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

Meriem DRISSI¹, Asmae NAKKABI², Mireille Ninon MBONZI OMBENGA³, M’Barek CHOUKRAD⁴ and Mohammed FAHIM⁴*  

¹Laboratory of Bio-Inorganic Chemistry, Molecular Materials and Environment, Faculty of Sciences, University Moulay Ismail, BP 11201, 50000 Meknes, Morocco.  
²Laboratory of Molecular Chemistry and Natural Substances, Faculty of Sciences, University Moulay Ismail, BP 11201, 50000 Meknes, Morocco.

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-phenylenediamine and 1,2-diaminopropane successively, and on the other hand their corresponding copper and zinc metal complex (L₁)₂MCl₂ (M = Zn: C₁, M = Cu: C₂) and (L₂)₂MCl₂ (M = Zn: C₁, M=Cu: C₂). The compounds thus obtained were characterized by IR spectroscopy, ¹H-NMR; ¹³C-NMR and mass spectrometry.

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

I. INTRODUCTION

The chemistry of transition metal complexes has been the subject of many studies during these recent years [1, 2, 3, 4, 5]. 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, 5] (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-phenylenediamine or 1,2-diaminopropane successively (Fig. 1). The prepared ligands were characterized by IR spectroscopy, NMR (¹H; ¹³C); 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-phenylene diamine and benzaldehyde disappearance of bands of vibration \( v_{C=O} \) of aldehyde located to 1710 to 1696 cm\(^{-1}\), carbonyl \( v_{CH} \) to 2695 cm\(^{-1}\) and \( v_{NH} \) 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 \( v_{C=\equiv N} \) [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-\( \phi \) appear at 8.25 ppm. For the \( ^{13} \)C NMR spectrums, there are the existences of eight signals located between 110 and 131 ppm corresponding to \( sp^2 \) carbons.

Mass spectrometry of the \( L_1 \) ligand shows fragmentations \( m/z \) of 283.07 (M - H\(^+\)); \( m/z \) = 207 [M-C\(_6\)H\(_4\)] and \( m/z \) = 194.04 [M-C\(_6\)H\(_4\)] 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 \( v_{CN} \) [9]. We also note the appearance of the vibration of \( v_{C\equiv O} \) band located at 1700 cm\(^{-1}\) [9], and \( v_{NH} \) 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 \( H_\alpha \) and 7.475 ppm and 7.704 ppm corresponding to aromatic protons \( H_\beta \). Both proton \( H_\alpha \) 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\(_2\)-C*.

In the \( ^{13} \)C NMR spectrums there are the existences 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 \( sp^3 \) CH\(_3\), two signals located at 66.45 and 67.48 ppm corresponding to \( sp^2 \) 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=\( \equiv N\).

Mass spectrometry of the \( L_2 \) ligand shows fragmentations \( m/z \) of 335 [M-H\(^+\)]; \( m/z \) = 306 [M-2CH\(_3\)], \( m/z \) = 216 [M-C\(_6\)H\(_4\)N(CH\(_3\))\(_2\)] and \( m/z \) = 203 [M-2CH\(_2\)C\(_6\)H\(_4\)N(CH\(_3\))\(_2\)] such that M = 336.

II.2 Synthesis of complexes \([L_1]_2\)MCl\(_2\) (M = Zn (C\(_1\)), M=Cu (C\(_2\)) and \([L_2]_2\)MCl\(_2\) (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 (dimine) \( L_1 \) and \( L_2 \) prepared in ethanol (Fig. 2).

![Figure 2: Synthesis of complexes of zinc(II) and copper(II) C\(_j\) (j = 1-4)](image)

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 \( v_{N-Zn} \) for the complex C\(_1\), and 526 cm\(^{-1}\) corresponding \( v_{C=N} \) for the complex C\(_2\). These results are consistent with literature [10]. The band of valence vibration \( v_{C\equiv N} \) 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 \( v_{Zn-N} \) for the complex C\(_3\), and a band at 520 cm\(^{-1}\) corresponding to the vibration of \( v_{C\equiv N} \) 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-\( \phi \) appear to 8.15 ppm.

The NMR\(^{13} \)C spectrum of complex C\(_2\) has eight signals between 111 and 130 ppm which correspond to \( sp^2 \) carbons for complex C\(_2\).
Mass spectrometry shows the fragmentation m/z=626 [M -C,H,]; m/z=600 [M - NCH,C,H,] (M=704.39) for the complex C. For the complex C, m/z=625 [M-C,H,]; m/z=344 [M- (2Cl + L, + 2H)] (M= 702.45).

In proton spectrum of complex C there are two doublets located at 7.66 and 7.8 ppm corresponding to aromatic protons H and H (Fig. 4). H, protons appear as a singlet at 8.4 ppm. The -CH,- protons HC, CH,-C* and CH,N- appear respectively at 3.5 ppm, 3 ppm, 2.498 ppm and 1.081 ppm.

In the NMR 13C spectrum there is the existence of signals located between 110 and 130 ppm corresponding to sp3 aromatic carbons.

The spectrum also has signals located between 39.16 and 47.82 ppm corresponding to the carbon sp3 - CH3, the signals located at 39.16 ppm and 47.82 ppm corresponding to sp3 carbons of -CH3, the asymmetric carbon C* and -CH-, and two signals located at 168.06 ppm and 190.33 ppm corresponding to the sp2 carbon - C=N-

The complex C mass spectrometry reveals the fragmentations m/z=642 [M - (C,H,N (CH,)+ 3CH,)]; m/z=470 [M-(L, + H)]; m/z= 441 [M - (L, + 2CH3)]; and m/z= 390 [M - (L, + 3CH3 + Cl)] such that M= 807. The proton spectrum of complex C shows the existence of multiplets located at 6.7ppm and 7.66 and 7.8 ppm corresponding to aromatic protons H and H. Protons -N=CH-φ group appear to 9,650 ppm. The protons HC, CH3, CH3-N and CH3-C* respectively appear to 3,392 ppm, 3,021 ppm, 2,70 ppm, 2,505 ppm. The complex C mass spectrometry reveals the fragmentations m/z= 625 [M - (C,H,N(CH,)+ 4 (CH3) + H)]; m/z= 440 [M - (L, + 2CH3)] and m/z= 399 [M - (L, + 2Cl)] such that M= 806.

### III. CONCLUSION

In this research we studies the preparation of diimine ligands N,N'-Bis(benzylidene)benzene-1,2-diamine L and N,N'-Bis(4-dimethylaminobenzylidene) propane-1,2-diamine L and their complexes of zinc (II) and copper (II). These complexes were characterized by IR spectroscopy, NMR (1H, 13C) and by mass spectrometry which permit us to determine the structure of the synthesized products.
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REFERENCES