Kinetics and Mechanism of the Ligand Exchange Reaction Between Tetraaza Macrocycle Ligand and Cu(II) Tetradeutate Amine-Amide Complexes

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Abstract

The kinetics of the ligand exchange reaction of tetraaza macrocycle, teazma (teazma is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene dihydrogen perchlorate) with Cu(bcen)²⁺ and Cu(bctn)²⁺, where bcen and bctn are N,N’-bis(β-carbamoylethyl) ethyldiamine and N,N’-bis(β-carbamoylethyl) propyldiamine, respectively, have been studied by visible spectrophotometry in dimethylformamide, DMF, solvent at 25 ± 0.2 °C. In the system of Cu(bctn)²⁺/teazma, the ligand exchange reaction proceeds in a two-step-consecutive manner, with two rate constants \( k_{bctn}^{obsd}(1) \) and \( k_{bctn}^{obsd}(2) \). The first reaction step was dependent on the concentration of teazma macrocycle, while the second reaction step was independent. However, it is found that the ligand exchange reaction in Cu(bcen)²⁺/teazma proceeds in an one-step with the rate constant \( k_{bcen}^{obsd} \). The rate constant is dependent on \([\text{teazma}]_{macrocycle}\). The ligand exchange reaction in the system of Cu(bcen)²⁺/teazma is not complete and after some progress, the reaction reaches equilibrium. On the basis of results, a reaction mechanism is proposed and discussed for the ligand exchange rate.

Keyword: Macrocycle, acyclic, diamine diamide, Cu complexes, ligand exchange

1. Introduction

Complexes with chelating ligands generally have increased stability relative to those of monodentate ligands, and even greater stability when the donor atoms are incorporated into a cyclic ligand that surrounds the metal ion, commonly referred to as a »macrocyclic effect«.1–3 The chemistry of transition metal ion with macrocyclic ligands is an interesting field in chemistry and has been the subject of extensive research due to their potential applications in different fields, such as coordination chemistry, environmental chemistry and the role they play as models for metallopeptidease and enzymes binding sites in biological systems.3–11

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. Cyclic tetraaza are among the most intensively studied macrocyclic ligands forming stable and inert complexes with many transition metal ions.9–15 Tetraaza macrocycles are coordinated by four donor atoms N to central ion, usually the central ion is coplanar with the four nitrogen atoms.3,8,16

Our group has studied the ligand exchange of copper(II) and nickel(II) complexes by acyclic tetradeutate ligands.17–19 As an extension of our study, we have been interested in the possibility of ligand exchange reaction between Cu(bcen)²⁺ and Cu(bctn)²⁺, where bcen and bctn are acyclic diamine-diamide tetradeutate ligand, N,N’-bis(β-carbamoylethyl) ethyldiamine and N,N’-bis(β-carbamoylethyl) propyldiamine, respectively, with tetraaza

![Scheme 1. A structural representation of copper complexes.](image-url)
macrocycles, teazma (5,7,7,12,14,14-hexamethyl-1,4,8, 11-tetraazaacyclo tetradeca-4,11-diene dihydrogen perchlorate, Scheme 1) in order to gain better understanding of the kinetic and mechanistic behavior of multidentate ligand exchange processes.

2. Experimental

2.1. Reagents

The acyclic diamine-diamide tetradentate ligand, bcn, bctn, and copper complexes were prepared as previously reported elsewhere by us and others.20,21

The macrocycle ligand teazma was prepared by the reported method.22 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. C₆H₁₂Cl₂N₄O₈; C, 39.92, H, 7.12; N, 11.64. Found: C, 40.15; H, 7.19; N, 11.73. IR (KBr, cm⁻¹): ν ＮΗ = 3147, ν Ｃ≡Ｎ = 1667, ν Ｃ≡Ｎ = 1175, ν ＣｌＯ₄ = 1052.

The macrocycle complex [Cu(teazma)](ClO₄)₂ was prepared as previously reported.23 Yield 82%. Anal. C₁₆H₃₂Cl₂CuN₄O₈; C, 35.40, H, 5.94; N, 10.32. Found: C, 35.35; H, 6.02; N, 10.23. IR (KBr, cm⁻¹): ν ＮΗ = 3212, ν Ｃ≡Ｎ = 1672, ν Ｃ≡Ｎ = 1175, ν ＣｌΟ₄ = 1037.

All other chemicals and solvent used in this work were of analytical grade, available commercially and were used without further purification.

2.2. Kinetic Measurements

The kinetic ligand exchanges of Cu(II) complexes, Cu(bcen)²⁺ and Cu(bctn)²⁺, were studied under pseudo first order conditions with an excess amount of [teazma] in dimethylformamide, DMF, as solvent. The concentration of Cu(II) complexes were kept constant at 6.50 × 10⁻³ M, while [teazma] was varied from 6.50 × 10⁻³ to 1.63 × 10⁻¹ M. All reactions were performed at 25 ± 0.2 °C and NaClO₄ was used to maintain a constant ionic strength of 1.0 M. The equal volumes (1 mL) of the isothermal reacting stock solutions of macrocycle ligand and NaClO₄ and copper complex were taken by a syringe and mixed in cell (1 cm path length). The ligand exchange reactions were monitored by a GBC UV-Visible Cintra 101 spectrophotometer and following the increase in absorbance at 515 nm due to the formation of Cu(teazma)²⁺ complex. The wavelength 515 nm is the maximum absorption of Cu(teazma)²⁺ complex (see Fig. 1). Each run was studied at least three times.

The absorbance versus time data were computer fitted by sigmaplot 12.0 software with equations 1 (monophasic reaction) and 2 (biphasic reaction) to find the best fit and $k_{obs}$.24,25

$$A = a_1 \exp[-k_{obs1}(1)t] + A_{\infty}$$ (1)

$$A = a_1 \exp[-k_{obs1}(1)t] + a_2 \exp[-k_{obs2}(2)t] + A_{\infty}$$ (2)

where $a_1$ and $a_2$ are comprised of rate constants and molar absorptivities.

3. Results and Discussion

3.1. Proposed Mechanism of Cu(bctn)²⁺/teazma System

The spectral changes associated with ligand exchange in Cu(bctn)²⁺ by teazma according to eq. 3 are shown in Fig. 2. The presence of only two absorbing species in the reaction mixture during the reaction course is confirmed by a sharp single isosbestic points at ca. 600 nm. The
change proceeds with a decrease in absorbance at ca. 675 nm and an increase at ca. 515 nm. The absorbance at 515 nm 675 nm due to Cu(teazma)2+ and Cu(bctn)2+ complexes, respectively (see Fig. 1).

Cu(bctn)2+ + teazma → Cu(teazma)2+ + bctn (3)

The kinetics of ligand exchange were followed by monitoring the increase in absorbance at 515 nm, the wavelength of maximum absorption due to the formation of Cu(teazma)2+ complex (Fig. 2). An example plot of absorbance versus time is shown in Fig. 3. The plot exhibited a monotonic increase and the pseudo-first-order rate constants (k_ \text{obsd}) were calculated from the absorbance changes at this wavelength.

The rate constants, k_ \text{obsd} were calculated by fitting the kinetic curves, absorbance vs. time with the help of a suitable exponential computer-fit program. The best fit was obtained by equation 2 (biphasic reaction) for Cu(bctn)2+ / teazma system. Therefore, the kinetics Cu(bctn)2+/teazma system are taking place in two consecutive steps, i.e. the ligand exchange reaction proceeds in a two-step-consecutive manner (A → B → C), with two the rate constants k_{bctn}^{(1)} and k_{bctn}^{(2)}. Table 1 summarizes values of k_ \text{obsd} for various concentration of teazma macrocycle.

| complex | \(10^4 \times k_{bctn}^{(1)}/s^-1\) | \(10^4 \times k_{bctn}^{(2)}/s^-1\) | \(10^4 \times k_{bcen}^{(1)}/s^-1\) |
|---------|---------------------------------|---------------------------------|---------------------------------|
| Cu(bctn)2+ | 5.40 ± 0.15                     | 6.21 ± 0.22                     | 7.48 ± 0.11                     |
| Cu(bcen)2+ | 10^4 × 10^3 × k_{bcen}^{(1)}/s^-1 | 10^4 × 10^3 × k_{bcen}^{(2)}/s^-1 | 10^4 × 10^3 × k_{bcen}^{(3)}/s^-1 |

The rate constants of the two consecutive steps are first order for Cu(bctn)3+ complex. The effect of the teazma concentration on the experimental rate constants, k_{bctn}^{(1)} and k_{bctn}^{(2)} is shown in Fig. 4. The rate constant of the first-step, k_{bctn}^{(1)} increases linearly with increasing [teazma]. Based on this, the first step is first order in [Cu(bctn)3+] and [teazma]. The rate constant of the second-step, k_{bctn}^{(2)} found to be independent on the concentration of teazma macrocycle. The small intercept confirms that the reverse reaction does not take place and also the negligible contribution of solvent to the overall rate.

Therefore, the rate law applicable to kinetic ligand exchange Cu(bctn)2+ / teazma system is given by eq. 4.

\[
\text{Rate} = k_{bctn}^{(1)} + k_{bctn}^{(2)} \text{[Cu(bctn)3+]} \quad (4)
\]

Where

\[
k_{bctn}^{(1)} = k_{bctn}^{(1)} [\text{teazma}] \quad (5)
\]

\[
k_{bctn}^{(2)} = k_{bctn}^{(2)} \quad (6)
\]

The k_{bctn}^{(1)} value was obtained from the slope of the linear plot k_{bctn}^{(1)} vs. [teazma] (eq. 5) and k_{bctn}^{(2)} which was independent on concentration teazma, was computed from the average of the values obtained for k_{bctn}^{(2)}, (Fig. 4 and Table 1). The rate constant for the second-step k_{bctn}^{(2)} = 3.44 ± 0.11 × 10^{-3}s^-1 is ca. 100 times slo-
The rate constants for ligand exchange reaction of Cu(bctn)$^{2+}$ complex by teazma were obtained by measuring the absorbance changes at 515 nm under the pseudo-first-order. The absorbance at 515 nm was found to increase with elapse of time (Fig. 5).

Under these conditions, the best fit of the absorbance versus time data were obtained by Equation 1 (monophasic reaction). Therefore, the rate constant $k_{\text{bcen}}^{\text{obsd}}$ in Cu(bcen)$^{2+}$/teazma system was obtained. The pseudo-first-order rate constant $k_{\text{bcen}}^{\text{obsd}}$ was found to increase with increase in teazma concentration (Fig. 6), the $k_{\text{bcen}}^{\text{obsd}}$ values are collected in Table 1.

Fig. 7 shows a consecutive series of spectra recorded in DMF solvent for the Cu(bcen)$^{2+}$/teazma system. Comparing Figure 7 with Figures 1 and 5 shows that the ligand exchange reaction is not complete and after some progress, the reaction reaches equilibrium (Eq. 7).

$$\text{Cu(bcen)}^{2+} + \text{teazma} \rightleftharpoons \text{Cu(teazma)}^{2+} + \text{bcen} \quad (7)$$

The effect of the teazma concentration on the rate constants, $k_{\text{bcen}}^{\text{obsd}}$ is shown in Fig. 6. The rate constant in-
creases linearly with increasing [teazma]. Likewise, as shown in Fig. 6, the dependence of rate constant $k_{bcen \text{obsd}}$ on the excess concentration of teazma is linear with non-zero intercepts confirms that the reverse reaction does take place. The rate law can be expressed by Eq. 8.

$$\text{Rate} = k_{bcen \text{obsd}}[\text{Cu(bcen)}^{2+}] = \left( k_{bcen} + k_{-1} \right) [\text{Cu(bcen)}^{2+}]$$ (8)

The rate constants $k_{bcen}$ value was calculated according to the Eq. 8 from the slope $k_{bcen \text{obsd}}$ vs. [teazma], whereas the value for the reverse rate constant ($k_{-1}$) was obtained from the intercept the plot (Table 1). The value $k_{bcen} = 3.99 \times 10^{-4}$ s$^{-1}$, is close to the rate constant of dissociation for Cu(bcen)$^{2+}$ ($k_{\text{diss}} = 8.81 \times 10^{-5}$ s$^{-1}$).\textsuperscript{21}

Chung reported the values of the rate constants of dissociation for Cu(bctn)$^{2+}$ and Cu(bcen)$^{2+}$ in water 7.94 $\times 10^{-3}$ and 8.81 $\times 10^{-5}$ s$^{-1}$, respectively.\textsuperscript{21} The ratio of the rate constants for the ligand exchange of the Cu(bctn)$^{2+}$/teazma and Cu(bcen)$^{2+}$/teazma systems ($k_{bctn}/k_{bcen} = 89.7$) are compatible with the ratio of the rate constants of dissociation reported by Chung for Cu(bctn)$^{2+}$ and Cu(bcen)$^{2+}$ (90.1).\textsuperscript{21} Comparisons of the ratios of the rate constants obtained in this study and the rate constants of dissociation for Cu(bctn)$^{2+}$ and Cu(bcen)$^{2+}$, show that the two reactions (ligand exchange and dissociation reactions) have the same rate determining step. The rate-determining step for dissociation Cu(bctn)$^{2+}$ and Cu(bcen)$^{2+}$ are the breakage of second copper nitrogen bond.\textsuperscript{21} The similarly of the values of $k_{bcen}$ and the rate constants of dissociation of Cu(bcen)$^{2+}$ can be the reason for the ligand exchange reaction was not complete and after some progress the forward reaction the reverse reaction is performed.

4. Conclusion

The ligand exchange reaction was investigated by using visible spectrophotometry in the dimethylformamide, DMF, as solvent. In the system Cu(bctn)$^{2+}$/teazma, the ligand exchange reaction proceeds in a two-step-consecutive manner, with two the rate constants (1) and (2), and the ligand exchange reaction was completed. The rate-determining step is the breaking of the second copper(II)-nitrogen bond. The ligand exchange reaction in the system Cu(bcen)$^{2+}$/teazma is not complete and is reversible reaction. The same value of the reverse rate constant in the system with the rate constant of dissociation of Cu(bcen)$^{2+}$ complex, can be the reason for the reversibility of the reaction.

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Povzetek

S pomočjo spektrofotometrije smo v dimetilformamidu (DMF) kot topili pri 25 ± 0.2 °C spremljali kinetiko izmenjave tetraaza makrocikličnega liganda teazma (teazma je 5,7,7,12,14,14-heksametil-1,4,8,11-tetraazaciklotetradeka-4,11-dien dihidroperklort) z Cu(bcen)2+ in Cu(bctn)2+, kjer sta bcn in bctn N,N'-bis(β-karbamoiletil) etilendiamin in N,N'-bis(β-karbamoiletil) propilendiamin. V sistemu Cu(bctn)2+/teazma, poteka izmenjava ligandov v dvostopenjskem zaporedju, z dvema hitrostnima konstantama (1) in (2). Prvi reakcijski korak je odvisen od koncentracije makrocikličnega liganda, medtem ko je drugi reakcijski korak neodvisen. Izmenjava ligandov pri sistemu Cu(bcen)2+/teazma poteka v eni stopnji s hitrostno konstanto k. Hitrostna konstanta je odvisna od koncentracije teazma makrocikličnega liganda. Izmenjava ligandov v sistemu Cu(bcen)2+/teazma ne poteče do konca, ampak se po določenem času vzpostavi ravnotežje. Na podlagi dobljenih rezultatov je predlagan reakcijski mehanizem in obravnavana hitrost izmenjave ligandov.