

**Spectroscopic and Conductance Studies of
New Transition Metal Complexes with a Schiff
Base Derived from 4-Methoxybenzaldehyde
and 1,2-bis(*p*-Aminophenoxy)ethane**

**Ümit Çakır,¹ Hamdi Temel,^{2,*} Salih İlhan,²
and H. İbrahim Uğraş¹**

¹Chemistry Department, Faculty of Arts and Sciences, Balıkesir
University, Balıkesir, Turkey

²Department of Chemistry, Faculty of Education, Dicle University,
Diyarbakır, Turkey

ABSTRACT

Four new metal complexes of Cu(II), Ni(II), Zn(II) and Co(III) with Schiff base derived from 4-methoxybenzaldehyde and 1,2-bis(*p*-aminophenoxy)ethane have been prepared and characterized by magnetic susceptibility, conductance measurements, elemental analyses, UV–Vis,

*Correspondence: Hamdi Temel, Department of Chemistry, Faculty of Education, Dicle University, Diyarbakır, Turkey; E-mail: htemel@dicle.edu.tr.



^1H NMR and IR spectra studies. The magnetic and spectroscopic data indicate an octahedral geometry for the six-coordinate complexes. The ligand was used for complexation studies. Stability constants were measured by means of a conductometric method. Furthermore, the stability constants for complexation between ZnCl_2 , $\text{Cu}(\text{NO}_3)_2$ and AgNO_3 salts and ligand (L) in 80% dioxane–water and pure methanol were determined from conductance measurements. In 80% dioxane–water, the stability constants ($\log K_e$) increase inversely with the crystal radii in the order $\text{Ag(I)} < \text{Zn(II)} < \text{Cu(II)}$.

Key Words: 1,2-bis(*p*-Aminophenoxy)ethane; 4-Methoxybenzaldehyde; Schiff base complexes; Spectra studies and stability constants.

INTRODUCTION

Schiff base metal complexes have been widely studied because of their industrial, antifungal and biological applications.^[1–6] In the present paper Cu(II), Ni(II), Zn(II) and Co(III) complexes of a Schiff base derived from 4-methoxybenzaldehyde and 1,2-bis(*p*-aminophenoxy)ethane are reported. Based on the physical and chemical data of some of these complexes, and adducts, structures for these compounds are proposed.

This is the first report about this ligand. The structure of the Schiff base ligand is shown in Figure 1.

We have used conductivity measurements to determine the stability (formation) constants for the Zn(II), Cu(II) and Ag(I) ion–ligand interaction.^[4,5] Also, this method yields accurate values for the ion association constants for the cation–ligand complexes with various anions. Our results suggest that a number of cation–Schiff base ligand complexes undergo ion association, and that this phenomenon is highly dependent on the nature of ion–solvent and ion–ligand interactions.

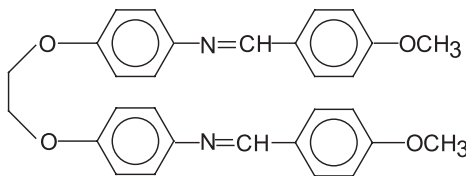


Figure 1. Structure of the ligand.

EXPERIMENTAL

Measurements

The electronic spectra of the complexes in the UV–Vis spectral region were recorded in DMF solutions using a Shimadzu Model 160 UV Visible Spectrophotometer. The IR spectra of the complexes were recorded with a Midac 1700 instrument in KBr pellets. ^1H NMR spectra were recorded on a Bruker GmbH DPX-400 MHz Digital FT-NMR spectrometer in $\text{DMSO}-d_6$, magnetic susceptibilities were determined on a Sherwood Scientific magnetic susceptibility balance (Model NO: MK1) at room temperature (23°C) using $\text{Hg}[\text{Co}(\text{SCN})_2]$ as a calibrant: diamagnetic corrections were calculated from Pascal's constants.^[7] The elemental analyses were conducted on a Carlo Erba instrument.

Complexation Studies and the Determination of the Stability Constants (K_e)

Anhydrous ZnCl_2 , $\text{Cu}(\text{NO}_3)_2$ and AgNO_3 of the highest purity were used. Stability constants were measured by means of a conductometric method. The water used in the conductometric studies was redistilled from alkaline potassium permanganate. Dioxane was dried over sodium metal, and anhydrous methanol was used without further purification (Merck; H_2O content less than 0.01%). The solutions were prepared with a constant 1:1 ratio of metal salt to ligand, in 80% dioxane–water mixture and in methanol. All solutions were prepared in a dry box and transferred to the dry conductivity cell. The conductances were measured at $25 \pm 0.05^\circ\text{C}$. The measuring equipment consisted of a glass vessel (type ingold) with an external jacket. At the same time, the system was connected to a thermostatted water-bath ($25 \pm 0.05^\circ\text{C}$) and a conductivity cell (Cole Parmer 19050-66) with a conductometer (Suntex SC-170 Model). The cell constant was determined to be 0.769 cm^{-1} at 25°C , by measuring the conductivity of aqueous potassium chloride solutions of various concentrations.^[8] $\text{Log } K_e$ and $-\Delta G^\circ$ values for the reaction of the ligand with the cations were determined by a conductometric procedure outlined previously. Results are reported as the average and standard deviation from the average of between four and six independent experimental determinations.

Materials

All the chemicals were obtained from Aldrich and were used without further purification. The compound 1,2-bis(*p*-aminophenoxy)ethane was synthesized by the earlier reported procedure.^[2,3]



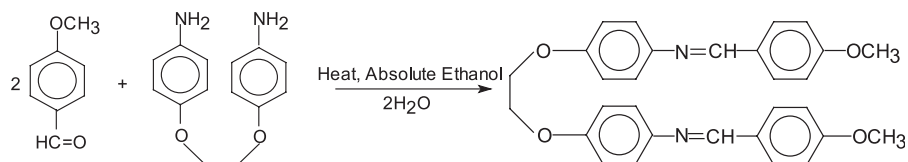


Figure 2. Synthesis scheme for the reaction of the 4-methoxybenzaldehyde and 1,2-bis(*p*-aminophenoxy)ethane.

Synthesis of Schiff Base

A solution of 4-methoxybenzaldehyde (10.00 mmole, 1.36 g) in 25 mL absolute ethanol was added dropwise, over 2 hours, to a stirred solution of 1,2-bis(*p*-aminophenoxy)ethane (5.00 mmole; 1.22 g) dissolved in 25 mL warm absolute ethanol. A solid mass separated out on cooling, which was kept in a refrigerator for better crystallization. It was then filtered, washed with ethanol, ether, and recrystallized from DMF. It was subsequently dried over anhydrous CaCl_2 in a desiccator. This ligand is insoluble in all common organic solvents, viz., acetone, alcohol, benzene, etc. and soluble in polar solvents viz. DMF and DMSO. M.p. 240°C ; yield: 2.04 g (85%). The reaction steps for the synthesis of ligand is given in Figure 2.

Synthesis of Metal Complexes

The analytical data for all these complexes are presented in Table 1. These were synthesized by adding a calculated amount of the Schiff base in DMF to the metal salt in the same solvent. The mixture was heated under reflux for 3–4 h, and then the volume was reduced to half. The solid complexes that separated out were filtered, washed with ethanol, recrystallized from a DMF–DMSO mixture (1:1) and dried in desiccators over silica gel. The reactions of the transition metal acetates with the Schiff base are indicated by the following equations:

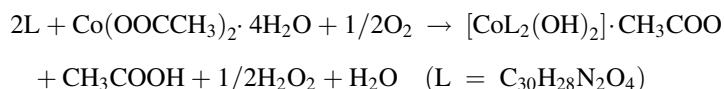
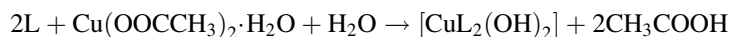
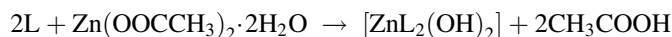


Table 1. Some properties of the ligand and its complexes.

Compound	F.W. g/mole	M.P. (°C)	Yield (%)	Elemental analyses % calculated (found)				μ_{eff}
				C	H	N		
Ligand (L) (yellow) (C ₃₀ H ₂₈ N ₂ O ₄)	480.00	240.0	85.0	75.00 (75.08)	5.83 (5.96)	5.83 (5.73)	—	
[CuL ₂ (OH) ₂] (brown) (C ₆₀ H ₅₈ N ₄ O ₁₀ Cu)	1057.54	280.0	60.0	68.08 (68.16)	5.48 (5.24)	5.29 (6.52)	1.73	
[NiL ₂ (OH) ₂] (red) (C ₆₀ H ₅₈ N ₄ O ₁₀ Ni)	1052.70	285.0	55.0	68.39 (68.21)	5.60 (5.71)	5.32 (5.46)	2.82	
[CoL ₂ (OH) ₂]·CH ₃ COO (Reddish brown) (C ₆₂ H ₆₁ N ₄ O ₁₂ Co)	1111.90	289.0	50.0	66.91 (67.11)	5.49 (5.22)	5.04 (4.88)	Dia	
[ZnL ₂ (OH) ₂] (white) (C ₆₀ H ₅₈ N ₄ O ₁₀ Zn)	1059.40	259.0	51.0	67.96 (67.97)	5.47 (5.40)	5.29 (5.20)	Dia	

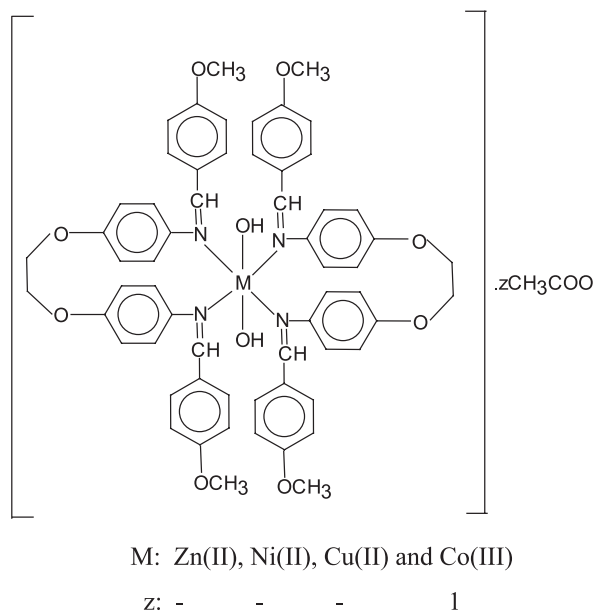


Figure 3. Suggested structures of the octahedral Zn(II), Ni(II), Cu(II), and Co(III) complexes of the ligand.

The ligand ratio of the Cu(II), Ni(II), Zn(II) and Co(III) complexes was found to be 1:2 (Figure 3). The complexes gave fine powders and we were not able to prepare single crystals for structure determination by X-ray spectroscopy. Hence, it was not possible to obtain unequivocal verification of the structures proposed here.

RESULTS AND DISCUSSION

Conductance Measurements

The Ni(II), Zn(II) and Cu(II) complexes are non-electrolytes as shown by their molar conductivity (Λ_M) measurements in DMF, which are in the range^[9,10] 4.10–10.20 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. The Co(III) complex is an electrolyte as shown by its molar conductivity (Λ_M) measurements in DMF, which is 36.70 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

Magnetic Susceptibility

The Ni(II) and Cu(II) complexes are paramagnetic and their magnetic susceptibilities are 2.82, 1.73 B. M., respectively. Since the Ni(II) and Cu(II) complexes were paramagnetic,^[11–13] their ¹H NMR spectra could not be obtained. However, the Zn(II) and Co(III) complexes were diamagnetic, and consequently, their ¹H NMR spectra were obtainable.

IR Spectra

Important IR bands of the Schiff base ligand and its complexes are given in Table 2. The IR spectra of the complexes are characterized by the appearance of a broad band in the region 3403–3469 cm⁻¹ due to OH groups.^[12] The coordination through the imine nitrogen is inferred from the shift of 1622 cm⁻¹ of the ligand to 1618–1619 cm⁻¹ for the complexes.^[12,13] The band at 1662 cm⁻¹ in the IR spectrum of the Co(III) complex is probably the C=O stretching vibration.^[8,9] Conclusive evidence of the bonding is also shown by the observation that new bands in the spectra of the metal complexes appear at 510–520 cm⁻¹, assignable to (M–N) stretching vibrations, which are not observed in the spectra of the ligand.^[13–15]

Electronic Spectra

The electronic spectra of all the complexes were recorded in 10⁻³ M DMF at room temperature. The spectrum of the free Schiff base exhibits

Table 2. Some IR frequencies (in cm⁻¹) of the ligand and its complexes.

Compound	IR spectra (cm ⁻¹) ^a					
	ν (OH)	ν (C–H) _{aromatic}	ν (C–H) _{aliphatic}	ν (C=O)	ν (CH=N)	ν (M–N)
Ligand (L)	–	3039 m	2954 m	–	1622 s	–
[CuL ₂ (OH) ₂]	3469 m	3043 m	2950 m	–	1618 s	515 w
[NiL ₂ (OH) ₂]	3450 m	3039 m	2953 m	–	1619 s	520 w
[ZnL ₂ (OH) ₂]	3403 m	3040 m	2954 m	–	1619 s	516 w
[CoL ₂ (OH) ₂]- CH ₃ COO	3439 m	3039 m	2954 m	1662 m	1618 s	510 w

^as (strong), m (medium), w (weak).



two absorption bands in the regions 252–275 and 305–324 nm. These bands are attributable to $\pi \rightarrow \pi^*$ transitions^[2–6,16] the first with those of the benzene ring and the second with those of the imino group. In the complexes, the imino $\pi \rightarrow \pi^*$ transition is shifted to a longer wavelength as a consequence of coordination when binding with the metal, confirming the formation of Schiff base metal complexes.^[12,17] The electronic spectrum of the Ni(II) complex shows absorption bands at 350–380 nm ($\epsilon = 822 \text{ L mol}^{-1} \text{ cm}^{-1}$) and 680 nm ($\epsilon = 62 \text{ L mol}^{-1} \text{ cm}^{-1}$) attributable to the ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ transition, which is compatible with this complex having an octahedral structure.^[8] The electronic spectrum of the Cu(II) complex shows an absorption band at 605 nm ($\epsilon = 383 \text{ L mol}^{-1} \text{ cm}^{-1}$) attributable to the ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ transition, which is compatible with this complex having an octahedral structure.^[9,12] The electronic spectrum of the Co(III) complex shows absorption bands at 424 nm ($\epsilon = 63 \text{ L mol}^{-1} \text{ cm}^{-1}$) and 460 nm ($\epsilon = 43 \text{ L mol}^{-1} \text{ cm}^{-1}$) attributable to the ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ transition, which is compatible with this complex having an octahedral structure.^[11] The electronic spectrum of the Zn(II) complex shows an absorption band at 360 nm ($\epsilon = 3925 \text{ L mol}^{-1} \text{ cm}^{-1}$) attributable to the L \rightarrow M (charge transfer) transition, which is compatible with this complex having an octahedral structure.^[12,16,17]

${}^1\text{H}$ NMR Spectra

The ${}^1\text{H}$ NMR spectra (in DMSO- d_6) of the ligand L showed signals at 3.68 (s, 6H) $-\text{OCH}_3$; 4.19 (s, 4H) $\text{O}-\text{CH}_2$; 7.02–7.06 (m, 8H), 7.24 (d, 4H, J: 8.82 Hz), 7.86 (d, 4H, J: 8.78 Hz), Ar-H; 8.54 (s, 2H) $\text{HC}=\text{N}$ ppm. The ${}^1\text{H}$ NMR spectra (in DMSO- d_6) of the Zn(II) complex showed signals at 3.74 (s, 2H), $-\text{OH}$; 3.85 (s, 12H) $-\text{OCH}_3$; 4.23 (s, 8H) $\text{O}-\text{CH}_2$; 7.07–7.26 (m, 24H), 7.86 (d, 8H, J = 8.80 Hz (ortho coupling) Ar-H; 8.45 (s, 4H) $\text{HC}=\text{N}$ ppm. The ${}^1\text{H}$ NMR spectra (in DMSO- d_6) of the Co(III) complex showed signals at 3.60 (s, 15H) $-\text{OCH}_3$; 3.74 (s, 2H) $-\text{OH}$; 4.37 (s, 8H) $\text{O}-\text{CH}_2$; 7.02–7.07 (m, 16H); 7.24 (d, 8H, J = 8.80 Hz); 7.8 (d, 8H, J = 8.75 Hz) Ar-H; 8.40 (s, 4H) $\text{HC}=\text{N}$ ppm.

From the ${}^1\text{H}$ NMR spectra, and IR absorption peaks of $-\text{OH}$ groups binding metal ions in complexes, it is thought that the $-\text{OH}$ groups are trans- to each other. They have slightly broad IR spectra for $-\text{OH}$ groups around $3403\text{--}3469 \text{ cm}^{-1}$, and only one peak for both $-\text{OH}$ groups in spectra of the complexes obtained by ${}^1\text{H}$ NMR. If the $-\text{OH}$ IR spectra have relatively broad peaks and show two different peaks on ${}^1\text{H}$ NMR, these are usually cis- because of the lack of symmetry of the molecule.

Conductometric Study of Ligand Zn(II), Ag(I), and Cu(II) Salts

Structures of ligand–cation complexes in a dioxan/water mixture and in pure methanol solvent were estimated from the conductance parameters (κ and Λ) as well as the complex formation constant, $K_e = (\Lambda_{MAM} - \Lambda) / (\Lambda - \Lambda_{MaLbAm}) [L]$.

Molar conductivities, Λ ($S\ cm^2\ mol^{-1}$), were calculated from the infinite frequency electrolytic conductances, κ , after correcting for the pure solvent conductance, i.e. $\Lambda = 1000\ \kappa / C_{MX}$ where C_{MX} is the total concentration of the metal salt. The experimental molar conductance equations and all calculations for stability constants and Gibbs free enthalpy values have been published in our previous works.^[4,5,8,18] All the experimental studies used the a 1:2 ratio of the metal–ion to the Schiff base ligand.

Our results suggest that a number of cation–ligand complexes undergo ion association and that this phenomenon is highly dependent on the nature of both ion–solvent and ion–ligand interactions. It was observed that, for the metal complexes with ligand in dioxan/water mixture, the K_e values were dependent on the chemical characteristics of ligand and solvents. This indicated that the electrostatic ion–dipole forces, which depend on the macroscopic dielectric constant of the solvents and on the dipole moment of the ligand, are the strongest factors in the complexation processes in such a system.

In 80% dioxane–water, the stability constants ($\log K_e$) increase inversely with the crystal radii in the order $Ag(I) < Zn(II) < Cu(II)$. We found that the stabilities of the complexes ions are affected not only by the relative sizes of the cationic radii but also by physical properties of the solvent. The high stability of the 1:2 complexes of Cu(II) with the ligand in both solvents is evident. This was the case with Cu(II)–L, and an essentially similar interpretation can be applied to the present chelating effect: a favourable orientation of ligand before chelation due to steric requirements and probably decreased complex solvation in the outer sphere.^[18–20]

Table 3. $\log K_e$ and $-\Delta G^\circ$ (kcal/mol) values for the interaction of ligand with $ZnCl_2$, $Cu(NO_3)_2$, and $AgNO_3$ in a 80% dioxan/water mixture at 25°C by the conductometric study.

Ligand	Value	Zn^{2+}	Cu^{+2}	Ag^+
L	$\log K_e$	3.21 ± 0.25	3.78 ± 0.13	2.34 ± 0.28
	$-\Delta G$	4370.29 ± 0.01	5148.70 ± 0.02	3190.34 ± 0.15



Table 4. Log Ke and $-\Delta G^\circ$ (kcal/mol) values for the interaction of ligand with ZnCl₂, Cu(NO₃)₂ and AgNO₃ in methanol at 25°C by the conductometric study.

Ligand	Value	Zn ²⁺	Cu ⁺²	Ag ⁺
L	Log Ke	3.31 ± 0.33	3.53 ± 0.05	2.56 ± 0.15
	$-\Delta G^\circ$	4517.37 ± 0.11	4812.21 ± 0.12	3487.21 ± 0.02

An explanation given for the former case deals with the ligand-solvation effects, while that for the latter is increased Cu–N and Cu–O bond strength, due to ligand cyclization.^[2,22] Zn(II) and Ag(I) differs from Cu(II) in that free enthalpy changes upon complex formation are almost the same regardless of the half ring size of the ligand. Planar complexes are expected to be stabilized by such a sequence of chelate half rings due to the removal of girdle strain. This stabilization is reflected in the greater heat of formation arising from the stronger Cu–N and Cu–O bonds in both solvents^[20,21] (see Tables 3 and 4).

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