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SOME NOVEL ASTATISTICAL FACTORS STABILIZING TERNARY COMPLEXES*

P K BHATTACHARYA *and* NEELA EMMANUEL

Department of Chemistry, Faculty of Science, M. S. University of Baroda, Baroda 390 002, India

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The formation constants of the mixed ligand complexes of the type [*MAL*], where *M* = Cu(II), Ni(II), *A* = 5-nitro-1,10-phenanthroline (nitrophen), dipyridylamine (dpa) or dipyridylketone (dpk), *L* = histidine or histamine have been determined by using SCOGS computer technique. It is observed that the formation constants follows the order [Cu nitro-phen *L*] > [Cudpk*L*] > Cudpk*L*. This is explained to be due to the electron withdrawing effect of nitro group making 5-nitro-1,10-phenanthroline a stronger π acid. In case of [Cudpk*L*], coordinated dpk is considered to be in equilibrium mixture of keto and diol form and the keto group increases the accepting tendency of dpk.

Histidine is found to coordinate in two forms—(*i*) from aminoacid and with protonated imidazole nitrogen. For such a complex [*MA* Hist H], the formation constant is found to be higher than the expected value. This has been explained in terms of hydrophobic interaction between the metal environment in *MA* and the non-coordinated protonated imidazole group. (*ii*) Histidine coordinating from imidazole nitrogen and amino nitrogen. In such complexes [*MA* Hist], the $\Delta \log K$ value is observed to be less positive where *M* = Cu(II) than where *M* = Ni(II). This has been explained by considering that in the complex, A occupies two position in the equitorial plane, whereas histidine occupies one equitorial and one axial position. The $\Delta \log K$ value becomes more negative in Cu(II) complexes due to the presence of Jahn-Teller effect.

Key Words : Mixed Ligand Complexes; Coordination Behaviour; Stability Constants; Jahn-Teller Effect

INTRODUCTION

COMPLEXES, in which more than one type of ligand is bound to one metal ion, are termed mixed ligand complexes. Systems with two different ligands bound to a metal ion are classified a ternary complexes. Last two decades have seen a tremendous increase in the study of the solution properties and solid state structures of the ternary complexes because of their role as homogeneous catalysts and also as synthetic models for explaining biochemical reactions.[1-8] It is observed that the delicate combinations of electronic and steric characteristics of the ligands exhibit a strong influence on the catalytic activity of the metal complex. By the help of

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solution studies, it is possible to design exactly the catalyst required for a particular process. The metalloenzymes can be regarded as naturally occurring ternary complexes with the combination of the most suitable metal ion and ligand molecules, attained by the nature in the early years of evolutionary process. Hence, the study of the properties of metal complexes involving biochemically important metal ions and ligands, provides simple models for complex biochmical reactions.[9-16]

It is expected from statistical consideration the formation constant K^{MA}_{MAL} or or K^{ML}_{MLA} should be less than K^{M}_{ML} or K^{M}_{ML}, respectively, *i.e.* $\Delta \log K = K^{MA}_{MAL} - K^{M}_{ML}$ should be negative.[17] It may become more negative because of electrostatic effect (when both ligands are negatively charged) or steric effects (when ligand A has bulky groups) on the coordinating atom.[17,18] However, it was observed that in the complexes where H = N-heteroaromatic bases, dipyridyl (dipy) or *o*-phenanthroline (*o*-phen), log K^{ML}_{MAL} is much greater than expected from statistical considerations.[9,19-24] This has been explained to be due to $M \longrightarrow$ bipy π interaction.[19,21] Consequently, effective electronegativity of $[MA]^{2+}$ is almost same as in $[M(H_2O)_6]^{2+}$ and hence log $K^{MA}_{MAL} \approx$ log K^{M}_{ML}.

It has been further observed that MA complexes discriminate between secondary ligands L coordinating from the sites N-N, N-O$^-$ and O$^-$-O$^-$, the order of stabilization being O$^-$O$^-$ > O$^-$-N > N-N.[15,19,25] This has been explained in terms of increase in class A character of M due to $M \longrightarrow A$ back donation in MA[19], resulting in lowering the repulsion between the metal dπ electrons and the additional lone-pair of electrons present on the secondary ligand L in the ternary complex MAL, compared to that in bidary complex ML.[26] The effect is maximum in the case of O$^-$-O$^-$ co-ordinating ligands with additional lone pairs on both O$^-$. The stabilization effect is more in the case of Cu(II) complexes resulting in positive Δ log K in [Cu A O$^-$-O$^-$] complexes.[26,27]

The effect of the mutual stabilization of the coordinating tendency of the two ligands in the above type of complexes and the relative order of stabilities can be observed in the d-d spectra of the complexes. In a mixed ligand complex $[MAL]$, the ligand field strength imposed by ligands is the average of the fields in binary complexes $[MA_2]$ and $[ML_2]$. A glance at the λ_{max} of [CuAL], [CuA_2] and [CuL_2] complexes where L = ligand having O$^-$O$^-$ or O$^-$-N coordination, show that the d-d transition in CuAL is at a higher energy than in CuA_2 or CuL_2.[28,29] This is because $M \longrightarrow A$ π interaction stabilizes $L \longrightarrow M$ σ bond due to the lowering of repulsion between metal dπ electrons and ligand lone pair of electrons over O$^-$-O$^-$ or O$^-$-N in the ternary complex. Thus ligands A and L can generate a stronger field in [CuAL] than in [CuA_2] or [CuL_2]. This leads to greater splitting of d orbitals in CuAL and d-d transition shifts to higher energy.

The deviation of d-d transition energy of CuAL from the average of [CuA_2] and [CuL_2] is less where L = O$^-$-N co-ordinating and is least where L = N-N

coordinating. Thus the spectral studies support the explanation that the stabilization of the ternary complex [*MAL*] is due to the reduction in the repulsion between the ligand π electrons and metal $d\pi$ electrons in the ternary complex.

The value of Δ log K of the ternary complex is also dependent on the nature of substitution over L.[30-33] Electron withdrawing groups lower the electron density on theO^--O^- and makes Δ log K more negative or less positive, whereas electron releasing group increases electron density on O^--O^- sites and makes Δ log K less negative or more positive.

Stability of the ternary complex has also been shown to be dependent on the π acid character of A.[32] Presence of an electron withdrawing group in the tertiary base makes it a stronger π acid, hence there is a stabilizing influence on the formation of the ternary complex. However, an electron releasing group over A decreases its acid character and thus destabilizes the ternary complex [*MAL*]. 5-nitro-1,10-phenanthroline with an electron withdrawing group is a stronger acid[34] and hence forms a more stable ternary complex, whereas dipyridyl amine (dpa)[35] with bridging –NH group between two pyridyl groups is a much weaker acid. The ternary complex, involving dpm are destabilized due to restricted π delocalization, formation of six membered ring and distortion in the planarity of the dpa ring.

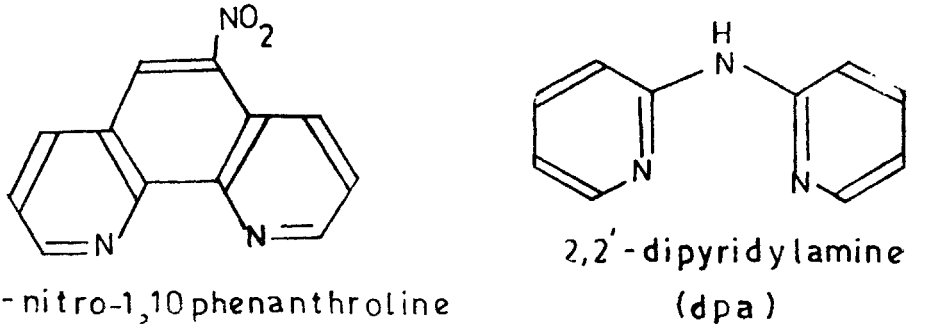

FIG 1

Another interesting ligand is dipyridyl ketone (dpk).[35,36] It is believed[35] to exist in the gem-diol form and coordinates from two nitrogens at lower *p*H. However, at *p*H above 4.5, deprotonation of one of the diol OH^- takes place and the coordinating site changes to N-O^-. An equilibrium of following type is known to exist.

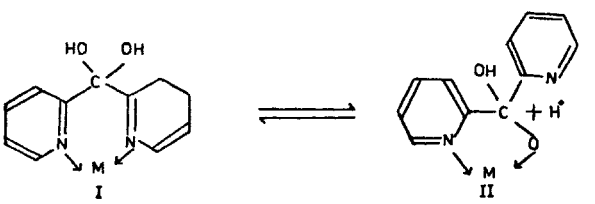

FIG 2

However, it has been recently observed by us[37] that a ternary complex [Cudpk$L$] where L is O⁻-O⁻ coordinating, dpk continues to coordinate from N-N end till *p*H 8. This has been attributed to the fact that in ternary complexes O⁻-O⁻ coordinating ligand prefer second ligand A coordinating from N-N, with possibility of $M \longrightarrow$ A π interaction, (I form) rather than A with σ bonding O⁻-N coordination (II form).

It has further been shown that dpk may not completely be in a geminal diol form, as it will necessitates sp^3 hybridization over the carbon atom and hence the planarity of the cordinated dpk ring will be lost. This should make dpk a weak π acid leading to destabilization of [Cudpk$L$] complex. Moreover, dpk forms a six membered ring and a five-six membered ring ternary complex is less stable. However, Cudpk$L$ complexes are observed to be more stable than that of the corresponding [Cudipy$L$] complex. A probable explanation has been extended[37] that coordinated dpk may not be fully in gem-diol form but there is an equilibrium between keto and gem-diol forms as follows :

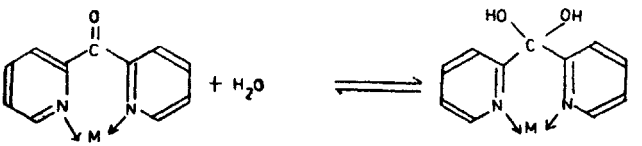

FIG 3

This is supported by the fact[38] that in the electronic spectrum of [Cudpk] the band at 256 nm due to $n \longrightarrow \pi^*$ transition of $> C = O$ group of dpk is retained till *p*H 8. Moreover, recently dpk has also been shown to form solid complexes both in diol and keto forms.[39,40] The keto form of dpk is a stronger π acid due to delocalisation of electrons over $> C = O$ part and hence the ternary complex is stabilized.

Another interesting observation of the structure of ligand on the stability of the ternary complexes is in [M dipy L] where L = an aminoacid with a non-coordinating phenyl or substituted phenyl group or indole group, as in phenylalanine, tryptophan or tyrosine, respectively. It has been suggested by Martin *et al.*[41,42] that in the binary complex non-coordinated hydrophobic phenyl or substituted phenyl group of the aminoacid have a preferential position near to the metal ion than in solution. This has been further confirmed by the X-ray analysis of the Cu(II) complexes of tyrosine and dipeptides containing tyrosine or tryptophan groups[43,44] and Pd (II) complexes of tyrosine.[45] They exhibit that the aromatic side group is tilted towards the metal ion, with the metal ion-aromatic ring separation less than the Van der Waals contact without bonding through the phenolic -OH or indole -NH.

In the ternary complex [MA aminoacid] with noncoordinating aromatic group $\Delta \log K$ is positive even though the coordination is from the aminoacid end as in glycine. The higher formation constant of the ternary complex can be explained

by considering that the aminocarboxylate end of the aminoacid coordinate with $[MA]$ and the phenyl or substituted phenyl part remains free. It may be expected to spread over the heteroaromatic N-base part of A leading to an intramolecular stacking interaction between the tertiary amine and the aromatic ring of the secondary ligand as suggested by Sigel[46,47] in case of [Cu(II) *o*-phen-phenylacetate] complex. However, in case of [CuAL] complexes, with bidentate L, construction of a space filling models shows that the aromatic ring of the aminoacid can spread only over the axial region of M(II) and not beyond. This makes intra-molecular interligand interaction less likely. The enhanced stability of these ternary complexes can be explained[48] by considering that the hydrophobicity of the metal ion environment increases on coordination with an aromatic base. Hence, the interaction of $[MA]$ with phenyl or hydroxyphenyl group is more, consequently the ligand L is more strongly bound with $[MA]$ in the ternary complex than with $[M(H_2O)_n]$ in the binary complex, resulting in more stable ternary complex. This leads to more positive $\Delta \log K$ in these ternary complexes.

The increase in the metal ion environment, aromatic ring hydrophobic interaction in ternary complex can be explained[48] as follows. The repulsion between electrons in metal ion dz^2 orbital and the delocalized π electron on the aromatic ring of the aminoacid (L) in the binary complex ML is lowered in the ternary complex MAL due to $M \longrightarrow A$ π interaction which reduces the electron density in the axial direction of the metal ion. Thus the aromatic ring can come closer to the metal ion in the ternary complex.

It has recently been observed by Yamauchi and workers[49] that even in the complexes [CuAL] where L = aminoacid with side chains and A = aliphatic diamine, there is stabilization of the ternary complex. It was explained that the greater stability of the [Cudiamine aromatic aminoacid] complex is due to the shift of electrons from the metal ion to the free aromatic ring of the aminoacid situated in the axial direction. This facilitates the coordination of the second ligand stabilizing the ternary complex. This fact, however, remains to be substantiated. If there is an electron shift from the metal ion to the aromatic ring of the aminoacid, it should facilitate the attachment of a σ bonding aliphatic diamine more than the σ and π bonding aromatic diamines. However, the observation points to the contrary. The value of $\Delta \log K$ is positive in [CuA aromatic amino acid] when A = dipyridyl or o-phenanthroline while it is negative when A = en.

The metal ion-aromatic side chain interaction seems to affect the coordinating tendency of L-dopa also in the ternary complexes. L-dopa is a compound of great biochemical importance as neurotransmitter. It is known to be ambidentate in the binary Cu(II) complexes[50] coordinating from the aminoacid end at lower pH and from catechol end at higher pH. However, in the ternary complexes [Cu dipy or *o*-phen L-dopa], L-dopa coordinates from the aminoacid end till pH 8.[48,51,52] The $\Delta \log K$ value is found to be positive, evidently due to interaction between the metal ion environment and non-coordinated dihydroxyphenol, as in case of analogous ternary complexes containing phenylalanine, tyrosine or tryptophan.

Another aminoacid of biochemical significance is histidine. It is also ambidentate in nature.[53] There are three coordinating sites, imidazole nitrogen, amino nitrogen and carboxyl oxygen. Only metal ions with an octahedral coordination sphere can combine with two tridentate histidinate anion. With metal ion having square planar coordination sphere, histidine forms stable *bis* complex but has little tendency to form *tris* complex because of steric factor. In [M(histidine)$_2$] complex there are two possible coordinating sites.[54'55]

(1) Both the histidinate anions bind to the metal ion histamine-like *i.e.* from imidazole nitrogen and amino nitrogen.

(2) Both the histidinate anions bound the metal ion glycine-like, *i.e.* the coordination is from amino nitrogen and carboxyl oxygen.

A third type of coordination was suggested earlier[56'57] considering that in the species [Cu(H. hist)], coordination is from imidazole nitrogen and carboxyl oxygen the amino nitrogen remaining non-coordinated and protonated. However, this will give rise to a less stable seven membered ring. A crystal structure study[58] has also shown that in the complex [Cu(LH)$_2$] the coordination is from amino nitrogen and carboxyl oxygen as in aminoacids and the imidazole nitrogen remains protonated. It has further been confirmed by Pettit *et al.*[59] by the determination of formation constants in solution. It has been shown that in the *p*H range 1.8 to 3.2 there is formation of [Cu(H. hist)] species involving glycine-like coordination and imidazole nitrogen remains protonated. In the *p*H range 3.5 to 4.7 species [Cu(hist)] is formed with coordination from amino nitrogen and imidazole nitrogen. There may be a weak coordination of carboxyl oxygen also. Thus, initially there is a formation of the species [Cu(H. hist)] or [Cu(hist)]. At still higher *p*H range 4.1 to 6, there is a coordination of the second histidinate moiety hist or H. hist respectively, resulting in the formation of [Cu(hist) (H. hist)]. In [Cu(hist) (H. hist)] one histidine molecule binds to Cu(II) from imidazole nitrogen and amino nitrogen and the other histidine molecule binds to the metal ion glycine like *i.e.* from amino nitrogen and carboxyl oxygen, imidazole nitrogen remaining protonated.

However, in [Ni(histidine) 1 or 2][60] complexes, histidine acts as tridentate, coordinating through imidazole nitrogen, amino nitrogen and carboxylate oxygen. The species with only bidentate aminocarboxylate coordination is not not formed.

In view of the fact that the two coordinated forms of histidine have non-coordinated side groups, protonated imidazole or carboxylate group, ternary complexes of the [MA histidine] were studied[53'61] where M = Cu(II) or Ni(II) and A = dipyridyl or *o*-phenathroline. The stability values have been compared with that of [MA histamine] or [MA alanine]. The present study has been extended to the cases of [MA histidine or histaminel where M = Cu(II) or Ni(II) and A = 5-nitrophenanthroline (nitrophen), dipyridylamine (dpa) or dipyridylketone (dpk). The values have been compared with the systems MA histidine or histamine where A = dipyridyl or *o*-phenanthroline.

Experimental

All reagents used were of A.R. grade and the titrations were carried out using the digital *p*H meter with an accuracy of ± 0.01. The proton ligand formation constants of histidine, histamine and *A*, formation constants of binary complexes of histidine, histamine and *A*, and mixed ligand formation constants were determined in 50 per cent dioxan-water (1:1, v/v) medium and 0.2 mol. dm^{-3} ($NaClO_4$) at 30° using SCOGS computer program.[62]

In case of binary Cu-histidine complex, species [Cu*L*], [Cu*L*H], [Cu*LL*H] were considered to be formed in 50 per cent dioxan medium as in water. The preliminary values of the formation constant of the mixed ligand species [Cu*AL*] and [Cu*AL*H] were determined by considering that the reaction occurs in steps. Precise values of stabilities are obtained by taking into account all possible species AH_2, *A*H, *A*, LH_3, LH_2, *L*, Cu(II), [Cu*A*], [CuA_2] [Cu*L*H], [Cu*L*], [Cu*LL*H], [CuL_2], [Cu*AL*], [Cu*AL*H].

In case of Ni(II) complexes, no convergency in values was obtained when the presence of protonated species [Ni(H.hist) is considered. The same result is obtained in mixed ligand complexes. It is thus indicated that Ni(II) combines with histidine from the histamine sites only. Hence the species considered were AH_2, *A*H, *A*, LH_3, LH_2, *L*H, *L*, Ni, [Ni*A*], [NiA_2], [Ni*L*], [NiL_2], and [Ni*AL*].

In case of CuA histamine complexes where M = Cu(II) or Ni(II) the species considered were LH_2, *L*H, *L*, AH_2, *A*H, *A*, Cu(II). [*MA*], [MA_2], [*ML*], [ML_2] and [*MAL*] in the second computer method.

The formation constants of the mixed ligand complexes have been tabulated in Table I.

Table I

Ternary complex stability constants of Cu(II) in dioxan-water (1 : 1, v/v) medium and 0.2M $NaClO_4$ at 30 °C with standard deviation σβ in parentheses

Ligands	$\log K^{CuA^1}_{CuA_1LH}$	$\log K^{CuA^1}_{CuA^1L}$	$\log K^{CuA^2}_{CuA^2LH}$	$\log K^{CuA^2}_{CuA^2L}$	$\log K^{CuA^3}_{CuA^2LH}$	$\log K^{CuA^3}_{CuAL}$
Histidine	10.17	10.13	10.01	9.96	9.48	9.6
	(±0.08)	(±0.06)	(±0.05)	(±0.08)	(±0.06)	(±0.11)
Δ log *K*	+0.23	−1.30	+0.07	−1.47	−0.56	−1.83
Histamine	—	8.7	—	8.55	—	7.92
		(±0.03)		(±0.09)		(±0.06)
Δ log *K*	—	−1.27	—	−1.42	—	−2.05

The plots of concentration of different species against *p*H in [CuA^1 histidine] and [NiA^1 histidine]. Systems are shown in Fig. 4 and 5. Electronic spectral studies were carried out using Carl-Zeiss Spectrophotometer.

In case of [Cu dpk histidine] system calculations was confined to *p*H 4.5 as the site of the coordinated dpk changes after that *p*H.

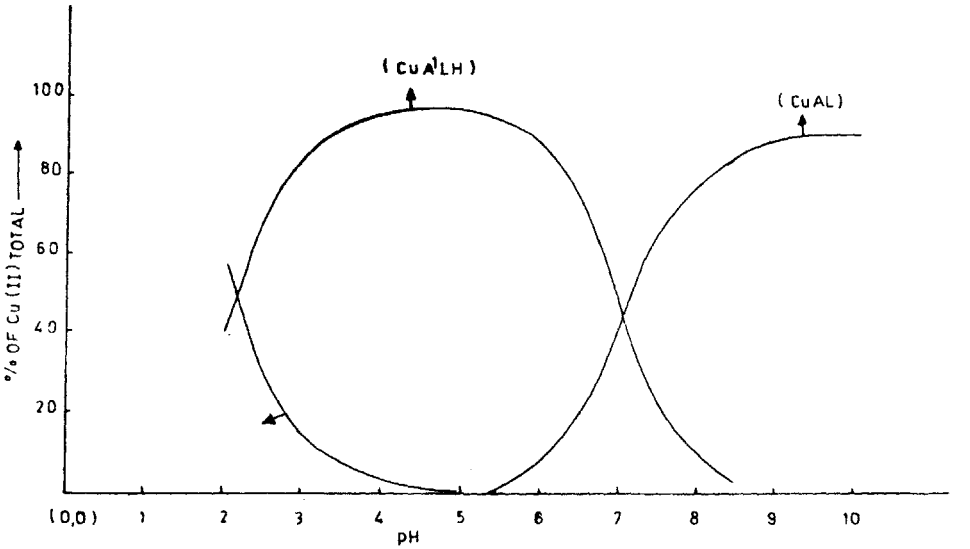

FIG 4

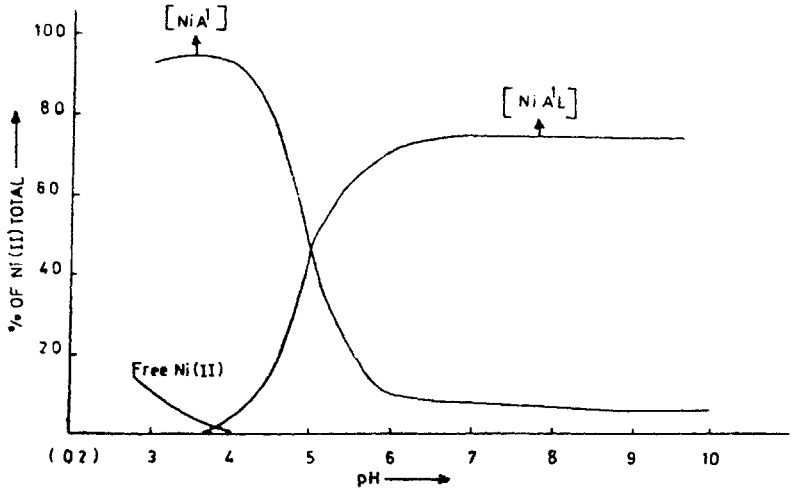

FIG 5

RESULTS AND DISCUSSION

The plot of concentration of the species against *p*H (Fig. 4) shows that [Cu*A*] is the major species in the lower *p*H range and the coordination of histidine takes place in steps

$$[CuA] + [\text{hist.H}] \rightleftharpoons [CuA\ \text{hist.H}]$$

$$[Cu]\ A + [\text{hist}] \rightleftharpoons [Cu\ A\ \text{hist}]$$

It is observed in the plot of the concentration of the species that [Cu *A* hist. H] is maximum (52 per cent) at *p*H 5 and [Cu*A* hist] is maximum (89 per cent at *p*H 6.5. In the lower *p*H range (*p*H 3.0 to 5.0) there is a formation of [Cu *A* hist. H] due to the coordination from amino nitrogen and carboxyl oxygen while imidazole nitrogen remain protonated, as in the binary complex [Cu hist. H]. The [Cu*A* hist] formation starts at higher *p*H due to coordination from imidazole nitrogen and amino nitrogen. As *p*H is increased, the concentration of [Cu*A* hist] also increases. In case of Ni(II) complexes, [Ni*A*] is formed at lower *p*H (4.5) and there is formation of [Ni*A* hist] with hist coordinating from imidazole nitrogen and amino nitrogen. As in the case of binary complex, there is no formation of the ternary complexes species [Ni *A* hist. H] with histidine coordinating from aminoacid end and imidazole nitrogen remain protonated.

In case of [*MA* histamine] systems also, [*MA*] is formed at lower H $p(< 4)$ and histamine coordination start at higher *p*H (> 4).

The coordination sites are further confirmed by the fact that in the lower *p*H range [Cu nitrophen histidine *M*] shows a d-d transition band at 610nm comparable to that in Cu nitrophen phenylalanine at 606nm. This shows that there is H^--N coordination from aminoacid part of histidine, imidazole nitrogen remain protonated resulting in the species [Cu nitro-phen hist H). In the higher *p*H range $\sim$ 6.5 the spectrum of [Cu*A* hist] shows a band at 666.7nm comparable to that of [Cu nitrophen histamine]. This shows a coordination from imidazole and amino nitrogen of histidine in [Cu*A* histidine], carboxylate part remain noncoordinated. It is observed that the stabilization of the ternary complexes [Cu 5-nitro-1, 10-phenanthroline] is more than [Cu phen *L*] or [Cu dipy *L*]. This can be explained by considering that the electron withdrawing nitro group makes nitro-phen stronger acid and hence $M \longrightarrow A$ π interaction is more resulting in greater stabilization of the ternary complexes.

In the case of [Cudpk *L*] complexes calculation has been done upto *p*H 4.5 considering coordination from N-N end only. This fact is confirmed by comparing the titration curves of [Cu dipy *L*] and [Cu dpk *L*]. They run parallel to each other upto *p*H 4 5.

Though both dya and dpk from six-membered ring, log *K* values of [Cudk hist] complexes is found to be greater than those of [Cu dpa hist] complexes. As disdussed earlier dpk in coordinated form may be in equilibrium mixture of keto and diol form. In 50 per cent dioxan solution, the equilibrium shifts more towards the right resulting in an increase in the keto form (Fig. 3).

The keto form of dpk is a stronger π acid due to π delocalization $> C=O$ part. Hence, the complex [Cudpk histidine] is more stable than [Cu dpa histidine].

In case of dpa, an electron withdrawing (–NH group) present between the two pyridyl moieties enhances the electron density on the ring. This should reduce the stability of the ternary complex. Moreover, dpa forms a six-membered ring. How.

TABLE II

Ternary complex stability constant of Nickel(II) in dioxan-water (1 : 1, *v/v*) *medium at* 0.2*M* $NaClO_4$ *at* 30 °C, *with standard deviation* $\sigma\beta$ *in parentheses*

Ligand	log $\frac{NiA}{NiAL}$					
	A^1	$\Delta \log K$	A^2	$\Delta \log K$	A^3	$\Delta \log K$
Histidine	9.92 (±1.12)	−0.27	9.82 (±0.09)	−0.37	9.65 (±0.13)	−0.54
Histamine	6.68 (±0.07)	−0.31	6.51 (±0.14)	−0.48	5.63 (±0.12)	−1.36

ever, the values of stability constants of the ternary complexes [Cu *A* histidine] with *A* = dipy or dpa are comparable. This may be due to the delocalization of electron density in dpa is over a larger area than that in dipyridyl.

It is interesting to compare the Δ log *K* value of [Cu*A* hist H] complexes with that of [Cu *A* alanine]. It is observed that the value is more positive as in case of [Cu *A* phenylalanine] complex. This can be explained by considering that the noncoordinated protonated imidazole part of the histidine spreads over the *A*, leading to an intramolecular stacking interaction between the tertiary amine and protonated imidazole part of histidine. However, as in the cases of [Cu*A*-phenylalanine] complex, in [Cu*A* hist H] complex also, the protonated imidazole part can spread only over the axial region of the metal ion and not beyond. This makes intramolecular interligand stacking interaction less likely. The increase in stability of [Cu*A* hist H] is due to an increase in the hydrophobicity of the metal environment in [Cu*A*] on coordination with the aromatic base *A* and consequent increase in the hydrophobic interaction of [Cu*A*] with the protonated imidazole compared to the hydrophobic inseraction in the binary complex. This effect is however less in the 50 per cent dioxan solvent as the less polar dioxan molecules may come between [Cu*A*] and the protonated imidazole.[63]

In the case of *MA* hist complex, the Δ log *K* value is found to be more negative. It is interesting to compare the Δ log *K* values of Cu(II) and Ni(II) complexes. It is generally obperved that Δ log *K* for [Cu*AL*] complexes is less negative than that for [Ni*AL*] complexes.[19] However, in the complexes [*MA* hist] with histidine coordinating through two nitrogens, the Δ log *K* values of Ni(II) complexes show less stability than the Cu(II) complexes. A probable explanation could be that in [*M*. hist] with tridentate histidine, the tridentate ligand is in an equatorial plane. In [*MA* hist] complexes, however, ligand *A* occupies two equatorial positions and hence histidine has to occupy two equatorial and one axial positions. In [Cu*A* hist] complexes axial coordination will be weak due to Jahn-Teller effect and hence the ternary complex is less stable.[22,64] In Ni(II) complexes, there is no destabilization in occupying the axial position and hence the Δ log *K* value of Ni(II) complexes is less negative than that of Cu(II) complexes. In [*MA* histamine]

TABLE III

Visible spectra of mixed ligand complexes in dioxan-water (1 : 1, *v/v*) *medium at different* pH

Complex	pH	λ_{max} nm
[CuA^1 H.Hist]	3.5	610
[CuA^1 Hist]	6.5	666.7
[CuA^1 Histamine]	4.0	666.0
[CuA^1 Histamine]	6.5	666.7

system also the Δ log K value is less negative than the corresponding Cu(II) complexes, though histamine acts in a bidentate fashion and can occupy two equatorial positions in both [Cu histamine] and [CuA histamine]. A probable reason could be sought from the structure of [CuL_2] complex with L co-ordinating from two tertiary nitrogens or one tertiary nitrogen and one $-NH_2$ group. In [Cu (biPy)$_2$ (H_2O)$_2$| complexes[65], two H_2O are at *cis* positions, one bipy occupies two equatorial positions and another bipy occupies one equatorial and one axial position. Similarly in [Cu(hist)$_2$] complex with both histidine having histamine type coordination, one ligand occupies two equatorial and another occupies one equatorial and another axial position. Similarly in the present [CuAL(H_2O)$_2$] complexes (L = histidine or histamine coordinating through one imidazole and one amino nitrogen). A occupies both equatorial positions and histidine or histamine occupy one equatorial and one axial position. Due to Jahn-Teller effect, the ligand L is strained in the formation of ternary complex and the value of log K^{CuA}_{CuAL} is lowered resulting in more negative Δ log K values.

In Ni(II) complexes, there is no Jahn-Teller distortion and hence L is not strained in the formation of *cis* [Ni bipy L(H_2O)$_2$] and Δ log K is less negative than in Cu(II) complexes.

It can thus be argued that Cu(II) bound to a tertiary amine does not prefer to coordinate with another tertiary amine molecule, but prefers O^--N or O^--O^- coordinating ligands. This may be extended as a possible reason of occurrence of Cu(II) in biological systems forming ternary complexes involving coordination of tertiary amine (imidazole, histidine or histamine) and aminoacid or peptide (O^--N) or phenolate (O^--O^-).

The study thus leads to following conclusions :

(1) In MAL complexes with A = π acid, there is astatistical stabilization due to $M \longrightarrow A$ bond formation.

(2) [MA] discriminate ligands L with different coordinating sites in the order O^--O^- > O^--N > N-N.

(3) Substitution over A and L affect the stability of the ternary complex.

(4) In case of [M dpk L] complexes there is an equilibrium between keto and diol form of coordinated dpk and in cases where L = O^--O^- coordinating ligand, dpk continues to coordinate from N-N end till high pH.

(5) Histidine forms two types of complexes *MA* hist H and [*MA* hist]. The former is stabilized due to an increase in the hydrophobic interaction between [*MA*] environment and noncoordinated protonated imidazole part of histidine. In the case of latter type of ternary complex the Δ log K value for Cu(II) complexes is more negative than Ni(II) complexes.

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