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Ternary Coordination Complex Formation between Glycylglycine, Copper(II) & DL-4-Aminobutyric Acid

M. SIVASANKARAN NAIR*†, K. VENKATACHALAPATHI & M. SANTAPPA‡
Central Leather Research Institute, Adyar, Madras 600 020

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Computer based analysis of the potentiometric data obtained at 37°C and I = 0.15 M; ($NaClO_4$) for the Cu(II)-glycylglycine (A)-DL-4-aminobutyric acid (B) system indicates the presence of two ternary complexes (CuAB and $CuABH_{-1}$) in addition to the binary complex species (HA, H_2A, CuA, $CuAH_{-1}$, HB, H_2B, and CuB). The results suggest that the five and seven-membered chelate rings in the CuAB complex is less favoured. It appears that the amide-deprotonated glycylglycine in the $CuABH_{-1}$ complex species is tridentate similar to that in the $CuAH_{-1}$ glycylglycine binary complex.

STUDIES on Cu(II)-dipeptide-amino acid ternary complex systems, though intermittent, have directed for a better understanding of the metal ion-enzyme-substrate complexes[1,2]. It is generally agreed[1-6] that initial complex formation between Cu(II) and a dipeptide results in a five-membered chelate ring involving N-amino and O-peptido donor groups in both the binary and ternary systems. At higher pH, the dipeptide undergoes deprotonation at the amide group and become[1-6] tridentate via N-amino, N-peptido and O-carboxylategroups in the Cu(II)-dipeptide binary systems. However, in the Cu(II)-dipeptide (A)-secondary ligand(B) ternary systems where B is bidentate or tridentate,[3,7-9], several workers favour the bidentate binding of amide-deprotonated dipeptides via N-amino and N-peptido groups, while others[5,10] favour its tridentate binding as is the case with $CuAH_{-1}$ dipeptide binary complex. Nair *et al.*[11] recently reported that amide-deprotonated dipeptide is tridentate in the presence of a monodentate ligand like imidazole in the Cu(II) ternary systems. The present communication deals with the coordination behaviour of a dipeptide, viz. glycylglycine (glgl) with Cu(II) in the presence of DL-4-aminobutyric acid (4-aba).

The potentiometric studies were carried out at 37°C and I = 0.15 M ($NaClO_4$) with the apparatus and procedure described previously[12,13]. Both glgl and 4-aba were obtained from Fluka. $Cu(ClO_4)_2$ and other reagents were prepared and estimated as described earlier[14].

Analysis of the potentiometric data in the pH range 3.00—8.00 in the Cu(II)-glgl(A)-4-aba(B) ternary system in this study using MINIQUAD-75 computer program[15] on an IBM-370 computer showed the presence of two ternary complexes (CuAB and $CuABH_{-1}$) in addition to the binary species[6,16] (HA, H_2A, CuA, $CuAH_{-1}$, CuA_2H_{-1}, HB, H_2B and CuB). The charges of all these complexes are neglected for clarity.

†Present address: Department of Chemistry, Post-Graduate Extension Centre, Madurai Kamaraj University, St. John's College Campus, Palayamkottai 627 002.

‡Present address: Vice Chancellor, University of Madras, Madras 20.

TABLE 1 — STABILITY CONSTANTS FOR Cu(II)-glgl(A)-4-aba (B) TERNARY SYSTEM

[I = 0.15 M ($NaClO_4$); temp. = 37°]

Constant	Value	Constant	Value
$\log \beta_{CuAB}$	12.29(10)	pK^{H}_{CuAB}	5.65
$\log \beta_{CuABH_{-1}}$	6.64(4)	$\log K^{CuAH}_{CuABH_{-1}}$	5.02
$\log K^{CuA}_{CuAB}$	6.59	$\log K^{CuB}_{CuABH_{-1}}$	0.57
$\log K^{CuB}_{CuAB}$	6.22	$\Delta\log K_{CuABH_{-1}}$	−1.05
$\Delta\log K_{CuAB}$	+0.52		

Stability constants of proton and binary complexes of glgl (ref. 6) and 4-aba (ref. 16) with Cu(II) used for the calculation of the above constants have been taken from our earlier published work.

It appears that complex formation between glgl(A) and Cu(II) in the CuAB species involves the formation of a five-membered chelate ring as is the case with CuA-glgl complex, because $\log K^{CuB}_{CuAB}$ (Table 1) and $\log K^{Cu}_{CuA}$ values[6] are comparable. Similarly comparison of the $\log K^{CuA}_{CuAB}$ (Table 1) and $\log K^{Cu}_{CuB}$ values[16] clearly indicate that 4-aba (B) forms a seven-membered chelate ring in the CuAB complex species. Thu the CuAB species would contain five-and seven-membered chelate rings. Since more coordination positions are available for binding the first ligand to a given multivalent metal ion than for the second ligand, negative values for $\Delta \log K_{CuAB}$ (Eqs 1 and 2) are expected. But this parameter for the title system

$$CuA + CuB \rightleftharpoons CuAB + Cu \qquad ...(1)$$

$$\Delta\log K_{CuAB} = \log \beta_{CuAB} - (\log \beta_{CuA} + \log \beta_{CuB}) \qquad ...(2)$$

is positive (Table 1). It indicates that 4-aba (B) ligand prefers to add on to CuA glgl binary complex rather than to aquated Cu(II). Also, the positive $\Delta\log K_{CuAB}$ value suggests that the formation of ternary complex, CuAB is preferred over the binary complexes, CuA or CuB. However, the maximum amount of the total Cu(II) present in CuAB complex is only 7.5% (Fig. 1), while the statistically expected value is 50% indicating that the CuAB formation is less favoured. This may be atributed to the steric factors associated with the five- and seven-membered chelate rings in this species.

Previously, Nair and coworkers[8,9] reported that amide-deprotonated glgl (AH_{-1}) is bidentate in the $CuABH_{-1}$, when B is a bidentate ligand like DL-2-aminobutyric acid, 3-aminobutyric acid, histamine or glycinamide; or a tridentate ligand like L-histidine, DL-2,3-diaminopropionic acid, DL-2,4-diaminobutyric acid or DL-ornithine. This conclusion was arrived at by considering (i) $\log K^{CuA}_{CuAB}$ and $\log K^{CuAH_{-1}}_{CuABH_{-1}}$, (ii) $\Delta\log K_{CuABH_{-1}}$ (Eqs 3 and 4) and (iii) pK^{H}_{CuAB} values in the Cu(II)-glgl(A)-B and Cu(II)-glycinamide (A)-B ternary systems.

$$CuAH_{-1} + CuB \rightleftharpoons CuABH_{-1} + Cu \quad \ldots(3)$$

$$\Delta \log K_{CuABH_{-1}} = \log \beta_{CuABH_{-1}} - (\log \beta_{CuAH_{-1}} + \log \beta_{CuB}) \quad \ldots(4)$$

One may expect the same type of binding of the ligand B in both CuAB and $CuABH_{-1}$ complexes and thus $\log K^{CuA}_{CuAB}$ and $\log K^{CuAH_{-1}}_{CuABH_{-1}}$ values must be comparable. This trend was seen[9] in the Cu(II)-glycinamide(A)-B systems, but in the Cu(II)-glgl (A)-B systems the $\log K_{CuABNA_{-1}}$ values were lower than $\log K^{CuA}_{CuAB}$ values by ~3 log units. This was explained by considering the bidentate binding of AH_{-1} glgl in $CuABH_{-1}$ unlike its tridentate binding in the $CuAH_{-1}$. Similar arguments have been put forward[9] to explain the negative Δ lo $K_{CuABH_{-1}}$ values (Eq. 4) with high magnitude in the case of Cu(II)-glgl(A)-B systems, while the $\Delta \log K_{CuH_{-1}}$ values in theCu(II)-glycinamide-B systems are in the order of statistically expected values. The bidentate mode of binding of AH_{-1} glgl in the ternary complex systems is further confirmed by the fact that pK^{H}_{CuAB} values in all the Cu(II)-glgl-B systems studied are nearly identical within the limits of experimental error to the corresponding Cu(II)-glycinamide-B systems. Sigel[3] also reported the bidentate binding of AH_{-1} glgl in the Cu(II)-glgl-2,2′-bipyridyl ternary system. For finding out the mode of coordination of AH_{-1} glgl in presently studied Cu(II)-glgl-4-aba system, the Cu(II) glyciannide-4-aba system was also investigated, but no appreciable complexing seems to have been revealed. If one compares the $\log K^{CuA}_{CuAB}$ and $\log K^{CuAH_{-1}}_{CuABH_{-1}}$ values in Table 1 for the title system, it may be noted that the latter parameter is lower than the former by only ~1.5 log units and its $\Delta \log K_{CuABH_{-1}}$ value is in the order of statistically expected values. Both these values suggest that the AH_{-1} glgl is tridentate in $CuABH_{-1}$ as in the case in $CuAH_{-1}$ glgl binary complex. Thus in the $CuABH_{-1}$ species three equatorial coordination sites would be occupied by AH_{-1} glgl, while the 4-aba (B) would occupy one equatorial and one axial position. This sturcture is similar to that of the $Cu(AH_{-1})A$ glgl complex[6], the difference is that the second glgl ligand is replaced by the 4-aba (B) ligand in the ternary system.

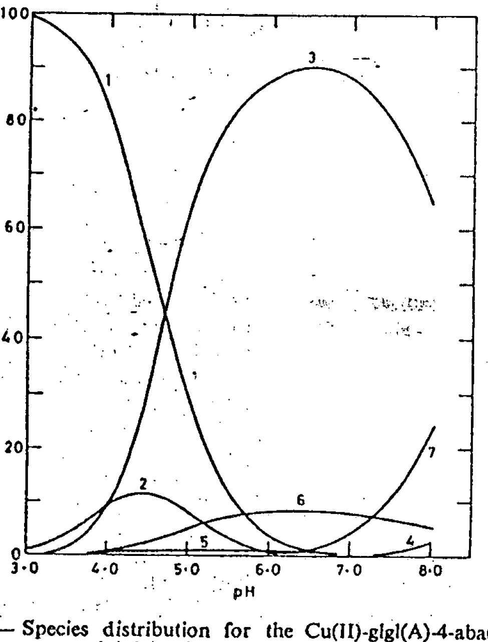

Fig. 1 — Species distribution for the Cu(II)-glgl(A)-4-aba(B) system at a metal-A-B ratio of 1:1:1 [(1) unbound Cu(II); (2) CuA; (3) $CuAH_{-1}$; (4) CuA_2H_{-1}; (5) CuB; (6) CuAB; and (7) $CuABH_{-1}$].

This tridentate binding of AH_{-1} glgl in the title system is surprising, because 4-aba(B) is also a bidentate ligand like DL-2-aminobutyric acid or 3-aminobutyric acid, under whose presence AH_{-1} glgl is found to be bidentate[9]. This may probably be accounted for by considering the fact that if AH_{-1} glgl binds in a bidentate manner, then the $CuABH_{-1}$ species in the title system would have five- and seven membered chelate rings, possibly less favoured due to steric reasons. The strain due to the seven-membered ring of 4-aba (B) would get reduced by its coordination in one equatorial position and one axial position at a greater distance. This is possible only by the coordination of AH_{-1} glgl in a tridentate manner, i.e. by occupying three equatorial sites similar to its binding in the $CuAH_{-1}$ glgl binary complex. The difference in the $\log K^{CuA}_{CuAB}$ and $\log K^{CuAH_{-1}}_{CuABH_{-1}}$ values of ~1.5 log units in the title system may thus be accounted for by the fact that in the CuAB complex, 4-aba (B) occupies two equatorial positions while in the $CuABH_{-1}$ complex, it occupies one equatorial and one axial position.

Thus, the present investigation shows that the coordination behaviour of amide-deprotonated dipeptide in the ternary Cu(II) complex systems is highly influenced by the chelate ring size-du e to the secondary ligand, B. The $CuABH_{-1}$ complex species is favoured above pH 6.5 and there is a steady increase in its concentration with rise in pH as shown in Fig. 1. At pH 8.0, about 24% of the total metal was found to be present in the form of $CuABH_{-1}$ species.

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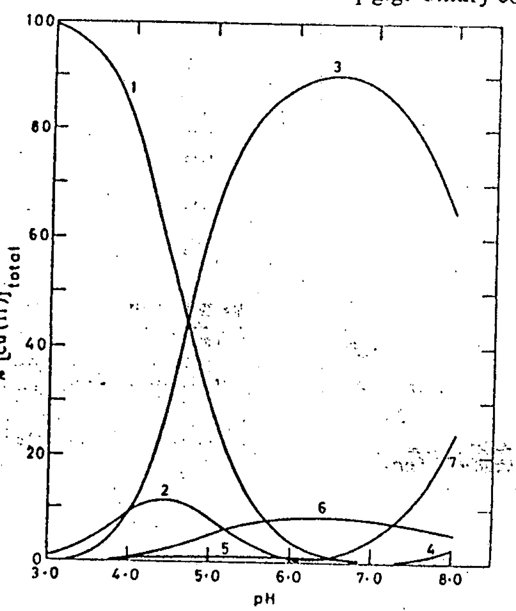

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The potentiometric studies were carried out at 37°C and $I = 0.15$ M ($NaClO_4$) with the apparatus and procedure described previously[12,13]. Both glgl and 4-aba were obtained from Fluka. $Cu(ClO_4)_2$ and other reagents were prepared and estimated as described earlier[14].

Analysis of the potentiometric data in the pH range 3.00—8.00 in the Cu(II)-glgl(A)-4-aba(B) ternary system in this study using MINIQUAD-75 computer program[15] on an IBM-370 computer showed the presence of two ternary complexes (CuAB and $CuABH_{-1}$) in addition to the binary species[6,16] (HA, H_2A, CuA, $CuAH_{-1}$, CuA_2H_{-1}, HB, H_2B and CuB). The charges of all these complexes are neglected for clarity.

It appears that complex formation between glgl(A) and Cu(II) in the CuAB species involves the formation of a five-membered chelate ring as is the case with CuA-glgl complex, because log K^{CuB}_{CuAB} (Table 1) and log K^{Cu}_{CuA} values[6] are comparable. Similarly comparison of the log K^{CuA}_{CuAB} (Table 1) and log K^{Cu}_{CuB} values[16] clearly indicate that 4-aba (B) forms a seven membered chelate ring in the CuAB complex species. Thu the CuAB species would contain five-and seven-membered chelate rings. Since more coordination positions are available for binding the first ligand to a given multivalent metal ion than for the second ligand, negative values for Δ log K_{CuAB} (Eqs 1 and 2) are expected. But this parameter for the title system

$$CuA + CuB \rightleftharpoons CuAB + Cu \quad ...(1)$$

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is positive (Table 1). It indicates that 4-aba (B) ligand prefers to add on to CuA glgl binary complex rather than to aquated Cu(II). Also, the positive Δlog K_{CuAB} value suggests that the formation of ternary complex, CuAB is preferred over the binary complexes, CuA or CuB. However, the maximum amount of the total Cu(II) present in CuAB complex is only 7.5% (Fig. 1), while the statistically expected value is 50% indicating that the CuAB formation is less favoured. This may be atributed to the steric factors associated with the five- and seven-membered chelate rings in this species.

Previously, Nair and coworkers[8,9] reported that amide-deprotonated glgl (AH_{-1}) is bidentate in the $CuABH_{-1}$, when B is a bidentate ligand like DL-2-aminobutyric acid, 3-aminobutyric acid, histamine or glycinamide; or a tridentate ligand like L-histidine, DL-2,3-diaminopropionic acid, DL-2,4-diaminobutyric acid or DL-ornithine. This conclusion was arrived at by considering (i) log K^{CuA}_{CuAB} and log $K^{CuAH_{-1}}_{CuABH_{-1}}$, (ii) Δlog $K_{CuABH_{-1}}$ (Eqs 3 and 4) and (iii) pK^{H}_{CuAB} values in the Cu(II)-glgl(A)-B and Cu(II)-glycinamide (A)-B ternary systems.

TABLE 1 — STABILITY CONSTANTS FOR Cu(II)-glgl(A)-4-aba (B) TERNARY SYSTEM

[$I = 0.15$ M ($NaClO_4$); temp. = 37°]

Constant	Value	Constant	Value
log β_{CuAB}	12.29(10)	pK^{H}_{CuAB}	5.65
log $\beta_{CuABH_{-1}}$	6.64(4)	log $K^{CuAH_{-1}}_{CuABH_{-1}}$	5.07
log K^{CuA}_{CuAB}	6.59	log $K^{CuB}_{CuABH_{-1}}$	0.57
log K^{CuB}_{CuAB}	6.22	Δlog $K_{CuABH_{-1}}$	−1.05
Δlog K_{CuAB}	+0.52		

Stability constants of proton and binary complexes of glgl (ref. 6) and 4-aba (ref. 16) with Cu(II) used for the calculation of the above constants have been taken from our earlier published work.

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$$CuAH_{-1} + CuB \rightleftharpoons CuABH_{-1} + Cu \quad \ldots(3)$$

$$\Delta \log K_{CuABH_{-1}} = \log \beta_{CuABH_{-1}} - (\log \beta_{CuAH_{-1}} + \log \beta_{CuB}) \quad \ldots(4)$$

One may expect the same type of binding of the ligand B in both CuAB and $CuABH_{-1}$ complexes and thus $\log K^{CuA}_{CuAB}$ and $\log K^{CuAH_{-1}}_{CuABH_{-1}}$ values must be comparable. This trend was seen[9] in the Cu(II)-glycinamide(A)-B systems, but in the Cu(II)-glgl (A)-B systems the $\log K_{CuABHA_{-1}}$ values were lower than $\log K^{CuA}_{CuAB}$ values by ~3 log units. This was explained by considering the bidentate binding of AH_{-1} glgl in $CuABH_{-1}$ unlike its tridentate binding in the $CuAH_{-1}$. Similar arguments have been put forward[9] to explain the negative Δ lo $K_{CuABH_{-1}}$ values (Eq. 4) with high magnitude in the case of Cu(II)-glgl(A)-B systems, while the $\Delta \log K_{CuH_{-1}}$ values in the Cu(II)-glycinamide-B systems are in the order of statistically expected values. The bidentate mode of binding of AH_{-1} glgl in the ternary complex systems is further confirmed by the fact that pK^{H}_{CuAB} values in all the Cu(II)-glgl-B systems studied are nearly identical within the limits of experimental error to the corresponding Cu(II)-glycinamide-B systems. Sigel[3] also reported the bidentate binding of AH_{-1} glgl in the Cu(II)-glgl-2,2′-bipyridyl ternary system. For finding out the mode of coordination of AH_{-1} glgl in presently studied Cu(II)-glgl-4-aba system, the Cu(II) glycianmide-4-aba system was also investigated, but no appreciable complexing seems to have been revealed. If one compares the $\log K^{CuA}_{CuAB}$ and $\log K^{CuAH_{-1}}_{CuABH_{-1}}$ values in Table 1 for the title system, it may be noted that the latter parameter is lower than the former by only ~1.5 log units and its $\Delta \log K_{CuABH_{-1}}$ value is in the order of statistically expected values. Both these values suggest that the AH_{-1} glgl is tridentate in $CuABH_{-1}$ as in the case in $CuAH_{-1}$ glgl binary complex. Thus in the $CuABH_{-1}$ species three equatorial coordination sites would be occupied by AH_{-1} glgl, while the 4-aba (B) would occupy one equatorial and one axial position. This structure is similar to that of the $Cu(AH_{-1})A$ glgl complex[9], the difference is that the second glgl ligand is replaced by the 4-aba (B) ligand in the ternary system.

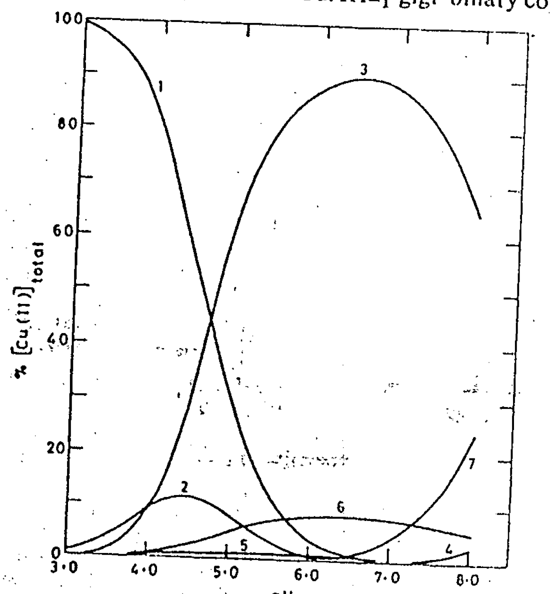

Fig. 1 — Species distribution for the Cu(II)-glgl(A)-4-aba(B) system at a metal-A-B ratio of 1:1:1 [(1) unbound Cu(II); (2) CuA; (3) $CuAH_{-1}$; (4) CuA_2H_{-1}; (5) CuB; (6) CuAB; and (7) $CuABH_{-1}$].

This tridentate binding of AH_{-1} glgl in the title system is surprising, because 4-aba(B) is also a bidentate ligand like DL-2-aminobutyric acid or 3-aminobutyric acid, under whose presence AH_{-1} glgl is found to be bidentate[9]. This may probably be accounted for by considering the fact that if AH_{-1} glgl binds in a bidentate manner, then the $CuABH_{-1}$ species in the title system would have five- and seven membered chelate rings, possibly less favoured due to steric reasons. The strain due to the seven-membered ring of 4-aba (B) would get reduced by its coordination in one equatorial position and one axial position at a greater distance. This is possible only by the coordination of AH_{-1} glgl in a tridentate manner, i.e. by occupying three equatorial sites similar to its binding in the $CuAH_{-1}$ glgl binary complex. The difference in the $\log K^{CuA}_{CuAB}$ and $\log K^{CuAH_{-1}}_{CuABH_{-1}}$ values of ~1.5 log units in the title system may thus be accounted for by the fact that in the CuAB complex, 4-aba (B) occupies two equatorial positions while in the $CuABH_{-1}$ complex, it occupies one equatorial and one axial position.

Thus, the present investigation shows that the coordination behaviour of amide-deprotonated dipeptide in the ternary Cu(II) complex systems is highly influenced by the chelate ring size-due to the secondary ligand, B. The $CuABH_{-1}$ complex species is favoured above pH 6.5 and there is a steady increase in its concentration with rise in pH as shown in Fig. 1. At pH 8.0, about 24% of the total metal was found to be present in the form of $CuABH_{-1}$ species.

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Ternary Coordination Complex Formation between Glycylglycine, Copper(II) & DL-4-Aminobutyric Acid

M. Sivasankaran Nair*†, K. Venkatachalapathi & M. Santappa‡

Central Leather Research Institute, Adyar, Madras 600 020

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Computer based analysis of the potentiometric data obtained at 37°C and $I = 0.15$ *M* ($NaClO_4$) for the Cu(II)-glycylglycine (A)-DL-4-aminobutyric acid (B) system indicates the presence of two ternary complexes (CuAB and $CuABH_{-1}$) in addition to the binary complex species (HA, H_2A, CuA, $CuAH_{-1}$, HB, H_2B, and CuB). The results suggest that the five and seven-membered chelate rings in the CuAB complex is less favoured. It appears that the amide-deprotonated glycylglycine in the $CuABH_{-1}$ complex species is tridentate similar to that in the $CuAH_{-1}$ glycylglycine binary complex.

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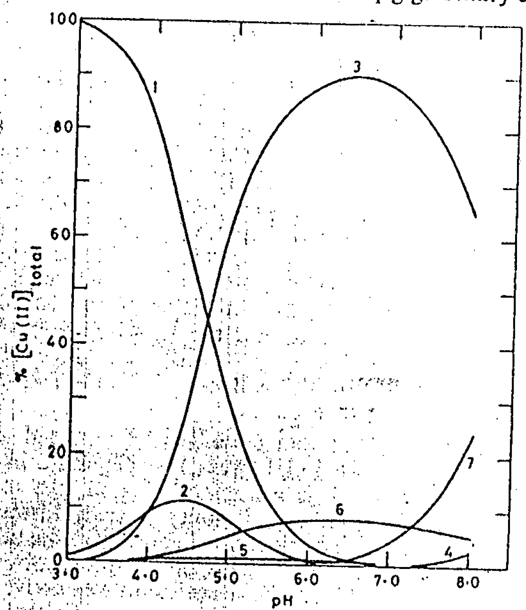

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