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Synthesis and Properties of some Azo Pyridone Dyes and their Cu(II) Complexes[1]

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ABSTRACT

A series of azo pyridone dyes derived by the coupling of 3-cyano-6-hydroxy-4-methyl 2 (1H) pyridone with diazotized para *and* meta *substituted anilines, and the Cu(II) complex of the dyes, have been synthesized. The azo dyes and complexes have been characterized by elemental analysis, IR, ^1H NMR and UV–visible spectra. The acid dissociation constants of the dyes and formation constants of the complexes have been determined spectrophotometrically. Substituent effects on these parameters have been discussed. © 1997 Elsevier Science Ltd. All rights reserved*

Keywords: azopyridone dyes, complex azo dyes, Cu(II) complexes of azopyridone dyes, ionization constants, formation contants, azo-hydrazone tautomerism, disperse dyes, substituent effect.

INTRODUCTION

It is well established that arylazopyridones have excellent coloration properties.[1,2,3] Very few investigations have been published with respect to the metal complexes of azopyridone dyes. Wang *et al.* reported the synthesis of some Cr(III) complexes of *o,o′*-dihydroxyazo pyridone dyes[4] but the Cu(II) complexes of azopyridone compounds have not been developed.

In this work, some azopyridone dyes and their Cu(II) complexes were synthesized and spectral properties of the dyes and complexes are compared.

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[1] Part of this work was presented at X National Congress of Chemistry, 1994, Bursa, Turkey.
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The acid dissociation constants of the dyes and formation constant of the complexes were also reported.

EXPERIMENTAL

General

IR spectra were determined (KBr) with a Mattson 1000 FTIR spectrophotometer. ^{1}H NMR spectra were recorded with a Varian EM60 in $CF_3COOH/CDCl_3$ with TMS as internal reference. Spectrophotometric measurements were carried out on a Bausch and Lomb Spectronic 2000 spectrophotometer. Copper concentration was analyzed using a Philips PU 9285 model flame AAS. Magnetic susceptibilities were measured with a Chistison Scientific Equipment Ltd Gouy Balance model MK-I at room temperature. pH measurements were carried out on a Corning M 240 pH meter with a combined glass electrode type 476050.

3-Cyano-6-hydroxy-4-methyl-2 (IH) pyridone was prepared from cyanoacetamide and ethyl acetoacetate by the previously reported potassium hydroxide method.[5]

General method for preparation of azo pyridone dyes[6]

3-Cyano-6-hydroxy-4-methyl-2 (IH) pyridone (1.50 g 0.01 mole) was dissolved in a solution of KOH (0.56 g, 0.01 mole) in water (4 ml). The resulting solution was cooled to 0–5°C and was treated with a cold (0–5°C) solution of the appropriate diazonium salt prepared by diazotizing the substituted aniline (0.01 mole) in 2.50 ml concentrated HCl and 4 ml water with $NaNO_2$ (0.76 g, 0.01 mole). The resulting diazonium salt liquor was then slowly added to the vigorously stirred solution and the mixture was stirred for 30 min. The precipitated orange solid was collected and washed thoroughly with cold water and dried. Crystallization from acetone or acetic acid gave orange needles. The yields were 90–95%. Characteristic IR and ^{1}H NMR spectral data of the dyes are given in Table 2.

Preparation of Cu(II) complexes of the azo dyes

All complexes were prepared from the azo dyes and copper-II-acetate as follows:

5 mmol azo dye was heated in methanol (250 ml) and a methanolic solution (20 ml) of 2.5 mmol copper-II-acetate was added slowly. The mixture was heated for 8 h under reflux, and the yellow–brown precipitate was

filtered, washed with warm water, methanol and ether, and then dried *in vacuo*. Complexes were not recrystallized because of their low solubilities of common organic solvents. The yields were in the region 60–78%. Elemental analysis and characteristic IR spectral bands of the complexes were tabulated in Tables 1 and 2.

Determination of pKa values of the azo dyes

The acid dissociation constants of the dyes were determined spectrophotometrically in 80% (v/v) ethanol–water mixture at $27 \pm 0.1°C$ and 0.1 M ionic strength; the pH meter was accurate to ±0.01 pH units and was calibrated with standard Beckman buffer solutions of pH 4.01 and 7.00. The pH meter readings recorded in ethanol–water solution were converted to hydrogen ion concentration as described by van Uitert and Haas.[7]

For the determination of pKa constants, a 50 ml solution of the azo pyridone dye was prepared such that it was $\sim 1.0 \times 10^{-5}$ M with respect to the azo pyridone, 0.1 M HCl and contained 80% (v/v) ethanol–water. The test solution was transferred to a thermostatted cell with a water-jacket. The pH of the solution was measured and the spectrum was recorded using either the ionic medium or 80% (v/v) ethanol as a blank. In both cases, identical absorbance values in the wavelength range employed were obtained. The pH of the test solution was increased by addition of small volume of concentrated carbonate-free potassium hydroxide made up from the same solvent. Since the total change in volume did not exceed 1.0%, no correction was made for dilution. After each spectral measurement, the pH was checked, and in all cases, the two values before and after the spectral measurements were found to be the same within the limits of the accuracy of the pH meter. In each run 12–16 pH readings were taken and the value of the pKa was calculated from each reading using the equation

$$\mathrm{pKa} = \mathrm{pH_i} + \log\frac{(A_a - A_i)}{(A_i - A_b)}$$

where A_i is the absorbance of solution at $\mathrm{pH_i}$; and A_a and A_b are the absorbance values of the strongly acidic and basic solution of compounds, respectively.

Determination of formation constants of the complexes

Complex formation equilibria and overall formation constants β for ML_2 type complexes can be given as

TABLE 1
Characterization Data for Dyes and Complexes

Substituent	*Dyes*					*Complexes*				
	Formula (Comp. number)	*m.p. (°C)*	*C% Found (Calcd)*	*H% Found (Calcd)*	*N% Found (Calcd)*	*Formula** Comp. number*	*C% Found (Calcd)*	*H% Found (Calcd)*	*N% Found (Calcd)*	*Cu% Found (Calcd)*
H	$C_{13}H_{10}N_4O_2$(**1**)	278–280	60.97(61.48)	4.01(3.97)	21.76(22.03)	ML_2(**1′**)	55.02(54.78)	3.11(3.16)	19.51(19.67)	10.99(11.15)
p-OEt	$C_{15}H_{14}N_4O_3$(**2**)	252–254	59.77(60.40)	4.72(4.74)	18.25(18.78)	ML_2(**2′**)	54.62(54.75)	3.91(3.95)	14.71(14.60)	9.81(9.66)
p-Me	$C_{14}H_{12}N_4O_2$(**3**)	270–272	62.50(62.68)	4.56(4.52)	20.52(20.88)	ML_2(**3′**)	56.41(56.23)	3.90(3.68)	18.20(18.74)	10.32(10.63)
p-Cl	$C_{13}H_9N_4O_2Cl$(**4**)	288–289	53.53(54.09)	3.18(3.15)	19.31(19.40)	ML_2(**4′**)	48.71(48.86)	2.62(2.51)	17.48(17.54)	9.79(9.95)
p-COOH	$C_{14}H_{10}N_4O_4$(**5**)	304–306	55.89(56.38)	3.96(3.39)	18.68(18.78)	ML_2(**5′**)	51.41(51.10)	2.66(2.74)	16.89(17.03)	9.41(9.66)
p-NO_2	$C_{13}H_9N_5O_4$(**6**)	326–328	51.71(52.19)	2.98(3.04)	22.98(23.40)	ML_2(**6′**)	47.31(47.62)	2.43(2.38)	21.23(21.43)	9.63(9.99)
m-OEt	$C_{15}H_{14}N_4O_3$(**7**)	254–256	59.85(60.40)	4.81(4.74)	18.62(18.78)	ML_2(**7′**)	54.49(54.75)	4.10(3.95)	14.58(14.60)	9.40(9.66)
m-Me	$C_{14}H_{12}N_4O_2$(**8**)	266–268	62.02(62.68)	4.55(4.52)	20.65(20.88)	ML_2(**8′**)	55.98(56.23)	3.78(3.68)	18.40(18.74)	10.32(10.63)
m-Cl	$C_{13}H_9N_4O_2$(**9**)	288–290	53.69(54.09)	3.14(3.15)	18.99(19.40)	ML_2(**9′**)	48.97(48.86)	2.47(2.51)	17.41(17.54)	9.82(9.95)
m-COOH	$C_{14}H_{10}N_4O_4$(**10**)	297–298	55.98(56.38)	3.52(3.39)	18.52(18.78)	ML_2(**10′**)	50.98(51.10)	2.69(2.74)	16.97(17.03)	9.72(9.66)
m-NO_2	$C_{13}H_9N_5O_4$(**11**)	279–280	51.97(52.19)	3.03(3.04)	23.22(23.40)	ML_2(**11′**)	47.89(47.62)	2.66(2.38)	21.46(21.43)	9.67(9.99)

*Melting points of all complexes are up to 350°C.
**L shows appropriate azo dye.

TABLE 2
Spectral Data of Dyes and Complexes

Compound	$\nu_{C\equiv N}$	$\nu_{C=O}$	$\nu_{C\text{-}O}$	$\nu_{Cu\text{-}O}$	*^1H NMR,* ppm*
1/1′	2250/2220	1681,1652/1651	/1281	421	15.4, 7.55, 2.76
2/2′	2220/2215	1665,1650/1652	/1272	463	15.3, 7.40, 4.01, 2.71, 1.35
3/3′	2220/2210	1660,1650/1649	/1265	460	15.4, 7.50, 2.45, 2.30
4/4′	2240/2210	1667,1651/1655	/1271	431	15.6, 7.35, 2.50
5/5′	2210/2200	1670,1658/1653	/1261	438	15.4, 7.50, 2.40
6/6′	2210/2195	1675,1651/1665	/1255	487	15.1, 7.85, 2.76
7/7′	2220/2215	1651,1630/1645	/1271	457	15.5, 7.45, 2.50, 2.35, 1.33
8/8′	2220/2210	1662,1648/1657	/1268	461	15.4, 7.50, 2.46, 2.35
9/9′	2220/2210	1681,1655/1661	/1259	443	15.2, 7.40, 2.50
10/10′	2240/2210	1674,1662/1660	/1256	451	15.3, 7.40, 2.55
11/11′	2240/2220	1671,1658/1665	/1263	469	15.1, 7.80, 2.75

*For azo dyes.

$$\mathrm{M} + 2\mathrm{L} \rightleftharpoons \mathrm{ML}_2 \; \beta = \frac{[\mathrm{ML}_2]}{[\mathrm{M}][\mathrm{L}]^2}, \quad \log\beta = \log\frac{[\mathrm{ML}_2]}{[\mathrm{M}][\mathrm{L}]^2}$$

[M], [L] and $[\mathrm{ML}_2]$ are represented molar equilibrium concentrations of metal ion, ligand azo dye and complex species, respectively. Charges are omitted for simplicity.

Complex formation constants of the dyes with Cu^{2+} ion were evaluated spectrophotometrically in methanol. The water-jacketted cell holder of the spectrophotometer was thermostatted at 27 ± 0.1°C. A series of solutions of known concentrations were prepared for both metal and ligand from the stock solutions of about 10^{-4} M for each. Complex solutions were prepared by mixing ligand and metal solutions. Metal to ligand mol ratios ranged between 25 and 5 in the resulting solutions. Absorbance values of all solutions were measured at maximum wavelength of the complexes. Molar absorbtivity coefficients of metal, ligand and complex (ϵ_m, ϵ_l and ϵ_c, respectively) were obtained from the slope of the plots of absorbances against concentrations. Correlation coefficients, r, were better than 0.996.

Equilibrium concentrations of the species were calculated using following equations.

$$[\mathrm{ML}_2] = \frac{\mathrm{A} - \mathrm{A}'}{\varepsilon}$$

$$[\mathrm{M}] = \mathrm{C_M}\frac{\mathrm{A} - \mathrm{A}'}{\varepsilon}$$

$$[\mathrm{L}] = \mathrm{C_L} - 2\frac{\mathrm{A} - \mathrm{A}'}{\varepsilon}$$

where $\mathrm{C_M}$ and $\mathrm{C_L}$ were concentration of metal and ligand solutions and $\mathrm{A}' = \varepsilon_\mathrm{M}\mathrm{C_M} + \varepsilon_\mathrm{L}\mathrm{C_L}, \varepsilon = \varepsilon_\mathrm{C} - \varepsilon_\mathrm{M} - 2\varepsilon_\mathrm{L}$.

TABLE 3
Visible Absorbtion Maxima, pKa and log β Values of the Compounds Studied

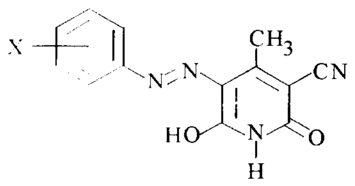
X	*Dyes*				*Complexes*	
	λ_{max} *(nm) in* $CHCl_3$	λ_{max} *(nm) in* CH_3OH	λ_{max} *(nm) in* C_2H_5OH-H_2O *80% (v/v)*	*pKa*	λ_{max} *(nm),* (ε_c) *in* CH_3OH	*log* β
H	440	452	454	8.07 ± 0.02	438 (4.88×10^4)	10.92 ± 0.02
p-OEt	473	488	494	7.84 ± 0.01	451 (5.98×10^4)	11.15 ± 0.01
p-Me	452	462	471	8.57 ± 0.02	437 (4.61×10^4)	11.25 ± 0.04
p-Cl	444	461	466	7.65 ± 0.05	443 (5.83×10^4)	10.39 ± 0.04
p-COOH	441	461	469	8.01 ± 0.02	458 (3.69×10^4)	10.80 ± 0.02
p-NO_2	436	451	461	7.20 ± 0.02	461 (5.53×10^4)	10.43 ± 0.01
m-OEt	474	466	464	8.06 ± 0.03	439 (4.05×10^4)	11.44 ± 0.01
m-Me	472	463	466	8.07 ± 0.05	435 (5.92×10^4)	10.91 ± 0.02
m-Cl	434	460	465	7.30 ± 0.01	437 (4.62×10^4)	10.87 ± 0.01
m-COOH	433	456	462	8.31 ± 0.02	439 (3.28×10^4)	10.54 ± 0.05
m-NO_2	426	447	445	6.98 ± 0.02	442 (4.71×10^4)	10.36 ± 0.01

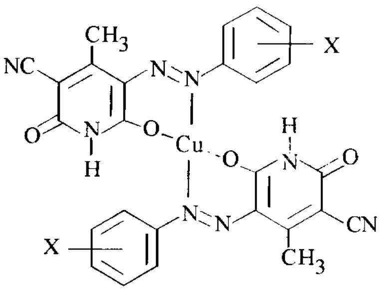
For determining a formation constant the absorbance values of a series metal + ligand mixtures which were prepared from their 10^{-5} M solutions as 1 ml + 9 ml, 1.5 ml + 8.5 ml, etc., were measured.

Formation constants were calculated for each mixture. Average values and standard deviations were calculated and tabulated in Table 3.

RESULTS AND DISCUSSION

The structure of the azopyridone dyes (**1–11**) prepared by coupling 3-cyano-6-hydroxy-4-methyl-2 (IH) pyridone with diazotized *p*- and *m*-substituted anilines and their Cu(II) complexes (**1′–11′**) were shown below.





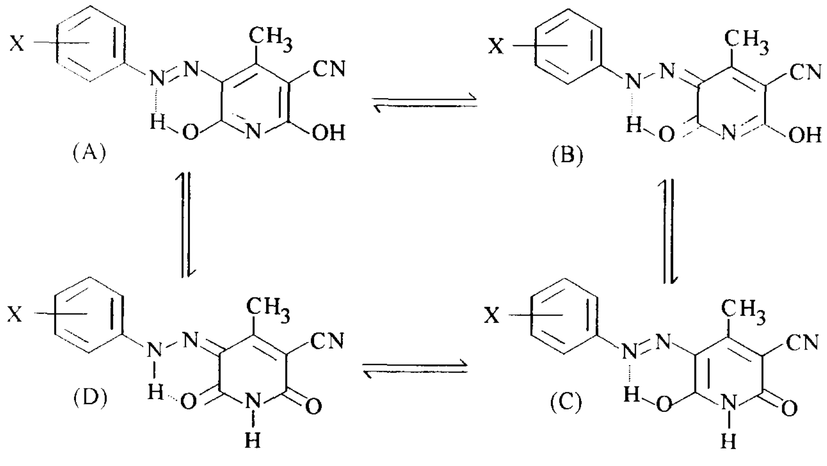
X = H m-OEt, m-Me, m-COOH, m-Cl, m-NO_2
p-OEt, p-Me, p-COOH, p-Cl, p-NO_2

The dyes prepared may exist in four tautomeric forms, namely A–D (Scheme 1). The infrared spectra of all the dyes showed two intense carbonyl bands at about 1681 and 1630 cm^{-1}, which were therefore assigned to the dikethoydrazone form D. The spectra exhibited a broad band in the region 3080–3200 cm^{-1}. The low frequency and the broadening of this band suggest that these compounds are strongly involved in hydrogen bonding in the solid state. The ^1H NMR spectra of dyes exhibit a broad signal near 15.1–15.6 ppm. This signal corresponds to imine NH proton resonance of the hydrazone form. It has been reported that the hydroxyazo OH proton resonance is 3–5 ppm higher than the hydrazone NH proton resonance.[8,9] Lycka and Machacek[10] and Mustroph,[11] from ^{13}C and ^{15}N NMR studies of some N-alkyl derivatives of azopyridones, concluded that the equilibrium was in favour of the diketohydrazone form D in solutions.

Furthermore, Peng *et al.*[12] have reported the ^1H NMR spectra of some azopyridone dyes in $CDCl_3$; these exist in the hydrazone form D and show NH peaks within the range of 14.30–16.09 ppm. These results suggest that the dyes prepared exist in the hyrazone form in the solid state and acidic solutions.

Visible absorption maxima of the dyes (Table 3) showed bathocromic shifts as the solvent polarity increases. This positive solvatochromism is also evident for the hydrazone form.[13]

Introduction of an electron accepter substituent into the diazo moiety at the para or meta position produces a slight effect (for dye **6** $\Delta\lambda$: 4 nm relative to dye **1**), whereas electron donor substitiuents produce strong bathocromic shifts (e.g. dye **2**, $\Delta\lambda = 33$ nm relative to dye **1**) in chloroform. Similiar results



Scheme 1

were also observed in methanol. However, in 80% (v/v) ethanol–water all of the substituents produced bathochromic shifts, with the exception of the *m*-nitro substituent.

All the synthesized complexes were brown insoluble solids. Magnetic measurements showed one unpaired electron ($\mu_{eff} = 1.78$–1.91 BM), as expected from the d^9 electronic structure of the Cu^{2+} ion. The results of the elemental analysis (Table 1) were in good agreement with those required by the suggested formulae.

In the IR spectra of the complexes (Table 2) the absorbtion of the nitrile group shifted to lower frequencies than those for the azo dyes. The complexes showed one strong single carbonyl absorbtion in the region 1665–1645 cm^{-1}. The second carbonyl absorbtion band, which appears in the spectra of the dyes, was not observed but new bands due to C–O and Cu–O vibrations in the range of 1281–1255 cm^{-1} and 476–421 cm^{-1} appeared in the spectra of the complexes.

The visible absorbtion maxima of all the complexes (except **6′**) shifted to lower wavelength; $\Delta\lambda_{max}$ values were in the range 3–37 nm. The absorbtion maximum of the complex **6′** in the visible region shifted bathochromically.

Ionization constants of the dyes

The pKa values of dyes **1–11** determined by the spectrophotometric titration method at 27 ± 0.1°C in 80% (v/v) ethanol–water mixture are given in Table 3. The absorption pattern was in each case characterized by the presence of two maxima in the ranges of 416–430 nm and 445–494 nm for the anionic and molecular species, respectively. The absorption spectra of the dyes in both strongly acidic and neutral solution were found to be the same. As the pH value of the solution increased the height of the former band increases and simultaneously that of the latter band decreases. Spectra recorded at different pH values in each case showed an isospestic point. This indicates that two species are in equilibrium.

Figure 1 shows the spectra of dye **2** at different pH values, taken as a typical example of the series. The spectral characteristics of the dyes are in agreement with Peng's results.[14] Therefore, the higher absorption frequencies of the dyes studied in basic solutions was assigned to the common anion E, which is the common conjugate base of both tautomers, as shown in Scheme 2.

The pKa values of the dyes were found to be within the range 6.98–8.57. Substituents in the diazo component do not exhibit the expected effect on pKa values. The pKa values for the dyes with electron-withdrawing substituents seem to be smaller than those for the dyes with electron-donating substituents. These results are also consistent with those of *N*-alkyl derivatives obtained in aqueous solutions.[15] In addition, no linearity has been observed

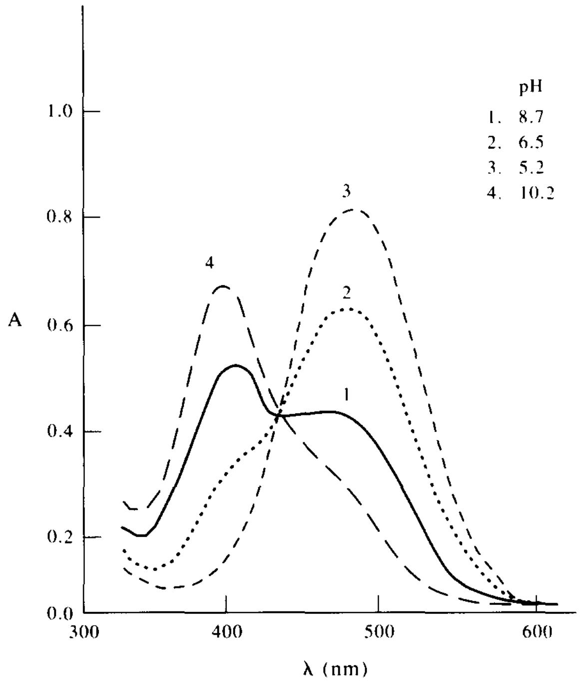
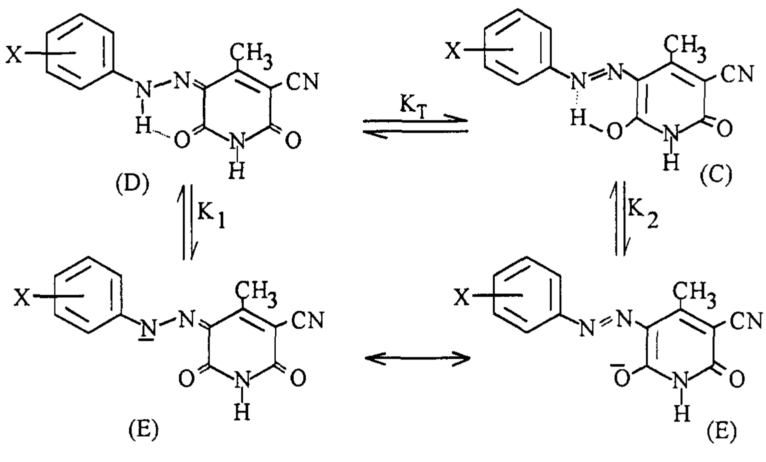


Fig. 1. Visible absorbtion spectra of dye **2** at different pH values.



Scheme 2

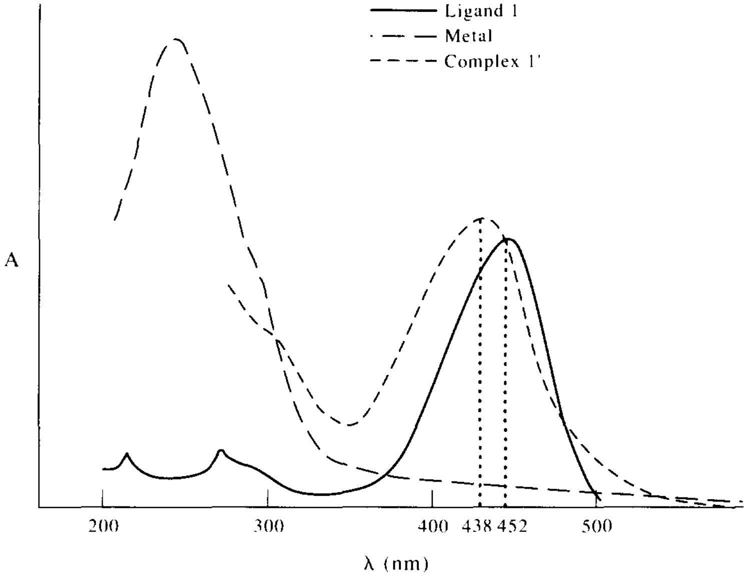


Fig. 2. UV–visible absorbtion spectra of Cu^{2+} ion, ligand dye **1** and complex **1'**.

between λ_{max} of dyes **1–11** and Hammett substituent constants in 80% (v/v) ethanol–water solvent system. The discrepancy from linearity may be attributed to the solvent system used, since the tautomeric equilibria are strongly affected by type of solvent used.[16]

Formation constants of the complexes

Formation constants of the ML_2 type complexes of the azo dyes **1'–11'** are given in Table 3. The UV–visible absorbtion spectra of Cu^{2+} ion, ligand azo dye **1** and complex **1'** are shown in Fig. 2 as an example.

Log β values of -Cl, -COOH and -NO_2 substituted complexes were lower than those of unsubstituted complex (**1'**). This is an expected result, since electron-withdrawing groups decrease the basicity of donor atoms and hence the chelation ability of the ligands decrease. On the other hand log β values of Me and OEt substituted complexes were higher than those of complex **1'**, since these groups increase the basicity of donor atoms (N and O) in the ligand molecules. Hence it may be concluded that more stable complexes are formed by stronger bases.

The log β value of *m*-Me substituted complex (**8'**) was almost the same as that of unsubstituted complex (11.91 and 11.92, respectively). Similiar results was also observed for pKa values of dyes **8** and **1** (8.07 for each).

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REFERENCES

1. Annen, O., Egli, R., Henzi, B., Jakob, H. & Matzinger, P., *Rev. Prog. Color.*, **17** (1987) 72.
2. Wang, I. J. & Wang, P. Y., *Textile Res. J.*, **60** (1990) 297.
3. Schwander, H. R., *Dyes and Pigments*, **3** (1982) 133.
4. Wang, I. J., Hsu, Y. J. & Tian, J. H., *Dyes and Pigments*, **16** (1991) 83.
5. Bobbitt, J. M. & Scola, D. A., *J. Org. Chem.*, **25** (1960) 560.
6. Brown, B. H. & Philpott, P. G., *J. Chem. Soc.*, 7185 (1965).
7. Van Uitert, L. G. & Haas, C. G., *J. Am. Chem. Soc.*, **75** (1953) 45.
8. Shawali, A. S., Harb, N. M. S. & Badahdah, K. D., *J. Heterocyclic Chem.*, **22** (1985) 1397.
9. Yoder, C. H., Barth, R. C., Ritcher, W. M. & Snavely, F. A., *J. Org. Chem.*, **37** (1972) 4121.
10. Lycka, A. & Machacek, V., *Dyes and Pigments*, **7** (1986) 171.
11. Mustroph, H., *Z. Chem.*, **29** (1989) 422.
12. Peng, Q., Li, M., Gao, K. & Cheng, L., *Dyes and Pigments*, **14** (1990) 89.
13. Stoyanov, S. & Antonov, L., *Dyes and Pigments*, **10** (1988) 33.
14. Peng, Q., Li, M., Gao, K. & Cheng, L., *Dyes and Pigments*, **18** (1992) 271.
15. Peng, Q., Li, M., Gao, K. & Cheng, L., *Dyes and Pigments*, **15** (1991) 263.
16. Kishimoto, S., Kitahara, S., Manabe, O. & Hiyama, H., *J. Org. Chem.*, **43** (1978) 3882.