Kinetics of the Ligand Exchange Reaction Between Tetradeutate Schiff Base N,N’-ethylen-bis (salicylaldimine) and Cu(N,N’-propylen-bis(salicylaldimine))

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Abstract

Visible spectrophotometry is used to study the kinetic of ligand exchange in the system Cu(salpn)/H₂salen with or without triethylamine (NEt₃) and H₂O in acetonitrile solvent at 25 ± 0.1°C and 0.01 M NaNO₃ (H₂salen and H₂salpn are N,N’-ethylen-bis(salicylaldimine) and N,N’-propylen-bis(salicylaldimine), respectively). It is found that the reaction rate is first-order with respect to Cu(salpn). In addition, the ligand exchange rate increases when NEt₃ is added to the reaction mixture, as shown by a break in the kobs vs. [NEt₃] plot. The effects of NEt₃ and H₂O on the ligand exchange rate are discussed, and reaction mechanism is proposed.

Keyword: Kinetic, mechanism, Schiff base, Cu complexes, ligand exchange, saturation kinetics

1. Introduction

Schiff base complexes of salen and its derivatives are one of the most exhaustively studied topics in coordination chemistry.¹ The magnetic properties,²⁻⁵ electronic spectra⁶,⁷ and the structures of copper(II) complexes of salen⁵,⁸,⁹ and its derivatives have been studied by various research groups.⁴,⁵ Tetradeutate Schiff bases generally react with divalent metal ions by losing of two hydroxyl protons to form neutral and stable complexes. The resulting complexes are monomers that have flexible structures. For example, it has been shown that the increasing the length of methylene chains in Cu(II) complexes of the salen ligand family cause their structures to change from a planar to distorted tetrahedral.²,³,¹⁰⁻¹² Moreover, in the presence of additional donors, they may form five or six coordinate species.¹²⁻¹⁶ Electronic spectral data indicate that the ligand field strength of the complexes decreases as the alkyl chain length increases.⁶,⁷

The stability of metal complexes is dependent upon both the metal center environment, and the ligand conformational flexibility. Ligand flexibility could be a driving force that causes the ligand exchange reaction to form a more stable complex. However, there is no report investigation on the relationship between metal complex geometrical structure and the kinetics of ligand exchange reaction of copper complexes of tetradeutate Schiff base. Therefore the present study on the kinetics of the ligand exchange between salen and salpn in Cu(salp) (reaction 1) was performed to investigate the influence of ligand flexibility on the stability of copper complexes.

\[ \text{Cu(salpn)} + \text{H}_2\text{salen} \rightarrow \text{Cu(salen)} + \text{H}_2\text{salpn} \]  \hspace{1cm} (1)

2. Experimental

2.1 Syntheses of Ligands

The Schiff base H₂salen and H₂salpn were prepared by a general method,¹²,¹⁷ involving the condensation reaction between 2 equivalents of salicylaldehyde and 1 equivalent of the appropriate diamine.

2.2 Syntheses of Cu(salen) and Cu(salpn) Complexes

The copper complexes (Scheme 1) were prepared by a general method,¹²,¹⁸,¹⁹ using the reaction between copper acetate and the Schiff base ligand (1:1 ratio) in methanol.

2. 3. Chemicals

Chemical reagents and all solvents, used in the syntheses and kinetic studies, were purified by standard methods.

2. 4. Kinetic Measurements

To measure the reaction rates, absorbance changes of reaction mixtures were followed using a GBC UV-Visible Cintra 101 spectrometer at 570 nm, where the greatest change in molar absorptivity between reactants and products occurred. Reaction mixtures were studied in acetonitrile, CH₃CN solvent (with and without triethylamine, NEt₃, and H₂O) at an ionic strength of I = 0.01 M in NaNO₃ 25 ± 0.1 °C. Both H₂salen and sodium nitrate have limited solubility in acetonitrile, and so their concentrations were restricted to 0.05 M and 0.01 M respectively.

To initiate reaction, equal volumes of Cu(salpn) at 2.00 × 10⁻³ M and H₂salen (2.00 × 10⁻³ – 5.00 × 10⁻²) were mixed, and absorbance versus time measurements were taken. It was found that the absorbance of the reaction mixture increases with time. Pseudo-first-order rate constants (k obs) given in table 1 are obtained from the plots of -ln(A₂₋₁) vs. time, where A₂ and A₁ represent the absorbance of the reaction mixtures at time t and infinity, respectively. At least three runs were made at each concentration and the average values of rate constants are reported.

The rate constants, k, were obtained by fitting data results of k obs vs. [H₂salen] using sigmaplot 9.0.

3. Results and Discussions

3. 1. Absorption Spectra

The visible absorption spectra of Cu(salen) and Cu(salpn) complexes in CH₃CN solvent show a maximum absorption due to d-d transition at 568 and 605 nm respectively (Fig.1).

![Visible spectra of Cu(salpn) and Cu(salen) complexes in CH₃CN](image1)

It is clear from the visible spectrum of Cu(salen) and Cu(salpn) complexes that, it is practical to follow the ligand exchange reaction spectrophotometrically. Fig. 2 shows a consecutive series of spectra recorded in CH₃CN solvent for Cu(salpn)/ H₂salen system, which indicates an increasing hypsochromic shift, with respect to the initial Cu(salpn) spectrum. In fact the changes observed in the spectrum are being caused by changing in the ligand field.

![Spectral changes recorded in CH₃CN solvent for the reaction of Cu(salpn) and H₂salen](image2)
complex. These observations indicate that the Cu(salpn) complex is converted to the Cu(salen) complex (reaction 1) by adding H$_2$salen ligand.

The spectrum produced by mixing corresponding amounts of Cu(salen) complex, H$_2$salpn and NaNO$_3$ in CH$_3$CN is similar to the last spectrum shown in Fig. 2. This similarity confirms the conversion of the Cu(salpn) to the Cu(salen) complex.

### 3.2. Kinetic Study

The rate law can be expressed as equation 2:

$$\text{Rate} = \frac{d[Cu(salen)]}{dt} = k_{\text{obs}} [Cu(salpn)]_0$$

where [Cu(salpn)]$_0$ is the concentration of Cu(salpn) at time initial. The pseudo-first-order rate constants were measured at various H$_2$salen ligand concentrations. The order of the reaction rate with respect to H$_2$salen ligand was determined by plotting $k_{\text{obs}}$ as a function of the concentration of H$_2$salen. As shown in Fig. 3, the variations of $k_{\text{obs}}$ vs. concentration of H$_2$salen showed saturation kinetics (See proposed mechanism).

The conversion of Cu(salpn) into Cu(salen) in CH$_3$CN solvent showed that Cu(salen) is thermodynamically more stable than Cu(salpn) complex. To confirm this conclusion, the reverse reaction, i.e. the conversion of Cu(salen) to the Cu(salpn) in the presence or in the absence of NEt$_3$ does not take place. Therefore, the reverse reaction and its equilibrium cannot be observed between two complexes in the studied condition.

The electronic spectra shown in Fig. 1, indicate that the Cu(salen) complex has a stronger ligand field ($\lambda_{\text{max}} = 568 \text{ nm}$) than Cu(salpn) complex ($\lambda_{\text{max}} = 605 \text{ nm}$). It is important to emphasize that the change in the ligand strength of the metal complex correlated with the geometry about the metal indicating that small structural changes cause profound effects in the ligand field strength.

The distortion about the copper center in Cu(salpn) complex causes a decrease in the ligand field strength due to a chelate effect caused by the extra methylene group. The Cu(salpn) is less stable because it forms larger chelate ring (six-member) than of the Cu(salen) complex (five-member). The size effect of chelate ring on complexes stability has been reported before. It has been shown that the complex stability decreases along with increasing the chelate ring size. The six-member chelated ring leads to less stable complexes than five-member chelate ring.

The decrease in the ligand field strength and stability of Cu(salpn) relative to the Cu(salen) is in agreement

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**Table 1.** Rate constants data for the reaction of Cu(salpn) with H$_2$salen ligand in the absence and in the presence at different concentration of NEt$_3$.

<table>
<thead>
<tr>
<th>$\text{[NEt}_3\text{]}$/M</th>
<th>$k \times 10^3$/s$^{-1}$</th>
<th>$\text{[NEt}_3\text{]}$/M</th>
<th>$k \times 10^3$/s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.031±0.11</td>
<td>0.90</td>
<td>2.504±1.51</td>
</tr>
<tr>
<td>0.18</td>
<td>1.298±0.65</td>
<td>1.08</td>
<td>2.987±0.64</td>
</tr>
<tr>
<td>0.36</td>
<td>1.688±0.78</td>
<td>0.08</td>
<td>0.031±0.11</td>
</tr>
<tr>
<td>0.54</td>
<td>1.383±1.04</td>
<td>1.08</td>
<td>1.347±0.51</td>
</tr>
<tr>
<td>0.72</td>
<td>1.831±1.03</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Solvent CH$_3$CN, at 25 ± 0.1 °C and I = 0.01 M NaNO$_3$

$^b$ in the presence of H$_2$O (0.28 M)

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The salen Schiff base forms square planar complex with the ion copper(II). Increasing the number of methylene units in the chain of the Schiff base ligand (Scheme 1) provides enough flexibility in Cu(salpn) in comparison with the Cu(salen), in such a way that it is inverted from a planar configuration to a distorted tetrahedral configuration.
with the trend observed in the ligand substitution (reaction 1). To propose a mechanism for this exchange reaction, the kinetic study of the reaction is investigated in the presence of non-coordinating amine (triethyl amine with a variable concentration and H₂O). The effect of triethyl amine and water on the kinetic behavior of the reaction is explained in the next section.

3. 3. Effect of Triethyl Amine

It is observed that, the rate of the exchange reaction increases when NEt₃ is added to the reaction mixture. Carrying out the reaction at different NEt₃ concentrations, indicates that the ligand exchange is strongly depends on the NEt₃ concentration. As shown in Fig. 4, by increasing NEt₃ concentration, the reaction rate become considerably faster than when carried out in the absence of NEt₃. However, as shown in Fig. 5 (plot of kobs vs. [NEt₃]), there is an obvious breaking point at ∼0.23 to 0.38 M concentration of NEt₃, dependent of [H₂salen]₀, which can be related to the change of the reaction species at these concentrations. As shown in Fig. 2, there are two isosbestic points at 487 and 646 nm. This means that the Cu(salpn) converts to the Cu(salen) without the formation of free Cu²⁺ ion, which has a different spectrum than Cu(salpn) and Cu(salen) complexes. In general, ligand exchange reactions between multidentate ligands proceed through intermediates in which the incoming ligand is partially coordinated to metal center and the leaving ligand is partially dissociated. Results from this study, namely that: (a) the ligand exchange rate did not change by adding H₂O to solvent and (b) the plot of kobs vs. [H₂salen] showed saturation kinetics indicates that a limiting value of kobs is reached at high [H₂salen]. This result implies that there is an association between Cu(salpn) and H₂salen prior to ligand exchange. We also know that because of the low acidity of H₂salen and its family ligands, Hsalen⁻ and salen²⁻ ions concentration were negligible so that H₂salen could be treated as the major reactive species under these conditions. This assumption was confirmed by performing the kinetic study of the exchange reaction in the presence of non-coordinating amine (triethyl amine with a variable concentration and H₂O). The effect of triethyl amine and water on the kinetic behavior of the reaction is explained in the next section.

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3. 4. Reaction in Presence of H₂O

The plot of kobs vs. [H₂salen] in the presence and absence of H₂O has been shown in Fig. 3 which shows that the rate of the ligand exchange reaction (Eq. 1) is not considerably changed by adding H₂O (0.28 M) to CH₃CN. However in presence of NEt₃, the ligand exchange reaction rate considerably decreases by adding H₂O (0.28 M) to solution of the reaction (Fig. 6). The effects of NEt₃ and H₂O show the importance of protonation/deprotonation on the rate of the ligand exchange reaction.

3. 5. Proposed Mechanism

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ligand exchange reaction in the presence of H2O with no changes in reaction rate.

In the absence and presence of H2O, the plot of kobs vs. [H2salen] showed saturation kinetics (Fig. 3), implying that a limiting value of kobs is reached at high [H2salen]. This leads us to assume that there is an association between Cu(salpn) and H2salen prior to ligand exchange.

\[ \text{Cu(salpn)} + \text{H2salen} \xrightarrow{K} [\text{Cu(salpn).H2salen}] \xrightarrow{k} \text{Cu(salen)} + \text{H2salpn} \]  

(3)

The theoretical rate law can be given as:

\[ k_{\text{obs}} = \frac{kK[H2\text{salen}]}{1 + K[H2\text{salen}]} \]  

(4)

Where K denotes the equilibrium constant between Cu(salpn) complex and H2salen ligand and k is the rate constant of the ligand exchange reaction. Detachment of salpn from the Cu(II) complexes likely involves initial coordination of oxygen groups of the H2salen to copper center in Cu(salpn) complex followed by protons-transfer from H2salen to salpn ligand, with the bond cleavage of two-end of salpn. Finally, the reaction is completed by replacing salpn with salen. (Scheme 2).

Fitting equation (3) with the experimental data yields K = 13.06 ± 3.12 M⁻¹ and k = (3.13 ± 1.06) × 10⁻³ s⁻¹ in the presence of H2O, K = 13.79 ± 3.84 M⁻¹ and k = (3.11 ± 1.08) × 10⁻³ s⁻¹ in the absence of H2O. Similar dependence of kobs on [H2salen], both in presence and absence of H2O (Fig. 3), is in agreement with our assumption that H2salen is the major reaction species. Therefore, no protonic equilibrium is expected for H2salen under the reaction conditions.

Fig. 7 shows a consecutive series of spectra recorded in CH3CN solvent for reaction of Cu(salpn) (2.00 × 10⁻³ M), H2salen (2.00 × 10⁻³ M) and NEt3 (0.90 M) system within 15 min.

Figure 7. Spectral changes recorded in CH3CN solvent for the reaction of Cu(salpn) (2.00 × 10⁻³ M), H2salen (2.00 × 10⁻³ M) and NEt3 (0.90 M) system within 15 min.

As shown in Fig 4, the ligand exchange rate will increase by adding NEt3. The effect of NEt3 could be due to its interaction with either Cu(salpn) or with the H2salen ligand. The spectrum of Cu(salpn) complex in the presence of NEt3 in CH3CN does not change with respect to its spectrum in the absence of NEt3. Therefore, adduct formation between NEt3 and Cu(salpn) is not observed. But, the absorption spectrum of H2salen ligand changes with increasing of NEt3.

The electronic spectrum of H2salen ligand in CH3CN shows three transitions in UV region, the bands at 212 and 254 nm assigned to the π→π* transition are due to transition involving molecular orbitals located on the phenolic chromophore and C = N chromophore to benzen ring, respectively. The last band at 314 nm is assigned to the n→π* transition involving the promotion of one of the lone-pair electrons of the nitrogen atom of C = N to the π* molecular orbital of benzene ring.26, 27 The n→π* transition at 314 nm is absent upon complex formation.
and this indicates that the imine nitrogen atom appears to be coordinated to the copper ion.\textsuperscript{28} The bands which assigned to the $\pi\rightarrow\pi^*$ transition have been shifted to the longer wavelength (lower energies) because of the extension of the conjugate system.\textsuperscript{28}

Upon increasing NEt$_3$, the band at 314 nm ($\pi\rightarrow\pi^*$ transition) does not change, however, the bands at 212 and 254 nm ($\pi\rightarrow\pi^*$ transition) change. The changes of the bands in the presence of NEt$_3$ indicate that there is interaction between H$_2$salen ligand and NEt$_3$. Therefore, the observed dependence of the reaction rate on concentration of NEt$_3$ can only be explained by consideration of the deprotonated of H$_2$salen ligand. With the increase of [NEt$_3$], the amount of anionic form of H$_2$salen (i.e. Hsalen$^-$ and salen$^{2-}$) increases significantly, and this is reflected in the rate constant values.

As shown in Fig. 5, there is strong dependence of the breaking point in the plot of $k_{\text{obs}}$ vs. [NEt$_3$] with H$_2$salen concentration. At higher concentration of H$_2$salen, the breaking point observed at lower NEt$_3$ concentration. The dependence of the breaking point on [H$_2$salen] confirms that the deprotonation of H$_2$salen ligand and formation Hsalen$^-$ and salen$^{2-}$ species.

The following observations (a) the increase of ligand exchange rate by adding NEt$_3$, (b) the decrease of reaction rate in the presence of NEt$_3$ by adding H$_2$O to reaction mixtures (Fig. 6) and (c) the break in the plot of $k_{\text{obs}}$ vs. [NEt$_3$], in the presence of NEt$_3$ as shown in Fig. 5, all suggest that Hsalen$^-$ and salen$^{2-}$ ions are major reactive species. At relatively low [NEt$_3$], the Hsalen$^-$ ion dominates while at high [NEt$_3$], the salen$^{2-}$ ion is major reactive species. A plausible mechanism explaining the NEt$_3$ effect can be given by scheme 3.

In the first step, the NEt$_3$ could quickly produce labile Hsalen$^-$ and salen$^{2-}$ ions, by the deprotonation of the phenolic group(s) (reaction 5 and 6).

\begin{equation}
\text{H}_2\text{salen} + \text{NEt}_3 \rightarrow \text{Hsalen}^- + \text{HNEt}_3^+ (5)
\end{equation}

\begin{equation}
\text{Hsalen}^- + \text{NEt}_3 \rightarrow \text{salen}^{2-} + \text{HNEt}_3^+ (6)
\end{equation}

Then coordination of oxygen group of the Hsalen$^-$ (path 1) or salen$^{2-}$ (path 2) to copper center in Cu(salpn) complex, is followed by a intramolecular proton transfer from Hsalen$^-$ to salpn (path 1). Finally, the bond cleavage of two-end of salpn and ligand exchange is completed similar to the reaction without NEt$_3$.

Using the proposed mechanism the rate law of ligand exchange can be expressed as

\begin{equation}
k_{\text{obs}} = \frac{k_1[H\text{salen}^-] + k_2[\text{salen}^{2-}]}{[H\text{salen}^-] + [\text{salen}^{2-}]} (7)
\end{equation}

At low concentration of NEt$_3$, the reaction 5 dominates with Hsalen$^-$ ion being the active species in promoting ligand exchange. Under this condition, [Hsalen$^-$] $>$ [salen$^{2-}$] and equation 7 is converted to $k_{\text{obs}} = k_1$. On the other hand, at high concentration of NEt$_3$, reaction 6 dominates with [salen$^{2-}$] $>$ [Hsalen$^-$], in which case equation 7 simplifies to $k_{\text{obs}} = k_2$. As shown Fig. 5, the slop of plot $k_{\text{obs}}$ vs. [NEt$_3$] at high [NEt$_3$] is smaller than at low [NEt$_3$], and therefore from equation 7, $k_2 < k_1$.

The rate of the reaction 1 is dependent on the NEt$_3$ concentration, in such a way that, by increasing NEt$_3$ concentration, the rate of reaction 1 increases because of increasing Hsalen$^-$ concentration. The Hsalen$^-$ ion rapidly coordinates to a copper center through its phenolic group, and this step is followed by intramolecular proton transfer from Hsalen$^-$ to salpn, causing Cu(salpn) to dissociate.
However, at the high concentration of NEt$_3$, the Hsalen$^-$ produced from reaction 5 is deprotonated and converted to salen$^{2-}$ ion. However, the salen$^{2-}$ quickly coordinates to a Cu complex, it cannot quickly undergo a bond cleavage, and therefore the rate of the ligand exchange reaction shows a small increase. A breaking point is observed in the plot of $k_{obs}$ vs. [NEt$_3$] at concentration of $0.23$ to $0.38$ M (dependent of [H$_2$salen]$_n$) as a result of a decrease in the concentration of Hsalen$^-$ ion. These results suggest that at high NEt$_3$ concentrations, reaction 6 is major reaction.

As shown in Fig. 6, the ligand exchange rate in the presence of NEt$_3$ will decrease by adding H$_2$O with respect to the reaction without H$_2$O. The decrease of ligand exchange rate by adding H$_2$O can be due to protonation of NEt$_3$ or Hsalen$^-$ and salen$^{2-}$ ions. The protoneated species give rise H$_2$salen ligand mainly species in ligand exchange reaction, and rate reaction decreases. Experimental observations confirm that the deprotonation/protonation H$_2$salen ligand and anionic form of H$_2$salen is important for the ligand exchange reaction.

4. Conclusion

The ligand exchange reaction was investigated in systems Cu(salpn)/H$_2$salen in the present or the absence of NEt$_3$ and H$_2$O by using visible spectrophotometry in the acetonitrile. The rate of reaction was not changed by adding H$_2$O, but the markedly increased by adding NEt$_3$. The marked increase suggests to the reaction without H$_2$O. The decrease of ligand exchange rate by adding H$_2$O can be due to protonation of NEt$_3$ or Hsalen$^-$ and salen$^{2-}$ ions. The protoneated species give rise H$_2$salen ligand mainly species in ligand exchange reaction, and rate reaction decreases. Experimental observations confirm that the deprotonation/protonation H$_2$salen ligand and anionic form of H$_2$salen is important for the ligand exchange reaction.

5. Acknowledgments

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6. References

Povzetek

Kinetiko izmenjave ligandov v sistemu Cu(salpn)/H$_2$salen v vodi, acetonitrilu in v raztopini 0.01 M NaNO$_3$, ob prisotnosti trietilamina (NEt$_3$) in brez njega smo proučevali z VIS-spektroskopijo pri 25 ± 0.1 °C (H$_2$salen in H$_2$salpn sta oznaki za N,N'-etilen-bis(salicilaldimin) oz. N,N'-propilen-bis(salicilaldimin)). Ugotovili smo, da je izmenjava reakcija prvega reda glede na Cu(salpn) kompleks ter da hitrost narašča z dodatkom NEt$_3$. Opisan je tudi predlagani mehanizem reakcije.