

## Research paper

# Structural characterization and electrochemical studies of Co(II), Zn(II), Ni(II) and Cu(II) Schiff base complexes derived from 2-((E)-(2-methoxyphenylimino)methyl)-4-bromophenol; Evaluation of antioxidant and antibacterial properties



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## ABSTRACT

Four transition-metal complexes [Co<sup>II</sup>(L)<sub>2</sub>] (**1**), [Zn<sup>II</sup>(L)<sub>2</sub>] (**2**), [Ni<sup>II</sup>(L)<sub>2</sub>] (**3**) and [Cu<sup>II</sup>(L)<sub>2</sub>] (**4**) have been synthesized from metal salts with tridentate Schiff base ligand (HL = 2-((E)-(2-methoxyphenylimino)methyl)-4-bromophenol) and characterized by elemental analyses, FT-IR, <sup>1</sup>H NMR, UV–Vis spectroscopy. The structures of **1** and **2** have been determined by X-ray crystallography. The geometry around the central cobalt ion is distorted octahedral. The *in vitro* antibacterial activity of the complexes against *Bacillus subtilis*, *Staphylococcus aureus*, *Enterobacter cloacae* and *Escherichia coli* and was found higher than the free ligand. Biological activity studies revealed that the antioxidant activity of the complexes was found to be enhanced in comparison with ascorbic acid. The electrochemical studies of **1**, **3** and **4** in acetonitrile solution showed that M<sup>II</sup>/M<sup>I</sup> reduction processes are electrochemically irreversible.

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## 1. Introduction

Metal complexes of Schiff-base ligands play an important role in material science and chemical research, due to their interesting properties and diverse structural aspects [1–3]. The structural variability of transition metal complexes of multidentate Schiff-base ligands with desired molecular geometry and the structure–function correlation of the resulting complexes has been the subject of intensive research recently [4–8]. Properties of these Schiff-base metal complexes depend on the nature of metal ions and ligands. Consequently, metal complexes have a variety of industrial applications in electrochemistry [9–10], catalysts [11–13], photochromic industry [14] and a wide range of biological activities [15–20]. Moreover, several studies [21,22] showed that due to the presence of a lone pair of electrons in nitrogen atom of the imine group, –C=N is of biological importance and attracts the interest of biological inorganic chemists. In addition, there have been several reports about the synthesis, crystal structure and biological evaluation of metal Schiff-base complexes with salicylaldehyde and its derivatives [23–28]. Thus, it seems worthwhile to continue to investigate this area. The present study is an extension to our work [29–31] on Schiff-base ligand through condensation of 2-methoxy aniline with 5-bromoSalicylaldehyde. We also report the synthesis of new complexes of Co(II) (**1**), Zn(II) (**2**), Ni(II) (**3**) and Cu(II) (**4**) derived from this tridentate Schiff-base ligand (Scheme 1). The complexes and ligand have been investigated by FT-IR, Visible spectra (UV–Vis) and proton nuclear magnetic resonance (<sup>1</sup>H NMR) and cyclic voltammetry (CV). Crystal structures of complexes **1** and **2** have been characterized by X-ray diffraction. The antibacterial activity against some selected bacterial strains and antioxidant properties of these metal complexes are also reported and discussed.

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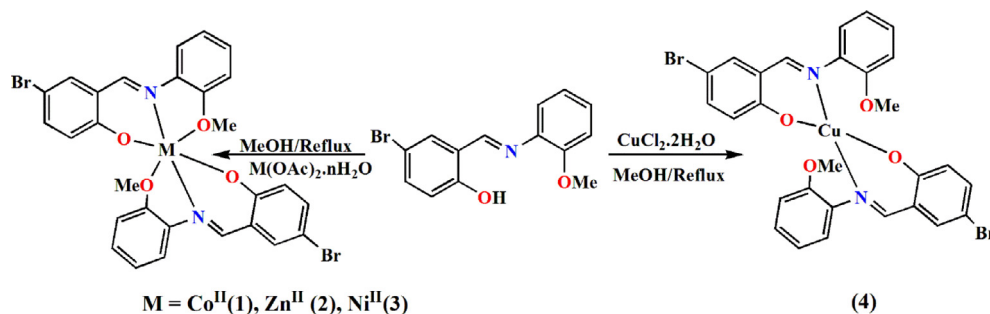
## 2. Experimental

## 2.1. Materials and instrumentations

All the chemicals and solvents used in this work were of reagent grade and used without further purification. FT-IR spectra (KBr pellets) were obtained on a FT-IR SHIMADZU (8400 s) spectrophotometer. UV–Vis spectra were recorded on a UV-1650 PC

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Scheme 1. Synthetic procedure for the preparation of complexes.

SHIMADZU spectrophotometer. The  $^1\text{H}$  NMR spectrum of the ligand was obtained on a Bruker DRX-500 NMR Spectrometer. To study the biological activity of the complexes, Stuart Shaking Incubator SI500 and Sigma-302 K Centrifuge were used. Cyclic voltammograms were recorded using a SAMA 500 Research Analyzer. Three electrodes were utilized in this system, a glassy carbon working electrode, a platinum disk auxiliary electrode and Ag wire as reference electrode. The glassy carbon working electrode (Metrohm 6.1204.110) with  $2.0 \pm 0.1$  mm diameter was manually cleaned with 1  $\mu\text{m}$  alumina polish prior to each scan. CV measurements were performed in acetonitrile with tetrabutylammonium hexafluorophosphate (TBAH) as a supporting electrolyte. The solutions were deoxygenated by purging with Ar for 5 min. All electrochemical potentials were calibrated versus  $\text{Fc}^{+/0}$  ( $E_0 = 0.4$  V versus SCE) couple under the same conditions [32]. Elemental analyses were performed by using a Perkin-Elmer 2400II CHNS-O elemental analyzer.

## 2.2. Synthesis of the Schiff-base ligand

The Schiff-base ligand HL was synthesized according to the literature procedure [33] by condensation of 5-bromosalicylaldehyde with 2-methoxyaniline (1:1 molar ratio) in 20 mL EtOH. The reaction mixture was stirred at room temperature for 3 h. An orange product was collected by filtration, washed with 10 mL absolute ethanol and dried in air. Yield: 60% m.p. 113 °C. FT-IR:  $\nu_{\text{max}}$   $\text{cm}^{-1}$  (KBr): 1616 (s, C=N), 1463, 1591 (s, C=C<sub>arom</sub>), 1284 (s, C-O), 1026 (s, C-Br). UV-Vis:  $\lambda_{\text{max}}$  (nm) ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ) ( $\text{CHCl}_3$ ): 362 (7710), 262 (6540), 245 (12,710).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz): 6.9 (m, 7H), 3.9 (s, 3H), 8.6 (s, 1H), 13.9 (s, 1H).

## 2.3. General procedure for synthesis of complexes (1–4)

To a solution of HL (2 mmol, 610 mg) in MeOH (20 ml) was added 1 mmol of appropriate metal salts ( $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (1),  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (2),  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (3) and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (4)) in MeOH (5 ml) and the mixture was refluxed for 3 h. The solid complex obtained was filtered off, washed with ethanol and then dried under vacuum. Dark red crystals of complex 1 and light yellow crystals of complex 2 suitable for X-ray crystallography were obtained by recrystallization of complexes in dichloromethane. Dark red solid product of 3 and green powder of 4 were for spectral studies were obtained.

$[\text{Co}(\text{L})_2]$  (1): Yield: 75%. m.p. 330 °C. Mol. Wt.: 666.93 Anal. Calcd. for  $\text{CoC}_{28}\text{H}_{22}\text{Br}_2\text{N}_2\text{O}_4$ : C, 50.25; H, 3.31; N, 4.19. Found: C, 50.12; H, 3.20; N, 4.13%. FT-IR:  $\nu_{\text{max}}$   $\text{cm}^{-1}$  (KBr): 1608 (s, C=N), 1494, 1514 (s, C=C<sub>arom</sub>), 1238 (s, C-O), 1018 (s, C-Br). UV-Vis:  $\lambda_{\text{max}}$ (nm) ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ) ( $\text{CHCl}_3$ ): 425 (2880), 330 (3910), 244 (10,570).

$[\text{Zn}(\text{L})_2]$  (2): Yield: 60%. m.p. 283 °C. Wt.: 671.92 Anal. Calcd. for  $\text{ZnC}_{28}\text{H}_{22}\text{Br}_2\text{N}_2\text{O}_4$ : C, 49.77; H, 3.28; N, 4.15. Found: C, 49.50; H,

3.15; N, 4.09%. FT-IR:  $\nu_{\text{max}}$   $\text{cm}^{-1}$  (KBr): 1606 (s, C=N), 1494, 1515 (s, C=C<sub>arom</sub>), 1244 (s, C-O), 1020 (s, C-Br). UV-Vis:  $\lambda_{\text{max}}$  (nm) ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ) ( $\text{CHCl}_3$ ): 410 (2220), 338 (2140), 247 (5620).  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 300 MHz): 3.4 (s, 6H), 6.70–7.3 (m, 14H), 8.2 (s, 2H).

$[\text{Ni}(\text{L})_2]$  (3): Yield: 80%. m.p. 351 °C. Wt.: 665.93 Anal. Calcd. for  $\text{NiC}_{28}\text{H}_{22}\text{Br}_2\text{N}_2\text{O}_4$ : C, 50.27; H, 3.31; N, 4.19. Found: C, 50.14; H, 3.12; N, 4.10%. FT-IR:  $\nu_{\text{max}}$   $\text{cm}^{-1}$  (KBr): 1610 (s, C=N), 1492, 1510 (s, C=C<sub>arom</sub>), 1238 (s, C-O), 1016 (s, C-Br). UV-Vis:  $\lambda_{\text{max}}$  (nm) ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ) ( $\text{CHCl}_3$ ): 446 (4870), 327 (4990), 251 (9800).

$[\text{Cu}(\text{L})_2]$  (4): Yield: 68%. m.p. 347 °C. Wt.: 670.92 Anal. Calcd. for  $\text{CuC}_{28}\text{H}_{22}\text{Br}_2\text{N}_2\text{O}_4$ : C, 49.91; H, 3.29; N, 4.16. Found: C, 49.37; H, 3.20; N, 4.12%. FT-IR:  $\nu_{\text{max}}$   $\text{cm}^{-1}$  (KBr): 1610 (s, C=N), 1463, 1591 (s, C=C<sub>arom</sub>), 1238 (s, C-O), 1016 (s, C-Br). UV-Vis:  $\lambda_{\text{max}}$  (nm) ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ) ( $\text{CHCl}_3$ ): 440 (2600), 329 (3640), 267 (2440).

## 2.4. X-ray crystallography

Diffraction data were collected at room temperature using  $\omega$ -scan technique on Agilent Technologies Xcalibur four-circle diffractometers with Eos CCD detector and graphite-monochromated  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71069$  Å). The data were corrected for Lorentz-polarization and absorption effects [34]. Precise unit-cell parameters were determined by a least-squares fit of 1021 (1) and 2261 (2) reflections of the highest intensity chosen from the whole experiment. The structures were solved with SIR92 [35] and refined with the fulmatrix least squares procedure on  $F^2$  by SHELXL-2013 [36]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and refined as 'riding model' with isotropic displacement parameters set at 1.2 (1.5 for methyl or hydroxyl groups) times  $U_{\text{eq}}$  of appropriate carrier atoms. In 2 weak restraints were applied to the shape of two atoms, O1 and C1A (ISOR). Non-standard space group I2/a was chosen as the transformation to more common C2/c results in  $\beta$  angles above 120°. Table 1 lists the relevant experimental data and refinement details.

## 2.5. Biological studies

### 2.5.1. Bacterial strains

The 1–4 complexes were tested against four pathogenic representatives, *Bacillus subtilis* (*B. subtilis*; PTCC No: 1023; ATCC 6633); *Staphylococcus aureus* (*S. aureus*; PTCC No: 1431; ATCC 25923) as Gram-positive and *Enterobacter cloacae* (*E. cloacae*; PTCC No: 1798; ATCC 13047) and *Escherichia coli* (*E. coli*; PTCC No: 1399; TCC 25922) as Gram negative. The organisms were purchased from Iranian Research Organization for Science and Technology (IROST).

### 2.5.2. Determination of minimum inhibitory concentrations (MIC)

The bacteriostatic activity studies of the active compounds were evaluated by three-fold serial dilution technique. The lowest concentration of an antimicrobial agent that prevents the appear-

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