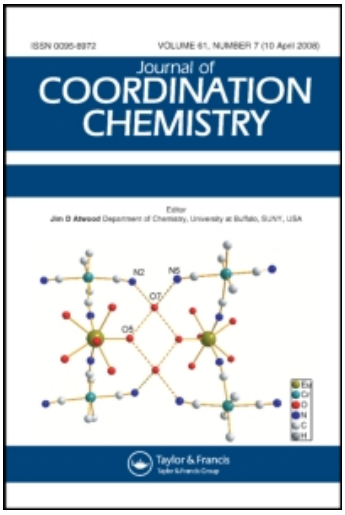

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BINARY AND TERNARY COMPLEXES INVOLVED IN THE SYSTEMS METHIONINEHYDROXAMIC ACID – GLYCYLGLYCINE – Ni(II) OR Cu(II) IONS

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The formation constants of binary and ternary complexes involved in the systems methioninehydroxamic acid (MX), glycylglycine (GG) and Cu(II) or Ni(II) were determined by pH-metric titration in aqueous solution at an ionic strength (I)=0.15 M NaCl) and $T=25^{\circ}$C. Ternary species of the type (MX : GG : Ni(II) or Cu(II) : H) = (1 : 1 : 1 : r), (2 : 1 : 1 : r) and (1 : 2 : 1 : r) exist in the pH range ~3 to ~10.

Differential pulse polarography (DPP) was used to follow complex formation and to study the reduction properties of these metal ions in the presence of MX, and GG. The metal oxidation states were more stabilized in the ternary systems than in the binary systems except for a few Ni(II) systems.

Spectral studies in the UV-Vis-nIR were used to monitor the presence of ternary species in the Ni(II) and Cu(II) systems. In addition, EPR studies were also used to record the magnetic properties of the binary and ternary species in the Cu(II) systems.

Keywords: Equilibria; Metal complexes; Formation constants; Polarography; EPR

INTRODUCTION

Aminohydroxamic acids and their metal complexes have received considerable interest in the last three decades due to their involvement in many chemical and biological systems [1–8]. They have found applications in the treatment of some diseases such as urolithiasis [4] and hepatic coma [5] and as tumor inhibitors [3]. In addition, their metal chelates are used as suitable oral sources of some metals for mammals [6].

Methioninehydroxamic acid, MX, was found to chelate Fe(III) in solution [7] with a dimer detected in aqueous solution in addition to other monomeric species. MX also has the ability to form mixed metal complexes in solution [8].

The study was conducted to test the interaction affinity of metal hydroxamates to peptides represented by glycylglycine.

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EXPERIMENTAL

Materials

Solutions of metal salts were prepared in doubly glass-distilled water. The concentration (0.10 M) was checked by complexometric EDTA titration using potentiometric methods, as was previously described [9]. Solutions of the ligands, (0.10 M) methioninehydroxamic acid (Sigma; >98%) and glycylglycine (BDH; >99%) were prepared in 0.10 M HCl solution.

The ionic strength, I, of the titrated solution was adjusted to 0.15 M by the addition of an appropriate amount of 2.0 M NaCl solution.

Measurements

The pH-metric titrations were done using a Metrohm titrator, model 670 titroprocessor, equipped with Metrohm glass and calomel electrodes. The titration cell was thermostated at (25 ± 0.01°C) by using Julabo circulator. Highly purified (humidified) nitrogen (99.999%) was purged above and below the surface (used as an additional stirring component) of the titrated solution. A pilot experiment was done to test for attainment of equilibrium after successive additions of 0.04 mL of the titrant to the titrand. Equilibrium attainment did not exceed 5 s (dictated by the constancy of pH) under the experimental conditions used. The titrator, however, was adjusted to a 40 s time interval after each successive addition of the titrant.

Three Schotte-Gerate buffers of pH values of 4.01, 6.87 and 9.18 were used to calibrate the electrode system. It was also calibrated by acid–base titration of standard 0.10 M HCl *vs* 0.10 M NaOH at an ionic strength of 0.15 M and 25°C. The differences between measured and calculated pH values, before the end point, were in the range of 0.013–0.030-log unit (the average was ~0.016). These differences correspond to the combined effects of the glass electrode junction potential and the activity coefficient of hydrogen ions at 0.15 M ionic strength and at $T = 25$°C. The direct pH-meter readings were used to calculate the formation constants in this work. Their positive logarithms given for aqueous solutions at $I = 0.15$ M NaCl and at $T = 25$°C may be converted into the corresponding concentration constants by subtracting ~0.016 n log unit from the listed log β values of the protonated species of the ligand and binary and ternary metal complexes in this work (where n is the coefficient of hydrogen in the ligand or the complex species) [10,11].

The data collected by an online IBM personal computer were further processed using the SUPERQUAD program [12]. The pH range used in the calculation was ~3.0–9.0. The experimental conditions for the titration sets are shown in Table I.

The polarographic measurements were obtained using a Metrohm Polarecord E 506 provided with a dropping mercury indicator electrode, saturated calomel reference electrode and a counter platinum-wire electrode. The settings of the polarographs were as follows: the voltage range varied depending on the metal ion under consideration, between 0.0 and −2.0 V (the voltage range was either 0.0 to −0.5 or −0.6 to −1.6 V for Cu(II) and Ni(II) systems, respectively). The pulse amplitude was −40 mV, the drop time was one second, the recorder speed was 0.5 mm/s and the temperature of the cell was room temperature (~23°C). The pH values were in the range of (~2.0 to ~11.0) and were obtained by a Radiometer pH meter type 84

TABLE I Summary of the pH-metric titrations experimental conditions

System	*Conc. of the ligand* $\times 10^3$ M	*Conc. of Ni(II)* $\times 10^3$ M	*Conc. of Cu(II)* $\times 10^3$ M	*No. of different runs*
MX (binary)	1.0–3.0 pH range ~4.5–11.0	1.0~3.0 pH range ~3.9–11.0	1.0–3.0 pH range ~3.3–11.0	8
GG (binary)	1.0–3.0 pH range ~3.0–11.0	1.0–3.0 pH range ~2.8–10.7	1.0–3.0 pH range ~2.8–11.0	6
MX–GG (ternary)		1.0–3.0 (MX) 1.0–3.0(GG) pH range ~2.8–10.8	1.0–4.0 (MX) 1.0–4.0 (GG) pH range ~2.9–10.7	6

provided with a Russell combination electrode (calibrated as previously mentioned). All solutions were deoxygenated by purging with pure humidified nitrogen before taking the differential pulse polarograms (DPP) and above the surface during the run.

The spectra of Cu(II) and Ni(II) systems were taken in the UV-Vis-nIR range using a Cary-500 spectrophotometer in the wavelength range 470–900 nm.

The EPR solution spectra of Cu(II) systems (at different pHs) were obtained at room temperature (~23°C) on an X-band (9.86 GHz) Brucker ECS 106 EPR spectrometer operating at 100 KHz modulated frequency with modulated amplitude of 10.115 G, in the magnetic field strength range of 2700–3700 G. The initial solution concentrations, placed in capillary tubes of 1 mm diameter, were 0.005 M in Cu(II) (T_{Cu}), 0.01 M in MX (T_{MX}) and 0.01 M in GG (T_{GG}). The pH of the solutions were adjusted using anhydrous Na_2CO_3 at pHs < 5.0, followed by CO_2 removal by passing purified nitrogen gas through the solution, and by dilute NaOH at pHs > 5.0.

Calculations

Stoichiometries and formation constants were simultaneously determined by the SUPERQUAD program [12]. The procedures used to select the correct equilibrium models were similar to those previously published [13].

RESULTS AND DISCUSSION

Equilibrium Study

The protonation constants of the ligands as well as the formation constants of the binary and ternary species are listed in Table II. The Cu(II)–MX system exhibits the formation of polynuclear complex 4 : 0 : 3 : 0 (MX : GG : Cu(II) : H). This kind of species has been previously reported for other systems [14–17]. Since there is a tendency for the metal ion to select either the nitrogen or oxygen donors of the hydroxamate group to form a five- or six-member chelate complex with the amino group, there are two ligation sites which may coordinate with another metal ion species. This can lead to the formation of the species 1 : 0 : 2 : 0 (MX : GG : Cu(II) : H). However, including this species in all equilibrium models of MX systems did not succeed. Moreover, there are several reports [14–16] indicating that Cu(II) forms dimeric species (2 : 0 : 2 : −1) with some aminohydroxamates. It is found that including this species in our model of Cu(II)–MX binary system failed in preference to the trimeric species (4 : 0 : 3 : 0), consistent with the previous report [17] of complexes of Cu(II) with N-hydroxy-D-asparagine.

TABLE II The formation constants of the binary and ternary complexes encountered in the systems MX–GG–Ni(II) or Cu(II). The stoichiometric coefficients p,q,r, and s stands for the MX, GG, Ni(II) or Cu(II) and H^+ species at $T=25°C$ and $I=0.15$ M NaCl

System	*p*	*q*	*r*	*s*	*Log β (±σ) this work*	*pH range, σ_D, χ^2, no. of data points*	*Reported Log β & remarks*
MX–H[a]	1	0	0	1	9.01(0.01)	6.5–10.2, 0.23, 9.5, 156	9.03(37°C)
	1	0	0	2	15.93(0.01)		15.80(37°C)
GG–H	0	1	0	1	8.11(0.01)	3.0–9.4, 1.67, 20.7, 161	8.15
	0	1	0	2	11.31(0.02)		11.31
MX–Ni(II)[a]	1	0	1	0	6.55(0.01)	5.4–7.5, 0.4, 14.8, 468	6.84(37°C)
	1	0	1	−1	−0.06(0.04)		0.41(37°C)
	2	0	1	0	13.46(0.01)		14.03(37°C)
	2	0	1	−1	4.29(0.16)		5.76(37°C) Red precipitate on standing overnight at pH's >7.5
MX–Cu(II)[a]	1	0	1	0	10.71(0.02)	3.4–6.0, 1.36, 8.5, 478	10.78(37°C)
	2	0	1	0	20.13(0.02)		20.06(37°C)
	4	0	3	0	49.44(0.03)		49.46(37°C) Green precipitate at pH's >7.2 for only 1:1 ratios
GG–Ni(II)[b]	0	1	1	1	–	2.8–9.1, 0.11, 35.6, 410	10.34
	0	1	1	0	3.96(0.01)		4.05
	0	1	1	−1	−4.83(0.02)		–
	0	2	1	0	7.19(0.01)		7.22
	0	2	1	−2	−11.45(0.06)		–
	0	3	1	0	–		9.40
GG–Cu(II)	0	1	1	0	5.51(0.01)	2.9–5.4, 0.05, 23, 506	5.50
	0	1	1	1	9.25(0.07)		–
	0	1	1	−1	1.34(0.01)		1.43
	0	2	1	1	19.23(0.08)	7.0–9.6, 0.14, 4.8, 149	–
	0	1	1	−2	−7.88(0.02)		–
	0	2	2	−1	11.71(0.14)		
	0	2	1	0	–		8.64
MX–GG–Ni(II)**	1	1	1	0	11.00(0.02)	2.9–9.4, 1.4, 14.8, 554	
	1	1	1	1	16.67(0.12)		
	1	2	1	0	13.45(0.16)		
	2	1	1	−1	7.74(0.02)		
MX–GG–Cu(II)**	1	1	1	0	18.31(0.03)	3.0–8.4, 2.14, 9.6, 567	
	1	1	1	−1	10.03(0.08)		
	1	2	1	0	21.44(0.14)		
	2	1	1	−1	12.81(0.11)		

[a][8]; [b][9]: ** The equilibrium reaction stands for the following: $p\ MX^- + q\ (GG^-) + r\ M^{2+} + s\ H^+ \rightleftarrows (MX_p\ GG_q\ M_r\ H_s)^z$; where z = no. of charges.

This species may be formed from the interaction of two binary species during the transition from 1:0:1:0 to 2:0:1:0 (MX:GG:Cu(II):H) i.e.

$$2Cu(MX) + Cu(MX)_2 \rightleftarrows Cu_3(MX)_4; \quad K_{34}=\beta_{4030}/\beta^2_{1010}\beta_{2010} \tag{1}$$

The $\log K_{34}$ has a positive value (6.89). Other possibilities lead to negative values.

Polymerization of Cu(II) with GG gives the species 0:2:2:−1, Table II. In this case Cu(II) may have a pentacoordinate structure. The species may be formed from the interaction of 0:1:1:0 and 0:1:1:−1 species. Ni(II) systems, on the other hand, did not show the formation of any polymeric species.

The presence of the species 1:0:1:−1, 2:0:1:−1, 0:1:1:−1 and 0:2:1:−2 in the Ni(II) (MX:GG:Ni(II):H) binary systems may indicate the formation of a hydroxy metal complex and/or the deprotonation of the hydroxamate moiety in the Ni(II)–MX binary system or the deprotonation of the peptidic linkage in the Ni(II)–GG system. The Cu(II)–GG binary system only shows 0:1:1:−1 and 0:1:1:−2 (MX:GG:Cu(II):H) species Table II.

The ternary system does not show formation of any polymeric species but it does show the formation of 1:1:1:−1 and 2:1:1:−1 (MX:GG:Cu(II):H) species with the possibility of formation of hydroxy species or the formation of a deprotonated peptidic linkage or deprotonated hydroxamate moiety.

The ternary enhancement for the 1:1:1:0 species can be rationalized if log K's of the following reactions are calculated: (charges are omitted for clarity)

$$\begin{aligned} &M(MX)H_i + M(GG)H_j \rightleftarrows M(MX)(GG)H_k + M; \\ &K_1 = \beta_{111k}/\beta_{1011}\beta_{011j} \quad (\text{where } k = i + j). \end{aligned} \tag{2}$$

$$\begin{aligned} &M(MX)_2H_i + M(GG)_2H_j \rightleftarrows 2M(MX)(GG)H_k; \quad (\text{M is either Ni(II) or Cu(II)}) \\ &K_2 = \beta^2_{111k}/\beta_{201i}\beta_{021j} \quad (k = i + j). \end{aligned} \tag{3}$$

The values of log K_1 (= 0.49, and 2.09 for Ni(II), and Cu(II) and log K_2 (= 1.35, and 7.49 for Ni(II), and Cu(II)), respectively), are always positive and greater than zero; when k is equal to zero.

Ternary complexes involving more than one ligand of the same type are illustrated by the presence of 1:2:1:0, and 2:1:1:−1 (MX:GG:Ni(II) or Cu(II):H) species in the Ni(II) and Cu(II) systems, Table II. These species reflect the flexibility of metal ions to have coordination environments different from that in the binary systems. This may be interpreted on the basis that ligands of the same nature in binary systems have more repulsion than different ligands in the ternary systems. Moreover, appreciable strain in the binary systems is expected if they are compared with ternary systems.

Polarographic Study

Table III shows the E_{max} (the potential at the maximum Faradaic current (δ_i)) of Ni(II) and Cu(II) ions in 0.15 M NaCl. The Ni(II) systems only exhibit reversible waves in the

TABLE III Representative values of E_{MAX} (mV) and $W^*_{1/2}$ (mV) for Ni(II) and Cu(II) in absence or presence of MX, GG or both at $T \sim 23^\circ$C and $I = 0.15$ M NaCl

Metal Ion	*Free metal ion* E_{MAX}, $W_{1/2}$ *(pH range)*	*Binary GG complexes* pH, E_{MAX}, $W_{1/2}$	*Binary MX complexes* pH, E_{MAX}, $W_{1/2}$	*Ternary complexes* pH, E_{MAX}, $W_{1/2}$
Ni(II)	−1020; 100 (3.0–4.5)	overlapped peaks at pHs > 5.7 6.14, −1040, ~108 6.14, −876, broad	overlapped peaks at pHs > 5.5 5.45, −1040, 120 5.45, −720, broad	overlapped peaks at pHs > 5.45 5.45, −1050, 129 5.45, −750, broad
Cu(II)	−64, −224; 87, 48 (3.0–4.0)	overlapped peaks at pHs > 4.1 4.1, −64, 112	overlapped peaks at pHs < 7.0 7.44, −332, 94 12.03, −422, 52	overlapped peaks at pHs < 7.0 7.38, −318, 60 12.0, −422, 60

*Half-peak width (mV).

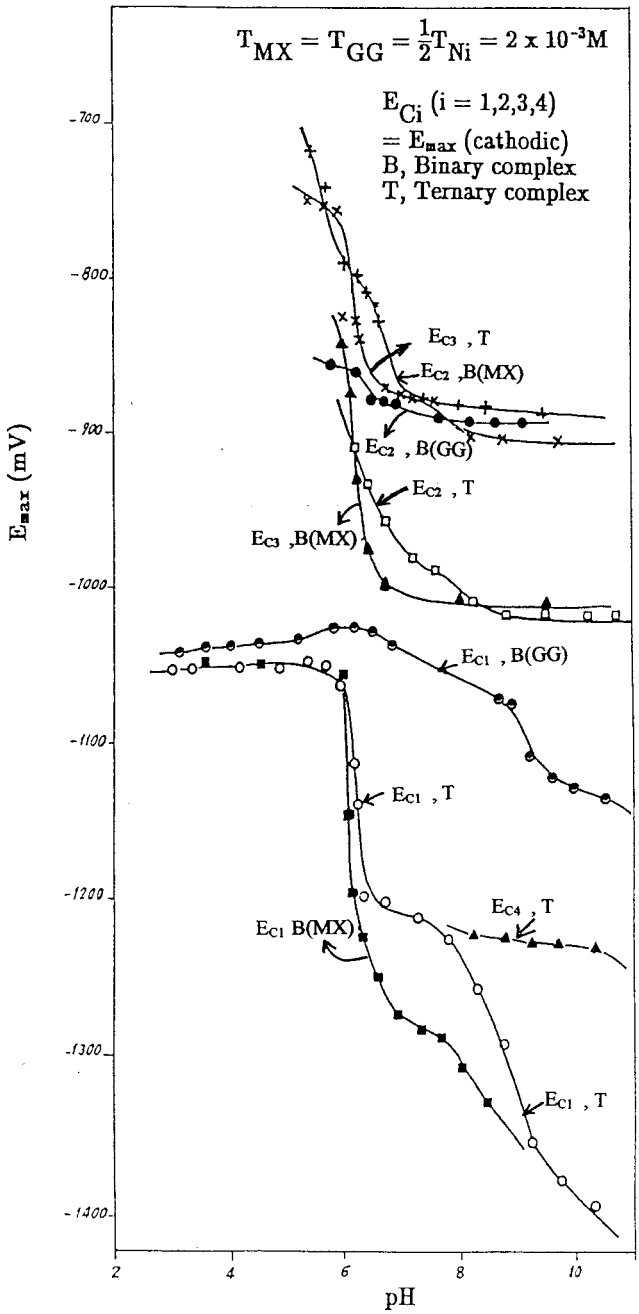

FIGURE 1 The effect of pH on E_{max} for Ni(II) systems.

chloride medium. The addition of GG, MX or both makes drastic changes in the DPP of these metal ions. Figures 1 and 2 illustrate the effect of pH on E_{max} of Ni(II) and Cu(II) systems. Complexing ligands lead to a relatively negative shift in the E_{max} of the metal ions. This can be attributed to the increase in electron density on the metal

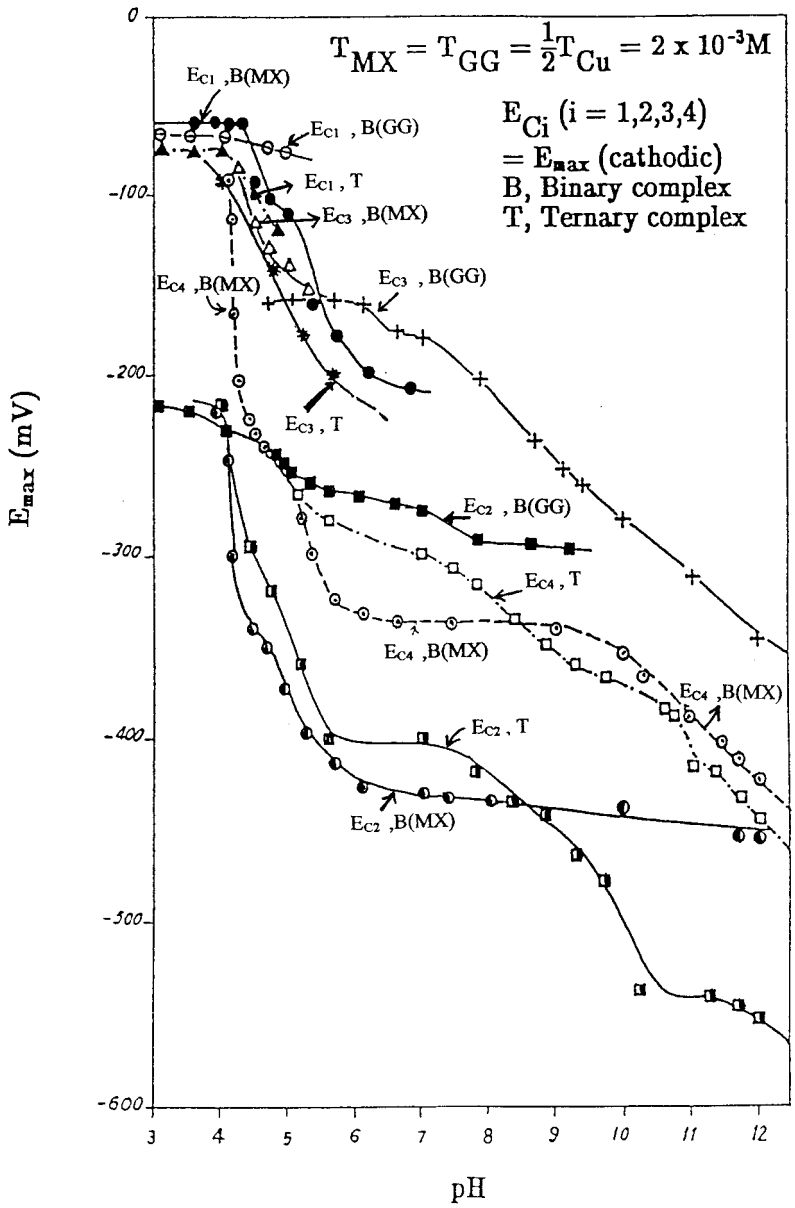

FIGURE 2 The effect of pH on E_{max} for Cu(II) systems.

ion as a result of the delocalization of the ligand electrons on the metal orbitals. This is found to be true for all systems studied except in a few cases in the Ni(II) system. The exception may be rationalized as due to the delocalization of metal ion electrons on ligand orbitals, leading to an increase in the positive character of the central metal ions rendering them more easily reduced.

The DPP of Ni(II) systems show, in general, overlapping peaks at pHs >5.5. The DPP of the Ni(II) systems (binary or ternary) show gradual negative shifts in

E_{max} (E_{C1}) as the pH increases above pH 5.8, indicating complex formation, Fig. 1. The DPP of the MX–Ni(II) system shows three E_{max} (E_{C1} , E_{C2} and E_{C3}) while the GG–Ni(II) system shows only two E_{max} (E_{C1} and E_{C2}). The addition of GG to the MX–Ni(II) binary system exhibits an extra peak, E_{C4}, at pH values >8. This is unique to the ternary system and may be assigned to the (MX : GG : Ni : H), 1 : 1 : 1 : 0 and 2 : 1 : 1 : -1 species; mainly the latter, which exists at pHs >8.0. The sum of δ_i of both E_{C1} and E_{C2} peaks corresponds to the δ_i of Ni(II) in absence of the ligands at pHs lower than ~6.0. Both peaks shift to more negative potential as pH increases above ~pH 6. A similar result is observed in the Ni(II)–SCN^- system [18] studied by DC polarography, however no interpretation was provided. E_{C2} and E_{C3} appear at more positive potentials than E_{C1}. A positive shift in E_{C3} of MX–Ni(II) system is observed on adding GG in the pH range 6.2–8.1. This type of shift is also shown by E_{C1}. It may be rationalized as due to the formation of the ternary species 1 : 1 : 1 : 0.

The DPP of Cu(II) systems, Table III, are mostly of the overlapped type specially at pHs <7.0 except for the GG–Cu(II) system where the overlapping takes place at pHs >4.1. The DPP of Cu(II) in the presence of 0.15 M NaCl consists of two peaks, E_{C1} and E_{C2}, Table III, interpreted [18] as due to the stepwise reduction of Cu^{2+} to Cu^{1+} and to Cu^0 ions. The reason for stepwise reduction was attributed to the special stability of CuCl. In the presence of GG, E_{C1} and E_{C2} are preserved. E_{C2} shifts to more negative potential as the pH increases while E_{C1}, on the contrary, almost stays constant with little shifts to negative potential. In fact, there is almost no free Cu(II) at pH values >4.5. One should expect that the stepwise reduction of Cu^{2+} to Cu^0 in chloride medium did not take place. It is replaced by the stepwise reduction of the binary complex species represented now by the new E_{C3} and E_{C2}. These two peaks are preserved at pHs >5.0. There is, however, no report about the stability of Cu^+ species of GG. The inflections in the E_{C2} and E_{C3} as a function of pH indicates the presence of more than one complex species in solution.

The DPP of the binary system of MX–Cu(II), Table III, is more complicated than that of GG–Cu(II) where an extra peak E_{C4} appeared. All peaks shift to more negative potential with respect to the Cl^- or GG–Cu(II) systems, (with the exception of E_{C3} in the GG system), Fig. 2. E_{C2} and E_{C4} of the MX–Cu(II) system show almost constant potential values in the pH range of ~6 to ~10. On the other hand, the shifts of E_{C1} toward more negative potential, in the pH range ~4.0 to ~7.0, indicate that the stepwise reduction of Cu^{2+} to Cu^0 is also taking place in the MX–Cu(II) system, where the presence of two inflections in the curve may indicate the reduction of more than one species. Moreover, E_{C4} and E_{C2} also show the same features of E_{C1} as a function of pH at pHs <7.0. Furthermore, E_{C4} shows an extra inflection at pH ~9.7 indicating the presence of another species. The $W_{1/2}$ (half-peak width; mV) for E_{C4} at pHs >6.0 varies between 94 and 52 mV indicating the variation between one electron reduction and two electron reduction processes; Table III.

The ternary system shows the same reduction behavior as the binary system of MX–Cu(II). However, E_{C1} and E_{C3} are shifted to more negative potentials, Fig.2. In addition, E_{C4} does not show any variation in $W_{1/2}$ by increasing the pH. The values are around 60 mV, which indicates a two-electron reduction process, Table III. This conclusion is quite important from the analytical point of view, since determination of Cu^{2+} is now feasible in the presence of these ligands at pHs >7.0; Cu^{2+} concentration cannot be determined easily by DPP, especially in chloride medium. The stability of the +2 oxidation state of Cu decreases in the ternary system at pHs less than 8.7,

compared to the binary species of MX–Cu(II) and increases at pHs greater than 8.7. This reflects the type of species below and above pH 8.7. There is only one fact pertinent to the DPP of these metal ions in presence of GG, MX or both that needs to be discussed. Most of these systems exhibit peaks with negative δ_i (they should all be positive since the pulse amplitude is -40 mV). This situation, however depends on the pH and system under consideration. It should be added that these peaks are highly reproducible either through scanning to more negative or to more positive potentials or from low to high pH or vice versa. They may be due to an adsorption process of the reduced, oxidized or both forms of the species.

Spectral Studies

UV-Vis-nIR Spectral Studies on Ni(II) and Cu(II) Systems

The absorption bands of aquated Ni(II) are weak with maximum wavelengths at ~395 ($\epsilon = 5.4$), ~690 ($\epsilon = 2.2$), and ~1149 ($\epsilon = 1.8$) nm. However, in the presence of MX or MX and GG, at least a 3 times increase in absorbance is observed (depending on the pH value) in addition to a blue shift in the wavelength maxima (~250 nm). Figure 3(a) shows the absorption spectra of the ternary system of Ni(II) as a function of pH

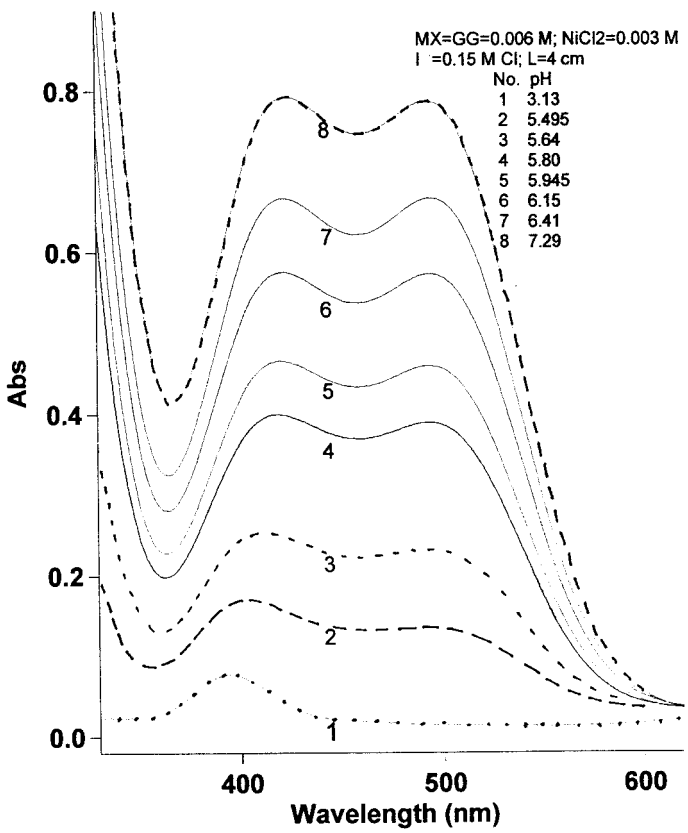

FIGURE 3 (a) The absorption spectra of Ni(II) ternary system; (b) The absorption spectra of Cu(II) ternary system.

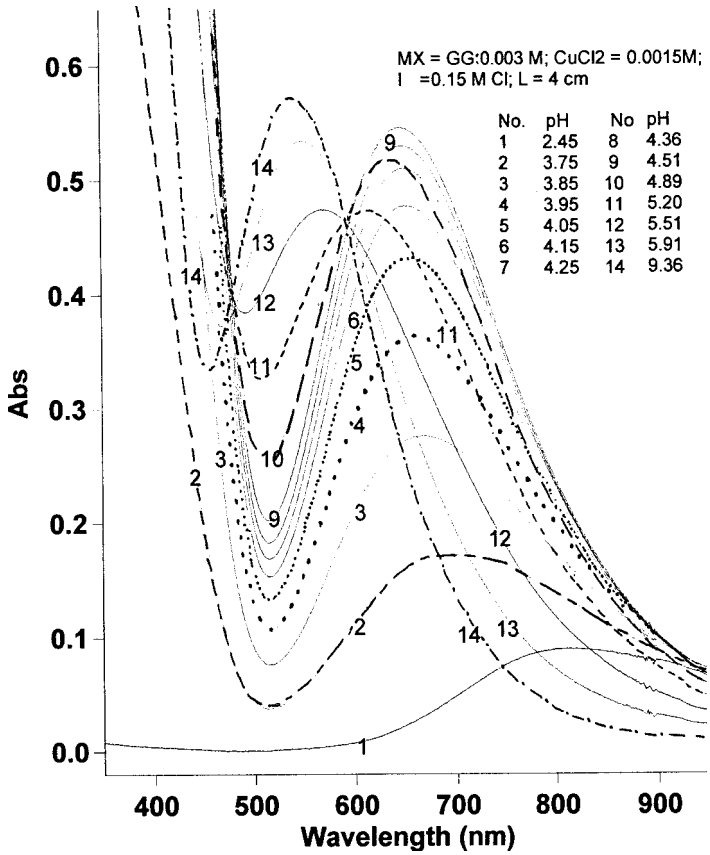

FIGURE 3 (Continued).

values. The spectra resemble the Ni(II)–MX binary system (not shown) with a slight decrease in absorbance. Figure 4(a) shows the variation of absorbance with pH values at a given wavelength. This dependence, unfortunately, does not definitely indicate a GG contribution to the spectra of the ternary complex. The absorption band of aquated Cu(II) is characterized by a broad asymmetric band at a maximum wavelength of ~812 nm ($\epsilon = 13.9$). This band shows a blue shift as well as an increase in absorbance as the pH values increase in presence of MX, GG or both. Figure 3(b) shows the spectra of the ternary system of Cu(II) as function of pH. Figure 4(b), on the other hand, shows the variation of absorbance as function of pH at a given wavelength. The spectra of the ternary system is quite similar to the Cu(II)–MX binary system except for the pronounced increase in absorbance observed in the presence of GG specially at pH values larger than ~3.9. These results indicate the contribution of GG to the absorption spectra of the Cu(II) ternary system.

EPR Spectral Studies on the Cu(II) Systems

The EPR spectra of Cu(II) consist of one signal at 3200 G indicating no nuclear spin-electron spin coupling in weakly complexing media. The g_{av} factor is 2.193. The major

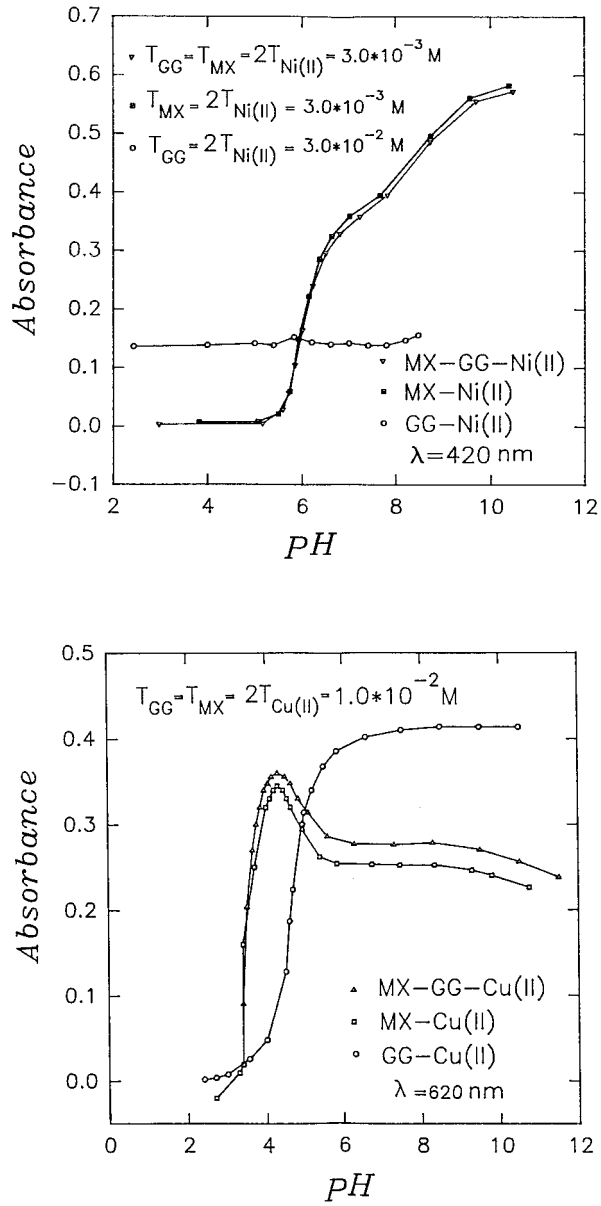

FIGURE 4 (a) Absorbance as a function of pH for Ni(II) systems; (b) Absorbance as a function of pH for Cu(II) systems.

cause of this broadness is the unresolved interaction of unpaired electrons with the protons of water molecules coordinated to the metal ions in aqueous solutions [19]. However, in the presence of GG the situation is different; splitting of the Cu(II) signal into four signals of unequal intensities occurs in the pH range ~3.9 to ~10.5. These signals correspond to the combination of the EPR of free hydrated Cu(II) ions and those of Cu(II) ions coordinated to GG where a single N atom is involved

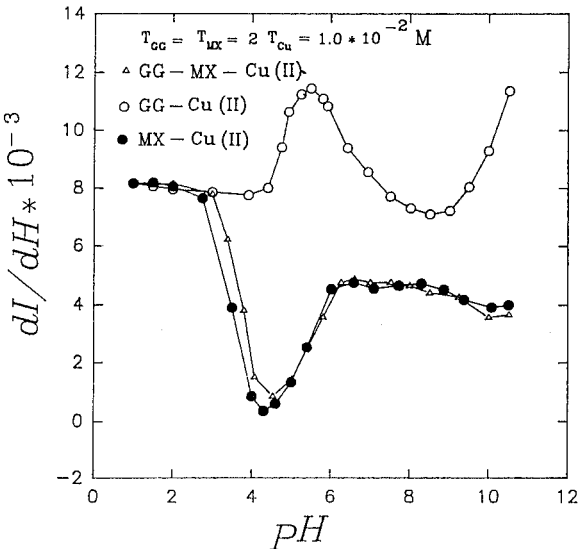

FIGURE 5 The variation of dI/dH as a function of H(G).

in chelation (0 : 1 : 1 : i (MX : GG : Cu(II) : H) species). Figure 5 shows the variation of the intensity of EPR signal as a function of pH at ~3150 G. The intensity increases as pH increases in the pH range 3.0–5.5 and decreases as pH increases in the pH range ~5.0–8.0 indicating the partial formation of the (antiferromagnetic) dimeric species of Cu(II) with GG, Table II. However, as the pH increases above 8.0, intensity increases, as dimerization of the complex decreases leading to formation of the monomeric species.

The EPR spectra of Cu(II) in the presence of MX are quite different in pattern from those in the presence of GG. Moreover, the split of the Cu(II) signal almost vanishes at pH ~4.3 due to the formation of an antiferromagnetic polymeric species, Table II. Figure 5 shows the variation of intensity at ~3150 G as a function of pH confirming the formation of several species in the course of the pH change. The intensity diminishes at pH ~4.3 indicating the formation of polymeric species, Table II. However, as the pH increases from ~4.3 to ~6.0, the intensity increases indicating the gradual formation of monomeric species. The intensity becomes almost constant above pH ~6.0. The number of split signals is always four at pHs > 5.0 and two to three below pH 3.5 with unequal intensities (noting that theoretically the number of Cu(II) nuclear spin-electron spin coupling signals is four of equal intensities). These results indicates that nitrogen atoms of MX are involved in ligation with Cu(II) such that the Cu(II) unpaired electrons are delocalized on N (covalent bonding). One can conclude that 0 : 1 : 1 : i species are formed at pH values < 4.0 and 0 : 2 : 1 : i species are formed at pH values > 5.0 and the polymer exists in the pH range ~3.7 to 6.0 . Typical coupling constant is ~80 G.

On the other hand, the EPR spectra of the ternary complexes of Cu(II) with GG and MX are similar to those of the MX–Cu(II) binary system especially at pHs > 4.5, Figure 5. At pHs < 4.5, the intensities are greater than that of the binary system, which may indicate the formation of 1 : 1 : 1 : i species. However, there is no clear

indication of ternary complex formation at pHs >4.5 although the potentiometric results show the formation of several species in the pH range under study.

CONCLUSION

Although GG binary complexes of Ni(II), and Cu(II), are less stable than their binary MX complexes, the ternary complexes involving both ligands are more stable than both binary species. In contrast to the binary Cu(II) systems, the ternary Cu(II) system does not involve any polymeric species.

The binary metal complexes of MX may assume five or six member chelate structures if the sulfur ligation of MX is ignored. The five-member chelate type may be one of three suggested structures depending on the ligation atoms involved, Fig. 6(a–c). It is expected that these structures may allow further formation of dimeric species (MX : 0 : 2**M** : s) by including another metal ion in the vacant sites. Unfortunately, this conclusion could not be confirmed in this work, Table II. However, it may allow complexation with a different hard metal ion such as Fe(III) or a soft metal ion such as Ni(II). The formation of the trimeric species in MX–Cu(II) system is peculiar. A suggested structure involving four MX molecules, two of them bridging between three Cu(II) ions may explain this stoichiometry. However, this kind of structure has the middle Cu(II) ion environment different from that of the other two Cu(II) ions,

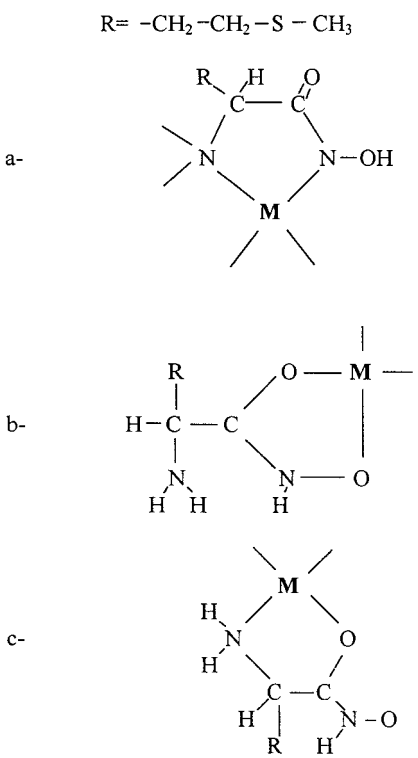

FIGURE 6 Predicted structures of the metal complexes of MX (five-member chelate).

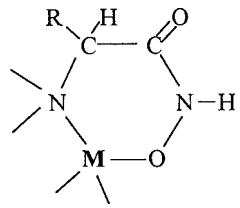

FIGURE 7 Predicted structures of the metal complexes of MX (six-member chelate).

which may impose some strain on the species. This conclusion can be supported by the EPR study where antiferromagnetism is observed in a very limited pH range ~4.3 to ~4.7.

If the chelation is of the six-membered type there is only one possible structure, shown in Fig. 7.

By comparing the formation constants of methionine [20], Meth, complexes with Cu(II) to that of MX, one can find that the stability of the latter is more than the former by ~3 log units for the 1 : 1 : 0 (MX or Meth: Cu(II) : s H) species and ~6 log units for the 2 : 1 : 0 species. These facts reflect the type of chelation one should expect in MX–Cu(II) system where the ligation atoms should be the nitrogen atoms of both the hydroxamate and the amino group, Fig. 6, rather than the oxygen atom of the hydroxamate group and the nitrogen atom of the amino group (in Meth the ligation is through the oxygen atom of the carboxylate and the nitrogen atom of the amino group). In (MX or Meth)–Ni (II) systems the same conclusion can be arrived at except that the differences in the formation constants are less being ~1 log unit and ~3 log units for 1 : 1 : 0 and 2 : 1 : 0 species, respectively. On the other hand, the complexation of these metal ions with GG may involve five, and/or seven-member chelates, Fig. 8. Although many ligation sites are available, the formation of dimeric species of this type 0 : 1 : 2 : s (MX : GG : **M** : s) does not occur, Table II. Instead, two ring structures may arise per molecule, Fig. 8. If the formation constants of the species encountered in GG–Cu (II) are compared with those species identical in composition to that in Gly(glycine)–Cu(II) system [20], one can find the latter species are more stable with a difference of ~3 log units than the former species. This observation probably reflects a different ring formation or due to the negative inductive effect of the carboxylate group in GG in complex formation with Cu(II). This interpretation may also be extended to Ni(II) systems.

GG–Cu(II) binary system shows, in addition to the formation of monomeric species, the formation of dimeric species i.e. 0 : 2 : 2 : − 1 (MX : GG : Cu (II) : −H), where –1 refer to the formation of hydroxy complex species or more probable, deprotonation of the peptidic proton, Table II. On the contrary, the GG–Ni(II) binary system did not show the formation of any polymeric species in solution under the same experimental conditions.

Ternary species for both Ni(II) and Cu(II) systems have the tendency to form hexa-coordinate species clearly represented by the species 1 : 2 : 1 : 0 and 2 : 1 : 1 : − 1 (pMX : qGG : rM : sH). This configuration cannot be definitely predicted in the binary systems.

The ternary species are either neutrally or negatively charged depending on their composition. It should be expected that the transport of these complexes in biological

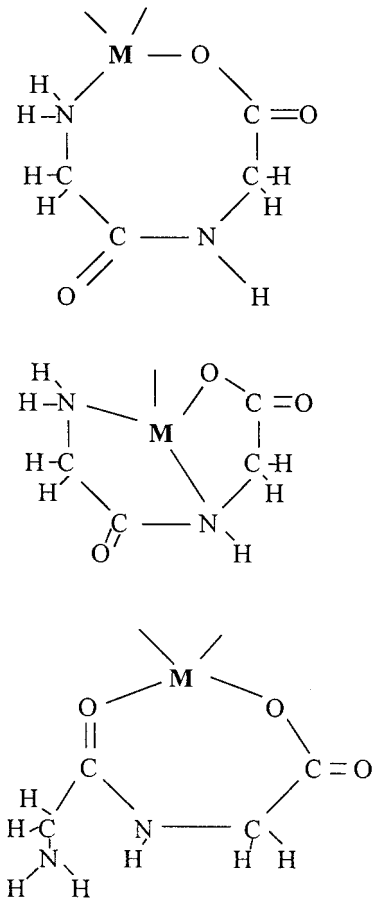

FIGURE 8 Predicted structures of the metal complexes of GG.

systems will be through active transport rather than passive transport if they are negatively charged, which is the case at biological pH values > 7.0.

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References

[1] J.B. Neilands, In: G. Eichorn (Ed.), Inorganic Biochemistry, Ch. 5 (Elsevier, Amsterdam, 1973), p. 167.
[2] D.A. Brown, M.V. Chidambaram and J.D. Glennon, *Inorg.Chem.* **19**, 3260 (1980).
[3] H. Kehl (Ed.), Chemistry and Biology of Hydroxamic Acids (Karger, New York, 1982).
[4] K. Munakata, K.K. Kobashi, S. Takebe and J. Hase, *J. Pharm. Dyn.* **3**, 451 (1980).
[5] W.N. Fishbein, C.L. Streeter and J.E. Daly, *J. Pharmacol. Exp. Ther.* **186**, 173 (1973).

[6] D.A. Brown, M.V. Chidambaram, In: H. Sigel (Ed.), Metal Ions in Biological Systems, Vol. 14 (Marcel Dekker, New York, 1982), p. 125.
[7] M.S. El-Ezaby, H.M. Marafie, M.M. Hassan and H.M. Abu Soud, *Inorg. Chim. Acta* **123**, 53 (1986).
[8] H.M. Marafie, M. Makhyoun, N. Al-Salem and M.S. El-Ezaby, *Electroanalysis* **4**, 611 (1992).
[9] N.M. Moussa, H.M. Marafie, M.S. El-Ezaby and M. Rashad, *Polyhedron* **6**, 1477 (1987).
[10] H. Sigel, A.D. Zuberbuhler and O. Yamauchi, *Anal. Chim. Acta* **255**, 63 (1991).
[11] H.M. Irving, M.G. Miles and L.D. Petit, *Anal. Chim. Acta* **38**, 475 (1967).
[12] P. Gans, A. Sabatini and A. Vacca, *J. Chem. Soc., Dalton Trans.* 1195 (1985).
[13] M.S. El-Ezaby, N.M. Shuaib, H.M. Marafie and M.M. Hassan. *J. Inorg. Biochem.* **33**, 161 (1988).
[14] B. Kurzak, K. Kurzak and J. Jesurska, *Inorg. Chim. Acta* **125**, 77 (1986).
[15] E. Leporati, *J. Chem. Soc., Dalton Trans.* 421 (1988).
[16] E. Farkas, J. Szoke, T. Kiss, H. Kozlowski and W. Bal, *J. Chem. Soc., Dalton Trans.* 2247 (1989).
[17] E. Leporati, *J. Chem. Soc., Dalton Trans.* 953 (1988).
[18] I.M. Kolthoff and J.J. Lingane, Polarography, Vol. II (Interscience Publ., New York, 1965).
[19] P.B. Ayscoughin, Electron Spin Resonance in Chemistry (Methuen & Co., London, 1967).
[20] R. Bruce Martin, In: H. Sigel (Ed.), Metal Ions in Biological Systems, Vol. 9 (Marcel Dekker, NY, 1979) p. 1.