

# Spectrophotometric Studies of the Behaviour of Multidentate Schiff Base Ligands with Copper(II) in Methanol Solution

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## ABSTRACT

Four formation reaction complexes of polydentate Schiff base ligands derived from condensation of ethylenediamine with salicylaldehyde ( $L_1$ ) and 2-pyridinecarboxaldehyde ( $L_2$ ) and of diethylenetriamine with salicylaldehyde ( $L_3$ ) and 2-hydroxy-1-naphthaldehyde ( $L_4$ ) as electron donors with copper (II) chloride as an electron acceptor in methanol were studied spectrophotometrically at 301 K. The absorption band wavelengths of the electron donors, the electron acceptor and their complexes were measured and studied. Parameters such as the molar absorptivities,  $\epsilon^{AD}$ , of these complexes and the equilibrium constants,  $K^{AD}$ , of their formation reactions obtained from the Benesi-Hildebrand equation were established and discussed. The absorption band energies of the complexes,  $E$ , the ionization potentials of the Schiff base ligands,  $I^D$ , and the Gibbs energy changes of the above reactions,  $\Delta G$ , were calculated. Finally, kinetic parameters such as the orders of the reactions, and the rate constants of the forward and reverse reactions,  $k_1$  and  $k_{-1}$ , were determined.

## KEYWORDS

UV-Visible, spectrophotometry, Schiff base ligand, transition metal complexes, copper(II) chloride, methanol, Benesi-Hildebrand.

## 1. Introduction

The polydentate Schiff bases are well known to coordinate with various metal ions to form metallic complexes with theoretical and practical applications of different types.<sup>1-5</sup>

A large number of Schiff base ligand complexes have been studied for their dioxygen uptake and oxidative catalysis.<sup>6-9</sup> Also complexes of transition metals such as Co(II) and Cu(II) involving derivatives of salicylaldehyde and aliphatic amines have received considerable attention because of their similarity to biological dioxygen carriers, as well as their potential as catalysts for the insertion of oxygen into organic substrates.<sup>10-13</sup>

Although their synthesis, structure, coordination chemistry and electrochemical behaviour have been extensively studied,<sup>14-22</sup> nothing has been reported concerning the spectrophotometric behaviour of these complexes in solution.

Studies of different complexes of mono-Schiff base ligands with non-metallic electron acceptors such as iodine and chloranil in solution using spectrophotometry have been described. Several parameters concerning these ligands and their complexes such as  $I^D$ ,  $K^{AD}$ ,  $\Delta E$ ,  $\epsilon^{AD}$  and  $G$  were established.<sup>23-29</sup>

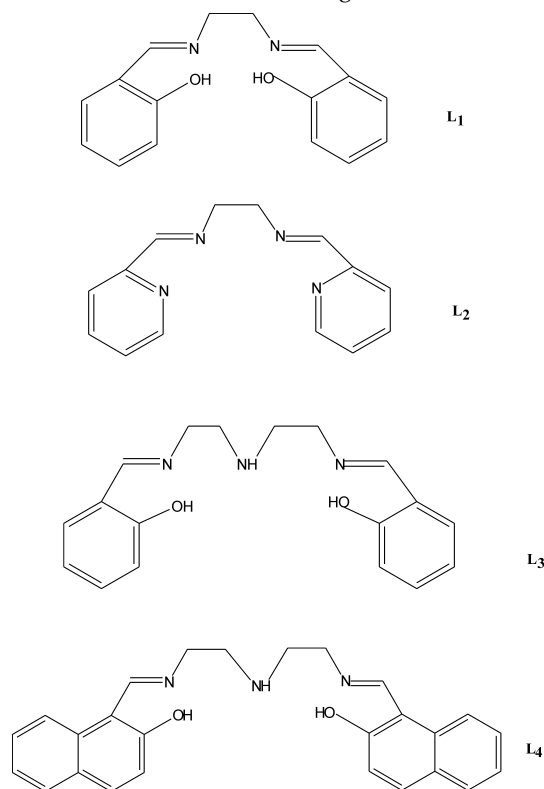
To our knowledge, no such studies have been done on transition metal complexes of these polydentate Schiff base ligands.

The present study aims to investigate the spectrophotometric behaviour of four polydentate Schiff base ligands (Scheme 1) with copper ion in methanol at 301 K.

Several parameters concerning complexation reactions such as equilibrium constant,  $K^{AD}$ , and Gibbs energy change,  $\Delta G$ , were evaluated, as well as the molar absorptivities,  $\epsilon^{AD}$ , absorption band energies,  $E$ , and ionization potentials,  $I^D$ , of the Schiff base ligands.<sup>30-36</sup>

The Schiff base ligands  $L_1$  to  $L_4$  were chosen according to their structures by changing both the aldehyde and the amine parts in order to study their influence on the metal coordination sphere.

$K^{AD}$  and  $\epsilon^{AD}$  were calculated using the Benesi-Hildebrand



Scheme 1

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**Table 1** Absorption band wavelengths (nm) for the Schiff base ligands and their complexes in methanol at 301 K.

Donors				Complexes			
L <sub>1</sub>	L <sub>2</sub>	L <sub>3</sub>	L <sub>4</sub>	L <sub>1</sub> /Cu <sup>2+</sup>	L <sub>2</sub> /Cu <sup>2+</sup>	L <sub>3</sub> /Cu <sup>2+</sup>	L <sub>4</sub> /Cu <sup>2+</sup>
205	220	225	200	220	269	245	220
255	292	275	220	247	278	275	315
315		316	270	285	282	360	375
405		402	310	352	288	579	562
			400	360	294		
			420	574	703		

equation which gave acceptable straight lines:<sup>37</sup>

$$\frac{[A_0]}{A} = \frac{1}{K^{AD}\epsilon^{AD}[D_0]} + \frac{1}{\epsilon^{AD}}, \quad (1)$$

where A = absorbance of the complex band at  $\lambda_{max}$ ,  $[A_0]$  = initial concentration of the acceptor,  $[D_0]$  = initial concentration of the donor,  $K^{AD}$  = equilibrium constant of the complex reaction in solution, and  $\epsilon^{AD}$  = molar absorptivity of the complex at  $\lambda_{max}$ .

The ionization potentials of the electron donors were calculated from the positions of the charge transfer (CT) bands for iodine complexes using the following equations:<sup>32-36</sup>

$$h\nu_{CT} = I^D - C_1 + \frac{C_2}{I^D - C_1} \quad (2)$$

$$h\nu_{CT} = a I^D + b \quad (3)$$

$$I^D = 4.39 + 0.857 h\nu_{CT} \quad (4)$$

$$I^D = 5.1 + 0.7 h\nu_{CT}, \quad (5)$$

where  $h\nu_{CT}$  is the absorption band energy of the CT complex in eV,  $I^D$  is the ionization potential of the electron donor in eV,  $C_1$ ,  $C_2$ ,  $a$  and  $b$  in Equations 2 and 3 are constants and their values for the iodine acceptor are as follows:

$$C_1 = 5.2 \text{ eV}, C_2 = 1.5 \text{ eV}^2, a = 0.67, b = -1.9 \text{ or } a = 0.87, b = -3.6.$$

Moreover, the kinetics of complexation reactions in methanol at 301 K were studied using the following equations:<sup>38-41</sup>

$$\frac{x_e}{a^2 - x_e^2} \ln \frac{x_e(a^2 - xx_e)}{a^2(x_e - x)} = k_1 t = y \quad (6)$$

$$\frac{k_1}{k_{-1}} = \frac{x_e}{(a - x_e)^2} = K^{AD}, \quad (7)$$

where  $a$  = initial concentration of donor and acceptor,  $x$  = concentration of the complex,  $x_e$  = concentration of the complex at equilibrium, and  $k_1$  and  $k_{-1}$  are the rate constants of the forward and the reverse reactions.

## 2. Experimental

All organic compounds used were obtained from Merck. Methanol and copper (II) chloride dihydrate were obtained from Fluka and used as received. The UV-visible spectra were measured using Perkin Elmer Lambda 20 and Shimadzu UV-1202 (Shimadzu Europa GmbH) UV-visible spectrometers and quartz cells of 1.0 cm path length. Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrometer, using KBr pellets.

<sup>1</sup>H NMR spectra were recorded with a Bruker AMX-300 spectrometer using CDCl<sub>3</sub> as solvent, and chemical shifts are reported relative to TMS as internal standard.

The polydentate Schiff base ligands derived from condensa-

tion of ethylenediamine with salicylaldehyde (L<sub>1</sub>) and 2-pyridinecarboxaldehyde (L<sub>2</sub>), and of diethylenetriamine with salicylaldehyde (L<sub>3</sub>) and 2-hydroxy-1-naphthaldehyde (L<sub>4</sub>) used throughout this work were prepared by condensation of the aldehyde and di- or triamine in 2:1 ratio and refluxing in ethanol for two hours.<sup>42</sup> The purity of these ligands was checked by their IR and <sup>1</sup>H NMR spectra.

• L<sub>1</sub>: green-yellow pellets; yield 98%; IR (KBr pellet, cm<sup>-1</sup>): 1634 (C=N); <sup>1</sup>H NMR (CDCl<sub>3</sub>, δppm): 13.1 (s, 2H, OH), 8.47 (s, 2H, CH=N), 6.90–7.40 (m, 8H, aromatic H), 4.01 (t, 4H, N-(CH<sub>2</sub>)<sub>2</sub>).

• L<sub>2</sub>: orange-yellow powder; yield 65%; IR (KBr pellet, cm<sup>-1</sup>): 1641 (C=N); <sup>1</sup>H NMR (CDCl<sub>3</sub>, δppm): 8.40 (s, 2H, CH=N), 7.30 (m, 2H, py), 7.71 (m, 2H, py), 7.95 (m, 2H, py), 8.62 (m, 2H, py), 4.05 (t, 4H, N-(CH<sub>2</sub>)<sub>2</sub>).

• L<sub>3</sub>: oil; yield 70%; IR (KBr pellet, cm<sup>-1</sup>): 1631 (C=N); <sup>1</sup>H NMR (CDCl<sub>3</sub>, δppm): 13.2 (s, 2H, OH), 8.35 (s, 2H, CH=N), 6.80–7.32 (m, 8H, aromatic H), 2.99 (t, 4H, =N-C-CH<sub>2</sub>-), 3.71 (t, 4H, =N-CH<sub>2</sub>-C-).

• L<sub>4</sub>: yellow-brown powder; yield 75%; IR (KBr pellet, cm<sup>-1</sup>): 1629 (C=N); <sup>1</sup>H NMR (CDCl<sub>3</sub>, δppm): 13.4 (s, 2H, OH), 8.78 (s, 2H, CH=N), 6.88–7.86 (m, 12H, aromatic H), 3.03 (t, 4H, =N-C-CH<sub>2</sub>-), 3.70 (t, 4H, =N-CH<sub>2</sub>-C-).

The complexes were prepared by mixing variable concentrations of donor (ranging between  $0.5 \times 10^{-4}$  and  $5 \times 10^{-4}$  mol dm<sup>-3</sup>) with a constant acceptor concentration ( $3 \times 10^{-4}$  mol dm<sup>-3</sup>) in methanol at 301 K.

The kinetic measurements were performed in methanol at 301 K on equimolar samples of donor and acceptor. Their concentrations ranged between  $3 \times 10^{-4}$  and  $5 \times 10^{-3}$  mol dm<sup>-3</sup>. These measurements were followed kinetically at the complex  $\lambda_{max}$  values in the visible region as reported in Table 1.<sup>41</sup>

The absorbances of the donor-acceptor mixtures were measured with change of time in the visible region at their  $\lambda_{max}$  values.

## 3. Results and Discussion

The absorption band wavelengths of the Schiff base ligands and their complexes were measured in methanol and are shown in Table 1. The four complexes exhibit new absorption bands in the visible region which can be associated with d-d transitions; their wavelengths are 574, 703, 579 and 562 nm for the L<sub>1</sub> to L<sub>4</sub> complexes, respectively. The differences among these values are probably due to the change in the nature of the metal environment in the four complexes.

The values of  $K^{AD}$  and  $\epsilon^{AD}$  obtained by plotting  $[A_0]/A$  against  $1/[D_0]$ , using the Benesi-Hildebrand equation, as shown in Fig. 1, are reported in Table 2.

The values of  $K^{AD}$  for the L<sub>1</sub> to L<sub>4</sub> complexes are 1677, 1218, 761 and 785 dm<sup>3</sup> mol<sup>-1</sup>, respectively. These results may indicate that Cu(II) complexes with the pentadentate ligands L<sub>3</sub> and L<sub>4</sub> are less stable than the corresponding complexes with the tetradentate ones, L<sub>1</sub> and L<sub>2</sub>. This is probably due to the differences in the

**Table 2** Absorption maxima, wavenumbers, equilibrium constants, molar absorptivities, absorption band energies and Gibbs energy changes of complex formation reactions in methanol at 301 K.

	L <sub>1</sub> /Cu <sup>2+</sup>	L <sub>2</sub> /Cu <sup>2+</sup>	L <sub>3</sub> /Cu <sup>2+</sup>	L <sub>4</sub> /Cu <sup>2+</sup>
λ <sub>max</sub> (nm)	574	703	579	562
ν (cm <sup>-1</sup> )	17422	14225	17271	17794
K <sup>AD</sup> (dm <sup>3</sup> mol <sup>-1</sup> )	1677 ± 27	1218 ± 22	761 ± 18	785 ± 17
ε <sup>AD</sup> (dm <sup>3</sup> cm <sup>-1</sup> mol <sup>-1</sup> )	598	471	402	937
E (eV)	2.160	1.764	2.142	2.207
-ΔG (kJ mol <sup>-1</sup> )	18.6	17.8	16.6	16.7

spatial configurations of the two types of complexes. In fact, the presence of the secondary amine nitrogen in the metal coordination sphere may lead to ligand distortion in the L<sub>3</sub> and L<sub>4</sub> complexes, unlike the less rigid L<sub>1</sub> and L<sub>2</sub> complexes, in which the planarity of the tetradentate ligands has been described.<sup>4,5,21</sup>

On the other hand, it seems that the stability of the L<sub>1</sub> complex containing the phenate group is higher than that of the L<sub>2</sub> complex containing pyridyl. This indicates that the phenate group coordinates more strongly with copper ion than does pyridyl.

Finally, the slight difference in the values of K<sup>AD</sup> for the L<sub>3</sub> and L<sub>4</sub> complexes indicates that the substitution of the phenyl by the naphthyl group does not affect the complex stability to a great extent.

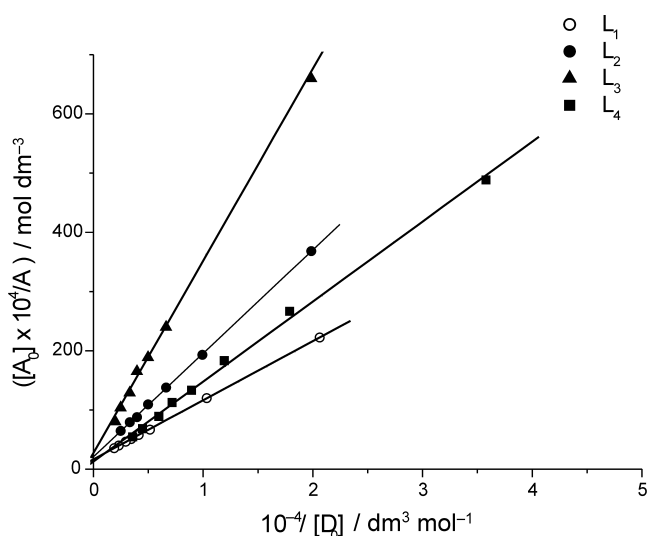
Molar absorptivities, ε<sup>AD</sup>, obtained from Equation 1, are 598, 471, 402 and 937 dm<sup>3</sup> cm<sup>-1</sup> mol<sup>-1</sup> for complexes L<sub>1</sub> to L<sub>4</sub>, as shown in Table 2.

The absorption band energies, E, are given in Table 2; these are 2.160, 1.764, 2.142 and 2.207 eV for the L<sub>1</sub> to L<sub>4</sub> complexes, respectively.

Moreover, the Gibbs energy changes for the four complex formation reactions, calculated from the values of K<sup>AD</sup>, are given in Table 2. These are -18.6, -17.8, -16.6 and -16.7 kJ mol<sup>-1</sup>, respectively. This shows that the spontaneity of these reactions follows the trend

$$L_1 > L_2 > L_4 > L_3.$$

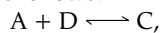
In order to calculate the ionization potentials of the Schiff base ligands, we utilized data for their complexes with iodine in methanol at 301 K. The absorption band wavelengths of the iodine complexes are 424, 386, 421 and 466 nm for the L<sub>1</sub> to L<sub>4</sub> complexes, respectively.

**Figure 1** Plots of  $([A_0]/A)$  versus  $1/[D_0]$ .**Table 3** Calculated ionization potentials of the Schiff base ligands.

Equation	I <sup>D</sup> /eV			
	L <sub>1</sub>	L <sub>2</sub>	L <sub>3</sub>	L <sub>4</sub>
2	7.46	7.85	7.50	7.05
3	7.20	7.63	7.23	6.81
	7.50	7.83	7.52	7.20
4	6.90	7.14	6.91	6.67
5	7.15	7.35	7.16	6.96
Average value	7.24	7.56	7.26	6.94

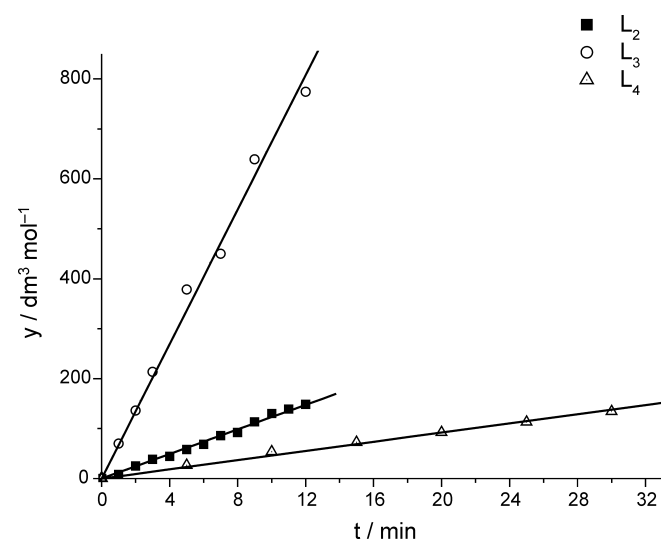
From these values, we established the ionization potentials of the four electron donors according to Equations 2–5 and these are tabulated in Table 3.<sup>43–46</sup> The average values of I<sup>D</sup> are 7.24, 7.56, 7.26 and 6.94 eV.

Finally, the kinetics of the complex formation reactions were studied at 301 K and are shown to be first order in each reactant. When equilibrium is reached the above reactions may be written as follows:



where A, D and C represent the acceptor, donor and complex, respectively.

The quantity y in Equation 6 is plotted against time in Fig. 2, from which the rate constant k<sub>1</sub> was obtained. The rate constant, k<sub>-1</sub>, for the reverse reaction was calculated using Equation 7.<sup>40,41</sup> The values of k<sub>1</sub> are shown in Table 4. The values of k<sub>1</sub> are 12.30, 67.35 and 4.60 dm<sup>3</sup> mol<sup>-1</sup> min<sup>-1</sup> for the L<sub>2</sub> to L<sub>4</sub> complex reactions, respectively. Those for k<sub>-1</sub> are 1.01 × 10<sup>-2</sup>, 8.85 × 10<sup>-2</sup> and 0.586 × 10<sup>-2</sup> min<sup>-1</sup>, respectively, while the L<sub>1</sub> complex formation reaction was found to be instantaneous.

**Figure 2** Plots of y versus time.

**Table 4** Values of complex reaction rate constants  $k_1$  and  $k_{-1}$  of Schiff base ligands with Cu(II) in methanol at 301 K.

Schiff base	$k_1/\text{dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$	$k_{-1} \times 10^2/\text{min}^{-1}$
L <sub>2</sub>	12.30 ± 0.19	1.01 ± 0.03
L <sub>3</sub>	67.35 ± 1.44	8.85 ± 0.40
L <sub>4</sub>	4.60 ± 0.09	0.586 ± 0.024

The values of  $k_1$  show that the ligand reaction rates are in the following order:

$$L_1 > L_3 > L_2 > L_4.$$

The vast differences between the values of  $k_1$  and  $k_{-1}$  for all complex formation reactions indicate that the equilibrium is greatly oriented towards complex formation.

Finally, we have been carrying out more extensive studies on these Schiff bases with other transition metals, such as Fe(III), Co(II) and Ni(II), and with non-metallic electron acceptors such as bromine and chloranil.

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