A P P E N D I X

ABSTRACTS OF THE PUBLICATIONS BASED ON PRESENT WORK

Intramolecular Interligand Interactions in Cu(II) Ternary Complexes Involving Dipeptides and Amino Acids

Journal of Inorganic Biochemistry, 39, 1, 1990.

The formation constants of the mixed - ligand complexes of the type (CuAL), where A refers to glycylglycine (A^1), glycyl - L - alanine (A^2), and glycyl - L - leucine (A^3) and L refers to α - alanine (L^1), phenylalanine (L^2), tryptophan (L^3), tyrosine (L^4), and L - dopa (L^5), were determined in 1:1 (v/v) dioxan - water medium at 30°C and I = 0.2 M ($NaClO_4$) using SCOGS computer program. The influence of the non-coordinated aromatic side groups of the amino acids on ternary complex formation is discussed.

Ternary Complex of Cu(II) involving Histidine and another Amino Acid or Dipeptide

Indian Journal of Chemistry, **29A**, 577, 1990.

The stability constants of ternary complexes of the type (CuLA) where A = histidine and L = glycylglycine (L^1), glycyl - L - alanine (L^2), glycyl - L - leucine (L^3), tryptophan (L^4), phenylalanine (L^5), tyrosine (L^6) and 3, 4 dihydroxyphenylalanine (L-dopa) (L^7) have been determined potentiometrically in aqueous medium at I = 0.2 M ($NaClO_4$) at 25°C. In the ternary complexes of copper (II) with histidine and dipeptides, where histidine acts as an ambidentate ligand coordinating through amino acid end with protonated imidazole or histamine end with weakly coordinated carboxylate, three types of species CuLAH, CuLA and CuL(-H)A have been detected. The species CuLAH is found to be most stable due to the hydrogen bonding between protonated imidazole and free COO^- group of the dipeptides. In the case of ternary complexes involving histidine and another amino acid (L), two types of species, CuLAH and CuLA, have been detected. (CuLAH) is stabilised due to intramolecular interligand stacking interaction and CuLA due to H - bonding between COO^- of histidine and non-coordinating - OH or - NH groups of amino acids.

Ternary Complexes of Substituted Catechols and Dipeptides with Copper(II)

Journal of Chemical Society Dalton Transactions, 3325, 1990.

The formation constants of the ternary complexes [CuA(L)], where A refers to the monoanions of glycylglycine (A^1), glycyl - L - alanine (A^2), or glycyl - L - leucine (A^3) and L to the dianion of catechol (L^1), pyrogallol (L^2), 4, 5 - dihydroxy benzene - 1, 3 - disulphonic acid (L^3), or napthalene - 2, 3 - diol (L^4), were determined by potentiometric titration in aqueous medium at 30°C and I = 0.2 mol dm^{-3} ($NaClO_4$) using the SCOGS computer program. The enhanced stability of the ternary complexes is attributed to possible hydrogen bonding between the two ligands through a water molecule.

Interligand Interactions in Ternary Copper(II) Complexes of Dipeptides and Auxins.

Journal of Inorganic Biochemistry, **41**, 57, 1991.

The formation constant of the mixed-ligand complexes of the type (CuAL) and ($CuA_{-H}L$), where A refers to glycylglycine, glycyl - L - alanine, and glycyl - L - leucine, and L refers to indole acetic acid, indole propionic acid, and indole butyric acid. They were determined in 1:1 (v/v) dioxan - water medium at 30°C and I = 0.2 M ($NaClO_4$), using SCOGS computer program. The astatistical stabilization of the ternary complexes has been attributed to intramolecular hydrogen bond formation between the two ligands.

Ternary Complexes of Copper(II) Involving Dipeptides and Aromation Amines : Effect of π - Acidity of Aromatic Amines on the Deprotonation of the Peptide Group in the Ternary Complex (Communicated).

Equilibrium constants have been measured potentiometrically for the mixed - ligand complexes Copper(II) - amines (A) - dipeptides (L). The aromatic amines (A) used are 5 - nitro - 1, 10 - phenanthroline (Nphen), 2 (2' - pyridyl) benzimidazole (pybz), 1, 10 - phenanthroline (phen) and 2 (2' - pyridyl) imidazoline (pyz). The dipeptides used are glycylglycine (gg), glycyl - L - alanine (ga) and glycyl - L - leucine (gl). The potentiometric titrations were carried out in 50% water - dioxan (1:1, v/v) medium at a constant ionic strength I = 0.2 mol dm^{-3} $NaClO_4$ and temp. = 30°C. Formation of two types of ternary complexes at different pH are reported. The values of the formation constants are compared with Cu - ethylenediamine (en) - dipeptide system. The effect of the increasing π - acid character of the amines (A) on the deprotonation of the dipeptides (L) in the ternary complex ($CuAL_{-H}$) has been discussed.

Electrochemical studies of the binary complex Cu-en and one of the ternary complexes Cu-en-gg was also carried out, in aqueous medium. The formation of two different ternary species at different pH with different reduction potentials was observed.

Electrochemical Studies of Ternary Complexes of Copper(II) Involving Dipeptide or Histidine and Another Amino Acid (Communicated).

The reduction steps of ternary complexes of Cu(II) involving (i) dipeptide, glycylglycine (gg) and amino acids, α - alanine (ala), tyrosine (tyr) and (ii) histidine and the amino acids α- alanine, tyrosine, phenylalanine (phe) and tryptophan (trp) have been studied by cyclic voltammetry in aqueous medium. The reduction proceeds through a one electron process resulting in the formation of Copper(I) ternary complexes. The Copper(I) - dipeptide - amino acid species were found to be unstable and undergo disproportionation generating Cu^{o} and Cu(II) complex at the mercury electrode. The imidazole coordination of histidine in binary and ternary complexes stabilizes the Cu(I) species and hence, in such complexes disproportionation does not take place and there is no generation of Cu^{o}. This emphasises the significance of imidazole coordination in stabilising Cu(I) state in biological redox processes.