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Novel Metal(II) Complexes with Bidentate Schiff Base Ligand: Synthesis, Spectroscopic Properties and Dye Decolorization Functions

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The bidentate Schiff base ligand 4-chloro-2-[1-(4-phenylphenyl)ethylideneamino]phenol and its mononuclear Co(II), Ni(II), Cu(II) and Zn(II) complexes have been synthesized. Ligand and metal complexes were characterized by elemental analyses, magnetic susceptibility, molar conductivity, ¹H- and ¹³C-NMR, the Fourier transform infrared, UV-Vis, inductively coupled plasma optical emission spectrometry, and thermogravimetric-differential thermogravimetric studies. The results suggest that the mononuclear complexes have a metal to ligand mole ratio of 1:2 and the metal(II) ions are coordinated with the phenolic oxygen and imine nitrogen atoms. Octahedral structures are proposed for the complexes of the Schiff base ligand. Furthermore, the complexes were checked for their efficiency to decolorize the dye methylene blue. In our experiments we found that metal(II) complexes had an acceptable decolorization efficiency against the dye methylene blue.

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1. Introduction

The Schiff bases can be formed by the condensation of a primary amine with a carbonyl compound and they contain an azomethine group (–CH=N–). The Schiff bases are usually bi- or tri-dentate ligands capable of forming stable transition metal complexes. The chemistry of the metal complexes of the Schiff bases containing nitrogen and other donor atoms has attracted a great deal of attention due to their stability, biological activity [1], and potential applications in many fields such as oxidation catalysis [2], electrochemistry [3], etc. Therefore synthesis of new Schiff bases and their metal complexes has been still the aim of many recent investigations. Transition metal complexes have been also used for degradation of the toxic dyes produced during dye production and textile manufacturing processes [4]. Due to the stability of modern textile dyes, conventional biological treatment methods are ineffective for their degradation [5, 6].

In the present work, we have synthesized a new bidentate Schiff base ligand (HL) using biphenyl as a starting material. Then, its Co(II), Ni(II), Cu(II) and Zn(II) complexes were obtained by the reaction of HL and appropriate metal salts. All of the synthesized compounds were characterized using several analytical and spectroscopic techniques. Additionally dye decolorization properties of the metal complexes were studied in detail.

2. Experimental

2.1. Material

All the solvents and the other chemicals used were of reagent grade and used as received.

2.2. Spectral measurements

Melting points were determined in open capillaries on an IA 9100 Electrothermal apparatus. Elemental analyses (CHN) were performed in a LECO 932 CHNS analyzer and metal contents of the complexes were determined by a Perkin-Elmer Optima 5300 DV ICP-OES spectrometer. ¹H- and ¹³C-NMR spectra were recorded with a Bruker AVANCE 300 MHz spectrometer in DMSO-*d*₆ with reference to Me₄Si (0.0 ppm). IR spectra were obtained on a Shimadzu IRPrestige-21 FT-IR spectrophotometer with samples prepared as KBr pellets with 2 cm⁻¹ resolution. Spectrophotometric measurements were performed on a PG T80+ spectrophotometer. Molar conductivities of the metal complexes were determined in dry DMF at room temperature using a Optic Ivymen System conductivity meter. Thermal analyses of metal complexes were carried out in atmospheric air using a Perkin Elmer Diamond TGA thermal analyzer. Magnetic susceptibilities of the complexes were measured by the Gouy method at room temperature using a model Sherwood Scientific MX1.

2.3. Synthesis of ligand (HL)

4-acetylbiphenyl was synthesized by the Friedel-Crafts acylation reaction of biphenyl with acetyl chloride in the 1:1 mole ratio according to literature method [7]. The Schiff base namely, 4-chloro-2-[1-(4-phenylphenyl)ethylideneamino]phenol was prepared

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by refluxing a mixture of equimolar quantities of 4-acetylbiphenyl with 2-amino-4-chloro phenol in absolute ethanol. The product was filtered off, washed with diethyl ether and dried over P_2O_5 .

2.4. Synthesis of complexes $[ML_2(H_2O)_2]$ [M : Co(II), Ni(II), Cu(II) and Zn(II)]

2 mmol of 4-chloro-2-[1-(4-phenylphenyl)ethylideneamino]phenol dissolved in methanol was mixed with Et_3N (2 mmol) and stirred for 0.5 h. Methanolic solution of metal acetates of Co(II), Ni(II), Cu(II), and Zn(II) (1 mmol) were added to the hot methanolic solution of the resulting solution which resulted in the precipitation of metal derivatives. The resulting mixture was refluxed for 2 h. The product was filtered off, washed with ethanol and diethyl ether and then dried over P_2O_5 .

2.5. Dye decolorization studies

A 150 mL round-bottom flask containing a 100 mL solution of the methylene blue in water (50 mg/L) and complex (1, 2, 3 or 4) (100 mg) was placed in a water bath (25 °C). While the solution was stirred, 15 mL H_2O_2 (30%, v:v) was added into it and the solution was stirred for 2 h. The absorbances were measured in a spectrophotometer at the maximum wavelength for the methylene blue (662 nm). The decolorization rate of the

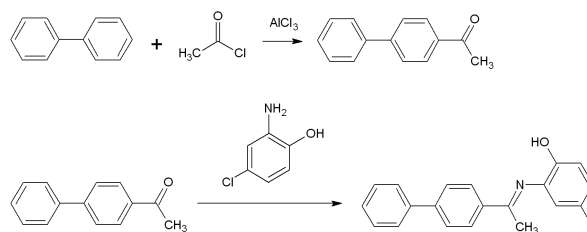
dye was determined as expressed in Eq. (1):

$$\text{dye decolorization \%} = [(A_0 - A_t)/A_0] \times 100, \quad (1)$$

where A_t is the absorbance at requested time and A_0 is the initial absorbance of each solution.

3. Results and discussion

Preparation of the Schiff base ligand was performed in two steps from biphenyl as shown below.



4-acetylbiphenyl was prepared from acetyl chloride and biphenyl by the Friedel-Crafts acylation in the presence of aluminium chloride [7]. Condensation of the 4-acetylbiphenyl with 2-amino-4-chloro phenol gave the Schiff base ligand. The analytical and physical data of the ligand and its mononuclear complexes are given in Table I. The analytical data indicated that the metal to ligand ratio is 1:2 for the complexes.

TABLE I

Physical properties and elemental analysis of the ligand and its metal complexes.

Compound	μ_{eff} [μ_B]	A_M^a	Color	m.p. [$^{\circ}C$]	Yield [%]	Calculated (found) [%]			
						C	H	N	Metal
HL	–	–	yellow	240 ^b	65	74.65 (74.51)	5.01 (5.43)	4.35 (4.21)	–
(1) CoL ₂ (H ₂ O) ₂	3.80	16	brown	260 ^b	56	65.23 (65.56)	4.65 (4.57)	3.80 (3.57)	8.00 (8.12)
(2) NiL ₂ (H ₂ O) ₂	2.88	16	brown	267 ^b	44	65.25 (65.04)	4.65 (4.43)	3.80 (3.63)	7.97 (7.81)
(3) CuL ₂ (H ₂ O) ₂	1.77	17	black	208 ^b	48	64.82 (64.49)	4.62 (4.51)	3.78 (3.96)	8.57 (8.34)
(4) ZnL ₂ (H ₂ O) ₂	dia	4	black	> 300	48	64.66 (64.93)	4.61 (4.82)	3.77 (3.91)	8.80 (8.66)

^aMolar conductivity [$\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$], ^bDecomposition point.

3.1. NMR spectra

The 1H - and ^{13}C -NMR spectra data of a DMSO- d_6 solution of the ligand HL show well-resolved signals as expected and can be given as follows: 1H -NMR: 6.49–7.67 (m, 12H, Ar-H), 3.73 (s, 1H , –OH), 1.38 (s, 3H, –CH₃), ^{13}C -NMR (DMSO- d_6 , ppm): 175.12 (imine), 116.13–148.93 (aromatic), 29.70 (aliphatic).

The 1H -NMR spectrum of the free ligand shows a multiplet in the range of 6.49–7.67 ppm due to aromatic pro-

tons. Also 1H -NMR spectrum of the HL shows a D_2O exchangeable peak at 3.73 ppm which is assigned to the aromatic –OH group. Furthermore, the singlet at 1.38 ppm has been attributed to the protons of the methyl group.

The ^{13}C -NMR of the ligand HL shows peaks at range 116.13–148.93 ppm, which are assignable to the carbons of the aromatic rings. The chemical shift of HL for imine carbon (C=N) was found at 175.12 ppm. The carbon atom of the methyl group was observed at 29.70 ppm

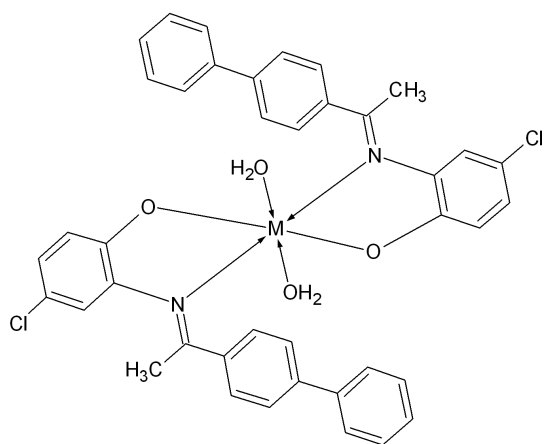


Fig. 1. Proposed structure for the metal complexes of the ligand. [M=Co(II), Ni(II), Cu(II), Zn(II)].

for HL. ¹H- and ¹³C-NMR spectra data of the ligand in DMSO-*d*₆ confirm the proposed structure of the ligand (HL) (Fig. 1).

3.2. IR spectra

FT-IR data of the ligand and its complexes are given in Table II. The infrared spectrum of the ligand (HL) shows a $\nu(\text{C}=\text{N})$ peak at 1605 cm^{-1} and the absence of a $\nu(\text{C}=\text{O})$ peak at around 1700 cm^{-1} is indicative of formation of condensation reaction. The broad band for the -OH group at 3317 cm^{-1} observed in the IR spectra of the free ligand is absent in the IR spectra of their metal complexes, indicating deprotonation of the OH group and formation of M-O bond. This is supported by the appearance of a new band in the region $517\text{--}552\text{ cm}^{-1}$ assigned to $\nu(\text{M}-\text{O})$ [8, 9].

TABLE II

Significant bands in the IR spectra of the ligand and its metal complexes (cm^{-1}).

Compound	O-H	C=N	C-N	C-O	M-O	M-N
HL	3317s	1605s	1416s	1227s	-	-
CoL(H ₂ O) ₂	3441b	1588m	1495s	1234m	552w	444w
NiL(H ₂ O) ₂	3448b	1591m	1481s	1253w	517w	437w
CuL(H ₂ O) ₂	3414b	1590m	1502w	1234s	527w	440w
ZnL(H ₂ O) ₂	3448b	1593w	1488m	1246w	541w	423w

b: broad, s: strong, m: medium, w: weak

The IR spectra of the mononuclear Co(II), Ni(II), Cu(II) and Zn(II) complexes also showed a broad band in the $3414\text{--}3448\text{ cm}^{-1}$ region, in line with the presence of water molecules coordinated to the metal ion [8].

The IR spectra of the metal complexes show bands between 1588 and 1593 cm^{-1} which indicates $\nu(\text{C}=\text{N})$ [10] and it is found that the $\nu(\text{C}=\text{N})$ bands in the complexes are shifted by $17\text{--}12\text{ cm}^{-1}$ to lower energy regions compared to the free ligand. This phenomenon appears to be due to the coordinated of azomethine nitrogens to the metal ion [11, 12].

The coordination mode of the ligand is further supported by new frequencies occurring in the $423\text{--}444\text{ cm}^{-1}$ ranges, which have been assigned tentatively to $\nu(\text{M}-\text{N})$.

3.3. Thermogravimetric analysis

The thermal decomposition behaviours of the ligand (HL) and its metal complexes were followed up to 1000°C in nitrogen atmosphere. The thermal decomposition of the ligand (HL) with the molecular formula $[\text{C}_{20}\text{H}_{16}\text{ClNO}]$ proceeds with three main degradation steps. The first step occurs within the temperature range $100\text{--}230^\circ\text{C}$ with an estimated mass loss 68.00% (calculated mass loss = 68.75%) which is reasonably accounted for the loss of one biphenyl, CH_3 , $-\text{Cl}$ and $-\text{OH}$ groups. The second step occurs within the temperature range $230\text{--}480^\circ\text{C}$ with an estimated mass loss 23.10% (calculated mass loss = 23.22%), which is reasonably accounted for the loss of one benzene group. The third estimated mass loss of 8.50% (calculated mass loss = 8.30%) within the temperature range $480\text{--}980^\circ\text{C}$ could be attributed to the liberation of one CN group. Total estimated mass loss is 7.95% (calculated mass loss = 8.03%).

The thermal decomposition of all synthesized complexes occurred in the similar manner. Because of this only thermogravimetric results of Ni(II) complex of HL are given. The thermal decomposition of the complex (2) with the molecular formula $[\text{NiL}_2(\text{H}_2\text{O})_2]$ also proceeds with four main degradation steps. The first estimated mass loss of 5.00% (calculated mass loss = 4.90%) within the temperature range $105\text{--}140^\circ\text{C}$ could be attributed to the liberation of two H_2O groups. The DTG curve gives a peak at 110°C . The second step occurs within the temperature range $135\text{--}165^\circ\text{C}$ with an estimated mass loss 9.40% (calculated mass loss = 9.00%), which is reasonably accounted for loss of two Cl groups. The third step corresponding to loss of two $-\text{CH}_3$ and two biphenyl groups (calculated mass loss = 45.00%), with estimated mass loss of 45.60% , were found within the temperature range $165\text{--}560^\circ\text{C}$. The last step probably accounted for the decomposition of remaining part of the complex. But decomposition did not finish at 1000°C . Therefore, last decomposition residue was not determined.

3.4. Magnetic susceptibility

The magnetic moment values of the complexes have been measured at room temperature and are listed in Table I. The magnetic susceptibility measurements show that the complexes except Zn(II) complex (4) are paramagnetic at ambient temperature. According to the magnetic moment results Co(II) complex (1) has a room temperature magnetic moment of 3.80 BM as expected for a high-spin octahedral Co(II) complex [13]. Synthesized Ni(II) complex (2) is paramagnetic with a magnetic susceptibility value of 2.88 BM , which is in agreement with the two-spin value of 2.83 BM . The magnetic moment data of the Cu(II) complex (3) at room temperature is *ca.* 1.87 BM , corresponding to one unpaired electron. The complex (3) may be considered to have octahedral geometry.

3.5. UV-Vis measurements

The electronic spectra data of the ligand (HL) and its metal complexes are summarized in Table III. The UV-vis spectra of the ligand exhibits 3 main peaks: at 295, 327, and 316 nm. The first and second peaks were attributed to $\pi \rightarrow \pi^*$ transitions of the benzene and imine group, respectively. The first peak of the ligand was not significantly affected by chelation. But the second peak was shifted to a shorter wavelength (16–57 nm). These shifts may be attributed to the chelation of the nitrogen atom of the ligand to the metal ion. It is further supported by the shifting the peak at 316 nm to a longer wavelength which was attributed to the $n \rightarrow \pi^*$ transitions.

TABLE III

UV-Vis absorption band data of the ligand and its complexes (nm).

Compounds	$\pi \rightarrow \pi^*$ (benzene)	$\pi \rightarrow \pi^*$ (imine)	$n \rightarrow \pi^*$	Charge transfer	$d \rightarrow d$
HL	295	327	316	–	–
CoL ₂ (H ₂ O) ₂	298	276	334	443	503
NiL ₂ (H ₂ O) ₂	295	311	352	412	506
CuL ₂ (H ₂ O) ₂	298	270	342	439	503
ZnL ₂ (H ₂ O) ₂	295	303	330	421	–

Another difference observed in the electronic spectra of the metal complexes, compared to the spectra of the corresponding free ligand, is associated with the appearance of a broad low intensity band at *ca.* 500 nm. This band is attributed to the $d-d$ transitions of the metal ions. The appearance of a strong band between 412 and 443 nm is assigned to charge transfer bands.

3.6. Conductivity measurements

The conductances of the solutions of the complexes in DMF (10^{-3} M) are shown in Table I. As can be seen from Table I, the molar conductances of the complexes are between 4 and $17 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ indicating the non-electrolytic nature of the complexes [14].

3.7. Dye decolorization studies

The catalytic activities of the complexes were evaluated in the decolorization of methylene blue at room temperature. Methylene blue shows several interesting features as a probe molecule for oxidation reactions, such as: (i) high solubility in water, (ii) the oxidation can be monitored simply by spectrophotometric measurements, and (iii) it simulates the behavior of textile dyes which are an important class of contaminant [15]. Experimental results show that Cu(II) complex (3) shows maximum decolorization at 25 °C.

The order of reactivity of the metal complexes is: $3 > 1 > 2 > 4$ (Fig. 3). It is believed that metal ion oxidized to hydrogen peroxide forming hydroxyl radical. Then the hydroxyl radical reacted with the methylene blue to oxidize it.

4. Conclusion

4-chloro-2-[1-(4-phenylphenyl)ethylideneamino]phenol ligand and its mononuclear Co(II), Ni(II), Cu(II), and Zn(II) complexes were synthesized and characterized by elemental analyses, magnetic susceptibility, molar conductivity, ¹H- and ¹³C-NMR, FT-IR, UV-Vis, ICP-OES and TG-DTG (thermogravimetric-differential thermogravimetric) analysis studies. Elemental analyses, stoichiometric and spectroscopic data of the metal complexes indicated that in the complexes, metal ion was complexed with nitrogen atom of imine group and phenolic oxygen (Fig. 2). Metal complexes of the ligand have a 1:2 metal:ligand ratio and all complexes of the ligand have octahedral geometry. Furthermore, the rate of catalytic decolorization of methylene blue using prepared metal complexes was successfully performed. The dye has been successfully decolorized 91% in the presence of Cu(II) complex (3) at 25 °C.

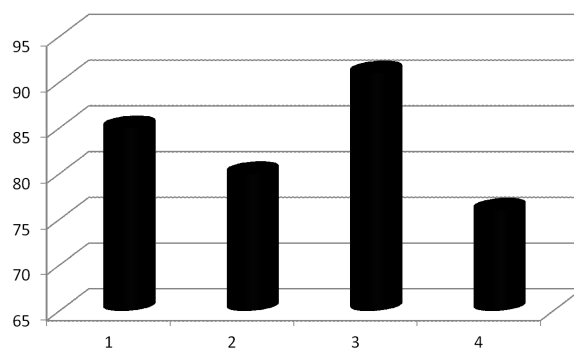


Fig. 2. Dye decolorization percentages of the metal complexes.

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