

Formation Constants of Binary & Ternary Chelates of Cu(II) with 2-(N,N-Diethylaminomethyl)benzimidazole & Amino Acids

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Proton-ligand and metal-ligand formation constants of 1:1 (MA) and 1:2 (MA₂) (binary) and 1:1:1 (MAL) (ternary) complexes [where M = Cu(II), A = 2-(N,N-diethylaminomethyl)benzimidazole and L = gly, α -ala, β -ala, pro and IMDA] have been determined *pH*-metrically in 50% (v/v) aq ethanol at 25°, 35° and 45° and *I* = 0.1 M (NaClO₄). The thermodynamic parameters ($\Delta G^\ddagger$, $\Delta H^\ddagger$ and $\Delta S^\ddagger$) associated with the formation of ternary chelates have been evaluated.

In continuation of our solution studies on the coordination of benzimidazoles¹ with metal ions, we report herein the formation constants of 1:1 and 1:2 (binary) and 1:1:1 (ternary) complexes of copper (II) with 2-(N,N-diethylaminomethyl)benzimidazole (DEAMB) as a primary ligand and amino acids such as glycine (gly), α -alanine (α -ala), β -alanine (β -ala), proline (pro) and iminodiacetic acid (IMDA) as secondary ligands in 50% (v/v) aq ethanol at 25°, 35° and 45° and *I* = 0.1 M (NaClO₄).

The proton-ligand and metal-ligand formation constants for binary systems were determined using the Irving-Rossotti *pH* titration technique², while those of ternary systems by the method of Ramamoorthy and Santappa³. The *pH*-meter readings (*B*) were corrected to get the actual $[H]^+$ in the non-aqueous medium by the method of Van Uitert and Haas. The general experimental details have been described earlier¹.

Binary complexes

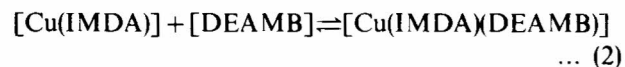
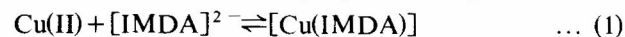
The proton-ligand formation constant, $\log K_{NH(am)}$ corresponds to the dissociation of proton of the N,N-diethylamino group, since the tertiary (the ring) nitrogen of benzimidazole, because of its low basicity, does not get protonated even in highly acidic medium (*pH* < 2.0). Therefore, its proton-ligand constant could not be determined. No dissociation of the imino proton ($-NH-$) of the imidazole ring has been observed even after *pH* 12.5¹.

The $\log K_{NH(am)}$ values⁴ (at 35°) of N-methyl-AMB (7.12) and N-ethyl-AMB (7.15) (AMB = aminomethyl-benzimidazole) are found to be higher than that of the unsubstituted AMB (6.86). This has been attributed to the electron releasing nature of the methyl or ethyl group. On the contrary, the lower value of $\log K_{NH}$ of N-butyl-AMB (6.98) may be attributed to the steric hindrance caused by the relatively bulkier butyl moiety. The $\log K_{NH(am)}$ of DEAMB (6.70) is lower than that of N-ethyl-AMB (7.15). Probably the two ethyl groups of DEAMB sterically hinder the protonation of the amino nitrogen.

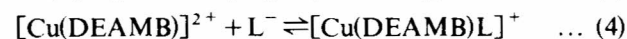
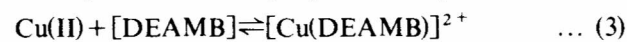
The $\bar{n}$ values ($0.1 < \bar{n} < 1.9$) for metal-ligand binary systems indicate the formation of both 1:1 and 1:2 complexes. The metal-ligand formation constants ($\log K_1$ and $\log K_2$) evaluated by various computational method² are in agreement with each other (Table 1). The standard deviations are within ± 0.03 log units.

Ternary complexes

Formation of ternary complexes has been inferred from (i) shift in *pH* of precipitation and (ii) colour change or intensification of colour of the solution³. The Cu(II)-IMDA-DEAMB titration curve coincides with 1:1 Cu(II)-IMDA curve in the *pH* range 2.4-3.5 and deviates at *pH* where coordination of Cu(II)-DEAMB system occurs, thus indicating the formation of ternary chelates in step equilibria (Eqs 1 and 2)



However, in the case of other systems, the mixed ligand curves coincide with 1:1 Cu(II) - DEAMB curve upto *pH* 3.8 and deviate at *pH* values where the complexation of 1:1 Cu(II)-L (where L = gly, α -ala, β -ala and pro) occurs. This suggests the formation of ternary chelates in step equilibria (Eqs 3 and 4).



Formation constants of the ternary systems have been evaluated using the method of Ramamoorthy and Santappa³ and are presented in Table 1.

The formation constants of ternary complexes at 25° with respect to the secondary ligand follow the order: IMDA > gly > pro > β -ala > α -ala. However, at 45° the position of IMDA and gly ternary systems is reversed over that of pro, α -ala and β -ala, suggesting destabilisation of $[Cu(IMDA)(DEAMB)]$ and $[Cu(DEAMB)(gly)]$ chelates at higher temperatures.

NOTES

Table 1 – Formation Constants and Thermodynamic Parameters of Binary and Ternary Cu(II)-DEAMB Complexes

[Medium: 50% v/v aq. ethanol; $I=0.1\ M$ (NaClO ₄)]							
System	Constant	Temp. (°C)			$\Delta G^\ddagger(35^\circ)$ kJmol ⁻¹	$\Delta H^\ddagger$ kJmol ⁻¹	$\Delta S^\ddagger$ J°K ⁻¹
		25	35	45			
[DEAMB]	$\log K_1^H$	6.80	6.70	6.61			
[Cu(DEAMB)]	$\log K_1$	6.28	5.74	5.23			
[Cu(DEAMB) ₂] ²⁺	$\log K_2$	3.80	3.67	3.47	-55.5	-131.0	-245
[Cu(IMDA)(DEAMB)]	$\log K_{MAL}^{MA}$	6.31	5.45	4.64	-32.1	-151.0	-388
[Cu(DEAMB(gly))] ⁺		5.10	4.73	4.38	-27.9	-65.6	-122
[Cu(DEAMB(α-ala))] ⁺		4.10	4.56	4.99	-26.9	+80.6	+348
[Cu(DEAMB(β-ala))] ⁺		4.41	4.74	5.05	-27.9	+58.1	+279
[Cu(DEAMB(pro))] ⁺		5.07	5.27	5.46	-31.0	+35.6	+216

A perusal of the stability data (Table 1) reveals that the ternary chelates are less stable than the corresponding binary chelates. Probably DEAMB being bulkier molecule offers more steric hindrance to the incoming amino acid molecule during the ternary complex formation. Further, if the formation of MA₂, ML₂ and MAL complexes is assumed to occur in step equilibria, then the observed order [$K_{MA_2}^{MA} < K_{MAL}^{MA}$, $K_{ML_2}^{ML}$] may be understood in the light of the bulkiness of the ligands.

The thermodynamic parameters ($\Delta G^\ddagger$, $\Delta H^\ddagger$ and $\Delta S^\ddagger$) evaluated from the pH-metric data and

calorimetric measurements are in good agreement (Table 1).

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References

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