Synthesis and Spectroscopic Studies of Some Macrocyclic Complexes Derived from Salicylaldehyde

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Abstract

The macrocyclic type Tetradentate ligand contain the nitrogen and oxygen as donor atoms have been prepared via the template reaction in two steps with their complexes of some metal ions, the reaction of one equivalent 1,2-phenylendiamine and two equivalent of salicylaldehyde obtained the precursor which the used in the template reaction since the 1,2-dibromoethane and metal salts [Co(II), Cu(II)] were added together as 1:1 ratio to the solution of precursor to form the macrocyclic complexes. The prepared compounds were characterized by Elemental analyses, FT-IR, UV-Vis, and ^{1}H,^{13}C-NMR. The spectral and physical studies show the suggested geometry around the all metals is octahedral.

Keywords: salicylaldehyde, macrocyclic complexes, Copper (II), Cobalt (II) complexes.

1. Introduction

Chemistry of macrocycles and their metal complexes has attracted much attention and has become a growing class of research [1-9], largely as a result of their remarkable applications in biology, supramolecular chemistry and new materials [2-9], etc. To some extent the interest in macrocyclic complexes especially those with polydentate ligands stems from the chemical properties that the macrocyclic ligands bring to the complexes as well as the variety of geometrical forms available and the possible encapsulation of the metal ion [10,11], The macrocyclic ligands are highly significant in bioinorganic chemistry, catalysis, extraction of metal ions from solution and many more[12], Macrocyclic when complexes with transition metal ions show some interesting properties and biological functions, such as being models for metalloproteins and oxygen carrier systems[13], Structural factors such as ligand rigidity, the type of donor atoms and their disposition have been shown to play significant roles in determining the binding features of macrocyclic ligands toward metal ions [14,15], Macrocyclic ligands containing a heteroatom are important complexing agents for cations, anions and molecules [16–17]. Cyclic and macrocyclic complexes of transition metals are of interest because of their use as diagnostic agents in magnetic resonance imaging and their resemblance to natural systems [18–20]. The macrocyclic Schiff bases have been widely studied due to their selective chelation to certain metal ions depending on the number, type and position of their donor atoms, the ionic radius of metal ion and coordinating properties of counterions [21–23], Because of their resemblance, synthetic macrocyclic complexes mimic naturally occurring macrocycles including metalloproteinase, porphyrins, and cobalamine[24–26]. Thus, biologically active macrocyclic complexes are used in the identification of diseased and normal tissues[27]. Transition metal macrocyclic complexes have received much attention because of their biological activities, including antiviral, anticarcinogenic[28], antifertility[29], Antibacterial, and antifungal activities[30]. Subsequently, Binding studies of transition metal complexes have become very important in the development of DNA probes [31] and chemotherapeutics.

2. Experimental

2.1. Apparatus and chemicals

Salicylaldehyde, 1,2-dibromoethane were obtained from (sigma-Aldrich), 1,2-phenylendiamine 98% (by MERK), cobalt chloride 6-hydrate 97% (by SCP), cupper(II)-chloride 2-hydrate 97% (by BDH), potassium hydroxide 97,88% (by BDH), absolute ethanol (by CHEMLAB).

UV/Vis spectroscopy (model: Hitachi U-1900), optical absorption spectrum infrared device model FT-IR-4100 from the Japanese company Jusco, rotar evaporator 4.91 model from the German company Normschiff, thin layer chromatographic of aluminum coated by Silica Gel 60F254 measuring 20 X 20 from the German company Merck.

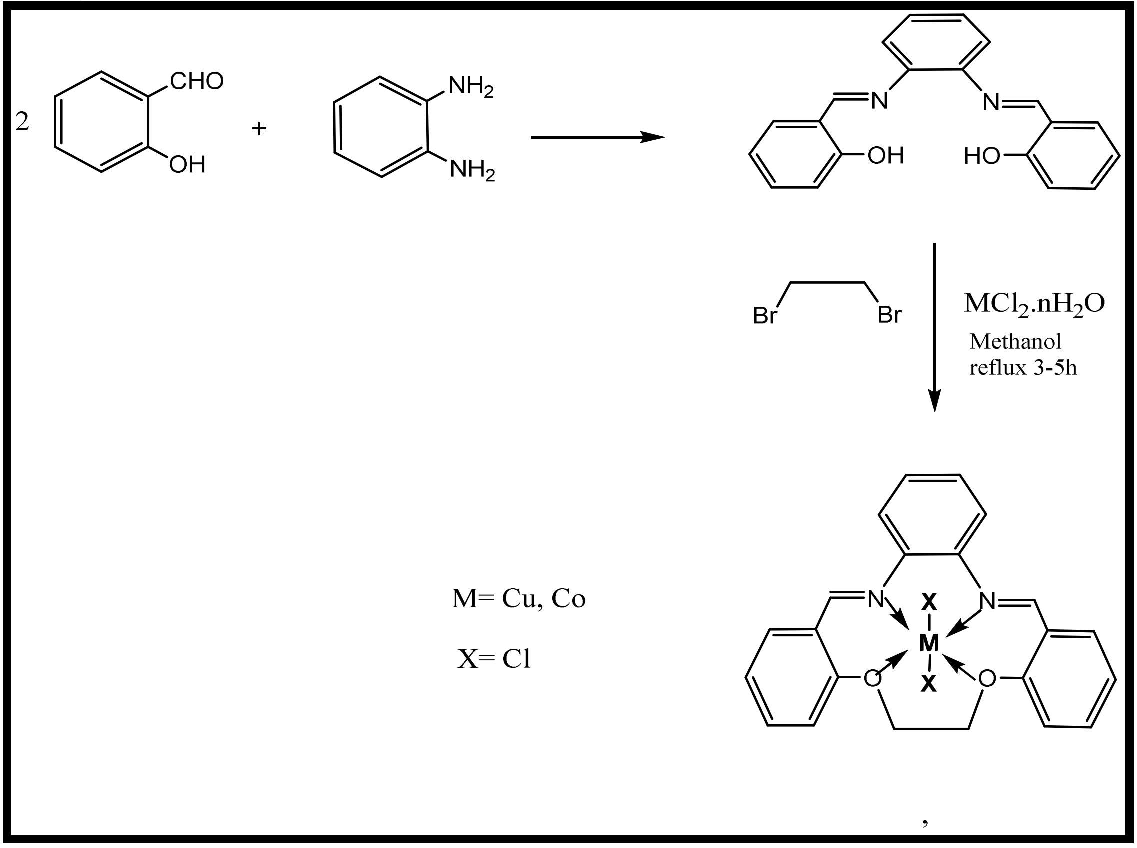
2.2. Experimental Procedure:

2.2.1. Preparation of precursor:

To 1,2-phenylendiamine (0.432g, 4 mmol) dissolved in absolute ethanol (8 mL) was added two equivalent of salicylaldehyde (0.977 g, 8 mmol) dissolved in absolute ethanol (12 mL). The mixture heated genteelly about 50°C for 0.5h, the color of solution became pale yellow stopped the heating and let the mixture to stirring only about 1.5 hours. The deep yellow precipitate was obtained, filtered washed with cold ethanol and ether, recrystallized from ethanol, dried gave orange crystals in color with a yield of (88 %). (**Scheme 1**)

2.2.2. Synthesis of metal complexes:

Isolation of the metal complexes. Any attempt to isolate the free macrocyclic ligand was unsuccessful so that all the complexes were obtained by template synthesis. To solution of precursor (0.316g, 1 mmol) dissolved in (5 mL) hot methanol added alcoholic KOH solution (0.086 g in 5 mL methanol), then a (0.186 g , 1 mmol) of 1,2-dibromoethane was added slowly to the solution, to the resulted mixture a solution of $CuCl_2.2H_2O$ (0.165 g, 1 mmol) were added as drop wise. The mixture reflux for 3-5h. The clear solution change to green in color. Cooled to room temperature the solvent removed with vacuum, the result precipitate collected, washed several times with cold ethanol and dry with ether and dried, Yield = 62%. The cobalt complex was carried out in the similar method which that showed in the preparation of Cupper complex accept the metal cobalt salt instead with Cupper ion salt. (**Scheme 1**)



(Scheme 1)

3. Results and Discussion:

3.1. Elemental analysis and characterization for precursor and their complexes:

The precursor was prepared by the condensation of salicylaldehyde and 1,2-phenylendiamine in their 2:1 molar ratio. All the complexes were obtained by template reaction deprotonation the OH protons, added the 1,2-dibromoethane, and the metal salts in their 1:1 molar ratio. The results of elemental analyses, colors, yields and the melting points are presented in **Table 1**.

Table 1. Elemental analysis, molecular weight and melting point of the precursor and their metal complexes.

Compounds	Mol. Weight	Color	Yield (%)	M.P (°C)	Elemental Analysis % Found (%Calc.)				
					C	N	O	Cl	M
precursor	316.36	orange	88	151-152	75.93 (76.6)	8.86 (8.90)	10.11 (9.56)	—	—
[Co L]	—	brown	55	305	55.80 (55.93)	5.88 (5.93)	6.69 (6.78)	14.95 (15.04)	12.44 (12.49)
[Cu L]	—	green	62	290	55.27 (55.40)	5.77 (5.87)	6.61 (6.71)	14.80 (14.89)	13.18 (13.33)

3.2. Infrared Spectra:

The infrared spectra for the present compounds taken in the range 400-4000 cm^{-1} help to indicate regions of absorption vibrations. The main stretching modes are for ν(C=N), ν(C=C) and ν(C-O). The IR data of the spectra of the precursor and their complexes are presented in **Table 2**.

The IR spectrum of the precursor **Fig.1** displays a broad band at (3438 cm^{-1}) due to the Ѵ(O-H) stretching with hydrogen bonding between two hydroxyl groups, the Ѵ(C-H) stretching of rings and aliphatic appeared at (3053 cm^{-1}). The characteristic band at (1614 cm^{-1}) assigned to Ѵ(C=N) stretching indicating the disappear the aldehyde carbonyl which that appear at (1720 cm^{-1}) [32].

The IR spectra of the complexes Co^{+2}, Cu^{+2} **Fig.2, Fig.3** respectively, The absence of Ѵ(OH), Ѵ(NH_2), Ѵ(C=O) bands and the appearance of a new weak absorption band in the 1590-1630 cm^{-1} region assignable to the Ѵ(C=N) comparable with reported for coordinated -C=N, provide evidence for the skeleton of the macrocyclic moiety, which was further supported by the negatively shifted band in the 1080-1090 cm^{-1} in all complexes corresponding to Ѵ(C-O-C) stretching vibrations, also indicate coordination through oxygen atoms[33].This was confirmed by the appearance of a strong intensity band in the 400-450 cm^{-1} region and the broad band in the 480-530 cm^{-1} in all complexes assignable to Ѵ(M-N) and Ѵ(M-O) stretching vibrations, respectively, consistent with those reported for complexes derived from nitrogen and oxygen ligands, whereas the bands occurring in 1470-1430, 1110-1090 and 780-750 cm^{-1} regions are assigned to benzene ring vibration.

Table 2. Characteristic infrared absorption frequencies (cm^{-1}) of the precursor and their complexes.

Compounds	**ν(OH) cm^{-1}**	**ν(C=N) cm^{-1}**	**ν(C-O-C) cm^{-1}**
precursor	3438	1614	———
[Co L]Cl_2	———	1606	1085
[Cu L]Cl_2	———	1602	1090

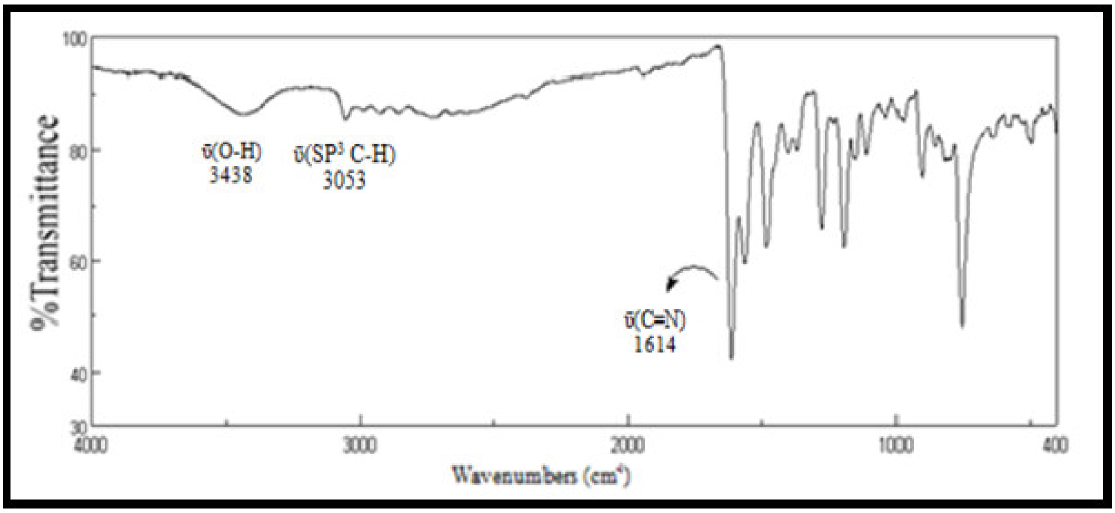


Fig 1. FT-IR spectrum of precursor

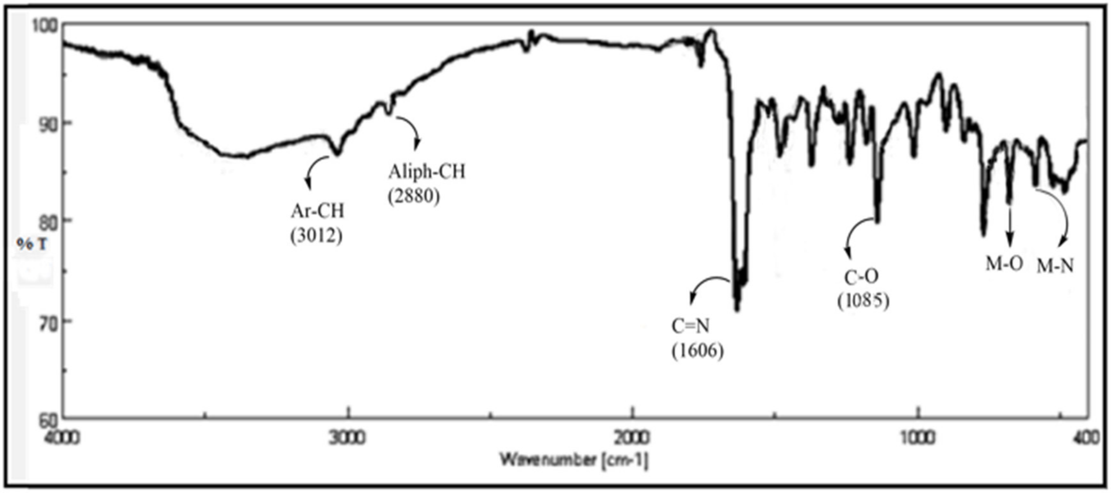


Fig 2. FT-IR spectrum of [Co L]Cl_2

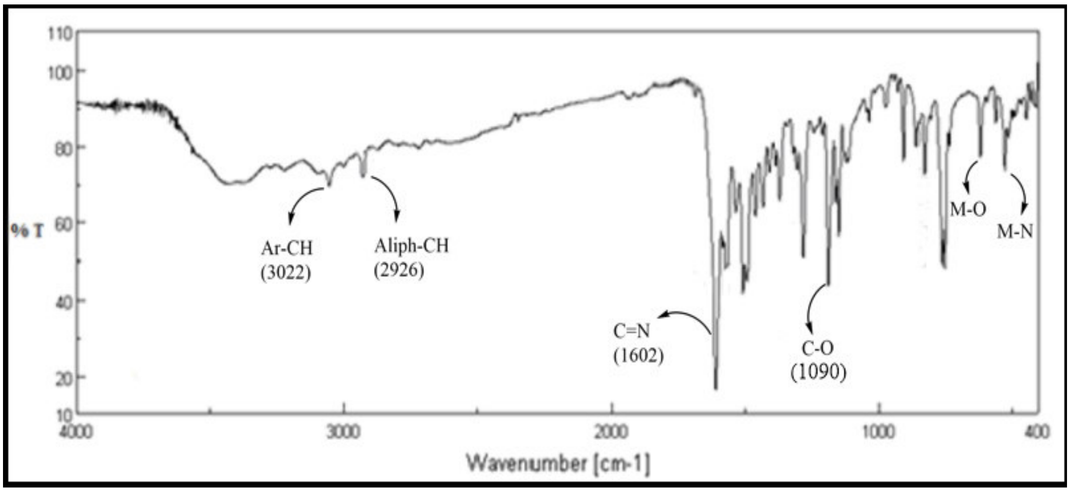


Fig 3. FT-IR spectrum of [Cu L]Cl_2

3.3. Electronic spectral data:

The data of the electronic spectra of the precursor and its complexes are given in **Table 3.** The spectrum of the precursor **Fig 4,** presented three bands in the UV interval at 275nm, 335nm and 340nm, assigned to (π→π*) and (n→π*) transitions.

The UV-Vis spectra of complexes **Figs. 5,6** for Co^{+2}, Cu^{+2} appears the absorption peaks for Co^{+2} complex showed the peaks at (524 nm) due to d-d transition type $^4T_2g(F)\rightarrow{}^4E_2g(F)$ and (510nm) due to d-d transition type $^4T_2g(F)\rightarrow{}^4E_2g(F)$ which that proper with octahedral geometry [34]. While the Cu^{+2} complex displays the twin head peak at (495 nm) due to d-d transition type $^2B_1g\rightarrow{}^2Eg$ and (590 nm) due to d-d transition type $^2B_1g\rightarrow{}^2B_2g$ corresponding with octahedral geometry [34], **Table 3.**

Table 3. Electronic spectral data and geometries of precursor and complexes.

Compounds	Electronic Spectra (nm)	Assignments	Geometry
precursor	270, 320, 340	π→π*, n→π*	——
[Co **L**]Cl_2	425 510	$^4T_2g(F)\rightarrow{}^4E_2g(F)$ $^4T_2g(F)\rightarrow{}^4E_2g(F)$	**octahedral**
[Cu **L**]Cl_2	495 590	$^2B_1g\rightarrow{}^2Eg$ $^2B_1g\rightarrow{}^2B_2g$	**octahedral**

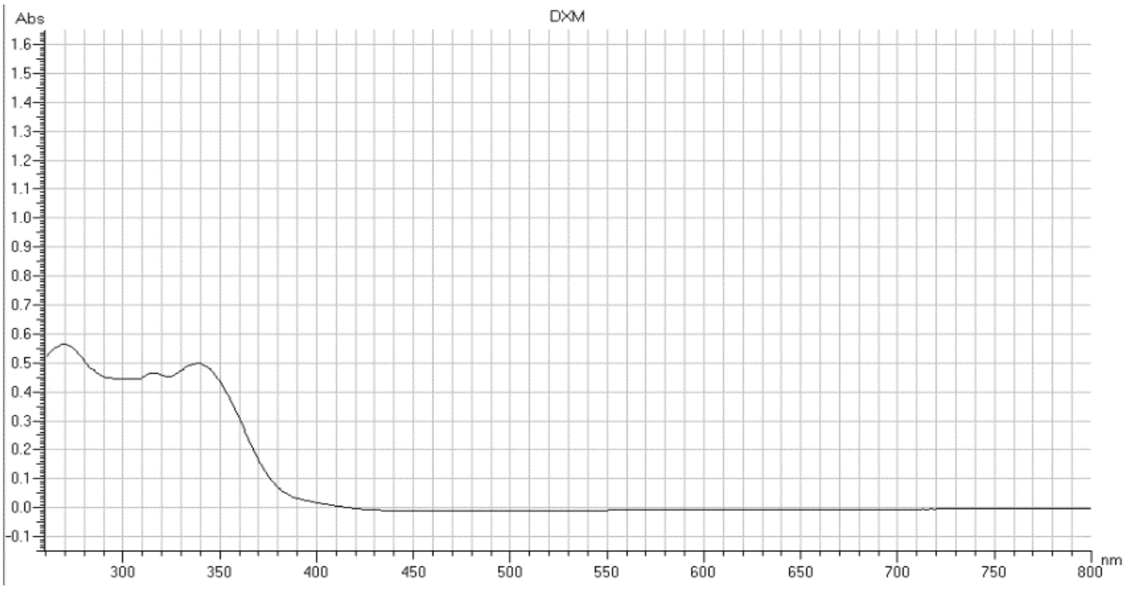


Fig 4. UV- vis spectrum of the precursor

The spectrum of precursor presented three bands in the UV interval at (270nm), (320nm) and (340nm), assigned to (π→π*, n→π*) transition.

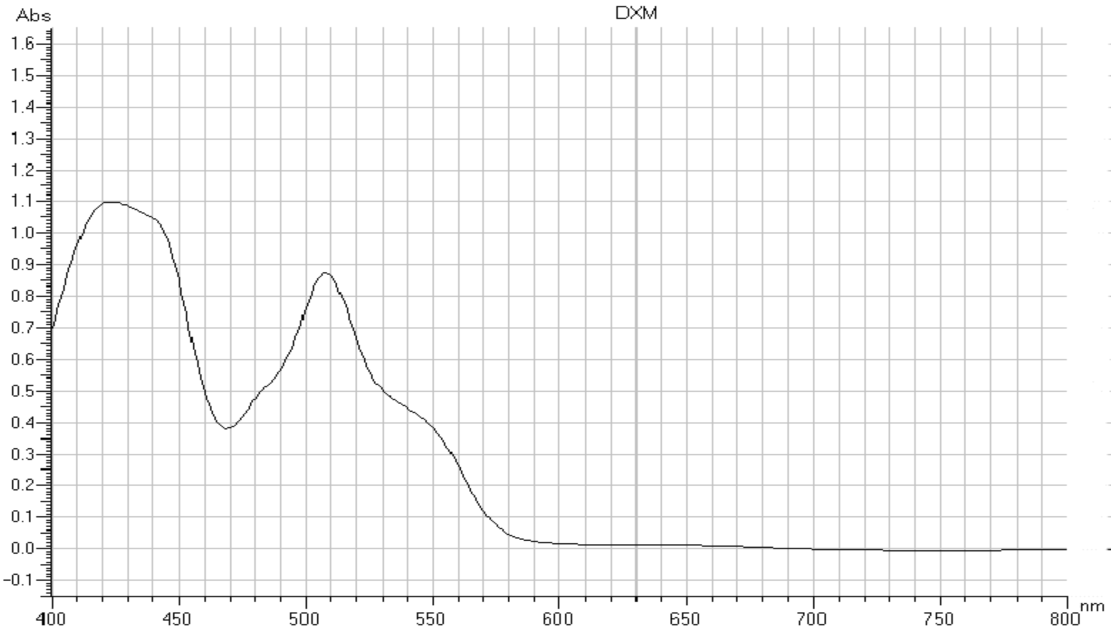


Fig 5. UV-vis spectrum of Co^{2+}

The electronic spectra of the [Co L]Cl_2 in DMF solution has two bands at (425nm), (510nm), these bands may be assigned to the transitions (d-d), The position of these bands suggests an octahedral environment [34] (**Fig 7**).

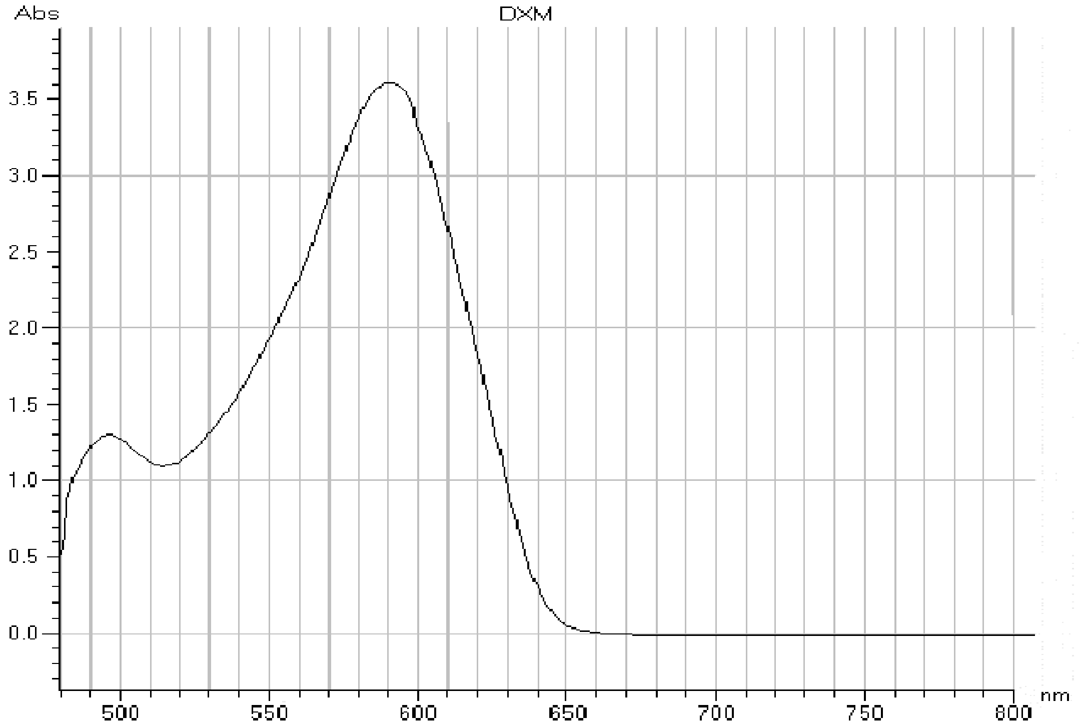


Fig 6. UV-vis spectrum of Cu^{2+}

The electronic spectra of the [Cu L]Cl_2 in DMF solution has two bands at (495nm) and (590nm), These bands may be assigned to the transitions (d-d), The position of these bands suggests an octahedral environment [34] (**Fig 7**).

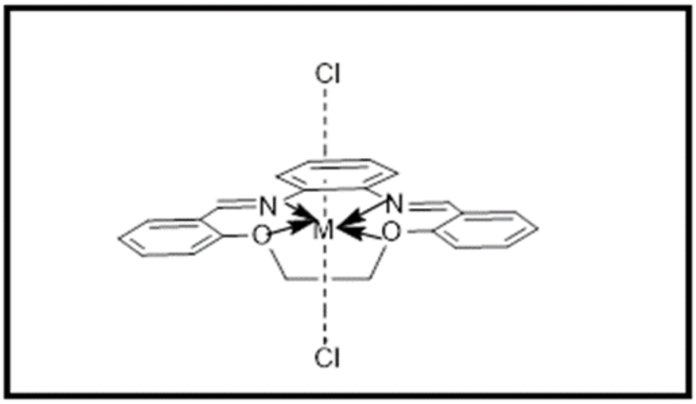


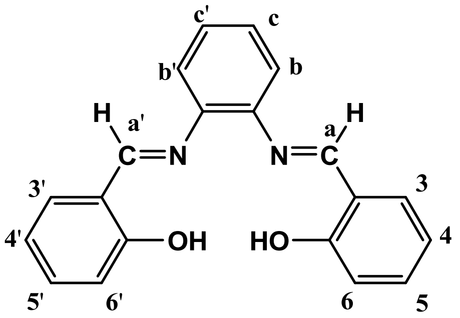
Fig 7. Suggested structure for all the complexes

3.4. ^{13}C and ^{1}HNMR spectroscopic measurements:

The (^{13}C and ^{1}HNMR) spectroscopic measurements of the precursor given in **Table 12**. Displays the data. The (^{1}H-NMR) spectra of the precursor showed the chemical shift at (δ= 8,91 ppm, 2H) assigned to imines proton (H-C=N), the signals at (**δ**=7.77-7.65 ppm, 4H , **δ**=7.57-7.49 ppm, 6H , **δ**=7.32-7.18 ppm, 2H) attributed to aromatic three rings in different environments, the signal at (δ= 5.71 ppm, 2H) assigned to (H-O) protons attached directed to aromatic ring.

The (^{13}CNMR) spectra of the precursor exhibits signals at (**δ**=164.94 ppm), these signal assigned to carbon azomethine group.

Table 5. The (^{13}C and ^{1}HNMR) spectroscopic measurements of the precursor.

Compound formula $C_{20}H_{16}N_2O_2$ [316.36 g/mol] mp: 151-152 ºC		
^{1}H-NMR (δ,ppm)	8.91 (s, 2H, HC=N) 7.77-7.65 (m, 4H, b, b`, $H_3$, $H_{3`}$) 7.57-7.49 (m, 6H, c, c`, $H_4$, $H_{4`}$, H_6, $H_{6`}$ ) 7.32-7.18 (m, 2H, $H_5$, $H_{5`}$) 5.71 (s, 2H, OH)	

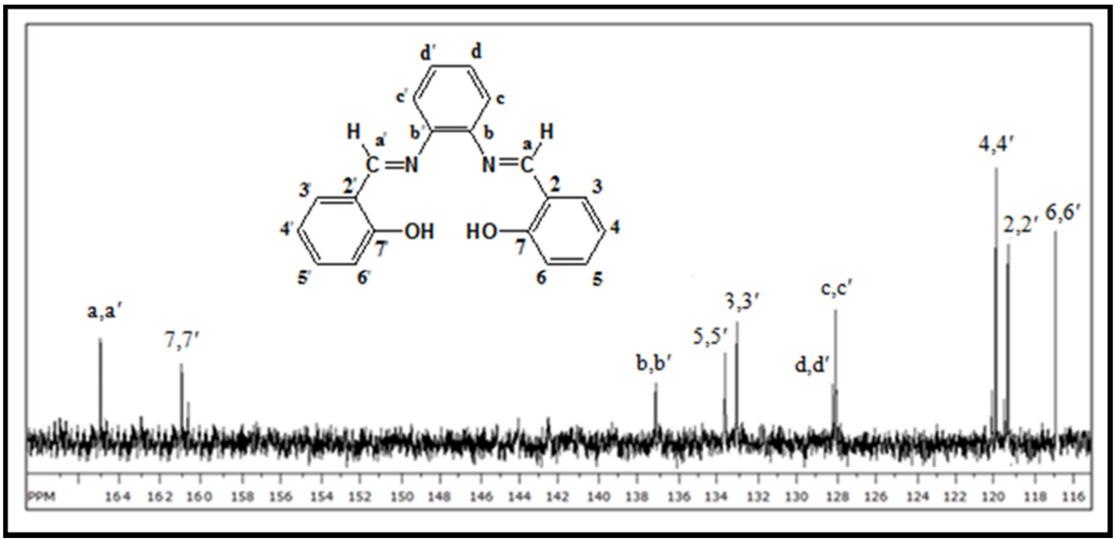


Fig 8. ^{13}CNMR spectrum of the precursor

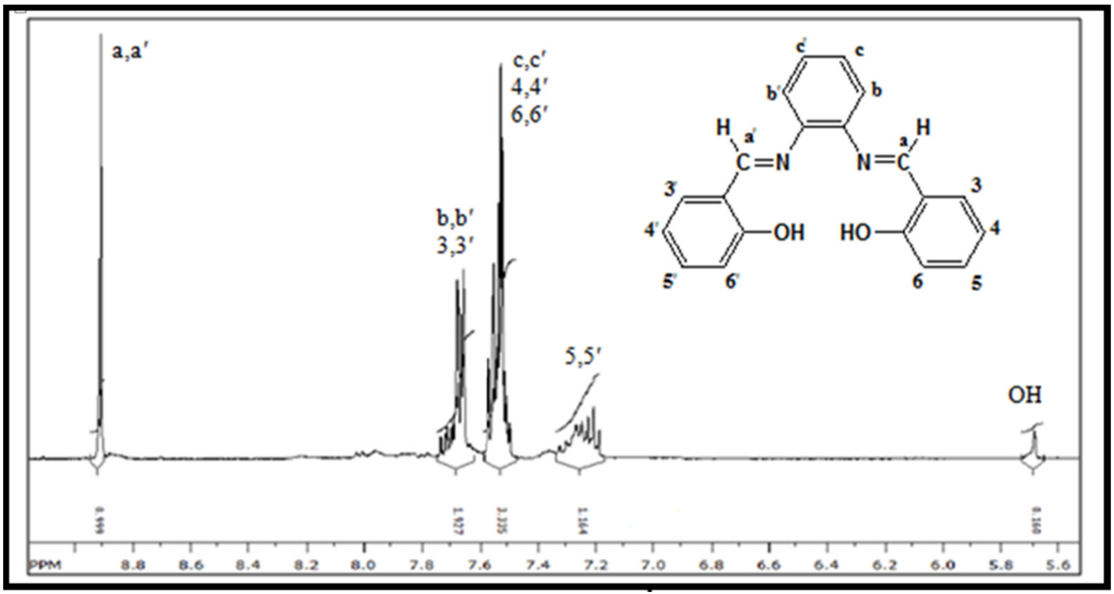


Fig 9. ^{1}HNMR spectrum of the precursor

Conclusions

In this paper, we reported the preparation, isolation and characterization of new macrocyclic complexes through the reaction of one equivalent of phenylenediamine with two equivalent of salicylaldehyde was obtained the precursor which that undergoes the template reaction with dibromoethane and the divalent metal ion (Cobalt and Copper). It is tentatively proposed that the precursor coordinates through the nitrogen of the azomethine group and the Oxygen of the benzene ring, forming a stable chelate ring structure.

In the light of the above discussion, octahedral structures for all the complexes, compounds are proposed (**Figure** 7).

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