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RESEARCH ARTICLE

SYNTHESIS AND CHARACTERIZATION OF NEW COMPLEXES OF COPPER (II) AND ZINC (II) A BASIS OF SCHIFF BASES LIGANDS N, N'-BIS (DIPHENYLMETHYLENE) ETHANE- 1, 2-DIAMINE (L₁) AND N, N'-BIS (DIPHENYLMETHYLENE) BENZENE -1, 2-DIAMINE (L₂)

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ABSTRACT

A new series of copper (II) and zinc (II) Schiff bases complexes containing the bidentate ligands N, N'-bis (diphenylmethylene) ethane-1, 2-diamine (L₁) and N, N'-bis (diphenyl methylene) benzene-1, 2-diamine (L₂) was prepared by the condensation of the ethylenediamine, or the orthophénylènediamine on benzophenone in ethanol at reflux. The Schiff base ligands and their corresponding complexes have been identified by IR spectroscopy, ¹H NMR, ¹³C NMR and by ESI MS spectrometry. The copper (II) and zinc (II) complexes obtained have a octahedral geometry; the metal cations are linked to the four nitrogen atoms of the imine grouping (C=N).

INTRODUCTION

The Chemistry of transition metal complexes with ligands of the Schiff base class has been the subject of numerous studies in the course of last years (Fahim *et al.*, 1986). It has been improved considerably through their many applications in the field of biology (Pember *et al.*, 1986), medicine (Gupta and Sutar, 2008), catalysis (Cozzi, 2004), organic synthesis and in the study of the active sites of metalloproteins (Pember *et al.*, 1986). These ligands show a wide biological activity and are the particular interest because of the various means by which they are bound to metal ions. It is known that the presence of the metal ion linked to biologically active compounds can improve their activities. Recently, many researchers have shown that the free ligands of Schiff base and their complexes have a wide variety of biological activities effective against the bacteria (Pember *et al.*, 1986), fungi (Pember *et al.*, 1986) and certain types of tumors (Gupta and Sutar, 2008). In this work, we present the synthesis of new complexes of copper (II) and zinc (II) with a basis of ligands bidentate Schiff base. The compounds obtained are characterized by various spectroscopic technics IR, ¹H-NMR, ¹³C-NMR and by ESI MS spectrometry.

EXPERIMENTAL

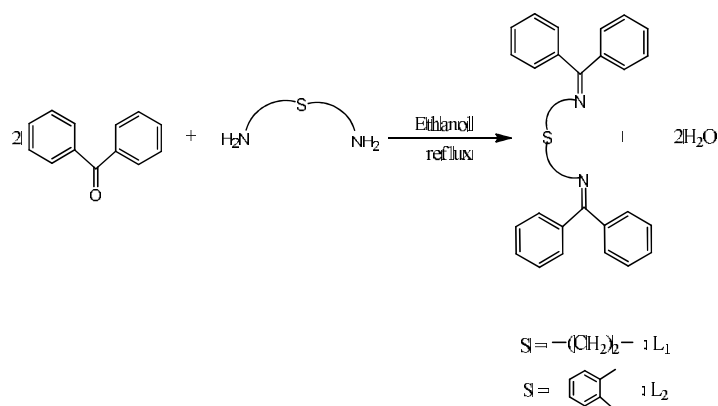
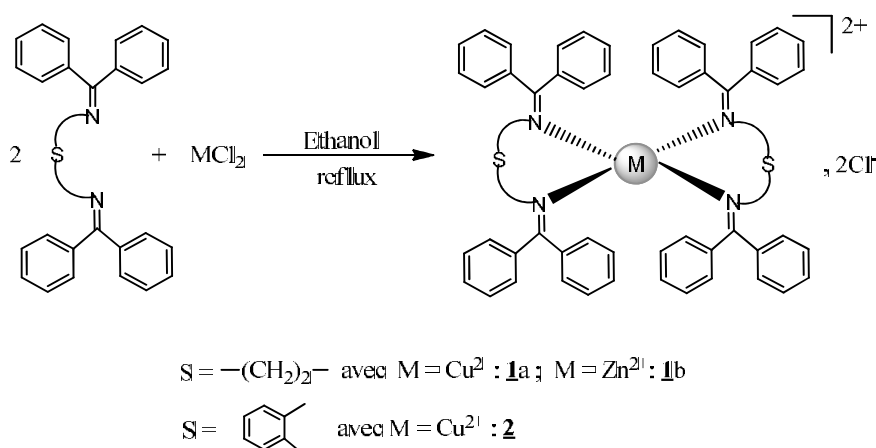
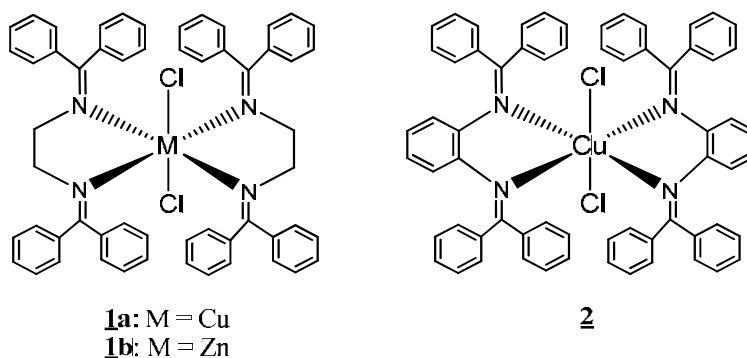
Ethylenediamine, orthophénylènediamine and benzophenone are from Fluka, Janssen and Aldrich. The metal salts CuCl₂ and ZnCl₂ are generated by Riedel, and Janssen. The solvents are generated by Aldrich. The infrared spectra were recorded by using a spectrometer FTIR (4000 - 400 cm⁻¹). The RMN spectra were recorded in DMSO solution, using a Bruker spectrometer ARX 400 MHz. Electrospray mass spectra were recorded in positive mode by using an API mass 1 spectrometer (Perkin-Elmer).

Synthesis of the ligand N, N'-bis (diphenylmethylene) ethane-1,2-diamine (L₁)

A solution of 3 g of benzophenone (16.66 mmol) in 20 ml of ethanol was added drop-wise, a solution of 0.5 g of ethylenediamine (8.33 mmol) in 10 ml of ethanol. The reaction mixture was refluxed for 4 hours at 65 ° C, after refroidissement, allowed in the refrigerator for two days. The beige crystals formed was filtered off and dried. yield 92%. IR (KBr; v/cm⁻¹): 3079 (ν_{CHar}); 2952-2870 (ν_{CH2}); 1648(ν_{C=N}); 1502 (ν_{C=C})_{ar}; 1102 (ν_{C-N}). ¹HNMR (DMSO-d₆) δ_H(ppm): 3,63 (CH₂); 7,28; 7,35; 7,40; 7,52 (H-aro). ¹³CNMR(DMSO-d₆) δ (ppm): 55,01(CH₂); 127,94; 128,32; 128,95; 139,87 (C-aro); 168,03 (C=N).

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Fig.1. Synthesis of the ligand L_1 and L_2 Fig.2. Synthesis of complexes $\underline{1a}$, $\underline{1b}$ and $\underline{2}$ Fig.3. Suggested structures of complex $\underline{1a}$, $\underline{1b}$ and $\underline{2}$

Synthesis of the ligand N, N'-bis (diphenylmethylene) benzene -1,2-diamine (L_2)

1,7g (9,2 mmol) benzophenone dissolved in 30 ml of absolute ethanol in the presence of two drops of HCl are heated at 60°C. To this mixture was added dropwise 15 ml of an ethanol solution containing 0,5 g (4,6 mmol) of orthophenylenediamine. The reaction mixture was refluxed for 4 hours and then allowed to stand over night at room temperature. The solvent was evaporated and the brown solid was washed with ether and dried. Yield: 84%. IR (KBr; ν/cm^{-1}): 3065 (ν_{CHar}); 1636 ($\nu_{\text{C=N}}$); 1498 ($\nu_{\text{C=C}}_{\text{ar}}$); 1136 ($\nu_{\text{C-N}}_{\text{ar}}$). $^1\text{H NMR}$ (DMSO- d_6) δ_{H} (ppm): 6,87; 7,16; 7,56; 7,58; 7,72; 7,75 (H-aro). $^{13}\text{C NMR}$ (DMSO- d_6) δ (ppm): 120,03; 122,45; 128,82; 131,29; 133,24; 138,63 (C-aro); 175,36 (C=N).

Synthesis of ((N, N'-bis (diphenylmethylene) ethane-1,2-diamine) $_2$ CuCl $_2$) ($\underline{1a}$)

A 0,04 g (0,283 mmol) of anhydrous copper chloride (CuCl_2) was suspended in 15 ml of ethanol, were added drop by drop 0.2 g (0,515 mmol) of ligand L_1 dissolved in 15 ml of ethanol. The mixture is refluxed for 2 hours, the green precipitates were filtered and dried. Yield: 77%. IR (KBr; ν/cm^{-1}): 3069 (ν_{CHar}); 2935-2857 (ν_{CH_2}); 1626 ($\nu_{\text{C=N}}$); 1502 ($\nu_{\text{C=C}}_{\text{ar}}$); 1100 ($\nu_{\text{C-N}}$); 440 ($\nu_{\text{Cu-N}}$). $^1\text{H NMR}$ (DMSO- d_6) δ_{H} (ppm): 3,66 (CH_2); 7,32; 7,42; 7,55; 7,71 (H-aro). $^{13}\text{C NMR}$ (DMSO- d_6) δ (ppm): 54,81 (C, CH_2); 129,07; 130,03; 133,24; (C-aro); 168,21 (C=N). ESI-MS: $m/z = 910,97$ ($\text{M}+\text{H}^+$).

Synthesis of complex ((N,N'-bis(diphenylmethylene)ethane-1,2-diamine)₂ZnCl₂) (1b)

The preparation was analogous to that of complex 1a, but anhydrous zinc chloride ZnCl₂ (0,038 g; 0,283 mmol) was used instead of CuCl₂. white solid, yield: 76%. IR (KBr; ν/cm^{-1}): 3065 (ν_{CHar}); 2936-2857 (ν_{CH_2}); 1629 ($\nu_{\text{C=N}}$); 1500 ($\nu_{\text{C=C}}_{\text{ar}}$); 1099 ($\nu_{\text{C-N}}$); 425 ($\nu_{\text{Zn-N}}$). ¹HNMR (DMSO-d₆) δ_{H} (ppm): 3,66 (CH₂); 7,32; 7,42; 7,55; 7,71 (H-aro). ¹³CNMR (DMSO-d₆) δ (ppm): 52,26 (C, CH₂); 128,91; 129,75; 132,94; (C-aro); 167,82 (C=N). ESI-MS: m/z = 912,29 (M+H)⁺.

Synthesis of complex ((N, N'-bis (diphenylméthylene) benzene -1.2-diamine)₂ CuCl₂) (2)

Complex 2 was synthesized using the same protocol as that used for the complex 1a. By reaction of 0,06 g (0,378 mmol) of CuCl₂ with 0,3 g(0,687 mmol) of ligand L₂. The khaki solid, yield: 74%. IR (KBr; ν/cm^{-1}): 3069 (ν_{CHar}); 1610 ($\nu_{\text{C=N}}$); 1500 ($\nu_{\text{C=C}}_{\text{ar}}$); 1118 ($\nu_{\text{C-N}}$); 436 ($\nu_{\text{Cu-N}}$). ¹HNMR (DMSO; δ ppm): 7,04; 7,18; 7,54; 7,59; 7,75; 7,80 (H-aro). ¹³C NMR (DMSO; δ ppm): 118,05; 120,62; 127,73; 130,29; 132,36; 137,68 (C- arom); 173,89 (C=N). ESI-MS: m/z = 970,24 (M-Cl)⁺, m/z = 891,6 (M-C₆H₅-C₃H₃)⁺.

RESULTS AND DISCUSSION

We have first of all carried out the synthesis of the Schiff base ligand by the condensation of an equivalent of 1,2-ethylenediamine or the orthophénylènediamine on two equivalents of benzophenone in ethanol at 65°C. After 4 hours of reflux were isolated ligands L₁ and L₂ with a yield of 92% and 84% respectively (Fig.1). On the one hand, The ligands L₁ and L₂ have been reacted by copper chloride anhydride (CuCl₂) in ethanol at reflux to give the complexes 1a and 2 (fig.2), with a respective yields 77% and 74%. On the other hand, the ligand L₁ has been reacted with zinc chloride (ZnCl₂) to give the complex 1b (figure 2) with a yield of 76%. The structures of these two ligands L₁, L₂ and their complexes 1a,1b and 2 have been identified by the spectroscopic techniques IR, ¹H-NMR, ¹³C-NMR and by ESI MS spectrometry. In the absence of technical by X-ray diffraction, infrared has proved to be the appropriate technic to obtain sufficient information and elucidate the nature of the binding of ligands (Siji, 2011).

The IR spectrum of ligand L₁ dispersed in KBr, shows absorption bands at 3079 cm⁻¹, (2952-2870) cm⁻¹, 1502 cm⁻¹ and 1102 cm⁻¹ attributed to stretching vibrations $\nu(\text{=CH})_{\text{ar}}$, $\nu(\text{CH}_2)$ asymmetric and symmetric, $\nu(\text{C=C})_{\text{ar}}$ and $\nu(\text{C-N})$, respectively. while IR spectrum of ligand L₂ in the solid state in KBr, shows the medium intensity bands at 3065 cm⁻¹, 1498 cm⁻¹ and 1136 cm⁻¹ assigned to stretching vibrations $\nu(\text{=CH})_{\text{ar}}$, $\nu(\text{C=C})_{\text{ar}}$ and $\nu(\text{C-N})$, respectively. On the two spectra of ligands, the absence of vibration band $\nu(\text{C=O})$ of starting ketone expected to 1685 cm⁻¹ and that of the amine (NH₂) groups between (3270-3225) cm⁻¹ correlated with the presence of the strong intensity band at 1648 cm⁻¹ for ligand L₁ and at 1636 cm⁻¹ for the ligand L₂ attributable to the stretching vibration azomethine $\nu(\text{C=N})$. it confirms complete condensation (Turkkan *et al.*, 2011) between benzophenone and ethylenediamine or O-phenylenediamine.

each IR spectrum of complex presents the medium intensity band at 1626 cm⁻¹, 1629 cm⁻¹ to 1610 cm⁻¹ attributable to the azomethine groups (C=N) stretching vibration for the complex 1a, 1b and 2 respectively. These bands have undergone a shift towards lower energies compared to their free ligands. This displacement suggests that the metal is coordinated to the macrocycle nitrogen atoms of the imine. More over, the complexation is confirmed by the appearance of a new medium intensity band at 440 cm⁻¹, 460 cm⁻¹ and 436 cm⁻¹ corresponding to the stretching vibration of metal-nitrogen bond (Cu-N), $\nu(\text{Zn-N})$ and $\nu(\text{Cu-N})$ (Siji *et al.*, 2011; Sharghi and Nasser, 2003) for the three complexes 1a, 1b et 2 respectively.

The ¹H NMR spectrum of ligand L₁ taken in DMSO-d₆ confirmed the condensation between the ketone and the amine. Indeed, the presence of a singlet at 3.63 ppm corresponding to the protons of the methylene group connected to the nitrogen atom (CH₂-N) and the absence of the signal of the protons of the amine (NH) expected 2.70 ppm show that the reaction took place. The signals of the aromatic protons of benzylidenimine appear as four triplet in the region 7.28-7.52 ppm. While the ¹H NMR spectrum of ligand L₂ taken in DMSO-d₆, presents on the one hand the signals carried by the protons of the aromatic ring benzylidenimine between 6.87-7.56 ppm and on the other hand of the signals carried by protons of the aromatic ring O-phenylenediamine appear in the region 7.58-7.75 ppm (Siji *et al.*, 2011). The analysis of ¹³C NMR spectrum of L₁ recorded in DMSO showed the presence of signals at 55.01 ppm; between 127.94 -139.87 ppm and 168.03 ppm attributed respectively to the methylene carbons (C-N) bound to the nitrogen atom, to carbons of the aromatic ring benzylidenimine (C aro) and to carbons the imine (C=N), while the ¹³C NMR spectrum of ligand L₂, present in addition to the signals in the region 120.03 -128.82 ppm corresponding to carbons of aromatic ring benzylidenimine, signals between 128.45 -135, 32 ppm have been attributed to aromatic rings of the o-phenylenediamine. We also observed a signal at 196.34 ppm that we assigned to the carbons of the imine (C=N) (Gao and Zheng, 2002). The ¹H NMR and ¹³C NMR spectra of the complex 1a, 1b and 2 show almost the same signals as those of the corresponding ligands. On the ¹H NMR spectrum of the complex 1a and 1b, the slight shift of the protons phenyl signals and protons methylene signals towards higher energies is certainly due to the coordination of the metal by the nitrogen atoms of the imine (C=N)(9). This movement of phenyl proton signals was also observed on the ¹H NMR spectrum of complex 2.

The ¹³C NMR spectrum of complex 1a shows a peak at 54.81 ppm attributed to the methylene carbon (CH₂). The peaks at 129.07; 130.03 and 133.24 ppm are assigned to the carbons belonging to the aromatic ring benzylidenimine. The peak at 168.21 ppm correspond to atoms carbons of the imine (C=N). The analysis of the ¹³C NMR spectrum of complex 2 showed nothing new apart from slight movement of signals towards to the low chemical shifts compared to the free ligand L₂. The results of NMR are consistent with those of IR. The complex 1a, 1b and 2 were characterized by ESI MS spectrometry. The mass spectrum of complex 1a shows a peak at m /z = 910.97 corresponding at molecular ion (M+ H)⁺ with a relative abundance of 37%, and the ions m/z = 643.28 (M-2Cl-N(CH₂)₂N-2 (C₆H₅))⁺ and m/z = 438 (M-2Cl-L₁-2CH₂)⁺ corresponding to the fragments resulting from the dissociation

of chloride, pattern ethylenediamine and benzylidenimine. while for the complex **1b**, molecular ion appears at $m/z = 912.29$ ($M+H$)⁺ with a relative abundance of 53%. different fragments are $m/z = 841.29$ ($M-2Cl$)⁺, $m/z = 687.23$ ($M-2Cl-2C_6H_5$)⁺, $m/z = 245.19$ ($M-L_1-2Cl-CN(CH_2)_2-2(C_6H_5)$)⁺. The molecular peak of complex **2** is not visible, but the ions $m/z = 970.24$ ($M-Cl$)⁺, $m/z = 891.60$ ($M-C_6H_5-C_3H_3$)⁺, $m/z = 782.97$ ($M-2Cl-2(C_6H_5)$)⁺ and $m/z = 499.56$ ($M-2Cl-L_2$)⁺ corresponding to the characteristic fragments of the loss of ligand L_2 , of chloride and benzene pattern confirm the structure of the complex **2**. the experimental mass found, are in agreement with the theoretical mass. The Fig.3, shows the proposed structures of complexes.

Conclusion

This work has allowed us to confirm the training of bidentate ligands L_1 and L_2 to the result of the condensation of 1,2-ethylenediamine or orthophénylènediamine with benzophenone. These ligands and their complex were obtained with good yields. The structures of these ligands as well as those of the complexes of copper(II) and zinc(II) correspondents have been determined by various methods of analysis. In these structures, the metal is hexacoordinate. It is linked to four nitrogens of azomethine groupings ($C=N$) and the other two coordination sites are occupied by chloride ion. The applications possibility of these ligands and their complexes in the field of catalysis, pharmacology and therapeutics offer at the coordination chemistry of immense potential, which explains the increase in research of Schiff bases ligands and complex (Gupta and Sutar, 2008; Balsells *et al.*, 1998).

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