Synthesis of New Azo Dyes and Copper(II) Complexes Derived from Barbituric Acid and 4-Aminobenzoylhydrazone

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Four new azo dyes, $\mathbf{L}^1$, $\mathbf{L}^2$, $\mathbf{L}^3$, and $\mathbf{L}^4$, were prepared by linking benzaldehyde *p*-aminobenzoylhydrazone (**3**) and *p*-hydroxybenzaldehyede *p*–aminobenzoylhydrazone (**4**) to barbituric acid and 1,3-dimethylbarbituric acid through diazo-coupling reactions. Reactions of the azo-dyes with copper chloride and bidentate ligand, 1,10-phenanthroline, produced mixed-ligand dinuclear complexes with general stoichiometry $[Cu_2L(phen)_2]Cl_2$ (**7**, **8**, **9**, and **10**). The structures of both azo dyes and their complexes were identified by elemental analyses, FT-IR, ^{1}H-NMR, UV-VIS, magnetic susceptibility, and mass spectral data.

Key Words: Azo-dyes, copper(II) complexes, barbituric acid, hydrazone, mixed-ligand.

Introduction

Azo compounds are a very important class of chemical compounds receiving attention in scientific research. They are highly colored and have been used as dyes and pigments for a long time.[1,2] Furthermore, they have been studied widely because of their excellent thermal and optical properties in applications such as optical recording medium,[3−6] toner,[7,8] ink-jet printing,[9,10] and oil-soluble lightfast dyes.[11] Recently, azo metal chelates have also attracted increasing attention due to their interesting electronic and geometrical features in connection with their application for molecular memory storage, nonlinear optical elements, and printing systems.[4,6,12] In this work, we synthesized 4 new azo-dyes by bringing together 2 important chemical compounds, barbituric acid and hydrazone, and copper(II) complexes by using these dyes and 1,10-phenanthroline. The chemical structures of both azo dyes and azo metal complexes were studied.

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Experimental

General

All the reagents and solvents were of reagent-grade quality and purchased from commercial suppliers. Melting points were determined on a Buchi SMP-20 melting point apparatus. Infrared spectra (in KBr pellets) were recorded on a Perkin–Elmer 1605 FT-IR spectrometer. ^{1}H-NMR spectra were recorded on a Bruker 250 MHz spectrometer in DMSO-d_6 using TMS as an internal reference. The electronic spectra of the ligands and complexes were recorded on a UV-1601 Shimadzu spectrophotometer in DMSO. Magnetic susceptibility measurements were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK 1) at room temperature (298 K) by using Hg[Co(SCN)$_4$] as a calibrant. Mass spectra were recorded on an Agilent 1100 MSD LC/MS Spectrometer. Metal concentrations were determined with a GBC Avanta Atomic Absorption Spectrometer in solution, prepared by decomposition of the complexes with HNO$_3$ followed by dilution with deionized water.

Synthesis of the azo dyes

4-Aminobenzohydrazide (**2**) was prepared by refluxing ethyl $p-$aminobenzoate (**1**) (10 mmol, 1.51 g) with hydrazine hydrate (2.5 mL) for 4 h.[13,14] Benzaldehyde 4-aminobenzyllhydrazone (**3**) and 4-hydroxybenzaldehyede 4-aminobenzoylhydrazone (**4**) were synthesized according to the reported method.[15−17]

Diazotization

Benzaldehyde 4-aminobenzoylhydrazone (**3**) and 4-hydroxybenzaldehyde 4-aminobenzoylhydrazone (**4**) (10 mmol) were dissolved in 5 mL of 2 M HCl. The solution was then cooled to 0-5 °C in an ice-bath and maintained at this temperature. Sodium nitrite (5 mmol, 0.345 g) solution in water (5 mL) was then added dropwise. Stirring was continued for 30 min to produce diazonium salts **5** and **6** at the same temperature.

Preparation of 4-[(*E*)-(2-hydroxy-4,6-dioxocyclohex-1-en-1-yl)diazenyl]-N'-[(1*E*)-phenylmethylene]benzohydrazide (L^1)

The diazonium solution of **5** was added portionwise to the coupling component solution prepared by mixing a suspension of barbituric acid (5 mmol, 0.64 g) in 75 mL of water with sodium carbonate (15 mmol, 1.6 g) dissolved in 40 mL of water. During the procedure the pH value was maintained within 9-10, and the temperature at 0-5 °C. The mixture was stirred for 6 h, and then the pH value was decreased to ∼6. The mixture was left overnight. The precipitated crude dyes were collected by filtration, and washed with water, ethanol, and acetone. EIMS, (positive ion) m/z (relative intensity): 379.1 [M$^+$+1, (95.6)], 380.0 [M$^+$+2, (20.2)]. ^{1}H-NMR (ppm): 14.30 (s, 1H, O-H···N), 11.90 and 11.60 (s, 1H, N-H), 11.35 (s, 1H, N-H), 8.71 (s, 1H, N=CH), 7.71-8.26 (m, 9H, Ar-H). UV (λ_{max}, nm, DMSO): 258, 294, and 395.

Preparation of 4-[(*E*)-(2-hydroxy-3,5-dimethyl-4,6-dioxocyclohex-1-en-1-yl)diazenyl]-N'-[(1*E*)-phenylmethylene]benzohydrazide (L^2)

The diazonium solution of **5** was added portionwise to the coupling component solution prepared by mixing a suspension of 1,3-dimethyl barbituric acid (5 mmol, 0.78 g) in 75 mL of water with sodium carbonate (15 mmol, 1.6 g) dissolved in 40 mL of water exactly as described above to give **L^2**. EIMS, (positive ion) m/z
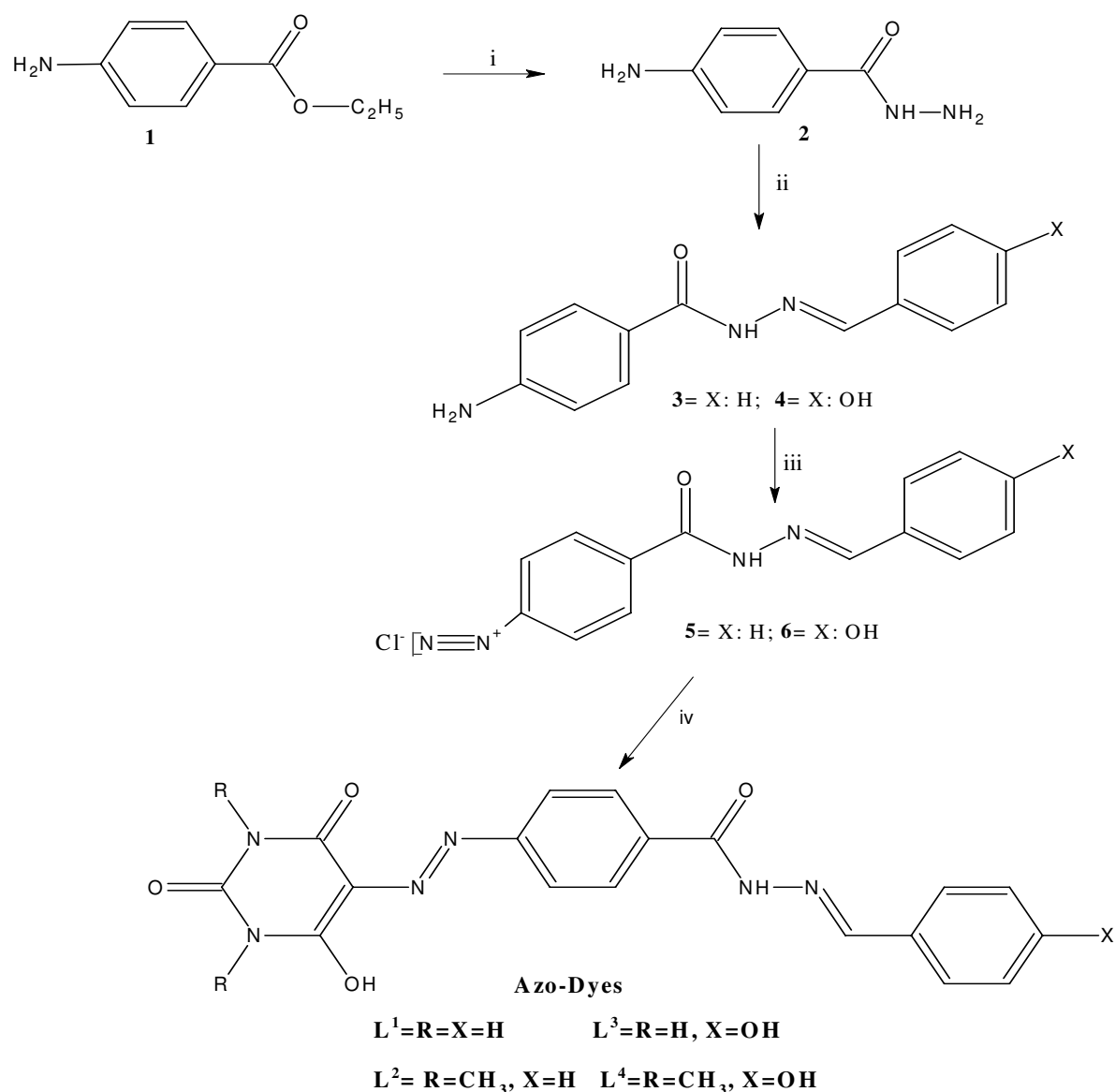
Scheme i) NH₂NH₂•H₂O, reflux 4 h; ii) benzaldehyde or p-hydroxybenzaldehyde, EtOH, HOAc, reflux 1 h; iii) NaNO₂, HCl, 0-5 °C; iv) barbituric acid or 1,3-dimethyl barbituric acid, Na₂CO₃, 0-5 °C, 6 h.

(relative intensity): 407.01 [M^++1, (100)], 408.0 [M^++2, (25.1)]. ^{1}H-NMR (ppm): 14.14 (s, 1H, O-H$\cdots$N), 11.87 (s, 1H, N-H$_{hyd}$), 8.47 (s, 1H, N=CH), 7.47-8.03 (m, 9H, Ar-H), 3.24 (s, 6H, N-CH₃). UV (λ_{max}, nm, DMSO): 253, 295, and 393.

Preparation of 4-[(E)-(2-hydroxy-4,6-dioxocyclohex-1-en-1-yl)diazenyl]-N'-[(1E)-(4-hydroxyp-henyl)methylene]benzohydrazide (L³)

The diazonium solution of **6** was added to portionwise to the coupling component solution prepared by mixing a suspension of barbituric acid (5 mmol, 0.64 g) in 75 mL of water with sodium carbonate (15 mmol, 1.6 g) dissolved in 40 mL of water exactly as described above for dye **L¹** to give **L³**. EIMS, (positive ion) m/z

(relative intensity): 395.0 [M^++1, (80.8)], 396.2 [M^++2, (13.5)]. ^{1}H-NMR (ppm): 15.11 (s, 1H, O-H$\cdots$N), 11.52, and 11.66 (s, 1H, N-H), 11.40 (s, 1H, N-H), 9.93 (s, 1H, O-H), 8.33 (s, 1H, N=CH), 8.02 (d, 2H, J=8.55 Hz, Ar-H), 7.71 (d, 2H, J=8.58 Hz, Ar-H), 7.57 (d, 2H, J=8.37 Hz, Ar-H), 6.85 (d, 2H, J=8.40 Hz, Ar-H). UV (λ_{max}, nm, DMSO): 257, 295, 312 sh, and 396.

Preparation of 4-[(*E*)-(2-hydroxy-3,5-dimethyl-4,6-dioxocyclohex-1-en-1-yl)diazenyl]-N'-[(1*E*)-(4-hydroxyphenyl)methylene]benzohydrazide (L^4)

The diazonium solution of **6** was added to portionwise to the coupling component solution prepared by mixing a suspension of 1,3-dimethylbarbituric acid (5 mmol, 0.78 g) in 75 mL of water with sodium carbonate (15 mmol, 1.6 g) dissolved in 40 mL of water exactly as described above to give L^4. EIMS, (positive ion) m/z (relative intensity): 423.1 [M^++1, (88.3)], 424.0 [M^++2, (14.9)]. ^{1}H-NMR (ppm): 14.13 (s, 1H, O-H$\cdots$N), 11.67 (s, 1H, N-H$_{hyd}$), 9.94 (s, 1H, O-H$_{fenol}$), 8.34 (s, 1H, N=CH), 8.01 (d, 2H, J=8.61 Hz, Ar-H), 7.75 (d, 2H, J=8.61 Hz, Ar-H), 7.56 (d, 2H, J=8.48 Hz, Ar-H), 6.85 (d, 2H, J=8.51 Hz, Ar-H), 3.24 (s, 6H, N-CH$_3$). UV (λ_{max}, nm, DMSO): 258, 298, 312 sh, and 398.

Preparation of copper(II) complexes (7, 8, 9, and 10)

To a solution of $CuCl_2?2H_2O$ (2 mmol, 0.35 g) in methanol (10 mL) was added dropwise a solution of 1,10-phenanthroline monohydrate (phen) (2 mmol, 0.38 g) in 10 mL of methanol with constant stirring. The resulting colored suspension was stirred and heated for 15 min. Then 1 mmol of ligand [L^1 (1 mmol, 0.378 g for complex **7**) or L^2 (1 mmol, 0.394 g for complex **8**) or L^3 (1 mmol, 0.406 g for complex **9**) or L^4(1 mmol, 0.422 g for complex **10**)] dissolved as a suspension in the same solvent (25 mL) was added and the resulting mixture was refluxed for 5 h. The colored precipitate was filtered off and washed several times with methanol and dried in vacuo.

Results and Discussion

Structure identification of azo-dyes

The azo-dyes having barbituric acid and hydrazone moieties as prepared in this study may exist in tautomeric forms as shown in Schemes 1 and 2. The infrared spectra of azo-dyes show 2 intense bands appearing at 1753 and 1710 cm^{-1} for L^1, 1724 and 1678 cm^{-1} for L^2, 1753 and 1711 cm^{-1} for L^3, and 1726 and 1664 cm^{-1} for L^4. These peaks are attributed to 2 carbonyl groups at the 2- and 6- positions of the pyrimidine ring. A broad hydroxyl (-OH) peak is observed within the region 3243-3359 cm^{-1}. The low frequency and the broadening of these bands suggest that these ligands have a strong hydrogen bonding (O-H$\cdots$N) in the solid state.[6,20−24,27] The peaks appearing in the region 1603-1611 cm^{-1} are attributed to ν(C=N) stretching vibration. Therefore, on the basis of 2 carbonyl groups and hydroxyl vibrations it may be concluded that there is a shift of equilibrium to the pyridine-2,4,6-trion configuration side of the azo-dyes and the ligands exist in diketoazo form **(III)** in the solid state (Scheme 1).[18−21] The band belonging to ν(N-H) stretching vibration is not observed probably due to overlapping with the broad hydroxyl peak. The hydrazone side of the azo-dyes also may exist in keto **(VI)** or enol **(VII)** tautomeric form in the solid state (Scheme 2).[6,26] The absorption of the strong ν(C=O) absorption band around 1645-1657 cm^{-1} in the infrared spectra of the azo-dyes suggests that the hydrazone side of the azo-dyes is in the keto form **(VI)** in the solid state.[14−17,27−29]

The tautomeric keto forms of the dyes are also indicated by ^{1}H-NMR spectroscopy. The enolic OH signals of the enol forms of the compounds are not observed while the amide NH signals of the keto forms appear around 11.30-11.87 ppm. The other characteristic peaks such as IR data of these compounds are given in Table 2. These data are in agreement with those previously reported for similar compounds.[13−17,30]

Table 1. Yields and characterization data for azo-dyes.

Dyes	Formula	Mp (°C)	Yield (%)	Color	μ_{eff} (BM)	Calculated (found) %			
						C	H	N	Cu
L^1	$C_{18}H_{14}N_6O_4$	328	68	Dark brown	-	57.14 (57.06)	3.70 (3.78)	22.22 (22.16)	
7	$C_{42}H_{28}N_{10}O_4Cl_2Cu_2$	>300	89	Dark green	1.95	53.96 (53.98)	3.00 (2.93)	14.99 (14.94)	13.60 (13.50)
L^2	$C_{20}H_{18}N_6O_4$	294	65	Light yellow	-	59.11 (58.98)	4.43 (4.29)	20.69 (20.61)	
8	$C_{44}H_{32}N_{10}O_4Cl_2Cu_2$	>300	85	Dark green	1.91	54.89 (54.82)	3.33 (3.27)	14.55 (14.49)	13.20 (13.15)
L^3	$C_{18}H_{14}N_6O_5$	325	70	Dark brown	-	54.82 (54.91)	3.55 (3.48)	21.32 (21.17)	
9	$C_{42}H_{28}N_{10}O_5Cl_2Cu_2$	>300	86	Dark green	2.06	53.05 (52.96)	2.95 (2.86)	14.74 (14.67)	13.37 (13.31)
L^4	$C_{20}H_{18}N_6O_5$	280	72	Light brown	-	56.87 (56.78)	4.27 (4.19)	19.91 (19.82)	19.91 (19.82)
10	$C_{44}H_{32}N_{10}O_5Cl_2Cu_2$	>300	85	Dark green	2.12	53.99 (53.92)	3.27 (3.21)	14.31 (14.26)	12.99 (12.93)

Table 2. The IR spectral data of the azo-dyes and their complexes, (KBr, cm^{-1}).

| Dyes	υ(O-H)	υ(C=O)	υ(>C=N-N=C>)	υ(C=N)	υ(N=N)	υ(C-N)	υ(C-O)
L^1	3254	1753, 1710, 1656	-	1605	1452	1354	1258
7	-	1751, 1709	1607	-	1434	1355	1258
L^2	3328	1724, 1678, 1645	-	1611	1456	1360	1280
8	-	1718, 1670	1615	-	1422	1363	1279
L^3	3343	1753, 1709, 1657	-	1605	1445	1354	1256
9	3407	1752, 1710	1620	-	1435	1355	1259
L^4	3359	1726, 1664, 1645	-	1603	1450	1359	1286
10	3437	1722, 1663	1518	-	1440	1361	1287
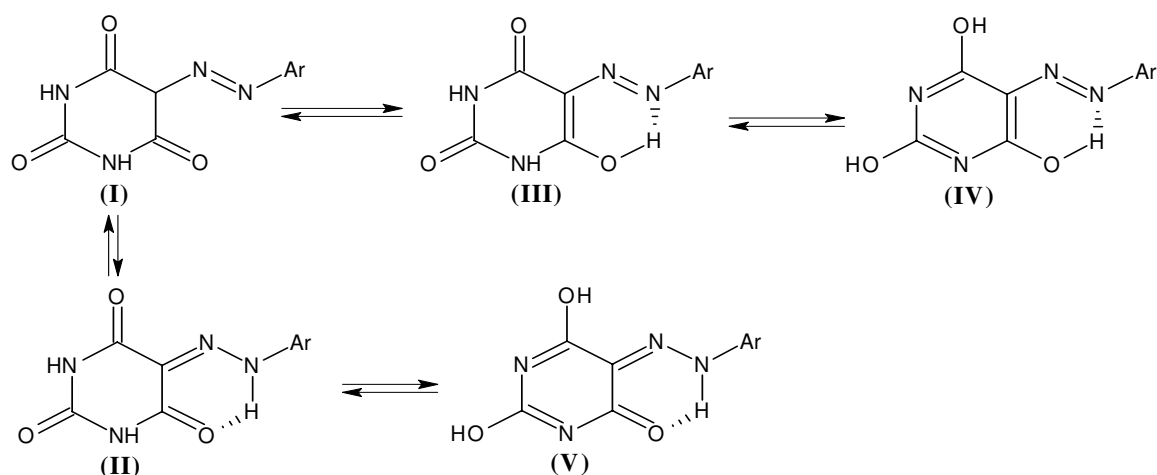
Tautomeric forms of L^1 and L^3
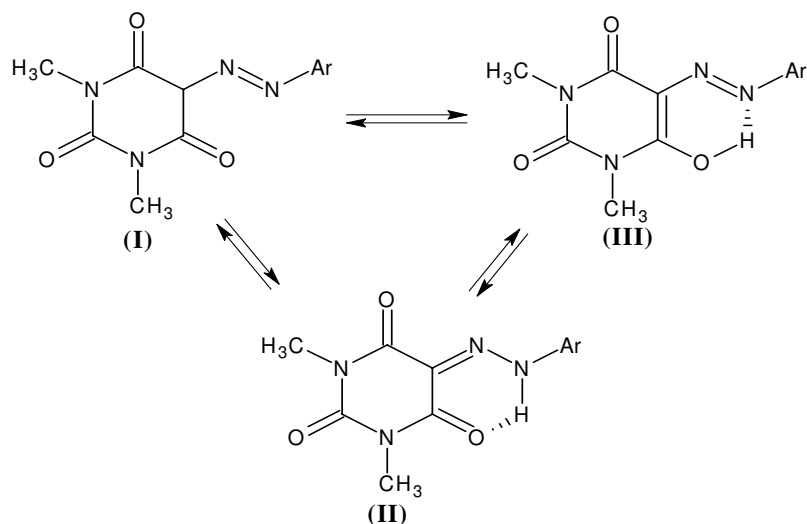
Tautomeric forms of L^2 and L^4

Scheme 1. Tautomeric forms of the barbituric acid moiety of the azo-dyes.
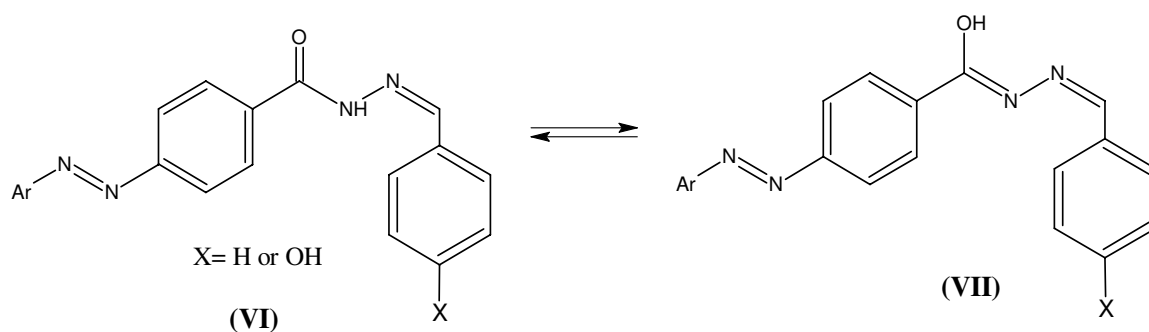
Scheme 2. Tautomeric forms of the hydrazone moiety of the azo-dyes.

The ^{1}H-NMR spectra of azo-dyes show a singlet due to the hydrogen bonded OH proton in the region of 14.13-15.11 ppm. It is well known that hydrogen bonded OH proton resonance appears at a lower field than that of NH proton resonance. Therefore, it may be concluded that these compounds also exist in the

azo form **(III)** in solutions.[21,23,24,31] On the other hand, the resonance of the phenolic OH proton of $\mathbf{L}^3$ and $\mathbf{L}^4$ is observed as a singlet at a relatively higher field, at 9.93 ppm and 9.94 ppm, respectively. Two singlet peaks between 11.52 and 11.90 ppm owing to NH protons, at the 1- and 3- positions of pyrimidine ring, are observed for $\mathbf{L}^1$ and $\mathbf{L}^3$ dyes. The proton of the amide group (NH) at the hydrazone side appears also as a singlet in the region of 11.35-11.87 ppm for all azo-dyes.[18,26] The other resonances observed for azo-dyes are given in the Experimental section.

Mass spectra (positive polarity) of azo-dyes show signals at 379.1 m/z and 380.0 m/z for $\mathbf{L}^1$, at 407.01 m/z and 408.0 m/z for $\mathbf{L}^2$, 395.0 m/z and 396.2 m/z for $\mathbf{L}^3$, and 423.1 m/z and 424.0 m/z for $\mathbf{L}^4$ corresponding to their $[M+1]^+$ and $[M+2]^+$ ion peaks, respectively. The results of the elemental analysis (Table 1) and mass spectra are in good agreement with those required for the proposed structure.

The electronic absorption spectral characteristics of the azo compounds in DMSO are given in the Experimental section. The azo-dyes have 3 strong absorptions (Figure 1). The shortest wavelength, appearing at 253-258 nm, may be attributed to $\pi \rightarrow \pi^*$ transition of the benzenoid moiety of the compounds and intra-ligand $\pi \rightarrow \pi^*$ transition. The second band, observed in the region of 294-312 nm, is attributed $n \rightarrow \pi^*$ electronic transition of the –N=N- group. The third band, appearing in the visible region (395-398 nm), can be assigned to $\pi \rightarrow \pi^*$ transition involving the whole electronic system of the azo-dyes.
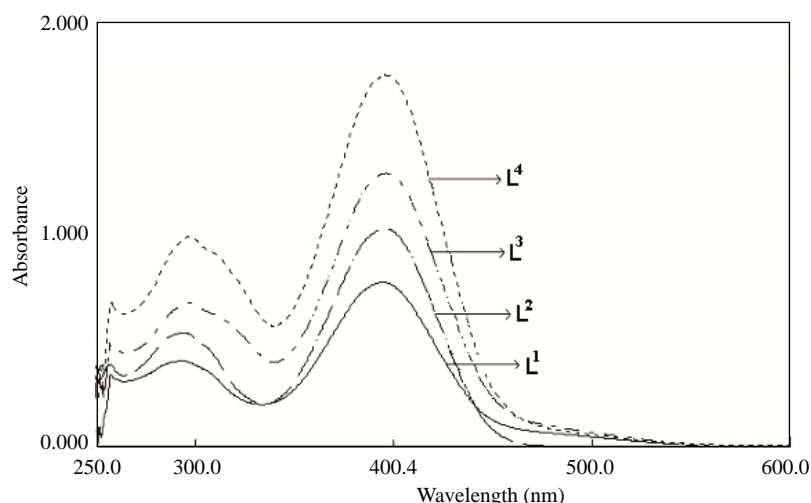

Figure 1. Absorption spectra of dyes; $\mathbf{L}^1$, $\mathbf{L}^2$, $\mathbf{L}^3$, and $\mathbf{L}^4$ in DMSO.

Structure identification of azo-metal complexes

The reaction of copper(II) chloride with 1,10-phenanthroline and azo-dyes in methanol gives mixed-ligand dinuclear copper(II) complexes with the general formula $[Cu_2L(phen)_2]Cl_2$. Elemental analysis, magnetic susceptibility, and IR spectroscopies were used to characterize the azo-copper complexes. The characteristic IR frequency values of the azo-dyes and their copper complexes are given in Table 2. The IR spectra of the complexes showed significant differences from those of the free dyes. In the IR spectra of the complexes, 2 strong carbonyl absorptions were observed in the region of 1751-1663 cm^{-1}. The third carbonyl absorption band and υ(C=N) stretching band at the hydrazone moiety of the azo-dyes appearing in the spectra of metal free azo compounds were not observed but a new band appeared between 1607 and 1620 cm^{-1} probably due to >C=N-N=C< stretching vibration suggesting that the NH proton of the hydrazone side of the dyes was lost via enolazition and the resulting enolic oxygen and the azomethine nitrogen are involved in

coordination.[14,15,27,28,30,31] The IR spectra of the complexes derived from L^3 and L^4 show a broad band at 3437 cm^{-1} and 3407 cm^{-1}, respectively, which can be attributed to the free OH stretching, indicating non-involvement of the phenolic OH group in coordination.[14,15] The movement of υ(N=N) stretch of the complexes to relatively lower energy $\sim$10 cm^{-1} compared to that of free dyes indicates coordination via the N=N group.[24-26] The υ(C=N) vibration of the phenanthroline ring could not be assigned since the spectra were complicated by many bands in the 1300-1600 cm^{-1} region. On the basis of IR spectral data we concluded that the barbituric acid side of azo-dyes exists in diketoazo form during complexation, while the hydrazone side exists in enol tautomeric form. In the complexes, the azo-dyes act as dianionic tetradentate ligands (Figure 2).
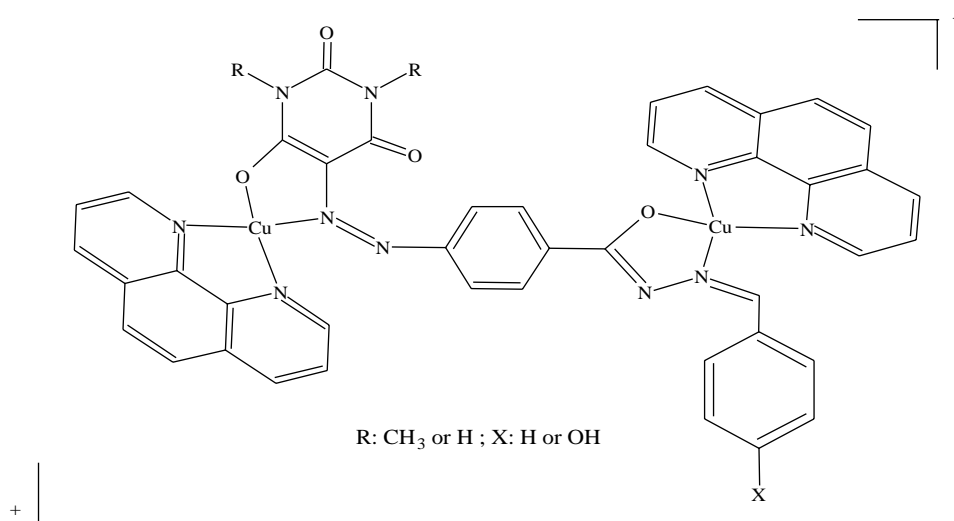

R: CH$_3$ or H ; X: H or OH

Figure 2. Proposed structure for the mixed-ligand dinuclear complexes.

The magnetic moment data of the solid state complexes at room temperature are reported in Table 1. The magnetic moment values of the copper(II) complexes are in the region of 2.91-2.12 μ_B at 298 K. It is seen that these magnetic moment values of copper complexes are slightly higher than the theoretical value of 1.73 μ_B for one d^9 copper ion, while they are also lower than that expected for dinuclear copper(II) complexes. These subnormal magnetic moment values of the dinuclear complexes may be explained by a weak antiferromagnetic intramolecular interaction since this situation can occur when 2 equivalent metal ions are coupled via an exchange interaction in a polynuclear complex.[15,32,33]

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