Conductivity Studies of Schiff Base Ligands Derived from *O*-Phenylenediamine and Their Co(II) and Zn(II) Complexes

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ABSTRACT

The coordination complexes of Co(II) and Zn(II) with Schiff bases derived from o-phenylenediamine and substituted 2-hydroxybenzaldehyde were prepared. All compounds were characterized by Fourier transform infrared (FTIR) spectroscopy and Nuclear magnetic resonance (NMR) spectroscopy elemental analyzers. They were analyzed using impedance spectroscopy in the frequency range of 100Hz–1MHz. L1 and L2 showed higher conductivity compared to their metal complexes, which had values of 1.37×10^{-7} *and* 6.13×10^{-8} *S/cm respectively.*

Keywords: *Schiff base, o-phenylenediamine, 2-hydroxy-3-methoxybenzaldehyde, 2-hydroxy-5-nitrobenzaldehyde, conductivity*

INTRODUCTION

Coordination chemistry, the chemistry of metal complexes is one of the most significant research areas in inorganic chemistry due to their facile synthesis and wide range of applications as antifungal, antibacterial, anticancer and anti-inflammatory agents, as well as their insecticidal and catalytic properties [1,2] which plays a major role in our lives. Schiff base ligands are able to coordinate with different metals and stabilize them in various oxidation states since they show electronic and magnetic properties [3]. In this paper, we report the synthesis, characterization and conductivity studies of Cu(II) and Ni(II) complexes with 6,6'-(1*E*,1'*E*)-(1,2-phenylenebis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)bis(2-methoxyphenol) (L1) and 2,2'-(1*E*,1'*E*)-(1,2-phenylenebis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)bis(4-nitrophenol) (L2). We focused on conjugated compounds which are more stable due to the effectiveness of their conjugation system [4]. Both ligands were synthesized using the same amine, which is *o*-phenylenediamine and substituted 2-hydroxybenzaldehyde.

MATERIALS AND METHODS

Preparation of Schiff Base Ligand (L1)

A Schiff base ligand 6,6'-(*1E*,1'*E*)-(1,2-phenylenebis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)bis(2-methoxyphenol) (L1) was successfully synthesized by condensation of 2-hydroxy-3-methoxybenzaldehyde and *o*-phenylenediamine in a 2:1 ratio. Both starting materials were dissolved separately in 25 cm^3 of ethanol. The yellow solution of 2-hydroxy-3-methoxybenzaldehyde was added to the *o*-phenylenediamine solution. The resulting orange mixture was refluxed for 6 h. Then, the product was filtered off, washed with diethyl ether and left to dry for a few days. The dried product was then collected.

Preparation of Metal Complexes (L1Co, L1Zn)

Metal complexes were prepared by the *in situ* method using 2-hydroxy-3-methoxybenzaldehyde, *o*-phenylenediamine and cobalt(II) acetate tetrahydrate mixed at a ratio of 2:1:1, by refluxing for 6 h in ethanol. The solution was then allowed to cool at room temperature, and the solvent removed using a rotary evaporator. After that, the product was filtered off and washed with diethyl ether. The final product was collected after being air dried. The same procedure was repeated for Zn(II) complexes.

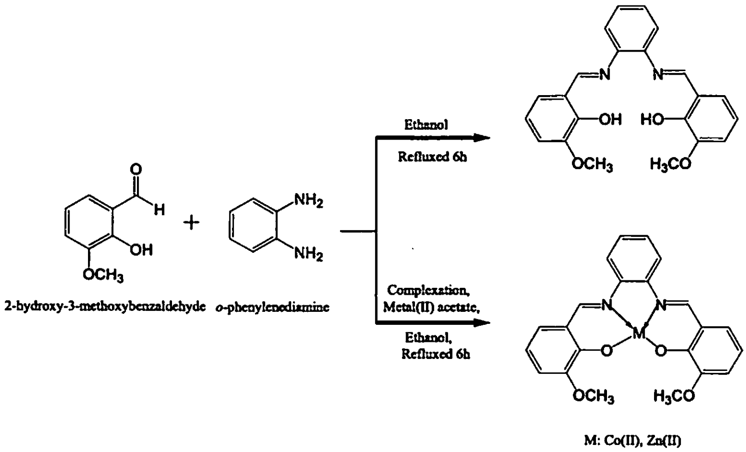

Figure 1: Reaction Scheme of the Preparation of L1 and its Complexes

Preparation of Schiff Base Ligand (L2)

Schiff base ligand 2,2'-(1*E*,1'*E*)-(1,2-phenylenebis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)bis(4-nitrophenol) (L2) was synthesized from the condensation of 2-hydroxy-5-nitrobenzaldehyde and *o*-phenylenediamine mixed at a ratio of 2:1 using ethanol as a solvent. Both starting materials were mixed and heated to reflux for 6 h. The product was filtered off and washed with diethyl ether. It was then left to air dry for few days before collection.

Preparation of Metal Complexes (L2Co, L2Zn)

Metal complexes were prepared by the in-situ method using 2-hydroxy-5-nitrobenzaldehyde, *o*-phenylenediamine and cobalt(II) acetate tetrahydrate mixed at a ratio of 2:1:1, by refluxing for 6 h in ethanol. The solution was then allowed to cool at room temperature and the solvent removed by using a rotary evaporator. After that, the product was filtered off and washed with diethyl ether. The final product was collected after being air dried. The same procedure was repeated for Zn(II) complexes.

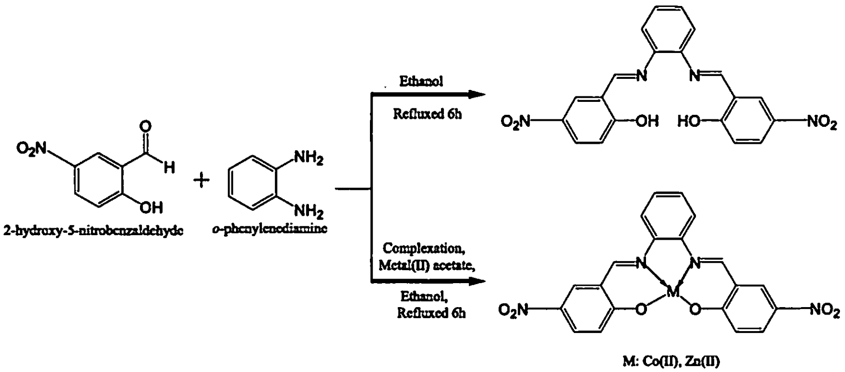

Figure 2: Reaction Scheme of the Preparation of L2 and its Complexes

RESULTS AND DISCUSSION

Elemental Analysis

The physical characteristics of metal complexes are summarized in Table 1. Elemental analysis showed that the experimental values were in agreement with the theoretical values for all compounds.

Table 1: Analytical Data and Physical Properties of Schiff Base Ligands and their Metal Complexes

Compound	Melting point (°C)	Yield (%)	Experimental Value (Calculated Value) (%)		
			C	H	N
L1	170.0	73.67	70.08 (70.20)	5.22 (5.36)	7.70 (7.44)
L1Co	247.3	70.63	54.19 (54.22)	4.57 (4.96)	5.35 (5.75)
L1Zn	261.6	77.10	57.66 (57.72)	4.67 (4.40)	6.01 (6.01)
L2	275.3	88.85	58.55 (59.12)	3.62 (3.47)	13.76 (13.79)
L2Co	>300	82.88	48.57 (51.85)	3.55 (2.61)	11.71 (12.09)
L2Zn	>300	86.20	47.48 (47.58)	3.64 (3.33)	9.58 (9.25)

Infrared Spectroscopy

Infrared spectroscopy was used to determine part of the structural information of a molecule. Structural information was determined by the presence or absence of a particular functional group in the structure. In this study structural analysis was carried out using the Perkin Elmer 1750X FTIR. Table 2 summarizes important peaks at different frequencies that appeared in the spectra for all compounds. In the IR spectrum of ligand L1, a peak at 1614 cm^{-1} was attributed to the C=N stretching band of the structure. After complexation with metal ions, the C=N band was shifted to lower frequencies between 1611 and 1614 cm^{-1}, indicating the coordination of nitrogen atom to the central metal ion. The coordination of nitrogen to the metal ion reduced the electron density of the azomethine link and caused a shift in the frequency of the C=N group [5]. The phenolic C-O stretching in free ligand L1 appeared at 1256 cm^{-1}. For complexes, the C-O stretching shifted to lower frequency in the region of 1237 to 1244 cm^{-1} due to the participation of the oxygen atom of the phenolic group in coordination with metal ions. New bands were observed in the spectra of both metal complexes in the regions of 509 to 526 cm^{-1} and 421 to 454 cm^{-1}, characteristic to M-N and M-O stretching vibrations, respectively. No metal-nitrogen and metal-oxygen peaks were observed in the spectrum of ligand L1 since it does not contains any metal. In the free L2 ligand, the C=N stretching band appeared at 1622 cm^{-1}. After complexation, the C=N stretching band shifted to lower frequencies of 1544 and 1525 cm^{-1} for Co(II) and Zn(II) complexes, respectively. The phenolic C-O stretching of L2 was observed at 1350 cm^{-1} while for both complexes they appeared at higher frequencies of 1351 to 1393 cm^{-1}. New peaks were observed at 500 to 542 cm^{-1} and 413 to 422 cm^{-1} representing M-N and M-O stretching vibrations, respectively. There were no observed M-N and M-O peaks for L2. N-O stretching frequencies were observed in the L2 spectrum. Symmetrical and asymmetrical N-O stretching vibrations appeared at 1487 and 1525 cm^{-1}, respectively [6]. For L2Co and L2Zn, symmetrical and asymmetrical N-O stretching vibrations were observed in the region of 1444 to1487 cm^{-1} and 1505 to 1526 cm^{-1}, respectively.

Table 2: Stretching Frequencies of Schiff Base Ligands and their Metal Complexes (cm^{-1})

Compound	Wavelength (cm^{-1})				
	v(C=N)	v(C-O)	v(NO_2)	v(M-N)	v(M-O)
L1	1614	1256	-	-	-
L1Co	1614	1244	-	526	454
L1Zn	1611	1237	-	509	421
L2	1622	1350	1487, 1525	-	-
L2Co	1544	1393	1444, 1505	542	422
L2Zn	1525	1351	1487, 1526	500	413

Magnetic Susceptibility

Magnetic susceptibility is a study of the degree of magnetization of a material in response to an applied magnetic field. The magnetic susceptibility value indicates the number of unpaired electron of a material. The value can be used to determine the geometric structure of a compound. By doing this, we can also determine the spin state whether its exhibit high spin or low spin behavior. Magnetic susceptibility of all compounds were measured at room temperature. The data is shown in Table 3. Co(II) complexes had effective magnetic moment values of 3.60 B.M and 3.60 B.M for L1Co and L2Co, respectively. Those values indicate three unpaired electron. According to the Crystal Field Splitting Theory, tetrahedral geometries for Co(II) complexes having three unpaired electron are as shown in Figure 3. Therefore, the geometry for L1Co and L2Co is tetrahedral. For Zn(II) complexes, both tetrahedral and square planar geometries splitting diagram of Zn(II) showed 0 unpaired electrons, indicating a diamagnetic nature. Since Zn(II) complexes had no unpaired electrons, they exhibited tetrahedral or square planar geometry (Figure 4).

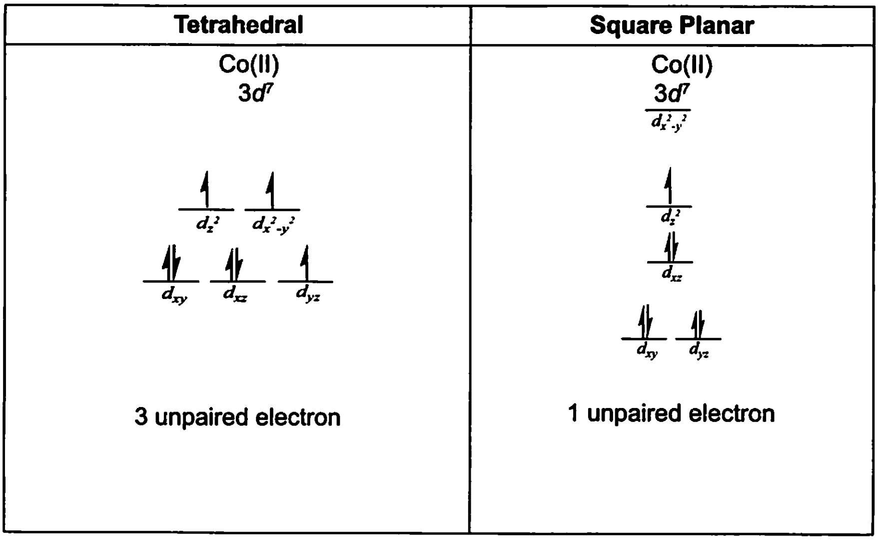

Figure 3: Crystal Splitting Diagram of Co(II) Complexes

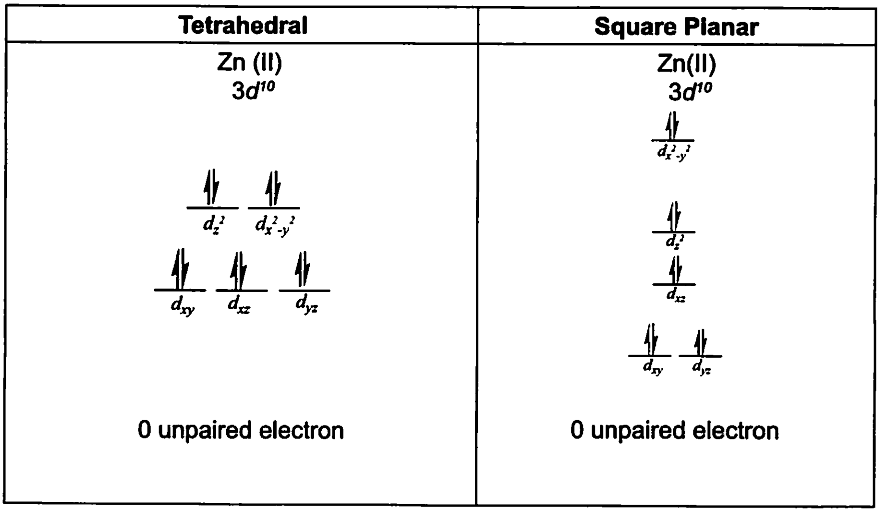

Figure 4: Crystal Splitting Diagram of Zn(II) Complexes

Table 3: Magnetic Susceptibility Data of Metal Complexes

Compound	μ_{eff} (B.M)	Number of unpaired electron	d^n	Suggested geometry
L1Co	3.67	3	d^7	Tetrahedral
L1Zn	Diamagnetic	0	d^{10}	Tetrahedral/ Square planar
L2Co	3.60	3	d^7	Tetrahedral
L2Zn	Diamagnetic	0	d^8	Tetrahedral/ Square planar

Conductivity Measurement

All synthesized compounds were further analyzed for their conductivity using impedance spectroscopy at room temperature. The analysis was conducted to observe the effect of complexation on the conductivity values of these Schiff base compounds. Conductivity of all compounds were measured using an impedance analyzer by applying alternating current (ac) voltage. The samples (0.25 g) were prepared in the form of pellets and their thickness measured. The pellets were then placed between two stainless steel blocking electrodes. Alternating current impedance spectroscopy (IS) was measured by using the Solartron Impedance 1260 in the frequency range of 100 Hz to 1 MHz at room temperature. Conductivity value was calculated using the following formula:

$$\frac{T}{R_b A} \tag{1}$$

Where T = thickness of the pellet
R_b = bulk resistance
A = surface area of the pellet

Table 4: Conductivity Value Calculated

Compound	Conductivity (S/cm)
L1	1.37×10^{-7}
L1Co	9.31×10^{-8}
L1Zn	1.63×10^{-8}
L2	6.13×10^{-8}
L2Co	2.65×10^{-8}
L2Zn	1.71×10^{-8}

Optical Properties

Measurement of the optical property represented by the band gap energy was done to support the conductivity data. The result can be acquired by conducting UV-Vis experiment. Optical band gap values can be obtained using the following equation:

$$\frac{hC}{\lambda_{onset}(1.6x10^{-19})} \qquad (2)$$

Where λ_{onset} = wavelength value from two tangents on the absorption edges

h = Planks constant

C = speed of light

The optical band gap energy is the energy taken by an electron to move from the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO). Table 5 shows the band gap energy of all synthesized compounds. Results of the optical band gap energy supports the conductivity values. The large optical band gap indicates that it was more difficult for electrons to excite from HOMO to LUMO, thereby reducing conductivity values. Conductivity values increase with decreasing band gap energy.

Table 5: Band Gap Energy of Schiff Base Ligands and their Metal Complexes

Compound	Band Gap Energy (eV)
L1	1.56
L1Co	2.69
L1Zn	2.53
L2	1.38
L2Co	1.45
L2Zn	1.75

CONCLUSION

Two Schiff base ligands with their Co(II) and Zn(II) complexes were synthesized and characterized. Conductivity studies showed that both ligands had higher conductivity values compared to metal complexes. Measurement of optical properties represented by the band gap energy was carried out to support the conductivity data.

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