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Synthesis and spectroscopic properties of new azo-dyes and azo-metal complexes derived from barbituric acid and aminoquinoline

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Abstract

Two new azo-dyes, 5-(quinoly-8-azo)pyrimidine-2,4,6-trione (**L_1**) and 5-(quinoly-8-azo)-1,3-dimethylpyrimidine-2,4,6-trione (**L_2**) were prepared by linking 8-aminoquinoline to barbituric acid and 1,3-dimethylbarbituric acid through diazo-coupling reactions. Reaction of new azo-dyes with Cu(II) or Ni(II) salts and unidentated ion gave mononuclear complexes with general stoichiometry [MLX], [M: Ni(II) or Cu(II); X: NO_3^-, SCN^-, CN^- or N_3^-]. On the other hand, two kinds of cobalt(II) complexes with different stoichiometries were prepared. Reaction of azo-dyes with $Co(AcO)_2$ with 2:1 molar ratio gave azo complexes with stoichiometry $Co(L)_2$ while reaction of cobalt salts with tridentate azo-dyes, bidentate ligand, 1,10-phenanthroline (**B**), and unidentate ion (X: NO_3^-, SCN^-, CN^- or N_3^-), mixed hard–soft donor sets, produced a new set of complexes with general stoichiometry CoLBX. The structures of both azo-dyes and their complexes were identified by elemental analyses, FTIR, ^{1}H NMR, UV–vis, magnetic susceptibility and mass spectral data. The elemental analyses and spectral data indicate that azo-dyes act as monobasic *O,N,N′*-tridentate ligand. The difference in absorption maximum from ligands to metal complexes was also studied.

Keywords: Azo-dyes; Complexes; Barbituric acid; (8-Quinolinyl)amine; Spectroscopy

1. Introduction

Azo compounds are highly colored and have been used as dyes and pigments for a long time. They have been receiving much attention and have been widely used in many practical applications such as coloring fibers [1,2], photoelectronic applications [3], printing systems [4,5], optical storage technology [6,7], textile dyes [8–10] as well as in many biological reactions [11–13] and in analytical chemistry [14,15]. Recently, metal complex dyes have also attracted increasing attention due to their interesting electronic and geometrical features in connection with their application for molecular memory storages, nonlinear optical elements, printing system, etc [4,6,16]. Therefore, several studies have been published on the synthesis and spectral properties of several azo barbiturates and aminoquinoline, as well as their transition metal complexes, so far [17–24].

In this work, we synthesized two new azo-dyes by bringing together two important chemical compounds barbituric acid and quinoline, and metal dye complexes by using new dyes, appropriate simple ligand and metal ions. The chemical structures of both azo-dyes and azo-metal complexes were studied. Also, the relationships between the difference in absorption maximum from ligands to their metal complexes and simple ligands to azo-metal complexes were studied.

2. Experimental

2.1. General

All the reagents and solvents were of reagent-grade quality and were purchased from Merck and Aldrich and used without

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further purification. Melting points were determined on a Bushi SMP-20, melting point apparatus. Infrared spectra (in KBr pellets) were recorded on a Perkin–Elmer 1605 FTIR 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 GBC Avanta Atomic Absorption Spectrometer in solution, prepared by decomposition of the complexes with HNO_3 followed by dilution with deionized water.

2.2. Synthesis of the azo-dyes

2.2.1. Diazotization

8-Aminoquinoline (10 mmol, 0.144 g) was 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 (10 mmol, 0.069 g) water (5 ml) solution was then added drop wise. Stirring was continued for 10 min at the same temperature.

2.2.2. Preparation of 5-(quinoly-8-azo)pyrimidine-2,4,6-trione (*L₁*)

The diazonium solution was added portion wise to the coupling component solution prepared by mixing a suspension of barbituric acid (1 mmol, 0.128 g) in 10 ml of water with sodium carbonate (3 mmol, 0.32 g) dissolved in 15 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, then the pH value was decreased to ∼6. The mixture was kept overnight. The precipitated crude dyes were collected by filtration, washed with water, ethanol and acetone (positive ion) *m/z* (relative intensity): 284.0 [M^+, (100)], 284.9 [M^{2+}, (17)]. ^{1}H NMR (ppm): 15.47 (s, 1H, O–H···N), 11.82 (s, 1H, N–H), 11.60 (s, 1H, N–H), 9.26 (d, 1H, $J = 4.15$ Hz, Ar-H), 8.72 (d, 1H, $J = 8.21$ Hz, Ar-H), 8.24 (d, 1H, $J = 7.60$ Hz, Ar-H), 8.09 (d, 1H, $J = 8.12$ Hz, Ar-H), 7.95 (m, 2H, $J = 7.93$, 3.89, 4.21 Hz, Ar-H).

2.2.3. Preparation of 5-(quinoly-8-azo)-1,3-dimethyl-arrimidine-2,4,6-trione (*L₂*)

The diazonium solution was added portion wise to the coupling component solution prepared by mixing a suspension of 1,3-dimethylbarbituric acid (1 mmol, 0.156 g) in 10 ml of water with sodium carbonate (3 mmol, 0.32 g) dissolved in 15 ml of water exactly as described above to give $\mathbf{L_2}$ (positive ion) *m/z* (relative intensity): 312.0 [M^+, (100)], 313.1 [M^{2+}, (12)]. ^{1}H NMR (ppm): 15.34 (s, 1H, O–H···N), 9.05 (d, 1H, $J = 4.20$ Hz, Ar-H), 8.52 (d, 1H, $J = 8.40$ Hz, Ar-H), 8.05 (d, 1H, $J = 7.34$ Hz, Ar-H), 7.90 (d, 1H, $J = 7.72$ Hz, Ar-H), 7.75 (m, 2H, $J = 7.86$, 4.25, 4.15 Hz, Ar-H).

2.3. Preparation of nickel and copper azo complexes

2.3.1. [NiLNO₃] and [CuLNO₃]

A solution of $Ni(NO_3)_2 \cdot 6H_2O$ (1 mmol, 0.74 g) or $Cu(NO_3)_2 \cdot 6H_2O$ (1 mmol, 0.293 g) in methanol (15 ml) was added to a magnetically stirred suspension of ligands (1 mmol) in methanol (50 ml). A distinct change in color and a decrease in the pH of the clear solution were observed. After adding an equivalent amount of methanolic solution of triethylamine (0.1 M), the mixture was refluxed for 3 h and then 60 ml of water was added. The colored precipitate was filtered off, washed several times with methanol and diethyl ether, dried in vacuo.

2.3.2. [MLX] [M: Ni(II) or Cu(II); X: SCN^-, CN^-, or N_3^-]

A solution of $Ni(CH_3COO)_2 \cdot 6H_2O$ (1 mmol, 0.245 g) or $Cu(CH_3COO)_2 \cdot 2H_2O$ (1 mmol, 0.20 g) in methanol (15 ml) was added to a magnetically stirred suspension of ligands (1 mmol) in methanol (50 ml). After the mixture was refluxed for 10 min, an aqueous solution (5 ml) of KSCN, NaCN or NaN_3 (1 mmol) was added and the resulting mixture was refluxed for further 3 h. Then, 60 ml of water was added, and the precipitated colored complexes were filtered off, washed several times with methanol and diethyl ether, and dried in vacuo.

2.4. Preparation of cobalt azo complexes

2.4.1. [Co(L)₂]

A solution of $Co(CH_3COO)_2 \cdot 4H_2O$ (0.5 mmol, 0.125 g) in 20 ml of methanol was added to a magnetically stirred suspension of the ligands (1 mmol) in methanol (40 ml). After the mixture was refluxed for 3 h, 50 ml of water was added. The reddish-brown precipitate was filtered off, washed several times with methanol and diethyl ether, and dried in vacuo.

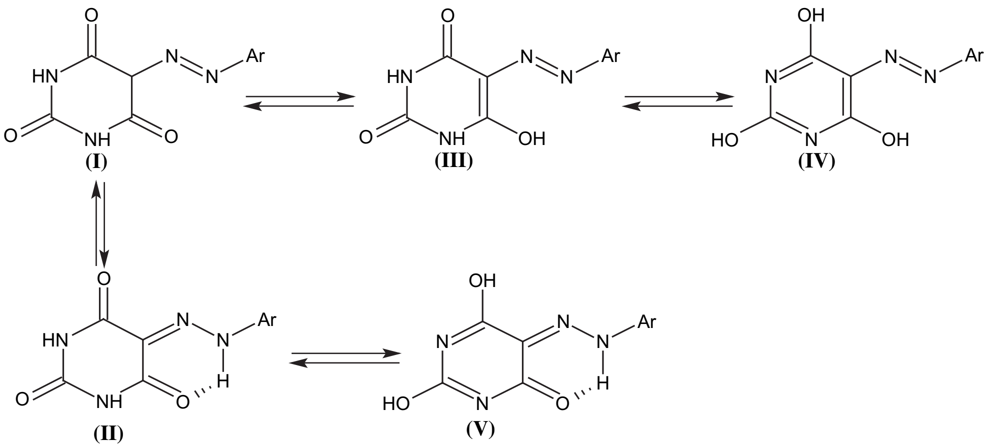
2.4.2. [CoLBX] (X: SCN^-, CN^- or N_3^-)

A solution of $Co(CH_3COO)_2 \cdot H_2O$ (1 mmol, 0.249 g) dissolved in 20 ml of methanol was added to a mixture $\mathbf{L_1}$ (1 mmol, 0.283 g) or $\mathbf{L_2}$ (1 mmol, 0.311 g) and 1,10-phenanthroline monohydrate (**B**) (1 mmol, 0.198 g) in 40 ml of methanol. The mixture was refluxed for 10 min. To this an aqueous solution (5 ml) of KSCN, NaCN or NaN_3 (1 mmol) was added, and refluxed for 3 h. After adding 60 ml water, the colored precipitate was filtered off, washed several times with methanol and finally with diethyl ether, and dried in vacuo.

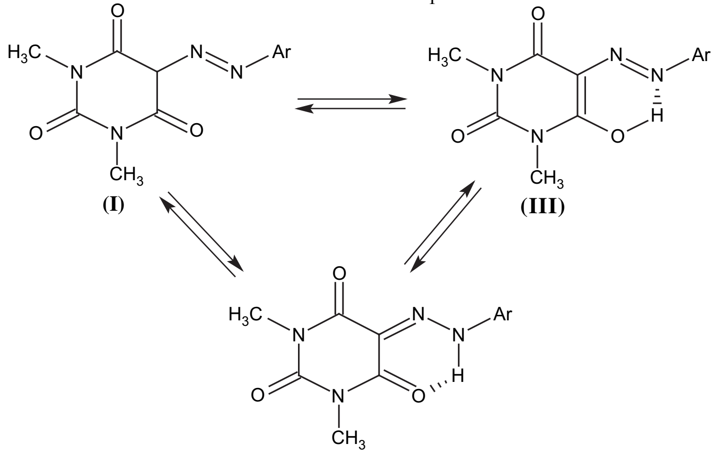
3. Results and discussion

3.1. Structure identification of azo-dyes

The azo-dyes prepared in this study may exist in tautomeric forms as shown in Scheme 1. The infrared spectra of $\mathbf{L_1}$ and $\mathbf{L_2}$ show three intense carbonyl bands appearing at 1714, 1678 and 1663 cm^{-1} for $\mathbf{L_1}$ and at 1711, 1667 and 1650 cm^{-1} for $\mathbf{L_2}$. The peaks appearing at 1636 cm^{-1} for $\mathbf{L_1}$



Tautomeric forms of L_1



Tautomeric forms of L_2

Scheme 1. Tautomeric forms of azo-dyes.

and at 1633 cm^{-1} for $\mathbf{L_2}$ are attributed to ν(C=N) stretching vibration. Also a broad band for hydroxyl group does not appear in the IR spectra of dyes. Therefore, on the basis of IR data we can conclude that there is a shift of equilibrium to pyridine-2,4,6-trione configuration and the ligands exist in triketohydrazo form (II) in the solid state [20,30]. The broad bands in the region of 3060–3200 cm^{-1} are attributed to ν(N–H) vibrations. The low frequency and the broadening of these bands suggest that these ligands have a strong hydrogen bonding (N–H···O) in the solid state [6,20–25,28]. The other characteristic peaks of these compounds appearing at 1386 cm^{-1} and 1085 cm^{-1} for $\mathbf{L_1}$ and at 1385 cm^{-1} and 1091 cm^{-1} for $\mathbf{L_2}$ are attributed to ν(C–N) and ν(N–N) modes, respectively.

The ^{1}H NMR spectra of ligands show a signal at 15.47 ppm for $\mathbf{L_1}$ and at 15.34 ppm for $\mathbf{L_2}$. These chemical shifts can be attributed to hydrogen bounded OH proton. It is well known that hydrogen bounded OH proton resonance appears at lower field than that of NH proton resonance. Furthermore, Song et al. [19,20] and Masoud et al. [23,24] have reported that azo-pyrimidine derivatives exist in the azo form in the absolute solvents. Therefore, it may be concluded that these ligands exist in the azo form (III) in solutions. In the ^{1}H NMR spectra of $\mathbf{L_1}$ two singlet peaks at 11.82 and 11.60 ppm are attributed to NH protons at the 1- and 3-positions of pyrimidine ring. A characteristic singlet for CH_3 groups at the 1- and 3-positions of pyrimidine ring appears at 3.28 ppm. The peaks appearing as a doublet in the 7.75–9.26 ppm are attributed to quinoline ring protons [25,27].

Mass spectra (positive polarity) of azo-dyes show signals at 284.0 *m/z* and 284.9 *m/z* for $\mathbf{L_1}$ and at 312.0 *m/z* and 313.1 *m/z* for $\mathbf{L_2}$ corresponding to their $[M+1]^+$ and $[M+2]^{2+}$ ion peaks. The results of the elemental analysis (Table 1) and mass spectra are in good agreement with those required by the proposed formulae.

3.2. Structure identification of azo-metal complexes

Reaction of azo-dyes with nickel and copper salts gave eight new complexes with general stoichiometry MLX [M: Ni(II) or Cu(II); X: NO_3^-, SCN^-, CN^- or N_3^-]. On the other hand, two kinds of cobalt(II) complexes with different stoichiometries were prepared. Reaction of azo-dyes with $Co(AcO)_2$ with 2:1 molar ratio gave azo complexes with stoichiometry $Co(L)_2$ while reaction of cobalt salts with tridentate azo-dyes, bidentate ligand, 1,10-phenanthroline (**B**),

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

Compounds	Yield (%)	Mp (°C)	Color	Formula	Calculated (found) (%)				
					C	H	N	S	M
$\mathbf{L_1}$	77	321	Dark yellow	$C_{13}H_9N_5O_3$	55.12 (54.78)	3.18 (3.49)	24.73 (25.13)	–	–
1	84	>350	Brown	$C_{13}H_{10}N_6O_7Ni$	37.05 (37.22)	2.38 (2.23)	19.95 (19.61)		14.01 (13.78)
2	85	>350	Light brown	$C_{14}H_{10}N_6O_4SNi$	40.29 (41.84)	2.40 (2.29)	20.14 (19.87)	7.67 (7.99)	14.15 (14.21)
3	86	>350	Light brown	$C_{14}H_8N_6O_3Ni$	45.90 (45.70)	2.18 (2.38)	22.95 (22.71)		15.85 (16.10)
4	85	>350	Light brown	$C_{13}H_{10}N_8O_4Ni$	38.90 (39.35)	2.49 (2.33)	27.43 (27.79)		14.71 (15.03)
5	83	>350	Brown	$C_{13}H_{10}N_6O_4Cu$	36.66 (36.39)	2.34 (2.43)	19.74 (19.49)		14.92 (15.28)
6	82	>350	Dark brown	$C_{14}H_{10}N_6O_4SCu$	39.86 (40.12)	2.37 (2.22)	19.93 (19.60)	7.59 (7.80)	15.07 (15.32)
7	86	>350	Brown	$C_{14}H_{10}N_6O_4Cu$	43.13 (43.21)	2.57 (2.50)	21.57 (21.73)		16.30 (16.51)
8	82	>350	Light brown	$C_{13}H_{10}N_8O_4Cu$	38.47 (38.67)	2.47 (234)	27.62 (27.40)		15.66 (15.37)
9	88	>350	Dark brown	$C_{26}H_{18}N_{10}O_7Co$	48.67 (48.29)	2.81 (2.73)	21.84 (21.43)		9.20 (9.59)
10	85	>350	Dark brown	$C_{25}H_{16}N_8O_6Co$	48.78 (49.29)	2.60 (2.53)	18.21 (18.45)		9.60 (10.02)
11	84	>350	Dark brown	$C_{26}H_{16}N_8O_3SCo$	53.87 (54.32)	2.76 (2.61)	19.34 (19.61)	5.53 (5.29)	10.19 (9.55)
12	87	>350	Brown	$C_{26}H_{16}N_8O_3Co$	57.04 (58.10)	2.93 (3.03)	20.48 (20.81)		10.79 (10.33)
13	83	>350	Dark brown	$C_{25}H_{16}N_{10}O_3Co$	53.29 (52.76)	2.84 (2.95)	24.87 (24.60)		10.48 (10.89)
$\mathbf{L_2}$	73	333	Yellowish green	$C_{15}H_{13}N_5O_3$	57.88 (58.30)	4.18 (3.86)	22.51 (22.15)	–	–
14	86	>350	Brown	$C_{15}H_{114}N_6O_7Ni$	40.09 (40.32)	3.12 (3.04)	18.71 (19.00)		13.14 (13.42)
15	89	>350	Brown	$C_{16}H_{12}N_6O_3SNi$	43.15 (43.57)	3.15 (2.04)	18.88 (19.19)	7.19 (7.36)	13.26 (13.42)
16	86	>350	Light brown	$C_{16}H_{14}N_6O_4Ni$	46.49 (46.23)	3.39 (3.21)	20.34 (20.19)		14.29 (14.57)
17	84	>350	Brown	$C_{15}H_{14}N_8O_4Ni$	41.96 (42.13)	3.26 (3.19)	26.11 (26.33)		13.75 (13.54)
18	85	>350	Brown	$C_{15}H_{14}N_6O_7Cu$	39.69 (39.44)	3.09 (3.21)	18.52 (18.29)		14.00 (14.31)
19	86	>350	Brown	$C_{16}H_{14}N_6O_4SCu$	42.71 (42.48)	3.11 (2.99)	18.69 (18.41)	7.12 (6.95)	14.13 (14.37)
20	81	345	Light brown	$C_{16}H_{14}N_6O_4Cu$	45.99 (46.25)	3.35 (3.22)	20.12 (19.90)		15.21 (15.60)
21	81	340	Dark brown	$C_{15}H_{14}N_8O_4Cu$	41.52 (41.19)	3.23 (3.18)	25.84 (25.26)		14.65 (14.79)
22	88	>350	Brown	$C_{32}H_{24}N_{10}O_7Co$	51.64 (51.85)	3.73 (3.52)	20.09 (20.38)		8.46 (8.31)
23	86	>350	Dark brown	$C_{27}H_{20}N_8O_6Co$	53.03 (53.47)	3.27 (3.42)	18.33 (17.86)		9.66 (9.18)
24	84	>350	Dark brown	$C_{28}H_{20}N_8O_3SCo$	55.35 (55.13)	3.29 (3.12)	18.45 (18.92)	5.27 (5.45)	9.72 (10.11)
25	84	>350	Dark brown	$C_{28}H_{20}N_8O_3Co$	58.43 (57.91)	3.48 (3.62)	19.48 (19.14)		10.26 (10.66)
26	83	>350	Dark brown	$C_{27}H_{20}N_{10}O_3Co$	54.82 (54.35)	3.38 (3.04)	23.69 (23.43)		9.98 (10.38)

and unidentate ion (X: NO_3^-, SCN^-, CN^- or N_3^-) produced a new set of complexes with general stoichiometry CoLBX. Elemental analysis, magnetic susceptibility, IR and UV–vis spectroscopies were used to characterize the azo-metal complexes.

In the IR spectra of the complexes (Table 2), two strong carbonyl absorptions are observed in the region of 1717–1661 cm^{-1}. The third carbonyl absorption band, appearing in the spectra of metal free ligand, is not observed but a new band due to C–O vibration appears around 1260 cm^{-1} in the spectra of all complexes indicating the coordination in the enolate form [19,20,28]. Moreover, another new band around 1360 cm^{-1} which is not observed in the spectra of metal free ligands is assigned as ν(N=N). The appearance of this peak at relatively lower field may indicate coordination via the N=N group [25–27]. On the basis of IR spectral data we can conclude that azo-dyes exist in diketoazo form during complexation and act as *O*,*N*,*N′*-monobasic tridentate ligand (III).

The ν(C=N) vibrations of quinoline and phenanthroline ring could not be assigned since the spectra were complicated with many bands in the 1300–1600 cm^{-1} region. The broad peaks in the 3450–3550 cm^{-1} region in the IR spectra of azo-metal complexes may be caused by water. The participation of nitrato group on coordination is indicated by three strong bands at ~1490, ~1390 and ~1290 cm^{-1} corresponding to ν_1, ν_2 and ν_4 of NO_3^- group in the IR spectra of complexes having nitrato group. The azido complexes exhibit two strong peaks at ~2050 cm^{-1} and ~1290 cm^{-1}. These peaks are attributed to ν_a and ν_s of the coordinated azido group. The complexes having CN group as an unidentate ion show a band at ~2130 cm^{-1} indicating ν(CN) vibration. The IR spectra of the complexes [NiLNCS], [CuLNCS] and [CoLBNCS] have two additional bands at ~2080 cm^{-1} and ~920 cm^{-1} corresponding to ν(CN) and ν(CS) modes of the coordinated NCS group, respectively. The position of these bands may be indicated by the coordination of NCS group through the nitrogen atom [29–31].

The magnetic moment data of the solid state complexes at room temperature are reported in Table 3. All nickel complexes [NiLX] are paramagnetic and show magnetic moment in the region 2.64–3.10 BM. On the basis of elemental analysis results and IR data, it can be concluded that the nickel complexes probably have distorted tetrahedral geometry; three coordination sites are occupied by tridentate ligand molecules and the fourth position is satisfied by unidentate ion (Fig. 1). Magnetic measurements of copper complexes [CuLX] show one unpaired electron (1.65–1.90 BM) as expected for the d^9 electronic structure of Cu^{2+} ion. All cobalt(II) complexes are paramagnetic and show magnetic moment in the region 3.87–4.49 BM. Cobalt complexes have probably distorted octahedral geometry; all coordination sites of the complexes with stoichiometry $[Co(L)_2]$ are occupied by the ligand molecules while three coordination sites are occupied by tridentate

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

Dyes	ν(C=O)	ν(N=N)	ν(C–O)	Others
$\mathbf{L_1}$	1714, 1678, 1663			3182 ν(NH), 1636 ν(C=N), 1386 ν(C–N), 1085 ν(N–N)
1	1715, 1668	1363	1267	1488, 1391, 1283 $\nu(NO_3)$
2	1714, 1667	1365	1255	2080 ν(CN), 918 ν(CS)
3	1716, 1654	1368	1263	2133 ν(CN)
4	1717, 1670	1364	1258	2050, 1288 $\nu(N_3)$
5	1720, 1665	1365	1260	1485, 1390, 1285 $\nu(NO_3)$
6	1718, 1663	1360	1261	2078 ν(CN), 922 ν(CS)
7	1713, 1669	1359	1266	2140 ν(CN)
8	1715, 1670	1361	1265	2053, 1291 $\nu(N_3)$
9	1727, 1661	1364	1267	
10	1718, 1665	1365	1256	1489, 1392, 1285 $\nu(NO_3)$
11	1716, 1663	1365	1260	2085 ν(CN), 920 ν(CS)
12	1718, 1667	1366	1263	2128 ν(CN)
13	1713, 1666	1360	1259	2045, 1294 $\nu(N_3)$
$\mathbf{L_2}$	1711, 1667, 1650			3150 ν(NH), 1633 ν(C=N), 1385 ν(C–N), 1091 ν(N–N)
14	1708, 1665	1352	1256	1490, 1392, 1385 $\nu(NO_3)$
15	1707, 1665	1353	1256	2082 ν(CN), 912 ν(CS)
16	1710, 1663	1356	1251	2130 ν(CN)
17	1713, 1660	1360	1258	2048, 1293 $\nu(N_3)$
18	1715, 1665	1364	1265	1489, 1389, 1295 $\nu(NO_3)$
19	1713, 1668	1361	1260	2077 ν(CN), 917 ν(CS)
20	1715, 1666	1359	1262	2129 ν(CN)
21	1706, 1680	1363	1262	2047, 1296 $\nu(N_3)$
22	1706, 1662	1362	1254	
23	1708, 1664	1358	1260	1487, 1390, 1286
24	1709, 1660	1366	1257	2075 ν(CN), 921 ν(CS)
25	1709, 1666	1362	1258	2128 ν(CN)
26	1707, 1670	1363	1261	2051, 1298 $\nu(N_3)$

Table 3
Magnetic moment and electronic spectral data of azo-dyes and their complexes

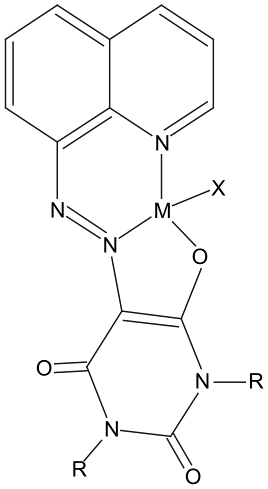
Dyes	λ_{max} (nm)	$\Delta\lambda_{max}$	μ_{eff} (BM)
$\mathbf{L_1}$	265.5, 319.5, 408.5		–
1	265.5, 437, 504.5 (sh)	28.5	2.78
2	266, 338.5, 437.5	29	2.64
3	255, 266.5, 327, 440	31.5	2.56
4	254.5, 266.5, 324, 376.5, 460	51.5	2.94
5	266.5, 323, 434.5	30.5	1.77
6	266.5, 341, 434.5	26	1.65
7	255, 266, 322, 429, 458 (sh)	20.5	1.89
8	266.5, 432, 459 (sh)	23.5	1.90
9	267, 328, 458.5	50	4.07
10	267, 331.5, 456	47.5	3.87
11	266.5, 413.5	5	4.12
12	271, 355.5, 376.5, 458.5	50	4.17
13	254, 266.5, 324, 376.5, 460	52.5	4.02
$\mathbf{L_2}$	265.5, 334.5, 410		–
14	265.5, 338.5, 437.5	27.5	2.89
15	265.5, 338.5, 438.5	28.5	2.81
16	255, 266, 337, 428	18	3.10
17	266.5, 433.5	23.5	2.75
18	254, 266, 437.5	27.5	1.87
19	266, 338, 435.5	25.5	1.74
20	266.5, 324, 335, 427.5	27.5	1.68
21	266, 432	22	1.86
22	265.5, 416	4	3.98
23	267.5, 331.5, 413.5	3.5	4.31
24	271.5, 415	5	4.23
25	270.5, 452.5	42.5	4.10
26	266.5, 324.5, 413.5, 550 (sh)	3.5	3.88

ligand molecules, the fourth, fifth and sixth positions are occupied by the bidentate base and unidentate ions in the complexes with stoichiometry [CoLBX] (Fig. 2).

3.3. Absorption spectral data

The electronic absorption spectral characteristics of the azo compounds and their transition metal complexes in DMSO are given in Table 3. The chemical shift values ($\Delta\lambda_{max}$) were determined by taking the difference between the absorption maximum of the azo-metal complexes with corresponding ligand. Figs. 3 and 4 show UV–vis spectra of the ligands and their complexes for comparative purposes. The ligands $\mathbf{L_1}$ and $\mathbf{L_2}$ have three strong absorptions as seen from Table 3 and Figs. 3 and 4. The band of shortest wavelength appearing at 265.5 nm may be attributed $\pi \rightarrow \pi^*$ transition of the heterocyclic moiety of azo compounds. The second band observed at 319.5 nm for $\mathbf{L_1}$ and at 334.5 for $\mathbf{L_2}$ is attributed to $n \rightarrow \pi^*$ electronic transition of –N=N– group. The third band appearing in the visible region (408.5 and 410 nm) can be assigned to $\pi \rightarrow \pi^*$ transition involving the whole electronic system of the azo-dyes.

In the spectra of azo-metal complexes, the absorption bands in the visible region of complexes are shifted to higher wavelengths relative to their corresponding metal free ligands. These strong absorptions of the complexes in the near ultraviolet region can be assigned as ligand to metal charge transition (LMCT). However, in the case of the complexes **1** and **26** a second band in the visible region is observed at 504.5 nm for **1** and at 550 nm for **26** as shoulder. These bands can come from the forbidden d–d transition, which is generally too weak. The expected d–d transitions in the visible region for the other complexes could not be detected. It may be



M = Cu(II) or Ni(II); X = NO_3^-, SCN^-, CN^- or N_3^-
R = H or CH_3

Fig. 1. Structure of nickel and copper complexes.

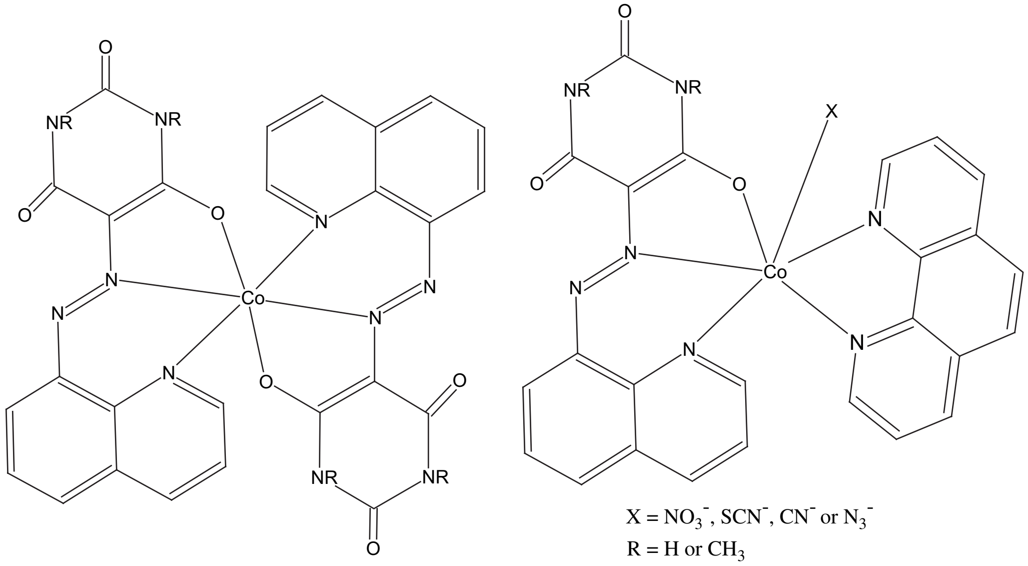


Fig. 2. Structure of cobalt complexes.

lost in the low-energy tail of the intense charge transfer transition.

3.3.1. The influence on $\Delta\lambda_{max}$ by ligands

When comparing the $\Delta\lambda_{\max}$ values of nickel, copper and cobalt complexes of $\mathbf{L_1}$, it can be easily noticed that in all three cases, unidentate azido ligand shows the highest ability to make red shift. The difference in absorption maximum of nickel and copper complexes from azo-metal complexes to $\mathbf{L_1}$ is almost same as that of nickel and copper complexes of $\mathbf{L_2}$. It can also be concluded from Table 3 that the chemical shift values of cobalt complexes of $\mathbf{L_1}$ (**9**, **10**, **11**, **12**, **13**) are higher than those of cobalt complexes of $\mathbf{L_2}$ (**22**, **23**, **24**, **25**, **26**). Furthermore, while comparing the cobalt complexes $[Co(L_1)_2]$ with $[CoL_1BX]$ of same ligand it is obviously seen that the precipitation of unidentate ligands on coordination does not efficiently effect the chemical shift since the $\Delta\lambda_{\max}$ of cobalt complexes of $\mathbf{L_1}$ except **11** is ~50 nm. The cobalt complexes of $\mathbf{L_2}$ except **25** show almost the same situation. Another interesting result of this study is the fact that $\Delta\lambda_{\max}$ values of cobalt complexes of azo-dyes bearing barbituric acid **9**, **10**, **12** and **13** except **11** are higher than those of copper and nickel complexes of the same ligand while the difference in absorption maximum of cobalt complexes of azo-dye containing 1,3-dimethylbarbituric acid moiety **22**, **23**, **24** and **26** except **25** is less than those of nickel and copper complexes of the same ligand. There is no simple explanation about this situation at this time.

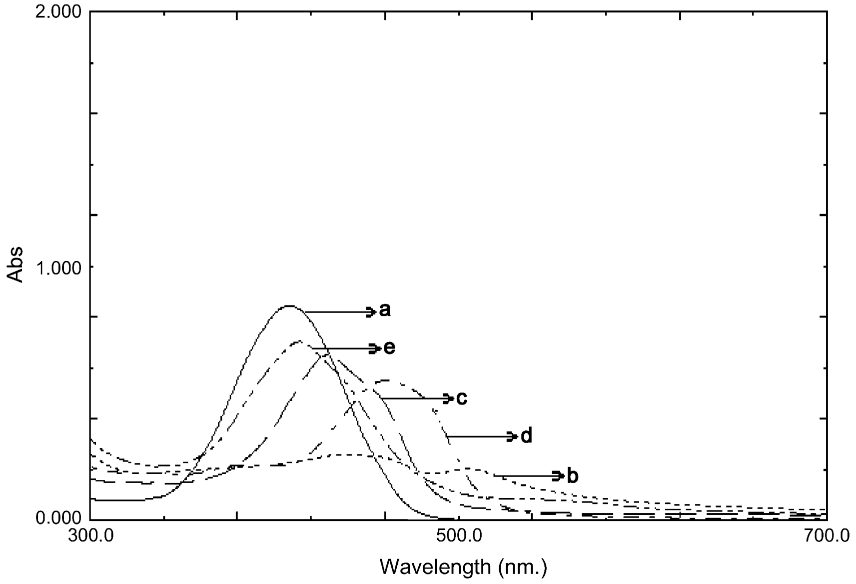


Fig. 3. Absorption spectra of dye $\mathbf{L_1}$ (a) and its complexes **1** (b), **7** (c), **9** (d) and **11** (e) in DMSO.

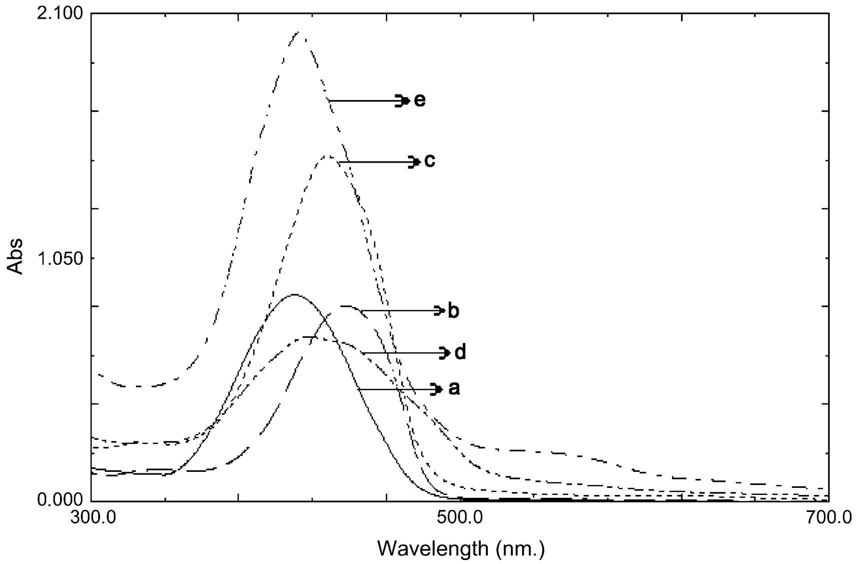


Fig. 4. Absorption spectra of dye L_2 (a) and its complexes **15** (b), **20** (c), **22** (d) and **26** (e) in DMSO.

4. Conclusion

In conclusion, we described the synthesis and some spectroscopic properties of the two new azo-dyes bearing barbituric acid and quinoline. We also prepared azo complexes (Ni, Cu and Co) containing synthesized azo-dyes, 1,10-phenanthroline and some unidentate simple ligands. It was found that these azo-dyes exist in the hydrazone form in the solid state while in the azo form during coordination. It was also noticed that in the case of some complexes, participation of the unidentate ligands increases the absorption maximum of azo-metal complexes. Unfortunately the effect of varying solvent on the absorption ability of new azo-dyes could not be examined due to the insolubility of new azo compounds in common organic solvents.

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