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Ternary complexes of substituted catechols and catecholamines

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Abstract. Stability constants of the ternary complexes [CuAL] where A = 5-Nitro-1,10-phenanthroline, *bis*(2-pyridyl) ketone (DPK) or *bis* (2-pyridyl)amine (DPA) and L is the dianion of catechol, tiron, protocatechic acid, pyrogallol, 1,8-dihydroxynaphthalene, catecholaldehyde, 2,3-dihydroxynaphthalene, dopamine or adrenaline have been determined by potentiometric titration in dioxane water (1 : 1 v/v) medium using a SCOGS computer programme. The observed trend of stability is explained on the basis of the nature of substitution over the ligands, chelate ring size and also the composition of mixed solvent in case of DPK. Structural changes in DPK have also been discussed as a function of pH, composition of medium and coordinating mode of the secondary ligand in the ternary complexes.

Keywords. Ternary complex; Cu(II) complex; complexes of catechol and derivatives; effect of substitution on ligand.

1. Introduction

In recent years, considerable attention has been paid to the coordination behaviour of heteroaromatic N-bases (A) in ternary transition metal complexes because of their similarity to imidazole systems commonly occurring in metalloenzymes. Contrary to the expectations from statistical consideration, the formation constants, log K^{MA}_{MAL}, of the mixed ligand complexes are found to be much greater than the binary systems. This has been explained in terms of $M \rightarrow A\pi$ interaction (Sigel 1967; Huber *et al* 1969; Griesser and Sigel 1970; Chidambaram and Bhattacharya 1970). The influence of the electronic character of the ligands on the stability of ternary complexes has, further, been confirmed by observing the discriminating behaviour of [MA] complexes towards the secondary ligands L having N or O^- coordinating sites (Walker *et al* 1972; Gopalkrishnan and Bhattacharya 1982a, b; Patel *et al* 1982a). Also the nature of substitution on two ligands has been shown to affect the stability of ternary complexes (Huber and Sigel 1972; Fischer and Sigel 1974, 1979; Sigel 1980; Patel and Bhattacharya 1985).

The present investigation considers potentiometric study of three series of ternary complexes [CuAL] where A = 5-nitro-1,10-phenanthroline (A^1), 2,2′-bipyridylketone (DPK, A^2), *bis* (2-pyridyl)amine (DPA, A^3) and L = catechol (L^1), tiron (L^2), protocatechuic acid (L^3), pyrogallol (L^4) 1,8-dihydroxynaphthalene (L^5), 2,3-dihydroxynaphthalene (L^6), catecholaldehyde (L^7), dopamine (L^8) or adrenaline in aqueous-dioxan (1 : 1, v/v) medium. The structures of catecholamines L^8 and L^9 are shown in chart 1.

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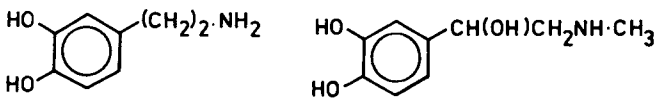


(L^8) **Chart 1.** (L^9)

2. Experimental

The instruments used and the method of determination of proton ligand and binary metal ligand formation constants were as detailed earlier (Patel *et al* 1982b).

For determination of formation constants of the ternary complexes [CuAL], potentiometric titrations were performed in dioxan-water medium at 30°C and I = 0·2M ($NaClO_4$). Calculations were done using computer programme SCOGS (Sayce 1968, 1971; Sayce and Sharma 1972) and considering the species LH_2, LH, L, AH, A, Cu(II), [CuA], [CuA_2], [CuL], [CuL_2] and [CuAL] to be present in the solution.

Electronic spectra of DPK and [CuDPK] were recorded at various pH on a Carl Zeiss Specord UV-VIS recording spectrophotometer.

3. Results and discussion

The formation constant calculations in the present study indicate that the formation of ternary complexes [CuAL], where $A = A^1$ to A^3 and $L = L^1$ to L^9, is in two steps, $Cu + A \rightleftharpoons [CuA]$ and $[CuA] + L \rightleftharpoons [CuAL]$ as in cases where A is *o*-phenanthroline (A^4) or dipyridyl (A^5) (Patel *et al* 1982b, Patel and Bhattacharya 1985). However, special attention is required for the [Cu DPK L] systems because of the special characteristics associated with DPK.

DPK is known to absorb a water molecule and exist in geminal diol form (DPK·H_2O). One of these two – OH protons can get dissociated at higher pH (> 5) (deprotonation is favoured in the presence of a metal ion) and the free O^- competes with one of the pyridyl nitrogens for coordination with the metal ion. Thus $(DPK{\cdot}OH)^-$ exhibits ambidentate nature with N–N or N–O^- as coordinating sites (Fischer and Sigel 1975, 1979). However, in the present study computer assisted calculations of formation constants of [Cu DPK L^{1-9}] in pH ranges 3 to 4·5 or 3 to 7 gave identical results, indicating that in these systems, DPK probably coordinates from the N–N end till high pH. To further confirm this, pH titration curves of [Cu DPK L] were compared with the corresponding curves for [Cu DIPY L]. Representative curves are shown in figure 1. The two curves run parallel till pH ~ 7·0 and there is no difference in the [Cu DPK L] and [Cu DIPY L] curves. This indicates that DPK continues to coordinate from the N–N site up to pH 7 as in the case of dipyridyl. Coordination from the –OH site in DPK would liberate extra protons resulting in deviation of the [Cu DPK L] curve from the [Cu DIPY L] curve. A reason for the preference for N–N coordination in [Cu DPK L] could be found in the fact that a combination of tertiary diimine (N–N) and O^- O^- coordinating ligands gives the most stable ternary copper complex because of $M \rightarrow A\pi$ interaction (Griesser *et al* 1969: Griesser and Sigel 1970, 1971; Chidambaram and Bhattacharya 1970; Patel *et al* 1982a, b).

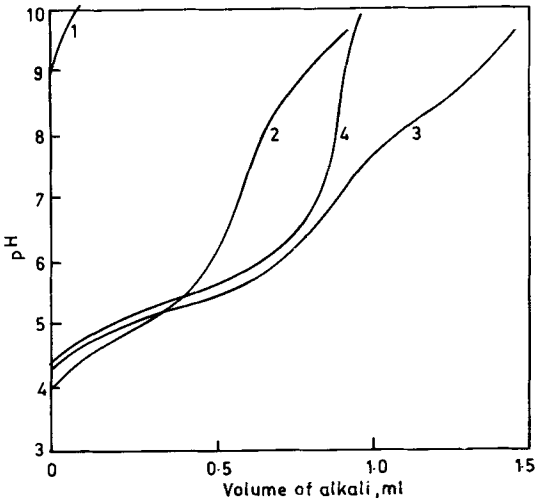
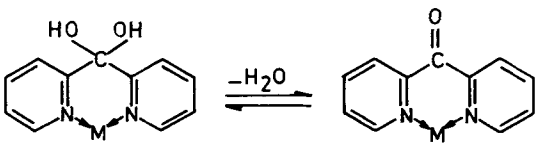


Figure 1. Titration curves for (1) DPK(0·001 M); (2) CuDPK (1 : 1); (3) CuDPK catechol (1 : 1 : 1); (4) CuDIPY catechol (1 : 1 : 1); solutions containing 0·01 M each of the ligands and/or Cu^{2+} have been titrated.

Verification of table 1 shows that [CuA^2L] complexes are more stable than other [CuAL] complexes. This can be explained only when DPK is considered to be in keto form. Loss of planarity of the chelate ring in gem-diol form with sp^3 hybridized carbon will result in considerable reduction in $M \rightarrow$ DPK. $H_2O\pi$-interaction which will destabilize the ternary complex.

An observation of the spectra of DPK and [CuDPK] at various pH supports this fact. In between pH 2 to 7 DPK exhibits two bands at 274 nm (π_1) and 244 nm (π_2) corresponding to transitions in the pyridyl ring. The π_2 band is shifted to lower energy due to the presence of the keto group. The weak $n \rightarrow \pi^*$ transition of the keto group occurs at $\sim$ 320 nm and is hidden under intense π_2 transition.

In the case of [Cu DPK] the corresponding π bands are observed at 248 and 272 nm with a small shift due to coordination with the metal ion. The presence of a π_2 band at higher wavelength (248 nm) till pH $\sim$ 5·5 indicates the existence of the keto form of the coordinated DPK and supports the following equilibrium.



This dynamic equilibrium is expected to be dependent on the percentage of nonaqueous solvent when mixed solvent systems are used. As a consequence stability constants are expected to depend considerably on the composition of the medium. Table 2 summarizes stability constants for some [Cu DPK L] systems in

Table 1. Stability constants log K^{CuA}_{CuAL} for ternary complexes of Cu(II).

Ligands[a]	A^1	$\Delta \log K$	A^2	$\Delta \log K$	A^3	$\Delta \log K$	A^{4b}	$\Delta \log K$	A^{5b}	$\Delta \log K$
L^1	13·76 (±0·10)	+0·96	14·65 (±0·08)	+1·85	13·58 (±0·03)	+0·78	13·48	+0·68	13·60	+0·80
L^2	14·56 (±0·07)	+0·15	15·06 (±0·05)	+0·65	14·35 (±0·09)	−0·06	14·25	−0·16	14·39	−0·02
L^3	15·51 (±0·10)	+0·10	15·66 (±0·04)	+0·25	15·39 (±0·03)	−0·02	14·77	−0·64	15·04	−0·37
L^4	16·05 (±0·07)	+0·49	15·90 (±0·07)	+0·34	14·88 (±0·10)	−0·68	15·24	−0·32	15·04	−0·52
L^5	10·66 (±0·10)	+0·09	10·18 (±0·10)	−0·39	9·54 (±0·08)	−1·03	8·93	−1·64	9·05	−1·52
L^6	15·35 (±0·09)	+0·80	15·15 (±0·10)	+0·60	14·80 (±0·09)	+0·25	14·71	+0·16	14·92	+0·37
L^7	14·39 (±0·09)	+0·54	14·35 (±0·09)	+0·50	13·39 (±0·10)	−0·06	13·70	−0·15	14·13	+0·28
L^8	14·28 (±0·05)	+0·28	14·78 (±0·07)	+0·78	13·85 (±0·10)	−0·15	13·47	−0·53	13·94	−0·06
L^9	15·67 (±0·10)	+1·01	16·11 (±0·10)	+1·45	15·48 (±0·05)	+0·82	15·22	+0·56	15·27	+0·61

Values in dioxane water (1:1, v/v) and μ = 0·2M $NaClO_4$ at 30°C, with standard deviation $\sigma\beta$ in parenthesis;
[a]See text for ligand description; [b]Values for A^4 and A^5 are taken from earlier work (Bhattacharya and Patel 1985), where A^4 = 1,10-phenanthroline and A^5 = 2,2′-dipyridyl.

Table 2. Stability constant of ternary complexes of [Cu DPK L] t = 30°C, μ = 0·2 mol dm^{-3} ($NaClO_4$) in different percentages of dioxan-water medium.

Percentage of dioxan	log $K^{CuA}_{CuAL^1}$	Δlog K	log $K^{CuAL^8}_{CuAl}$	Δlog K
Aqueous	14·78[a]	+0·82	10·91	+0·05
25%	14·14	+1·34	11·53	+0·53
50%	14·65	+1·85	14·78	+0.78

[a]Sigel *et al* (1971)

aqueous 25% and 50% dioxan-water media. The value of $K^{CuA}_{CuAL^1}$ in aqueous solution is taken from literature (Fischer and Sigel 1979), where the conditions used for the determination are different, and hence the value of $K^{CuA}_{CuAL^1}$ is higher. However, both temperature and ionic strength affect binary and ternary formation constants to the same extent and hence the $\Delta \log K$ value can be considered for comparison with the present study. It is observed that there is an increase in the positive value of $\Delta \log K$ with increase in dioxan content of the medium, indicating shift of equilibrium (I) towards right. The keto form being more π acidic in character stabilizes the ternary complex.

$\Delta \log K$ values for the complexes [CuA^1L] are higher than those for corresponding DIPY or PHEN complexes. This is because of the presence of electron withdrawing $-NO_2$ group which depleted the electron density over the ring, making it a stronger π acid. As a result, the class *A* character of the metal ion is increased and coordination with a $O^- - O^-$ containing ligand is favoured resulting in greater stabilization of the ternary complex. The electron releasing > NH group over DPA should decrease the π-acidity of the ligand. However, there is no destabilization of the ternary complex involving DPA. This may be because of the larger size of the chelate ring formed by DPA.

Comparison within the series of secondary ligands indicates that $\Delta \log K$ values for [Cu*A* catecholate] are higher than those for the respective complexes formed by tiron, photocatechuic acid, catechol aldehyde or 2,3-dihydroxynaphthalene. This is because of the electron withdrawing nature of the substitutents, sulphonate, carboxylate, carbonyl or phenyl, respectively, over the catecholate ring. These decrease the electron density over the coordinating O^- resulting in lower release of repulsion in the ternary complex than in the binary complex and ultimately lower stabilization of the ternary complex. The ternary complexes formed by 1,8-dihydroxy naphthalene are still less stable probably because of the direct participation of the second phenyl ring in electron delocalization and formation of a six-membered chelate ring.

In case of catecholamines the amino group remains protonated and hence exert an electron withdrawing effect. Consequently, in ternary complexes of dopamine, $\Delta \log K$ values are lower than those for [Cu *A* catecholate]. However, in adrenaline the electron withdrawing effect of the protonated amino group is partly compensated by the $-OH$ group present on the same side chain and, hence, the stabilization is just comparable with the corresponding catechol complexes.

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