Full Paper

Complexation Studies of Zn²⁺, Cu²⁺, Co²⁺, Ni²⁺ and Cd²⁺ Ions with a Schiff Base Ligand

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Abstract: The complex-formation reactions between Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+} and Cd^{2+} ions with, *N,N'*–Bis-(salicylidene)1,8-diamino-3,6-dioxaoctan Schiff base ligand, has been studied by spectrophotometric method in acetonitrile at various temperatures. The formation constant (K_f) and the molar absorptivity (ε) of the resulting complexes between ligand and different cations were calculated by fitting the observed absorbance at various $[M^{2+}]/[L]$ mole ratios and found that the stability of the resulting L-M^{2+} complexes varied in the order $Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+} > Cd^{2+}$. The enthalpy and entropy changes of the complexation reaction were determined from the temperature dependence of the formation constants.

Keywords: complexation; formation constants; Schiff bases; spectrophotometry

1. INTRODUCTION

The condensation of an amine with an aldehyde, forming what is called a Schiff base, is one of the oldest reactions in chemistry. Schiff base ligands coordinate to a metal through the imine nitrogen and another group, usually oxygen, situated on the origin aldehyde [1-2]. When a diamine was first combined with two equivalents of salicylaldehyde, the Salen ligands came into being [3]. These ligands are quite familiar as tetradentate ligands in metal complexes [4-6]. These ligands with N_2O_2 donor atom set are very well known to coordinate to inorganic and organic cations to give rise to chelate complexes [7-8]. Diamine Schiff bases are different from monoamine Schiff bases in having two chromophores bridged by a methylene chain in a molecule, and thus the mutual interactions between the chromophores appears to affect their chemical and physical properties. Therefore, interesting optical properties derived from the interaction between the two chromophores in the diamine Schiff bases could be expected. Some of optical properties of diamine Schiff base ligands have been reported in literature [9], but the complexation reactions of these complexes in nonaqueous solvents have not been reported. Schiff bases derived from salicylaldehyde (salens) as polydentate ligands are well known to form very stable complexes with transition metal ions

[10]. Salen complexes of transition metals have been frequently used as catalysts in such diverse processes as oxygen and atom – transfer [11], enantioselective epoxidation [12], mediating organic redox reactions [13] and recently as ionophores in ion – selective studies [14].

Since the nature of solvent may strongly influence the stoichiometry and formation constant of transition metal complexes in solution, we decided to study the complexation reaction between the *N,N'*–Bis-(salicylidene)1,8-diamino-3,6-dioxaoctan Schiff base ligand (**L**) (Figure 1) and some transition metal ions in acetonitrile solvent.
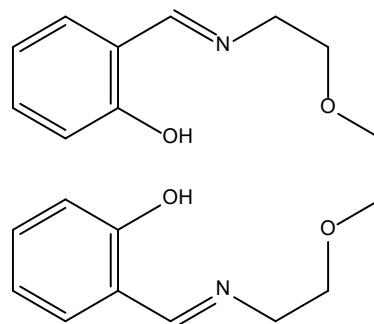
Figure 1. Chemical structure of *N,N'*–Bis-(salicylidene)1,8-diamino-3,6-dioxaoctan (**L**).

Crystallographic data shown that the Zn²⁺-**L**

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complex is formed in solid state [15], and the Ni^{2+}-**L** complex effect on DNA-protein interaction have reported [16]. In this research, we report the spectrophotometric studies of the stoichiometry, formation constant, and thermodynamics of complexes between the Schiff bases ligand (**L**) with Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+} and Cd^{2+}ions in acetonitrile solvent.

2. MATERIAL AND METHODS

Reagent grade metal nitrates and acetonitrile (AN) all from Merck and recently synthesized Schiff base (**L**) were of highest purity available was used without any further purification. All Uv-Visible spectra recorded on a computerized double–beam Shimadzu 2550 spectrophotometer, using two matched 10 mm quartz cell.

In a typical experiment, 2.0 mL of ligand solution (5.0×10^{-5} – 1.0×10^{-4} M) in AN was placed in the spectrophotometer cell and the absorbance of solution was measured. Then known amounts of the concentrated solution of metal ions in AN (1.3×10^{-3} M – 1.3×10^{-2} M) was added in a stepwise manner using an l0µL Hamilton microliter syringe. The electronic absorption spectra of the solution were recorded after each addition. The metal ions solution was continually added until the desired metal to ligand mole ratio was achieved.

For evaluation of the formation constant from absorbance *vs* [M]/[L] mole ratio data, the KINFIT [17] program was also used [18-19]. Adjustable parameters are the K_f, absorbance of free ligands, and absorbance of metallic complexes. The ligand concentration, [**L**], was calculated by a Newton-Raphson procedure. When the value of [**L**] have been obtained, the concentration of all other species involved are calculated from the mass balance equations, by using the estimated value of the formation constant at the current interaction step of the program. Refinement of the parameters was continued until the sum-of-squares of the residuals between calculated and observed absorbance for all experimental points was minimized. The output of the KINFIT program comprises the refined parameters, the sum-of-squares and the standards deviation of the data [20-22].

The formation constant (K_f) and the molar absorptivity (ε) of the resulting complexes between ligands and different cations were calculated by fitting the observed absorbance, A$_{obs}$, at various [M^{2+}] / [**L**]

mole ratios to the previously derived equation (equation 1 and 2), which express the A$_{obs}$ as a function of the free and complexed metal ions, and the formation constant evaluated from a non – linear least – squares program KINFIT [17].

$$K_f[L]^2 + (1 + K_f(C_L - C_M)[L] - C_L = 0 \qquad (1)$$

The observed absorbance of solution is also given by:

$$A_{obs} = A_L \times \varepsilon_L + A_{ML} \times \varepsilon_{ML} \qquad (2)$$

3. RESULTS AND DISCUSSION

The complex – formation reaction between Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+} and Cd^{2+} ions with N,N'–Bis-(salicylidene)1,8-diamino-3,6-dioxaoctan (**L**), has been studied spectrophotometrically in AN solvent at various temperatures. Formation constants of the 1:1 complexes were evaluated from computer fitting of the absorbance–mole ratio data at different temperatures, and listed in Table 1. At 25ºC the stability of the resulting complexes for **L** ligand varied in the order Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+} > Cd^{2+}. Stabilities of the resulting complexes were investigated at various temperatures and enthalpies and entropies of complexation were determined from the temperature dependence of the formation constants, and the results have listed in Table 1 too.

The electronic absorption spectra of **L** ligand and its Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+} and Cd^{2+} complexes in AN are shown in Figure 2, and in the increasing concentration of metallic ions were recorded at room temperature. A typical curve for Cu^{2+} ion with **L** ligand is shown in Figure 3. As shown in Figure 2, the main ligand peak appears at about 310-320 nm, while the main peak of the formed complexes with metal ions is about 365-380 nm. Therefore as the complexes are formed, there appears a shift in the absorption band with the wavelength of about 50-60 nm. According to Figure 3 original absorption peak of the Schiff base ligand at about 310-320 nm gradually vanished and intensity of the original absorption peak of Cu**L** complexes at about 360-380 nm increases with the increase in the concentration of Cu^{2+} ion with clear isobestic point. The absorption bands about 260-280 nm in the spectrum of the ligand was related to π → π* transition of the phenoxy groups, and other band in about 310-320 nm related with the π → π* transition of the imine nitrogen atoms in conjugation of the aromatic ring group [23].

The stoichiometry of the **L** metallic ions

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complexes in acetonitrile was examined by the method of continuous variation [24]. A sample of the resulting plot for Cu^{2+} and Zn^{2+} ions complexes is shown in Figure 4, and it is evident that 1:1 complexes are formed in solution. The formation of such complexes in acetonitrile at various temperatures was further supported by mole ratio method, and typical mole ratio plots for Cu^{2+} ion are shown in Figure 5.

The formation constants of the resulting 1:1 ligand to metal ions complexes were obtained at various temperatures by absorbance measurements of solutions in which varying concentrations of metal ions were added to fixed amounts (5.0×10^{-5} M - 1.0×10^{-4} M) of ligand solution, at λ_{max} of complexes. All the resulting absorbance – mole ratio data were best fitted to equation 1, which further supports the formation of 1:1 complexes in solution.

For evaluation of the formation constants and molar absorptivity coefficients from absorbance *vs* [M]/[L] mole ratio data, a non- linear least squares curve fitting program KINFIT was used. Sample computer fits of the absorbance – mole ratio data for Cu^{2+} metal ions at 25°C are shown in Figure 6.

In order to have a better understanding of the thermodynamics of complexation between **L** and metal ions in acetonitrile, it is useful to consider the enthalpic and entropic contributions to these reactions. The enthalpy and entropy of the complexation reactions were determined by measuring the formation constants of the resulting 1:1 complexes as a function of temperature. All of the $\log K_f$ values evaluated from the computer fitting of the corresponding absorbance – mole ratio data are listed in Table 1. Vant's Hoff plots of $\log K_f$ *vs* 1/T, for metals complexes in acetonitrile were linear and for two ligands are shown in Figure 7. $\Delta H°$ and $\Delta S°$ values were determined from Vant's Hoff equation (equation 3) in the usual manner from the slopes and intercepts of the plots, respectively, and the results are also listed in Table 1.

$$\log K_f = - \Delta H/2.303R \, (1/T) + \Delta S /2.303R \quad (3)$$

**Table 1**. Formation constants, enthalpy and entropy values for different $L–M^{2+}$ complexes.

| L-ions complexes	$\mathbf{Log}K_f$					$\mathbf{\Delta H°}$	$\mathbf{\Delta S°}$	$\mathbf{\Delta G°}$
	20 °C	25 °C	30 °C	35 °C	40 °C	Kj mol^{-1}	Jmol^{-1}K^{-1}	Kj mol^{-1}
Cd^{2+}	4.00±0.01	3.96±0.01	3.90±0.01	3.84±0.01	3.78±0.01	-19.6±0.7	9.7±2.4	-22.5±1
Zn^{2+}	5.28±0.01	5.26±0.01	5.20±0.01	5.13±0.01	5.09±0.01	-18.1±1.5	39.5±5.9	-29.9±2.5
Co^{2+}	5.09±0.01	5.02±0.01	4.94±0.01	4.89±0.01	4.84±0.01	-21.5±1.2	23.8±3.9	-28.7±1.7
Ni^{2+}	4.10±0.01	4.06±0.01	4.01±0.01	3.95±0.01	3.90±0.01	-18.3±1.5	16.4±5.2	-23.1±2.2
Cu^{2+}	5.46±0.01	5.40±0.01	5.34±0.01	5.30±0.01	5.27±0.01	-16.7±1.0	47.4±3.4	-30.8±1.5
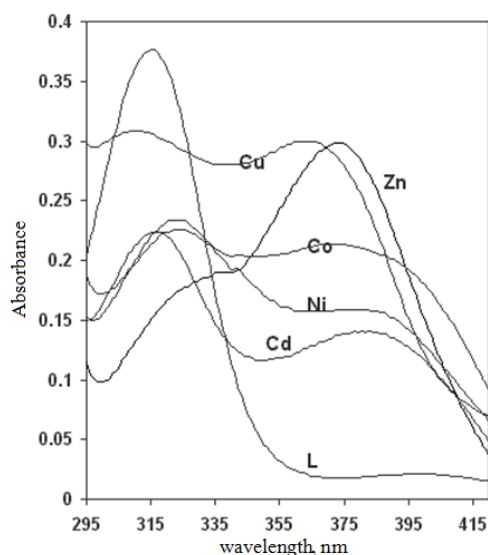
**Figure 2**. Electronic absorption spectra of **L**-metallic ions complexes.
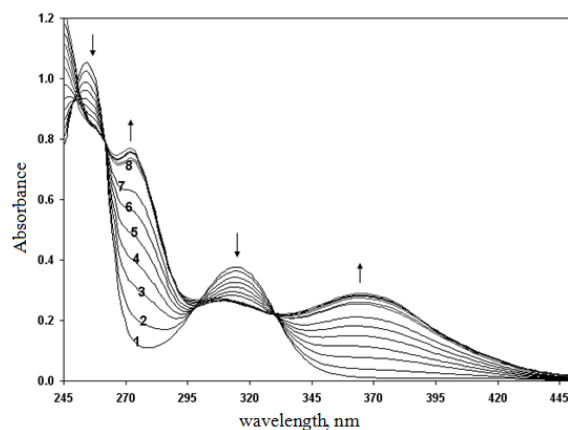
Figure 3. Electronic absorption spectra of **L** (5×10^{-5}M) in the presence of increasing concentration of $Cu(NO_3)_2$ at 25°C, in different [M]/[L] mole ratio, (1) spectrum of **L**, (2) 0.18, (3) 0.36, (4) 0.54, (5) 0.72, (6) 0.9, (7) 1.08, (8) 1.26.

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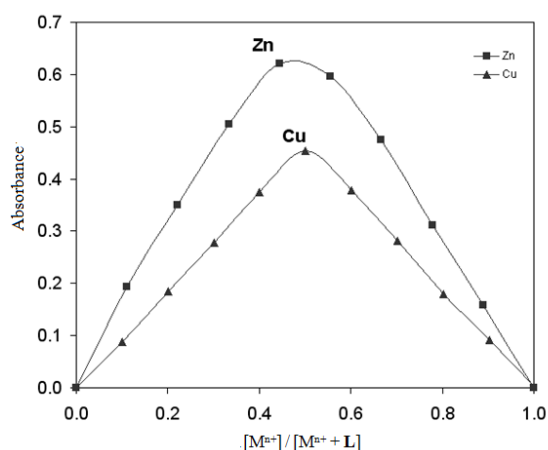
**Figure 4**. Continuous variation plots for Cu^{2+} and Zn^{2+} ions complexes with **L**.
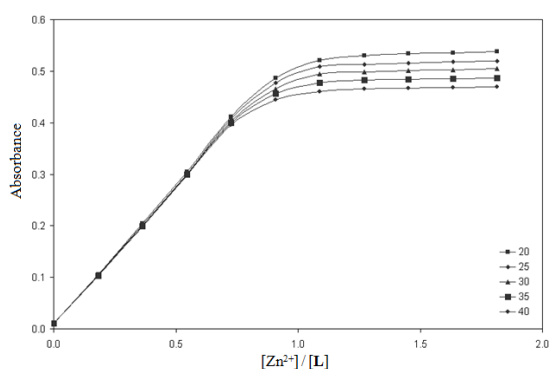
Figure 5. Mole ratio plots of **L** (5.0×10^{-5}M) with Zn(NO$_3$)$_2$ solution (372nm) at various temperatures.
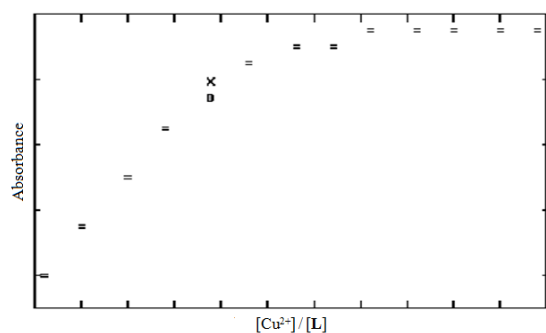
Figure 6. Computer fit of absorbance *vs* [Cu^{2+}]/[**L**] at 25°C (X) experimental point, (O) calculated point, (=) experimental and calculated points are the same within the resolution of the plot.

4. CONCLUSION

The stability of the resulting M**L** complexes varied in the order Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+} > Cd^{2+}. The ligand can be used for solid phase extraction and determination of trace amounts of these metallic ions in aqueous samples.
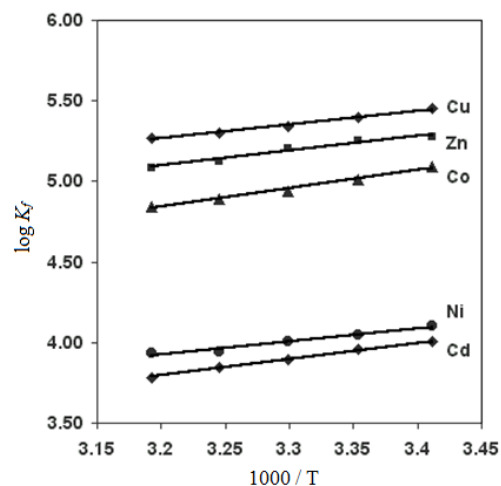
Figure 7. Vant's Hoff plots of **L**-metallic ions system.

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