Kinetics and Mechanism of Ligand Substitution Reaction of Tetraamine Macrocyclic Ligand with Tridentate Schiff Base in Copper(II) Complexes

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Abstract: The kinetics of the substitution reaction in the CuLX complexes, where L is the salicylaldehyde semicarbazone tridentate Schiff base ligand and X = NO_3, Br and ClO_4 with $N_4H_2 \cdot 2ClO_4$ macrocyclic ($N_4H_2 \cdot 2ClO_4$ is *5,7,7,12,14,14*-Hexaniethyl-*1,4,8,11*-tetraazacyclo tetradeca-*4,11*-diene dihydrogen perchlorate) were studied spectrophotometrically in DMF solvent at 25 ± 0.1 °C and an ionic strength of 0.5 M $NaNO_3$. The rate constants for ligand exchange reactions were obtained under the pseudo-first-order by measuring the absorbance changes at 700 nm, where equal to the greatest change in molar absorptivity between reactants and products. Under these conditions, the overall process is biphasic reaction. Therefore, two rate constants k_{obs} (1) and k_{obs} (2) were obtained. The k_{obs} (1), was fast and depended on $N_4H_2 \cdot 2ClO_4$ concentration and the k_{obs} (2) was not significantly affected by the concentration of $N_4H_2 \cdot 2ClO_4$ ligand. Based on the results, a mechanism for the ligand substitution reaction is proposed.

The kinetics of the substitution reaction in the CuLX complexes, where L is the salicylaldehyde semicarbazone tridentate Schiff base ligand and X = NO_3, Br and ClO_4 with $N_4H_2 \cdot 2ClO_4$ macrocyclic ($N_4H_2 \cdot 2ClO_4$ is *5,7,7,12,14,14*-Hexaniethyl-*1,4,8,11*-tetraazacyclo tetradeca-*4,11*-diene dihydrogen perchlorate) were studied spectrophotometrically in DMF solvent.

$$CuLX + N_4H_2 \cdot 2ClO_4 \rightarrow CuN_4(ClO_4)_2 + HL + HX$$
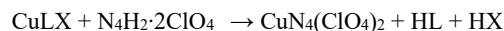
1. INTRODUCTION

The chemistry of macrocycles has been extensively studied for many years to improve the coordination chemistry and because of their potential applications as models for the active sites of important biological systems.[1-6] Macrocyclic ligands form stable and inert complexes with many transition metal ions. The chemistry of transition metal complexes of macrocyclic ligands is an area that has attracted considerable interest in recent years.[5-10] These complexes exhibit a range of characteristic properties that are markedly different from those of their acyclic analogs which has led to the concept of the "*macrocyclic effects*".[1,11,12] Among macrocyclic ligands, cyclic tetraaza ligands are the more readily available macrocyclic ligands, and these ligands have been coordinated to most metal ions, usually, the central ion is coplanar with the four nitrogen atoms.[12-16] The stability of metal complexes is dependent upon both the metal center environment, and the ligand conformational. Macrocyclic ligands represent an interesting class of ligands in compared with acyclic multidentate ligands. Macrocyclic complexes show thermodynamic and kinetic stabilities and the characteristic properties inaccessible to the complexes of non-cyclic chelate ligands. From the thermodynamic point of view the stability of metal complexes with macrocyclic, one would expect that there is a driving force for replacing the ligand coordinated with the macrocyclic free ligand to form more stable complexes.[1,11,12]

In previous studies, we reported kinetics of the ligand exchange in the CuL′/H₂L″ systems, where L′ and L″ are salen and its derivatives tetradentate Schiff base ligands.[17,18] In this article, we extend our investigations into the possibility of ligand exchange reaction between L in the CuLX (L = tridentate Schiff base ligand and X = NO_3, Br and ClO_4) and tetraaza macrocyclic $N_4H_2 \cdot 2ClO_4$ ligand (reaction 1, Scheme 1).

$$CuLX + N_4H_2 \cdot 2ClO_4 \rightarrow CuN_4(ClO_4)_2 + HL + HX \quad (1)$$
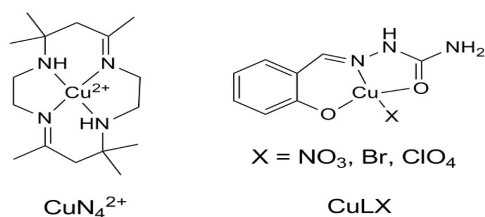
Scheme 1. A structural representation of copper complexes

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

The synthesis of the tridentate Schiff base ligand, HL was carried out as previously reported by us and others,[19,20] by condensation an aqueous solution containing semicarbazidehydrochloride (1 g, 0.008 mol) and sodium acetate (1.5 g, 0.01 mol), salicylaldehyde (0.5 g, 0.004 mol) at room temperature for 1 h to give a white precipitate. The precipitate was filtered, washed with distilled water and dried at room temperature. Yield 67%. IR (KBr, cm^{-1}): $\upsilon C{=}N = 1621$, $\upsilon C{=}O = 1682$.

Copper(II) complexes, CuLX (X = NO$_3$, Br and ClO$_4$) were synthesized and characterized by elemental analysis, FT-IR, UV-Vis and single-crystal X-ray diffraction analyses as previously reported elsewhere by us.[19] Briefly, A solution CuX$_2$ (2 mmol, X = NO$_3$, Br and ClO$_4$) in water (3 mL) was added to the solution of HL ligand (0.358 g, 2 mmol) in methanol (30 mL). The resulting solution (for X = NO$_3$ and Br) was heated to reflux for 3 h and X = ClO$_4$, was stirred for 24 h at room temperature. The resulting green solution was filtered, and the green precipitates were obtained by evaporation of the solvent.

[CuLNO$_3$].H$_2$O. After two days, Green small crystals appeared at the bottom of the vessel upon slow evaporation of the solvents, which were washed with ethanol:water (1:1 v/v) and dried in air. Yield 83%. Anal. Calcd. for C$_8$H$_{10}$CuN$_4$O$_6$: C, 29.86; H, 3.13; N, 17.41. Found: C, 29.28; H, 3.35; N, 17.50. IR (KBr, cm^{-1}): $\upsilon C{=}N = 1602$, $\upsilon C{=}O = 1657$.

[CuLBr].1.5H$_2$O. After two days, Green block-shaped crystals appeared upon slow evaporation of the solvents at room temperature, which was washed with ethanol:water (1:1 v/v) and dried in air. Yield 80%. Anal. Calcd. for C$_8$H$_{11}$CuN$_3$O$_{3.5}$: C, 27.56; H, 3.18; N, 12.05. Found: C, 27.45; H, 3.11; N, 11.92. IR (KBr, cm^{-1}): $\upsilon C{=}N = 1602$, $\upsilon C{=}O = 1646$.

[CuLClO$_4$]$_2$. The green precipitates were obtained by evaporation of the solvent. The green solid product was recrystallized from methanol/2-propanol (5:2 v/v). Green block-shaped crystals appeared upon slow evaporation of the solvents, which were washed with ethanol and dried in air. Yield 83%. Anal. Calcd. for C$_{16}$H$_{16}$Cl$_2$Cu$_2$N$_6$O$_{12}$: C, 28.16; H, 2.36; N, 12.32. Found: C, 28.44; H, 2.31; N, 12.00. IR (KBr, cm^{-1}): $\upsilon C{=}N = 1602$, $\upsilon C{=}O = 1654$, $\upsilon ClO_4 = 1047$.

The Macrocycle ligand, N$_4$H$_2$·2ClO$_4$ was prepared by the reported method.[21] The reaction of perchloric acid with ethylenediamine (1:1 molar ratio) in acetone solvent at room temperature for 15 min to give a white precipitate. m.p. > 110 °C, Yield 70%. Anal. Calcd. for C$_{16}$H$_{34}$Cl$_2$N$_4$O$_8$: C, 39.92, H, 7.12; N, 11.64. Found: C, 40.15; H, 7.19; N, 11.73. IR (KBr, cm^{-1}): $\upsilon N{-}H = 3147$, $\upsilon C{=}N = 1667$, $\upsilon C{-}N = 1175$, $\upsilon ClO_4 = 1052$.

The Macrocycle complex CuN$_4$(ClO$_4$)$_2$ was prepared by a method similar to that described by *Kang*.[22] The copper(II) acetate monohydrate (0.198 g, 1 mmol) was added to s of the N$_4$H$_2$·2ClO$_4$ ligand (0.481 g, 1 mmol) in methanol (30 mL). The resulting suspension was heated to reflux for 30 min. The red precipitates were obtained by evaporation of the solvent. Yield 82%. Anal. Calcd. for C$_{16}$H$_{32}$Cl$_2$CuN$_4$O$_8$: C, 35.40, H, 5.94; N, 10.32. Found: C, 35.35; H, 6.02; N, 10.23. IR (KBr, cm^{-1}): $\upsilon N{-}H = 3212$, $\upsilon C{=}N = 1672$, $\upsilon C{-}N = 1175$, $\upsilon ClO_4 = 1037$.

Kinetic measurements
Kinetic measurements of ligand exchanges were carried out on a GBC UV-Visible Cintra 101 spectrophotometer. The experiments were carried out in dimethylforamide, DMF, an aprotic polar solvent, under pseudo-first order limiting conditions. The concentration of Cu(II) complexes were kept constant at 5.0×10^{-3} M, while [N4] was varied from 5.0×10^{-3} to 1.5×10^{-1} M. All reactions were performed at 25 ± 0.1 °C and NaNO$_3$ were used to maintain a constant ionic strength of 0.5 M. The equal volumes (1 mL) of the isothermal reacting stock solutions of macrocycle ligand and NaNO$_3$ and copper complex were taken by a syringe and mixed in cell (1 cm path length). The ligand exchange reactions were monitored by following the decrease in absorbance versus time at 700 nm, this wavelength showed the greatest change in absorbance between the copper Schiff base complexes (CuLX) and the product complex, CuN$_4$(ClO$_4$)$_2$. Each run was studied at least three times.

The conventional mixing technique was employed for all the reactions. To initiate the reaction, equal volumes of the solution of the Cu(II) complex in DMF with the solution containing macrocycle N$_4$H$_2$·2ClO$_4$ and NaNO$_3$ were mixed. The reaction mixture absorbance values at 700 nm were followed as a function of time. At each concentration, at least three runs were recorded.

The rate constants k$_{obs}$ values were evaluated by fitting the data variation the absorbance of versus time data using *Sigmaplot 12.0* software with equations 2 (*irreversible first-order reaction*), 3 (*biphasic reaction*), and 4 (*triphasic reaction*) to find the best fit:[12]

$$A = a_1 \exp[-k_{obs}(1)t] + A_\infty \qquad (2)$$

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

$$A = a_1 \exp[-k_{obs}(1)t] + a_2 \exp[-k_{obs}(2)t] + a_3 \exp[-k_{obs}(3)t] + A_\infty \qquad (4)$$

where a$_1$ and a$_2$ are comprised of rate constants and molar absorptivities.

$$a_1 = \varepsilon_A[A]_0 + \frac{\varepsilon_B[A]_0 k_1}{k_2 - k_1} + \frac{\varepsilon_C[A]_0 k_2}{k_1 - k_2}$$

$$a_2 = \frac{k_1[A]_0(\varepsilon_B - \varepsilon_C)}{k_1 - k_2}$$

The rate constant k, has been obtained by fitting data results of k_{obs} versus N$_4$H$_2$·2ClO$_4$ using sigmaplot 12.0.

3. RESULTS AND DISCUSSION
Absorption spectra
The visible absorption spectra of the CuLX (X = NO$_3$, Br and ClO$_4$) and CuN$_4$(ClO$_4$)$_2$ complexes at equal concentrations in DMF solvent show maximum absorption due to d–d transition at about 700 and 515 nm, respectively (Figure 1). The visible spectrum of the copper complexes could be used to monitor ligand exchange reaction of CuLX with N$_4$H$_2$·2ClO$_4$ (reaction 1) and study the kinetics of the reaction.
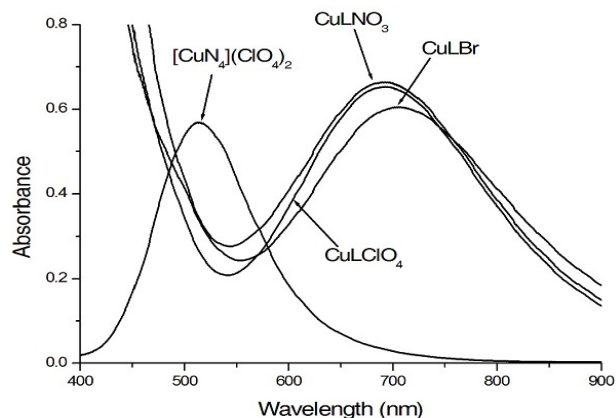
Figure 1. Visible spectra of CuLX, X = NO₃, Br and ClO₄ (5.0 × 10^{-3} M) and CuN₄(ClO₄)₂ (5.0 × 10^{-3} M) complexes in DMF (1 cm quartz cell).

Figure 2 shows a consecutive series of spectral changes associated with ligand exchange in the complexes CuLX by N₄H₂·2ClO₄ with an equal concentration in DMF according to reaction 1. Figure 2 indicates a decrease of absorption at about 700 nm and an increase of absorption at 520 nm with respect to the starting CuLX spectrum. The spectrum CuN₄(ClO₄)₂ complex in DMF was similar to the last spectrum shown in Figure 2. These observations indicate that the CuLX (X = NO₃, Br and ClO₄) complexes converted to a CuN₄(ClO₄)₂ complex when the N₄H₂·2ClO₄ ligand was added (reaction 1). The decrease of absorption at about 700 nm was used to monitor and study the kinetics of the reaction.

Kinetic study

The rate constants for ligand exchange reaction were obtained under the pseudo-first-order by excess and different N₄H₂·2ClO₄ ligand concentrations. The reactions were monitored by following the changes of absorption at the 700 nm band, where the difference absorption between the substrate and the product was the largest. The absorbance at 700 nm was found to decrease with elapse of time, due to the formation of CuN₄(ClO₄)₂ complex (Figure 2). A typical plot of the absorbance versus time data at 700 nm is shown in Figure 3.

Under these conditions, the best fit for the results of data was obtained by equation 3 (biphasic reaction). Therefore, two rate constants k_{obs} (1) and k_{obs} (2) were obtained. The pseudo-first-order rate constants were measured at different ligand concentrations. The order of the reaction rate with respect to N₄H₂·2ClO₄ ligand was determined by plotting k_{obs} as a function of ligand concentration. Figure 4 shows the variation in k_{obs} versus macrocycle ligand concentration, which indicates that the first-step reaction, k_{obs} (1) was fast and dependent on N₄H₂·2ClO₄ while the two-step reaction k_{obs} (2) was slower than the first-step and independent on N₄H₂·2ClO₄ ligand concentration.
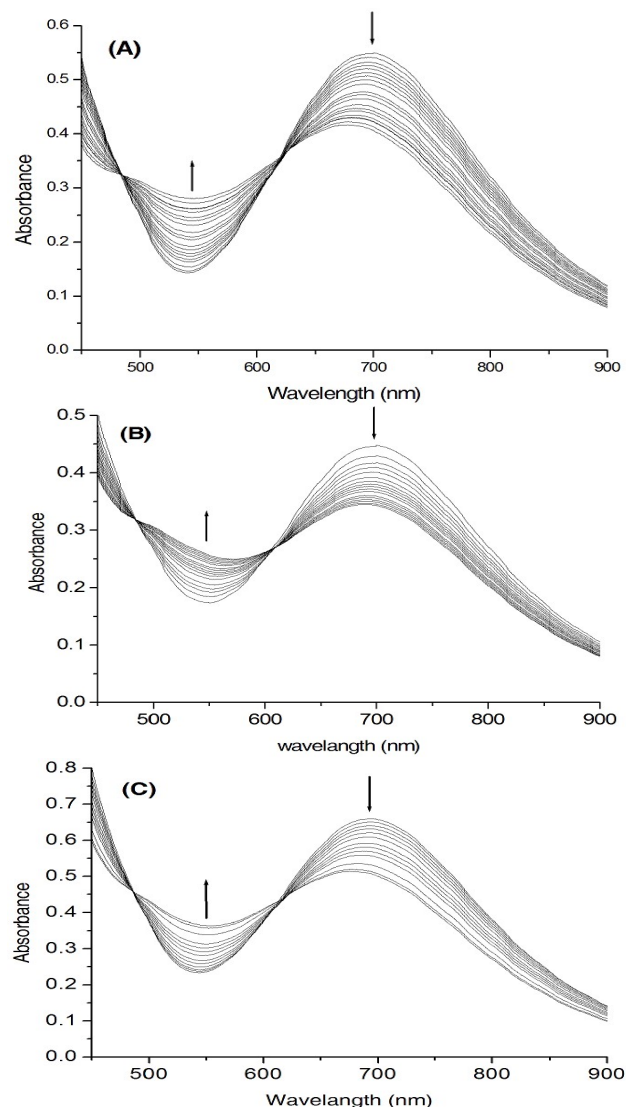

Figure 2. Spectral changes recorded in DMF solvent for the reaction of CuLX (5.00 × 10^{-3} M)/N₄H₂·2ClO₄ (5.00 × 10^{-3} M) system (**A**) X = NO₃, (**B**) X = Br, (**C**) X = ClO₄.
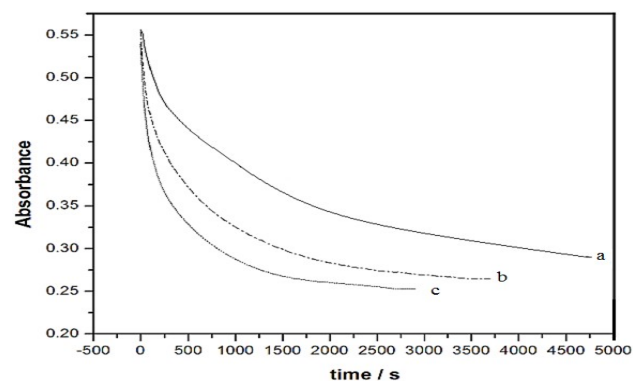

Figure 3. Plot of absorbance vs. time for reaction of CuNO₃ (5.0 × 10^{-3} M) and N₄H₂·2ClO₄, a = 1.00 × 10^{-2} M, b = 7.50 × 10^{-2} M, c = 1.50 × 10^{-1} M recorded in DMF solvent.

These results can be described by equations 5 and 6.

$$k_{obs}(1) = k_1 [N_4H_2 \cdot 2ClO_4] \qquad (5)$$

$$k_{obs}(2) = k_2 \qquad (6)$$

The second-order rate constants k_1 were obtained from the slope of the linear plots $k_{obs}(1)$ versus $[N_4H_2 \cdot 2ClO_4]$. The first-order rate constants k_2 were found by the mean of the experimentally obtained data for $k_{obs}(2)$, which was independent of the concentration of ligand (Table 1).
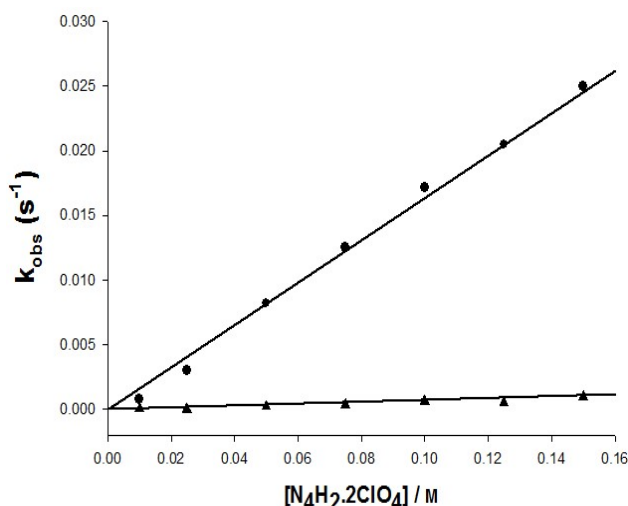

Figure 4. Plot of the rate constants $k_{obs}(1)$, ● and kobs (2), ▲ vs. $N_4H_2 \cdot 2ClO_4$. for CuLClO$_4$ complex.

Table 1. Rate constants data for the reaction of CuLX complexes with macrocyclic $N_4H_2 \cdot 2ClO_4$ ligand

X	$10^1 \times k(1)$ (M^{-1}.s^{-1})	$10^3 \times k(2)$ (s^{-1})
NO$_3$	1.78 ± 0.07	3.83 ± 0.12
Br	1.25 ± 0.06	2.92 ± 0.17
ClO$_4$	3.45 ± 0.11	3.60 ± 0.27

The conversion of CuLX by adding $N_4H_2 \cdot 2ClO_4$ ligand to $CuN_4(ClO_4)_2$ complex in DMF solvent showed that $CuN_4(ClO_4)_2$ complex was thermodynamically more stable than the CuLX complexes. To confirm this, the reverse of reactions i.e., the conversion of $CuN_4(ClO_4)_2$ by adding L ligand to the CuLX does not take place. In this condition, a reverse reaction and equilibrium cannot be observed between the two complexes.

In comparison with acyclic multidentate ligands, cyclic ligands form stable and inert complexes with many transition metal ions.[1,4,23] The increase in the ligand field strength (decrease wavelength) and stability of $CuN_4(ClO_4)_2$ relative to the CuLX complexes are in accord with the trend observed in the ligand exchange reaction (reactions 1). This is consistent with previous results reported on the reaction of ligand exchange and metal exchange in the polydentate with the formation of more stable complexes.[17,18,24-26]
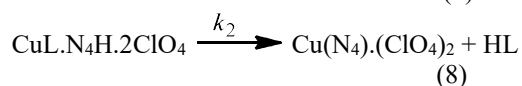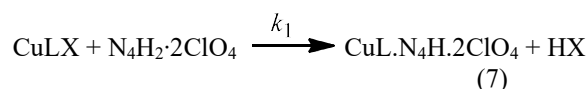
Proposed mechanism

The ligand exchange reaction 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 $k_{obs}(1)$, was fast and depended on the concentration of $N_4H_2 \cdot 2ClO_4$ ligand, according to equation 5. The $k_{obs}(2)$ was not significantly affected by the increase in the concentration of $N_4H_2 \cdot 2ClO_4$ ligand (Figure 4). The kinetic results indicate that the reaction occurs in two consecutive steps, namely $[N_4H_2 \cdot 2ClO_4]$ dependent and $[N_4H_2 \cdot 2ClO_4]$ independent steps. It is reasonable to assume that the concentration dependent step, $k_{obs}(1)$ is the first-step in a series of two consecutive steps.

The presence of only two absorbing species ($CuN_4(ClO_4)_2$ and CuLX) in the reaction mixture in visible region during the reaction course is confirmed by sharp isosbestic points at about 485 and 610 nm (Figure 4). This indicates that the CuLX converted to the $CuN_4(ClO_4)_2$ without the formation of a free Cu^{2+} ion, which has a different spectrum from the copper Schiff base complexes.[12] In general, the ligand exchange reactions between multidentate ligands proceed via intermediates where the incoming ligand is partially coordinated to the metal center and the leaving ligand is partially dissociated.[12,27]

In addition, Figure 4 shows a representative graph for k_{obs} dependence on the free ligand concentrations with zero intercepts at the extrapolated zero concentration. The zero intercepts confirms that the reverse reaction does not take place and also the negligible contribution of solvent to the overall rate.

The possible reactions for the ligand exchange reaction would thus be given by equations 7 and 8.

$$CuLX + N_4H_2 \cdot 2ClO_4 \xrightarrow{k_1} CuL.N_4H.2ClO_4 + HX \qquad (7)$$

$$CuL.N_4H.2ClO_4 \xrightarrow{k_2} Cu(N_4).(ClO_4)_2 + HL \qquad (8)$$

It follows from equation 7, that rate constant $k_{obs}(1)$ should be increased linearly with $[N_4H_2 \cdot 2ClO_4]$ according to $k_{obs}(1) = k_1 [N_4H_2 \cdot 2ClO_4]$ (equation 5). Ligand exchange reactions likely involve the fast bond cleavage of the X at CuLX complex and coordination of nitrogen atom of macrocycle to the copper center in the Cu complex followed by proton transfer from $N_4H_2 \cdot 2ClO_4$ to the X ligand (Scheme 2) with the rate constant k_1 and formation of an intermediate ternary complex, $CuL.N_4H.2ClO_4$ (equation 7). As indicated by equation 7, the formation of the intermediate $CuL.N_4H.2ClO_4$ species is dependent on the concentration of both reactant species (CuLX and $N_4H_2 \cdot 2ClO_4$) and dependent on the nature of X ligand also. The postulate of adduct formation is in

good agreement with a number of studies on the ligand exchange of multidentate ligands in transition metal complexes.[17,18,27]
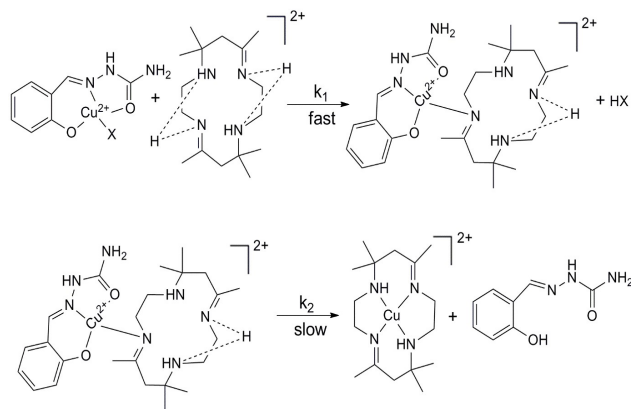
Scheme 2. The suggest mechanism for ligand exchange reaction in the system CuLX/$N_4H_2 \cdot 2ClO_4$

The second-step of the reaction is an intramolecular reaction and is independent of the [$N_4H_2 \cdot 2ClO_4$] concentration and slower than first-step (rate-determining step, RDS). We suggest that the second-step (eq. 8), with rate constants k_2 (same order in all CuLX complexes), is associated with the proton transfer from $N_4H.2ClO_4$ ligand with the bond cleavage of Schiff base ligand and finally, the reaction is completed by replacing Schiff base ligand with $N_4H_2 \cdot 2ClO_4$ (Scheme 2). The k_2 values are the same for all the ligand exchange reactions in CuLX complexes and independent on nature of X ligand. This is consistent with the mechanism suggested (Scheme 2). Despite the points of difference between the CuLX (X = NO_3, ClO_4 and Br) systems, the same general mechanism is proposed to hold for the present system also. Since this step is slow compared with the first step, it controls the overall rate of reaction and can be regarded as rate-determining step.

4. CONCLUSIONS

The ligand exchange reaction was investigated in CuLX/$N_4H_2 \cdot 2ClO_4$ systems by using visible spectrophotometry in the DMF under pseudo-first-order conditions. Experimental data were computer-fitted to appropriate exponential functions using a non-linear least-square iterative method. It was found that the reaction rate was a two-step process; the first-step was rapid and dependent on the concentration of $N_4H_2 \cdot 2ClO_4$ macrocyclic and the nature of X ligand. The second-step was slow and independent of $N_4H_2 \cdot 2ClO_4$. The conversion of the CuLX into the $Cu(N_4) \cdot (ClO_4)_2$ indicated that $Cu(N_4) \cdot (ClO_4)_2$ should be more stable than CuLX.

CONFLICTS OF INTEREST

There is no conflict of interest to declare.

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