



# A selective naked-eye chemosensor derived from 2-methoxybenzylamine and 2,3-dihydroxybenzaldehyde - synthesis, spectral characterization and electrochemistry of its bis-bidentates Schiff bases metal complexes



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## ABSTRACT

A new colorimetric receptor **HL**, acting as a bidentate Schiff base ligand, has been synthesized by condensation of 2-methoxybenzylamine on 2,3-dihydroxybenzaldehyde in a methanolic solution. Interestingly, this chelating agent can selectively detect  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions with a simple and an easy-to-make, well defined naked-eye visible color changes in two different solvents like acetonitrile and methanol. This bidentate ligand coordinates three metal ions of Co(II), Cu(II) and Fe(II) via nitrogen and oxygen atoms. The molecular structures of the synthesized compounds were elucidated by various physicochemical properties such as the elemental analysis, FT-IR, HNMR, UV-Vis and the Mass spectrometry. The resulting general formulae  $[\text{M}(\text{L})_2 \cdot \text{H}_2\text{O}]$  ( $\text{M}(\text{II}) = \text{Cu}, \text{Fe}, \text{Co}$ ) are proposed as mononuclear complexes. The solvatochromism properties of these compounds were studied with their absorption spectra using different solvents as methanol (**MeOH**), acetonitrile (**AN**), tetrahydrofuran (**THF**), dimethylformamid (**DMF**), dimethylsulfoxid (**DMSO**) and dichloromethane (**DC**). The Electrochemical behavior of copper complex was explored in DMF solutions by cyclic voltammetry (**CV**) with two working electrodes: glassy carbon (**GC**) and platinum electrode (**Pt**). This study reveals that copper complex shows successively two redox systems as  $\text{Cu}^{\text{III/II}}$  and  $\text{Cu}^{\text{II/I}}$ . The  $\text{Fe}^{\text{III/II}}$  and  $\text{Co}^{\text{III/I}}$  redox systems have also been studied in DMF and DMSO media.

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## 1. Introduction

The Schiff base ligands proved to be an important class of the chelating agents as far as the coordination chemistry is concerned, and this is mainly due to their easy synthesis, electronic properties and the tendency to form stable complexes with most of the transition metals [1–4]. These properties attract a large number of applications like those involved in the analytical chemistry field [5]. They can even serve as electrochemical catalysts [6] either in homogeneous or heterogeneous catalysis for alkanes oxidation, alkenes epoxidation [7], sensors [8] and corrosions inhibitors [9] as well.

Colorimetric sensors have attracted much attention to allow a “naked-eye” detection in an uncomplicated and an inexpensive manner

so as to offer qualitative and quantitative information. During the last couple of decades, there have been numerous works which focused on the design and the synthesis of the artificial receptors based on this kind of Schiff base chelates [10]. The aim was to detect selectively and efficiently diverse cations or anions [11,12]. In fact, the colorimetric chemosensors of cations can be generated basically through the right combination of a receptor and a chromophore. Consequently, these chemosensors have been widely investigated for their fundamental role in environmental, analytical and biological applications [13–15]. As a consequence, the designing and the synthesizing chemosensors that can detect certain metal ions such as the bivalent ones:  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$  [16–21], or the trivalent cations such as  $\text{Fe}^{3+}$ ,  $\text{Mn}^{3+}$  and  $\text{Al}^{3+}$  [22,23] with high selectivity and sensitivity were induced by most studies in the literature. This research attracts both university and industry researchers.

The coordination chemistry of metal(II) complexes via the use of the bidentate Schiff base ligands has been thoroughly investigated during the last years, especially in the oxidation reactions [24]. It has always

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been a subject of considerable attention due to its various properties. A large number of copper complexes with such ligands has been prepared and characterized for their involvement in several applications [25].

Therefore, in the present work, we report the synthesis and isolation of novel mononuclear metal(II) complexes that were derived from a bidentate Schiff base ligand. These compounds have been characterized by  $^1\text{H}$  NMR, FT-IR, a Mass spectrometry, an Elemental analysis and an UV-Vis spectrophotometry. Moreover, the colorimetric sensing characteristics of the corresponding synthesized receptor (**HL**) were investigated through the use of an UV-Vis absorption spectrophotometry in organic solutions at the expense of the presence of different metal ions such as  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$ . Furthermore, the cyclic voltammetric behavior has also been reported and discussed using two different working electrodes in two different media. The synthetic route of the Schiff base precursor (**HL**) and its Cu(II), Fe(II) and Co(II) Schiff base complexes is outlined in the following Scheme 1.

## 2. Experimental

### 2.1. Physicochemical Characterization

All solvents and chemicals are of reagent grade and were used as received. The solutions of metal ions were prepared from their salts  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{FeCl}_3$ ,  $\text{CdCl}_2$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{ZnCl}_2$ ,  $\text{Al}(\text{NO}_3)_3$ ,  $\text{BaCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{LiCl}$ ,  $\text{KCl}$ ,  $\text{NaCl}$ ,  $\text{PbCl}_2$ .

The  $^1\text{H}$  NMR spectra were recorded on a Bruker AC300 Y 400 at 25 °C using tetramethylsilane (TMS) as an internal reference. All chemical shifts  $^1\text{H}$  are given in ppm using deuterated DMSO- $d_6$  as solvent. While the FT-IR spectra were recorded on a Perkin Elmer 1000-FT-IR Spectrometer using KBr disks and electronic spectra (UV-Vis) were obtained with a Unicam UV-300 Spectrophotometer having 1 cm path length cell. The Elemental analysis was performed using a (C, N, H, S) LECO analyser (Micro TruSpec model). As for the experimental description of mass spectrometry, we have employed a HPLC Agilent 1100 series coupled to UV-Vis and MS with ionic trap detector (Agilent model 1100 Series LC/MSD Trap SL).

The Cyclic voltammetry was performed on Voltalab 40, Potentiostat-Galvanostat equipment. All measurements were carried out in a 5cm<sup>3</sup> Metrohm single compartment cell with three conventional electrodes. The employed working electrodes are GC (3 mm) or Pt (2 mm). They were polished with a diamond paste and thoroughly rinsed with large amounts of acetone and finally with acetonitrile. The counter electrode was a platinum (Pt) wire and the potentials refer to the Saturated Calomel Electrode (SCE). DMF and DMSO solutions were used with  $10^{-3}$  M of Schiff base metal complexes and their ionic

strength was maintained at  $10^{-1}$  M with tetra-*n*-butylammonium perchlorate (TBAP).

### 2.2. Synthesis of the Schiff Base Receptor Ligand (HL)

138 mg of 2,3-dihydroxybenzaldehyde (1 mmol) were dissolved in methanol (10 mL) and stirred at a room temperature. Then, this solution was added drop-wise to 10 mL of methanol containing 137 mg (1 mmol) of 2-methoxybenzylamine. This mixture is held under stirring until it turns into yellow color which indicates that the Schiff base is formed. The solution was stirred again for 2 h at a room temperature producing a yellow to an orange colored precipitate. The obtained precipitate was filtered off, washed with cold methanol and diethylether, and then dried under vacuum. The expected compound **HL** was obtained with yield of 90%.

**HL**:  $^1\text{H}$  NMR (DMSO- $d_6$ ,  $\delta$ , ppm): 8.85 and 13.75 (s, 2H, O—H), 8.59 (s, 1H, N=CH), 6.50–7.50 (m, 7H, Ar—H), 4.76 (s, 2H, Ph—CH<sub>2</sub>), 3.83 (s, 3H, methoxy O—CH<sub>3</sub>).  $\text{C}_{15}\text{H}_{15}\text{NO}_3$  (**HL**): calcd. C 70.02, H 5.88, N 5.44; found C 69.82, H 5.55, N 5.45. FT-IR (KBr pellet,  $\text{cm}^{-1}$ ): 3350–3650 (br, O—H, phenolic), 2800–3100 (w, C—H aliphatic and aromatic), 1644 (s, C=N), 1240 (m, C—O). (MS-LC): ( $m/z$ ) 257.2 ( $[\text{HL}]^+$ ).

### 2.3. Synthesis of the Cobalt(II)-, Copper(II)- and Iron(II)-Schiff Base Complexes

Cobalt(II), copper(II) and iron(II) complexes were prepared by the same method. To a hot solution of 1 mmol of the appropriate acetate metal salt in 10 mL of methanol was slowly added under stirring to a solution of 2 mmol of **HL** dissolved 10 mL of methanol. This mixture was heated to reflux with stirring for 4 h. The resulting metal (II) complex was isolated by a simple addition of petroleum ether that led to the formation of precipitate which can easily be recovered by filtration. After that, this complex was washed with small portions of cold methanol, and then with diethylether. As a result, the novel bis-bidentate Schiff base metal(II) complexes with their general formulae  $[\text{M}^{\text{II}}(\text{L})_2 \cdot \text{H}_2\text{O}]$  and yields ranging from 75 to 85% were obtained. (L = bidentate Schiff base ligand) (Scheme 1).

$\text{Co}^{\text{II}}(\text{L})_2 \cdot \text{H}_2\text{O}$ : Anal. Calc. for  $\text{C}_{30}\text{H}_{30}\text{N}_2\text{O}_7\text{Co}$ : C 61.21; H 5.13; N 4.75 Found: C 61.22; H 4.29; N 4.13%. FT-IR (KBr pellet,  $\text{cm}^{-1}$ ): 3300–3700 (br, O—H, phenolic), 2800–3120 (w, C—H aliphatic and aromatic), 1628 (s, C=N), 1248 (m, C—O), [510–650] (m, Co—O), [410–510] (m, Co—N). (MS-LC): ( $m/z$ ) 569.4 ( $[\text{CoL}_2]^+$ ).

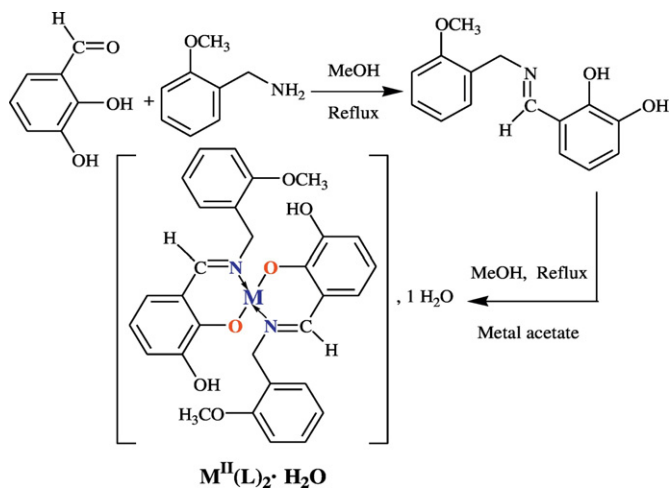
$\text{Cu}^{\text{II}}(\text{L})_2 \cdot \text{H}_2\text{O}$ : Anal. Calc. for  $\text{C}_{30}\text{H}_{30}\text{N}_2\text{O}_7\text{Cu}$ : C 60.65; H 5.09; N 4.72 Found: C 60.81; H 4.61; N 4.26%. FT-IR (KBr pellet,  $\text{cm}^{-1}$ ): 3300–3700 (br, O—H, phenolic), 2840–3100 (w, C—H aliphatic and aromatic), 1627 (s, C=N), 1248 (m, C—O), [510–610] (m, Cu—O), [405–490] (m, Cu—N). (MS-LC): ( $m/z$ ) = 576.1 ( $[\text{CuL}_2]^+$ ).

$\text{Fe}^{\text{II}}(\text{L})_2 \cdot \text{H}_2\text{O}$ : Anal. Calc. for  $\text{C}_{30}\text{H}_{30}\text{N}_2\text{O}_7\text{Fe}$ : C 61.45; H 5.16; N 4.78 Found: C 61.53; H 4.81; N 4.51%. FT-IR (KBr pellet,  $\text{cm}^{-1}$ ): 3300–3700 (br, O—H, phenolic), 2820–3100 (w, C—H aliphatic and aromatic), 1635 (s, C=N), 1256 (m, C—O), [510–590] (m, Fe—O), [400–510] (m, Fe—N). (MS-LC): ( $m/z$ ) 568.3 ( $[\text{FeL}_2]^+$ ).

## 3. Results and Discussion

### 3.1. Chemistry

The Schiff base **HL** (Scheme 1) was prepared by refluxing of equimolar amounts of 2-methoxybenzylamine and 2,3-dihydroxybenzaldehyde in methanolic solution. The resulting chelate which could be involved in the UV-Vis studies requires the knowledge of its dissolving properties in diverse solvents. Its molecular structure was obviously established by using FT-IR,  $^1\text{H}$  NMR, mass spectrometry and CHN analysis. Therefore, the synthesized Schiff base ligand appears as soluble in common organic solvents such as AN, DC, THF, DMF, DMSO and MeOH. This compound was further used in the complexation



Scheme 1. Preparation of Schiff base ligand and its metal complexes.

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