



ISSN: 0067-2904

## Preparation and Characterization of New (Halogenated Azo-Schiff) Ligands with Some of their Transition Metal Ions Complexes

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Received: 16/10/2021

Accepted: 1/1/2022

Published: 30/8/2022

### Abstract

Two new halogenated azo-Schiff ligands were prepared in two steps. The first step included a condensation between 4-amino acetophenone and 2-fluoro-4-bromo aniline to give the corresponding Schiff base. In the second step, the diazonium salt of this Schiff base reacted with 2-naphthol and 4,5-diphenylimidazole to form two new azo-Schiff base derivatives as ligands; (3-((E)-(4-((E)-1-((4-bromo-2-fluorophenyl) imino)ethyl) phenyl) diazenyl) naphthalen-2-ol (HSBAN) (L1) and ((E)-N-(4-bromo-2-fluorophenyl)-1-(4-((E)-(4,5-diphenyl-1H-imidazol-2-yl) diazenyl) phenyl) ethan-1-imine) (HSBAI) (L2), respectively. These new ligands were characterized by mass spectrometry, FT-IR, <sup>1</sup>H NMR, UV-Visible spectroscopy and elemental microanalysis (CHN). Five divalent transition metal ion complexes (Co, Ni, Cu, Cd, and Hg) were prepared and characterized, beyond the determination of the optimal condition (concentration, pH value, and the mole ratio M:L) using UV-visible studies. Additionally, complementary techniques, such as atomic absorption, electrical conductivity and magnetic susceptibility, were performed to deduce their geometries. The comprehensive study suggested an octahedral geometry for all complexes except Cd and Hg complexes of the first ligand.

**Keywords:** Schiff base; Azo compounds; azo-schiff compounds; TMI complexes; optimal conditions.

### تحضير وتشخيص ليكاندات ازو - شف هاليدية جديدة مع بعض معقداتها لايونات العناصر الانتقالية

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#### الخلاصة

حضرت اثنان من ليكاندات الازو-شف الهاليدية بخطوتين. الخطوة الاولى تضمنت تكاثف بين 4-امينواسيتوفينون و 2-فلورو-4-برومو انيلين لاعطاء قاعدة شيف المقابلة. في الخطوة الثانية، ملح الديازونيوم لقاعدة شيف المحضرة تفاعل مع قواعد الازواج 2-نفثول وال 4,5-داي فنيل ايميدازول لتكوين اثنين من مشتقات الازو - شيف الجديدة كليكاندات: (L1) (HSBAN) و (L2) (HSBAI)، على التوالي. هذه الليكاندات الجديدة شخصت باستخدام طيف الكتلة، تقنية الاشعة تحت الحمراء، طيف الرنين النووي المغناطيسي البروتوني، مطيافية الاشعة فوق بنفسجية-المرئية و التحليل العنصري الدقيق. ولكل ليكاند تم تحضير خمس من معقدات ايونات العناصر الانتقالية ثنائية الشحنة (للكوبلت والنيكل والنحاس والكاديوم والزنك) اضافة

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لتشخيصها في بعض من التقنيات المسبقة الذكر، حيث حضرت المعقدات الصلبة بعد معرفة الظروف المثلى للتحضير من تركيز ودالة حامضية pH ومعرفة النسبة المولية اللازمة لتحضير المعقدات والتي كانت (M:L)1:2 ولجميع المعقدات المحضرة. فيما استخدمت تقنيات تكاملية لإقرار الصيغة البنائية الهندسية للمعقدات (كالاتصاف الذري والتوصيلية المولارية والحساسية المغناطيسية)، ومن خلال نتائج البحث يمكن اقتراح الشكل الهندسي ثماني السطوح لجميع المعقدات عدا معقدي (الكاديوم والزنك) لليكاند الأول.

## 1. Introduction

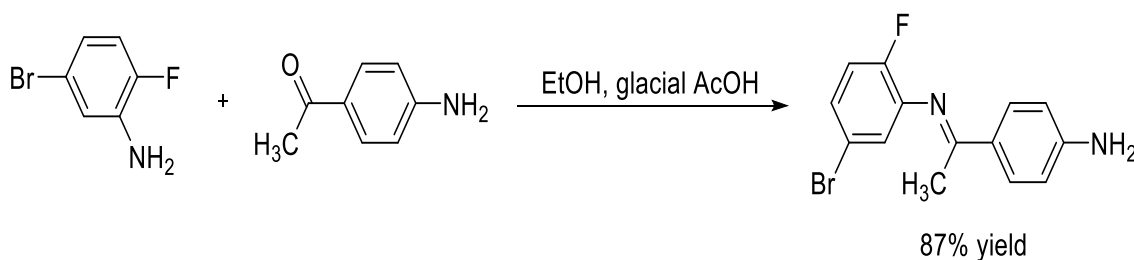
The presence of multiple functional groups in the molecules may improve their properties [1] especially when oriented in essential fields such as medical [2] and industrial [3]. Schiff base (azo-methene) group compounds [4] are one of the most important compounds that have had great importance over the past decades [5,6]. It is synthesized from the primary amine reaction with carbonyl compounds under different conditions [7,8]. The reaction conditions may act as catalysts, corrosion inhibitors, and intermediates in organic synthesis [9-12]. In homocyclic and heterocyclic forms, azo compounds (-N=N-) play an essential role in the dye and pigment industries [13-16]. They have extensively entered the analytical chemistry fields [17,18], indeed into the manufacturing of drugs and other medications [19], and LCD color filters [20].

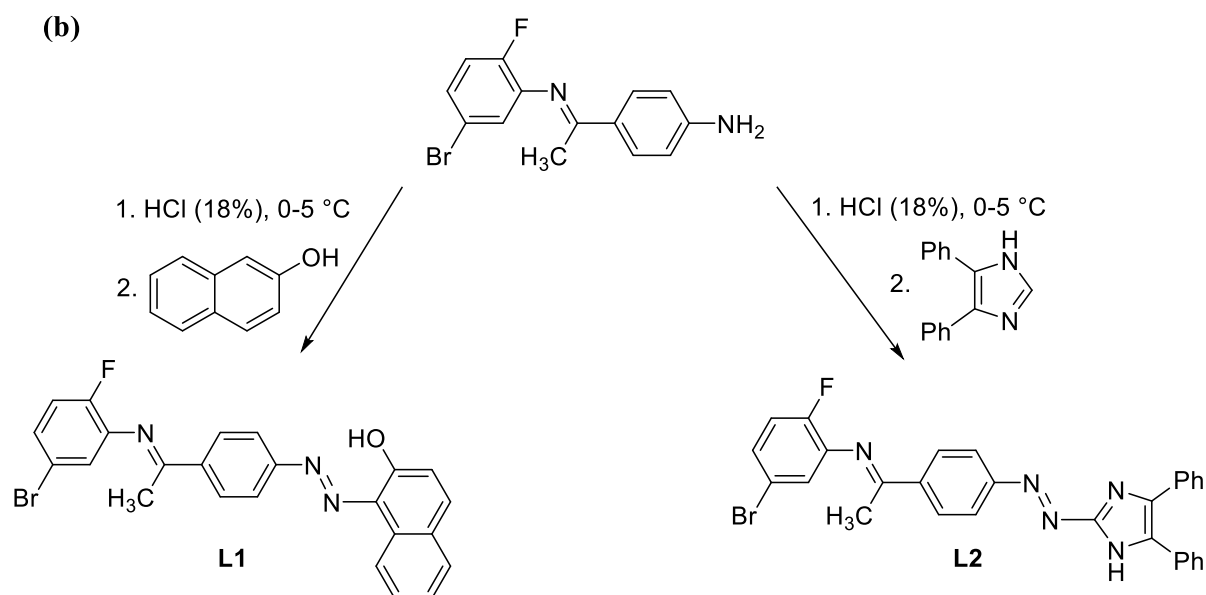
Azo-Schiff base compounds can be prepared according to the compound's characteristics and reaction conditions in two ways. The first way is by synthesizing the azo-moiety, then the Schiff base reaction [21]. The second way is the Schiff base synthesized and then coupled to form azo compounds [22]. These compounds and their complexes have received significant attention in order to gain access to a variety of biological [23] and industrial applications such as textile dye and photoelectronic [24].

## 2. Material and Methods

All chemicals and solvents used in this research are of analytical grades. The stoichiometric analysis (CHN) of the ligands and their complexes was performed using the ECS 4010 CHNOS Elemental analyzer. Metal contents were estimated based on the flame atomic absorption (Shimadzu AA 6800). The FT-IR spectra were recorded using a Burker FTIR spectrophotometer and KBr pellets. The ultra-violet spectra were recorded in the absolute ethanol as a solvent using a Shimadzu 1650 PC.  $^1\text{H}$  NMR spectral data were recorded using a Varian 500MHz frequency. Chemical shifts are quoted in ppm downfield from tetramethylsilane (TMS) as the internal standard and deuterated DMSO in  $^1\text{H}$  NMR as a reference (2.5 ppm). Mass spectrometry data were recorded using Agilent technology (HP) and an ion source of 70eV. Info Lab Terminal recorded the conductivity values for the new complexes, and the magnetic susceptibility data were collected using the Sheward instrument for magnetic measurements.

(a)





**Scheme 1** - (a) Preparation of the amino Schiff base (AHSB), (b) preparation of the azo-Schiff bases ligands

#### Schiff Base Synthesis (AHSB)

A mixture of 4-aminoacetophenone (2.7 gm, 0.02 mol) and 2-fluoro-4-bromo aniline (3.8 gm, 0.02 mol) in absolute ethanol (100 ml), and a few drops of glacial acetic acid were added as a catalyst. When the reaction had reached completion, as mentioned by TLC, the solution was reduced to a minimum and cooled using the iced bath as the reaction was performed. The colored precipitate was developed, and it was filtered and dried; m.p. 65°C, in 87% yield [25].

#### Azo-Schiff Base Ligands Synthesis

Amino Schiff base (3.06 g, 0.01 mol) was dissolved in HCl solution (18%) at 0-5°C. A cooled solution of sodium nitrite (0.69 g, 0.01 mol) in iced distilled water (10 ml) was added drop by drop to the reaction mixture and stirred for 15 minutes. The coupling components 2-naphthol (for L<sub>1</sub>) (1.44 g, 0.01mol) and 4,5-diphenylimidazole (for L<sub>2</sub>) (2.2 g, 0.01 mol) were solvated with an alkaline alcoholic solution. The diazonium salt solution was gently added to the coupling solutions with stirring, keeping in mind that the temperature did not exceed 5°C. The colored precipitates were developed, and their solutions were neutralized to improve the maximum number of azo yields. The new ligands were then filtered and washed twice with deionized water to eliminate the formed salts.

#### Complexes Synthesis

After determining the mole ratio (M:L), the solid transition metal ion complexes for the new ligands L<sub>1</sub> and L<sub>2</sub> were synthesized. These ligands (0.01 mol) were dissolved in hot ethanol (50 ml), and the solution of the selected metal ion chlorides (0.005 mol) was added to the reaction mixture and heated at 50 °C for 1 hour. The formed precipitates in the reaction mixture were filtered and dried over CaCl<sub>2</sub> overnight.

### 3. Results and Discussion

The condensation of 2-fluoro-4-bromo aniline with 4-amino acetophenone produced a Schiff base derivative (AHSB), as shown in Figure 1a. This product was utilized as a precursor (diazonium salt) to prepare new ligands. The ligand L<sub>1</sub> was prepared when AHSB was coupled with 2-naphthol. While the ligand L<sub>2</sub> was prepared when AHSB was coupled with 4,5-diphenylimidazole, as shown in Figure 1b. The newly prepared ligands are stable solids, non-hygroscopic, and easy to access in their solid complexes. Meanwhile, most of them are soluble in organic solvents such as DMF, DMSO, and ethanol; slightly soluble in methanol, chloroform, and acetone; and insoluble in water.

**Table 1** - Analytical and physical data of the ligands and their complexes.

| No. | Compound<br>(Empirical formula)   | Color          | m.p.<br>(°C) | Yield<br>(%) | Elemental analysis (calc./found)<br>(%) |              |                |                |
|-----|---|----------------|--------------|--------------|---|--------------|----------------|----------------|
|     |   |                |              |              | C                                       | H            | N              | M              |
| 1   | Schiff base (AHSB)  | Bright -green  | 65           | 87           | -                                       | -            | -              | -              |
| 2   | L <sub>1</sub> (C <sub>24</sub> H <sub>17</sub> N <sub>3</sub> OBr)   | Reddish-Orange | 165-166      | 77           | 62.35<br>61.33                          | 3.71<br>3.67 | 9.09<br>9.01   | -              |
| 3   | [Co(C <sub>24</sub> H <sub>16</sub> N <sub>3</sub> OBr) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]                | Deep Brawn     | 213-214      | 83           | 56.66<br>56.05                          | 3.57<br>3.52 | 8.26<br>8.19   | 5.79<br>5.74   |
| 4   | [Ni(C <sub>24</sub> H <sub>16</sub> N <sub>3</sub> OBr) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]                | Greenish-Brawn | 221-222      | 90           | 56.67<br>55.98                          | 3.57<br>3.55 | 8.26<br>8.24   | 5.77<br>5.27   |
| 5   | [Cu(C <sub>24</sub> H <sub>16</sub> N <sub>3</sub> OBr) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]                | Brisk-Red      | 225-226      | 78           | 56.40<br>56.22                          | 3.55<br>3.49 | 8.22<br>8.20   | 6.22<br>6.12   |
| 6   | [Cd(C <sub>24</sub> H <sub>16</sub> N <sub>3</sub> OBr) <sub>2</sub> ]  | Red            | 291-292      | 76           | 55.70<br>55.33                          | 3.12<br>3.10 | 8.12<br>8.08   | 10.86<br>10.44 |
| 7   | [Hg(C <sub>24</sub> H <sub>16</sub> N <sub>3</sub> OBr) <sub>2</sub> ]  | Brawn          | 160-161      | 83           | 51.33<br>-                              | 2.87<br>-    | 7.48<br>-      | 17.86<br>-     |
| 8   | L <sub>2</sub> (C <sub>29</sub> H <sub>21</sub> N <sub>5</sub> FBr)   | Orange         | 114-115      | 79           | 64.69<br>63.96                          | 3.93<br>3.77 | 13.01<br>12.54 | -              |
| 9   | [Co(C <sub>29</sub> H <sub>21</sub> N <sub>5</sub> FBr) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> Cl] <sub>2</sub> | Deep-Brawn     | 230-231      | 88           | 56.88<br>56.13                          | 3.62<br>3.44 | 11.44<br>11.04 | 4.81<br>4.18   |
| 10  | [Ni(C <sub>29</sub> H <sub>21</sub> N <sub>5</sub> FBr) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> Cl] <sub>2</sub> | Brawn          | 229-230      | 81           | 56.07<br>55.90                          | 3.73<br>3.70 | 11.27<br>11.11 | 4.72<br>4.21   |
| 11  | [Cu(C <sub>29</sub> H <sub>21</sub> N <sub>5</sub> FBr) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> Cl] <sub>2</sub> | Dark-Red       | 200-201      | 73           | 56.67<br>56.44                          | 3.61<br>3.26 | 11.39<br>11.31 | 5.17<br>5.08   |
| 12  | [Cd(C <sub>29</sub> H <sub>21</sub> N <sub>5</sub> FBr) <sub>2</sub> Cl] <sub>2</sub>                                 | Maron          | 206-205      | 76           | 55.28<br>55.05                          | 3.36<br>3.13 | 11.12<br>11.09 | 8.92<br>8.77   |
| 13  | [Hg(C <sub>29</sub> H <sub>21</sub> N <sub>5</sub> FBr) <sub>2</sub> Cl] <sub>2</sub>                                 | Deep-Red       | 203-204      | 88           | 51.67<br>-                              | 10.39<br>-   | 10.39<br>-     | 14.88<br>-     |

### Spectroscopic Studies

#### FT-IR spectroscopy

When a powerful technique such as single-crystal X-ray crystallography is absent, the less powerful (infrared spectroscopy) may act as a suitable tool that gives information about the nature of the functional groups of the organic ligands [26] and the coordinating sites of the metallic ions with these groups. The spectrum AHSB shows two adjacent amine group frequencies at 3389 and 3325 cm<sup>-1</sup>, respectively, while the azo-methene (C=N) group appeared at 1585 cm<sup>-1</sup>, as shown in Figure 1. In the first ligand (HSBAN), the amine group disappeared clearly, and new frequency was appeared at 1445 cm<sup>-1</sup> due to the azo group of HSBAN [27]. The stretching vibration of the naphthol hydroxyl group (OH) appeared at 3308 cm<sup>-1</sup>. Additionally, the azomethene group observed at 1592 cm<sup>-1</sup> as shown in Figure 2.

Because of the coordination with the metal ions, the intensities and sites of the HSBAN complexes differed. For instance, the absence of the naphthol hydroxyl group and the shifting of the azo group tend to lower the frequency. New frequencies were observed within these complexes' spectra at frequencies around 3300-3100 cm<sup>-1</sup>, related to the coordination of water [28]. Other support frequencies (M-O) were discovered to be less than 500 cm<sup>-1</sup>, which may improve the coordinated and complex formation [28]. These frequencies are shown in Table 2 and Figure 3.

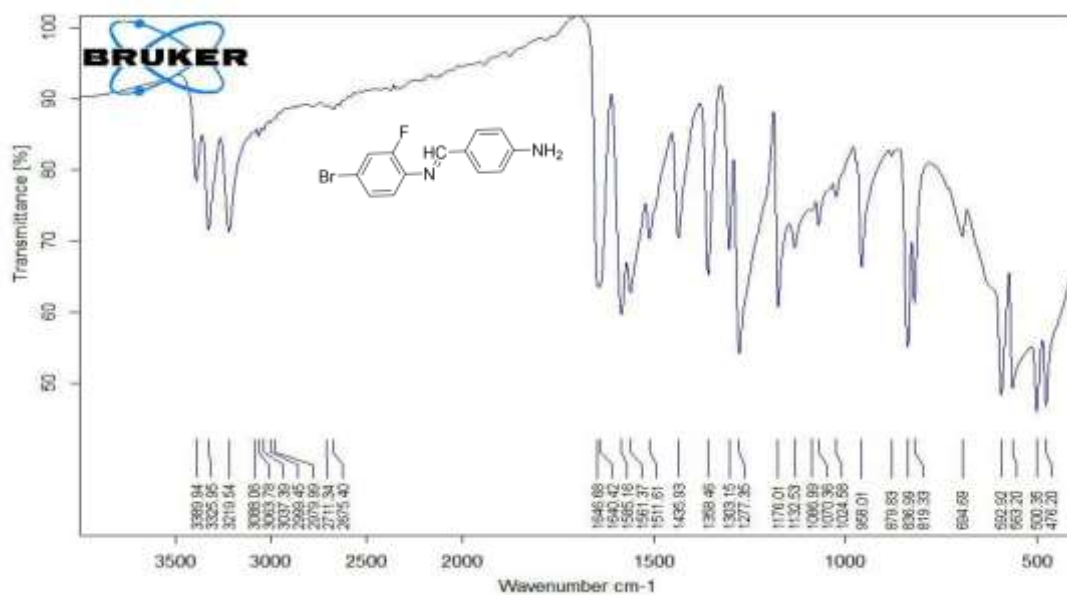


Figure 1 - FT- IR spectrum of amino Schiff base AHSB

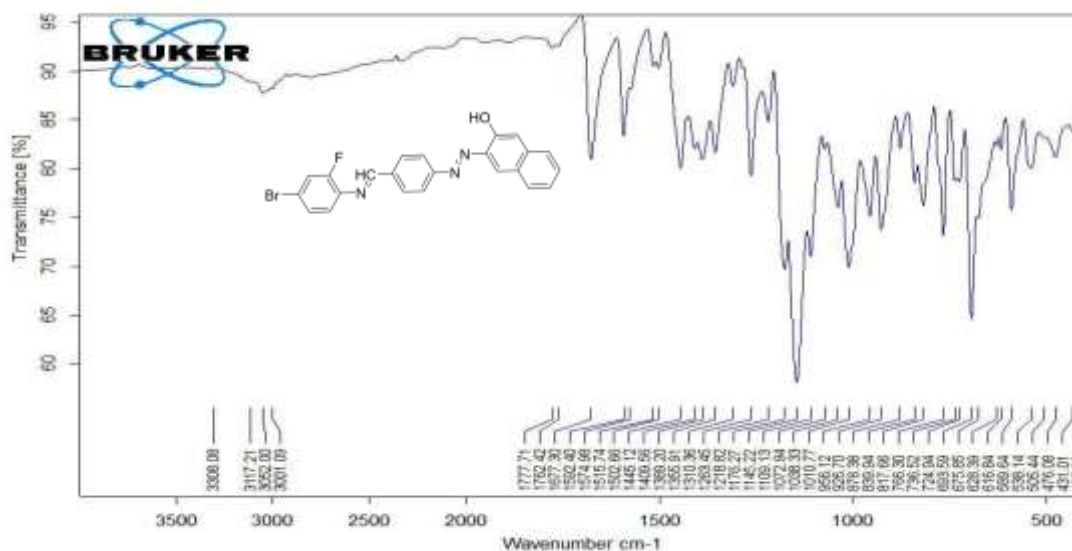


Figure 2 - FT-IR spectrum of HSBAN (L<sub>1</sub>)

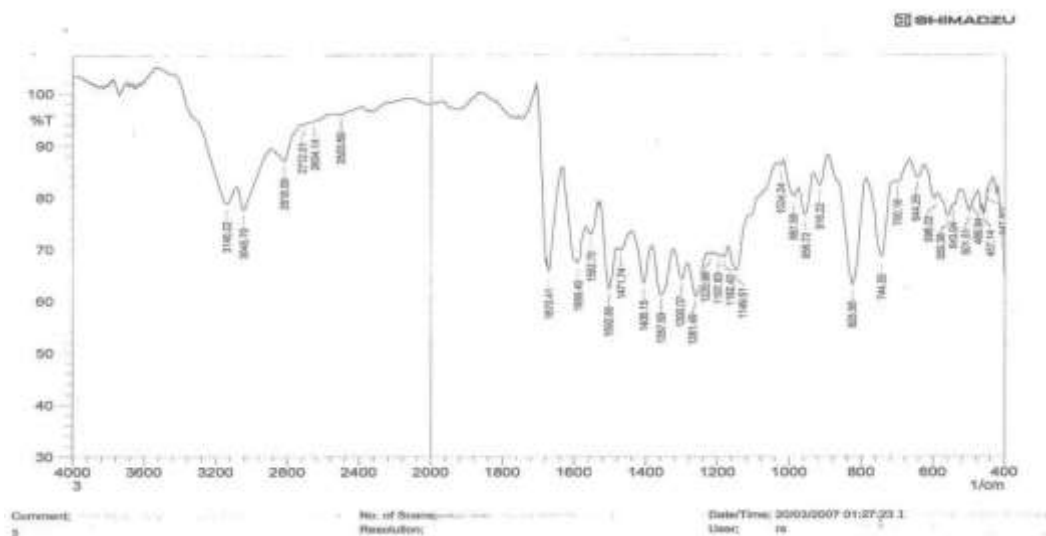


Figure 3 - FT-IR spectrum of CuL<sub>1</sub> complex

The FT-IR spectral data of the second ligand (HSBAI) and its complexes developed the stretching band of the NH group within the  $3600\text{ cm}^{-1}$  frequency region. Due to intramolecular hydrogen bonding [29], these frequencies vanished for other complexes such as Cu, Cd, and Hg. Other influential bands, such as the azo group, appeared at the  $1444\text{ cm}^{-1}$  frequency.

The frequency of the imidazole azo-methene group ( $-\text{C}=\text{N}-$ ) may shift toward low wave numbers or changes in shape and intensity due to coordination with the metal ions. The Schiff base azo-methene is still in approximately the same region. The azo group ( $\text{N}=\text{N}$ ) shifted 10 to  $40\text{ cm}^{-1}$  from the ligand sites, indicating the coordination.

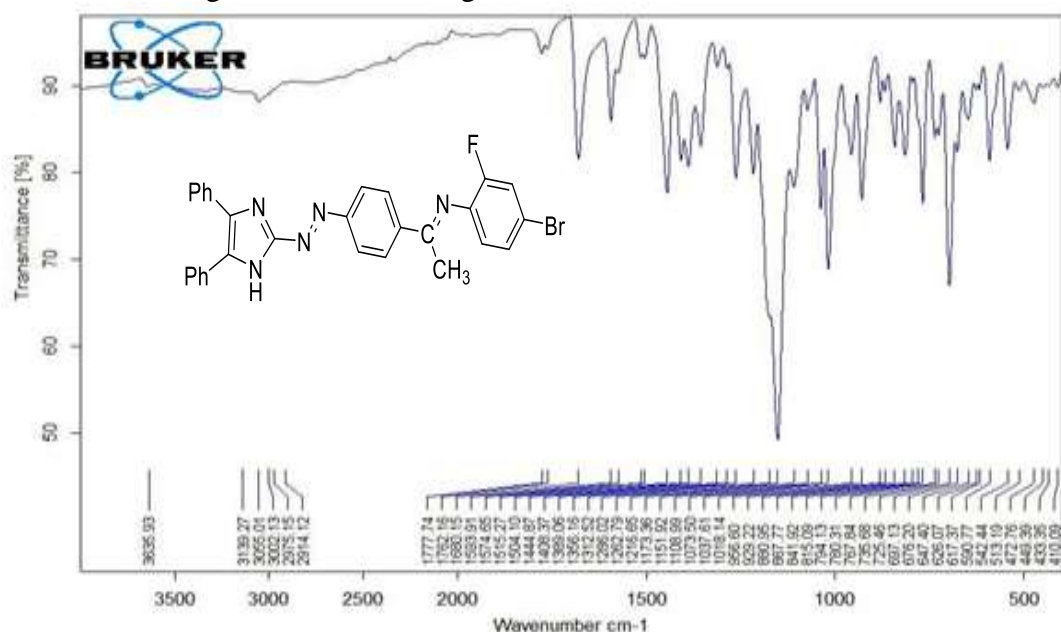


Figure 4 - FT-IR spectrum of HSBAI (L<sub>2</sub>)

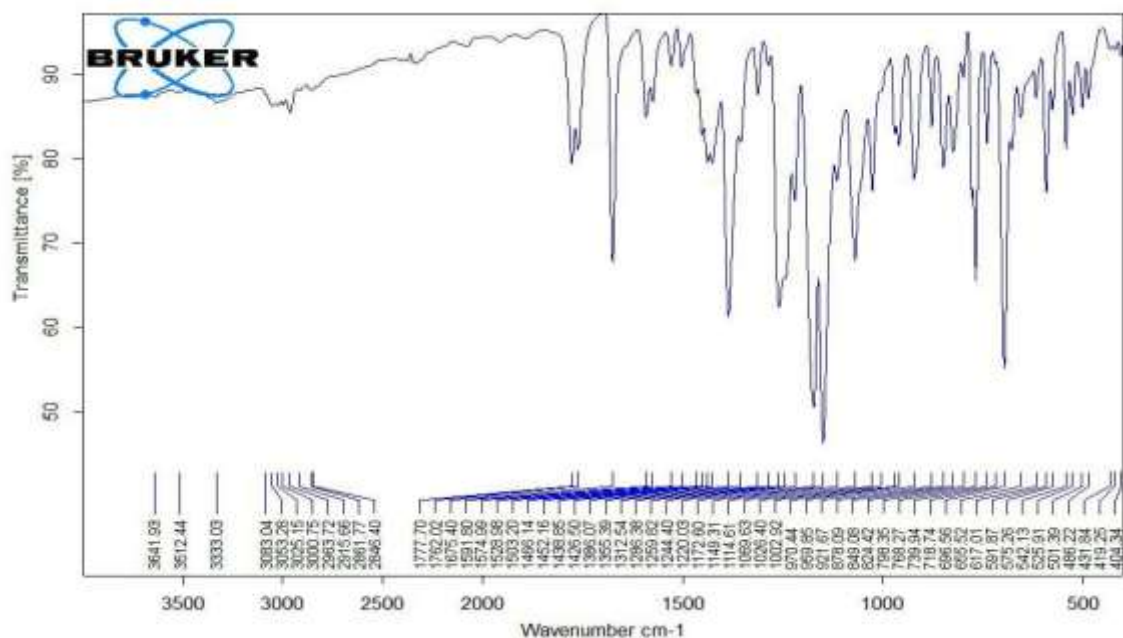


Figure 5 - FT-IR spectrum of NiL<sub>2</sub> complex

**Table 2** - Spectroscopic data (FT-IR and electronic) for the new ligands and their complexes

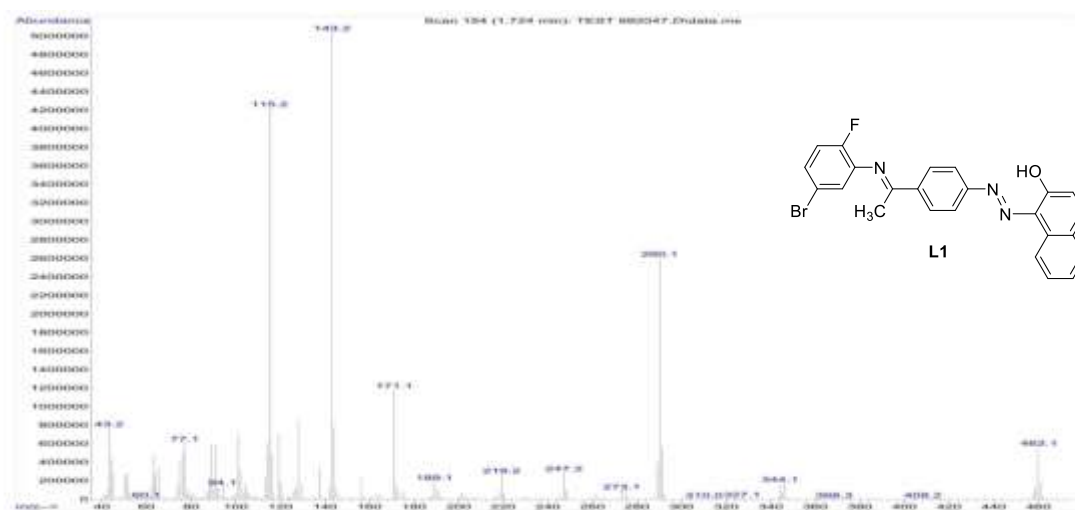
| No. | Compound   | FT-IR data (cm <sup>-1</sup> ) |      |                            |      |     | Electronic (nm) |
|-----|--|--------------------------------|------|----------------------------|------|-----|-----------------|
|     |  | OH                             | NH   | C=N <sub>sf</sub>          | N=N  | M-O |                 |
| 1   | L <sub>1</sub> (HSBAN)   | 3308                           |      | 1592                       | 1445 | -   | 486<br>342      |
| 2   | [Co(L <sub>1</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]                | 3182(co <sub>H2O</sub> )       | -    | 1592                       | 1410 | 586 | 508<br>318      |
| 3   | [Ni(L <sub>1</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]                | 3147(co <sub>H2O</sub> )       | -    | 1597                       | 1408 | 584 | 500<br>341      |
| 4   | [Cu(L <sub>1</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]                | 3140(co <sub>H2O</sub> )       | -    | 1589                       | 1406 | 559 | 492<br>343      |
| 5   | [Cd(L <sub>1</sub> ) <sub>2</sub> ]  | -                              | -    | 1589                       | 1402 | 580 | 507<br>317      |
| 6   | [Hg(L <sub>1</sub> ) <sub>2</sub> ]  | -                              | -    | 1587                       | 1402 | 586 | 502<br>317      |
| 7   | L <sub>2</sub> (HSBAI)   | -                              | 3635 | 1593 <sub>im</sub><br>1574 | 1444 | -   | 444<br>316      |
| 8   | [Co(L <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O)Cl]Cl                          | 3340(co <sub>H2O</sub> )       | 3615 | 1591 <sub>im</sub><br>1574 | 1432 | 587 | 509<br>301      |
| 9   | [Ni(L <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub> | 3333(co <sub>H2O</sub> )       | 3641 | 1591 <sub>im</sub><br>1574 | 1426 | 575 | 488<br>292      |
| 10  | [Cu(L <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) Cl]Cl                         | 3350(co <sub>H2O</sub> )       | -    | 1581 <sub>im</sub><br>1565 | 1418 | 589 | 515<br>294      |
| 11  | [Cd(L <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub> ]                                | -                              | -    | 1593 <sub>im</sub><br>1575 | 1433 | 589 | 496<br>297      |
| 12  | [Hg(L <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub> ]                                | -                              | -    | 1594 <sub>im</sub><br>1575 | 1431 | 589 | 493<br>297      |

- co<sub>H2O</sub> = coordination water, sf = Schiff base, im = imidazole

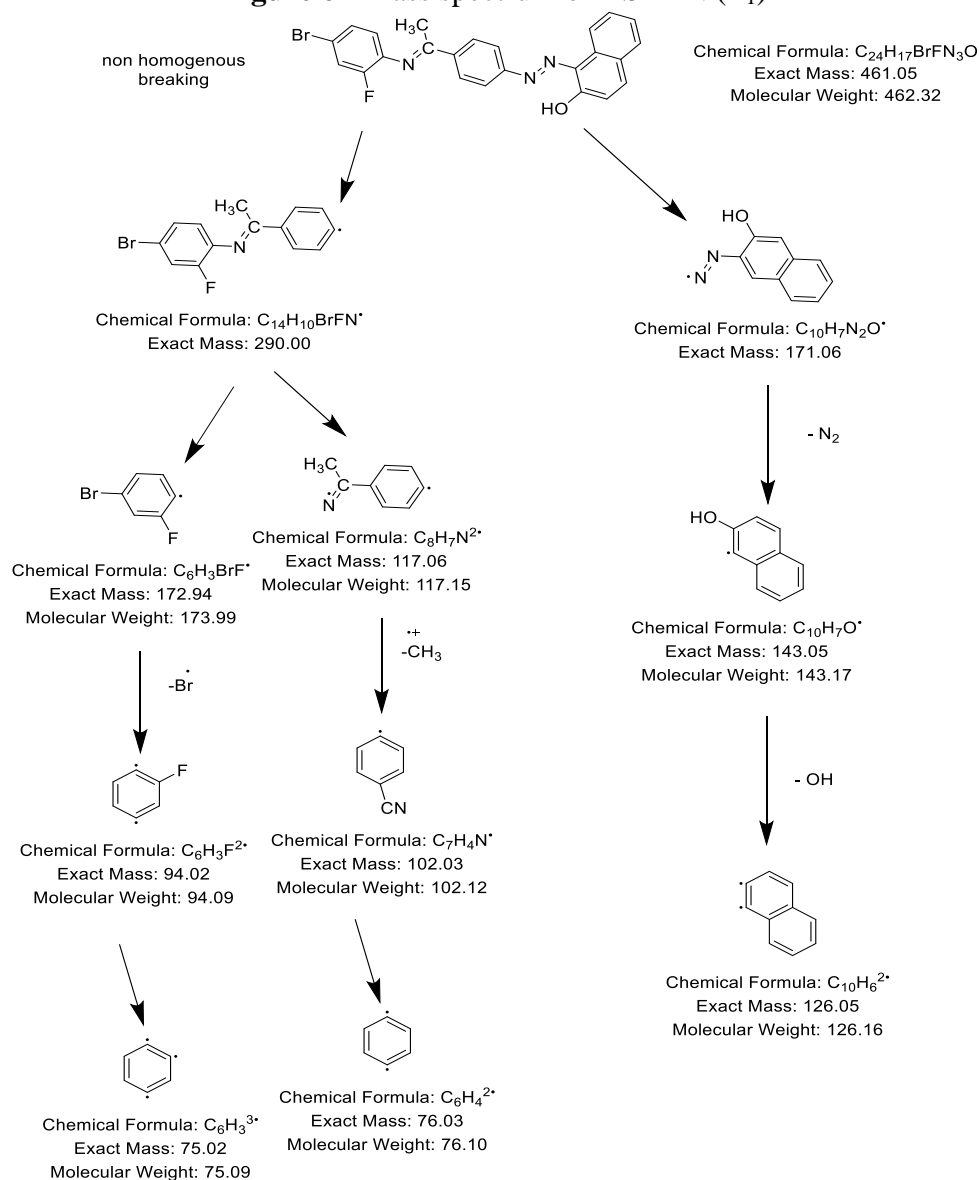
#### Mass Spectrometry

The investigation of molecular species can be successfully conducted using an appropriate technique such as mass spectroscopy. The mass spectroscopy gives the precise successive degradation of the target compounds, the stability of the fragments expressed by the intensity, and the masses of the organic and non-organic compounds [30]. The two ligands were synthesized within this study and the copper complex of the second ligand (CoL<sub>2</sub>) was measured with a high degree of precision.

The HSBAN gives [M, M+1] fragments at M/z of 462.1 and 463.0, equivalent to L<sub>1</sub>. The naphthol fragment appeared clearly with its charged ion at M/z of 144.0 and 143.0. This indicates the right compound preparation as shown in Figure 6 and the fragmentation mechanism in Scheme 2. The other ligand (HSBAI) gives a mass fragment M with its [M+1] ion at 537.2 and 538.0. These values return to the L<sub>2</sub> mass value. The presence of the 4,5-diphenylimidazole fragment and its [M-2] ion is shown at 220.0 and 218.1, respectively. This is an excellent evidence for this ligand synthesis, as shown in Figure 7. Figure 8 shows the CoL<sub>2</sub> mass spectrum that was measured using the electro-ionization mass technique. The electro-ionization mass technique is suitable for complex fragmentation. It gives a mass fragment at 1225.0 m/z equivalent to the [M+1] cobalt complex CoL<sub>2</sub> mass and its fragments, including the 4,5-diphenyl imidazole ion at 221.6 M/z. In addition to the other complementing procedures, this enabled us to conclude the complex formula.



**Figure 6 - Mass spectrum of HSBAN (L<sub>1</sub>)**





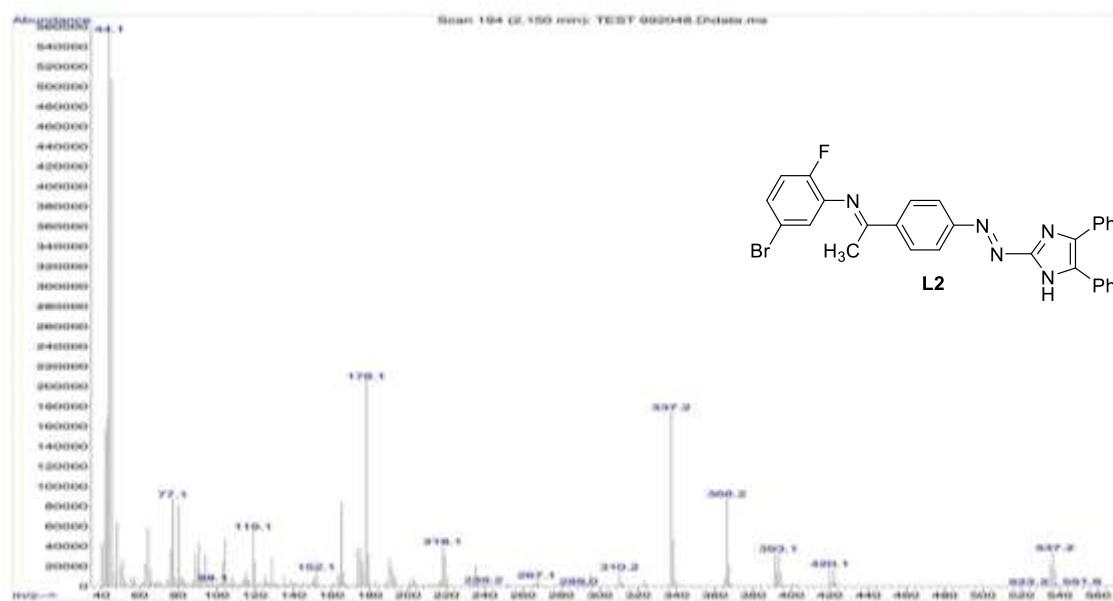


Figure 7 - Mass spectrum of HSBAI ( $L_2$ )

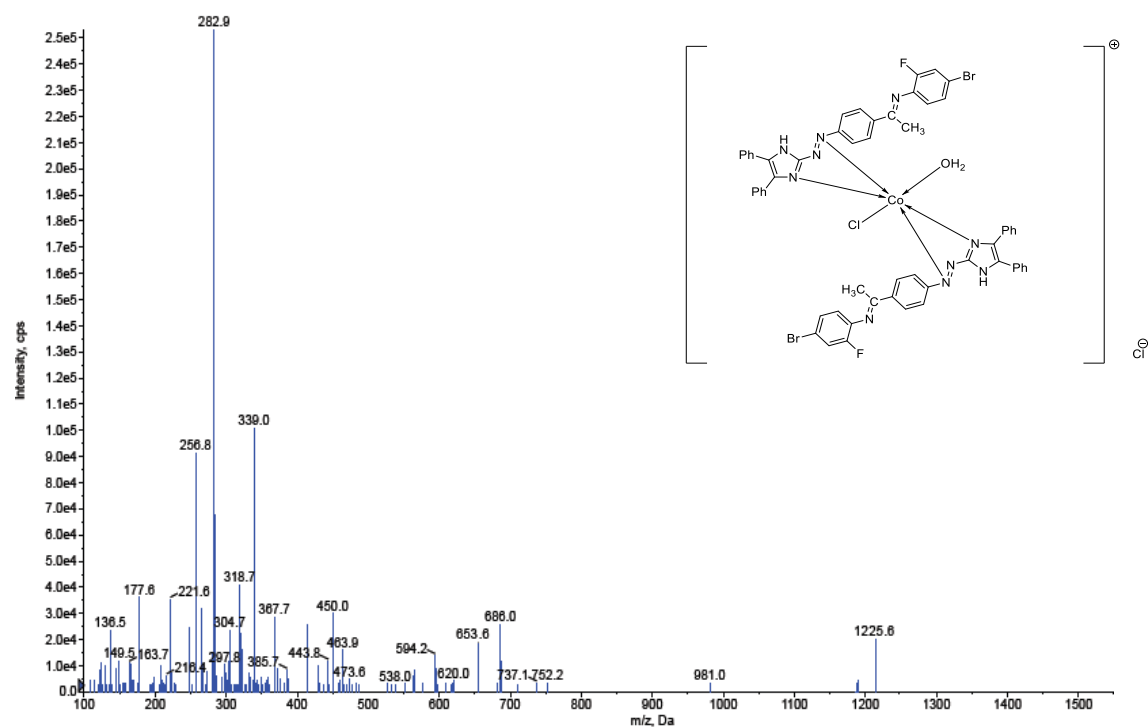


Figure 8 - Mass spectrum of  $CoL_2$  complex

### $^1H$ NMR spectroscopy

Magnetic resonance techniques are essential techniques used to determine the structure of organic molecules in solutions [31]. The  $L_1$  and  $L_2$  ligands and the nickel complex of the azo-naphthol were identified using  $^1H$  NMR spectroscopy to ensure their structural formula. Figure 9 shows a singlet signal at 9.77 ppm related to the naphthol (OH) proton [32], and multiple signals at 8.17-7.34 ppm for the aromatic rings of the naphthol and benzene. The protons of the methyl group in acetophenone appeared as a singlet signal at 2.65 ppm.

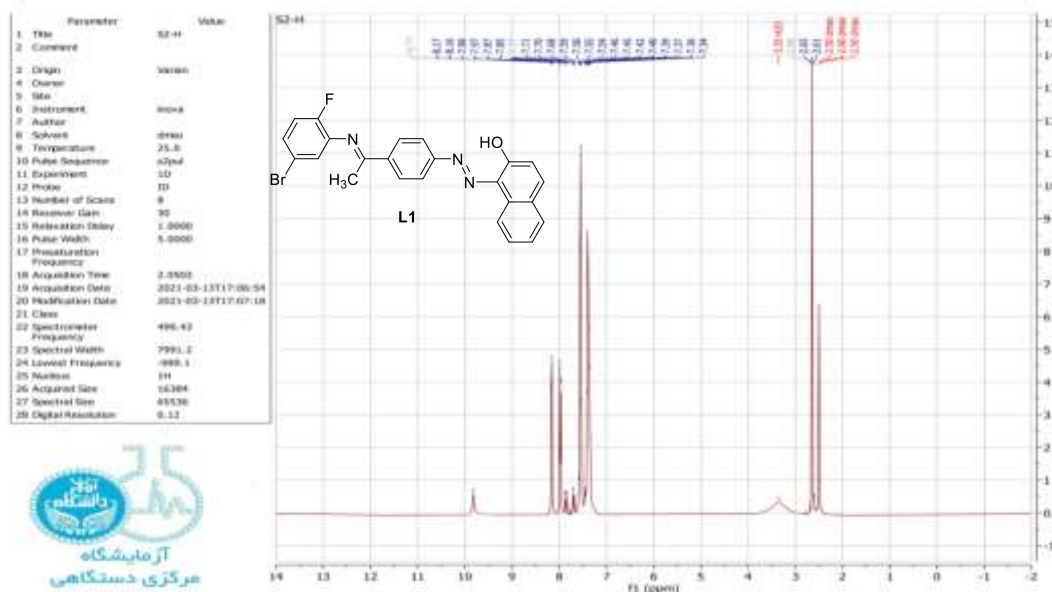


Figure 9 -  $^1\text{H}$  NMR spectrum of HSBAN ( $L_1$ )

The nickel complex of HSBAN ligand proved the disappearance of the naphthol phenolic proton (coordination's absence of its signal) and the presence of the coordination of water protons with an intense signal of 3.34 ppm. This method is a straightforward approach to confirm the complex geometry, as illustrated in Figure 10.

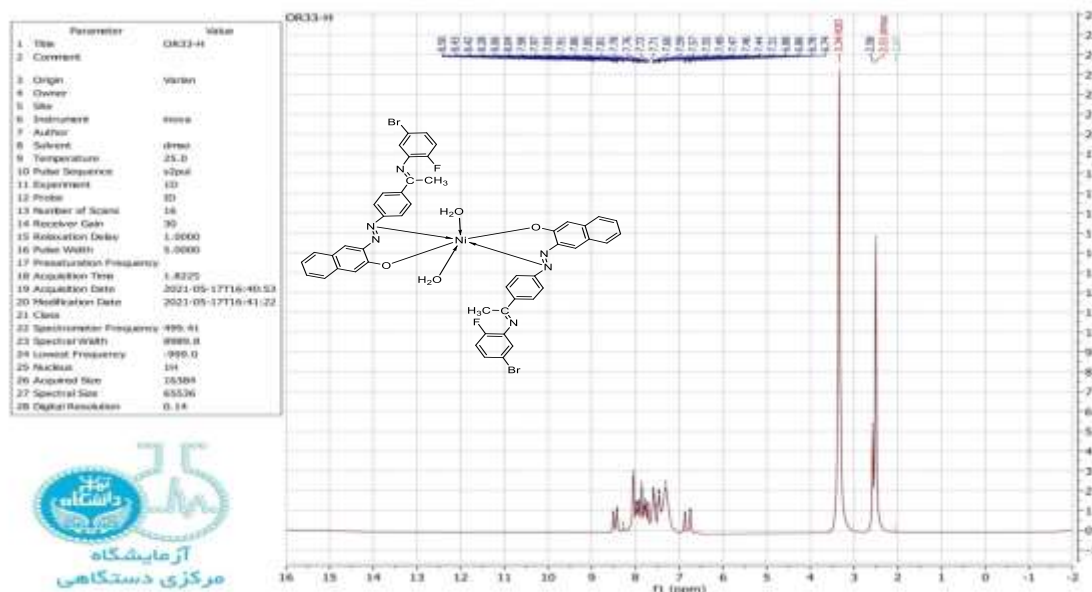


Figure 10 -  $^1\text{H}$  NMR spectrum of  $\text{Ni}L_1$  complex

The  $^1\text{H}$  NMR spectrum in Figure 11 of the HSBAN ( $L_2$ ) shows a singlet signal at 15.86 ppm due to the NH-imidazole proton, and multiplet signals ranging from 6.75 to 9.70 related to the aromatic rings. The methyl protons in acetophenone show a singlet signal at 2.64 ppm [33].

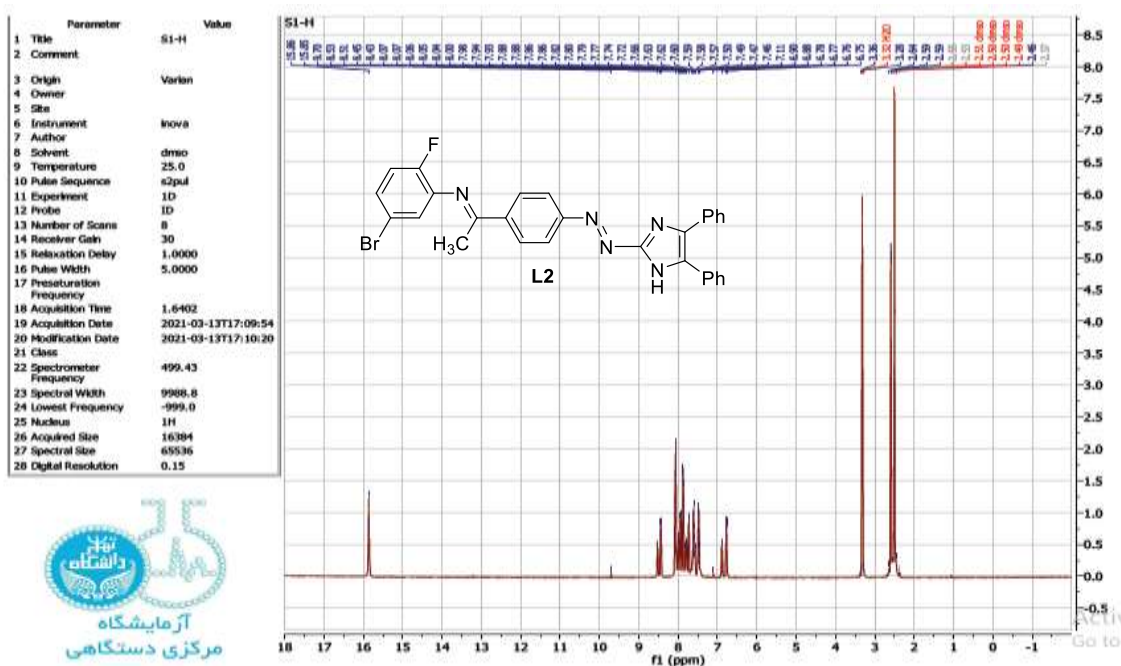
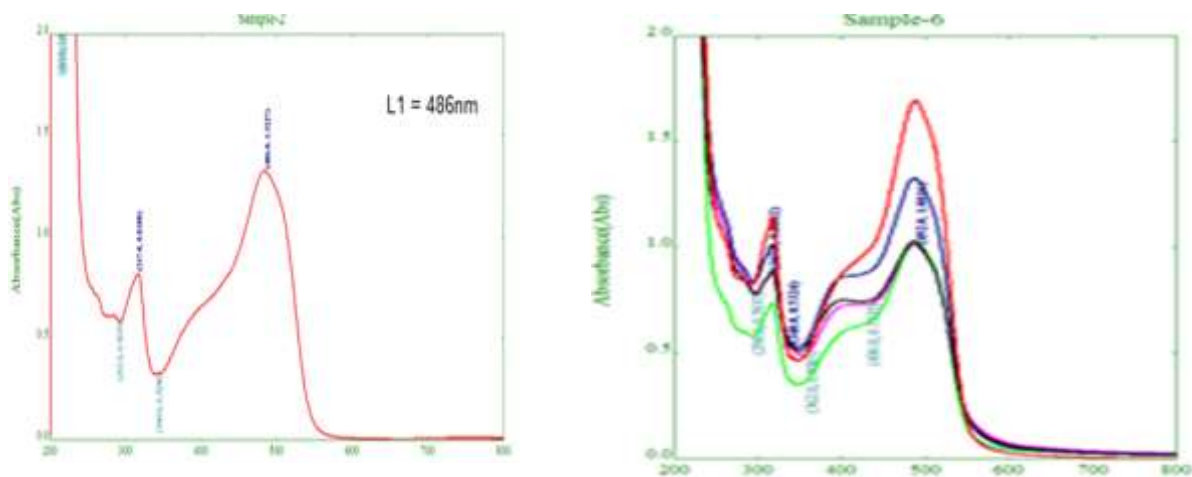


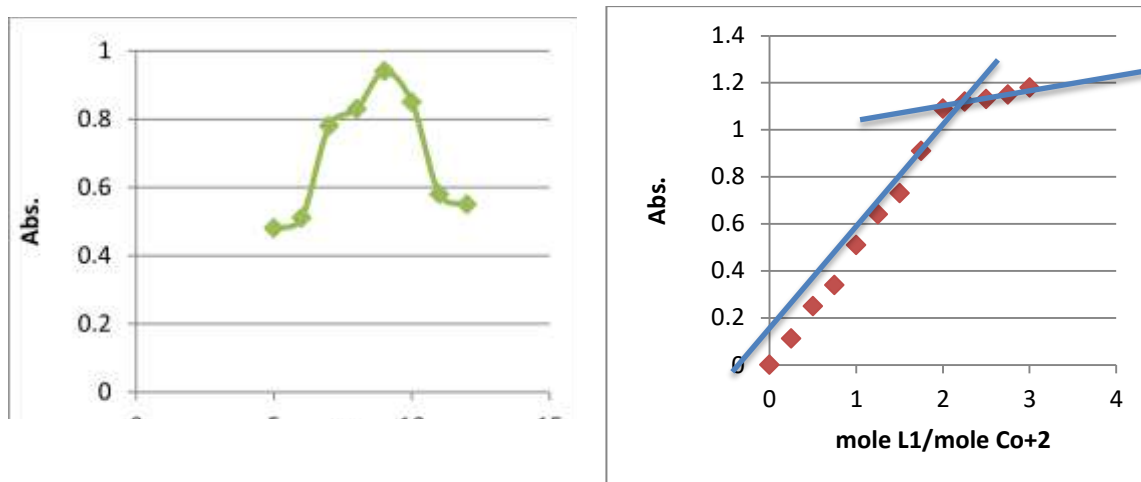
Figure 11 -  $^1\text{H}$  NMR of HSBAl ( $\text{L}_2$ )

### UV-Visible Spectrophotometry

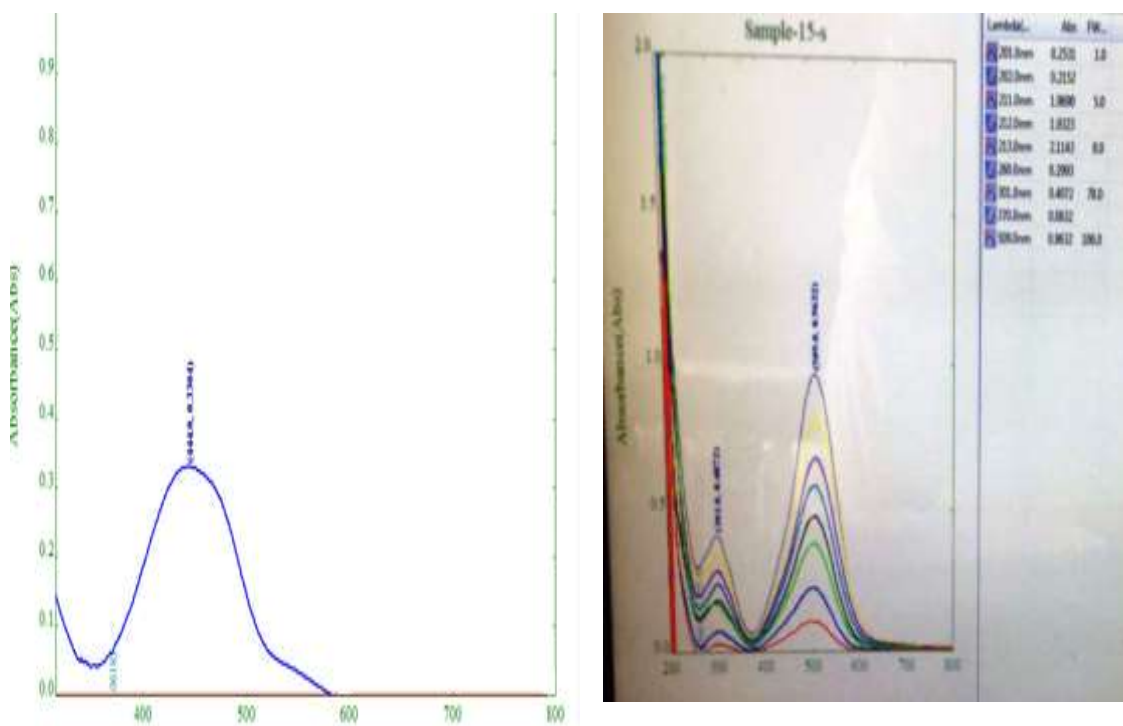
UV-visible spectrophotometry is an analytical technique that determines how many discrete wavelengths of UV or visible light are absorbed or transmitted by samples when compared to a blank or reference solution. These can be enhanced by determining the clear solutions that obey the Lambert-Beer equation [34]. The free  $\text{L}_1$  and  $\text{L}_2$  ligands have two principal bands, at 486 and 342 for  $\text{L}_1$  and 444 and 316 nm for  $\text{L}_2$  are assigned to the  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions, respectively, when ethanol is used as a solvent, as shown in Figures 12 and 13.

When the aqueous solutions of some transition metal ions were mixed with these ligands, they formed aqueous complexes due to the coordination between the lone pairs of the electrons in the ligand atoms and the vacant orbitals of these ions with the observation of a redshift toward high wavelength values. Choosing optimal conditions (concentration and pH) to determine the appropriate mole ratio (M:L) may prepare the solid complexes with the right percentage. This may be shown in Figures 12 and 13, and in Table 2. The molar ratio of all complexes in the current study (M:L) is 1:2.

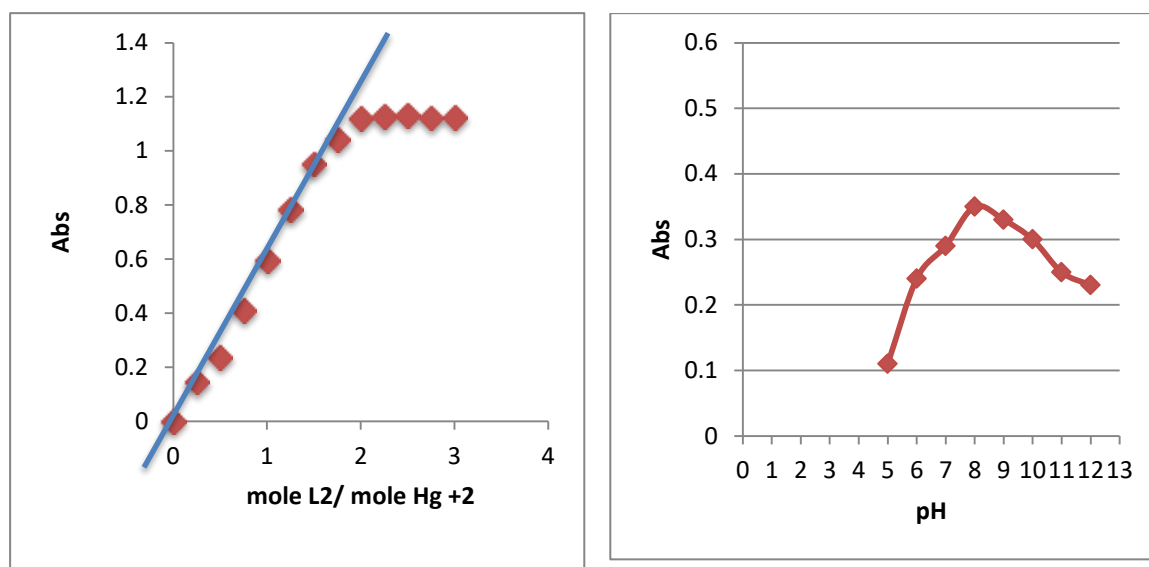




**Figure 12** - (a) UV-Visible spectrum of HSBAN ligand at  $1 \times 10^{-4} \text{M}$ , (b) UV-Visible spectrum of  $\text{CuL}_1$  complex at different concentrations, (c) the optimal pH value determination for  $\text{NiL}_1$  at  $500 \text{nm}$  and  $7 \times 10^{-5} \text{M}$ , (d) the mole ratio M/L for the  $\text{Co}^{2+}$  ion at optimal conditions.



**Figure 13** - (a) UV-Visible spectrum of HSBAl ligand at  $1 \times 10^{-4} \text{M}$ , (b) UV-Visible spectrum of  $\text{CoL}_2$  complex at different concentrations, (c) the optimal pH value determination for  $\text{CuL}_2$  at  $515 \text{nm}$  and  $2 \times 10^{-5} \text{M}$ , (d) the mole ratio M/L for the  $\text{Hg}^{2+}$  ion at optimal conditions.



### Conductivity and Magnetic Susceptibility

Molar electrical conductivity is a complementary technique that enhances the derivation of the suggested structural formula in complexes [35]. The conductivity values were raised when increasing the charged species in the solution. A high dielectric constant and low viscosity solvents were used in conductivity measurement (ethanol, methanol, DMSO, DMF, acetonitrile, and other components) when the complexes were insoluble in water (water was excluded).

In this study, two solvents (DMF and DMSO) were used at a  $1 \times 10^{-3}$  M concentration at room temperature. The low conductivity values for the first ligand (HSBAN) complex indicate non-electrolyte naturality. In contrast, the conductivity values of the second ligand (HSBAI) complexes were diverted from high to low values, with the indication of the charged coordination sphere of some of them as illustrated in Table 3.

Magnetic measurements of the complexes are guided by the electronic configuration and the oxidation state of the central atom or ions in their complexes depends on the effect of the secondary shells occupied by the odd electrons. The number of these odd electrons can be detected from the magnetic susceptibility values, and the geometrical structure of the complexes can be suggested.

The effective magnetic moments ( $\mu_{\text{eff}}$ ) of the HSBAN ( $L_1$ ) complexes are:

- The cobalt(II) complex gives 5.5 BM. This indicates three odd electrons and agrees with the octahedral high spin ( $t_2g^5 e_g^2$ ) complex [36].
- The nickel (II) complex gives 3.919 BM. This indicates the existence of two odd electrons and is compatible with the octahedral nickel complex [37].
- A 2.008 BM value of the copper complex pointed to a unique electron of the octahedral copper complex [36].
- The zero values of the (cadmium and mercury) complexes indicate no odd electrons due to filled electron shells.

While the magnetic moments for the HSBAI ( $L_2$ ) complexes are:

- 6.10 BM for the cobalt complex. The presence of three odd electrons in the octahedral cobalt complex and the incremental value indicates the orbital contribution in this complex [36].
- A 2.852 BM value for the nickel complex indicates two odd electrons in the octahedral nickel configuration [37].

- The copper complex owned a 1.8 BM value appointed to the unique odd electron in the octahedral copper complex configuration [38].

The diamagnetic properties of the electron are fully occupied in the configuration for cadmium and mercury complexes, making them insensitive to the magnetic fields, and no values were detected for these complexes.

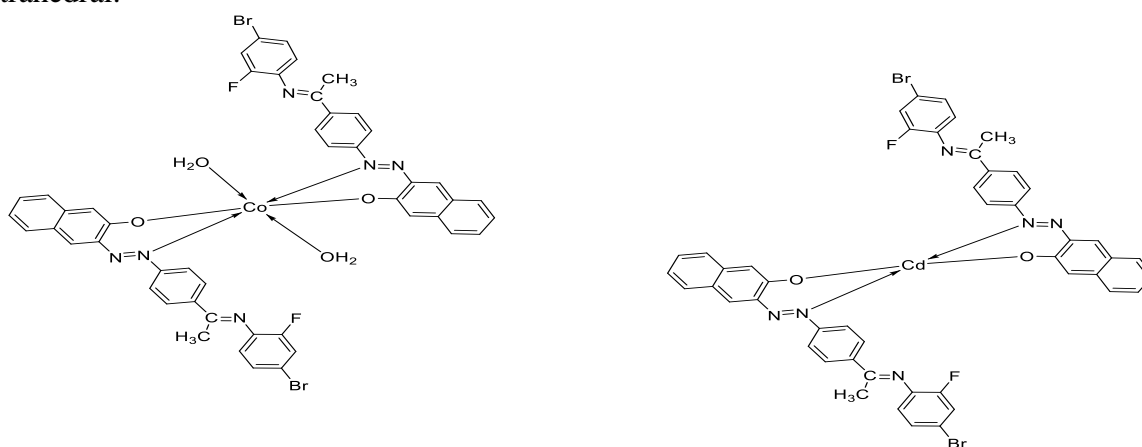
**Table 3** - Molar conductivity and magnetic moments for the metallic complexes measured at 25 °C.

| No. | Complex  | Molar Conductivity |     | Magnetic moment B.M |
|-----|--|--------------------|-----|---------------------|
|     |  | DMSO               | DMF |                     |
| 1   | [Co(L <sub>1</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]                | 16                 | 35  | 5.500               |
| 2   | [Ni(L <sub>1</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]                | 26                 | 38  | 3.919               |
| 3   | [Cu(L <sub>1</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]                | 08                 | 37  | 2.008               |
| 4   | [Cd(L <sub>1</sub> ) <sub>2</sub> ]  | 04                 | 36  | 0                   |
| 5   | [Hg(L <sub>1</sub> ) <sub>2</sub> ]  | 28                 | 05  | 0                   |
| 6   | [Co(L <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O)Cl]Cl                          | 65                 | 102 | 6.100               |
| 7   | [Ni(L <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub> | 116                | 146 | 2.852               |
| 8   | [Cu(L <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O)Cl]Cl                          | 79                 | 93  | 1.800               |
| 9   | [Cd(L <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub> ]                                | 48                 | 07  | 0                   |
| 10  | [Hg(L <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub> ]                                | 45                 | 15  | 0                   |

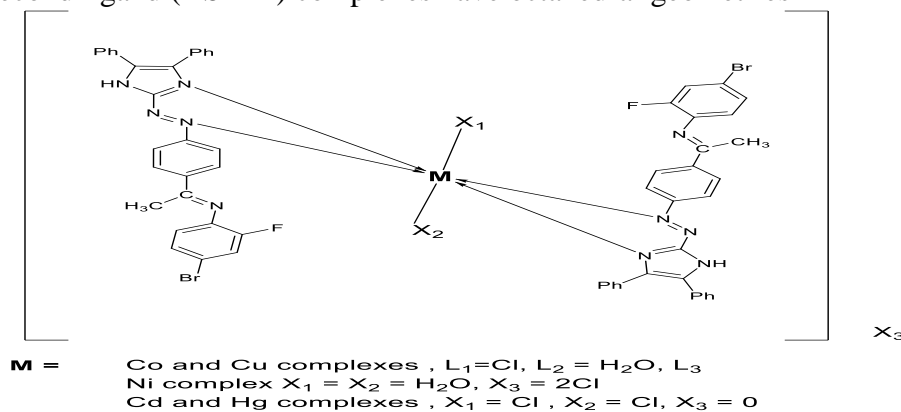
### Suggested Geometry

From the whole results, it can be proposed to suggest the complexes geometries as the following:

The Co, Ni, and Cu complexes of HSBAN are octahedral, while the Cd and Hg complexes are tetrahedral.



**Figure 14** - Suggested geometry for the cobalt and cadmium complexes of HSBAN ligand. While the second ligand (HSBAI) complexes have octahedral geometries



**Figure 15** - Suggested geometry for HSBAI ligand complexes

#### 4. Conclusion

Starting from the precursor synthesis [amino Schiff base (AHSB)], two new azo-Schiff base ligands were synthesized. These ligands were utilized as a diazonium salt component to synthesize the HSBAN and HSBAl azo ligands. Based on various techniques used and spectroscopic data presented and discussed above, five divalent transition metal ion complexes were prepared for each ligand.

The complexes were suggested to have an octahedral arrangement around the central ion, except for the cadmium and mercury complexes of HSBAN ( $L_1$ ). The cadmium and mercury complexes were proposed to have a tetrahedral environment. The HSBAN ( $L_1$ ) serves as a monobasic bidentate chelating ligand ( $HL_1$ ) *via* the azo nitrogen atom and the oxygen of the naphthol ring. In contrast, the HSBAl ( $L_2$ ) serves as a bidentate chelating ligand *via* both the nitrogen atoms of the azo group and the  $N_1$  of the imidazole ring.

The magnetic studies of the complexes show the high spin nature of the complexes due to the accounted-for presence of three, two, and one unpaired electron for  $Co^{2+}$ ,  $Ni^{2+}$ , and  $Cu^{2+}$  complexes, respectively. Zero values for the ions filled with  $Cd^{2+}$  and  $Hg^{2+}$  complexes were obtained. On the other hand, the complexes are more thermally stable than the ligands. The results are in accordance with the compositions of the ligands and their complexes as determined *via* elemental analysis.

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