

Hydrolytic Cleavage of the Imino Bond in Schiff Base Ligand N, N'-bis[3(4-Dodecyloxy-Benzylideneamino)-Propyl]-Piperazine by Complexation. The study of the New Cu(II) and Ni(II) Complexes Containing 1,4-bis(3-Aminopropyl)Piperazine as Ligand

C.M. Bucovicean, L. Cseh, C. Cretu and O. Costisor

Institute of Chemistry Timisoara of Romanian Academy, Bv. Mihai Viteazu, No. 24, RO-300223, Timisoara, Romania
e-mail: bucovicean@yahoo.com

Abstract: Present study reveals that during the reaction of the Schiff base ligand N, N'-bis[3(4-dodecyloxy-benzylideneamino)-propyl]-piperazine (L) with the copper and nickel perchlorate, the imino bond is destroyed. In order to explain this behaviour, the influence of the metal ions nature was studied. In this frame, the following complexes $[\text{CuL}'(\text{ClO}_4)] \cdot \text{ClO}_4 \cdot 4\text{H}_2\text{O}$ (1) and $[\text{NiL}'(\text{ClO}_4)] \cdot \text{ClO}_4 \cdot \text{H}_2\text{O}$ (2) containing (L') as ligand, where L'=1,4-Bis(3-aminopropyl)piperazine, have been obtained and their nature has been established on the basis of results of elemental analysis, atomic absorption spectroscopy (AAS), electric molar conductivity, electronic (UV-Vis) and infrared (IR) spectroscopy.

Keywords: Schiff base ligand; copper(II) complex; nickel(II) complex; 1,4-Bis(3-aminopropyl)piperazine; perchlorate counter anion.

1. Introduction

In the field of coordination chemistry the Schiff bases represents a very usefull class of compounds due to their versatility to act as ligands with metal ions. The characteristic bond of the Schiff bases, C=N, has reversible nature which allows by hydrolysis, obtaining the initial corresponding aldehyde and amine compounds [1-9].

We describe here the synthesis of new copper(II) and nickel(II) complexes containing 1,4-bis(3-aminopropyl)piperazine as the ligand, obtained as a result of hydrolytic cleavage of the imino bond of Schiff base N, N'-bis[3(4-dodecyloxy-benzylideneamino)-propyl]-piperazine by complexation. Also we study the influence of metal ions on the stability of Schiff base N, N'-bis[3(4-dodecyloxy-benzylideneamino)-propyl]-piperazine.

2. Experimental

2.1. Materials

All the reagents and solvents were purchased from Merck, Aldrich, and used without further purification, except ligands were obtained as follows: N, N'-bis[3(4-dodecyloxy-benzylideneamino)-propyl]-piperazine (L) was synthesized according to literature [9] and 1,4-bis(3-aminopropyl)piperazine (L'), obtained as a result of hydrolytic cleavage of the imino bond of Schiff base N, N'-bis[3(4-dodecyloxy-benzylideneamino)-propyl]-piperazine by complexation.

2.2. Physical Measurements

The complexes characterization was performed by elemental analysis, electric molar conductivity, UV-VIS and IR spectroscopy.

Analytical data were obtained by a Perkin Elmer model 240C elemental analyzer and the metal ions were determined with GBC SENSAA apparatus.

Electric molar conductivities were measured at room temperature on DMF and CH_3CN solutions with a WTW LF 340 – A conductivity meter.

Electronic absorbtion spectra of freshly prepared solutions of complexes in DMF and CH_3CN were measured with a Perkin Elmer LAMBDA 12 spectrophotometer.

IR spectra were recorded in KBr pellets on a Jasco FT/IR-430 spectrophotometer, in the $400\text{-}4000\text{ cm}^{-1}$ range.

2.3. Synthesis

ATTENTION! Perchlorate salts are potentially explosive; they should be handled with care and in small quantities.

$[\text{CuL}'(\text{ClO}_4)] \cdot \text{ClO}_4 \cdot 4\text{H}_2\text{O}$ (1) A solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.1 mmol, 0.0370 g) dissolved in 5 ml tetrahydrofurane (THF) was added to a solution containing the Schiff base N, N'-bis[3(4-dodecyloxy-benzylideneamino)-propyl]-piperazine (L) (0.1 mmol, 0.0747 g) dissolved in 10 ml tetrahydrofurane (THF). The mixture was refluxed for 4h, when a mauve precipitate was formed. The solid formed was filtered, washed with tetrahydrofurane (THF) an dried at room temperature. Yield: 73 % (0.0545g).

Elem. Anal. for $[\text{CuL}'(\text{ClO}_4)]\cdot\text{ClO}_4\cdot 4\text{H}_2\text{O}$ (1) (534.84g/mol): calcd (%) C 22.44; H 6.01; N 10.45; Cu 11.86; found: C 22.46; H 6.03; N 10.48; Cu 11.88; $\Lambda_M(\text{DMF})$: 75 $[\Omega^{-1}\text{cm}^2\text{mol}^{-1}]$

UV-Vis (DMF) λ [nm]: 575 (in a $2.2\cdot 10^{-3}$ M solution of complex (1))

IR (KBr pellet) ν_{max} $[\text{cm}^{-1}]$: 3734, 3617, 3313, 3268, 2952, 2932, 2875, 1652, 1646, 1600, 1099, 1023, 914, 648, 621

$[\text{NiL}'(\text{ClO}_4)]\cdot\text{ClO}_4\cdot\text{H}_2\text{O}$ (2) A solution of $\text{Ni}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ (0.1 mmol, 0.0365g) dissolved in 5 ml tetrahydrofurane (THF) was added to a solution containing the Schiff base N, N'-bis[3(4-dodecyloxy-benzylideneamino)-propyl]-piperazine (L) (0.1 mmol, 0.0747 g) dissolved in 10 ml tetrahydrofurane (THF). The mixture was refluxed for 4h, when an orange precipitate was formed. The solid formed was filtered, washed with tetrahydrofurane (THF) and dried at room temperature. Yield: 81.7 % (0.0610g).

Elem. Anal. for $[\text{NiL}'(\text{ClO}_4)]\cdot\text{ClO}_4\cdot\text{H}_2\text{O}$ (2) (475.93 g/mol): calcd (%) C 25.22; H 5.50; N 11.76; Ni 12.31;

found: C 25.24; H 5.51; N 11.77; Ni 12.33; $\Lambda_M(\text{CH}_3\text{CN}) = 130$ $[\Omega^{-1}\text{cm}^2\text{mol}^{-1}]$

UV-Vis (CH_3CN) λ [nm]: 473, 650 (in a $2.4\cdot 10^{-3}$ M solution of complex (2))

IR (KBr pellet) ν_{max} $[\text{cm}^{-1}]$: 3735, 3614, 3297, 3175, 2950, 2927, 2880, 1652, 1646, 1602, 1268, 1142, 1108, 1087, 941, 690

3. Results and Discussion

Starting from Schiff base ligand N, N'-bis[3(4-dodecyloxy-benzylideneamino)-propyl]-piperazine (L), and metallic salts: copper(II) and nickel(II) perchlorate hexahydrate, the formation of a rigid core by complexation of the aminic groups failed due to the destruction of the imino bond. Thus the complexes $[\text{CuL}'(\text{ClO}_4)]\cdot\text{ClO}_4\cdot 4\text{H}_2\text{O}$ (1) and $[\text{NiL}'(\text{ClO}_4)]\cdot\text{ClO}_4\cdot\text{H}_2\text{O}$ (2) containing 1,4-Bis(3-aminopropyl)piperazine (L') were obtained.

Complex compounds and related reactions are sketched in Figure 1.

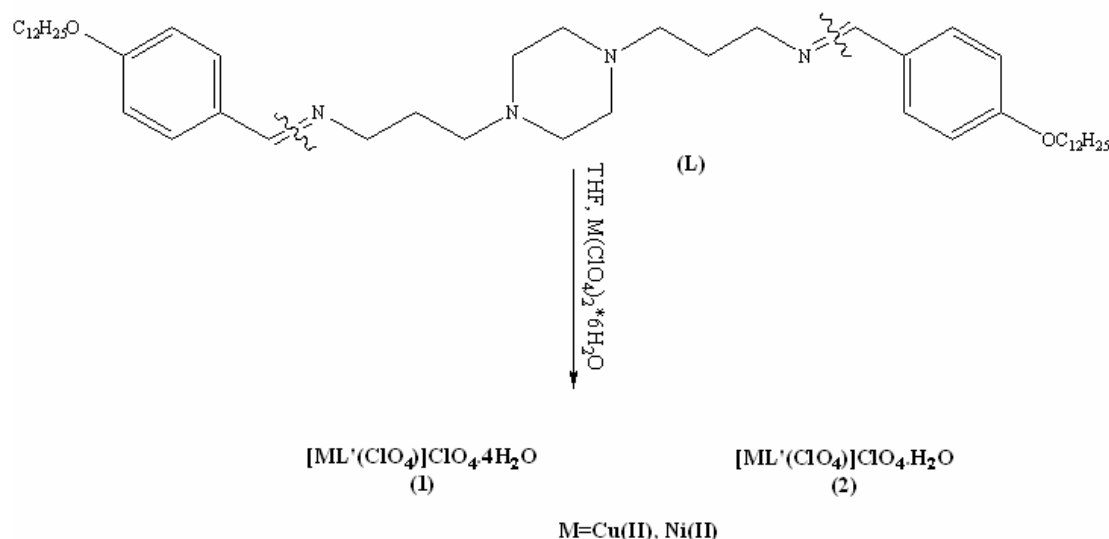


Figure 1. Reagents and conditions: (1) N, N'-bis[3(4-dodecyloxy-benzylideneamino)-propyl]-piperazine (L), tetrahydrofurane solution (THF), $\text{Cu}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$, 1,4-Bis(3-aminopropyl)piperazine (L')

3.1. Molar conductivity measurement

The molar conductivities (Λ_M) of 10^{-3} M solutions of complexes (1) and (2) were measured at 20°C in DMF and CH_3CN which demonstrates their behaviour as 1:1 electrolytes [10].

3.2. Electronic spectra

The electronic spectra of the complexes have been recorded with the aim to obtain informations regarding the geometry of the metal ions. The electronic spectrum of the complex (1) shows a broad band centered at 575 nm

assigned to the spin allowed transition ${}^2\text{T}_2 \rightarrow {}^2\text{E}$ which denotes the square-pyramidal geometry around copper (II) [8, 11-13]. For the compound (2) it was observed two absorption bands at 473 and 650nm, respectively, that suggest the octahedral geometry around nickel (II). These bands are assigned to the transition ${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{A}_{2g}$, ${}^3\text{T}_{1g}(\text{F}) \leftarrow {}^3\text{A}_{2g}$ [13, 16].

3.3. Infrared spectra

The broad bands at 3734, 3617 cm^{-1} (for 1) and 3735, 3614 cm^{-1} (for 2) in the spectra of complexes (1) and (2)

can be attributed to stretching vibrations (ν_{OH}) of water molecules [14].

Examination of the infrared spectra of the complexes (1) and (2) shows the characteristic bands of the piperazine ligand. However some changes demonstrate the coordination to the metal ion. Thus, in the spectrum of complex (1), the bands assigned to the $\nu(\text{NH})$ stretching asymmetric and symmetric vibrations of NH_2 group, are shifted towards lower frequencies at 3313 and 3268 cm^{-1} , compared to the free ligand (3369 and 3283 cm^{-1}).

In the infrared spectrum of complex (2) can be also observed the $\nu(\text{NH})$ bands shifted towards lower frequencies, namely at 3297, 3175 cm^{-1} [14, 17]. The shift of these bands towards lower frequencies compared to that of the free ligand, indicates their involvement in coordination of the metal center. The bands attributable to $\nu(\text{C-H})$ of N-CH_2 modes of the piperazinic moiety disappear, in the case of both the complexes (1) and (2) suggesting the involvement of piperazine nitrogen atoms in coordination of the metal ion, when acts as a tetradentate ligand and adopts a *bath* conformation [14]. The relatively weak bands around 3000 cm^{-1} observed in the spectra of complexes (1) and (2) are assigned to the $\nu(\text{CH}_2)$ mode of the propylene groups.

The metal-nitrogen vibrations can be assigned at 648 cm^{-1} and 690 cm^{-1} , respectively, for complexes 1 and 2 [15].

The strong absorption bands at 1099, 1023, 914 cm^{-1} and 621 cm^{-1} are attributable for monodentate and ionic perchlorate groups, for complex (1). In the case of complex (2) the bands attributable for bidentate and ionic perchlorate can be observed at 1268, 1142, 1087, 941 cm^{-1} and 1108 cm^{-1} [14-16].

4. Conclusions

The present study shows that the metal ions nature is not responsible for the hydrolytic cleavage of the Schiff base N, N' -bis[3(4-dodecyloxy-benzylideneamino)-propyl]-piperazine. We assume that the presence of the trace amounts of water arising from copper (II) and nickel (II) perchlorate hexahydrate destabilises the imino

bond with the formation of the complexes $[\text{CuL}'(\text{ClO}_4)]\cdot\text{ClO}_4\cdot 4\text{H}_2\text{O}$ (1) and $[\text{NiL}'(\text{ClO}_4)]\cdot\text{ClO}_4\cdot\text{H}_2\text{O}$ (2) where $\text{L}' = 1,4\text{-Bis}(3\text{-aminopropyl})\text{piperazine}$ [6, 7, 18]. Their physico-chemical characterization, indicates the obtaining of two new mononuclear complexes. In both cases, the ligand L' acts as a tetradentate, through N_2 set of donor atoms of piperazine and one or two oxygen atoms from perchlorate group, when adopts a *bath* conformation.

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