

Structure of blue copper proteins: electron-transfer kinetics of Cu(II/I) copper complex with macrocyclic ligand with N₂S₂ donor set

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Abstract: In electron-transfer, the change in the oxidation state of the reactants is generally accompanied by structural changes, which influence the electron-transfer kinetics. Previous studies on the systems of Cu(II/I) complexes involving cyclic tetrathiaether ligands indicated that inversion of coordinated donor atoms may be a primary factor in controlling gated electron transfer. Complex formation and isomerization studies on [14]aneN₄ type complexes have demonstrated that coordinated N atoms are shown to invert since they must undergo a hydrogen abstraction prior to inversion. In the systems with [14]aneN_xS_{4-x} ligands, there is a choice of N or S inversion. This study has been conducted to determine the effect of inversion of coordinated N atoms on electron-transfer rates as a function of different concentrations of water as hydrogen ion acceptor existing in aprotic solvent (acetonitrile). Data on electron-transfer kinetics are presented here. Possible conformational changes and kinetics pathways for N-S mixed donor complexes are discussed.

INTRODUCTION

Copper proteins perform a variety of functions in biological systems including uptake, storage and release of electrons. The blue copper proteins are small proteins, with type 1 copper center close to the periphery of the protein. Based on structural work, the type 1 copper proteins, azurin and plastocyanin contain one copper ion which is strongly coordinated by the N^δ of two histidines and S^γ of cysteines, with elongated axial S (methionine) bond completing distorted tetrahedral environment (Figure 1).

A comparison of azurin (Cascella, Magistrato, Tavernelli, et al., 2006) with plastocyanin shows that the geometry is closer to a trigonal bipyramid, so azurin has weakly bound glutamine oxygen unlike plastocyanine. Active site in an enzyme is constrained by surrounding protein matrix to impose the distorted tetrahedral geometry that is normally favored by Cu(I) state resulting in a relatively high reduction potential of the type 1 copper sites, unique spectral properties and relatively high self-exchange rate constant. Number of studies attempted to explain this unique behavior of active metal center in blue copper proteins using complexes mimicking a structure and

geometry of the blue copper protein active site or computational methods.

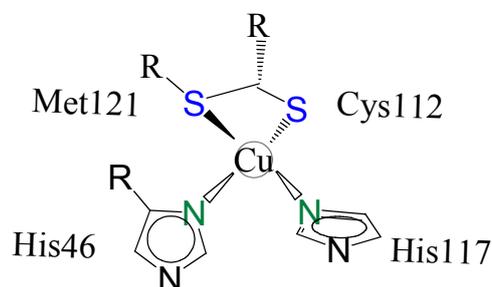
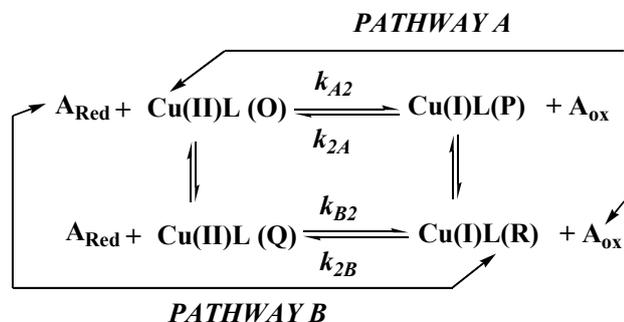


Figure 1. Structure of metal center in blue copper proteins.

Extensive studies on biomimetic complexes of copper (II/I) with tetrathiamacrocyclic ligands of different ring size attempted to elucidate this unique structure-function relationship. (Malkin and Malsmstrom, 1970; Randall, Gamelin, LaCroix, et al., 200; Valle, and Williams, 1968). The differences between the calculated self-exchange rate constants obtained from copper (II) reductions and copper (I) oxidations were several orders of magnitude. (Comba,

2000). To explain this behavior, a dual pathway square scheme was proposed which involves conformational changes of the reduced and oxidized form, preceded or followed by the electron-transfer. Comba, 2000, Solomon, Hare, and Gray, 1976; Gray, Malmstrom, and Williams, 2000). Dual-pathway square ET scheme mechanism was proposed to explain Cu(II/I) ET cross reactions (Scheme 1).



Scheme 1. Dual-pathway square scheme mechanism proposed for Cu(II/I) ET cross reactions (Dunn, Ochrymowycz, and Rorabacher, 1997).

Cu(II)L(A) and Cu(I)L(B) forms represent stable forms of two oxidation states, while Cu(II)L(Q) Cu(I)L(P) represent metastable intermediates with distorted geometry. A_{ox} and A_{red} are the oxidized and reduced forms of the counter reagent. Horizontal reactions symbolize electron transfer reactions, and vertical reactions conformational change processes. In the absence of conformational changes, electron transfer reactions will occur in a single step, resulting in specific rate constant for the two ET processes being equivalent. Thus, pathway A is preferred for the Cu(II)L reduction reaction, and Cu(I)L oxidation will follow Pathway A in the absence of conformation-limited behavior.

Conformational control in electron transfer kinetics of copper systems.(Comba,2000; Leggett, Dunn, Vande Linde, et al., 1993; Villeneuve, Schroeder, Ochrymowycz, et al.,1997) is highly dependable on donor atom inversion of ligands (N or S donors). Complex formation and isomerization studies on [14]ane N_4 type complexes have shown that coordinated N atoms are slow to invert since they must undergo a hydrogen ion abstraction prior to inversion, followed by donor atom rotation and reprotonation. By contrast, sulfur inversion requires simple rotation of the sulfur lone pair. In the systems with [14]ane N_xS_{4-x} ligands, (Figure 2), there is a choice of N or S inversion.

For the copper complex with [14]aneNS₃ ligand no nitrogen inversion is required for the conformational change from Cu(II)L to Cu(I)L. For other systems, with two nitrogen atoms each in the macrocycle, the different placement of the nitrogen is expected to cause unique electron-transfer kinetic behavior.

In this study, we focused on an investigation of the effect of the relative placement of nitrogen and sulfur atoms in the macrocyclic ring of [14]aneN₂S₂ ligand in copper (II/I) complexes (Figure 3) upon the electron-transfer rate constant as a function of water content acting as a proton acceptor in acetonitrile solution.

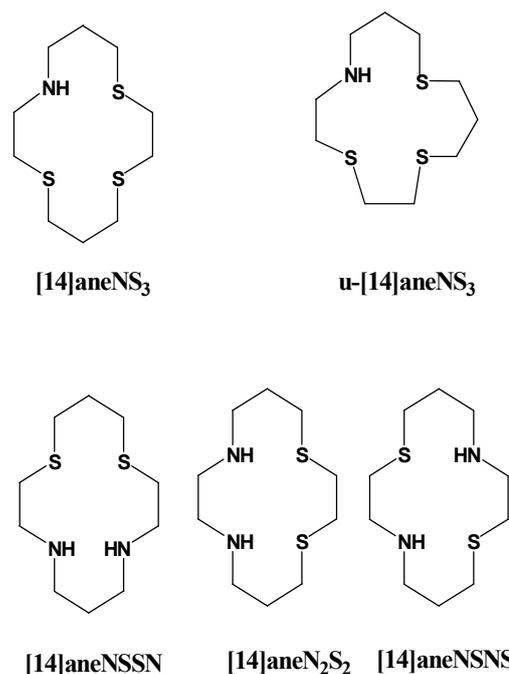


Figure 2. [14]ane N_xS_{4-x} ligands with different position of S and N atoms, resulting in distinguished kinetic behavior based on necessity of S and N donor atom inversion.

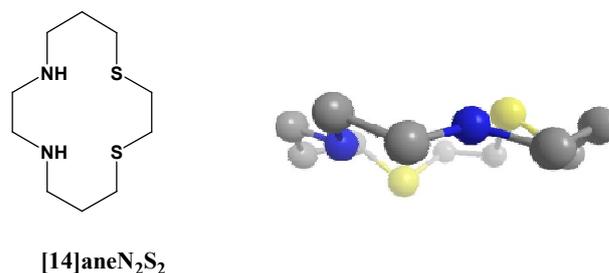


Figure 3. Structure of ligand with N and S donor sets obtained by using MM 2 force field energy minimization. Calculated steric energy was 15.13074 Kcal/mole. Blue balls represent N atoms, while yellow balls represent S atoms. Hydrogen atoms from structure were excluded because of clarity.

In the case of systems with one nitrogen donor atom, there is no need for the nitrogen to invert and, thus the water content in nonaqueous solution should have no effect on the kinetic behavior of these systems. For macrocycles containing two or more nitrogen donor atoms, the addition of a proton acceptor (water) might show changes in mechanistic behavior if one or more nitrogen atoms were required to invert. This is directly related on position of nitrogen atoms within macrocycle acting as a ligand in copper complex. Based on this line of reasoning, Cu (II/I) complexes with N₂S₂ macrocycle as a ligand studied in this work was expected to show different kinetic behavior reflecting the number of nitrogen required to invert during Cu(II/I) electron transfer. The electron-transfer kinetics of Cu(II/I) complexes with N₂S₂ ligands was investigated as a function of water content in acetonitrile utilizing cross reaction kinetics between the copper (II/I) complexes and appropriate counter reagents chosen on the basis of their formal potential and self-exchange rate constants.

EXPERIMENTAL

Materials

Reagents. Copper perchlorate was prepared by adding HClO_4 to CuCO_3 , as previously described. The product was first recrystallized as hydrate salts from water and then recrystallized from acetonitrile by evaporation to yield the acetonitrile-solvated salts.

Counter reagents. (S)-(1,3,6,8,10,13,16,19-octaazabicyclo-[6.6.6]-eicosane)cobalt(III) perchlorate ($\text{Co}(\text{sep})\text{Cl}_3$), pentaammineisonicotinamideruthenium(II)perchlorate ($\text{Ru}(\text{NH}_3)_5(\text{isn})(\text{ClO}_4)_2$), tetraamminebipyridineruthenium(II) perchlorate ($[\text{Ru}(\text{NH}_3)_4(\text{bpy})](\text{ClO}_4)_2$) were prepared using standard and modified literature methods (Stanbury, Haas, and Taube, 1986).

Polyaminothiaether Ligand. Stock solutions of ligand were prepared by an extraction of formed unprotonated ligand by using dichloromethane in five repeated extractions. The neutral ligand was then dissolved in acetonitrile and the concentrations were determined spectrophotometrically.

Copper(II) Complexes formed with polyaminothiaether ligand. Solutions of the copper(II) complexes with $[\text{14}] \text{aneN}_2\text{S}_2$ ligand were prepared by adding an appropriate volume of copper(II) perchlorate solution of known concentration to the ligand solution where the ligand was in excess over copper(II) perchlorate.

Copper(I) Complexes. In acetonitrile, solutions were prepared by dissolving at least ten-fold excess of ligand in a previously standardized solution of copper(I) perchlorate in 0.1 M $\text{NaClO}_4/\text{CH}_3\text{CN}$ that had been purged with nitrogen. The concentration of the complex was assumed to be identical to that of the original copper(I) perchlorate.

Karl-Fischer Reagents. Karl-Fischer (KF) reagents were used for the determination of water in acetonitrile. The KF titrant (titer 1 mg/ml), as obtained from GFS Chemicals consisted of a solution of iodine in methanol and KF solvent contained pyridine, sulfur dioxide and methanol and served as a solvent for the sample.

All starting chemicals were obtained from Sigma Aldrich, USA.

Methods

Stopped-Flow Kinetic Measurements. The cross-reaction kinetic data for the reduction and oxidation of the copper complexes were collected by using a stopped-flow spectrophotometer. For the reactions in acetonitrile, a modified Durrum-Gibson stopped-flow spectrophotometer interfaced to an Insight 486 PC was used. All reactions were thermostated at 25 ± 0.2 °C using a Forma Scientific 2095 water bath.

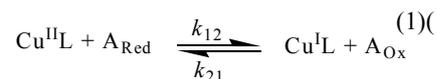
UV-visible Spectra. The general UV-visible spectra of the copper complexes were obtained using a Hewlett-Packard 8452A diode array spectrophotometer. A Cary-17D dual-beam spectrophotometer thermostated at 25 ± 0.2 °C was used to perform all quantitative absorbance measurements.

Formal Potentials. Formal potentials of copper complexes and counter reagents were determined by cyclic voltammetry (CV) using a BAS-100 Electrochemical Analyzer. A three-electrode electrochemical cell was used with a 3 mm glassy carbon disk or silver wire working electrode, a Pt wire auxiliary electrode and a Ag/AgCl (3 M NaCl) reference electrode. The ionic strength was

maintained at 0.10 M using 0.10 M $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ or $\text{NaClO}_4 \cdot \text{CH}_3\text{CN}$. Ferriin ($E^\circ = 1.112$ V vs. SHE) was used as an internal standard in aqueous solutions, and ferrocene ($E^\circ = 0.400$ V vs. SHE) was used in acetonitrile solutions. Reference electrodes were stored in 3 M NaCl . The glassy carbon-working electrode was polished with Micropolish Alumina 2 and 3 prior to use.

Analysis of Electron-Transfer Kinetic Data

The major focus of this study was to determine the self exchange rate constant, k_{11} , for copper(II/I) complexes with mixed donor macrocycle. This was accomplished by measuring the electron-transfer kinetics of selected cross-reaction



Here, the terms A_{Red} and A_{Ox} represent the reduced and oxidized form of the counter reagent. These reactions can be described by the following rate equation:

$$-\frac{d[\text{Cu}^{\text{II}}\text{L}]}{dt} = k_{12}[\text{Cu}^{\text{II}}\text{L}][\text{A}_{\text{Red}}] - k_{21}[\text{Cu}^{\text{I}}\text{L}][\text{A}_{\text{Ox}}]$$

where k_{12} and k_{21} are second-order rate constants for the copper(II) complex reduction reaction and copper(I) complex oxidation reaction, respectively. For some of the systems studied, the data analysis could be simplified by doing experiments under pseudo-first order conditions. This was accomplished by using at least ten-fold excess of one of the reactants over the other, so that the concentration of the major reactant did not change significantly during the reaction. If the counter reagent is in excess, the observed pseudo-first order rate constant, k_{obs} , for $\text{Cu}^{\text{II}}\text{L}$ reduction can be defined as:

$$k_{\text{obs}} = k_{12}[\text{A}_{\text{Red}}]$$

so that the resulting pseudo-first-order rate equation is:

$$-\frac{d[\text{Cu}^{\text{II}}\text{L}]}{dt} = k_{\text{obs}}[\text{Cu}^{\text{II}}\text{L}]$$

presuming that the reduction proceeds to the completion. A similar relationship can be derived for $\text{Cu}^{\text{I}}\text{L}$ oxidation. The kinetic data obtained under these conditions were then fitted to the integrated first-order expression:

$$\ln \frac{A - A_{\text{eq}}}{A_0 - A} = -k_{\text{obs}} t$$

where A represents the absorbance of the reaction mixture at any time t , A_{eq} represents the absorbance of the reaction mixture at $t = \infty$ and A_0 represents the absorbance at $t = 0$.

If the reaction of interest was too fast to monitor by the stopped-flow method, then second-order conditions were employed and the kinetic data were fitted to the general reversible second-order rate expression.

RESULTS AND DISCUSSION

Physical Parameters for Copper(II) $[\text{14}] \text{aneN}_2\text{S}_2$

In the current study, cyclic voltammetric experiments were carried out in acetonitrile to determine the standard potentials of the copper complexes with $[\text{14}] \text{aneN}_2\text{S}_2$,

All potential values for the corresponding systems in aqueous and acetonitrile solution are listed in Table 1.

Table 1. Physical Parameters for Copper(II) complexes in acetonitrile and in water at 25 °C, $\mu = 0.10$ M (NaClO₄).

| Complexed ligand | E ^f , V vs. Fc. | λ_{max} , nm | $10^{-3} \epsilon$, M ⁻¹ cm ⁻¹ |
|--|----------------------------|-----------------------------|---|
| [14]aneN ₂ S ₂ in acetonitrile | -0.363 | 370 ^a | 8.2(1) ^a |
| [14]aneN ₂ S ₂ in water | 0.04 ^b | 337 ^a | 7.6(1) ^a |

^aKoenigbauer, 1986; ^bWesterby 1988.

Standard potential of Copper(II) [14]aneN₂S₂ is lower when compared with the standard potential of Cu(II/I)([14]aneNS₃). In general, the replacement of a sulfur atom with a nitrogen atom in the macrocyclic ligand lowers the Cu(II/I) potential as is observed for all these systems in both solvents (Westerby, Juntunen, and Leggett, et al., 1991). This phenomenon is due to the fact that the stability constants for the copper(II) cyclic polyamino polythiaethers showed an increase by five to six orders of magnitude (Westerby, Juntunen, Leggett, et al., 1991) with each additional substitution of a nitrogen atom for a sulfur donor atom. However, the calculated copper(I) stability constant values were found to be relatively constant with the majority having values of approximately 10^{15} M^{-1} .

The near-UV absorption peak exhibited by the copper-polyaminothiaether complexes shifts to higher energies when the sulfur atoms are replaced by nitrogens. If the maximum wavelengths of the absorption band for these systems are compared to the value of 390 nm for the Cu(II)([14]aneS₄) and 255 nm for the Cu(II)([14]aneN₄), it is clear that these observations are consistent with the assignment of this peak to the S→Cu(II) charge transfer band (Westerby, Juntunen, and Leggett, et al., 1991) and, therefore, as the number of sulfur donor atoms increases, the energy of the electron transfer decreases.

Electron-Transfer Kinetics of Cu(II/I)([14]aneN₂S₂).

The self-exchange rate constant values for Cu(II/I)([14]aneN₂S₂) as determined from reduction reactions, $k_{11(\text{Red})}$, cover a 9.3-fold range which is within the limits of experimental error (Table 2). The range of the $k_{11(\text{Ox})}$ values determined for the six oxidation reactions with two different oxidation reagents are within a 5.3-fold range (Table 3).

Since no increase in $k_{11(\text{Ox})}$ or $k_{11(\text{Red})}$ was observed as a function of water content in acetonitrile, we can conclude that the presence of a proton acceptor does not affect the electron-transfer rate. The mean value of $\log k_{11(\text{Red})} = 1.68$ is nearly three orders of magnitude larger than the mean values of $\log k_{11(\text{Ox})} = -1.17$. Based on this observation, we can conclude that the Cu(II/I)([14]aneN₂S₂) system shows the characteristic “square-scheme” behavior in which pathway A is preferred, that is, the value of $k_{11(\text{Red})}$ represents the self-exchange rate constant via Pathway A ($k_{11(\text{A})}$) while the values of $k_{11(\text{Ox})}$ represent the self-exchange rate constant for Pathway B.

The two stable conformations of copper(II) complexes are generally Conformer I and Conformer III (Figure 4).

Conformer I exists as a five-coordinate species, where the lone electron pairs on all sulfur atoms and the hydrogens on the nitrogen atoms are oriented in the same direction relative to the macrocyclic ring. In Conformer III, the lone electron pairs of sulfur atoms and/or the hydrogens attached

to nitrogen atoms that are bridged by one trimethylene group are oriented in one direction, while the hydrogens attached to the nitrogens and/ or the sulfur lone electron pairs bridged by the other trimethylene bridge are oriented in the opposite direction. Copper(I) complexes exist as distorted 4-coordinate tetrahedral complexes in Conformer V in which the direction of the lone electron pairs on the sulfurs and the hydrogens on the nitrogens alternating as one proceeds around the ring.

Table 2. Mean cross-reaction rate constant and self-exchange rate constants calculated for Cu^{II}([14]aneN₂S₂) with selected counter reagents in acetonitrile at 25°C, $\mu = 0.10$ M (NaClO₄).

| Counter Reagent | % H ₂ O (w/w) | $k_{12}(\text{or } k_{21})$ M ⁻¹ s ⁻¹ | k_{11} M ⁻¹ s ⁻¹ | log k_{11} |
|------------------------|--------------------------|---|--|--------------|
| Reductions | | | | |
| Co ^{II} (sep) | 0.007 | 1.3 (5) × 10 ³ | 12.95 | 1.11 |
| | 0.010 | 3.0 (12) × 10 ³ | 70.80 | 1.85 |
| | | 2.9 (6) × 10 ³ | 66.17 | 1.82 |
| | 0.10 | 2.7 (16) × 10 ³ | 57.22 | 1.76 |
| | | 1.9 (9) × 10 ³ | 28.01 | 1.45 |
| | 1.0 | 3.9 (3) × 10 ³ | 120.91 | 2.08 |

Table 3. Mean cross-reaction rate constant and self-exchange rate constants calculated for Cu^{III}([14]aneN₂S₂) with selected counter reagents in acetonitrile at 25°C, $\mu = 0.10$ M (NaClO₄).

| Counter Reagent | % H ₂ O (w/w) | $k_{12}(\text{or } k_{21})$ M ⁻¹ s ⁻¹ | k_{11} M ⁻¹ s ⁻¹ | log k_{11} |
|---|--------------------------|---|--|--------------|
| Reductions | | | | |
| Ru ^{III} (NH ₃) ₄ (bpy) | 0.010 | 0.6 (2) × 10 ⁶ | 0.027 | -1.57 |
| | 0.10 | 1.5 (10) × 10 ⁶ | 0.209 | -0.68 |
| | 1.0 | 1.3 (4) × 10 ⁶ | 0.137 | -0.87 |
| Ru ^{III} (NH ₃) ₅ (isn) | 0.010 | 0.8 (5) × 10 ⁵ | 0.023 | -1.64 |
| | 0.10 | 1.9 (9) × 10 ⁵ | 0.123 | -0.91 |
| | 1.0 | 1.2 (5) × 10 ⁵ | 0.046 | -1.34 |

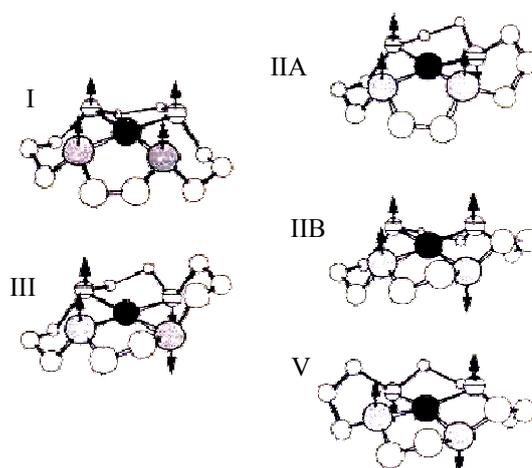


Figure 4. Schematic representation of the five conformers for the copper complexes formed with [14]aneN₂S₂ ligand. The solid circle represents the copper atom, the shaded circles represent nitrogen atoms, the striped circles represent sulfur atoms, and the open circles represent carbon atoms. Hydrogen atoms have been omitted for clarity. The arrows represent the orientation of the hydrogen atom attached to nitrogen or the unshared electron pair on sulfur relative to the macrocyclic ring. Conformers I and III are stable forms for Cu(II) complexes and Conformer V is a stable form Cu(I). In converting from Conformer I or III to Conformer V either Conformer IIA or IIB must be accessed as an intermediate. These two intermediate conformers differ only in the fact that one sulfur donor atom is oriented in a unique direction relative to the “plane” of the macrocyclic ring in Conformer IIA while in Conformer IIB it is a nitrogen donor atom that is oriented in the unique direction.

If Cu(II)([14]aneN₂S₂) exists in Conformer I, one nitrogen hydrogen and one sulfur lone electron pair must invert. If the Cu(II) complex is in Conformer III, the inversion of only the two sulfur donor atoms is necessary (**Figure 4**). Since no increase in the $k_{11(\text{Red})}$ values was observed as a function of water content in acetonitrile, we presume that the dominant form of the Cu(II) complex is Conformer III.

Previous studies (Koenigbauer, 1986; Westerby, 1988) of Cu(II/I)([14]aneN₂S₂) system showed kinetic behavior in aqueous solution at different pH values. For the oxidations conducted at low pH (1.0 to 2.5), the k_{11} values are much smaller than those obtained in acetonitrile solution. At higher pH (5.45 and 5.60), Koenigbauer observed two reactions, where the faster reaction was pseudo-first-order and the slower one was truly first-order. The k_{11} value for the faster reaction is approximately 2000 times higher than that for the oxidation at lower pH. The slower reaction appears to represent "gated" oxidation with the average k_{obs} value calculated to be $2.47 \times 10^{-3} \text{ s}^{-1}$. The self-exchange rate constant obtained for the oxidation at high pH (5.3) is in agreement with the $k_{11(\text{Ox})}$ values obtained in acetonitrile. Since $k_{11(\text{Ox})}$ decreases significantly with decreasing pH, we can assume that inversion of at least one nitrogen is involved in the conformational change. At very low pH, the concentration of hydrogen ion is high and deprotonation of coordinated nitrogen becomes difficult. The result is a very slow nitrogen inversion. However, at high pH, conformational change becomes the rate limiting-step and gated behavior is observed where the conformational change (R→P) controls the rate of the oxidation of reaction. Thus, the system is not following Pathway B, but a more complex scheme involving a number of metastable conformers Galijasević, Krylova, Koenigbauer, et al.,(2003).

CONCLUSIONS

Electron-Transfer Kinetics of Cu(II/I)([14]aneN₂S₂) followed square scheme mechanism but for current system is a free from significant donor atom inversion barriers. By controlling the amount of water in aprotic solvent, any dependence on proton acceptance and need for donor inversion would significantly affect the self-exchange rate constant values for reduction and oxidation reactions. For Cu(II) complex with [14]aneN₂S₂ ligand in the acetonitrile, the only possible conformation was Conformer III, where the inversion of only the two sulfur donor atoms is necessary that does not depend on hydrogen extraction. Thus, the position of donor sets in this type of ligand significantly directs electron-transfer process and in general overall complex geometry.

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Summary/Sažetak

U elektron transfer procesu, promjena oksidacionog stanja reaktanata je generalno praćena strukturalnim promjenama, koje direktno uslovljavaju kinetiku posmatranih reakcija. Ranije studije na Cu(II/I) kompleksima sa cikličnim tetraoeter ligandima su pokazale da inverzija koordiniranih donorskih atoma u kompleksu je vjerovatno osnovni faktor u kontrolisanom tzv. "gated" elektronskom transferu. Studije formiranja Cu(II/I) kompleksa i izomeracije sa [14]aneN₄ tipovima kompleksa su pokazale da dolazi do inverzije koordiniranih N atoma zbog abstrakcije vodikovih atoma. U sistemima sa [14]aneN_xS_{4-x} ligandima, postoji mogućnost inverzije N ili S atoma. Cilj ovog istraživanja je bilo određivanje inverzije N atoma i efekat iste strukturne promjene na konstante brzine elektron transfera ali u funkciji niskih koncentracija vode u aprotičnom rastvaraču (acetonitril). Rezultati koji opisuju elektron transfer kinetiku i moguće konformacijske promjene kompleksa Cu(II/I) te kinetički mehanizam za ligande sa N-S donor atomima su predstavljeni i objašnjeni u ovom radu.