

## Potentiometric studies on mixed-ligand complexes of copper (II) with Schiff bases as primary ligands and amino acids as secondary ligands

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### ABSTRACT

The formation constant of mixed ligand complexes of copper (II) with Schiff bases (1-(2-hydroxy benzamido)-2-(4-methoxyphenyl)-azomethine ( $L_1$ ) and (1-2-hydroxyhexamido)-2-(3,4,5,trimethoxy)-azomethine ( $L_2$ ) as primary ligands and glycine ( $R_1$ ), DL-Valine ( $R_2$ ) as secondary ligands have been determined potentiometrically in 40% (v/v) THF-water mixture at 30°C and ionic strength of 0.1 M NaClO<sub>4</sub>. The proton ligand stability constants of free ligands and stability constants for ternary metal complex systems involving Schiff bases and amino acids were also determined under identical conditions. The P<sup>H</sup> titration data were analysed using the computer SCOGS programme. The relative stability of ternary complexes as compared to that of corresponding binary complexes has been quantitatively explained in terms of  $\Delta \log K$ ,  $K_R$ ,  $K_L$  and  $K_T$  values. The concentration distribution of various complex species as a function of pH was evaluated.

**Keywords:** Formation constants, Transition metals, Schiff bases, Amino acids, Ternary complexes.

### 1. INTRODUCTION

Schiff bases and their metal complexes exhibit a wide range of biological activities and applications as a marker in the study of biological process [1-3]. The complexing properties of Schiff bases and azo-linked Schiff bases are related to the presence of the electron donor imines, diazo and hydroxyl sites, which are of importance in binding to metals, and the stability of resulting complex [4-5]. Diazo compounds and ortho hydroxyl Schiff bases have intermolecular hydrogen bonded planar structure [6-7]. The hydroxyl group and the azo group account for the chelation of these compounds with transition and non transition metal ions [8-11], which has led to a great deal of study of these compounds as an analytical reagent. The use of chelating agents in the treatment of heavy metal ions from industrial waste water is a field of great interest to environmental applications [12]. It is well known that several Schiff base and their complexes have anti-inflammatory, antipyretic, analgesic, anti-diabetic, antibacterial, anti-cancer and anti-HIV, activity [13-16]. The literature survey reveals that no systematic study has been reported on the binary and ternary complexes of Cu (II) with present Schiff bases. In view of this fact and the continuation of our earlier studies on binary and

ternary complexes of Schiff bases [17-21] we have undertaken the study of complex equilibria of binary and ternary Cu(II) complexes of some newly synthesized Schiff bases as primary ligands and amino acids, DL-Glycine and DL-Valine as secondary ligands.

### 2. Experimental

All the reagents used were of AR grade and all the solutions were prepared in doubly distilled water and standardized by usual procedure [22]. The Schiff bases (1-(2-hydroxy benzamido)-2-(4-methoxyphenyl)-azomethine)  $L_1$ , (1-2-hydroxyhexamido)-2-(3,4,5,trimethoxy)-azomethine)  $L_2$  were synthesized by refluxing equimolar quantities of salicylhydrazine and respective aldehyde in ethanol for six hours. The products obtained were filtered, washed with ethanol and dried over calcium chloride. The purity was tested by elemental analysis, melting point, TLC and IR spectra. The melting point of  $L_1$  is 218°C (found: C, 66.60%; H, 5.10%; N, 10.14% calculated for C<sub>15</sub>H<sub>14</sub>O<sub>3</sub>N<sub>2</sub>: C, 66.65%; H, 5.22%; N, 10.36%). The melting point of  $L_2$  is 181°C (found: C, 61.89%; H, 5.67%; N, 8.27% calculated for C<sub>17</sub>H<sub>18</sub>O<sub>5</sub>N<sub>2</sub>: C, 61.81%; H, 5.49%; N, 8.48%) The two IR bands appearing at 1600-1630 cm<sup>-1</sup> and 1190-1205 cm<sup>-1</sup> were assigned to stretching vibration modes  $\nu_{C=O}$ ,  $\nu_{C-OH}$  deformation. The

phenolic. -OH stretching was found to be absent due to strong intramolecular hydrogen bonding with orthocarbonyl group. The observed lowering in normal carbonyl group frequency may be due to the effect of intramolecular hydrogen bonding. [23,24]. The titrations were carried out using a digital pH meter (Elico model L1-120) in conjugation with combined electrode. All titrations were carried out at  $30 \pm 0.1^\circ\text{C}$ . For the determination of formation constants of ternary complexes, following solutions were prepared., 0.02M perchloric acid, 0.01M metal solutions and for ionic strength, 0.1M sodiumperchlorate. The titrations were plotted by using experimental data, which were utilized to analyze the proton ligand formation constants of primary and secondary ligands and stability constants of their metal complexes. Concentration of total metal, total ligand, free metal, free ligand and various possible species that are formed during the complexation are calculated using SCOGS programme [25]. Complex formation equilibria were elucidated with the help of species distribution curves obtained [26].

### 3. RESULT AND DISCUSSION

#### 3.1. Binary metal complexes

The proton ligand and metal ligand stability constants of primary ligands (1-(2-hydroxy benzamido)-2-(4-methoxyphenyl)-azomethine)  $L_1$ , (1-2-Hydroxyhexamido)-2-(3,4,5,trimethoxy)-azomethine)  $L_2$  and secondary ligands ( $R_1$ ), DL- Glycine and DL- Valine ( $R_2$ ) with Cu (II) ions determined in 40% (v/v) THF:water medium at  $30^\circ\text{C}$  and ionic strength 0.1m  $\text{NaClO}_4$  have been determined by Irving-Rossoti technique after appropriate pH corrections determined by using the method suggested by Van Uitert. Their stepwise metal-ligand formation constants were also determined for the comparison with those of the ternary systems under identical conditions. The values are presented in Table1. The primary as well as secondary ligands both form 1:1 and 1:2 complexes with Cu(II) ions. The complexing tendency of Cu(II) is found to be more with  $L_2$  than  $L_1$ .

**Table - 1: Proton - ligand and metal -ligand stability constants in binary system.**

Ligand	$K_1^H$	$K_2^H$	$\text{Log}K_{ML}^M$	$\text{Log}K_{ML_2}^{ML}$
$L_1(\text{C}_{15}\text{H}_{14}\text{O}_3\text{N}_2)$	8.49	-	6.36	5.92
$L_2(\text{C}_{17}\text{H}_{18}\text{O}_5\text{N}_2)$	8.30	-	6.46	6.02
$R_1$	3.13	9.75	3.98	5.69
$R_2$	3.27	9.81	3.51	5.65

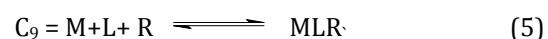
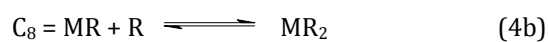
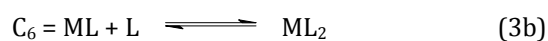
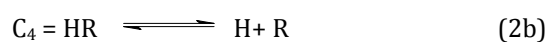
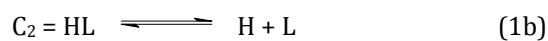
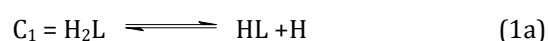
#### 3.2. Ternary metal complexes

In the ternary system ( $L_1R_1\text{Cu}$ ), the pH titration curves are represented in figure 1. The pH of precipitation of these mixed ligands was 5.0 while that of simple systems was 4.70. The mixed ligand curve coincides with A+L curve up to 2.6 pH and then it deviates. The deviation of mixed ligand curves from the theoretical composite curves towards right indicates 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 simultaneous equilibria was interred. After the pH of precipitation 5.0, mixed ligand curve deviates towards x-axis due to the formation of hydroxide species.

The Schiff base  $L_1$  and amino acid (glycine)  $R_1$  both form 1:1 and 1:2 complexes with

Cu (II). The percentage distribution curve of free metal ( $F_M$ ), free ligand ( $F_L$ ) and free ligand ( $F_R$ ) are shown for the system  $L_1R_1\text{Cu}$  in figure 2, 3 and 4. The sharp decrease in the concentration of free metal from about 46% to 3% up to pH-4 indicates the maximum complexation of the metal in this pH range. After pH-4 there is slow decrease in concentration of free metal till it reaches to zero at pH-5. The percentage of free ligand, though it is very low (0.1 to 0.5%) found to increase with increasing pH. This major amount of  $F_L$  and  $F_R$  increases to 3.5 and 0.9% respectively up to pH 6.0 and then remains constant. This increase in concentration may be due to the dissociation of excess ligand present in the system.

The formation of 1:1:1 ternary complex by involving various stepwise possible species that are formed during the complexation process is calculated by using "SCOGS" computer programme. According to this method, the concentrations of different species distributed are as follows.



In order to demonstrate the nature of formation of ternary complex, the speciation diagram obtained for the system  $\text{Cu}L_1R_1$  is represented in figure 5. From the speciation curve of  $\text{Cu}L_1R_1$  system, the concentration of ternary

species ( $C_8$ ) is initially low i.e. 36% then it increases sharply up to pH-4 and reaches to maximum value of 95.3% and then remains constant. The curve indicates the formation of ternary complex to the maximum extent.

The reaction (1b and 2b) for the formation of L and R represented by  $C_2$  and  $C_3$  show continuous decrease with increasing pH which indicates the formation of  $CuL_1R_1$  by reaction (5). The concentration of these species is minimum at pH-5, where the concentration of  $CuL_1R_1$  is maximum which confirms the formation of ternary complex by reaction (5). The formation of  $CuL$  and  $CuR$  represented by  $C_5$  and  $C_7$  shows continuous decrease with increasing pH and the concentration of these species is minimum at pH 5.5. The concentration of  $CuL$  is 8.0% at 3.8 pH and that of  $CuR$  is 11% at 3.8 pH which decrease with increase in pH value. Concentration of  $CuL_2$  and  $CuR_2$  remains negligible throughout the pH range which indicates nonformation of these complexes and confirms the formation of ternary complex by the reaction (5) represented by  $C_9$ . Species The species distribution curves permit us to select the best condition of pH, concentration and ligand metal ratio for the preparation of the complex in solid state. The species distribution diagram of  $CuL_2R_1$  system shows in figure 6 the similar trends as that of  $CuL_1R_1$  system. Other systems,  $CuL_1R_2$  and  $CuL_2R_2$  also show similar behavior. The stability of binary species  $ML, MR$  and ternary species  $MLR$  complex is in the expected order. The stability constants of ternary

complexes were found to be greater in  $L_1$  than in  $L_2$ . The relative stabilities of the binary and ternary complexes are quantitatively expressed in terms of  $\beta_{111}, \beta_{20}, \beta_{02}, K_L, K_R, K_f$  and  $\Delta\log K$  values which are presented in Table (2). The comparison of  $\beta_{111}$  with  $\beta_{20}$  and  $\beta_{02}$  of this system reveals the preferential formation of ternary complexes over binary complexes of primary as well as secondary ligands. The considerably high positive values of  $K_L$  and  $K_R$  indicate more stability of ternary complex with respect to that of binary once of primary as well as secondary ligands. The  $K_f$  values of this complex is positive which indicates higher stability of ternary complexes. The negative  $\Delta\log K$  values of this complex indicate that the ternary complexes is less stable than the binary 1:1 metal- $L_1$ , and metal-glycine complex. This is in accordance with the statistical considerations. The negative  $\Delta\log K$  values doesn't mean that the complexes are not formed. The negative value may be due to the higher stability of its binary complexes and the reduced number of coordination sites. In  $Cu L_1R_1$  system, the primary as well as secondary ligands individually form 1:1 and 1:2 complexes with  $Cu (II)$ . It has been observed from Table (2) that the stability of mixed ligand complexes of  $L_1$ , are higher than that of the mixed ligand complexes of  $L_2$ . The positive values of  $K_R, K_L$  and  $K_f$  confirm the stability of mixed ligand complexes but comparatively these complexes are less stable than the 1:1 complexes of binary ones and hence we get negative values of  $\Delta\log K$ .

**Table - 2: Stability constants of ternary complexes.**

L	R	$\beta_{111}$	$\beta_{20}$	$\beta_{02}$	$K_R$	$K_L$	$K_f$	$\Delta\log K$
$L_1$	Glycine	14.83	12.48	12.94	7.57	8.27	4.24	1.01
$L_1$	DL-Valine	16.77	12.48	13.19	9.27	10.21	7.87	2.71
$L_2$	Glycine	15.02	12.48	12.94	7.76	8.56	4.62	1.30
$L_2$	DL-Valine	16.21	12.48	13.19	8.71	9.75	6.75	2.25

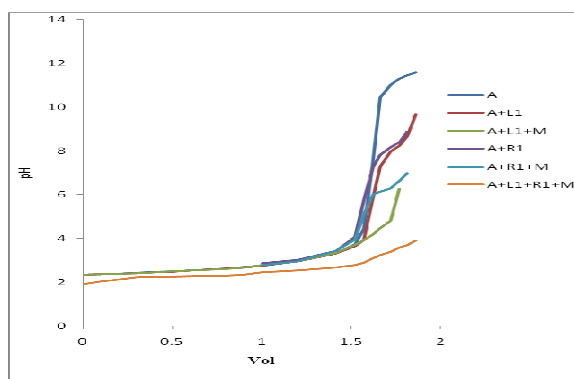


Figure - 1: Potentiometric titration curve in  $L_1R_1Cu$  system

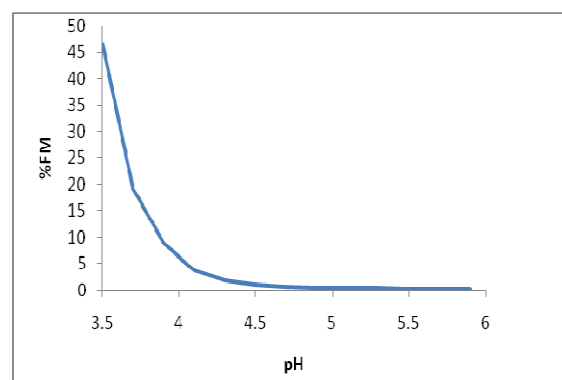


Figure - 2: Percentage distribution curve of  $F_M$ , in  $L_1R_1Cu$  system.

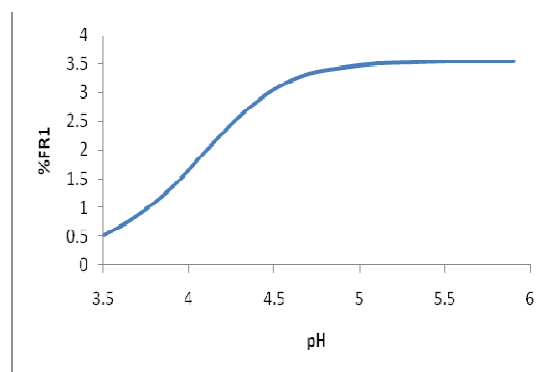


Figure - 3: Percentage distribution curve of  $F_M$ ,  $F_{R1}$ , and  $F_{R2}$  in  $L_1R_1Cu$  system.

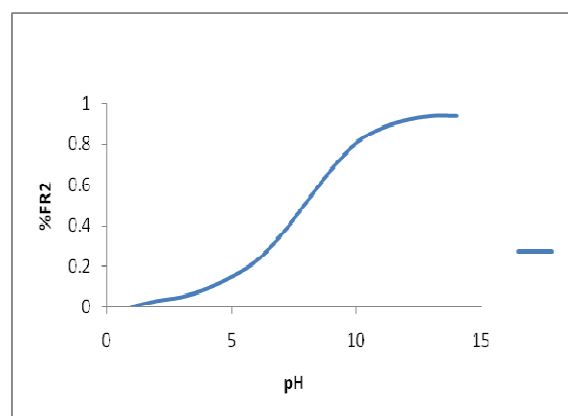


Figure - 4: Percentage distribution curve of  $F_{R2}$  in  $L_1R_1Cu$  system.

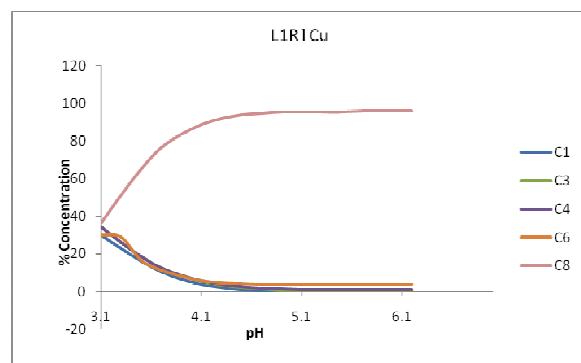


Figure - 5: Species distribution diagram for  $L_1R_1Cu$ .

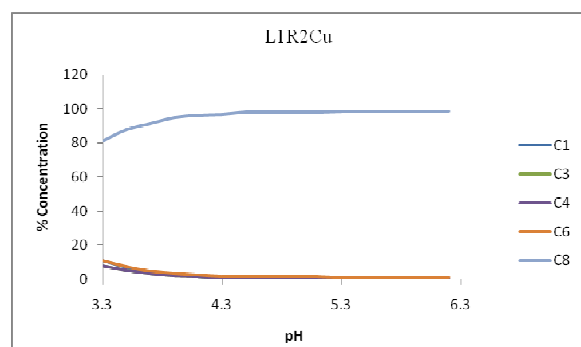


Figure - 6: Species distribution diagram for  $L_1R_2Cu$  system.

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