Stability of Binary and Ternary Copper(II) Complexes with 1,10-Phenanthroline, 2,2′-Bipyridyl and Some α-Amino Acids in Aqueous Medium

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Interactions of certain amino acids with some metal ions have significant consequences in biological systems. Metal ions can act as co-factors in the regulation of enzymatic reactions. Interactions of metal ions with amino acid side chains or with different organic complexes is also essential for many biological events. In this study, the stability constants of 1 : 1 : 1 ternary complexes of Cu(II) with 1,10-phenanthroline (Phen) as the primary ligand, and 2,2′-bipyridyl (Bpy) and some selected α-amino acids [(glycine (Gly), leucine (Leu), glutamine (Gln)] as secondary ligands, were identified in I=0.1 M ionic medium at t=(25±0.1) °C in aqueous solutions, by potentiometry. The protonation constants of the free ligands and the stability constants of the binary and ternary systems were also determined under the same experimental conditions. The protonation constants of all of the ligands and the stability constants of the formed complexes were evaluated by using the BEST computer program. The stabilities of the ternary complexes have been quantitatively compared with those of the corresponding binary complexes in terms of the some parameters. The concentration distributions of the complexes in solution were also evaluated. Species distributions as a function of pH reveal that the MAB ternary complexes predominate over a pH range, where M=Cu(II); A=Phen; B=Bpy, Gly, Leu and Gln.

Key words potentiometry; stability constant; ternary complex; α-amino acid; 1,10-phenanthroline; 2,2′-bipyridyl

In recent years, considerable research has been carried out on model mixed-ligand complexes in an effort to understand the nature of metal-ion complexation in biological systems. The formation of complexes containing two different ligands has become of interest to coordination chemists, and the formation constants of some of these complexes have been determined.[1] The chemical speciation[2,3] and simultaneous determination[4] of metal ions have been increasingly needed in areas such as clinical chemistry, biochemistry, environmental pollution and industrial control.

It is well-known that ternary coordination plays an important role in biological processes. Ternary complex formation occurs commonly in biological fluids, with several potential ligands, including certain amino acids, peptides, peptide derivatives or their analogues. Heterocyclic N-bases are likely to compete for biologically important transition metal ions found *in vivo*, such as Cu(II), Ni(II), Zn(II), Co(II) and Mn(II).[5]

Metallic copper and silver both have antibacterial properties, while Au–thiol complexes have found increasing use in the treatment of rheumatoid arthritis.[1] However, within this group of metals, only copper has shown significant biological functions in diverse organisms. Copper is widely distributed in the plant and animal worlds, and its redox chemistry is involved in a variety of oxidation processes. It is known that an adult human contains around 100 mg of copper, mostly attached to proteins. Daily intake of copper in different forms is 3—5 mg for people with a normal metabolism, and copper deficiency results in anemia. Moreover, a congenital inability to excrete copper can result in toxic levels of copper accumulation, which leads to a metabolic disease known as Wilson's disease.[6,7]

The 1,10-phenanthroline and 2,2′-bipyridyl ligands used in this study have been extensively used as ligands in both analytical and preparative coordination chemistry. The 1,10-phenanthroline unit is an important building block and plays an important role in the development of supramolecular chemistry.[8—11]

Glycine (Gly) is the simplest of the amino acids, but has significant function as a starting metabolite for the biosynthesis of other compounds (such as creatine) in living organisms.[12,13] Glycine is synthesized from serine.[14] Leucine, a neutral amino acid, is also a very important bioligand for human health. It has a function in protein dimerization and forms a structure known as a leucine zipper.[14] Glutamine (Gln), a basic amino acid, plays an important role in living organism as an NH_4^+ donor.[14,15]

Because amino acids are structural units for proteins, some properties of amino acids are of high interest.[16] Amino acids are essential low molecular weight ligands for humans and in other biosystems.[17—22] Transition metal ion chelate complexes are also exploited by industry in the large-scale purification of α-amino acids. A wide range of drugs and drug precursors contains an aminocarboxylic acid moiety.[23,24]

Recently, the interaction of Cu(II) complexes with nucleic acids has attracted attention due to its proposed role in gene mutations in therapeutic approaches,[25—29] because DNA is thought to be the target of chemotherapy in the treatment of tumors.[30] It is also known that certain ternary complexes of Cu(II) with 1,10-phenanthroline (Phen) have antitumor activity.[31]

Yadoshi, *et al.* (2007) determined the crystal structures of a series of three complexes—$[Cu(Gly)(bpy)Cl]\cdot 2H_2O$ (1), $[Cu(Gly)(phen)Cl]_2\cdot 7H_2O$ (2) and $[Cu(Gly)(bpa)(H_2O)Cl]$ (3)—using X-ray crystallography, and compared the coordination modes of Cu(II) in these ternary complexes. These authors reported that the central Cu(II) atoms of complexes 1 and 3 have similar distorted octahedral coordination geometry, while the Cu(II) atom of complex 2 has a distorted square pyramidal coordination. In all of the complexes, the

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aromatic heterocyclic compounds bpy, phen, and bpa behave as bidentate N,N′ ligands, and Gly behaves as a bidentate N,O ligand.[32)]

In order to obtain further information on the driving forces that lead to the complexation of copper in biological systems, we have analyzed the formation equilibria of binary and ternary complexes of Cu(II) metal ion involving: Phen as a primary ligand as well as 2,2′-bipyridyl (Bpy) and some α-amino acids—glycine (Gly), leucine (Leu), glutamine (Gln)—as secondary ligands. The protonation constants of selected ligands and the stability constants of the investigated complexes were studied at 25 °C and I=0.1 M KCl, using potentiometric pH titrations in aqueous solutions. The value of protonation constants of the free ligands and the stabilities of the binary and ternary complexes were determined by using the BEST software program.[33)] The concentration distribution curves of each complex species in solution were also evaluated. In our analysis, $\Delta \log K$ parameters indicate the effect of the bonded primary ligand towards an incoming secondary ligand. Log X is the statistical parameter that shows the charge neutralization in mixed-ligand complexes and includes both enthalpy and entropy. Log X is generally accepted as 0.6.[34—36)]

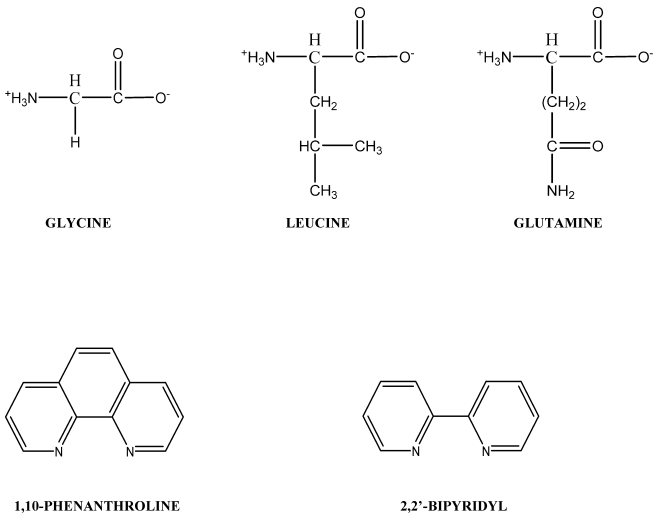

Fig. 1. Structural Formula of the Ligands Used in This Study

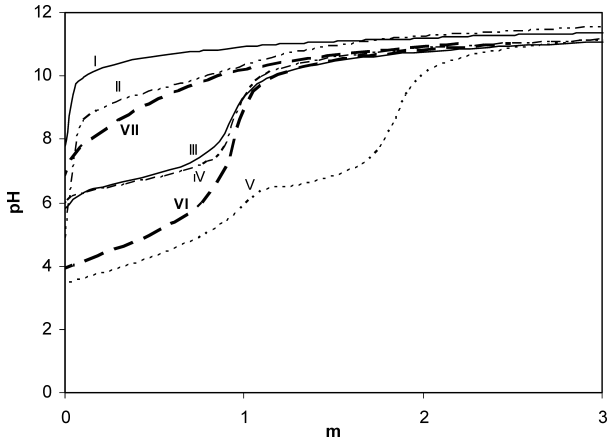

Fig. 2. Potentiometric Titration Curves of Binary (1 : 1) and Ternary Complexes (1 : 1 : 1) (I=0.1 M KCl at 25 °C)

Curve I. Phen alone; II. Gly alone; III. Cu(II) : Bpy (1 : 1); IV. Cu(II) : Phen (1 : 1); V. Cu(II) : Gly(1:1); VI. Cu(II) : Phen : Gly (1 : 1 : 1); VII. Cu(II) : Phen : Bpy.

Experimental

Chemicals and Solutions All of the chemicals used in this study were of analytical grade and were used without further purification. The purity of chemicals was checked and the exact concentrations of the solutions were determined by the Gran method with standard HCl.[37)] Phen (99.5%) was purchased from Merck. Bpy (98%) and Gly (99%) were purchased from Fluka. Leu (98%) and Gln (99%) were purchased from Sigma. The copper stock solution (*ca.* 0.01 M) was prepared from analytical grade chloride in a small excess of HCl (Merck, 37%, d=1.18) in order to avoid hydrolysis. The copper(II) stock solution was standardized complexometrically by EDTA titration with an appropriate indicator.[38)] All solutions were made with double-distilled, deionized and CO_2-free water. 0.1 M potassium hydroxide solution, free of carbonate, was prepared and standardized with potassium hydrogen phthalate, $HKC_8H_4O_4$ (99.9%, Merck, dried at 120 °C prior to use). The supporting electrolyte was potassium chloride (98%, Fluka) and all measurements were performed in an oxygen-free nitrogen atmosphere. Structures of α-amino acids, Phen and Bpy are given in Fig. 1.

Potentiometric Titrations Potentiometric titrations were performed on a Schott Titroline Alpha Plus automatic titrator with a combined pH electrode (Schott), which is connected to a computer. The combined glass electrode was calibrated daily with two Merck standard buffer solutions, first with a pH 4.01 solution followed by a pH 8.96 solution at 25 °C. The potentiometric cell was also calibrated before each titration so as to measure the hydrogen ion concentration rather than its activity.[39,40)]

For potentiometric titrations, the volumes were made up to 50 ml with deionized water prior to the titration being performed. Sample solutions were titrated in a double-walled glass cell maintained at (25±0.1) °C by circulating water using a thermostat (VWR 11405), and they were stirred magnetically under a continuous flow of nitrogen.

The following mixtures were prepared at different ratios (1 : 1, 1 : 2, 1 : 3 in binary systems and 1 : 1 : 1, 1 : 2 : 1, 1 : 1 : 2, 1 : 2 : 2 in ternary systems) for the determination of the formation constants of binary complexes MA or MB, as well as for MAB ternary complexes. Binary MA or MB complexes and ternary MAB complexes were titrated against standard 0.1 M KOH:

1: 5 ml 0.1 M HCl+2.5 ml 2 M KCl (for cell calibration)
2: 0.1 M HCl+5 ml 0.01 M ligand+2.5 ml 2 M KCl (for the determination of protonation constants of ligands)
3: 0.1 M HCl+5 ml 0.01 M ligand A or B+5 ml 0.01 M $CuCl_2$+2.5 ml 2 M KCl (for the determination of formation constants of Cu(II) complexes)
4: 0.1 M HCl+5 ml 0.01 M ligand A and B+5 ml 0.01 M $CuCl_2$+2.5 ml 2 M KCl (for the determination of formation constants of ternary complexes Cu(II): A : B)

All calculations were performed with the micro computer program BEST.[41)] The BEST program begins with the set of known and unknown (estimated) overall stability constants and computes [H^+] at the equilibrium for each quantity of added base. For each equilibrium point, the fitting process consists of the minimization of the differences between the observed and calculated pH values, by using a weighted least-squares method. The process is repeated until no further minimization is obtained. All other mathematical aspects are described elsewhere.[42—44)] In addition, the selection of the equilibrium models was based on a critical evaluation of the least-squares fitting results (σ_{fit}). All of the protonation, binary and ternary systems titrations contained at least 99 experimental points between pH 2 and 10. The concentration distribution diagrams were obtained using the program SPE.[45)]

Results and Discussion

Typical titration curves of Phen and Gly solutions in either the absence or presence of Cu(II) metal ions at (25±0.1) °C and I=0.1 M KCl are shown in Fig. 2, where m is moles of base added per mole of ligand. Similar behavior was observed for Gly with the other amino acids and for Phen with Bpy. For free amino acids, buffer regions between m=0 to 1, indicating dissociation of a proton from the $-NH_3^+$ group, gave one proton during titrations. Protonated Phen and Bpy has two protons. The buffer region when m=0 indicates the dissociation of protons from protonated H_2L^{2+}.

In order to see the effect of ligand concentration on the protonation constant, different concentrations of ligands were

analyzed in different hydrogen ion concentrations.

The potentiometric titration curves in Fig. 2 indicate that the addition of Cu(II) metal ion to the free ligand solutions lowered the pH value. This shows that the complexation reactions proceed by the release of protons. The constructed titration curves for Cu(II) : amino acids clearly reveal the formation of binary complexes in solution, and these complexes started forming at about pH 3.5. For Cu(II) : Phen (Bpy), the color of the solution of these complexes was blue when these ligands and the metal ion were put into the glass cell.

This result indicates that this complex forms at a low pH and the complexed ligand exists in solution at pH 6.0 and $m=0$. The titration curves of 1 : 1 binary Cu(II) : amino acid complex solutions display two equivalence points, around pH ranges of 5—6 and 8—9. The first equivalence point, corresponding to $m=1$, proved that one amino acid molecule is bound to Cu(II) by release of a proton from the amino group, and a strong MB complex is formed.

Cu(II) : ligands binary stability constants were computed considering all of the possible species (H_2A, HA, A, M, MA, MA_2, MA_3, MAH, $MA_2H\cdots$). These complexes are very stable up to high pH values. Precipitation occurred at pH >10 and, thus, no calculations have been performed beyond this point. Therefore, a critical evaluation of the hydroxocomplexes will not be performed in the present evaluation. Equilibrium constants for metal complexation are defined as shown below (K is the stepwise stability constant and charges are omitted for the intention of clarity).

For amino acids (Gly, Leu, Gln):

$$M+HA \rightleftarrows MA+H \qquad K_{MA}=[MA]\cdot[H]/[M]\cdot[HA] \tag{1}$$

$$MA+HA \rightleftarrows MA_2+H \qquad K_{MA_2}=[MA_2]\cdot[H]/[MA]\cdot[HA] \tag{2}$$

$$MA+H \rightleftarrows MAH \qquad K_{MAH}=[MAH]/[MA]\cdot[H] \tag{3}$$

$$MA_2+H \rightleftarrows MA_2H \qquad K_{MA_2H}=[MA_2H]/[MA_2]\cdot[H] \tag{4}$$

For N-based ligands (Phen, Bpy):

$$M+A \rightleftarrows MA \qquad K_{MA}=[MA]/[M]\cdot[A] \tag{5}$$

$$MA+A \rightleftarrows MA_2 \qquad K_{MA_2}=[MA_2]/[MA]\cdot[A] \tag{6}$$

$$MA_2+A \rightleftarrows MA_3 \qquad K_{MA_3}=[MA_3]/[MA_2]\cdot[A] \tag{7}$$

Values of the potentiometric constants of free ligands and the stability constants of the binary complexes are given in Table 1. The data obtained are in good agreement with previously published values.[46—53] The results show that the stability order of the binary system in terms of amino acids is Gly>Leu>Gln and Phen>Bpy for N-based ligands. This is in accordance with their basicity and the order of protonation constants. For a series of similar ligands, the higher the basicity of the ligand, the greater the stability of the metal complex.[54]

The ligands used in this study act as bidentate ligands. Cu(II) : amino acid complexes contain 5-membered chelate rings formed *via* the coordination of amino-N and carboxylate-O donors,[55] while Phen and Bpy each provide two aromatic nitrogens whose unshared electron pairs are properly placed to act cooperatively in binding Cu(II) cations. Since these ligands are π electron deficient, they are excellent π-acceptors.[56,57] Cu(II) : Phen(Bpy) complexes also formed 5-membered chelate rings.

Metal–Ligand Ternary Systems A set of typical titration curves for the different Cu : Phen : Gly (1 : 1 : 1) and Cu : Phen : Bpy (1 : 1 : 1) systems at (25±0.1) °C and $I=0.1$ M KCl are shown in Fig. 2. Similar behavior was observed for Gly with the other amino acids.

Analysis of the titration curve for the Cu : Phen : Bpy (1 : 1 : 1) ternary complex formation showed that Cu : Phen or Cu : Bpy forms at lower pH values and exists in solution at pH <6 and $m=0$. As shown in titration curve (VI) in Fig. 2, the Cu : Phen : Gly complex exists in solution at pH 4. The titration curve (VI) corresponding to the (1 : 1 : 1) ternary Cu : Phen : Gly complex shows one equivalence point, at pH=8. However, when $m=1$, the binary complex Cu : Gly (1 : 1) is present in the solution.

The best-fit computer models in the investigated ternary systems showed only the 1 : 1 : 1 species, while the other species were negligible below pH 6. Furthermore, it is worth mentioning that these systems show no precipitation during titration. Thus, they are not hydrolyzed under experimental conditions even in high pH ranges. Ternary chelates are more polar than the binary chelates because of the electron density of their metal–ligand bonds, so ternary complexes are not easily hydrolyzed in the high pH region.

The overall stability constant β^{M}_{MAB} may be presented by Eq. 8.

$$M+A+B \rightleftarrows MAB \qquad \beta^{M}_{MAB}=[MAB]/[M]\cdot[A]\cdot[B] \tag{8}$$

In the presence of both ligands, Phen is ligated to the

Table 1. Protonation Constants for Phen, Bpy, Gly, Leu, Gln and Stability Constants of Binary Complexes for This Ligands with Cu(II) (25 °C and $I=0.1$ M KCl) (log K_{MABH} and log β_{MABH})

	log K_{HA}	log K_{H2A}	log K_{MA}	log K_{MA_2}	Log β_{MA_2}	log K_{MAH}	Log β_{MA_2H}	log K_{MA_3}	Log β_{MA_3}
Glycine	9.50	2.42	8.15	6.91	15.06				
	9.58[a] (2)	2.34[a] (2)	8.14[a] (1)		14.98[a] (1)		19.00[a] (1)		
Leucine	9.55	2.33	8.12	6.79	14.91	4.57	19.48		
	9.52[b] (2)	2.34[b] (2)	8.10[b] (3)		14.71[b] (1)		19.50[c] (1)		
Glutamine	9.00	2.20	7.70	6.43	14.13				
	9.00[d]	2.15[d]	7.74[e]		14.20[e]				
1,10-Phenanthroline	4.95	—	9.10	6.75	15.85			5.08	20.90
	4.93[f] (2)	1.8[c] (1)	9.0[g]		15.7[g]				20.90[g]
2,2′-Bipridyl	4.41	—	8.08	5.59	13.67			3.15	16.82
	4.40[f] (2)	1.3[c] (1)	8.10[h]		13.60[h]				17.00[c] (3)

$\sigma_{fit}\times0.02$. *a*) Ref. 46 ($I=0.1$ M KCl; $t=25$ °C), *b*) ref. 47 ($I=0.1$ M KNO_3; $t=25$ °C), *c*) ref. 48 ($I=0.1$ M KCl; $t=25$ °C), *d*) ref. 49 ($I=0.2$ M KCl; $t=25$ °C), *e*) ref. 50 ($I=0.1$ M KNO_3; $t=25$ °C), *f*) ref. 51 ($I=0.1$ M; $t=25$ °C), *g*) ref. 52 ($I=0.1$ M KCl; $t=25$ °C), *h*) ref. 53 ($I=0.1$ M; $t=25$ °C).

Table 2. Stability Constants for Ternary Complexes in Cu(II) : Phen : B (Gly, Leu, Gln, Bpy) Systems (25 °C ve I=0.1 M KCl)

Ligand A	Ligand B	$\log \beta_{MAB}$	$\log K^{MA}_{MAB}$	$\log K^{MB}_{MAB}$	$\Delta \log K$	$\log X$
Phen	Gly	16.45	7.35	8.30	−0.80	1.99
Phen	Leu	16.61	7.51	8.49	−0.61	2.46
Phen	Gln	16.55	7.45	8.85	−0.25	3.12
Phen	Bpy	15.27	6.17	7.19	−1.91	1.02

Cu(II) metal ion, followed by interaction of the amino acid or Bpy; that is, ternary complex formation could be considered in stepwise equilibriums (Eqs. 9, 10).

$$M+A \rightleftarrows MA \qquad K^{M}_{MA}=[MA]/[M]\cdot[A] \tag{9}$$

$$MA+B \rightleftarrows MAB \qquad K^{MA}_{MAB}=[MAB]/[MA]\cdot[B] \tag{10}$$

where A=Phen and B=Bpy and amino acids (Gly, Leu, Gln)

As shown in Table 2, mixed–ligand complexes with stoichiometry [MAB] are formed in all systems. Comparison of $\log K^{MA}_{MAB}$ and $\log K^{MB}_{MAB}$ constants indicates which ligand is the primer ligand for binding to the Cu(II) metal ion. The equilibrium constants are derived from the computed values of $\log \beta_{MAB}$ according to the following equations:

$$\log K^{MA}_{MAB}=\log \beta^{M}_{MAB}-\log K^{M}_{MA} \tag{11}$$

$$\log K^{MB}_{MAB}=\log \beta^{M}_{MAB}-\log K^{M}_{MB} \tag{12}$$

However, this equilibrium equation shows how tightly the B ligand is bound to the simple MA complex. $\log K^{MA}_{MAB}$ and $\log K^{MB}_{MAB}$ values listed in Table 2 clearly show that formation of the Cu : Phen complex is favored instead of formation of Cu : B (Bpy and amino acids), while Phen acts as a primary ligand in all ternary systems (Cu : Phen : B).

The relative stability of the ternary complexes, as compared with the corresponding binary species, could be evaluated in different ways. A review of those methods[58] has shown that, for a variety of reasons, the most suitable comparison for these studies is in terms of $\Delta \log K$, as defined by the following equation:

$$\Delta \log K=\log K^{MA}_{MAB}-\log K^{M}_{MB}=\log K^{MB}_{MAB}-\log K^{M}_{MA} \tag{13}$$

This reaction represents the following overall equilibrium,

$$MA+MB \rightleftarrows MAB+M \quad \text{and hence,}$$
$$\Delta \log K=\log \beta_{MAB}-(\log K_{MA}+\log K_{MB}) \tag{14}$$

As Table 2 shows, $\Delta \log K$ values are negative, depending on the geometry of the complex. This is expected based upon prior statistical analyses of steric and electrostatic factors.[34,59,60] This phenomenon can be explained by the availability of fewer coordinating sites for the second ligand on the primary complex (MA), compared to that on free Cu^{2+} ions.[61] Also, charge neutralization occurs on the species during ternary complex formation. It can be seen in Table 2 that $\Delta \log K$ values obtained for Cu : Phen : Bpy species are more negative (−1.91) than the values obtained for all Cu : Phen : Amino acids systems: (−0.2)—(−0.8). This suggests that interaction is favored with an anionic donor (amino acids) as compared to a neutral donor (Bpy). However, there is π acidic character in the primary ligand (Phen) and Bpy, due to back-donation from the metal d orbital into the vacant π-orbital of the aromatic amine (M→Nπ). This behavior is similar to that observed previously in [M-dipyridyl-L] complexes by Chidambaram and Bhattacharya.[60] The absence of stabilization is compatible with the explanations given by Sigel *et al.*[61—63] for the possible stabilization of ternary complexes.

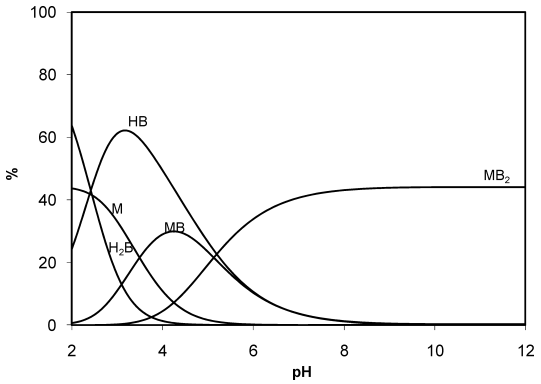

Fig. 3. Distribution Diagram of the Species in the 1 : 2 Cu(II) : Gly Binary System (M: Cu(II), A: Glycine)

As an alternate way to further characterize the trend in MAB ternary complex stabilities, disproportionation constants X[36,58] were calculated for all of the systems in Table 2.

The $\log X$ parameter is defined by the following equation:

$$MA_2+MB_2 \rightleftarrows 2MAB, \quad \text{hence} \quad X=[MAB]^2/[MA_2]\cdot[MB_2]$$
$$\log X=2\log \beta^{M}_{MAB}(\log \beta^{M}_{MA_2}+\log \beta^{M}_{MB_2}) \tag{15}$$

The value expected for X on statistical grounds is 4 and $\log X$=0.6[36] for all geometries. The observed values for $\log X$ can be compared with the statistical values of 0.6. For all systems, obtained values are larger than the statistical value, indicating a significant stabilization of these mixed ligand complexes when compared with the corresponding 1 : 2 binary systems.

Distribution Diagrams The concentration distributions of various complex species existing in solution as a function of pH can be obtained by means of the SPE program. Figure 3 depicts the distribution diagrams of the species found in equilibrium between Gly and Cu(II). The species distribution for the Cu : Phen system, taken as a representative, is given in Fig. 4. Similar trends were obtained for the other systems. The distribution diagrams were drawn in the titration where the metal to ligand ratio was 1 : 2 for Cu : Gly and 1 : 3 for Cu : Phen.

From the concentration distribution curves (Fig. 3), at lower pH's (2—4) almost all Cu(II) ions were present as free ions (about maximum concentration of 40.0%). The Cu : Gly (1 : 1) species has a maximum concentration of 35.0% at pH 4.5. Only the Cu : $(Gly)_2$ species predominates at a pH higher than 6.

From the species distribution diagram in Fig. 4, it can be

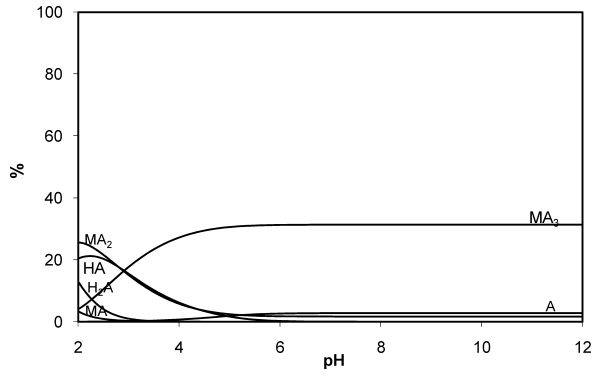

Fig. 4. Distribution Diagram of the Species in the 1 : 3 Cu(II) : Phen Binary System (M: Cu(II), A: 1,10-Phenanthroline)

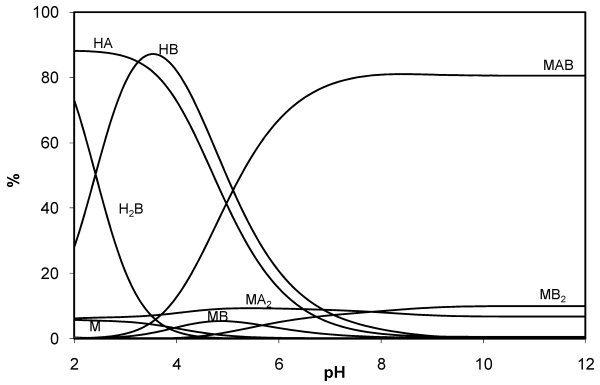

Fig. 5. Distribution Diagram of the Species in the 1 : 1 : 1 Cu(II) : Phen : Gly Ternary System (M: Cu(II), A: 1,10-Phenanthroline, B: Glycine)

concluded that the 1 : 1 and 1 : 2 binary Cu : Phen complexes prevail at acidic pH values (maximum concentration of *ca.* 27.0% for 1 : 2 and *ca.* 5.0% for 1 : 1 binary systems). The 1 : 3 binary Cu : Phen complexes start to form at pH *ca.* 2 and reach a maximum concentration of *ca.* 30.0 at pH *ca.* 5.

The species distribution diagram of Cu : Phen : Gly is shown in Fig. 5. In acidic pH values, the protonated ligand species prevail; after pH *ca.* 8, the species Cu : Phen : Gly is the most abundant and reaches a maximum of *ca.* 85.0% while the concentrations of binary systems are small.

Figure 6 shows that the ternary Cu–Phen–Bpy (1 : 1 : 1) complexes predominate in all of the pH ranges, start to form at very low pH values, and reach a maximum concentration of *ca.* 55.0% at pH *ca.* 4. However, the binary 1 : 2 complexes are less favored. They reach a maximum of *ca.* 15.0% at pH *ca.* 3. This suggests that ternary complex formation is favored.

In conclusion, our results clearly indicate that the primary ligand is 1,10-phenanthroline, due to its basicity and its π-interactions with metals. In addition, we have found that the binary and ternary complexes formed with Phen and Cu(II) are very stable. Moreover, results presented in this research showed that the ternary complexes are more stable than the binary complexes with respect to the stability parameters. When the ligands used in this research are compared for their donor atoms, N,N donors are preferred over N,O donors.

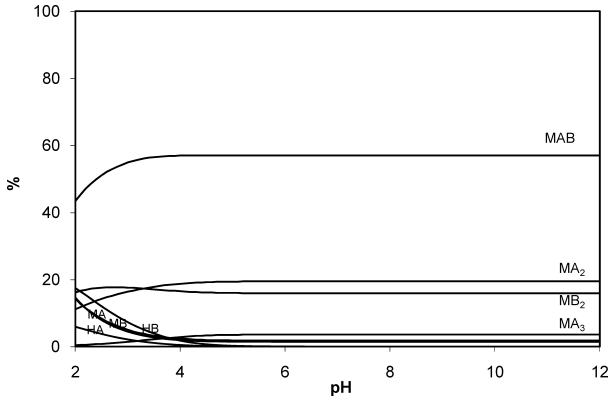

Fig. 6. Distribution Diagram of the Species in the 1 : 1 : 1 Cu(II) : Phen : Bpy Ternary System (M: Cu(II), A: 1,10-Phenanthroline, B: 2,2′-Bipyridyl)

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