

Synthesis, characterization and spectroscopic properties of new azo-dyes and azo-metal complexes derived from 8-hydroxyquinoline

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Abstract

Two new azo-dyes [5-(4-anisidinyl azo)-8-hydroxyquinoline] (**L₁**) and [5-(4-acetyl phenyl azo)-8-hydroxyquinoline] (**L₂**) were synthesized by linking 8-hydroxyquinoline to P-Anisidine and P-amino acetophenone through mono azo-coupling reactions. Reaction of new azo-dyes with Ni(II), Co(II), Cu(II), VO(IV) salts gave mono nuclear complexes with general stereochemistry $[M(L)_2]$. The ratio 1:2 (M:L) complexes showed square planer geometry around M(II) ions but showed square bi pyramidal geometry around VO(IV) ion. Their structures were identified by FTIR, UV-visible and the molar conductivity measurements. FTIR spectra showed that ligand is coordinated to the metal ions in bidentate (O group and N atom) in 8-hydroxyquinoline. The molar conductance data reveal that the new complexes are good electrolytes. Molar conductivity in zero concentration Λ_0 and dissociation constant K_d for these complexes were obtained. The molar conductivity values of **dye L₁** complexes are higher than these values to their corresponding **dye L₂** complexes. The solvatochromic properties of new azo-dyes and their complexes in different solvents were investigated; they are strongly solvent dependent and exhibited azo-common anion equilibrium in DMSO and DMF. The acid and base effects on this equilibrium are also examined. Substituent effect of dyes on absorption spectra in various solvents was also studied. The absorption band of complexes are shifted to higher wavelengths relative to their corresponding metal free ligands.

Keywords: Azo-dyes, Complexes, 8-hydroxyquinoline, Spectroscopy, Solvent effect, Substituent effect.

1- Introduction

the other hand, 8-hydroxyquinoline azo-dyes derived from the sulphonamides derivatives were employed in textile industry. Mordant dyeing with these acid azo-dyes showed very good fastness properties on wool and nylon fibers^[14]. In addition, some of 8-hydroxyquinoline and azo derivatives found numerous applications in analytical chemistry as chromophoric and metallochromic indicators^[15]. 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^[16], photo electronic applications^[17], printing system^[18], optical storage technology^[19], textile dyes^[20], as well as in many biological reactions and in analytical chemistry^[21]. Azo-dyes and pigments constitute the largest and most varied group of synthetic organic colorants in use today. Hence, in addition to their conventional application as colorants for wools, fabrics, paints, inks and toners, azo compounds have also found their way into high-technology areas, such as colorants for liquid-crystalline materials and a photoconductor for photoreceptor in copiers and laser printer^[22]. Recently, metal complex dyes have also attracted increasing attention due to their interesting electronic and geometrical features in connection with their

The chemical properties of quinoline and its derivatives have been widely discussed because of their biological relevance, coordination capacity and their use as metal extracting agent^[1]. They have attracted special interest due to their therapeutic properties. On the other hand, quinoline sulphonamides have been used in treatment of cancer, tuberculosis and malaria^[2]. Several quinoline derivatives possess chemotherapeutic activity and act as antimalaria and antiallergic agents^[3]. They show broad spectrum efficiency against multiple herpes viruses and they have a potential role for the treatment of a variety of infections^[4]. 8-hydroxyquinoline is one of the most important derivatives of quinoline. 8-hydroxyquinoline, its derivatives and their complexes with transition metals have high antibacterial activities^[5-7]. In addition azo compounds based on 8-hydroxyquinoline derivatives play a central role as chelating agents for a large number of metal ions^[8-11]. In recent years a number of novel merocyanine dyes have been synthesized which contain the 8-hydroxyquinoline nucleus and these dyes exhibit strong metallochromic behavior against some heavy and transition metals ions^[12,13]. Although 8-hydroxyquinoline azo-dyes have bacteriostatic action, they have not been indicated of having commercial value as textile dyes. On

between (400-4000 cm^{-1}) of the synthesized azo compounds and their complexes were recorded by FT-IR spectrophotometer (FTIR-8400 Shimadzu-Japan) as KBr disc. The electronic spectra were recorded on the UV-visible spectrophotometer type (spectro SC) in various solvents. The melting point was recorded on "Gallen Kamp Melting Point Apparatus". The conductance measurements were recorded on W.T.W conductivity Mester LBR meter (Germany).

2.2. Synthesis

2.2.1. Synthesis of the azo-dyes

2.2.1.1 Synthesis of 5-(4-anisidinyl azo)-8-hydroxyquinoline

a) Diazotization

p-anisidine (1.233 g , 10 mmole) was dissolved in of 2M HCl (15 ml). The solution was then cooled to 0-5 $^{\circ}\text{C}$ in an ice-bath and maintained at this temperature. Sodium nitrite (0.69 g , 10 mmole) in water (10 ml) solution was then added dropwise and Stirred was for 10 minutes at same temperature.

b) Azo coupling

The cold diazonium solution was added portion wise to the coupling component solution prepared by mixing of 8-hydroxyquinoline (1.452 g , 10 mmole) and KOH (0.56 g , 10 mmole) in water (20 ml). The solution was stirred at 0-5 $^{\circ}\text{C}$ for 1 h meanwhile, the swell PH of the reaction mixture was maintained at 4-6 by the simultaneous addition of saturated sodium carbonate solution. The mixture was stirred

application for molecular memory storage, nonlinear optical elements, printing system and these type of molecule have several advantages, for example the azo group is photocromic, redox responsive PH-sensitive; stabilizes low valent metal oxidation states due to the presence of low-lying azo centered π^* molecular orbital serves as a molecular switch, is used as metal ion indicator in complexometric titration. Azo compounds are known to be involved in a number of biological reactions such as inhibition of DNA, RNA and protein synthesis, carcinogenesis and nitrogen fixation. Furthermore, they were proved to have biological activity against bacteria and fungi^[23].

In this work, we synthesized two new azo-dyes by bringing together two important chemical compounds 8-hydroxyquinoline and aromatic amines such as P-Anisidine and P-amino acetophenone, and metal dye complexes by using new dyes, appropriate simple ligand and metal ions such as Ni(II), Co(II), Cu(II) and VO(IV) with study the spectroscopic properties of new azo-dyes and their complexes.

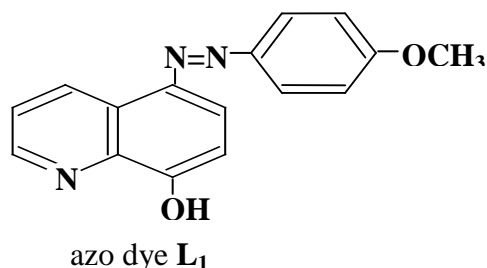
2- Experimental

2.1. General

All the chemical compounds, the reagent and the solvents were purchased from BDH and Fluka and used without further purification except P-anisidine was purified by recrystallization method. Infra-red spectra

dried. Recrystallization from EtOH gave light brown crystalline. M.P. 209 C⁰, yield 79% .

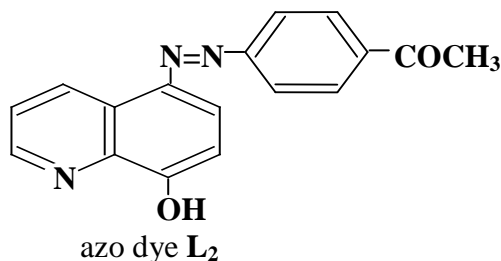
for 24 h at room temperature and the resulting solid was filtered, washed with cold water and



2.2.1.2 Synthesis of 5-(4-acetyl phenyl azo)-8-hydroxyquinoline

The same procedure is followed to prepare azo dye **L₂** using (1.352 g , 10 mmole) of P-amino acetophenone, (0.690 g , 10 mmole) of Sodium nitrite,(1.452 g , 10

mmole) of 8-hydroxyquinoline, (0.560 g , 10 mmole) of KOH. The resulting solid was filtered, washed with cold water and dried. Recrystallization from EtOH gave dark red crystalline. M.P. 235C⁰, yield 81%



2.2.2. Synthesis of metal complexes

2.2.2.1.Synthesis of nickel(I I) and copper(I I) azo complexes

(I I) or Cu(I I) ; X: (CH₃COO)₂ and Cl₂] (L₁Ni or L₁Cu) [M: Ni a) [M (L₁)₂]X A solution of Ni(CH₃COO)₂.4H₂O (0.373 g , 1.5 mmole) or CuCl₂.2H₂O (0.257 g , 1.5 mmole) in MeOH (20 ml) was added drop

wise into the solution of the azo dye L₁ (0.838 g , 3.0 mmole) in MeOH (30 ml) with strong stirring for 2 h at room temperature. Then, of water (25 ml) was added, and the precipitated colored complexes were filtered off, washed with MeOH ,diethyl ether, and dried in vacuum (I I) or Cu(I I) ; X: (CH₃COO)₂ and Cl₂] (L₂Ni or L₂Cu) [M: Ni b) [M(L₂)₂]X This preparation method is

similar to the above, using (0.373 g , 1.5 mmole) of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ or (0.257 g , 1.5 mmole) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, (0.874 g , 3.0 mmole) of the azo dye L_2 . The precipitated colored complexes were filtered off, washed with MeOH , diethyl ether and dried in vacuum.

2.2.2.2.Synthesis of cobalt(I I) and oxovanadium(I V) azo complexes

(I I) and VO(I I) ; X: $(\text{CH}_3\text{COO})_2$ and SO_4] (L_1Co or L_1VO) [M: Co a) [M (L_1)₂]X (0.272 g , 1.5 mmole) A solution of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.374 g , 1.5 mmole) or $\text{VOSO}_4 \cdot \text{H}_2\text{O}$ in MeOH (25 ml) was added to a stirred solution of the azo dye L_1 (0.838 g , 3 .0 mmole) in MeOH (40ml). After the mixture was refluxed for 3 h , water (40 ml) was added. the precipitated colored complexes were filtered off, washed with MeOH , diethyl ether and dried in vacuum.

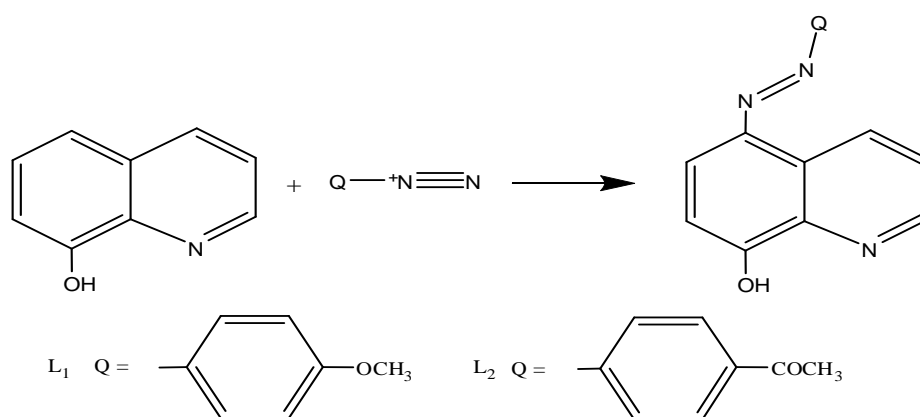
(I I) and VO(I I) ; X: $(\text{CH}_3\text{COO})_2$ and SO_4] (L_2Co or L_2VO) [M: Co b) [M (L_2)₂]X The

preparation method is similar to the above, using (0.374 g , 1.5 mmole) of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ or (0.272 g , 1.5 mmole) of $\text{VOSO}_4 \cdot \text{H}_2\text{O}$, (3 .0 mmole, 0.874 g) of the azo dye L_2 . The precipitated colored complexes were filtered off, washed with MeOH , diethyl ether and dried in vacuum.

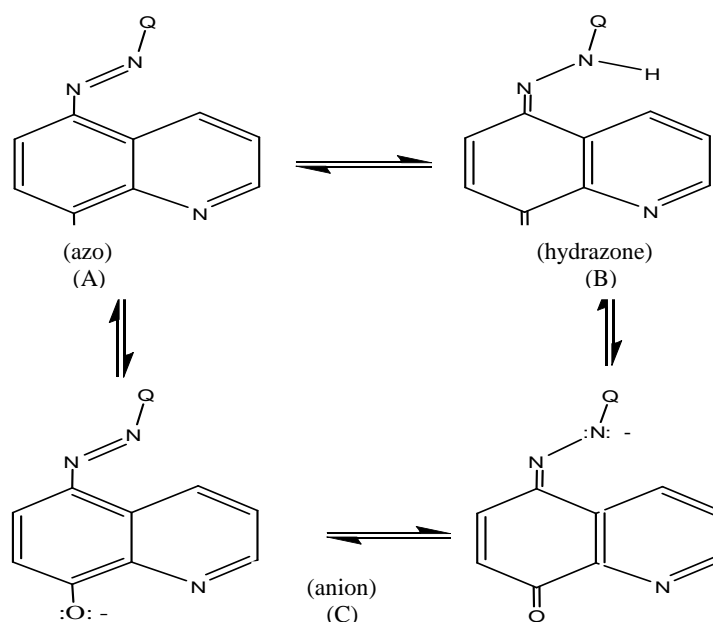
* The physical properties for all synthesized complexes are shown in Table 5.

3- Resultes and discussion

In the present work, two new azo-dyes (L_1 and L_2) were synthesized by coupling 8-hydroxy quinoline with diazotized P-anisidine [4-methoxy aniline] , P-amino acetophenone in nitrosyl hydrochloric acid (scheme 1). The synthesized dyes from 8-hydroxyquinoline(L_1 and L_2) may existed in two possible tautomeric forms, namely azo form A and hydrazone B as depicted in scheme 2. The deprotonation of two tautomers leads to common anion C.



Scheme1. structures of dyes L_1 , L_2



Scheme 2. Azo-hydrazone tautomerism and anionic form of synthesized azo 8-hydroxyquinoline

3.1. Analysis of FTIR spectra and mode of bonding:

The infrared spectra of the azo-dyes (L_1 and L_2) and their complexes with Ni(I I), Co(I I), VO(IV), Cu(I I) ions were obtained in KBr disc. The appearance of the azo band at ($1450\text{--}1600\text{ cm}^{-1}$) confirmed that all the synthesized dyes and their complexes containing azo group in the solid state.^[24,25] The binding sites in these complexes are deduced from their infrared spectra. See Figure 1. Table 1 summarize the IR data for azo-dyes (L_1 and L_2) and their synthesized complexes. The IR spectra showed that values of --N=N-- stretching frequency (1501 cm^{-1}) in dye L_1 and its synthesized complexes and (1504 cm^{-1}) in dye L_2 and its synthesized complexes remain practically unchanged indicating that --N=N-- group have no part in

coordination whereas the carbonyl group C=O stretching frequency (1668 cm^{-1}) in dye L_2 have unchanged values as well, indicating that carbonyl group is not taking part in coordination. However, the high changing in the shape and the position of O–H stretching and O–H in plane bending and O–H out of plane bending and C–O stretching in phenol group and changing in the position of C=N stretching in pyridyl group as compared to spectra of free ligands indicate that H₂O group and N atom) in 8-hydroxyquinoline are involved in coordination between azo-dyes (L_1 and L_2) with their synthesized complexes. In addition, in the complexes ($L_1\text{Ni}$, $L_1\text{Co}$, $L_1\text{Cu}$; $L_2\text{Ni}$, $L_2\text{Co}$, $L_2\text{Cu}$) we obtained two new bands in every complex and they are assigned to M–N stretching, M–O stretching frequency. In ($L_1\text{Ni}$ and $L_2\text{Ni}$) complexes,

These bands observed at 505–513 cm^{-1} and 420–467 cm^{-1} region can be assigned to Ni–N and Ni–O stretching frequency respectively. In (**L₁Co** and **L₂Co**) complexes, The bands centered at 517–528 cm^{-1} and at 424–449 cm^{-1} are assigned to Co–N and Co–O stretching frequency respectively. But new weak bands centered at 509 cm^{-1} , 438 cm^{-1} in **L₁Cu** and at 511 cm^{-1} , 469 cm^{-1} in **L₂Cu** are assigned to Cu–N and Cu–O stretching frequency

respectively^[26].

In (**L₁VO** and **L₂VO**) complexes, three new bands were obtained in every complexes. New two weak bands observed at 488–492 cm^{-1} and 451–455 cm^{-1} region can be assigned to V–N and V–O stretching frequency and the strong and sharp band observed at 978–980 cm^{-1} region can be assigned to V=O stretching frequency respectively^[26].

Table 1 : Selected IR data (400-4000 cm^{-1}) of azo-dyes (L₁** and **L₂**) and their complexes.**

(s=strong, m=medium, w=weak, br=broad)

IR bands	Compounds									
	L₁	L₁Ni	L₁C o	L₁VO	L₁Cu	L₂	L₂Ni	L₂Co	L₂VO	L₂C u
O-H Stretching (br,s)	3250 3528	3231 3512	3206 - 3514	3200- 3490	3230- 3495	3279- 3532	3250- 3520	3270- 3500	3235- 3497	3255 3550
C=N Stretching (s)	1595	1576	1582	1587	1585	1597	1580	1578	1586	1591
In plane O-H bending (m)	1412	1400	1389	1394	1391	1382	1373	1372	1367	1369
C-O Stretching (s)	1252	1243	1248	1242	1240	1273	1265	1270	1264	1271
Out of plane O-H bending (m)	795	791	760	764	764	758	743	748	750	748
M-N Stretching (w)	-----	513	517	492	509	-----	505	528	488	511
M-O Stretching (w)	-----	467	449	451	438	-----	420	424	455	469
V=O Stretching (s)	-----	-----	-----	980	-----	-----	-----	-----	978	-----

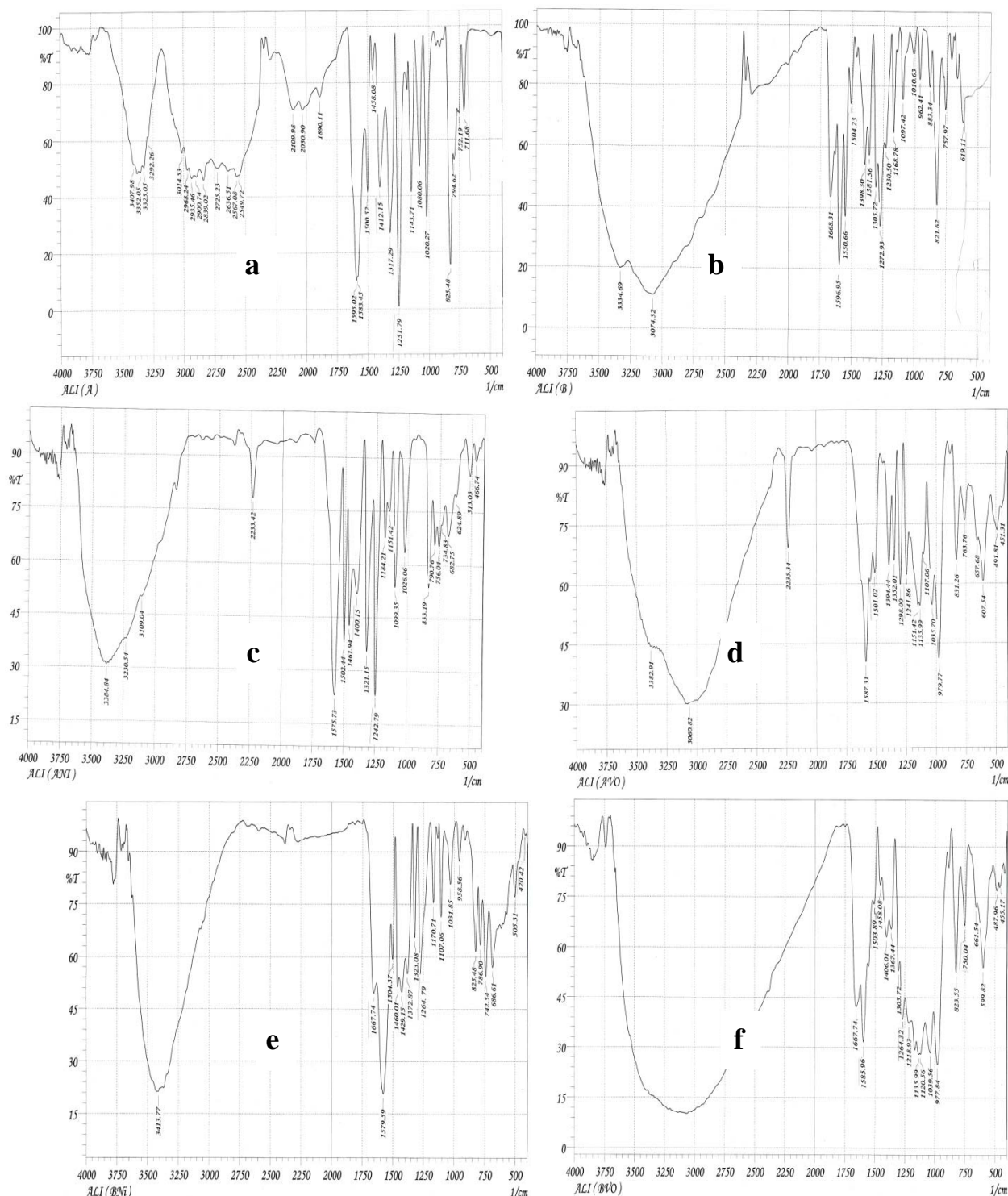


Figure 1 : Infrared spectrum for (a): dye L_1 , (b): dye L_2 , (c): $L_1 Ni$, (d): $L_1 VO$, (e): $L_2 Ni$, (f): $L_2 VO$.

3.2. Solvent effect on absorption spectra of the synthesized azo-dyes and their complexes

Since the tautomeric equilibria strongly depend on the nature of media, the behavior of dyes (L_1 and L_2) and their transition metal complexes in various solvents was studied.

For this purpose, the absorption spectra of them were measured in various solvents at a concentration approximately (10^{-6} - 10^{-8} M) and these are run at different concentration because of solubility problems and the results are given in Table 2. It was found that the absorption maximum of these dyes and their complexes are strongly solvent dependent and vary with solvent polarity. They show generally bathochromic shifts as the polarity of the solvents is increased. The influence of solvents for the dyes increases in the order DMSO > DMF > acetonitrile > methanol > acetic acid > chloroform. The spectral shifts of dye **L₁**, **L₁Ni**, **L₁Co** and dye **L₂**, **L₂Ni**, **L₂Co** in various solvents are shown in Figures (2 and 3) respectively.

Dye **L₁** have one strong absorption maximum as seen from Table 2 and Figure 2. This band observed at 402 nm in DMSO, 401 nm in DMF, 389 nm in acetonitrile, 388 nm in methanol, 385 nm in acetic acid and 374 nm in chloroform is attributed to $\pi \rightarrow \pi^*$ electronic transition of --N=N-- group; so dye **L₁** exhibit significantly larger bathochromic shifts in stronger polar solvents (DMSO and DMF) than the weaker polar solvents (acetic acid and chloroform). The same results were observed in absorption maximum of dyes (**L₁** and **L₂**) and their complexes as shown in Table 2. For example, for **L₁Ni**, $\Delta\lambda_{\text{max}} = 92$ nm in DMSO, $\Delta\lambda_{\text{max}} = 89$ nm in DMF, $\Delta\lambda_{\text{max}} = 48$ nm in acetonitrile, $\Delta\lambda_{\text{max}} = 32$ nm in methanol, $\Delta\lambda_{\text{max}} = 24$ nm in acetic

acid relative to those in chloroform. The absorption spectra of dye **L₁** showed only one absorption maximum in all solvents used whereas the dye **L₂** and all its complexes showed two absorption maxima in all solvents used. It is known that two maxima are observed for compounds exhibiting azo-hydrazone tautomerism. These results suggest that the dyes and their complexes may exist as a mixture of two forms in solutions except for dye **L₁**. Especially for **L₂Ni**, **L₂Co** were observed two absorption maxima in DMSO, DMF, acetonitrile and methanol as shown in Figure 3 and Table 2. On the other hand, the absorption spectra of dyes (**L₁** and **L₂**) and their complexes in acetic acid and chloroform showed only one absorption maxima in the range 383-426 nm and 348-395 nm respectively except for **L₁Ni**, dye **L₂**, **L₂Ni**. The absorption spectra of **L₁Ni**, dye **L₂**, **L₂Ni** exhibit two absorption maximum, for example, the absorption spectra of **L₁Ni** exhibit at 429 nm, 519 nm in acetic acid and at 405 nm, 557 nm in chloroform. But the absorption spectra of dye **L₂** exhibit at 350 nm, 461 nm in acetic acid and at 348 nm, 452 nm in chloroform. These results show that the dyes (**L₁** and **L₂**) and their complexes are in favor of the predominantly single tautomeric form in acetic acid and chloroform except **L₁Ni**, dye **L₂**, **L₂Ni**. **L₁Ni**, dye **L₂**, **L₂Ni** may exist as a mixture of two tautomeric forms in acetic acid and chloroform. Furthermore, the absorption patterns of the dyes and their

complexes are changed with solvents. The spectra of **L₂Co** in acetic acid and chloroform show one maximum at 393 nm, 384 nm respectively, whereas DMSO, DMF, acetonitrile and methanol the intensity of this band is decreased and a new more intensive band is appeared in the range 482-497 nm, show Figure 3. Thus, the absorption curves almost pass through an isosbestic point approximately 410 nm characteristic of equilibrium. This equilibrium may exist between the tautomeric forms (azo and hydrazone) or between the one tautomeric form and the anionic form. Because the equilibrium depends on the acidity of the solvents used. The effect of solvents on the equilibria is somewhat different from that of solvents on azo-hydrazone tautomerism. In proton donating solvents such as acetic acid and chloroform, the dyes and their complexes give a hypsochromic shift of λ_{\max} and are basically in the neutral form. In proton-accepting solvents, such as DMSO, DMF and methanol, the dyes (**L₁** and **L₂**) and their complexes give a bathochromic shift of λ_{\max} and exist mainly in the common anion form. Such as order of the effect of solvents is consistent with the phenomenon of dissociation rather than azo-hydrazone tautomerism.

In the spectra of azo-metal complexes, the absorption band of complexes are shifted to higher wavelengths relative to their corresponding metal free ligands. For

example, when DMSO solvent used the absorption maximum of dye **L₁** observed at 402 nm But it is shifted at 497 nm, 478 nm, 457 nm and 438 nm of **L₁Ni**, **L₁Co**, **L₁Cu**, **L₁VO** respectively. The influence of dye **L₁** complexes increases in λ_{\max} the order **L₁Ni** > **L₁Co** > **L₁Cu** > **L₁VO** > dye **L₁**.

Unfortunately, the some expected weak d-d transition in the visible region for some complexes can not be detected even with concentrated solution. It may be lost in the low energy tail of the charge transfer transitions.^[27,28] We obtained from the absorption maximum of dye **L₂** and their complexes that dye **L₂** have one strong absorption maximum as seen from Table 2 and Figure 3. This band observed at 370 nm in DMSO, 370 nm in DMF, 361 nm in acetonitrile, 354 nm in methanol, 350 nm, 461 nm in acetic acid and 348 nm, 452 nm in chloroform is attributed to $\pi \rightarrow \pi^*$ electronic transition of $-\text{N}=\text{N}-$ group; The absorption maximum of dye **L₂** complexes are shifted to higher wavelengths relative to dye **L₂**. For example, The absorption maximum of **L₂Ni** observed at 391 nm and 487 nm in DMSO, 387 nm and 485 nm in DMF, 377 nm and 461 nm in acetonitrile, 368 nm and 458 nm in methanol, 358 nm and 465 nm in acetic acid, 352 nm, 457 nm in chloroform. The first absorption maximum is attributed to $\pi \rightarrow \pi^*$ electronic transition of $-\text{N}=\text{N}-$ group; but the second absorption maximum is attributed to expected d-d transition in the visible region.

The other complexes of dye **L₂** are similar for this state. The influence of dye **L₂** complexes dye **L₂** increases in absorption maximum in the order **L₂Co** > **L₂Cu** > **L₂Ni** > **L₂VO** > dye **L₂**. It was also observed that the absorption maximum curves of azo-dyes (**L₁** and **L₂**) and their complexes were very sensitive to acids and bases. λ_{\max} values of the dyes and their complexes showed the large bathochromic shifts when a small amount of piperidine was added to each dyes and their complexes solutions in chloroform. as shown in Table 3. The absorption curves of the dyes resembled those in DMSO, DMF and methanol. Atypical example is shown in Figures 4 and 5. There was no significant change in the spectra of the dyes and their complexes when a small amount of piperidine was added to their solutions in DMSO, DMF. Similar effects were observed when a small amount of 0.1 M KOH was added to methanolic solutions of dye **L₁**, **L₁Ni**, **L₁VO**, dye **L₂**, **L₂Cu**. the addition of 0.1 M KOH to methanolic solutions of **L₁Co**, **L₁Cu**, **L₂Co**, **L₂Ni**, **L₂VO**, the maxima at the shorter wave lengths was disappeared and λ_{\max} values at longest wave length did not significantly change, as shown in Table 3. For example, the absorption bands of **L₂VO** observed at 361 nm and 450 nm in methanol when a small amount of 0.1 M KOH to methanolic solution, we obtained one band at 453 nm.

λ_{\max} values of the dyes (**L₁** and **L₂**) and their complexes in methanol showed large hypsochromic shifts when 0.1 M HCl was added, being nearly the same as those observed in chloroform. This indicates that dye **L₁** and their complexes exist in dissociated state in DMSO, DMF and methanol with the exception of **L₁Co**, **L₁Cu** in methanol. In contrast, the dyes and their complexes exist in a single tautomeric form in chloroform with the exception of **L₁Ni**, dye **L₂**, **L₂Ni**. These results also indicate that **L₂Ni**, **L₂Co**, **L₂Cu**, **L₂VO** in a partly dissociated state in DMSO, DMF and methanol with the exception of the **L₂Cu** in methanol. **L₁Co** and **L₁Cu** also exist **Substituent effect on** in partly dissociated state in methanol.

3.2.1. absorption spectra of dyes in various solvents

Substituent effect of the dyes (**L₁** and **L₂**) and their complexes was also studied. As apparent in Table 2, introduction of electron-donating **-OCH₃** group at the 4-position into benzene ring in dye **L₁** and its complexes resulted in bathochromic shifts as comparing with dye **L₂** and its complexes, that have electron-accepting **-COCH₃** group at the same position of benzene ring in all solvents used. For example, for dye **L₁** $\Delta\lambda_{\max}$ =32 nm in DMSO, $\Delta\lambda_{\max}$ =31 nm in DMF, $\Delta\lambda_{\max}$ =28 nm in acetonitrile, $\Delta\lambda_{\max}$ =26 nm in chloroform relative λ_{\max} of dye **L₂** in the same solvents; for **L₁Cu** $\Delta\lambda_{\max}$ =53 nm in

DMSO, $\Delta\lambda_{\max}=51\text{nm}$ in DMF, $\Delta\lambda_{\max}=48\text{ nm}$ in acetonitrile, $\Delta\lambda_{\max}=27\text{ nm}$ in chloroform relative λ_{\max} of dye **L₂Cu** in the same solvents. Thus, the bathochromic shifts can be obtained by enhancing the electron donor properties of the diazo component. On the other hand, the absorption spectra of the dyes and their complexes in chloroform and acetic acid showed only one absorption maximum with the exception of **L₁Ni**, dye **L₂** and **L₂Ni**. In addition, when electron-donating group –**OCH₃** introduced into the 4-position of benzene ring (**L₁Co** and **L₁VO**) and when electron-accepting group –**COCH₃** introduced into the same position in (**L₂VO** and **L₂Cu**) one tautomeric form is observed in acetic acid and chloroform. Moreover, while two tautomeric forms are observed in DMSO, DMF for **L₂VO** and **L₂Co**, only single tautomeric form is observed for **L₁VO** and **L₁Cu** in DMSO, DMF. This showed that with the introduction of electron donor Substituents to benzene ring, the dyes and their complexes existed predominantly in one tautomeric form in proton donating solvents when the introduction of electron-acceptor Substituent to benzene.

3.2.2. The influence on $\Delta\lambda'_{\max}$ by ligands

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. Table

4, Figure 6 show Uv-visible spectra of the ligands dyes (**L₁** and **L₂**) and their complexes in DMSO solvent respectively, for comparative purposes. When comparing the $\Delta\lambda'_{\max}$ values of the dyes complexes, it can be easily noticed that in all four cases, the ligands dyes (**L₁** and **L₂**) shows the highest ability to make red shift. $\Delta\lambda'_{\max}$ values of dyes (**L₁** and **L₂**) complexes are higher than their free ligands. It can also be concluded from Table 4 that λ'_{\max} values of dye **L₁** complexes (**L₁Ni**, **L₁Co**, **L₁Cu** and **L₁VO**) are higher than those of dye **L₂** complexes (**L₂Ni**, **L₂Co**, **L₂Cu** and **L₂VO**) respectively and this result due to that dye **L₁** complexes have electron-donating –**OCH₃** group at the 4-position into benzene ring, while dye **L₂** complexes have electron-accepting –**COCH₃** group introduced into the same position of benzene ring. Another interesting results of this study is the fact that $\Delta\lambda'_{\max}$ value of **L₁Ni** is higher than **L₁Co**, **L₁Cu** and **L₁VO** respectively, while $\Delta\lambda'_{\max}$ value of **L₂Ni** is less than **L₂Co** and **L₂Cu** except **L₂VO**. we observed that **L₁VO** is less than **L₂Ni**, **L₂Co** and **L₂Cu** and **L₂VO** is less than **L₂Ni**, **L₂Co** and **L₂Cu**. Therefore, we can arrange the influence on $\Delta\lambda'_{\max}$ of dyes complexes in the order (**L₁Ni** > **L₁Co** > **L₁Cu** > **L₁VO**) and (**L₂Co** > **L₂Cu** > **L₂Ni** > **L₂VO**).

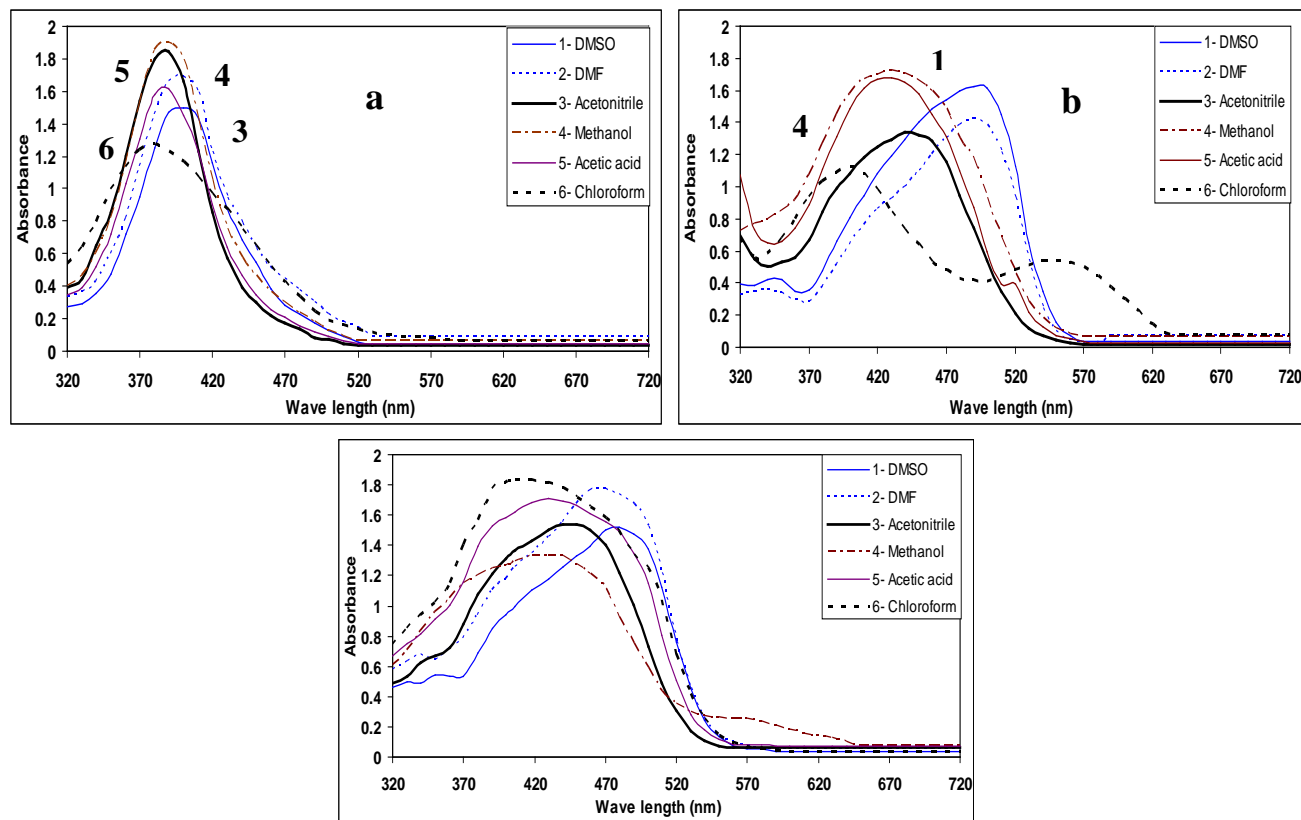
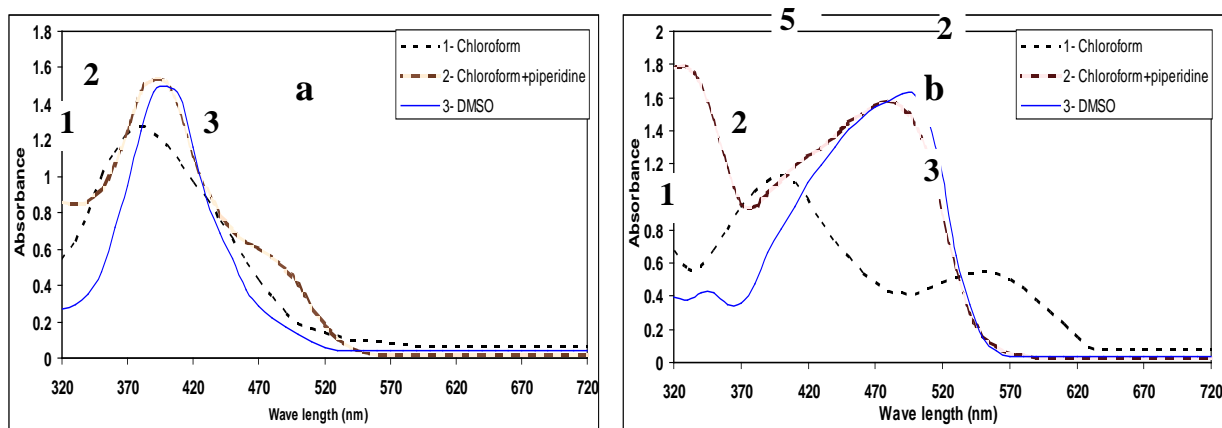


Figure 2 : Absorption spectra of dye L_1 and its complexes in various solvents, (a): L_1 , (b): L_1 Ni, (c): L_1 Co.



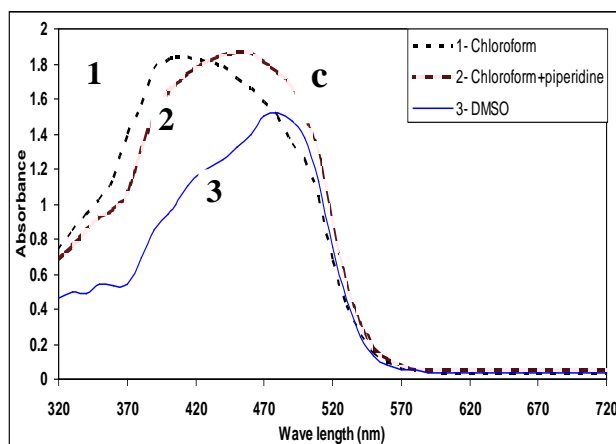


Figure 4: Absorption spectra of dye L_1 and its complexes in neutral and basic solutions, (a): L_1 , (b): $L_1 Ni$, (c): $L_1 Co$.

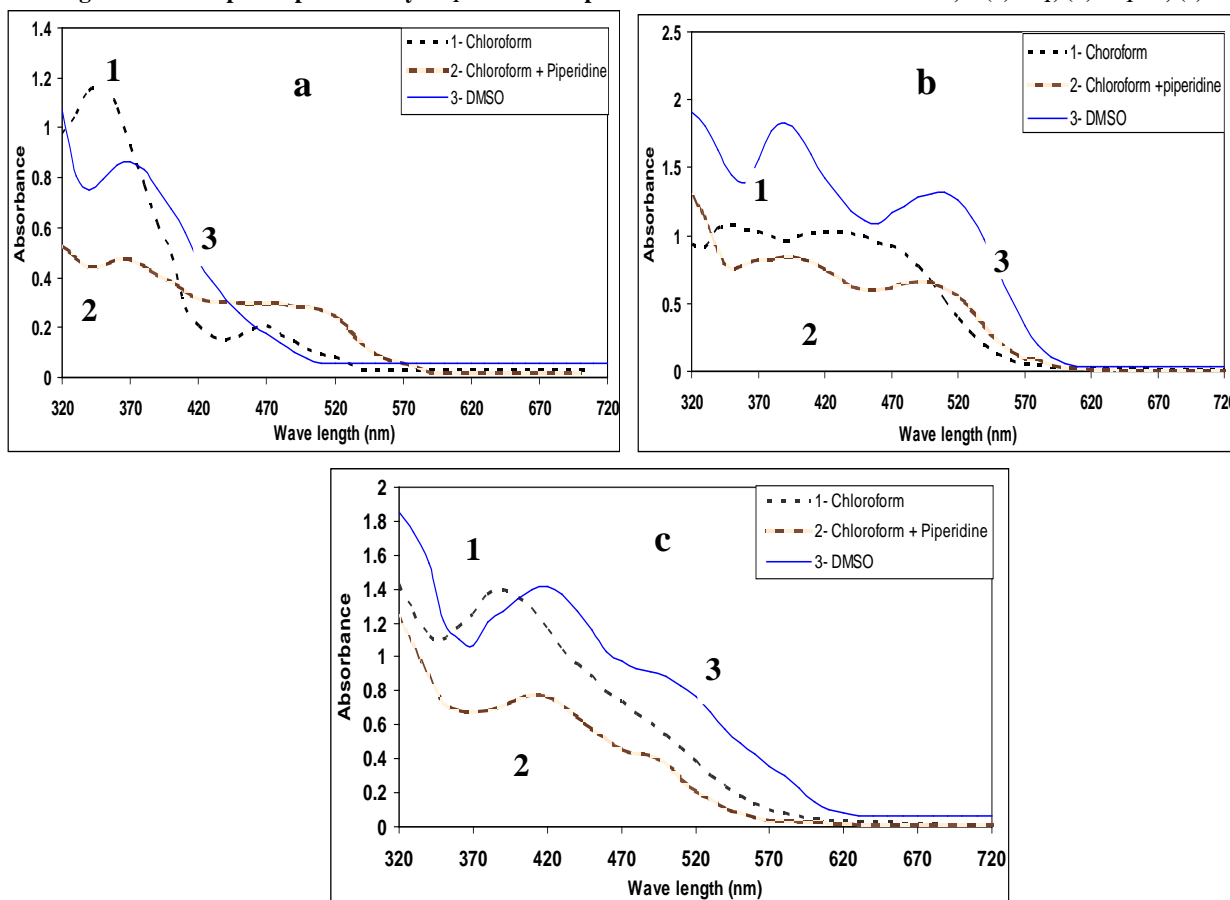
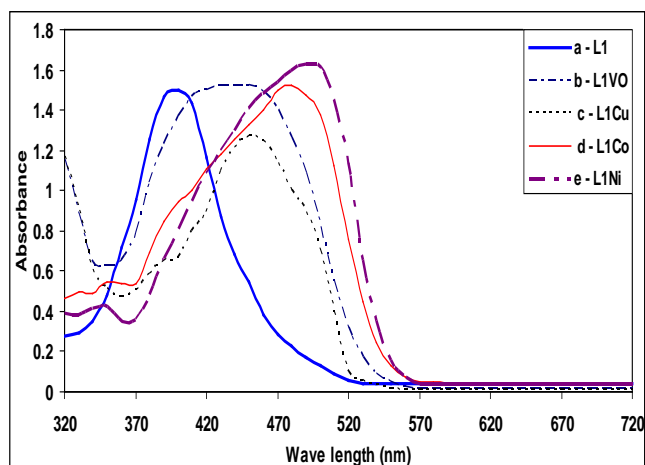


Figure 5: Absorption spectra of dye L_2 and its complexes in neutral and basic solutions, (a): L_2 , (b): $L_2 Ni$, (c): $L_2 Co$.



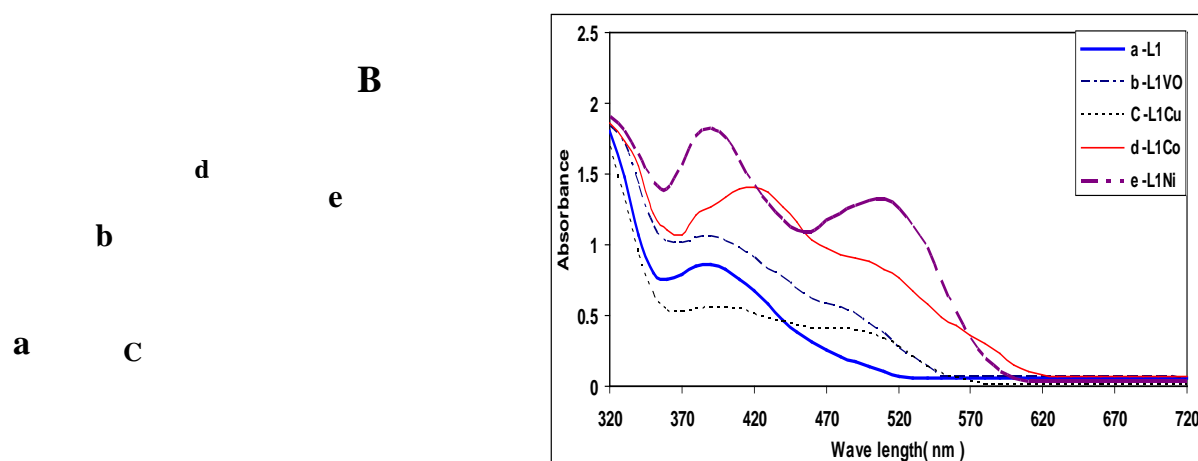


Figure 6 : Absorption spectra of (A): dye L_1 and its complexes in DMSO solvent, (a): L_1 , (b): $L_1 VO$, (c): $L_1 Cu$ (d): $L_1 Co$ (e) $L_1 Ni$.
(B) : dye L_2 and its complexes in DMSO solvent, (a): L_2 , (b): $L_2 VO$, (c): $L_2 Cu$ (d): $L_2 Co$ (e) $L_2 Ni$.

Table 2 : Influence of solvents on λ_{max} (nm) of azo-dyes (L_1 and L_2) and their complexes ($L_1 Ni$, $L_1 Co$, $L_1 VO$, $L_1 Cu$) ; ($L_2 Ni$, $L_2 Co$, $L_2 VO$, $L_2 Cu$).

compounds	DMSO	DMF	acetonitrile	methanol	Acetic acid	chloroform
L_1	402	401	389	388	385	374
$L_1 Ni$	497	494	449	437	441,519	405,557
$L_1 Co$	478	471	447	433,577	426	395
$L_1 VO$	438	432	407,561	397	389	381
$L_1 Cu$	457	454	442	400,450	392	389
L_2	370	370	361	354	350,461	348,452
$L_2 Ni$	391,487	387,485	377,461	368,458	358,465	352,457
$L_2 Co$	381,483	379,477	370	361,450	351	348
$L_2 VO$	417,497	417,497	411,486	407,482	393	384
$L_2 Cu$	404,490	403,487	394,465	389	383	362

Table 3 : Absorption maximum on λ_{max} (nm) of azo-dyes (L_1 and L_2) and their complexes ($L_1 Ni$, $L_1 Co$, $L_1 VO$, $L_1 Cu$) ; ($L_2 Ni$, $L_2 Co$, $L_2 VO$, $L_2 Cu$) in acidic and basic solutions.

compounds	DMSO	DMSO + piperidine	DMF	DMF + piperidine	methanol	Methanol + KOH	Methanol + HCl	chloroform	chloroform + piperidine
L_1	402	402	401	401	388	389	371	374	392,470
$L_1 Ni$	497	501	494	496	437	437	398	405,557	485
$L_1 Co$	478	479	471	471	433,577	581	390	395	459
$L_1 VO$	432	438	438	432	397	397	380	381	432
$L_1 Cu$	457	459	456	456	400,450	456	395	389	441
L_2	370	370	370	371	354	354	331	348,452	355,459
$L_2 Ni$	391,487	400,488	387,485	387,483	368,458	437	338,451	352,457	361,468
$L_2 Co$	417,497	428,497	417,497	424,496	407,482	485	386	384	425
$L_2 VO$	381,483	386,485	379,477	489,477	361,450	453	340	348	411
$L_2 Cu$	404,490	409,491	403,487	411,85	389	390	359	362	418

Table 4 : Electronic spectral data and $\Delta\lambda'_{\max}$ of azo-dyes (L_1 and L_2) and their synthesized complexes in DMSO solvent.

compounds	λ_{\max} (nm)	$\Delta\lambda'_{\max}$
L_1	402
L_1Ni	497	95
L_1Co	478	76
L_1VO	438	36
L_1Cu	457	55
L_2	370
L_2Ni	391,487	21
L_2Co	417,497	47
L_2VO	381,483	11
L_2Cu	404,490	34

3.3.Molar conductance data

The solubility of the synthesized complexes in DMF permitted determination of the molar conductivity Λ_m of (25×10^{-6} - 1×10^{-2} M) solutions at 25 °C and by comparison, the electrolytic nature for each complex. The high values of the molar conductance data listed in table 5 when the concentration of these complexes are equal to 10^{-4} M and these values indicate that the complexes are good electrolytes. The specific conductivity increased when the concentration of the solution was increased, this property is due to the increase of the number of ions that are found in solution. This increasing perhaps is due to the change in the concentration of electrolyte or the change in the degree of dissociation [29], for these reasons molar conductivity should be used to explain the variation of the conductivity with concentration. Kolorash

equation was applied to synthesized complexes, plot of Λ_m versus $(C)^{1/2}$ were shown, See Figure 7 for L_1Ni , L_1VO and L_2Ni , L_2VO .

$$\Lambda_m = \Lambda_0 - S \sqrt{C} \quad (1)$$

It was shown that molar conductivity for complexes increased in dilute concentration. We obtained the molar conductivity in zero concentration Λ_0 and dissociation constant K_d for these complexes when kraos equation was drawn and we obtained linear function, for example Figures 8. Table 6 shows Λ_0 and K_d values for synthesized complexes.

$$\Lambda_m \cdot C = K_d \cdot \Lambda_0^2 (1 / \Lambda_m) - K_d \cdot \Lambda_0 \quad (2)$$

Λ_m = Molar conductivity. C = The molar concentration.

K_d = Dissociation constant. Λ_0 = Molar conductivity at infinite dilution.

From table 5 , we obtained that the molar conductivity values of dye **L₁** complexes with Ni(I I), VO(I V), Cu(I I) and Co(I I) ions are higher than the molar conductivity values of dye **L₂** complexes with the same ions. The reason of this result may be that dye **L₁** and their complexes are containing donating group $-\text{OCH}_3$ group in the benzene ring, but in dye **L₂** and their complexes are containing accepting group $-\text{COCH}_3$ group in the benzene ring. For example, the molar conductance at 10^{-4} M of **L₁Ni** =136 $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ but in **L₂Ni**=120 $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ and the molar conductance of **L₁VO**= 72 $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ while for **L₂VO**= 41 $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$.

$\text{cm}^2\text{mole}^{-1}$. Another interesting results of this study is the fact that the molar conductance of Ni(I I) complexes of azo-dyes(**L₁**and **L₂**) (**L₁Ni** and **L₂Ni**) are higher than those of VO(I V), Cu(I I) and Co(I I) complexes with the same ligand, (**L₁VO**, **L₁Cu** and **L₁Co**) and (**L₂VO**, **L₂Cu** and **L₂Co**) respectively. See table5. For example, the molar conductance at 10^{-4} M of **L₁Ni** =136 $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$, **L₁VO**=72 $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$, **L₁Cu**=56 $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$, **L₁Co**=38 $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$. Therefore, we can arrange the influence on molar conductance of synthesized complexes for dye **L** (**L** = **L₁** or **L₂**) in the order **LNi** > **LVO** > **LCu** > **LCo**

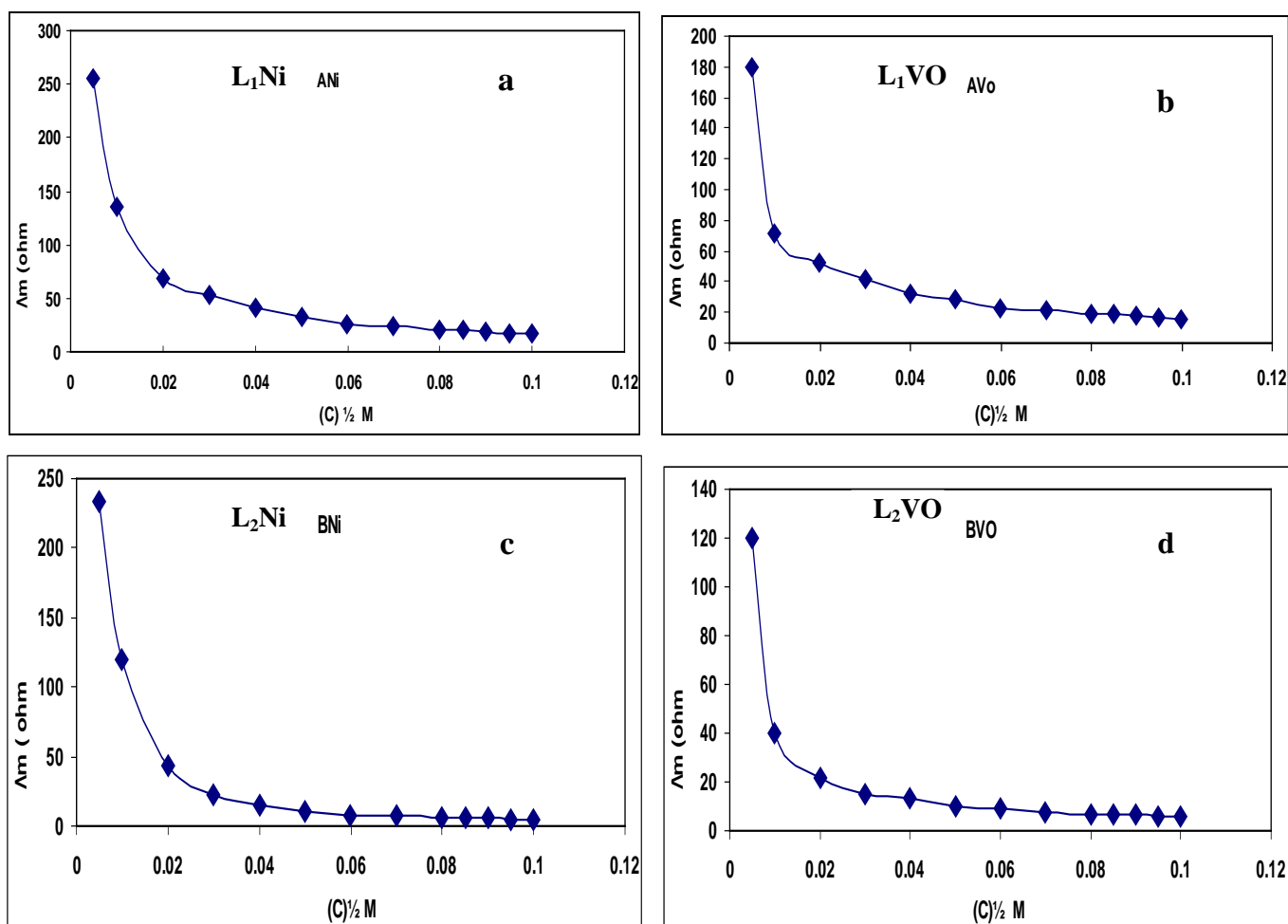


Figure 7 : Molar conductivity Λ_m against $(C)^{1/2}$ for
(a): **L₁Ni**, (b): **L₁VO**, (c): **L₂Ni**, (d): **L₂VO** .

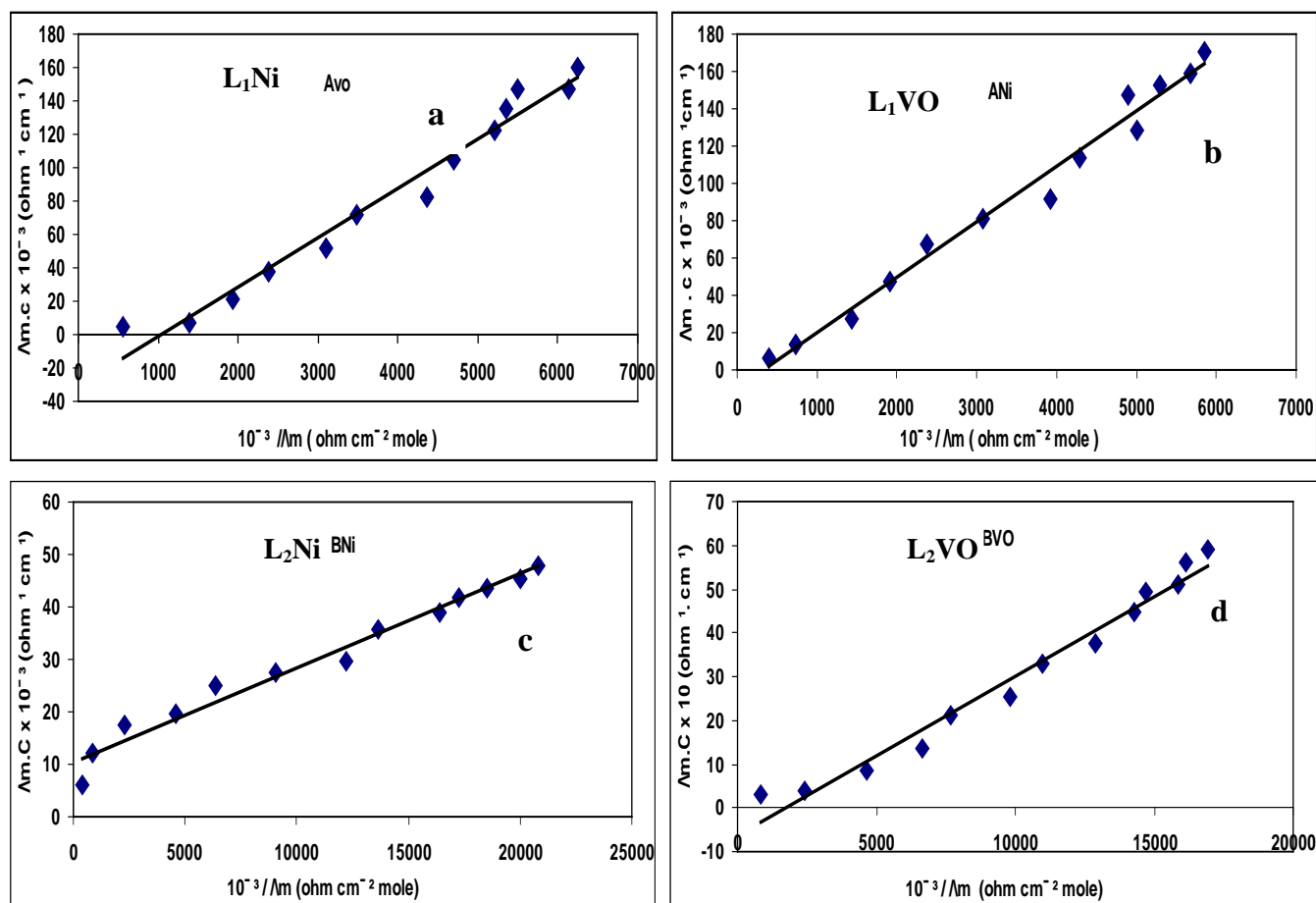


Figure 8 : Molar conductivity $\Lambda_m.C \times 10^{-3}$ against $10^{-4} / \Lambda_m$ for (a): L_1Ni , (b): $L_1 VO$, (c): $L_2 Ni$, (d): $L_2 VO$.

Table 5: Physical data of metal complexes of azo-dyes (L_1 and L_2).

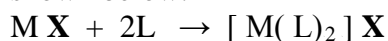
Compounds	Colour	% Yield	M.p. (C°)	Conductance at $10^{-4}M$ ($\text{Ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$)
$L_1 Ni$ [(C ₁₆ H ₁₃ N ₃ O ₃) ₂ Ni](CH ₃ COO) ₂	Light Brown	84	>320	136
$L_1 Co$ [(C ₁₆ H ₁₃ N ₃ O ₃) ₂ Co](CH ₃ COO) ₂	Violet	82	>330	38
$L_1 VO$ [(C ₁₆ H ₁₃ N ₃ O ₃) ₂ VO] SO ₄	Violet	89	>338	72
$L_1 Cu$ [(C ₁₆ H ₁₃ N ₃ O ₃) ₂ Cu] Cl ₂	Dark Brown	92	>290	56
$L_2 Ni$ [(C ₁ H ₁₃ N ₃ O) ₂ Ni](CH ₃ COO) ₂	Light Brown	75	>350	120
$L_2 Co$ [(C ₁ H ₁₃ N ₃ O) ₂ Co](CH ₃ COO) ₂	Light Brown	80	>350	35
$L_2 VO$ [(C ₁ H ₁₃ N ₃ O) ₂ VO] SO ₄	Dark Brown	83	>340	41
$L_2 Cu$ [(C ₁ H ₁₃ N ₃ O) ₂ Cu] Cl ₂	Dark Brown	79	>315	36

*Decomposition point.

Table 6: Molar conductivity at infinite dilution Λ_o and Dissociation constant K_d for complexes between azo-dyes (L_1 and L_2) and their complexes with Ni(I I),Co(I I),VO(I I), Cu(I I) ions.

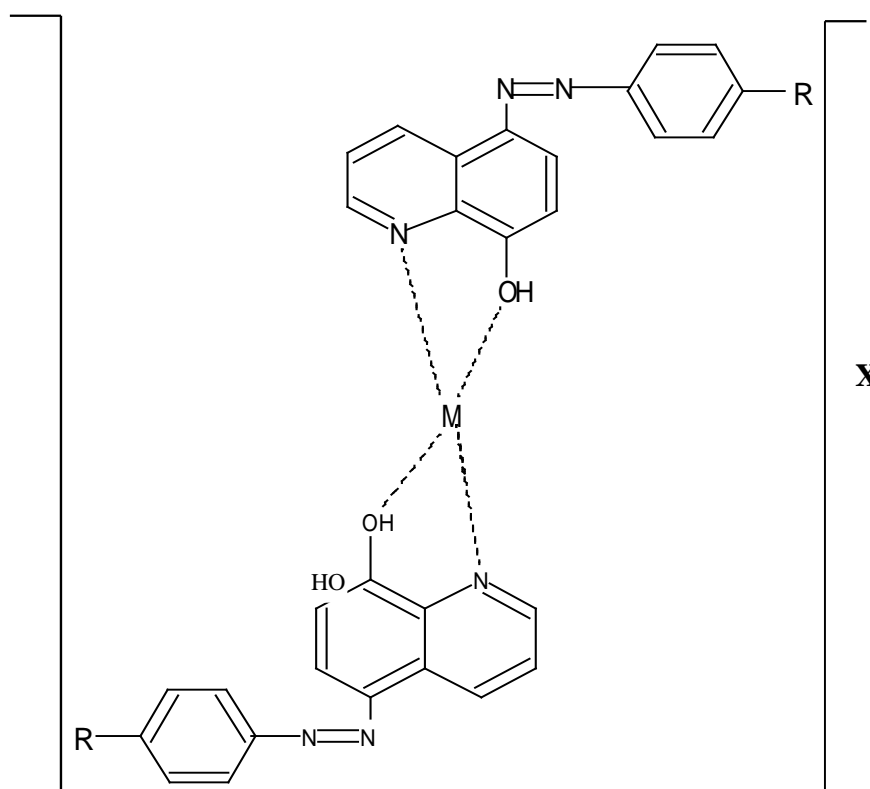
complexes	Λ_o ($\text{Ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$)	$K_d \times 10^{-4}$ (mole.cm^{-3})
$L_1 \text{ Ni}$	310	42.9032
$L_1 \text{ Co}$	143	0.9326
$L_1 \text{ VO}$	223	2.3364
$L_1 \text{ Cu}$	153	1.9450
$L_2 \text{ Ni}$	280	39.6429
$L_2 \text{ Co}$	118	0.3559
$L_2 \text{ VO}$	148	1.9572
$L_2 \text{ Cu}$	138	1.3861

The general reaction for the synthesis of the metal complexes of azo-dyes (L_1 and L_2) is shown below:

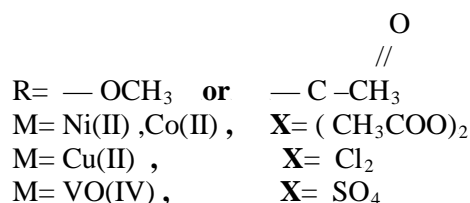


From the IR spectra, we observed that nitrogen atom and H O group of 8-hydroxyquinoline have been considered partially in coordination in the synthesis of

complexes whereas the HO group still existed. We concluded from the high molar conductance that these complexes have ionic structure. It is possible to suggest the geometrical structure for the synthesized complexes between azo-dyes (L_1 and L_2) with Ni (I I), Co(I I),VO(I V) and Cu(I I) ions, as shown below :



where:



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الملخص

تم تحضير صبغتين جديدتين من أصباغ الأزو (L₁) [5-(4-anisidinyl azo)-8-hydroxyquinoline] و (L₂) [5-(4-acetyl phenyl azo)-8-hydroxyquinoline] بواسطة إرتباط 8-hydroxyquinoline مع p-anisidine و p-amino acetophenone من خلال تفاعلات الإزدواج أحادية الأزو. لقد تمت مفاعلة الأصباغ الجديدة المحضرة مع أملاح VO(IV)، Cu(I)، Co(I)، Ni(I) والتي أعطت معقدات أحادية نواة العنصر ذات هيئة فراغية عامه بالشكل [M(L)₂]. لقد أوضحت النسبة 1:2 (M:L) بلن الشكل الهندسي حول أيونات Cu(I)، Co(I)، Ni(I) هو مربع مستوي غير أن الشكل الهندسي حول أيونات VO(IV) هو مربع الهرم الثلاثي. كما تم تشخيص تراكيب كل من الأصباغ ومعقداتها الجديدة المحضرة بواسطة الأشعة تحت الحمراء FTIR والأشعة المرئية وفوق البنفسجية UV-visible وقياسات التوصيلية المولارية. لقد وضحت قياسات FTIR بلن الليكاندات (الأصباغ) تتناسق مع أيونات العناصر بحيث تسلك كليكاندات ثنائية السن bidentate ligand وتكون معقدات مع الأصباغ الجديدة المحضرة (صبغة الأزو L₁ و صبغة الأزو L₂) من خلال تناسق كل من مجموعة O-H وذرة النتروجين في 8-hydroxyquinoline مع أيون العنصر. لقد تم قياس التوصيلية المولارية للمعقدات الجديدة ووجدنا بلن هذه المعقدات هي الكتروليتات قوية وأنها تمتلك تراكيب أيونية. كما تم حساب التوصيلية المولارية عند التركيز الصفر Λ₀ و ثابت التفكك K_d للمعقدات المحضرة. لوحظ بأن قيم التوصيلية المولارية لمعقدات الصبغة L₁ مع أيونات (Ni(I)، VO(IV)، Cu(I)، Co(I)) أعلى قيمه مقارنة بقيم التوصيلية المولارية لمعقدات الصبغة L₂ مع نفس الأيونات. كما تم التحري عن خواص الذائبية للأصباغ ومعقداتها في مذيبات مختلفة، ووجد بلنّها اعتمدت بقوة على طبيعة المذيب وتقوم بتحفيز حالة التوازن و صبغة الأنيون لأصباغ الأزو هي الأكثر شيوعا في مذيبات DMSO، DMF. كذلك تمت دراسة تأثير كل من الحامض والقاعدة على حالة التوازن هذه. كما حصلنا من أطياف الأمتصاص لمعقدات الأصباغ المحضرة، بلن حزم الأمتصاص تزداد نحو طول موجي أعلى مقارنة مع الليكاندات الحرة المقترنه بالأيون.