

Study of ternary complexes involving auxins and amino acids with side groups

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Abstract. Stability constants of mixed ligands complexes [MAL] (where $M = \text{Cu}^{2+}$, Ni^{2+} , Zn^{2+} , A = indole acetic acid, (IAA) indole propionic acid (IPA) and indole butyric acid (IBA); L = α -alanine, phenylalanine, tyrosine and tryptophan) were determined using the SCOGS computer program. The stabilization of ternary complexes has been attributed to intramolecular interactions between the two ligands.

Keywords. Mixed ligand complexes; ternary complexes; intramolecular interactions; auxins.

1. Introduction

Auxins are growth hormones which regulate cell enlargement in plants. In biochemical systems, auxins may coordinate with metalloproteins or other such biomolecules, thus resulting in the formation of ternary complexes. As auxins are monodentate, there may be intramolecular interligand interaction between the non-coordinated indole moiety of the auxin and the side group of the other ligand. Study of ternary complexes MAL where A = auxins and L = dipeptides has been reported (Chakraborty and Bhattacharya 1991). For interactions to occur effectively the non-coordinating side groups should be oriented suitably for effective overlap (Chaudhuri and Sigel 1977; Emanuel and Bhattacharya 1985). The central metal ion plays an important role in orienting the interacting groups (Amico *et al* 1981). In Zn(II) complexes with tetrahedral geometry, interligand interactions between the non-coordinated side groups of the two ligands are more pronounced than in square planar Cu(II) or Ni(II), where both the ligands in the ternary complex are bidentate (Varghese and Bhattacharya 1992).

In order to see whether the same is true when one ligand is bidentate and another is monodentate, the formation constants of ternary complexes (MAL) (where A is indole acetic acid (IAA) (A^1), indole propionic acid (IPA) (A^2) or indole butyric acid (IBA) (A^3); L = α -alanine (L^1), phenylalanine (L^2), tyrosine (L^3) or tryptophan (L^4); and $M = \text{Cu}^{2+}$, Zn^{2+} or Ni^{2+}) have been studied in the present investigation.

2. Experimental

All the reagents used were of AnalaR grade. The potentiometric titrations were carried out in 50% v/v aqueous dioxan medium. Using the method detailed earlier (Patel and

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Bhattacharya 1993), the corrections in pH parameters have been made. Other experimental parameters for the mixed ligand systems have been given in § 2.1.

2.1 Solution compositions

Mixed ligands: (a) 0.02 M HClO_4 ; 0.004 M ligand A, 0.002 M ligand L, 0.002 M $(\text{M}(\text{ClO}_4)_2)$; 0.172 M NaClO_4 . (b) 0.02 M HClO_4 ; 0.002 M ligand A, 0.002 M ligand L, 0.002 M $(\text{M}(\text{ClO}_4)_2)$; 0.174 M NaClO_4 . Ionic strength, electrolyte: 0.2 mol m^{-3} , NaClO_4 .

2.2 Method

pH titration was done using a pH meter (G P Electronics, accuracy ± 0.01). The glass electrode was calibrated using buffer solutions of pH 4 and 9. pH range – M(II) complexation at 4.00 to 7.00; temperature – 25°C ; Method of calculation – SCOGS (Sayce 1968, 1971; Sayce and Sharma 1972); species considered – binary system; HA, MA, MAOH (metal–auxins) HA, MA, MAOH (metal–auxins). In the case of Ni(II) complexes MA_2 was also considered; HL, H_2L , ML, ML_2 (metal amino acid). mixed ligand complex system – HA, MA, MAOH, HL, H_2L , ML, ML_2 , MA(OH)L and MAL. In the case of Ni(II) complexes MA(OH)L is not formed.

The refined values of protonation constants and formation constants of binary complexes have been used as fixed parameters for the refinement of mixed ligand species. The formation constants of the mixed ligand complexes and their $\Delta \log k$ values have been presented in tables 1 and 2.

3. Results and discussion

The relative stability of a mixed ligand complex, as compared to that of a binary complex, is best quantified by

$$\Delta \log K = \log K_{\text{MAL}}^{\text{M}} - [\log K_{\text{MA}}^{\text{M}} + \log K_{\text{ML}}^{\text{M}}].$$

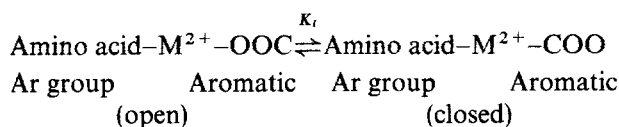
This is a measure of the difference in the strength of binding of the ligand to the free metal ion and to the metal ion already bound to another ligand. From statistical considerations, $\Delta \log K_{\text{Td}}$ assuming a tetrahedral coordination sphere, as in Zn(II) complexes, works out to be 0.3 (Td-tetrahedral) (Balakrishnan *et al* 1985). For the Jahn–Teller distorted tetragonal coordination sphere of Cu^{2+} , the theoretical value of $\log K_{\text{Cu}}$ should be -0.5 . As the two ligands in the present study have negative charges, it can be expected that the tendency of amino acids to coordinate with (M–auxin) will be less due to the interligand repulsions between negatively charged ligands resulting in more negative values of $\Delta \log K$.

However, in the present complexes of amino acids with side groups, it was observed that the $\Delta \log K$ values are less negative or more positive than expected from statistical considerations. The enhanced stability of the ternary complex is attributed to intramolecular interligand interactions between non-coordinated groups like the phenyl, phenol or indole groups of phenylalanine, tyrosine and tryptophan respectively, and the flexible indole group of the auxins. This drives the equilibrium of complex formation to the right, resulting in higher stability than expected from statistical considerations for the mixed ligand complex. The schematic structure of the possible ligand arrangement in such a complex is as in figure 1. The ternary complex is not fully in the above form. There exists an equilibrium between the open and the closed forms in

Table 1. Mixed ligand stability constants of K_{MAL}^M and $\Delta \log K$ in 50% v/v water dioxane medium ($I = 0.2 \text{ M NaClO}_4$).

Complex	$\log K_{MAL}^M$			$\Delta \log K$		
	Cu	Ni	Zn	Cu	Ni	Zn
MA ¹ L ¹	12.09 (0.10)	10.13	7.62 (0.1)	-0.27	+0.66	-0.86
MA ¹ L ²	12.30 (0.09)	9.45	7.47 (0.08)	-0.63	+1.30	-0.32
MA ¹ L ³	12.66 (0.03)	9.85	7.65 (0.05)	+0.37	+1.90	-0.27
MA ¹ L ⁴	12.99 (0.03)	10.44	7.94 (0.01)	+0.50	+1.94	-0.18
MA ² L ¹	11.85 (0.10)	9.76	7.36 (0.09)	-0.62	+0.30	-1.12
MA ² L ²	11.77 (0.10)	9.08	7.16 (0.02)	-0.50	+1.00	-0.70
MA ² L ³	11.84 (0.08)	8.96	7.47 (0.08)	-0.38	+1.18	-0.50
MA ² L ⁴	12.15 (0.12)	9.67	7.82 (0.10)	-0.28	+1.24	-0.40
MA ³ L ¹	11.40 (0.15)	8.85	7.51 (0.02)	-0.85	+0.60	-1.44
MA ³ L ²	11.36 (0.08)	8.43	7.47 (0.05)	-0.74	+0.37	-0.85
MA ³ L ³	11.50 (0.06)	8.45	7.67 (0.03)	-0.66	+0.54	-0.78
MA ³ L ⁴	11.86 (0.15)	9.10	8.03 (0.08)	-0.50	+0.64	-0.62

solution.



The greater the intramolecular interligand interaction, the greater is the value of K_I . This results in higher stability of the ternary complex and less negative $\Delta \log K$.

The order of stabilities of the ternary complexes containing auxins is IAA > IPA > IBA. The ideal chain length for effecting a stronger intramolecular interaction is only one methylene group long, i.e. ($n = 1$), as in indole acetic acid. The stabilization of the ternary complex is lower with increasing chain length of the complex.

It is observed that these interactions are influenced by the geometry of the coordination sphere of the metal ion. It was observed earlier that in Zn(II) complexes, with tetrahedral geometry, the hydrophobic interactions are more pronounced than in square planar Ni(II) or Cu(II) complexes, where the two ligands are bidentate

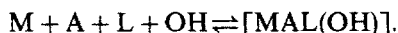
Table 2. Mixed ligand stability constants of $K_{MAL(OH)}^M$ and $\Delta \log K$ in 50% v/v water dioxane medium ($I = 0.2 \text{ M NaClO}_4$).

Complex	$\log K_{MAL(OH)}^M$		$\Delta \log K$	
	Cu	Zn	Cu	Zn
MA ¹ L ¹ (OH)	5.07	1.88	-1.01	-2.22
MA ¹ L ² (OH)	5.16	1.30	-0.73	-0.07
MA ¹ L ³ (OH)	5.28	1.67	-0.57	+0.22
MA ¹ L ⁴ (OH)	5.75	2.00	-0.30	+0.33
MA ² L ¹ (OH)	5.34	1.51	-1.14	-1.10
MA ² L ² (OH)	5.16	1.12	-1.04	-0.78
MA ² L ³ (OH)	5.70	1.32	-0.76	-0.69
MA ² L ⁴ (OH)	5.66	1.81	-0.66	-0.44
MA ³ L ¹ (OH)	5.24	1.65	-1.69	-1.20
MA ³ L ² (OH)	5.15	1.50	-1.42	-0.84
MA ³ L ³ (OH)	5.51	1.72	-1.02	-0.75
MA ³ L ⁴ (OH)	5.86	2.07	-0.87	-0.60

(Varghese and Bhattacharya 1992). However, in the present complexes, where one ligand A is monodentate and the other ligand L is bidentate, $\Delta \log K$ is more negative in Zn(II) than in the corresponding Cu(II) complexes. Space-filling molecular models indicate that in case of tetrahedral Zn(II) complexes, the non-coordinating indole group on the monodentate ligand A is at a greater distance from the non-coordinating groups of the second ligand L. Hence, the intramolecular interaction is lower, resulting in lower stability of the ternary complex.

In the present systems, $\Delta \log K$ in the Ni(II) complex was found to be more positive than in the corresponding Cu(II) complex. A similar more negative $\Delta \log K$ for Cu(II) complexes involving one monodentate and one tridentate ligand was observed (Manjula *et al* 1995). The side group of auxin or the aromatic part of the amino acid acts as an additional coordination site in the axial direction of the metal ion, which results in some interaction between the metal orbitals and the π cloud over the aromatic side group as proposed by Yamauchi (Masuda *et al* 1993). This amounts to a ligand field in the axial direction. The additional electron cloud in the axial direction causes a destabilization effect in Cu(II) complexes due to the Jahn–Teller effect. However, in corresponding Ni(II) complexes there is no destabilization due to the absence of the Jahn–Teller effect.

Apart from the (MAL) species, it was observed that a hydroxo species [MAL(OH)] is formed in the present system. The equilibrium corresponding to this species can be represented as



Stability of the hydroxo complex species was quantified by the expression.

$$\Delta \log K = \log K_{MAL(OH)}^M - [\log K_{MA(OH)}^M + \log K_{ML}^M].$$

The $\Delta \log K$ values for [MAL(OH)] are seen to be more negative or less positive than the corresponding (MAL) complex. This in turn is attributed to electrostatic repulsion. The coordination of two anionic A and OH reduces the negative charges on the M(II). When a second ligand L with one negative charge coordinates with MA(OH) there is

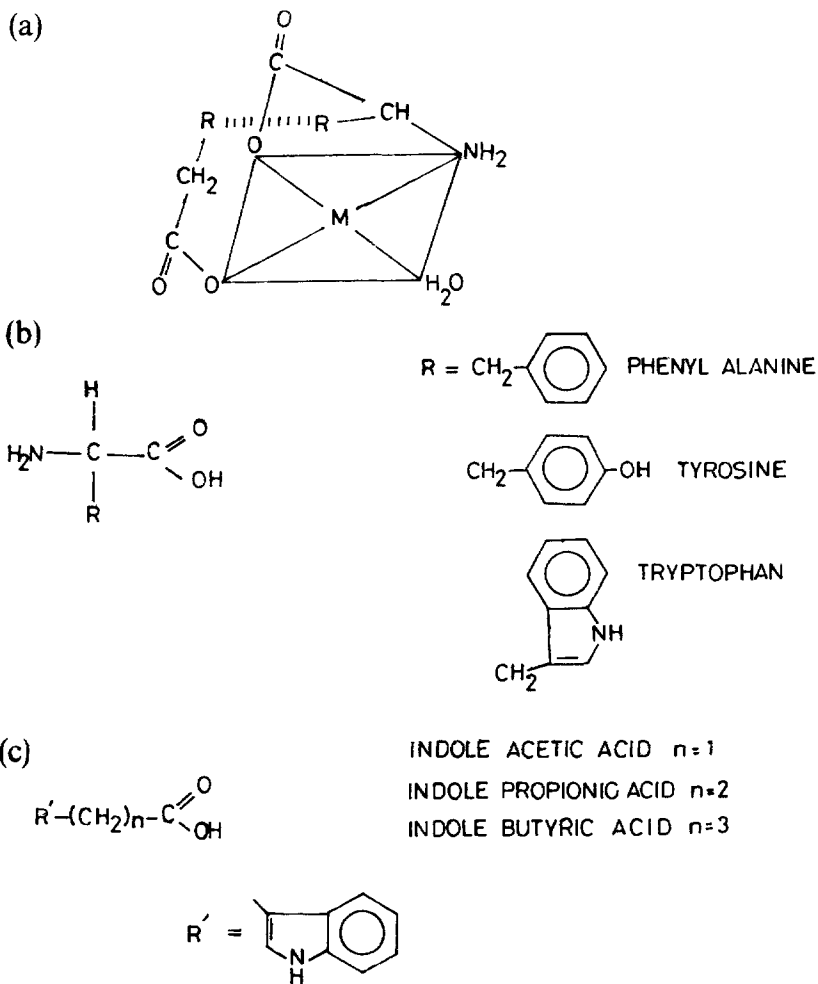


Figure 1. (a) Schematic structure of the possible ligand arrangement in the complex. (b) & (c) Structures of the amino acids and auxins respectively.

an electrostatic repulsion between OH^- , the amino acid anion and the auxin anion. This repulsion leads to lowering in stability of the ternary complex.

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