Spectrophotometric Study of Fe(III) Complexes with the Newly Synthesized Schiff Base Compound Derived from 4,4'-Diaminodiphenylmethane

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ABSTRACT

Two new chromogenic Schiff base ligands were synthesized by the condensation reaction of 4,4'-diaminodiphenylmethane as a primary amine with 2-hydroxy-3-methoxybenzaldehyd and 4-hydroxy-3-methoxybenzaldehyde. The structures of the compounds were characterized by elemental analysis, FT-IR, and ^{1}H NMR. The complexation behavior of the ligands towards some transition metal ions (Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^+, Pb^{2+} and Sn^{2+}) was studied using UV-Vis spectrophotometry. The effects of some experimental parameters on the complex formation such as solvent, metal ions and ligand concentrations were investigated. Both ligands exhibited excellent chromogenic properties towards the complexation with Fe^{3+} ions over other studied metal ions in DMSO. The addition of Fe^{3+}ions to both ligands gave rise to a large bathochromic shift (from 400 to 610 nm). Thus, resulting in a change of color from orange to green (610nm) and from yellow to green (630nm) for both ligands, respectively, which provided a naked-eye detection of Fe^{3+} ions in addition to spectroscopic detection. Job's continuous variation and mole ratio methods were used to determine the stoichiometry of ligands-Fe^{3+} complexes. Stability constants of the 1:1 (ligand : metal) complexes were found to be equivalent to 5.7×10^5 and 1.3×10^5, for both complexes, respectively.

الملخص العربي

تهدف هذه الدراسة إلى تحضير اثنان من قواعد شيف اللونية عن طريق التفاعل التكثيفي بين الأمين الأولي 4و4–ثنائي أمين ثنائي فينيل ميثان و 2–هيدروكسي–3–ميتوكسي بنزالدهيد و 4–هيدروكسي–3– ميتوكسي بنزالدهيد بنسبة تفاعل 1:1 في وسط حمضي . لقد تم تشخيص المركبات الناتجة باستخدام بعض الطرق الطيفية المتبعة (التحليل الدقيق للعناصر ومطيافية الاشعة تحت الحمراء ومطيافية الرنين المغناطيسي) . وتمت ايضا دراسة قدرة هذه المركبات في تكوين معقدات مع بعض العناصر الانتقالية (مثل: ,Fe^{3+} Sn^{2+} Pb^{2+} ,Ag^+ ,Cu^{2+} ,Ni^{2+} ,Co^{2+}) باستخدام مطيافية الضوء فوق البنفسجي–المرئي (UV–Vis). وبينت الدراسة انتقائية هذه المركبات في تشكيل معقدات ملونة مع الحديد الثلاثي (Fe^{3+}) في الوسط العضوي ثنائي ميثيل السلفوكسيد (DMSO) . حيث امكن من الدراسة ملاحظة تكون المعقدات الناتجة مباشرة بالعين المجردة عن طريق تغير لون المحلول (من البرتقالي الى الاخضر) بمجرد اضافة

أيون الحديد الثلاثي الى محلول المركب. وتم تحديد المعقد عند الطول الموجي (630nm=λ). واظهرت النتائج ان هذه القواعد تتفاعل تفاعلا مباشرا مع الحديد الثلاثي وتنتج معقدات ثنائية النواة وبنسبة 1:1 مولار [Fe^{3+}:L] بالنسبة للمركب الاول , وبنسبة 1:3 للمركب الثاني . وقد اثبتت الدراسات التحليلية التي اجريت ان لكلا المعقدين الناتجين من تفاعل المركبين مع الحديد الثلاثي ثباتيه عالية تصل الى (5.7×10^5) و (1.3×10^5) على التوالي.

INTRODUCTION

Schiff bases have been playing an important part in the development of coordination chemistry, organic chemistry, and bio-organic chemistry. Over the past few years, their complexes with metal ions have been extensively studied due to their attractive chemical and physical properties, and their potential applications in various scientific areas (Nejati *et al.,* 2009 ; Tai *et al.,* 2003).

Schiff base is a compound that contains the azomethine group with a general formula RHC=N−R' was first reported by Hugo Schiff in 1864 (Collinson and. Fenton,1996). They are usually formed by condensation of a primary amine with a carbonyl compound (usually aldehyde or ketone (Bruice, 2004). The reaction is a reversible reaction, and usually takes place under an acid catalysis, base catalysis, or upon heating. Schiff bases are generally bi- or tridentate ligands which have the capability to forming very stable complexes with transition metal ions (due to C=N chelating group), but less affinity towards alkali metal and alkaline earth metal cations (Sheng *et al.,* 2008). Owing to the relative easiness of preparation, synthetic flexibility, and the special property of C=N group, Schiff bases are generally excellent chelating agents (Marczenko, 1986), especially when a functional group like –OH or –SH is close to the azomethine group so as to form a five or six membered ring with the metal ion. Schiff base compounds have a wide range of applications in different fields. Their complexes with transition metal are amongst the most widely studied compounds in inorganic chemistry (Tai *et al.,* 2003).

A large number of Schiff bases and their complexes have been studied for their interesting and important properties, such as their ability to reversibly bind with oxygen (Jones *et al.,* 1979), catalyze reactions on oxygenation, hydrolysis, electro-reduction, decomposition (Kumar *et al.,* 2009), photochromic properties (Margerum and. Miller, 1971), and complexing ability towards some toxic metal ions (Sawodny and Riederer, 1977). In addition, the biological activities of the Schiff bases and their complexes are considered one of the most interesting applications. These include antimicrobial, antiviral and antifungal activities (Kumar *et al.,* 2010; Jarrahpour, *et al.,* 2007), synergistic action on insecticides, anti-tumor and cytotoxic activities (Geweely,2009; Koneru *et al.,* 1993). Transition Schiff bases complexes also have electroluminescence and photoluminescence properties and find interesting applications in material science (Hou *et al.,* 2007). In analytical chemistry, Schiff bases, with N and O as donor atoms, are well known to form strong complexes with transition metal ions (Abbaspour *et al.,* 2002).

Chromogenic reagents are the reagents which give color reaction in spectrophotometric methods. They are related to the change in the absorption behavior of radiation, which leads to a color change upon interaction with an analyte (Tai *et al.,* 2003). The development of chromogenic reagents is an interesting field because it can provide a visual detection, giving qualitative information without resort to any expensive instrument, since a specific color change of solution upon complexation is observed. Schiff base compounds are very good chromogenic reagents with excellent complexation ability towards ionic species. There applications were focused on the detection of various metal ions by using spectroscopic methods. Many chromogenic Schiff base compounds provide naked eye detection in addition to UV-Vis spectroscopic detection, due to the change in color (Singh *et al.,* 2009). 4,4'-diaminodiphenylmethane (DADPM) is a diamine compound which also known as *p,p'*-methylenedianiline (MDA), is consider an important chemical intermediate. The syntheses of Schiff base ligands using DADPM as amine has been the interest of many research groups [(Mohanty *et al.,* 1997;Huang *et al.,* 2005;Yoshida *et al.,* 1999; Salavati-Niasari and Bazarganipour, 2007; Kruger *et al.,* 2001). for a variety of applications. The use of DADPM for the synthesis of chromogenic Schiff base compounds was not frequently reported before as most studied focused on the complexes with double or triple helical structure as its interest in the field of coordination chemistry. Therefore, the present work is focused on the chromogenic properties of Schiff base ligands derived from

DADPM and its complexation ability towards transition metal ions.

MATERIALS AND METHODS

A Hitachi U-2000 spectrophotometer was used to obtain UV spectra for all solutions over the 380-800 nm range with a quartz cell of 1.0 cm path length. The infrared spectra (IR) were recorded on a Perkin Elmer 2000 FT-IR spectrophotometer as KBr disk in the region of 400-4000 cm^{-1}. The ^{1}HNMR spectra were recorded on a Bruker 300 MHz spectrometer. An elemental analyzer-Perkin Elmer, Series II, 2400 CHN/O was used for the C, H and N microanalysis.

Chemicals and Reagents

All chemicals and reagents used in this study were of analytical grade, and were used without further purification. A 4,4'-diaminodiphenylmethane (Fluka), 2-hydroxy-3-methoxybenzaldehyde (Merck), 4-hydroxy-3-methoxybenzaldehyde (Aldrich), methanol (Aldrich), ethanol (Qrec), acetonitrile (Lab-scan), acetone (Qrec), THF (Qrec), $Cu(NO_3)_2.2.5H_2O$ (Aldrich), CH_3COOAg (Ajax-Chemicals), $SnCl_2$ (Sigma), $FeCl_3.6H_2O$ (Sigma), $CoCl_2$ (Merck), $Ni(NO_3)_2.6H_2O$ (Fluka), and $Pb(NO_3)_2$ (Alfar), were commercially available pure compounds.

Syntheses of Ligands
- **2-hydroxy-3-methoxybenzaldehyd-bis(4,4'-diaminodiphenylmethane) (L1)**.

A 0.39g (0.002 M) of DADPM was dissolved in 25 mL of hot ethanol, and then added to a round bottom flask containing 0.61g (0.004M) of 2-hydroxy-3-methoxybenzaldehyde in 25 mL of hot ethanol. The reaction mixture was refluxed on a water bath for 30 minutes, where upon a light orange precipitate was formed. The precipitate was filtered, washed with fresh amount of cold alcohol, and dried at room temperature. The ligand was then recrystallized from hot alcohol with a 70% yield.

- **4-hydroxy-3-methoxybenzaldehyde-bis(4,4'-diaminodiphenylmethane) (L2).**

A 0.39g (0.002M) of DADPM was dissolved in 25 mL of hot methanol, and then added to around bottom flask containing 0.61g (0.004M) of 4-hydroxy-3-methoxybenzaldehyde in 25 mL of hot methanol. The mixture was refluxed on a water bath for two and half hours. The solution was left to cool at room temperature, where a yellow precipitate was formed. The resulted yellow precipitate was filtered, washed with fresh amount of cold methanol, and left dried at room temperature. The ligand was then recrystallized from hot alcohol, with 62% yield.

- **Synthesis of L1-Fe^{3+} Complex**

A 25 mL solution of **Fe^{3+}** chloride hexahydrate (0.027g, 1×10^{-4} M) in an acetonitrile was slowly added to an acetonitrile (25 mL) solution of L1 (0.047g, 1×10^{-4} M). The color of the mixture was turned brown immediately. The mixture was then refluxed for two hours, and the volume reduced to one third of the initial volume on a water bath. A black precipitate was formed by drop wise addition of 0.01M ammonia solution. The precipitate was then collected by suction filtration, washed thoroughly with acetonitrile and air dried at room temperature. The product was obtained in 64% yield.

- **Synthesis of L2-Fe^{3+} Complex**

A 25 mL solution of **Fe^{3+}** chloride hexahydrate in acetonitrite (0.027g, 1×10^{-4} M) was added to an acetonitrile solution (25mL) of L2 (0.093g, 2×10^{-4} M). The color of the mixture was turned to green immediately upon addition. The mixture was then refluxed for two hours. A dark green precipitate was formed and then filtered, washed thoroughly with acetonitrile and air dried completely at room temperature. The product was obtained in 61% yield.

RESULTS AND DISCUSSION

- **. Synthesis and characterization of the ligands.**

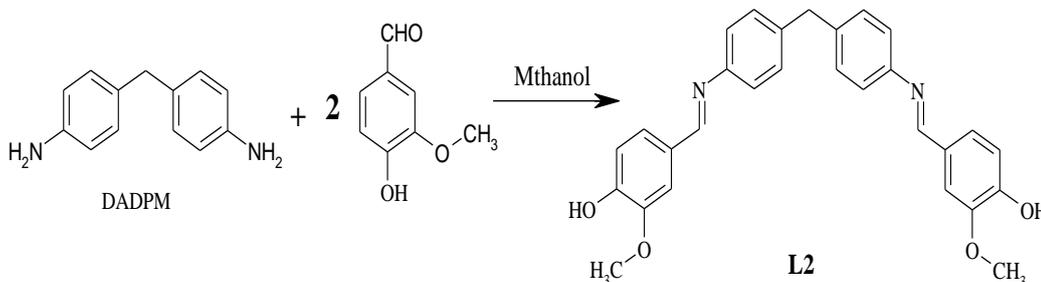***Ligand-1* (L1):** The synthetic route for the preparation of 2-hydroxy-3-methoxybenzaldehyd-bis(4,4'-

diaminodiphenylmethane) (**L1**) is given in **Scheme 1**. The ligand was synthesized by heating 2-hydroxy-3-methoxybenzaldehyd with

DADPM in a 2:1 mole ratio. The melting point of the solid was 181˚C.
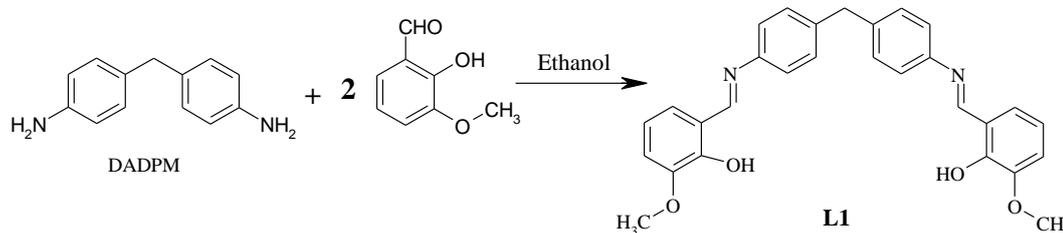
Scheme 1: The synthetic route for the preparation of 2-hydroxy-3-methoxybenzaldehyd bis(4,4'-diaminodiphenylmethane) (**L1**).

Ligand-2 (L2): The synthetic route for the preparation of 4-hydroxy-3-methoxybenzaldehyde-bis(4,4'-diaminodiphenylmethane) (**L2**) is given in **Scheme 2**. L2 was synthesized by heating two equivalents of 4-hydroxy-3-methoxybenzaldehyde with one equivalent of DADPM. The product was obtained in a yield of 62% as a yellow powder. The melting point is 80˚C.

Scheme 2: The synthetic route for the preparation of 4-hydroxy-3-methoxybenzaldehyde bis(4,4'-diaminodiphenylmethane) (L2).

3.2 Elemental Analysis

Table-1 shows the results of the determination of carbon, hydrogen and nitrogen (CHN) for both synthesized ligands and their complexes with Fe^{3+}. The percentages of elements found were in good agreement to the predicted percentage obtained by calculations

Table 1: The elemental analysis (CHN) of ligands and their Fe^{3+} complexes.

| %	L1	L1-Fe^{3+}	L2	L2-Fe^{3+}
	Calculated (Found)	Calculated (Found)	Calculated (Found)	Calculated (Found)
C	74.59 (75.27)	55.30 (50.28)	74.59 (72.63)	30.76 (29.02)
H	5.57 (5.35)	4.13 (3.54)	5.57 (5.27)	2.29 (3.66)
N	6.00 (6.13)	4.45 (4.33)	6.00 (5.84)	2.47 (2.35)

FT-IR Analysis.

Ligand 1: The most important feature in the IR spectrum of L1 is the presence of absorption band at 1618 cm^{-1}. This indicated that a new C=N bond was formed (Pavia, 2009). The absence of the strong band at 1639 cm^{-1} corresponding for the C=O band indicating the involvement of the carbonyl group of the aldehyde in the reaction. However, the disappearance of the NH stretching absorption bands (3442 cm^{-1}, 3413 cm^{-1}, and 3353 cm^{-1}) on 4,4-diaminodiphenylmethane (starting material) is also another evidence of the interaction between the diamine and carbonyl groups (Schiff base reaction). The broad band at 3447 cm^{-1} was attributed to the presence of the OH functional group. Furthermore, an important characteristic adsorption band observed at 1256 cm^{-1} was assignable to the C–N stretching vibration (Pavia, 2009).

Ligand 2 : In this ligand (L2), the formation of the compound was confirmed by the presence of

the C=N bond at 1581 cm⁻¹ region. As mentioned in the first ligand, the disappearance of the C=O band (at 1669 cm⁻¹) of the aldehyde group (CHO) confirmed the involvement of this group in the condensation reaction, and therefore the formation of L2 compound**.**

Iron (Fe³⁺) Complex: The IR study confirmed the complexation of both ligands with F³⁺ ions. A comparison between the IR spectra of ligands with their Fe^{3+} complexes indicated that the ligands are principally coordinated to the metal ions in two ways. The bands that appeared at 1618 cm⁻¹ and 1581 cm⁻¹ due to the stretching of C=N group were shifted to 1637 cm⁻¹ and 1606 cm⁻¹ in the L1-Fe^{3+} and L2-Fe^{3+} complexes, respectively, indicating the participation of the azomethine nitrogen in the coordination with the Fe^{3+} ions. A broad bands appeared at 3447 cm⁻¹ and 3395 cm⁻¹ assignable to the OH group were also shifted to 3422 cm⁻¹ and 3385 cm⁻¹ for both complexes, respectively. This indicated the involvement of the group in the complexation with Fe^{3+} ion [24]. These shifting also confirmed the participation of the O and N atoms in the coordination with Fe^{3+} ions (**Figure 1**).
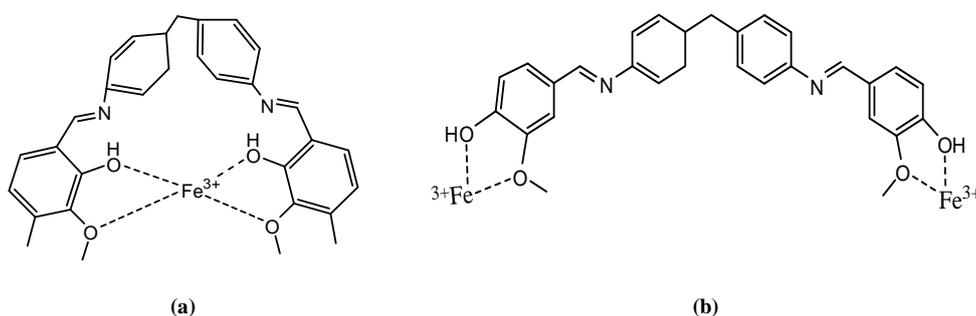
Figure 1: The propose structure of the (**a**) L1-Fe^{3+} and (**b**) L2-Fe^{3+} complexes.

3.4 ¹H NMR Analysis

The spectrum of L1 (**Figure 2**) showed nine groups of resonance (δ; 2.5, 3.8, 4.02, 6.9, 7.1, 7.2, 7.3, 8.9, and 13.3 ppm). The first signal (2.5 ppm) was attributed to the deuterated DMSO-d_6 solvent. Additionally, both methyl groups in the ligand (Ha) are equivalent by symmetry giving rise to a singlet at δ 3.8 ppm. The CH₂ protons (Hf) were observed at δ 4.02 ppm. The spectrum also displayed the OH proton of the phenolic groups and azomethine protons (H–C=N), as two singlets at δ 13.3 (Hc) and δ 8.9 ppm (Hb), respectively (Keypour, *et al.,* 2010; Issa *et al*. 2009).
. The data of the L1 spectrum was summarized in condensed format as: Ha: δ 3.8 ppm (singlet, 6H), Hf δ 4.02 ppm (singlet, 2H), Hi δ 6.9 ppm (triplet, 2H), Hd δ 7.1 ppm (doublet, 4H), He δ 7.2 ppm (doublet, 4H), Hg and Hh δ 7.3 ppm (multiple, 4H), Hc δ 8.9 ppm (singlet, 1H), Hb δ 13.3 ppm (singlet, 1H). This result was in agreement with the FT-IR spectrum confirming that the Schiff base condensation process had taken place.

The difference between the ¹H NMR spectra of ligand 1, and its complex with Fe^{3+} could be noticed from the downfield shift of the signal at 13.3 ppm (OH group, free L1) to 10.23 ppm (Δδ= 3.1 ppm) upon complexation (**Figure 1**). Additionally, the signal at 8.9 ppm (H−C=N) had also shifted downfield to 8.9 (Δδ = 0.03 ppm), thus indicating the coordination of the hydroxyl oxygen to the metal atom.

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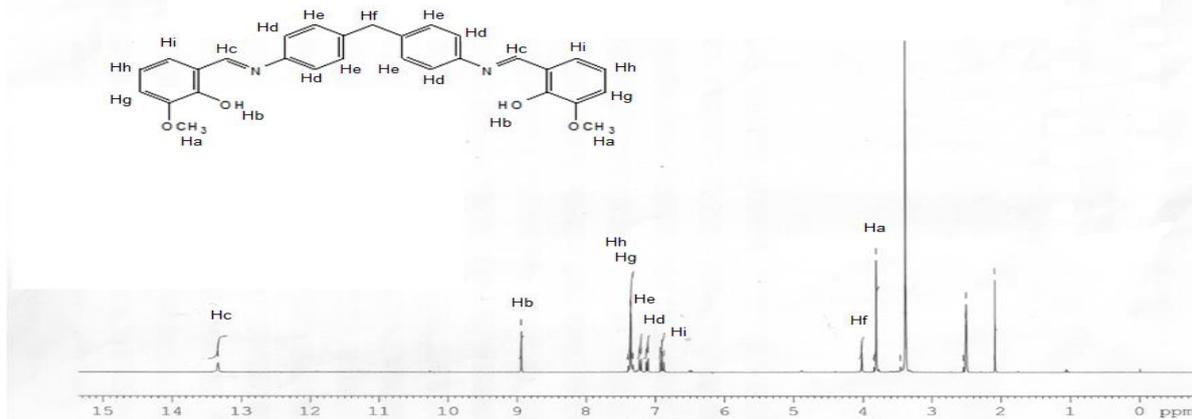
Figure 2: The ^1H NMR spectrum of the L1 in DMSO-d_6.

The ^1H NMR spectrum of L2 (**Figure 3**) also showed nine groups of resonance (3.8, 3.9, 6.9, 7.1, 7.2, 7.3, 7.5, 8.4 and 9.7 ppm), including the solvent signal at 2.5 ppm (DMSO-d_6). The spectrum data of L2 were summarized in a condensed format as: Ha: δ 3.83 ppm (singlet, 6H), Hc δ 3.95 ppm (singlet, 2H), Hg δ 6.90 ppm (doublet, 2H), He δ 7.14 ppm (doublet, 4H), Hd δ 7.24 ppm (doublet, 4H), Hf δ 7.32 ppm (doublet , 2H), Hj δ 7.5 ppm (singlet, 2H), Hb δ 8.43 ppm (singlet, 1H), Hh δ 9.7 ppm (singlet, 1H). Additionally, the phenolic (OH) and azomethine protons gave rise to two singlet signals at 9.7 ppm and 8.4 ppm, respectively. The spectrum confirmed the structure of the ligand.
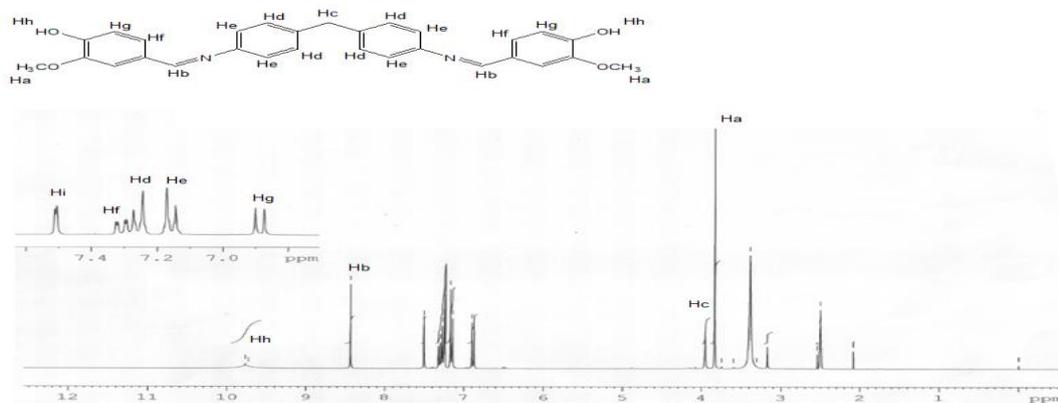
Figure 3: The ^1H NMR spectrum of the L2 in DMSO-d_6.

The complexation of L2 with Fe^{3+} could be noticed at the 9.7 ppm (OH) and the 8.4 ppm (H−C=N) signals (spectrum not showed). The two signals were shifted upfield to 10.31 ppm (Δδ = 0.6 ppm), and 9.76 (Δδ = 1.3 ppm), respectively, indicating the coordination of the hydroxyl oxygen and azomethine nitrogen to the metal ion. This confirms the participation of the O and N atoms in the coordination.

3.2 Chromogenic properties of the ligands
3.2.1 Solvent effect
- ***On the absorption spectra of the free ligands.***

The effect of solvent on the chromogenic properties of the free ligands was investigated. The absorption spectra of L1 and L2 were recorded in various solvents at a concentration

of 1×10^{-4}M for L1 and 8×10^{-4} M for L2. Their corresponding λ_{max} and absorption are given in **Table 2.** Results showed that both ligands did not show large variation with the polarity of the solvents. The main absorption band was located in the visible region within a range of 390-410 nm which could be assigned to π-π^* transition in the large conjugated system. As both ligands had low solubility in relatively high polar solvents (methanol and ethanol) their absorbance were very low.

Table 2: The effect of solvent on the λ_{max} for Ll and L2 ligands.

Solvent	Dielectric constant	L1		L2	
		λ_{max} nm	Absorbance	λ_{max} (nm)	Absorbance
Methanol	33.0	410	0.181	390	0.119
Ethanol	24.5	400	0.220	390	0.111
Acetone	21.0	400	0.523	390	0.260
THF	7.5	400	0.548	390	0.326
DMSO	18.4	400	0.528	390	0.374
Acetonitrile	37.5	400	0.510	390	0.301
Chloroform	4.8	400	0.513	390	0.322

- ***On the ligands-metal ions complexation.***

Both ligands have an azomethine ($-N=C-$) and OH groups, therefore, they could form a potential chromogenic complexes with metal ions (Fakhari *et al*. 2005). It was proofed that these compounds are highly dependent on solvent system in their complexations with metal ions (Farias de Lima, *et al*., 1998 ; Boca *et al.,* 2005). Accordingly, their metal complexation with selected transition metal ions such as Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^{+}, Pb^{2+}, and Sn^{2+} was investigated at different solvents. The donor ability of the solvent plays the most important role in non-aqueous solvent systems. Solvents with low dielectric constants show poor ion solvating properties, while solvents with high donor ability and dielectric constants are unfavorable in complexation, because the solvent molecules will compete with ligands for metal ions (Rounaghi *et al*., 2010). As both ligands in this study were not soluble in water, some common organic solvents (DMSO, THF, ethanol, methanol) were used to investigate their chromogenic complexation behavior with metal ions.

Results showed that both ligands exhibited high absorption values in DMSO (Table 2). Therefore, their complexation properties with metal ions were carried out using DMSO. The absorption spectra of L1 (1×10^{-4} M) in DMSO upon addition of an equivalent of Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^{+}, Pb^{2+} and Sn^{2+} are shown in **Figure 4a,** while those of L2 (8×10^{-4} M) in DMSO with the same group of metal ions are shown in **Figure 4b.**
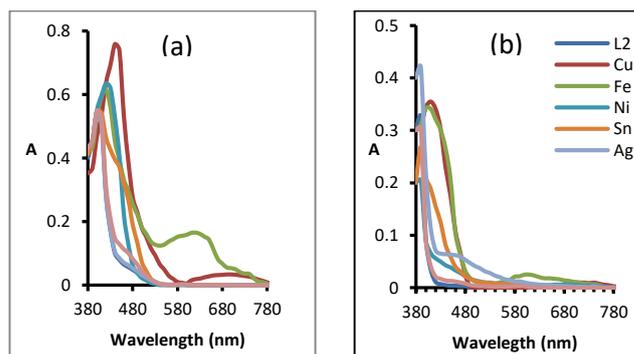

Figure 4: Absorption spectra of (a) L1 (1×10^{-4}M) and (b) L2 (8×10^{-4} M) in DMSO upon addition of transition metal ions (1×10^{-4}M).

The addition of the metal cations to the ligand solutions showed no change in the solution color, except for the Fe^{3+} ions. By adding Fe^{3+} ions to L1, the color changed from light orange to green immediately, while the color changed from yellow to green when Fe^{3+} ions were added to L2. A new absorption band at 610 nm for both ligands was observed, indicating that the complex formation had taken place. Meanwhile, no noticeable change was observed when other metal ion solutions were added. The chromogenic complexation behavior of both ligands was further investigated in THF. Similar behavior towards Fe^{3+} was observed. The color of the solutions changed from light orange to green and from yellow to green immediately upon addition of Fe^{3+} to both ligands, respectively. A new absorption band (610 nm) was also observed upon complexation. Since $Fe^{3+}$is the only metal ion showed a remarkable change in color upon complexation with both ligands, therefore, it was selected for further studies.

3.2.3 Effect of ligand concentration

An optimum ligand concentration is essential to give maximum sensitivity on the absorbance of Fe^{3+} complex. Therefore, the effect of ligands concentration on the absorbance of their complex with Fe^{3+} was studied by mixing the metal ion (1.0×10^{-3}M) with different concentration of ligands in DMSO. The color intensity of the test solution increased with an increase in the ligand concentration. The absorbance of ligands-Fe^{3+} complexes was found to be linearly proportional to the ligand concentration in the range from 1.0×10^{-4} to 1.0×10^{-3}M for L1 and from 1.0×10^{-3} - 8.0×10^{-3}M for L2. Increasing the concentration of ligands did not lead to a significant increase in the absorbance of the complexes. The maximum absorbance was obtained at 1.0×10^{-3}M and 8.0×10^{-3} M, with a ratio equivalent to 1:1 and 8:1 for both ligands, respectively. This ratio was essential to obtain an optimal color development for maximum absorbance. Figure 5, shows the linear correlation ($R^2 = 0.9919$ and 0.9857) for ligands, respectively.
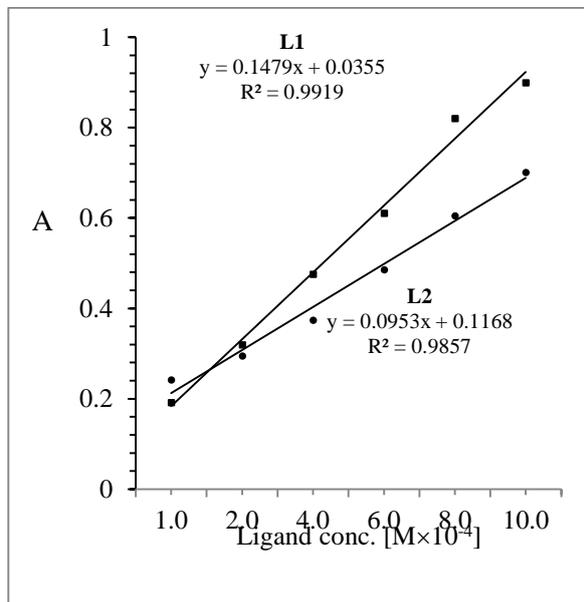

Figure 5: Plot of absorbance of studied ligands upon complexation with Fe^{3+} in DMSO, λ_{max} 610 nm

3.2.4 Effect of Fe^{3+} ions concentration

At a fixed ligand concentration (L1= 1.0×10^{-3} M and L2= 8.0×10^{-3} M) the effect of Fe^{3+} ions was investigated. The concentration of Fe^{3+} was varied within the range of 0.1×10^{-3} to 1.0×10^{-3} M to investigate the absorption profile as a function of Fe^{3+}concentration (**Figure 6**). The absorbance of the complexes were found to be linearly proportional to the concentration of Fe^{3+}. The maximum absorbance of L1- Fe^{3+} complex was found at 1.0×10^{-3} M of Fe^{3+} ions, with a mole ratio of 1:1 (L1: Fe^{3+}), while that for L2-F^{3+} was obtained when the Fe^{3+}concentration reached a 1.0×10^{-3} M, corresponding to a mole ratio of 8:1.
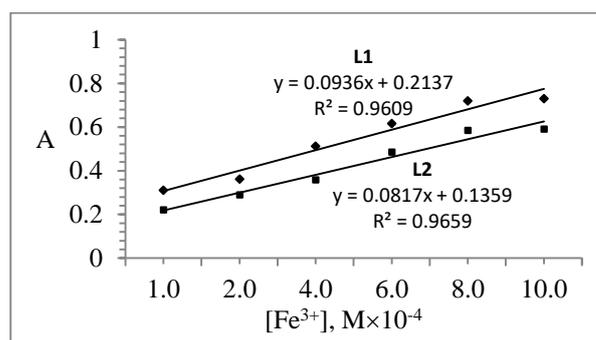
Figure 6: The mole ratio method for ligands-Fe^{3+} complexes.

3.2.5 Stoichiometry of the complexes

In addition to the mole ratio method presented earlier, the stoichiometry of the complex was also studied by Job's continuous variations method in order to confirm the previous findings. In L1-Fe^{3+} complex the curve displayed a maximum at a mole fraction $x_{metal} = 0.5$ (**Figure 7**) which indicated the formation of this complex in a 1:1 mole ratio. For L2, the variation method showed that the ratio of the metal ion to L2 in the complex was 1:8 (mole fraction 0.8). These findings agreed well with the results obtained from the mole ratio method in the previous section. The stability constants, K_s (**Table 3**) for both complexes could be determined from the plot of Job's method, using the following corresponding equations (Tahir *et al.,* 2010) and found equals to 5.7×10^5 and 1.6×10^5 for both complexes, respectively.

$$Ks = \frac{[ML]}{[M] \times [L]} \qquad Ks = \frac{A2/A1}{(1 - \frac{A_2}{A_1}) \times (C_L - (C_m \times \frac{A_2}{A_1}))}$$

where, A_1 and A_2 are the observed and extrapolated absorbance, while C_L and C_m are ligand and metal ion concentrations, respectively.

Table 3: Stability constants for the studied complexes at 1.0×10^{-3}M.

Complex	A_1	A_2	K_s
L1-Fe^{3+}	0.70	0.73	5.7×10^5
L2-Fe^{3+}	0.62	0.67	1.6×10^5

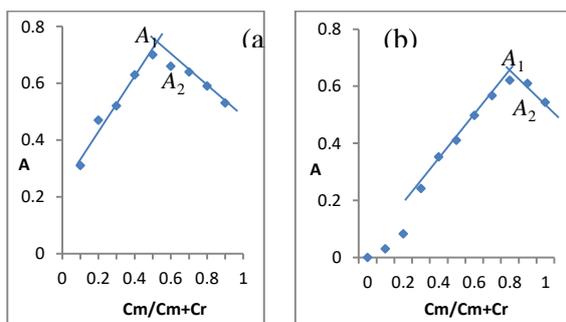Figure 7: Determination of M:L ratio of the complexes by Job's method. 1.0×10^{-3} M Fe^{3+}, 1.0×10^{-3} M ligand1, $\lambda_{max} = 610$nm.

3.2.6. Interferences

The interferences of foreign metal ions on the complexation of Fe^{3+} with both ligands was investigated. Fe^{3+} (1.0×10^{-3}M) was added to different solutions of L1 and L2 in the presence of one equivalent of other metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^+, Pb^{2+} and Zn^{2+}). The absorbance of the solutions mixture was measured at 610 nm. The interferences (%I) of the metal ions studied are shown in **Table 4.** Most of the metal ions examined have no interference on the complexation of Fe^{3+} ions. The addition of Cu^{2+} ions showed the highest interference on the detection of L1-Fe^{3+} complex ($\Delta A= 0.014$) among all the other metal ions. The addition of Zn^{2+} ions showed the highest interference in the detection of L2-Fe^{3+} ions ($\Delta A= 0.571$). The addition of Zn^{2+} ions caused the color of the solution mixture to change to yellow, indicating a strong interference with Fe^{3+} ions. This may be due to the ability of Zn^{2+} ion to form complex with ligand 2.

Table 4: The interferences of foreign metal ions on the complexation of Fe^{3+} with L1 and L2. The $\lambda_{max}= 630$nm

Metal ion	L1			L2		
	A	**ΔA**	**%I**	**A**	**ΔA**	**%I**
Fe^{3+}	0.723	-	-	0.571	-	-
$Fe^{3+}+Co^{2+}$	0.717	0.006	0.8	0.568	0.003	0.5
$Fe^{3+}+Zn^{2+}$	0.720	0.003	0.4	0	0.571	100
$Fe^{3+}+Pb^{2+}$	0.719	0.004	0.5	0.570	0.001	0.17
$Fe^{3+}+Ag^+$	0.721	0.002	0.3	0.563	0.008	1.4
$Fe^{3+}+Ni^{2+}$	0.722	0.001	0.1	0.571	0	0
$Fe^{3+}+Cu^{2+}$	0.709	0.014	1.9	0.555	0.016	2.8

$$\Delta A = A_{(Fe^{3+}+foreign\ metal\ ions)} - A_{(Fe^{3+})}, \qquad \%I = \frac{\Delta A}{A(F^{3+})} \times 100$$

CONCLUSION
----*-------------------------------------*----

In this study, two chromogenic Schiff base ligands as well as their complexes with Fe^{3+} were investigated. The chromogenic complexation properties of both ligands were studied through spectrophotometric method. Different transition metal cations (Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^+, Pb^{2+}, and Sn^{2+}) were used. Among these cations, both ligands displayed selectivity for Fe^{3+} in DMSO. Upon addition of Fe^{3+} ions, in solution containing L1, an obvious color change from light orange to green was immediately noticed, while in L2 solutions, the color changed from yellow to green, noticeable via naked eye detection. A ligand to Fe^{3+} molar ratio of 1:1 and 8:1 for L1-Fe^{3+} and L2-Fe^{3+} complexes were reported, respectively. The stability constants (K_s) were found to be equivalent to 5.7×10^5 and 1.3×10^5 for both ligands, respectively. Therefore, it could be concluded that L1 exhibited excellent chromogenic properties towards Fe^{3+} ion as compared with L2, as it showed the ability to complex with Fe^{3+} ions in a mole ratio of 1:1 with no significant interference from other transition metal ions in this study.

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