I.A.U.
Karaj Branch

-Journal of Applied Chemical Research, 9, 2, 59-65 (2015)

Journal of Applied Chemical Research
www.jacr.kiau.ac.ir

Synthesis and Characterization of New Schiff Bases of Ethylenediamine and Benzaldehyde Derivatives, Along with Their Iron Complexes

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Abstract

Two new symmetrical Schiff bases have been prepared by the condensation of ethylenediamine and two benzaldehyde derivatives, 2-hydroxybenzaldehyde and 2,4-dimethoxybenzaldehyde. The electronic transitions within these Schiff bases molecules in chloroform solvent have been investigated by UV-Vis spectroscopy. The ^{1}H NMR and IR spectra were studied and assigned to related groups. Furthermore, Two iron complexes with mentioned Schiff base have been synthesized by the reaction of titled ligands and transition metal ion, Fe (III) in the ratio of 1:1. The iron complexes have been characterized as well.

Keywords: *Schiff base, Benzaldehyde derivatives, Iron complex, ^{1}H NMR, IR.*

Introduction

The preparation of a new ligand is perhaps the most important step in the development of metal complexes which exhibit unique properties and novel reactivity [1-3]. Schiff base compounds (-RC=N-) are usually formed by the condensation of a primary amine with an active carbonyl. The cross-linking agents can also be derived from metal complexes with O, N or S ligands. For example, an intra coordination salt such as salicylates or anthranilates and aliphatic or aromatic amines can form strong five or six membered chelate rings which are able to produce metal containing cross-linking agents with the required properties [4-7].

Schiff bases are the important class of ligands and have wide applications in biological, clinical, analytical and industrial studies in addition to their important roles in catalysis and organic synthesis [8-9]. Some Schiff bases were tested for fungicidal activity which

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is related to their chemical structure [10]. Aromatic Schiff bases or their metal complexes catalyze reactions on oxygenation, hydrolysis, electro-reduction and decomposition [11-15]. The field of Schiff base complexes is fast developing because of the wide variety of possible structures for the ligands, depending on the aldehyde and amine used. Many Schiff bases and their complexes have been widely studied because of their industrial and biological applications [16, 17]. Moreover in recent years, metal complexes of Schiff bases have attracted considerable attention due to their remarkable antibacterial, antifungal and antitumor activities [18-22].

In the present article, two symmetrical Schiff bases have been prepared by the condensation of ethylenediamine with benzaldehyde derivatives, 2-hydroxybenzaldehyde and 2,4-dimethoxybenzaldehyde, as well as two metal complexes with mentioned Schiff bases, N,N-bis(2-hydroxybenzilidene)ethylene -diamine and N,N-bis (2,4-dimethoxybenzilidene) Ethylene diamine, where transition metal ion was Fe(III). The Schiff base ligands and their iron complexes were characterized by elemental analysis, UV-Vis., ^{1}H NMR and IR spectroscopy.

Experimental

Materials

All chemicals were purchased from Merck and Aldrich. Infrared spectra (4000–250 cm^{-1}) of solid samples were taken as a 1% dispersion in KBr pellets using a Shimadzu-470 spectrometer. ^{1}H NMR spectra were acquired on a Bruker AC-300 MHz spectrometer at ambient temperature in $CDCl_3$. The melting points are uncorrected and were obtained by a Kofler Heizbank Rechart type 7841 melting point apparatus. UV–Vis. spectra were recorded on a UNICO-4802 spectrometer using a 1 cm path length cell. Elemental analyses were performed using a Heraeus CHN–O Rapid analyzer.

Synthesis of ligand L1

0.2 ml (3 mmol) of Ethylenediamine and 0.63 ml (6 mmol) of 2-hydroxybenzaldehyde were added to 20 ml of absolute ethanol. The reaction mixture was refluxed for 3h at 40 °C. The powder was collected by vacuum filtration and dried overnight in vacuum (yellow, yield 0.65 g, 80.8 %, m.p. 135-140 °C). ^{1}H NMR δ_H ($CDCl_3$): 3.96 (s, 2H, $-CH_2-N=$), 6.87 (dd, 1H, Hc_{Ar}), 6.95 (d, 1H, Ha_{Ar}), 7.24 (d, 1H, Hd_{Ar}), 7.30 (d, 1H, Hb_{Ar}), 8.3 (s, 1H, -CH=N-) and 13.2 (s, 1H, OH). IR (KBr, cm^{-1}): 470, 644, 741, 852, 1042, 1146 (ν C-N), 1198, 1283 (ν C-C), 1423, 1495, 1573 (ν C=C), 1636 (ν -CH=N-), 2896, 2930, 3048 (ν C-H, Ar), 3427 (ν O-H). UV–Vis. λ_{max} ($CHCl_3$): 260 nm, 325 nm. Anal. Calc. for H_2L1: C, 76.07; H, 4.27; N, 9.96. Found: C, 71.64; H, 5.97; N, 10.45%.

Synthesis of ligand L2

0.2 ml (3 mmol) of Ethylenediamine and 1 g (6 mmol) of 2,4-dimethoxybenzaldehyde were added to 20 ml of absolute ethanol. The reaction mixture was refluxed for 3h at 40 ºC. A powder was collected by vacuum filtration and dried overnight in vacuum (opalescent, yield 0.89 g, 83.2 %, m.p. 143-159 ºC). Fig. 1 demands synthetic scheme of the ligands L1 and L2. 1H NMR δH ($CDCl_3$): 3.81 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.91 (s, 2H, -CH_2-N=), 6.42 (s, 1H, Hd_{Ar}), 6.51 (d, 1H, Hb_{Ar}), 7.27 (s, 1H, Ha_{Ar}), 7.88 (s, 1H, Hc_{Ar}) and 8.62 (s, 1H, -CH=N-). IR (KBr, cm^{-1}): 533, 578, 830, 1031 (ν C-O), 1124, 1165 (ν C-N), 1205, 1265 (ν C-C), 1421, 1466, 1503, 1607 (ν C=C), 1636 (ν -CH=N-), 2833 (ν C-H, Ar), 2881, 2996 (ν C-H, Me). UV–Vis. λ_{max}(CHCl3): 275 nm, 320 nm. Anal. Calc. for H_2L2: C, 72.37; H, 4.96; N, 10.74. Found: C, 65.75; H, 6.57; N, 7.67%.

Synthesis of Fe(III) complexes

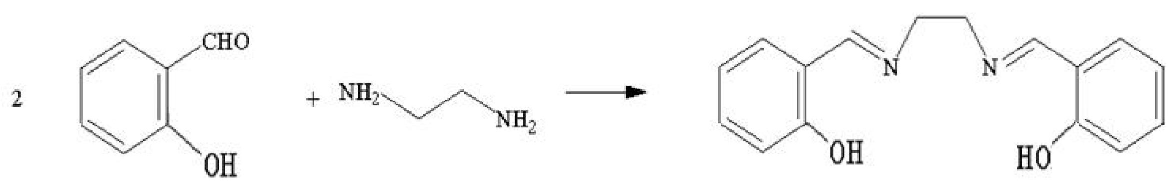
$FeCl_3.6H_2O$ (0.3 g, 1 mmol) was dissolved in methanol (20 ml) and reacted with mentioned ligands (1 mmol) dissolved in 20 ml of methanol. The mixture was stirred at 40 °C for 2 h, and then the resulting precipitate was filtered, washed with cold methanol and dried under vacuum over silica gel.

Complex **1** (brown, yield 0.31 g, 72 %, m.p. 264-272 °C)

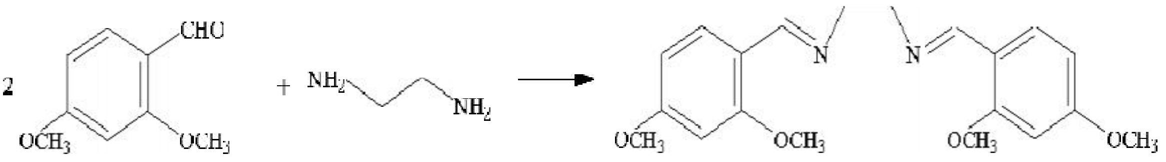
IR (KBr, cm^{-1}): 474, 570, 800, 838, 938, 1020, 1038, 1107, 1161 (ν C-N), 1209, 1276, 1324 (ν C-C), 1440, 1503 (ν C=C), 1603 (ν -C=N-), 2833, 2915, 3004 (ν C-H, Ar), 3439 (ν O-H). UV–Vis. λ_{max} (CH_3OH): 235 nm, 260 nm and 325 nm. Anal. Calc. for **1**: C, 46.47; H, 6.13; N, 9.81. Found: C, 44.62; H, 3.27; N, 6.50%.

Complex **2** (orange, yield 0.38 g, 73 %, m.p. 135-145 ºC)

IR (KBr, cm^{-1}): 611, 804, 860, 1027 (ν C-O), 1165 (ν C-N), 1217, 1298 (ν C-C), 1365, 1458, 1503, 1555 (ν C=C), 1614 (ν -C=N-), 1781, 2833 (ν C-H, Ar), 2930, 2989 (ν C-H, Me), 3149, 3338, 3517. UV–Vis. (CH_3OH) λ_{max}: 230 nm, 275 nm, 320 nm and 400 nm. Anal. Calc. for **2**: C, 39.11; H, 0.37; N, 4.86. Found: C, 46.31; H, 4.63; N, 5.4%.



N,N-bis(2-hydroxybenzilidene)ethylenediamine



N,N-bis(2,4-dimethoxybenzilidene)ethylenediamine

Figure 1. Synthetic scheme of Schiff base ligands.

Results and discussion

Synthesis of the compounds

Ligands L1 and L2 have been prepared by the condensation of ethylenediamine and two benzaldehyde derivatives, 2-hydroxybenzaldehyde and 2,4-dimethoxybenzaldehyde, as Figure 1 is described the schematic scheme of two Schiff base ligands. Both compounds were characterized with ^{1}H NMR, IR and UV-Vis spectroscopy.

Complex 1 was obtained from reaction of one equivalent of $FeCl_3.6H_2O$ with one equivalents of ligand **1** in methanol at 40 °C, in 72% yield. Complex **2** was prepared in 73% yield similarly except for the replacement of L2 with L1. The mentioned iron complexes were characterized with spectroscopic methods, also.

IR Spectra

In the absence of a powerful technique such as single x-ray crystallography, infrared spectra has proven to be the most suitable technique to give enough information to elucidate the nature of bonding of the ligand to the metal ions. The free Schiff base ligands show a strong band in the region 1636 cm^{-1} which is characteristic of the azomethine group [23]. Coordination of the Schiff bases to the metal through the nitrogen atom is expected to reduce electron density in the azomethine ring and lower the C=N absorption frequency, as in the metal complexes, the vibration mode of C=N absorption is shifted to lower frequencies and appears around 1603-1614 cm^{-1}, indicating coordination of the azomethine nitrogen to metal ions [24]. Furthermore, a strong band at 1031 cm^{-1} is observed in the free Schiff base L2, which is characteristic of the C-O group. Coordination of the Schiff bases to the metal leads that the C-O absorption frequency appears around 1027 cm^{-1} [25].

^{1}H NMR spectra

^{1}H NMR spectra of Schiff base ligands were recorded in CDCl3 solution on a Bruker Advance 300 instrument, in room temperature. The ^{1}H NMR spectrum of the Fe (III) complexes illustrate paramagnetic nature. 1H NMR spectrum of L1 shows two doublets for the H_a and H_d at 6.9 ppm and 7.2 ppm, where Hc and H_b are observed at 6.9 ppm and 7.3 ppm (as dd), respectively. The hydroxy proton of L1 appears as a singlet at 13.2 ppm (Figure 2, a). ^{1}H NMR spectrum of L2 shows two doublets for the H_b and H_c at 6.5 ppm and 7.9 ppm, whereas H_d and Ha are observed as two singlets at 6.4 ppm and 7.3 ppm, respectively. The methoxy protons appear as singlet at 3.1 ppm. The imine protons are observed as singlets, at 8.4 ppm for L1 and 8.6 ppm for L2 (Figure 2, b).

Absorption spectra

The UV-Vis spectra were recorded on UNICO spectrophotometer (model 4802) with quartz cells of 1 cm^{-1} path length. The UV-Vis spectra of the ligands were recorded in chloroform solution in the wavelength range from 200-400 nm and UV-Vis spectra of the complexes were recorded in methanol solution in the wavelength range from 200-800 nm (Table 1). The band appearing in the range of 260-280 nm is attributed to π→π* transition of the benzene ring of the ligands, where these bands are slightly shifted to lower wavelength in the spectra of the complexes. Furthermore, the absorption spectra of the free ligands illustrate a band in the 320-325 nm range that is assigned to the n→π* transitions of the azomethine group. During the formation of the complexes these bands are shifted to lower wavelength suggesting that the nitrogen atom of the azomethine group is coordinated to the metal ion [27]. The electronic spectrum of Fe(III) complexes shows an absorption band around 530 nm for complex **1** and 400 nm for complex **2**, attributed to the $^{5}T_{2}g \rightarrow {}^{5}Eg$ transition [28]. Moreover a signal around 320 nm is observed in the spectra of both complexes, which can be assigned to LMCT.

Table 1. UV-Visible spectra (nm).

Compounds	Absorbance (nm)	Assignment
L_1 [$C_{16}H_{16}N_2O_2$]	260	π→π*
	325	n→π*
L_2 [$C_{20}H_{24}N_2O_4$]	275	π→π*
	320	n→π*
complex **1** [$C_{16}H_{16}N_2O_2Cl_3Fe$]	235	π→π*
	260	n→π*
	325	LMCT
	530	$^5T_2g \rightarrow {}^5Eg$
complex **2** [$C_{20}H_{24}N_2O_4Cl_3Fe$]	230	π→π*
	275	n→π*
	320	LMCT
	400	$^5T_2g \rightarrow {}^5Eg$

Conclusions

In the present paper two symmetrical Schiff bases have been prepared by the condensation of ethylenediamine and benzaldehyde derivatives; and characterized by electronic absorption spectra, ^1H NMR and IR spectroscopies, Two iron complexes with mentioned Schiff base have been synthesized by the reaction of titled ligands and transition metal ion, Fe(III) in the ratio of 1:1. The iron complexes have been characterized by elemental analysis, infrared and UV-Vis. spectra. Metal complexes involved coordination of metal ion through azomethine nitrogen atom.

Acknowledgements

The authors are grateful to Islamic Azad University, North Tehran Branch for its financial support.

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