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Synthesis, characterization and spectroscopic properties of new azo dyes derived from aniline derivatives based on acetylacetone and azo-metal (II) complexes and singular value decomposition (SVD) investigation

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Abstract

Four new azo-dyes, 3-phenyl azopentane-2,4-dion (L_A), 3-(4-nitro phenyl azo)-pentane-2,4-dion (L_P), 3-(2-nitro phenyl azo)-pentane-2,4-dion (L_O) and 4-(1-acetyle-2-oxo-propyl azo)-benzene sulfonate sodium (L_S), were synthesized from aniline, 4-nitroaniline, 2-nitroaniline and sulfanilic acid with acetylacetone, respectively. Reaction of these new dyes with acetate salts of copper(II), nickel(II) and cobalt(II) in molar ratios of 1:2 were carried out to produce azo metal (II) complexes with the general stoichiometry; CuL_2, CoL_2 and NiL_3 in complexes. Structure of azo dyes was characterized using FT-IR,^{1}H NMR,^{13}C NMR, UV-Visible and also the corresponding metal (II) complex were characterized by FT IR, UV-Visible and CHN and XRD analysis techniques. Elemental analysis and spectral data indicated that the dye as a ligand with two teeth, N and O, acts as a bidentate ligand. Differences in absorption maxima of azo ligands compared to those corresponding complexes were also studied. Also, in this work, singular value decomposition (SVD) as a chemometric method was used to determine the Cu(II), Co(II) and Ni(II) complexes with the mentioned ligands in methanol by UV-Vis spectrophotometry. SVD method confirmed the formation of CuL_2, CoL_2 and NiL_3 complexes.

Keywords: Azo dye; sulfanilic acid; acetylacetone; bifurcated intramolecular H-bond; azo-metal (II) complex; tautomeric forms; MATLAB.

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]. With their vast applications, there is another aspect to these molecules which is sometimes

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underplayed for obvious reasons [16–19]. While some azo compounds are mildly toxic and produce measurable toxic effects with prolonged use, others are quick to impart a toxicological effect.

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]. Complex formation of the azo-metal has varied advantages from an industrial standpoint, because the role played by metal ions is twofold, one that it strengthens interaction of the azo compound (dye) with the material on which it is applied and two, that it is also able to enhance the intensity of color. On the other hand, recent studies [20] show that complex formation of azo dye with metals such as Co(II) reduce cytotoxicity even at low concentration of the complex.

Several studies have been published on the synthesis and spectral properties of several azo dye and their complexes [21-23], as we searched in the literature, there is no report azo dye based on acetylacetone. With this idea in mind, herein, we report the synthesis of new azo dyes based on acetylacetone with aniline derivatives and its azo-metal (II) complexes. The chemical structures of both azo-dyes and azo-metal (II) complexes were studied. Also, absorption properties and effects of various solvents on the maximum adsorption of dyes and their corresponding complexes were studied.

Within the background of kinetic and equilibrium considerations, there are two fundamentally different ways of extracting information: model-based analysis and model-free analysis [24]. For the determination of active components in the studying system, singular value decomposition (SVD), as a powerful mathematical tool, was enlisted. SVD can be looked at from three mutually compatible points of view. On the one hand, it, as a method for transforming correlated variables into a set of uncorrelated ones, can better expose the various relationships among the original data items. This method is also used for identifying and ordering the dimensions along with data points which exhibit the most variation. Briefly, SVD can be seen as a method for data reduction and can be used simply to find out the number of significant components in a data matrix [25-28].

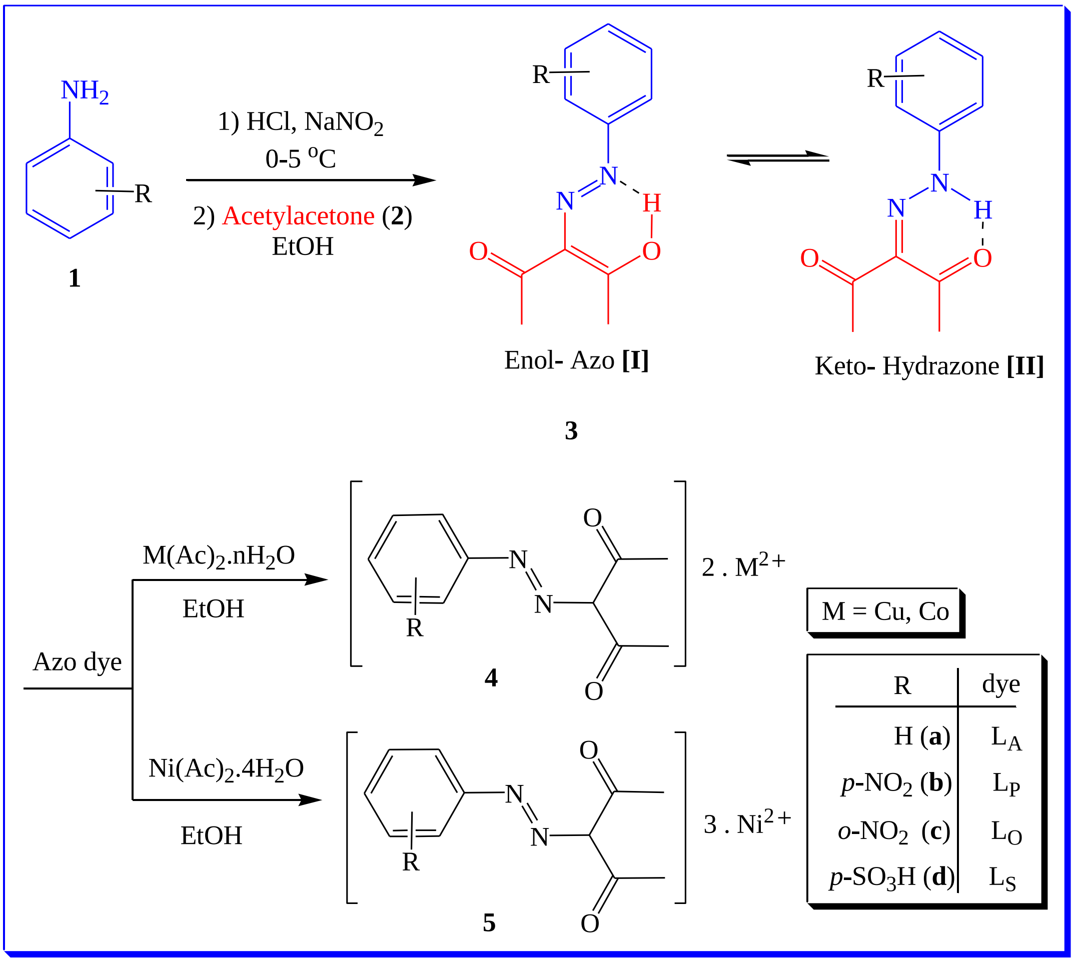
Recently we have reported some chemometrics items on 5-(2-hydroxybenzylidene)-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione and their complexation with copper(II) and mercury(II) ions [29].

Experimental

General

All the reagents and solvents were of reagent-grade quality and were purchased from Merck and Fluka and used without further purification. Melting points were determined on a Electrothermal 9200, melting point apparatus. Infrared spectra (in KBr pellets) were recorded on a Thermo Nicolet Nexus 670 FT-IR spectrometer (Urmia University, Urmia, Iran). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 and 100 MHz Ultrashield Spectrometer in DMSO and $CDCl_3$ using TMS as an internal reference, respectively (University of Tabriz, Tabriz, Iran). The electronic spectra of the ligands and complexes were recorded on a UV-2450 Shimadzu spectrophotometer in MeOH, chloroform and acetonitrile (Tabriz Payame Noor University, Tabriz, Iran).

Elemental analyses (CHN) were carried out on an Elemental, Vario, EL III analyzer (University of Tabriz, Tabriz, Iran). Powder X-ray diffraction (XRD) measurements were performed on a Shimadzu 6000 X-ray diffractometer using CuKα (λ = 0.15418 nm) radiation (Urmia University, Urmia, Iran).



Scheme 1. Synthesis of azo dyes (**3**) and their metal (II)-azo complexes (**4** and **5**).

Methods

All solutions were prepared in methanol. Microliter amounts of concentrated metal cation solutions (every step by adding of 10 µL from 10^{-3} M; 25 step) were added to ligand solutions in increments (100 µL 10^{-3} M). The solutions were kept constant at 25 ± xx °C for determination of stability constants. After every addition, we waited about 2 min, until reaction completed. Afterward, absorbance data were recorded. Moreover, all analizing data were done by MATLAB.

Synthesis of the azo-dye ligands of L_A, L_P, L_O

Each of aniline (0.91 mL, 10 mmol), *o*-nitroaniline (1.38 g, 10 mmol) and *p*-nitroaniline, 1.38 g, 10 mmol) was dissolved in a suitable volume of water containing 10 mL of HCl (conc.). The solution was then cooled to 0-5 °C in an ice-bath and maintained at this temperature. The solution of sodium nitrite (0.69 g, 10 mmol) in 2 mL water was then added dropwise. Stirring was continued for 10 min at the same temperature. The obtained diazonium salt solution was added portion wise to the solution of acetylacetone (1.02 mL, 10 mmol) in 7 mL EtOH and the corresponding dye precipitate then dried.

(E)-3-(Phenyldiazenyl)pentane-2,4-dione (LA)

Orange powder, m.p.=76 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 14.7 (s, 1H, OH/NH), 7.42 (d, 4H, *J* = 4.04 Hz), 7.22 (m, 1H), 2.61 (s, 1H), 2.49 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.93, 196.12 (C=O), 140.48 (ar.), 132.16 (ar.), 128.63 (ar.), 124.87 (ar.), 115.23 (=C-N/C=N-N), 30.66 (CH_3), 25.62 (CH_3). FT-IR (KBr, cm^{-1}): ν = 3443 (O-H), 3060 (C-H, ar.), 1676 (C=O), 1521 (N=N), 1271 (C-O).

(E)-3-((4-Nitrophenyl) diazenyl) pentane-2,4-dione (LP)

Brown powder, m.p. =182 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 14.53 (s, 1H, OH/NH), 8.31 (d, 2H, *J* = 9 Hz), 8.25 (d, 2H, *J* = 9 Hz), 7.51 (d, 2H, *J* = 9 Hz), 7.25 (d, 2H, J = 9 Hz), 2.64 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.74 (C=O), 145.58 (ar.), 137.48 (ar.), 127.20 (ar.), 124.48 (ar.), 114.80 (=C-N/C=N-N), 30.66 (CH_3), 25.66 (CH_3). FT-IR (KBr, cm^{-1}): ν = 3439 (OH), 3079 (C-H, ar.), 1671 (C=O), 1505 (N=N), 1334 (NO_2), 1162 (C-O).

(E)-3-((2-Nitrophenyl)diazenyl)pentane-2,4-dione (LO)

Orange brown powder, m.p. = 110 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 15.48 (s, 1H, OH/NH), 11.18 (s,1H, N-H), 8.28 (d, 1H, *J* = 8.4 Hz), 8.22 (d, 1H, J = 8.4 Hz), 8.14 (d, 1H, J = 8.4 Hz), 7.94 (d, 1H, *J* = 8.4 Hz), 7.73 (t, 1H, J = 8 Hz), 7.63 (t, 1H, J = Hz), 7.41 (s, 1H), 7.26 (t, 1H, J = 8 Hz), 7.06 (t, 1H, J = Hz), 2.65 (s, 3H), 2.55 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.11, 196.04 (C=O), 139.37 (ar.), 137.41 (ar.), 135.25 (ar.), 134.79 (ar.), 125.07 (ar.), 124.99 (ar.), 122.97 (ar.), 120.69 (ar.), 119.97 (ar.), 116.18 (=C-N/C=N-N), 115.50 (=C-N/C=N-N), 30.65 (CH_3), 25.60 (CH_3). FT-IR (KBr, cm^{-1}): ν = 3449 (OH), 3304 (N-H), 3104 (C-H, ar.), 1685 (C=O), 1492 (N=N), 1266 (C-O).

Synthesis of the azo-dye ligand of LS

Sulfanilic acid (1.73 g, 10 mmol) was dissolved in solution of sodium carbonate (5 mmol, 0.529 g) in 12 mL of water. The solution of sodium nitrite in water (5 mmol, 0.344 g) was then added drop wise to the mixture. Immediately, the final solution moved into the vessel containing 1 mL hydrochloric acid and 2 g ice. The diazonium solution was added portion wise to the coupling component solution of acetylacetone (1.02 mL, 10 mmol) in 7 mL EtOH. During the procedure the temperature was maintained at 0-5 °C. The mixture was stirred for 10 minutes, then was kept for 2 weeks. The precipitated crude dyes were collected by filtration and washed with ethanol.

Sodium 4-(1-acetyl-2-oxo-propylazo)-benzenesulfonate (LS)

Yellow powder, m.p. = 292 °C (decomps.). ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.94 (s, 1H, OH/NH), 7.63 (d, 2H, *J* = 8.4 Hz), 7.48 (d, 2H, *J* = 8.4 Hz), 2.52 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.99, 196.48 (C=O), 144.93 (ar.), 141.87 (ar.), 133.77 (ar.), 127.09 (ar.), 115.52 (=C-N/C=N-N), 31.25 (CH_3), 26.45 (CH_3). FT-IR (KBr, cm^{-1}): ν = 3447 (OH), 1678 (C=O), 1524 (N=N), 1268 (C-O).

Preparation of cobalt, nickel and copper azo complexes

In a round bottom flask equipped with a magnetically stirrer, a solution of $Co(CH_3COO)_2.4H_2O$ (0.285 g, 1 mmol) or $Ni(CH_3COO)_2.4H_2O$ (0.249 g, 1 mmol) or $Cu(CH_3COO)_2.H_2O$ (0.200 g, 1 mmol) in ethanol (10 mL) was added to the suspension of ligands (2 mmol) in

20 mL of the mixture of equal parts of ethanol-chloroform (1:1). A distinct change in color was observed. The mixture was refluxed for 3 h. The colored precipitate was filtered off, washed several times with ethanol and then dried in vacuum (For the spectral data see Table 3).

Results and discussion

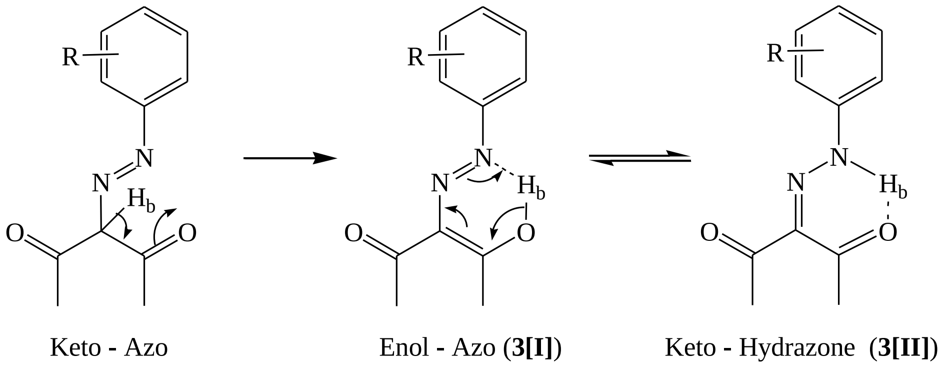
Synthesis

This article describes the formation of azo dyes (**3**) derived from the reaction of diazonium salts of aniline and its derivatives (**1**) with acetylacetone (**2**) and formation of the corresponding azo-metal (II) complexes (**4** and **5**). The diazonium salt was easily obtained using sodium nitrite in acidic condition and azo dyes **3** were easily synthesized by azo coupling. Metal (II)-azo complexes (**4** and **5)** were synthesized by the chelation between different metal ions (Cu^{2+}, Ni^{2+} and Co^{2+}) and azo dyes **3** (Scheme 1).

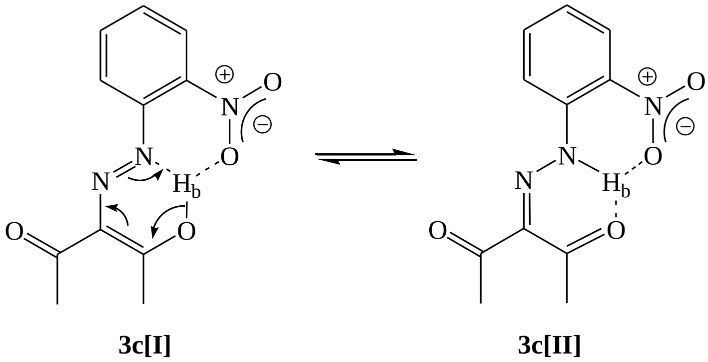
Structure identification of azo-dyes

The azo-dyes prepared in this study may exist in equilibrium of two tautomeric forms of enol-azo (**3[I]**) and keto-hydrazone form (**3[II]**) as shown in Scheme 2. No keto-azo form was existed in the equilibrium mixture due to the lack of C-H_b chemical shift. These compounds were confirmed by ^1H NMR, ^{13}C NMR, FT IR and UV–vis spectra. The ^1H NMR spectra of ligands show a signal at δ 14.70, 14.53, 15.48 and 13.94 ppm for L_A (**3a**), L_P (**3b**), L_O (**3c**) and L_S (**3d**), respectively. These deshielded chemical shifts can be attributed to intramolecular hydrogen bonded OH/NH proton (this proton assigned by H_b). ^1H NMR spectrum of dye **3a** shows two distinct methyl protons at δ 2.61 and 2.49 ppm due to the restricted rotation about C-N and/or C=N bonds. This compound also shows two peaks for the carbonyl carbon atoms at δ 196.9 and 196.1 ppm. These observations supported the one distinct tautomer of enol-azo (**3a[I]**) form. The percentages of tautomeric forms of all ligands are summarized at Table 1. ^{13}C NMR spectrum of **3a** shows nine distinct peaks that confirms a distinct form. Compound **3b** show an equilibrium mixture of two tautumeric forms of **3b[I]** and **3b[II]** in ratio of 72% : 28%, respectively (Figure 1). The peaks at δ 14.5 and 8.7 ppm also correspond to H_b of **3b[I]** and **3b[II]** in ratio of ≈72% : 28%, respectively (Table 1). The peak appeared at δ 8.7 ppm is broadened so the broadening of this peak indicated the H_b bonded to nitrogen atom in keto-hydrazone form.

One of the most interesting phenomena in this work is the equilibrium mixture of tautomeric forms in **3c**. Obviously, this compound shows an equilibrium mixture of tautomeric forms of **3c[I]** and **3c[II]** in ratio of 42.4%: 57.6%, respectively. A distinct deshielded peak at δ 15.84 ppm corresponds to H_b bonded to oxygen atom (for more information see supplementary material). The chemical shift of H_b in **3c** is higher than other compounds due to the existence of bifurcated intramolecular hydrogen bond (Figure 2 and Scheme 3). In **3c**, the peaks at δ15.84 and 11.18 ppm can be attributed OH in **3c[I**] and NH in **3c[II]** forms, respectively (Scheme 3). According to ^1H and ^{13}C NMR spectra, compound **3d** shows a distinct tautomeric form of enol-azo (**3d[I]**) form (see experimental section and supplementary material). These spectral data also confirms the assigned tautomeric forms for each dye in the solid state (Table 1).



Scheme 2. Possible tautomeric forms of azo-dyes



Scheme 3. Bifurcated intramolecular hydrogen bond in **3c**

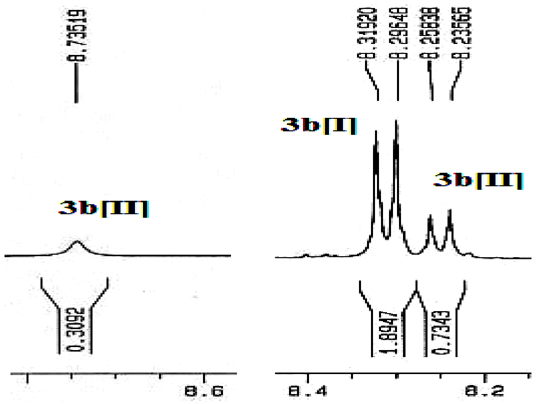


Figure 1. The ratio of the equilibrium mixture of tautomeric forms in **3b**

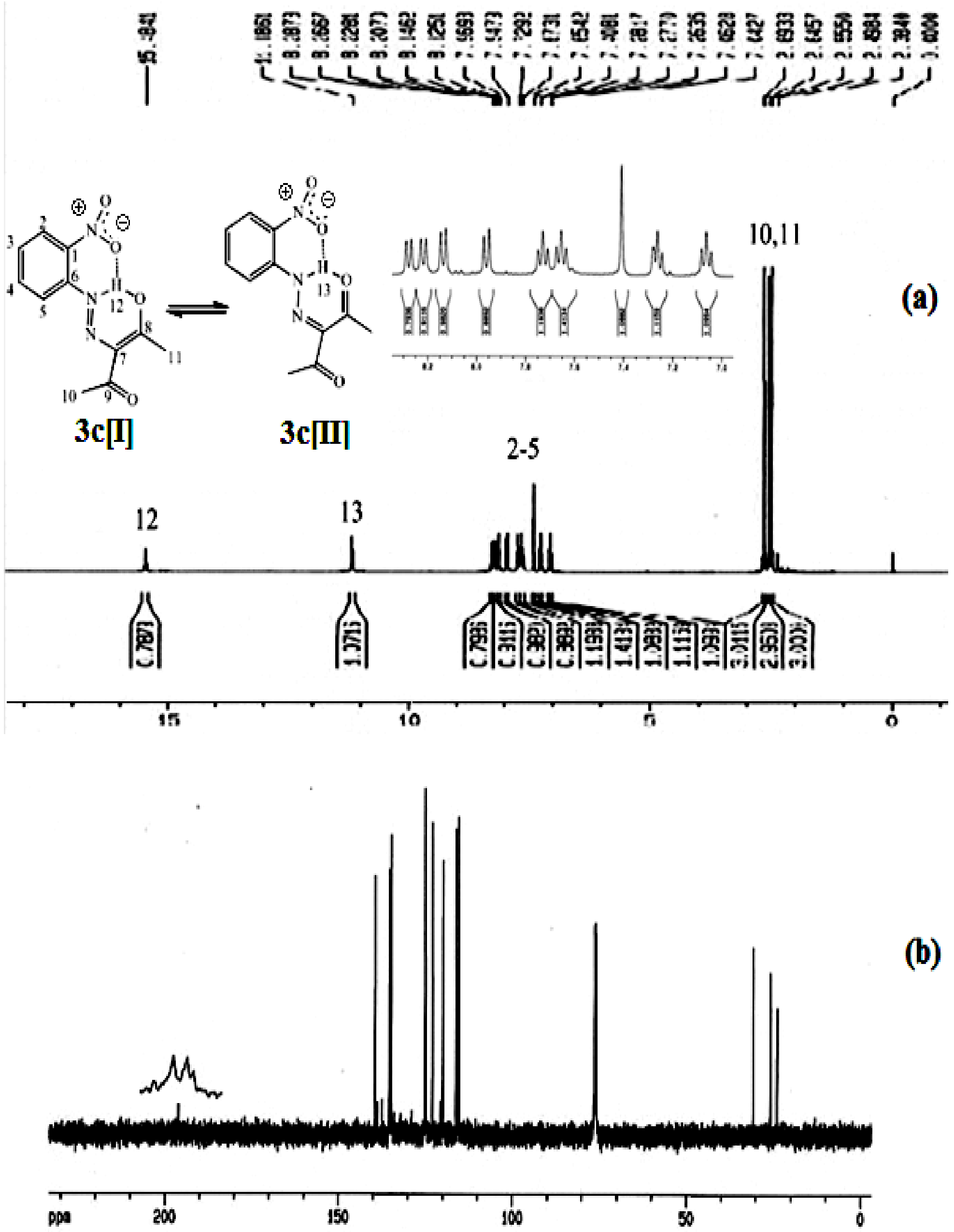


Figure 2. The ^{1}H (a) and ^{13}C NMR (b) spectra of an equilibrium mixture of ligand L_O (**3c**) in $CDCl_3$

The FT-IR spectra of the synthesized azo dyes also showed the characteristic absorption peaks due to stretching frequency of the OH and/or NH group in the region 3439-3449 cm^{-1}. The broad band in the region of 3300 and 3305 cm^{-1}, attributed to ν(N-H) was observed for the azo dye of L_O and L_P while this band in the spectrum of L_A, and L_S does not appeared. Therefore, on the basis of FT-IR data we conclude that ligands of L_O and L_P exist an equilibrium of enol-azo (**3[I]**) and keto-hydrazone forms (**3[II]**) in the solid state. Strong bands at the regions of 1521, 1505, 1492 and 1524 cm^{-1} can be attributed to the ν(N=N) stretching frequency for L_A, L_P, L_O and L_S, respectively. Carbonyl bands appearing at 1676, 1671, 1685 and 1678 cm^{-1} correspond to L_A, L_P, L_O and L_S, respectively. Absorption peaks of ν(C-O) appear in the FT-IR spectra of these dyes.

Electronic spectral data for compounds **3a-3d** in $CHCl_3$, acetonitrile and MeOH as a nonpolar, aprotic polar and protic polar solvents are summarized in Table 2. Representatively, electronic absorption spectra of ligands **3a-3d** in MeOH are shown in Figure 3 (For more information see Supplementary material).

Table 1. The percentage of tautomeric forms of ligands **3a-3d**

Entry	Compd.	Enol-azo (%)	Keto-hydrazone (%)
1	**3a (L_A)**	100	0
2	**3b (L_p)**	72	28
3	**3c (L_O)**	42.4	57.6
4	**3d (L_s)**	100	0

Table 2. Electronic absorption spectral data of the ligands **3a-3d**

	λ_{max}(nm)		
Azo dye	**$CHCl_3$**	**MeCN**	**MeOH**
L_A	366	361	362
L_P	376	376	374
L_O	330, 398	397[a]	391
L_S	367	365	363

[a] A shoulder appeared at λ ≈ 330 nm

Structure identification of azo-metal complexes

Reaction of azo-dyes with cobalt, nickel and copper salts gave eight new complexes with general stoichiometry of CoL_2, CuL_2 and three complexes with stoichiometry of $Ni(L)_3$. Elemental analysis, FT-IR and UV-Vis spectroscopies were used to characterize the azo-metal complexes. The physical properties and elemental analyses for some complexes are outlined in Table 3.

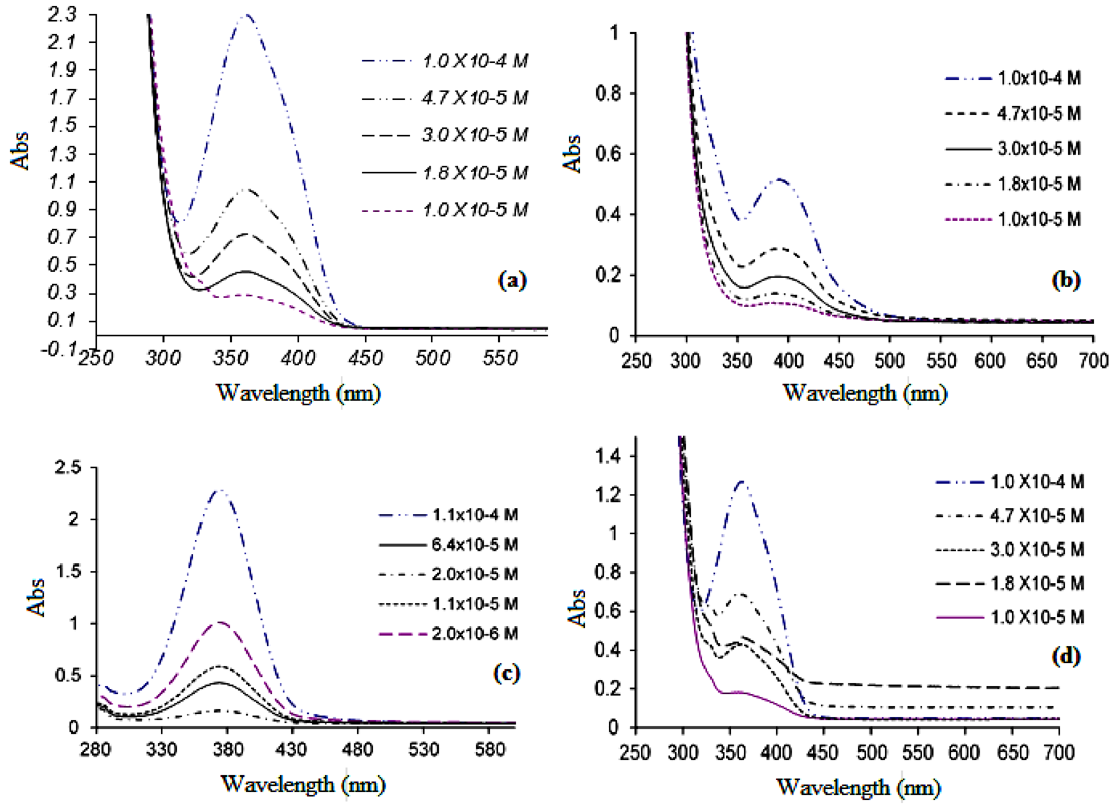


Figure 3. Representatively, absorption spectra of ligand dyes L_A (a), L_O (b), L_P (c) and L_S (d) in MeOH in different concentrations

Table 3. Characterization data for azo-metal (II) complexes

Complex	M.p(℃)	Color	Formula	Calculated (found) (%)		
				C	H	N
Cu-L_A	80	Green jade	$(C_{11}H_{12}N_2O_2)_2Cu$	-b	-	-
Cu-L_P	164	Brown	$(C_{11}H_{11}N_3O_4)_2Cu$	-	-	-
Cu-L_O	120	Light brown	$(C_{11}H_{11}N_3O_4)_2Cu$	46.37(47.13)	3.98(4.22)	14.41(14.2)
Cu-L_S	290^a	Light green	$(C_{11}H_{11}N_2O_5S)_2Cu$	-		-
Co-L_A	79	Green jade	$(C_{11}H_{12}N_2O_2)_2Co$	-	-	-
Co-L_P	217	Dark brown	$(C_{11}H_{11}N_3O_4)_2Co$	-	-	-
Co-L_O	161	Brown	$(C_{11}H_{11}N_3O_4)_2Co$	-	-	-
Co-L_S	230^a	Light green	$(C_{11}H_{11}N_2O_5S)_2Co$	37.45(37.44)	3.35(4.12)	7.29(6.89)
Ni-L_P	180	Dark brown	$(C_{11}H_{11}N_3O_4)_3Ni$	49.49(51.82)	4.27(4.12)	14.84(15.16)
Ni-L_O	165	Brown	$(C_{11}H_{11}N_3O_4)_3Ni$	-	-	-
Ni-L_S	290^a	Light green	$(C_{11}H_{11}N_2O_5S)_3Ni$	-	-	-

[a] Decomposed at this temperature
[b] The elemental analysis not measured

Table 4. The FT-IR and electronic spectral data of the azo-metal (II) complexes

	ν (cm^{-1})				**λ_{max}(nm)**		
Complex	**ν(O-H)**	**ν(C=O)**	**ν(N=N)**	**ν(C-O)**	**$CHCl_3$**	**MeOH**	**MeCN**
Cu-L_A	3447	1675	1523	-	367, 591	369, 585	361, 539
Cu-L_P	3448	1671	1505	1240	374, 583	375, 589	374, 578
Cu-L_O	3449	1684	1494	1266	397, 549	389, 572	395, 621
Cu-L_S	3444	1682	1523	1268	361, 579	363, 601	366, 615
Co-L_A	3434	1676	1522	1271	366, 673	362, 626	363
Co-L_P	3435	1671	1507	1261	379, 582	375, 617	376
Co-L_O	3549	1685	1491	1266	395, 597	322, 390, 667	394, 601
Co-L_S	3432	1683	1524	-	378, 543	363, 549	366, 523
Ni-L_P	3437	1671	1516	-	378, 654	375, 633	375, 578
Ni- L_O	3442	1685	1489	1267	338, 395, 617	390, 596	330, 395, 657
Ni-L_S	3441	1676	1522	1268	366, 547	363, 537	366, 523

The results of elemental analyses are in good agreement with those required by the proposed formula given in Table 3. The FT-IR spectra of metal (II)-azo complexes show broad-stretching vibration bands at 3432-3549 cm^{-1} (Table 4) which could be attributed to OH of the solvent molecules (Methanol). A strong band in the region of 1671–1685 cm^{-1} assigned to ν(C=O), that at least one conjugated C=O group is present in the complexes. These C=O bands are markedly shifted to lower frequency in the complexes of M-L_A (M: Cu and Co) M-L_O, and M-L_S (M: Cu, Co and Ni) compared to those in the azo dyes (L_A, L_O and L_S). This indicates that in the complexes the structure of azo ligand may be changed and it may produce increased effective conjugation. Also, absorption bands of N=N group are shifted to lower or higher frequency. These spectral data show that in these complexes the azo ligand may act as keto-hydrazone form (**II**). It was also noticed in the spectra of the M-L_P (M: Cu, Co and Ni) complexes, a new band corresponded to C-O vibration appears around 1260-1240 cm^{-1} and strong bands assigned as ν N=N appeared at low frequency. These spectral data show that in the complexes the azo ligand acts as azo-enol form [30] which coordinated through hydroxyl oxygen and azo group nitrogen to the center metal ions. On the basis of FT-IR spectral data we can conclude that azo-dyes exist in keto-hydrazone or enol-azo forms during complexation and act as O,N-bidentate ligand.

On the basis of elemental analysis results and FT-IR data, it can be concluded that the nickel complexes probably have distorted octahedral geometry and all coordination sites are occupied by three molecules of the bidentate ligand (Figure 4A).While cobalt and copper complexes have probably distorted tetrahedral geometry, four coordination sites are occupied by bidentate ligand molecules (Figure 4B).

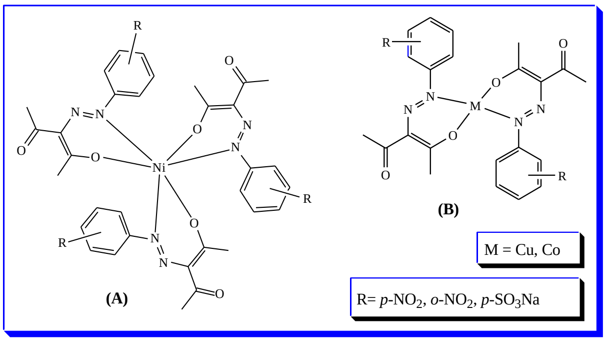


Figure 4. Proposed structure of nickel (A), cobalt and copper (B) complexes

Electronic absorption spectra of the azo-ligands and their complexes

The formation of the azo dyes and metal (II)-azo complexes is also confirmed by UV-visible spectra in solution. UV-vis absorption spectra of the azo dyes and their complexes were recorded over the wavelength range of 200-700 nm, in different organic solvents at five different concentrations (Tables 2 and 4). The λ_{max} peak observed in the range of 360-398 nm in the spectra of ligands may be attributed to a $\pi\rightarrow\pi^*$ transition contributing the whole π -electronic system of the compound in conjugation with the chromophor [31].

In the spectra of azo-metal complexes, the absorption bands in the visible region of complexes (~322-395 nm) are shifted to higher or lower 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). Also, a second band in the visible region is observed at 523-672 nm as shoulder. These bands can come from the forbidden d-d transition, which is generally too weak. The complexes spectrum of Co-L_O in MeOH, Ni-L_O in MeCN and $CHCl_3$ show a third absorption band at 322, 330 and 338 nm, respectively, which indicate the presence of both tautomeric forms **(I** and **II)** of azo ligand. Differences of concentration has not effect in the maximum absorption of both ligand and complex dye (Figure 5). Representatively, absorption spectra of $Cu(L_A)_2$ in the solvents of acetonitrile, $CHCl_3$ and in MeOH in different concentrations is shown in Figure 6.

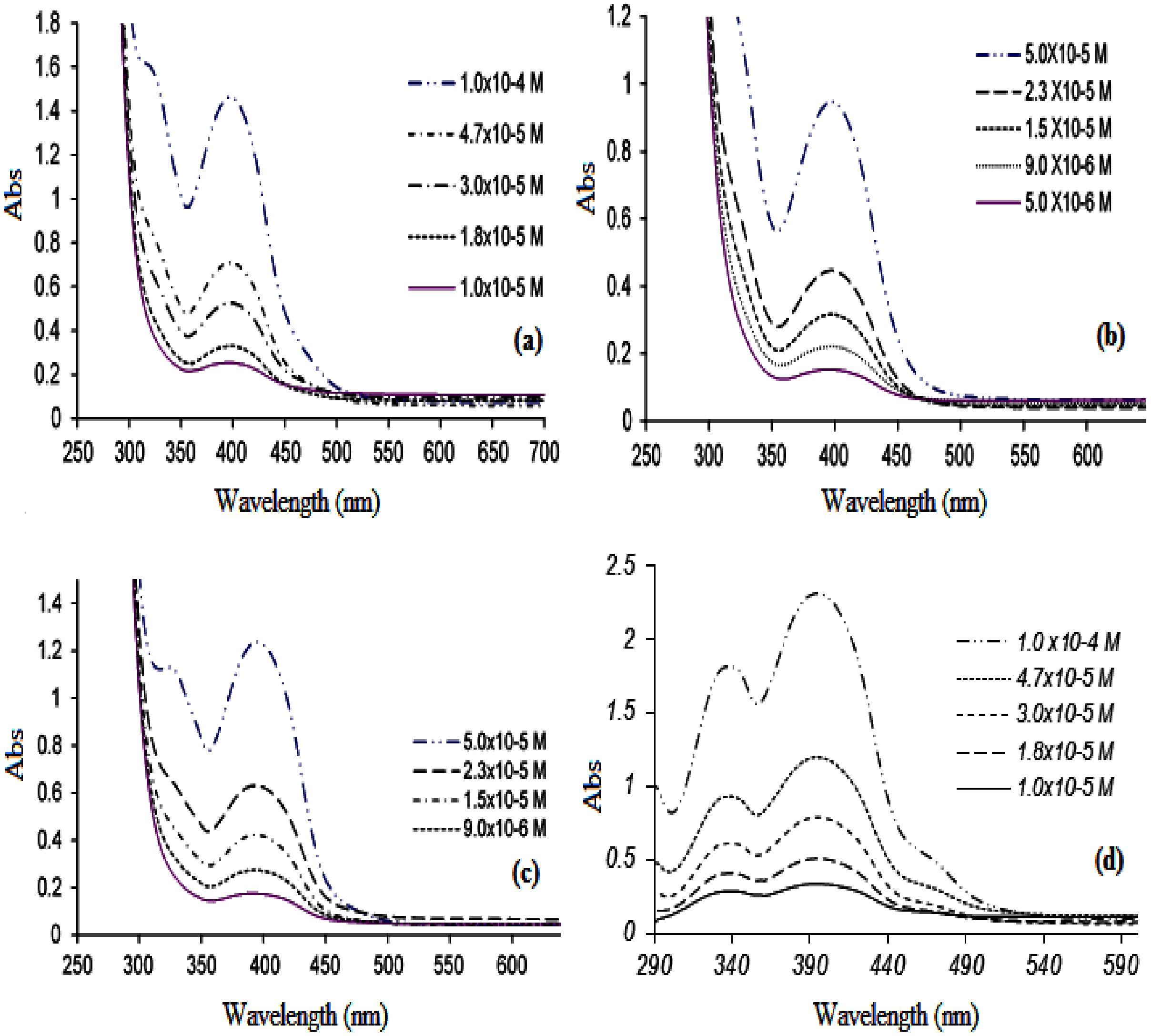


Figure 5. Representatively, absorption spectra of dyes L_O (a), $Cu(L_O)_2$ (b), $Co(L_O)_2$ (c) and $Ni(L_O)_3$ (d) in $CHCl_3$ in different concentrations (the forbidden d-d transitionat 523-672 nm are not shown for the clarity)

Investigateing the effects of different solvents on the maximum absorption values of ligands and their complexes show that chloroform is relatively higher than that of other solvents. In other words, in solvents with lower polarity the $\pi\rightarrow\pi^*$ transitions are easier than polar solvents. This phenomenon may arise from the intermolecular hydrogen bond between solvent – ligand and also solvent – complex.

The effect of hydrogen bonding on the electronic spectra

The effect of hydrogen bonding on the electronic spectra of ligands **3a-3d** and corresponding complexes **4a-4d** and **5a-5d** were investigated. The λ_{max} of azo compounds **3a-3d** increased in $CHCl_3$ as compared to that of MeOH and acetonitrile. This observation attributed to the increasing hydrogen bonding between azo ligand – polar solvent (MeOH and/or acetonitrile). When hydrogen bonding increases the polarity of the solute molecule (azo ligand), the absorption spectra moves to longer wavelengths (Red shift), and when the polarity of the molecule is decreased the absorption spectra tends to move to shorter wavelengths (Blue shift) [32]. According to Table 2, the λ_{max} of the all azo ligands bathochromically shifted from polar solvents (as MeOH or acetonitrile) to chloroform. We conclude that the absorption spectra tend to move to longer wavelengths in nonpolar solvents (as $CHCl_3$) and the polarity of the azo ligand is increased. The polarity of these dyes is decreased in MeOH and/or acetonitrile via intermolecular hydrogen bond. No significant difference was observed between the effect of MeOH and acetonitrile on λ_{max} of the all azo ligands. According to Table 4, in azo-metal complexes, no significant difference was observed between the effects of hydrogen bond on λ_{max} and azo-metal complexes. Representatively, the electronic absorptions of $Cu(L_A)_2$ in chloroform, methanol and acetonitrile in different concentration is shown in Figure 6.

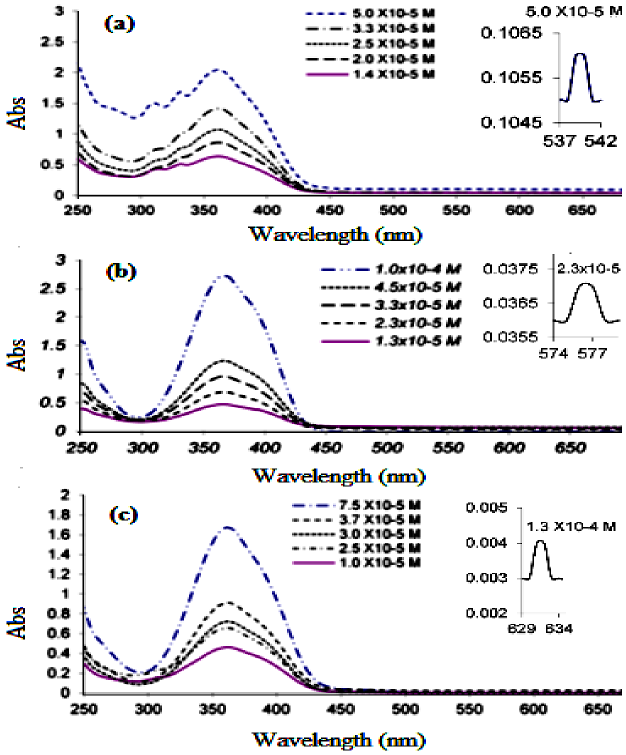


Figure 6. Representatively, absorption spectra of $Cu(L_A)_2$ in acetonitrile (a), $CHCl_3$ (b) and in MeOH (c) in different concentrations

The powder X-ray diffraction patterns of azo-metal complexes

Representatively, the XRD patterns of two azo-metal complexes of $Co(L_O)_2$ (a) and $Cu(L_S)_2$ (b) are shown in Figure 7. The Scherrer equation, in X-ray diffraction and crystallography, is a formula that relates the size of particles, or crystallites, in a solid to the broadening of a peak in a diffraction pattern [33]. According to the Scherrer equation ($\tau = K\lambda/\beta \cos \theta$); where τ is the crystallite size which may be smaller or equal to the grain size, K is a dimensionless shape factor, with a value close to unity (0.9), but it varies with the actual shape of the crystallite, besides, λ is the X-ray wavelength based on Bragg equation ($\lambda = 2d \sin \theta$), and obtained 1.54 Å; β is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians. The maximum peaks of the $Co(L_O)_2$ and $Cu(L_S)_2$ complexes appeared at 2θ = 7 and 13 degree, respectively. The second maximum peak in $Co(L_O)_2$ was also appeared at 2θ = 27 degree (Fig. 7). According to Scherrer equation, the particle size of these complexes were found in results of 59.7 nm for $Co(L_O)_2$ and 71.9 nm for $Cu(L_S)_2$, respectively. These observations confirmed the formation of nanoparticles of the mentioned complexes.

Analysis of experimental data

UV-Vis absorption spectra of L_O in methanol solvent is shown in Figure 8. Appearance of isosbestic points in UV-Vis diagram is the other evidence for kinetic complex formation. The two isosbestic points can be found at 371 nm and 423 nm. These results admit that the system may obey a two-step complexation reaction between Cu^{2+} and L_O (Figure 8).

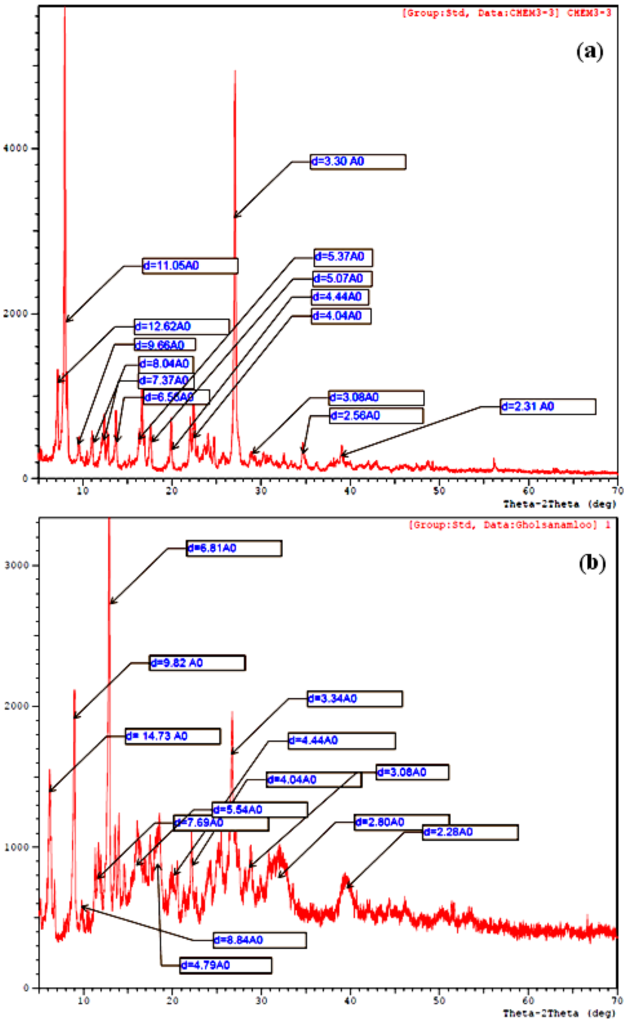


Figure 7. Powder X-ray diffraction patterns for $Co(L_O)_2$ (a) and $Cu(L_S)_2$ (b) powder forms

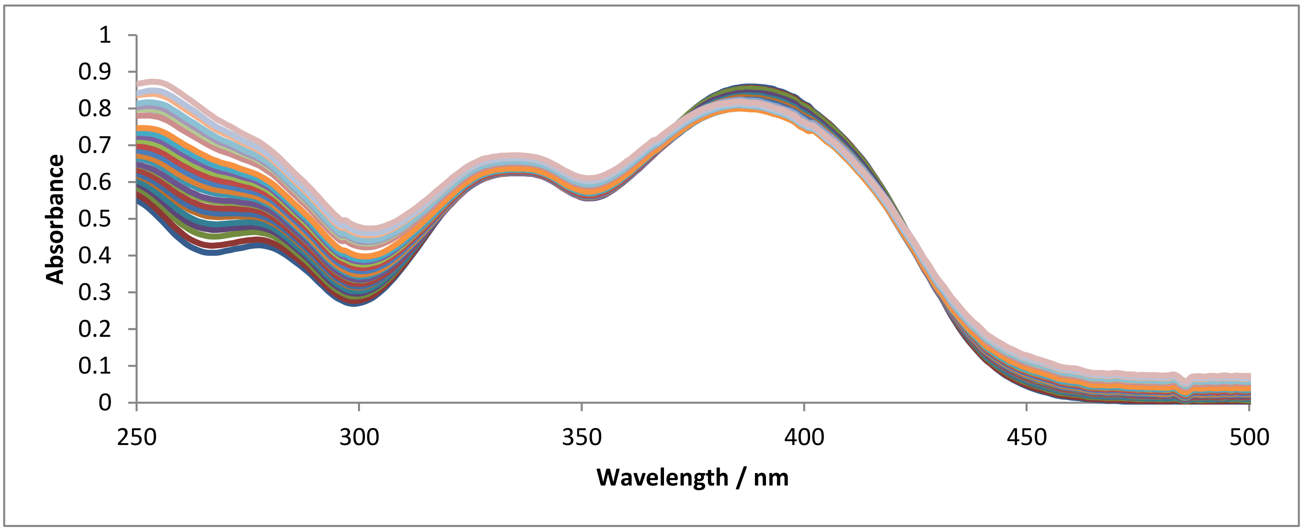


Figure 8. Changes in UV-Vis absorption spectra of L_O in methanol solvent (4.76 × 10^{-5} mole/L) by adding Cu^{2+}. [Cu^{2+}, s] mole/L: 10×10^{-6}, 20×10^{-6}, 30×10^{-6}, 40×10^{-6}, 50×10^{-6}, 60×10^{-6}, 70×10^{-6}, 80×10^{-6}, 90×10^{-6}, 100×10^{-6}, 110×10^{-6}, 120×10^{-6}, 130×10^{-6}, 140×10^{-6}, 150×10^{-6}, 160×10^{-6}, 170×10^{-6}, 180×10^{-6}, 190×10^{-6}, 200×10^{-6}, 210×10^{-6}, 220×10^{-6}, 230×10^{-6}, 240×10^{-6}, 250×10^{-6}

Singular value decomposition (SVD) showed that there were 3 components in the investigated wavelength range of 250-500 nm (Figure 9). Therefore, the absorbing components in this system could be assumed to be L, CuL, and Cu^{2+} (solvated cation) that can undergo in next step of complexation to give CuL_2.

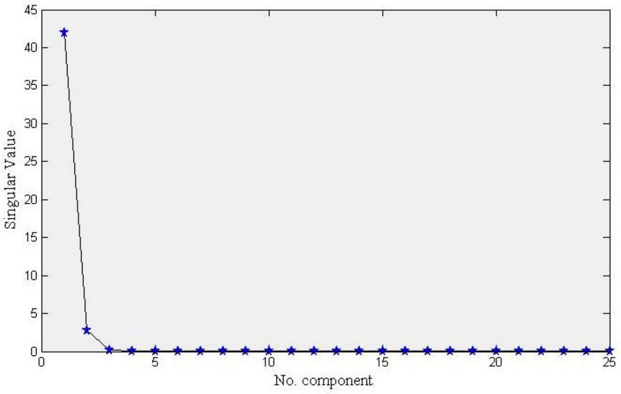


Figure 9. Consecutive singular values of singular value decomposition of Cu^{2+}-NDPD complexometric data matrix as a function of number of components

However, the only isosbestic point in range of studying can be found at 427 nm. These results admit that the system may obey a one-step complexation reaction between Co^{2+} and NDPD (in comparison with Cu^{2+}) (Figure 10).

SVD showed that there were 3 components in the investigated wavelength range of 250-500 nm (Figure 11). Therefore, the absorbing components in this system could be assumed to be L, CoL_2, and Co^{2+} (solvated cation).

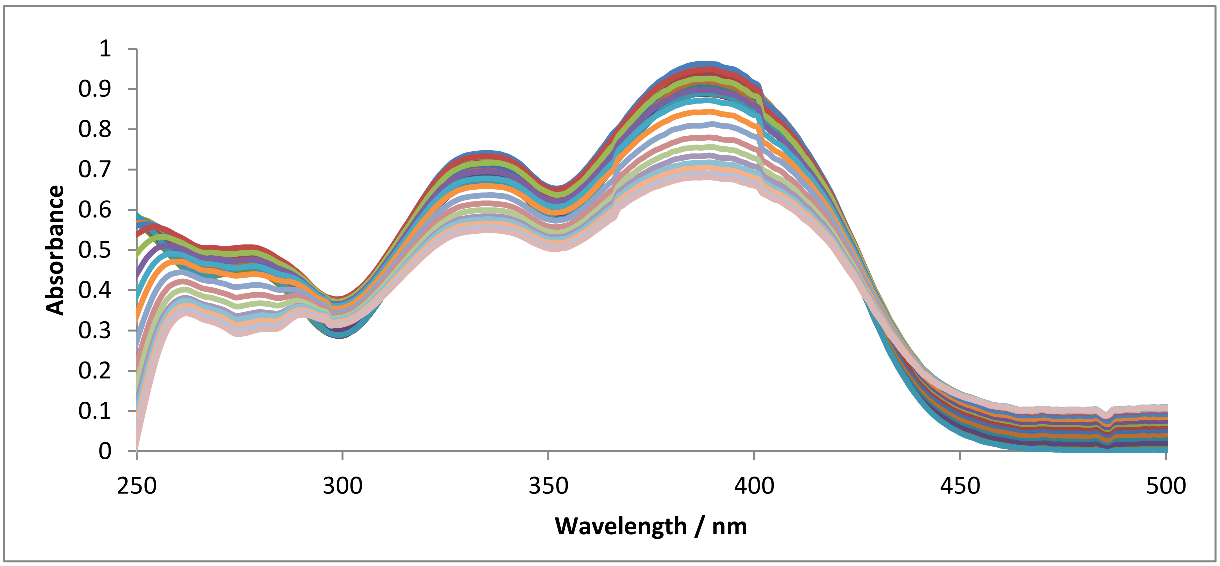


Figure 10. Changes in UV-Vis absorption spectra of L_O in methanol solvent (4.76×10^{-5} mole/L) by adding Co^{2+}. [Co $^{2+}$, s] mole/L: 10×10^{-6}, 20×10^{-6}, 30×10^{-6}, 40×10^{-6}, 50×10^{-6}, 60×10^{-6}, 70×10^{-6}, 80×10^{-6}, 90×10^{-6}, 100×10^{-6}, 110×10^{-6}, 120×10^{-6}, 130×10^{-6}, 140×10^{-6}, 150×10^{-6}, 160×10^{-6}, 170×10^{-6}, 180×10^{-6}, 190×10^{-6}, 200×10^{-6}, 210×10^{-6}, 220×10^{-6}, 230×10^{-6},240×10^{-6},250×10^{-6}

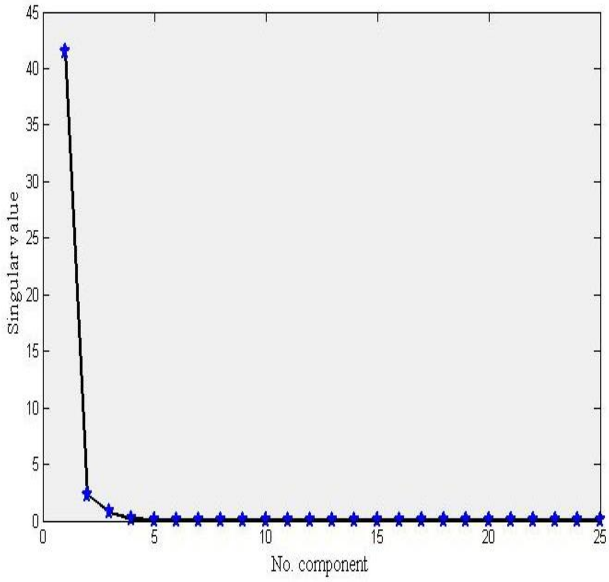


Figure 11. Consecutive singular values of singular value decomposition of Co^{2+}-NDPD complexometric data matrix as a function of number of components

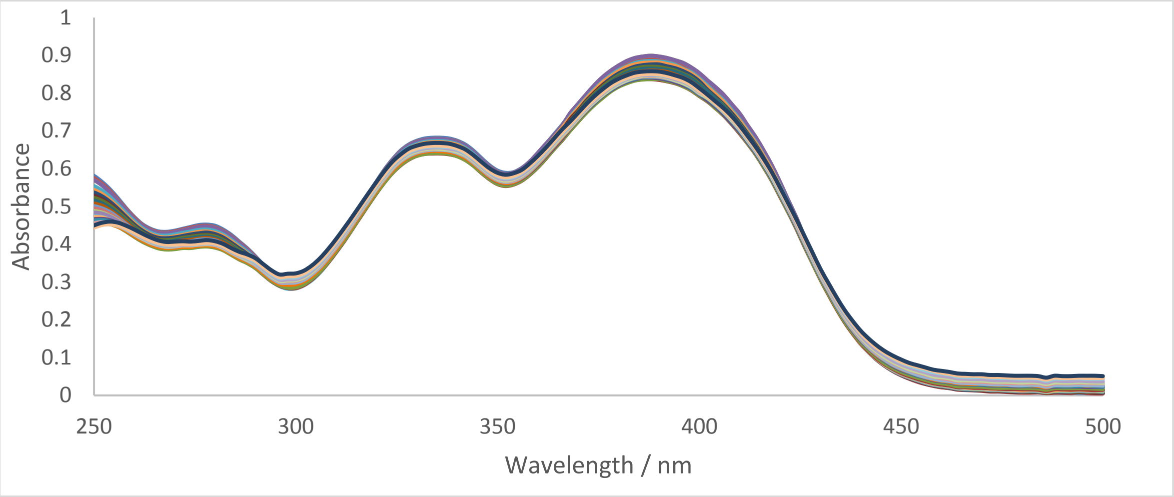


Figure 12. Changes in UV-Vis absorption spectra of L_O in methanol solvent (4.76×10^{-5} mole/L) by adding Ni^{2+}. [Ni^{2+}, s] mole/L: 10×10^{-6}, 20×10^{-6}, 30×10^{-6}, 40×10^{-6}, 50×10^{-6}, 60×10^{-6}, 70×10^{-6}, 80×10^{-6}, 90×10^{-6}, 100×10^{-6}, 110×10^{-6}, 120×10^{-6}, 130×10^{-6}, 140×10^{-6}, 150×10^{-6}, 160×10^{-6}, 170×10^{-6}, 180×10^{-6}, 190×10^{-6}, 200×10^{-6}, 210×10^{-6}, 220×10^{-6}, 230×10^{-6},240×10^{-6},250×10^{-6}

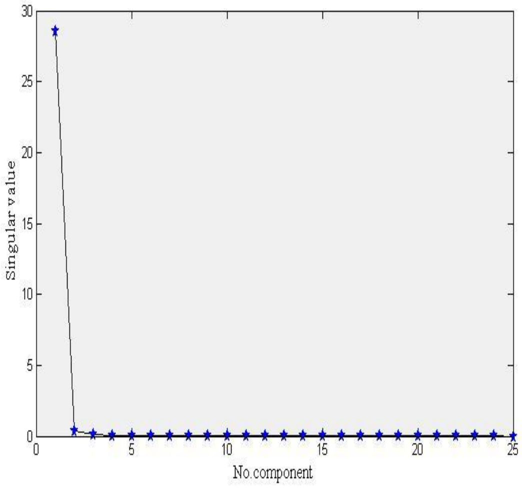


Figure 13. Consecutive singular values of singular value decomposition of Ni^{2+}-L_O complexometric data matrix as a function of number of components

SVD also showed that there were 3 components in the investigated wavelength range of 250-500 nm (Figure 12). Therefore, the absorbing components in this system could be assumed to be L, NiL_2, and NiL_3. Because the investigated wavelength range for this data was 250-500 nm and also because the Ni^{2+} (solvated form) had no absorbance in this range, it can be concluded that the spectroscopic active components were the ligand itself and both types of produced complex NiL_2 and NiL_3. Consecutive singular values of SVD of Ni^{2+}-LO complexometric data matrix is shown in Figure 13. Both Figures 14 and 15 show the range of components. It is clearly distinguished that in the nickel case, absorption range of metal salt is out of studying range; unlike copper and cobalt case (not shown).

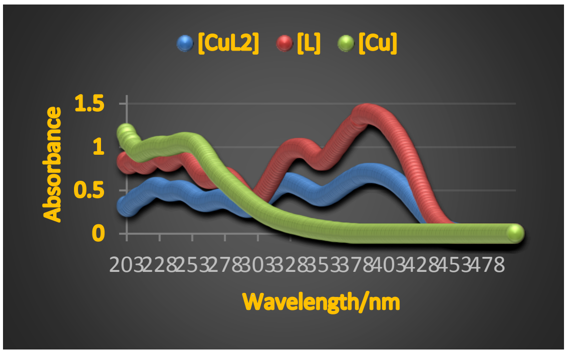


Figure 14. The UV-Vis absorption of ligand (L_O), metal salt (copper acetate) and complex

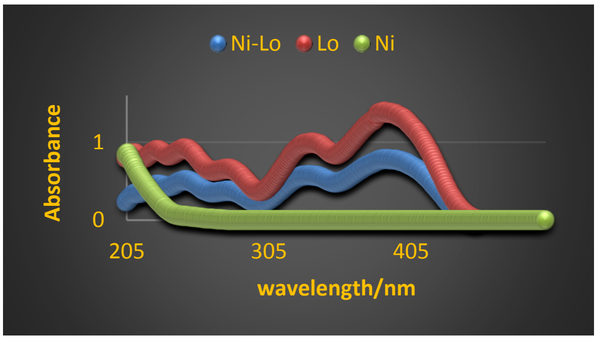


Figure 15. The UV-Vis absorption of ligand (L_O), metal salt (nickel acetate) and complex

Conclusion

Four new azo dyes in the reaction with acetylacetone were synthesized and fully characterized by spectroscopic techniques. We also prepared azo complexes (Ni, Cu and Co) from the corresponding synthesized azo-dyes ligands. The results show that two azo-dyes of L_A and L_S solely exist in the azo-enol form while dyes L_P and L_O are existing in an equilibrium mixture of azo-enol and keto-hydrazone forms in detaile. Also, the mentioned ligands act as N, O bidentate ligand in the coordination with metal cation. Investigating the effect of different solvents on the λ_{max} show that the $\pi \rightarrow \pi^*$ transitions were done easily in the solvents with lower polarity. The XRD patterns showed that these complexes were found in results of nanoparticles. Singular value decomposition (SVD) was used to determine the Cu(II), Co(II) and Ni(II) complexes with the mentioned ligands in methanol by UV-Vis spectrophotometry and confirmed the formation of CuL_2, CoL_2 and NiL_3 complexes.

Supplementary material

Full characterization data for compounds **3a-3d**, **4a-4d** and **5a-5d** are available in pdf file.

Acknowledgements

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