

Study of formation Constant of Schiff base ligand

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Abstract

Ternary complex formation equilibria of Cu(II) metal involving tetradentate Schiff base ligand (L) 4-hydroxy-3(1-(2-(benzylideneamino) phenylimino) ethyl) -6-methyl-2H-pyran- 2-one as primary ligand and DL- Glycyl-Amino butyric acid (R), dipeptide as secondary ligand have been investigated potentiometrically. The ionic strength $\mu = 0.1$ M was kept constant using NaClO₄ in THF: Water (60:40) medium. Ternary complexes are formed by simultaneous reactions. Concentration of total metal, total ligand, free metal, free ligand and various possible species that are formed during complexation process are calculated by using "SCOG" computer programme. The comparative study of Cu(II) ternary complexes is discussed.

Keywords: Ternary complexes, tetradentate Schiff base ligand, dipeptides.

Introduction

Amino acids and their ternary complexes are used in various fields Thermodynamics and Potentiometric Studies of Mixed Ligand Complexes of Salicylic Acid. They are involved in metabolism, pain treatment, toxins removal and inflammation control.^{1,2} Metallic complexes including 2 – amino pyridine shows therapeutic agent for Wilson disease.³ Ternary metal complexes play a potential role in biological processes. They manifest as metallic enzyme substrate complexes. Now the stability constants of drugs has been done potentiometrically.⁴ The stability constant of metal complexes with drugs is useful for knowing the appropriate dose of a drug and its effect with all other components of the bloodstream as well as for measuring the strength of metal ligand bonds. All these studies indicate the importance of Potentiometric study of Ternary complexes. So in continuation of earlier work⁵ here we report the solution equilibrium of complexes including Cu(II) with tetra dentate Schiff bas ligand have been investigated potentiometrically. The ionic strength $\mu = 0.1$ M was kept constant using NaClO₄ in THF: Water (60:40) medium. Stability constants of ternary systems were determined by potentiometric method using the computer program named "SCOGS" at

25±0.1°C. The relative stabilities of the ternary complexes are compared with those of the corresponding binary complexes in terms of $\Delta \log K$.

Experimental

Titration were performed in a double walled glass cell in an inert atmosphere (nitrogen) at ionic strength of 0.1 M (NaClO₄). The solutions were titrated pH metrically against (0.2N) NaOH. Since the Schiff base and its metal complexes were found to be either insoluble or sparingly soluble in water, a reaction mixture consisting (60:40) THF-water solution was used as a solvent for potentiometric studies. THF used in the present investigation was obtained from E. Merk and was further purified by known literature method.⁶ All metal ion solutions were prepared from their AR grade metal chlorides and standardized by known literature methods. A standard 0.2N NaOH solution (E.Merk) was used for titrations. Standard solutions of AR grade HClO₄, NaClO₄ (1.0M) were prepared and standardized by known methods.⁶ The ligand solution (0.1M) was prepared in distilled THF. All other solvents used during the entire research work were of AR grade

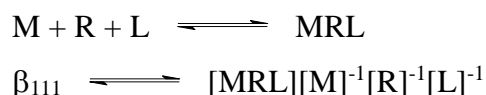
Apparatus

Elico digital pH meter (model LI-127) equipped with a CL-51B combined electrode was used for pH measurements. The pH meter was calibrated against standard buffers (pH 4.02 and 9.18) before measurements. pH meter readings were corrected for organic-aqueous media. The protonation constants and stability constants of the Schiff bases and their complexes were determined by means of the data obtained from potentiometric titrations in 60% THF-water medium. Through out the experimental work glass distilled water was used. This was obtained by double distillation of deionised water in presence of crystals of potassium permagnate and potassium hydroxide pallets. For synthesis of Schiff bases, ethanol and methanol were used as commercial solvents

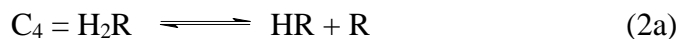
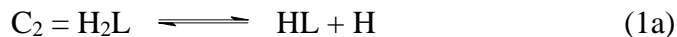
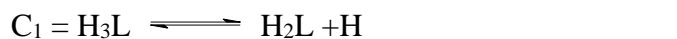
Potentiometric measurements

The synthesis and characterisation of ligand is reported earlier.⁷ Stock solutions of ligand (0.1M) was prepared in THF. The protonation constants of primary ligand L₁ and secondary ligands DL- Glycyl-Amino butyric acid (R), have been determined by Irving-Rossotti technique after appropriate pH corrections determined by using method suggested by Van Uitert.⁸ The protonation constant and metal- ligand stability constant of ligands is given in the

(Table 1) All titrations were carried out between pH 3 to 11 under nitrogen atmosphere. The pH metric data were used to find the stoichiometry, deprotonation and stability constants. The primary as well as secondary ligands form both 1:1 and 1:2 complexes with Cu(II) ion. Here ternary system has been presented in the above work. Concentration of total metal, total ligand, free metal, free ligand and various possible species that are formed during the complexation process are calculated by using “SCOGS” computer programme^{9, 10} The equilibrium constant β_{111} for the reaction is calculated.



According to this method, the concentration of different species distributed are as follows:



The $\Delta \log K$, K_r , K_R and K_L parameters are generally used to indicate the relative stability of ternary complexes as compared to binary complexes. These parameters are defined by the equations.

$$\Delta \log K = \log \beta_{111} - \log K_{10} - \log K_{01}$$

$$K_r = \beta_{111}^2 / (K_{20}K_{02})$$

$$K_R = \beta_{111} / K_{01}$$

$$K_L = \beta_{111} / K_{10}$$

Results and Discussion

The concentration of various species HL, L, R, CuL, CuR, CuLR and CuLR, at different pH were obtained as computer outputs. The concentrations of these species were plotted against pH values to study complexing equilibria and the relative predominance of mixed ligand complexes over binary complexes. The plots of these systems i.e. L-Cu(II)- DL- Glycyl- Amino butyric acid (R), systems are presented in the paper (Fig.1-4). All the graphs were critically analysed to understand the possible equilibria in the ternary chelation.

In these systems the pH of precipitation of mixed ligand complexes was about 7.7. The mixed ligand curves coincide with A+L curve up to pH 4.5 and then deviates. The deviation of mixed ligand curve from the theoretical composite curve towards left indicate the formation of ternary complex. Since the mixed ligand curve did not coincide with either of the individual metal complex titration curves, the formation of 1:1:1 complex by a simultaneous equilibria was inferred. In Cu(II)-L-N –butyric acid system it is observed from (Fig. 3.6) that the mixed ligand titration curve coincides with A+L curve up to pH 3.8 and later on deviates. Non super impossible nature of the composite curve over mixed ligand curve confirms the formation of ternary complex.

i). Cu(II)-L -(R) System

The tetradentate Schiff base (L) as primary ligand forms both 1:1 and 1:2 complexes with Cu(II), while the secondary ligand, dipeptides, copper. The percentage distribution curves of free metal (F_M), free primary ligand (F_L) and free secondary ligand (F_R) are shown in (Fig. 2-4). The initial percentage of free metal at pH = 3.2 is very less i.e. 0.4 which indicates the maximum consumption of metal ions in the complex formation at this pH. It sharply decreases up to pH 4.4 after which the concentration remains constant indicating the maximum complexation in the pH- range 3.2 to 4.4. The percentage of free primary ligand (L) and secondary ligand R, though extremely low (~0.03%) found to increase with increasing pH. The percentage of F_L and F_R reaches to 3.2 and 1.1 percent respectively at pH-5.5 and then remains constant. This increase in free ligand concentrations may be due to the dissociation of excess ligands present in the system.

Terms of β_{111} , β_{20} , β_{02} , K_L , K_R , K_T and $\Delta \log K$ values which are presented in (Table3) shows relative stabilities of binary, ternary complexes.

The comparison of β_{111} with the product of β_{20} and β_{02} i.e. K_r of the system reveals preferential formation of ternary complexes over binary complexes of primary as well as secondary ligands since they show positive value. Relatively higher positive value of K_r than K_L indicates more stability of ternary complexes with respect to the binary complexes of secondary ligand than that of primary ligand.

The negative $\Delta \log k$ value of the complex indicates that the ternary complex is slightly less stable than either of the binary 1:1, Cu(II)-L and Cu(II)-R complexes. This is in accord with the statistical considerations. The negative $\Delta \log k$ value is due to the higher stability of binary complexes than the ternary one and may be due to the reduced number of co-ordination sites.

To understand the mechanism and extent of formation of ternary complex at different pH, the species distribution curves are most useful. The speciation diagram obtained for the system Cu(II)-L is presented in (Fig.1)

From the curve, C_{10} , it can be observed that the initial concentration of ternary species is very less i.e. 5.54 percent. Above this pH, it increases very sharply to attain maximum value at pH 5.2 and then remains constant at about 93 percent for the whole pH range up to pH 7.2. Thus more than 93 percent metal ion is present in the form of ternary complex at pH 7.2.

The reactions 1b and 2b represent the formation of HL(C_2) and R(C_5). Their continuous decrease with increasing pH indicate the formation of Cu(II)- L-R by reaction (5). It can be seen from the (Fig.3.5) that the concentration of HL is 93% and that of R is about 4% at the initial pH 3.2 which sharply decrease up to pH 5.2 .The formation of ternary complex also takes place to the maximum extent i.e. up to 92% in the same pH range which supports the possibility of reaction (5). The formation of CuLR in the present investigation is also possible by equilibria



The other way of characterizing the ternary complexes is by following disproportionation reactions



This reaction is possible only if both the ligands from 1:1 and 1:2 complexes individually with the metal ion .Other disproportionation reactions are



The reaction 9 and 10 correspond to the system consisting of one ligand which forms only 1:1 complex and other forms both 1:1 and 1:2 complexes. The equilibrium reaction (II) represent the system containing the ligands which form only 1:1 binary complexes of metal .The reaction is possible only if the sufficient concentration of ML and MR are available.

In addition to this, the formation of ternary complex may also be possible by reaction (7) since concentration of MR (C_8) decreases from 90 to 6.2% .However disproportion reaction (11) can not be ruled out. Since in the present system, primary ligand L forms both 1:1 and 1:2 complexes while the secondary ligand forms only 1:1 complex, the formation of MRL is also possible by the disproportionation reaction (9).

Table 1 P^k values of Primary ligand

Ligands	pK ₁	pK ₂	pK ₃
L ₁	2.93	9.83	-

Table 2 pK and logk values of Cu(II) chelates of dipeptides

Peptides	pK ₁	pK ₂	log k ₁	logk ₂	log β
DL- Glycyl –Amino butyric acid(R ₃)	4.3137	7.2352	7.8960	-	7.8960

Table 3 Parameters based on some relationship between formations of mixed ligand complexes of Cu(II) with L₁ and dipeptides

Dipeptides	logβ ₂₀	β ₀₂	β ₁₁	k _L	k _R	k _r	Δlogk
Amino-N butyric acid	18.1333	7.896	18.0489	7.8933	10.1529	-	-0.0027

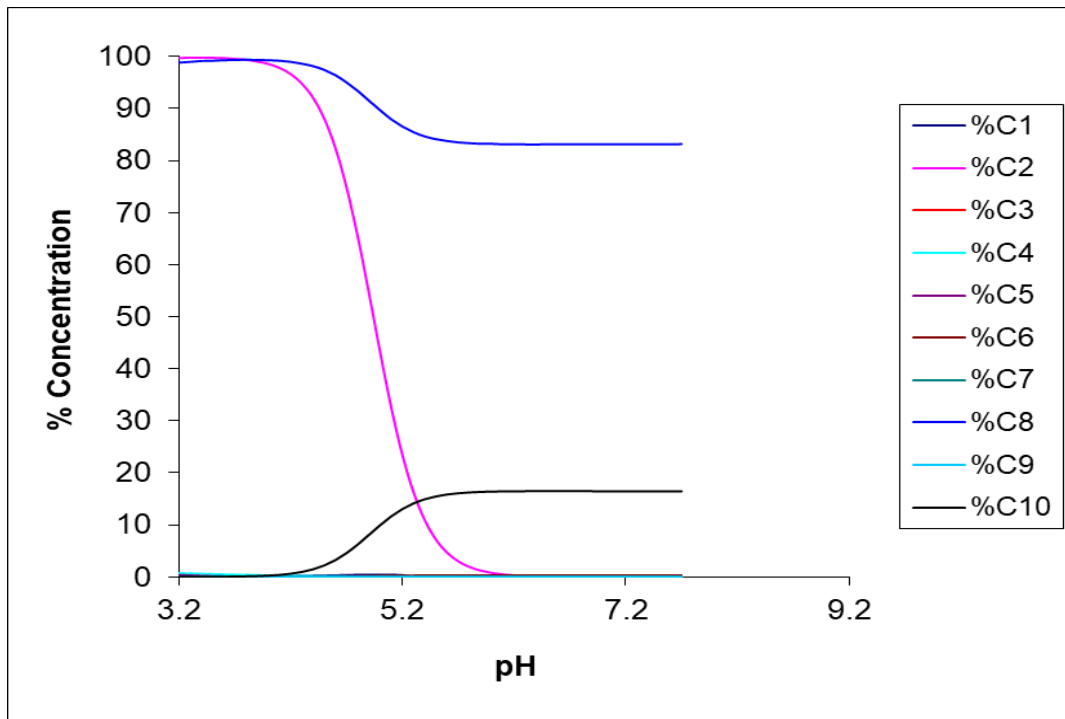


Figure1. Species distribution graph of LCuR

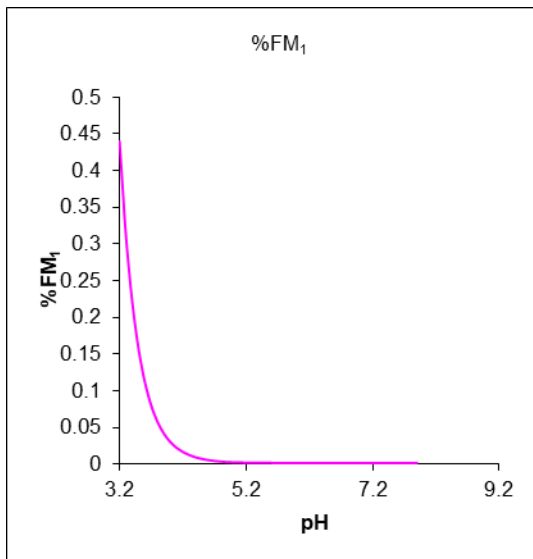


Figure 2. %FM Vs pH graph

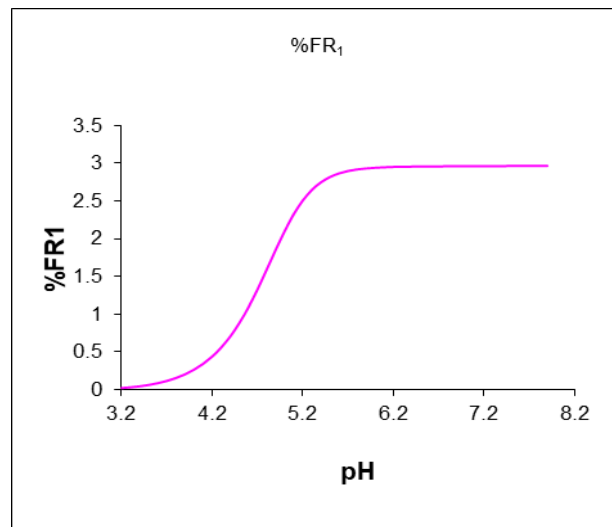


Figure 3. %FR Vs pH graph

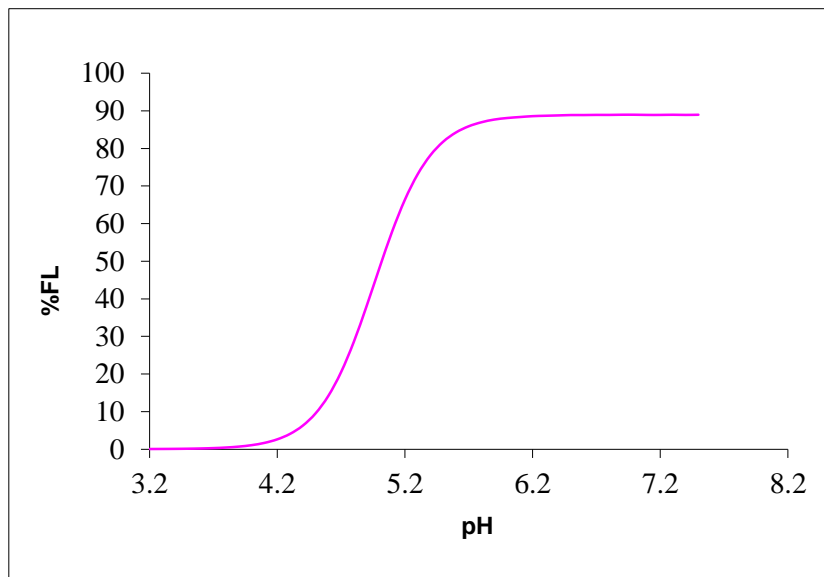


Figure 4. % FL vs pH

Result

In the present study include ternary complex formation equilibria of Cu(II, metal involving tetradentate Schiff base ligand (L) 4-hydroxy-3(1-{2--(benzylideneamino) phenylimino) ethyl) -6-methyl-2H-pyran- 2-one as primary ligand and DL- Glycyl-Amino butyric acid (R), dipeptide as secondary ligand have been investigated potentiometrically. T 0.1 ionic strength. System form both 1;1 and 1;2 metal bcomplexes. The negative value of $\Delta \log k$ shows more stability of ternary metal complex.

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