

Effect of substitution on the catecholate ring on ternary complex stability

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Abstract. The formation constants of the complexes of the type $[CuAL]$, where $A = 2,2'$ -bipyridyl, 1,10-phenanthroline, 2-(2'-pyridyl)benzimidazole, or 2-(2'-pyridyl)imidazoline and $L =$ a dianion of catechol, tiron, protocatechuic acid, pyrogallol, 1,8-dihydroxynaphthalene, 2,3-dihydroxynaphthalene, dopamine, or adrenaline, have been determined in a dioxan-water (1:1, v/v) medium and $\mu = 0.2 \text{ mol dm}^{-3} \text{ NaClO}_4$ at 30°C , using SCOGS method. The effect of the π acid character of A and substitution on ligand L on the ternary complex stability have been discussed.

Keywords. Ternary complexes; catechol complexes; effect of substitution on ligand.

1. Introduction

The complexes $[MAL]$, where $A =$ heteroaromatic N-bases, are known to have a statistical stability due to $M \rightarrow A\pi$ interaction (Sigel 1967; Bhattacharya and Chidambaram 1970; Griesser and Sigel 1970). The complex $[MA]$ shows a discriminating effect towards ligands L , preferring them in the order $O^- - O^- > O^- - N > N - N$ (Griesser and Sigel 1970; Griesser *et al* 1969, 1973; Bhattacharya *et al* 1982a). The effect is maximum in case of Cu(II) complexes and $\Delta \log K$ is positive in $[CuA O^- - O^-]$ complexes. Larger positive values of $\Delta \log K$ have been observed in $[CuAL]$ complexes where L is the aromatic ligand with $O^- - O^-$ co-ordinating sites (Griesser *et al* 1971, 1973; McCormick *et al* 1972).

The stabilization of the ternary complex depends on the π acid character of the base A . The greater the $M \rightarrow A \pi$ interaction, the stabler is the ternary complex (Bhattacharya *et al* 1982b). It has also been shown that substitution on the ligand L affects the stability of the ternary complex. It was observed (McCormick *et al* 1972; Huber *et al* 1971) that the substitution of an electron withdrawing group on the secondary ligand L in $[CuAL]$ complexes destabilizes the ternary complex, and of an electron-releasing group increases the stability of the ternary complex. It has recently been observed by Bhattacharya and Patel (1984a) that in $[CuAL]$ complexes where $L =$ salicylaldehyde and its derivatives, $\Delta \log K$ becomes less positive with the increasing electron-withdrawing tendency of the substituted groups. In order to investigate this further, complexes $[MAL]$ have been studied where $M = \text{Cu(II)}$, $A = 2,2'$ -bipyridyl (A^1), 1,10-phenanthroline (A^2), 2-(2'-pyridyl)benzimidazole (A^3), 2-(2'-pyridyl)imidazoline (A^4), and $L =$ the dianion of catechol (L^1), tiron (L^2),

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pyrogallol (L³), protocatechuic acid (L⁴), 1,8-dihydroxynaphthalene (L⁵), 2,3-dihydroxynaphthalene (L⁶), dopamine (L⁷), or adrenaline (L⁸). Some of the systems have already been studied (Griesser and Sigel 1970; McCormick *et al* 1972; Huber *et al* 1971) in aqueous media but the formation constants have again been determined in 50% dioxan-water (1:1, v/v) media for comparison under identical experimental conditions.

2. Experimental

All reagents used were of AR grade except 2-(2'-pyridyl)benzimidazole and 2-(2'-pyridyl)imidazoline, which were synthesised (Frieser and Walter 1954). The pH was measured to an accuracy of ± 0.01 . Necessary pH corrections for the dioxan-water medium were made (Haas and Van Uitert 1953).

The proton-ligand, binary metal-ligand and ternary complex formation constants were determined in dioxan-water (1:1, v/v) medium and $\mu = 0.2 \text{ mol dm}^{-3} \text{ NaClO}_4$ at 30°C by using SCOGS computer technique (Sayce 1968, 1971; Sayce and Sharma 1972). In every case, the titration was repeated for two different concentrations and similar values were obtained as shown in tables 1 and 2.

The formation constants of proton-ligand entities LH, LH₂ and those of the binary complexes [CuL] and [CuL₂] were first obtained. The formation constants of [CuA] and [CuA₂] were determined as done earlier (Bhattacharya and Gopalakrishnan 1982). These values were used as fixed parameters in the refinement of the ternary complex formation constants, $\log K_{\text{CuAL}}$. The species present in the solution were considered to

Table 1. Proton-ligand and binary complex stability constants.

Ligand ^a	$\log K_1^{\text{H}}$	$\log K_2^{\text{H}}$	$\log K_3^{\text{H}}$	$\log K_{\text{CuL/A}}^{\text{Cu}}$	$\log K_{\text{CuL}_2/\text{A}_2}^{\text{CuL/A}}$
L ¹	12.97 (0.00)	8.97 (0.05)	—	12.80 (0.03)	10.00 (0.01)
L ²	12.98 (0.01)	8.07 (0.02)	—	14.41 (0.01)	12.91 (0.02)
L ³	12.38 (0.03)	9.61 (0.00)	5.85 (0.02)	15.56 (0.10)	10.82 (0.20)
L ⁴	12.54 (0.10)	9.79 (0.10)	—	15.41 (0.10)	13.33 (0.30)
L ⁵	10.04 (0.06)	8.35 (0.00)	—	10.57 (0.04)	9.09 (0.06)
L ⁶	12.78 (0.01)	9.62 (0.01)	—	14.55 (0.06)	11.92 (0.10)
L ⁷	11.40 (0.10)	10.76 (0.08)	8.83 (0.10)	14.00 (0.04)	11.66 (0.07)
L ⁸	13.11 (0.10)	9.86 (0.02)	8.75 (0.10)	14.66 (0.20)	12.22 (0.02)
A ¹	3.70 (0.04)	—	—	7.00	4.15 (0.15)
A ²	4.40 (0.03)	—	—	8.82	5.46 (0.12)

Values in dioxan-water (1:1, v/v) and $\mu = 0.2 \text{ M NaClO}_4$ at 30°C, with standard deviation $\sigma\beta$ in parentheses; ^a see text for ligand description.

Table 2. Stability constants for ternary complexes of Cu(II).

Ligands ^b	$\log K_{\text{CuAL}}^{\text{CuA}^*}$							
	A ¹		A ²		A ³		A ⁴	
	log K	$\Delta \log K$	log K	$\Delta \log K$	log K	$\Delta \log K$	log K	$\Delta \log K$
L ¹	13.60 (0.08)	+0.80	13.48 (0.07)	+0.68	14.12 (0.09)	+1.32	12.33 (0.01)	-0.47
L ²	14.39 (0.01)	-0.02	14.25 (0.01)	-0.16	14.50 (0.02)	+0.09	12.80 (0.05)	-1.61
L ³	15.04 (0.10)	-0.52	15.24 (0.10)	-0.32	15.71 (0.10)	+0.15	14.40 (0.09)	-1.16
L ⁴	15.04 (0.10)	-0.37	14.77 (0.10)	-0.79	15.74 (0.06)	+0.18	14.27 (0.06)	-1.29
L ⁵	9.05 (0.00)	-1.52	8.93 (0.03)	-1.64	10.64 (0.03)	+0.07	8.91 (0.03)	-1.66
L ⁶	14.92 (0.01)	+0.37	14.71 (0.01)	+0.16	15.14 (0.02)	+0.59	13.79 (0.02)	-0.76
L ⁷	13.94 (0.10)	+0.06	13.47 (0.02)	-0.53	14.75 (0.04)	+0.75	13.29 (0.04)	-0.71
L ⁸	15.27 (0.10)	+0.61	15.22 (0.10)	+0.56	16.58 (0.05)	+1.92	14.38 (0.05)	-0.28

Values in dioxan-water (1:1, v/v) and $\mu = 0.2 \text{ M NaClO}_4$ at 30°C, with standard deviation $\sigma\beta$ in parentheses; * using computer method; ^b see text for ligand description.

be AH, A, LH₂, LH, [CuA], [CuA₂], [CuL], [CuL₂] and [CuAL]. The preliminary value of $\log K_{\text{CuAL}}^{\text{Cu}}$ supplied to the computer, was obtained by considering the reaction to be of the type $[\text{CuA}] + \text{L} \rightleftharpoons [\text{CuAL}]$ (Bhattacharya *et al* 1982b).

Spectra were recorded (Carl Zeiss Specord UV visibile spectrophotometer) using dioxan-water (1:1, v/v) as solvent. The spectra of Cu(II) + A + L mixed in 1:1:1 mole ratio were recorded at pH 5.8, where mixed ligand complex formation is maximum. The observed spectral bands in the visible range are presented in table 3.

3. Results and discussion

From the plot of the concentration of the species against pH, it is observed that in the lower pH range (pH 1.8–3.0) Cu(II) and [CuA] are the major species and in the higher pH range (pH 4.0–7.0) the species [CuA] and [CuAL] predominate. Formation of [CuA₂], [CuL] and [CuL₂] is low. In all cases upto 98% of the mixed-ligand complexes are formed and the sum of [CuAL] and [CuA] is almost 100%. This shows that these complexes are formed in steps $\text{Cu} + \text{A} \rightleftharpoons [\text{CuA}]$ and $[\text{CuA}] + \text{L} \rightleftharpoons [\text{CuAL}]$, equilibrium constants for which are given in tables 1 and 2.

The formation constants show that in the complexes [CuAL] where A = A¹, A² or A³ and L = L¹, L⁶ or L⁸, $\Delta \log K$ ($\log K_{\text{CuAL}}^{\text{CuA}} - \log K_{\text{CuL}}^{\text{Cu}}$) is positive.

In cases where A = A⁴, $\Delta \log K$ is negative for all the mixed ligand complexes. In cases where L = L², L³, L⁴, L⁵ or L⁷, $\Delta \log K$ is negative except where A = 2-(2'-pyridyl)benzimidazole.

Table 3. Electronic spectra of binary and ternary complexes.

Compound ^a	λ max in cm^{-1}
[CuA ₂ ¹]	13 500 (2.79)
[CuA ₂ ²]	13 500 (2.75)
[CuL ₂ ¹]	22 120 (1.59), 14 600 (1.19)
[CuL ₂ ²]	22 500 (1.36), 13 250 (1.16)
[CuL ₂ ³]	25 000 (sh) (2.27), 14 390 (1.44)
[CuL ₂ ⁴]	24 700 (1.89), 14 490 (1.58)
[CuL ₂ ⁵]	21 000 (sh) (1.95), 13 160 (1.31)
[CuL ₂ ⁷]	17 000 (1.79), 12 900 (0.95)
[CuL ₂ ⁸]	21 500 (2.16), 12 660 (0.65)
[CuA ¹ L ¹]	22 000 (1.85), 13 790 (1.11)
[CuA ¹ L ²]	22 500 (1.90), 14 390 (1.32)
[CuA ¹ L ³]	24 000 (2.08), 15 030 (1.20)
[CuA ¹ L ⁴]	23 250 (2.49), 15 000 (1.11)
[CuA ¹ L ⁶]	21 000 (2.02), 13 160 (1.30)
[CuA ¹ L ⁷]	22 000 (2.04), 16 000 (2.04)
[CuA ¹ L ⁸]	22 500 (1.95), 14 290 (1.07)

Values in dioxan-water (1:1, v/v) medium; ^a see text for ligand descriptions; Values of $\log \epsilon$ (epsilon in units of $\text{M}^{-1} \text{cm}^{-1}$) are given in parentheses.

For all complexes the order of formation constants is $[\text{CuA}^3\text{L}] > [\text{CuA}^1\text{L}] \approx [\text{CuA}^2\text{L}] > [\text{CuA}^4\text{L}]$, as expected from the increasing order of $\text{Cu} \rightarrow \text{A} \pi$ interaction (Bhattacharya *et al* 1982a). As $\text{Cu} \rightarrow \text{A}$, π interaction goes on increasing, $\Delta \log K$ becomes more positive in $[\text{CuAL}]$ where $\text{L} = \text{L}^1, \text{L}^6$ or L^8 and less negative in cases, where $\text{L} = \text{L}^2, \text{L}^3, \text{L}^4, \text{L}^5$, or L^7 .

The positive $\Delta \log K$ in the complexes $[\text{CuAL}]$, where $\text{L} = \text{L}^1, \text{L}^6$ or L^8 , is as expected in cases of $\text{O}^- - \text{O}^-$ coordinating ligands (Griesser and Sigel 1970; Griesser *et al* 1973; Bhattacharya *et al* 1982a). This has been explained as due to the increasing class A character of Cu(II) in $[\text{CuA}]$, with consequent decrease of repulsion between the metal $d\pi$ electrons and the lone pair of electrons over the ligand atom in the ternary complex (Bhattacharya *et al* 1982a). The effect is maximum in case of $\text{O}^- - \text{O}^-$ ligands with lone pairs of electrons over both O^- (Griesser and Sigel 1970; Bhattacharya *et al* 1982a). The effect is larger when the two O^- are over the aromatic ring (McCormick *et al* 1972; Griesser and Sigel 1971, 1973).

With the substitution of the aromatic ring H by electron withdrawing groups, the electron density over O^- is reduced. This destabilizes the ternary complex and makes $\Delta \log K$ less positive. An electron releasing group increases the electron density over O^- and stabilizes the ternary complex resulting in more positive $\Delta \log K$.

In cases, where $\text{L} =$ the dianion of 2,3-dihydroxynaphthalene (L^6), $\Delta \log K$ is less positive than in cases where $\text{L} =$ catecholate (L^1). This can be explained by considering that the lone pair electrons on the two O^- of 2,3-dihydroxynaphthalene get delocalized over two rings and hence, the effective electron density on the O^- is less in case of L^6 than in case of catecholate. Thus, the additional phenyl ring acts as an electron-withdrawing group.

In cases, where $L = 1,8$ -dihydroxynaphthalene (L^5), $\Delta \log K$ is negative, even though the ligand co-ordinates through two O^- . This is because the two O^- are on different benzene rings and hence the effective negative charge on the two O^- is less, which leads to negative $\Delta \log K$.

It is also seen that in $[CuA \text{ tiron}]$, $[CuA \text{ protocatechuate}]$ or $[CuA \text{ pyrogallolate}]$ complexes, $\Delta \log K$ values are negative or less positive than in case of $[CuA \text{ catecholate}]$. This is expected because the substituted sulphonate, carboxylate and hydroxy groups on the rings of ligands L^2 , L^3 and L^4 , respectively, reduce the electron density on the ring. Thus, the negative charge over two O^- is less in these ligands than in the case of unsubstituted catecholate, and $\Delta \log K$ is less positive.

In cases where $L = \text{dopamine } (L^7)$ or $\text{adrenaline } (L^8)$ also, co-ordination is from the phenolate O^- . This has been confirmed by observing visible spectral bands. There is difference in the $d-d$ spectral band positions of $[CuA^1L^7]$ ($16,000 \text{ cm}^{-1}$), $[CuA^1L^8]$ ($14,290 \text{ cm}^{-1}$) and $[CuA^1L^1]$ ($13,790 \text{ cm}^{-1}$) because of the substitution effect in the first two cases. But a band at $\sim 22,000 \text{ cm}^{-1}$ is seen in all these complexes (table 3), which is characteristic of the $L \rightarrow M$ charge transfer in catecholate complexes (Mainer and Rajan 1978). This shows that the amine group is not involved in co-ordination. The proton association constant of the amine in these ligands is higher and the proton does not dissociate till pH 7.5. Hence, in the pH range 3.0–6.0, where L co-ordinates with $[CuA]$, it can be considered to be in the monoprotinated form LH , the amine proton remaining undissociated. The formation constants show that in the case of $[CuAL^8H]$, $\Delta \log K$ is less positive than in the case of $[CuAL^1]$ and in the case of $[CuAL^7H]$, $\Delta \log K$ is negative when $A = A^1, A^2$, or A^4 . Decrease in the $\Delta \log K$ values in the case of catecholamines is because the protonated amine group withdraws electron density from the ring; hence, the ternary complex is not stabilized to the same extent as $[CuAL^1]$. The electron withdrawing effect is less in adrenaline (L^8) than in dopamine (L^7), probably because of the additional methyl group.

Thus, the present study shows the effect of substituted groups, not directly co-ordinated to the metal ion, on ternary complex stability. Catechol and its derivatives, like catecholamines, are of biochemical importance and their degradation is brought about by the metalloenzymes co-ordinating with the two phenolate O^- of the catechol part, which is then oxidized to quinone. The present study also shows that the substituted amine group in catecholamines may make them less susceptible to co-ordination with metalloenzymes involving imidazole type of ligands (Bhattacharya and Patel 1984b).

3.1 Visible spectra

It is normally expected that in a mixed-ligand complex $[MAL]$, the ligand field created by the two ligands is the average of the ligand fields in the binary complexes $[MA_2]$ and $[ML_2]$ (Kida 1961). This is true in complexes $[CuAL]$, where L co-ordinates through N-N or O^- -N (Bhattacharya *et al* 1982a). However, in the complex $[CuAL]$ studied in the present paper, where L co-ordinates through two O^- , the $d-d$ transition band in $[CuAL]$ is at a higher energy level than in $[CuA_2]$ or $[CuL_2]$. This shows that the $M \rightarrow \text{bipy } \pi$ interaction stabilizes the $L \rightarrow M \sigma$ interaction (where L co-ordinates through two O^-). Conversely, the $L \rightarrow M \sigma$ interaction increases the $M \rightarrow \text{bipy } \pi$ interaction. Thus the two ligands mutually stabilize each other. Consequently, ligand A and L create a stronger field in $[CuAL]$ than in $[CuA_2]$ or $[CuL_2]$.

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