

Comparison of chelating ability of NO-, NS-, ONS-, and ONO-type Schiff base derivatives and their stability constants of Bis-complexes with copper(II)

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Received: 21.03.2013 • Accepted: 09.07.2013 • Published Online: 16.12.2013 • Printed: 20.01.2014

Abstract: The present study includes important findings relating to the number of donor atoms, species of ligands, and stabilities of complexes. Stabilities of complexes between Cu(II) ion and NO-, NS-, ONS-, and ONO-type Schiff bases were compared. Acid-base properties of the Schiff bases were explained at 25 ± 0.1 °C and ionic strength (I) of 0.1 M supported by NaCl. The Hyperquad computer program was used for calculation of dissociation and stability constants. The overall stability constants of their Cu(II) complexes were calculated and the various formed complexes between the Schiff bases with Cu(II) ion formulated as CuL_2 , CuHL_2 , CuH_2L_2 , and $\text{CuH}_{-1}\text{L}_2$ ($\text{Cu}(\text{OH})\text{L}_2$). The complexes of ONS- and ONO-type tridentate ligands were more stable than those of NO- and NS-type bidentate ligands.

Key words: Schiff bases, potentiometric titration, Hyperquad, stability constants

1. Introduction

Schiff bases have been used extensively as ligands in the field of coordination chemistry.¹⁻⁴ By attaching donor atoms of Schiff bases to transition metal ions very stable complexes are formed in the tetrahedral structures. Recently, Schiff base complexes have been attracting continuous attention for different applications.⁵⁻¹⁰ Transition metals play an important role in the construction of molecular materials that display magnetic properties and they are used in materials, supramolecular, and biochemistry.¹¹⁻¹⁵ It is well known that the metal complexes of some drugs have higher activity than free ligand forms. In particular, most Cu(II) complexes have been found to be antibacterial agents.^{16,17} The predication of acidity constants of organic reagents is important in estimating their physical and biological activity. They play a fundamental role in many analytical procedures such as acid-base titration, solvent extraction, and complex formation.¹⁸⁻²⁰ The potentiometric titration method is regarded as a powerful electro-analytical technique²¹ and is used for the determination of ionic equilibrium of many ligands and the stability constants of complexes in solutions.²²⁻²⁹ In the present study, the protonation-deprotonation equilibrium of a series of Schiff bases and the coordination properties of their binary complexes with Cu(II) ion were investigated using the potentiometric titration method.

2. Results and discussion

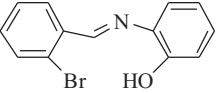
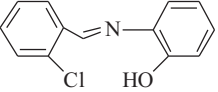
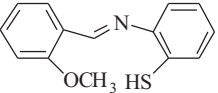
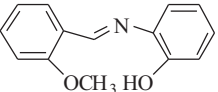
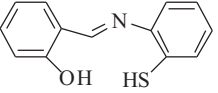
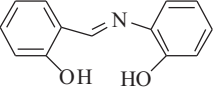
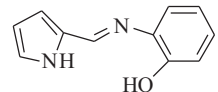
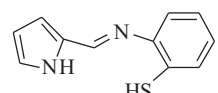
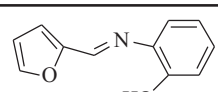
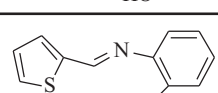
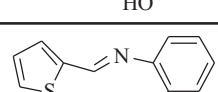
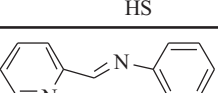
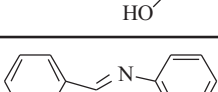
2.1. Synthesis of the Schiff bases

The studied Schiff bases were prepared³⁰ from the reactions of 2-aminophenol and 2-aminothiophenol with related aldehyde derivatives (such as 2-Br-, 2-Cl-, 2-OCH₃-, 2-OH-benzaldehyde, pyrrol-2-carbaldehyde,

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furfural, thiophene-2-carbaldehyde, and pyridine-2-carbaldehyde) in ethanol at reflux conditions for 5 h (Figure 1; Table 1).

Table 1. The structure of ligands and their physical properties.

Entry	Ligands	M.p. (°C)	Yield (%)	Ref.
1	1a 	73-76	89	10
2	1b 	93-94	84	30,31
3	1c 	95-98	91	This work
4	1d 	103-105	90	32
5	1e 	110-114	94	33
6	1f 	182-184	96	32
7	2a 	119-121	68	34
8	2b 	76-78	73	This work
9	2c 	168-170	86	35
10	2d 	46-48	95	35
11	2e 	78-80	92	36
12	3a 	172-174	96	37,38
13	3b 	119-121	75	40

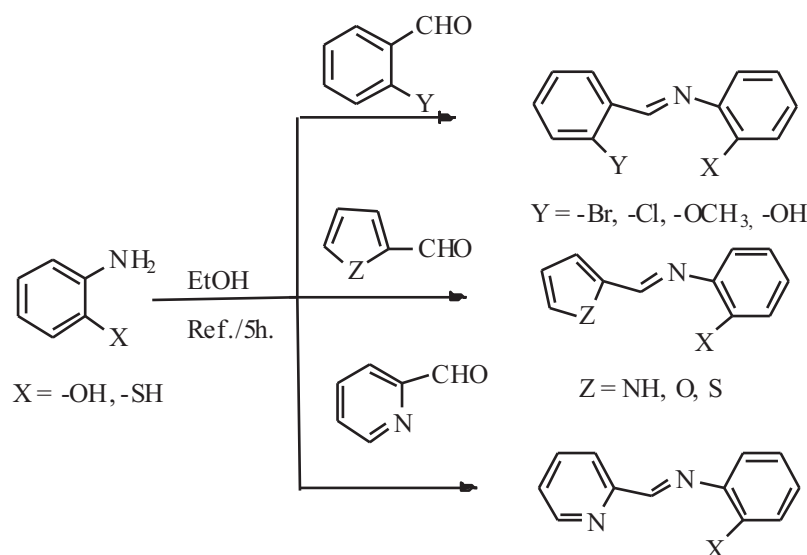


Figure 1. General synthesis route for Schiff bases.

2.2. Dissociation constants

Dissociation constants were potentiometrically obtained from a series of several independent measurements. Many NO-, NS-, ONS-, and ONO-type Schiff base ligands were investigated and **1e**, **1f**, **2a**, and **3b** represent ONS-, ONO-, NO-, and NS-type Schiff bases, respectively. The distribution curves of ligands having different coordination properties with respect to the chelating ability of **1e**, **1f**, **2a**, and **3b** are shown in Figure 2a–2d.

All the studied ligands have 2 or 3 donor atoms. For example, while **1e**, **1f**, **3a**, and **3b** have 3 protonable donor atoms, other ligands have 2 protonable donor atoms. Consequently, if the fully protonated forms of the Schiff bases are denoted as LH_n , the general notation of its protonation equilibrium is as follows:



In each stage, one proton dissociates and dissociation constants are given as

$$K_n = \frac{[LH_{n-1}] \cdot [H_3O^+]}{[LH_n]} \quad (2)$$

Dissociation constants of all ligands are calculated using the Hyperquad program under our experimental conditions and are given in Table 2 in comparison with literature data.

Compound **3b** was studied potentiometrically by Issa et al. using the Calvin–Bjerrum titration technique as modified by Irving and Rossotti at 25 °C and an ionic strength of 0.1 M (NaCl) in 70% (v/v) aqueous ethanol and dissociation constant of –SH group was determined as 10.12.⁵ This value is the same as that found in our study (10.12). Dissociation constants of **3a** were studied by Geary et al., Gürkan et al., and Sengupta et al. in 50% (v/v) aqueous methanol and 50% (v/v) aqueous dioxin, respectively.^{6–8} Dissociation constants of azomethine nitrogen of **3a** have been determined as about pK_a 6. The value is higher than our determined pK_a value (4.36). Additionally, while pK_a values reported by Friedrich et al. are 10.46 and 12.46 in 75% (v/v) aqueous dioxin,⁹ Gürkan et al.'s values are 9.19 and 10.40 using potentiometric titration at ionic strength of 0.1 M (NaClO₄) in 50% (v/v) aqueous methanol for **1f**.⁷ On the other hand, 3 pK_a values were obtained as

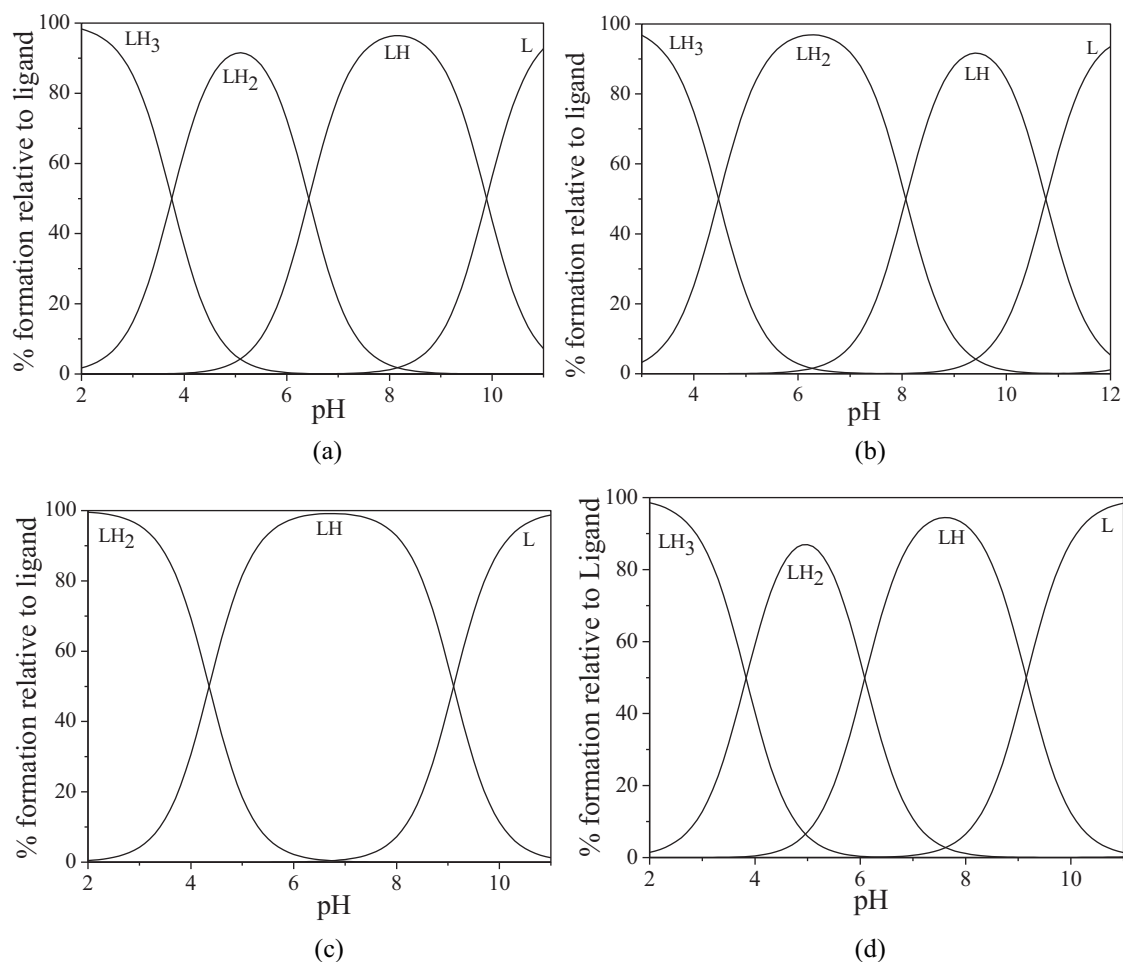


Figure 2. The species distribution curves of the ligands (a) **1e**, (b) **1f**, (c) **2a**, and (d) **3b** (25.0 ± 0.1 °C, I : 0.1 M by NaCl, 0.05 mmol HCl).

8.07, 10.76, and 4.47, which were for azomethine nitrogen in **1f** in the experimental conditions in this study. In addition, Demirelli et al. have studied the determination of dissociation constants of **1a**, **1d**, and **1f** in 20%, 40%, and 60% (v/v) aqueous dioxane, respectively, and shown the solvent effect on dissociation constants.¹⁰

As a result, different solvent and solvent ratios are shown to have changed the polarity of the solutions. Therefore, increasing the solvent ratios in solutions causes increasing dipole–dipole interaction among molecules. Thus, the measured pK_a values in an organic solvent–water mix might be different from those in an aqueous solution. It may also be thought that the high polarity of the solution media causes decreasing electron density of the azomethine nitrogen. Similarly, high polarity of the solution media increases the electron density of the phenolic groups. In this case, the pK_a values of phenolic groups of the ligands are increased (see Table 2).

2.3. Stability constants

The stability constants of binary complexes between Schiff bases and Cu(II) ion were determined following the refinement of data by the Hyperquad computer program. The cumulative stability constants (β_{mlh}) are defined by Eqs. (3) and (4).

Table 2. Dissociation constants of Schiff bases in the literature and this work (25.0 ± 0.1 °C, I : 0.1 M by NaCl, 0.05 mmol HCl).

Ligands	pK_{a1}	pK_{a2}	pK_{a3}	$\log\beta_2$	$\log\beta_3$	References
1a	4.26	10.14	-	-	-	Ref. ¹⁰
	4.21	10.57	-	-	-	Ref. ¹⁰
	3.90	11.35	-	-	-	Ref. ¹⁰
	3.38 ± 0.03	9.46 ± 0.08	-	12.84 ± 0.03	-	This work
1b	3.29 ± 0.03	9.38 ± 0.09	-	12.68 ± 0.03	-	This work
1c	3.05 ± 0.03	9.75 ± 0.08	-	12.80 ± 0.02	-	This work
1d	4.45	10.22	-	-	-	Ref. ¹⁰
	4.22	10.56	-	-	-	Ref. ¹⁰
	3.95	11.35	-	-	-	Ref. ¹⁰
	3.18 ± 0.01	9.21 ± 0.06	-	12.39 ± 0.03	-	This work
1e	-	9.32	10.34	-	-	Ref. ⁸
	3.94 ± 0.02	9.16 ± 0.03	11.33 ± 0.08	20.45 ± 0.06	24.43 ± 0.07	This work
1f	-	9.19	10.40	-	-	Ref. ⁷
	-	10.46	12.46	-	-	Ref. ⁹
	4.28	8.62	10.11	-	-	Ref. ¹⁰
	4.11	8.73	10.25	-	-	Ref. ¹⁰
	4.01	9.61	11.30	-	-	Ref. ¹⁰
	4.47 ± 0.04	8.07 ± 0.01	10.76 ± 0.08	18.83 ± 0.07	23.29 ± 0.07	This work
2a	3.83 ± 0.03	-	9.15 ± 0.08	12.99 ± 0.03	-	This work
2b	3.75 ± 0.03	-	9.69 ± 0.07	13.44 ± 0.03	-	This work
2c	5.43 ± 0.03	9.15 ± 0.02	-	14.58 ± 0.02	-	This work
2d	4.07 ± 0.01	9.28 ± 0.02	-	13.34 ± 0.03	-	This work
2e	6.35 ± 0.02	9.74 ± 0.03	-	16.09 ± 0.06	-	This work
3a	6.41	-	9.25	-	-	Ref. ⁷
	6.58	-	9.13	-	-	Ref. ⁸
	6.37	-	9.77	-	-	Ref. ⁶
	4.36 ± 0.04	6.09 ± 0.09	9.11 ± 0.01	15.19 ± 0.04	19.55 ± 0.03	This work
3b	-	-	10.12	-	-	Ref. ⁵
	3.38 ± 0.04	6.54 ± 0.09	10.12 ± 0.04	16.66 ± 0.04	20.03 ± 0.04	This work



$$\beta_{mlh} = \frac{[M_m L_l H_h]}{[M]^m [L]^l [H]^h}, \quad (4)$$

where M is Cu(II) ion, L is ligand, and H is proton, and m , l , and h are the respective stoichiometric coefficients. The potentiometric data for the Cu(II) – L₂ systems indicate that there is a significant tendency toward the formation of ML₂ species. Cu(II) ion complexes were formed by releasing 2 of the hydrogen ions from the fully protonated form of the ligands.¹¹ Compounds **1e** and **1f** serve as tridentate ligands by the coordinating of imino, phenolic –OH and –SH groups with Cu(II) ion. The others (**1a**, **1b**, **1c**, **1d**, **2a**, **2b**, **2c**, **2d**, **2e**, **3a**, and **3b**) serve as bidentate ligands. Thus, the stability constants of Cu(II) complexes of **1e** and **1f** are higher than those of the others.

Coordination numbers of a central atom can change to 6 or 4 depending on the ligand structures in the complex formation. For example, the coordination number of Cu(II) ion was observed as 4 against all studied ligands except **1e** and **1f** in this study. Therefore, tetrahedral complexes were obtained. On the other hand, the coordination number of Cu(II) ion was 6 against **1e** and **1f**, because they are tridentate ligands. The molecular structures of 4- and 6-coordinated complexes of copper with **1a** and **1f** are given in Figure 3a and 3b.

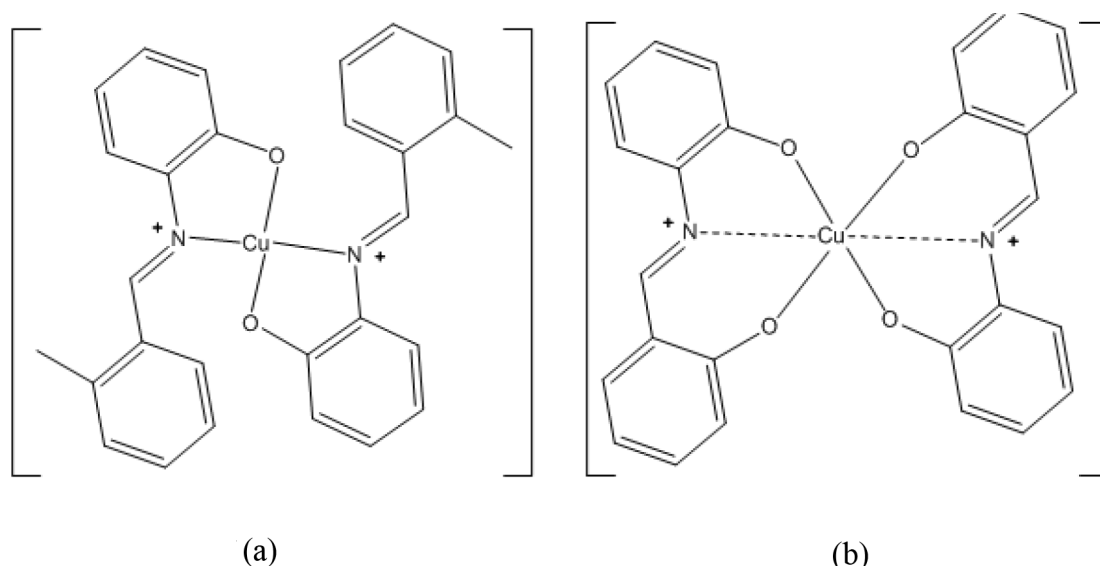


Figure 3. Molecular structures of 4- and 6-coordinated complexes of Cu(II) with **1a** and **1f** (a) Cu(II)–**1a**₂ (b) Cu(II)–**1f**₂.

Complexes having 6 coordination numbers form an octahedral structure and they can be formulated as MX₂, where MX₂ is a structure of bis-complex, M is Cu(II) ion, and X is the ligand **1e** (or **1f**). Therefore, the octahedral complexes between **1e** and **1f** and Cu(II) ion are more stable than the tetrahedral complexes. This situation was supported by the experimental (Table 3) and the semiempirical molecule orbital (SE-MO) PM3 method. 3D structures of complex species and their formation heats (H_f) are calculated by PM3 method. Accordingly, formation heats (H_f) of Cu–**1e**₂/**1f**₂/**2a**₂/**3b**₂ complexes were determined as 608.78 kcal/mol, 613.42 kcal/mol, 728.96 kcal/mol, and 776.13 kcal/mol, respectively, and the findings are given in Figure 4a–4d.

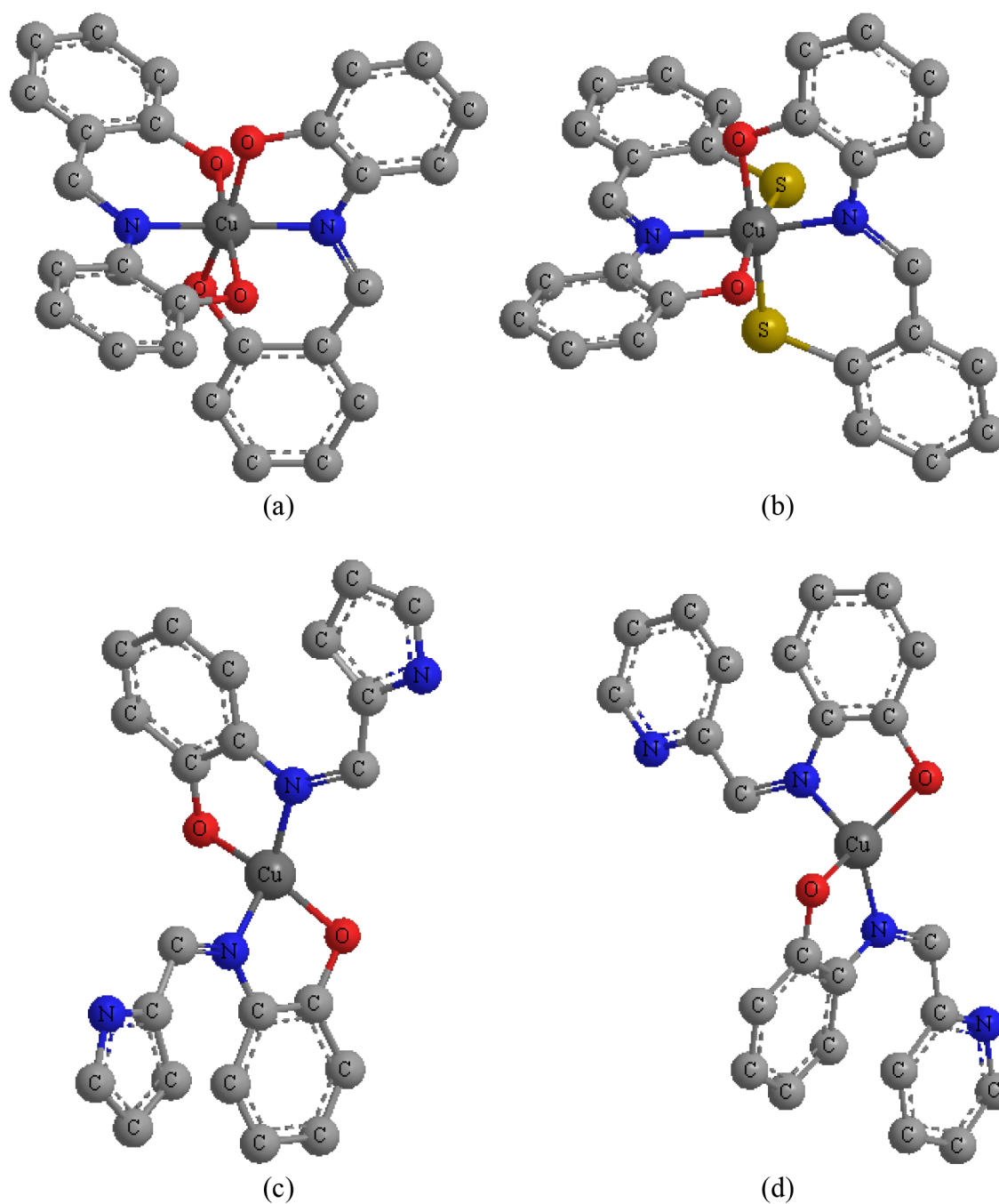


Figure 4. Comparison of 3D structure of complex species and their formation heats (H_f) (a) Cu(II)-**1e**₂ complex (ONS type) (H_f : 608.78 kcal/mol) (b) Cu(II)-**1f**₂ complex (ONO type) (H_f : 613.42 kcal/mol) (c) Cu(II)-**2a**₂ complex (NO type) (H_f : 728.96 kcal/mol) (d) Cu(II)-**3b**₂ complex (NS type) (H_f : 776.13 kcal/mol).

As a result, different electron densities on the donor atoms are an important factor affecting the stability of the Cu(II) complexes with the ligands. The various complexes between Cu(II) ion and the Schiff bases were formulated as CuL_2 , $CuHL_2$, CuH_2L_2 , and $CuH_{-1}L_2$ ($Cu(OH)L_2$), depending on pH. The overall stability constants of detectable Cu(II)- L_2 species are given in Table 3.

Table 3. Overall stability constants in Cu(II)–L₂ binary system (25.0 ± 0.1 °C, I: 0.1 M by NaCl, 0.05 mmol HCl).

Ligands	<i>m</i>	<i>h</i>	<i>l</i>	logβ	Ligands	<i>m</i>	<i>h</i>	<i>l</i>	logβ
	1	0	2	14.07 ± 0.05		1	0	2	15.88 ± 0.03
1a	1	1	2	20.38 ± 0.08	2a	1	1	2	22.90 ± 0.05
						1	-1	2	6.68 ± 0.07
	1	0	2	13.43 ± 0.05		1	0	2	16.18 ± 0.03
1b	1	1	2	19.97 ± 0.08	2b	1	1	2	22.96 ± 0.03
	1	-1	2	5.99 ± 0.09		1	-1	2	5.99 ± 0.07
1c	1	0	2	13.65 ± 0.15	2c	1	0	2	11.59 ± 0.08
	1	-1	2	6.56 ± 0.10		1	1	2	18.94 ± 0.15
1d	1	0	2	11.24 ± 0.04	2d	1	0	2	13.71 ± 0.05
	1	-1	2	1.67 ± 0.09		1	-1	2	5.45 ± 0.11
	1	0	2	18.85 ± 0.09	2e	1	0	2	13.29 ± 0.04
1e	1	1	2	28.64 ± 0.05		1	-1	2	3.84 ± 0.07
	1	2	2	35.55 ± 0.07					
					3a	1	0	2	13.60 ± 0.06
	1	0	2	17.51 ± 0.05		1	1	2	18.91 ± 0.04
1f	1	1	2	26.33 ± 0.04		1	-1	2	4.76 ± 0.01
	1	2	2	34.11 ± 0.02					
					3b	1	0	2	14.65 ± 0.06
						1	1	2	21.52 ± 0.08
						1	-1	2	6.93 ± 0.08

Electron pairs on donor atoms play a critical role for complex formation. Mobility of the electron pairs facilitates participation in coordination. However, electron-withdrawing groups on the ligands cause decreasing stability in the complexes because of the limitation of electron mobility. This situation is clearly seen in Table 3. Differences in electronegativity of Br and Cl atoms cause different stability constants in the Cu(II)–**1a**₂ and Cu(II)–**1b**₂ complexes. The same case can be said for the –OH and –SH groups.

The species distribution curves of the complexes between Cu(II) ion and **1e**, **1f**, **2a**, and **3a** ligands are given in Figure 5a–5d.

In Figure 5, the species distribution curves of **1e** differ from those of **1f** because of the different electron density of the –OH and –SH groups. In the Cu(II)–**1e**₂ system, 3 main complexes (CuL₂, CuHL₂, and CuH₂L₂) were obtained at between pH 5 and 11. The CuHL₂ species start occurring at pH 5 and reach the maximum at pH 8–9 by 90%; and the CuL₂ species start to form at pH 8 and reach the maximum at pH 11 by 99%. In the Cu(II)–**1f**₂ system, similarly, CuL₂ and CuH₂L₂ complex species were observed in the acidic and basic region at 99%, the same as in the Cu(II)–**1e**₂ system. However, CuHL₂ species reach the maximum at pH 8–9 and approx. 60%.

In Cu(II)–**2a** and Cu(II)–**3a** systems, the main complexes (CuL₂ and CuHL₂) were obtained in neutral and acidic regions. The CuL₂ and CuHL₂ species exist above pH 7 at 90% and 98%, respectively. For both complexes (Cu(II)–**2a** and Cu(II)–**3a**), hydrolysis species (CuH₋₁L₂) were also observed at pH 11 and at 99%. The logβ_{CuL2} values are shown in Figure 6.

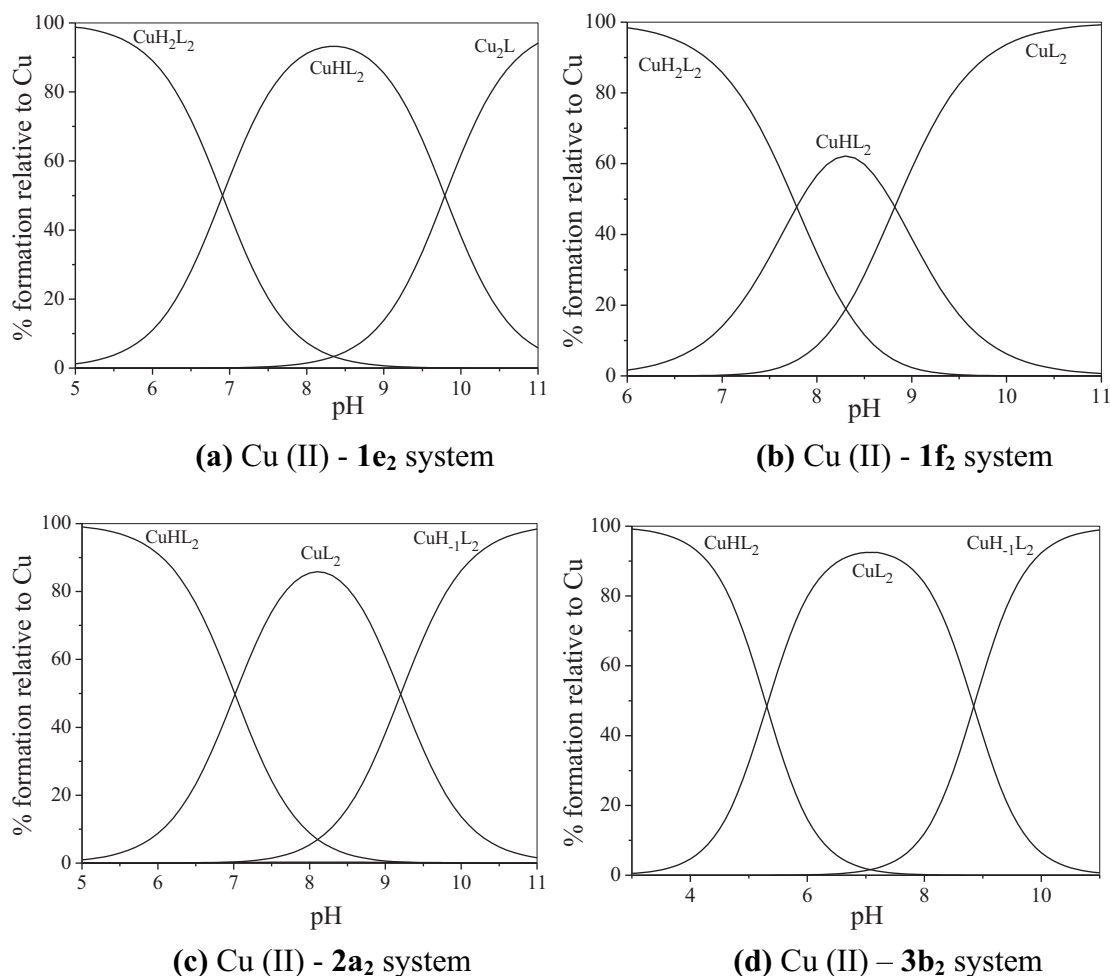


Figure 5. The species distribution curves of complexes between Cu(II) ion and **1a**, **1e**, **2a**, and **3a** ligands (a) Cu(II)–**1e**₂ system (b) Cu(II)–**1f**₂ system (c) Cu(II)–**2a**₂ system (d) Cu(II)–**3b**₂ system (25.0 ± 0.1 °C, I: 0.1 M by NaCl, 0.05 mmol HCl).

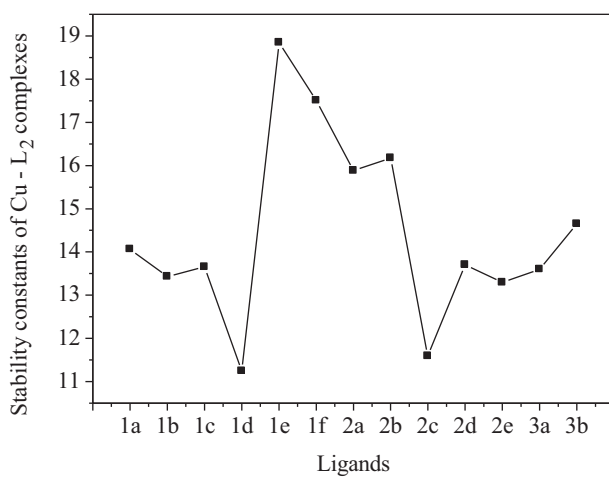


Figure 6. Changing of the log β_{CuL2} values for the ligands.

3. Experimental procedure and methods

3.1. Preparation of the Schiff bases

The studied Schiff bases were synthesized by a procedure reported by Perumal et al.³⁰ To a stirred solution of 2-methoxybenzaldehyde (1.36 g, 10 mmol) in ethanol (10 mL) was added a solution of 2-aminothiophenol (1.87 g, 15 mmol) in ethanol (10 mL). The mixture was refluxed for 5 h. After cooling the reaction mixture, the precipitated substance was filtered and recrystallized in ethanol. The other Schiff bases were prepared by the above-mentioned procedure. The physical data of unknown compounds:

(*E*)-2-(2-methoxybenzylideneamino)benzenethiol (**1c**): (yield 91%; mp 95–98 °C); ¹H NMR (400 MHz, CDCl₃) δg= 8.64 (d, *J* = 7.6 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.0, Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.42 (s, 1H, HC = N), 7.28 (t, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 4.04 (s, 3H, -OCH₃), 3.88 (brs, 1H, -SH). ¹³C NMR (100 MHz, CDCl₃): δ = 163.21, 159.16, 157.29, 136.49, 131.87, 129.57, 125.99, 124.68, 122.85, 121.31, 121.20, 116.42, 111.74, 55.89. IR (Liquid): 3544, 3475, 3413, 3226, 1612, 1563, 1415, 1138, 1041, 884, 863, 747, 605, 482. Elemental Anal. Calcd: C, 69.11; H, 5.39; N, 5.76; S, 13.18. Found: C, 68.91; H, 5.27; N, 5.72; S, 13.28.

(*E*)-2-((1H-pyrrol-2-yl)methyleneamino)benzenethiol (**2b**): (yield, 73%; mp 76–78 °C); ¹H NMR (400 MHz, CDCl₃) δg= 11.74 (s, -NH), 8.36 (s, 1H, HC = N), 7.44 (d, *J* = 8.0 Hz, 1H), 7.24–7.21 (d, *J* = 8.0, Hz, 1H), 7.16–7.11 (m, 3H), 6.80 (bs, 1H), 6.24 (m, 1H), 4.56 (s, 1H, SH). ¹³C NMR (100 MHz, CDCl₃): δ = 151.22, 149.74, 130.80, 130.61, 127.62, 126.30, 126.02, 125.28, 118.22, 117.89, 110.54. IR (Liquid): 3554, 3482, 3415, 3235, 1616, 1567, 1413, 1132, 1037, 881, 867, 744, 601, 480. Elemental Anal. Calcd: C, 65.32; H, 4.98; N, 13.85; S, 15.85. Found: C, 65.28; H, 5.18; N, 13.78; S, 15.98.

3.2. Apparatus and materials

Firstly, Schiff bases were dissolved in sufficient ethanol and diluted at a ratio of 1/10. Next, 1×10^{-3} M stock solution was prepared for each ligand. Ethanol, NaCl, and CuCl₂ were purchased from Merck, potassium hydrogen phthalate (KHP) and borax (Na₂B₄O₇) from Fluka, and 0.1 M NaOH and 0.1 M HCl as standard from Aldrich. All reagents were of analytical quality and were used without further purification. A solution of metal ion (1×10^{-3} M) was prepared from CuCl₂ as received and standardized with ethylenediaminetetraacetic acid (EDTA).⁴⁰ Next, 1.0 M NaCl stock solution was prepared from the original bottle. For all solutions, CO₂-free double-distilled deionized water was obtained with an aquaMAX-*Ultra* water purification system (Young Lin Inst.). Its resistivity was 18.2 MΩ cm⁻¹.

3.3. Potentiometric measurements

All potentiometric pH measurements were carried out on solutions in a 100-mL double-walled glass vessel using the Molspin pH meter with Orion 8102BNUWP ROSS ultra combination pH electrode and the temperature was controlled at 25.0 ± 0.1 °C by circulating water through the double-walled glass vessel, from a constant-temperature bath (DIGITERM 100, SELECTA). The electrode was calibrated according to the instructions in the Molspin Manual.⁴¹ An automatic burette was connected to the Molspin pH-mV-meter. The pH electrode was calibrated with a buffer solution of pH 4.005 (KHP) and pH 9.180 (borax)⁴² at $25.0 (\pm 0.1)$ °C. During the titration, nitrogen (99.9%) was purged through the cell. The Hyperquad⁴³ computer program was used for the calculation of both dissociation and stability constants.

The cell was equipped with a magnetic stirrer. Atmospheric CO₂ was excluded from the titration cell with a purging steam of purified N₂. The system was maintained at an ionic strength of 0.1 M by NaCl as a supporting electrolyte. A solution containing about 0.01 mmol of the ligands, and the required amount of 1.0 M NaCl and 0.1 M HCl were put into the titration cell. Finally, doubly distilled deionized water was added to the cell to a total volume of 50 mL and titration was started. The pH data points were collected after each addition of 0.03 mL of the standardized NaOH solution. The second solution contained the same amounts of components plus 0.005 mmol of Cu(II) solution and doubly distilled deionized water was added to the same total volume. The potentiometric studies were carried out at the metal:L molar ratios of 1:2 and each titration was repeated 3 times.

4. Conclusion

In this work, the effect of substituents on the Cu(II)-L₂ complexes was discussed. Different electron densities on the donor atoms are an important factor affecting the stability of the Cu(II) complexes with the ligands. The various complexes between Cu(II) ion and Schiff bases were formulated as CuL₂, CuHL₂, CuH₂L₂, and CuH₋₁L₂ (Cu(OH)L₂) depending on pH. Stability constants of binary complexes between Cu(II) and Schiff bases were determined in 0.1 M ionic strength (NaCl) and at 25.0 ± 0.1 °C, using the combined glass electrode, potentiometrically. The logβ_{CuL₂} values for the ligands are shown in Figure 4. The dissociation constants and overall stability constants were calculated using Hyperquad and the results are given in Tables 1 and 2. The coordination number of Cu(II) ion was 4 against all studied ligands except **1e** and **1f** in this study. Therefore, tetrahedral complexes were obtained. However, the coordination number of Cu(II) ion was 6 against **1e** and **1f** because they are tridentate ligands. Cu(II)-**1e** and -**1f** complexes are in octahedral structure. As a result, the complexes of ONS- and ONO-type tridentate ligands are more stable than those of NO- and NS-type bidentate ligands. The logβ_{CuL₂} values are changed as **1e** > **1f** > **2b** > **2a** > **3b** > **1a** > **2d** > **1c** > **3a** > **2c** > **1b** > **2e** > **1d**.

Acknowledgment

The authors gratefully acknowledge the financial support of this work from the Scientific Research Council of Gaziosmanpaşa University.

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