Preferential Formation of Ternary Copper(II) Complexes Involving Substituted Ethylenediamines and Amino Acids with an Aromatic Side Chain

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Abstract

The stability constants have been determined potentiometrically for the ternary copper(II)–amine–amino acid systems, where amine refers to ethylenediamine(en), N,N′-dimethylethylenediamine-(dmen), N,N,N′,N′-tetramethylethylenediamine(tmen), or N,N′-dibenzylethylenediamine(dben), and amino acid to L-alanine(ala), L-valine(val), L-phenylalanine(phe), L-tyrosine(tyr), O-methyl-L-tyrosine(mtyr), L-tryptophan(trp), or 5-hydroxy-L-tryptophan(htrp). The tendency of the ternary complex formation ($\Delta \log K$) decreased in the order, dben > tmen > dmen > en for the amines and htrp ≃ trp > tyr ≃ mtyr ≃ phe > val ≃ ala for the amino acids. The preferred ternary complex formation of the systems containing dben or htrp was comparable with that observed for phenanthroline. The stability enhancement was found to be additive and proportional to the aromatic ring size. These observations suggest that the proximity of an aromatic ring around the copper(II) ion increases the electronegativity of copper(II) by both the copper(II)–aromatic ring interaction and decreased hydration.

Introduction

Aromatic rings contribute to the stability of ternary complexes through π-back donation and aromatic ring stacking [1, 2]. Close contact of an aromatic ring with a metal ion, which has been revealed by X-ray analysis of Cu(II)–glycyl-L-tryptophanate [3], Cu(II)–L-tyrosinate [4], *etc.* to be less than the van der Waals contact, indicates a weak bonding between them and could also be a stabilizing factor. For biological systems, a proximal aromatic ring can be an electron transfer pathway connecting a metal ion and the environment. In fact, the copper sites of plastocyanin and azurin, which are involved in electron transfer, are located in a hydrophobic environment with an array of aromatic rings of the peptide side chains, through which electrons are supposed to be transferred to and from the outside [5–8]. A similar proximity of an aromatic ring at the active center has also been assumed in hemocyanin [9, 10] and cytochrome oxidase [11]. In tyrosinase phenols as substrates have been proposed to approach the active copper site apically [12]. Although the metal ion–aromatic ring interactions in solution are supported by a body of experimental results such as stereoselectivity observed for ternary copper(II) systems [13] and rotamer populations in palladium(II)- and nickel(II)–peptide complexes as studied by NMR spectroscopy [14–18], their existence and effects on the properties of complexes have not been explored in detail.

In view of the biological importance of the aromatic ring in the copper coordination sphere, we carried out a potentiometric study of the ternary systems consisting of a bidentate amine and an amino acid (Fig. 1) in order to shed light on the electronic effects of aromatic rings by careful examination of the stability constants.

Experimental

Materials

N,N′-Dibenzylethylenediamine(dben) diacetate was obtained from Wako Chemical Co., O-methyl-L-tyrosine (mtyr) from Aldrich, and 5-hydroxy-L-tryptophan(htrp) from Sigma. Ethylenediamine(en), N,N′-dimethylethylenediamine(dmen), N,N,N′,N′-tetramethylethylenediamine(tmen), alanine(ala), valine(val), phenylalanine(phe), tyrosine(tyr), and tryptophan(trp) were purchased from Nakarai. Amines were converted to the corresponding hydrochlorides and recrystallized from aqueous methanol. All other chemicals employed were of the highest grade available.

pH Titrations

pH Titrations were carried out at 25 °C and I = 0.1 *M* (KNO_3) in the same way as described previously [19] for solutions of binary and ternary systems containing copper(II), amine, and amino acid in the molar ratios of 1:2:0, 1:0:2 ~ 4, and

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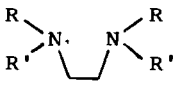
amine	R	R'	abbreviation
	H-	H-	en
	CH_3-	H-	dmen
	CH_3-	CH_3-	tmen
	CH_2-	H-	dben

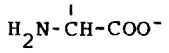
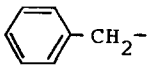
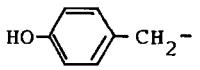
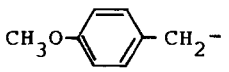
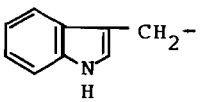
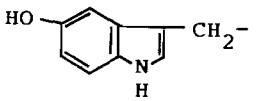
amino acid	R''	
	CH_3-	ala
	$(CH_3)_2CH$-	val
	CH_2-	phe
	CH_2-	tyr
	CH_2-	mtyr
	CH_2-	trp
	CH_2-	htrp

Fig. 1. Structures and abbreviations of ligands used.

TABLE I. Stability Constants (log β_{pqrs}) of Binary Complexes of B and AA at 25 °C and I = 0.1 *M* (KNO_3).

	log β_{pqrs}[a]						
pqrs	dben		tmen		dmen		en[b]
1100	7.963(0.002)		7.622(0.001)		10.071(0.001)		10.523
1200	12.754(0.009)				17.140(0.002)		19.505
110−1			1.489(0.002)				
0101	8.938(0.001)		9.328(0.001)		10.148(0.000)		9.976
0102	14.941(0.002)		15.284(0.002)		17.261(0.001)		17.148
	log β_{pqrs}[a]						
	ala[c]	val[b]	phe[b]	tyr[d]	mtyr	trp[b]	htrp
1010	8.33	8.049	7.931	10.64	7.742(0.003)	8.020	
1011				17.99			18.606(0.022)
1020	15.27	14.913	14.834	15.36	14.663(0.003)	15.562	15.259(0.026)
1021				25.47			26.258(0.023)
1022				34.90			36.760(0.017)
0011	9.82	9.573	9.194	10.142	9.068(0.008)	9.312	10.764(0.001)
0012	12.16		11.452	19.170	11.159(0.012)		20.128(0.001)
0013				21.051			22.559(0.003)

[a]Values in parentheses denote standard deviations. [b]Data taken from ref. 13. [c]Data taken from ref. 22. [d]Data taken from ref. 21.

TABLE II. Stability Constants (log β_{pqrs}) of Ternary Complexes, $Cu_pB_q(AA)_rH_s$, at 25 °C and I = 0.1 *M* (KNO_3).

AA	pqrs	log β_{pqrs}[a]			
		dben	tmen	dmen	en
ala	1110	15.853(0.002)	15.349(0.001)	17.696(0.000)	17.949(0.003)
val	1110	15.695(0.001)	15.052(0.005)	17.423(0.001)	17.726(0.002)
phe	1110	15.487(0.004)	15.119(0.002)	17.412(0.001)	17.746(0.001)
tyr	1111	26.616(0.002)	25.116(0.002)	27.450(0.001)	27.772(0.003)
	1110	16.164(0.002)	15.676(0.005)	18.249(0.002)	18.462(0.003)
mtyr	1110	15.325(0.001)	14.848(0.002)	17.138(0.001)	17.580(0.001)
trp	1110	16.113(0.002)	15.499(0.020)	17.748(0.003)	18.078(0.003)
htrp	1111	26.750(0.002)	25.988(0.005)	28.379(0.002)	28.655(0.002)
	1110	16.424(0.002)	–[b]	18.274(0.002)	18.585(0.002)

[a]Values in parentheses denote standard deviations. [b]The value could not be obtained.

1:1:1. The stability constants, β_{pqrs}, which are defined by eqn. 1 (charges are omitted for simplicity), were calculated by the method of nonlinear least-squares using the computer program MINIQUAD [20] with the aid of a FACOM M-170F computer at the Kanazawa University Computation Center:

$$pCu + qB + rAA + sH \rightleftarrows Cu_pB_q(AA)_rH_s$$

$$\beta_{pqrs} = \frac{[Cu_pB_q(AA)_rH_s]}{[Cu]^p[B]^q[AA]^r[H]^s} \quad (1)$$

where p, q, r, s are the numbers of copper(II), amine (B), amino acid (AA), and proton (H), respectively, in the complex $Cu_pB_q(AA)_rH_s$. The apparent ion product of water $pK_w' = 13.96$ and the difference between pH and $-\log[H]$ (0.063) were used for computer simulation. Some of the pK_a values and the stability constants of the binary complexes were taken from the literature [13, 21, 22].

Results and Discussion

The calculated stability constants log β_{pqrs} of the binary and ternary systems are shown in Tables I and II, respectively.

The tendency of ternary complex formation can be evaluated in various ways, but $\Delta\log K$ as defined by eqn. 2 [2] may be the most convenient because there is no change in the net charge of the complexes in the present ternary systems.

$$Cu(AA) + CuB \rightleftarrows Cu(AA)B + Cu$$

$$10^{\Delta\log K} = \frac{[Cu(AA)B]\,[Cu]}{[Cu(AA)]\,[CuB]} \quad (2)$$

The $\Delta\log K$ value of the species without proton in the ternary complex is given by eqn. 3 and that of the species involving tyr or htrp with a phenol proton can be calculated by eqn. 4:

$$\Delta\log K = \log \beta_{1110} - \log \beta_{1100} - \log \beta_{1010} \quad (3)$$

$$\Delta\log K = \log \beta_{1111} - \log \beta_{1100} - \log \beta_{1011} \quad (4)$$

TABLE III. The $\Delta\log K$ Values of Ternary Complexes, $Cu_pB_q(AA)_rH_s$.

AA	pqrs	$\Delta\log K$			
		dben	tmen	dmen	en
ala	1110	–0.44	–0.60	–0.71	–0.90
val	1110	–0.32	–0.62	–0.70	–0.85
phe	1110	–0.41	–0.43	–0.59	–0.71
tyr	1111	–0.34	–0.50	–0.61	–0.74
	1110	–2.44	–2.59	–2.46	–2.70
mtyr	1110	–0.38	–0.52	–0.68	–0.69
trp	1110	+0.13	–0.14	–0.34	–0.47
htrp	1111	+0.18	–0.24	–0.30	–0.47

The $\Delta\log K$ values are listed in Table III. Because the values for the systems involving tyr and mtyr are comparable irrespective of the phenol OH group, the use of $\Delta\log K$ of protonated species for comparison of the values for non-protonated species is probably justified. However, the $\Delta\log K$ values of the species with a deprotonated phenol may not directly represent the tendency of ternary complex formation, because in the species 1010 of the corresponding binary systems it is the coordinated water and not the phenol that is deprotonated [21]. Therefore, it is difficult to compare the stability of a ternary complex involving a deprotonated phenol with that of the other species by referring to $\Delta\log K$. Comparisons of such ternary species with the other ones are readily possible through the pK_a of the phenol given by log β_{1111} –

TABLE IV. The Differences log β_{1111} − log β_{1110} Observed for Ternary Complexes, $Cu_pB_q(AA)_rH_s$.

B	log β_{1111} − log β_{1110}	
	tyr	htrp
dben	9.45	10.33
tmen	9.34	–[a]
dmen	9.20	10.11
en	9.31	10.07

[a]The value could not be obtained.

log β_{1110} (Table IV), which reflects the stabilization of the species 1111 relative to 1110.

Cu(II)–amine–ala (or val) Systems

Since the Δlog K value for the Cu(II)–en–ala system was found to be –0.90, which is identical with the theoretical Δlog K value in the case of a distorted octahedral copper(II) complex [2], the tendency of ternary complex formation was compared with this value and Δlog K greater than –0.90 was taken to indicate that the ternary complex is favored. Cu(II)–en–val has Δlog K = –0.85 and may also serve as a standard.

With amine = N-methylated diamine (dmen and tmen) the Δlog K values increase in the order dmen (–0.71) < tmen (–0.61), indicating that N-methylation results in enhancement of Δlog K, which is useful for estimating the ternary complex stability. This is indicated by the enhanced electron density on the nitrogen atom due to N-methylation, but correlation [2] between the sums of the pK_a values of the amines and the Δlog K values is not evident.

Though the chemical effect of the benzyl substituent appears to be similar to that of the methyl group, the Δlog K values for dben-containing systems are greater than those for dmen- and surprisingly also for tmen-containing ones.

The values for Cu(II)–dben–ala (–0.44) and Cu(II)–dben–val (–0.32) are comparable with those of Cu(II)–phenanthroline(phen)–ala (–0.45) and Cu(II)–phen–val (–0.31) [23], which indicates that dben favors ternary complexes just as phen does.

Cu(II)–en(or tmen)–Aromatic Amino Acid Systems

The Cu(II)–en–aromatic amino acid systems favor ternary complexes more than the Cu(II)–en–ala(or val) system. The Δlog K values increased in the order of amines, phe (–0.71) ≃ tyr (–0.74) ≃ mtyr (–0.69) < trp (–0.47) ≃ htrp (–0.47), where the first three involve a benzene ring and the rest an indole ring. The result suggests that the stabilization of ternary complexes depends upon the aromatic ring size. The Cu(II)–en–trp (or htrp) system has a Δlog K value

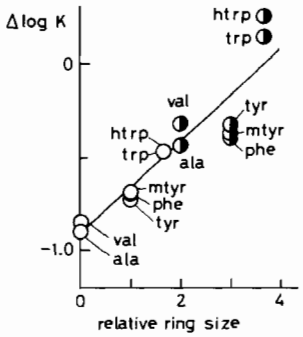


Fig. 2. Relationship between Δlog K and aromatic ring size in Cu(en)(amino acid) (○) and Cu(dben)(amino acid) (●) systems. The relative ring size is an approximate ratio of an aromatic ring size to benzene as the standard.

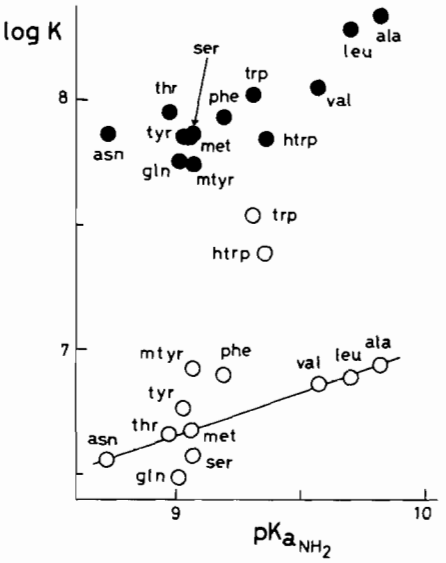


Fig. 3. Correlation between $pK_{a_{NH_2}}$ and log K_1 (●) or log K_2 (○) in copper(II)–neutral amino acid systems. The amino acids used were ala, val, phe, tyr, mtyr, trp, htrp, L-leucine(leu), L-methionine(met), L-serine(ser), L-threonine(thr), L-asparagine(asn), and L-glutamine(gln). The stability constants were taken from this work, refs. 13, 22 and 24.

similar to that for Cu(II)–dben–ala, further indicating the relationship between the Δlog K enhancement and the aromatic ring size (Fig. 2). A similar trend has been reported for the 1:2 Cu(II)–neutral amino acid systems [24]. The aromatic amino acids are positioned above the correlation line between log K_2 of Cu(amino acid)$_2$ and the ligand pK_a shown in Fig. 3, which indicates that stability enhancement is in the order trp ≃ htrp > tyr ≃ mtyr ≃ phe. Further, the deviations from the correlation line of aromatic amino acids were almost comparable with the stability enhancement of Cu–en–aromatic amino acid ternary systems (Fig. 4). On the other hand, such deviations were not observed for log K_1. These enhancements may be explained by the copper(II)–

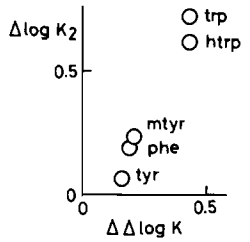


Fig. 4. Relationship between the enhancements of Δlog K (ΔΔlog K) in the Cu(en)(aromatic amino acid) system and log K_2 (Δlog K_2) in the Cu(aromatic amino acid)$_2$ system. ΔΔlog K was calculated by ($\Delta\log K_{Cu(en)(\text{aromatic amino acid})} - \Delta\log K_{Cu(en)(ala)}$). Δlog K_2 was evaluated from the deviation from the correlation line for log K_2 in Fig. 3.

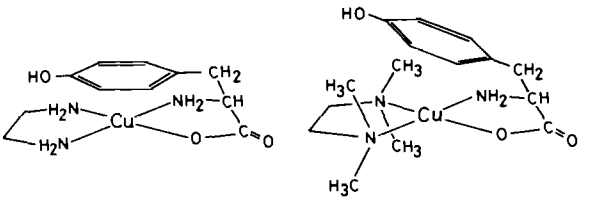


Fig. 5. Preferred structures of Cu(en)(tyr) and Cu(tmen)-(tyr).

aromatic ring interaction, which increases the positive charge of copper(II) by electron transfer to the aromatic ring [25] and thus favors binding of another ligand in proportion to the π-acceptor capacity of the aromatic ring. ESR spectral data also indicated the delocalization of the unpaired electron of copper-(II) in the system with tyr but not with ala and val [26]. This type of electron flow is opposite to that found in the usual organometallic π-complexes [27]. To confirm this point we tested the systems involving tmen instead of en; in the system Cu(II)–tmen–aromatic amino acid, the aromatic ring can not approach copper(II) because of the steric hindrance due to the methyl groups of tmen (Fig. 5). If the copper(II)–aromatic ring interaction is the main cause of the Δlog K enhancement, the Δlog K values of Cu(II)–tmen–aromatic amino acid systems should be as low as the value of the Cu(II)–tmen–ala system (–0.60), but they were actually enhanced (–0.43 ~ –0.14). The Δlog K enhancements of the Cu(II)–tmen–aromatic amino acid systems compared with those of the corresponding Cu(II)–en–aromatic amino acid systems (0.2 ~ 0.3) were observed, in addition to the increment due to tmen as observed for the tmen systems involving ala or val in place of an aromatic amino acid. An appreciable electron flow through the copper(II)–aromatic ring interaction should increase the pK_a of the OH groups, which is contrary to the observation that the systems Cu(II)–tmen–tyr and Cu(II)–en–tyr have nearly the same pK_a values for the phenol OH group estimated from the difference $\log \beta_{1111} - \log \beta_{1110}$.

TABLE V. The Differences[a] between Experimental and Calculated[b] Δlog K Values.

AA	pqrs	B		
		dben	tmen	dmen
val	1110	0.07	–0.07	–0.04
phe	1110	–0.19	–0.02	–0.07
tyr	1111	–0.06	–0.06	–0.06
	1110	–0.20	–0.19	0.05
mtyr	1110	–0.16	–0.13	–0.13
trp	1110	0.14	–0.03	–0.06
htrp	1111	0.19	–0.07	–0.02

[a]Δlog K(experimental) – Δlog K(calculated). [b]Calculated according to eqn. 5.

Cu(II)–dben(or dmen)–Aromatic Amino Acid Systems

The values for Cu(II)–dben–aromatic amino acid are enhanced relative to those for Cu(II)–dmen–aromatic amino acid, but the Δlog K differences between Cu(II)–dben–amino acid and Cu(II)–dmen–amino acid are approximately the same irrespective of the amino acid involved. This indicates that the preferential formation of ternary complexes Cu(dben)(aromatic amino acid) is not due only to the interaction of copper(II) with the aromatic side chain of dben and amino acids, because two aromatic rings can not occupy the space above the coordination plane at the same time.

Additivity of Δlog K

The Δlog K values of the Cu(II)–amine–amino acid systems were found to be an additive function of the Δlog K values exhibited by the component amine and amino acid coupled with ala and en, respectively, with Cu(en)(ala) as standard, and can be calculated according to eqn. 5:

$$\Delta\log K_{Cu(\text{amine})(\text{amino acid})} =$$

$$= (\Delta\log K_{Cu(\text{amine})(ala)} - \Delta\log K_{Cu(en)(ala)}) +$$

$$+ (\Delta\log K_{Cu(en)(\text{amino acid})} - \Delta\log K_{Cu(en)(ala)}) +$$

$$+ \Delta\log K_{Cu(en)(ala)}$$

$$= \Delta\log K_{Cu(\text{amine})(ala)} + \Delta\log K_{Cu(en)(\text{amino acid})} +$$

$$+ 0.90 \qquad (5)$$

Table V indicates that the calculated values agree satisfactorily with the observed ones to within 0.2 log unit, which is useful for estimating the ternary complex stability. Deprotonation of tyr and htrp does not affect the additivity. The ternary systems with trp and htrp have Δlog K values which are

greater than the estimated values, and this may suggest stacking [2] between the benzene ring of dben and the indole ring of trp or htrp. The systems having Δlog K values lower than the estimated ones may suffer steric repulsion between aromatic rings.

Enhancement of Δlog K by a Proximal Aromatic Ring

The preference of formation of the ternary complexes involving an aromatic ring is apparently proportional to the ring size (Fig. 2). The presence of an aromatic ring above the Cu(II) coordination plane is probably essential for preferential formation of ternary complexes. 1,2-Diaminobenzene does not contribute to Δlog K enhancement [23] because the benzene ring is not above the plane. Comparison of thermodynamic parameters for log K_2 of $Cu(trp)_2$ with those of $Cu(ala)_2$ showed an increase of $-\Delta H$ [28] which is the dominant component of ΔG, indicating a stronger copper(II)–ligand bonding. An aromatic ring which is located above the copper(II) plane is considered to increase the electronegativity of copper(II) and thus its affinity for the second ligand through the copper(II) → aromatic ring electron flow and to decrease hydration of copper(II) including removal of the apically coordinated water molecule. Both effects are inferred to be proportional to the aromatic ring size. Further, in support of this, the log K_2 enhancement observed for $Cu(tyr)_2$ and $Cu(trp)_2$ in water disappears in 50% dioxane–water [29] which mimics the decreased hydration of copper(II) complexes as a whole by side chain aromatic rings. The importance of solvation was also proposed in determining the preferential orientation of the aromatic side chain [30]. The influence of the solvent–side chain interaction on stability constants was indicated in various systems such as copper(II)–dipeptide systems [31].

Taken together, the results obtained in this study show that the direct effects of the copper(II)–aromatic ring interaction on stability constants are small but that the increased electronegativity due to the presence of an aromatic ring favors ternary complex formation. Therefore, careful treatment of the Δlog K values is necessary when the systems involve possible metal ion–aromatic ring interactions and aromatic ring stacking. Proper orientation of an aromatic ring at the active site of copper proteins appears to be essential for effective electron transfer, oxygenation, and substrate specificity, for all of which the copper(II)–aromatic ring interaction and the hydrophobicity produced by aromatic rings may be responsible.

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