Table III. Controlled-Potential Coulometric Determination of Solubility of O_2 in Liquid NH_3 (0.1 M KBr)

temp, °C	Q_a,[a] C	Q_b,[b] C	concn,[c] mol/L	solubility,[d] mol/L
−60	−7.20	−6.20	0.0034	0.0045
−50	−5.20	−4.75	0.0022	0.0038
−40	−2.88	−2.54	0.0012	0.0039

[a] Number of coulombs recorded until current dropped to a constant value, with O_2 in the gas phase. [b] Q without O_2 in the gas phase. [c] 1 atm total pressure ($O_2 + NH_3$). [d] 1 atm O_2 partial pressure.
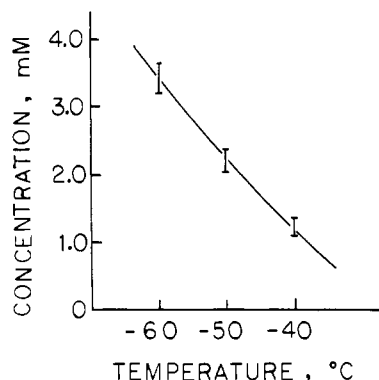

Figure 5. Concentration of O_2 in liquid NH_3 (M) vs. temperature (1 atm total pressure).

those calculated from data given by Ahrens and Heusler.[5] These differences are not too large in light of the uncertainty of the enthalpy of solution and the uncertainties of our experimental determination.

Diffusion Coefficient of O_2. Potential step chronoamperometry was employed to determine the diffusion coefficient, *D*,

for O_2 in NH_3 at −55 °C.[18] A potential step from +0.10 to −0.35 V vs. AgRE for 5 s was employed and the slope of the plot of *i* vs. $r^{-1/2}$ was determined to be 14.1 ± 0.7 μA $s^{-1/2}$. From the known area of the electrode (0.0145 cm²) and the solution concentration determined from the coulometric measurements (2.7 mM) a value of *D* in saturated $MeBu_3NI$ of 4.4×10^{-5} cm²/s was obtained. This value is generally of the order of that expected on the basis of diffusion coefficients found in other nonaqueous solvents[2,4a,16] when account is taken of the low viscosity of NH_3 (0.317 cP at −50 °C).[19] The diffusion coefficient estimated from the Stokes–Einstein equation[20] with a radius for O_2 of 1.4 Å and *T* = 223 K is 3.6×10^{-5} cm²/s.

Conclusions

The results presented here suggest that the electroreduction of O_2 in liquid ammonia provides a convenient procedure for preparing stable solutions or precipitates of O_2^-. Liquid ammonia may also be a useful solvent for carrying out and studying reactions of O_2^-, since NH_3 is a good solvent for both organic and inorganic compounds, provides a very low proton availability, and has a wide low-temperature liquid range. Studies of reactions of O_2^{2-} may also be possible since this species shows some stability in this medium.

Registry No. O_2, 7782-44-7; NH_3, 7664-41-7; KO_2, 12030-88-5.

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Effect of Two Ligands on Ternary Complex Stability

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The formation constants for 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 = ethylenediamine, 1,2-diaminopropane, *N*-methylethylenediamine, *N*-ethylethylenediamine, glycine, α-alanine, or malonate, have been determined in dioxane–water (1:1 v/v) solutions and 0.2 mol dm⁻³ $NaClO_4$ at 30 °C. The formation constant values have been determined by a graphical method and further refined by using a computer program. The value of $\Delta \log K = \log K^{MA}_{MAL} - \log K^{M}_{ML}$ is small negative or positive showing astatisticality, and an increase in the value of mixed-ligand complexes is due to a lowering in repulsion between metal dπ electrons and the ligand electrons in the mixed-ligand complex.

Introduction

In the study of mixed-ligand complexes of the type [MAL], where A is a heteroaromatic N base, it has been observed that the stability constant of the ternary complex is higher than expected from statistical consideration.[1,2] This has been explained to be due to a M → bpy π interaction.[3–6] Sigel has

shown that the complex [MA] shows discrimination toward secondary ligands L with coordinating atoms N–N, N–O⁻, and O⁻–O⁻.[7,8] In cases of ternary complexes in which L coordinates through two nitrogen atoms or one nitrogen and one oxygen atom, $\Delta \log K = \log K^{MA}_{MAL} - \log K^{M}_{ML}$ is a small negative quantity. However, when L coordinates through two oxygen atoms, $\Delta \log K$ in [CuAL] complexes is positive. Sigel extended this observation to explain the greater stability of mixed-ligand complexes in biological systems involving the imidazole ring.[9,10] However, in a recent publication Abbott

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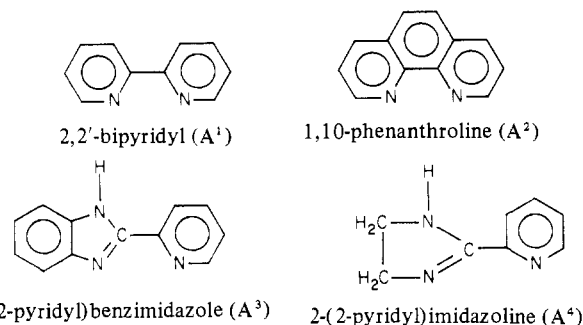(9) Sigel, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 394.

2,2'-bipyridyl (A[1])

1,10-phenanthroline (A[2])

2-(2-pyridyl)benzimidazole (A[3])

2-(2-pyridyl)imidazoline (A[4])

Figure 1.

and co-workers[11] have shown that ternary complexes containing imidazole do not exhibit as much astatisticalilty as those containing tertiary amines and $\Delta \log K$ in [Cu(Im)L] complexes is negative. Sigel has clarified in a communication[12] that "a negative $\Delta \log K$ does not exclude a stability increasing influence of imidazole...a less negative value may already indicate a positive effect", due to M → imidazole π interaction.

So that the relative effects of the imidazole ring and the tertiary amine on the stabilities of ternary complexes could be seen, formation constants and spectra of ternary complexes of the type [CuAL] have been studied, where A = 2,2'-bipyridyl (A[1]), 1,10-phenanthroline (A[2]), 2-(2-pyridyl)benzimidazole (A[3]), and 2-(2-pyridyl)imidazoline (A[4]) and L = ethylenediamine (L[1]), 1,2-diaminopropane (L[2]), *N*-methylethylenediamine (L[3]), *N*-ethylethylenediamine (L[4]), glycinate (L[5]), α-alanine (L[6]), or malonate (L[7]). The structures of the ligands A are as shown in Figure 1.

Experimental Section

General Considerations. All reagents used were of AR grade, except 2-(2-pyridyl)benzimidazole and 2-(2'-pyridyl)imidazoline, which were prepared by the known method.[13]

The proton–ligand and metal–ligand formation constants were determined in dioxane–water (1:1 v/v) solution and 0.2 mol dm^{-3} NaClO$_4$ at 30 °C.

The values of $\bar{n}_H$, K_1^H, K_2^H, $\bar{n}$, pL, $\log K_1$, and $\log K_2$ were calculated by carrying out normal Irving–Rossotti titrations.[14,15] The formation constants of ternary complexes were determined by using an extension of Irving–Rossotti titration technique.[6] The values of $\bar{n}$ and pL were calculated in the pH range 3–6 with the same equations as for binary systems.[15]

At $\bar{n} = 0.5$ in the formation curve, pL = $\log K^{MA}_{MAL}$. More precise values were obtained by plotting pL at each point against log (($1 - \bar{n})/\bar{n}$) and obtaining a straight line. At each point on the straight line $\log K^{MA}_{MAL}$ = pL – log (($1 - \bar{n})/\bar{n}$). The average values have been recorded in Table II. In each individual measurement pH values were corrected for 50% dioxane medium with use of the method suggested by Van Uitert and Haas.[16]

All the formation constants were subjected to refinement by using the computer program SCOGS.[17] This is a powerful physical technique capable of calculating, simultaneously or individually, association constants for any of the species formed in solution containing up to two metal ions and two ligands, provided that the degree of formation is pH dependent. The subroutine COGSNR of the SCOGS computer program calculates the concentration of all the selected species, and a table of the same is printed in the program output. The refinement was carried out in steps. The refined values of the proton–ligand formation constant K_1^H and K_2^H of ligands A and L and metal–ligand

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Table I. Proton–Ligand and Binary Stability Constants of Cu(II) in Dioxane–Water (1:1 v/v) and $\mu = 0.2$ M (NaClO$_4$) at 30 °C

ligand	K_1^H	K_2^H	log K^{Cu}_{CuL}	log $K^{CuL}_{CuL_2}$
L[1]	9.72 ± 0.03	6.98 ± 0.04	10.59 ± 0.18	10.03 ± 0.16
L[2]	9.26 ± 0.03	6.35 ± 0.03	10.10 ± 0.19	9.59 ± 0.16
L[3]	9.64 ± 0.03	6.89 ± 0.04	10.13 ± 0.09	9.41 ± 0.12
L[4]	9.64 ± 0.01	6.88 ± 0.02	9.64 ± 0.09	8.18 ± 0.10
L[5]	9.71 ± 0.01	3.29 ± 0.01	8.73 ± 0.17	8.44 ± 0.10
L[6]	9.43 ± 0.01	3.38 ± 0.02	9.01 ± 0.20	7.61 ± 0.17
L[7]	7.09 ± 0.07	4.20 ± 0.10	8.25 ± 0.00	3.63 ± 0.08

formation constants of [CuL] and [CuL$_2$] were first obtained. The values of formation constants of [CuA] and [CuA$_2$] used were same as in our previous work.[18] These refined values were used as fixed parameters for the refinement of the mixed-ligand complex formation constants in two ways: (i) by considering the species present in the solution to be LH$_2$, LH, L, [CuA], and [CuAL]; (ii) by taking into account all possible species present in solution, i.e., LH$_2$, LH, L, AH$_2$, AH, A, [CuL$_1$], [CuL$_2$], [CuA$_1$], [CuA$_2$], and [CuAL].

The refined values of the proton–ligand, binary metal–ligand formation constants, and mixed-ligand formation constants obtained by the computer technique have been presented in tables I and II. In cases of [CuA^{3}L] and [CuA^{4}L], calculation of mixed-ligand stability constants considering all possible species could not be done. This is because the formation of [CuA^3] and [CuA^4] is complete at very low pH, and hence the formation constants of [CuA^3] and [CuA^4] could not be determined by a pH-metric method. The formation constants of the ternary complexes [CuA^{3}L] and [CuA^{4}L] were, therefore, determined with the first computer method presuming complete formation of [CuA].

Spectral Measurement. The spectra were recorded on a Carl Zeiss Specord UV–visible spectrophotometer with 1-cm quartz cells and dioxanewater (1:1 v/v) as solvent. Solutions of concentrations 10^{-4} and 10^{-2} mol dm^{-3} were used for the UV and visible regions, resp. Spectra were recorded of A, L, [CuA$_1$], [CuA$_2$], [CuL], [CuL$_2$], and [CuAL]. A solution of [CuA]$^{2+}$ was prepared by mixing Cu(II) and A in a 1:1 ratio and maintaining the pH at 3.5. Solutions of [CuA$_2$]$^{2+}$ and [CuL$_2$] were prepared by mixing metal ion and ligands in a 1:2 ratio, and spectra were recorded at pH 5.5. For [CuAL], the metal ion and two ligands were mixed in the ratio 1:1:1. The pH of the solution was raised to 6.5. The pH values in all cases were fixed where the concentration of selected species was maximum in computer output data. The spectral bands have been recorded in Table III.

Results and Discussion

It is interesting to observe that in the case of the ternary complexes [CuAL], where L = L[1]–L[7], the values of the mixed-ligand formation constants obtained by the use of the extension of Irving–Rossotti titration technique, with the presumption that the formation of the complex is in steps Cu + A ⇌ [CuA] and [CuA] + L ⇌ [CuAL], and the values obtained by using the computer method are nearly equal. This shows that [CuA] formation is almost complete in the lower pH range and L combines with [CuA] in the second step, forming [CuAL]. This is further confirmed by the plot of the computer output of the concentrations of various species (as percentages of total Cu(II) present) against pH as shown in Figures 2 and 3. It is observed that in the lower pH range (pH 1–3) Cu(II) and [CuA] are the major species and in the higher pH range (pH 3–7) the major species are [CuA] and [CuAL]. In cases of [Cu(A)malonate)] systems 99% of the mixed-ligand complex is formed and the sum of the percentages of [Cu(A)(malonate)] and [CuA] totals to almost 100%. The concentrations of other species [CuA$_2$], [CuL], and [CuL$_2$] are negligible. In case of [Cu(A)(amino acid)] the maximum percentage of mixed-ligand complex is 91%, and in the case of [Cu(A)(diamine)] the percentage of mixed-ligand complex formed is 68%. This is in accordance with the

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Table II. Stability Constants of Ternary Complexes of Cu(II) in Dioxane-Water (1:1 v/v) and $\mu = 0.2$ M (NaClO$_4$) at 30 °C

| | A^1 | | | A^2 | | | A^3 | | | A^4 | | |
| | $\log K^{CuA}_{CuAL}$ | | | $\log K^{CuA}_{CuAL}$ | | | $\log K^{CuA}_{CuAL}$ | | | $\log K^{CuA}_{CuAL}$ | | |
	I^a	II^b	$\Delta \log K$	I	II	$\Delta \log K$	I	II	$\Delta \log K$	I	II	$\Delta \log K$
L^1	9.62	9.51 ± 0.08	−1.08	9.52	9.32 ± 0.18	−1.27	10.00	9.94 ± 0.13	−0.65	9.38	9.43 ± 0.11	−1.16
L^2	9.28	9.10 ± 0.00	−1.00	9.28	9.26 ± 0.1	−0.84	9.64	9.80 ± 0.13	−0.30	9.00	9.13 ± 0.03	−0.97
L^3	8.77	8.57 ± 0.15	−1.56	8.84	8.61 ± 0.09	−1.52	9.18	9.18 ± 0.10	−0.95	8.55	8.59 ± 0.10	−1.54
L^4	7.63	7.73 ± 0.14	−1.91	7.94	7.76 ± 0.18	−1.88	8.55	8.55 ± 0.08	−1.09	7.48	7.44 ± 0.08	−2.2
L^5	9.12	8.29 ± 0.20	−0.44	9.06	8.70 ± 0.02	−0.03	9.40	8.93 ± 0.03	+0.20	7.99	7.68 ± 0.02	−1.05
L^6	8.59	8.51 ± 0.03	−0.51	8.42	8.35 ± 0.00	−0.66	8.74	8.61 ± 0.03	−0.40	7.64	7.30 ± 0.03	−1.71
L^7	7.99	8.73 ± 0.04	+0.48	7.99	8.73 ± 0.04	+0.48	8.28	8.97 ± 0.04	+0.72	7.36	7.91 ± 0.03	−0.34

^{a} An extension of the Irving-Rossotti titration technique. ^{b} Computer method.

Table III. Electronic Spectra (λ_{max} in nm) of Free Ligands, Binary Complexes, and Ternary Complexes in a Dioxane-Water (1:1 v/v) Medium

compd	λ_{max}
A^1	236.9, 289.1
L^1	
L^5	
L^7	
[CuA^1$_2$]	243.9, 301.2, 312.5, 714.3
[CuL^1$_2$]	232.5, 568.7
[CuL^5$_2$]	232.5, 689.6
[CuL^7$_2$]	248.7, 763.3
[CuA^{1}L^1]	239.2, 299.0, 312.5, 613.4
[CuA^{1}L^5]	212.7, 243.9, 303.0, 312.5, 666.6
[CuA^{1}L^7]	243.9, 300.0, 312.5, 632.9

(Cudipy, ethylenediamine)

(Cudipy, Glycine)

Figure 2.

(Cudipy, malonate)

Figure 3. Variation of concentrations of different species with pH.
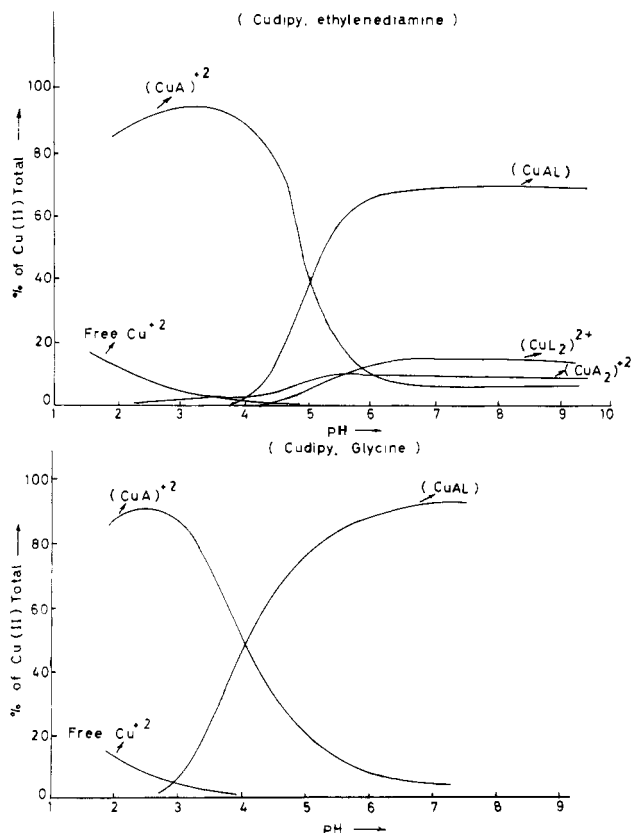
stabilities of mixed-ligand complexes with O⁻–O⁻, O⁻–N, and N–N coordination.

The formation constant values show that in the complex [CuAL], where L = L^1–L^6, coordinating through two nitrogen atoms or one nitrogen and one oxygen atom, $\Delta \log K$ has a small negative value. In cases where coordination is from N–N, the $\Delta \log K$ is more negative than where coodination is from N–O⁻. In cases where L has two oxygen coordination
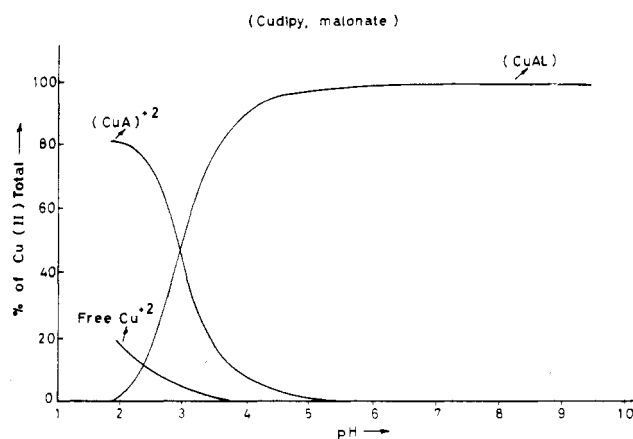
sites like malonate, $\Delta \log K$ is positive in the complexes [CuAL], where A = A^1, A^2, or A^3.

The astatistical stabilization of [CuAL] complexes can be explained by considering that there is a Cu → A π interaction and hence the electron density on the metal ion is reduced and the effective electronegativity of [CuA]$^{2+}$ is almost the same as that of [Cu(H$_2$O)]$^{2+}$.[3,6] Thus the σ-bonding tendency of L to combine with [CuA]$^{2+}$ and [Cu(H$_2$O)]$^{2+}$ is not significantly different.

As the Cu → A π interaction goes on increasing, $\Delta \log K$ becomes less negative in [CuAL], where L = N–N or N–O⁻ coordinating ligands and more positive in the case of malonate. The order of formation constants of the complexes [CuAL] is [CuA^{3}L] > [CuA^{1}L] ≈ [CuA^{2}L] > [CuA^{4}L].

This shows that the Cu → A π interactions in [CuA^1] and [CuA^2] are of equal extent. However, in [CuA^3] the coordination is from one pyridine N and one benzimidazole ring N, and hence the Cu → A π interaction is greater. This results in an increase in the formation constants of ternary complexes [CuA^{3}L], and $\Delta \log K$ becomes less negative or more positive. In the case of [CuA^4], the ligand coordination is from one pyridine N and one imidazoline ring N. π interaction is possible only with the pyridine ring. The imidazoline ring is saturated and hence has no delocalized π-electron cloud. Thus A^4 is less π interacting than bipyridyl. This results in negative $\Delta \log K$ values. The $\Delta \log K$ is negative even in the case of [CuA^{4}L], where L is coordinating through two O⁻. It has been reported[11] earlier that in cases where A is imidazole or histamine [CuAL^7] also shows negative $\Delta \log K$ values. Thus the small negative or positive value of $\Delta \log K$ depends on the extent of Cu → A π interactions. Where A is unidentate with imidazole or bidentate with imidazole and a second aliphatic nitrogen coordinating atom (histamine) or pyridyl and saturated imidazoline ring nitrogen coordinating atom (A^4), [CuAL] complexes show negative $\Delta \log K$. However, when A = 4-(2-pyridyl)imidazole, [CuAL^7] shows a small positive value of $\Delta \log K$.[10] In the present study it is observed that

in cases of [CuA³L], where A³ has a combination of one benzimidazole and another tertiary amine ring, Δ log K shows the highest positive or minimum negative Δ log K values. The stabilization effect is more than that in cases where A = bipyridyl or o-phenanthroline. It is to such an extent that even the complex [CuA³(glycine)] shows a positive Δ log K value, though the coordination of amino acid is from one nitrogen and one oxygen atom. Thus a ligand A with an imidazole or benzimidazole and a tertiary amine nitrogen as coordinating atoms (4-(2-pyridyl)imidazole or 2-(2-pyridyl)benzimidazole) appears to bring maximum stabilization of the ternary complex [CuAL]. This observation may be of interest in explaining the specificity in the choice of carrier base in the metallo-enzymes. Besides a Cu → A π interaction, Sigel has attributed greater stabilization in [CuAL] complexes to Jahn–Teller effects in Cu(II) complexes. Sigel[4] considered that, on co-ordination of the stronger field ligand bipyridyl, [Cu(bpy)₂-(H₂O)₄] will be somewhat more distorted to square-planar geometry, thus creating the right geometry for the coordination of the secondary ligand. He has proposed that the effect is especially favored when L is O⁻–O⁻. However, no reason has been assigned. The greater stabilization of [CuA(O⁻–O⁻)] complexes can be better understood in terms of an explanation recently extended by us considering repulsion between metal ion electrons and ligand lone-pair electrons.[20,21] In the formation of binary complexes, there is electron repulsion between the metal ion dπ electron and a lone pair of electrons (if any) present on the co-ordinating atom of the σ-bonding ligand L. However, in the ternary complex there is back-donation of electrons through π bonding between the metal ion and the A molecule, and hence the electron density on [CuA] is reduced. This reduces the repulsion between metal dπ electrons and the additional lone pair of electrons over the ligand L in the ternary complex. In the case of malonate (L⁷) there are lone pairs of electrons over both carboxylate anions, and hence electronic repulsion in [CuL⁷] formation is greater. The release of repulsion is, thus, more pronounced in the ternary complex [CuAL⁷], and this leads to positive Δ log K. In N–O⁻-coordinating ligands there is a lone pair of electrons only over the carboxylate O⁻. Due to the decrease of electron repulsion in ternary complexes, Δ log K is a small negative quantity in [CuAL] complexes with L = N–O⁻ coordinating ligands. There is no extra lone pair of electrons present on the σ-bonding nitrogen atom, and hence the favorable electron-release effect is not felt in the formation of [CuAL], where L = N–N coordinating ligands. In cases where L = L³ or L⁴, there is greater lowering in the ternary complex formation constant and Δ log K values are more negative because of steric hindrance in the ternary complex formation due to the alkyl groups on the N atoms.

Electronic Spectra of the Complexes. The spectral bands in a representative case involving Cu²⁺, A¹, L⁵, or L⁷ are discussed. The absorption spectrum of free bipyridyl shows bands at 236.9 and 289.1 nm. The band in the low-energy region (289.1 nm) corresponds to the π → π* transition. On co-ordination with metal ion, the bands are observed in [CuA¹₂]²⁺ at 243.9, 301.2, and 312.5 nm. The appearance of a new band at 312.5 nm and a shift in the π → π* transition to 301.2 nm show that there is interaction between π orbitals of Cu(II) and those of the bipyridyl molecule.

L¹, L⁵, and L⁷ show no band in the UV region, because the σ → σ* transition occurs in the far-UV region. There are new bands observed in the spectra of [CuL¹₂] at 232.5 nm, in [CuL⁵₂] at 232.5 nm, and in [CuL⁷₂] at 248.7 nm. The appearance of a new band in each is due to L → M charge-transfer interactions.

The ternary complex [CuAL] exhibits a band at ∼300 nm. This corresponds to the π → π* transition and occurs at nearly the same place as in [CuA¹₂], showing thereby that the π interaction in [CuA] is not significantly affected due to the formation of the ternary complex [CuAL]. The stabilization of the ternary complex is only due to the lowering of electron repulsion between the ligand lone pair of electrons and Cu²⁺ dπ electrons and the increase in σ bonding of L. This effect is significant in the case of [CuA¹L⁷], with L⁷ coordinating through oxygen atoms. This effect is reflected in d–d transition bands.

It is normally expected that in a mixed-ligand complex [MAL] the ligand field created is an average of the ligand field in the binary complexes [MA₂] and [ML₂]. However, in the complexes [CuA¹L⁷], the d–d transition band is at higher energy than in [CuL⁷₂] or [CuA¹₂]. In the cases of L coordinating through N–O⁻ also, the d–d band of [CuAL] is at higher energy, though not to the same extent as in the case of O⁻–O⁻-coordinating malonate. This is because the M → bpy π interaction stabilizes the L → M σ interaction where L coordinates through two O⁻. Thus the ligands A and L create a stronger field in [CuAL] than in [CuL₂] or [CuA₂]. This leads to greater splitting of the d orbitals in [CuAL], and the d–d transition band shifts to a higher energy region. The band corresponding to the σ → σ* transition (L → M charge transfer) also moves to a higher energy region in the case of ternary complexes containing O⁻–O⁻- or N–O⁻-coordinating ligands. In the case of [CuA¹(diamine)], the shift of the σ → σ* transition is less and the d–d transition band of [CuA¹(diamine)] is intermediate between the d–d transition bands of [CuA¹₂] and [Cu(diamine)₂] as normally expected. This observation of the mutual effect of the two ligands in increasing the ligand field strength and consequent stabilization of the mixed-ligand complex will help in explaining the stabilities of various metalloenzymes and designing tailor made metalloenzyme models.

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