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Synthesis and characterization of ligand diimines and their complexes of copper (II) and zinc(II)

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Abstract:- In recent years, the importance of metal complexes bases ligands polyamines increased in various directions due to their biological activities and their applications in organic synthesis, catalysis, medicine and materials. In this article we will examine the synthesis of bidentate ligands derived from Schiff bases (diimine) N,N'-Bis(benzylidène)benzene-1,2-diamine L1 and N,N'-Bis(4-dimethyaminobenzylidene) propane-1,2-diamine L2 from precursors ortho-phenylendiamine and 1,2-diaminopropane successively, and on the other hand their corresponding copper and zinc metal complex $(L_1)_2MCl_2$ (M = Zn: **C1**, M = Cu: **C2**) and $(L_2)_2MCl_2$ (M = Zn: **C3** M=Cu: **C4**). The compounds thus obtained were characterized by IR spectroscopy, ^{1}H-NMR; ^{13}C-NMR and mass spectrometry.

Keywords: Schiff bases, zinc complex, copper complex, IR, ^{1}H-NMR; ^{13}C-NMR, mass spectrometry.

I. INTRODUCTION

The chemistry of transition metal complexes has been the subject of many studies during these recent years [1, 2]. Schiff base ligands have played an important role in our understanding of the coordination chemistry of transition metal ions, his complexes have a broad range of applications including, biological systems [3, 4] (enzyme inhibition, anti-microbial action), therapy (Antimicrobial activity [5], anti-tumor cytotoxic and [6]), catalytic activity, and the Schiff base complexes can be as a contrast agent for MRI [7].

Some Schiff bases have the activity of the simple harmonic generation. The Schiff's base chelates amido form with the Cu (II) and Fe (II) acts as an inhibitor of thrombin [8].

II. RESULTS AND DISCUSSION

II.1 Synthesis of N,N'-Bis(benzylidène)benzene-1,2-diamine L1 and N,N'-Bis(4-dimethyaminobenzylidene) propane-1,2-diamine L2.

Diimine ligands N,N'-Bis(benzylidène)benzene-1,2-diamine L1 and N,N'-Bis(4-dimethyaminobenzylidene) propane-1,2-diamine L2 propane were prepared by the condensation at reflux in ethanol with two equivalents of benzaldehyde or 4-dimethylaminobenzaldehyde on an equivalent ortho-phenylendiamine or 1,2-diamiopropane successively (Fig. 1).

The prepared ligands were characterized by IR spectroscopy, NMR (^{1}H; ^{13}C); and mass spectrometry.

Table captions appear centered above the table in upper and lower case letters. When referring to a table in the text, no abbreviation is used and "Table" is capitalized.

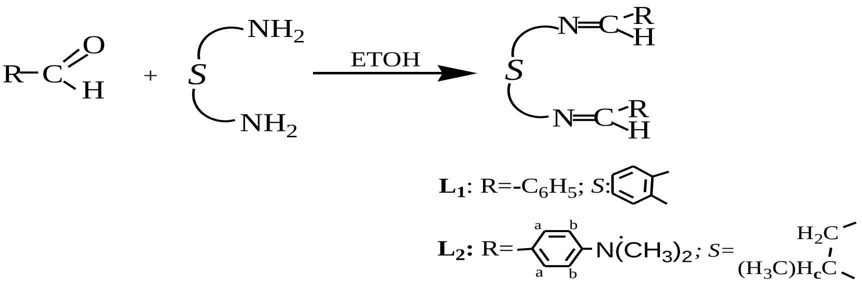


Fig. 1: Synthesis of ligands N,N'-Bis(benzylidène)benzene-1,2-diamine L1 and N,N'-Bis(4-dimethyaminobenzylidene) propane-1,2-diamine L2

IR spectroscopy of the ligand **L_1** shown by comparison with the infrared spectrum of ortho-phenylendiamine and benzaldehyde disappearance of bands of vibration $\upsilon_{C=O}$ of aldehyde located to 1710 to 1696 cm^{-1}, carbonyl υ_{CH} to 2695 cm^{-1} and υ_{NH2} at 3300 cm $^{-1}$ characteristic of a primary amine and the appearance of a broad band and less intense at 1601.19 cm $^{-1}$ corresponding to the vibration $\upsilon_{C=N}$ [9].

In proton spectrum of the ligand **L_1** we note the presence of a multiplet located at 7 and 7.75 ppm corresponding to aromatic protons. The protons of the N=CH-φ appear at 8.25 ppm.

For the ^{13}C NMR spectrums, there are the existences of eight signals located between 110 and 131 ppm corresponds to sp^2 carbons.

Mass spectrometry of the **L_1** ligand shows fragmentations m/z=283.07 [M – H$^+$]; m/z=207 [M-C_6H_5] and m/z= 194.04 [M-C_7H_6] such that M=284.

The infrared spectrum of ligand **L_2** shows the appearance of a thin and very intense band at 1620 cm^{-1} corresponding to the stretching vibration $\upsilon_{C=N}$ [9]. We also note the disappearance of the vibration of $\upsilon_{C=O}$ band located at 1700 cm $^{-1}$ [9], and υ_{NH2} vibration band at 3300 cm^{-1}.

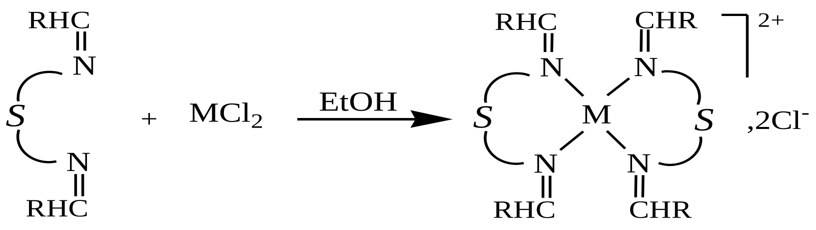
The proton spectrum of this ligand shows the presence of doublets located at 6.67 and 6.8 ppm corresponding to aromatic protons H_b and 7.475ppm and 7.704 ppm corresponding to aromatic protons H_a. Both proton H_c group appear as a singlet at 8.1 ppm. Also we detected 4 singlets located respectively; at 3.4 ppm, 2.9 ppm to 2.5 ppm and 1.1 ppm corresponding to the protons N-CH_3, H-C*, CH_2 and CH_3-C*.

In the ^{13}C NMR spectrum there are the existence of signals located between 110 and 130 ppm corresponding to sp^2 aromatic carbons. The spectrum also has signals located between 39.16 and 40.83 ppm corresponding to the carbon sp^3 CH3, two signals located at 66.45 and 67.48 ppm corresponding to sp^3 carbons of the asymmetric carbon C* and -CH_2-, two signals located at 159.63 and 161.59 ppm corresponding to the sp^2 carbon -C=N.

Mass spectrometry of the L_2 ligand shows fragmentations m/z = 335 [M-H$^+$]; m/z = 306 [M-2CH_3], m/z= 216 [M-$C_6H_4N(CH_3)_2$] and m/z = 203 [M-$CHC_6H_4N(CH_3)_2$] such that M = 336.

II.2 Synthesis of complexes $[L_1]_2MCl_2$ (M = Zn (C_1), M=Cu (C_2)) and $[L_2]_2MCl_2$ (M=Zn (C_3), M = Cu (C_4)).

Complex of zinc and copper mentioned were prepared by the reflux condensation MCL_2 anhydrous metal salt (M=Cu, Zn) on the base ligands Schiff (diimine) **L_1** and **L_2** prepared in ethanol (Fig. 2).



Li (i=1;2)

Cj (j=1-4)
M = Zn;Cu

Fig. 2: Synthesis of complexes of zinc(II) and copper(II) Cj (j = 1-4)

Infrared spectroscopy of complexes **C_1** and **C_2** compared with that of the ligands **L_1** and **L_2** shows the appearance of a new thin band at 444.56 cm^{-1} corresponding to the $\upsilon_{N\text{-}Zn}$ for the complex **C_1**, and 526 cm $^{-1}$ corresponding $\upsilon_{Cu\text{-}N}$ for the complex **C_2**. These results are consistent with literature [10]. The band of valence vibration $\upsilon_{C=N}$ for complexes **C_1** and **C_2** are respectively 1606 cm^{-1} and 1628 cm^{-1} with a delay of 5 to 27 cm^{-1} compared to their precursors **L_1** and **L_2.**

For complexes **C_3** and **C_4**, the infrared spectrum shows the appearance of a thin and very intense band at 480 cm^{-1} corresponding to the vibration of $\upsilon_{Zn\text{-}N}$ for the complex **C_3**, and a band at 520 cm^{-1} corresponding to the vibration of $\upsilon_{Cu\text{-}N}$ for the complex **C_4** [10].

The proton spectrum of the complex **C_1** shows the presence of two multiplets located at 6.9 and 7.72 ppm which correspond to the aromatic protons (Fig. 3), two protons of the N=CH-φ appear to 8.15 ppm.

The NMR^{13}C spectrum of complex **C_1** has eight signals between 111 and 130 ppm which correspond to sp^2 carbons for complex **C_1**.

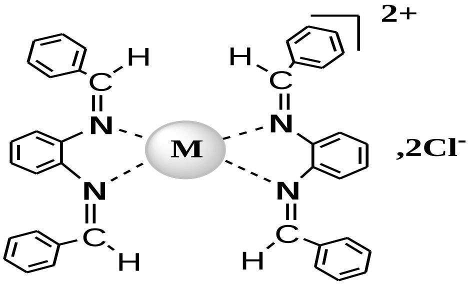


Fig. 3: Complexes C_1 (M=Zn) and C_2 (M=Cu)

Mass spectrometry shows the fragmentation m/z=626 [M -C_6H_6]; m/z=600 [M - $NCHC_6H_5$] (M=704.39) for the complex **$\underline{C_1}$**. For the complex **$\underline{C_2}$** m/z=625 [M-C_6H_6]; m/z=344 [M- (2Cl + $\underline{L_1}$ + 2H)] (M= 702.45).

In proton spectrum of complex **$\underline{C_3}$** there are two doublets located at 7.66 and 7.8 ppm corresponding to aromatic protons H_a and H_b (Fig. 4). H_C protons appear as a singlet at 8.4 ppm. The -CH_2- protons HC*-, CH_3-C*- and CH_3-N- appear respectively at 3.5 ppm, 3 ppm, 2.498 ppm and 1.081 ppm.

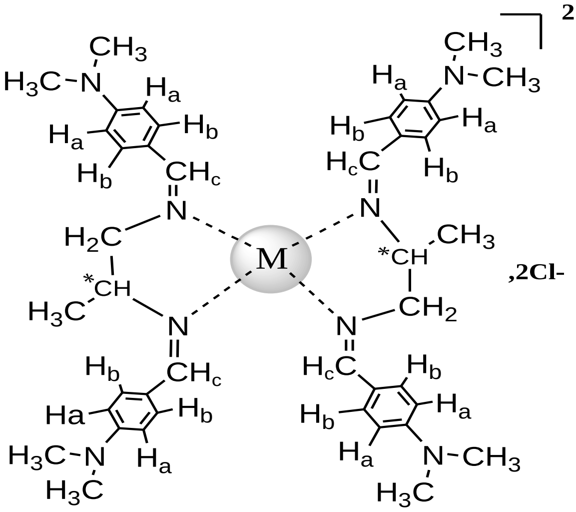


Fig. 4: Complexes $\underline{C_3}$ (M=Zn) and $\underline{C_4}$ (M=Cu)

In the NMR^{13}C spectrum there is the existence of signals located between 110 and 130 ppm corresponding to sp^2 aromatic carbons.

The spectrum also has signals located between 39.16 and 47.82 ppm corresponding to the carbon sp^3 -CH_3, the signals located at 39,16ppm and 47,82 ppm corresponding to sp^3 carbons of -CH_3 the asymmetric carbon C* and -CH_2-, and two signals located at 168.06 ppm and 190,33 ppm corresponding to the sp^2 carbon -C=N-.

The complex **$\underline{C_3}$** mass spectrometry reveals the fragmentations m/z=642 [M - (C_6H_4N $(CH_3)_2$ + $3CH_3$)]; m/z=470 [M-($\underline{L_2}$ + H)]; m/z= 441 [M - ($\underline{L_2}$ + $2CH_3$)]; and m/z= 390 [M - (**$\underline{L_2}$** + $3CH_3$ + Cl)] such that M= 807.
The proton spectrum of complex **$\underline{C_4}$** shows the existence of multiplets located at 6.7ppm and 7.662 ppm corresponding to aromatic protons H_a and H_b. Protons -N=CH-φ group appear to 9,650 ppm. The protons HC*, CH_2, CH_3-N and CH_3-C* respectively appear to 3,392 ppm, 3,021 ppm, 2.70 ppm, 2,505 ppm.
The complex **$\underline{C_4}$** mass spectrometry reveals the fragmentations m/z= 625 [M - ($C_6H_4N(CH_3)_2$ + 4 (CH_3) + H)]; m/z= 440 [M - (**$\underline{L_2}$** + $2CH_3$] and m/z= 399 [M - (**$\underline{L_2}$** + 2Cl] such that M= 806.

III. CONCLUSION

In this research we studies the preparation of diimine ligands N,N'-Bis(benzylidène)benzene-1,2-diamine $\underline{L_1}$ and N,N'-Bis(4-dimethyaminobenzylidene) propane-1,2-diamine $\underline{L_2}$ and their complexes of zinc (II) and copper (II). These complexes were characterized by IR spectroscopy, NMR (^{1}H, ^{13}C) and by mass spectrometry which permit us to determine the structure of the synthesized products.

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