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

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ABSTRACT
Visible spectrophotometry is used to study the kinetics of ligand exchange in the system Ni(salpn)/H₂salen with or without triethylamine (NEt₃) and H₂O in dimethylformamide (DMF) solvent at 25 ± 0.1 °C and 0.01 M NaNO₃. It was found that the reaction rate is of the first-order with respect to Ni(salpn). In addition, the effect of NEt₃ and H₂O on the rate of the reaction was examined. The rate of the ligand exchange reaction was accelerated by adding NEt₃ to the reaction mixture. However, the ligand exchange reaction rate was not changed by adding H₂O to the mixture reaction. The effects of NEt₃ and H₂O on the ligand exchange rate show that deprotonation/protonation of the H₂salen ligand and anionic form of H₂salpn is important. On the basis of these results, the reaction mechanism is discussed.

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1. Introduction
Ligand substitution reaction on planar four-coordinate metal complexes with central metal ions of d⁶ electronic configuration, such as Ni(II), have been generally studied using replaceable monodentate ligands. The results of these studies have almost universally suggested an associative mechanism with a five-coordinate intermediate.
Polydentate ligand exchange reactions are very interesting from a mechanistic point of view due to their importance in coordination chemistry. However, the kinetics of polydentate ligands exchange reactions have not been studied in the same detail as monodentate ligands. In general, such systems proceed through intermediates, where the incoming polydentate ligand is partially coordinated and the leaving ligand is partially dissociated. The driving force for ligand exchange reactions in metal-complexes with polydentate ligands is the formation of a more stable complex.

The structures of the Ni(II) and Cu(II) complexes of multidentate ligands such as salen Schiff base ligands and its derivatives (Scheme 1) have been studied by various groups. These studies have indicated that the increase in the number of CH₂ groups allows sufficient flexibility to the structure of complexes by changing their structure from a planar to distorted tetrahedral form or by forming five- or six-coordinate species in the presence of additional donors. In addition, the metal complex stability decreases as the alkyl chain length (number of CH₂ groups) increases.

In our previous work, we reported the kinetics of ligand exchange in the systems Cu(salpn)/H₂salen, Cu(salbn)/H₂salen and Cu(salbn)/H₂salpn, where H₂salen, H₂salpn and H₂salbn are N,N'-ethylen-bis(salicylaldimine), N,N'-propylen-bis(salicylaldimine) and N,N'-butylen-bis(salicylaldimine), respectively (reactions 1–3). In order to investigate the effect of the metal on the kinetics of ligand exchange, we carried out a kinetic study for the ligand exchange reaction salpn with the Ni(salen) complex, Ni(N,N'-propylen-bis(salicylaldimine)), reaction 4).

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**Ni(salpn):** Brown needle-shaped crystals, m.p. >250, Yield = 70 %, IR (cm$^{-1}$): $\nu$(C=N) 1606, $\nu$(C–O) 1355, $\nu$(C=C) 1540. Electronic spectra in DMF solvent: $\lambda_{\text{max}}$ (log $\epsilon$, M$^{-1}$ cm$^{-1}$) = 650 (1.86), 350 (3.81), 275 (4.81) nm. Found: C, 60.01; H, 4.66; N, 8.38 %. Calc. for $\text{C}_{17}\text{H}_{16}\text{N}_{2}\text{NiO}_{2}$ (339.02); C, 60.23; H, 4.76; N, 8.26 %.

2.2. Kinetics Measurements
To measure the ligand exchange reaction rate, the absorbance changes of reaction mixtures were recorded as a function of time using a GBC UV-Visible Cintra 101 spectrophotometer. The greatest change in molar absorbance between reactants and products was observed at 530 nm. Therefore, all kinetic measurements of absorbance versus time were made at this wavelength. Reaction mixtures were made in dimethylformamide, DMF, an aprotic polar solvent, ionic strength 0.1 M (adjusted with NaNO$_3$) and the Ni(salpn) complex concentration was held constant at $5.0 \times 10^{-3}$ M, while concentration of H$_2$salen ligand (with and without triethylamine, NEt$_3$ and/or H$_2$O) was varied from $5.0 \times 10^{-3}$ to $1.0 \times 10^{-1}$ M at 25 ± 0.1 °C. Under these conditions, pseudo-first-order kinetic behaviour was observed for reaction 4.

To initiate the reaction, equal volumes of Ni(salpn) and H$_2$salen were mixed and the absorbance of reaction product at 530 nm was followed as a function of time. At least three runs at each concentration were recorded. The absorbance $A$ versus time $t$ data were computer-fitted with the sigmaplot 12.0 software using Equation 5 (irreversible first-order reaction), 6 (biphasic reaction), and 7 (triphasic reaction) to find the best fit and $k_{\text{obs}}$:

$$A_t = a_1 \exp[-k_{\text{obs}}(1)t] + a_2$$  \hspace{1cm} (5)

$$A_t = a_1 \exp[-k_{\text{obs}}(1)t] + a_2 \exp[-k_{\text{obs}}(2)t] + A_\infty$$  \hspace{1cm} (6)

$$A_t = a_1 \exp[-k_{\text{obs}}(1)t] + a_2 \exp[-k_{\text{obs}}(2)t] + a_3 \exp[-k_{\text{obs}}(3)t] + A_\infty$$  \hspace{1cm} (7)

where $a_1$ and $a_2$ comprise rate constants and molar absorptivities, respectively:

$$a_1 = e_{\text{A}_0} [\text{A}_0] + e_{\text{B}[\text{A}]0} k_1 - k_1 + e_{\text{C}[\text{A}]0} k_2$$

$$a_2 = \frac{k_1 [\text{A}_0] (k_2 - e_{\text{C}})}{k_1 - k_2}$$

3. Results and Discussion

3.1. Kinetics study
The visible absorption spectra of Ni(salen) and Ni(salpn) complexes in DMF solvent show a maximum absorption due to d-d transition at 540 and 600 nm, respectively (Fig. 1). The UV-Vis absorption spectra recorded after mixing Ni(salpn) and H$_2$salen in DMF (Fig. 2) shows a consecutive series of spectra recorded in DMF for the Ni(salpn)/H$_2$salen system, indicating that the Ni(salpn) complex is converted to the Ni(salen) complex by adding H$_2$salen ligand. The spectrum of Ni(salen) in DMF (Fig. 1), was similar to the last spectrum shown in Fig. 2. This similarity confirms the conversion of the Ni(salpn) to the Ni(salen) complex (reaction 4).

The rate constants for the ligand exchange reaction were obtained by measuring the absorbance changes at 530 nm under pseudo-first-order conditions, [H$_2$salen] $>>$ [Ni(salpn)] (Figs. 3 and 4). The absorbance at 530 nm was found to increase with time, due to formation of Ni(salen) complex (Fig. 3). Under these conditions, the best fit for the absorbance versus time data was obtained utilizing Equation 6 (biphasic reaction). Therefore, two rate constants $k_{\text{obs}}(1)$ and $k_{\text{obs}}(2)$ were obtained. The plots of the two observed constants, $k_{\text{obs}}$ vs. [H$_2$salen], are shown in Fig. 4. The figure indicates that the first reaction step was fast and dependent on the [H$_2$salen], while the second reaction step was slow and independent of the concentration of H$_2$salen ligand. These results can be described by Equations 8 and 9.

$$k_{\text{obs}}(1) = k_1 [\text{H}_2\text{salen}]$$  \hspace{1cm} (8)

$$k_{\text{obs}}(2) = k_2$$  \hspace{1cm} (9)

The $k_1$ (second-order rate constant) value was obtained from the slope of line $k_{\text{obs}}(1)$ vs. [H$_2$salen], $k_1 = 5.80 \pm 0.28 \times 10^{-7}$ M$^{-1}$ s$^{-1}$ and $k_2 = 2.56 \pm 0.89 \times 10^{-6}$ s$^{-1}$ was determined as the mean of the experimentally obtained data for $k_{\text{obs}}(2)$ (Fig. 4), which was independent of [H$_2$salen]. The rate constant for the second step of the ligand exchange reaction of the Ni(salpn)/H$_2$salen system is similar to the analogous reactions of the Cu(salpn)/H$_2$salen system (3.11 1.06 $\times 10^{-6}$ s$^{-1}$).

The kinetic study of the ligand exchange reaction was investigated in the presence of H$_2$O (protic solvent) and/or NEt$_3$. 

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**Scheme 1**
A structural representation of the Schiff base ligands and complexes.

**Figure 1** Visible spectra of Ni(salpn) ($5.0 \times 10^{-3}$ M) and Ni(salen) ($5.0 \times 10^{-3}$ M) complexes in DMF (1 cm quartz cell).
3.2. Effect of Triethylamine

The rate of the ligand exchange reaction was observed to be accelerated by adding NEt₃ to the reaction mixture. Consequently, the effect of [NEt₃] on the rate of the reaction was examined. The absorbance at 530 nm was found to increase with time, due to formation of Ni(salpn) complex (Fig. 3). The rate of the ligand exchange reaction at different NEt₃ concentrations indicated that the rate of reaction strongly depends on [NEt₃]. The plots of k₁ and k₂ values vs. [NEt₃] are shown in Fig. 5. As shown in Fig. 5, the value of k₁ initially increased by increasing the NEt₃ concentration, while the k₂ value was independent of the concentration of NEt₃ amine. However, as shown in Fig. 5, for the plot of k₁ vs. [NEt₃] there is an obvious break between the 0.1–0.3 M concentrations of NEt₃ – this could be related to a change of the reaction species at these concentrations of NEt₃. This effect on the reaction rate is also found in the salen-type copper(II) complexes.⁹,¹⁰

3.3. Effect of H₂O

Like the analogous reaction of copper(II) complexes,⁹,¹⁰ the ligand exchange rate of H₂salen for salpn in Ni(salpn) complex does not significantly change with the addition of H₂O to the mixture reaction. The values of k₁ and k₂ in the presence and the

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Figure 2 Spectral changes recorded in DMF solvent for the reaction of Ni(salpn) (5.0 × 10⁻³ M)/H₂salen (5.0 × 10⁻³ M) system within 20 min; (A): visible region; (B): UV region (1 cm quartz cell).

Figure 3 Plot of absorbance vs. time for reaction of Ni(salpn) (5.0 × 10⁻³ M), (—): H₂salen (5.0 × 10⁻³ M) and (----): H₂salen (5.0 × 10⁻² M).

Figure 4 Plot of the rate constants k₁ vs. [H₂salen] ([Ni(salpn)] = 5.0 × 10⁻³ M, I = 0.1 M NaNO₃ and 25 ± 0.1 °C).

Figure 5 Plots of k₁ vs. [NEt₃] for ligand exchange reaction [Ni(salpn)] = 5.0 × 10⁻³ M and [H₂salen] = 7.5 × 10⁻² M, k₁(1), M⁻¹ s⁻¹ • and k₁(2), s⁻¹ •.
The rate of the exchange reaction Ni(salpn) with H$_2$salen in presence of NEt$_3$ and H$_2$O was studied for three different conditions: 1) [NEt$_3$] < 0.1 M (before break in plot in Fig. 5); 2) [NEt$_3$] > 0.3 M (after break in plot in Fig. 4); 3) 0.1 < [NEt$_3$] < 0.3 M (break limits in plot in Fig. 5). In the first and second condition, the ligand exchange reaction rate was considerably decreased by adding H$_2$O (0.4 M). In the last condition, 0.1 < [NEt$_3$] < 0.3 M, the rate of reaction was decreased by adding H$_2$O (0.4 M) to the reaction mixture (Table 1). In spite of this, the reaction rate in this condition (0.1 < [NEt$_3$] < 0.3 M) was increased by adding of H$_2$O up to 0.05 M. The effects of NEt$_3$ and H$_2$O show the importance of protonation/deprotonation on the rate of the ligand exchange reaction (vide infra).

### 3.4. Reaction in Presence of H$_2$O and NEt$_3$

The rate of the exchange reaction Ni(salpn) with H$_2$salen in presence of NEt$_3$ and H$_2$O was studied for three different conditions: 1) [NEt$_3$] < 0.1 M (before break in plot in Fig. 5); 2) [NEt$_3$] > 0.3 M (after break in plot in Fig. 4); 3) 0.1 < [NEt$_3$] < 0.3 M (break limits in plot in Fig. 5). In the first and second condition, the ligand exchange reaction rate was considerably decreased by adding H$_2$O (0.4 M). In the last condition, 0.1 < [NEt$_3$] < 0.3 M, the rate of reaction was decreased by adding H$_2$O (0.4 M) to the reaction mixture (Table 1). In spite of this, the reaction rate in this condition (0.1 < [NEt$_3$] < 0.3 M) was increased by adding of H$_2$O up to 0.05 M. The effects of NEt$_3$ and H$_2$O show the importance of protonation/deprotonation on the rate of the ligand exchange reaction (vide infra).

### 3.5. Proposed Mechanism

The ligand exchange reaction Ni(salpn) with H$_2$salen was found to be a two-step process (biphasic reaction) as described by the experimental rate constants $k_{\text{obs}}(1)$ and $k_{\text{obs}}(2)$. The $k_{\text{obs}}(1)$ is dependent on the concentration of the H$_2$salen ligand, according to Equation 8. The $k_{\text{obs}}(2)$ is H$_2$salen concentration independent (Fig. 4).

A similar effect on reaction rate was also found for the salen-type ligands copper(II) complexes, suggesting a common mechanism for the ligand exchange reactions (vide infra).

As observed from the experimental data, the ligand exchange rate in the absence of NEt$_3$ did not change with addition of H$_2$O (protic solvent) to the reaction mixture, it is reasonable to assume that Hsalen$^-$ and salen$^{2-}$ ion concentrations are negligible, so that H$_2$salen can be treated as the major reactive species. The acidity of H$_2$salen and its family of ligands enable us to assume that under these reaction conditions neutral H$_2$salen ligand was the original species.

These observations lead us to suggest a possible mechanism for the reaction when a Ni(salpn) complex reacts with H$_2$salen ligand (Equations 10 and 11):

1. **Ni(salpn) + H$_2$salen $\rightarrow$ Ni(salpn)$\cdot$H$_2$salen**
2. **[Ni(salpn)]$\cdot$H$_2$salen $\rightarrow$ Ni(salpn) + H$_2$salen**

### Table 1: Rate constants data for the reaction of Ni(salpn) with H$_2$salen ligand in the absence and in the presence of NEt$_3$ and H$_2$O $^a$ ($k_1$ = second-order rate constant).

<table>
<thead>
<tr>
<th>[NEt$_3$] (M)</th>
<th>0</th>
<th>0.1</th>
<th>0.2</th>
<th>0.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>[H$_2$O] (M)</td>
<td>0</td>
<td>0.05</td>
<td>0.4</td>
<td>0.4</td>
</tr>
</tbody>
</table>

$k_1 \times 10^5$ (M$^{-1}$ s$^{-1}$) | 5.80 ± 0.28 | 7.07 ± 0.34 | 6.04 ± 0.22 | 5.81 ± 0.18 |

$^a$Solvent DME, [Ni(salpn)] = 5.0 × 10$^{-3}$ M, [H$_2$salen] = 5.0 × 10$^{-3}$ – 1.0 × 10$^{-1}$ M at 25 ± 0.1 °C and I = 0.1 M NaNO$_3$.

It is clear from Equation 10 that rate constant $k_{\text{obs}}(1)$ should increase linearly with [H$_2$salen], according to Equation 8. The formation of the adduct [Ni(salpn)$\cdot$H$_2$salen in Equation 10 is in agreement with a number of studies on the polydentate ligand exchange reaction. The lone pairs electron on the phenolic oxygen atoms of H$_2$salen provide a reasonable basis to propose the formation of adduct [Ni(salpn)$\cdot$H$_2$salen as the first step in the reaction.

The second reaction step is first-order and independent of [H$_2$salen] (Equation 11) with rate constant $k_2$. As indicated in Scheme 2, substitution of salpn from the Ni(II) complexes involves initial coordination of phenolic oxygen atoms of H$_2$salen to the nickel centre in the Ni(salpn) complex followed by proton-transfer from H$_2$salen to salpn, with bond cleavage of two-ends of salpn. The ligand exchange reaction is completed by substituting salpn with salen.

As shown in Fig. 5, the reaction rate increases by adding NEt$_3$. The effect of NEt$_3$ could be due to its interaction with either Ni(salpn) or with Schiff base ligand. The UV-Vis spectrum of the Ni(salpn) complex in DMF solvent does not change with the addition of NEt$_3$, to the solvent, therefore, the formation of the adduct Ni(salpn) and NEt$_3$ is not observed. In our previous study, we have explained that interaction between H$_2$salen and NEt$_3$ could lead to the formation of Hsalen$^-$ and salen$^{2-}$ ions (dependent on [NEt$_3$]) by the deprotonation phenolic group(s) of H$_2$salen (reactions 12 and 13):

1. **H$_2$salen + NEt$_3$ $\rightarrow$ Hsalen$^-$ + HNEt$_3^+$**
2. **Hsalen$^-$ + NEt$_3$ $\rightarrow$ salen$^{2-}$ + HNEt$_3^+$**

It is clear that in the presence of NEt$_3$, the major reactive species are Hsalen$^-$ and salen$^{2-}$ ions. At relatively low [NEt$_3$], the Hsalen$^-$ ion and at high [NEt$_3$] the salen$^{2-}$ ion is the original reactive species. This suggests that a plausible mechanism in the presence of NEt$_3$ is that presented in Scheme 3. In the first step, NEt$_3$ quickly produced labile Hsalen$^-$ and salen$^{2-}$ ions. Then, Hsalen$^-$ ion (path 1) or salen$^{2-}$ ion (path 2) coordinated to a nickel centre in Ni(salpn) complex by lone pairs electron on the pheno-
lic oxygen atoms. This is followed by intramolecular proton transfer from the coordinated Hsalen⁻ to one of the phenolic oxygen atoms coordinated to the salpn ligand with bond-cleavage of one end of salpn (path 1).

As shown in Fig. 5, the slope of the plot at high [NEt₃] (0.97 ± 0.07 M⁻¹.s⁻¹, salen⁻² is the major reactive species, Equation 13) is less than with low [NEt₃] (1.18 ± 0.13 M⁻¹.s⁻¹, Hsalen⁻ is the major reactive species, Equation 12). Therefore, we can assume that the Hsalen⁻ ion is a more active species than the salen⁻² ion in the ligand exchange reaction.⁹,¹⁰ At high concentration of [NEt₃] (> 0.3 M), although the salen⁻² ion is similar to the Hsalen⁻ ion and can be quickly coordinated to a Ni(II) centre in the Ni(salpn) complex, the salen⁻² ion has no available proton for intramolecular proton transfer and thus cannot quickly undergo bond cleavage of salpn in the Ni(salpn) complex. Therefore, the rate of the reaction increases less under these conditions. At concentration 0.1 < [NEt₃] < 0.3 M there is equilibrium between Hsalen⁻ and salen⁻² ions.

To ensure the validity of the mechanism shown in Scheme 3, the reactions have been performed in the presence of H₂O and NEt₃. These experiments are studied with three different concentrations of NEt₃:

1. In the first case, [NEt₃] < 0.1 M (before the break in the plot in Fig. 5), the ligand exchange rate was decreased by adding H₂O. The decrease of the reaction rate could be due to protonated NEt₃ and Hsalen⁻ ion. The protonated Hsalen⁻ ion gave rise to the formation of neutral H₂salen ligand and the rate of reaction decreased.

2. In the second case, [NEt₃] > 0.3 M (after break in plot in Fig. 5), the reaction rate was decreased by adding H₂O (0.4 M). In this condition, salen⁻² ion was protonated by adding H₂O, Hsalen was formed and the reaction rate deceased.

3. In 0.1 < [NEt₃] < 0.3 M (break limits in plot in Fig. 5), the effect of H₂O on the rate of reaction was dependent on the concentration of H₂O. The reaction rate of ligand exchange was increased by increasing the concentration of H₂O up to 0.05 M. The increase of the reaction rate at low [H₂O] could be due to the formation of Hsalen⁻ ion by protonated salen⁻² ion. However, the reaction rate was decreased by adding more H₂O (≥0.4 M) due to complete protonation of salen⁻² and Hsalen⁻ ions and formation of neutral H₂salen.

4. Conclusion
The distortion of Ni(II) in the Ni(salpn) complex due to the formation of the larger chelate ring cause a less stable complex than the Ni(salen) complex. This is the driving force for replacing salen with salpn in Ni(salpn) complex. In the presence of NEt₃, the ligand exchange reaction rate will be increased due to the formation of salen⁻² ion. However, at high concentration of NEt₃, the reaction rate partially decreases in comparison with low [NEt₃], due to the formation of salen⁻² ion. These observations confirm that, as with similar reactions of salen-type Cu(II) complexes, the deporotonation/protonation H₂salen ligand and the anionic form of H₂salen are important for the ligand exchange reaction.

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