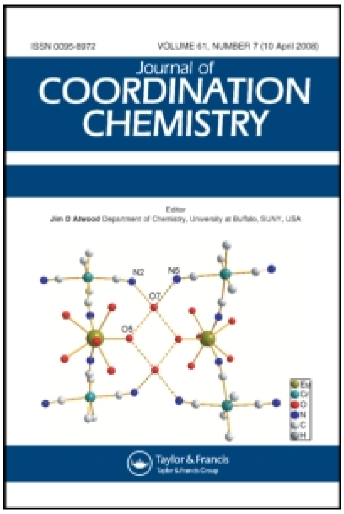

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A STUDY OF π INTERACTIONS IN MIXED LIGAND COMPLEXES AND EFFECTS ON SUBSTITUTION

Paresh J. Patel[a]; P. K. Bhattacharya[a]
[a] Department of Chemistry, M.S. University of Baroda, Baroda, India

To cite this Article Patel, Paresh J. and Bhattacharya, P. K.(1984) 'A STUDY OF π INTERACTIONS IN MIXED LIGAND COMPLEXES AND EFFECTS ON SUBSTITUTION', Journal of Coordination Chemistry, 13: 2, 113 — 118
To link to this Article: DOI: 10.1080/00958978408079762
URL: http://dx.doi.org/10.1080/00958978408079762

J. Coord. Chem., 1984, Vol. 13, pp. 113–118
0095-8972/84/1302-0113 $18.50/0

Printed in Great Britain

A STUDY OF π INTERACTIONS IN MIXED LIGAND COMPLEXES AND EFFECTS ON SUBSTITUTION

PARESH J. PATEL and P.K. BHATTACHARYA†
Department of Chemistry, M.S. University of Baroda, Baroda 390002, India.

(Received March 21, 1983)

The formation constants of complexes of the type [CuAL], where A = 2, 2′-dipyridyl, 1,10-phenanthroline, 2-(2′-pyridyl)benzimadazole, or 2-(2′-pyridyl)imidazoline and L = salicylaldehyde, 5-bromosalicylaldehyde, 5-nitrosalicylaldehyde, 2-hydroxyacetophenone, or 2-hydroxy-1-naphthaldehyde have been determined in dioxan-water (1:1 v/v) solutions and μ = 0.2 mol dm^{-3} NaClO$_4$ at 30°. The formation constants have been determined by a graphical method and further refined using a computer programme. The values of Δlog K (log K^{MA}_{MAL} – log K^{M}_{ML}) is positive. ΔLog K is less positive in the case of complexes involving 2-hydroxyl-1-naphthaldehyde, nitrosalicylaldehyde and bromosalicylaldehyde. The solid mixed ligand complexes have been isolated.

INTRODUCTION

The mixed-ligand complexes [MAL], involving tertiary diimines are being studied exhaustively.[1–3] They exhibit astatistical stabilization due to metal to ligand π interactions.[4–6] It has been observed that [MA] prefers to coordinate with 0^--0^- ligands,[4,7–9] because of an increase in the class A character of M in [MA][10] leading to a lessening of electron repulsion between the metal dπ electrons and 0^--0^- lone pairs in the ternary complex [MA(0^--0^-)] compared to the binary complex [M(0^--0^-)].[11,12] It has also been observed[13–15] that electron-releasing groups on L increase the positive value of Δlog K and electron-withdrawing groups on L reduce the positive value of Δlog K.

In order to further investigate the effect of the nature of the ligands on mixed-ligand complex stability, a study of the complexes [CuAL] has been carried out where A = 2,2′-bipyridyl (A^1), 1,10-phenanthroline (A^2), 2-(2′-pyridyl)benzimidazole (A^3) or 2-(2′-pyridyl)imidazoline (A^4) and L = salicylaledehyde (L^1), 5-bromosalicyladehyde (L^2) 5-nitrosalicyladehyde (L^3), 2-hydroxyacetophenone (L^4), or 2-hydroxyl-1-naphthaldehyde (L^5).

RESULTS AND DISCUSSION

It is interesting to observe that in case of the ternary complexes [CuAL], where L = L^1 to L^5, the values of the mixed-ligand formation constants obtained by the use of the two computer techniques are nearly equal in all cases. This shows that $[CuA]^{2+}$ formation is almost complete in the lower pH range and L combines with $[CuA]^{2+}$ forming [CuAL]. This is further confirmed by a plot of the concentration of the various species (as a percentage of the Cu(II) present) against pH as shown in Fig. 1. It is observed that in the lower pH range (2 to 4) the major species are Cu(II) and [CuA^1] and in the higher pH range the major species are [CuA^1] and [CuA^{1}L^1]. The same is true in other cases where A = A^2 to A^4 and L = L^2 to L^5. The concentrations of species such as [CuA$_2$], [CuL] and [CuL$_2$] are very low (below 1%). Values for the equilibrium constants are given in Tables I and II.

---

† To whom correspondence should be addressed.

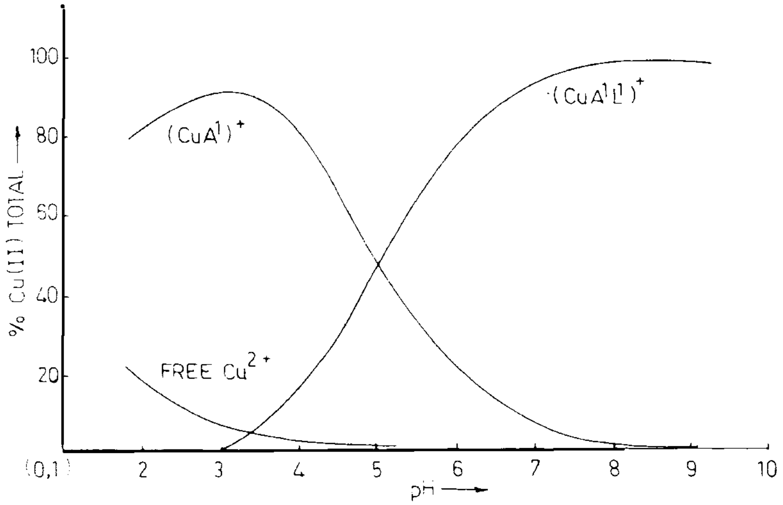

FIGURE 1 Relative concentrations of binary and ternary complex species in $[CuA^1L^1]^+$ systems; T = 30°, μ = 0.2M.

It is observed that the values of the formation constants of the mixed-ligand complexes are much higher than expected from statistical considerations. In the cases of $[CuA^1L]$, $[CuA^2L]$ and $[CuA^3L]$, Δlog K values are positive. The value however depend on the extent of $Cu \rightarrow A(\pi)$ interaction and the order is found to be $[CuA^1L] > [CuA^2L] > [CuA^3L] > [CuA^4L]$.

In case of $[CuA^4L]$, Δlog K is found to be negative and this is thought to be because there is coordination from one pyridine and one imidazoline nitrogen atom. In this case any π interaction is possible only with the pyridine ring. A similar dependence of Δlog K on the nature of A was observed by Sigel.[16]

The formation constants of the ternary complexes depend on the nature of and substitution on L also. 2-Hydroxy-acetophenone shows a more positive Δlog K value in the ternary complex than salicylaldehyde because the methyl group increases the electron density in the ring. However, in the case where L = 2-hydroxy-1-naphthaldehyde, Δlog K is less positive. This may be because the electron density is delocalized over the two phenyl rings and hence the effective electron density on the oxygen is less.

TABLE I

Proton-ligand and binary complex stability constants in dioxan-water (1:1 v/v) and μ = 0.2M $NaClO_4$ at 30°.

Ligand[a]	log K_1^H	log $K^{Cu}_{CuL/A}$	log $K^{CuL/A}_{CuL_2/A_2}$
L^1	9.23 ± 6.01	6.64 ± 0.07	6.03 ± 0.09
L^2	7.98 ± 0.01	6.07 ± 0.02	4.78 ± 0.02
L^3	5.78 ± 0.02	4.17 ± 0.04	3.30 ± 0.03
L^4	10.90 ± 0.01	8.04 ± 0.05	6.90 ± 0.05
L^5	8.04 ± 0.02	6.07 ± 0.14	5.07 ± 0.05
A^1	3.70 ± 0.04	7.00	4.15 ± 0.15
A^2	4.40 ± 0.03	8.82	5.46 ± 0.12

[a] See text for ligand description.

TABLE II
Stability constants for ternary complexes of Cu(II) in dioxan-water (1:1 v/v) and μ = 0.2M NaClO$_4$ at 30°.

	Log $K_{CuAL}^{Cu\,a}$							
	A$^{1\,b}$		A$^{2\,b}$		A$^{3\,b}$		A$^{4\,b}$	
	log K	Δlog K	log K	Δlog K	log K	Δlog K	log K	Δlog K
L$^{1\,b}$	7.58 ±0.1	+ 0.94	7.39 ±0.14	+ 0.75	7.08 ±0.07	+ 0.44	6.13 ±0.08	− 0.53
L$^{2\,b}$	6.67 ±0.18	+ 0.60	6.42 ±0.08	+ 0.35	6.21 ±0.17	+ 0.14	5.25 ±0.13	− 0.82
L$^{3\,b}$	4.59 ±0.09	+ 0.42	4.41 ±0.18	+ 0.24	4.17 ±0.19	+ 0.00	2.83 ±0.16	− 1.77
L$^{4\,b}$	9.18 ±0.13	+ 1.14	9.00 ±0.13	+ 0.96	8.87 ±0.09	+ 0.83	8.12 ±0.18	+ 0.08
L$^{5\,b}$	6.80 ±0.12	+ 0.73	6.69 ±0.13	+ 0.62	6.11 ±0.15	+ 0.04	5.62 ±0.10	+ 0.45

[a]Using computer methods. [b]See text for ligand description.

The effect can also be seen in the case of ternary complexes of nitrosalicylaldehyde and bromosalicylaldehyde. Δlog K is less positive, compared to salicylaldehyde. This is because the nitro and bromo groups being electron-withdrawing decrease the negative charge density on the ligand. The order of Δlog K and formation constants of the ternary complexes is [CuAL^1] > [CuAL^2] > [CuAL^3], and the same order holds good in all cases involving A. Thus the present study shows how substitution of the ligands effects the stability of the mixed-ligand complexes, though the substituting group does not take part in coordination with the metal ion.

The mixed-ligand complexes were isolated. Analysis of the compounds indicated the composition [CuAL] [BF$_4$]. Molar conductances of all the complexes correspond to the expected range for 1:1 electrolytes. Details and magnetic moments are given in Table III.

TABLE III
Analytical, Magnetic and Conductance data

Compound	Analysis (%)^a				μ_{eff} (B.M.)	Conductance (cm^2/mol^{-1}) in methanol
	Cu	N	C	H		
[CuA^{1}L^1][BF$_4$]^b	14.8 (14.9)	6.1 (6.6)	48.1 (47.7)	3.01 (3.04)	1.88	113.8
[CuA^{2}L^1][BF$_4$]	14.0 (14.1)	5.7 (6.2)	50.2 (50.5)	3.08 (2.98)	1.82	97.8
[CuA^{1}L^4][BF$_4$]	14.7 (14.4)	6.4 (6.3)	47.0 (48.9)	3.37 (3.39)	1.87	107.7
[CuA^{2}L^4][BF$_4$]	14.2 (13.7)	5.6 (6.0)	51.0 (51.5)	3.30 (3.14)	1.88	107.8
[CuA^{1}L^5][BF$_4$]	13.2 (13.3)	5.5 (5.9)	52.4 (52.8)	3.29 (3.14)	1.88	112.8
[CuA^{2}L^5][BF$_4$]	12.9 (12.7)	5.1 (5.6)	54.9 (55.1)	3.38 (2.99)	1.88	95.8

[a]Calculated values are given in parentheses. [b]See text for ligand descriptions.

The ligand field spectra of the complexes are interesting. It is normally expected that in a mixed-ligand complex [MAL], the ligand field splitting should be average of that in two binary complexes [MA_2] and [ML_2]. However, in the complexes of the present study the d-d transition in [CuA^1L] is at a higher energy than in [CuL_2^1] or [CuA_2^1]. The shift in the d-d band position of the [CuAL] complexes from the average of those of [CuA_2] and [CuL_2] can be considered to be due to the additional stabilization of the ternary complex. Some spectral details are included in Table IV.

EXPERIMENTAL

All reagents used were of A.R. grade, except for 2-(2′-pyridyl)benzimidazole or 2-(2′ pyridyl)imidazoline, which were prepared by known methods.[17]

The proton-ligand, metal-ligand formation constants were determined in dioxan-water (1:1 v/v) solutions and μ - 0.2 mol dm^{-3} $NaClO_4$ at 30°. The values of $\bar{n}H$, K_1^H, $\bar{n}$, pL, log K_1 and K_2 were calculated by the normal Irving-Rossotti titrations.[18,19] The titrations were carried out under an atmosphere of nitrogen in a thermostatic bath. In each measurement, pH values were corrected for the medium using the method suggested by Van Uitert and Haas.[20] The preliminary values of the formation constants of the ternary complexes were determined by using an extension of the Irving-Rossotti technique.[6]

TABLE IV
Electronic spectra of binary and mixed-ligand complexes in dioxan-water (1:1 v/v)

Compound[a]	λ_{max}[b]
$[CuA_2^1]^{2+}$	13.5 (2.79)
$[CuA_2^2]^{2+}$	13.5 (2.75)
$[CuL_2^1]$	13.7
$[CuL_2^2]$	13.8
$[CuL_2^3]$	13.8
$[CuL_2^4]$	14.0
$[CuL_2^5]$	13.8
$[CuA^1L^1]^+$	16.0 (1.85)
$[CuA^2L^1]^+$	15.8 (1.90)
$[CuA^1L^2]^+$	15.8 (1.90)
$[CuA^2L^2]^+$	15.7 (2.02)
$[CuA^2L^3]^+$	15.5 (1.60)
$[CuA^1L^4]^+$	15.8 (1.89)
$[CuA^2L^4]^+$	15.8 (1.80)
$[CuA^1L^5]^+$	15.8 (1.80)
$[CuA^2L^5]^+$	15.8 (2.07)
$[CuA^1L^3]^+$	15.8 (2.22)

[a]See text for ligand descriptions. [b]λ_{max} in cm^{-1} multiplied by 10^{-3}. Values of log ϵ (ϵ in units of $M^{-1}cm^{-1}$) are given in parentheses.

All the formation constants were subjected to refinement using the computer programme SCOGS.[21] The refined values of proton-ligand formation constants K_1^H of LH, AH^+ and the binary metal-ligand formation constants for [CuL] and [CuL_2] were first obtained. The formation constants of [CuA] and [CuA_2] were determined as in previous work.[12] These values were used for the refinement of the ternary complex formation constants in two ways:

(i) by considering the species present in the solution to be LH, L, [CuA] and [CuAL] and (ii) by taking into account all possible species in solution, including AH, A, [CuL], [CuL_2], and [CuA_2].

The subroutine COGSNR of the SCOGS programme was used to calculate the concentrations of all the selected species. The refined values, obtained by the computer technique, are given in Tables I and II. In the cases of [CuA^3L] and [CuA^4L], calculation of mixed-ligand formation 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 titration.

The mixed-ligand complexes [CuAL] [BF_4], where A = A^1 or A^2 and L = L^1, L^4 or L^5 were isolated. The compounds were prepared as follows. To 0.002 mol dm^{-3} cupric acetate in alcohol (25 cm^3) was added equimolar quantities of ligand (A) and ligand (L) in alcohol (25 cm^3). The solution was refluxed for 15-20 minutes and then a 0.1 mol dm^{-3} solution of sodium tetrafluoroborate in alcohol was added until precipitation was complete. The solid was filtered, washed with alcohol and dried.

Spectra were recorded on a Carl Zeiss SPECORD U.V. visible spectrophotometer dioxan-water (1:1 v/v) as solvent. The spectra of Cu(II) + A + L mixed in 1:1:1 mol ratio were also recorded at pH 6.5 where mixed-ligand complex formation is at a maximum. The spectral bands were observed at the same positions as those of isolated [CuAL] in solution. This shows that the Cu(II) ternary complexes are formed quickly after mixing the components. Spectra of the binary complexes $[CuA_2]^{2+}$ and [CuL_2], prepared by mixing of solutions of Cu(II) and ligands in ratios of 1:2, 1:3 and 1:5, were recorded at pH 3.5 and 5.5, respectively (the pH values were fixed where the calculated concentrations of such species was at a maximum). The spectral bands were identical at all three ratios showing that the same species, $[CuA_2]^{2+}$ or [CuL_2] is present in solution. The data is given in Table IV.

ACKNOWLEDGEMENT

We wish to thank Professor K.N. Trivedi for providing the necessary laboratory facilities. We are also thankful to the CSIR New Delhi, for financial support.

REFERENCES

1. H. Sigel, (Ed), "Metal ions in Biological Systems", Marcel Dekker, New York, Vol. 2, 1973, p. 64.
2. H. Sigel, *Inorg. Chem.*, **19**, 1411 (1980).
3. P.K. Bhattacharya, *J. Sci. Ind. Res.*, **40**, 382 (1981).
4. H. Sigel, *Chimia*, **21**, 489 (1967).
5. R. Griesser and H. Sigel, *Inorg. Chem.*, **9**, 1238 (1970).
6. M.V. Chidambaram and P.K. Bhattacharya, *J. Inorg. Nucl. Chem.*, **32**, 3271 (1970).
7. G.A. L'Heaureux and A.E. Martell, *J. Inorg. Nucl. Chem.*, **28**, 481 (1966).
8. U. Doraswamy and P.K. Bhattacharya, *Indian J. Chem.*, **13**, 1069 (1975).
9. H. Sigel and B. Prijs, *Chimia*, **29**, 134 (1975).

10. F.A. Walker, H. Sigel and D.B. McCormick, *Inorg. Chem.*, **11**, 2756 (1972).
11. P.J. Patel, V.K. Patel and P.K. Bhattacharya, *Indian J. Chem.*, **21**, 590 (1982).
12. P.J. Patel, V.K. Patel and P.K. Bhattacharya, *Inorg. Chem.*, **21**, 3163 (1982).
13. F.A. Walker, H. Sigel and D.B. McCormick, *Inorg. Chem.*, **11**, 2756 (1972).
14. H. Sigel, P.R. Huber, R. Griesser and B. Prijs, *Inorg. Chem.*, **12**, 1198 (1973).
15. K. Gopalakrishnan and P.K. Bhattacharya, *J. Chem. Soc. Dalton*, 353 (1982).
16. B.E. Fischer and H. Sigel, *Inorg. Chem.*, **18**, 425 (1979).
17. J.L. Walter and H. Frieser, *Anal. Chem.*, **26**, 217 (1954).
18. H.M. Irving and H.S. Rossotti, *J. Chem. Soc.*, 3397 (1953).
19. H.M. Irving and H.S. Rossotti, *J. Chem. Soc.*, 2904 (1954).
20. L.G. Van Uitert and L.G. Haas, *J. Amer. Chem. Soc.*, **75**, 451 (1953).
21. I.G. Sayce, *Talanta*, **15**, 1397 (1968); I.G. Sayce, *ibid.*, **18**, 653 (1971); I.G. Sayce and V.S. Sharma, *ibid.*, **19**, 83 (1972).