

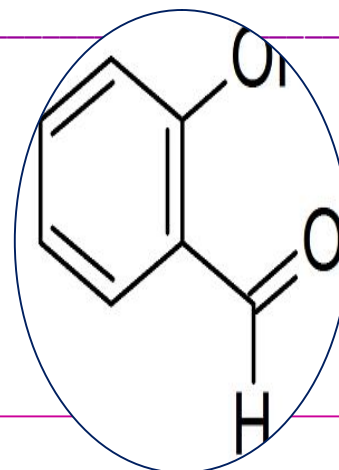


STUDIES OF SOME MACROCYCLIC COMPLEXES DERIVED FROM SALICYLALDEHYDE

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ABSTRACT

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.

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-phenylenediamine 98% (by MERK), cobalt chloride 6-hydrate 97% (by SCP), copper(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 FTIR- 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.

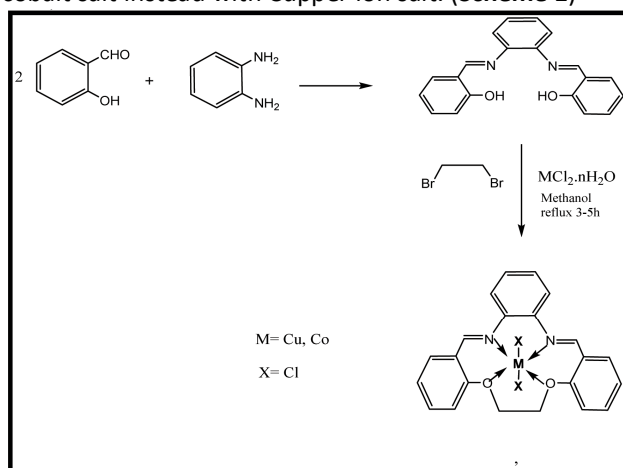
2.2. Experimental Procedure:

2.2.1. Preparation of precursor:

To 1,2-phenylenediamine (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 gently 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 $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (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 Copper complex accept the metal cobalt salt instead with Copper 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-phenyldiamine 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 $\nu(\text{C}=\text{N})$, $\nu(\text{C}=\text{C})$ and $\nu(\text{C}-\text{O})$. 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 $\nu(\text{O}-\text{H})$ stretching with hydrogen bonding between two hydroxyl groups, the $\nu(\text{C}-\text{H})$ stretching of rings and aliphatic appeared at (3053 cm^{-1}). The characteristic band at (1614 cm^{-1}) assigned to $\nu(\text{C}=\text{N})$ 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 $\nu(\text{OH})$, $\nu(\text{NH}_2)$, $\nu(\text{C}=\text{O})$ bands and the appearance of a new weak absorption band in the $1590\text{-}1630 \text{ cm}^{-1}$ region assignable to the $\nu(\text{C}=\text{N})$ comparable with reported for coordinated $-\text{C}=\text{N}$, provide evidence for the skeleton of the macrocyclic moiety, which was further supported by the negatively shifted band in the $1080\text{-}1090 \text{ cm}^{-1}$ in all complexes corresponding to $\nu(\text{C}-\text{O}-\text{C})$ stretching vibrations, also indicate coordination through oxygen atoms [33]. This was confirmed by the appearance of a strong intensity band in the $400\text{-}450 \text{ cm}^{-1}$ region and the broad band in the $480\text{-}530 \text{ cm}^{-1}$ in all complexes assignable to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ stretching vibrations, respectively, consistent with those reported for complexes derived from nitrogen and oxygen ligands, whereas the bands occurring in $1470\text{-}1430$, $1110\text{-}1090$ and $780\text{-}750 \text{ cm}^{-1}$ regions are assigned to benzene ring vibration.

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

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

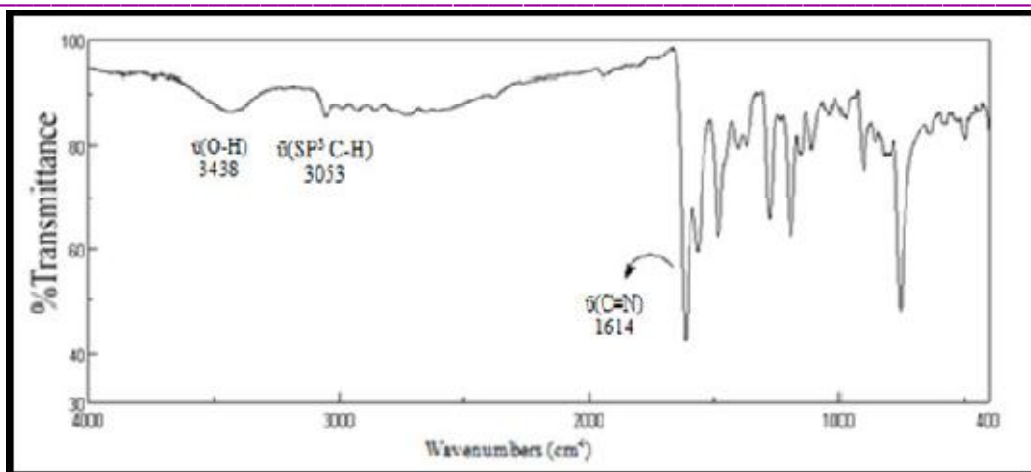


Fig 1. FT-IR spectrum of precursor

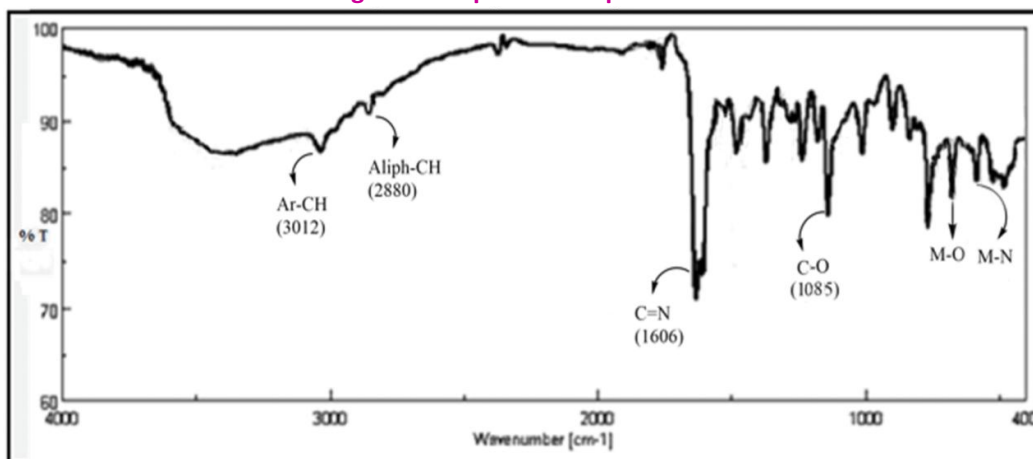


Fig 2. FT-IR spectrum of [Co L]Cl₂

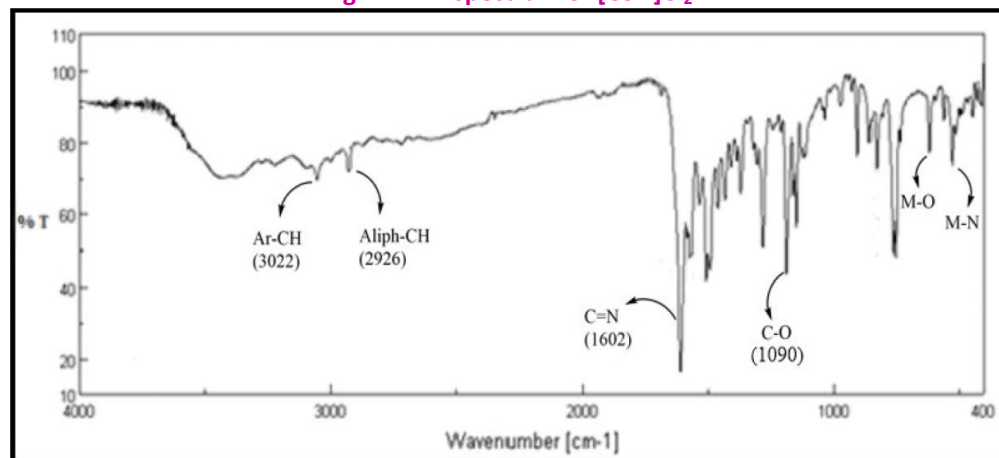


Fig 3. FT-IR spectrum of [Cu L]Cl₂

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 ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) 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 ${}^4\text{T}_{2g}(\text{F}) \rightarrow {}^4\text{E}_{2g}(\text{F})$ and (510nm) due to d-d transition type ${}^4\text{T}_{2g}(\text{F}) \rightarrow {}^4\text{E}_{2g}(\text{F})$ 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 ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ and (590 nm) due to d-d transition type ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ 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 | $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ | — |
| [Co L]Cl ₂ | 425 | ${}^4\text{T}_{2g}(\text{F}) \rightarrow {}^4\text{E}_{2g}(\text{F})$ | octahedral |
| | 510 | ${}^4\text{T}_{2g}(\text{F}) \rightarrow {}^4\text{E}_{2g}(\text{F})$ | |
| [Cu L]Cl ₂ | 495 | ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ | octahedral |
| | 590 | ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ | |

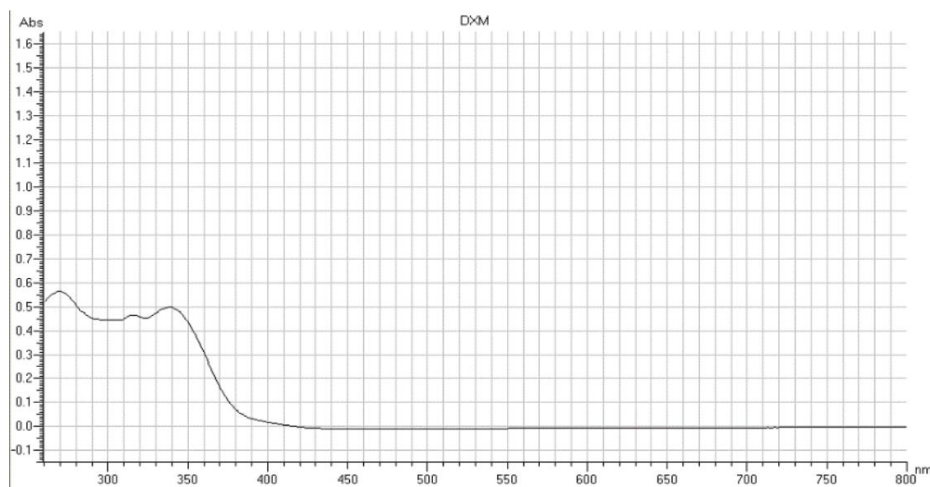


Fig 4. UV- vis spectrum of the precursor

The spectrum of precursor presented three bands in the UV interval at (270nm), (320nm) and (340nm), assigned to $(\pi \rightarrow \pi^*, n \rightarrow \pi^*)$ transition.

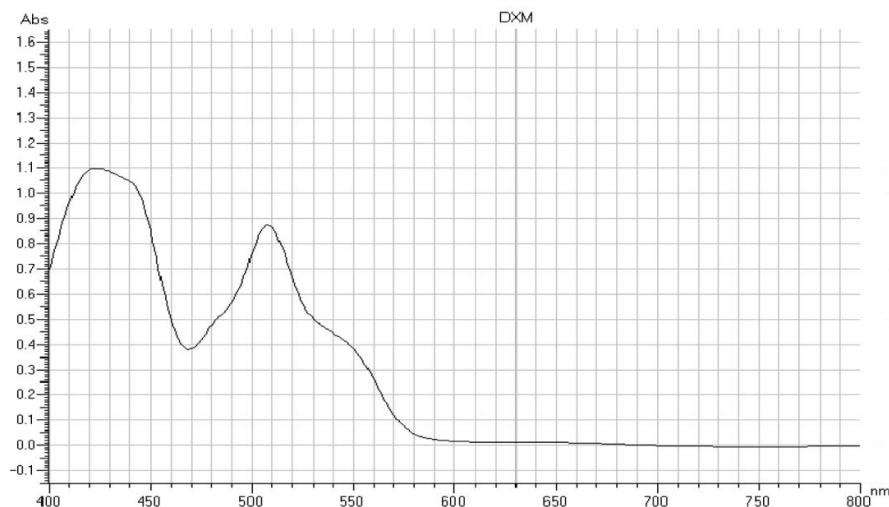


Fig 5. UV-vis spectrum of Co^{2+}

The electronic spectra of the $[\text{Co L}]\text{Cl}_2$ 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**).

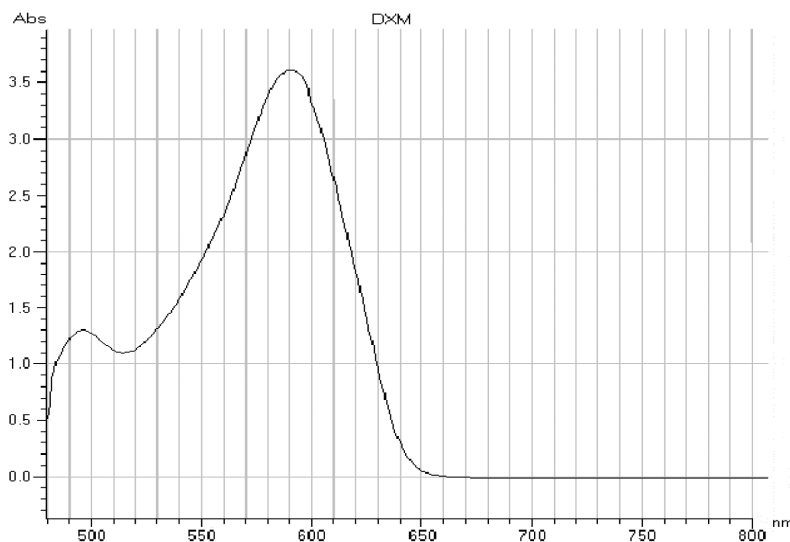


Fig 6. UV-vis spectrum of Cu_2^+

The electronic spectra of the $[\text{Cu L}]\text{Cl}_2$ 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**).

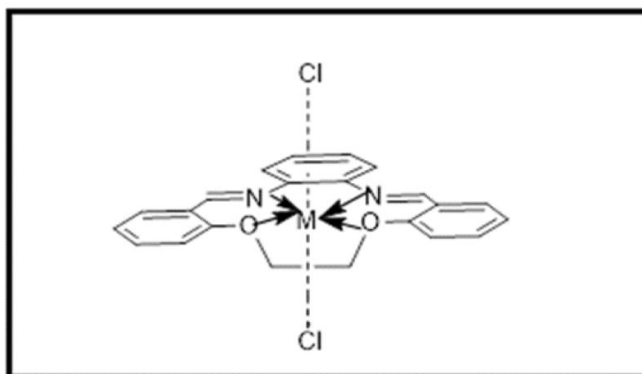


Fig 7. Suggested structure for all the complexes

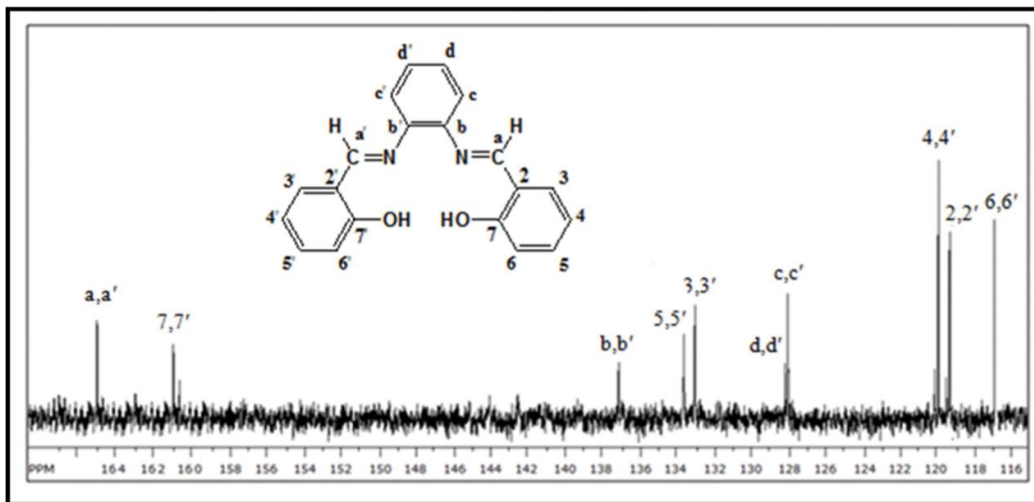
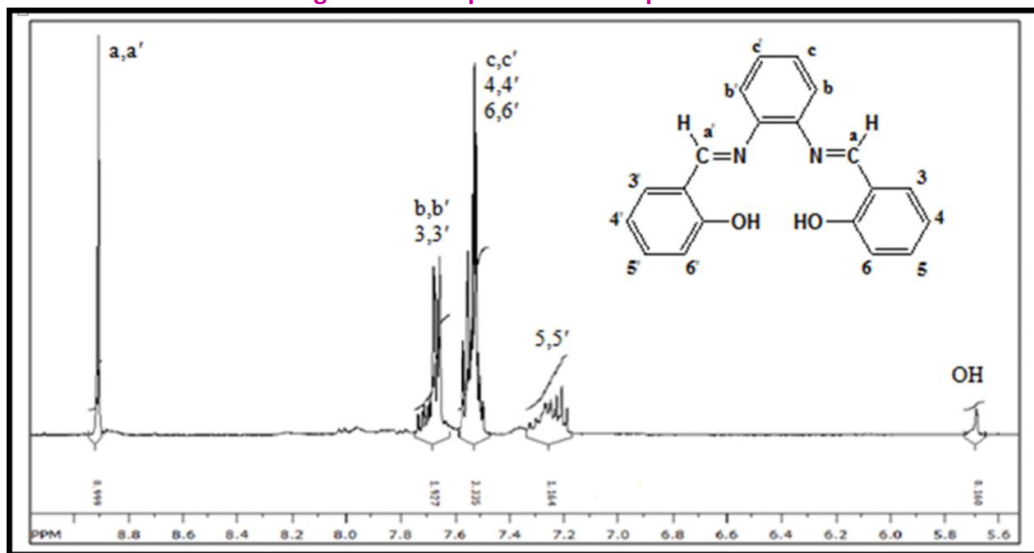
3.4. ^{13}C and ^1H NMR spectroscopic measurements:

The (^{13}C and ^1H NMR) spectroscopic measurements of the precursor given in **Table 12**. Displays the data. The (^1H -NMR) spectra of the precursor showed the chemical shift at ($\delta = 8.91$ ppm, 2H) assigned to imines proton ($\text{HC}=\text{N}$), the signals at ($\delta = 7.77\text{--}7.65$ ppm, 4H, $\delta = 7.57\text{--}7.49$ ppm, 6H, $\delta = 7.32\text{--}7.18$ ppm, 2H) attributed to aromatic three rings in different environments, the signal at ($\delta = 5.71$ ppm, 2H) assigned to (H-O) protons attached directed to aromatic ring.

The (^{13}C NMR) spectra of the precursor exhibits signals at ($\delta = 164.94$ ppm), these signal assigned to carbon azomethine group.

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

| Compound formula $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_2$ [316.36 g/mol] mp: 151-152 $^\circ\text{C}$ | | |
|---|---|--|
| ^1H -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}C NMR spectrum of the precursor****Fig 9. ^1H NMR spectrum of the precursor**

CONCLUSIONS

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- phenyldiamine 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.

REFERENCES

- [1] D.Singh, V. Malik, K. Kumar, C. Sharma, K. Aneja, *Spectrochim. Acta A*, V.76, (2010), P.45-49.
- [2] L.Gupta, S. Chandra, Spectroscopic characterization and EPR spectral studies on transition metal complexes with a novel tetradentate, 12-membered macrocyclic ligand, *Spectrochim Acta*, V.65, (2006), P.792-796.
- [3] S.Rani, S.Kumar, Spectroscopic and biological approach in the characterization of a novel 14-membered [N4] macrocyclic ligand and its Palladium(II), Platinum(II), Ruthenium(III) and Iridium(III) complexes, *Spectrochim Acta*, V.118, (2014), P.244–250.
- [4] S.Chandra, L.Gupta, Spectroscopic approach in characterization of chromium(III), manganese(II), iron(III) and copper(II) complexes with a nitrogen donor tetradentate, 14-membered azamacrocyclic ligand, *Spectrochim. Acta A* V.61, (2005), P.2139-2144.
- [5] S.Chandra, S.Verma, Spectroscopic studies of transition metal complexes with a N-donor tetradentate(N4) 12- membered macrocyclic ligand, *Spectrochim. Acta*, V.71, (2008), P.458-464.
- [6] J.Timmos, T.Hubin, Coord Preparations and applications of synthetic linked azamacrocyclic ligands and complexes, *Chem. Rev.* V.254, (2010), P.1661-1685.
- [7] L. Mandal, S. Sasmal, Crystal structure, catecholase activity and ESI-MS of a mixed valence cobalt(III)–cobalt(II) complex derived from a macrocyclic ligand: Identification/proposition of hydrogen bonded metal complex solvent aggregates in ESI-MS, *Inorg Chim Acta*, V.412, (2014), P.38–45.
- [8] D. Kong,Y. Xie, Synthesis, structural characterization of tetraazamacrocyclic ligand, five-coordinated zinc(II) complex, *Inorg Chim Acta*, V.338, (2002), P.142-148.
- [9] N. Raman, R. Rajakumar, Bis-amide transition metal complexes: Isomerism and DNA interaction Study, *Spectrochim. Acta A*, V.120, (2014) 428–436.
- [10] G.Ferraudi, J.Canales, Synthetic N-substituted metal aza-macrocyclic complexes: Properties and applications, *J.Coord Chem*, V.58, (2005), P.89–109.
- [11] A.Chaudhary, N.Bansal, A ntifertility, antibacterial, antifungal and percent disease incidence aspects of macrocyclic complexes of manganese(II), *J. Inorg Biochem*, V.96, (2003), P.393-400.
- [12] Salih I, Hamdi T, Ismail, Synthesis and characterization of new macrocyclic Schiff base derived from 2,6- diaminopyridine and 1,7-bis(2-formylphenyl)-1,4,7-trioxaheptane and its Cu(II), Ni(II), Pb(II), Co(III) and La(III) complexes, *Polyhedron*, V.29, (2007), P.2795
- [13] R. Kumar and R.Singh, Chromium(III) Complexes with Di_erent Chromospheres Macrocyclic Ligands: Synthesis and Spectroscopic Studies, *Turk J. Chem*, V.30 (2006), P.77.
- [14] M.Liu, W.Yuan, Synthesis, characterization and DNA interaction studies of complexes of lanthanide nitrates with tris{2-[(3,4-dihydroxybenzylidene) imino] ethyl}amine, *Spectrochim Acta*, V.70, (2008), P.1114
- [15] S.Chandra, M.Tyagi, Lanthanide complexes derived from hexadentate macrocyclic ligand: Synthesis, spectroscopic and thermal investigation, *Spectrochim. Acta*, V.75, (2010), P.835.
- [16] B.Ghanbari, M.Zarepour, Structural relevance of N2O2-donor naphthodiaza-crown macrocyclic ligands to selective fluorescence signaling behavior towards aliphatic tertiary amines, *Journal of Photochemistry and Photobiology A: Chemistry* V.314, (2016), P.42–51.
- [17] A.Khandar, S.Hosseini-Yazdi, Synthesis, characterization and structure of nickel(II) complexes of a 16-membered mixed-donor macrocyclic Schiff base ligand, potentially hexadentate, bearing two pendant alcohol functions, *Polyhedron*, (2007) P.26-33.

-
- [18] K. Kumar, M.F. Twiddle. Synthesis, characterization and antimicrobial activity of a new macrocycle and its transition metal complexes, *Chem.*, 65, 512 (2008).
- [19] F.Fry, B.Graham, L.Spicca, Tetra- and hexadentate Schiff base ligands and their Ni(II), Cu(II) and Zn(II) complexes. Synthesis, spectral, magnetic and thermal studies, *J. Chem. Soc. Dalton Trans.*, 827 (2012).
- [20] S.Ilhan, H.Baykara, Synthesis and characterization of 1,2-bis(2-(5-bromo-2-hydroxybenzylidenamino)-4-chlorophenoxy)ethane and its metal complexes: An experimental, theoretical, electrochemical, antioxidant and antibacterial study, *Spectrochimica Acta*, 118 (2014) 632–642
- [21] Vallarino, L.M.J.; In: *Handbook on the Physics and Chemistry of Rare Earths*, Gschneidner Jr., K.A.; Eyring, L. (Eds.). Elsevier, Amsterdam, 1991, pp. 191–285.
- [22] Hernandez-Molina, R.; Mederos, A. In: *Comprehensive Coordination Chemistry II*, McCleverty, J.A.; Meyer, T.J. (Eds.). Elsevier, Amsterdam, 2004, pp. 12–28.
- [23] Gerbeleu, N.V.; Arion, V.B.; Burges, J. *Template Synthesis of Macrocyclic Compounds*, Wiley-VCH, Weinheim, 1999.
- [24] T.Khan, S.Hasan, Template synthesis and spectroscopic studies of 13-membered oxotetraaza macrocyclic complexes. *Indian J Chem* 1998, 37A:1123–5.
- [25] Kumar DS, Alexander V. Synthesis of lanthanide(III) complexes of chloro and bromo substituted 18-membered tetraaza macrocycles. *Polyhedron* 1999;18:1561–8.
- [26] S.Ilhan, H.Temel, Synthesis and spectral characterization of macrocyclic Schiff base by reaction of 2,6-diaminopyridine and 1,4-bis(2- arboxyaldehydophenoxy) butane and its Cu(II), Ni(II), Pb(II), Co(III), La(III) complexes. *Transit Met Chem*, V.32, (2007), P.584–590.
- [27] M.Shakir, S.Khatoun, Synthesis and spectral studies of a 12-membered tetraimine macrocyclic ligand and its complexes. *Transit Met Chem*, V.32, (2007), P.4–6.
- [28] S.Chandra, S.Sharma, Synthesis and spectral studies of transition metal complexes with dibenzo-[b,i]-8,10,19,21 -tetramethyl-[1,5,8,12] –tetraazatetradeca -1,3,5,7,10,12, 14,16,18,21-decane a fourteen membered tetradentate macrocyclic ligand. *J Indian Chem Soc*, V.83, (2006), P.988–992.
- [29] S.Chandra, M.Pundir, Spectroscopic characterization of chromium (III), manganese(II) and nickel(II) complexes with a nitrogen donor tetradentate, 12-membered azamacrocyclic ligand. *Spectrochim Acta A*, V.69, (2008), P.1–7.
- [30] R.Prasad, A.Upadhyay, Chromium(III), iron(III) and cobalt(II) complexes of 14 and 16-membered tetraazamacrocycles. *J Indian Chem Soc*, V.83, (2006), P.857–60.
- [31] J. Liu, T. Lu, Synthesis, DNA-binding and cleavage studies of macrocyclic copper(II) complexes, *Transition Met. Chem*, V.28, (2003), P.116-121.
- [32] E.Pretsch, P.Buhlmann, *Structure Determination of Organic Compounds*, Springer-Verlag Berlin Heidelberg, (2009).
- [33] W.Sun, P.Yan, J.Zhang, N,N'-bis(salicylidene)propane-1,2-diamine lanthanide(III) coordination polymers: Synthesis, crystal structure and luminescence properties, *J.Solid State Chem*, V.182, (2009), P.381-388.
- [34] A.KALAM, V.TRIPATHI, Template synthesis and characterization of 16-membered octaazamacrocyclic complexes: a photoelectron spectroscopic study, *Turk J Chem*, V.34, (2010), P.147–155.
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