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# A cyclic voltammetry investigation of the complex formation between $Cu^{2+}$ and some Schiff bases in binary acetonitrile/dimethylformamide mixtures

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## Abstract

The complex formation between $Cu^{2+}$ ions and some Schiff base ligands was studied in binary solvent mixtures of acetonitrile (AN)/dimethylformamide (DMF) systems at 25 °C using the cyclic voltammetric technique. The stoichiometry and stability of the complexes were determined by monitoring the shift in the half-wave potential of the CV peaks of the copper against the ligands concentration. The stoichiometry of all the complexes was found to be 1:1 and the complexation constants increased with decreasing amounts of dimethylformamide in these binary systems. In all cases, the variation of the stability constant with composition of the solvents was monotonic and showed good correlation with the inherent solvation ability of the neat solvents which form the mixture.

*Keywords:* Schiff base; Cyclic voltammetry; Mixed solvents; Copper; Stability constants

## 1. Introduction

Schiff base ligands are considered privileged ligands because they are easily prepared by the condensation between aldehydes and imines. Stereogenic centers or other elements of chirality (planes, axes) can be introduced in the synthetic design. Schiff base ligands are able to coordinate many different metals [1–5], and to stabilize them in various oxidation states. Schiff bases can be used to obtain optical materials and conducting polymers [6]. Thus, new optical and organic conducting materials can be produced by these compounds. The Schiff base ligands have been used in construction of membrane sensors [7–14] and as models for biological systems [15,16]. During the past two decades, considerable attention has been paid to the chemistry of the metal complexes of Schiff bases containing nitrogen and other donors [17–22]. This may be attributed to their stability [23] and potential applications in many fields such as oxidation catalysis [17] and electrochemistry [18]. It is well known that some drugs have higher activity when administered as metal complexes than as free ligands [24].

Schiff bases and their biologically active complexes have been often used as chelating ligands in the coordination chemistry of transition metals as radiopharmaceuticals for cancer targeting, agrochemicals, as catalysts and as dioxygen carriers.

Copper is an important trace element for plants and animals, and is involved in mixed ligand complex formation in a number of biological processes. Copper complexes containing Schiff base ligands are of great interest since they exhibit numerous biological activities such as antitumor

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[25], anticandida [26], antimicrobacterial [27] antimicrobial [28] activities, etc.

In this work, we study the possibility of complex formation of $Cu^{2+}$ with Schiff bases. This can affect the concentration of free Schiff bases and therefore the activation of substituted Schiff bases in biological systems.

Among the strategies that can be applied for the study of binding, the use of potentiometric and spectroscopic techniques deserves special attention, due to the ability of potentiometry to determine accurate values for the stability constants and due to the large variety of structural information that can be obtained from the different spectroscopic methods analysis [28]. However, these techniques are limited by their low sensitivity, which makes their application impossible when a large concentration of the ligand cannot be reached (e.g. to prevent complex precipitation). In such situations, voltammetric techniques can be a suitable alternative [29]. In this method the effect of the variables such as ligand topology, nature and number of binding sites and type of is studied for the stability complex formation.

Due to the low solubility of the selected Schiff base, we choose DMF, AN and their mixtures for study of $Cu^{2+}$–Schiff base complexation. DMF and AN have about the same dielectric constants ($\varepsilon_{DMF} = 36.7$; $\varepsilon_{AN} = 37.5$), but quite different donating abilities [30] ($DN_{DMF} = 26.6$; $DN_{AN} = 14.1$). Thus, by the use of different DMF–AN mixtures, the influence of the solvating ability of the solvent medium on the complexation process can be investigated.

In this paper, we report the cyclic voltammetry study of copper complexes with 2,2′-(1*E*,1*E*′)-(butane-2,3-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)bis(4-methylphenol) (L1), 2,2′-(1*E*,1*E*′)-(1,3-phenylenebis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)diphenol (L2), 2-(1-(2-hydroxyphenyl)ethylideneamino)-3-phenylpropanoicacid (L3), (*z*)-2-(1-(2-mercaptophenylimino)ethyl)phenol (L4), tris(2-(hydroxyamino)ethyl)amine (L5), (*z*)-2-(1-(2-methoxyphenylimino)ethyl)phenol (L6) and ($N^1E$, $N^2E$)-$N^1$,$N^2$-bis(4-chlorobenzylidene)ethane-1,2-diamine (L7) in binary acetonitrile–dimethylformamide mixtures (see Fig. 1).

## 2. Experimental

### 2.1. Reagents

The solvents, acetonitrile (AN) and dimethylformamide (DMF) were refluxed for several days over the dehydration

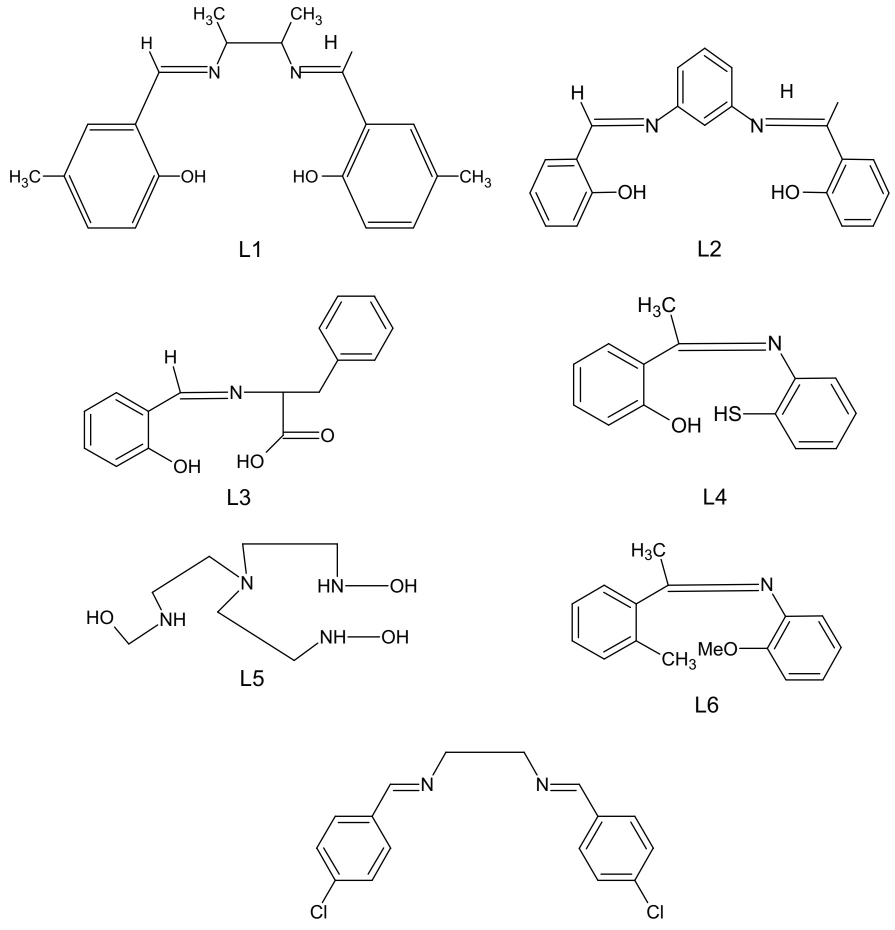
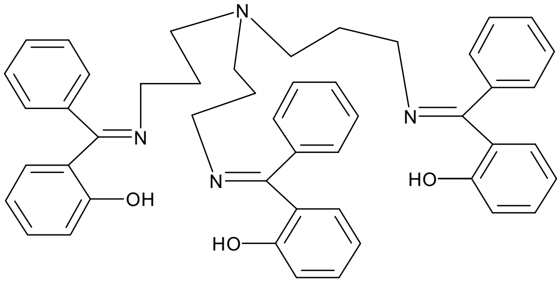


Fig. 1. Structures of Schiff bases.

agent $P_2O_5$, and then fractionally distilled. All of these solvents were transferred into a dry box and dried over $P_2O_5$. Reagent grade copper nitrate (from Merck) was used without further purification except for drying over $P_2O_5$ in a vacuum desiccator for 48 h. Tetrabutylammonium perchlorate (TBAP) was prepared by dissolving an equimolar mixture of the tetrabutylammonium chloride (Merck) and perchloric acid (Merck) in water, and then filtering the resulting mixture. The filtrate (TBAP) was purified by recrystallization in distilled water several times and, was then oven dried at 110 °C for 2 days. Ligands, L1, L2, L3, L4, L6 and L7 were synthesized, purified and dried as described elsewhere [31–36].

### 2.2. Synthesis of L5

The heptadentate Schiff base ligands were easily prepared by reaction of tris(3-aminopropyl) amine with 3 equivalent of 2-hydroxybenzophenone as shown in Scheme 1. Tris(3-(2-hydroxybenzophenone)propyl)amine: to a solution of 2-hydroxybenzophenone (2.06 g, 12 mmol) in diethyl ether (12 ml) was added tris(3-aminopropyl)amine (0.75 g, 4 mmol) in absolute ethanol (40 ml). After the addition of additional diethyl ether (40 ml) and cooling in an ice bath for 50 min, the yellow precipitate formed was filtered off, washed with diethylether and dried *in vacuo*. Yield: 80%. Found: C, 80.50%; H, 6.61%; N, 5.95%. $C_{48}H_{48}N_3O_3$ requires: C, 80.64%; H, 6.77%; N, 5.87%; $^1$H NMR (400 MHz, $CDCl_3$, internal reference TMS): $\delta$ 13.25 (br s, 3 H, OH), $\delta$ 2.17 (m, 6H), 3.06 (t, 6H), 3.66 (t, 6H), 6.95 (15H, s, $C_6H_5$), 7.34 (6H, s, naphthyl), 8.43 (6H, s, naphthyl); IR (Nujol mull) cm$^{-1}$: 3000–2300 (b, $\nu_{O-H}$), 1633.6, 1614.2 (sh), 1580, 1496.6 (s, $\nu_{C=N}$ and $\nu_{C=C}$). Complete condensation of all primary amino groups is confirmed by the lack of N—H stretching bands in the IR 3150–3450 cm$^{-1}$ region and the presence of strong C=N stretching bands for ligand. This conclusion is also supported by the $^1$H NMR data which shows not only the absence of N—H hydrogen resonances but also the presence of C=N.



Scheme 1.

### 2.3. Apparatus

Cyclic voltammetric measurements were performed with the aid of a setup, comprising a PC PIII Pentium 300 MHz microcomputer equipped with a data acquisition board (PCL-818PG, PC-Labcard Co.) and a custom made potentiostat [37]. A Pt wire auxiliary electrode and a glassy-carbon working electrode polished with alumina and sonicated in deionised water after measurements were used. A double junction silver–silver chloride reference electrode was placed in 0.05 M TBAP (with same solvent) and connected to the electrolyzed solution by mean of a bridge containing the base electrolyte. A solution of 0.05 M tetrabutylammonium perchlorate (TBAP) was used as a base electrolyte. All solutions were deaerated for 10 min with pure nitrogen and an inert atmosphere was maintained over the solutions during the reduction. All experi-

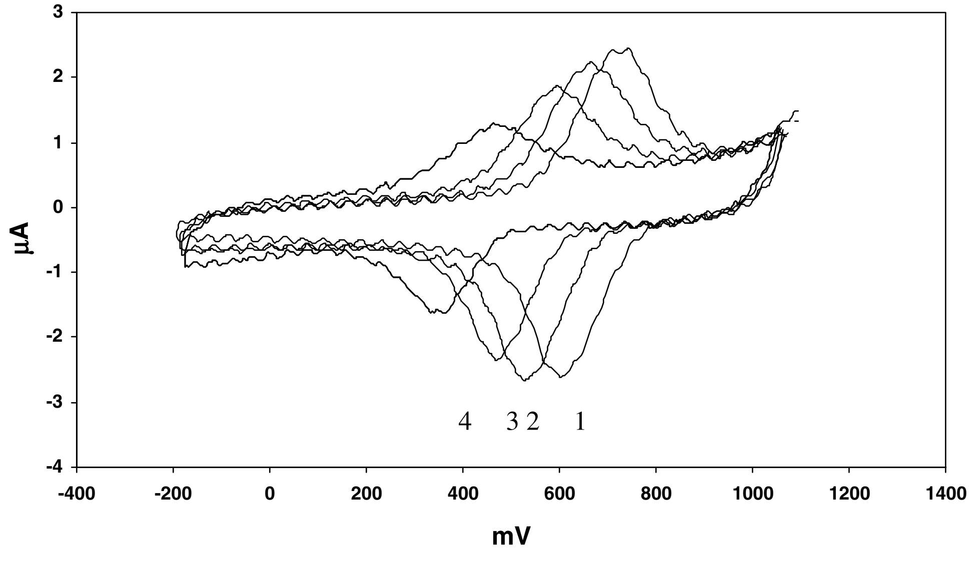


Fig. 2. CV polarograms of 5 × 10$^{-4}$ M $Cu^{2+}$ ion in DMF/AN (40% DMF + 60% AN) binary system with different concentrations of L3 ligand: (1) 0.0; (2) 0.3; (3) 1.0; (4) 8 mM.

ments were carried out at 25 ± 0.1 °C using a model FK2 Haake thermostat with water bath. Concentration of Cu(II) was $5 \times 10^{-4}$ M and the volume of the sample was 5.0 ml. Redox potentials shown in the paper were obtained at 5 mV/s of scan rate. All potentials were referenced internally against the Fe/Fe$^{+}$ couple.

## 3. Results and discussion

In cyclic voltammetry investigation, the significant quantity for studying the stability of the metal–ion complexes is the half-wave potential ($E_{1/2}$) of the cyclic voltammogram peak potential of the complex and the free metal ion. The difference in $E_{1/2}$ between the complex and the metal ion is used in the calculation of the stability constant of the complexes. The interaction between L1–L7 with Cu$^{2+}$ was studied in acetonitrile/dimethylformamide binary mixtures of various compositions at 25 °C. The addition of the ligands to Cu$^{2+}$ solutions in 0.05 M TBAP, shifts the reduction potential $E_{1/2}$ of the metal ions towards a more negative value. As an example, the cyclic voltammograms of the Cu$^{2+}$ ion in the presence of different concentrations of L3 in one of the AN/DMF binary systems is shown in Fig. 2. The shift in half-wave potential towards more negative values upon the addition of excess ligand was observed to be in accordance with the simple Lingane equation:

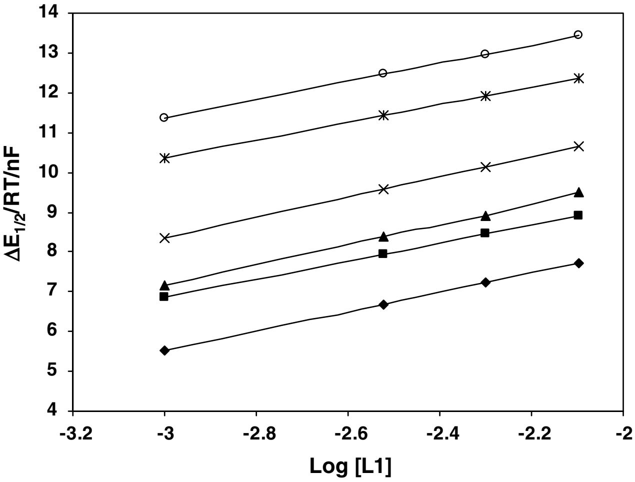


Fig. 3. Linear plots of $\Delta E_{1/2}/(RT/nF)$ versus log[L1] for the L1–Cu$^{2+}$ complex in AN and DMF and their binary mixtures.

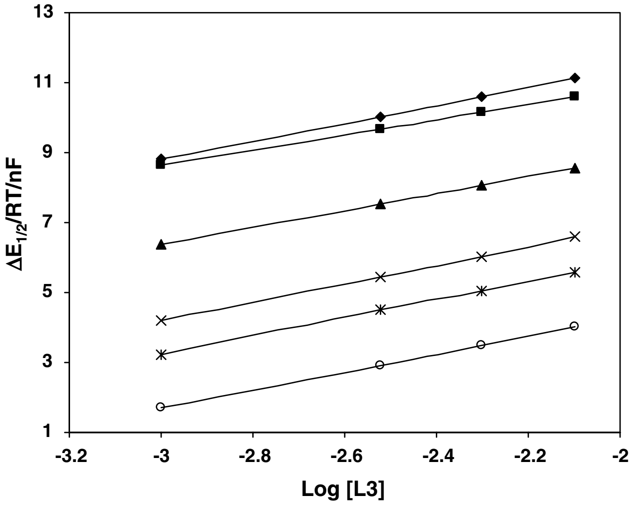


Fig. 4. Linear plots of $\Delta E_{1/2}/(RT/nF)$ versus log[L3] for the L3–Cu$^{2+}$ complex in AN and DMF and their binary mixtures.

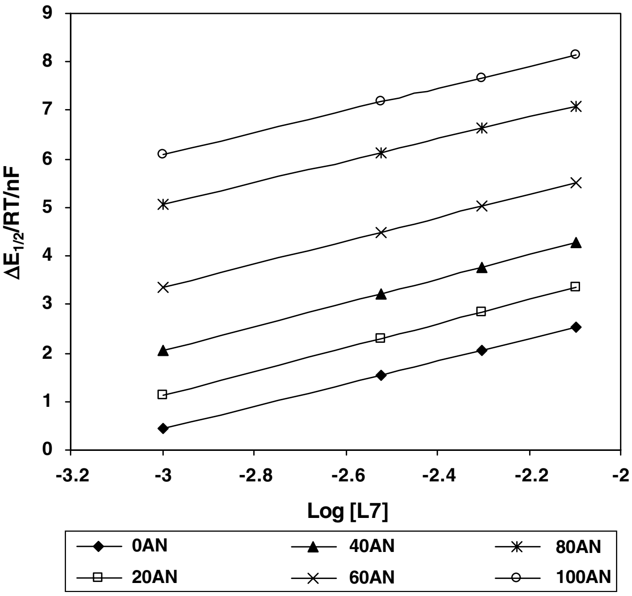


Fig. 5. Linear plots of $\Delta E_{1/2}/(RT/nF)$ versus log[L7] for the L7–Cu$^{2+}$ complex in AN and DMF and their binary mixtures.

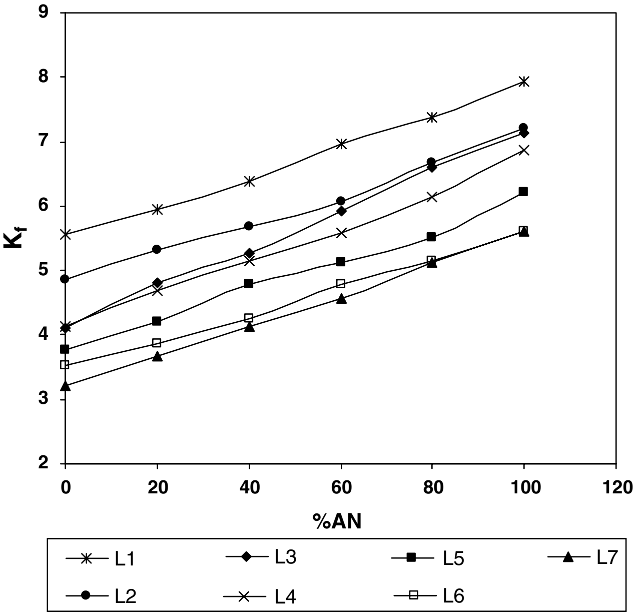


Fig. 6. Variation of log $K_f$ of different Cu$^{2+}$–Schiff bases complexes with $X_{AN}$.

Table 1
Stability constant of $Cu^{2+}$ complexes with different Schiff bases in AN–DMF mixtures at 25 °C

| Composition wt% of DMF in AN | $\log K_f \pm SD$ | | | | | | |
|---|---|---|---|---|---|---|---|
| | L1 | L2 | L3 | L4 | L5 | L6 | L7 |
| 0 | 7.94 ± 0.05 | 7.2 ± 0.04 | 7.14 ± 0.05 | 6.87 ± 0.02 | 6.21 ± 0.05 | 5.61 ± 0.1 | 5.61 ± 0.05 |
| 20 | 7.38 ± 0.04 | 6.67 ± 0.05 | 6.6 ± 0.04 | 6.13 ± 0.02 | 5.52 ± 0.05 | 5.15 ± 0.07 | 5.12 ± 0.05 |
| 40 | 6.96 ± 0.07 | 6.08 ± 0.09 | 5.92 ± 0.07 | 5.58 ± 0.04 | 5.12 ± 0.06 | 4.78 ± 0.05 | 4.57 ± 0.08 |
| 60 | 6.39 ± 0.03 | 5.69 ± 0.06 | 5.28 ± 0.07 | 5.14 ± 0.05 | 4.78 ± 0.07 | 4.25 ± 0.06 | 4.12 ± 0.02 |
| 80 | 5.95 ± 0.08 | 5.31 ± 0.03 | 4.8 ± 0.1 | 4.68 ± 0.03 | 4.21 ± 0.09 | 3.87 ± 0.03 | 3.68 ± 0.09 |
| 100 | 5.55 ± 0.04 | 4.86 ± 0.03 | 4.1 ± 0.08 | 4.12 ± 0.03 | 3.76 ± 0.04 | 3.52 ± 0.04 | 3.2 ± 0.05 |

$$\Delta E_{1/2} = (E_{1/2})_{\mathrm{ML}} - (E_{1/2})_{\mathrm{M}} = -(RT/n\mathrm{F})(LnK_f + m\ln[\mathrm{L}]_t) \tag{1}$$

where $(E_{1/2})_{\mathrm{ML}}$ and $(E_{1/2})_{\mathrm{M}}$, are the half-wave potentials of the complexed and free metal ion, $n$ is the number of electrons involved in the reaction, $K_f$ is the formation constant of the complexes, $m$ is the stoichiometry of the complex and $[\mathrm{L}]_t$, is the analytical concentration of the ligand. A linear graph of $\Delta E_{1/2}$ versus $\ln[\mathrm{L}]_t$ will have a slope of $(-RT/n\mathrm{F})m$ and an intercept of $-RT/n\mathrm{F} \ln K_f$. The $m$ and $K_f$, therefore, can be obtained from the slope and intercept of the linear plot (Figs. 3–5).

The variations of $\Delta E_{1/2}$ as a function of $\log[\mathrm{L}]_t$ for complex formation between L1, L3, L7 and $Cu^{2+}$ ions in acetonitrile/dimethylformamide binary systems are shown in Figs. 3–5. Similar linear plot was obtained for other systems which is an indication of the formation of a single complex in solution. The slope of these linear plots gave a value of $m \approx 1$, which confirms the formation of a 1:l complex in solution. The formation constants were obtained by fitting the voltammetric data to Eq. (1) by computer. The results are given in Table 1. The data collected in this table show that the values of the stability constant of all of the complexes increase as the concentration of dimethylformamide is lowered in acetonitrile/dimethylformamide binary systems. DMF is a solvent of high solvating ability (DN = 26.6) [38], which can compete strongly with the ligands for $Cu^{2+}$ ion. Thus, it is not surprising that the addition of DMF to the AN as a low donicity solvent (DN = 14.1) [36] will decrease the extent of interaction between the ligand donating atoms and $Cu^{2+}$ ion. It is immediately obvious that the nature of the medium plays an important role in the complexation process, and it seems that the donor ability of the solvents as expressed by the Gutmann donor numbers [39] plays a very important role in determining the stabilities of these complexes. The variations of the formation constants of ligands–$Cu^{2+}$ as a function of solvent composition in acetonitrile/dimethylformamide solutions are shown in Fig. 6. Investigation of these figures shows that the complexation process in these mixed non-aqueous solvents is sensitive to the solvent composition. In all cases, the variation of the stability constant with composition of the solvents is monotonic and shows a good correlation with the inherent solvating ability of the neat solvents which form the mixtures. In another word, this behavior probably indicates that the donocity of each solvent will not change in the presence of another solvent (Fig. 6).

From Table 1 it can be seen that the stability of the resulting 1:1 complexes of $Cu^{2+}$ ion with different Schiff base decreases in the order of L1 > L2 > L3 > L4 > L5 > L6 > L7.

*The effect of the ligands structure on the complexes stability.* Some of the factors, such as the size of the semi-cavity of the ligand, the number and the nature (based on the soft and hard theory) of the donor atoms in the ligand, are important in the stability of the formed complexes. Among them, however, the most significant factor is the number of the ligand donor atoms. Therefore, the L1 and L2 ligands are expected to form the most stable complexes (Table 1) with $Cu^{2+}$ among all the examined ligands. Owing to the benzene electron withdrawing agent, the L2 donor ability was lower than that of L1. Therefore, the L2 complexes were weaker than the L1 complexes. The same phenomenon was observed for the L3 and L4 ligands. The previous ligands formed a semi-cavity, enhancing the formation power of the complexes. Nevertheless, L5 could not form such a cavity and the L5 complexes were weaker than the L1–L4 complexes. The number of the donor atoms in L6 and L7 was smaller compared with the number of the other ligands. As a consequence, these ligands formed weaker complexes than the complexes of the other ligands.

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