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RESEARCH ARTICLE

SYNTHESIS AND CHARACTERIZATION OF LIGAND DIIMINES N-(1-(PROPIONYLOXY) PROPYLIDENE) BENZÉNAMINE, N-(2-METHYL-1, 4-DIPHENYL-4-(PHENYLIMINO)BUTYLIDENE) BENZENAMINE AND THEIR COMPLEXES OF COPPER AND ZINC

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ABSTRACT

The objective of this study is to synthesize Schiff base ligand, (diimine) N-(1-(propionyloxy)propylidene) benzenamine L_1 and N-(2-methyl-1,4-diphenyl-4-(phenylimino) butylidene) benzenamine L_2 from precursors propionic anhydride and 1,4-diphenyl-2-methylbutane-1,4-dione successively, and on the other hand their corresponding copper and zinc metal complex $(L_1)_2MCl_2$ (M = Zn: C_1 , M = Cu: C_2) and $(L_2)_2MCl_2$ (M = Zn: C_3 , M=Cu: C_4). The compounds thus obtained were characterized by IR spectroscopy, ¹H-NMR; ¹³C-NMR and mass spectrometry.

INTRODUCTION

In the past decades, the complexes containing transition metal ions and various Schiff-base ligands have been extensively investigated due to their novel structures and potential applications in many fields (Fahim *et al.*, 2010 ; Drissi *et al.*, 2015 ; Bendifi *et al.*, 2007 ; Mbonzi *et al.*, 2014 ; Dede *et al.*, 2009). Particularly, the accessibility of diverse structural modifications, biological modeling applications (Neelakantan *et al.*, 2008 ; Li *et al.*, 2005 ; Nakamura *et al.*, 2001), catalysis, design of molecular ferromagnets and materials chemistry (Kotha, 2003 ; Donnell, 2004 ; Wu *et al.*, 2006 ; Zhong *et al.*, 2005 ; Wezenberg *et al.*, 2008 ; Das *et al.*, 2006). These complexes are also biologically important species that have numerous applications, such as in the treatment of cancer, as antibactericide agents, antiviral agents, fungicide agents and for other biological properties (Ferrari *et al.*, 2000; Wang *et al.*, 2001; Charo *et al.*, 2004; Zhang *et al.*, 2003).

RESULTS AND DISCUSSION

Synthesis of N-(1-(propionyloxy) propylidene) benzenamine L_1 and N-(2-methyl-1,4-diphenyl-4-(phenylimino) butylidene) benzenamine L_2

Diimine ligands N-(1-(propionyloxy) propylidene) benzenamine L_1 and N-(2-methyl-1,4-diphenyl-4-

(phenylimino) butylidene)benzenamine L_2 were prepared by the condensation at reflux in ethanol with two equivalents of aniline on an equivalent of anhydride propionique and 1,4-diphenyl-2-methylbutane-1,4-dione 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.

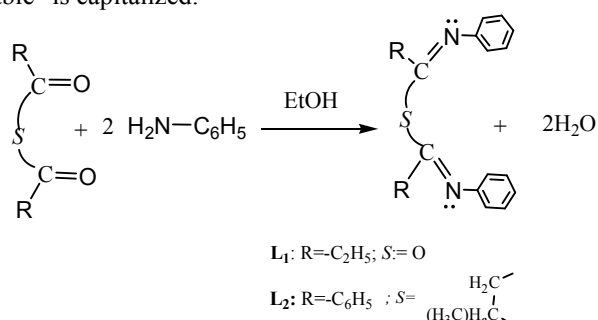


Fig. 1. Synthesis of ligands N-(1-(propionyloxy)propylidene) benzenamine L_1 and N-(2-methyl-1,4-diphenyl-4-(phenylimino)butylidene) benzenamine L_2

IR spectroscopy of the ligand L_1 show by comparison with the infrared spectrum of aniline and 1,4-diphenyl-2-méthylbutane-1,4-dione disappearance of bands of vibration $\nu_{C=O}$ of ketone located at 1710 to 1696 cm^{-1} , carbonyl ν_{CH} at 2695 cm^{-1} and ν_{NH_2} at 3300 cm^{-1} characteristic of a primary amine and the appearance of a broad band and less intense at 1640 cm^{-1} corresponding to the vibration $\nu_{C=N}$ (Adly *et al.*, 2013).

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In proton spectrum of the ligand \underline{L}_1 we note the presence of a doublet at 7.60 ppm corresponding to aromatic protons (Haa') and two triplets at 7.30 et 7.03 ppm corresponding respectively to aromatic protons (Hbb' and Hc). Also we detected a triplet and quadruplet at 1.10 – 2.30 ppm corresponding respectively to protons CH_3 and CH_2 .

For the ^{13}C NMR spectrums, there is the existence of four signals located between 119.49 and 139.85 ppm corresponds to sp^2 of aromatic carbons. The signals located at 10,11 and 29,97 ppm corresponds to Carbons sp^3 of CH_3 and CH_2 and signals located at 172.40 ppm corresponding to carbon $\text{C}=\text{N}$. Mass spectrometry of the \underline{L}_1 ligand shows fragmentations $m/z=281$ [$\text{M} + \text{H}^+$]; $m/z=267$ [$\text{M}-\text{CH}_3 + 2\text{H}^+$] and $m/z=189$ [$\text{M}-(\text{C}_6\text{H}_5 + \text{N})$] such that $\text{M}=280$. The infrared spectrum of ligand \underline{L}_2 shows the appearance of a thin band at 1635 cm^{-1} corresponding to the stretching vibration $\nu_{\text{C}=\text{N}}$ (Tumer *et al.*, 2007). We also note the disappearance of the vibration of $\nu_{\text{C}=\text{O}}$ band located at 1700 cm^{-1} (Tumer *et al.*, 2007), and ν_{NH_2} vibration band at 3300 cm^{-1} .

The proton spectrum of this ligand shows the presence of a multiplet located at 7.50 and 7.80 ppm corresponding to aromatic protons. Also we detected three signals: two doublets and one multiplet located respectively at 1.16 ppm, 2.48 ppm and 3.04 ppm corresponding to the protons CH_3 , CH_2 and Hc. In the ^{13}C NMR spectrum there is the existence of four signals located between 127.65 and 135.17 ppm corresponding to sp^2 aromatic carbons. The spectrum also shown signals located at 8.93 ppm corresponding to the carbon sp^3 CH_3 , two signals located at 18.43 and 45.93 ppm corresponding to sp^3 carbons of CH_2 and the asymmetric carbon C^* , two signals located at 166.50 and 167.33 ppm corresponding to the sp^2 carbon $\text{C}=\text{N}$. Mass spectrometry of the \underline{L}_2 ligand shows fragmentations $m/z = 295$ [$\text{M}-(\text{C}_6\text{H}_5 + \text{CH}_3 + \text{H}^+)$]; $m/z=106$ [$\text{C}_6\text{H}_5\text{N} + \text{CH}_3 + \text{H}^+$] and $m/z = 91$ [$\text{C}_6\text{H}_5\text{N}$] such that $\text{M} = 402$.

Synthesis of complexes $[\underline{L}_1]_2\text{MCl}_2$ ($\text{M} = \text{Zn}$ (\underline{C}_1), $\text{M}=\text{Cu}$ (\underline{C}_2)) and $[\underline{L}_2]_2\text{MCl}_2$ ($\text{M}=\text{Zn}$ (\underline{C}_3), $\text{M} = \text{Cu}$ (\underline{C}_4))

Complex of zinc and copper mentioned above were prepared by the reflux condensation MCl_2 anhydrous metal salt ($\text{M}=\text{Cu}$, Zn) on the base ligands Schiff (diimine) \underline{L}_1 and \underline{L}_2 prepared in ethanol (Fig 2).

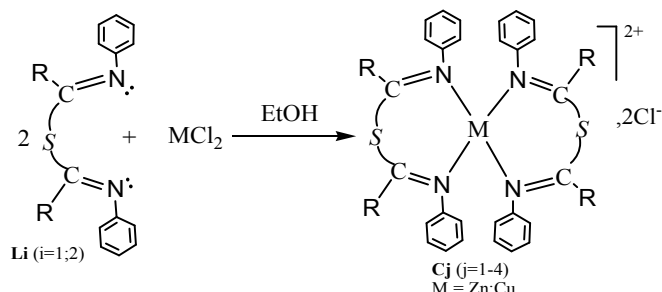


Fig. 2. Synthesis of complexes of zinc (II) and copper (II) C_j ($j = 1-4$)

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 420 cm^{-1} corresponding to the $\nu_{\text{N}-\text{Zn}}$ for the complex C_1 , and 510 cm^{-1} corresponding $\nu_{\text{C}-\text{N}}$ for the complex C_2 . These results are consistent with literature (Tumer *et al.*, 2007).

The band of valence vibration $\nu_{\text{C}=\text{N}}$ for complexes C_1 and C_2 are respectively 1600 cm^{-1} with a delay of 40 cm^{-1} compared to their precursors L_1 . For complexes C_3 and C_4 , the infrared spectrum shows the appearance of a thin and very intense band at 420 cm^{-1} corresponding to the vibration of $\nu_{\text{Zn}-\text{N}}$ for the complex C_3 , and a band at 480 cm^{-1} corresponding to the vibration of $\nu_{\text{Cu}-\text{N}}$ for the complex C_4 (Zhang *et al.*, 2003). The band of valence vibration $\nu_{\text{C}=\text{N}}$ for complexes C_1 and C_2 are respectively 1640 cm^{-1} and 1648 cm^{-1} with a delay of 5 and 13 cm^{-1} compared to their precursors L_2 . The proton spectrum of the complex C_1 shows the presence of one doublet and two triplets located respectively at 7.57 – 7.27 and 7.01 ppm which correspond to the aromatic protons (Haa', Hbb' and Hc) (Fig 3). Also we detected two signals which are a triplet and quadruplet located respectively at 1.05 and 2.27 ppm corresponding to the protons CH_3 and CH_2 .

The NMR ^{13}C spectrum of complex \underline{C}_1 has four signals between 119.51 and 139.00 ppm which correspond to sp^2 aromatic carbons for complex \underline{C}_1 . Also we detected two signals located respectively at 10.11 and 29.98 ppm corresponding to the protons CH_3 and CH_2 . The carbon of the $\text{N}=\text{C}$ appear at 172.40 ppm.

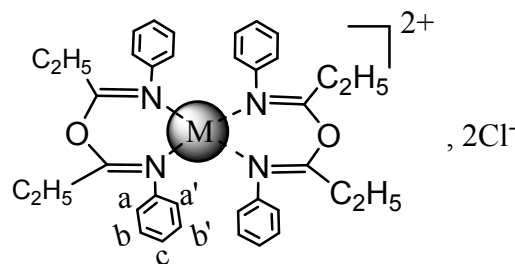


Fig. 3. Complexes \underline{C}_1 ($\text{M}=\text{Zn}$) and \underline{C}_2 ($\text{M}=\text{Cu}$)

In proton spectrum of complex \underline{C}_3 there are a multiplet located between 7.01 and 7.86 ppm corresponding to aromatic protons (Fig 4) and two doublets located at 1.10 and 3.02 ppm corresponding respectively of protons CH_3 and CH_2 . Hc protons appear as a multiplet at 3.43 ppm.

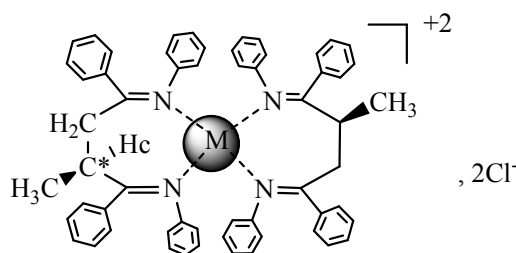


Fig. 4. Complexes \underline{C}_3 ($\text{M}=\text{Zn}$) and \underline{C}_4 ($\text{M}=\text{Cu}$)

In the NMR ^{13}C spectrum there is the existence of signals located between 119.50 and 135.27 ppm corresponding to sp^2 aromatic carbons. Also the spectrum shows signals located at 10.13 ppm corresponding to the carbon sp^3 CH_3 , two signals located at 44.73 and 45.93 ppm corresponding to sp^3 carbons of CH_2 and the asymmetric carbon C^* , and two signals located at 166.45 and 167.29 ppm corresponding to the sp^2 carbon $\text{C}=\text{N}$. The proton spectrum of complex C_4 shows the existence of two signals located at 7.41 ppm and 7.79 ppm corresponding to aromatic protons. The protons H_c , CH_2 and CH_3-C^* respectively appear at 3.04 ppm, 2.43 ppm, 1.13 ppm.

In the NMR¹³C spectrum there is the existence of signals located between 127.64 and 135.17 ppm corresponding to sp² aromatic carbons. The spectrum also shows signal located at 9.03 ppm corresponding to the carbon sp³ CH₃, two signals located at 18.43 and 45.93 ppm corresponding to sp³ carbons of CH₂ and the asymmetric carbon C*, and two signals located at 166.50 and 167.33 ppm corresponding to the sp² carbon C=N.

Conclusion

In this research we studied the preparation of diimine ligands N-(1-(propionyloxy) propylidene) benzenamine L₁ and N-(2-methyl-1, 4-diphenyl-4-(phenylimino) butylidene) benzenamine L₂ and their complexes of zinc (II) and copper (II). These complexes were characterized by IR spectroscopy, NMR (¹H, ¹³C) and by mass spectrometry which permitted us to determine the structure of the synthesized products.

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