

# Synthesis and Study of an Azo-azomethine Dyes with N,O Donor Set of Atoms and Their Cu (II), Co (II) and Ni(II) Complexes

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## Abstract

The Synthesis of azo-azomethine ligand H<sub>2</sub>L, 2,2'(1,2-phenylenebis(azanylidene)bis (methanylydene) bis(4-phenyldiazenyl) phenol were carried out by the condensation of phenyl -1,2-diamine with 2-Hydroxy -5-(phenyldiazenyl)benzaldehyde. Reaction of this ligand with Nickel (II), Cobalt (II) and Cooper (II) ions were carried out by using metal chloride salts by the 1:1 molar ratio. Three new organometallic complexes were obtained, the Cu (II), and Ni (II) are tetracoordinate binding to two phenolic oxygens and two imine nitrogen in approximate square planar geometry. Co (II) also coordinates using the same sites like other metals but gave octahedral configuration. The structure of the ligand and its metal complexes were elucidated by elemental analyses, IR, <sup>1</sup>H <sup>13</sup>C NMR, electronic spectra.

**Keywords:** Azo-azomethine, tetracoordinate, phenolic, imine.

## Introduction

Dyes used before the nineteenth century were either of vegetable or animal origin and belonged to various chemical types<sup>[1]</sup>. Colorants, which include chromophores of dyes have been widely used owing to their versatility in various fields. This colorants usually consisting of C=C, N=N, C=N, and aromatic and heterocyclic rings, containing oxygen, nitrogen or sulfur. Synthetic dyes are extensively used in industry and the main synthetic dye classes include azo. Azo compounds are versatile molecules and have received much attention in research both fundamental and application<sup>[2]</sup>. This interesting feature maybe because of the existence of both hard nitrogen and/or oxygen donor atoms in the backbones of these compounds, some of which have interesting physical and chemical properties<sup>[3]</sup>. Apart from this interest, azo-azomethine has been used in many practical applications such as coloring fibers<sup>[4]</sup>, photoelectronics<sup>[5]</sup>, printing systems<sup>[6]</sup>, optical storage technology<sup>[7]</sup> and textile dyes<sup>[8]</sup> as well as in many biological reactions<sup>[9]</sup> and in analytical chemistry<sup>[10]</sup>.

Regarding the industrial importance of azo dyes relative to their structures, they can be classified into two main types: those in which the azo group participates in coordination to the metal ion with formation of the chelate ring and those in which it is not<sup>[11]</sup>. Schiff bases derived from the salicylaldehydes are known as polydentate ligands. Schiff base ligands have significant importance in chemistry; especially in the development of Schiff base complexes, because Schiff base ligands are potentially capable of forming stable complexes with metal ions<sup>[12]</sup>. These transition metal complexes have also grown in the areas of biology due to biological activities, such as antiviral<sup>[13]</sup>, antitumor<sup>[14]</sup>, bactericidal<sup>[15]</sup>, fungicidal<sup>[16]</sup> and nonlinear optical properties<sup>[17]</sup>. This type of the compounds have been used for metal analyses, for device applications related to telecommunications, optical computing<sup>[18]</sup>, storage<sup>[19]</sup>, and information processing<sup>[20]</sup>.

Because of the importance of azo-containing Schiff base compounds and in continuance of the interest in syntheses of azo based compounds, herein syntheses and characterization of a series of azo-linked salicylidenic Schiff bases named 2,2'(1,2-phenylenebis(azanylidene) bis(methanylydene) bis(4-phenyldiazenyl) phenol and its metal complexes, are reported. The ligands in this study were synthesized by the reaction of phenyl -1,2-diamine with 2-hydroxy -5-(phenyldiazenyl)benzaldehyde.

The Ni(II) , Cu(II) and Co(II) complexes of this Schiff base ligands were also prepared and their structures were confirmed by elemental analysis, IR and UV-visible spectral data.

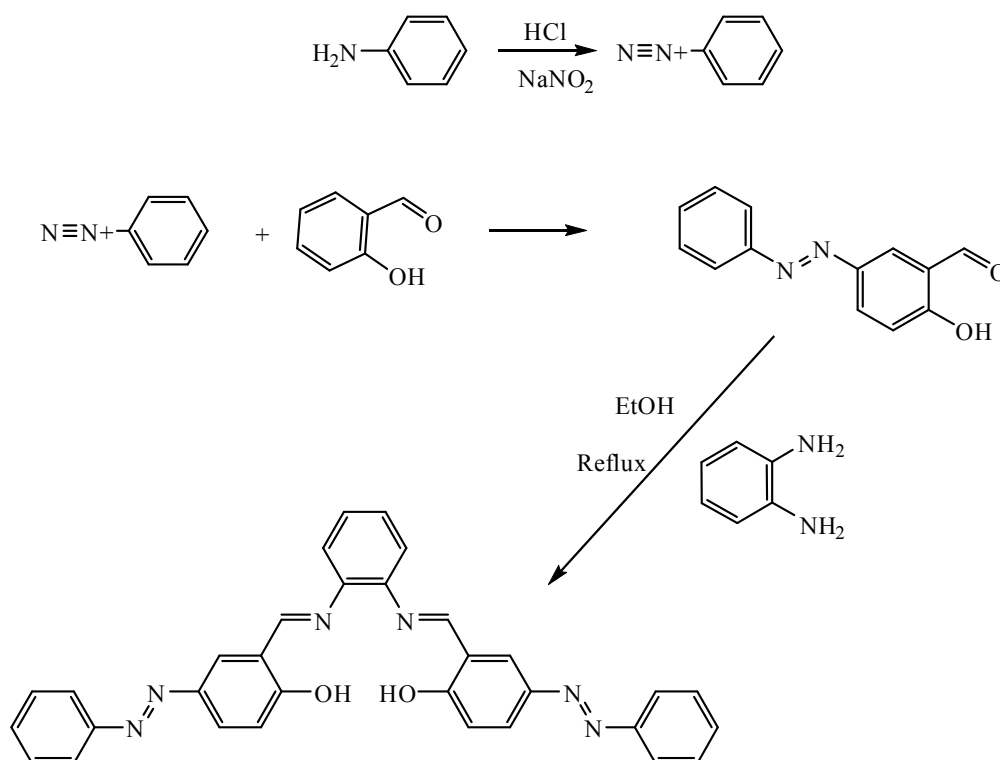
## Experimental

### Reagents and physical measurements

NiCl<sub>2</sub>.6H<sub>2</sub>O (Aldrich, 98.99%), CuCl<sub>2</sub>.2H<sub>2</sub>O (BDH, 98.99%), CoCl<sub>2</sub>.6H<sub>2</sub>O (SCP, 98.99%), and phenyl-1,2-diamine (Merck, 99%). Dimethylformamide (DMF), chloroform (CHCl<sub>3</sub>), hexane, toluene, methanol, ethanol acetone and diethyl ether were purchased from Aldrich Chem. Co. and Merck and used as received. Carbon, hydrogen and nitrogen analyses were performed with a model CE-440 elemental analyzer. The proton NMR spectrum of the azo ligand was determined in the Scientific Studies and Research Center (SSRC), Damascus. The infrared spectra (KBr disc) were recorded in the 4000–400 cm<sup>-1</sup> range on a Perkin Elmer spectrum model FT-IR-4100 spectrophotometer. The electronic spectra were obtained on a Shimadzu 160A UV spectrometer. The melting points were measured with an Electrothermal LDT 9200 apparatus in open capillaries , 2-Hydroxy -5-(phenyldiazenyl)benzaldehyde was prepared as described previously<sup>[21]</sup>, using aniline and salicylaldehyde (Aldrich, 99%) as starting materials.

### Synthesis of H<sub>2</sub>L ligand

A typical procedure for the synthesis of H<sub>2</sub>L is as follows: a solution containing phenyl-1,2-diamine (0.054 g, 0.5 mmol) in 25 mL of EtOH was added drop-wise into a solution involving (0.226 g, 1 mmol) of 2-Hydroxy-5-[(E)-phenyldiazenyl] benzaldehyde in 25 mL of EtOH. The obtained mixture under magnetic stirring was refluxed for 3 h to produce an orange precipitate. The orange H<sub>2</sub>L precipitate was filtered and washed with cold EtOH several times, and finally dried at 50°C in vacuum. The H<sub>2</sub>L ligand was analyzed by <sup>1</sup>H, <sup>13</sup>C NMR and FT-IR spectroscopy. Yield: 59%, m.p. 232–233°C. Anal. Calc. for C<sub>32</sub>H<sub>24</sub>N<sub>6</sub>O<sub>2</sub> (FW:524.57 g/mol): C, 73.27; H, 4.61; N, 16.02. Found: C, 73.16; H, 4.57; N, 15.93%. <sup>1</sup>H NMR (CDCl<sub>3</sub> as solvent, δ in ppm): 13.23 (*b*, 2H, O-H); 8.58 (*s*, 2H, CH=N), 7.86–7.19 (*m*, 20H, aromatic C-H). <sup>13</sup>C NMR (CDCl<sub>3</sub> as solvent, δ in ppm): <sup>13</sup>C NMR (CDCl<sub>3</sub> as solvent, δ in ppm): 118.19 (C<sup>9</sup>), 119.00 (C<sup>8</sup>), 121.10 (C<sup>3</sup>, C<sup>6</sup>), 122.58 (C<sup>13</sup>), 127.39 (C<sup>11</sup>), 127.57 (C<sup>4</sup>, C<sup>5</sup>), 127.88 (C<sup>16</sup>, C<sup>18</sup>), 129.15 (C<sup>15</sup>, C<sup>19</sup>), 130.55 (C<sup>17</sup>), 145.59 (C<sup>12</sup>), 152.57 (C<sup>1</sup>, C<sup>2</sup>), 160.20 (C<sup>14</sup>) 163.88 (C<sup>9</sup>-O), 165.90(C<sup>8</sup>=N). IR (KBr, cm<sup>-1</sup>): 3409 ν(phenolic O–H), 3038 ν(C–H, aromatic), 1586 ν(phenolic C–O), 1624 ν(CH=N), 1484 ν(N=N).



Scheme – The Synthesis of the Azo-azomethine H<sub>2</sub>L Ligand

### Synthesis of Co(II) complex, [CoL(H<sub>2</sub>O)<sub>2</sub>]

A CoCl<sub>2</sub>·6H<sub>2</sub>O (0.237 g, 1 mmol) in 15 mL MeOH was added to a stirring solution of H<sub>2</sub>L(0.524 g, 1 mmol) of in 25 mL hot EtOH/CHCl<sub>3</sub> mixture (15:10). The brownish solution formed was refluxed for an hour and the brown precipitate formed was isolated by filtration, washed with EtOH and dried in air. Yield: 78%, m.p.> 300 °C. Anal. Calc. for Co(C<sub>32</sub>H<sub>26</sub>N<sub>6</sub>O<sub>4</sub>)·2H<sub>2</sub>O (M<sub>w</sub>: 617.53 g/mol): C, 62.24; H, 4.24; N, 13.61. ;Co, 9.54. Found: C, 62.18; H, 4.20; N, 13.56. ;Co, 9.50 %. IR (KBr, cm<sup>-1</sup>): 3790-3350 ν(O-H, hydrated), 3030 ν(C-H, aromatic), 1597 ν(phenolic C–O), 1611 ν(CH=N), 1475 ν(N=N), 540 ν(Co–O), 420 ν(Co–N).

### Synthesis of Cu(II) complex, [CuL]

The complex was prepared by the addition of CuCl<sub>2</sub>·2H<sub>2</sub>O (0.170 g, 1 mmol) in 20 mL EtOH into a stirring solution of the ligand (0.524 g, 1 mmol) in 40 mL hot EtOH/CHCl<sub>3</sub> mixture (25:15). The resulting purple solution formed was refluxed for three hours and left to cool to room temperature. The brownish precipitate obtained was filtered, washed with EtOH and dried. Recrystallization from hot EtOH yielded as a brown solid. Compound purity was followed by T.L.C. and a single spot was observed. Yield: 78%, m.p. > 300 °C. Anal. Calc. for Cu(C<sub>32</sub>H<sub>22</sub>N<sub>6</sub>O<sub>2</sub>) (M<sub>w</sub>: 585.11 g/mol): C, 65.58; H, 3.78; N, 14.34; Cu, 10.84. Found: C, 65.50; H, 3.70; N, 14.31; Cu, 10.82%. IR (KBr, cm<sup>-1</sup>): 3020 ν(C–H, aromatic), 1599 ν(CH=N), 1598 ν(phenolic C–O), 1456 ν(N=N), 510 ν(Cu–O), 414 ν(Cu–N).

### Synthesis of Ni(II) complex, [NiL]

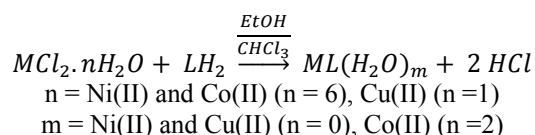
Nickel (II) complex was prepared by mixing a hot  $\text{CHCl}_3$  solution (10 mL) of  $\text{H}_2\text{L}$  (0.524 g, 1 mmol) and methanolic solution (10 mL) of the  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.237 g, 1 mmol). The solution was refluxed for 4 h and then allowed to stand. Yield: 74%, m.p. > 300°C. Anal. Calc. for  $\text{Ni}(\text{C}_{32}\text{H}_{22}\text{N}_6\text{O}_2)$  ( $M_w$ : 581.26 g/mol):

C, 66.12; H, 3.82; N, 14.46; Ni, 10.10. Found: C, 66.07; H, 3.76; N, 14.38; Ni, 10.07%. IR (KBr,  $\text{cm}^{-1}$ ): 3025  $\nu(\text{C-H, aromatic})$ , 1603  $\nu(\text{CH=N})$ , 1593  $\nu(\text{phenolic C-O})$ , 1470  $\nu(\text{N=N})$ , 525  $\nu(\text{Ni-O})$ , 419  $\nu(\text{Ni-N})$ .

## Results and discussion

### Preparation and solubility

The elemental analyses agreed well with 1:1 metal to ligand stoichiometry for all the metal complexes. The complexes are in various colours varied from purple, pale green to brownish colour different from the colour of the ligand  $\text{H}_2\text{L}$  indicating that the colours formed depend on the transition metal ions. The melting points of the complexes are different (higher) than that of the azo Schiff base ligand, an evidence for complexation. All the metal complexes were soluble in EtOH, MeOH,  $\text{CHCl}_3$ ,  $(\text{Me})_2\text{CO}$ , and DMF. In Ni(II) and Cu(II) complexes of the bisazo Schiff base ligand acts as a tetradentate ligand and binds through the oxygen of the phenoxyl group and nitrogen of  $\text{CH=N}$  azomethine to give square planar geometry while Co(II) gave octahedral geometry. The formation of the metal complexes may be represented by the general equation:



The structures of the complexes of Ni(II), Cu(II) and Co(II) were proposed by the analytical and spectroscopic data.

### $^1\text{H}$ and $^{13}\text{C}$ NMR spectroscopy

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the ligand were recorded. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the  $\text{H}_2\text{L}$  ligand are shown in Figs. 1 and 2, respectively. In the  $^1\text{H}$  NMR spectrum of shown a signal at  $\delta$  13.23 ppm assigned to the phenolic -OH protons [22]. The presence of this singlet, due to the H-bonded OH-group, indicates a high contribution of the enolic structure. A characteristic singlet signal at  $\delta$  8.58 ppm is assignable to azomethine protons ( $-\text{CH=N}-$ ) [23]. In addition the  $^{13}\text{C}$  NMR of the ligand shows aromatic carbons in the region of  $\delta$  160.20-118.19 ppm. In the spectrum the signals at  $\delta$  163.88 and  $\delta$  165.90 ppm are due to phenolic C-OH and  $\text{CH=N}$ , respectively.

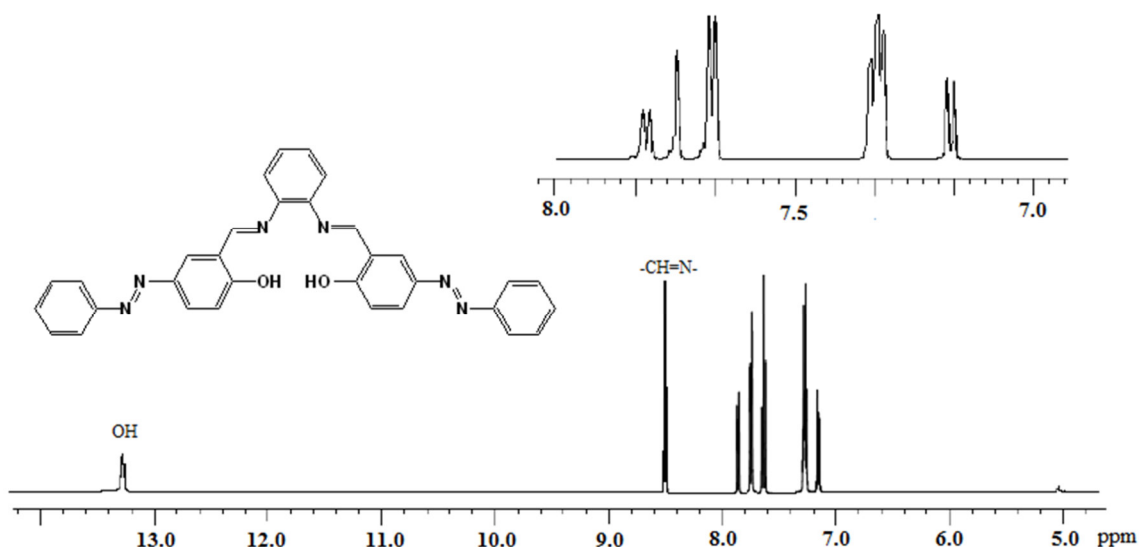


Fig. 1.  $^1\text{H}$  NMR spectrum of the ligand  $\text{H}_2\text{L}$

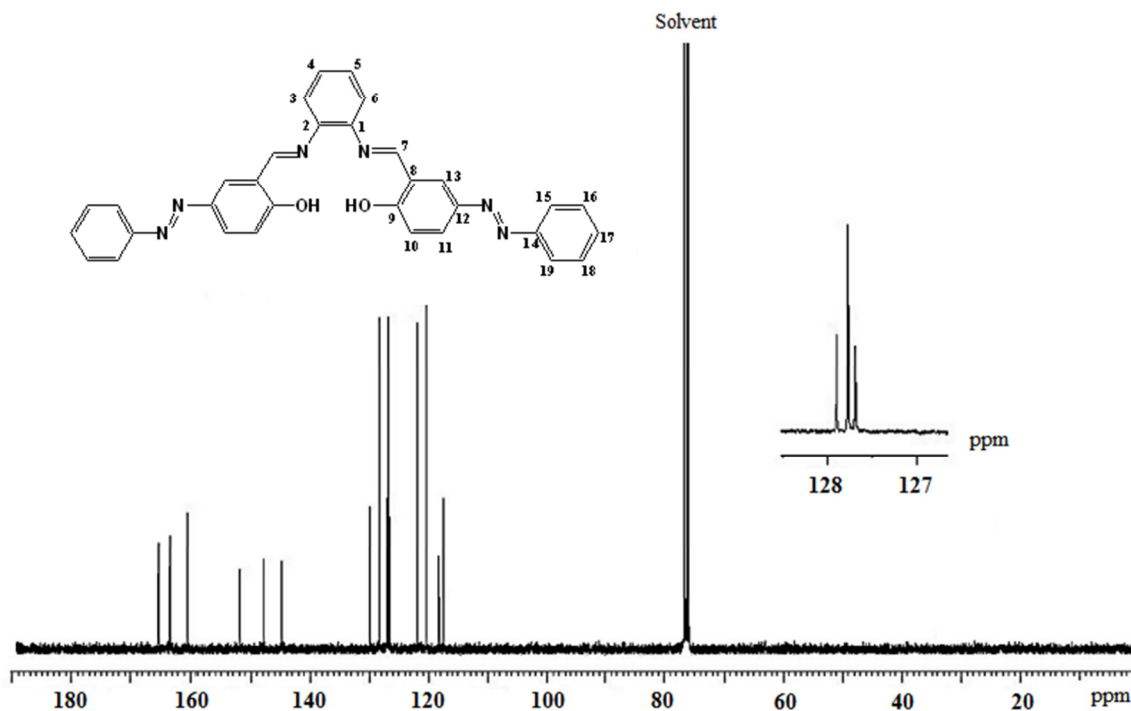


Fig. 2.  $^{13}\text{C}$  NMR spectrum of the ligand  $\text{H}_2\text{L}$

### Vibrational spectroscopy

The characteristic IR data of the ligand 2,2'(1,2-phenylenebis(azanylidene)bis (methanylydene) bis(4-phenyldiazenyl) phenol and its metal complexes listed in Table 2.

In order to clarify the mode of bonding, the IR spectra of the ligand  $\text{H}_2\text{L}$  and its complexes were studied on careful comparison of the latter with the former. The IR spectrum of the ligand exhibit bands at  $3409\text{cm}^{-1}$  and  $3038\text{cm}^{-1}$  that are assignable to  $\nu(\text{OH})$  and  $\nu(\text{Ar}-\text{CH})$  [24-25], and the appearance of absorptions bands at  $1624\text{v}$  ( $\text{C}=\text{N}$ ),  $1586\text{v}$  ( $\text{C}-\text{O}$ ),  $1484\text{v}$  ( $\text{N}=\text{N}$ ),  $1521-1425\text{v}$  ( $\text{C}=\text{C}$ ),  $1286\text{v}$  (bs,  $\text{C}-\text{N}$ ) is in agreement with the structure proposed of the ligand. In the IR spectra of all complexes, show vibrational bands at  $1611-1599$ ,  $1575-1556$ ,  $1470-1459\text{cm}^{-1}$  assigned for  $\nu_s$  and  $\nu_{as}$  of the  $\text{C}=\text{N}$ , phenolic  $\text{C}-\text{O}$ ,  $\text{N}=\text{N}$  groups, respectively. Also, the IR spectra of the all complexes show that the stretching frequency of the  $\text{C}=\text{N}$  band was shifted to lower wave numbers (ca.  $13-25\text{cm}^{-1}$ ) in comparison with the free ligand after coordination. This shift is due to the reduction of the double bond character of the  $\text{C}=\text{N}$  bond, which is caused by the coordination of nitrogen to the metal center and is in agreement with the results obtained from the other similar complexes described previously [26-27]. On the Other hands, the disappearance of the OH band of the free ligands in the spectra of the metal complexes indicates that the OH group has been deprotonated and coordinates to the metal ion as  $-\text{O}-$  indicating that ligand  $\text{H}_2\text{L}$  bind to metal ions in a binegative tetradentate fashion through two  $\text{C}=\text{N}$  and two OH groups with deprotonation of OH groups. Upon coordination of the ligand with metals, the absorption of new weak bands near  $547-506\text{cm}^{-1}$  and  $430-410\text{cm}^{-1}$  range are observed from the spectra of all complexes may contribute to  $\text{M}-\text{O}$  and  $\text{M}-\text{N}$  starching. [28-31]

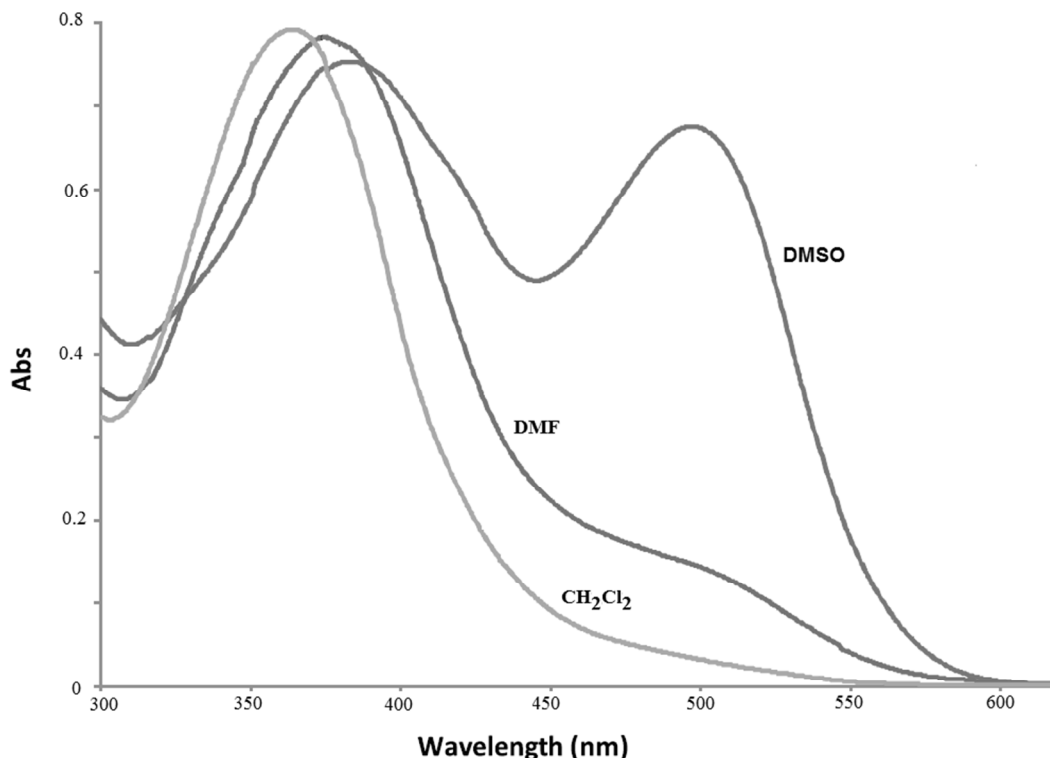
Table 2 Characteristic IR bands of the ligand  $\text{H}_2\text{L}$  and its metal complexes ( $\text{cm}^{-1}$ , KBr)

Compound	$\nu(\text{OH})$	$\nu(\text{Ar}-\text{C}-\text{H})$	$\nu(\text{CH}=\text{N})$	$\nu(\text{N}=\text{N})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
$\text{H}_2\text{L}$	3409	3038m	1624s	1484s	-	-
$\text{CoL}(\text{H}_2\text{O})_2$	-	3030m	1611s	1475m	540m	420w
$\text{CuL}$	-	3020m	1599s	1456m	510m	414w
$\text{NiL}$	-	3025m	1603s	1470m	525m	419w

### The Electronic spectra

The electronic absorption spectra of the  $\text{H}_2\text{L}$  ligand were recorded various solvents with different polarities such as dichloromethane, dimethylformamide and dimethylsulfoxide between 250 and 600 nm were taken and the spectrum of the  $\text{H}_2\text{L}$  in various solutions is shown in Figs. 3. The spectroscopic data obtained in this work are agreed well with the previous work [32-33]. Electronic spectrum of the  $\text{H}_2\text{L}$  ligand in these solvents showed two absorption bands. The maximum absorptions in the range of 360-380 nm can be attributed to  $\pi \rightarrow \pi^*$  transitions of  $\pi$  electrons within the structure [34]. The  $\pi \rightarrow \pi^*$  transition of the ligand observed in different wavelengths in

different solvents, which can be attributed to the polarity of the used solvent, since the azo-azomethine ligand contains an imine ( $-\text{HC}=\text{N}-$ ) and an azo ( $-\text{N}=\text{N}-$ ) chromophore groups. In general, the  $\pi \rightarrow \pi^*$  transitions shift to longer wavelengths as the polarity of the solvent increases ( $\text{DMSO} > \text{DMF} > \text{CH}_2\text{Cl}_2$ ). Due to the dipole moment of the solvent, a new dipole moment on the ligand is formed. This solvent effect is greater on the  $\pi^*$  orbital than the  $\pi$  orbital. Therefore, the energy level of the  $\pi^*$  orbital decreases as the result of that the energy of the  $\pi \rightarrow \pi^*$  transitions decreases and the  $\pi \rightarrow \pi^*$  transition absorption red shifts. The second electronic absorption band at 480-500 nm regions which appears as a shoulder in DMF and as an intense band in DMSO solvent might be attributed to the  $n \rightarrow \pi^*$  transition.



**Fig.3. The UV-Vis spectra of the ligand H<sub>2</sub>L in three organic solvents**

The electronic spectra of Co(II) complex have multiple bands observed at 490 nm, 540 nm and 650 nm. These bands are ascribed to  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}$ ;  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$  and  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}$  transitions respectively, which is consistent with the octahedral geometry<sup>[35]</sup>. The Ni(II) complexes have two spin allowed transitions at 450 nm, and 550 nm. These bands are correlated to  ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$  and  ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$  transitions, respectively in a square planar stereochemistry<sup>[36]</sup>. The electronic spectra of Cu(II) complexes shows a band in the range 580–595 nm for  ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$  in a square planar<sup>[37]</sup>.

## Conclusion

In this article three new nickel (II), copper (II) and zinc (II) complexes of azo-Schiff base ligand 2,2'(1,2-phenylenebis(azanylidene)bis(methanylydene)bis(4-phenyldiazenyl) phenol was reported. Characterization of these metal complexes was carried out by elemental analyses, infrared, Electronic and NMR spectra. The bisazo-Schiff base coordinates to the metal ions through the four donor atoms (ONNO type). In the light of the above discussion, distorted square planar structures for Cu (II), and Ni (II) complexes, and octahedral structure for Co (II) chelate is proposed.

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