

Synthesis, Characterization, and Spectroscopic Properties of a Symmetrical Schiff Base Ligand and its Bimetallic Complexes

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This article presents the synthesis of new Schiff base ligand and preparation of its transition metal complexes with copper (II), nickel (II), zinc (II), and cobalt (II). Furthermore, absorption and fluorescence properties of ligand and its metal complexes are investigated. The effect of the solvents, such as N,Ndimethylformamide (DMF), dimethyl sulfoxide (DMSO), ethanol, methanol, 1,4-dioxane on fluorescence properties of metal complexes, are performed and obtained results are summarized. All of the structures were characterized by using spectroscopic techniques.

Keywords bimetallic complex, bissalophen, Schiff base, tetradentate ligand

INTRODUCTION

Schiff bases are an important class of ligands in coordination chemistry and find extensive application in different fields.^[1–5] Complexes of transition and non-transition metals with Schiff bases are investigated extensively for many years because the complexes are important in chemical applications.^[6,7] These metal Schiff-base complexes are frequently used as model compounds for metallo-proteins, and have interesting catalytic, magnetic, spectral, chemical, electrochemical, and non-liner optical properties that are often strongly dependent on the detailed ligand structure.^[6,8] Also, metal ions using the complexation reaction have a important role in biological processes such as the functions of enzymes, the transport of oxygen, the health of teeth, and diseases such as Alzheimer's, Parkinson's, Huntington's, and Wilson's diseases.^[9,10] Zinc(II) ion, the second most abundant transition metal in the human body, plays many roles in numerous cellular functions such as the regulation of gene expression, apoptosis, co-factors in metalloenzyme catalysis, anorexia, prevention of prematurely pregnancy, and neurotransmission in biological systems.^[11,12] The deficiency of copper, a trace mineral that is essential to good health, can cause growth retardation, anemia, osteoporosis, osteoarthritis, rheumatoid arthritis, and pancytopenia in humans.^[12] Cobalt and nickel share right/left-sided cell receptors and are considered essential to human health, too. While a cobalt and vitamin B₁₂ relationship is well documented, a similar, less documented affiliation applies to nickel and vitamin C.[12] The fluorescence properties of the Schiff-base ligands with various metal ions along with zinc ion, copper ion, cobalt ion, and nickel ion are documented in the literature.^[13-15] In consideration of the reported fluorescence properties for salen and its transition metal complexes, the authors report synthesis, characterization, and spectroscopic properties of new salen type Schiff base and its transition metal complexes with copper (II), nickel (II), zinc (II), and cobalt (II).

EXPERIMENTAL

All of the reagents used in this study were obtained from Merck or Fluka and used without further purification. Dry THF was distilled from the ketyl prepared from sodium and benzophenone. Thin layer chromatography (TLC) was performed using silica gel on glass TLC plates (silica gel H, type 60, Merck). Generally solvents were dried by storing them over molecular sieves (Aldrich; 4 Å, 8-12 mesh). Melting points were determined on a Gallenkamp apparatus. ¹H and ¹³C NMR spectra were obtained using a Varian 400 MHz spectrometer operating at 400 MHz at room temperature using DMSO-d₆ as solvent. IR spectra were recorded on a Perkin-Elmer 1605 FTIR spectrometer as KBr pellets. UV-Vis absorption and fluorescence spectra were recorded on a Shimadzu UV-1700 spectrometer and on a Perkin-Elmer LS-55 spectrometer, respectively. Elemental analyses were performed using a Leco CHNS-932 analyzer. Conductivities were measured in DMF using a LF 330 / SET conductivity meter and performed at

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 24° C. Magnetic moments were measured by the Gouy method by using Hg[Co(SCN)₄] as calibrant.

Synthesis and Characterization of the Schiff Base Ligand and its Bimetallic Complexes

The Schiff base ligand was prepared by adding dropwise a solution of 3,3'-diaminobenzidine (0.214 g, 1 mmol) in THF (10 mL) to a THF solution (20 mL) of 2,4-dihydroxybenzaldehyde (0.58 g, 4.2 mmol) and one drop of glacial acetic acid (catalytic amount, not necessary) under stirring at room temperature. The resultant reaction mixture was then refluxed for 9 h with an exclusion of moisture. The resulting dark orange solution was cooled to room temperature and evaporated to dryness. The solid was recrystallized from THF and dried in vacuo. Yield: 90% of orange crystals. ¹H NMR (400 MHz, DMSO-d₆): δ 13.50 (s, 4H, OH), 10.25 (s, 4H, OH), 8.85 (s, 4H, CH = N), 7.35–7.65 (m, 8H, ArH), 6.20–6.35 (m, 10H, ArH); ¹³C NMR (400 MHz, DMSO-d₆): δ 163.9, 159.6, 147.8, 141.9, 137.1, 130.5, 127.1, 124.5, 122.2, 113.0, 109.9, 101.5. FT-IR (KBr pellet, ν (cm⁻¹)): 3400, (OH), 3100, 3050 (C-H_{ar}), 1645 (C = N), 1600, 1550, 1480 (C = C). MS (FAB), m/z: 695 [MH⁺, [C₄₀H₃₁N₄O₈]⁺,%40]. Anal. calc.: C₄₀H₃₀N₄O₈. C, 69.16; H, 4.35; N, 8.07%. Found: C, 69.13; H, 4.31; N, 8.13%.

Preparation of Bimetallic Complexes

All of the transition metal complexes were prepared as follows. To a solution of 3,3'-diaminobenzidine (0.107 g, 0.5 mmol) and 2,4-dihydroxybenzaldehyde (0.29 g, 2.1 mmol) in THF (20 mL) was added dropwise a solution of the corresponding metal salts The metal complexes were prepared by treatment of ligand with appropriate metal salts such as Cu(II), Ni(II), Zn(II), and Co(II) chlorides (2.3 mmol) in THF (10 mL). The suspension obtained was refluxed for 9 h, and then the solvent was partially evaporated. The resulting precipitate was filtered, washed several times with methanol, and then dried *in vacuo* to yield the crude product.

RESULTS AND DISCUSSION

In this article, we describe the synthesis of Schiff base ligand **3** by the reaction of 3,3'-diaminobenzidine **1** with 2,4dihydroxybenzaldehyde **2** in boiling THF and the preparation of its bimetallic complexes with copper (II), nickel (II), zinc (II), and cobalt (II). The chemical equations concerning the formation of the Schiff base and the complexes represented as follows (Scheme 1 and 2):

The molecular structure of novel ligand **3** and its complexes were characterized by FT-IR, UV-vis, ¹H NMR spectra, magnetic susceptibility measurements, and elemental analysis. Table 1 shows the analytical and physical data for the ligand **3** and its metal complexes. The IR spectral data of the ligand **3** and metal complexes are listed in Table 2.



SCH. 1. Synthesis of binucleating tetradentate Schiff base ligand (i: THF, reflux, 9 h).

FT-Infrared Spectra

Significant frequencies were selected by comparing the IR spectra of the free ligand **3** and its metal complexes. Since there are no C = O and NH₂ absorption in the IR spectra of the ligand **3**, these peaks indicate the formation of the expected compound. In the IR spectra of the Schiff base ligand around 2700–2565 cm⁻¹ range, the ligand exhibit broad medium intensity bands that are assigned the intermolecular H-bonding vibrations (O-H…N). This situation is common for aromatic azomethine compounds containing *o*-OH groups.^[16] In the IR spectra of the bimetallic complexes, these bands disappear thoroughly. The infrared spectrum of the Schiff base exhibits a band at 1645 cm⁻¹ assignable to ν (C = N) of the azomethine. In the



SCH. 2. Structure of symmetric bimetallic salphen complexes (M: Cu, Ni, Zn or Co).

Compounds	Empirical formula	M.S. (FAB) m/z	Color	M.p. (°C)	Yield (%)	Found (calcd)%		
						С	Н	N
Salphen	C ₄₀ H ₃₀ N ₄ O ₈	695 [MH ⁺ ,%40]	Orange	155–156	90	69.13 (69.16)	4.31 (4.35)	8.13 (8.07)
Bis[Cu-(salphen)]	$C_{40}H_{26}N_4O_8Cu_2\\$	818 [MH ⁺ ,%55]	Dark Green	300 ^d >	40	58.57 (58.46)	3.59 (3.68)	6.89 (6.82)
Bis[Ni-(salphen)]	$C_{40}H_{26}N_4O_8Ni_2\\$	808 [MH ⁺ ,%60]	Dark Green	300 ^d >	33	59.05 (59.16)	3.69 (3.72)	6.94 (6.90)
Bis[Zn-(salphen)]	$C_{40}H_{26}N_4O_8Zn_2\\$	821 [MH ⁺ ,%35]	Pale Brown	300 ^d >	30	58.27 (58.20)	3.77 (3.66)	6.85 (6.79)
Bis[Co-(salphen)]	$C_{40}H_{26}N_4O_8Co_2{\cdot}2H_2O$	844 [MH ⁺ ,%55]	Dark Brown	300 ^d >	38	54.49 (54.56)	3.77 (3.89)	6.46 (6.36)

 TABLE 1

 Some analytical data and physical properties of newly synthesized ligand 3 and its metal complexes

^dDecomposition points of the corresponding molecule.

IR spectra of the bimetallic complexes, this band shifts to lower frequencies and, at the same time, its intensity is lowered. This situation indicates that the imine nitrogen must be coordinated to the metal ion. Additionally, the characteristic carbonyl peak is not seen around 1700 cm⁻¹ in the IR spectra of the free ligand. A broad band in the 3430-3435 cm⁻¹ region indicating the presence of water molecules is observed in the spectra of the Co (II) complex. This was also confirmed by elemental analysis of Co (II) complex. All of these data support the proposed structures of the complexes and free ligand. In the IR spectra of the free ligand and its complexes, the bands at 1110 cm^{-1} and 1210–1220 cm⁻¹ can be attributed to C-N and C-O bonds, respectively. In the free ligand 3, a strong band at 1210 cm^{-1} due to C–O (phenolic) shifts to higher frequency by 20–43 cm⁻¹ in the complexes indicating coordination of the phenolic oxygen atom to the metal ion. The practically unchanged p(O-H)at 3400–3480 cm⁻¹ reveals that this group does not coordinate to metal atoms by oxygen atoms.^[17] The appearance of new bands at 430–500 cm⁻¹ and 640–680 cm⁻¹, that attributed to $\nu_{(M-N)}$ and $\nu_{(M-O)}$ vibrations supporting the participation of the nitrogen atom of the azomethine group and oxygen atom of the phenolic OH (*orto* position) group of the ligand in the complexation with metal ions. The ratios of the ligand to metal (M/L = 2:1) are founded by means of both UV spectra^[18] (Figures 1 and 2) and elemental analyses.

The elemental analysis data of the Schiff base **3** and its complexes show the formation of 2:1 [M:L]. We found that the theoretical values are in a good agreement with the found values. The purity of the Schiff base and its complexes are assured by the elemental analyses and TLC techniques.

Magnetic Measurements and Mass Spectra

The magnetic measurements of the complexes are measured at room temperature. From magnetic measurements, copper (II), Ni (II), and Co (II) complexes are paramagnetic. The magnetic moment of cobalt (II) complex is 4.61 B.M., which suggests the high spin octahedral arrangement around the metal ion. The copper (II) complex shows a magnetic moment 1.79 B.M.

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Compounds	<i>р</i> -ОН	$C = N_{\text{imin}}$	$C = C_{Ar}$	C-H _{Ar}	Ar-O	M-N	M-O	$\mu_{\rm eff}$ (B.M.)
Salphen	3400	1645	1480 1550	3100 3050	1210	-	_	_
Bis[Cu-(salphen)]	3420	1633	1480 1549	3100 3050	1245	420	560	1.79
Bis[Ni-(salphen)]	3480	1635	1450 1580	3100 3050	1230	480	540	2.83
Bis[Zn-(salphen)]	3455	1623	1480 1550	3100 3050	1253	440	580	Diam.
Bis[Co-(salphen)]	3435 ^b	1645	1480 1550	3100 3050	1240	410	520	4.61

TABLE 2 Illustration of IR data of newly prepared ligand **3** and its metal complexes (ν , cm⁻¹)

^bbroad.





FIG. 1. Determination of metal to ligand ratio for Ni(II) and Co(II) by use of absorbance values.

corresponding to one unpaired electron and magnetic susceptibility of nickel (II) complex is 2.83 B.M consisting with its proposed tetrahedral configuration. Zinc (II) complex is diamagnetic as expected for the d^{10} configuration. The FAB mass spectra of Schiff base **3** and its transition metal complexes exhibit the (M⁺) peaks, which are in agreement with the estimated values for compounds. The mass spectral data for transition metal complexes are consistent with deprotonation of four of



FIG. 2. Determination of metal to ligand ratio for Cu(II) and Zn(II) by using absorbance values. (Figure is provided in color online.)

FIG. 3. Absorption spectra of the ligand and its complexes in DMF at room temperature. (Figure is provided in color online.)

the eight hydroxyl groups of the ligand **3**, giving neutral complexes (Scheme 2).

¹H and ¹³C NMR Spectra

¹H NMR spectrum of the free ligand **3** clearly demonstrates the presence of a (CH = N) environment at 8.80-8.85 ppm, which also indicates the occurrence of the condensation reaction. The ¹H NMR spectra of **3** exhibits the absorption of the phenolic hydrogens at low field, 13.50 ppm, which shows that they are very acidic and the presence of intramolecular hydrogen bonding. The absence of this peak in the zinc complex indicates loss of OH proton due to complexation. Comparing the azomethine proton signal of free ligand 3 and Zn(II) complex, this peak is shifted downfield in the Zn complex suggesting deshielding of the azomethine group due to coordination with zinc. There is no appreciable change in the other proton signals of this complex.^[19,20] Furthermore, the appearance of a new signal at 10.25 ppm may be assigned to the existence of -OH group (para position) of the ligand 3, and aromatic C-H protons are observed at 6.20–7.65 ppm. In the ¹³C NMR spectra of Schiff base ligand 3, it is obvious that compound 3 possesses certain symmetry elements, and therefore the number of signals observed in the 13C NMR is lesser than the number of C atoms in the Schiff base ligand 3. Furthermore, in the ¹³C NMR for Schiff base compound 3, one signal is hidden because of the overlapped peaks. The molar conductance values of the synthesized binucleating tetradentate Schiff base bissalophen 3 and its Cu (II), Ni (II), Zn (II), and Co (II) complexes are in range from 2.5 to 33.5 Ω^{-1} cm² mol⁻¹ in DMF solutions indicating the non-electrolyte nature of these compounds. These values provide some indication to support the proposed structural conformation for complexes.

UV-visible Spectra

Electronic absorption spectral data show π - π * transitions related to benzene ring at 220–260 nm and imine π - π * transition at 332–343 nm. Comparing the free ligand 3 and its transition metal complexes, it can be seen that the imine π - π * transitions are shifted to some extent because the imine nitrogen is involved in coordination with metal ion. In the complexes, the low intensity bands around the 630-500 nm range are consistent with d \rightarrow d transitions of the metal ions and intraligand n $\rightarrow \pi^*$ transitions.^[21] At the same time, around 430–355 nm range, the more intense band for complexes may be due to the coincidence of charge transfer $d \rightarrow \pi^*$ and $L \rightarrow M$ transition.^[22] The UV-Vis spectrum of the Ni(II) and Cu(II) complexes exhibits absorption bands at 585 and 625 nm assignable to the transitions ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}(F)$ for Ni(II) attributable tetrahedral complex,^[17] and ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ for Cu(II), supporting square planar structure, which is in agreement with the measured μ_{eff} values of the Cu(II) complexes.^[23,24] The electronic spectra of the high spin Co(II) complex shows a broad band at 570 nm, which may be assigned to ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$ transition compatible with octahedral geometry.^[19] The absorption spectra of the ligand **3** and its corresponding Cu (II), Ni (II), Zn (II), and Co (II) complexes in DMF solutions are shown in Figure 3. It can be seen that the absorption peaks of Co (II) complex are obviously different from the ligand 3. In comparison with Co (II) complex, an important feature of the absorption spectrum of ligand 3 is shown that one absorption peak is observed at 348 nm, which are absent in the spectrum of Co (II) complex. The other feature is that the absorption peak at 348 nm in the ligand 3 is shifted to 345 nm in Co (II) complex, and a new absorption peak at 418 nm was observed in Co (II) complex, indicating that the coordination of Co atom with the ligand **3**. Figure 3 shows the change in the absorption spectra for Zn (II) complex between 275 and 550 nm.

As seen from Figure 3, new peak was observed at 394 nm. The absorption peak at 348 nm in the ligand 3 is shifted to 316 nm in Zn (II) complex. The absorption spectra of Cu (II) and Ni (II) complexes in diluted DMF solution show that the spectra of Cu (II) and Ni (II) complexes are similar to each other. Compared with the absorption peak of the ligand 3, a corresponding absorption peak at 422 nm is observed in Cu (II) complex. There is a blue shift by 14 nm in the 348 nm absorption band for Cu (II) complex. The new absorption peaks at 316 nm and 393 nm are observed in Ni (II) complex. The absorption peak at 348 nm in the ligand 3 is shifted to 316 nm with formation of Ni (II) complex. Furthermore, a new absorption peak is observed at 393-416 nm in Cu (II), Ni (II), Zn (II), and Co (II) complexes, which is assigned to the n- π^* charge transfer transition from the filled π orbital of the bridging phenolic oxygen to the vacant d-orbital of the metal ions.^[25]

Fluorescence Properties

In Figure 4, the effects of the solvents such as N,Ndimethylformamide (DMF), dimethyl sulfoxide (DMSO), ethanol, methanol, 1,4-dioxane on the fluorescence spectra of ligand **3** are shown. The ligand **3** in DMF display enhanced emission intensities compared to the other solvents when excited with the same amount of energy. This result might be related to the dipol moments and the viscosities of solvents.



FIG. 4. Emission spectra of the ligand in the different solvents at room temperature (ligand concentration: 5×10^{-5} M, λ_{ex} : 460 nm). (Figure is provided in color online.)



FIG. 5. Emission spectra of the ligand and its complexes at room temperature (ligand concentration: 5×10^{-5} M, complex concentration: 5×10^{-5} M, λ_{ex} : 460 nm). (Figure is provided in color online.)

Figure 5 shows the fluorescence spectra of the ligand 3 and its Co (II), Cu (II), Ni (II), and Zn (II) complexes in DMF solutions. In comparison with the corresponding free ligand 3 $(\lambda_{em} = 476 \text{ nm}), \text{Zn}$ (II) complex exhibits blue-shift with $\lambda_{em} =$ 503 nm and shows a significant increase in fluorescence intensity at 503 nm. This anomaly can be explained by the fact that excited states resulting from complexes of Zn (II) are typically ligand-centered in nature owing to the inability of the d¹⁰ metal center to participate in low-energy charge transfer for metalcentered transitions.^[26-29] So, factors like an increased rigidity in complex structure,^[29] a restriction in the photoinduced electron transfer (PET),^[22,27] etc. are assigned to the increase in the fluorescence intensity.^[25] A decrease of the fluorescence intensity is observed for the complexes for Cu (II), Co (II), and Ni (II) ions. A decrease of the fluorescence intensity caused by Cu (II), Co (II), and Ni (II) ions is probably a result of the "heavy atom effect" causing the increase of intersystem crossing rate constant, ligand-to-ions electronic energy transfer, redox-activity, and magnetic perturbation.^[25,30–32]

CONCLUSIONS

As a result, the potential binucleating tetradentate Schiff base bissalophen **3** was prepared and employed to synthesize binuclear transition metal complexes with Cu (II), Ni (II), Zn (II), and Co (II). Furthermore, absorption and fluorescence properties of tetradentate Schiff base ligand **3** and its transition metal complex were described. Comparing the fluorescent intensity of ligand **3** and the transition metal complexes, it can be seen that Zn (II) complex is higher, and this result is provided specifically for Zn (II) complex in the fluorometric metal determination. Moreover, it was observed that the emission intensity of ligand **3** and its transition metal complexes usually increased in different solvents with increasing dipol moments and decreasing viscosities of the solvents in fluorometric experiments.

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