	-0.25	-0.20	90	100	1.004	1.004
	5.0	0.00	0.05	-0.24	-0.19	90	90	1.004	1.004
	3.9	0.00	0.05	b	b	---	---	---	---

[a]Peak observed from the second scan. [b]Peak absent. [c]$n = 90.4/W_{\frac{1}{2}}$.

5.5.1 Spectral data

Electronic spectra were recorded for all the complexes, **1-10** and **17-21** in aqueous media in the presence of various N-donor ligands, ammonia, imidazole, pyrazole and pyridine at 1:2, complex to ligand ratio at pH *ca.* 7. The spectra do not exhibit any change in the d-d band position due to the presence of the N-donor ligands. However, frozen glassy ESR spectra of of the complexes in the presence of ammonia exhibit decrease in $g_{\|}$ and $A_{\|}$ values. Figure 5.5 (A) shows the frozen glassy ESR profile of the complex **21** taken at 120 K in the absence of ammonia. All the complexes exhibit similar spectra and are typical of Cu(II) ion in axial environments. The spectra showed $g_{\|} > g_{\perp} > 2.0$, characteristic of tetragonally distorted octahedral, square-base pyramidal or square planar stereochemistries all Cu(II) geometries associated with a $d_{x^2-y^2}$ ground state.[24] The ESR data for all the complexes are collected in Table 5.5. As it can be observed from the data, except for the complexes, **4** and **5**, all the complexes have the $g_{\|}$ values in the range 2.250-2.269 and the $A_{\|}$ values in the range 169-177 G. These values are comparable to the known values of Cu(II) complexes of simple α-amino acids.[9,25] Hence, the ESR data suggests tetragonally distorted octahedral geometry for the complexes, with two apical water molecules for the present set of complexes. ESR parameters are also known to reflect the extent of interaction between the central Cu(II) ion and the apical water molecules; more the interaction higher is the $g_{\|}$ value and lower is the $A_{\|}$ value.[9,15-19] Low $g_{\|}$ and high $A_{\|}$ values (Table 5.5) observed for complexes **4** and **5** reveal that

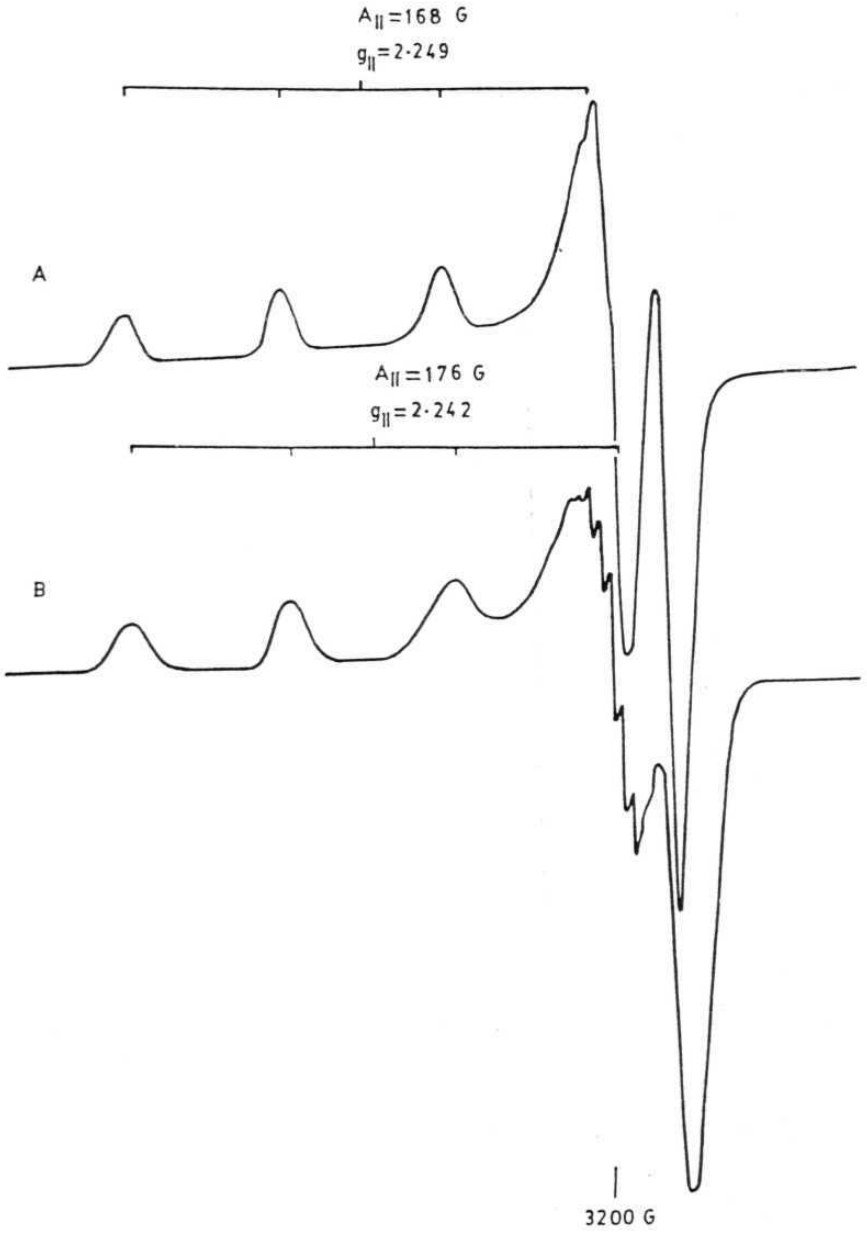


Figure 5.5. Frozen glassy ESR spectra (at 120 K) of the complex **21** in the absence (A) and in the presence of ammonia at pH 7.2.

Table 5.5. ESR data for the complexes **1-10** and **17-21** in the absence and presence of ammonia (1 : 2, complex to ammonia ratio, pH ca. 7.0).

Complex	in absence of ammonia			in presence of ammonia		
	$g_{\parallel}$	$g_{\perp}$ [a]	$A_{\parallel}$ (G)	$g_{\parallel}$	$g_{\perp}$ [a]	$A_{\parallel}$ (G)
1	2.264	2.060	169	2.245	2.057	175
2	2.259	2.062	175	2.251	2.055	176
3	2.269	2.067	165	2.262	2.061	173
4	2.244	2.060	177	2.247	2.061	176
5	2.229	2.059	181	2.224	2.052	180
6	2.258	2.061	169	2.242	2.051	177
7	2.260	2.062	172	2.251	2.059	173
8	2.258	2.059	170	2.244	2.055	175
9	2.259	2.057	170	2.246	2.059	180
10	2.254	2.060	172	2.245	2.057	178
17	2.252	2.057	174	2.251	2.056	177
18	2.254	2.057	173	2.248	2.061	175
19	2.256	2.056	173	2.244	2.057	179
20	2.259	2.057	177	2.244	2.061	183
21	2.249	2.055	168	2.242	2.056	176

[a] $g_{\perp} = (3g_{iso} - g_{\parallel})/2$

the interaction of their central Cu(II) ions with the solvent H_2O molecules is very weak, i.e., these complexes are more tetragonally distorted and more planar is the CuN_2O_2 chromophore. On addition of ammonia (1:2, complex to ammonia ratio, pH 7-7.5) all the complexes exhibit the same four-line ESR profiles as shown in Figure 5.5 (B). However, the spectra reveal measurable changes in the ESR parameters. Consistently, except for the complexes, **4** and **5**, decrease of $g_{\|}$ and increase of $A_{\|}$ values have been observed for all the complexes. The ESR data in the absence and presence of ammonia are presented in Table 5.5. It is known that the replacement of oxygen donors by nitrogen donors affect oppositely the ESR parameters. For example, in the case of Cu(II) complexes of tridentate ligands with an equatorial water molecule, the $g_{\|}$ values increase and $A_{\|}$ decreases when the axial bonds become more covalent[15-19] and $g_{\|}$ values decrease and $A_{\|}$ increases on planar coordination of the donor base.[21-23] The change in ESR parameters is due to the change in geometry as a result of axial or planar coordination of the strong N-donor ligands. For the present set of complexes, only axial coordination will be possible due to the reason that the axial water molecules are weakly bound as already mentioned. Nevertheless, the decrease in $g_{\|}$ and increase in $A_{\|}$ values observed in the presence of ammonia can be viewed as replacement of 'hard' or class (a) donor atoms by 'soft' or class (b) donor atoms, which tends to decrease $g_{\|}$ and increase $A_{\|}$ values.[26] Therefore, the experimental observation of lower $g_{\|}$ and higher $A_{\|}$ values indicate that the softer ammonia ligand replaces the apical water molecules without effecting considerable change in the geometry of the complexes.

Absence of considerable change in $g_{\|}$ and $A_{\|}$ values for the complexes, **4** and **5**, further supports the conclusion that these complexes are more tetragonally distorted and the interaction of their central Cu(II) ion with the solvent water molecules or ammonia is very weak. The ESR parameters for the complexes, except for **4** and **5**, are $g_{\|}$ in the range 2.242-2.251 and $A_{\|}$ in the range 173-183 G and the values are reasonable for tetragonal six coordinated Cu(II) complexes.[27]

5.5.2 Electrochemical data

For all the complexes CV and DPV data were collected in aqueous media in the presence of various proportions of ammonia at neutral pH. The complexes **4** and **5** did not exhibit any change in their CV and DPV profiles on addition of ammonia. All other complexes, namely, **1-3**, **6-10** and **17-21** exhibit the following changes after the addition of ammonia at pH 7-7.5: (i) the general pattern of two redox couples, namely, C-D (Cu(II)/Cu(I)) and A-B (Cu(0)(Hg)/Cu(II)(aq)) is observed (ii) the potential of the C-D couple shifts to less negative values on addition of ammonia (iii) for 1:1, complex to ammonia ratio the shift is about 30 mV and for 1:2 ratio, about 60 mV (vi) on further addition of ammonia no pronounced shift of the C,D redox couple is observed, however, for 1:6 ratio a shift of *ca.* 10-20 mV is observed (v) when ammonia is added in excess (> 10 times) the CV profiles change and resemble that of free Cu(II) ion in the presence of ammonia (vi) the peaks A and B do not shift on addition of ammonia. These changes for a representative complex are shown in Figure 5.6 and the CV data collected in Table 5.6.

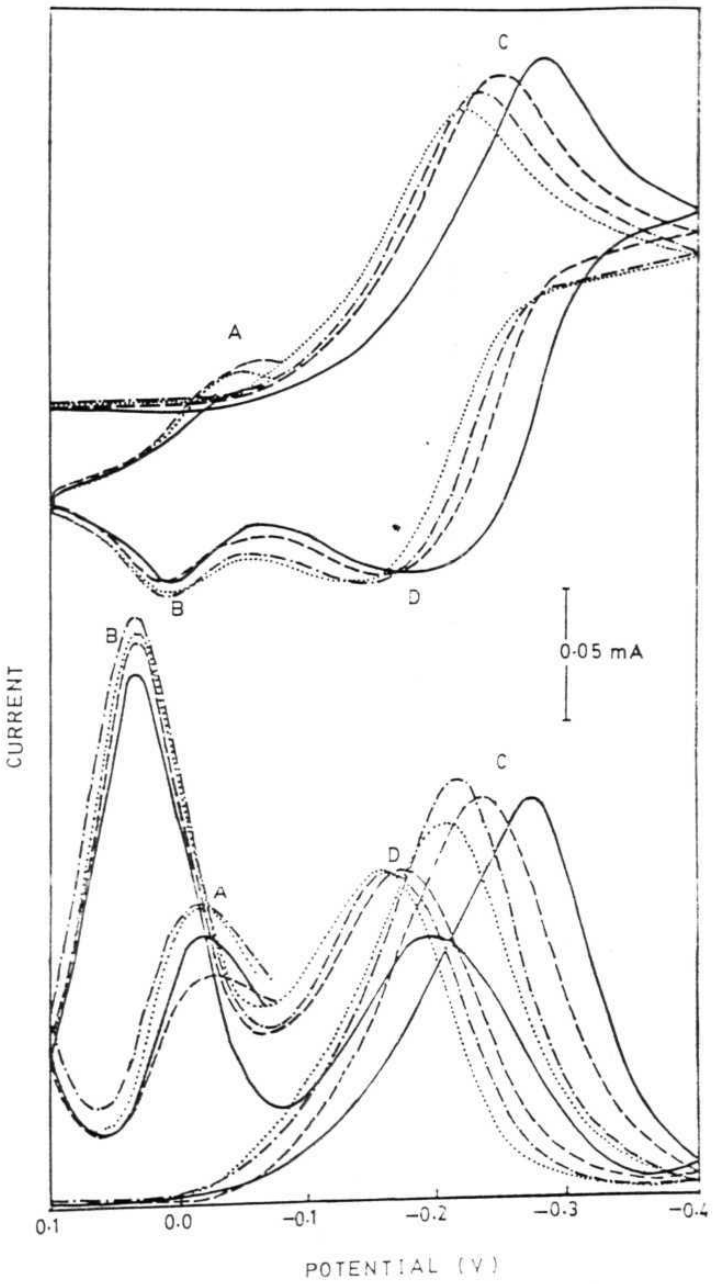


Figure 5.6. CV and DPV profiles of the complex **10** in aqueous media in presence of various proportions of ammonia: 1:0, complex to ammonia ratio (——), 1:1 (----), 1:2 (-·-·-) and 1:6 (·····) at pH 7.0.

Table 5.6. CV data for the complexes **1-10** and **17-21** in aqueous media in the presence of ammonia at various proportions at scan rate 0.050 V/s.

Complex	complex : ammonia	E_p (V) A[a]	B	C	D	ΔE_p(V)	$E_{\frac{1}{2}}$(V)	$-i_c/i_a$
1	1:0	-0.01	0.03	**-0.27**	**-0.20**	0.07	-0.235	1.04
	1:1	-0.01	0.03	-0.23	-0.16	0.07	-0.195	1.00
	1:2	-0.01	0.03	-0.20	-0.12	0.08	-0.160	1.04
	1:6	-0.01	0.03	**-0.20**	**-0.12**	0.08	-0.160	**1.04**
	1:10	-0.01	0.03	-0.18	**-0.10**	0.08	-0.140	1.00
2	1:0	-0.03	0.01	**-0.26**	**-0.18**	0.08	-0.220	1.06
	1:1	-0.03	0.01	**-0.24**	**-0.15**	0.09	-0.195	1.00
	1:2	-0.03	0.01	-0.21	**-0.14**	0.07	-0.175	1.04
	1:6	-0.03	0.00	-0.20	-0.12	0.08	-0.160	1.00
	1:10	-0.03	0.00	-0.18	-0.11	0.07	-0.145	1.02
3	1:0	-0.03	0.03	-0.28	-0.20	0.08	-0.240	1.00
	1:1	-0.04	0.01	-0.25	-0.15	0.10	-0.200	1.00
	1:2	-0.03	0.01	-0.21	-0.14	0.07	-0.175	1.06
	1:6	-0.03	0.01	-0.19	-0.12	0.07	-0.155	1.06
	1:10	-0.03	0.01	-0.19	-0.12	0.07	-0.155	1.00
4	1:0	-0.01	0.03	-0.51	b	--	--	--
	1:1	-0.01	0.03	-0.51	b	--	--	--
	1:2	-0.01	0.03	-0.51	b	--	--	--
	1:6	-0.01	0.03	-0.51	b	--	--	--
	1:10	-0.01	0.03	-0.51	b	--	--	--
5	1:0	-0.01	0.03	-0.53	b	--	--	--
	1:1	-0.01	0.03	-0.53	b	--	--	--
	1:2	-0.01	0.03	-0.53	b	--	--	--
	1:6	-0.01	0.03	-0.53	b	--	--	--
	1:10	-0.01	0.03	-0.53	b	--	--	--
6	1:0	**-0.02**	**0.02**	**-0.27**	**-0.20**	**0.07**	**-0.235**	**1.03**
	1:1	**-0.03**	**0.02**	**-0.23**	**-0.15**	0.08	-0.190	1.00
	1:2	-0.03	0.02	-0.22	-0.14	0.08	-0.180	1.00
	1:6	-0.03	0.02	-0.21	-0.13	0.08	-0.170	1.00
	1:10	**-0.03**	**0.02**	**-0.20**	**-0.12**	0.08	-0.160	1.00
7	1:0	-0.02	0.03	-0.29	**-0.21**	0.08	-0.250	1.04
	1:1	-0.02	0.02	-0.26	-0.18	0.08	-0.220	1.00
	1:2	-0.02	0.02	-0.23	-0.16	0.07	-0.195	1.04
	1:6	-0.02	0.02	-0.22	-0.15	0.07	-0.185	1.04
	1:10	-0.02	0.02	-0.20	-0.14	0.06	-0.170	1.00
8	1:0	-0.03	0.03	-0.26	-0.17	0.09	-0.235	1.00
	1:1	-0.04	0.00	-0.23	-0.15	0.08	-0.190	1.00
	1:2	-0.04	0.00	-0.22	-0.15	0.07	-0.185	1.00
	1:6	-0.03	0.01	-0.21	-0.14	0.07	-0.175	1.00
	1:10	-0.04	0.00	-0.19	-0.12	0.07	-0.155	1.00
9	1:0	-0.03	0.01	-0.28	-0.20	0.08	-0.240	1.00
	1:1	-0.04	0.01	-0.25	-0.18	0.07	-0.215	1.00
	1:2	-0.04	0.01	-0.23	-0.16	0.07	-0.195	1.04
	1:6	-0.04	0.01	-0.22	-0.15	0.01	-0.185	1.00
	1:10	-0.04	0.00	-0.21	-0.13	0.08	-0.170	1.00

Table 5.6 (Contd.)

10	1:0	-0.03	0.03	-0.28	-0.19	0.09	-0.235	1.03
	1:1	-0.03	0.03	-0.22	-0.13	0.09	-0.175	1.00
	1:2	-0.03	0.03	-0.18	-0.11	0.07	-0.145	1.04
	1:6	-0.03	0.01	-0.17	-0.11	0.06	-0.140	1.00
	1:10	-0.02	0.01	-0.16	-0.10	0.06	-0.130	1.04
17	1:0	b	b	-0.27	-0.20	0.07	-0.235	0.91
	1:1	b	b	-0.26	-0.20	0.06	-0.230	1.00
	1:2	b	b	-0.25	-0.19	0.06	-0.220	1.00
	1:6	b	b	-0.25	-0.19	0.06	-0.220	1.00
	1:10	b	b	-0.25	-0.18	0.06	-0.220	0.96
18	1:0	-0.05	0.01	-0.28	-0.22	0.06	-0.250	1.00
	1:1	-0.03	0.02	-0.25	-0.19	0.06	-0.220	1.00
	1:2	-0.03	0.02	-0.23	-0.15	0.08	-0.190	1.05
	1:6	-0.03	0.02	-0.20	-0.13	0.07	-0.165	1.00
	1:10	-0.03	0.03	-0.19	-0.12	0.07	-0.155	0.96
19	1:0	-0.04	0.02	-0.28	-0.21	0.07	-0.245	0.96
	1:1	-0.03	0.02	-0.23	-0.17	0.06	-0.200	1.00
	1:2	-0.02	0.02	-0.21	-0.15	0.06	-0.180	1.00
	1:6	-0.02	0.02	-0.20	-0.13	0.07	-0.165	0.96
	1:10	-0.02	0.02	-0.18	-0.11	0.07	-0.145	1.06
20	1:0	-0.03	0.03	-0.28	-0.22	0.06	-0.250	1.05
	1:1	-0.03	0.02	-0.25	-0.19	0.06	-0.220	1.00
	1:2	-0.03	0.01	-0.22	-0.15	0.07	-0.185	1.06
	1:6	-0.03	0.02	-0.20	-0.13	0.07	-0.165	0.96
	1:10	-0.03	0.01	-0.20	-0.12	0.08	-0.160	1.00
21	1:0	-0.03	0.01	-0.27	-0.20	0.07	-0.235	1.00
	1:1	-0.03	0.01	-0.24	-0.18	0.06	-0.210	1.00
	1:2	-0.03	0.01	-0.21	-0.14	0.07	-0.175	0.96
	1:6	-0.03	0.01	-0.20	-0.13	0.07	-0.165	1.04
	1:10	-0.03	0.01	-0.20	-0.12	0.08	-0.160	1.10

[a]Peak appeared from second scan onwards; [b]peak absent.

Since the pattern of the CV profiles does not show any change, the same mechanism (equations 3.1 to 3.3) can explain the redox process; C-D peaks correspond to Cu(II)/Cu(I) couple and A-B peaks correspond to Cu(0)(Hg)/Cu(II)(aq) couple. Absence of any change in the CV profiles of the complexes **4** and **5** reveals that the interaction between the central Cu(II) ions and water or ammonia is too weak to effect any change in the redox behaviour of the complexes. For the rest of the complexes the interaction

is considerable as the ESR data suggests and hence the change in their electrochemical behaviour. The observations (iii) and (iv) shows that two NH_3 molecules are involved in the replacement of the apical H_2O molecules. The shift of Cu(II)/Cu(I) couple to less negative values is in agreement with the general trend of increase in Cu(II)/Cu(I) reduction potential upon replacing oxygen donor ligands by nitrogen donor ligands.[4] A comparison of changes observed in spectral and redox behaviour of the complexes upon replacement of apical H_2O molecules by NH_3, reveals that the redox behaviour is more sensitive. Addition of other N-donor bases does not effect any shift of Cu(II)/Cu(I) redox potential values indicating the inability of these ligands to interact with the central Cu(II) ions of the complexes replacing the apical water molecules. This may be due to the larger size of the N-donor ligands, making them sterically unsuited for apical coordination. DPV data were also collected for the complexes. Representative DPV profiles are shown in Figure 5.6. The DPV data are in agreement with the CV data.

5.6 Conclusions

Copper(II) complexes of the alicyclic- -amino acids investigated form protonated species, $[CuL]^+$, at pH < 4.5. Only the bis complex species, CuL_2, exhibit reversible one-electron redox process. In general, Cu(II) complexes which exist as hexa coordinated in aqueous media with two solvent H_2O molecules at the apical sites, on addition of ammonia exhibit change in ESR parameters and shift of Cu(II)/Cu(I) redox potential towards less negative potentials commensurate with the replacement of apical H_2O by ammonia.

5.7 References

1. T.A. Connors, L.A. Elson and W.C.J. Ross, Biochem. Pharm. 1958, **1**, 239.
2. L.W. Mapson and D.A. Wardle, Plant Physiol. 1966, **41**, 376.
3. D.D. Adams and S.F. Yard, Proc. Natl. Acad. Sci. U.S.A. 1979, **76**, 170.
4. N. E. Hoffman, S.F. Yang, Y. Ichihara and S. Sakamura, Plant Physiol. 1982, **70**, 195.
5. R.A. Adlington, J.E. Baldwin and B.J. Rawlings, J. Chem. Soc. Chem. Commun. 1983, 290.
6. J.E. Baldwin, D.A. Jackson, R.M. Adlington and B.J. Rowlings, ibid. 1985, 206.
7. D.P. Graddon and L. Munday, J. Inorg. Nucl. Chem. 1961, **23**, 231.
8. D.P. Graddon and L. Munday, ibid. 1963, **25**, 215.
9. H. Yokoi and T. Isobe, Chem. Lett. 1972, 95; H. Yokoi, M. Sai, T. Isobe and S. Ohsawa, Bull. Chem. Soc. Jpn. 1972, **45**, 2189.
10. J.K. Beattie, D.J. Fensom and H.C. Freeman, J. Am. Chem. Soc. 1976, **98**, 500.
11. H. Irving and L.D. Pettit, J. Chem. Soc. 1963, 1546.
12. B.A. Goodman, D.B. McPhail and H.K.J. Powell, J. Chem. Soc. Dalton Trans. 1981, 822.
13. G. Thomas and P.S. Zacharias, Polyhedron 1985, **4**, 811.
14. A.J. Bard and L.R. Faulkner, 'Electrochemical methods, Fundementals and Applications', Wiley, New York, 1980, p.190.
15. K.E. Falk, E. Ivanova, B. Roos and T. Vanngard, Inorg. Chem. 1970, **9**, 556.

16. J. Pradilla-Sorzano and J.P. Fackler, Jr., ibid. 1974, **13**, 38.

17. B.B. Wayland and V.K. Kapur, ibid. 1974, **12**, 2517.

18. R.D. McMillin, R.S. Drago and J.A. Nusz, J. Am. Chem. Soc. 1976, **98**, 3120.

19. T. Kogane, R. Hirota, K. Abe and M. Hirata, J. Chem. Soc. Perkin Trans. 2 1981, 652.

20. Y. Sugiura and Y. Hirayama, Inorg. Chem. 1976, **15**, 679.

21. J. Peisach and W.E. Blumberg, Arch. Biochem. Biophys. 1974, **165**, 691.

22. G.D. Shields, S. Christiano and R.D. Bereman, J. Inorg. Nucl. Chem. 1978, **40**, 1953.

23. H. Okawa and D.H. Busch, Inorg. Chem. 1974, **18**, 1555.

24. B.J. Hathaway and D.E. Billing, Coord. Chem. Rev. 1970, **5**, 143.

25. C. Ou, D.A. Powers, J. Thich, T.R. Felthouse, D.N. Hendrickson, T.A. Potenza and H.J. Schugar, Inorg. Chem. 1978, **17**, 34.

26. U. Sakaguchi and A.W. Addison, J. Chem. Soc. Dalton Trans. 1979, 600.

27. H.M. Swartz, J.R. Bolton and D.C. Borg, 'Biological Applications of Electron Spin Resonance', Wiley-Interscience, New York, 1972, p.428-429, 434-435.

CHAPTER VI

COPPER(II)-N-SALICYLIDENE-AMINO ACIDATO COMPLEXES AND THEIR IMIDAZOLE, PYRAZOLE AND PYRIDINE ADDUCTS

6.1 Abstract

Copper(II) Schiff base complexes derived from salicylaldehyde and amino acids, namely, glycine, L-alanine, L-serine, L-threonine, and ß-alanine, Cu(sal-aa)(H_2O), and their imidazole, pyrazole and pyridine adducts, Cu(sal-aa)L, have been prepared. Their electronic spectral and ESR data in water concur with data obtained in dioxane-H_2O mixture; cyclic voltammetric and differential pulse voltammetric data collected in aqueous media suggest involvement of Cu(I) intermediate species in their redox process; a three-step electrode mechanism has been proposed. In the 5-3.5 pH range, presence of protonated species, [Cu(sal-aaH)-(H_2O)]$^+$, is evident from CV profiles. The electronic spectra of Cu(sal-aa)L adducts show a shift of ca. 10-20 nm in the d-d band

position to lower wavelengths. ESR parameters g_{iso}, $g_{\|}$ and $A_{\|}$ are lower and A_{iso} higher for the adducts compared to the parent complexes. These changes are commensurate with increased planar covalency resulting from the replacement of H_2O molecule by N-donor ligands. The electrochemical behaviour of pyridine adducts is similar to that of Cu(sal-aa)(H_2O) complexes. Imidazole and pyrazole adducts show irreversible one-electron reduction, this difference in electrochemical behaviour being related to the difference in electron acceptor ability of the N-donor ligands. At low pHs, the electrochemical behaviour of the adducts is similar to that of the parent complexes.

6.2 Introduction

Most of the transformations that amino acids undergo during metabolism are catalyzed by enzymes requiring pyridoxal phosphate as cofactors.[1] These reactions also proceed in non-enzymatic pyridoxal-amino acid systems and in many cases addition of metal ions such as copper(II) and zinc(II) to these binary systems has been found to enhance the reaction rates. The role of metal ions in these reactions has been extensively reviewed.[2] The mechanisms proposed for the pyridoxal catalysis however have been derived from studies on model systems such as N-salicylidene-α-amino acidato Schiff bases and their metal complexes.[3] Metal ions may simulate some of the features of enzymic activities by acting as a trap for the Schiff base formed between pyridoxal and the amino acid and more importantly by labilizing the bonds adjacent to the coordinating groups of the amino acid residue. Due to the large interest, many metal ion containing model systems have been

studied. These include 1:1, Cu(II) complexes of N-salicylidene-α-amino acids.[2,4-14] The chelate ring structure of these complexes has been established by X-ray structural studies.[10-14] The structure involves coordination of the tridentate Schiff base ligand through phenolic oxygen, the imino nitrogen and carboxylato oxygen donors. Although structural data on the metal complexes of salicylaldehyde-amino acid Schiff bases are available, there is very little information available on their redox properties, particularly on the Cu(II) complexes. Therefore, we have investigated the redox properties of selected Cu(II) salicylidene-amino acidato complexes, the amino acid moieties therein being glycine, L-alanine, L-serine, L-threonine and ß-alanine. These Cu(II) complexes are abbreviated as Cu(sal-aa)(H_2O), where aa = amino acid residue.

The Cu(II) complexes with nearly planar geometry are able to form adducts with various N-donor ligands such as imidazole, pyrazole and pyridine etc., which is likely to influence redox properties. This has been examined by electrochemical methods. Adduct formation and geometry have been studied by UV-Vis and ESR spectral methods and the results obtained are discussed in the subsequent sections. The adducts are of the general formula, Cu(sal-aa)L, (aa = amino acid; L = N-donor ligand). The electrochemical results are compared with those obtained for Cu(II) complexes of α-amino acids, peptides and related ligands.[15-17]

6.3 Experimental

6.3.1 Preparation of complexes

The complexes, Cu(sal-aa)(H_2O), were prepared from Schiff

base ligands derived from salicylaldehyde and the amino acids, glycine, L-alanine, L-serine, L-threonine and ß-alanine and their imidazole, pyrazole and pyridine adducts, Cu(sal-aa)(H_2O) were prepared as described in Section 2.2

6.3.2 Physical measurements

The general techniques employed are discussed in Section 2.3.

6.4 Results and discussion

The Cu(sal-aa)(H_2O) complexes and the adducts are dark green in colour and are soluble in water and methanol except for Cu(sal-gly)(H_2O) which is insoluble in methanol. In general the adducts were more soluble in methanol. The purity of the complexes was checked by analytical data and IR spectra. The analytical data for all the complexes are given in Table 2.2.

6.4.1 Electronic and ESR spectra

Cu(sal-aa)(H_2O) complexes

Electronic spectra in aqueous media exhibit a band at 660 nm and three UV bands at ca. 360, 270 and 240 nm, in agreement with the previous reports.[6,9] Relevant data are given in Table 6.1. The complexes possess near planar geometry with one H_2O molecule completing the coordination sphere.[10-14] The electronic spectra were studied at low pHs in order to check for any spectral changes, since electrochemical experiments show the presence of protonated species at low pHs as will be discussed later. At low pH, the d-d band decreases and finally disappears at the decomposition pH, 2.5 and no additional bands were observed in the wavelength range 800-400 nm. ESR data have been reported previously

in 3:2 dioxane:H_2O mixture.[18] Since our electrochemical measurements were carried out in aqueous media, ESR data were collected in this medium and the important parameters are: g_{iso} = 2.129-2.135, A_{iso} = 66-72 G, $g_{\|}$ = 2.258-2.279 and $A_{\|}$ = 168-180 G (Table 6.1). The data are close to the values reported in dioxane:H_2O mixture and are compatible with square planar geometry.[18]

Cu(sal-aa)L complexes

Analytical, electronic and ESR spectral data are known[19] only for the Cu(sal-aa)(H_2O) adducts, and ESR data in pyridine solvent are known for a few Cu(sal-aa)(H_2O) complexes.[18] For a systematic investigation the imidazole, pyrazole and pyridine adducts of Cu(sal-gly)(H_2O), Cu(sal-ala)(H_2O), Cu(sal-ser)(H_2O), Cu(sal-thr)(H_2O) and Cu(sal-ß-ala)(H_2O) are prepared. Analytical and IR data on these adducts suggest the replacement of H_2O by the N-donor ligands. The electronic spectra of the adducts exhibit the d-d band at ca. 640 nm, ca. 20 nm lower than the parent complexes. The shift in the d-d band position indicates that the adducts are more planar than their parent complexes. The electronic spectral behaviour at lower pHs differs from that of the parent complexes. In the pH range 6-5 the d-d band of the imidazole adducts gradually shifts from 640 nm to higher wavelengths. At pH 4, the band is at 660 nm and on further lowering of pH, only absorbance decreases. The pyrazole and pyridine adducts do not show such a shift of d-d band on lowering pH up to 5 but at pH 4 the band shifts to 660 nm and on further lowering of pH absorbance decreases. The general ESR pattern is similar to that of the parent complexes. However there is a

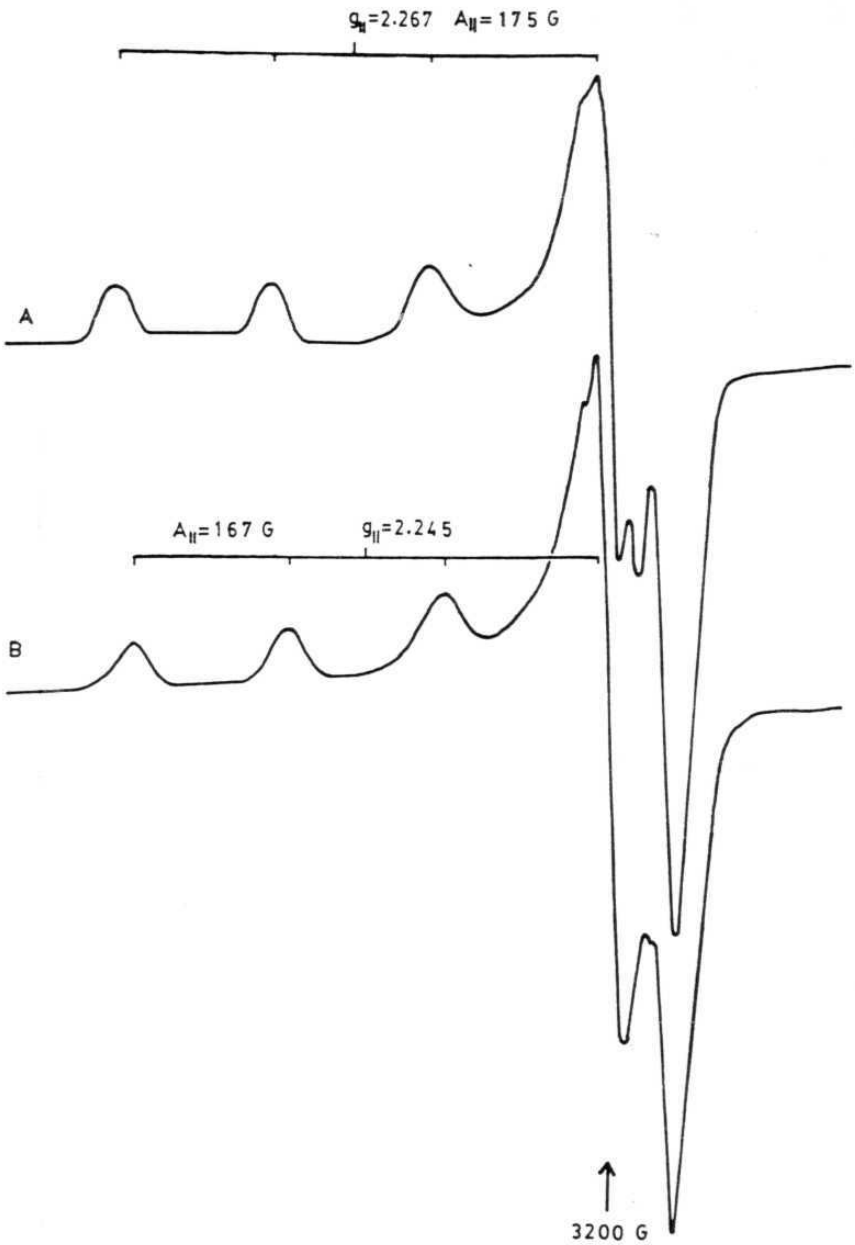


Figure 6.1. Frozen glassy ESR spectra of Cu(sal-ser)(H_2O) (A) and Cu(sal-ser)im (B) in 95:5, water:methanol mixture at 120 K.

Table 6.1. Electronic and ESR spectral data of Cu(sal-aa)(H_2O) complexes and their (im), (py) and (py) adducts in aqueous media.

Complex	$\lambda_{max}(\varepsilon_{max})$ nm($M^{-1}cm^{-1}$)	g_{iso}	A_{iso} (G)	$g_{\parallel}$	$g_{\perp}$ [a]	$A_{\parallel}$ (G)
Cu(sal-gly)H_2O	660 (73)	2.130	71	2.260	2.065	180
Cu(sal-gly)im	640 (95)	2.128	72	2.246	2.069	164
Cu(sal-gly)pz H_2O	655 (92)	2.122	75	2.238	2.064	179
Cu(sal-gly)py	650 (98)	2.128	75	2.249	2.067	177
Cu(sal-ala)H_2O	660 (82)	2.129	71	2.263	2.044	177
Cu(sal-ala)im	645 (89)	2.126	73	2.247	2.065	165
Cu(sal-ala)pz	650 (84)	2.125	74	2.249	2.063	177
Cu(sal-ala)py	650 (88)	2.126	73	2.247	2.065	173
Cu(sal-ser)H_2O	660 (92)	2.132	72	2.267	2.045	175
Cu(sal-ser)im	640 (86)	2.121	73	2.245	2.059	167
Cu(sal-ser)pz	650 (82)	2.121	76	2.242	2.060	175
Cu(sal-ser)py	650 (81)	2.125	73	2.245	2.065	173
Cu(sal-thr)H_2O	660 (91)	2.132	72	2.269	2.058	174
Cu(sal-thr)im	640(103)	2.126	73	2.251	2.063	167
Cu(sal-thr)pz	655(101)	2.132	72	2.248	2.077	175
Cu(sal-thr)py	655(108)	2.130	71	2.247	2.071	172
Cu(sal-ß-ala)H_2O	660 (59)	2.135	66	2.279	2.063	168
Cu(sal-ß-ala)im	650 (54)	2.129	69	2.258	2.065	163
Cu(sal-ß-ala)pz	660 (75)	2.131	73	2.255	2.069	172
Cu(sal-ß-ala)py	660 (72)	2.128	66	2.268	2.058	168

[a] $g_{\perp} = (3g_{iso} - g_{\parallel})/2$

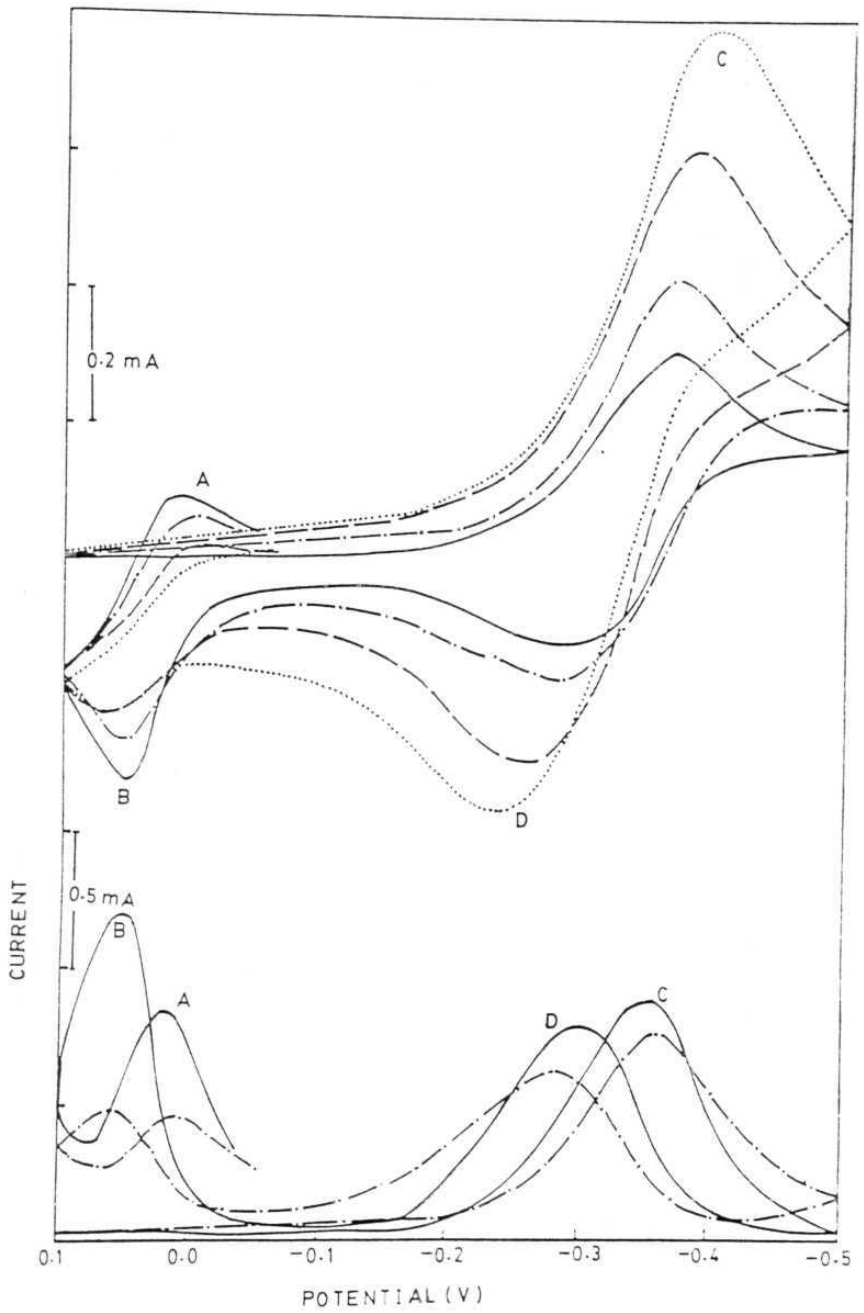
slight decrease of g_{iso} and increase of A_{iso} values by ca. 2-4 G. Frozen glass ESR spectra were also recorded for the Cu(sal-aa)(H_2O) complexes and the adducts. The spectra could be fitted for $g_{\parallel} > g_{\perp} > 2.0$, showing the pattern typical for tetragonal symmetry. Though both the Cu(sal-aa)(H_2O) complexes and the adducts exhibit similar ESR profiles (Figure 6.1), measurable decrease in $g_{\parallel}$ and $A_{\parallel}$ values is observed for the adducts. The ESR data are presented in Table 6.1. Such changes indicate stronger planar covalent bonds resulting from the replacement of H_2O molecule by the N-donor ligand.[6,8,20-26]

6.4.2 Electrochemical data

Cyclic voltammetric data were collected for the complexes in aqueous media. The Schiff bases and the N-donor ligands did not exhibit any redox peaks in the potential range investigated, +0.01 to -1.00 V. The complexes and the adducts did not exhibit any redox peaks in the high negative region(-1.00 to -1.80 V).

Cu(sal-aa)(H_2O)

These complexes exhibited two sets of redox peaks C,D at ca. -0.33 V and A,B at ca. +0.03 V. The electrochemical behaviour can be summarized as follows: (i) a reduction peak (C) at -0.36 V is observed during the first cathodic scan (ii) an oxidation peak (D) appears at -0.30 V on reverse scan along with another oxidation peak (B) at ca. +0.04 V (iii) a new reduction peak (A) is observed from the second scan onwards (iv) when the scan is reversed at -0.30 V (before the appearance of peak C) A,B peaks do not appear (v) if the potential is held at -0.50 V (after the appearance of peak C), the peak heights of A,B peaks increase



ure 6.2. CV and DPV profiles of Cu(sal-ala)(H_2O) in aqueous media at neutral pH at various scan rates: 0.010 V/s (——), 0.020 V/s (—·—·—), 0.050 V/s (----) and 0.100 V/s (·····).

Table 6.2. CV data of Cu(sal-aa)(H_2O) complexes in aqueous media at dissolution pH at different scan rates.

Complex	Scan rate (V/s)	E_p (V)				$\Delta E_{p\,C,D}$ (V)	$E_{\frac{1}{2}\,C,D}$ (V)	$-i_c/i_a$ C,D
		A[a]	B	C	D			
Cu(sal-gly)H_2O	0.01	0.00	0.04	-0.36	-0.29	0.07	-0.325	1.07
	0.02	0.00	0.04	-0.36	-0.29	0.07	-0.325	1.00
	0.05	0.00	0.04	-0.36	-0.27	0.09	-0.315	1.03
	0.10	-0.02	0.06	-0.36	-0.27	0.09	-0.315	0.94
Cu(sal-ala)H_2O	0.01	0.01	0.05	-0.37	-0.30	0.07	-0.335	1.00
	0.02	0.00	0.05	-0.37	-0.30	0.07	-0.335	1.00
	0.05	0.00	0.06	-0.38	-0.28	0.10	-0.330	1.00
	0.10	0.00	0.06	-0.39	-0.25	0.16	-0.330	1.00
Cu(sal-ser)H_2O	0.01	0.00	0.05	-0.37	-0.30	0.07	-0.335	1.00
	0.02	0.00	0.05	-0.37	-0.30	0.07	-0.335	1.00
	0.05	0.00	0.05	-0.38	-0.26	0.12	-0.320	1.00
	0.10	0.00	0.05	-0.39	-0.25	0.14	-0.320	1.00
Cu(sal-thr)H_2O	0.01	0.00	0.05	-0.38	-0.25	0.13	-0.315	1.30
	0.02	0.00	0.05	-0.38	-0.28	0.15	-0.305	1.36
	0.05	0.00	0.05	-0.41	-0.19	0.22	-0.300	1.32
	0.10	0.00	0.00	-0.43	-0.15	0.28	-0.290	1.20
Cu(sal-βala)H_2O	0.01	0.00	0.04	-0.30	-0.24	0.06	-0.270	1.00
	0.02	0.00	0.04	-0.30	-0.24	0.06	-0.270	1.00
	0.05	b	b	-0.31	-0.23	0.08	-0.280	1.00
	0.10	b	b	-0.32	-0.22	0.10	-0.270	1.00

[a]Peak appeared after the second scan; [b]peak absent.

considerably while there is no change in the heights of C,D peaks (vi) peak separation value for the C,D peaks, ΔE_p (C,D), is about 60-80 mV and the current ratio $-i_c/i_a$ (C,D) is ca. 1 (vii) at fast scans the heights of C,D peaks increase while that of A,B peaks decrease (viii) repeated scans do not have much influence on the profiles. CV profiles of a representative complex are shown in Figure 6.2 and the data are given in Table 6.2. Peak C can be due to a one-electron process, Cu(II) $\overset{1e}{\rightleftharpoons}$ Cu(I) or a two-electron Cu(II) $\overset{2e}{\rightleftharpoons}$ Cu(0) process. If it is due to the one-electron process, on reversing the scan the electrochemically generated Cu(I) species may be reoxidised to Cu(II) species resulting a peak (D). The electrochemically generated Cu(I) intermediate species can undergo the chemical decomposition/disproportionation to Cu(0). The two-electron oxidation of Cu(0) to Cu(II) species results peak B and the subsequent reduction of Cu(II) accounts for the peak A. The A,B peaks are shown to result from Cu(II) $\overset{2e}{\rightleftharpoons}$ Cu(0) process by an independent experiment on pure Cu(II) salts. The ΔE_p values are about 60 mV and $-i_c/i_a$ values about 1 for the C,D peaks suggesting reversible one-electron redox process. The absence of peak A in the first scan and its appearance after second scan show that Cu(II) has to be electrochemically generated for the appearance of this peak. The electrode sequence explains this. The second alternative of two-electron reduction for the appearance of peak C cannot explain the experimental observations and therefore is not considered in detail. Electrochemical behaviour of these complexes is very similar to that of Cu(II)-amino acid complexes[17] and some of their condensation products described in Chapter III, for which a

similar mechanism (equations 3.1 to 3.3, ligands are omitted in the equations) has been established.

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

$$2Cu(I) \xrightarrow{\text{Chemical reaction}} Cu(0)(Hg) + Cu(II)(H_2O)$$

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

Inspection of Table 6.2 reveals a shift of C,D peaks to less negative values by 60 mV for Cu(sal-ßala)(H_2O) compared to other complexes. This trend is compatible with an increased degree of tetrahedral distortion[27] as evidenced by the ESR data (decrease of A_{iso} and $A_{\parallel}$ and increase of $g_{\parallel}$ values). More tetrahedral distortion is expected for this complex due to increase in chelate ring size.

To study the effect of pH, CV data were collected at low pHs. The major changes observed are: (i) C,D peaks decrease in height gradually and at pH ca. 4 disappear completely (ii) at pH ca. 4, a new reduction peak (C′) at ca. -0.18 V and an oxidation peak (D′) at ca. -0.12 V appear, and shift to less negative values on further decrease of pH (iii) at pH < 2.5, only A,B peaks are observed (iv) the process is reproducible on increasing pH but heights of C,D peaks are decreased. These changes are shown for a representative complex in Figure 6.3 and the data are presented in Table 6.3. The observation of peaks C′,D′ at pH ca. 4 indicates the formation of a new species which is capable of undergoing one-electron redox process. The new species appears to be, $[Cu(sal\text{-}aaH)(H_2O)]^+$ since Cu(II) salicylaldehyde or amino acid complexes, which can be other possible products, have completely

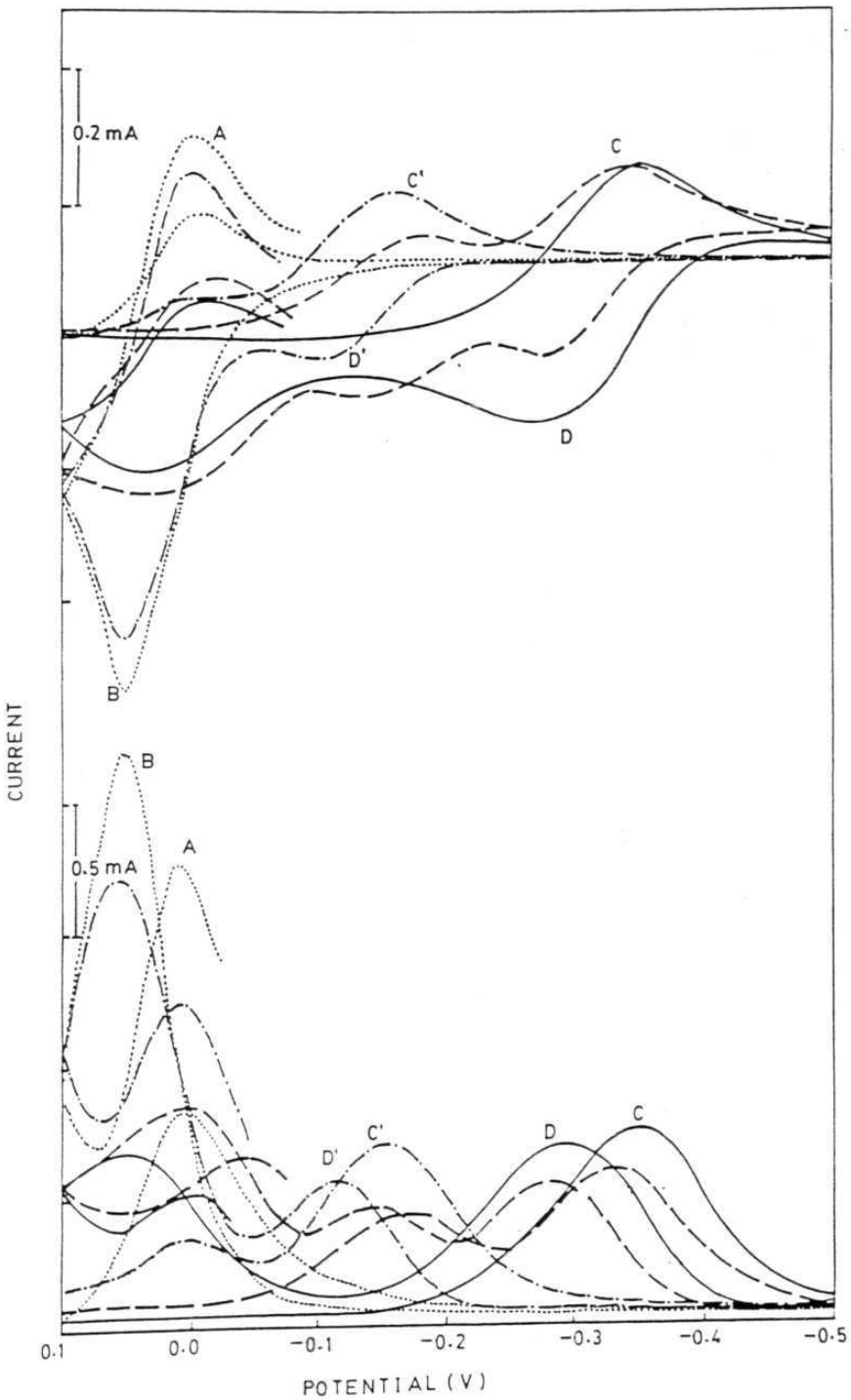


Figure 6.3. CV and DPV profiles of Cu(sal-ser)(H_2O) in aqueous media at various pHs: 7.2 (——), 4.5 (----), 3.0 (-·--) and 2.1 (·····) at scan rates 0.050 and 0.010 V/s respectively.

Table 6.3. CV data of the Cu(sal-aa)(H_2O) complexes in aqueous media at different pHs at scan rate 0.02 V/s.

Complex	pH	E_p (V)				ΔE_p C,D (C',D') (V)	$E_{\frac{1}{2}}$ C,D (C',D') (V)	$-i_c/i_a$ C,D (C,'D')
		A[a]	B	C (C')	D (D')			
Cu(sal-gly)H_2O	7.0	0.00	0.04	-0.36	-0.29	0.07	-0.325	1.07
	6.2	-0.04	0.00	-0.35	-0.27	0.08	-0.310	1.00
	4.4	-0.06	0.00	-0.34	-0.27	0.07	-0.305	1.07
				(-0.18)	(-0.12)	(0.06)	(-0.150)	(1.00)
	3.9	-0.06	-0.02	(-0.16)	(-0.10)	(0.06)	(-0.130)	(1.17)
	3.1	-0.08	-0.02	b	b	..	..	..
Cu(sal-ala)H_2O	7.2	0.00	0.05	-0.37	-0.30	0.07	-0.335	1.00
	4.9	0.00	0.05	-0.37	-0.27	0.10	-0.320	1.11
	4.2	0.00	0.05	-0.36	-0.29	0.07	-0.325	1.00
				(-0.19)	(-0.12)	(0.07)	(-0.155)	(1.11)
	3.4	0.00	0.05	(-0.14)	(-0.07)	(0.07)	(-0.105)	(1.00)
	3.1	0.00	0.05	b	b	..	..	..
Cu(sal-ser)H_2O	7.2	0.00	0.05	-0.37	-0.30	0.07	-0.335	1.00
	5.9	-0.05	0.00	-0.35	-0.27	0.08	-0.310	1.00
	4.5	-0.05	0.00	-0.34	-0.28	0.06	-0.310	1.00
				(-0.18)	(-0.12)	(0.06)	(-0.150)	(1.00)
	3.0	0.00	0.05	(-0.16)	(-0.10)	(0.06)	(-0.130)	(1.20)
	2.1	-0.01	0.04	b	b	..	..	..
Cu(sal-thr)H_2O	7.2	0.00	0.05	-0.38	-0.23	0.15	-0.305	1.36
	5.0	0.00	0.04	-0.38	-0.25	0.13	-0.315	1.20
	3.8	0.00	0.04	-0.34	-0.26	0.06	-0.290	1.33
				(-0.18)	(-0.12)	(0.06)	(-0.150)	(1.10)
	3.0	0.00	0.05	(-0.14)	(-0.08)	(0.06)	(-0.110)	(1.00)
	2.4	-0.04	0.06	b	b	..	..	..
Cu(sal-βala)H_2O	7.2	0.00	0.04	-0.30	-0.24	0.06	-0.270	1.00
	5.9	0.00	0.04	-0.30	-0.24	0.06	-0.270	1.00
	4.6	0.00	0.04	-0.28	-0.22	0.06	-0.250	1.00
				(-0.18)	(-0.12)	(0.06)	(-0.150)	(1.00)
	4.1	0.00	0.04	(-0.15)	(-0.05)	(0.10)	(-0.100)	(0.90)
	3.1	-0.01	0.04	b	b	..	..	..

Values in parentheses correspond to C',D' peaks; [a]Peak appeared from the second scan onwards; [b]peak absent.

different CV profiles at this pH. Though Cu(II)-α-amino acid complexes and similar systems can be protonated the species produced do not undergo one-electron redox process.[15-17] The $[Cu(sal\text{-}aaH)(H_2O)]^+$ undergoes one-electron redox process, stability of the intermediate Cu(I) species arising from increased chelation present in the $Cu(sal\text{-}aa)(H_2O)$ complexes compared to the Cu(II)-α-amino acidato complexes.

Cu(sal-aa)L complexes

The CV behaviour of pyridine adducts at neutral pH is very similar to the parent $Cu(sal\text{-}aa)(H_2O)$ complexes implying that replacement of H_2O by pyridine does not substantially affect the electrochemical behaviour. However, the imidazole and pyrazole adducts exhibit the following changes: (i) peak C appears at more negative potentials (ca. -0.40 V) (ii) peak D is absent even at high scan rates but A, B peaks appear at the same potentials. Representative CV profiles are shown in Figure 6.4 and the data collected in Table 6.4. Absence of peak D implies that the Cu(II)/Cu(I) redox process is not reversible i.e., the Cu(I) intermediate species generated is unstable for these adducts and undergoes immediate chemical disproportionation/decomposition excluding its reoxidation. The pyridine adducts show reversible one-electron redox behaviour (presence of peak D) indicating higher stability of their Cu(I) intermediate species. It is well known that Cu(I) complexes are stabilized by 'softer' ligands.[27] The greater π-acceptor ability (softness) of pyridine compared to imidazole and pyrazole can be inferred from the CV behaviour. Origin of the peaks B and A relates to two-electron oxidation-reduction of Cu(0) as in the case of parent complexes.

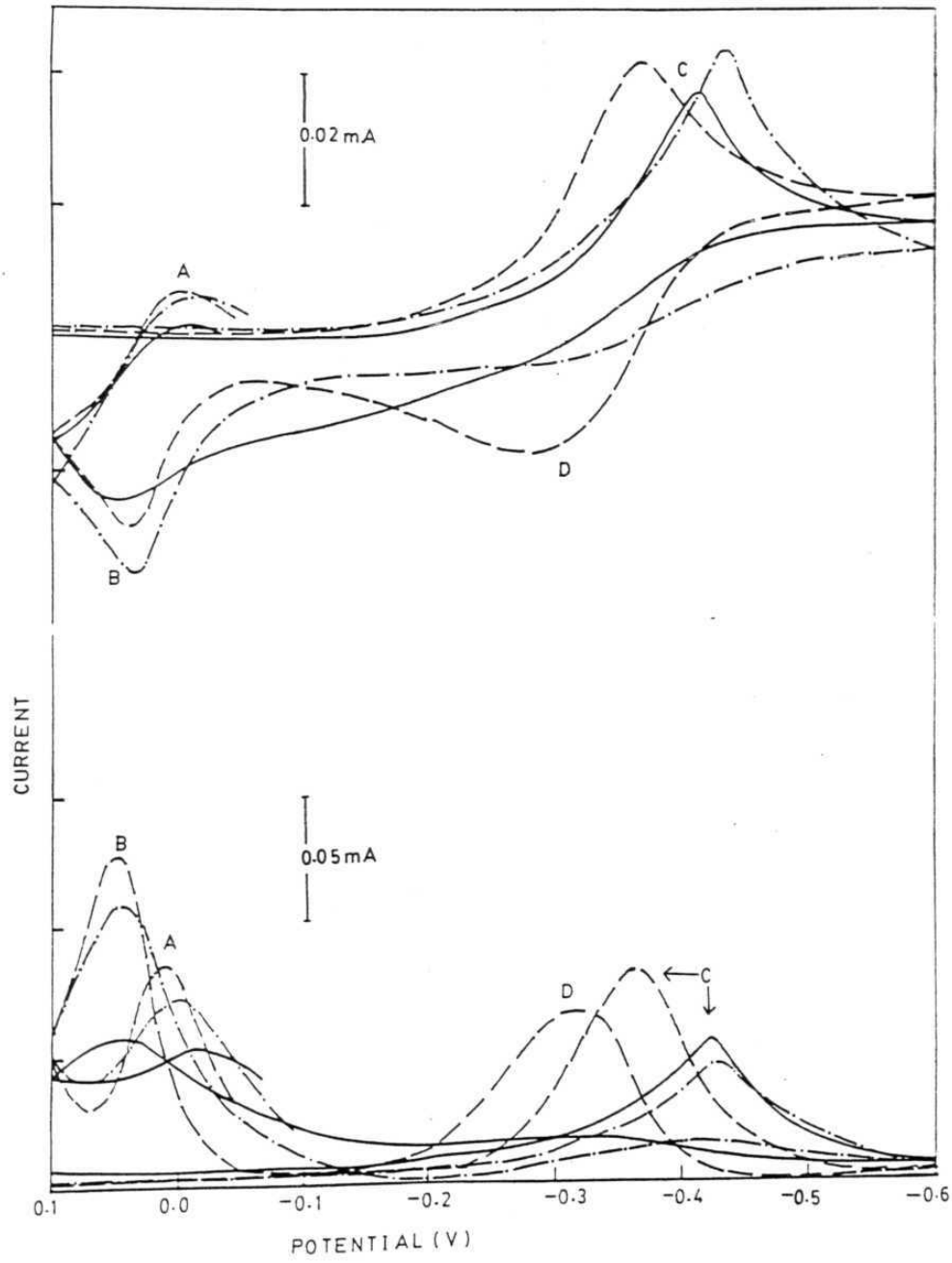


Figure 6.4. CV and DPV profiles of Cu(sal-ala)im (——), Cu(sal-ala)pz (—·—·—) and Cu(sal-ala)py (----) at scan rates 0.050 and 0.010 V/s respectively.

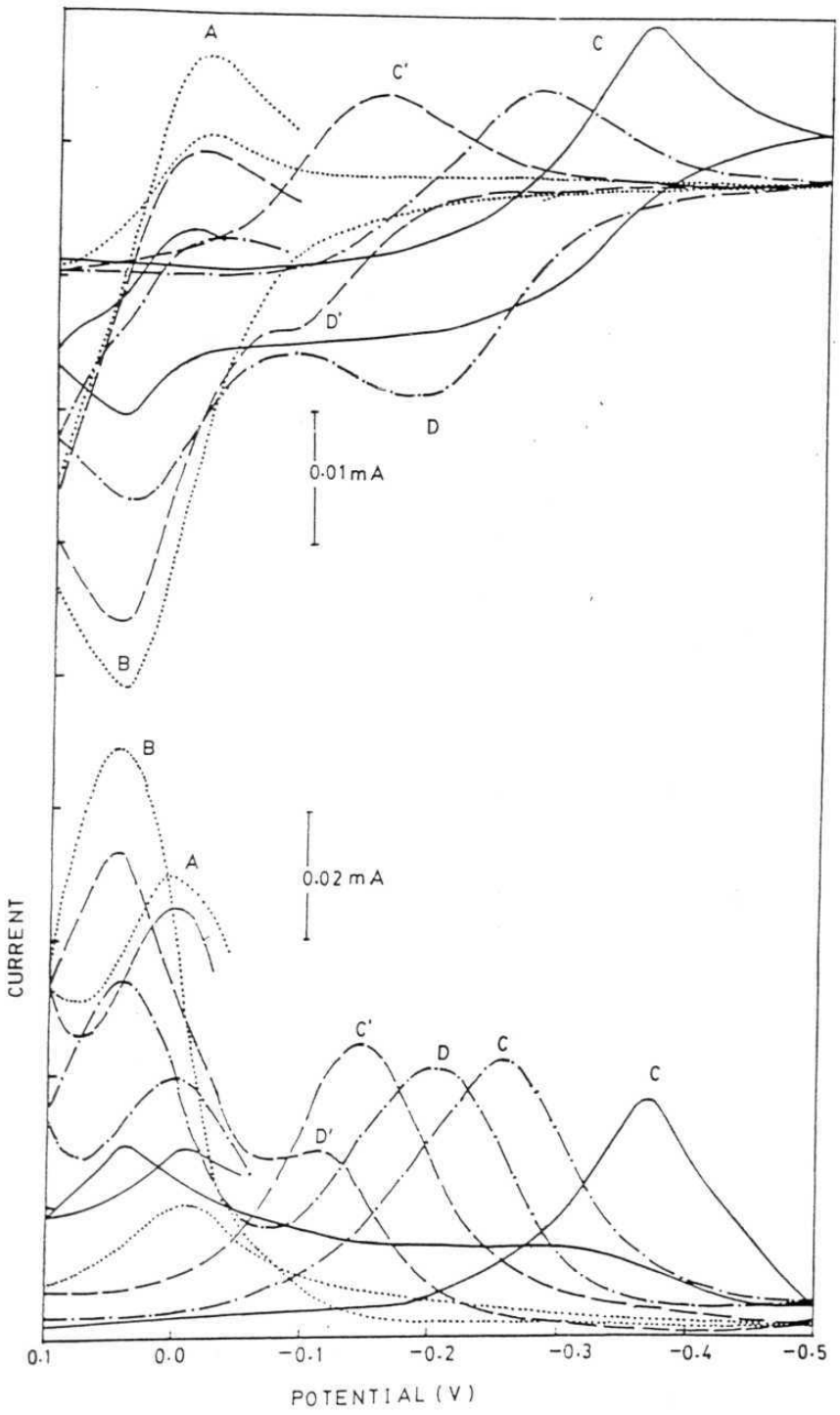


Figure 6.5. CV and DPV profiles of Cu(sal-gly)im in aqueous media at various pHs: 7.5 (——), 5.6 (—·—·—), 4.6 (----) and 3.3 (·····) at the scan rates 0.050 and 0.010 V/s respectively.

Table 6.4. CV data of the adducts in aqueous media at various pHs at scan rate 0.020 V/s.

Complex	pH	E_p (V)				ΔE_p C,D (C',D') (V)	$E_{\frac{1}{2}}$ C,D (C',D') (V)	$-i_c/i_a$ C,D (C',D')
		A[a]	B	C (C')	D (D')			
Cu(sal-gly)im	7.5	0.00	0.04	-0.36	b	..	..	..
	5.6	-0.01	0.04	-0.27	-0.17	0.10	-0.22	1.13
	4.6	-0.01	0.04	(-0.20)	(-0.14)	(0.06)	(-0.17)	(1.36)
	3.3	-0.01	0.04	(-0.08)	b	..	..	..
Cu(sal-gly)pz H_2O	7.3	0.01	0.04	-0.40	b	..	..	..
	5.0	0.00	0.04	-0.39	b	..	..	..
	3.6	0.00	0.04	(-0.12)	(-0.09)	(0.03)	(-0.105)	(1.00)
	2.5	0.00	0.04	b	b	..	..	..
Cu(sal-gly)py	7.6	0.00	0.04	-0.36	-0.27	0.09	-0.315	1.07
	5.1	0.00	0.04	(-0.22)	(-0.17)	(0.05)	(-0.195)	(1.33)
	4.2	0.00	0.04	(-0.15)	(-0.10)	(0.05)	(-0.125)	(1.30)
	3.1	0.01	0.04	b	b	..	..	..
Cu(sal-ala)im	7.6	-0.01	0.05	-0.42	b	..	..	..
	6.1	-0.10	-0.02	-0.34	-0.20	0.14	-0.27	0.83
	4.9	-0.10	-0.06	-0.30	-0.20	0.10	-0.25	0.93
	3.6	-0.16	-0.07	b	b	..	..	..
Cu(sal-ala)pz	7.2	-0.01	0.04	-0.40	b	..	..	..
	6.0	0.00	0.04	-0.41	b	..	..	..
	4.2	0.00	0.04	(-0.15)	(-0.09)	(0.06)	(-0.12)	(1.58)
	2.8	0.00	0.04	b	b	..	..	..
Cu(sal-ala)py	7.6	0.00	0.04	-0.37	-0.29	0.08	-0.33	1.06
	6.0	0.00	0.04	-0.37	-0.30	0.07	-0.225	1.00
				(-0.23)	(-0.17)	(0.06)	(-0.200)	(1.00)
	5.2	0.00	0.04	(-0.23)	(-0.17)	(0.06)	(-0.200)	(1.20)
	4.0	0.00	0.04	(-0.17)	(-0.12)	(0.05)	(-0.145)	(1.24)
Cu(sal-ser)im	7.4	-0.01	0.05	-0.39	b	..	..	..
	5.0	0.00	0.04	-0.29	-0.16	0.13	-0.225	1.21
	3.5	0.00	0.04	(-0.15)	(-0.10)	(0.05)	(-0.125)	(1.29)
	2.1	0.00	0.04	b	b	..	..	..
Cu(sal-ser)pz	7.4	0.00	0.04	-0.43	b	..	..	..
	5.2	0.00	0.04	-0.38	b	..	..	..
				(-0.22)	(-0.16)	(0.06)	(-0.190)	(1.35)
	4.4	0.00	0.04	(-0.17)	(-0.13)	(0.04)	(-0.150)	(2.37)
	2.5	0.00	0.04	b	b	..	..	..
Cu(sal-ser)py	7.5	0.00	0.04	-0.37	-0.28	0.09	-0.325	1.06
	6.2	0.00	0.04	-0.36	-0.28	0.08	-0.320	0.92
				(-0.21)	(-0.17)	(0.04)	(-0.190)	(1.26)
	4.6	0.00	0.03	(-0.21)	(-0.15)	(0.06)	(-0.180)	(1.13)
	3.6	0.00	0.03	(-0.11)	(-0.08)	(0.03)	(-0.095)	(2.50)
Cu(sal-thr)im	7.5	0.00	0.04	-0.37	b	..	..	..
	5.0	0.00	0.04	-0.28	-0.17	0.11	-0.225	0.87
	4.1	0.00	0.04	(-0.18)	(-0.12)	(0.06)	(-0.150)	(1.11'
	2.9	0.00	0.04	b	b	..	..	..

Table 6.4 (contd.)

Cu(sal-thr)pz	7.3	0.00	0.05	-0.41	b	..	..	..
	5.3	0.01	0.05	-0.39	b	..	..	..
				(-0.15)	(-0.11)	(0.04)	(-0.130)	(1.32)
	3.5	0.01	0.05	(-0.11)	(-0.07)	(0.04)	(-0.090)	(1.43)
	3.0	0.00	0.04	b	b	..	..	..
Cu(sal-thr)py	7.2	0.01	0.04	-0.37	-0.22	0.15	-0.295	1.50
	6.0	0.01	0.05	-0.35	-0.29	0.06	-0.320	1.00
				(-0.22)	(-0.16)	(0.06)	(-0.190)	(1.44)
	5.0	0.01	0.05	(-0.20)	(-0.14)	(0.06)	(-0.170)	(1.10)
	3.5	0.01	0.05	(-0.11)	(-0.06)	(0.05)	(-0.085)	(1.10)
Cu(sal-βala)im	7.6	b	0.04	-0.31	b	..	..	..
	6.0	0.00	0.04	-0.22	-0.16	0.06	-0.190	1.07
	4.2	0.00	0.04	(-0.14)	(-0.07)	(0.07)	(-0.105)	(1.09)
	3.6	0.01	0.04	b	b	..	..	..
Cu(sal-βala)pz	7.2	0.0	0.04	-0.37	b	..	..	..
	5.5	0.0	0.04	-0.36	b	..	..	..
	4.6	0.0	0.04	(-0.15)	(-0.09)	(0.06)	(-0.120)	(1.00)
	3.7	0.0	0.04	b	b	..	..	..
Cu(sal-βala)py	7.3	0.01	0.04	-0.31	-0.25	0.060	-0.280	1.00
	5.5	0.01	0.04	-0.30	-0.24	0.060	-0.270	1.00
	3.9	0.01	0.04	(-0.11)	(-0.06)	(0.050)	(-0.085)	(1.43)
	2.5	0.01	0.04	b	b	..	..	..

Values in parentheses correspond to C',D' peaks; [a]peak appeared from the second scan onwards; [b]peak absent.

Major changes in the CV behaviour of the adducts at lower pHs can be summarized as follows: (i) at pH ca. 6 peak C shifts to less negative potentials by ca. 60-80 mV along with the appearance of peak D for the imidazole adducts (ii) peak D does not appear even at pH 5 for the pyrazole adducts (iii) at pH 6, the pyridine adducts exhibit C',D' peaks along with the C,D peaks and at pH 5 only the C',D' peaks are observed (iv) for the imidazole and pyrazole adducts only at pH ca. 4, the C',D' peaks appear (v) for all the adducts, C',D' peaks shift to less negative values on further decrease of pH and finally disappear at pH ca. 2.5 (vi)

these electrochemical changes are reproducible on increasing pH from 2.5 to 7 but there is a decrease in their peak heights. The CV profiles of a representative adduct are shown in Figure 6.5 and the data collected in Table 6.4. Similarity with the parent Cu(sal-aa)(H_2O) complexes at or below pH 4 indicates that the coordinated N-donor ligands are displaced as the pH is lowered generating the parent complex. This may be due to the protonation of the donor ligands thereby weakening the ligand-metal bonds. Presence of C′,D′ peaks for the adducts at pH ca. 4 therefore will have the same origin as C′,D′ peaks of the parent complexes.

Differential pulse voltammograms were recorded for all the Cu(sal-aa)(H_2O) complexes in aqueous media at the same experimental conditions as those of CV experiments. DPV data have been compared with the CV data. DPV profiles of a representative complex are given in Figure 6.2. They show the four peaks C,D and A,B. The n value calculated from $W_{\frac{1}{2}}$ values[28] for C,D peaks is ca. 1, indicating one-electron transfer process, a conclusion drawn from the CV data. relevant DPV data are given in Table 6.5. Differential pulse voltammograms have been recorded for all the complexes at lower pHs also. DPV profiles of a representative complex are given in Figure 6.3. Appearance of C′,D′ peaks and other changes observed with the CV profiles could be seen with the DPV profiles also. DPV data have been collected for the adducts in aqueous media at neutral and low pHs. The imidazole and pyrazole adducts exhibit the presence of peak C at more negative values but the oxidation peak D is absent at neutral pH.

Table 6.5. Differential pulse voltammetric data of the Cu(sal-aa)(H_2O) complexes at different pHs at scan rate 0.010 V/s.

Complex	pH	E_p (V)				n^a	
		A[b]	B	C (C')	D (D')	C (C')	D (D')
Cu(sal-gly)H_2O	7.0	0.00	0.05	-0.35	-0.29	0.82	0.82
	6.2	0.00	0.05	-0.34	-0.29	0.90	0.90
	4.4	-0.05	0.00	-0.33	-0.27	0.90	0.82
				(-0.18)	(-0.11)	(0.90)	(0.82)
	3.9	-0.06	-0.01	(-0.13)	(-0.07)	(0.82)	(0.82)
	3.1	-0.00	-0.01	c	c	..	..
Cu(sal-ala)H_2O	7.2	0.02	0.06	-0.37	-0.30	1.00	0.90
	4.9	0.02	0.06	-0.37	-0.30	0.90	0.82
	4.2	0.01	0.05	-0.36	-0.30	0.90	0.90
				(-0.19)	(-0.12)	(0.90)	(1.00)
	3.4	0.00	0.05	(-0.13)	(-0.08)	(1.00)	(1.00)
	3.1	0.00	0.05	c	c	..	..
Cu(sal-ser)H_2O	7.2	0.00	0.04	-0.35	-0.29	0.90	0.90
	5.9	0.00	0.05	-0.34	-0.29	0.90	0.90
	4.5	-0.05	0.00	-0.33	-0.28	0.90	0.90
				(-0.17)	(-0.11)	(1.00)	(0.90)
	3.0	0.00	0.04	(-0.15)	(-0.10)	(1.00)	(1.00)
	2.1	0.00	0.04	c	c	..	..
Cu(sal-thr)H_2O	7.2	0.01	0.05	-0.37	-0.28	1.00	0.82
	5.0	0.01	0.05	-0.37	-0.28	0.90	0.82
	3.8	0.01	0.05	-0.31	-0.25	0.82	0.82
				(-0.18)	(-0.12)	(0.90)	(1.00)
	3.0	-0.01	0.05	(-0.14)	(-0.08)	(1.00)	(0.90)
	2.4	-0.01	0.05	c	c	..	..
Cu(sal-βala)H_2O	7.2	0.00	0.05	-0.30	-0.24	0.90	0.90
	5.9	0.00	0.05	-0.30	-0.24	0.90	0.90
	4.6	0.00	0.05	-0.28	-0.22	0.90	0.90
				(-0.18)	(-0.12)	(0.90)	(1.00)
	4.1	0.00	0.05	(-0.15)	(-0.09)	(0.90)	(1.00)
	3.1	-0.01	0.05	c	c	..	..

Values in parentheses correspond to C',D'peaks; [a] $n = 90.4/W_{\frac{1}{2}}$;
[b] peak appeared from the second scan onwards; [c] peak absent.

Table 6.6. DPV data of the Cu(sal-aa)L adducts in aqueous media at various pHs at scan rate 0.010 V/s.

Complex	pH	E_p (V)				n^a	
		A[b]	B	C (C')	D (D')	C (C')	D (D')
Cu(sal-gly)im	7.5	0.00	0.05	-0.36	c	0.82	..
	5.6	0.00	0.05	-0.28	-0.22	0.82	0.82
	4.6	0.00	0.04	(-0.20)	(-0.14)	(0.82)	(1.00)
	3.3	0.00	0.04	c	c	..	..
Cu(sal-gly)pz H_2O	7.3	0.01	0.04	-0.41	c	1.00	..
	5.0	0.00	0.04	-0.40	c	1.13	..
	3.6	0.00	0.04	(-0.13)	(-0.08)	(1.29)	(1.29)
	2.5	0.00	0.04	c	c	..	..
Cu(sal-gly)py	7.6	0.00	0.05	-0.36	-0.30	1.00	1.00
	5.1	0.00	0.04	(-0.22)	(-0.17)	(1.00)	(1.13)
	4.2	0.00	0.04	(-0.14)	(-0.10)	(1.29)	(1.13)
	3.1	0.01	0.05	c	c	..	..
Cu(sal-ala)im	7.6	0.00	0.04	-0.44	c	1.00	..
	6.1	-0.06	-0.02	-0.34	-0.25	0.82	0.90
	4.9	-0.10	-0.06	-0.32	-0.25	0.90	1.00
	3.6	-0.16	-0.08	c	c	..	..
Cu(sal-ala)pz	7.2	0.00	0.04	-0.44	c	1.00	..
	6.0	0.00	0.04	-0.43	c	1.00	..
	4.2	0.00	0.04	(-0.15)	(-0.09)	(1.13)	(1.13)
	2.8	0.00	0.04	c	c	..	..
Cu(sal-ala)py	7.6	0.00	0.04	-0.38	-0.32	1.00	1.00
	6.0	0.00	0.04	-0.37	-0.31	1.00	1.00
	5.2	0.00	0.04	(-0.23)	(-0.17)	(1.00)	(0.90)
	4.0	0.00	0.04	(-0.17)	(-0.12)	(1.29)	(1.29)
Cu(sal-ser)im	7.4	0.00	0.04	-0.41	c	1.00	..
	5.0	0.00	0.04	-0.32	-0.27	1.00	1.00
	3.5	0.01	0.05	(-0.15)	(-0.10)	(1.13)	(1.29)
	2.1	0.01	0.05	c	c	..	..
Cu(sal-ser)pz	7.4	0.0	0.05	-0.44	c	1.13	..
	5.2	0.00	0.04	-0.40	c	1.13	..
				(-0.22)	(-0.15)	(1.00)	(1.00)
	4.4	0.00	0.04	(-0.17)	(-0.11)	(1.00)	(1.00)
	2.5	0.00	0.04	c	c	..	..

Table 6.6 (Contd.)

Cu(sal-ser)py	7.5	0.00	0.04	-0.38	-0.30	0.90	0.90
	6.2	0.00	0.0	-0.37	-0.31	1.00	1.00
				(-0.22)	(-0.18)	(1.29)	(1.29)
	4.6	0.00	0.04	(-0.21)	(-0.16)	(1.00)	(1.00)
	2.5	0.00	0.04	c	c	..	..
Cu(sal-thr)im	7.5	0.00	0.04	-0.39	c	0.90	..
	5.0	0.00	0.05	-0.29	-0.20	0.90	0.82
	4.1	0.00	0.05	(-0.19)	(-0.14)	(0.82)	(0.90)
	2.9	0.00	0.05	c	c	..	..
Cu(sal-thr)pz	7.3	0.01	0.04	-0.42	c	0.90	..
	5.3	0.01	0.05	-0.41	c	1.13	..
	3.5	0.01	0.05	(-0.11)	(-0.07)	(1.29)	(1.29)
	3.0	0.01	0.05	c	c	..	..
Cu(sal-thr)py	7.2	0.01	0.05	-0.37	-0.30	1.00	1.00
	6.0	0.01	0.05	-0.35	-0.29	1.00	1.00
				(-0.22)	(-0.16)	(1.00)	(1.00)
	5.0	0.01	0.05	(-0.20)	(-0.14)	(1.00)	(1.13)
	3.5	0.01	0.05	(-0.11)	(-0.06)	(1.29)	(1.29)
Cu(sal-βala)im	7.6	0.00	0.05	-0.31	c	..	..
	6.0	0.00	0.05	-0.23	-0.18	1.00	1.00
	4.2	0.00	0.05	-0.14	(-0.07)	(1.00)	(1.13)
	3.6	0.01	0.05	c	c	..	..
Cu(sal-βala)pz	7.2	0.00	0.04	-0.38	c	1.00	..
	5.5	0.00	0.04	-0.37	c	1.00	..
	4.6	0.00	0.04	(-0.15)	(-0.09)	(1.00)	(1.29)
	3.7	0.00	0.04	c	c	..	..
Cu(sal-βala)py	7.3	0.01	0.04	-0.31	-0.25	1.00	1.00
	5.5	0.01	0.04	-0.30	-0.25	1.00	1.00
	3.9	0.01	0.04	(-0.10)	(-0.05)	(1.29)	(1.29)
	2.5	0.01	0.04	c	c	..	..

Values in parentheses correspond to the C',D' peaks; [a] $n = 90.4/W_{\frac{1}{2}}$;

[b] peak appeared from the second scan onwards; [c] peak absent.

The pyridine adducts exhibit similar DPV behaviour as that of the parent complexes at neutral and low pHs. Imidazole and pyrazole adducts show presence of C′,D′ peaks at pH ca. 4 as the parent complexes. DPV data of the adducts are presented in Table 6.6 and profiles of a representative adduct are shown in Figure 6.5. These data are supportive of the conclusions drawn from the CV data.

6.5 Conclusions

The Cu(sal-aa)(H_2O) complexes are of planar geometry as evidenced by the ESR data. Their CV behaviour is similar to that of Cu(II)-α-amino acid complexes at neutral pH but at low pHs there are observable differences. An electrode mechanism involving Cu(I) intermediate is suggested and discussed. At lower pHs, protonated species such as $[Cu(sal\text{-}aaH)(H_2O)]^+$ are formed, which undergo one-electron redox process at a less negative potential. Electronic and ESR spectral data show that the N-donor ligands replace the equatorial H_2O molecule of the parent complexes during adduct formation enhancing the planar covalency of the copper-N-donor ligand bond. This is reflected in their redox behaviour. The imidazole and pyrazole adducts undergo irreversible Cu(II)/Cu(I) redox process in contrast to the pyridine adducts. The greater 'softness' (π-acceptor ability) of pyridine has been attributed to the reversibility shown by the pyridine adducts.

6.6 References

1. H.C. Dunathan, Adv. Enzymol. 1971, **35**, 79; D.E. Metzler, ibid. 1979, **50**, 1; J.C. Vedras and H.G. Floss, Acc. Chem. Res. 1980, **13**, 455.
2. D.A. Phipps, J. Mol. Catal. 1979, **5**, 81.
3. R.D. Gillard and R. Wootton, J. Chem. Soc. B 1970, 364; H.R. Mohler and E.H. Corders, in 'Biological Chemistry', Harper and Row, New York, 1971, p.393.
4. G.N. Weinstein, M.J. O'Connor and R.H. Holm, ibid. 1970, **9**, 2104.
5. G.O. Carlisle and L.J. Theriot, J. Inorg. Nucl. Chem. 1973, **35**, 2093.
6. L.A. Zyzyck, H. Frummer and J.F. Villa, ibid. 1975, **37**, 1653.
7. G.C. Percy, ibid. 1975, **37**, 2071.
8. L. Casella, M. Gullotti, A.Pasini and M. Visca, Inorg. Chim. Acta 1976, **19**, L9; L. Casella, M. Gullotti, A. Pasini and A. Rockenbauer, Inorg. Chem. 1979, **18**, 2825.
9. M.R. Wagner and F.A. Walker, ibid. 1983, **22**, 3021.
10. T. Ueki, T. Ashida, Y. Sasada and M. Kakudo, Acta Crystallogr. 1967, **B22**, 870.
11. T. Ueki, Y. Sasada and M. Kakudo, ibid. 1969, **B25**, 329.
12. Y. Nakao, K. Sakurai and A. Nakahara, Bull. Chem. Soc. Jpn. 1967, **40**, 1536.
13. K. Korhonen and R. Hamalainen, Acta Crystallogr. 1981, **B37**, 829.
14. T. Ueki, T. Ashida, Y. Sasada and M. Kaguto, ibid. 1968, **B24**, 1361.

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

16. G. Thomas and P.S. Zacharias, ibid. 1985, **4**, 299.

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

18. J. Jazierska, ibid. 1987, **6**, 1669.

19. G. Plesch, C. Friebel, O. Svajlenova and Kratsmar-Smogrovic, Inorg. Chim. Acta 1987, **129**, 81.

20. H. Yokoi, M. Sai, T. Isobe and S. Ohsawa, Bull. Chem. Soc. Jpn. 1972, **45**, 2189.

21. I. Adato, A.H.I. Ben-Bassat and S. Sarel, J. Phys. Chem. 1971, **75**, 3828.

22. H. Yokoi and T. Isobe, Bull. Chem. Soc. Jpn. 1969, **42**, 2187.

23. H.A. Kùska and M.T. Rogers J. Chem. Phys. 1965, **43**, 1744.

24. H.A. Kuska, M.T. Rogers and R.E. Drullinger, J. Phys. Chem. 1967, **71**, 109.

25. J. Peisach and W.E. Blumberg, Arch. Biochem. Biophys. 1974, **165**, 691.

26. L. Casella, M. Gullotti and G. Pacchioni, J. Am. Chem. Soc. 1982, **104**, 2386.

27. H. Yokoi and A.W. Addison, Inorg. Chem. 1977, **16**, 1341.

28. A. J. Bard and L. R. Faulkner, 'Electrochemical Methods Fundamentals and applications' Wiley, New York, 1980, p.190.

PUBLICATIONS

1. Spectral and electrochemical investigations on some condensation products of copper(II)-amino acid complexes.
   N. Arulsamy, B. Srinivas and P.S. Zacharias, Transition Met. Chem. 1990, **15**, 309.

2. Spectral and electrochemical investigations of copper(II)-N-salicylidene-amino acidato complexes and their imidazole, pyrazole and pyridine adducts.
   N. Arulsamy and P.S. Zacharias, Transition Met. Chem. in press.

3. Catalytic and magnetic properties of a new series of binuclear copper(II) complexes.
   B. Srinivas, N. Arulsamy and P.S. Zacharias, Polyhedron in press.

4. Spectral and electrochemical properties of copper(II) complexes of some alicyclic-α-amino acids.
   N. Arulsamy and P.S. Zacharias, Polyhedron in press.

5. Condensation reaction of bis(ß-alaninato)copper(II) with formaldehyde and ammonia.
   N. Arulsamy and P.S. Zacharias, Inorg. Chim. Acta communicated.

6. Interesting redox properties of an intermolecularly interacting copper(II) system.

N. Arulsamy and P.S. Zacharias, J. Chem. Soc. Chem. Comm. communicated.

Presentation

1. Redox properties of copper(II)-alicyclic-α-amino acid complexes. P.S. Zacharias and N. Arulsamy, Presented at the 'Symposium on Modern Trends in Inorganic Chemistry' held at Bombay, 1989.