

Synthesis and spectroscopic studies of some transition metal complexes of a novel Schiff base ligands derived from 5-phenylazo-salicylaldehyde and *o*-amino benzoic acid

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Abstract

Cu(II), Mn(II), Ni(II), and Zn(II) metal complexes with novel heterocyclic Schiff base derived from 5-phenyl azo-salicylaldehyde and *o*-amino benzoic acid have been synthesized and characterized on the basis of elemental analyses, electronic, IR, and ¹H NMR spectra, and also by aid of scanning electron microscopy (SEM), X-ray powder diffraction, molar ratio measurements, molar conductivity measurements, and thermogravimetric analyses. It has been found that the Schiff base behaves as neutral tridentate (ONO) ligand forming chelates with 1:1 (metal:ligand) stoichiometry.

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1. Introduction

During the past two decades, considerable attention has been paid to the chemistry of the transition metal complexes of Schiff bases containing nitrogen and other donors [1–4]. The ligands, derived by the condensation of a primary amine and an active carbonyl group, contain the azomethine group [5,6]. Schiff bases are a class of important compounds in medicinal and pharmaceutical field. They show biological activities including antibacterial [7–10], antifungal [11,12], anticancer [13–15], and herbicidal [16] activities. Furthermore, Schiff bases are utilized as starting material in the synthesis of industrial [17] and biological compounds such as β -lactams [18]. Azo compounds have been used for a long time as dyes in industry [19]. In addition, azo compounds are used in analytical chemistry as indicators in pH, redox, or complexometric titration [20,21]. Some azo compounds have shown a good antibacterial activity [22,23]. The existence of an azo moiety in different types of compounds has caused them to show pesticidal activity [16]. Based on the mentioned properties for Schiff bases and azo compounds, we

reported herein the syntheses and spectroscopic studies as well as thermal investigation of a novel Schiff base derivatives ligand (H₂L) (L₁ = 2-[5-phenyl azo-2-hydroxy benzylidene amino]-benzoic acid; L₂ = 2-[5-(2-chlorophenyl) azo-2-hydroxy benzylidene amino] benzoic acid; L₃ = 2-[5-(4-methyl phenyl) azo-2-hydroxy benzylidene amino] benzoic acid) and its Cu(II), Mn(II), Ni(II), and Zn(II) complexes. Mass spectra and ¹H NMR spectra were obtained to determine the structure of the ligands HL₁, HL₂, and HL₃.

2. Experimental

2.1. Materials

o-Chloroaniline, *o*-amino benzoic acid, *p*-toluidine, salicylaldehyde, aniline, metal salts (Cu(CH₃COO)₂·3H₂O, NiSO₄·7H₂O, MnSO₄·4H₂O, and ZnSO₄·7H₂O), and other chemicals were obtained from Porlabo (reagent grade).

2.2. Synthesis of the azo compounds

Aniline (4.65 ml, 50 mmol), *o*-chloroaniline (6.40 ml, 50 mmol), or *p*-toluidine (5.35 g, 50 mmol) was mixed with hydrochloric acid (37%, 6.0 ml, 40 mmol) in distilled water

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(30 ml) and diazotized below 5 °C with sodium nitrite (40.0 mmol, 2.8 g) in distilled water (30 ml). The diazotized aniline, *o*-chloroaniline, or *p*-toluidine compounds were coupled with salicylaldehyde in alkaline media below 5 °C. The pH value during the coupling was kept fixed between 7 and 9. Coupling to the salicylaldehyde occurred in basic media at the *para* position to the hydroxyl group (Scheme 1) [24].

All diazo compounds were recrystallized several times from ethyl alcohol (95%) and the addition of hydrochloric acid to pH 3. All organic impurities were then extracted by washing with small portion of diethyl ether. The precipitated compounds were dried under vacuum at 70 °C. The other, all diazo compounds (L₂ and L₃) were synthesized in the same manner. The purity of all diazo compounds was evaluated by thin layer chromatography.

2.3. Synthesis of the Schiff base ligand

The Schiff base ligands were synthesized according to the known condensation method [25]. The methanol solution (50 ml) of *o*-amino benzoic acid (6.85 g, 50 mmol) was mixed with a solution of the derivatives of 5-phenyl azo-salicylaldehyde (11.3 g, 50 mmol, L₁; 13.02 g, 50 mmol, L₂; 12.0 g, 50 mmol, L₃) in water (100 ml). The mixture was refluxed and stirred magnetically for 2 h at 70 °C on a hot plate. After cooling, the

solution of the Schiff base was filtered, and the solid was washed several times with methanol. All organic impurities were then extracted by washing with small portions of diethyl ether. The ligands were dried in vacuo over calcium chloride, and were recrystallized several times from ethyl alcohol. The purity of the ligands was evaluated by thin layer chromatography. Elemental analysis CHN, IR, UV–vis, mass, and ¹H NMR spectra confirm the composition of the ligands. The formulas of the azo-linked Schiff base ligands are given in Scheme 1.

2.4. Synthesis of metal complexes

All of the complexes were synthesized by adding of the appropriate metal salts (1.0 mmol, in 20 ml ethyl alcohol–water (1:1)) to a hot solution of the ligands (1.0 mmol, in 30 ml ethyl alcohol (95%)). The pH was adjusted to 6.00–7.00 using alcoholic sodium hydroxide (0.01 M). The resulting solutions were stirred and heated on a hot plate at 70 °C for 30 min. The volume of the obtained solution was reduced to one-half by evaporation. One day later, the colored solid of the complexes formed was filtered, the solids washed with ethanol and diethyl ether, and finally dried under vacuum. The synthesized complexes were recrystallized from ethanol–water (1:1). The purity of all complexes was evaluated by thin layer chromatography. All complexes were prepared by the same method and isolated as powdered material. Elemental analysis CHN, IR, mass spectra, UV–vis, ¹H NMR, XRD, SEM, and thermogravimetric analyses as well as atomic absorption spectra confirmed the composition of metal complexes.

2.5. Apparatus and experimental conditions

2.5.1. Elemental analysis and metal percentage

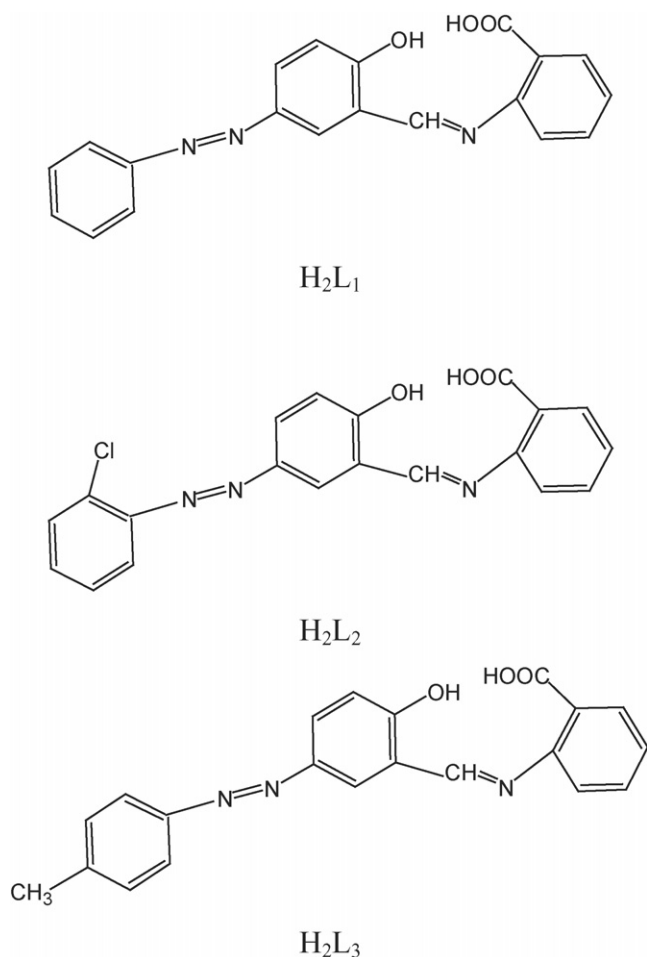
Elemental analyses (C, H, and N) were performed using a Perkin-Elmer CHN 2400 elemental analyzer. Percentages of the metal ions of the complexes were determined using PYE-UNICAM SP 1900 atomic absorption spectrophotometer supplied with the corresponding lamp used for this purpose.

2.5.2. Infrared spectra

IR spectra (4000–400 cm⁻¹) were recorded as KBr pellets on Perkin-Elmer spectrum RXI FT-IR system spectrophotometer.

2.5.3. Electronic spectra

UV spectra were measured with a Jenway 6405 spectrophotometer, using 1 cm Quartz cell, slit fixed at 2 nm. The range of wavelength was from 200 to 800 nm. The concentrations of ligands (H₂L₁, H₂L₂, and H₂L₃) were 5 × 10⁻⁴ mol/l (pH 7), each of these ligands was added into five 5 ml cuvettes, each containing 1 ml of this solution, then metal ions (Cu(II), Mn(II), Ni(II), or Zn(II)) solutions of 5 × 10⁻⁴ mol/l (regulated at pH 7) from 0 to 4.00 ml were added into cuvettes, respectively, and diluted to 5 ml with ethanol (95%). The final concentration of ligands was 10⁻⁴ mol/l in each cuvette, the final concentrations of metal ions were 0.00, 0.25 × 10⁻⁴, 0.50 × 10⁻⁴, 0.75 × 10⁻⁴, 1.00 × 10⁻⁴, 1.50 × 10⁻⁴, 2.00 × 10⁻⁴, 2.50 × 10⁻⁴, 3.00 × 10⁻⁴, 3.50 × 10⁻⁴, and 4.00 × 10⁻⁴ mol/l. Until equilibrium was reached, each UV absorption was recorded.



Scheme 1. Azo-linked Schiff base ligands.

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