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Hexacoordinated Ternary Chelates of Cu(II) with Amino Acids

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Evidence for the formation of hexacoordinated Cu(II) chelates of the type MA_2B and MAB_2 where A and B are two of the amino acids glycine, threonine or phenylalanine has been obtained from potentiometric and spectrophotometric studies. Stability constant and stabilization constant data reveal that formation of MA_2B and MAB_2 can not be ignored at physiological *p*H.

IN spite of possessing capacity to form hexacoordinated complexes (example aquo complexes), Cu(II) is known to form predominantly tetra-coordinated complexes in solution[1]. It is observed in the present investigation that hexacoordinated 1:3 complexes of Cu(II) with glycine, threonine or phenylalanine are formed in significant amounts only when the ligand is present in 100 times excess.

Since the expansion of coordination sphere of metal ions is known to occur through ternary chelate formation[2], it was thought worthwhile to investigate whether formation of hexacoordinated Cu(II) chelates could be realized through ternary chelate formation. Present study establishes the formation of ternary chelates of Cu(II) of the type MA_2B and MAB_2 containing pairs of amino acids (glycine and threonine; threonine and phenylalanine; and phenylalanine and glycine) in the solution containing Cu(II) and amino acids in 1:2:1 and 1:1:2 ratio.

Glycine, threonine and phenylalanine were E. Merck reagents. $Cu(ClO_4)_2$ was prepared and estimated by the standard methods. All other chemicals used were of AR grade. All the *p*H measurements were carried out on an Elico digital *p*H meter fitted with combined electrode No. CL 67. Beckmann DB manual spectrophotometer with 1 cm cells was used to record absorption spectra of solutions.

Evidence for the formation of MA_2B and MAB_2 species was obtained from the *p*H-titration of solutions containing Cu(II) and amino acids (HA or HB) in 1:3 ratio; Cu(II), HA and HB in 1:1:1, 1:2:1 and 1:1:2 ratios against carbonate-free NaOH. In the *p*H region 7.00-9.00, the curves for the systems 1:2:1 and 1:1:2 were found to be significantly different from the curves for 1:3 system and were considerably lower than the composite curves constructed out of 1:1:1 curves and HA or HB curve. This indicates an interaction between MAB and HA or HB which in all probability leads to the formation of MA_2B and MAB_2 in solution. Further support for the MA_2B and MAB_2 formation in solution comes from the experimental observation that hydrolysis sets in at a significantly higher *p*H in 1:2:1 and 1:1:2 titrations as compared to 1:3 or 1:1:1 titrations.

Absorption spectra of the 1:2:1 and 1:1:2 solutions were significantly different from those of 1:2, 1:3 or 1:1:1 solutions (*p*H of all the solutions was raised to 8.50 by the addition of NaOH) suggesting that 1:2:1 and 1:1:2 solutions contain some new species, which in all probability are MA_2B and MAB_2.

The experimental observation that in 1:2:1 and 1:1:2 titrations, Cu(II) was not hydrolysed even in the high *p*H region could be understood in terms of Polar Solvent Model[7]. As per this model electron density of the metal-ligand bonds in ternary chelates is redistributed in such a way that the ternary chelates are more polar than the binary chelates and hence more stable in the high dielectric constant medium. Thus, in aqueous medium ternary chelates

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are not easily hydrolysed and are stable in the high *p*H region.

The log $K^{MA_2}_{MA_3}$ values were determined adopting the Irving-Rossotti method[3,4] from the *p*H-titration data of 1:100 solutions. The log K^{M}_{MAB} values were determined in the same manner as reported earlier[5,6]. Stability constant values of MA_2B were evaluated using the data in the *p*H region 7.00 - 9.00, where value of m (moles of base added per mole of metal ion) was between 2.0 and 3.0 by considering the species HA, A, HB, B, MA_2, and MA B (charges are omitted here and elsewhere for the sake of simplicity). The species M, MA and MB were ignored because $m > 2.0$.

After writing down relevant expressions for the total metal ion (T_M), total ligand ($T_L = T_A + T_B$) and total titrable proton (T_H), the following expression for [A] was derived,

$$[A] = \frac{(1-a)T_L - [H] + [OH]}{[H]/K_A + [K^{M}_{MA_2}(1+[H]/K_A)/(1+[H]/K_B)K^{M}_{MAB}][H]^{1/2}/K_B} \quad ..(1)$$

where a is the moles of base added per mole of ligand (T_L). Values of [B], [M] and $K^{M}_{MA_2B}$ were then obtained from Eqs 2-4.

$$[B] = [A]\left[K^{M}_{MA_2} + (1+[H]/K_A)/(1+[H]/K_B)K^{M}_{MAB}\right]^{\frac{1}{2}} \quad ..(2)$$

$$[M] = (1+[H]/K_A)/K^{M}_{MAB}[B] \quad ..(3)$$

$$K^{M}_{MA_2B} = (T_M - K^{M}_{MAB}[M][A][B] - K^{M}_{MA_2}[M][A]^2)/[M][A]^2[B] \quad ..(4)$$

The log $K^{M}_{MA_2B}$ values were calculated at different a values and the average values are noted in Table 1.

TABLE 1 — STABILITY CONSTANTS AND STABILISATION CONSTANTS OF BINARY AND TERNARY CHELATES AT TEMP. = 30°C; μ=0.1

Stability Constant/ Stabilisation Constant	Ligands		
	HA=Gly HB=Thn	HA=Thn HB=Pha	HA=Pha Hb=Gly
log $K^{M}_{MA_2}$	15.15	14.77	14.90
log $K^{MA_2}_{MA_3}$	3.30±0.03	3.30±0.03	2.90±0.07
log K^{M}_{MAB}	15.71±0.04	15.36±0.02	15.56±0.21
log $K^{M}_{MA_2B}$	19.01±0.08	19.01±0.07	18.20±0.15
log $K^{M}_{MAB_2}$	19.78±0.07	18.30±0.12	17.82±0.10
log $K^{MA_2}_{MA_2B}$	3.86	4.24	3.30
log $K^{MB_2}_{MAB_2}$	5.01	3.40	2.67
log x	0.27	1.06	0.15
log x'	0.00	0.35	—0 26
log x''	0.77	0.04	—1.04

The pK_a values of glycine (Gly), threonine (Thn) and phenylalanine (Phn) are 9.60, 9.20, and 8.95, respectively.

The log $K^{M}_{MAB_2}$ values were obtained in a similar manner. The log $K^{MA_2}_{MA_2B}$ and log $K^{MB_2}_{MAB_2}$ values were computed for the sake of comparison and presented in Table 1. The uncertainties mentioned against log K values in Table 1 are three times the standard deviation.

Amino acids are known to act as bidentate ligands coordinating through the carboxylate and amino groups. Since 1:2:1 and 1:1:2 curves are lower than the 1:2 and 1:1:1 curves, it is not unreasonable to assume that amino acids which exist as Zwitter ions ($R-\underset{\displaystyle NH_3^+}{\underset{|}{CH}}-COO^-$) in the physiological *p*H region, lose proton on coordination to MA_2 or MAB and are hence coordinated through amino group. The log $K^{MA_2}_{MA_2B}$ and log $K^{MB_2}_{MAB_2}$ values are large enough to suggest the formation of a chelate ring and thus the carb xylate group of the third amino acid is also coordinated to the metal ion. Hence Cu(II) is hexacoordinated in MA_2B and MAB_2.

Comparison of log $K^{MA_2}_{MA_2B}$ and log $K^{MB_2}_{MAB_2}$ with log $K^{MA_2}_{MA_3}$ and log $K^{MB_2}_{MB_3}$, respectively (keeping in view the differences in pK_a values of HA and HB) reveals that all the ternary chelates except Cu(II)$(Pha)_2(Gly)$ and Cu(II)(Pha)$(Gly)_2$ are significantly more stable than the binary chelates.

The best way of discussing the stabilisation effects in ternary chelates is through the computation of stabilisation constants. The stabilisation effects in MA_2B and MAB_2 could be understood by considering the following equilibrium,

$$MA_3 + MB_3 \overset{x}{\rightleftharpoons} Ma_2B + MAB_2 \quad ..(I)$$

Statistically expected value of log x is 0.95. If log $x > 0.95$, MA_2B and MAB_2 are favoured over the 1:3 chelates. Observed log x values (Table 1) reveal that Cu(II)$(Gly)_2(Thn)$ and Cu(II)$(Gly)(Thn)_2$ are significantly stabilised over Cu(II)$(Gly)_3$ and Cu(II)$(Thn)_3$; Cu(II)(Thn) (Pha) and Cu(II)(Thn) $(Pha)_2$ are as stable as Cu(II)$(Thn)_3$ and Cu(II)$(Pha)_3$; Cu(II)$(Pha)_2(Gly)$ and Cu(II) (Pha)$(Gly)_2$ are significantly less stable than Cu(II)$(Pha)_3$ and Cu(II) $(Gly)_3$. It is surprising that Cu(II)(Pha)$(Gly)_2$ and Cu(II)(Pha) (Gly) are easily formed in spite of unfavourable log x values. A reasonable explanation for this trend could be given in terms of Polar Solvent Model[7]. Ternary chelates being more polar and less susceptible to hydrolysis are readily formed in solution, in spite of unfavourable log x values and are stable at high *p*H.

To know whether the formation of MA B and MAB_2 occurs at the expense of MAB or the bis-chelates, the following equilibria were considered,

$$MA_3 + MAB \overset{x'}{\rightleftharpoons} MA_2B + MA_2 \quad ..(II)$$

$$MB_3 + MAB \overset{x''}{\rightleftharpoons} MAB_2 + MB_2 \quad ..(III)$$

Statistically expected values of log x' and log x'' are 0.18 each. If log $x' > 0.18$, MA_2B is formed at the expense of MAB. Similarly, if log $x'' > 0.18$, MAB_2 is formed at the expense of MAB. The observed log x' and log x'' values (Table 1) reveal that glycine and phenylalanine coordinate to the bischelates preferably as compared to the 1:1:1 chelates, whereas threonine preferably coordinates to 1:1:1 chelates. Hence, Cu(II) $(Gly)(Thn)_2$ and Cu(II)(Thn)(Pha) are formed at the expense of 1:1:1 chelates but all other chelates studied are formed at the expense of bischelates. Thus, 1:1:1 chelates could be neglected if threonine is present in large excess. Concentrations of MA_2B and MAB_2 calculated at different *p*H values reveal that these species cannot be ignored at *p*H > 7.00.

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Potentiometric Determination of Stability Constants of Some Bivalent Metal Complexes with 3-Hydroxy-2-methyl-1,4-naphthoquinone Monoxime

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Dissociation constant of 3-hydroxy-2-methyl-1,4-naphthoquinone monoxime (HMNQM) and stability constants of its complexes with Mn(II), Mg(II), Fe(II), Co(II), Ni(II), Zn(II), Cd(II) and Pb(II) have been determined *p*H-metrically at 30± 1°C in 75% dioxan at different ionic strengths adjusted with sodium perchlorate. The stability constants have been calculated by weighted least-squares method.

THE present work deals with the determination of dissociation constant of 3-hydroxy-2-methyl-1,4-naphthoquinone monoxime (HMNQM) and formation constants of its complexes with bivalent transition metal ions. The studies have been carried out in 75% dioxan medium at 30 ± 1°C. The formation constants of the metal-HMNQM complexes have also been studied at different ionic strengths of sodium perchlorate.

A digital *p*H-meter (Elico, model LI-120) with a glass electrode (0–13 *p*H range) was used for *p*H measurements. The *p*H-meter was standardised with potassium hydrogen phthalate and phosphate buffers before performing the titrations. 3-Hydroxy-2-methyl-1,4-naphthoquinone (phthiocol) was prepared by the method of Fieser[1] and its purity was checked by elemental analysis and TLC.

The solution of HMNQM was prepared in freshly distilled dioxan. All the metal ion solutions were prepared from AR(B.D.H.) samples of the corresponding nitrates or sulphates and were standardised by conventional methods. Sodium perchlorate (Riedel) was used to keep the ionic strength constant. A 0.204*M* solution of tetramethyl ammonium hydroxide (TMAH) (E. Merck, A.G., Darmstadt) in 75% dioxan (aqueous) was used as the titrant. It was standardised with a standard solution of oxalic acid. The dioxan used was freed from peroxide by refluxing it with sodium metal for 24 hr and was freshly distilled over sodium before use. All the other chemicals used were of reagent grade.

All measurements were carried out at 30 ± 1°C. Presaturated nitrogen (with 75% dioxan) was passed through the solution during titrations.

The method of Bjerrum and Calvin, as modified by Irving and Rossotti[2] was used to determine $\bar{n}$ and *p*L values. The following solutions (total volume = 19.67 ml instead of 20 ml, due to contraction in volume on mixing dioxan and water) were titrated potentiometrically against standard 0.204*M* TMAH, in 75% dioxan to determine $\bar{n}$ and *p*L values of the complexes.

(i) 0.8 ml of $HClO_4$ (0.02 *M*) + 2.0 ml of $NaClO_4$ (2*M*) + 1.7 ml of H_2O + 0.5 ml of KNO_3 or K_2SO_4 (0.02 *M*) + 15.0 ml dioxan

(ii) 0.8 ml of $HClO_4$ (0.02 *M*) + 2.0 ml of $NaClO_4$ (2*M*) + 1.7 ml of H_2O + 0.5 ml of KNO_3 or K_2SO_4 (0.02 *M*) + 5.0 ml of ligand (0.02 *M*) + 10.0 ml of dioxan

(iii) 0.8 ml of $HClO_4$ (0.02 *M*) + 2.0 ml of $NaClO_4$ (2*M*) + 1.7 ml of H_2O + 0.5 ml of metal nitrate or sulphate (0.02 *M*) + 5.0 ml of ligand (0.02 *M*) + 10 ml of dioxan.

In sets i, ii and iii, requisite amounts of $NaClO_4$ were added to maintain the ionic strength at 0.1, 0.01 and 0.005*M*.

Due to the presence of oxime group the acidity of the *ortho*-phenolic hydroxyl group is enhanced and during complexation it is replaced by an equivalent of metal(II) and thus the ligand (I) acts as a mono-