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N_2 Schiff Ligand with Mercury (II) Complex: Preparation and Characterization

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P A P E R I N F O

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A B S T R A C T

The Bi dentate ligand type N_2 molecule have been prepared through one step reaction between one equivalent of acetyl acetone with two equivalent of 4-phenoxy aniline, using ethanol as a solvent. This ligand was used to manufacture the target Hg (II) complex from action of the ligand and Mercury with a 1:1 ratio.The ligand and complex were characterized by infrared spectroscopy, the ultraviolet spectrum, the precise analysis of the elements (C.H.N.). ^{1}H-NMR spectrum and the mass spectrum of the new ligand were taken. The prepared complex was also diagnosed with molar conductivity and magnetic susceptibility. Suggested geometry around the Mercury ion is Tetrahedral.

1. INTRODUCTION

Chemical compounds containing the imine group are known as Schiff bases.They consist of a carbon atom double-bonded to a nitrogen atom (C=N)[1] .Alphabetic or aromatic primary amines, certain amino acids, and aldehydes combine to form aliphatic or aromatic ketones (carbonyl compounds) [2]. Colored crystals, which are often yellow in color, are typical in Schiff bases. Carbony l compounds and the type of amines - aliphatic or aromatic have a major influence on the characteristics and stability of Schiff bases .The used aldehyde, ketone, or amine also affects the stability of these types of compounds[3]. The most stable bases are Schiff bases prepared from an aromatic aldehyde and an aromatic amine. This is due to the increased stability by resonance. The availability, electronic features, and simplicity of Schiff base ligands have all led to great deal of investigations. Recent years have seen a tremendous increase in interest in Schiff base coordination chemistry because of its important applications in analytical chemistry[4], organic synthesis, electroplating, metal refining, metallurgy, and photography[5]. Both the advancement of bioinorganic chemistry and contemporary coordination chemistry depend strongly on schiff bases[6].They have several usages in medicine because of their pharmacological characteristics. The biological activity of azomethine derivatives[7] depends on the (C=N). A number of azomethines were therefore found to have diuretic, anticancer, and antimicrobial (antibacterial, antifungal) properties[8]. Schiff bases are widely used in agrochemicals, analytical chemistry[9], food and dye industrie, catalysis[10], and fungicidal characteristics. There have been numerous reports on applications over the past few decades, particularly in biology. Among these reports are the ones that have antiviral, antifungal[11], antioxidant, anticancer, anti-inflammatory, and antimalarial properties[12]. Thus,it necessary to do a review that emphasizes the uses of Schiff base ligands and their complexes.

2. APPARATUS

Melting point, /SMP30/ , Strut, England, HOT plate with magnetic stirrer MR Hei - standard ,Heldolph ,Germany, Balance BL 2105, Sartorius, Germany, Oven BS size two, Gallenkamp, England, UV-Visible spectra recorded by UV-Visible spectrophotometer (Shimadzu- UV-1700), FT-IR Test scan Shimadzu model 8000, the IR spectra of the compound (400-4000 cm-1), ^{1}H-NMR spectra by using Varian-Ultra Shield 500 MHz (Switzerland) with DMSO-d^6 solvent, as well as Auto Magnetic susceptibility Balance Sherwood Scientific the electrical conductivity was measured using a digital conductivity meter WT-720-inolab (Germany), and mass spectra Work mass selective Detector 5973 and using an energy of 70 Electron Volt.

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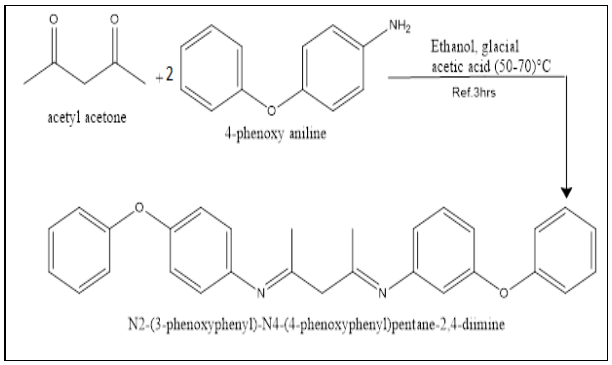
3. EXPERMINTAL

3.1 Materials

There is sufficient purification for every chemical that is utilized from Merek, Aldrich, and Fluka.

3.1.1 Synthesis of new ligand(2E,4E)

(0.001mol,1.0216 mL) of acetyl acetone dissolved in 10 ml of pure ethanol) was placed with the addition of three drops of glacial acetic acid,(solution. 1). Next, we took (0.1852 mol 0.001 g) of 4-phenoxy aniline that was well dissolved in 20 ml of absolute ethanol,(Solution .2), in a sublimation device. Place (Solution.1) and gradually add (Solution .2) to it.Then, we begin the reverse sublimation process (Reflux) for 3h at a temperature of (50 -60) °C with the circular-bottomed reaction flask with a capacity of (100 mL) placed submerged in a water bath. After the reaction, the mixture is left to dry in the air for 24h. at room temperature before it is being washed and recrystallized using diethyl ether. It forms a yellowish-brown precipitate, yelled %70 as in (Scheme1)



Scheme 1. Reagent preparation step

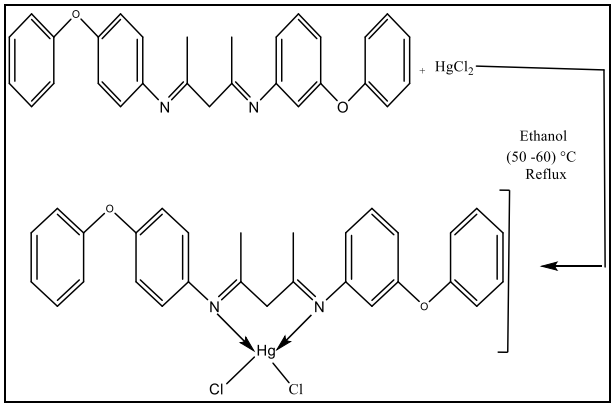
Elemental Analysis: C, 80.16(79.16); H, 6.03(5.03); N, 6.45(5.25); O, 7.36(6.16), the chemical composition of the ligand as well as certain physical characteristics are presented in Table (1).

TABLE 1. Explains the physical properties and chemical formula of the ligand**.**

Color	Proportion of roduct	M.P (C°)	M.wt	Chemical Formula	Name and symbol
yellowish-brown	yelled:70.0 %	280-283	434.5	$C_{29}H_{26}N_2O_2$	(2E,4E)-N2-(3-phenoxyphenyl)-N4-(4-phenoxyphenyl)pentane-2,4-diimine

3.1.2 . Preparation of the Hg(II) complex

reflex and stirring with(0.11g),of $HgCl_2$ for 3h at(50–60)°C, with a mixture containing (0.2g) of ligand dissolves in (25 mL) of absolute Ethanol. The brown precipitate form, is filtered out, and is allowed to air dry. MP:277-280°C; yelled:70.0%; Chemical Formula: $C_{29}H_{26}Cl_2HgN_2O_2$ 4; M.wt: 706.0 Elemental Analysis: Elemental Analysis: C, 49.33(48.83); H, 3.71(2.71); Hg, 28.41(27.41); N, 3.97(2.47); O, 4.53(3.53) as in **(Scheme2)**.



Scheme 2. Preparation of Mercury complex

4. PRODUCT DESCRIPTION

Ultraviolet-visible (UV-Vis), infrared (FT-IR), and the precise analysis of the elements (C.H.N.), melting point analysis were used to characterize the produced ligand and complex. while the ^{1}H-NMR spectrum and the mass spectrum of the new ligand were taken. Aside from that, the generated complex was assessed by using molar conductivity and magnetic successptibility.

5- RESULTS AND DISCUSSION

5.1 UV-Visible spectra for ligand

The electronic absorption spectra of the Schiff base ligand were obtained at room temperature in an absolute ethanol solution (1×10^{-3}) mole [13]. It is seen in **(Figure 1)**. There are two electron transitions in the ultra violet region of the ligand's UV-Vis electronic transition.: the $\pi \longrightarrow \pi^*$ transition which occurs at (λ = 240nm) with absorbance 0.669 while the $n \longrightarrow \pi^*$ transition occurs at(λ = 334nm)with absorbance 0.233.

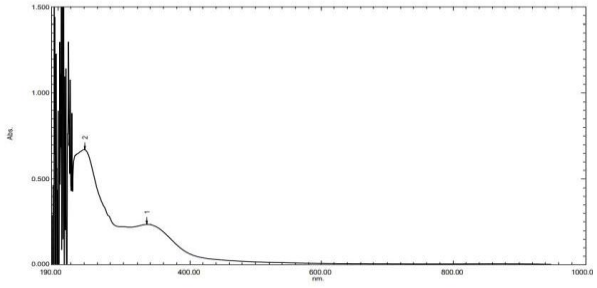


Figure 1. The UV-Vis spectrum of ligand

5.2 UV- Visible spectra for Mercury complex

The Schiff base complex's electronic absorption spectra were obtained in an absolute ethanol solution 10^{-3}mole at room temperature[14]. Just as (Figure 2) shows, the compound undergoes electronic transitions at wavelengths of (λ = 244nm), where the absorbance is 0.448, and (λ =221nm), when the absorbance is 0.472. C.T. is characterized by charge transfers ,There are no d-d transitions in the visible spectrum because Mercury is of the d^{10} type, which indicates that the d orbital is filled with electrons.

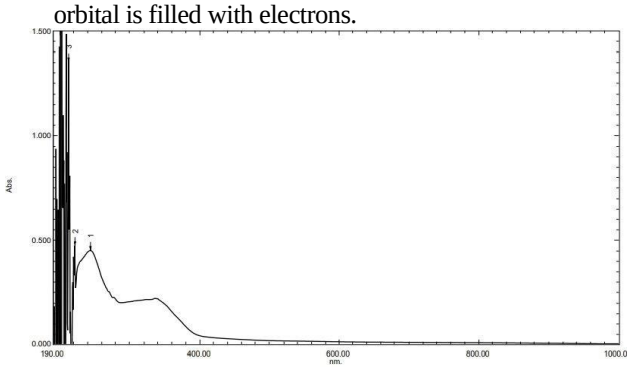


Figure 2. UV-Visb for Mercury complex

5.3 FT-IR spectra

As exposed in figure (3), we can distinguish the ligand's (L) IR spectra[15] by the appearance of some bands with distinct frequencies such as υ (-CH) at (3167) cm^{1-} belonging to the aromatic rings and υ ($-CH_2$) at (2980) cm, υ ($-CH_3$) at (2889) cm^{1-}. A distinct band also appeared at (1633) cm^{1-} originating from the azomethine group υ (C=N) frequency, finally, at (1394) cm^{1-} represents the frequency of the ether group (C-O-C).

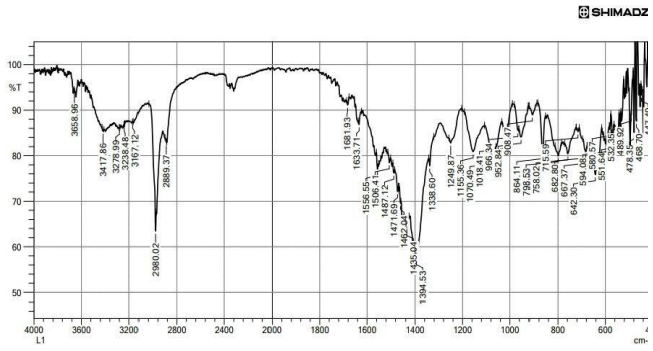


Figure 3. Schiff base ligand spectrum in FT-IR

When comparing the ligand's spectrum to the Mercury complex (HgL) spectrum displayed in Figure (4), it was found that different shifts occurred for the same groups mentioned above, with the appearance of new frequencies for other groups, such as the frequency of υ (M-N) at (422-470)cm^{1-}, suggesting that there is coordination in the aforementioned complex[16].

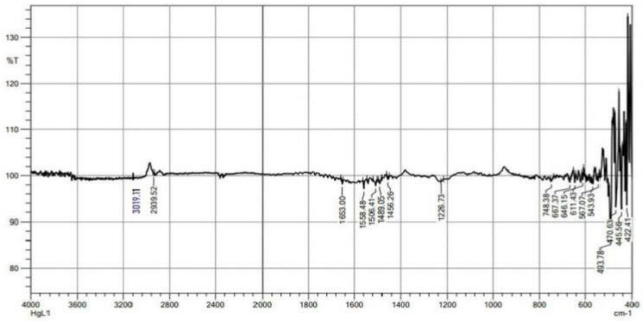


Figure 4. FT-IR spectrum of the Mercury complex

5.4. Proton NMR spectrum for ligand

The 1H-NMR spectra of the Schiff base ligand obtained by using the solvent DMSO-d^6, reveals the synthesis process as described in **Figure (5).** With its chemical shift displayed at (δ = 2.522 ppm), a signal for two groups (-CH3) in the range (δ=1.1-1.3 ppm,6H) , another signal for the group (CH2) at the chemical shift (δ = 3.4ppm,2H) and further signal in the range (δ = 6.9-8.9ppm,18H) refer to aromatic rings in which C-H groups form in different environments[17].

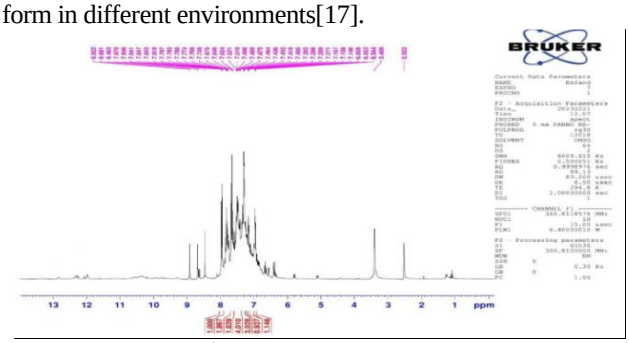


Figure 5. ^{1}H-NMR spectra of The ligand

5.5. Mass spectrum of the ligand

Figure (6) offers free ligand (L) mass spectrum displayed the charge to-mass ratio M/Z^+(M.wt=434), which is proportional to the molecular weight of the compound[18].

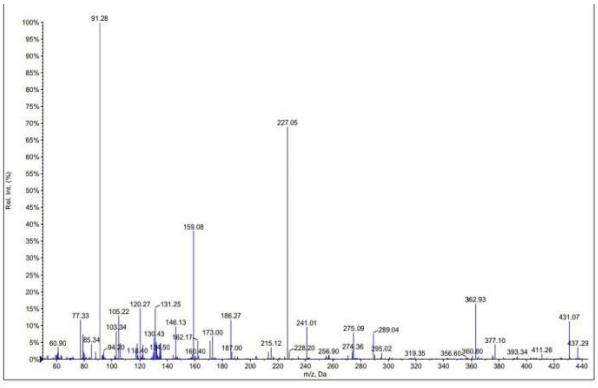
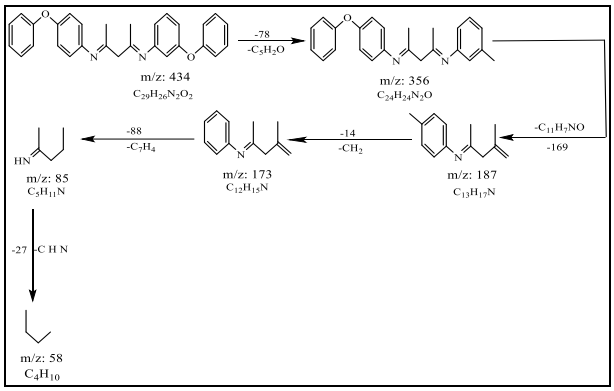


Figure 6. Mass spectrum of the ligand

The Scheme (3) shows the partitioning method for the mass spectrum of the compound



Scheme 3. Ligand fragmentation

5.6. Magnetic susceptibility and molar conductivity of Mercury complex

Mercury's complex is classified as dia-magnetic because it possesses the d^{10} system, which, in a hybridized state, has no single electron[19]. The complex's molar conductivity was measured at room temperature (25°C) using DMSO as the solvent. The complex's concentration was 0.001 M, and the resultant value of 18.6 $S.mol^{-1}. cm^2$ demonstrated the complex's non-electrolytic character[19], which supports its tetrahedral geometry.

6. CONCLUSION

The Bi dentate ligand typeN_2 was prepared in one step by reacting one equivalent of acetylacetone with two equivalent of 4-phenoxyaniline using ethanol as a solvent.This research includes the preparation of a Schiff base ligand and a Mercury complex. The prepared ligand and complex were characterized by infrared spectroscopy,The ultraviolet spectrum, the precise analysis of the elements (C.H.N.). ^{1}H-NMR spectrum and the mass spectrum of the new ligand were taken .The prepared complex was also diagnosed with magnetic susceptibility.This confirmed the proposed tetrahedral shape of the Mercury ion, in addition to the molar conductivity, which revealed that the complex is non electrolytic.

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Arabic Abstract

تم تحضير الليكاند ثنائي السن من النوع N_2 من خلال خطوة واحدة تضمنت التفاعل بين مكافئ واحد من الأسيتيل أسيتون مع مكافئين من 4-فينوكسي أنيلين، باستخدام الإيثانول كمذيب. يستخدم الليكاند بعد ذلك لتحضير معقد Hg (II) بنسبة مولية 1:1، وشخص الليكند والمعقد المقترح بواسطة التحليل الطيفي للأشعة تحت الحمراء، وطيف الاشعة فوق البنفسجية، والتحليل الدقيق ،و طيف ^{1}H-NMR والطيف الكتلي لليكند الجديد، كما تم تشخيص المعقد المحضر من خلال التوصيلية المولارية والحساسية المغناطيسية . وكان الشكل الهندسي المقترح لأيون الزئبق هو رباعي السطوح.