Scientific paper

Kinetics of the Ligand Exchange Reaction Between Tetradentate 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)/H_2salen with or without triethylamine (NEt_3) and H_2O in acetonitrile solvent at 25 ± 0.1°C and 0.01 M $NaNO_3$ (H_2salen and H_2salpn 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 NEt_3 is added to the reaction mixture, as shown by a break in the k_{obs} vs. [NEt_3] plot. The effects of NEt_3 and H_2O 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 spectra[6, 7] and the structures of copper(II) complexes of salen[5, 8, 9] and its derivatives have been studied by various research groups.[4, 5] Tetradentate 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 methylen 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 tetradentate 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.

$$\text{Cu(salpn)} + H_2\text{salen} \rightarrow \text{Cu(salen)} + H_2\text{salpn} \qquad (1)$$

2. Experimental

2. 1. Syntheses of Ligands

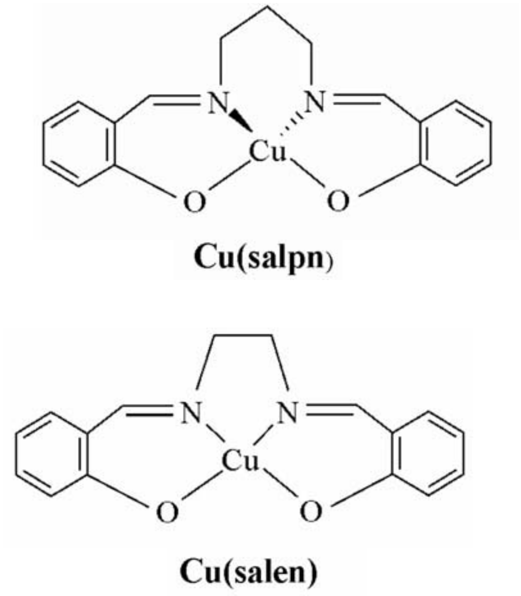
The Schiff base H_2salen and H_2salpn were prepared by a general method,[12, 17] involving the condensation reaction between 2 equivalents of salicylaldehyde and 1 equivalent of the appropriate diamine.

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.

- **Cu(salen):** Yield 51%. Anal. Calculated for $C_{16}H_{14}CuN_2O_2$: C, 58.26; H, 4.28; N, 8.49. Found : C, 58.09; H, 4.23; N, 8.61.

- **Cu(salpn):** Yield 50%. Anal. Calculated for $C_{17}H_{16}CuN_2O_2$: C, 59.38; H, 4.69; N, 8.15. Found : C, 59.12; H, 4.63; N, 8.21.



Scheme 1

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, CH_3CN solvent (with and without triethylamine, NEt_3 and H_2O) at an ionic strength of I = 0.01 M in $NaNO_3$ 25 ± 0.1 °C. Both H_2salen 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 H_2salen ($2.00 \times 10^{-3} – 5.00 \times 10^{-2}$) 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 $-\ln(A_\infty – A_t)$ vs. time, where A_t and A_∞ 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. [H_2salen] using sigmaplot 9.0.

3. Results and Discussions

3. 1. Absorption Spectra

The visible absorption spectra of Cu(salen) and Cu(salpn) complexes in CH_3CN solvent show a maximum absorption due to d-d transition at 568 and 605 nm respectively (Fig.1).

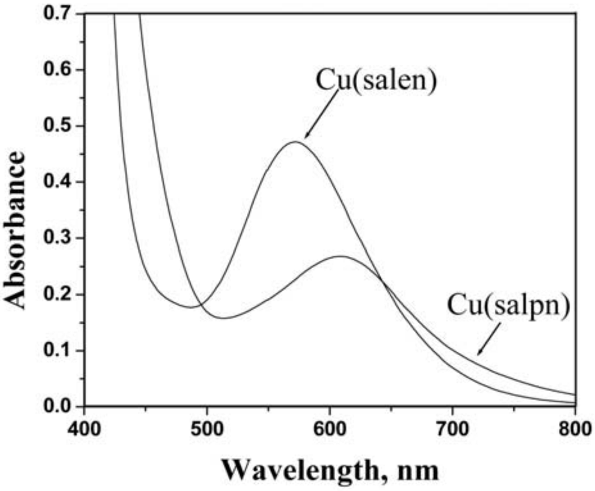


Figure 1. Visible spectra of Cu(salpn) (6.0×10^{-3} M) and Cu(salen) (6.0×10^{-3} M) complexes in CH_3CN.

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 CH_3CN solvent for Cu(salpn)/ H_2salen 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

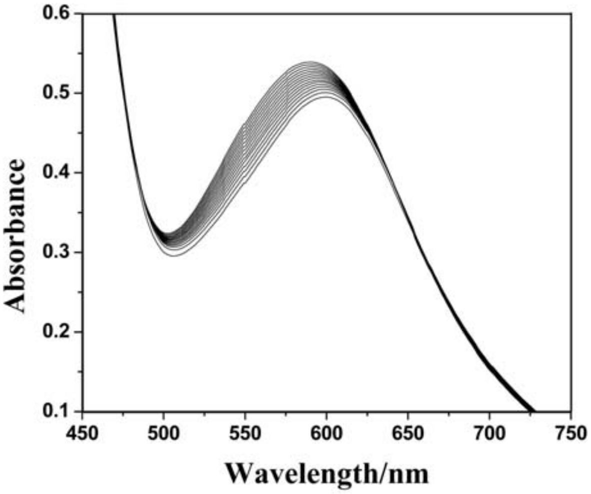


Figure 2. Spectral changes recorded in CH_3CN solvent for the reaction of Cu(salpn) (2.00×10^{-3} M)/ H_2salen (2.00×10^{-3} M) system within 40 min.

complex. These observations indicate that the Cu(salpn) complex is converted to the Cu(salen) complex (reaction 1) by adding H_2salen ligand.

The spectrum produced by mixing corresponding amounts of Cu(salen) complex, H_2salpn and $NaNO_3$ in CH_3CN 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:

$$\text{Rate} = \frac{d[Cu(salen)]}{dt} = k_{obs}\,[\text{Cu(salpn)}]_0 \qquad (2)$$

where $[\text{Cu(salpn)}]_0$ is the concentration of Cu(salpn) at time initial. The pseudo-first-order rate constants were measured at various H_2salen ligand concentrations. The order of the reaction rate with respect to H_2salen ligand was determined by plotting k_{obs} as a function of the concentration of H_2salen. As shown in Fig. 3, the variations of k_{obs} vs. concentration of H_2salen showed saturation kinetics (See proposed mechanism).

The conversion of Cu(salpn) into Cu(salen) in CH_3CN 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 (λ_{max} = 568 nm) than Cu(salpn) complex (λ_{max} = 605 nm).[14]

Table 1. Rate constants data for the reaction of Cu(salpn) with H_2salen ligand in the absence and in the presence at different concentration of NEt_3[a]

$[NEt_3]$/M	$k\times10^3/s^{-1}$	$[NEt_3]$/M	$k\times10^3/s^{-1}$
0	0.031±0.11	0.90	2.504±1.51
0.18	1.298±0.65	1.08	2.987±0.64
0.36	1.688±0.78	0[b]	0.031±0.11
0.54	1.383±1.04	1.08[b]	1.347±0.51
0.72	1.831±1.03		

[a] Solvent CH_3CN, at 25 ± 0.1 °C and I = 0.01 M $NaNO_3$

[b] in the presence of H_2O (0.28 M)

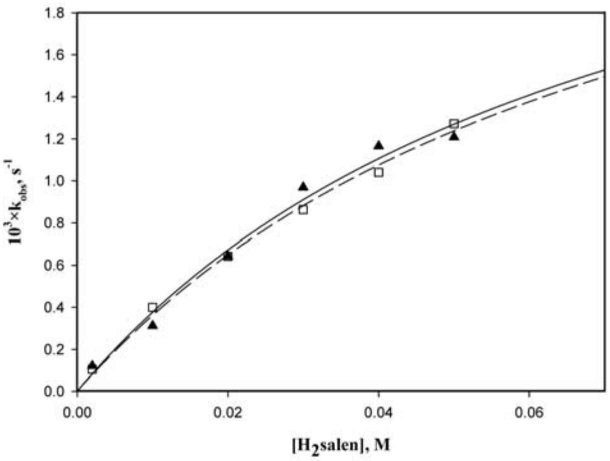


Figure 3. Plots of k_{obs} vs. $[H_2salen]$ for ligand exchange reaction of salpn in Cu(salpn) by H_2salen in the absence H_2O (▲) and in the presence H_2O, $[H_2O]$ = 0.28 M (☐)

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.[12, 14, 18] 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.[12, 20–22] 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

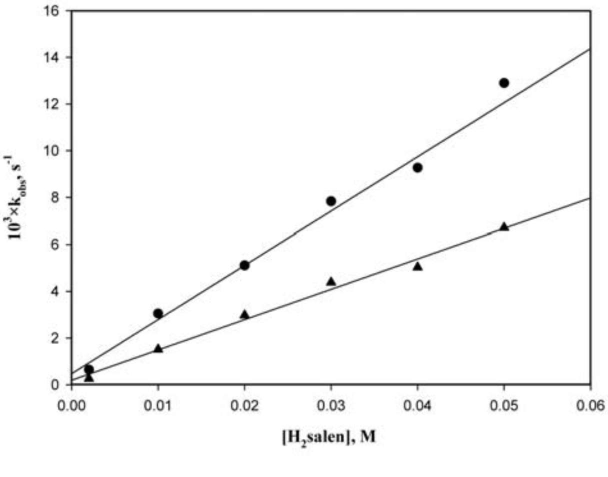


Figure 4. Plots of k_{obs} vs. $[H_2salen]$ for ligand exchange reaction of salpn in Cu(salpn) by H_2salen in the presence NEt_3, $[NEt_3]$ = 0.18 M (▲) and $[NEt_3]$ = 0.90 M (●)

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 H_2O). 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 NEt_3 is added to the reaction mixture. Carrying out the reaction at different NEt_3 concentrations, indicates that the ligand exchange is strongly depends on the NEt_3 concentration. As shown in Fig. 4, by increasing NEt_3 concentration, the reaction rate become considerably faster than when carried out in the absence of NEt_3. However, as shown in Fig. 5 (plot of k_{obs} vs. $[NEt_3]_0$), there is an obvious breaking point at ~0.23 to 0.38 M concentration of NEt_3, dependent of $[H_2salen]_0$, which can be related to the change of the reaction species at these concentration of NEt_3. As shown in Fig. 5, by increasing H_2salen concentration, the break point on the plot of k_{obs} vs. $[NEt_3]_0$ observed in lower NEt_3 concentration.

3. 4. Reaction in Presence of H_2O

The plot of k_{obs} vs. $[H_2salen]$ in the presence and absence of H_2O has been shown in Fig. 3 which shows that the rate of the ligand exchange reaction (Eq. 1) is not considerably changed by adding H_2O (0.28 M) to CH_3CN. However in presence of NEt_3, the ligand exchange reaction rate considerably decreases by adding H_2O (0.28 M) to solution of the reaction (Fig. 6). The effects of NEt_3 and H_2O show the importance of protonation/deporotonation on the rate of the ligand exchange reaction.

3. 5. Proposed Mechanism

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 Cu^{2+} ion,[23] which has a different spectrum than Cu(salpn) and Cu(salen) complexes. In general, ligand exchange reactions between multidentatate ligands proceed through intermediates in which the incoming ligand is partially coordinated to metal center and the leaving ligand is partially dissociated.[23, 24] Results from this study, namely that: (a) the ligand exchange rate did not change by adding H_2O to solvent and (b) the plot of k_{obs} vs. $[H_2salen]$ showed saturation kinetics indicates that a limiting value of k_{obs} is reached at high $[H_2salen]$. This result implies that there is an association between Cu(salpn) and H_2salen prior to ligand exchange. We also know that because of the low acidity of H_2salen and its family ligands,[25] $Hsalen^-$ and $salen^{2-}$ ions concentration were negligible so that H_2salen could be treated as the major reactive species under these conditions. This assumption was confirmed by performing the

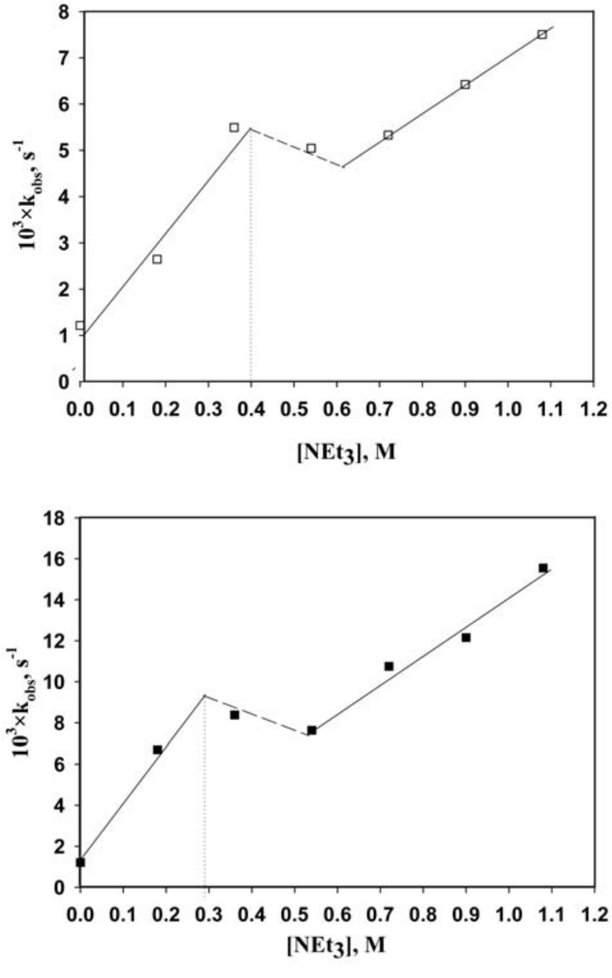


Fig 5. Plots of k_{obs} vs. $[NEt_3]$ for ligand exchange reaction $[Cu(salpn)] = 2.00 \times 10^{-3}$ M and $[H_2salen] = 2.00 \times 10^{-3}$ M (☐)and $[H_2salen] = 0.05$ M (■)

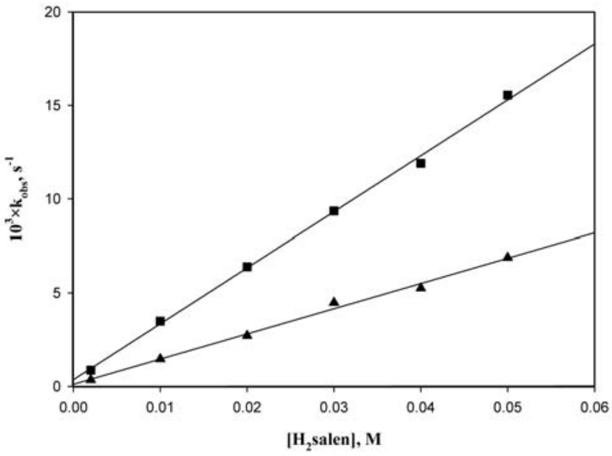


Figure 6. Plots of k_{obs} vs. $[H_2salen]$ for ligand exchange reaction of salpn in Cu(salpn) by H_2salen, $[NEt_3] = 1.018$ M in the absence H_2O (■) and in the presence, $[H_2O] = 0.28$ M (▲)

ligand exchange reaction in the presence of H_2O with no changes in reaction rate.

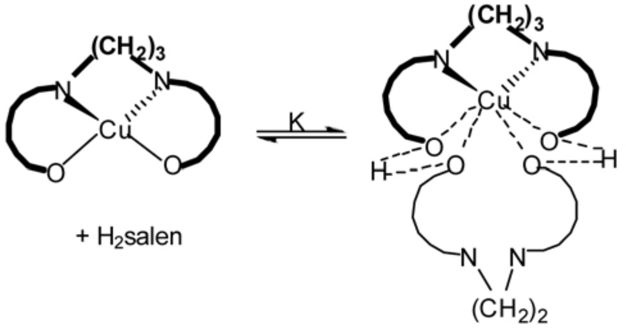
In the absence and presence of H_2O, the plot of k_{obs} vs. [H_2salen] showed saturation kinetics (Fig. 3), implying that a limiting value of k_{obs} is reached at high [H_2salen]. This leads us to assume that there is an association between Cu(salpn) and H_2salen prior to ligand exchange.

$$\mathrm{Cu(salpn)} + \mathrm{H_2salen} \underset{}{\overset{K}{\rightleftharpoons}} [\mathrm{Cu(salpn).H_2salen}] \xrightarrow{k} \mathrm{Cu(salen)} + \mathrm{H_2salpn} \quad (3)$$

The theoretical rate law can be given as:

$$k_{obs} = \frac{kK[H_2salen]}{1 + K[H_2salen]} \quad (4)$$

Where K denotes the equilibrium constant between Cu(salpn) complex and H_2salen 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 H_2salen to copper center in Cu(salpn) complex followed by protons-transfer from H_2salen to salpn ligand, with the bond cleavage of two-end of salpn. Finally, the reaction is completed by replacing salpn with salen. (Scheme 2).



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 H_2O, K = 13.79 ± 3.84 M^{-1} and k = (3.11 ± 1.08) × 10^{-3} s^{-1} in the absence of H_2O. Similar dependence of k_{obs} on [H_2salen], both in presence and absence of H_2O (Fig. 3), is in agreement with our assumption that H_2salen is the major reaction species. Therefore, no protonic equilibrium is expected for H_2salen under the reaction conditions.

Fig. 7 shows a consecutive series of spectra recorded in CH_3CN solvent for reaction of Cu(salpn) with H_2salen in the presence of NEt_3. The absorption spectra indicate a shift towards smaller wavelength with respect to the starting Cu(salpn) spectrum, which is similar to Fig. 2 . In fact the changes observed in the spectrum indicate that the Cu(salpn) complex is converted to the Cu(salen) complex by adding H_2salen ligand, in the presence of NEt_3.

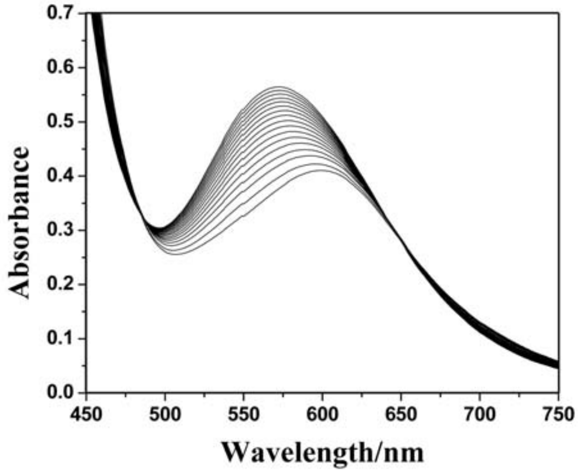


Figure 7. Spectral changes recorded in CH_3CN solvent for the reaction of Cu(salpn) (2.00 × 10^{-3} M), H_2salen (2.00 × 10^{-3} M) and NEt_3 (0.90 M) system within 15 min.

As shown in Fig 4, the ligand exchange rate will increase by adding NEt_3. The effect of NEt_3 could be due to its interaction with either Cu(salpn) or with the H_2salen ligand. The spectrum of Cu(salpn) complex in the presence of NEt_3 in CH_3CN does not change with respect to its spectrum in the absence of NEt_3. Therefore, adduct formation between NEt_3 and Cu(salpn) is not observed. But, the absorption spectrum of H_2salen ligand changes with increasing of NEt_3.

The electronic spectrum of H_2salen ligand in CH_3CN shows three transitions in UV region, the bands at 212 and 254 nm assigned to the $\pi \rightarrow \pi^*$ transition are due to transition involving molecular orbitals located on the phenolic chromophore and C = N chromophore to benzene ring, respectively. The last band at 314 nm is assigned to the $n \rightarrow \pi^*$ 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 $n \rightarrow \pi^*$ 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.[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.[28]

Upon increasing NEt_3, the band at 314 nm ($n \rightarrow \pi^*$ 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_2salen 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_2salen ligand. With the increase of $[NEt_3]$, the amount of anionic form of H_2salen (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_{obs} vs. $[NEt_3]_0$ with H_2salen concentration. At higher concentration of H_2salen, the breaking point observed at lower NEt_3 concentration. The dependence of the breaking point on $[H_2salen]$ confirms that the deprotonation of H_2salen 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_2O to reaction mixtures (Fig. 6) and (c) the break in the plot of k_{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).

$$H_2salen + NEt_3 \xrightleftharpoons{K_1} Hsalen^- + HNEt_3^+ \qquad (5)$$

$$Hsalen^- + NEt_3 \xrightleftharpoons{K_2} salen^{2-} + HNEt_3^+ \qquad (6)$$

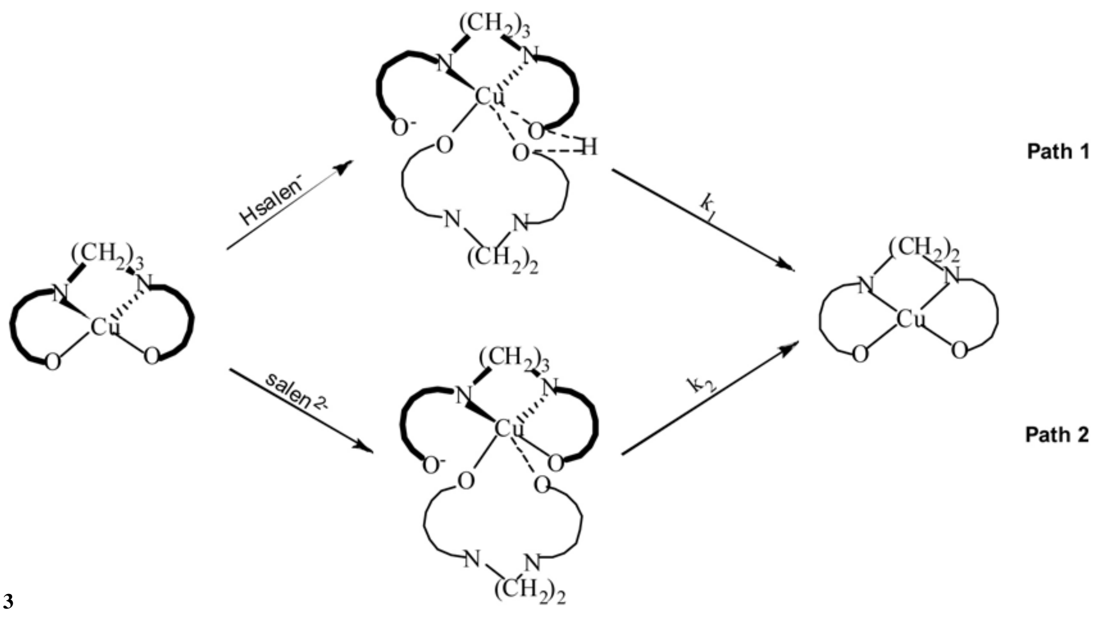
Then coordination of oxygen group of the $Hsalen^-$ (path 1) or $salen^{2-}$ (path 2) to copper center in Cu(salpn) complex, is followed by a intramolecular proton transfer from $Hsalen^-$ to salpn (path 1). Finally, the bond cleavage of two-end of salpn and ligand exchange is completed similar to the reaction without NEt_3.

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

$$k_{obs} = \frac{k_1[Hsalen^-] + k_2[salen^{2-}]}{[Hsalen^-] + [salen^{2-}]} \qquad (7)$$

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 $k_{obs} \approx k_1$. On the other hand, at high concentration of NEt_3, reaction 6 dominates with $[salen^{2-}] >> [Hsalen^-]$, in which case equation 7 simplifies to $k_{obs} \approx k_2$. As shown Fig. 5, the slop of plot k_{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.



Scheme 3

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 $[H_2salen]_0$) 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_2O with respect to the reaction without H_2O. The decrease of ligand exchange rate by adding H_2O can be due to protonated of NEt_3 or $Hsalen^-$ and $salen^{2-}$ ions. The protoneated species give rise H_2salen ligand mainly species in ligand exchange reaction, and rate reaction decreases. Experimental observations confirm that the deprotonation/protonation H_2salen ligand and anonic form of H_2salen is important for the ligand exchange reaction.

4. Conclusion

The ligand exchange reaction was investigated in systems Cu(salpn)/H_2salen in the present or the absence of NEt_3 and H_2O by using visible spectrophotometry in the acetonitrile. The rate of reaction was not changed by adding H_2O, but the markedly increased by adding NEt_3. These observations show the importance of protonation/deprotonation of H_2salen ligand in the rate of the ligand exchange reaction. The conversion of the Cu(salpn) into the Cu(salen) in the Cu(salpn)/H_2salen system indicated that Cu(salen) should be more stable than Cu(salpn). The decrease in the stability of the Cu(salpn) complex (distorted tetrahedral configuration) relative to the Cu(salen) complex (square planer) may be due to an extra methylene group in the chain of the Schiff base ligand.

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Povzetek

Kinetiko izmenjave ligandov v sistemu Cu(salpn)/H_2salen v vodi, acetontrilu 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_2salen in H_2salpn sta oznaki za N,N'-etilen-bis(salicilaldimin) oz. N,N'-propilen-bis(salicilaldimin)). Ugotovili smo, da je izmenjava rekacija prvega reda glede na Cu(salpn) kompleks ter da hitrost narašča z dodatkom NEt_3. Opisan je tudi predlagani mehanizem reakcije.