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SYNTHESIS, SPECTROSCOPIC, THERMAL, BIOLOGICAL ACTIVITIES STUDIES FOR Ni(II),Cu(II) AND Zn(II) COMPLEXES WITH PHTHALOHYDRAZIDE DERIVED LIGAND AND EVALUATION AS ANTIOXIDANTS

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ABSTRACT. The present article discusses the synthesis of tetradentate Schiff base complexes formed by the condensation reaction of 2-hydroxy benzaldehyde and phthalohydrazide. The ligand (LH2) was detected using FT-IR spectra, ^{1}H, ^{13}C-NMR, UV-Vis spectroscopy, elemental microanalysis CHN, and mass spectrometry. The obtained solid complexes have been assessed using physicochemical and spectroscopic techniques, including UV-Vis, FT-IR, nuclear magnetic resonance (^{1}H-NMR, ^{13}C-NMR), mass spectrometry, thermal gravimetric analysis (TGA), and atomic absorption, in addition to complex conductivity and magnetic moment measurements. The infrared results demonstrated that ligands functioning as tetradentate ligands are chelated to metal ions via the phenolic oxygen and nitrogen of the azomethine group. Specific metal ions join with chloride ions (Cu^{+2}, Zn^{+2}) to reach their coordination numbers. The generated compounds' antibacterial effect in vitro was measured towards *Candida albicans* as a fungal species, Gram-positive *Bacilla* and *pseudomonas*, and Gram-negative *Staph* and *E. coli* using the agar well diffusion technique. The ligand generated an octahedral geometry around the (Cu^{+2} and Zn^{+2}) and a tetrahedral form around the Ni^{+2} metal ion, per the measurement and spectroscopic tests. Ascorbic acid is used as a standard in the phosphomolybdate technique to assess the antioxidant activity of the ligand and complexes.

KEY WORDS: Antioxidant activity, Phosphomolybdate, Tetradentate ligand, Coordination number, Condensation reaction.

INTRODUCTION

One of the most famous compound classes is Schiff bases because of their remarkable variety and simplicity of production. The Schiff base ligand is involved throughout design and synthesis of various metal complexes. It is conveniently generated via the condensation reaction between an aromatic amine and a carbonyl molecule [1]. These molecules' thermal and chemical stability makes them significant for advancing modern coordination chemistry. These substances are commonly used because of their applications in inorganic biochemistry, catalysis, and optical materials [2, 3]. Extensive research has been conducted recently on transition metal complexes derived from bidentate Schiff base ligands that include both -NH_2 (amine) and -OH (hydroxyl) groups. The Schiff base-metal complexes, which have donor atoms of nitrogen and oxygen together with a variety of transition metal elements (such as Ni(II), Cu(II), and Zn(II)), have a wide range of applications, including catalytic biological (antibacterial, antibiofilm, antifungal, antimalarial, antioxidant, anticancer, and antiviral) [4-6], luminescence, fluorescence, nonlinear optical characteristics, and prospective uses as sensors and photovoltaic materials. In this work, a novel Schiff base ligand complex with Ni(II), Cu(II), and Zn(II) was produced, and their structures were elucidated using a variety of spectroscopic and analytical methods [7, 8].

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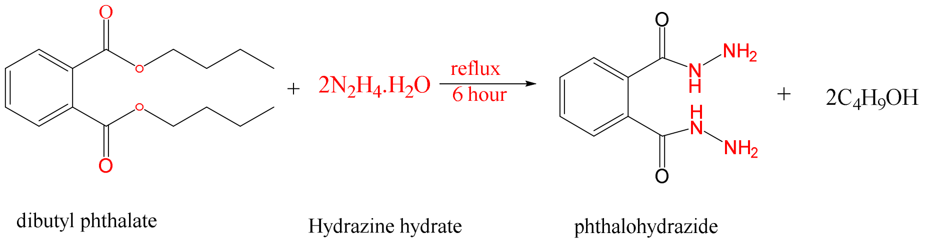
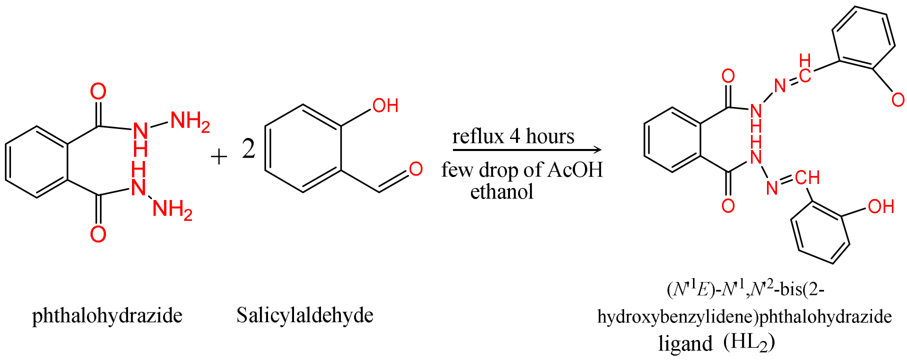
Experimental

Step 1 explains the method of generating phthalohydrazide by dissolving 1.0 g of dibutyl phthalate (0.0036 mol) in 15 mL of ethanol while the mixture is still at the temperature of the room in a round-bottom flask. Following an ongoing stirring period, 3.604 g (0.072 mol) of aqueous hydrazine monohydrate was put in gradually in a 1:2 molar ratio. The resulting mixture then refluxed for 6 hours. After the reaction ended, the white precipitate was removed by filtering, let to settle to room temperature, and finally washed using dry ether and methanol. As seen in Scheme 1, re-crystallization of a white precipitate made completely of ethanol provided an extremely high 87% melting point at 294 °C [9].



Scheme 1. Phthalohydrizized initial substance synthesized.

In step two, phthalohydrazide (1 g, 0.005 mol) was dissolved in a 25 mL round-bottom flask containing 10 mL of ethanol. Together with the resulting ligand (LH_2) amount as shown in Scheme 2. With a 1:2 molar ratio of salicylaldehyde (1.221 g, 0.010 mol) and a 3–4 drop of anhydrous acetic acid, the mixture was raised to 50 °C and refluxed for four hours. The yellow crystal was dried after being formed, filtered, washed, and re-crystallized. The melting point was between 281 and 283 °C, and the yield was 80%. FTIR, UV-Vis, mass, ^{1}H-NMR, ^{13}C-NMR, CHN elemental analysis and TGA were applied to analyze the ligand.

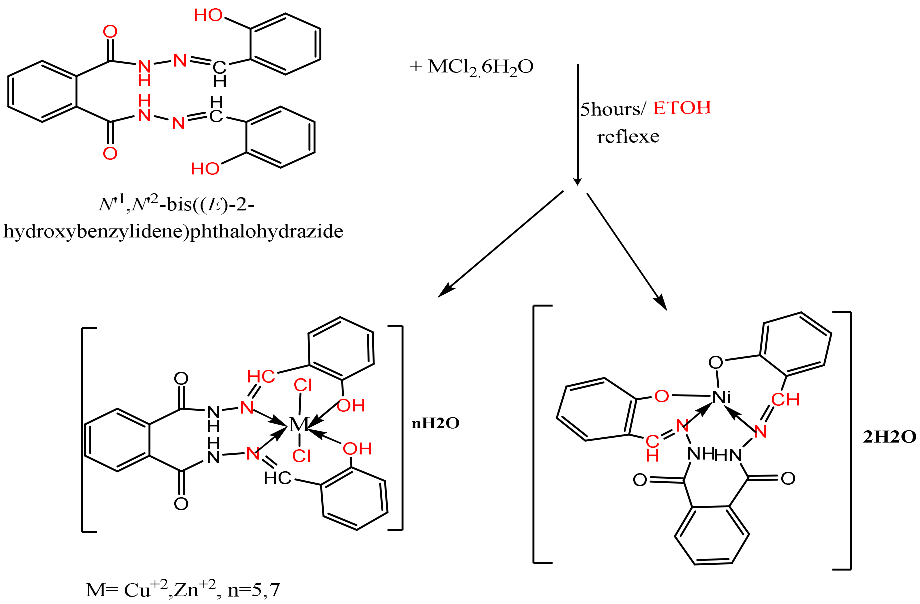


Scheme 2. Schiff bases ligand preparation (LH_2).

Preparation of metal complexes

Ten milliliters of pure ethanol dissolved 0.200 g (0.497 mmol) of ligand in a 25 mL round-bottom flask. In a 1:1 molar ratio, metal chloride [M = Ni^{2+}, Cu^{2+}, and Zn^{2+}] (0.118, 0.085 g, and 0.067g) was added to a flask having a ligand solution after being dissolved in 10 mL of 100% ethanol.

Table 1 shows how the mixture's color varied after five hours of reflux heating to 40 °C. The final yields were great to high, ranging from 75-82%, when the precipitate had been filtrated off, cleaned with ethanol, and dried at room temperature for 24 hours. As per Scheme 3 [10].



Scheme 3. The prepared complexes of Schiff bases ligand (LH2).

RESULTS AND DISCUSSION

A high yield of the ligand and its complexes was generated. The resulting ligand's physical characteristics, micro elemental studies, and metal complexes are listed in Table 1. The indicated structural model and the outcomes are very similar. The elemental analyses predicted and observed results were accepted, showing that the ligand and complexes have been created successfully.

Table 1. The physical features of generated chemicals and elemental microanalysis of C, H, N, %Cl using Mohr's method and M% percent using atomic absorption .

Ligand/complexes	M.p. (°C)	Color	Calculated (found)				
			C%	H%	N%	Cl%	M%
$LH_2(C_{22}H_{18}N_4O_4)$	281–283	yellow	65.60	4.47	13.91	----	----
(402. 41)			(64.81)	(4.84)	(13.37)		
$[Ni\ LH_2].2H_2O$	290Dec	Yellowish-green	53.37	4.04	11.31	----	11.85
(494.60)			(52.55)	(3.64)	(12.11)		(11.25)
$[CuLH_2Cl_2].5H_2O$	260-264	Olive	42.11	4.46	9.03	11.33	10.13
(626. 56)			(42.22)	(4.25)	(10.05)	(11.00)	(9.91)
$[ZnLH_2Cl_2].7H_2O$	270-273	Light-yellow	39.71	4.81	8.42	10.68	9.83
(664.40)			(39.41)	(3.83)	(8.01)	(10.04)	(8.92)

Schiff base ligand FTIR spectra and its complexes

FTIR is a helpful technique for identifying the Functional groups and forming new bands in chemical compounds. Due to phenolic OH, the Schiff base ligand shows a broad band at 3463 and 3442 cm^{-1}. The wideness of this band is due to intermolecular hydrogen bonding between the phenolic and azomethine groups. This band shifted to 3425 and 3431 cm^{-1} in Cu(II) and Zn(II) complexes, respectively, and vanished in Ni(II) complexes, indicating that the hydroxide group coordinated after deprotonation with metals. The frequency of the (C=N) value shifts downward due to the metal ions' coordination with the nitrogen azomethine [11, 12]. This comes as a result of the azomethine's reduced electron density. The IR spectra of the complexes show specific lines in the 1608-1622 cm^{-1} region, representing how the metal ions coordinate with the ligand via the azomethine's nitrogen atom [13]. New stretching modes at 451–489, 513–586, and 351–397 cm^{-1} appear in the complexes' far-infrared spectra, and these are attributable to M–N, M–O, and M–Cl, respectively [14]. Bonds are formed between divalent metal ions, and the nitrogen azomethine, hydroxyl group, and chloride, sequentially, are enabled by these stretching modes as in Table 2 shows the previously described results.

Table 2. FTIR spectroscopy data of Schiff base ligand and its complexes (cm^{-1}).

Symbol	ν(O-H) phenolic	ν(H_2O) lattice	ν(N-H)	ν(C=N)	ν(C=C)	ν(M-O)	ν(M-N)	ν(M-Cl)
Ligand (LH_2)	3463	----	3325	1622	1573	---	---	---
$[NiLH_2]$.2H2O	----	3452-694	3082	1608	1539	586	451	397
$[CuLH_2Cl_2].5H_2O$	3425	3434-640	3153	1606	1583	524	464	351
$[ZnLH_2Cl_2].7H_2O$	3431	3425-661	3112	1623	1579	513	489	378

Measuring ligand and its complexes using UV-Vis spectroscopy

At room temperature, the electronic spectra of complexes and ligands were taken in DMF solution between the 200–1100 nm range. The data that was gathered is displayed in Table 3. The Schiff base ligand's UV-Vis spectra produced substantial intensity absorption peaks at 248, 297, and 357 nm, which were attributed to charge transfer transitions of carbonyl and azomethine, respectively, and intra-ligand (π–π*, n–π*) [15]. The complexes' spectra displayed shifts in the locations of absorption bands, which suggested that the hydroxyl phenol and azomethine functional groups [16] were coordinating the metal ions. The Ni(II) complex in DMF's electronic spectra exhibited bands at around 240, 405, and 923 nm, which were attributed to π→π*, charge transfer, and $^3T_1 \rightarrow {}^3T_1(p)$, $^3T_1 \rightarrow {}^3T_2$. The possibility of the creation of a high-spin tetrahedral shape [17] is given by the magnetic moment of 3.11 BM and the observed electronic spectrum of the Ni(II) complex. The spectrum bands at 353, 592 and 922 nm, which correspond to the electronic transition (C.T., $^2B_1g \rightarrow {}^2Eg$, $^2B_1g \rightarrow {}^2A_2g$), demonstrate that the Cu-complex has an octahedral geometry. A charge transfer band was seen in the d^{10} Zn(II) complex at 354 and 435 nm [18]. All produced complexes are non-electrolyte complexes relative to the molar conductivities.

Ligand identification by ^{1}H-NMR spectroscopy

The ^{1}H NMR data of the ligand table 4 in DMSO indicates that the solvent is responsible for the wide signal at $\delta = 2.5$ ppm. At 9.0 ppm, two symmetrical imine groups connected to a signal attributed to the (CH=N) proton of the azomethine Schiff base. The chemical shifts were attributed to the aromatic ring's hydrogen in the 6.94–7.71 ppm area, the amid group's proton at $\delta = 11.12$ ppm, and two signals at 11.86 ppm from the two-phenolic group [9].

Table 3. UV-Vis spectroscopy studies of the ligand and the molar conductivity of metal complexes.

Compound	λ_{max} (nm)	Absorption (cm^{-1})	Assignments	μ_{eff} (B.M.) Exp.	Molar Cond. $Ohm^{-1}\ cm^2\ mol^{-1}$	Geometry
Ligand (LH_2)	248 297 357	4032.25 3367.00 28490.0	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ C.T.	----	----	----
$[NiLH_2].2H_2O$	923 543 405 240	1083.42 1841.62 2468.13 4166.66	$^3T_1 \rightarrow {}^3T_1(p)$ $^3T_1 \rightarrow {}^3T_2$ CT $\pi \rightarrow \pi^*$	3.11	3.40	Tetrahedral
$[CuLH_2Cl_2].5H_2O$	922 592 353 293	1084.59 1689.18 2832.86 3412.96	$^2B_1g \rightarrow {}^2A_1g$ $^2B_1g \rightarrow {}^2Eg$ CT $n \rightarrow \pi^*$	3.76	3.50	Octahedral
$[ZnLH_2Cl_2].7H_2O$	354 293 217	2824.86 3412.97 4608.29	CT $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	Di	4.40	Octahedral

Ligand characterization using ^{13}C-NMR spectroscopy

One helpful method for determining the chemical makeup of the synthesized ligand is ^{13}C-NMR spectroscopy. The ^{13}C-NMR spectrum, displays the critical peaks in the appropriate locations to depict the chemical structure of the generated ligand. The carbon atom N=CH in two imine groups generates one peak at 148.65 ppm; however, carbonyl groups display a peak at 163.22 ppm due to oxygen's stronger electronegativity than nitrogen, resulting in more de-shielding. The phenolic group peak, connected to the DMSO solvent and located at 43.33 ppm, remains at 158.81 ppm [20].

Schiff base ligand characterization via mass spectroscopy

The ligand's (LH2) mass spectra exhibit a parent peak and a fragmentation ion pattern. The mass spectrum of the ligand is displayed in Figure 1. The peak at m/z = 403.23 can be observed as the molecular ion peak correlated with the ligand formula weight. Additional peaks in the spectrum may be seen at (m/z) 239.64, 222.71, 146.74, 120.81, and 76.83. As it broke apart piece by piece, the ligand formed fresh, distinct peaks [21].

Characterization of Schiff bases ligand and its complexes by thermal studies

Thermal analysis was used to investigate the Schiff base's thermal behavior and its complexes. The thermograms were recorded in a nitrogen atmosphere within the 25 to 1000 °C temperature range, with a heating rate of 10 °C/min. The findings stated a weight loss agreement between the calculated and thermal decomposition values, supporting the recommended formulae in Table 4 and supporting the elemental analysis results [22].

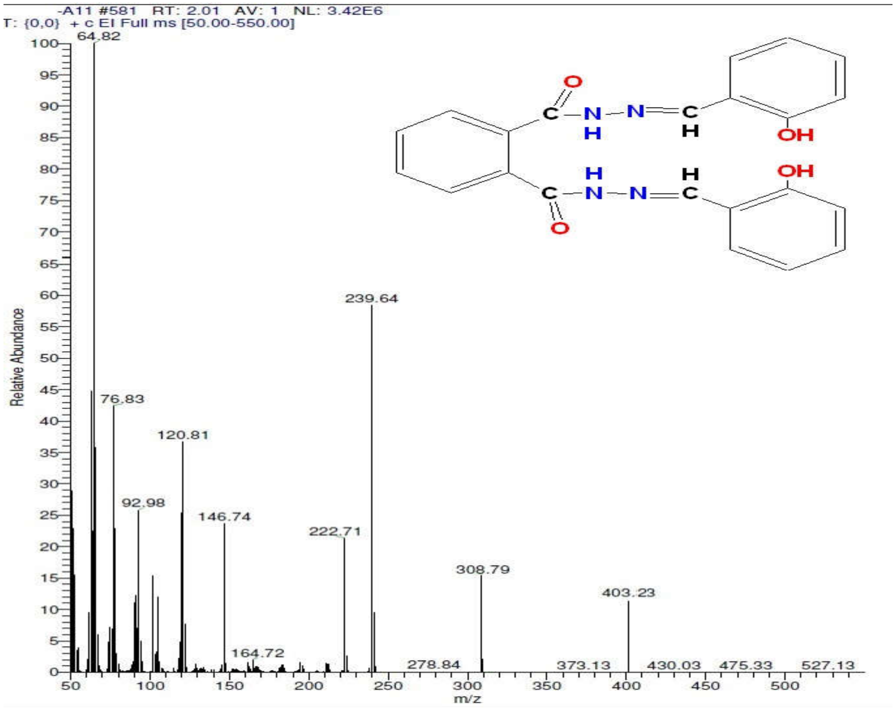


Figure 1. Mass spectrum of (LH_2).

Table 4. Summarizes the pyrolysis processes of compounds.

Compounds	Decomposition	Weight loss (%)			Lost species
		T_{max} (C)	Calcd.	Found	
$LH_2(C_{22}H_{18}N_4O_4)$	Step 1	50-250	41.74	41.73	$-C_8H_{12}N_2O_2$
	Step 2	250- 950	5.76	5.80	$-CH_2$
	Residue				$C_{12}H_4N_2O_2$
$[NiLH_2].2H_2O$	Step 1	50-300	3.63	4.28	$-H_2O$
	Step 2	300-375	16.15	16.82	$-C_2H_5NO+H_2O$
	Step 3	375-425	21.89	21.85	$-C_5HNO$
	Step 4	425-850	21.56	20.50	$-C_2H_2N_2O$
	Step 5	850-980	7.85	7.32	$-C+4H_2$
	Residue				NiO+12C
$[CuLH_2Cl_2]. 5H_2O$	Step 1	50-135	5.10	4.34	$-2H_2O$
	Step 2	135-254	12.10	12.0	$-2H_2O+Cl$
	Step 3	254-325	19.17	19.20	$-H_2O+Cl+C_2H_6+NH_2$
	Step 4	325-785	24.00	24.11	$-C_4H_8N_2O$
	Step 5	785-820	9.07	9.70	-CHO
	Step 6	820-858	11.00	11,30	$-C_2H_2$
	Step 7	858-980	8.90	7.88	-2C
	Residue				CuO+NO+12C

$[ZnLH_2Cl_2]$.$7H_2O$	Step 1	0-350	5.42	5.20	$-2H_2O$
	Step 2	350-430	8.6	7.6	$-3H_2O$
	Step 3	430-780	25.07	24.97	$-Cl_2+2H_2O+CHO+NH_2$
	Step 4	780-935	6.16	5.86	-NO
	Residue				$ZnO+C_{18}H_{11}+N_2H_4+$ $3CO_2$

Phosphomolybdate assay (total antioxidant capacity) (TAC)

Phosphomolybdate assay were used in the present investigation to assess the Schiff base ligand and its complexes decreased papillitis. As stated in Table 5, the samples were evaluated for their capacity to scavenge radicals at concentrations of 50, 100, and 150 µg/mL. When the complexes' outcomes were compared to ascorbic acid, the TAC assay's dropping graph proved that when compared to the standard, all three of the complexes had similar effects against phosphomolybdenum cation. Compared to other complexes, the Ni-complex, in particular, showed the most potent antioxidant activity at all doses. However, it had less activity than the current standard [23].

Table 5. Total antioxidant of ligand and complexes.

	50 µg/mL		100 µg/mL		150 µg/mL	Sample
Conc.	Absorbance	Conc.	Absorbance	Conc.	Absorbance	
4.848	0.032	8.40825	0.056	14.9985	0.099	LH_2
8.21885	0.054	11.55185	0.076	17.30885	0.114	Ni-complex
5.26465	0.035	11.13525	0.074	14.6955	0.097	Cu-complex
6.969	0.046	9.127875	0.060	14.3925	0.095	Zn-complex
17.31	0.144	18.75	0.124	20.11	0.133	Vit. C

Evaluation of the ligand's and its complexes' bioactivity [24]

The *in vitro* antibacterial activity of the ligand was examined using both Gram-positive (*Bacilla* and *Pseudomonas*) and Gram-negative (*Staph.* and *E. coli*) bacteria. The evidence on antibacterial activity confirmed that the resultant Ligand and complexes were physiologically active, as shown in Table 6. The final results demonstrated that these substances favorably impacted the species under investigation. Zn complexes were more efficient against *E. coli* bacteria than against copper complexes, which had the maximum antifungal activity against *Candida*. Ni complexes were most active against *Staph* bacteria, and Zn(II) complexes were most active against *Bacillus* bacteria. The antibacterial capabilities of Cu(II) and Zn(II) corresponding complexes have increased activity against *pseudomonas*. Tetracycline is an antibiotic, but many complexes have further activity than it does, and ligands that promote complexation improve antibacterial and antifungal properties [25-26].

Table 6. Antibacterial and antifungal properties of synthetic ligands and their complexes.

Candida	*E. coli*	*Staph*	*Bacilla*	*Pseudomonas*	*Complexes*
13	16	16	9	14	Ni
19	12	9	9	16	Cu
15	17	15	12	16	Zn
10	13	13	10	11	Ligand
13	11	12	9	10	Tetracycline

CONCLUSIONS

The newly created Schiff bases ligand, as well as its complexes with Ni(II), Cu(II), and Zn(II), were created and examined using a range of distinct physical and analytical analyses. The gathered information demonstrated that the ligand acts as a N_2O_2 tetra-dentate ligand chelated through the two nitrogen atoms of azomethine groups and two oxygen atoms of phenolic groups forming thermally stable (1:1) (M:L) metallic complexes. Based on the final results of various methods, we propose an octahedral environment surrounding Cu(II), Zn(II) and tetrahedral around Ni(II) metal ion. The produced substances exhibited good inhibitory behavior towards a few selected (gram-positive, gram-negative, and Candida fungus) bacteria and fungi for the solution of 10^{-3} M. The antioxidant activity of the synthetic compounds was evaluated by the phosphomolybdenum assay using ascorbic acid as standard. Results show that all complexes and ligands have antioxidant activity, but the Ni- complex is the best.

Supplementary information

The carbon, hydrogen, and nitrogen amounts were taken using the Euro Vector EA 3000 A, and FT-IR spectra were obtained using a Shimadzu FT-IR-8100 spectrometer. Using TMS as an internal standard, the ligand (LH_2) ^{1}H and ^{13}C-NMR spectra were collected in d6 - DMSO solvent on a Bruker 300 MHz. The electronic spectra were recorded at 25 ^{o}C using a Shimadzu UV1650 PC spectrophotometer. The complexes' electrical conductivity was measured using a Philips PW-digital conductivity meter at 25 °C ± 2 °C for a 1×10^{-3}M solution in DMF. Magnetic susceptibility measurements were also obtained at 25 ^{o}C in the solid state using Gouy balance. The molecular weight of the synthesized Ligand was calculated using a GCMS-QP2010 PLUS; DI analysis Shimadzu, Japan spectrometer in the University of Samarra laboratory. Also, all melting point results were recorded on (the Gallen Kamp melting apparatus) at the College of Science for Women, University of Baghdad.

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