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Kinetics and Mechanism of the Ligand Exchange Reaction Between Tetradentate 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)/H_2salen with or without triethylamine (NEt_3) and H_2O in dimethylformamide (DMF) 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 was found that the reaction rate is of the first-order with respect to Ni(salpn). In addition, the effect of NEt_3 and H_2O on the rate of the reaction was examined. The rate of the ligand exchange reaction was accelerated by adding NEt_3 to the reaction mixture. However, the ligand exchange rate was not changed by adding H_2O to the mixture reaction. The effects of NEt_3 and H_2O on the ligand exchange rate show that deprotonation/protonation of the H_2salen ligand and anionic form of H_2salen is important. On the basis of these results, the reaction mechanism is discussed.

KEYWORDS

Kinetic, mechanism, Schiff base, Ni complexes, ligand exchange.

1. Introduction

Ligand substitution reaction on planar four-coordinate metal complexes with central metal ions of d^8 electronic configuration, such as Ni(II), have been generally studied using replaceable monodentate ligands.[1,2] The results of these studies have almost universally suggested an associative mechanism with a five-coordinate intermediate.[1,3]

Polydentate ligand exchange reactions are very interesting from a mechanistic point of view due to their importance in coordination chemistry.[4,5] 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.[5–7] The driving force for ligand exchange reactions in metal-complexes with polydentate ligands is the formation of a more stable complex.[8–10]

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.[11–17] These studies have indicated that the increase in the number of CH_2 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.[17–21] In addition, the metal complex stability decreases as the alkyl chain length (number of CH_2 groups) increases.[22,23]

In our previous work, we reported the kinetics of ligand exchange in the systems Cu(salpn)/H_2salen, Cu(salbn)/H_2salen and Cu(salbn)/H_2salpn, where H_2salen, H_2salpn and H_2salbn are N,N′-ethylen-bis(salicylaldimine), N,N′-propylen-bis(salicylaldimine) and N,N′-butlen-bis(salicylaldimine), respectively (reactions 1–3).[9,10] 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).

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

$$\text{Cu(salbn)} + H_2\text{salen} \rightarrow \text{Cu(salen)} + H_2\text{salbn} \quad (2)$$

$$\text{Cu(salbn)} + H_2\text{salpn} \rightarrow \text{Cu(salpn)} + H_2\text{salbn} \quad (3)$$

$$\text{Ni(salpn)} + H_2\text{salen} \rightarrow \text{Ni(salen)} + H_2\text{salpn} \quad (4)$$

2. Experimental

2.1. Materials

The Schiff bases H_2salen and H_2salpn were prepared from a general method,[9,10] namely the condensation reaction between two equivalents of salicylaldehyde and one equivalent of the appropriate diamine (1,2-ethylendiamine and 1,3-propandiamine), in ethanol. The yellow products were obtained in yields typically 70 % or better. Purity of products was verified by comparing with literature melting points (m.p.), 124 and 53 °C for H_2salen and H_2salpn, respectively.[19,20,23]

H_2salen: Yield = 80 %, IR (cm^{-1}): ν(O-H) 3000–3500, ν(C=N) 1633, ν(C–O) 1281, ν(C=C) 1578. Electronic spectra in DMF solvent: λ_{max} (log ε, M^{-1} cm^{-1}) = 403 (2.23), 316 (3.49), 256 (4.20) nm.

H_2salpn: Yield = 70 %, IR (cm^{-1}): ν(O-H) 3000–3500, ν(C=N) 1629, ν(C–O) 1276, ν(C=C) 1580. Electronic spectra in DMF solvent: λ_{max} (log ε, M^{-1} cm^{-1}) = 404 (2.36), 313 (4.02), 253 (4.37) nm.

The nickel complexes were prepared by a general method, using the reaction solution of nickel(II) acetate with the Schiff base ligand (1:1 molar ratio).[24,25]

Ni(salen): Red needle-shaped crystals, m.p. >250, Yield = 61 %, IR (cm^{-1}): ν(C=N) 1619, ν(C–O) 1345, ν(C=C) 1530. Electronic spectra in DMF solvent: λ_{max} (log ε, M^{-1} cm^{-1}) = 540 (2.18), 345 (3.98), 270 (4.79) nm. Found: C, 59.13; H, 4.34; N, 8.62 %. Calc. for $C_{16}H_{14}N_2NiO_2$ (324.99); C, 58.99; H, 4.27; N, 8.75 %.

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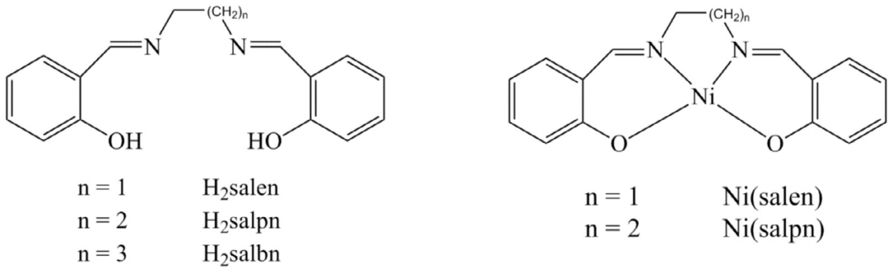


Scheme 1
A structural representation of the Schiff base ligands and complexes.

Ni(salpn): Brown needle-shaped crystals, m.p. >250, Yield = 70 %, IR (cm^{-1}): ν(C=N) 1606, ν(C–O) 1355,ν(C=C) 1540. Electronic spectra in DMF solvent: λ_{max} (log ε, 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 $C_{17}H_{16}N_2NiO_2$ (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 5.0×10^{-3} M, while concentration of H_2salen ligand (with and without triethylamine, NEt_3 and/or H_2O) was varied from 5.0×10^{-3} to 1.0×10^{-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_2salen 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_{obs}:

$$A_t = a_1\exp[-k_{obs}(1)t] + A_\infty \quad (5)$$

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

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

where a_1 and a_2 comprise rate constants and molar absorptivities, respectively:[1]

$$a_1 = \varepsilon_A[A]_0 + \frac{\varepsilon B[A]0k1}{k2 - k1} + \frac{\varepsilon C[A]0k2}{k1 - k2}$$

$$a_2 = \frac{k1[A]0(\varepsilon B - \varepsilon C)}{k1 - k2}$$

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_2salen in DMF (Fig. 2) shows a consecutive series of spectra recorded in DMF for the Ni(salpn)/H_2salen system, indicating that the Ni(salpn) complex is converted to the Ni(salen) complex by adding H_2salen 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).

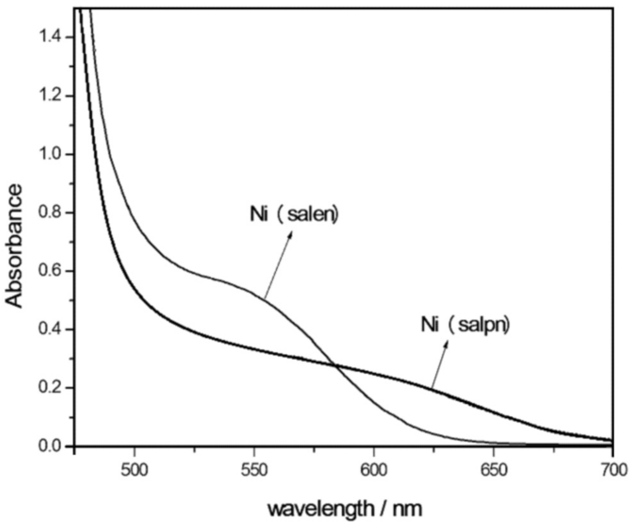


Figure 1 Visible spectra of Ni(salpn) (5.0×10^{-3} M) and Ni(salen) (5.0×10^{-3} M) complexes in DMF (1 cm quartz cell).

The rate constants for the ligand exchange reaction were obtained by measuring the absorbance changes at 530 nm under pseudo-first-order conditions, [H_2salen] >> [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 $k_{obs}(1)$ and $k_{obs}(2)$ were obtained. The plots of the two observed constants, k_{obs} *vs.* [H_2salen], are shown in Fig. 4. The figure indicates that the first reaction step was fast and dependent on the [H_2salen], while the second reaction step was slow and independent of the concentration of H_2salen ligand. These results can be described by Equations 8 and 9.

$$k_{obs}(1) = k_1[H_2\text{salen}] \quad (8)$$

$$k_{obs}(2) = k_2 \quad (9)$$

The k_1 (second-order rate constant) value was obtained from the slope of line $k_{obs}(1)$ *vs.* [H_2salen], $k_1 = 5.80 \pm 0.28 \times 10^{-1}$ M^{-1} s^{-1} and $k_2 = 2.56 \pm 0.89 \times 10^{-3}$ s^{-1} was determined as the mean of the experimentally obtained data for $k_{obs}(2)$ (Fig. 4), which was independent of [H_2salen]. The rate constant for the second step of the ligand exchange reaction of the Ni(salpn)/H_2salen system is similar to the analogous reactions of the Cu(salpn)/ H_2salen system (3.11 1.06 × 10^{-3} s^{-1}).[9]

The kinetic study of the ligand exchange reaction was investigated in the presence of H_2O (protic solvent) and/or NEt_3.

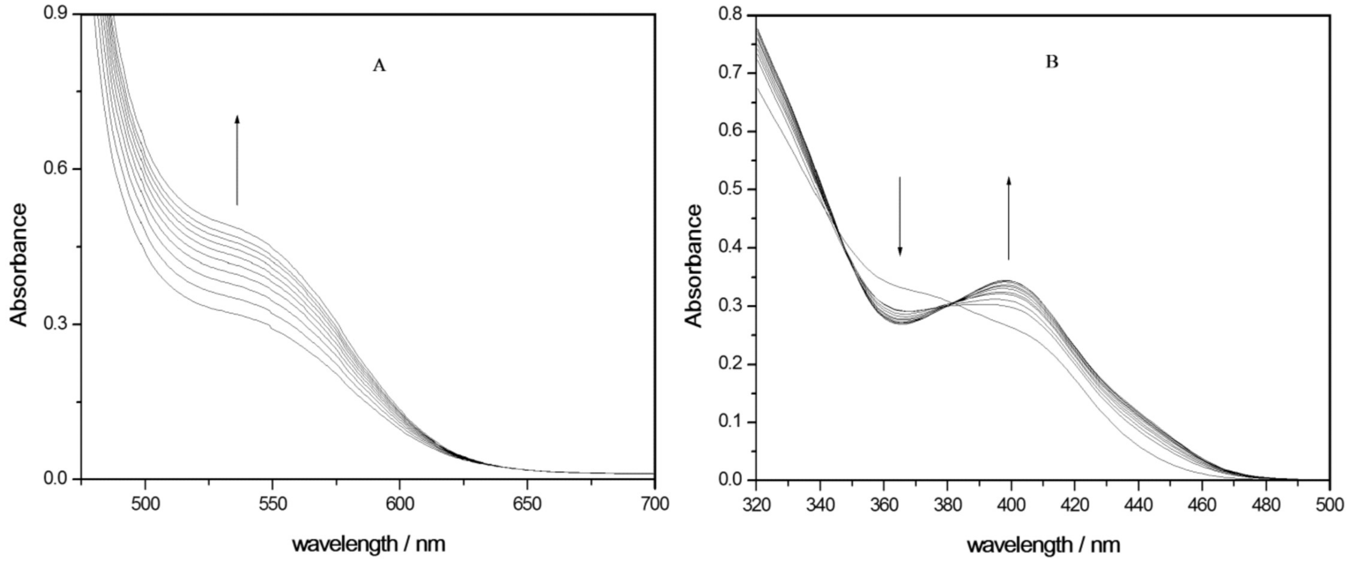


Figure 2 Spectral changes recorded in DMF solvent for the reaction of Ni(salpn) (5.0×10^{-3} M)/H_2salen (5.0×10^{-3} M) system within 20 min; (**A**): visible region; (**B**): UV region (1 cm quartz cell).

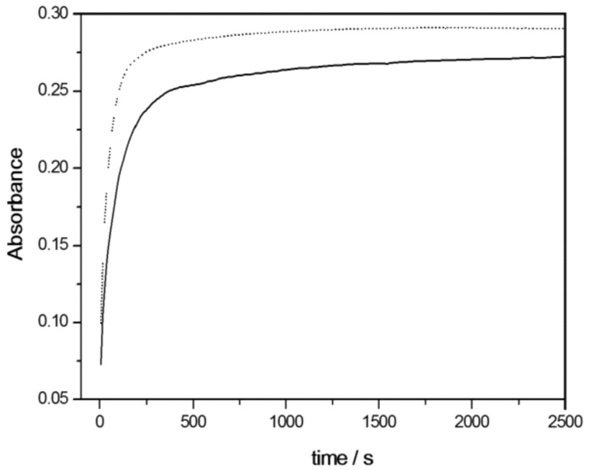


Figure 3 Plot of absorbance *vs.* time for reaction of Ni(salpn) (5.0×10^{-3} M), (—): H_2salen (5.0×10^{-3} M) and (----): H_2salen (5.0×10^{-2} M).

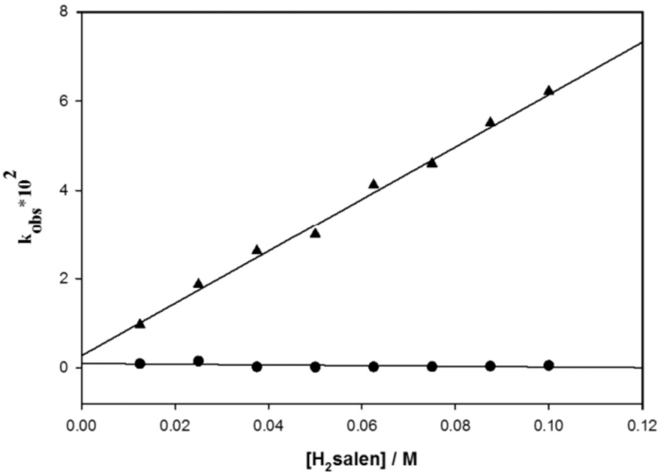


Figure 4 Plot of the rate constants $k_{obs}(1)$, ▲ and $k_{obs}(2)$, ■ *vs.*[H_2salen] ([Ni(salpn)] = 5.0×10^{-3} M, I = 0.1 M $NaNO_3$ and 25 ± 0.1 °C).

3.2. Effect of Triethylamine

The rate of the ligand exchange reaction was observed to be accelerated by adding NEt_3 to the reaction mixture. Consequently, the effect of [NEt_3] 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 NEt_3 concentrations indicated that the rate of reaction strongly depends on [NEt_3]. The plots of k_1 and k_2 values *vs.* [NEt_3] are shown in Fig. 5. As shown in Fig. 5, the value of k_1 initially increased by increasing the NEt_3 concentration, while the k_2 value was independent of the concentration of NEt_3 amine. However, as shown in Fig. 5, for the plot of k_1 *vs.* [NEt_3] there is an obvious break between the 0.1–0.3 M concentrations of NEt_3 – this could be related to a change of the reaction species at these concentrations of NEt_3. This effect on the reaction rate is also found in the salen-type copper(II) complexes.[9,10]

3.3. Effect of H_2O

Like the analogous reaction of copper(II) complexes,[9,10] the ligand exchange rate of H_2salen for salpn in Ni(salpn) complex does not significantly change with the addition of H_2O to the mixture reaction. The values of k_1 and k_2 in the presence and the

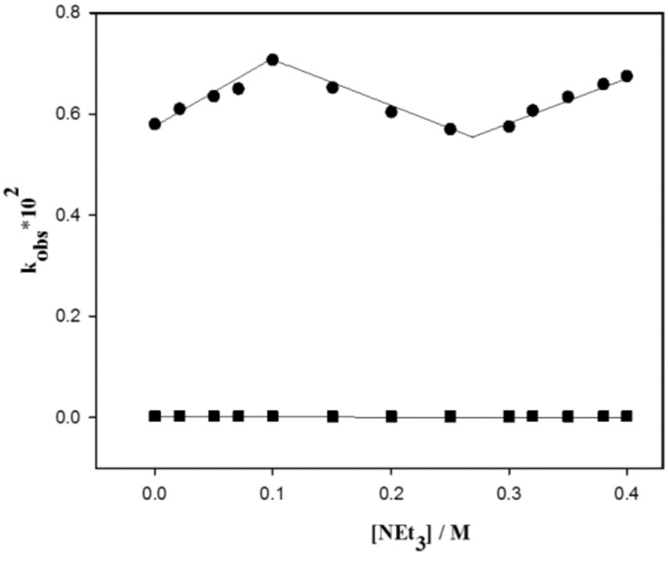


Figure 5 Plots of k_{obs} *vs.* [NEt_3] for ligand exchange reaction [Ni(salpn)] = 5.0×10^{-3} M and [H_2salen] = 7.5×10^{-2} M, $k_{obs}(1)$, $M^{-1} s^{-1}$ ● and $k_{obs}(2)$, s^{-1} ■.

Table 1 Rate constants data for the reaction of Ni(salpn) with H_2salen ligand in the absence and in the presence of NEt_3 and H_2O [a]. (k_1 = second-order rate constant).

$[NEt_3]$ (M)	0	0	0.1	0.1	0.2	0.2	0.2
$[H_2O]$ (M)	0	0.05	0	0.4	0	0.4	0.05
$k_1 \times 10$ (M^{-1} s^{-1})	5.80 ± 0.28	5.90 ± 0.27	7.07 ± 0.34	5.88 ± 0.30	6.04 ± 0.22	5.81 ± 0.18	6.13 ± 0.39

[a] Solvent DMF, [Ni(salpn)] = 5.0×10^{-3} M, [H_2salen] = $5.0 \times 10^{-3} - 1.0 \times 10^{-1}$ M at 25± 0.1 °C and I = 0.1 M $NaNO_3$

absence of H_2O were of the same order (Table 1). This result allowed us to propose that reactive species were similar in both the reaction conditions (*vide infra*).

3.4. Reaction in Presence of H_2O and NEt_3

The rate of the exchange reaction Ni(salpn) with H_2salen in presence of NEt_3 and H_2O 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_2O (0.4 M). In the last condition, $0.1 < [NEt_3] < 0.3$ M, the rate of reaction was decreased by adding H_2O (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_2O up to 0.05 M. The effects of NEt_3 and H_2O show the importance of protonation/deprotonation on the rate of the ligand exchange reaction (see proposed mechanism).

3.5. Proposed Mechanism

The ligand exchange reaction Ni(salpn) with H_2salen was found to be a two-step process (biphasic reaction) as described by the experimental rate constants $k_{obs}(1)$ and $k_{obs}(2)$. The $k_{obs}(1)$, is depended on the concentration of the H_2salen ligand, according to Equation 8. The $k_{obs}(2)$ is H_2salen 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*).[9,10]

As observed from the experimental data, the ligand exchange rate in the absence of NEt_3 did not change with addition of H_2O (protic solvent) to the reaction mixture, it is reasonable to assume that $Hsalen^-$ and $salen^-$ ion concentrations are negligible, so that H_2salen can be treated as the major reactive species. The acidity of H_2salen and its family of ligands enable us to assume that under these reaction conditions neutral H_2salen ligand was the original species.[26]

These observations lead us to suggest a possible mechanism for the reaction when a Ni(salpn) complex reacts with H_2salen ligand (Equations 10 and 11):

$$\text{Ni(salpn)} + \text{H}_2\text{salen} \xrightarrow{kobs(1)} [\text{Ni(salpn)}]\cdot\text{H}_2\text{salen} \qquad (10)$$

$$[\text{Ni(salpn)}]\ \text{H}_2\text{salen} \xrightarrow{kobs(2)} [\text{Ni(salen)}] + \text{H}_2\text{salen} \qquad (11)$$

It is clear from Equation 10 that rate constant $k_{obs}(1)$ should increase linearly with [H_2salen], according to Equation 8. The formation of the adduct [Ni(salpn]·H_2salen in Equation 10 is in agreement with a number of studies on the polydentate ligand exchange reaction.[5–7] The lone pairs electron on the phenolic oxygen atoms of H_2salen provide a reasonable basis to propose the formation of adduct [Ni(salpn]·H_2salen as the first step in the reaction.

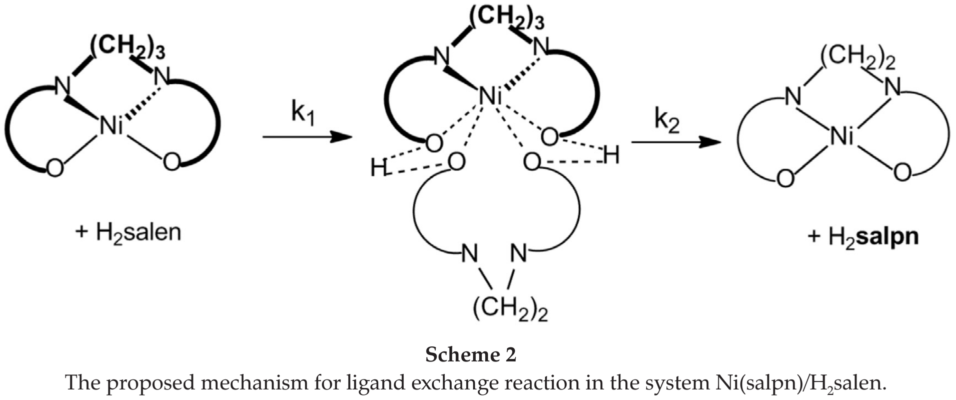
The second reaction step is first-order and independent of [H_2salen] (Equation 11) with rate constant k_2. As indicated in Scheme 2, substitution of salpn from the Ni(II) complexes involves initial coordination of phenolic oxygen atoms of H_2salen to the nickel centre in the Ni(salpn) complex followed by protons-transfer from H_2salen 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,[9,10] we have explained that interaction between H_2salen 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_2salen (reactions 12 and 13).

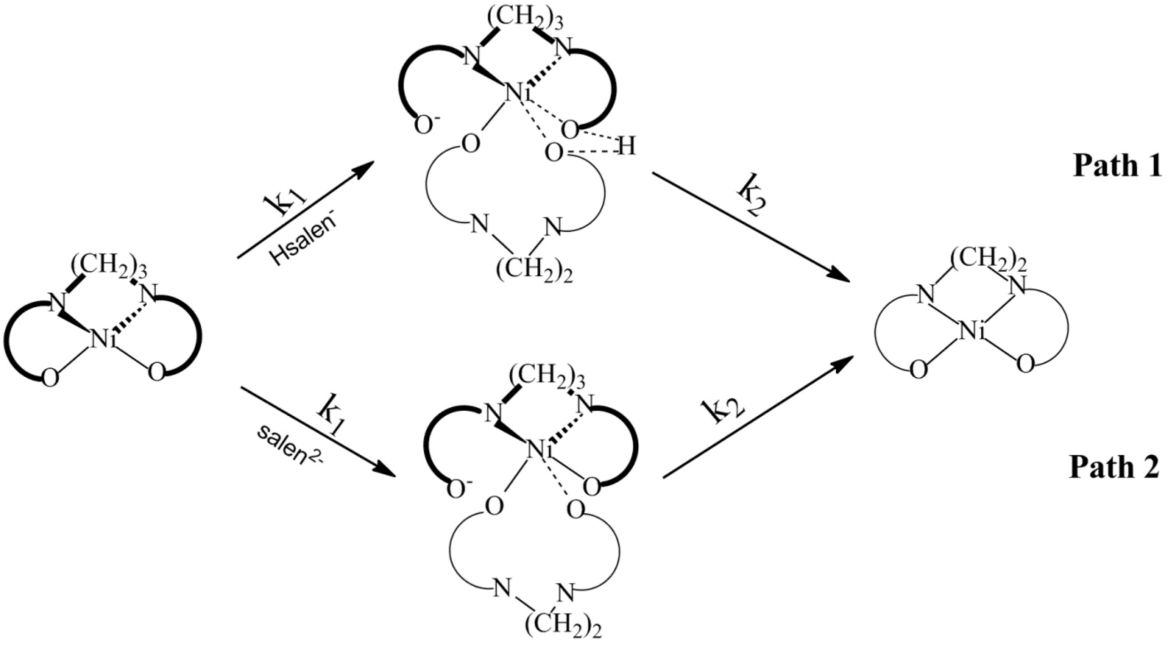
$$\text{H}_2\text{salen} + \text{NEt}_3 \rightarrow \text{Hsalen}^- + \text{HNEt}_3^+ \qquad (12)$$

$$\text{Hsalen}^- + \text{NEt}_3 \rightarrow \text{salen}^{2-} + \text{HNEt}_3^+ \qquad (13)$$

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-



Scheme 2
The proposed mechanism for ligand exchange reaction in the system Ni(salpn)/H_2salen.



Scheme 3
The proposed mechanism for ligand exchange reaction in the system Ni(salpn)/H_2salen in the presence of NEt_3.

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 [NEt_3] (0.97 ± 0.07 $M^{-1}.s^{-1}$, salen^{2-} is the major reactive species, Equation 13) is less than with low [NEt_3] (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 [NEt_3] (> 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<[NEt_3]<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 H_2O and NEt_3. These experiments are studied with three different concentrations of NEt_3:

1. In the first case, [NEt_3] < 0.1 M (before the break in the plot in Fig. 5), the ligand exchange rate was decreased by adding H_2O. The decrease of the reaction rate could be due to protonated NEt_3 and Hsalen$^-$ ion. The protonated Hsalen$^-$ ion gave rise to the formation of neutral H_2salen ligand and the rate of reaction decreased.
2. In the second case, [NEt_3] > 0.3 M (after break in plot in Fig. 5), the reaction rate was decreased by adding H_2O (0.4 M). In this condition, salen^{2-} ion was protonated by adding H_2O, H_2salen was formed and the reaction rate deceased.
3. In 0.1 <[NEt_3] < 0.3 M (break limits in plot in Fig. 5), the effect of H_2O on the rate of reaction was dependent on the concentration of H_2O. The reaction rate of ligand exchange was increased by increasing the concentration of H_2O up to 0.05 M. The increase of the reaction rate at low [H_2O] could be due to the formation of Hsalen$^-$ ion by protonated salen^{2-} ion. However, the reaction rate was decreased by adding more H_2O (≥0.4 M) due to complete protonation of salen^{2-} and Hsalen$^-$ ions and formation of neutral H_2salen.

4. Conclusion

The distortion of Ni(II) in the Ni(salpn) complex due to the formation 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 NEt_3, the ligand exchange reaction rate will be increased due to the formation of Hsalen$^-$ ion. However, at high concentration of NEt_3, the reaction rate partially decreases in comparison with low [NEt_3], 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 H_2salen ligand and the anionic form of H_2salen are important for the ligand exchange reaction.

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